SOME STUDIES OF THE HOMOLYTIC REACTIONS OF CHLORINATED BENZENES

by

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DECLARATION

ABSTRACT

The homolytic aromatic substitution reactions of chlorinated benzenes was investigated by studying their phenylation reactions. Dibenzoyl peroxide was used as the source of phenyl radicals and reactions were effected in sealed, thick walled tubes at different temperatures with various additives.

All the chlorosubstituted benzenes (chlorine = 1 - 6) were investigated namely chlorobenzene, three isomers each of di-, tri and tetra-chlorobenzenes, penta- and hexachlorobenzenes. The methylation of polychlorobenzenes was examined qualitatively, using tertiary butyl peroxide as the source of methyl radicals.

The phenylation of chlorosubstituted benzenes was found to involve the normal processes of displacement, disproportionation and dimerisation. Products which could be formed by displacement of hydrogen (phenyldehydrogenation) and of chlorine (phenyldechlorination) occurred in all cases where possible. In addition, as the number of chlorine atoms increased, other novel reaction products became important and suggestions are made as to the mechanisms of their formation.

It is suggested that σ-complexes formed could take up a hydrogen atom and then form products involving the elimination of hydrogen chloride or less commonly of molecular chlorine. Ipso σ-complexes formed by the attack of a phenyl radical at a carbon bearing chlorine could give products arising from migration of either phenyl or chlorine to the ortho or meta position. Occasionaly it might be possible for these pathways to give a novel route to a conventional product.

Thus in the phenylation of the isomeric di-, tri- and tetra-, and penta- and hexachlorobenzenes, the products are those of phenyl-dehydrogenation and phenyldechlorination reactions. However, additional novel by-products were also found in these reactions which possibly arise by the addition - elimination reaction sequence described above and the ipso rearrangement reaction.

Therefore the products of the phenylation reactions of the chloro-substituted benzenes differ substantially from those of the corresponding fluorosubstituted benzenes which were only reported to undergo replacement of hydrogen and fluorine.

The relative rates of the isomeric chlorosubstituted benzenes were determined and also the partial rate factors at the various positions of the aromatic ring in the absence and presence of several additives.

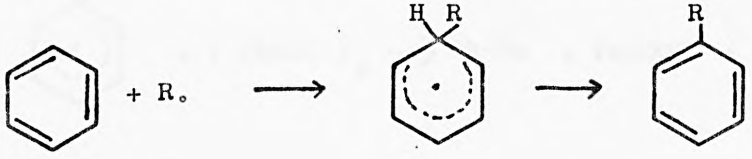
CHAPTER ONE

INTRODUCTION

1.1 INTRODUCTION

For many years, aromatic substitution reactions were [1] regarded as being divided into two classes, those involving attack by an electrophilic species (e.g. nitration) and those involving reaction of a nucleophilic species (e.g. amination). [2] More recently, however, there has been a great deal of interest in aromatic substitution reactions in which the attacking entity is a non-polar, free radical species, neither electrophilic or nucleophilic. [3] This class of reaction has become known as homolytic aromatic substitution and was first recognised by Hey in 1934. [4]

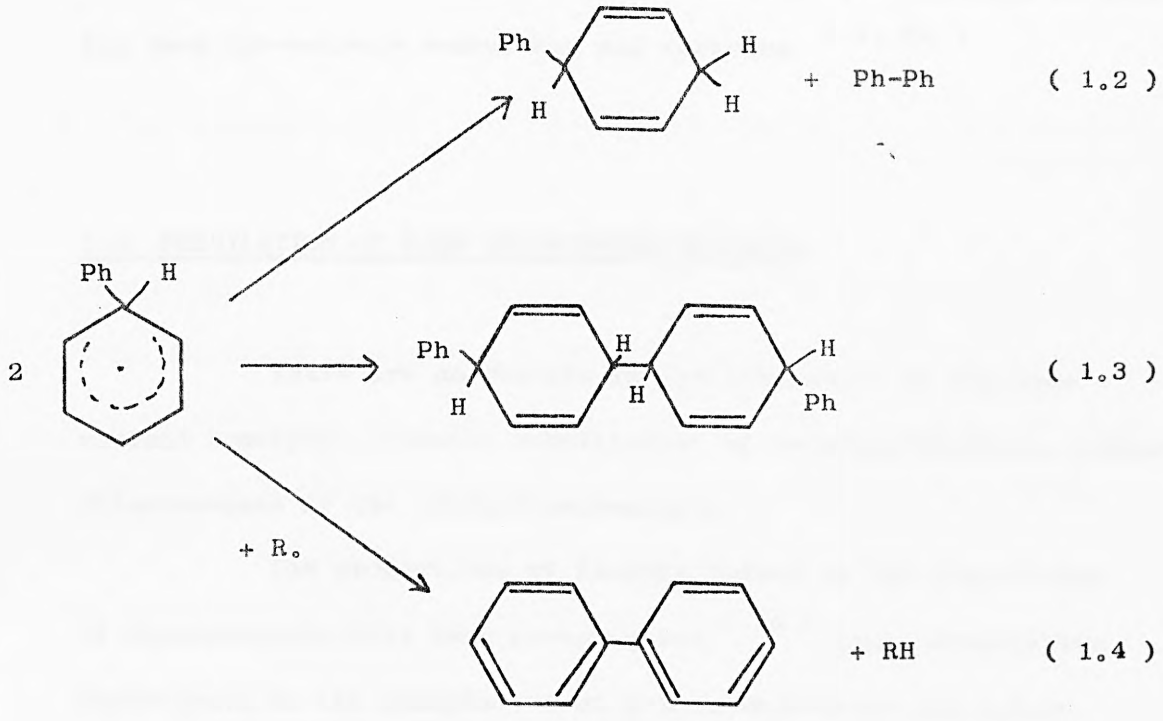
Arylation (i.e. attack by an aryl radical) has been the most widely researched homolytic aromatic substitution reaction [5] and has been the subject of several reviews. [6,7,8] The most general description of homolytic aromatic substitution is the displacement of a substituent (usually hydrogen) in an aromatic system by a radical R. as represented by (1.1). [9]

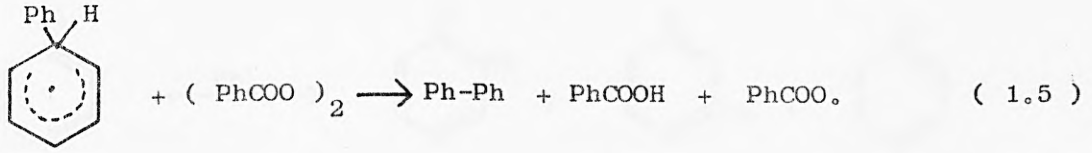


(1.1)

The phenylcyclohexadienyl radicals (σ-complex or radical adduct) can react further in three ways: they can disproportionate to give biphenyl and a dihydrobiphenyl (1.2), dimerise to yield a tetrahydroquaterphenyl (1.3) or be oxidised to biphenyl (1.4). Biphenyl is also generated in a chain-transfer reaction with dibenzoyl peroxide as shown in (1.5).

Thus it can be seen that this sort of reaction can lead to many and varied products, particularly biaryl (synthetic use) and other polycyclic systems. [10]





Homolytic aromatic substitutions are distinguished from electrophilic aromatic substitutions by their relative insensitivity to polar influences either in the substrate or in the attacking radical.

Since 1952 important work has been done by Hey and Williams [11, 12] on the quantitative study of the arylation of different monosubstituted benzenes. The proportions in which the three mono-aryl isomers were formed were determined. On combination of these data, partial rate factors for the arylation in the

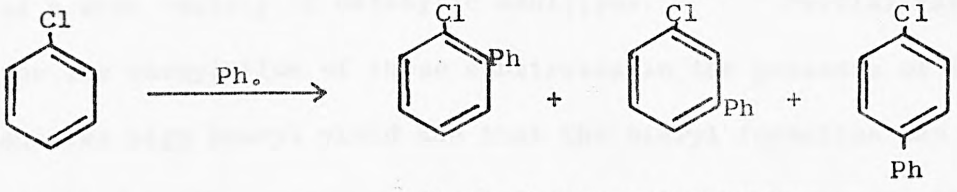
different aromatic positions of the compounds were calculated. The partial rate factor measured the activating or deactivating effect of each orienting substituent on each of the remaining positions.

The chemistry of the behaviour of free radicals in solution has been extensively researched and reviewed. (1, 61)

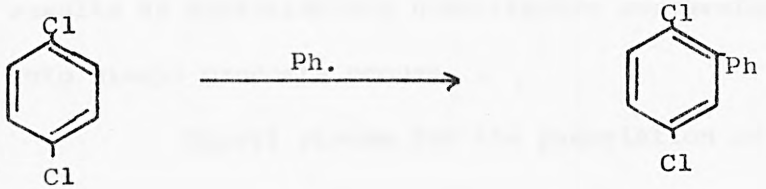
1.2 PHENYLATION OF SOME CHLORINATED BENZENES

There are no reports in the literature on the free radical homolytic aromatic substitution of hexachlorobenzene, pentachlorobenzene or the tetrachlorobenzenes.

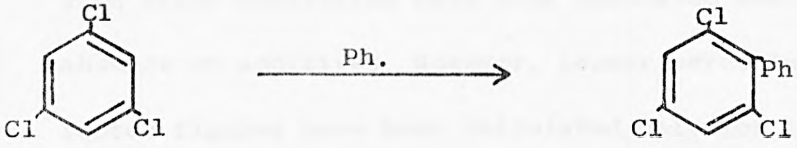
The proportions of isomers formed in the phenylation of chlorobenzene have been investigated. (14) Also, competitive experiments on the phenylation of p-dichlorobenzene and 1,3,5-trichlorobenzene have been reported. (15) Scheme 1.1 shows the reported products of phenylation.



2-,3-,4-chlorobiphenyls



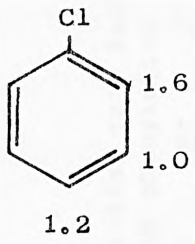
2,5-dichlorobiphenyl



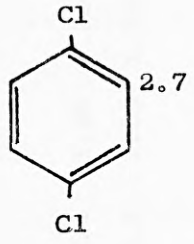
2,4,6-trichlorobiphenyl

Scheme 1.1

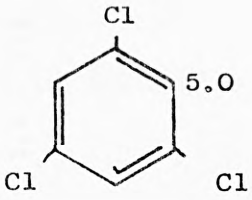
Figure 1.1 Partial rate factors (p.r.f.) for phenylation



chlorobenzene



p-dichlorobenzene



1,3,5-trichlorobenzene

Partial rate factors of these compounds were also determined and these are shown in Figure 1.1. The main product of phenylation of p-dichlorobenzene was 2,5-dichlorobiphenyl. The only other by-products reported were chloroterphenyls, which were yellow, glassy resins. (15)

Similarly, the main product of phenylation of 1,3,5-trichlorobenzene was 2,4,6-trichlorobiphenyl, formed by replacement of hydrogen. (13, 15)

Recently, these arylation reactions have been studied with single and mixed substrates in both the absence and presence of a wide variety of catalytic additives. (13) Partial rate factors for the phenylation of these substrates in the presence of additives ensures high biaryl yield and that the biaryl formation was not affected by the selective loss of σ-complexes by dimerisation reactions. (13) This means more reliable partial rate factor results as approximately quantitative conversion of σ-complexes into biaryl products occurs.

Biaryl yields for the phenylation of chloro-, fluoro- and bromobenzene, p-dichlorobenzene, 1,3,5-trichlorobenzene along with other substrates have been tabulated both in the presence and absence of additives. However, isomer percentage and partial rate factor figures have been calculated only for the monohalogenobenzenes and are listed in Table 1.1.

Table 1.1 Reactions of benzoyl peroxide (1 g) with equimolar mixtures (50 ml.) of benzene and arenes (ArH) in the presence and absence of additives at 80 °C

ArH	additive	total binuclear products (mole per mole peroxide)	ArH k PhH	isomers (%) in biaryls o-	m-	p-	partial rate factors for phenylation o-	m-	p-
chlorobenzene	none	0.573	1.14	54.6	27.2	18.2	1.9	0.9	1.2
	iron benzoate (0.5 g)	0.866	1.43	57.6	26.1	17.3	2.5	1.1	1.5
bromobenzene	none	0.741	1.47	54.2	30.5	15.3	2.4	1.35	1.35
	iron benzoate (0.5 g)	0.907	1.53	54.5	29.5	16.0	2.3	1.35	1.50
fluorobenzene	none	0.619	1.08	48.2	51.8*		1.5	1.1	1.2
	iron benzoate (0.5 g)	0.800	1.23	55.0	45.0*		2.0	1.1	1.1

* = combined m- and p-

(source: reference 13)

Table 1.2 Reactions of benzoyl peroxide (1 g) with equimolar mixtures (50 ml.) of benzene and p-dichlorobenzene or 1,3,5-trichlorobenzene (ArH) in the presence and absence of additives (0.5 g) at 80 °C

ArH	additive	$\frac{k_{ArH}}{k_{PhH}}$	$\frac{k_{ArH}}{k_{PhH}}$ (calculated)
p-dichlorobenzene	none	1.65	1.15
	iron benzoate	1.98	1.76
	copper benzoate	2.13	2.01
1,3,5-trichlorobenzene	none	4.99	2.15
	iron benzoate	4.86	4.48

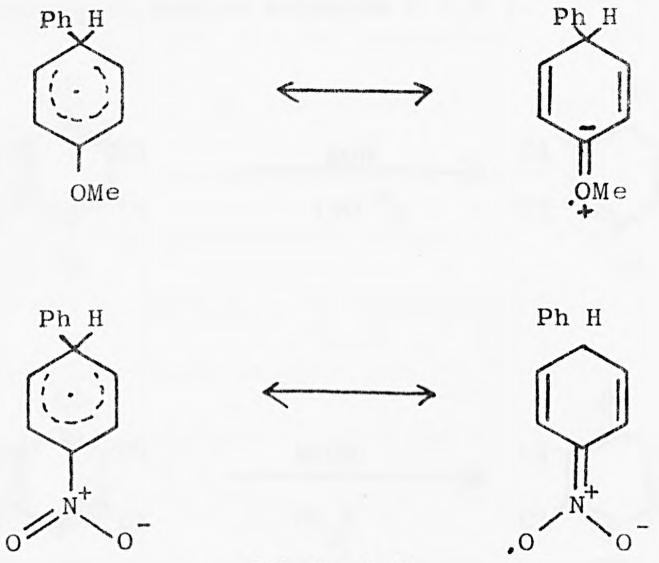
(source: reference 13)

Figures obtained for the isomer percentages in the presence of the additive differ slightly from those obtained in their absence, but the difference is not large enough to change the pattern of homolytic phenylation. (13)

Sometimes the difference between results obtained with and without additives was considerable, e.g. in the phenylation of chlorobenzene yields were low in the uncatalysed reaction but much improved on the addition of iron (III) benzoate. However, in the phenylation of bromobenzene which gave good yields of bromobiphenyl in the uncatalysed reaction, the difference between the uncatalysed and catalysed reactions was small.

Isomer distribution results obtained in the phenylation rections with single and mixed substrates were found to be quite similar. (13) In general, a slight increase in the ortho- product is accompanied by a slight decrease in the amounts of meta- and para- product.

Activation of the ortho- and para- positions arises from the ability of some conjugated groups to contribute to the delocalisation of the unpaired electron in the σ-complexes, as shown in Scheme 1.2, thus increasing the stability of these complexes



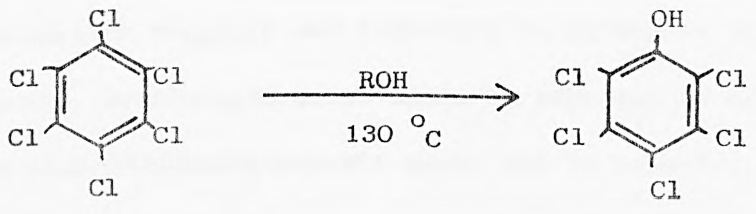
Scheme 1.2

and the reactivities in the ortho- and para- positions of these aromatic substrates.[9] However, the meta- positions are not affected as this type of delocalisation is not possible.

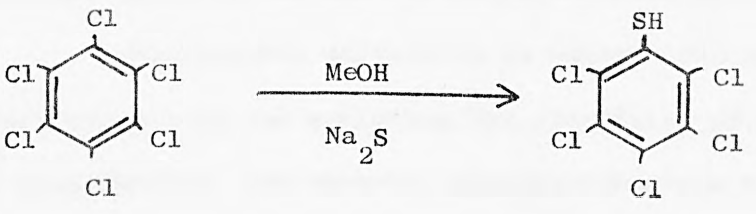
1.3 GENERAL PROPERTIES OF HEXACHLOROBENZENE

Compared with hexafluorobenzene, the substitution reactions of hexachlorobenzene have not been investigated in such great depth. Hexachlorobenzene appears to be inert as shown by its failure to react with Grignard reagents[16] and its resistance to attack by molten sodium hydroxide as well as other active substances. However, it has been attacked by certain reactive reagents, but only under extreme conditions e.g. reaction with vigorous fluorinating agents.[17] Thus, hexachlorobenzene appears to be an unreactive compound.

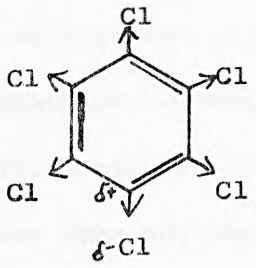
Despite this apparent unreactivity, several reactions are known to proceed under moderate conditions. Hexachlorobenzene can be hydrolised to pentachlorophenol in an alcoholic solution at 130 °C (1.6) and pentachlorothiophenol is produced by reaction with methanolic sodium sulphide (1.7).[19]



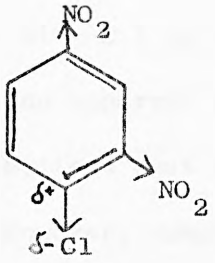
(1.6)



(1.7)



(I)



(II)

The low reactivity, at least towards electrophilic attack, of hexachlorobenzene can be understood by a consideration of the charge distribution in the molecule. The six chlorine atoms exert strong inductive and mesomeric effects (-I and +M) on the ring carbon atoms leaving them positively charged. (3) In this respect, hexachlorobenzene (I) resembles 2,4-dinitrochlorobenzene (II). The nitro-groups are also strongly electron withdrawing and leave the benzene ring positively charged. However, in the case of hexachlorobenzene, the electron withdrawing effect (-I) is counteracted to a certain extent by the +M effect and so hexachlorobenzene would be expected to be less reactive (to nucleophilic attack) than 2,4-dinitrochlorobenzene. (20, 21)

As 2,4-dinitrochlorobenzene is susceptible to attack by nucleophilic reagents and resistant to attack by electrophilic reagents, hexachlorobenzene would be expected to have similar reactions. Hexachlorobenzene would not be expected to undergo typical electrophilic aromatic substitution reactions such as nitration, sulphonation and the Friedel-Crafts reaction.

Considerable difficulty is experienced in obtaining the correct conditions for achieving the reactivity of hexachlorobenzene with nucleophiles. For example, hexachlorobenzene does not react

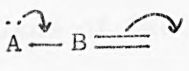
with sodium methoxide in boiling methanol, but will react to form pentachloroanisole if the temperature is raised to 120 °C. (22) When methylamine is bubbled through hot (310 °C) or cold solutions of hexachlorobenzene in various solvents, no apparent reaction occurs. Thus, one could easily be led to believe that hexachlorobenzene does not react with methylamine. However, complete reaction occurs with methylamine in a closed vessel at 150 °C. In spite of the mild conditions, the probability of discovering these reactions is much smaller than if they occurred at atmospheric pressure.

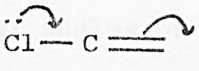
Another aspect of this 'inconvenience factor' is the remarkably low solubility of hexachlorobenzene in common organic solvents. At room temperature, its solubility is less than 1 % in alcohol, diethyl ether, acetone and dimethylformamide. Since it is customary to study substitution reactions in solution, it can be seen how poor solubility could obscure its reactivity and discourage further investigations.

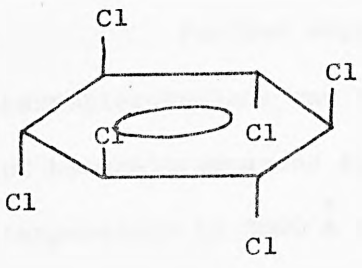
It has been found that hexachlorobenzene does indeed react with nucleophilic reagents (23, 24) as predicted.

1.3.1 THE STRUCTURE OF HEXACHLOROBENZENE

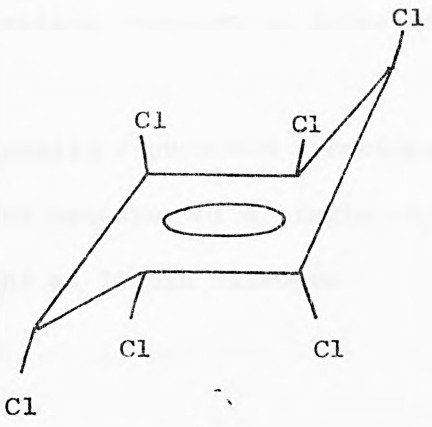
Research has been carried out to elucidate the structure of hexachlorobenzene by various workers. (25) In a system where an atom A with a lone pair of electrons is connected to an atom B by a single bond, B having a double bond, then resonance possibilities exist. Due to the resonance, the length of the carbon-chlorine bond







(III)



(IV)

is shorter than that in chloromethane. Thus, hexachlorobenzene, like the chloroethens, experiences a shortening of the C - Cl bond length. [25] The C - Cl distance is 1.70 ± 0.03 Å as compared to the value of 1.76 Å found in saturated aliphatic chlorine compounds. The decrease is attributed to the introduction of a degree of double bond character to the C - Cl bond. There were also distortions in the benzene ring which increase the C - C distance by 0.02 Å. [25]

Electron diffraction [26] shows that hexachlorobenzene molecules are distorted with the chlorine atoms being alternately displaced above and below the mean plane of the benzene ring, as shown at (III). [27] In the vapour state, the hexachlorobenzene molecule adopts a chairlike conformation, as shown at (IV).

Studies by Coulson on the steric forces in halogen substituted benzenes showed that hexachlorobenzene was puckered. Contributions of the formal charges on carbon and chlorine, the bond dipoles in the C - Cl bond, were taken into account.

On analysis of a quadrupole spectrum of hexachlorobenzene, Duchesne et al [29] showed that the chlorine atoms were bent away from the plane of the ring alternately at angles of 25°. Each ring carbon is partially shielded from attack by the two ortho- chlorine

atoms which protrude forward, thus limiting reaction to those reagents of a suitable geometry.

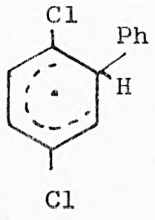
Further support for a corrugated / puckered structure for hexachlorobenzene was obtained from the spectrum of a single crystal of hexachlorobenzene in polarised light at liquid nitrogen temperature in 3000 Å range. (27)

1.4 REVERSIBILITY OF HOMOLYTIC AROMATIC SUBSTITUTION

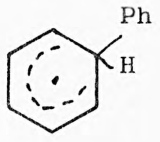
The addition of aroyloxy radicals to arenes is known to be reversible. (30, 31, 32, 33) However, it has been considered that low temperature homolytic aromatic substitution reactions were irreversible processes, (34, 35, 36) on the basis of an insignificant kinetic isotope effect for the phenylation of benzene. (37) Thus Atkinson et al showed that the addition of phenyl radicals at 80 °C was irreversible. (38) Similarly, thermochemical data for radical reactions with benzenoid compounds indicated that phenylation was irreversible below 200 °C, (39) whilst the formation of σ-complexes was a reversible process at high temperatures. In contrast, a Japanese report (40) and work by Henriquez and Nonhebel (41, 42, 43) suggest that the phenylcyclohexadienyl radicals are formed reversibly in the addition of phenyl radicals to substituted benzenes. The latter workers demonstrated the reversibility of the addition of phenyl radicals to benzene compounds by a study of the phenylation of ortho- and para-dichlorobenzenes. (41, 42) They questioned the irreversibility of the addition of phenyl radicals to an aromatic substrate on the basis of variations of isomer ratios and rate constants obtained by the phenylation of isomeric dichlorobenzenes in the presence of oxidising agents. (41, 42, 43) They found that

the partial rate factors for the phenylation of p-dichlorobenzene (42) decreased with increasing temperature, providing evidence for the reversible formation of the phenylcyclohexadienyl radical, especially when the cylohexadienyl radical has an ortho-substituent. Table 1.3 shows such variation of partial rate factor with temperature.

Thus the phenyldichlorocyclohexadienyl radical (V) was formed reversibly and was more liable to undergo dissociation than the phenylcyclohexadienyl radical (VI).



(V)



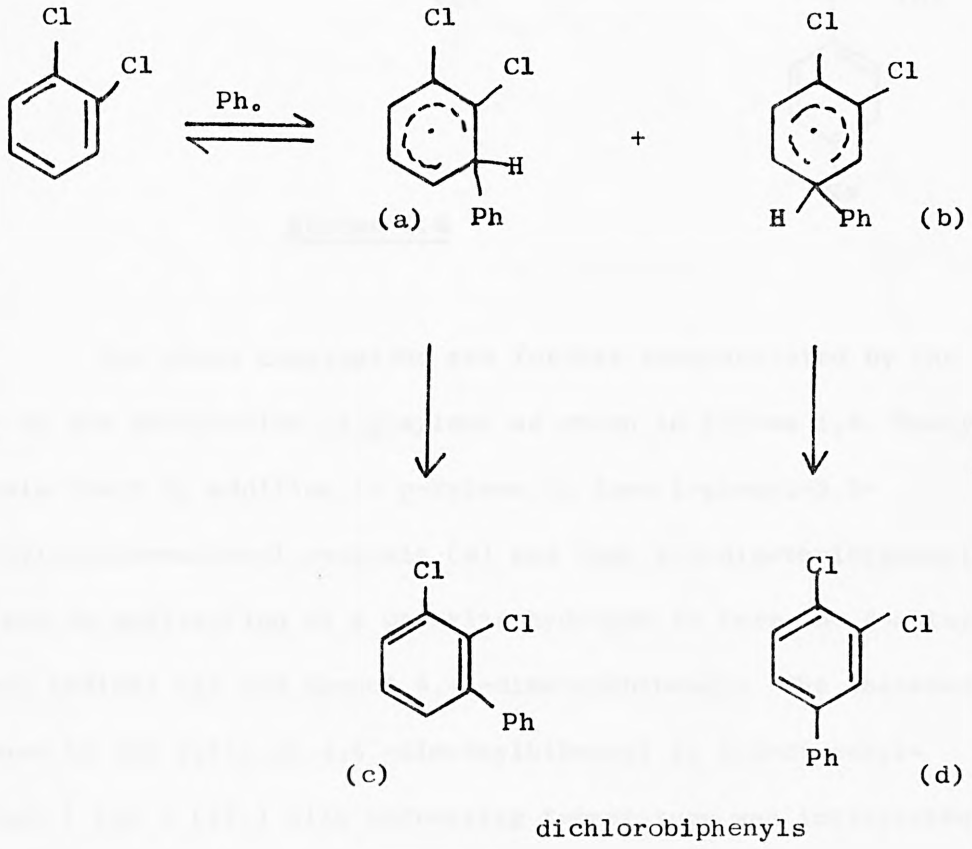
(VI)

Henriquez and Nonhebel also reported the o-dichlorobenzene on phenylation yielded 2,3- and 3,4-dichlorobiphenyls, with an increase in temperature. Scheme 1.3 represents the formation of 2,3- and 2,4-dichlorobiphenyls (structures (c) and (d)) which were formed through the corresponding isomeric phenyldichloro-cyclohexadienyl radicals (structures (a) and (b)) respectively. On steric ground, radical (a) was less stable than radical (b). Therefore there was an increase in the yield of the more thermo-dynamically stable product, namely 3,4-dichlorobiphenyl with an increase in temperature. Thus the ratio of 2,3-dichlorobiphenyl to 3,4-dichlorobiphenyl decreases with an increase in temperature due to the higher yields of the 3,4-dichlorobiphenyl isomer.

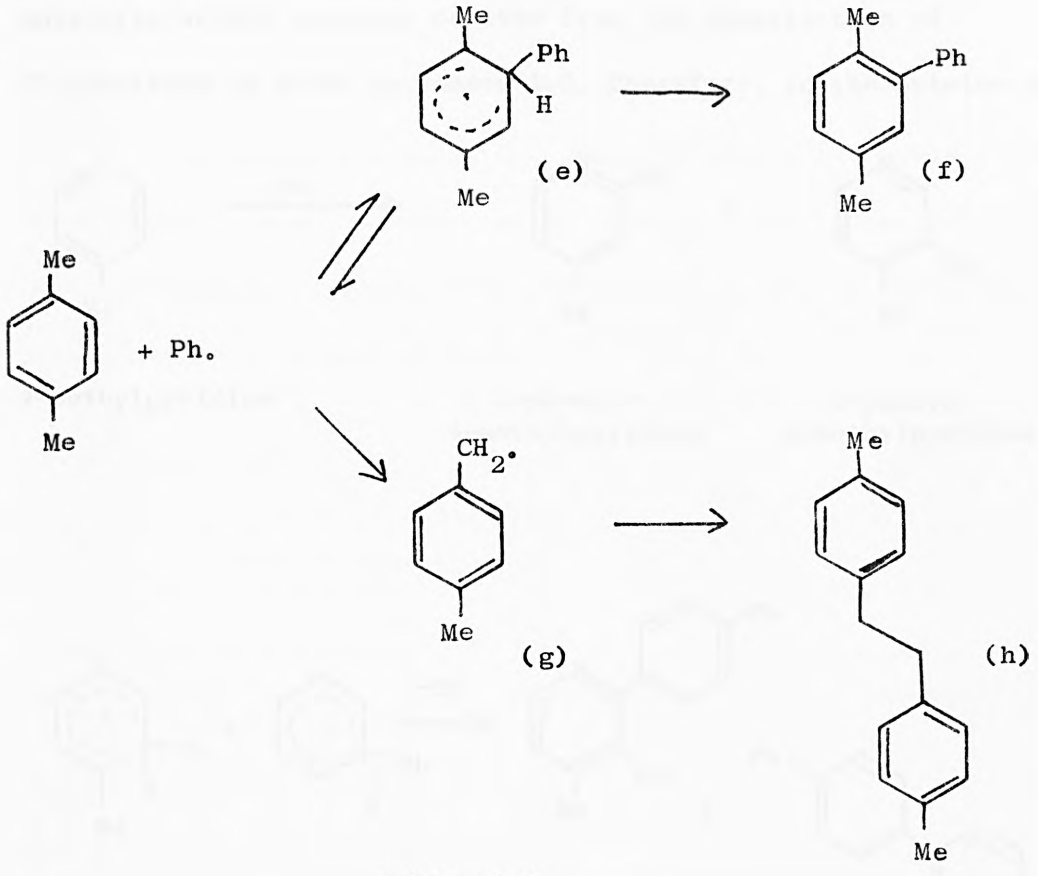
Particularly when the attacking radical enters ortho-to the substituent, then the formation of the σ-complex (phenyl-cyclohexadienyl radical) may be reversible. (41)

Table 1.3 Partial rate factors for the phenylation of p-dichlorobenzene

temperature (^{o}C)	partial rate factor
60	5.98
80	2.75
100	2.43



Scheme 1.3

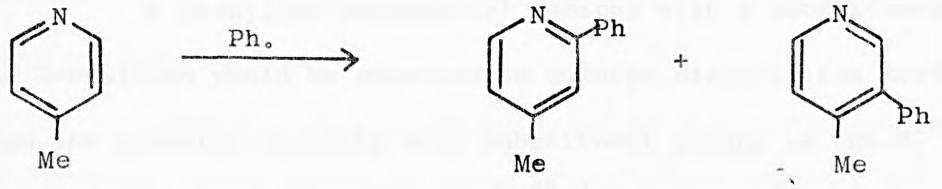


Scheme 1.4

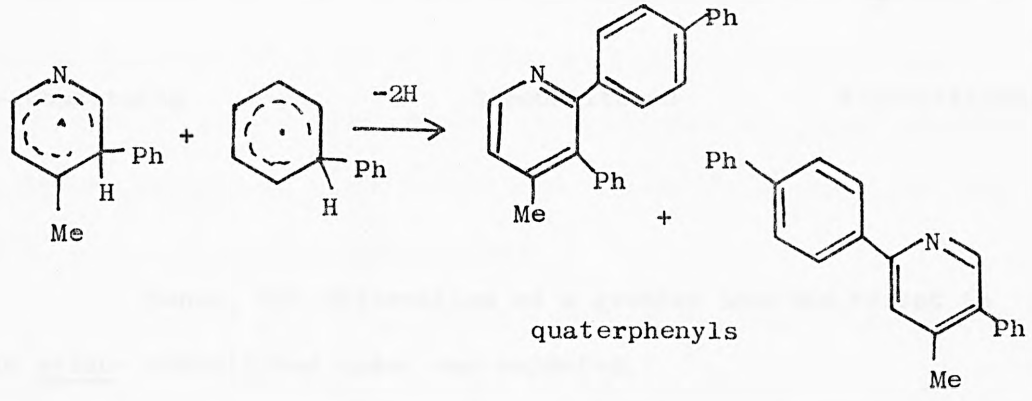
The above conclusions are further substantiated by the study of the phenylation of p-xylene as shown in Scheme 1.4. Phenyl radicals react by addition to p-xylene to form 1-phenyl-2,5-dimethylcyclohexadienyl radicals (e) and then 2,5-dimethylbiphenyl (f), and by abstraction of a benzylic hydrogen to form the 4-methylbenzyl radical (g) and thence 4,4'-dimethylbibenzyl. The observed increase in the ratio of 4,4'-dimethylbibenzyl to 2,5-dimethylbiphenyl ((h) : (f)) with increasing temperature was interpreted as indicating that the formation of the 1-phenyl-2,5-dimethylcyclohexadienyl radical (e) was reversible. (37)

Variations in isomer ratios and rate constants were also observed in the reaction of benzoyl peroxide with 4-methylpyridine in the presence of an oxidising agent. (43, 44) However, these

variations were interpreted as due to the formation of high molecular weight products derived from the dimerisation of σ-complexes as shown in Scheme 1.5. Therefore, in the opinion of



4-methylpyridine — 2-phenyl-4-methylpyridine — 3-phenyl-4-methylpyridine



quaterphenyls

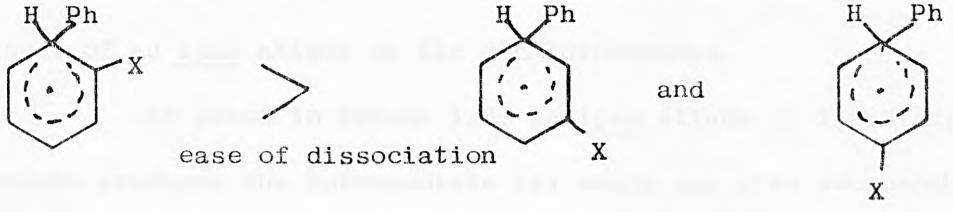
Scheme 1.5

Vidal et al [44] it was unnecessary to question the irreversibility of phenyl radical attack on aromatic substrates. Furthermore, the dimerisation of intermediate complexes explained the variation in isomer percentages in the case of 4-methylpyridine. Therefore, before deciding on the irreversibility of the attack by phenyl radicals on aromatic hydrocarbons, it is essential to ensure the absence of products of dissociation and dimerisation of the intermediate complexes, which is known to occur in heteroaromatic (4-methylpyridine) and aromatic (benzene) systems. [44]

Further indication of the reversibility of the formation of the σ-complex was received from the presence of a definite

kinetic isotope effect in the phenylation of chloro- and nitro-benzenes.[45] Also, the isotope effect was found to be the greatest for the formation of ortho-substituted products.

A phenylcyclohexadienyl radical with a substituent in the 2-position would be expected to undergo dissociation more readily than the isomeric radicals with substituent groups in the 3- and 4-positions due to steric effects,[45] thus :-



2-substituted 3-substituted 4-substituted

Hence, the observation of a greater isotope effect in the ortho- substituted cases was expected.

1.5 HOMOLYTIC AROMATIC IPSO SUBSTITUTION

Homolytic aromatic ipso substitution appears to be a general process at least in heteroaromatic systems.[46, 47] Also, some examples of substitution by phenyl radicals at the ipso position of a substituted benzene ring have been reported.[50, 51] Investigations have shown[52] the significance of ipso attack in some electrophilic nitrations of disubstituted benzenes.[53]

Similarly, there is increasing evidence of the importance and occurrence of an ipso attack in free radical aromatic substitution reactions.[54] In general, the ipso intermediate

leads to the loss of the original substituent or to a substitution product by ortho- or meta- migration of the attacking radical or substituent as shown in the following examples (it should be noted that reference 54 refers to meta- migration but does not give any specific examples) :-

Consider the photobromination of 1,2-dichlorobenzene. [55] An unusually large amount of ortho-substitution products and extensive halogen rearrangement products were observed and interpreted as the result of an ipso attack on the dichlorobenzene.

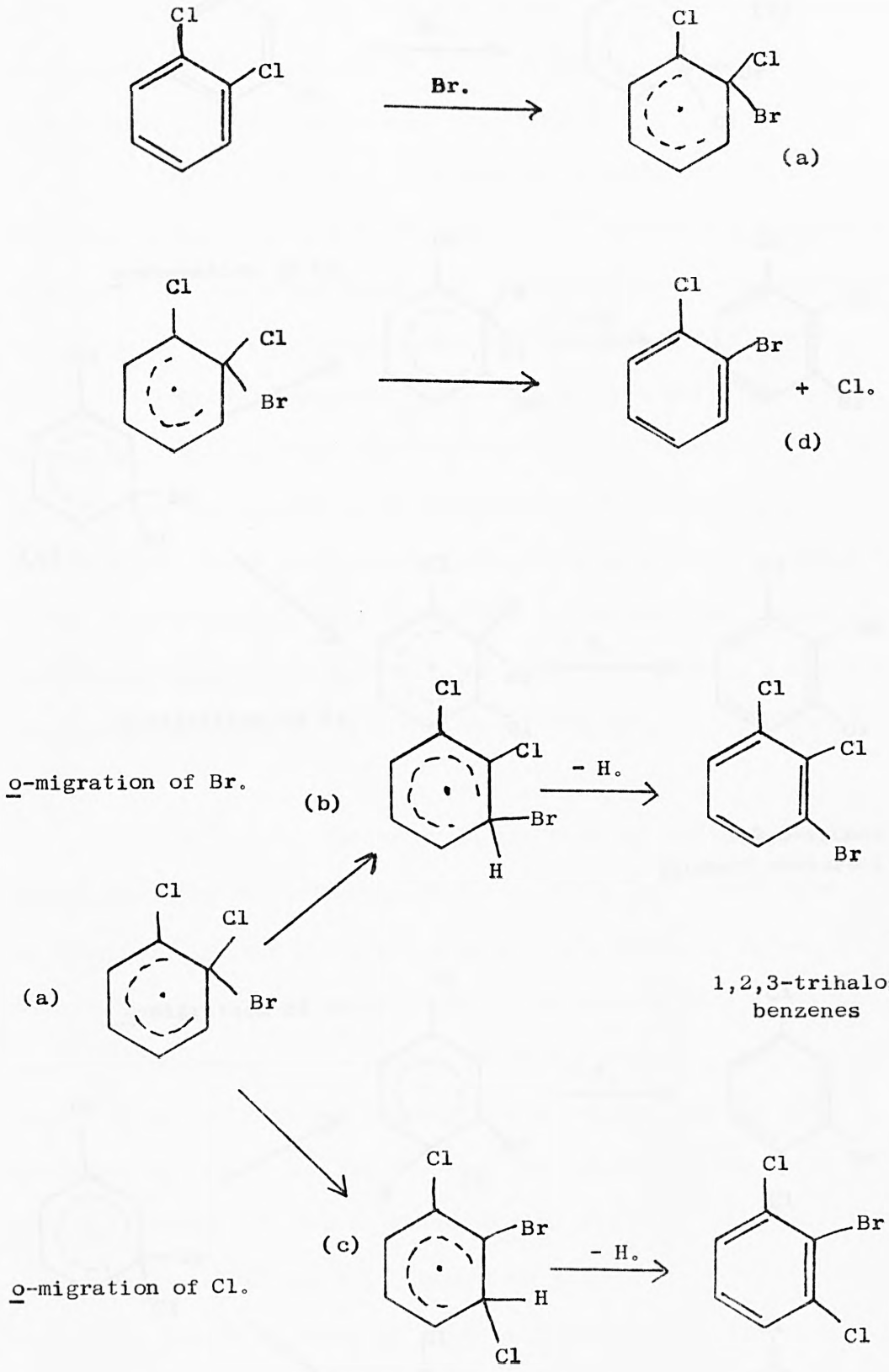
As shown in Scheme 1.6, an ipso attack on 1,2-dichlorobenzene produces the intermediate (a) which can give 2-bromochlorobenzene (d) with the loss of a chlorine radical. However, the intermediate (a) can also undergo rearrangement by ortho- migration of either halogen to yield structures (b) and (c), which, by loss of H. give 1,2,3-trihalogenobenzene. [56]

In the ipso attack of 1,3-dichlorobenzene (Scheme 1.7), ortho- migration of either halogen in the intermediate (e) can occur either of two directions giving 1,2,3- isomers and 1,2,4- isomers.

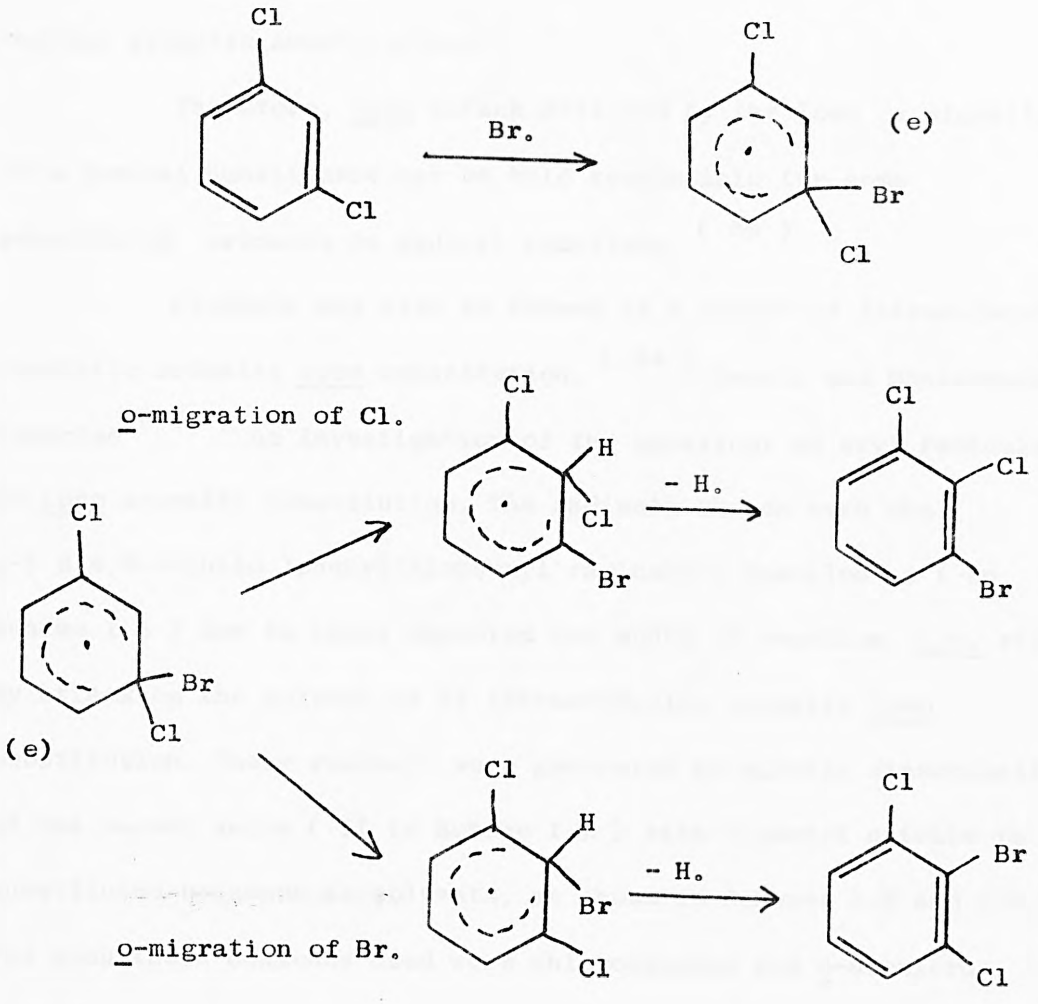
It can therefore be seen that the rearrangement products are particularly relevant to an ipso mechanism.

Apart from several halogen exchanges, [57, 58] free radical replacements of halogen by hydrogen [59] has also been observed.

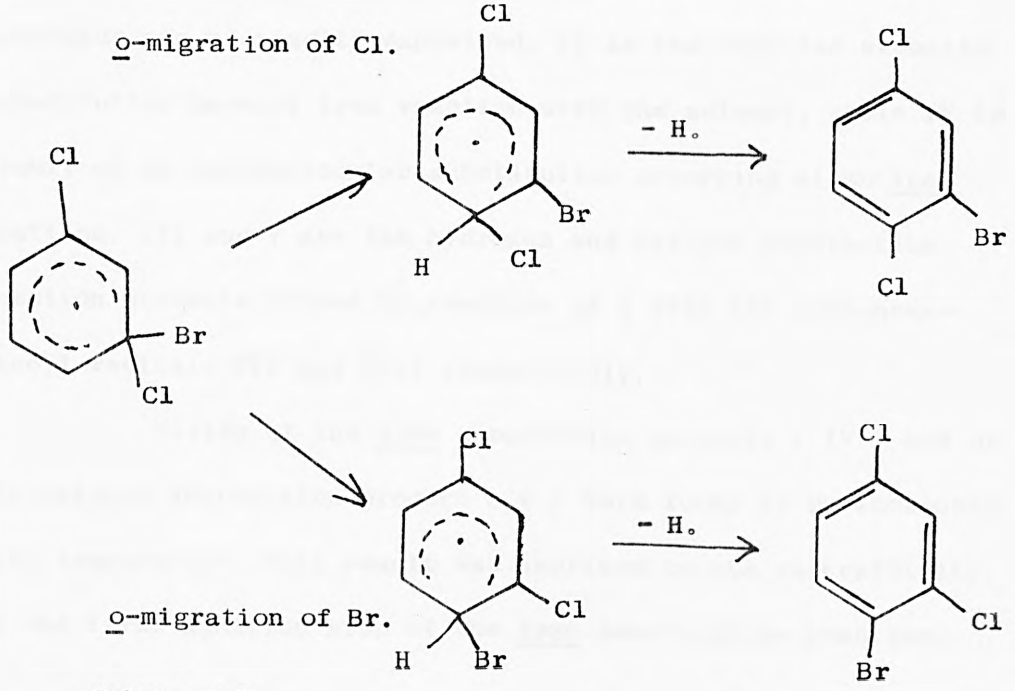
The presence of halogen in the benzene ring deactivates all the positions toward electrophilic attack. However, the ipso position is actually less deactivated than the other positions. [135] There is no reason to expect the ipso position to be unfavourable for radical reactions as electronic effects of substituents affect rates or product distribution negligibly [61, 62] in the free


Cl
Cl
Br.
Cl
Cl
Br
(a)
Cl
Cl
Br
Cl
Br
+ Cl.
(d)
o-migration of Br.
(b)
Cl
Cl
Br
H
- H.
Cl
Cl
Br
1,2,3-trihalogeno-benzenes
(a)
Cl
Cl
Br
o-migration of Cl.
(c)
Cl
Br
H
Cl
- H.
Cl
Br
Cl

Scheme 1.6



1,2,3-isomer
product mixture (above)



Scheme 1.7

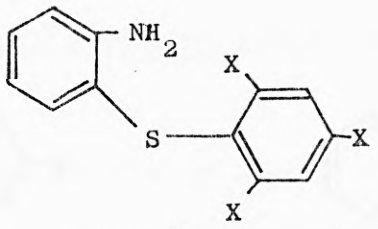
radical aromatic substitutions.

Therefore, ipso attack followed by the loss or migration of a geminal substituent can be held responsible for some substituted products in radical reactions. (59)

Products may also be formed as a result of intramolecular homolytic aromatic ipso substitution. (54) Benati and Montevecchi reported (63) an investigation of the behaviour of aryl radicals in ipso aromatic substitution. The radicals chosen were the o-(2,4,6-trihalo)phenylthiophenyl radicals (labelled as I in Scheme 1.8) due to their expected two modes of reaction, i.e. either by attack on the solvent or by intramolecular aromatic ipso substitution. These radicals were generated by aprotic diazotisation of the parent amine (II in Scheme 1.8) with n-pentyl nitrite in substituted benzenes as solvents, as shown in Schemes 1.8 and 1.9. (64) The subsituted benzenes used were chlorobenzene and o-dichlorobenzene.

Analysis of the reaction mixtures by column chromatography afforded the following products, which were identified by spectral data and elemental analysis. Formation of these compounds can be readily explained. VI is the expected aromatic substitution product from reaction with the solvent, while IV is the result of an intramolecular substitution occurring at an ipso position. III and V are the hydrogen and halogen abstraction reaction products formed by reaction of I with the cyclohexadienyl radicals VII and VIII respectively.

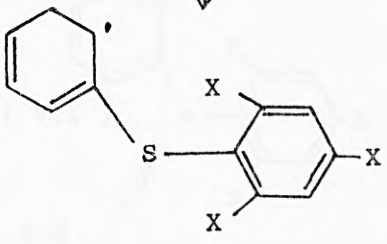
Yields of the ipso subsitution products (IV) and of the halogen abstraction product (V) were found to be increased with temperature. This result was ascribed to the reversibility of the first addition step of the ipso substitution reaction.



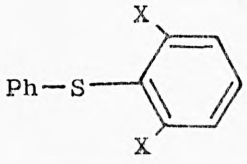
(II)

Ar-H

Ar = Ph, PhCl, $PhCl_2$

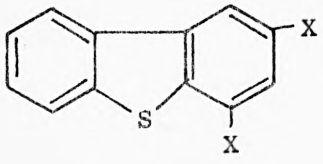


(I)



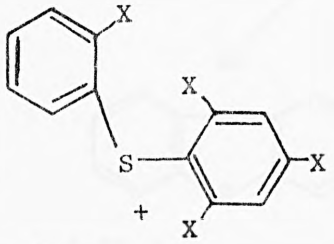
X (III) 2,4,6-trihalodiphenylsulphide
hydrogen abstraction product

+

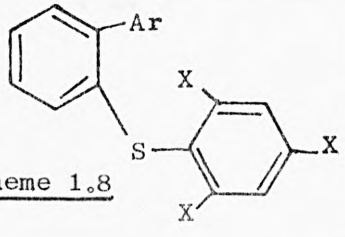


(IV) 2,4-dihalodibenzothiophen
intramolecular ipso substitution
product

+

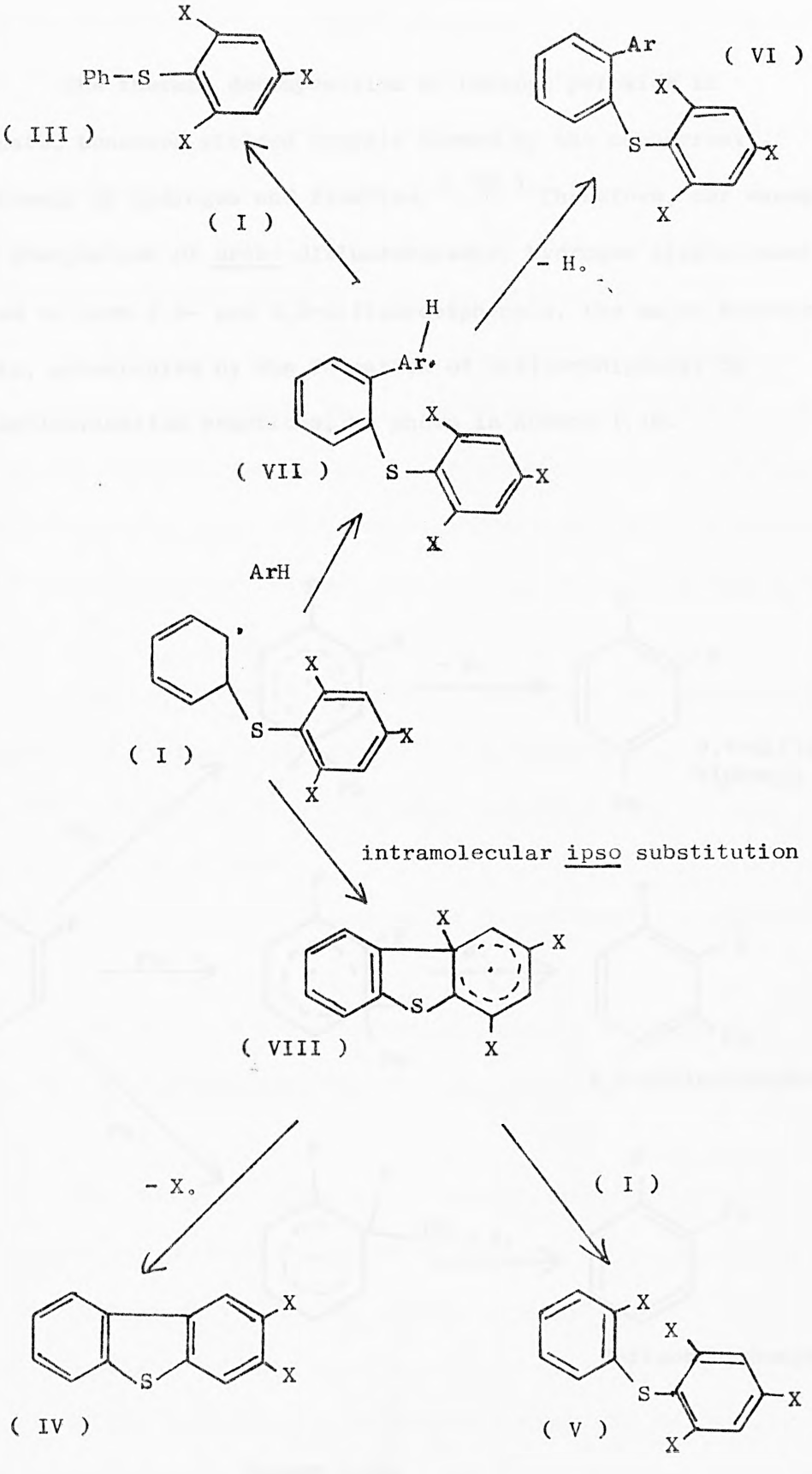


(V) 2,2',4,6-tetrahalodiphenylsulphide
halogen extraction product



(VI) 2,4,6-trihalo-2'-aryldiphenyl-
sulphide
aromatic substitution product

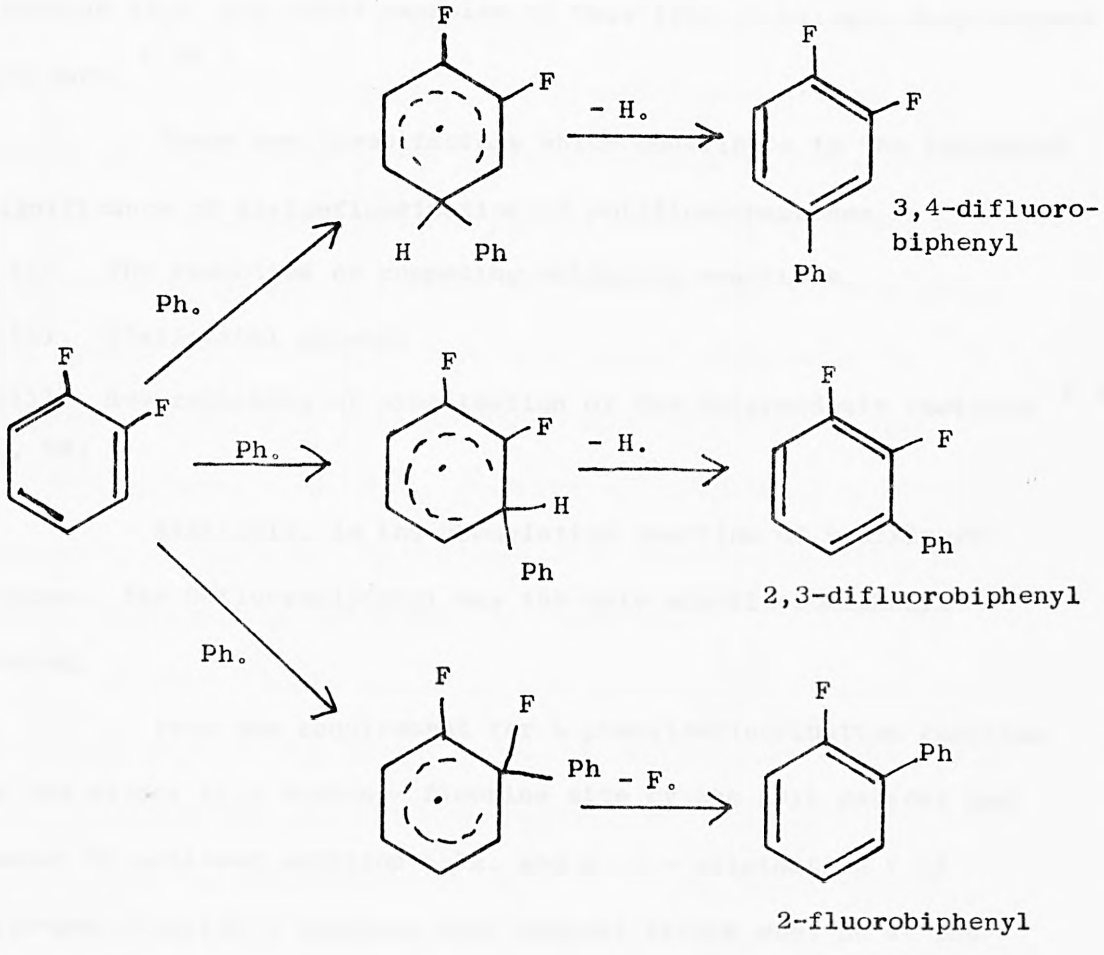
Scheme 1.8


X
Ph—S
X
X
(III)
(I)
Ar
(VI)
X
S
X
X
- H.
H
Ar.
(VII)
S
X
X
X
ArH
(I)
X
S
X
X
intramolecular ipso substitution
X
X
S
(VIII)
X
- X.
(I)
X
S
X
(IV)
X
X
S
X
X
(V)

Scheme 1.9

1.6 PHENYLATION REACTIONS OF FLUORINATED BENZENES

The thermal decomposition of benzoyl peroxide in fluorinated benzenes yielded biaryls formed by the concurrent displacement of hydrogen and fluorine.[65] Therefore, for example, in the phenylation of ortho-difluorobenzene, hydrogen displacement occurred to form 3,4- and 2,3-difluorobiphenyls, the major reaction products, accompanied by the formation of 2-fluorobiphenyl by phenyldefluorination reactions, as shown in Scheme 1.10.



Scheme 1.10

Phenyldefluorination was found to occur in all the phenylation reactions of the polyfluoroarenes. However, it was dominant only in the case of 1,2,3,4-tetra- and pentafluorobenzenes. (65) Thus it appears that phenyldefluorination becomes a more significant reaction as the number of fluorine atoms in the benzene ring increases, presumably due to the statistical factor involved i.e. more available fluorine sites as compared to hydrogen.

R. Bolton et al (66, 67) have proposed a mechanism for the fluorine displacement in the phenyldefluorination reactions. The proposed mechanism for fluorine displacement involves hydrogen bonding between the aroic acid formed concomitantly and the expelled fluorine atom. Any other examples of this type of halogen displacement are rare. (65)

There are three factors which contribute to the increased significance of aryldefluorination of polyfluorobenzenes :-

(i) The reduction of competing oxidation reactions.

(ii) Statistical grounds

(iii) Reversibility of dimerisation of the intermediate radicals. (48, 68, 69)

Similarly, in the phenylation reaction of m-difluorobenzene, the 3-fluorobiphenyl was the only monofluorobiphenyl formed.

Thus the requirement for a phenyldefluorination reaction is the attack at a carbon - fluorine site by the aryl radical and cannot be achieved addition (Ph. and H.) - elimination (of hydrogen fluoride) sequence when radical attack must be at the carbon - hydrogen position. In the polyfluorobenzene, hydrogen radical uptake can be excluded due to the ease with which the radical can undergo reactions of dimerisation or oxidation even in hydrogen rich reaction mixtures. (65)

The yields of biaryl obtained by the phenylation of the isomeric di-, tri- and tetrafluorobenzenes along with experimental isomer ratios have been tabulated. (65)

In the phenylation reaction of hexafluorobenzene, the pentafluorobiphenyl yield could be increased by pyrolysis of the high boiling residues, (68) when dimerisation and disproportionation reactions of the σ-complexes occurred. However, this type of secondary decomposition was precluded from reactions of the polyfluoroarenes where the yields of biaryl can be taken to reflect the extent of phenylation of each substance. (65)

Phenyldehydrofluorination (elimination of hydrogen fluoride) as defined by Bolton et al (65) was found not to occur, thus for example in the phenylation of o-difluorobenzene, the 2-fluorobiphenyl found in the reaction products is not contaminated with any other isomeric fluorobiphenyl. Hence, as described by these workers, phenyldefluorination reactions must involve attack at a carbon site bearing fluorine and cannot arise from the addition - elimination sequence where an aryl radical attacks a carbon - hydrogen site. Thus, the take up of hydrogen in such systems is excluded due to the ease with which the radicals may undergo dimerisation and oxidation reactions.

Biaryl yield can be held to reflect the relative extents of primary phenylation in each case and partial rate factors have been determined for phenyldehydrogenation and phenyldefluorination reactions of the polyfluorobenzenes. (65) The observed partial rate factors for the relative rates of phenylation of fluorobenzene and benzene can be successfully used in predicting the relative rates of attack of polyfluorobenzenes at hydrogen bearing sites. (65) However, partial rate factors for phenyldefluorination are

considerably inaccurate in their predictions and an empirical factor of 0.27 was incorporated in the case of the di- and trifluorobenzenes. This factor indicates the great difficulty of aryldefluorination in comparison to aryldehydrogenation. As the number of fluorine atoms increases in the benzene ring, the greater the difference between calculated and experimental partial rate factors. (65)

The complications which may arise when there are contributions due to the formation of complexes (13) between substrates in competition and radicals (or their precursors) will be discussed in section 1.10 of this introduction. These effects are clearly visible in pentafluorobenzene (70) and in the arylation of derivatives of pentafluorobenzene, (66, 67) causing the failure of the additivity principle.

The relative rates of phenyldefluorination and phenyldehydrogenation in a molecule are governed by two factors. The first one indicates the reactivity of the aromatic site to phenyl radical attack and the second one involves the relative yields of each biaryl from the relevant radical intermediate. (65)

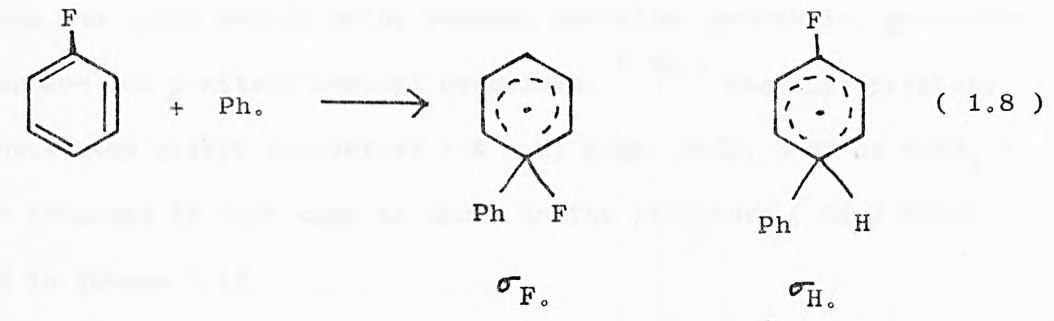
The relative rates of formation of these biaryls determine their yields and are dependent on the following factors :-

(i) The individual rate constants (k_H, k_F) of aromatisation.

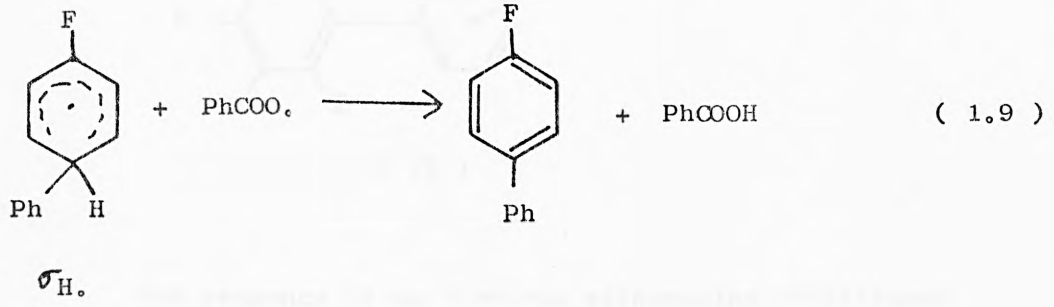
(ii) The relative concentrations of the two radical intermediates σ_H. and σ_F. (see Scheme 1.11).

(iii) The concentration of the aromatising reagents.

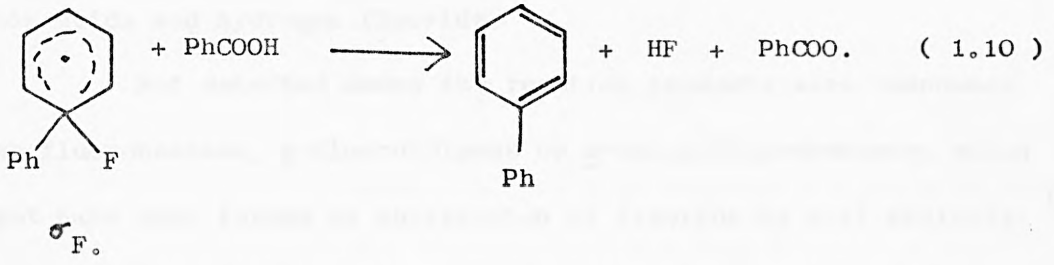
Consider the phenylation of fluorobenzene as shown in Scheme 1.11, with the phenyl radical attack at C-H and C-F sites. The benzoic acid formed (equation (1.9)) is the necessary reagent in the defluorination of the σ_F. intermediate in equation (1.10). A decrease in the amount of benzoic acid formed must



$\sigma_{F.}$ $\sigma_{H.}$ (1.8)



$\sigma_{H.}$ (1.9)



$\sigma_{F.}$ (1.10)

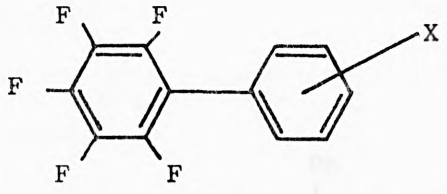
Scheme 1.11

cause a corresponding decrease in the extent to which defluorination can compete with dimerisation as the pathway of the σ-intermediate. (65)

1.7 ARYLATION OF HEXAFLUOROBENZENE

The thermal decomposition of aroyl peroxides in hexafluorobenzene (48, 67) yielded the appropriately substituted pentafluorobiphenyl as the major product (70) with the homolytic substitution

of fluorine. The arylation reactions were carried out in sealed tubes and under reflux using benzoyl peroxide, m-methyl-, m-chloro-, m-bromo- and p-nitro- benzoyl peroxides. (48) The appropriately substituted biaryl derivative (X = H, 3-Me, 3-Cl, 3-Br or 4-NO_2) was obtained in each case as shown in the structure (IX) below and in Scheme 1.12.



(IX)

The presence of an electron withdrawing substituent such as Cl-, Br- or -NO_2 decreased the yield of the biaryl.

Some of the by-products consisted of benzene derivatives, aroic acids and hydrogen fluoride.

Not detected among the reaction products were compounds like fluorobenzene, m-fluorotoluene or m-chlorofluorobenzene, which might have been formed by abstraction of fluorine by aryl radicals. (48)

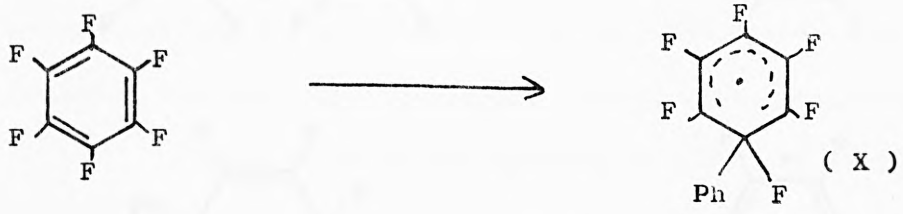
The biaryl yield increased after distillation of the total reaction products, indicating that some pentafluorobiphenyl was being formed by secondary reactions. These secondary reactions during the distillation of reaction products probably involved the breakdown of substituted dimers such as fluorinated biphenyls and quaterphenyls as shown in Scheme 1.13. (2, 71)

Thus, biaryl (2,3,4,5,6-pentafluorobiphenyl) may be formed in reactions (1.14), (1.16) and (1.17) in Scheme 1.12, and it can be seen that reactions (1.11) and (1.12) show the formation of the aryl radicals whilst in equation (1.13) the complex (X) is formed.

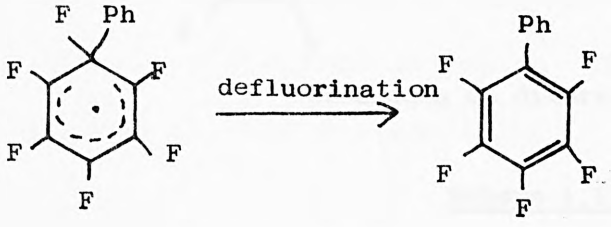
$PhCOO - OOCPh \longrightarrow 2\ PhCOO\cdot$ (1.11)

$2\ PhCOO\cdot \longrightarrow 2\ Ph\cdot + 2\ CO_2$ (1.12)

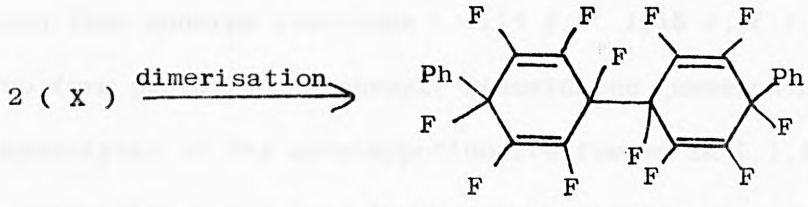
$C_6F_6 + Ph\cdot \longrightarrow PhC_6F_6\cdot$ ($\sigma_{F\cdot}$) (1.13)



(X)

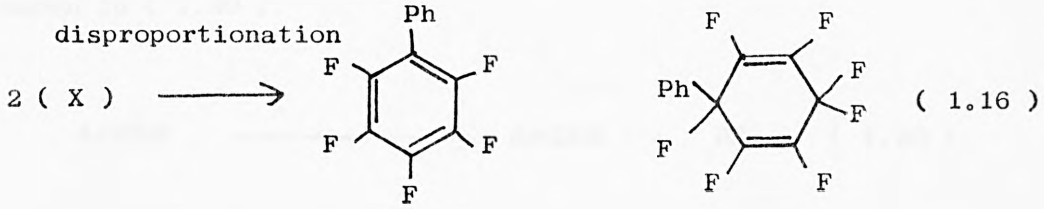


+ F· (1.14)



(XI) (1.15)

(plus 2,2' and 2,4' isomers and stereoisomers)

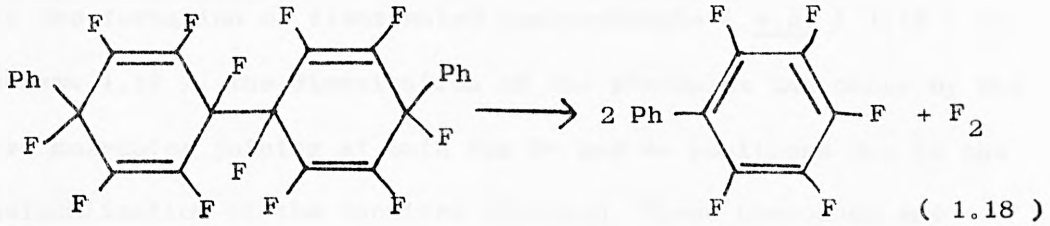


(1.16)

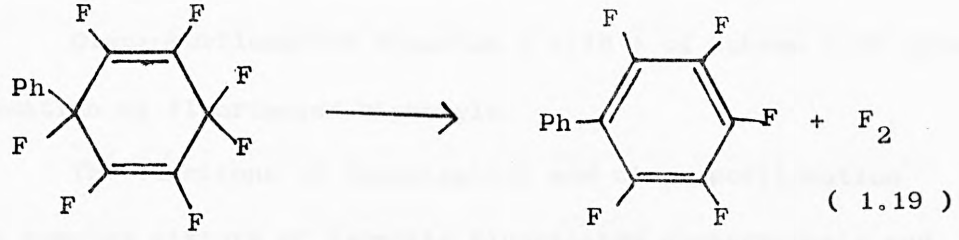
(X) + $PhCOO\cdot \longrightarrow C_6F_5\text{-}C_6H_5 + PhCOOF$ (1.17)

Scheme 1.12

(XI)



(1.18)



(1.19)

breakdown of dimers of σ-complexes

Scheme 1.13

The σ-complex or hexafluorophenylcyclohexadienyl radical can then undergo reactions (1.14), (1.15), (1.16) and (1.17) to form pentafluorobiphenyl, fluorinated quaterphenyls and biphenyls. Hydrolysis of the aroylhypofluorite formed in (1.17) would yield aroic acids and eventually hydrogen fluoride would be formed, as shown in (1.20).

$$ArCOOF \longrightarrow ArCOOH + HF \qquad (1.20)$$

If Z-H represents a hydrogen donor, such as water, which may be present, the following reactions show the formation of aroic acids and benzene derivatives. (48)

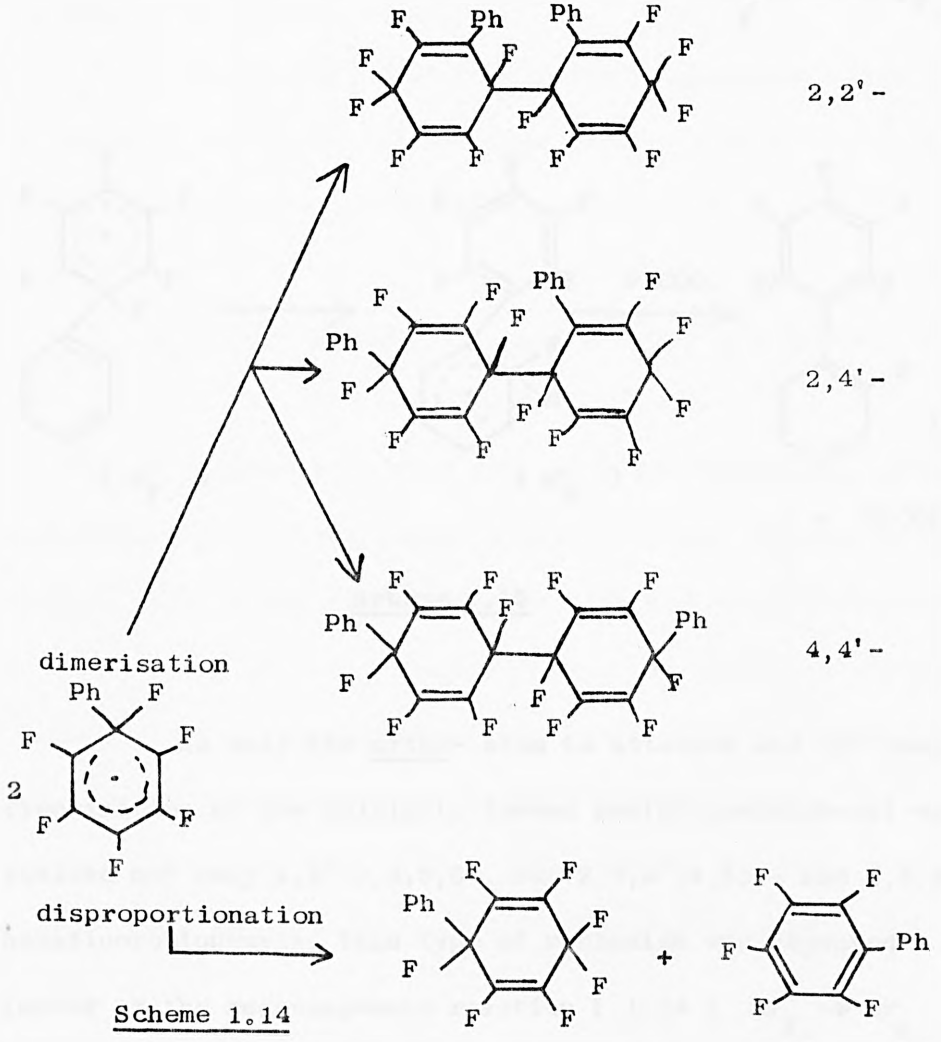
$$Ph\cdot + Z\text{-}H \longrightarrow Ph\text{-}H + Z\cdot \qquad (1.21)$$

$$PhCOO\cdot + Z\text{-}H \longrightarrow PhCOOH + Z\cdot \qquad (1.22)$$

Dimerisation of the phenylcyclohexadienyl radical leads to the formation of fluorinated quaterphenyls (e.g. (1.15) in Scheme 1.12). The dimerisation of the σ-complex can occur by the two molecules joining at both the 2- and 4- positions due to the delocalisation of the unpaired electron. These compounds may comprise any high boiling residues formed in the reaction.

Disproportionation equation (1.16) of Scheme 1.12 shows the formation of fluorinated biphenyls.

The reactions of dimerisation and disproportionation yield a complex mixture of isomeric fluorinated quaterphenyls and biphenyls as shown in Scheme 1.14.

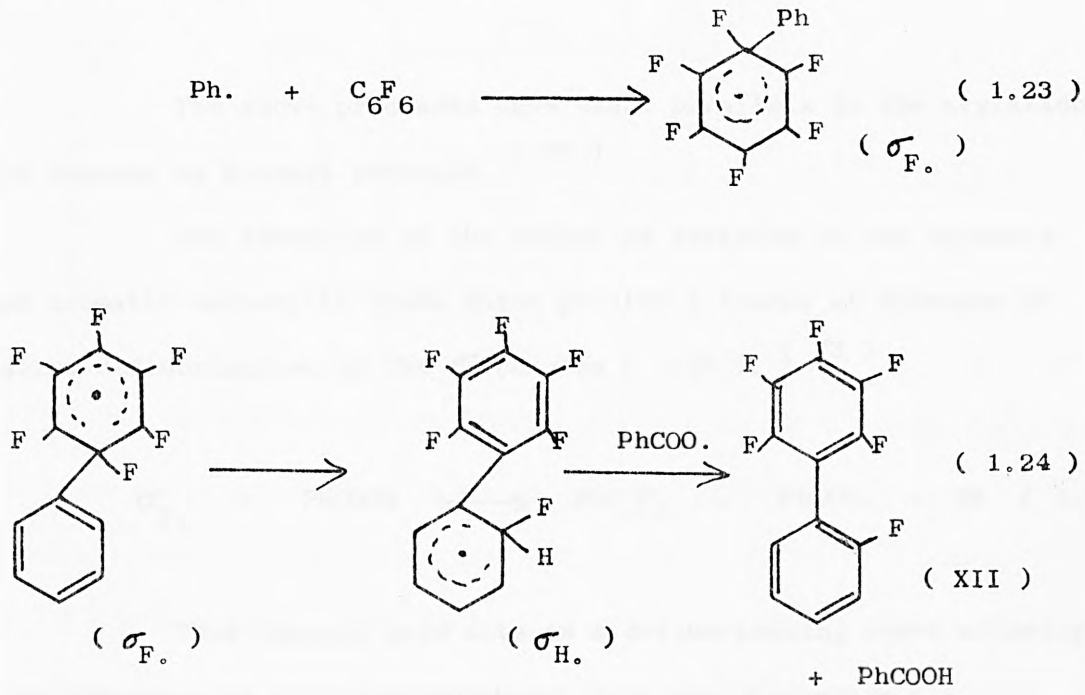


Scheme 1.14

Furthermore, it has been found that in the phenylation of hexafluorobenzene an induced decomposition process occurs alongside the homolysis of the peroxide oxygen-oxygen bond. (72)

Products associated with the occurrence of induced decomposition are 2,2',3,4,5,6-hexafluorobiphenyl (XII), (73) benzoic acid and hydrogen fluoride. However, 2,3,4,5,6-pentafluorobiphenyl is the main arylation product at all concentrations of peroxide. (72)

The above products could form from the reaction between benzoyl peroxide and the rearrangement product ($\sigma_{H.}$) of the initially formed complex ($\sigma_{F.}$) as shown in Scheme 1.15.



Scheme 1.15

As only the ortho- atom is attacked and the homolytic fluorination at the initially formed pentafluorobiphenyl would have yielded not only 2,2',3,4,5,6-, but 2,3,3',4,5,6- and 2,3,4,4',5,6-hexafluorobiphenyls, this type of mechanism was rejected (72) in favour of the rearrangement reaction (1.24) $\sigma_{F.} \rightarrow \sigma_{H.}$

The induced decomposition of the peroxide can occur by the σ-complex ($\sigma_{F.}$) and by its rearrangement product ($\sigma_{H.}$) as shown in Scheme 1.16 :-

$$\sigma_{F.} \longrightarrow \sigma_{H.}$$

$$\sigma_{F.} + (PhCOO)_2 / BzO. \longrightarrow \sigma_{F.}\text{-OOCPh} + PhCOO.$$

$$\sigma_{F.}\text{-OBz} + BzO.$$

(Bz = PhCO-)

$$\sigma_{H.} + (PhCOO)_2 / BzO. \longrightarrow \underline{o}\text{-F-Ph-}C_6F_5 + PhCOOH + PhCOO.$$

Scheme 1.16

The above processes have exact parallels in the arylation of benzene by benzoyl peroxide. (67)

The formation of the biaryl is assisted by the presence of aromatic carboxylic acids which provide a source of hydrogen to allow defluorination of the σ-complex (1.25). (73)

$$\sigma_{F.} + PhCOOH \longrightarrow PhC_6F_5 + PhCOO. + HF \quad (1.25)$$

Thus benzoic acid acts as a defluorinating agent allowing the formation of pentafluorobiphenyl from the σ-complex i.e. benzoic acid is the essential source of hydrogen in the defluorination process (74) of the σ-complex $\sigma_{F.}$. The amount of hydrogen fluoride evolved was also increased when the decompositions were carried out in the presence of added aromatic acids. (73) Some benzoic acid is formed in the rearrangement reaction of $\sigma_{F.}$ which leads to the formation of 2,2',3,4,5,6-hexafluorobiphenyl $\sigma_{H.}$.

$$\sigma_{F.} \longrightarrow \sigma_{H.} + BzOH \quad (1.26)$$

The benzoic acid may then cause the defluorination of another $\sigma_{F\cdot}$ radical (1.25). The benzoyloxy radicals may decarboxylate to yield phenyl radicals and eventually $\sigma_{F\cdot}$, add to hexafluorobenzene to yield a new radical intermediate $\sigma_{F'\cdot}$ or undergo radical - radical addition as shown in (1.28), (1.29) and (1.30) of Scheme 1.17.

$$PhCOO\cdot \longrightarrow Ph\cdot + CO_2 \qquad (1.27)$$

$$C_6F_6 + Ph\cdot \longrightarrow \sigma_{F\cdot} \qquad (1.28)$$

$$C_6F_6 + PhCOO\cdot \longrightarrow \left[PhCOO\text{-}C_6F_6\right]\cdot \; \sigma_{F'\cdot} \qquad (1.29)$$

$$PhCOO\cdot + \sigma_{F\cdot} \longrightarrow \sigma_{F\cdot}\text{-}OOCPh \qquad (1.30)$$

Scheme 1.17

The formation of tertiary esters (1.30) allows benzoic acid to be regenerated by means of transesterification with hydrogen fluoride as shown in (1.31) and (1.32). [66] Benzoic acid can thus be returned to the defluorination point whilst the process is limited by the presence of tertiary esters to provide benzoic acid or of the $\sigma_{F\cdot}$ radicals to be defluorinated.

$$\sigma_{F'}\text{-}\sigma_{F'} \quad (PhCOO\text{-}C_6F_6)_2 + 2\,HF \longrightarrow C_{12}F_{14} + 2\,PhCOOH \qquad (1.31)$$

$$PhC_6F_6\text{-}OOCPh + HF \longrightarrow PhC_6F_7 + PhCOOH \qquad (1.32)$$

On the addition of p-fluorobenzoic acid [75] to the thermal decomposition of benzoyl peroxide in hexafluorobenzene, the yields of pentafluorobiphenyl were greatly increased (1.33). No 2,2'3,4,5,6-hexafluorobiphenyl could be found although 2,3,4,4',5,6-hexafluorobiphenyl was present in quantities proportional to the amount of added p-fluorobenzoic acid. This suggests the formation of p-fluorophenyl radicals arising from p-fluorobenzoic acid (1.34).

$$\sigma_{F\cdot} + \text{p-F-C}_6\text{H}_4\text{-COOH} \longrightarrow \text{PhC}_6\text{F}_5 + \text{HF} + \text{p-F-C}_6\text{H}_4\text{COO}\cdot \quad (1.33)$$

$$\text{p-F-C}_6\text{H}_4\text{-COO}\cdot \longrightarrow \text{p-F-C}_6\text{H}_4\cdot + \text{CO}_2 \quad (1.34)$$

The pentafluorobiphenyl arises mainly from the defluorination of the radical intermediate and not through the decomposition of adducts (1.34).

The phenylation of hexafluorobenzene is summarised in Scheme 1.18.

1.7.1 FLUORINATED TERPHENYLS

The thermal decomposition of benzoyl peroxide in hexafluorobenzene gave the corresponding biaryls and mass spectrometry of the residues showed evidence of biphenylyl radicals derived from the arylation of the peroxide or of aroic acids. [76] Fluorinated terphenyls were also found and it was shown that arylation of binuclear species was not the main source of terphenyls. The arylation of benzoyl peroxide would only become significant in concentrated solutions where the ratio of solvent to peroxide was

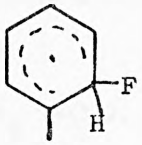
initiation :

$PhCOO\text{-}OCPh \longrightarrow 2\ PhCOO\cdot$

$PhCOO\cdot + C_6F_6 \longrightarrow \left[PhCOO\text{-}C_6F_6\right]\cdot = \sigma_{F'\cdot}$

$PhCOO\cdot \longrightarrow Ph\cdot + CO_2$

$Ph\cdot + C_6F_6 \longrightarrow \left[Ph\text{-}C_6F_6\right]\cdot = \sigma_{F\cdot}$

$\sigma_{F\cdot} \xrightarrow{\text{rearrange}}$  $= \sigma_{H\cdot}$

C_6F_5

induced decomposition :

$\sigma_{H\cdot} + BzO\cdot\ (Bz_2O_2) \longrightarrow \underline{o}\text{-}F\text{-}C_6H_4\text{-}Ph + BzOH + BzO\cdot$

$\sigma_{F\cdot} + BzO\cdot\ (Bz_2O_2) \longrightarrow \sigma_{F\cdot}\text{-}OBz + BzO\cdot$

defluorination :

$\sigma_{F\cdot} + BzOH \longrightarrow Ph\text{-}C_6F_5 + HF + BzO\cdot$

termination :

$2\ \sigma_{F\cdot}\ (2\ \sigma_{F'\cdot}) \longrightarrow (\sigma_F)_2\ (\sigma_{F'})_2$

$\sigma_{F\cdot}\ (\sigma_{F'\cdot}) + Ph\cdot \longrightarrow \sigma_F\text{-}Ph\ (\sigma_{F'}\text{-}Ph)$

$\sigma_{F\cdot}\ (\sigma_{F'\cdot}) + BzO\cdot \longrightarrow \sigma_F\text{-}OBz\ (\sigma_{F'}\text{-}OBz)$

transesterification :

$(\sigma_{F'})_2 + 2\ HF \longrightarrow C_{12}F_{14} + 2\ BzOH$

$\sigma_F\text{-}OBz + HF \longrightarrow \sigma_F\text{-}F + BzOH$

$\sigma_{F'}\text{-}OBz + HF \longrightarrow \sigma_{F'}\text{-}F + BzOH$

Scheme 1.18

small, or when the solvent was unusually inert.

The initial arylation of benzoyl peroxide or benzoic acid can yield biphenylyl radicals which would undergo reactions parallel to the aryl radicals.

$$PhCOOH + Ph\cdot \longrightarrow Ph\text{-}(C_6H_4)\text{-}COOH \qquad (1.35)$$

$$Ph\text{-}(C_6H_4)\text{-}COOH \longrightarrow Ph\text{-}(C_6H_4)\text{-}COO\cdot \longrightarrow Ph\text{-}C_6H_4\cdot \qquad (1.36)$$

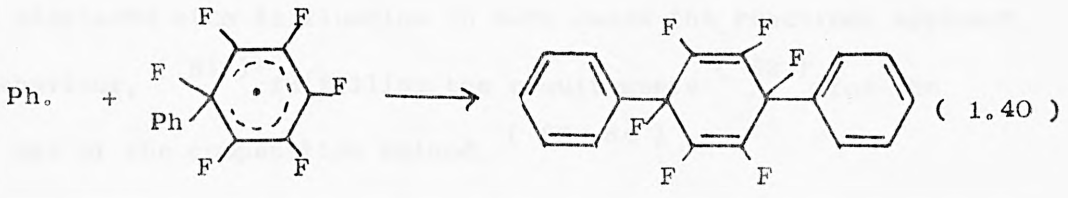
$$Ph\text{-}C_6H_4\cdot + C_6F_6 \longrightarrow Ph\text{-}C_6H_4\text{-}C_6F_6\cdot \qquad (1.37)$$

$$Ph\text{-}C_6H_4\text{-}C_6F_6\cdot \xrightarrow{-F\cdot} Ph\text{-}C_6H_4\text{-}C_6F_5 \qquad (1.38)$$

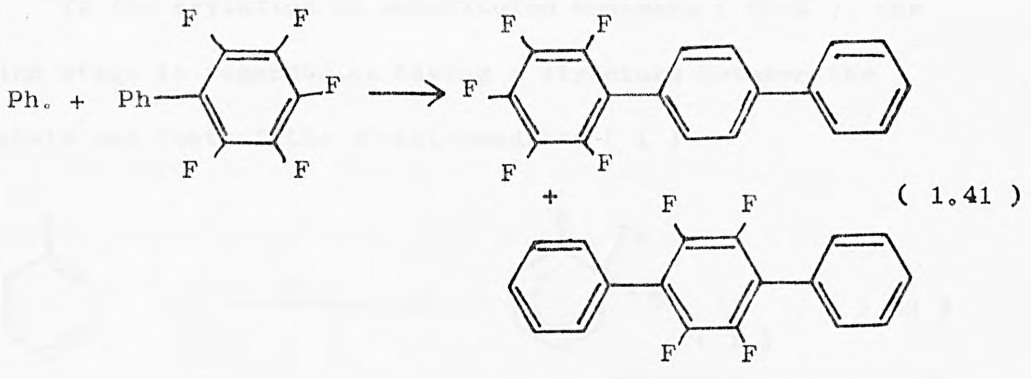
Scheme 1.19

Fluorinated terphenyls may also be formed by radical-radical combination reactions (1.39), (1.40) or by the arylation of biaryl (1.41). (76)

$$C_6F_6\text{-}Ph\cdot + Ph\cdot \longrightarrow Ph\text{-}C_6F_6\text{-}Ph \qquad (1.39)$$



(1.40)



(1.41)

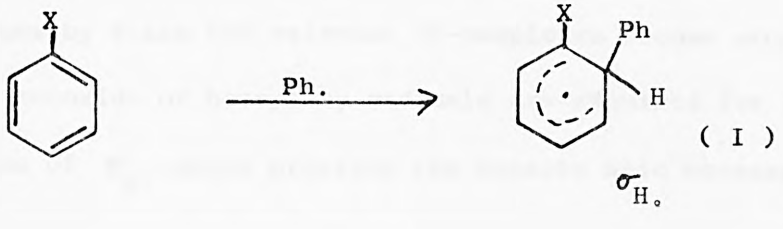
The arylation of pentafluorobiphenyl (1.41) would give 2,3,4,5,6-pentafluoroterphenyl and tetrafluoroterphenyl depending on the displacement of hydrogen or fluorine.

1.8 PHENYLATION OF PENTAFLUOROBENZENE, BROMOPENTAFLUOROBENZENE AND OCTOFLUOROTOLUENE

Homolytic phenylation reactions of the title compounds were carried out using hexafluorobenzene as the reference compound. (77) The thermolysis of benzoyl peroxide in hexafluorobenzene (48, 78) yields 2,3,4,5,6-pentafluorobiphenyl in considerable yields despite the energy differences involved in displacing fluorine and not hydrogen, whilst the pentafluorophenyl analogues behave similarly. Thus, bromopentafluorobenzene yields the three isomeric bromotetrafluorobiphenyls, (79) and the mechanism of this reaction involving the displacement of fluorine has been discussed. (66, 67) This mechanism is different from that proposed for the phenylation of benzene. (80)

As hexafluorobenzene was used as the reference compound and the displaced atom is fluorine in both cases the reactions approach ideal behaviour, (81) fulfilling the requirements (82) for the correct use of the competition method. (83, 84)

In the arylation of substituted benzenes (Ph-X), the transition stage is regarded as having a structure between the ground state and that of the σ-intermediate (I)



(1.42)

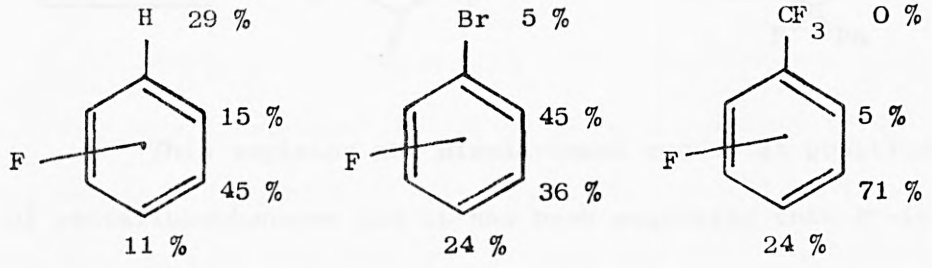
(I)

$\sigma_{H.}$

It has been found that partial bonding occurs between the incoming radical and the attacked carbon atom with the delocalisation of electrons through the ring and substituents. (77) In polyfluoroaromatic systems (C_6F_5-X), a choice is available in structures using either fluorine or -X as the substituents for delocalisation unlike the (C_6H_5-X) systems where hydrogen cannot participate in this manner. This could then account for different isomer distribution patterns found in the arylation of (C_6F_5-X) as compared to (C_6H_5-X) systems, where the ortho- position is the most activated site.

Yields of isomeric biaryls obtained in the phenylation of pentafluorobenzene, bromopentafluorobenzene and octafluorotoluene by the thermolysis of benzoyl peroxide in these solvents are shown in Figure 1.2

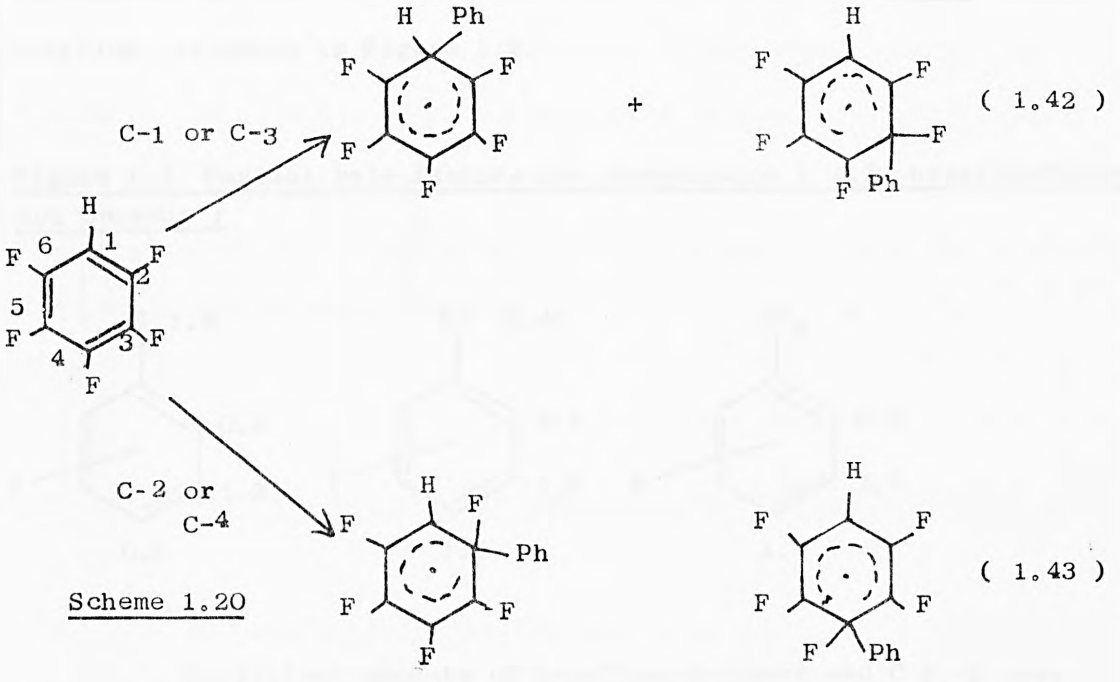
Figure 1.2 Yields of isomeric biaryls from the phenylation reaction



In the arylation of pentafluorobenzene, hydrogen is displaced more readily than fluorine, reflecting the various mechanisms by which the relevant σ-complexes become aromatic again. Benzoyl peroxide or bezoyloxy radicals are required for the oxidation of σ_H. which provides the benzoic acid necessary for the

defluorination of σ_F. and an essential requirement for the latter reaction. (66)

In pentafluorobenzene the σ-complex obtained by phenyl radical attack at C-1 or C-3 sites can be stabilised by resonance contributions from three fluorine atoms and can therefore be more readily formed than those complexes arising from attack at C-2 or C-4 positions where only 2 fluorine substituents may take part in the resonance structures (1.42), (1.43), (77) see Scheme 1.20.



Scheme 1.20

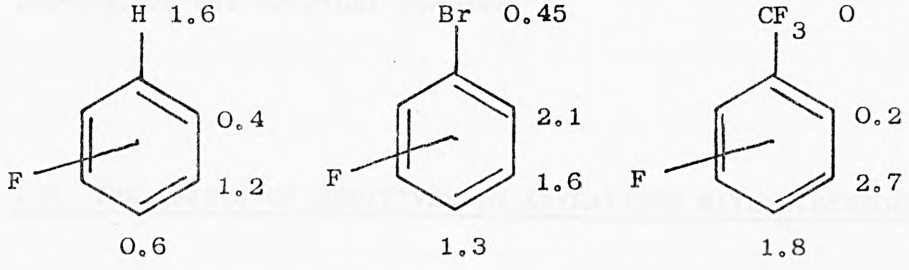
This explains why displacement occurs at positions 1 and 3 of pentafluorobenzene and it has been suggested that σ-intermediates are better stabilised by ortho- substituents than by para substituents as the C-4 position is flanked by two ortho- atoms whilst the C-2 position has only one ortho- fluorine atom.

A similar effect was observed in the phenylation of octafluorotoluene with an additional steric effect further lowering the reactivity at the C-2 site. The C-3 position (meta) in octafluorotoluene

is the most reactive site for reasons similar to those of pentafluorobenzene. Thus the relative reactivities of positions C-3 and C-4 in pentafluorobenzene and octafluorotoluene systems arises from the presence of three fluorine substituents contributing to the stability of the resulting σ-intermediate.

All positions of attack in bromopentafluorobenzene by phenyl radicals yield a σ-intermediate which may be stabilised by three fluorine atoms. It also appears that from the phenylation yields, bromine is more effective than fluorine in the ortho-position, as shown in Figure 1.2.

Figure 1.3 Partial rate factors for phenylation (c.f. hexafluorobenzene not benzene)



Equivalent amounts of hexafluorobenzene and C_6F_5-X were used in competition reactions which yielded relative rates of attack. On combining these results with the isomer ratios, it is possible to calculate partial rate factors in which the rate of attack at one position in C_6F_5-X is compared with that of attack at a position in hexafluorobenzene. The high values for the partial rate factor for the C-2 position in pentafluorobenzene, bromopentafluorobenzene and octafluorotoluene (see Figure 1.3) were considered to be a reflection of the stabilisation by substituents as described above. (77)

Similarly, the deactivation of C-3 in pentafluorobenzene

can be readily explained, however it is difficult to explain the activation of this site in bromopentafluorobenzene and octafluorotoluene.

It appears that although the relative rates of attack in one molecule can be explained, the relative rates of attack between different molecules are more difficult to explain. (77)

These results indicate that the entity responsible for distinguishing between different molecules (intermolecular) is different from the entity responsible for the intramolecular selection.

Thus the apparent activation of the meta- position in C_6F_5-X systems results from the formation of complexes of different stabilities between the phenyl radical precursor and the aromatic substrates such that eventually a phenyl radical attacks the aromatic portion of the original complex. (77)

1.9 THE EFFECT OF ADDITIVES IN ARYLATIONS WITH DIBENZOYL PEROXIDE

The use of homolytic arylation as a synthetic method would be enhanced if the dimerisation reactions of the intermediate σ-complexes could be prevented or reduced.

A high yield of biaryl has been achieved by the use of various catalytic additives, notably gaseous oxygen, (85, 7) quinol, (78) copper II salts, (2, 86) iron salts, (13) nitro- and nitroso-compounds (87, 88) and transition metal salts. (86) In each case the σ-complex is efficiently oxidised to biaryls before diverting dimerisation or diproportionation reactions can occur. (89) Therefore the addition of additives causes the biaryl

formation to be maximised, with Cu(II) and Fe(III) benzoates being the most efficient [13] and causing near theoretical yields of biaryl and aroic acid to form.

Any partial rate factors measured under such conditions would be free from any uncertainties arising from the selective removal of σ-complexes by side reactions e.g. dimerisation.

It was found (within the ranges investigated) that the concentration of the additive had little effect on biaryl yields and very small amounts of copper II benzoate were extremely effective, causing biaryl yields to approach theoretical maximum. [13]

1.9.1 OXYGEN

Oxygen acts by abstracting hydrogen with the generation of a hydroperoxy radical. [85] Investigation of the influence of oxygen on phenylation reactions showed that although the biaryl yields are affected, the isomer distribution of the products remained the same. That is, the relative rates of phenylation at different positions in a substrate are not dependent on diversionary reactions of the σ-complexes.

1.9.2 NITRO-COMPOUNDS

The mechanism of the action of nitro-compounds is less certain. They may be reduced to the corresponding nitroso-compound which could scavenge phenyl radicals to generate a nitroxide. The nitroxide could dehydrogenate the phenylcyclohexadienyl radicals

as shown in Scheme 1.21. (91)

$$PhNO_2 \longrightarrow PhNO \qquad (1.44)$$

$$PhNO + Ph\cdot \longrightarrow Ph_2NO\cdot \qquad (1.45)$$

$$[Ph\text{-}PhH]\cdot + Ph_2NO\cdot \longrightarrow Ph_2 + Ph_2NOH \qquad (1.46)$$

$$Ph_2NOH + (PhCOO)_2 \longrightarrow Ph_2NO\cdot + PhCOOH + PhCOO\cdot \qquad (1.47)$$

Scheme 1.21

1.9.3 METAL AROATES

D. H. Hey et al suggested (86) that in the thermal decomposition of benzoyl peroxide in benzene, the resonance stabilised σ-complex may be oxidised by the paramagnetic divalent copper as shown in Scheme 1.22

$$(PhCOO)_2 + Cu(I) \longrightarrow PhCOOCu(II) + PhCOO\cdot \qquad (1.48)$$

$$PhCOO\cdot \longrightarrow Ph\cdot + CO_2 \qquad (1.49)$$

$$Ph\cdot + Ph\text{-}H \longrightarrow [Ph\text{-}PhH]\cdot \qquad (1.50)$$

$$[Ph\text{-}PhH]\cdot + PhCOOCu(II) \longrightarrow Ph_2 + PhCOOH + Cu(I) \qquad (1.51)$$

Scheme 1.22

However, a different mechanism was proposed by Williams et al where they considered the reaction with copper II salts proceeded by an oxidation and proton loss from the σ-complex. (13)

Therefore the addition of copper II salts affects the conversion of the σ-radical to the corresponding cation, which loses a proton to yield the biaryl (92) as shown in Scheme 1.23.

$$\left[\text{Ph-PhH}\right]^{\bullet} + \text{Cu(II)} \longrightarrow \left[\text{Ph-PhH}\right]^{+} + \text{Cu(I)} \quad (1.52)$$

$$\left[\text{Ph-PhH}\right]^{+} \longrightarrow \text{Ph}_2 + \text{H}^{+} \quad (1.53)$$

$$(\text{PhCOO})_2 + \text{Cu(I)} \longrightarrow \text{PhCOOCu(II)} + \text{PhCOO}\bullet \quad (1.54)$$

Scheme 1.23

Similarly, the mechanism for the action of iron III benzoate is shown in Scheme 1.24 with Fe(III) being regenerated in (1.56) in its higher valency state. This is required as the amount of metal salt equimolar with the peroxide is not required to yield near theoretical amounts of biaryl and benzoic acid.

$$\left[\text{Ph-ArH}\right]^{\bullet} + \text{Fe(III)} \longrightarrow \text{PhAr} + \text{H}^{+} + \text{Fe(II)} \quad (1.55)$$

$$\text{PhCOO}\bullet + \text{Fe(II)} \longrightarrow \text{PhCOO}^{-} + \text{Fe(III)} \quad (1.56)$$

$$\text{PhCOO}^{-} + \text{H}^{+} \longrightarrow \text{PhCOOH} \quad (1.57)$$

Scheme 1.24

Scheme 1.24 explains the effect of iron benzoate and was consistent with observed kinetics.[13] Therefore the dimerisation reaction of the σ-complexes can be minimised and suppressed by the addition of certain additives which promote the oxidation of the σ-complex by chain transfer reactions and use the dimerisation reaction as the main chain termination process.[13]

Dihydrobiphenyls are formed in the arylation reactions in the absence of additives by the disproportionation of the σ-complexes, as shown in equations (1.58) and (1.59). These dihydrobiphenyls can undergo oxidation by additives to form the biaryls after the completion of the thermal decomposition of the benzoyl peroxide. However, this is not an efficient method to increase

biaryl yields. (13)

$$2\left[ArAr'H\right]^{\cdot} \longrightarrow ArAr' + ArAr'H_2 \quad (1.58)$$

$$ArAR'H_2 \longrightarrow ArAr' + H_2 \quad (1.59)$$

However, the most efficient and convenient addities were found to be the transition metal salts, in particular Cu(II) and Fe(III) benzoates. (13) The latter were more soluble in aromatic substrates, however a deposition of a form of Fe(III) benzoate occurred during the reaction. Many of the reactions of metal salts were not homogeneous, thus ruling out accurate kinetic investigation.

The catalytic effect of Fe(III) benzoate was found to be proportional to its concentration up to a maximum. Metal salts other than the aroates were less effective and unadvantageous.

An example of the influence of copper salts on thermal decomposition reactions is provided by the reaction of benzoyl peroxide in benzene. (86) The major products without additive would be biphenyl and benzoic acid in yields of below 50 % along wih high boiling polymeric material. The higher boiling products are formed by dimerisation of the intermediate σ-complex. However, the yield of biphenyl can be increased to about 80 % by effecting the efficient, rapid oxidation of the phenylcyclohexadienyl radical by an additive.

Further results of yields of products of reactions with benzoyl peroxide with benzene in the presence of various additives exist in the literature. (2, 86)

Another example of the effect of an oxidising agent's presence in a phenylation reaction is provided by the reaction with p-dichlorobenzene. (42) Thus the addition of copper benzoate

Table 1.4 Partial rate factors for the phenylation of p-dichlorobenzene

temperature	partial rate factor (no additive)	partial rate factor in presence of copper benzoate
80 °C	2.60	4.13
100 °C	2.43	2.62

It should be noted that these figures are derived from reference 42 whereas those for the phenylation of p-dichlorobenzene quoted in Table 1.2 are derived from a separate investigation, reference 13

increases the biaryl yields and hence the partial rate factors as shown in Table 1.4. It can be seen that in the phenylation of p-dichlorobenzene at 80 °C, the partial rate factor increased from 2.60 in the absence of additive to 4.13 in the presence of copper benzoate. (42) This implies that the copper benzoate interacted with the two different σ-complexes (i.e. one from benzene and one from p-dichlorobenzene) by differing extents.

1.10 THE ELIMINATION OF POSSIBLE COMPLICATIONS IN THE MEASUREMENT OF PARTIAL RATE FACTORS FOR PHENYLATION

The thermolysis of aroyl peroxides in aromatic substrates has been used for the synthesis of biaryls and for the measurement of partial rate factors. (2, 93) However, biaryl yields can be low due to the formation of resinous products consisting of mixtures of isomeric tetrahydroquaterphenyls arising from σ-complex dimerisation reactions, (1.60 and (1.61) in Scheme 1.24.

$$Ar\cdot + Ar'H \longrightarrow [Ar\text{-}Ar'H]\cdot \qquad (1.60)$$

$$2\,[Ar\text{-}Ar'H]\cdot \longrightarrow \text{dimers} \qquad (1.61)$$

$$[Ar\text{-}Ar'H]\cdot + (ArCOO)_2 \longrightarrow Ar\text{-}Ar' + ArCOOH + ArCOO\cdot \qquad (1.62)$$

$$[Ar\text{-}Ar'H]\cdot + ArCOO\cdot \longrightarrow Ar\text{-}Ar' + ArCOOH \qquad (1.63)$$

Scheme 1.24

In these reactions (e.g. Ar'H = PhH, Ph-R, Ph-F) only a small proportion of the σ-complexes give biaryls by chain transfer reactions as shown in (1.63). However, with some substrates (e.g. Ar'H = Ph-Br, $Ph\text{-}NO_2$) the dimerisation reaction (1.61)

occurs to a much smaller extent, whilst chain transfer processes are the main reactions producing biaryls in higher yields with residue formation being minimised. Partial rate factors obtained in reactions where the σ-complex undergoes a chain transfer type reaction are less likely to have possible errors arising from the different rates of dimerisation and hence selective removal of σ-complexes leading to biaryls. (13)

Furthermore, the dimerisation reaction of the σ-complexes can be reduced or suppressed by the addition of small amounts of certain catalytic additives which promote the oxidation of the σ-complex by chain transfer reactions and use the dimerisation reaction as the main chain termination reaction.

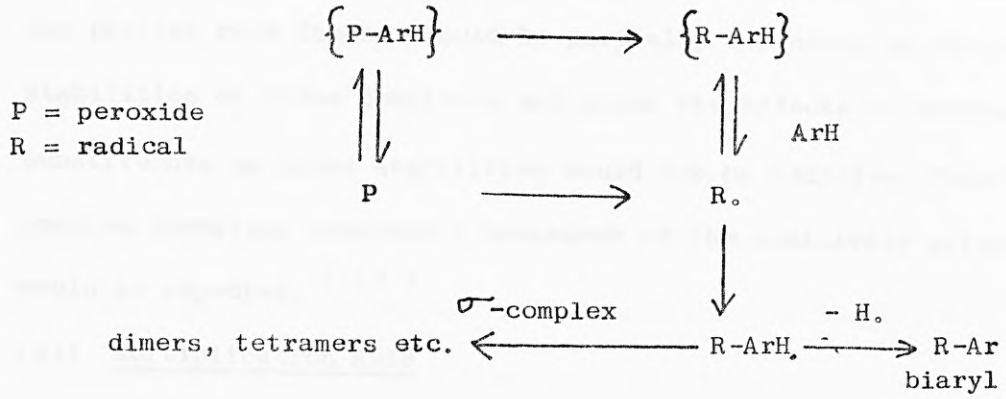
Accurate results for partial rate factors for phenylation have been collected in two reviews. (2, 7) There are two possible complexities which can occur in the measurement of partial rate factors. (13) :-

Problem 1

This refers to the possibility of intermediate σ-complexes being diverted by different amounts in varying side reactions. The chief side reaction is the dimerisation reaction which occurs on the combination of two σ-complexes. This can lead to significant errors in the values for rates of arylation, isomer distributions and derived from these two measurements, the partial rate factors.

Problem 2

This concerns the fact that radicals (or the relevant precursor) may form complexes which are of a greater stability than the radicals (or the precursors), with the aromatic substrates in a step which occurs before σ-complex formation (see Scheme 1.25).



Scheme 1.25

If this type of complex formation occurs then the intermolecular selection amongst different aromatic substrates by radicals will be affected by the relative stabilities of any complexes which may be formed. It will also be affected by the reactivities of the aromatic substrates in the addition of radicals to their nuclei thus yielding σ-complexes. However, intramolecular selection in an aromatic substrate (isomer distributions) would be affected to a much smaller degree.

This type of complex formation would be expected to occur only if a large difference in polarity existed between the substrate and radicals, as is found in the pentafluorophenylation (70) and phenylation of polyfluoroarenes. (67)

It was possible to check for this type of complex formation by applying the following three tests and noting any discrepancies (Problem 2). (13)

(i) Additivity Principle

As the partial rate factors reflect the activation energies of the reactions of the addition of free phenyl radicals to the different sites in the various substrates, then the effects of several substituents in a particular substrate on these activation

energies will be additive. Therefore, if complex formation occurred the partial rate factors would be partially dependent on the relative stabilities of these complexes and hence the effects of several substituents on these stabilities would not be additive. Thus if complex formation occurred a breakdown of the additivity principle would be expected. (13)

(ii) Multiplication Rule

$$k^{A}_{C} = k^{A}_{B} \times k^{B}_{C} \qquad (1.64)$$

Equation (1.64) shows the multiplication rule for the relative rates of phenylation of the pairs of A, B and C. If complex formation occurred, and the relative stabilities of these complexes were solvent dependent, this multiplication rule would be expected to break down. (13)

(iii) Relative Proportions of Competing Substrates

If complex formation occurred then relative rates measured would be expected to vary with relative proportions of competing substrates in the mixture, after having made corrections for unequal concentration of substrates. Such a variation would not be observed if phenyl radicals were free and selected freely between the substrates. (13)

These tests for complex formation were applied for the reactions of phenyl radicals and benzene, p-dichlorobenzene, 1,3,5-trichlorobenzene, bromobenzene, toluene and anisole. However, there was no evidence for the formation of complexes of the substrates and phenyl radicals or its precursor, which is in contrast to the results with polyfluorinated radicals and substrates. It was considered that this may be due to the small difference in polar character between phenyl radicals and these substrates, which was

not conducive to complex formation to a sufficient degree to have noticeable effects on the partial rate factors for phenylation of these substrates. (13)

Therefore the possibility that arenes form complexes with aryl radicals (or the precursors) as an essential part of the selection process between substrate molecules was not confirmed in studies of the application of the additivity principle, the multiplication rule and of the variation of relative concentration of the two competing aromatic substrates.

1.11 OBJECTIVES OF THE PRESENT STUDY

It can be seen from the preceding sections that in recent years, the homolytic phenylation reactions of several fluorinated benzenes have been extensively investigated under various conditions.

However, there seems to have been only limited investigation of chlorinated benzenes, particularly the higher chlorinated compounds. Considering the bond energy of the C-Cl bond of 79 kcal mol^{-1} compared with the C-F energy of 116 kcal mol^{-1} and the chlorine atomic radius of 0.99 A compared with a value of 0.64 A for fluorine, it is interesting to speculate whether analagous phenylation reactions occur in the chlorinated benzene systems.

Accordingly, the objective of this work is to study the phenylation reactions of chlorobenzene (Chapter Three), dichlorobenzenes (Chapter Four), trichlorobenzenes (Chapter Five), tetrachlorobenzenes (Chapter Six), pentachlorobenzene (Chapter Seven) and hexachlorobenzene (Chapter Eight) at 80 ^{o}C both in the absence and presence of various additives, which may or may not

promote high biaryl yield.

It is intended that these studies should include the identification of the products of the reactions, the yields of the products with relation to the amount of radical source used and the relative reactivities of the various reactive sites compared with one of the positions of benzene (partial rate factors or p.r.f.'s).

Since the most likely reaction products are the various chlorinated biphenyls, with the chlorine substituents on one ring, it is proposed to synthesise these compounds by methods which insure that their structure is unambiguous.

CHAPTER TWO

EXPERIMENTAL

2.1 LIST OF CHLORINATED BIPHENYLS TO BE SYNTHESISED

4-chlorobiphenyl

2-chlorobiphenyl

3-chlorobiphenyl

2,6-dichlorobiphenyl

2,4-dichlorobiphenyl

3,4-dichlorobiphenyl

2,3-dichlorobiphenyl

2,5-dichlorobiphenyl

3,5-dichlorobiphenyl

2,4,6-trichlorobiphenyl

2,3,4-trichlorobiphenyl

2,4,5-trichlorobiphenyl

2,3,5-trichlorobiphenyl

2,3,5-trichlorobiphenyl

2,3,6-trichlorobiphenyl

2,3,4,5-tetrachlorobiphenyl

2,3,5,6-tetrachlorobiphenyl

2,3,4,6-tetrachlorobiphenyl

2,3,4,5,6-pentachlorobiphenyl

2.1.1 PURIFICATION OF REAGENTS

Some chemicals were analytical reagent grade and were used without furhter purification unless specifically stated. The purity of the polychlorobenzenes was ascertained by gas-liquid chromatography (g.l.c.) which showed the absence of any significant impurity.

Benzene

AnalaR benzene was washed with concentrated sulphuric acid [14] until the washings were colourless, followed by washing with aqueous sodium hydrogen carbonate and finally with water. The benzene was then fractionally distilled and dried over sodium-lead alloy.

Dibenzoyl peroxide

Dibenzoyl peroxide was dissolved in chloroform and the upper aqueous layer removed. [14] To the filtered chloroform solution, methanol was added dropwise and the crystalline solid which separated out was filtered off. The dibenzoyl peroxide was then dried in a vacuum desiccator over calcium chloride and stored in the dark.(melting point 105 ^{o}C *cf* literature value 104 to 106 ^{o}C.)

2.2 GENERAL METHOD OF PREPARATION OF STANDARD POLYCHLOROBIPHENYLS

Small amounts of pure polychlorobiphenyls were required for identification of reaction products and for the determination of response factors for a flame ionisation detector. As very few of the required polychlorobiphenyls were available commercially, they had to be synthesised by various unambiguous methods. [94]

The general method used was a diazotisation reaction in

which the appropriately substituted polychloroaniline was diazotised with sodium nitrite. (95) The substitited diazonium salt underwent a replacement reaction, with the loss of nitrogen and subsequent substitution of a benzene ring to form the appropriately substituted polychlorobiphenyl. (96) The equations (2.1) and (2.2) show the formation of 2-chlorobiphenyl from 2-chloroaniline.

$$\underline{o}\text{-}C_6H_4\text{-}Cl.N^+H_3.Cl^- \xrightarrow{\text{sodium nitrite}} \left[\underline{o}\text{-}C_6H_4\text{-}Cl.N^+\equiv N\right] Cl^- \quad (2.1)$$

$$\left[\underline{o}\text{-}C_6H_4\text{-}Cl.N^+\equiv N\right] Cl^- + C_6H_6 \xrightarrow{\text{sodium acetate}} \underline{o}\text{-}C_6H_4\text{-}Cl.C_6H_5 + N_2 + HCl \quad (2.2)$$

In some cases, the substituted chloroaniline had to be synthesised, using the substituted polychlorobenzene as the starting material.

The appropriate polychlorobenzene (4 g.) was nitrated with fuming nitric acid (40 ml.) at 100 ^{o}C for 20 minutes, under conditions for mononitration. Occasionally, certain positions of the polychlorobenzene were blocked with a suitable group such that preferential nitration occurred. The solution was poured onto crushed ice and the solid was filtered off. After recrystallisation, the solid polychloronitrobenzene was dried and its melting point was determined. (All the yields reported in this chapter are based on the initial starting material unless specifically stated otherwise.)

The polychloronitrobenzene was then reduced to the appropriate polychloroaniline with hydrazine hydrate and palladium charcoal. (97) Reduction with iron filings and hydrochloric acid proved to be ineffectual. Before proceeding to diazotise the prepared polychloroaniline, an infra-red spectrum (98) of the sample was obtained to ascertain the required transformation of C-NO_2 to C-NH_2

Primary amine (literature) [99] :-

symmetrical stretch:	3250 to 3450 cm^{-1}
asymmetrical stretch:	3330 to 3550 cm^{-1}
observed from sample:	3470 cm^{-1}
	3360 cm^{-1}

2.3 PREPARATION OF MONOCHLOROBIPHENYLS

2.3.1 PREPARATION OF 2-CHLOROBIPHENYL BY THE DIAZOTISATION METHOD

Ortho-chloroaniline (7 g.) was dissolved or suspended in an aqueous solution of mineral acid. More acid was used than the two equivalents per mole of amine than are required to protonate the aniline and form nitrous acid from the sodium nitrite. The mixture of amine and acid was cooled in an ice-salt mixture to a temperature between 0 and 5 ^{o}C. A concentrated solution of sodium nitrite was added slowly, dropwise, at such a rate that the temperature did not rise above 5 to 10 ^{o}C. As there was some loss of nitrous acid (as nitric oxide and nitrogen dioxide) it was necessary to test the reaction mixture with starch / iodide paper to see when sufficient sodium nitrite had been added. [96]

The cold diazotised solution was filtered through glass wool into a round bottom flask containing cold benzene (250 ml.). This mixture was vigorously stirred and a solution of 5N sodium hydroxide was added dropwise whilst maintaining the temperature of the reaction mixture in the range 5 to 10 ^{o}C for one hour. The reaction mixture was left stirring for at least 24 hours and up to 48 hours at ambient temperature, when the reaction was complete.

The organic layer was separated from the aqueous layer.

The benzene fraction was washed with distilled water three times and then dried with magnesium sulphate. Any excess of benzene in the organic layer was removed by distillation at atmospheric pressure, yielding a dark orange / yellow coloured viscous oil. The desired 2-dichlorobiphenyl was separated from the tarry oil by column chromatography. (96)

A three foot glass column was first filled with activated alumina and fitted with a dropping funnel containing petroleum ether (boiling range 60 - 80 ^{o}C, 500 ml.) as eluant. The tarry oil was dissolved in a minimum quantity of benzene and then introduced on to the column. Several fractions of the eluant were collected until a test run of the eluant on an alumina thin layer chromatography (t.l.c.) plate showed under ultra-violet light that the eluant contained no other compounds.

The different fractions of eluant containing 2-chlorobiphenyl were concentrated and any solids that crystallised were collected, recrystallised from ethanol and identified by melting point determination, elemental analysis (carbon, hydrogen and chlorine content) and g.l.c. retention times. (35 % yield, melting point 30 ^{o}C *cf* literature value 32 ^{o}C. Calculated analysis for

$C_{12}H_9Cl$: C = 77.21 %, H = 4.83 %, Cl = 19.03 %

found : C = 76.82 %, H = 4.30 %, Cl = 18.89 %)

2.3.2 PREPARATION OF 4-CHLOROBIPHENYL BY THE PENTYL NITRITE METHOD

$$\underline{p}\text{-Cl.}C_6H_4NH_2 + C_6H_6 + CH_3(CH_2)_4.ONO \longrightarrow \underline{p}\text{-Cl.}C_6H_4.C_6H_5 + N_2 \qquad (2.3)$$

The preparation of polychlorobiphenyls by the diazotisation

of an aqueous amine in the presence of the aromatic compund to be arylated gave poor yields of chlorobiphenyls (Gomberg - Hey process). The low yields can be attributed to the instability of the diazonium solution and the heterogeneity of the reaction. These disadvantages were overcome in some cases by using an alkyl nitrite such as pentyl nitrite (101) as the diazotising agent.

Para-chloroaniline (7 g.), benzene (200 ml.) and pentyl nitrite (9 g.) were heated until a vigorous reaction was set up with the evolution of gas. After 30 minutes, the effervescence had subsided and the mixture was boiled for 2 hours under reflux.

The excess of benzene and low boiling products were removed under reduced pressure and on distilling the residue, 4-chlorobiphenyl was obtained. (38 % yield, melting point 75 ^{o}C, cf literature value 77 ^{o}C (100a). Calculated analysis for

$C_{12}H_9Cl$: C = 77.21 %, H = 4.83 %, Cl = 19.03 %

found : C = 76.97 %, H = 4.42 %, Cl = 18.93 %)

2.3.3 PREPARATION OF 3-CHLOROBIPHENYL

$$\underline{m}\text{-Cl.C}_6\text{H}_4\text{.NH}_2 + \text{NaNO}_2 + 2\,\text{HCl} \longrightarrow \underline{m}\text{-Cl.C}_6\text{H}_4\text{.N}_2^{+}\text{Cl}^{-} + \text{NaCl} + 2\,\text{H}_2\text{O} \quad (2.4)$$

$$\underline{m}\text{-Cl.C}_6\text{H}_4\text{.N}_2^{+}\text{Cl}^{-} + \text{C}_6\text{H}_6 \xrightarrow[0 \text{ to } 5\ ^{o}\text{C}]{\text{sodium acetate}} \underline{m}\text{-Cl.C}_6\text{H}_4\text{.C}_6\text{H}_5 \quad (2.5)$$

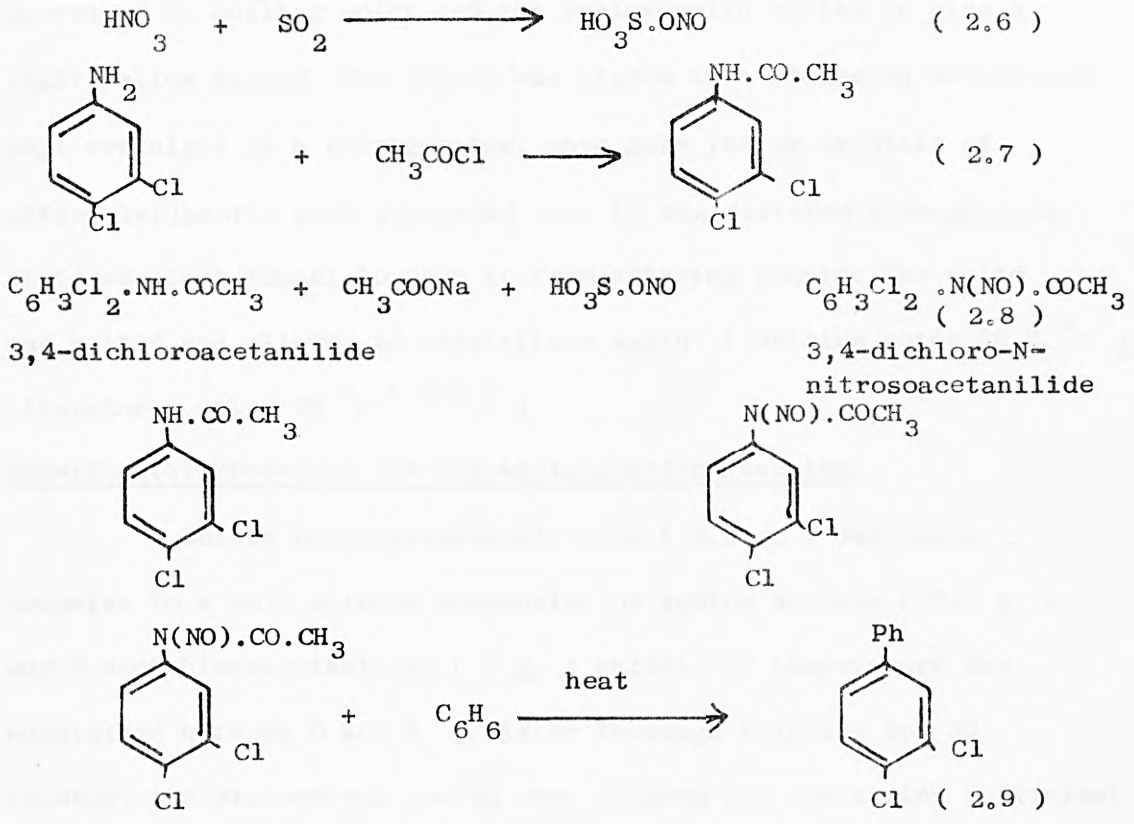
The experimental procedure followed has been described in section 2.3.1 and 3-chlorobiphenyl was obtained as an oil. (Boiling point 287 ^{o}C cf literature value 284 ^{o}C (100a)

calculated analysis for $C_{12}H_9Cl$: C = 77.21 %, H = 4.83 %, Cl = 19.03 %

found : C = 76.52 %, H = 4.55 %, Cl = 18.86 %)

2.4 PREPARATION OF DICHLOROBIPHENYLS

2.4.1 PREPARATION OF 3,4-DICHLOROBIPHENYL BY THE ACYLARYLNITROSAMINE REACTION



Scheme 2.1

The Acylnitrosamine Reaction

The decomposition of the N-nitroso- derivative of an acylarylamine in benzene yields unsymmetrical biaryl in improved yields. (102) The reaction occurs in a homogeneous phase and nitrosylsulphuric acid (103) is used as the nitrosating agent. When protected from moisture, nitrosylsulphuric acid remains stable on storage at room temperature. (104)

Preparation of Nitrosylsulphuric Acid

Dry sulphur dioxide was bubbled (4 to 8 bubbles s^{-1})

through fuming nitric acid (200 ml.) in an efficient fume cupboard. Large volumes of nitrogen oxides were evolved and after 3 hours a yellow solid started to separate out. After a further 2 hours, the flask was placed in a water bath and dry air was passed through the reaction vessel. Gradually, the temperature of the water bath was increased to boiling point and the yellow solid melted to give a light yellow liquid. The liquid was placed in a stoppered bottle and kept overnight in a refrigerator, when pale yellow crystals of nitrosylsulphuric acid separated out. It was filtered through a dry, sintered glass funnel to free it from adhering liquid. The solid was melted and allowed to crystallise again. (melting point 68.5 ^{o}C cf literature value 70 ^{o}C (102))

Experimental Procedure for the Acylarylation Reaction

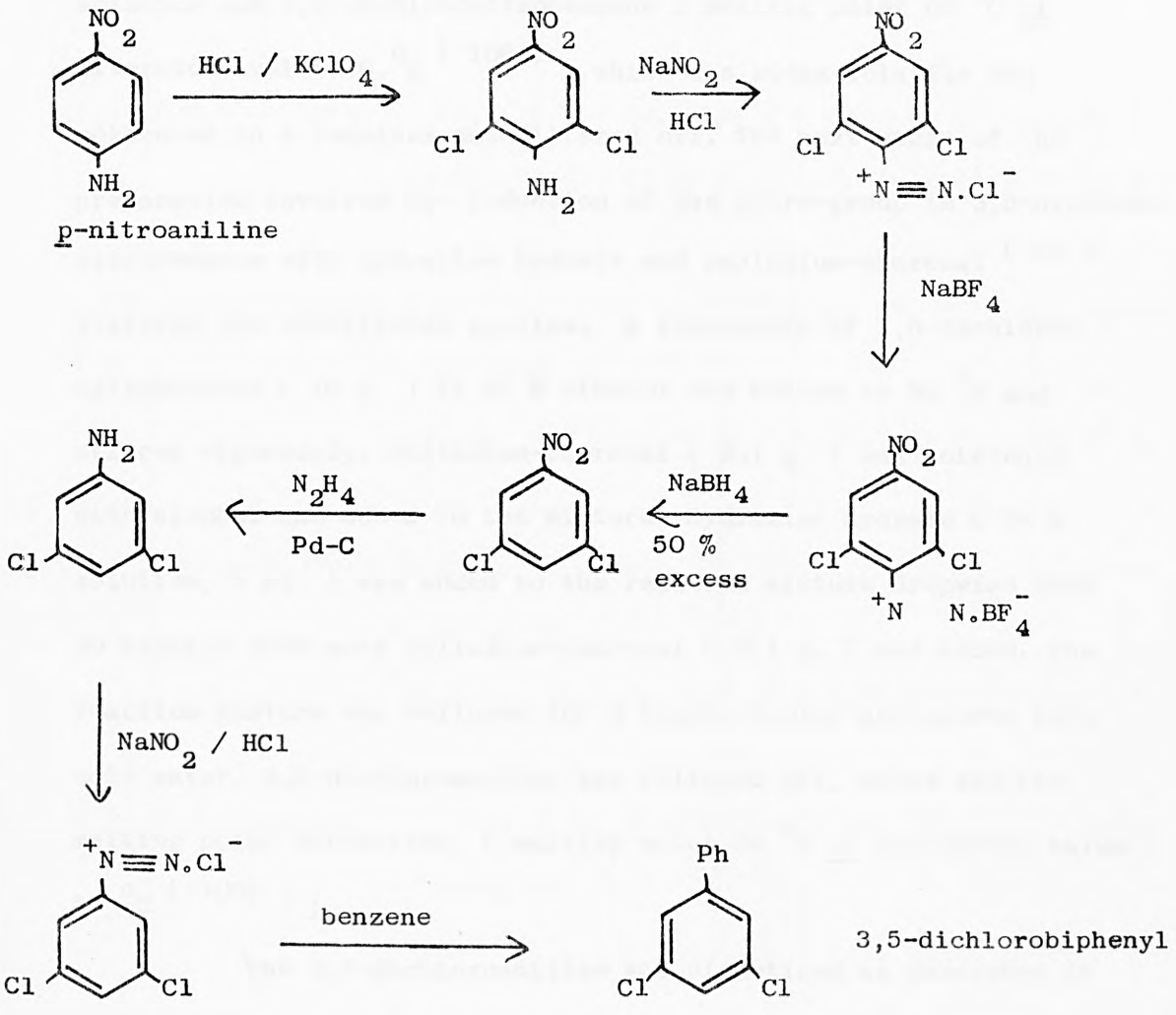
Molten nitrosylsulphuric acid (3.9 g.) was added dropwise to a well stirred suspension of sodium acetate (7.5 g.) and 3,4-dichloroacetanilide (3 g.) whilst the temperature was maintained between 0 and 5 ^{o}C. After thorough stirring for 30 minutes, the mixture was poured over crushed ice containing sufficient alkali to neutralise any acids present. A yellow oil, the nitroso-derivative, separated out and solidified. This was the 3,4-dichloro-N-nitrosoacetanilide. (Yield 70 % melting point 66 ^{o}C cf literature value 67 ^{o}C (102))

A solution of the above nitroso-derivative in benzene (150 ml.) was heated under reflux for 4 hours. Nitrogen was evolved and the solution turned dark red. The unreacted benzene was removed and the residue dissolved in a minimum quantity of benzene. This solution was passed down a column of activated alumina. using light petroleum as the eluant. The 3,4-dichlorobiphenyl was obtained as pale yellow crystals. (Yield 35 % melting point 43 ^{o}C cf literature value 45 to 46 ^{o}C (105))

Analysis calculated for $C_{12}H_8Cl_2$: C = 62.84 %, H = 3.01 %, Cl = 30.26 %

found : C = 64.89 %, H = 3.36 %, Cl = 31.15 %

2.4.2 PREPARATION OF 3,5-DICHLOROBIPHENYL FROM p-NITROANILINE



Scheme 2.2

Para-nitroaniline was used as the starting material in the synthesis of 3,5-dichlorobiphenyl. (106) The first stage was the chlorination of p-nitroaniline (14 g.) with hydrochloric acid (200 ml.) and potassium perchlorate (7 g.) when chlorine was introduced into the 2 and 6 positions, yielding 2,6-dichloro-4-nitro-

-aniline was effected with sodium tetrafluoroborate (3 g.) and sodium borohydride (4 g.) via a diazotisation reaction as shown in Scheme 2.2. With chlorine present in the nucleus, the replacement of a diazo- group by hydrogen is facilitated and little ether formation occurs. (107) Steam was passed through the reduced solution and 3,5-dichloronitrobenzene (melting point 65 ^{o}C cf literature value 66 ^{o}C (106)) which was steam volatile was collected in a receiver and filtered off. The next stage of the preparation involved the reduction of the nitro-group in 3,5-dichloro-nitrobenzene with hydrazine hydrate and palladium-charcoal (97) yielding the substituted analine. A suspension of 3,5-dichloro-nitrobenzene (10 g.) in 95 % ethanol was heated to 50 ^{o}C and stirred vigorously. Palladium-charcoal (0.1 g.) was moistened with alcohol and added to the mixture. Hydrazine hydrate (64 % solution, 5 ml.) was added to the reaction mixture dropwise over 30 minutes when more palladium-charcoal (0.1 g.) was added. The reaction mixture was refluxed for 2 hours, cooled and poured into cold water. 3,5-dichloroaniline was filtered off, dried and its melting point determined. (melting point 56 ^{o}C cf literature value 57 ^{o}C (100b)).

The 3,5-dichloroaniline was diazotised as described in section 2.3.1 and reacted with benzene to yield 3,5-dichloro-biphenyl. (36 % yield, melting point 35 ^{o}C cf literature value 36 ^{o}C (100b)).

Calculated analysis for $C_{12}H_8Cl_2$: C = 62.84 %, H = 3.01 %, Cl = 30.26 %

found : C = 64.57 %, H = 3.59 %, Cl = 31.84 %

2.4.3 PREPARATION OF 2,3-, 2,4-, 2,5-, 2,6-DICHLOROBIPHENYLS

The experimental procedure followed has been described in section 2.3.1 and the isomeric dichloroanilines were commercially available.

2,6-dichlorobiphenyl : yield 30 %, melting point 34 ^{o}C *cf* literature value 36 ^{o}C (95)

calculated analysis $C_{12}H_8Cl_2$: C = 62.84 %, H = 3.01 %, Cl = 30.26 %

found : C = 63.59 %, H = 2.93 %, Cl = 30.61 %

2,4-dichlorobiphenyl : yield = 34 %, melting point 23 ^{o}C *cf* literature value 25 ^{o}C (95)

found : C = 62.57 %, H = 3.10 %, Cl = 30.07 %

2,3-dichlorobiphenyl : yield 40 %, boiling point 175 ^{o}C *cf* literature value 172 ^{o}C (100b)

found : C = 63.11 %, H = 2.87 %, Cl = 30.14 %

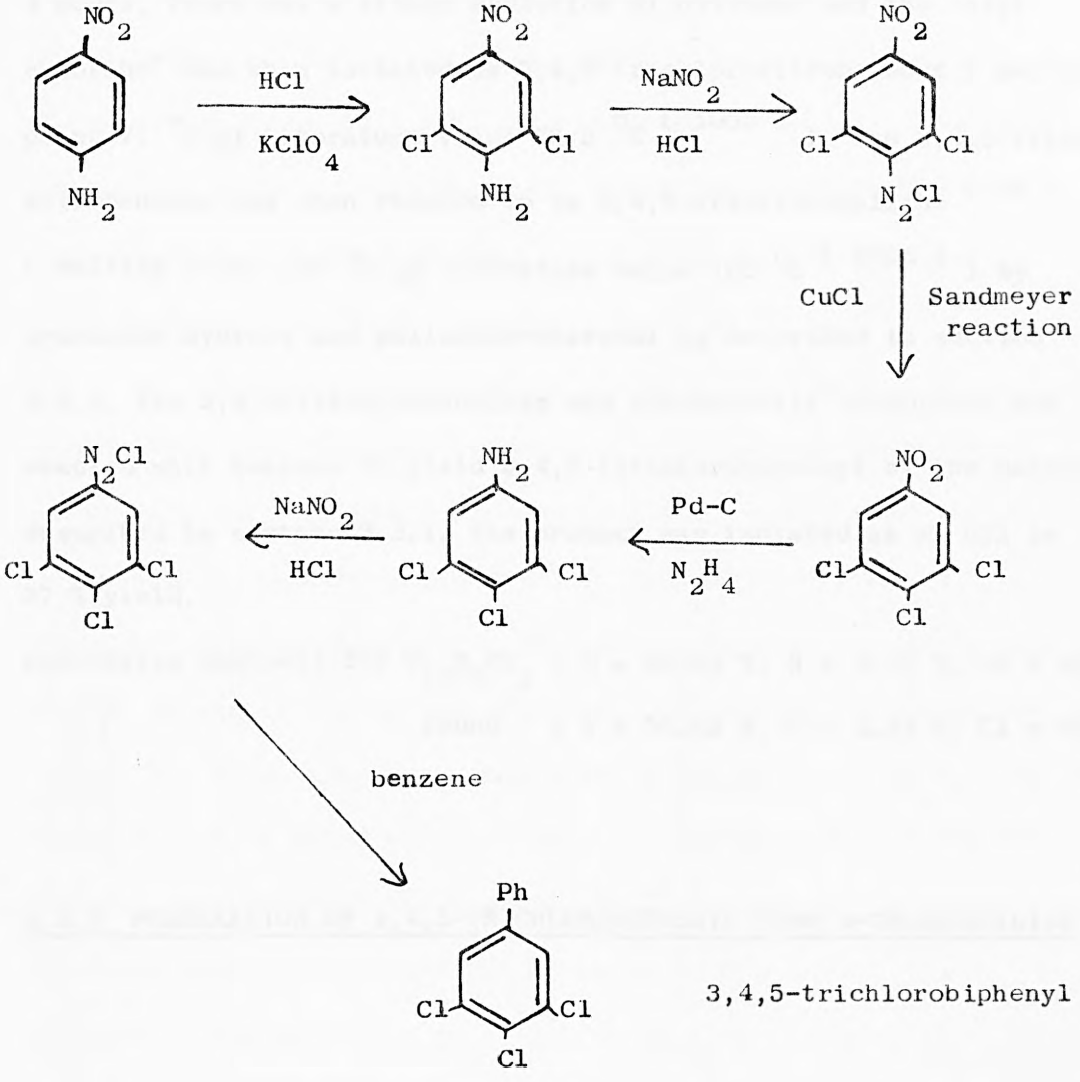
2,5-dichlorobiphenyl : yield 33 %, boiling point 183 ^{o}C *cf* literature value 182 ^{o}C (100b)

found : C = 62.95 %, H = 3.08 %, Cl = 30.20 %

2.5 PREPARATION OF TRICHLOROBIPHENYLS

The preparation of unsymmetrical trichlorobiphenyls is a complicated, multistage synthesis. During the preparation of the trichlorobiphenyls, certain positions on the aromatic ring have to be blocked or protected. For example, during chlorination or nitration reactions, in order to introduce chlorine or nitro-groups selectively.

2.5.1 PREPARATION OF 3,4,5-TRICHLOROBIPHENYL



3,4,5-trichlorobiphenyl

Scheme 2.3

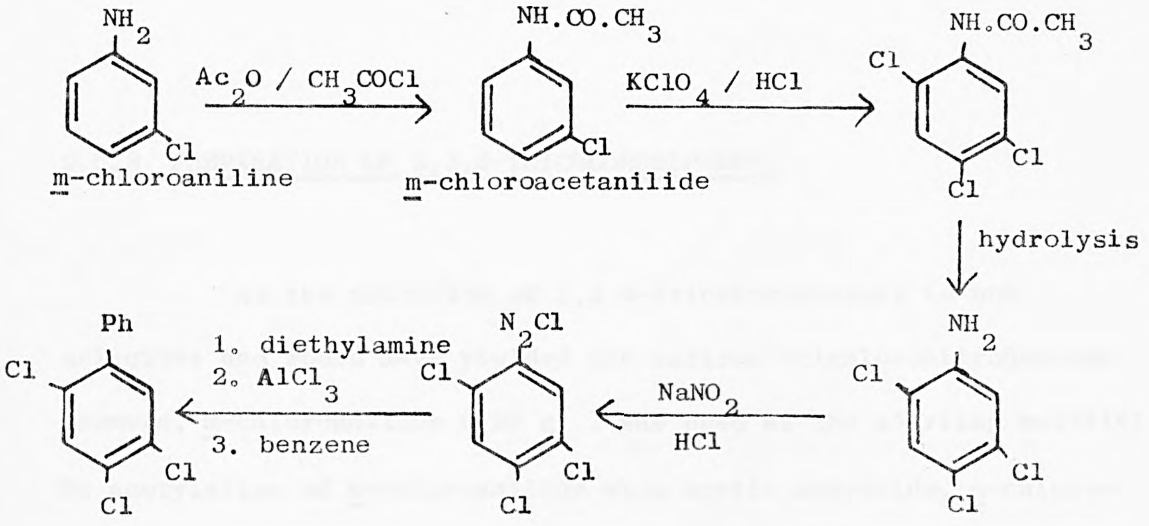
The first step in this synthesis involves the chlorination of p-nitroaniline which has been described in section 2.4.2, followed by the diazotisation of 2,6-dichloro-4-nitroaniline as described in section 2.3.1. After diazotisation, the diazonium salt underwent a Sandmeyer reaction with the replacement of the diazonium group by chlorine. (96) This replacement was carried out by mixing a solution of the freshly prepared diazonium salt with cuprous chloride in concentrated hydrochloric acid at -5 ^{o}C to form the

dark coloured complex ($C_6H_3Cl_2N_2^+[CuCl_2]^-$). The mixture was allowed to warm up to room temperature and stirred for a further 4 hours. There was a steady evolution of nitrogen and the 'aryl chloride' was then isolated as 3,4,5-trichloronitrobenzene (melting point 71 °C cf literature value 72.5 °C (100c)). The 3,4,5-trichloronitrobenzene was then reduced to to 3,4,5-trichloroaniline (99) (melting point 100 °C cf literature value 100 °C (100c)) by hydrazine hydrate and palladium-charcoal as described in section 2.4.2. The 3,4,5-trichloroaniline was subsequently diazotised and reacted with benzene to yield 3,4,5-trichlorobiphenyl by the method described in section 2.3.1. The product was isolated as an oil in 37 % yield.

calculated analysis for $C_{12}H_7Cl_3$: C = 55.92 %, H = 2.72 %, Cl = 41.36 %

found : C = 55.02 %, H = 2.34 %, Cl = 40.81 %

2.5.2 PREPARATION OF 2,4,5-TRICHLOROBIPHENYL FROM m-CHLOROANILINE



2,4,5-trichlorobiphenyl

Scheme 2.4

Meta-chloroaniline was used as the starting material for this synthesis and was readily available commercially. On acetylation with acetic anhydride, m-chloroacetanilide was formed which was chlorinated with potassium perchlorate as described in section 2.4.2. Chlorine was found to enter the m-chloroacetanilide at positions ortho- and para- to the $-NH.CO.CH_3$ group. Upon hydrolysis the appropriately substituted 2,4,5-trichloroaniline was formed (melting point 93 °C cf literature value 95 °C (100c)).

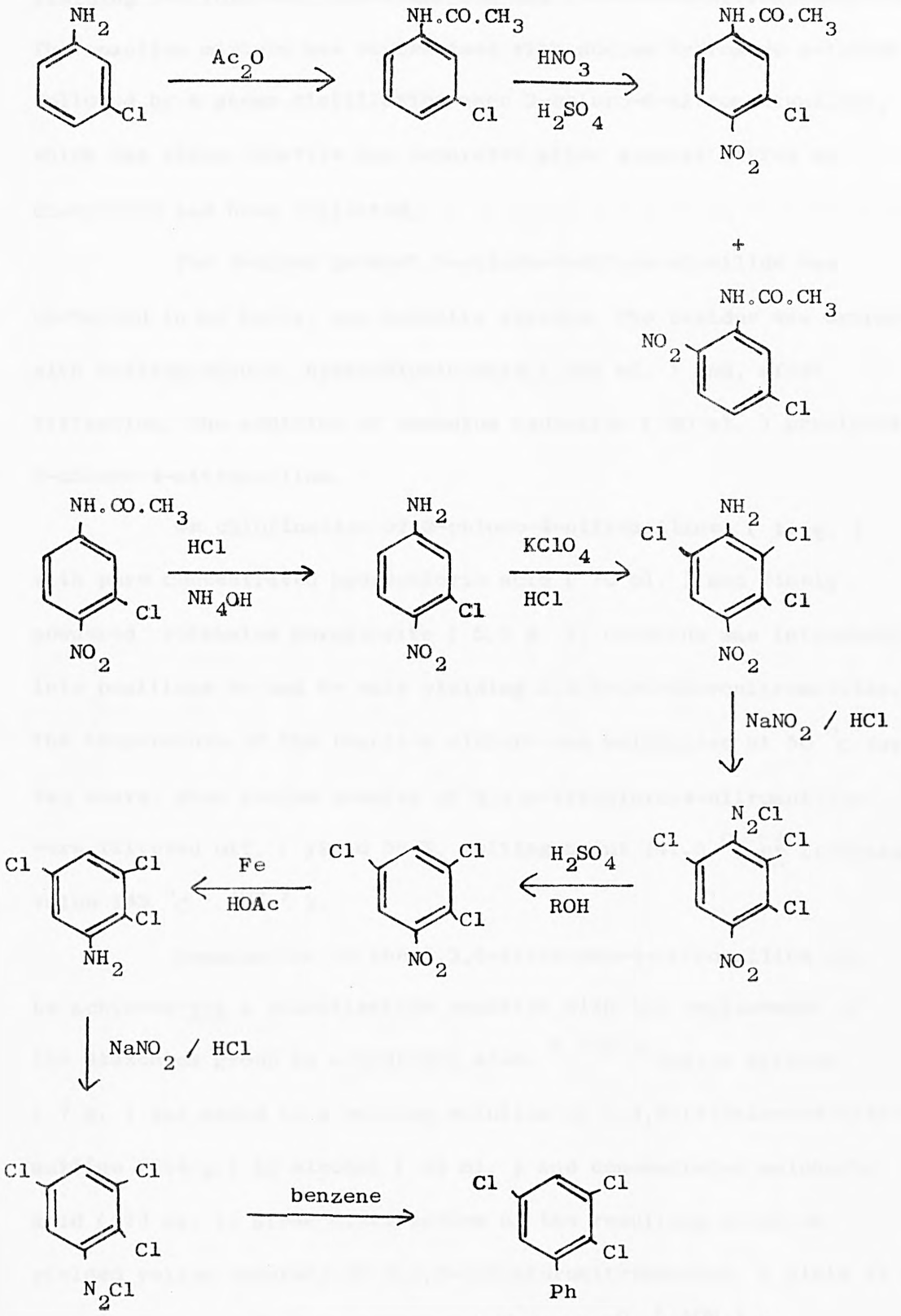
2,4,5-trichloroaniline was diazotised with sodium nitrite and mineral acid followed by reaction with benzene as described in section 2.3.1 to yield the required 2,4,5-trichlorobiphenyl (yield 23 %, melting point 75 °C cf literature value 76 °C). However, this reaction of the diazonium salt gave extremely poor yields of biaryl and the reaction was modified at the diazonium stage. The freshly prepared diazonium solution was treated with diethylamine in water and the reaction products were boiled with benzene and aluminium trichloride. (108) The yield of 2,4,5-trichlorobiphenyl was improved by about 40 %.

calculated analysis $C_{12}H_7Cl_3$: C = 55.92 %, H = 2.72 %, Cl = 41.36 %

found : C = 55.97 %, H = 2.74 %, Cl = 41.29 %

2.5.3 PREPARATION OF 2,3,5-TRICHLOROBIPHENYL

As the nitration of 1,2,4-trichlorobenzene is not selective and would have yielded the various trichloronitrobenzene isomers, m-chloroaniline (20 g.) was used as the starting material. On acetylation of m-chloroaniline with acetic anhydride, m-chloroacetanilide was formed. (109) Mixed acids (sulphuric / nitric) were used to nitrate the m-chloroacetanilide where the nitro-group was



2,3,5-trichlorobiphenyl

Scheme 2.5

introduced into the 4- and 6- positions as shown in Scheme 2.5, yielding 3-chloro-4-nitroacetanilide and 3-chloro-6-nitroacetanilide. The reaction mixture was neutralised with sodium hydroxide solution followed by a steam distillation when 3-chloro-6-nitroacetanilide, which was steam volatile was separated after several litres of distillate had been collected.

The desired product 3-chloro-4-nitroacetanilide was contained in the tarry, non-volatile residue. The residue was extracted with boiling dilute hydrochloric acid (200 ml.) and, after filtration, the addition of ammonium hydroxide (80 ml.) precipitated 3-chloro-4-nitroaniline.

On chlorination of 3-chloro-4-nitroaniline (11 g.) with pure concentrated hydrochloric acid (10 ml.) and finely powdered potassium perchlorate (5.5 g.), chlorine was introduced into positions 2- and 6- only yielding 2,3,6-trichloronitroaniline. The temperature of the reaction mixture was maintained at 50 ^{o}C for two hours, when yellow needles of 2,3,6-trichloro-4-nitroaniline were filtered off. (yield 58 %, melting point 141.5 ^{o}C *cf* literature value 143 ^{o}C (109)).

Deamination of the 2,3,6-trichloro-4-nitroaniline can be achieved *via* a diazotisation reaction with the replacement of the diazonium group by a hydrogen atom. (110) Sodium nitrite (7 g.) was added to a boiling solution of 2,3,6-trichloro-4-nitroaniline (14 g.) in alcohol (63 ml.) and concentrated sulphuric acid (13 ml.). Steam distillation of the resulting solution yielded yellow crystals of 2,3,5-trichloronitrobenzene. (yield 51 %, melting point 44 ^{o}C, *cf* literature value 45 ^{o}C (109)).

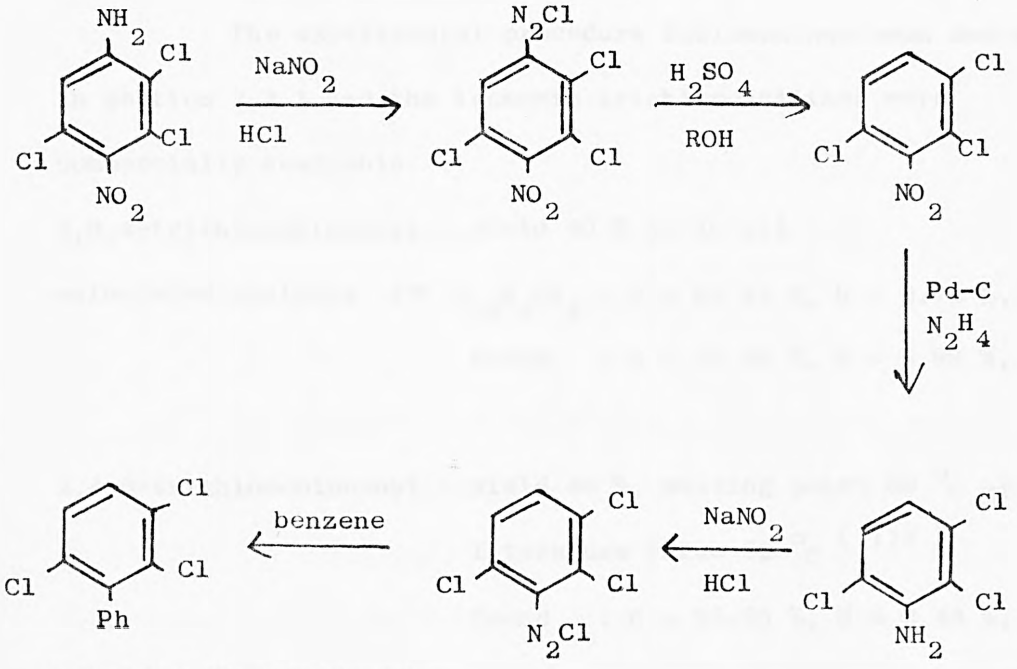
Reduction of the 2,3,5-trichloronitrobenzene (8 g.) with iron filings (4 g.) and acetic acid (20 ml.) produced the

corresponding aniline,[111] which was then diazotised (as described in section 2.3.1) and reacted with benzene to form 2,3,5-trichlorobiphenyl.[112] (yield 38 %, melting point 40 °C cf literature value 41 °C [100c]).

calculated analysis $C_{12}H_7Cl_3$: C = 55.92 %, H = 2.72 %, Cl = 41.36 %

found : C = 56.03 %, H = 2.44 %, Cl = 41.11 %

2.5.4 PREPARATION OF 2,3,6-TRICHLOROBIPHENYL



2,3,6-trichlorobiphenyl

Scheme 2.6

The preparation of 2,3,6-trichloro-4-nitroaniline has been described in section 2.5.3. On diazotisation (described in section 2.3.1) and reaction with alcohol (20 ml.) and concentrated

sulphuric acid (15 ml.), deamination was effected with the formation of 2,3,6-trichloronitrobenzene.[111, 112] Reduction of 2,3,6-trichloro-4-nitrobenzene was carried out with hydrazine and palladium-charcoal as described in section 2.4.2 yielding 2,3,6-trichloroaniline. The substituted aniline was then diazotised and reacted with benzene as described in section 2.3.1 yielding 2,3,6-trichlorobiphenyl (35 % yield) as an oil.

calculated analysis for $C_{12}H_7Cl_3$: C = 55.92 %, H = 2.72 %, Cl = 41.36 %

found : C = 55.25 %, H = 2.89 %, Cl = 41.47 %

2.5.5 PREPARATION OF 2,3,4- AND 2,4,6-TRICHLOROBIPHENYLS

The experimental procedure followed has been described in section 2.3.1 and the isomeric trichloroanilines were commercially available.

2,3,4-trichlorobiphenyl : yield 40 % as an oil

calculated analysis for $C_{12}H_7Cl_3$: C = 55.92 %, H = 2.72 %, Cl = 41.36 %

found : C = 55.48 %, H = 2.99 %, Cl = 41.74 %

2,4,6-trichlorobiphenyl : yield 48 %, melting point 60 ^{o}C cf literature value 62 ^{o}C [113]

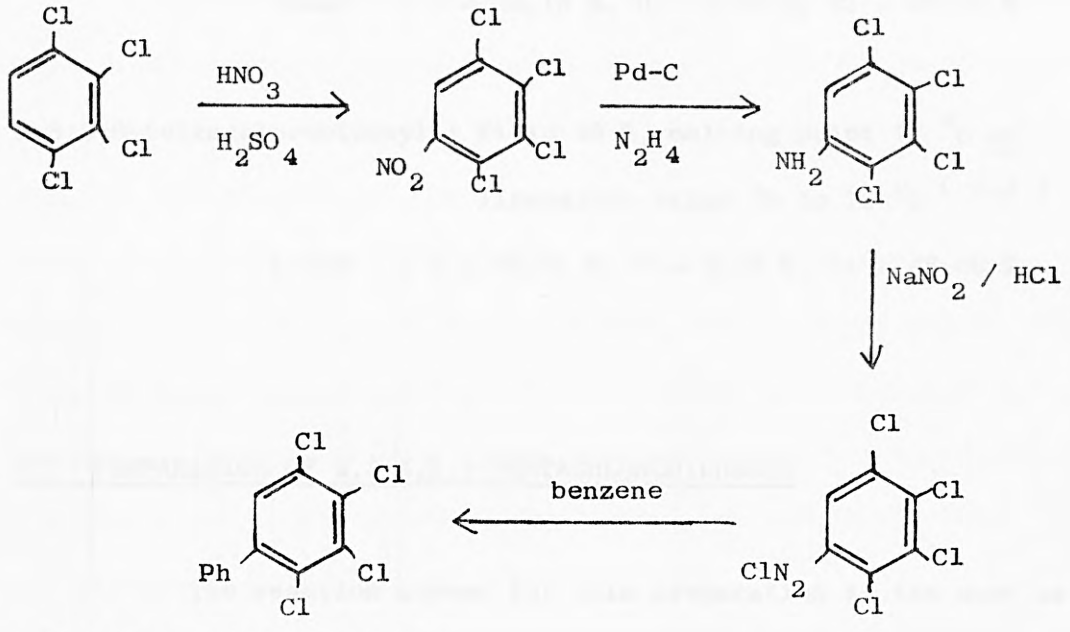
found : C = 55.25 %, H = 2.43 %, Cl = 41.18 %

2.6 PREPARATION OF TETRACHLOROBIPHENYLS

The appropriate tetrachloroanilines were not available commercially and were prepared by nitrating the tetrachlorobenzene isomer under conditions giving rise to monosubstitution by the nitro-

group as described in section 2.2

2.6.1 PREPARATION OF 2,3,4,5-TETRACHLOROBIPHENYL



2,3,4,5-tetrachlorobiphenyl

Scheme 2.7

The tetrachloronitrobenzene (10 g.) was reduced in the presence of palladium-charcoal by hydrazine hydrate as described in section 2.4.2 to yield the aniline. The tetrachloroaniline was then diazotised as described in section 2.3.1 and reacted with cold benzene to yield tetrachlorobiphenyl. The 2,3,4,5-tetrachloro-biphenyl was isolated from the tar by column chromatography as described in section 2.3.1 on a silica column (4 foot) using n-hexane as the eluant. (Yield 46 %, melting point 90 ^{o}C cf literature value 91 to 92 ^{o}C (114)).

calculated analysis $C_{12}H_6Cl_4$: C = 49.32 %, H = 2.05 %, Cl = 48.63 %

found : C = 49.36 %, H = 2.07 %, Cl = 48.56 %

The following tetrachlorobiphenyls were also prepared using the same method :-

2,3,4,6-tetrachlorobiphenyl : Yield 51 %, melting point 47 ^{o}C *cf* literature value 49 ^{o}C (115)

calculated for $C_{12}H_6Cl_4$: C = 49.32 %, H = 2.05 %, Cl = 48.63 %

found : C = 49.18 %, H = 2.09 %, Cl = 48.70 %

2,3,5,6-tetrachlorobipneyl : Yield 49 %, melting point 77 ^{o}C *cf* literature value 78 to 79 ^{o}C (115)

found : C = 49.41 %, H = 2.02 %, Cl = 48.60 %

2.7 PREPARATION OF 2,3,4,5,6-PENTACHLOROBIPHENYL

The reaction scheme for this preparation is the same as that for the preparation of 2,3,4,5-tetrachlorobiphenyl except that the starting material is pentachlorobenzene (see Scheme 2.7).

Pentachlorobenzene (10 g.) was nitrated with nitric acid to yield pentachloronitrobenzene followed by reduction with hydrazine hydrate and palladium-charcoal as described in section 2.4.2 yielding pentachloroaniline. (Yield from pentachlorobenzene = 58 %, melting point 231 ^{o}C *cf* literature value 232 ^{o}C (100c)).

Pentachloroaniline (5 g.) was diazotised and reacted with benzene as described in section 2.3.1 yielding 2,3,4,5,6-pentachlorobiphenyl. (Yield 37 %, melting point 122 ^{o}C *cf* literature value 123 ^{o}C (95)).

calculated analysis $C_{12}H_5Cl_5$: C = 44.10 %, H = 1.53 %, Cl = 54.36 %

found : C = 44.56 %, H = 1.38 %, Cl = 54.81 %

2.8 PREPARATION OF COPPER(II) BENZOATE FOR USE AS AN ADDITIVE IN THE PHENYLATION REACTIONS OF POLYCHLOROBENZENES

$$CuCO_3 + 2\ PhCOOH \longrightarrow Cu(PhCOO)_2 + H_2O + CO_2 \qquad (2.10)$$

Green copper carbonate (6.5 g.) was mixed in an intimate mixture with finely powdered benzoic acid (12.5 g.). The mixture was heated in a paraffin oil bath at 150 ^{o}C for 3 hours, when the reaction mixture changed colour to pale blue. The salt was then transferred to an evaporating basin and a perforated filter paper placed over it, along with a glass funnel. The dish was heated over a bunsen burner and any excess of benzoic acid was removed by its sublimation. The light blue powder was then heated for 3 hours in a drying pistol under vacuum. (Yield 63 %, melting point 186.5 ^{o}C cf literature value 188 ^{o}C [116]).

An alternative method used the reaction of copper and benzaldehyde, [117] however the yields were poor.

2.9 SUMMARY OF PREPARATIONS

Table 2.1 shows a summary of the starting materials, yields and melting points of the chlorinated biphenyls prepared by various unambiguous pathways.

Table 2.1 Summary of preparations of chlorinated biphenyls

compound	source	melting point (°C)	yield* (%)
2-chlorobiphenyl	o-chloroaniline	30	35
3-chlorobiphenyl	m-chloroaniline	oil	43
4-chlorobiphenyl	p-chloroaniline	75	38
3,4-dichlorobiphenyl	3,4-dichloroacetanilide	43	35
3,5-dichlorobiphenyl	p-nitroaniline	35	36
2,6-dichlorobiphenyl	2,6-dichloroaniline	34	30
2,4-dichlorobiphenyl	2,4-dichloroaniline	23	34
2,3-dichlorobiphenyl	2,3-dichloroaniline	oil	40
2,5-dichlorobiphenyl	2,5-dichloroaniline	oil	33
3,4,5-trichlorobiphenyl	p-nitroaniline	oil	37
2,4,5-trichlorobiphenyl	m-chloroaniline	75	40
2,3,5-trichlorobiphenyl	m-chloroaniline	40	38
2,3,6-trichlorobiphenyl	m-chloroaniline	oil	35
2,3,4-trichlorobiphenyl	2,3,4-trichloroaniline	oil	40
2,4,6-trichlorobiphenyl	2,4,6-trichloroaniline	60	48
2,3,4,5-tetrachlorobiphenyl	1,2,3,4-tetrachlorobenzene	90	46
2,3,4,6-tetrachlorobiphenyl	1,2,3,5-tetrachlorobenzene	47	51
2,3,5,6-tetrachlorobiphenyl	1,2,4,5-tetrachlorobenzene	77	49
2,3,4,5,6-pentachlorobiphenyl	pentachlorobenzene	122	37

* it should be noted that all yields are based on the amount of original starting material i.e. compound quoted as source

2.10 METHODS USED FOR FREE RADICAL PHENYLATION REACTIONS

2.10.1 METHOD 1 : REFLUX UNDER NITROGEN

The initial experiments were carried out in a three necked round bottom flask as shown in Figure 2.1. The reactants were weighed and placed together in the flask. Dry nitrogen gas was bubbled through the reactants and the reaction mixture was refluxed on a steam bath for 8 hours. The mixture was heterogeneous in the cold, but after the first hour of heating the reaction mixture turned pale yellow and became homogeneous. 2 μl. samples of the reaction mixture were withdrawn every hour for g.l.c. analysis through the rubber 'subaseal' (septum).

Due to non-reproducibility of the p.r.f. results, this method of phenylation was abandoned.

2.10.2 METHOD 2 : SOLVENT BATH

A glass tube was sealed in the centre of the three necked flask as shown in Figure 2.2.

The reaction tube was fitted with a mechanical stirrer and a water condenser for the reaction products. A constant temperature bath was achieved by placing a suitable solvent in the flask. The temperature of the bath was noted form the thermometer and was dependent on the solvent used. Samples of the reaction mixture could be withdrawn with a syringe once the stirrer motor was removed.

Figure 2.1 Apparatus used for refluxing phenylation reactions

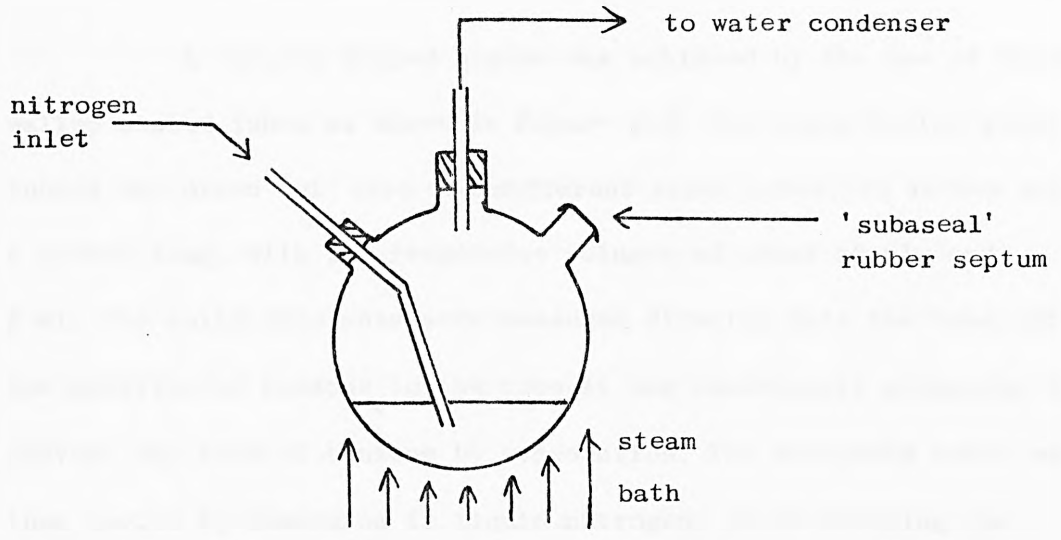


Figure 2.2 Apparatus used for solvent bath phenylation reactions

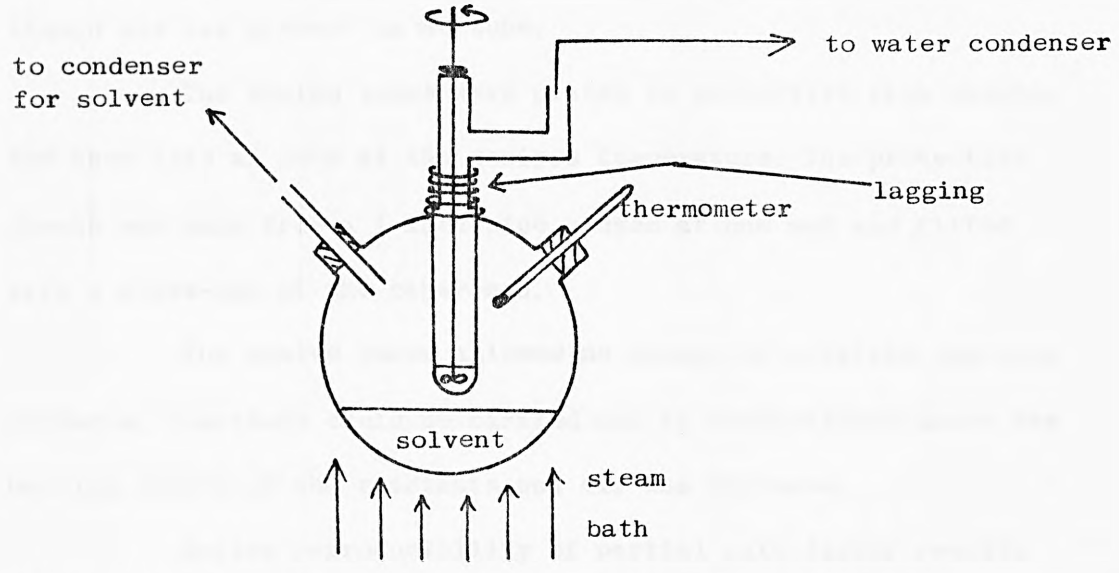
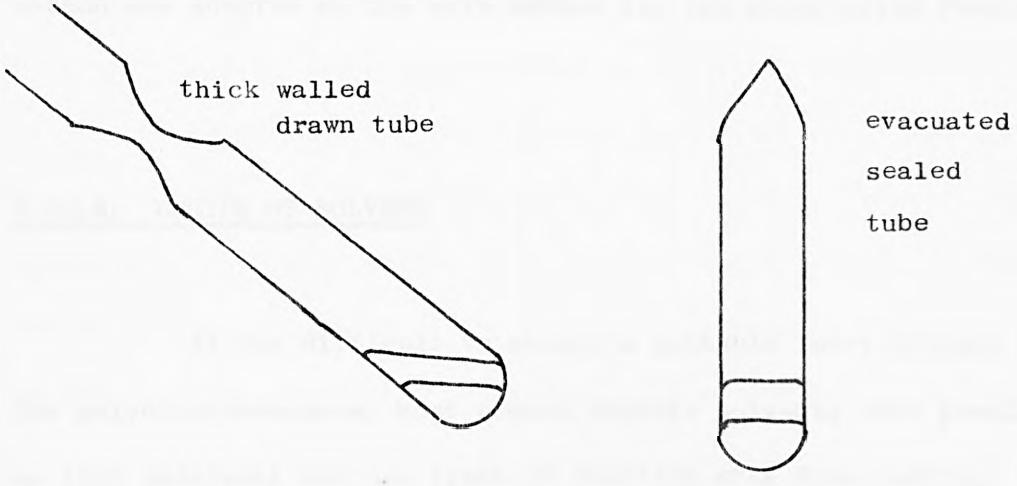


Figure 2.3 Tubes used in sealed tube phenylation reactions



2.10.3 METHOD 3 : SEALED TUBE

A totally sealed system was achieved by the use of thick walled sealed tubes as shown in Figure 2.3. The heavy walled glass tubing was drawn out into two different sized tubes, 12 inches and 6 inches long, with the respective volumes of about 15 ml. and 8 ml. The solid reactants were measured directly into the tube, after the addition of benzene to the tube it was immediately stoppered to prevent any loss of benzene by evaporation. The stoppered tubes were then cooled by immersion in liquid nitrogen. After freezing the contents, the tubes were evacuated and sealed, taking care that no liquid air was present in the tube.

The sealed tubes were placed in protective iron sheaths and then into an oven at the desired temperature. The protective sheath was made from a 1 inch pipe closed at one end and fitted with a screw-cap at the other end.

The sealed tubes allowed no escape of volatile reaction products, reactions could be carried out at temperatures above the boiling points of the reactants and air was excluded.

Better reproducibility of partial rate factor results was achieved by the use of the smaller sealed tubes. The sealed tube method was adopted as the main method for the phenylation reactions.

2.10.4. CHOICE OF SOLVENT

It was difficult to obtain a suitable inert solvent for the polychlorobenzenes. Most common organic solvents were precluded, as they underwent various types of reaction with free radical.

One exception was the relatively inert carbon tetrachloride,

which was frequently chosen as a solvent in the study of homolytic reactions. However, its non-polar character limited its usefulness as a solvent and chlorine abstraction often occurred. (74)

It was considered that a perfluorinated compound might be sufficiently inert to phenyl radicals to be suitable to act as a solvent for polychlorobenzenes. With this in mind, perfluorodecalin was investigated, but was found to be unsatisfactory in that it reacted to a significant extent with the phenyl radicals, thus setting up an undesired competition for the free radicals.

It was possible to use one of the reactants as the solvent but here again there were several limitations. However, this was the method that was eventually adopted and reaction temperatures used were often above the melting point of the particular polychlorobenzene. After the first half-hour of heating, all the reaction mixtures were homogeneous.

2.11 IDENTIFICATION AND QUANTITATIVE ANALYSIS OF THE PRODUCTS OF THE PHENYLATION REACTIONS

The products of the phenylation of the chloro-substituted benzenes were analysed by gas-liquid chromatography (g.l.c.) and by in-line g.l.c./ mass spectrometry as described below.

Identification was achieved by comparison of the g.l.c. retention times of the products with those of the authentic compounds prepared as described above, when analysed under identical conditions, and also by a comparison of their relative retention times as described below, determined using biphenyl as the reference compound.

Quantitative studies consisted of the determination of

partial rate factors (p.r.f.'s) using benzene itself as the reference compound and also the measurement of the yields of the reaction products as moles per mole of the radical precursor (benzoyl peroxide) consumed . These yields were determined by the addition of a known weight of an internal standard to the complete reaction mixture at the end of the reaction. The compound chosen as internal standard was p-chlorotoluene as this was of a similar chemical nature as the reaction products and appeared in the chromatograms as a peak well separated from them and from excess of the reactants.

2.11.1 GAS CHROMATOGRAPHY

Polychlorobiphenyls are normally assayed in extracts of materials by g.l.c. Analytical conditions are usually those employed for chlorinated pesticides involving liquid phases such as SE 30,[118] OV-1,[118] OV-101,[119] XE-60.[119]

Quantitative analysis of phenylation reaction mixtures is complicated by the large number of peaks appearing in the chromatograms and by the variation in detector response to each component.[120, 121] This variation may be 3000 fold by using an electron capture detector.[95]

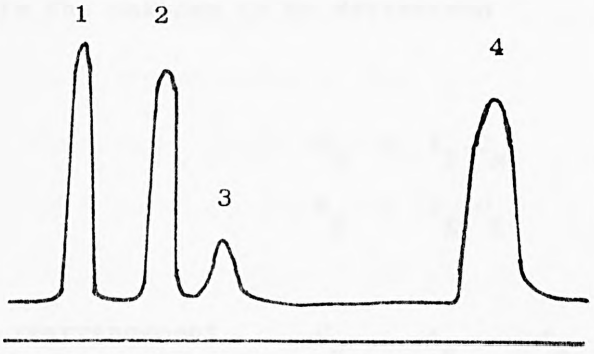
Therefore it was chosen to carry out the analysis of phenylation reaction mixtures on flame ionisation detectors and determining response factors for all the product components.[122]

The instruments used for the analysis of the phenylation reaction products were the Pye 104 gas chromatograph and the Perkin-Elmer F 11 model, both fitted with a dual flame ionisation

detector (F.I.D.). Temperature programming was used for the analyses, all of which were carried out under two sets of conditions. The first run was carried out at a high sensitivity i.e. low attenuation to observe all the phenylation product peaks which were small trace amounts compared to the amount of reactants present. The second run was carried out at a low sensitivity i.e. a highly attenuated signal to see the tops of the remaining reactant peaks. Figure 2.4 gives an example of these two runs.

Figure 2.4 Chromatograms obtained form 1,3,5-trichlorobenzene reaction

first sensitive run
(low attenuation)



second run
(high attenuation)

Phenylation product analysis was carried out by g.l.c. under the conditions described in Table 2.2. Relative response factors were determined for the polychlorobenzenes and also for the polychlorobiphenyls.[95] The relative response factors of the chlorinated compounds were measured with respect to a given internal standard which was added to the sample prior to analysis.[120] Para-chlorotoluene was chosen as the internal standard. Earlier work had been carried out with chlorobenzene as the internal standard, but its use was discontinued when a detectable small amount of chlorobenzene was found in certain phenylated reaction mixtures.

For mass detectors, the area (A) of a given peak is proportional to the concentration (C) of the respective solute.

$$A \propto C$$

hence $A = f.C$ where f is a constant

The proportionality factor, f, is called the detector response factor and its value will depend not only upon the type of detector but also upon the chemical character of the component. Using the above expression, it is possible to obtain expressions for two peaks of components S and X, where S is the standard and X is the unknown to be determined

$$A_S = f_S \cdot C_S$$

$$A_X = f_X \cdot C_X$$

on rearrangement

$$\frac{C_X}{C_S} = \frac{A_X}{A_S} \cdot \frac{f_S}{f_X}$$

Table 2.2 Gas chromatography conditions

A. Operating conditions for the analysis of phenylation reaction products of polychlorobenzenes (except 1,2,4,5-tetrachlorobenzene).

Column : 10 % SE 30 coated on high performance Chromasorb W, column length, 6 feet

Carrier gas : nitrogen at 55 ml. min^{-1}

Initial temperature : 100 ^{o}C

Rate of temperature rise : 4 $^{o}C\ min^{-1}$

Final temperature : 260 ^{o}C

Final hold : 20 minutes

Detector temperature : 310 ^{o}C

Hydrogen flow rate : 30 ml. min^{-1}

Air flow rate : 300 ml. min^{-1}

B. Operating conditions for the analysis of the phenylation reaction products of 1,2,4,5-tetrachlorobenzene.

Column : 12 % OV-101 on high performance Chromasorb W, column length, 5 feet

Carrier gas : nitrogen at 40 ml. min^{-1}

Initial temperature : 125 ^{o}C

Rate of temperature rise : 6 $^{o}C\ min^{-1}$

Final temperature : 250 ^{o}C

Final hold : 20 minutes.

Detector temperature : 300 ^{o}C

Hydrogen flow rate : 30 ml. min^{-1}

Air flow rate : 300 ml. min^{-1}

The ratio f_S/f_X is referred to as the response factor and is determined by measurements from chromatograms obtained from standard solutions of unknown and internal standard. (See Table 2.4) The response factor is used to calculate the concentration of a given unknown thus :-

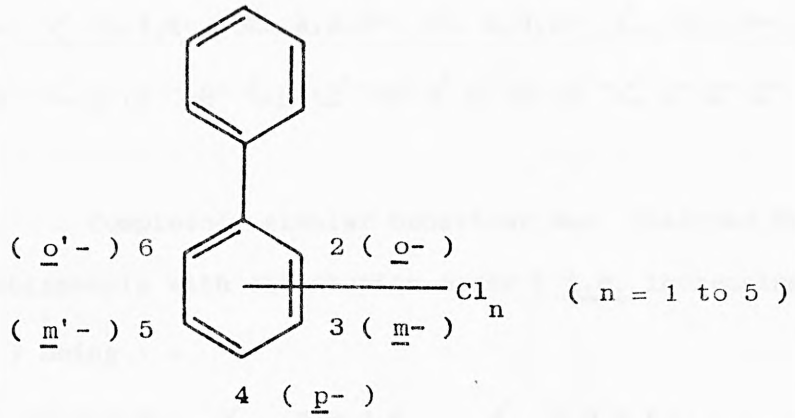
$$C_X = C_S \cdot \frac{A_X}{A_S} \cdot \frac{f_S}{f_X}$$

where A_x and A_S refer to peak areas or peak weights of the unknown and internal standard respectively.

2.11.2 GAS CHROMATOGRAPHY - THE BEHAVIOUR OF SOME CHLORINATED BIPHENYLS

The gas chromatographic retention behaviour of a series of polychlorinated biphenyls was studied on an SE 30 column to enable the ultimate analysis of phenylation reaction mixtures of polychlorobenzenes. (123) Good resolution and separation was achieved with this non-polar stationary phase. From the relative retention times shown in Table 2.3, it is evident that small polar and steric effects operate in the determination of retention behaviour on the column. Relative retention times decrease with an increase in temperature with the elution order of polychlorobiphenyls unaltered. All isomers with a particular number of chlorine atoms e.g. trichlorobiphenyls, are eluted before the first isomer of the next series with one more chlorine substituent i.e. tetrachlorobiphenyls. (124)

The structure of the polychlorobiphenyls is shown below, the numbers and symbols indicating the chlorinated positions



relative to the phenyl group, with ortho- as o- and o'-, meta- as m- and m'- and para- as p-.

The monochlorobiphenyl isomers (2-, 3- and 4-) are eluted according to their boiling points, the retention increasing with increase in the distance between the chlorine and phenyl group (i.e. in the order o-, m-, p-). The difference in the retention times of the 3- and 4- isomer is small.

With the dichlorobiphenyls, the lowest retention time is shown by the 2,6-isomer where the substitution occurs in both positions ortho- to the phenyl group. The 2,4- and 2,5- isomers are close in retention times with increased retention of meta-disubstituted 3,5-isomer. Greater retention is observed by the 2,3-isomer due to reinforcement of polar effects by their close proximity, while the highest retention is shown by the 3,4-isomer.

Order of elution of dichlorobiphenyls

With increasing retention time :-

2,6- < 2,5- < 2,4- < 2,3- < 3,5- < 3,4-

o-,o'- < o-,m'- < o-,p- < o-,m- < m-,m'- < m-,p-

The order of retention times of the isomeric trichlorobiphenyl isomers is shown below, the behaviour following that of the monochloro- and dichloro- isomers.

2,4,5- < 2,4,6- < 2,3,6- < 2,3,5- < 2,3,4- < 3,4,5-

o-,p-,m'- < o-,o'-,p- < o-,o'-,m- < o-,m-,m'- < o-,m-,p- < m-,m'-,p-

Completely similar behaviour was observed for the tetrachlorobiphenyls with the elution order (i.e. increasing retention times) being : -

2,3,5,6- < 2,3,4,6- < 2,3,4,5-

o-,o'-,m-,m'- < o-,o'-,m-,p- < o-,m-,m'-,p-

Generally, therefore, molecules with substitution in the para- and meta- positions, and especially together, show the greatest retention.

Figure 2.5 shows the elution order of polychlorobiphenyls on SE 30 and Table 2.3 lists the relative retention times observed.

2.11.3 DETERMINATION OF RELATIVE RETENTION TIMES OF CHLORINATED BIPHENYLS

Definition :

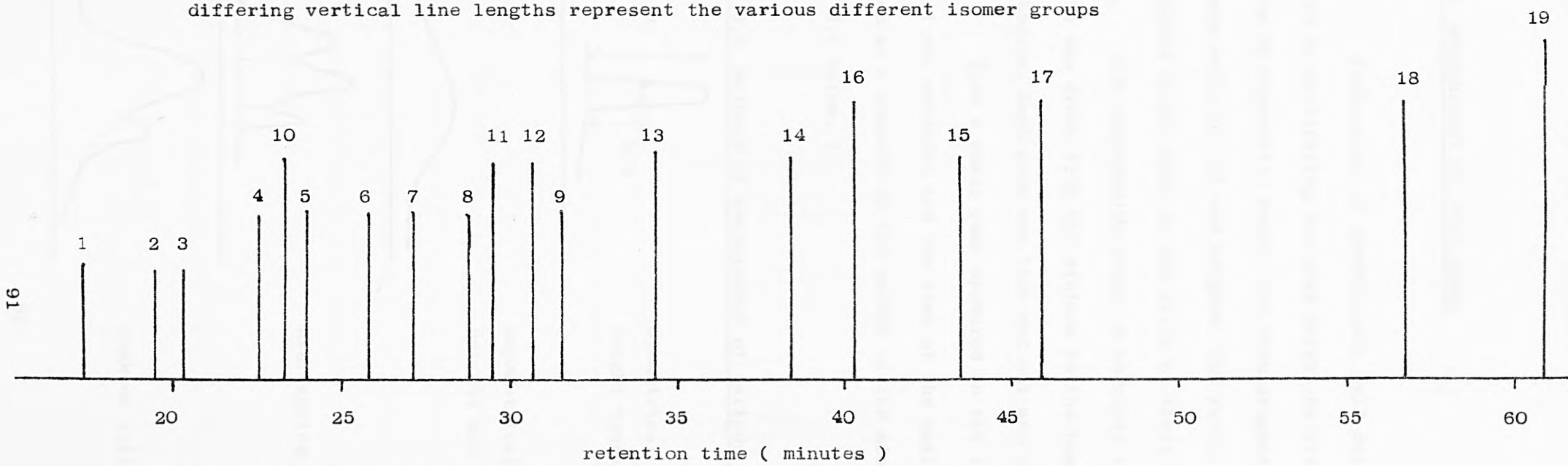
The volume of a carrier gas required to elute a compound from the gas chromatograph column is called the retention volume. Under constant pressure conditions, the flow rate is linear with time and one could speak of retention time. This retention time is characteristic of the sample and the liquid phase and can therefore be used to identify the sample whilst column temperature remains constant. Identification is based on a comparison of the retention time of the unknown compound with that obtained from a known compound analysed under identical conditions. Relative retention time is that time reported relative to that of a standard component.

Table 2.3 Relative retention times of polychlorobiphenyls

polychlorobiphenyl	relative retention time (min.)
2-chlorobiphenyl	17.2
3-chlorobiphenyl	19.6
4-chlorobiphenyl	20.3
2,6-dichlorobiphenyl	22.5
2,5-dichlorobiphenyl	24.0
2,4-dichlorobiphenyl	25.9
2,3-dichlorobiphenyl	27.1
3,5-dichlorobiphenyl	28.8
3,4-dichlorobiphenyl	31.6
2,4,5-trichlorobiphenyl	23.3
2,4,6-trichlorobiphenyl	29.6
2,3,6-trichlorobiphenyl	30.8
2,3,5-trichlorobiphenyl	34.3
2,3,4-trichlorobiphenyl	38.4
3,4,5-trichlorobiphenyl	43.5
2,3,5,6-tetrachlorobiphenyl	40.3
2,3,4,6-tetrachlorobiphenyl	45.9
2,3,4,5-tetrachlorobiphenyl	56.8
2,3,4,5,6-pentachlorobiphenyl	60.9
(biphenyl)	(1.0)

Figure 2.5 Elution sequence of polychlorobiphenyls on SE 30

differing vertical line lengths represent the various different isomer groups



1. 2-chlorobiphenyl
2. 3-chlorobiphenyl
3. 4-chlorobiphenyl
4. 2,6-dichlorobiphenyl
5. 2,5-dichlorobiphenyl
6. 2,4-dichlorobiphenyl
7. 2,3-dichlorobiphenyl
8. 3,5-dichlorobiphenyl
9. 3,4-dichlorobiphenyl
10. 2,4,5-trichlorobiphenyl
11. 2,4,6-trichlorobiphenyl
12. 2,3,6-trichlorobiphenyl
13. 2,3,5-trichlorobiphenyl
14. 2,3,4-trichlorobiphenyl
15. 3,4,5-trichlorobiphenyl
16. 2,3,5,6-tetrachlorobiphenyl
17. 2,3,4,6-tetrachlorobiphenyl
18. 2,3,4,5-tetrachlorobiphenyl
19. 2,3,4,5,6-pentachlorobiphenyl

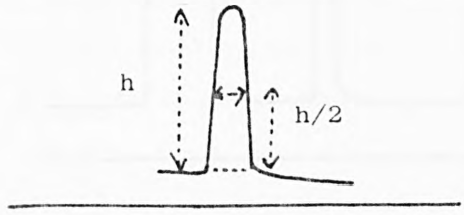
2.11.4 MEASUREMENT OF PEAK AREAS

Peak areas of symmetrical, well defined peaks were obtained by multiplying the peak height by its width at half height. In cases of asymmetric peaks, the chromatogram was photocopied and the peaks were cut out and weighed. The ratio of the peak weights was assumed to be equal to the ratio of their areas.

For overlapping peaks, a vertical straight line separating thepeaks was drawn from the minimum to the base line of the chromatogram. Each peak was then cut out and weighed.

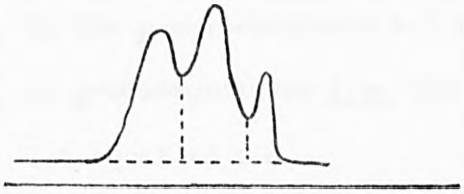
When a small peak appeared on the tail of a larger peak, the tail was extended and the area of the small peak above the tail was used as a measure of the amount of the minor component. (See Figure 2.6 below.)

Figure 2.6 Methods of measurement of various peak shapes

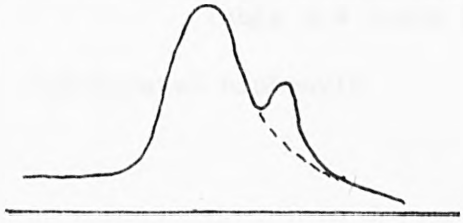


symmetrical peak
height times width at half height

asymmetrical peak
cut out and weigh



overlapping peaks

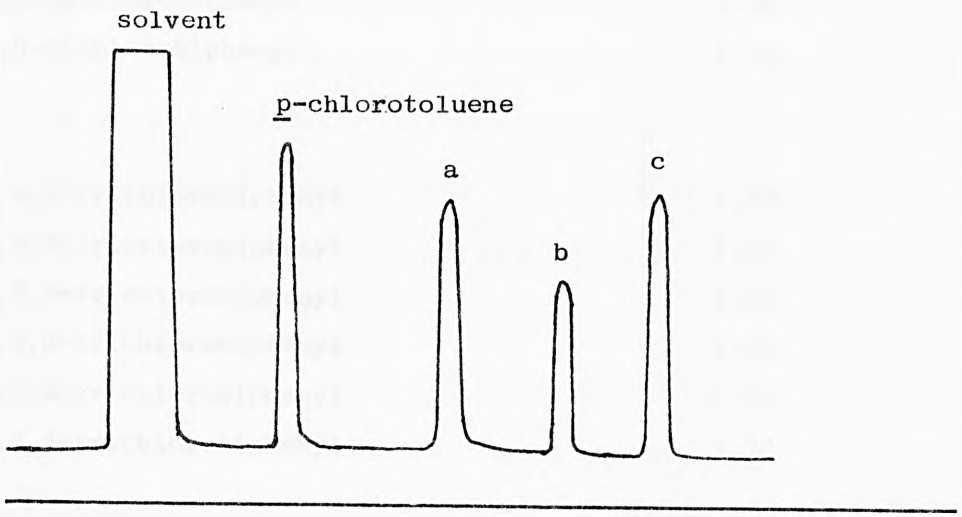


peak on tail

2.11.5 DETERMINATION OF RESPONSE FACTORS

Section 2.11.1 shows the derivation of the expression linking weights, peak areas of a compound and its response factor. A method for calculating F.I.D. weight percent response factors is to make up a standard solution of each polychlorobiphenyl, say a, b, and c, and p-chlorotoluene (the reference compound) and then produce a chromatogram of the mixture as shown in Figure 2.7.

Figure 2.7 Chromatogram used in calculation of F.I.D. response factors



The weights, W, injected are known and the areas, A, can be measured. The ratio A / W is calculated for each peak. The response factor, F, is calculated by dividing the A / W of each peak by the p-chlorotoluene A / W. These response factors are relative to p-chlorotoluene i.e. the p-chlorotoluene factor is arbitrarily set equal to 1.0.

Table 2.4 lists the response factors obtained for the chlorinated biphenyls.

Table 2.4 Response factors relative to p-chlorotoluene for chlorinated biphenyls

compound	response factor
2-chlorobiphenyl	1.06
3-chlorobiphenyl	1.19
4--chlorobiphenyl	1.16
2,6-dichlorobiphenyl	1.21
2,5-dichlorobiphenyl	1.28
2,4-dichlorobiphenyl	1.32
2,3-dichlorobiphenyl	1.35
3,4-dichlorobiphenyl	1.56
3,5-dichlorobiphenyl	1.62
2,4,5-trichlorobiphenyl	1.63
2,4,6-trichlorobiphenyl	1.66
2,3,6-trichlorobiphenyl	1.68
2,3,5-trichlorobiphenyl	1.65
2,3,4-trichlorobiphenyl	1.72
3,4,5-trichlorobiphenyl	1.76
2,3,5,6-tetrachlorobiphenyl	1.82
2,3,4,6-tetrachlorobiphenyl	1.87
2,3,4,5-tetrachlorobiphenyl	2.04
2,3,4,5,6-pentachlorobiphenyl	2.28
(biphenyl)	1.15

2.11.6 USE OF GC / MASS SPECTROMETRY FOR THE IDENTIFICATION OF REACTION PRODUCTS

The effluent from a gas chromatograph is usually a pure compound in small quantity in the gas phase. The quantity and condition is ideal for transfer into a mass spectrometer source, providing the carrier gas can be largely removed.

The gas chromatograph is thus directly coupled to the mass spectrometer, and the spectrum of each component is obtained as it leaves the column. [98] Identification of substances in very small quantities is therefore possible in complex reaction products. [125] Each peak from the gas chromatograph can be bled to the mass spectrometer in succession. [126] The mass spectrometer was interfaced to a computer as data output is enormous when fast scanning a succession of peaks eluting rapidly from a gas chromatograph. [127, 128]

The mass spectra of the products of phenylation of the polychlorobenzenes was run on a Kratos MS 30 single beam mass spectrometer with a mass range of 28 to 495 mass units. Quaterphenyls, which were the heaviest compounds likely to have been formed in the phenylation reactions had a mass of 306 mass units.

Computer analysis of the individual peak mass numbers was used to identify the compound giving rise to the peak. The computer print-out of the results gave plots of ion abundance *versus* m / e ratio. These results, along with fragmentation patterns of the polychlorobiphenyls are listed in the various Tables in the Appendix. The base peak is assigned a relative abundance of 100 and the relative abundances of all the other peaks in the spectrum are reported as percentages of the abundance of the base peak.

Chlorine posesses two isotopes differing by 2 mass units, ^{35}Cl and ^{37}Cl, in the abundance ratio 3 : 1 and one can calculate the abundance of the 3 species $X^{35}Cl_2$, $X^{35}Cl^{37}Cl$ and $X^{37}Cl_2$ where X is the remaining molecule, as 9 : 6 : 1. (The natural abundance of ^{37}Cl is 32.5 % that of ^{35}Cl.)

The ions from chlorine compounds are very characteristic and in an ion containing one chlorine atom, the relative intensities of the lines separated by 2 mass units is 3 : 1.

For each element in a given ion, the relative contributions to m + 1, m + 2 peaks etc. can be calculated from the binomial expansion of $(a + b)^n$, where a and b are the relative abundances of the isotopes and n is the number of these atoms present in the ion. (125)

Thus for three chlorine atoms in an ion, expansion gives $a^3 + 3a^2b + 3ab^2 + b^3$, whilst four peaks are found where the first contains three ^{35}Cl atoms and each successive peak has ^{35}Cl replaced by ^{37}Cl until the last peak contains three ^{37}Cl atoms.

The m / e values are separated by 2 mass units at m, m + 2, m + 4, m + 6. As the relative abundances of ^{35}Cl and ^{37}Cl are 3 : 1 (a = 3, b = 1) the intensities of the four peaks are :-

$a^3 = 27$, $3a^2b = 27$, $3ab^2 = 9$, $b^3 = 1$ i.e. 27 : 27 : 9 : 1

A compound that contains one chlorine atom will have an m + 2 peak approximately one third the intensity of the molecular ion peak because of the presence of molecular ions containing ^{37}Cl isotope.

A compound that contains two chlorines will show a distinct m + 4 peak, in additon to m + 2 peak because of the presence of molecular ions containing two atoms of the heavy isotope.

Therefore, the number of chlorine atoms in a molecule can be ascertained by the number of alternate peaks beyond the parent

peak. Thus, three chlorine atoms in a molecule will give peaks at m, m + 2, m + 4 and m + 6. (129)

Also, in polychloro-compounds, the peak of the highest mass may be so weak as to escape notice.

The relative abundances of the peaks (molecular ion, m + 2, m + 4 *etc.*) have been calculated and are presented in Table 2.5, showing the isotope contributions in terms of percentage of the parent peak. (130)

The mass spectrum of dichlorobiphenyls shows chlorine randomisation over both phenyl rings, except in the case of both chlorine atoms being *ortho*- to a C - C bond *e.g.* 2,2'- and 2,6-dichlorobiphenyls. Similar results are obtained with tetrachloro-biphenyls. (126)

In dichlorobiphenyls, fragmentation patterns showed both loss of chlorine and hydrogen chloride from the molecular ion and the occurrence of metastable peaks. All dichlorobiphenyl isomers were found to have a common breakdown pattern and hence the isomers were indistinguishable. Similarly, the chlorobiphenyl breakdown pattern was common with the *ortho*- isomer being indistinguishable from the *meta*- and *para*-isomers.

Tri- and tetrachlorobiphenyls were both found to fragment with successive loss of chlorine atoms with their primary ion spectra being virtually indistinguishable. Therefore isomeric polychlorobiphenyls lose their positional identity upon electron impact. (131)

Table 2.5 Intensities of isotope peaks for ^{35}Cl and ^{37}Cl

halogen present	m	% m + 2	% m + 4	% m + 6	% m + 8	% m + 10	% m + 12
Cl	100	32.6					
Cl_2	100	65.3	10.6				
Cl_3	100	97.8	31.9	3.47			
Cl_4	100	131.0	63.9	14.0	1.15		
Cl_5	100	163.0	106.0	34.7	5.66	0.37	
Cl_6	100	196.0	161.0	69.4	17.0	2.23	0.11

Table 2.6 Multiplicity of chlorine peaks

number of chlorine atoms present	possible molecular ions in fragmentation pattern
1	m, m + 2
2	m, m + 2, m + 4
3	m, m + 2, m + 4, m + 6
4	m, m + 2, m + 4, m + 6, m + 8
5	m, m + 2, m + 4, m + 6, m + 8, m + 10
6	m, m + 2, m + 4, m + 6, m + 8, m + 10, m + 12

Table 2.7 Possible molecular ions from polychlorobenzenes

polychloro-benzene	m	m + 2	m + 4	m + 6	m + 8	m + 10	m + 12
chlorobenzene	112.5	114.5					
dichlorobenzene	147.0	149.0	151.0				
trichlorobenzene	181.5	183.5	185.5	187.5			
tetrachlorobenzene	216.0	218.0	220.0	222.0	224.0		
pentachlorobenzene	250.5	252.5	254.5	256.5	258.5	260.5	
hexachlorobenzene	285.0	287.0	289.0	291.0	293.0	295.0	297.0

Table 2.8 Possible molecular ions from polychlorobiphenyls

polychloro-biphenyl	m	m + 2	m + 4	m + 6	m + 8	m + 10
chlorobiphenyl	188.5	190.5				
dichlorobiphenyl	223.0	225.0	227.0			
trichlorobiphenyl	257.5	259.5	261.5	263.5		
tetrachlorobiphenyl	292.0	294.0	296.0	298.0	300.0	
pentachlorobiphenyl	326.5	328.5	330.5	332.5	334.5	336.5

2.11.7 ATTEMPTED USE OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (H.P.L.C.) FOR THE ANALYSIS OF THE REACTION PRODUCTS OF THE PHENYLATION REACTIONS

The possible use of H.P.L.C. as the main analytical technique for the separation of the products of the phenylation of polychlorobenzenes was investigated. [133, 134] Chromatography was performed with a Waters liquid chromatograph M 6000 equipped with a suitable injection valve. Detection was carried out by plotting the absorption at 254 nm. on a variable wavelength Perkin Elmer spectrophotometer. This wavelength was found to be a reasonable average of λ_{max} for all the polychlorocompounds investigated.

The phenylated reaction mixtures and the standard polychlorobiphenyls were dissolved in carbon tetrachloride. The eluant flow rate used was between 1 and 2 ml. min^{-1}, and prior to use the column was allowed to equilibrate with the mobile phase for 2 hours.

As the samples were complex mixtures, linear gradient elution was attempted to achieve shorter retention times, better resolution and reduced tailing effects. However, separation of the phenylated reaction mixtures was incomplete with extensive overlapping of the peaks from isomeric chlorobiphenyls. Due to this poor separation capability, the H.P.L.C. method of analysis was abandoned in favour of g.l.c.

H.P.L.C. columns investigated for the separation of the phenylated reaction mixtures :-

Corasil I and II, Carbowax 400, Reverse phase C_8, C_{18}, Hypersil, Porasil

Eluants investigated were :-

Hexane, pentane, cyclohexane, 5 to 25 % ethyl acetate / cyclohexane, 5 to 20 % ethyl acetate / hexane, methanol / water.

2.11.8 DETERMINATION OF RELATIVE POSITIONAL REACTIVITIES (PARTIAL RATE FACTORS)

A substituent group is classified as activating if the remaining positions on the ring it is attached to are each more reactive than one position on benzene, and is classified as deactivating if they are less reactive.

For an exact, quantitative comparison under identical reaction conditions, competitive reactions can be carried out, in which the compounds to be compared are allowed to compete for a limited amount of reagent.

Equimolar amounts of two compounds to be compared are mixed together and allowed to react with a very limited amount of a particular reagent. Since there is not enough reagent for both compounds, the two compete with each other. Analysis of the reaction products shows which compound has consumed most of the reagent and hence is more reactive.

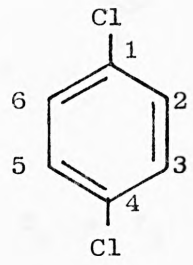
For this work, the two compounds were benzene and the appropriate polychlorobenzene, competing for a limited supply of phenyl radicals from dibenzoyl peroxide.

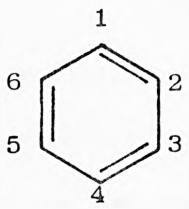
For convenience in experimentation, some of the competition experiments have actually used mixtures containing the two competing compounds in molar ratios other than 1 : 1.

Calculation of Partial Rate Factors

The Partial Rate Factor (p.r.f.) is the numerical value given for the reactivity at a certain position in a molecule compared to the reactivity of one position in benzene. (132)

Consider the structures of p-dichlorobenzene and benzene :-





As there are four equivalent C - H positions in p-dichlorobenzene (viz 2,3,5 and 6) and six in benzene, these figures must be taken into account in the p.r.f. calculation as shown below.

$$\text{p.r.f} = \frac{\text{rate of reaction at position 2 or 3 or 5 or 6 in p-dichlorobenzene}}{\text{rate of reaction at one position in benzene}}$$

if

$$A = \frac{\text{weight of 2,5-dichlorobiphenyl peak x response factor for p-dichlorobiphenyl}}{4 \times \text{concentration of p-dichlorobenzene}}$$

and

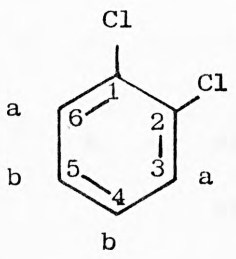
$$B = \frac{\text{weight of biphenyl peak x response factor for biphenyl}}{6 \times \text{concentration of benzene}}$$

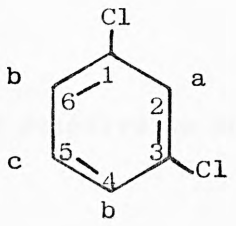
then

$$\text{partial rate factor of compound} = \frac{A}{B}$$

Where there were more than one p.r.f to be evaluated as in ortho-

and meta-dichlorobenzenes a similar calculation procedure utilising response factors was followed.





$f_a = f_3 = f_6$

$f_b = f_4 = f_5$

$f_a = f_2$

$f_b = f_4 = f_6$

$f_c = f_5$

The products of the phenylation reactions indicated that attack by phenyl radicals also occurred at positions occupied by chlorine and a rate factor for attack at these positions was determined in a similar manner i.e. p.r.f.'s for phenyldechlorination reactions.

2.11.9 DETERMINATION OF THE YIELDS OF REACTION PRODUCTS

Section 2.11.1 shows a detailed explanation and derivation of the relationship between the peak area and weight of a substance as shown below.

On opening the sealed tubes, the phenylated products were completely transferred into a flask with 10 ml. carbon tetrachloride. Two further 5 ml. portions of carbon tetrachloride were used to ensure complete transfer of reaction products. A known quantity of p-chlorotoluene was then added to the phenylated products as the internal standard.

Therefore,

$$\frac{W_X}{W_S} = \frac{A_X}{A_S} \times k \times F$$

where :-

k = response factor for X relative to the internal standard compound

W_X, W_S = the weights of X and S (the internal standard) respectively in the reaction mixture

A_X, A_S = the peak areas of the compound X and the internal standard S respectively

Therefore,

$$W_X = W_s \times \frac{A_X}{A_S} \times k \times F$$

where :-

F = any signal attenuation adjustment

example :-

$$\text{weight of 2,5-dichlorobiphenyl} = \text{weight of internal standard} \times \frac{\text{area of 2,5-dichlorobiphenyl peak}}{\text{area of internal standard peak}} \times \text{response factor for 2,5-dichlorobiphenyl}$$

(assuming that the same attenuation was used for both peaks)

Percentage yield

Biaryl yield was expressed as the number of moles produced per mole of dibenzoyl peroxide.

Let

x = weight of compound X

$(MW)_X$ = molecular weight of compound X

p = weight of peroxide P

$(MW)_P$ = molecular weight of peroxide P

then

$$\text{yield of compound X} = \frac{\frac{x}{(MW)_X}}{\frac{p}{(MW)_P}}$$

expressed in moles per mole of peroxide

The percentage yield in moles per mole peroxide = yield x 100

CHAPTER THREE

PHENYLATION OF CHLOROBENZENE

3.1 METHOD OF PHENYLATION OF CHLOROBENZENE

The phenylation of chlorobenzene and the other chlorinated benzenes was carried out by the competition method as described in section 2.10 using benzene as the reference compound.

After carrying out several phenylation reactions at various temperatures for different lengths of time, it was decided after product analysis to carry out all the phenylation reactions at 80 ^{o}C for 50 hours.

The phenylation of chlorobenzene was also carried out in the presence of various additives such as copper benzoate to promote the efficient oxidation of the phenylcyclohexadienyl radical.

Some competitive phenylation reactions were also carried out by varying the substrate ratio from polychlorobenzene : benzene 1 : 1 to 1 : 2 and 1 : 3. The partial rate factor values obtained from these reactions were of the same order as results tabulated in this work. However, due to insufficient experiments, these results have not been included.

Sections 3.2 to 3.4 show the chromatograms obtained and their identification followed by tables listing experimental quantities leading to tables of results tabulating partial rate factors, yields and calculated isomer ratios.

3.2 CHROMATOGRAMS

Figure 3.1 shows the chromatogram of the reaction products from the phenylation of chlorobenzene run at high attenuation. Figure 3.2 shows the same thing run at low attenuation. Figure 3.3 is a reconstructed chromatogram, being a combination of the above.

Figure 3.1

Reaction of chlorobenzene - high attenuation

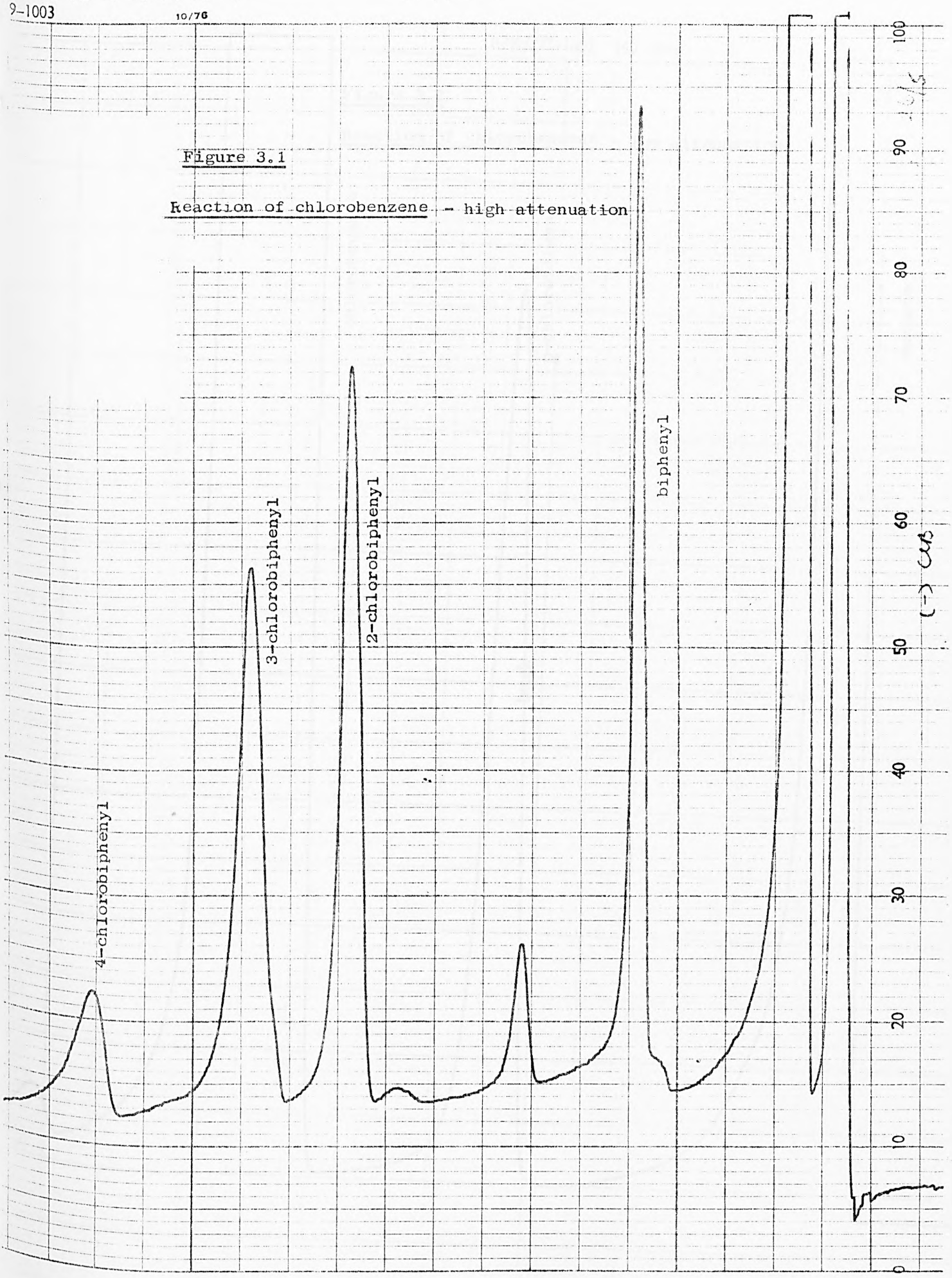


Figure 3.2

Reaction of chlorobenzene - low attenuation

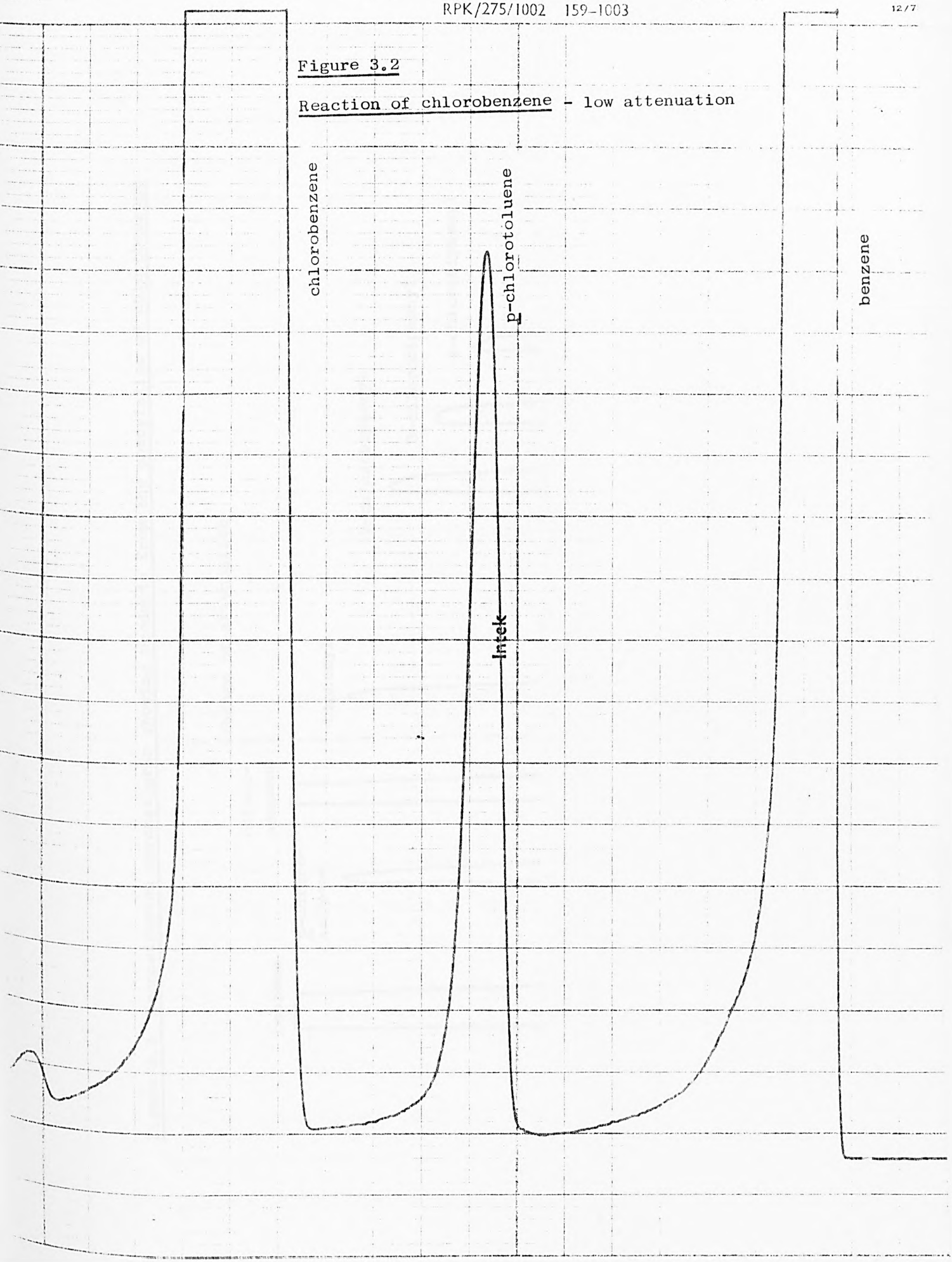
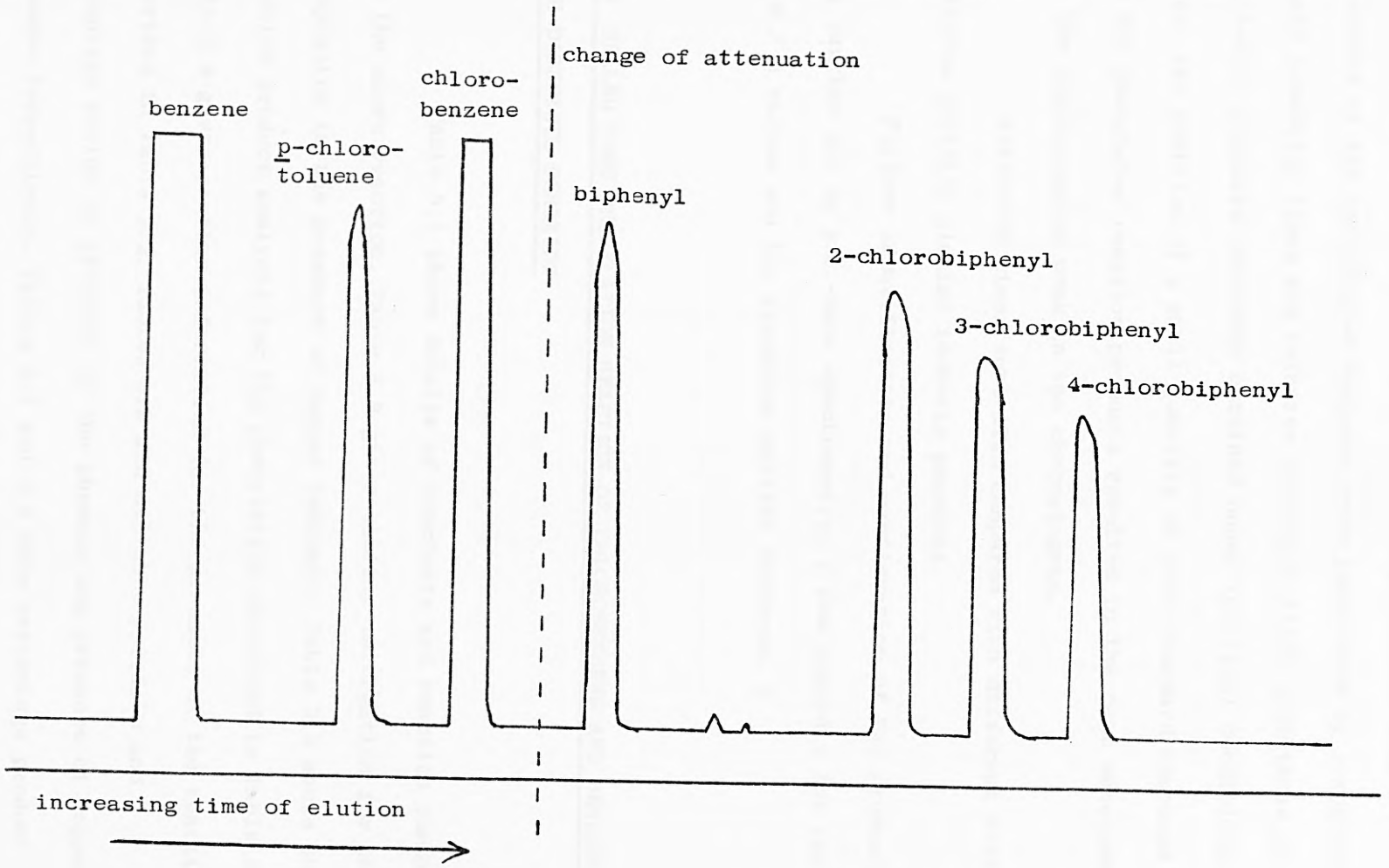


Figure 3.3 Reconstructed chromatogram showing products from the phenylation of chlorobenzene



3.3 PEAK IDENTIFICATION

Peaks on the chromatograms for the phenylated reaction products of the chlorinated benzenes were identified by comparing their retention times and relative retention times with those of authentic standard compounds obtained under identical conditions. Also, the addition of a small quantity of pure standard compound to the phenylated reaction products resulted in the peak enhancement of the corresponding peak in the chromatogram.

Retention times were also compared with different reaction mixtures yielding similar isomeric products.

Further identification and confirmation of the products was carried out by g.c.-mass spectrometry. (See appendix for the m^+, m / e values and the breakdown pattern observed.)

3.4 SEALED TUBE PHENYLATION REACTION OF CHLOROBENZENE AND BENZENE WITH DIBENZOYL PEROXIDE

Table 3.1 shows details of reactants and reaction conditions for the above reaction. Table 3.2 gives similar information for the phenylation in the presence of copper benzoate. Table 3.3 shows the reaction product analysis for the phenylation described in Table 3.1. Table 3.4 gives similar information for the products of the reaction described in Table 3.2. Tables 3.5 and 3.6 show p.r.f.'s and percentage yields of products in the absence and presence of copper benzoate respectively. Tables 3.7 and 3.8 show percentage product isomer ratios calculated from partial rate factors only in the absence and presence of copper benzoate respectively.

Table 3.1 Composition of reaction mixtures

experiment number	benzene weight		chlorobenzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^2	g x 10	mol x 10^2	g x 10	mol x 10^2
1	8.726	1.12	1.2655	1.12	2.155	1.0
2	8.734	1.12	1.2648	1.12	2.467	1.0
3	8.739	1.12	1.2643	1.12	2.459	1.0
4	8.722	1.12	1.2654	1.12	2.450	1.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

substrate ratio : 1 : 1

Table 3.2 Composition of reaction mixture (presence of copper benzoate)

experiment number	benzene weight		chlorobenzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^2	g x 10	mol x 10^2	g x 10	mol x 10^2
1	8.746	1.12	1.2505	1.12	2.485	1.0
2	8.740	1.12	1.2516	1.12	2.479	1.0
3	8.736	1.12	1.2508	1.12	2.473	1.0
4	8.737	1.12	1.2513	1.11	2.481	1.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

substrate ratio : 1 : 1

weight of copper benzoate added in each case : 0.1 g.

Table 3.3 Analysis of the phenylation reaction products of chlorobenzene (absence of copper benzoate)

experiment number	2-chlorobiphenyl					3-chlorobiphenyl					4-chlorobiphenyl					p-chlorotoluene internal std.
	peak weight (g.)	cpd. weight (g.)	peak weight Ph_2 (g.)	Ph_2 weight (g.)	peak weight std. (g.)	peak weight (g.)	cpd. weight (g.)	peak weight Ph_2 (g.)	Ph_2 weight (g.)	peak weight std. (g.)	peak weight (g.)	cpd. weight (g.)	peak weight Ph_2 (g.)	Ph_2 weight (g.)	peak weight std. (g.)	(g.)
1	0.0519	0.0998	0.0679	0.1244	0.0906	0.0218	0.0422	0.0782	0.1284	0.1011	0.0114	0.0209	0.0577	0.0921	0.1040	0.1644
2	0.0496	0.0965	0.0656	0.1217	0.0850	0.0206	0.0412	0.0747	0.1267	0.0929	0.0129	0.0213	0.0680	0.0978	0.1097	0.1561
3	0.0527	0.1003	0.0681	0.1244	0.0816	0.0215	0.0419	0.0765	0.1265	0.0895	0.0137	0.0219	0.0729	0.1015	0.1063	0.1465
4	0.0502	0.0986	0.0652	0.1220	0.0910	0.0229	0.0426	0.0763	0.1205	0.1079	0.0118	0.0210	0.0647	0.1003	0.1099	0.1687

1. p-chlorotoluene, the internal standard, was added to the phenylation reaction after the completion of the reaction
2. response factors : biphenyl = 1.01, 2-chlorobiphenyl = 1.06, 3-chlorobiphenyl = 1.19, 4-chlorobiphenyl = 1.16
3. peaks were cut out and weighed
4. the above results were obtained from three different chromatograms at various attenuations of the same reaction mixture, giving better comparison of the biphenyl peak with the chlorobiphenyl peaks

Table 3.4 Analysis of the phenylation reaction products of chlorobenzene (presence of copper benzoate)

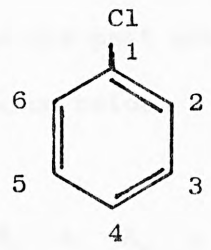
experiment number	2-chlorobiphenyl					3-chlorobiphenyl					4-chlorobiphenyl					p-chlorotoluene internal std.
	peak weight (g.)	cpd. weight (g.)	peak weight Ph_2 (g.)	Ph_2 weight (g.)	peak weight std. (g.)	peak weight (g.)	cpd. weight (g.)	peak weight Ph_2 (g.)	Ph_2 weight (g.)	peak weight std. (g.)	peak weight (g.)	cpd. weight (g.)	peak weight Ph_2 (g.)	Ph_2 weight (g.)	peak weight std. (g.)	(g.)
1	0.0561	0.1060	0.0488	0.0879	0.0865	0.0247	0.0437	0.0825	0.1239	0.1037	0.0153	0.0234	0.0673	0.0897	0.1169	0.1542
2	0.0554	0.1055	0.0497	0.0901	0.0850	0.0251	0.0442	0.0791	0.1182	0.1032	0.0146	0.0228	0.0693	0.0943	0.1134	0.1527
3	0.0569	0.1062	0.0515	0.0916	0.0856	0.0259	0.0445	0.0901	0.1315	0.1044	0.0154	0.0231	0.0710	0.0928	0.1166	0.1508
4	0.0550	0.1054	0.0486	0.0908	0.0838	0.0240	0.0436	0.0713	0.1099	0.1013	0.0161	0.0238	0.0729	0.0939	0.1216	0.1550

the notes at the foot of Table 3.3 also apply to this table

additive = 0.1 g. copper benzoate in each case

estimated percentage error = ± 5 %

Calculation of partial rate factors



If f_x = partial rate factor for position x

$$f_x = \frac{\text{rate of reaction at position x (mol dm}^{-3}\text{ s}^{-1}\text{)}}{\text{rate of reaction at one position of benzene under identical conditions (mol dm}^{-3}\text{ s}^{-1}\text{)}}$$

f_o = ortho- partial rate factor = f_2 = f_6

f_m = meta- partial rate factor = f_3 = f_5

f_p = para- partial rate factor = f_4

For an ideal equimolar mixture of chlorobenzene and benzene :-

$$f_o = \frac{\text{weight of 2-chlorobiphenyl formed}}{\text{Molecular weight of 2-chlorobiphenyl}} \times \frac{\text{M. Wt biphenyl}}{\text{weight of biphenyl formed}} \times \frac{6}{2}$$

From Table 3.3, experiment number 1

$$f_o = \frac{0.0998}{188.5} \times \frac{154}{0.1244} \times \frac{6}{2} = 1.97$$

similarly, f_m = 0.81 and f_p = 1.11

Further results are given in Table 3.5. Table 3.6 gives similar information from the reaction in the presence of copper benzoate.

Calculation of chlorobiphenyl yields

Section 2.11 lists the explanation and derivation of the relationship between the peak area and the weight of a substance as shown in the expression below.

$$W_X = W_S \times \frac{A_X}{A_S} \times R_X$$

where :

W_X, W_S = the weights of the product X formed during the reaction and the added internal standard, S

A_X, A_S = the peak areas of the compound X and the internal standard S determined as described in Chapter 2

R_X = the response factor for X relative to the internal standard

Taking values from experiment number 1 of Table 3.3, the above expression may be evaluated thus :

weight of 2-chlorobiphenyl formed during the reaction $= 0.1644 \times \frac{0.0519}{0.0906} \times 1.06$

$= 0.0998$ g.

similarly :

weight of 3-chlorobiphenyl formed during the reaction $= 0.1644 \times \frac{0.0218}{0.1011} \times 1.19$

$= 0.0422$ g.

and :

weight of 4-chlorobiphenyl formed during the reaction $= 0.1644 \times \frac{0.0114}{0.1040} \times 1.16$

$= 0.0209$ g.

These weights for 2-, 3- and 4-chlorobiphenyl were expressed in moles per mole of peroxide x 100 using values from Table 3.1 for composition of the reaction mixture.

for example :

$$\text{\% yield of compound X (as moles per mole of peroxide x 100)} = \frac{\frac{W_X}{\text{molecular wt. of X}}}{\frac{W_P}{\text{molecular wt. of P}}} \times 100$$

where :

W_X = weight of compound X

W_P = weight of peroxide

Threrfore percentage yields of the chlorobiphenyls in mole per mole of peroxide x 100 were obtained as shown using figures from Tables 3.1 and 3.3.

$$\text{\% yield 2-chlorobiphenyl} = \frac{\frac{0.0998}{188.5}}{\frac{0.2455}{242}} \times 100$$

$$= 52.2\ \%$$

$$\text{\% yield 3-chlorobiphenyl} = \frac{\frac{0.0422}{188.5}}{\frac{0.2455}{242}} \times 100$$

$$= 22.1\ \%$$

$$\text{\% yield 4-chlorobiphenyl} = \frac{\frac{0.0209}{188.5}}{\frac{0.2455}{242}} \times 100$$

$$= 10.9\ \%$$

Further results are in Tables 3.5 and 3.6 for phenylation in the absence and presence of copper benzoate respectively.

Table 3.5 Partial rate factors and percentage yields for the phenylation of chlorobenzene (absence of copper benzoate)

experiment number	p.r.f.	2-chloro-biphenyl yield	p.r.f.	3-chloro-biphenyl yield	p.r.f.	3-chloro-biphenyl yield
	f_o	%	f_m	%	f_p	%
1	1.97	52.2	0.81	22.1	1.11	10.9
2	1.94	50.5	0.80	21.6	1.07	11.1
3	1.98	52.5	0.81	21.9	1.05	11.5
4	1.99	51.6	0.87	22.3	1.03	11.0
(mean values)	1.97	51.7	0.82	22.0	1.07	11.1

yield in moles per mole benzoyl peroxide x 100

Table 3.6 Partial rate factors and percentage yields for the phenylation of chlorobenzene (presence of copper benzoate)

experiment number	p.r.f. f_o	2-chloro-biphenyl yield %	p.r.f. f_m	3-chloro-biphenyl yield %	p.r.f. f_p	4-chloro-biphenyl yield %
1	2.98	55.4	0.87	22.9	1.29	12.2
2	2.89	55.2	0.92	23.1	1.19	11.9
3	2.87	55.5	0.83	23.3	1.23	12.1
4	2.87	55.1	0.98	22.8	1.26	12.5
(mean values)	2.90	55.3	0.90	23.0	1.24	12.2

yield in moles per mole benzoyl peroxide x 100

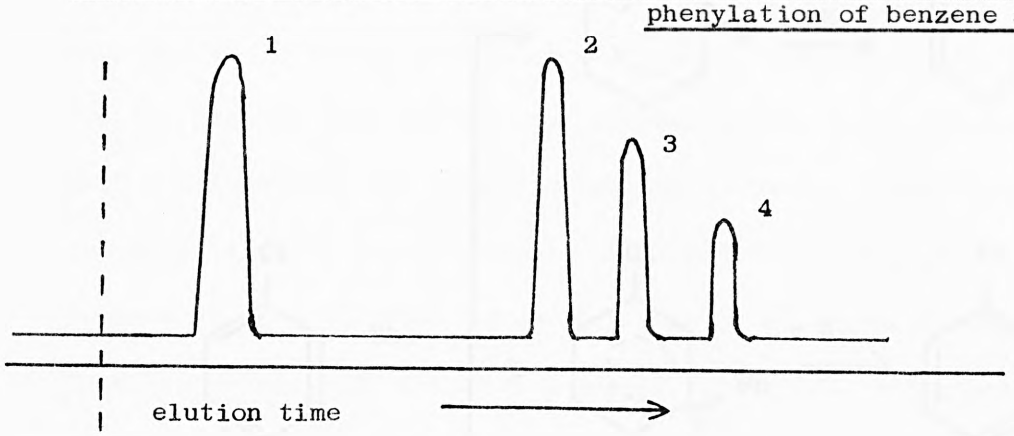
Table 3.7 Percentage isomer ratios calculated from partial rate factors (phenylation of chlorobenzene in absence of copper benzoate)

experiment number	% o- (2-chlorobiphenyl)	% m- (3-chlorobiphenyl)	% p- (4-chlorobiphenyl)
1	50.6	20.8	28.5
2	50.9	21.0	28.1
3	51.6	21.1	27.3
4	51.2	22.4	26.5

Table 3.8 Percentage isomer ratios calculated from partial rate factors (phenylation of chlorobenzene in the presence of copper benzoate)

experiment number	% o- (2-chlorobiphenyl)	% m- (3-chlorobiphenyl)	% p- (4-chlorobiphenyl)
1	58.0	16.9	25.1
2	57.8	18.4	23.8
3	58.2	19.9	25.6
4	56.1	19.2	24.7

Figure 3.4 Reconstructed chromatogram showing only products of phenylation of benzene and chlorobenzene



peak 1 = biphenyl

peak 2 = 2-chlorobiphenyl

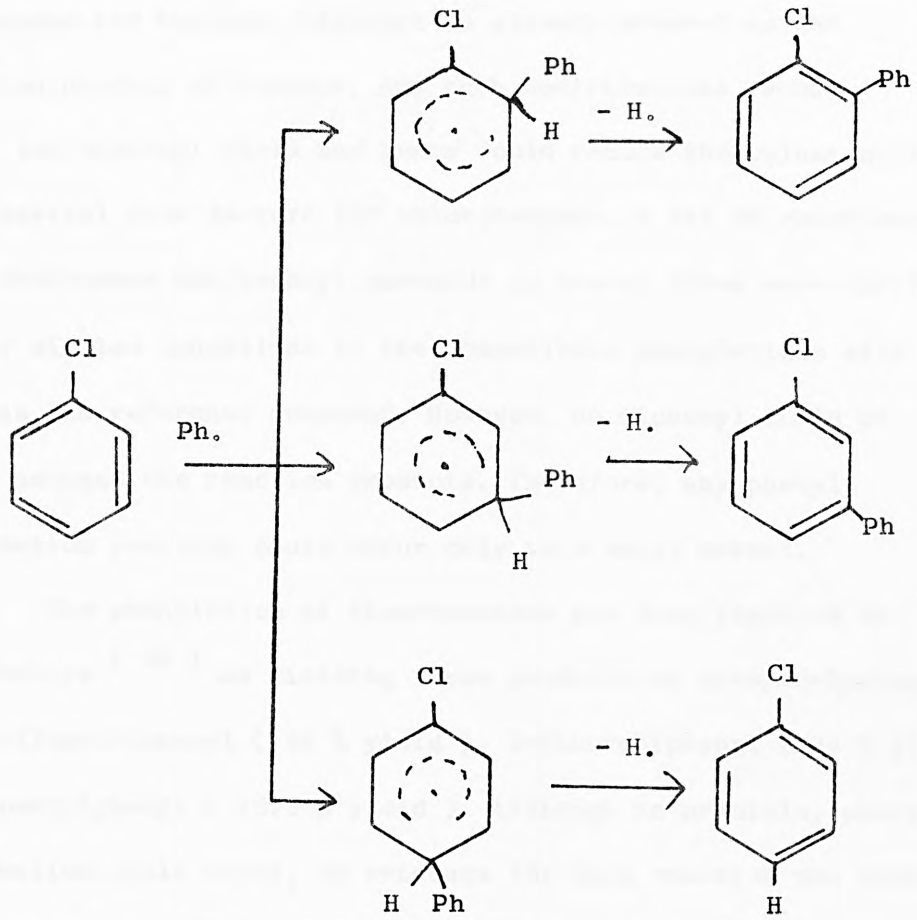
peak 3 = 3-chlorobiphenyl

peak 4 = 4-chlorobiphenyl

The competitive phenylation of chlorobiphenyl has been reported in the literature (14, 15) and has been discussed in section 1.2. The main products obtained were the isomeric 2-, 3- and 4-chlorobiphenyls.

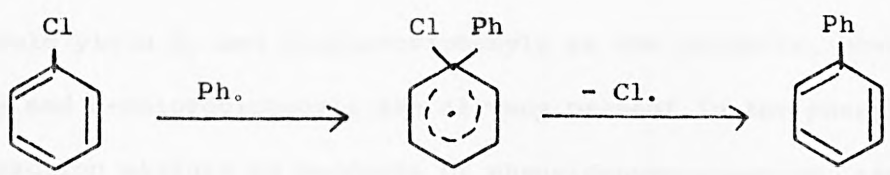
In the present study, the sealed tube phenylation of chlorobenzene and benzene yielded identical products. The simplest explanation of these results is that phenyldehydrogenation is the major reaction with phenyl radical attack at a carbon - hydrogen site followed by hydrogen displacement. Phenyl radical attack at position 2 or 6 in chlorobenzene yielded 2-chlorobiphenyl in 51.7 % yield, whilst attack at position 3 or 5 yielded 3-chlorobiphenyl in 22 % yield and attack at position 4 gave 4-chlorobiphenyl in 11.1 % yield.

The suggested pathway for the formation of the isomeric chlorobiphenyls by phenyldehydrogenation (hydrogen displacement) is shown in Scheme 3.1



Scheme 3.1

In the phenylations of the isomeric di-, tri-, tetra-, penta- and hexafluorobenzenes (see Chapters 4 to 8) the reaction products obtained by chlorine displacement and other associated reactions became increasingly significant. If phenyl radical attack occurred at C-1 in chlorobenzene (C - Cl site), followed by chlorine elimination in a phenyldechlorination reaction, the resultant product would be biphenyl as shown in Scheme 3.2.



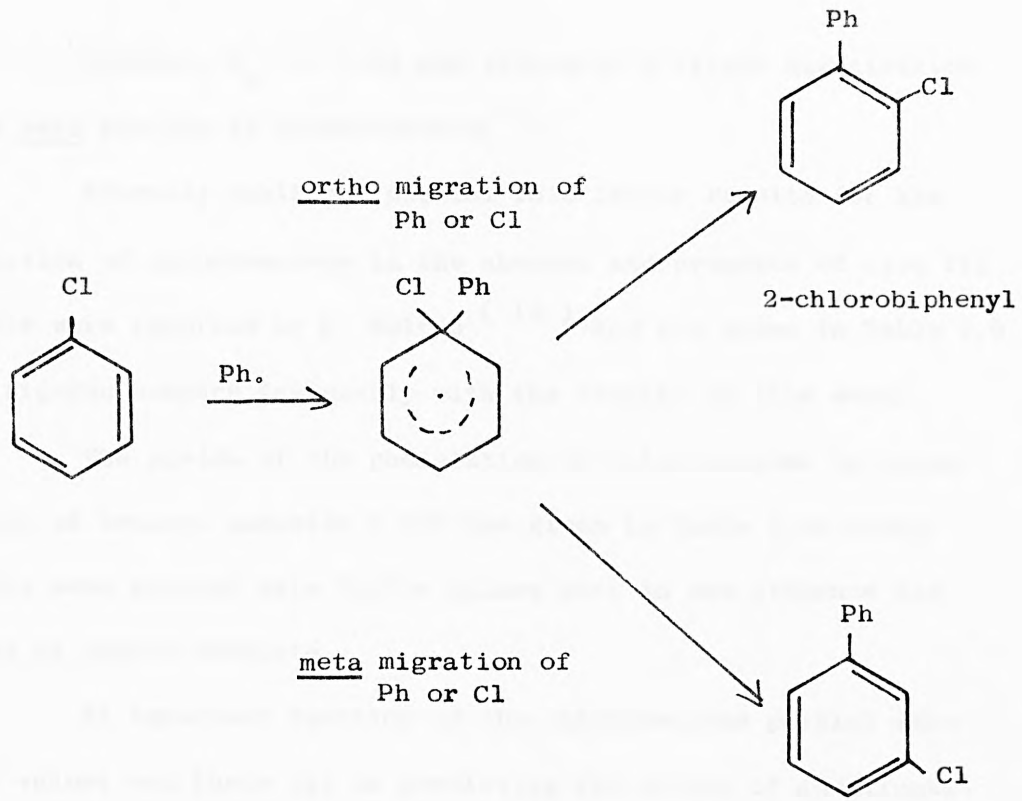
Scheme 3.2

However, in the competitive phenylation reaction of chlorobenzene and benzene, biphenyl is already present as the phenylation product of benzene. Any such contributions would increase the biphenyl yield and hence would reduce the values obtained for the partial rate factors for chlorobenzene. A set of reactions with chlorobenzene and benzoyl peroxide in sealed tubes were carried out under similar conditions to the competitive phenylations with benzene as the reference compound. However, no biphenyl could be detected amongst the reaction products. Therefore, any phenyl-dechlorination reaction could occur only to a small extent.

The phenylation of fluorobenzene has been reported in the literature [65] as yielding three products of phenyldehydrogenation, namely 2-fluorobiphenyl (48 % yield), 3-fluorobiphenyl (34 % yield) and 4-fluorobiphenyl (13.3 % yield). Although in priciple, phenyl-defluorination could occur, no evidence for this reaction was found either in phenylation or pentafluorophenylation reactions of fluorobenzene.[65] Chlorobenzene behaves similarly.

Ipso-type rearrangement reactions were found to occur in several of the more chlorinated benzenes (Chapters 4 to 8). Such reactions required ipso-type attack by phenyl radicals at the carbon - chlorine site in the chlorobenzene followed by an ortho or meta migration of either geminal group (Cl or Ph) as shown in Scheme 3.3 for chlorobenzene itself. There were no parallel reactions reported in the phenylation of fluorobenzene.[65]

If an ipso-type attack followed by the rearrangement of the intermediate complex occurred in chlorobenzene itself, this would yield 2- and 3-chlorobiphenyls as the products, however, as 2- and 3-chlorobiphenyls are already present in the phenylation reaction mixture as products of phenyldehydrogenation, the ipso rearrangement pathway would enhance the values obtained for the



Scheme 3.3

partial rate factors f_o and f_m. It is not possible to comment on this possibility except to note that no phenyldechlorination, which would involve the same σ-complex, is observed.

From Table 3.5 it can be seen that the yields of the chlorobiphenyl isomers are in the following decreasing order of 2-chlorobiphenyl (51.7 %), 3-chlorobiphenyl (22 %) and 4-chlorobiphenyl (11.1 %). From a statistical point of view, these results might be expected as there are two positions available for the formation of both the 2- and 3-chlorobiphenyls, whilst substitution at one C - H position only leads to the formation of 4-chlorobiphenyl.

The partial rate factors for chlorobenzene as shown in Table 3.5 show an activation for both the ortho- and para- positions of the molecule towards attack by a phenyl radical as compared to benzene.

$$f_o = 1.97 > f_p = 1.07 > f_m = 0.82$$

However, f_m = 0.82 and indicates a slight deactivation of the meta postion in chlorobenzene.

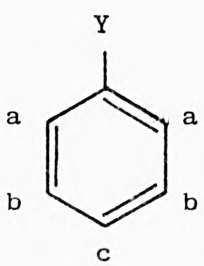
Recently published partial rate factor results for the phenylation of chlorobenzene in the absence and presence of iron III benzoate were reported by R. Bolton [13] and are shown in Table 3.9. These figures compare favourably with the results in this work.

The yields of the phenylation of chlorobenzene in moles per mole of benzoyl peroxide x 100 are given in Table 3.10 along with the mean partial rate factor values both in the presence and absence of copper benzoate.

An important function of the chlorobenzene partial rate factor values was their use in predicting the effect of additional chlorine atoms according to Holleman's product rule. [132]

When dealing with several substituent groups in the ring then as an approximation it is satisfactory to assume that the partial rate factor at a given position is the product of the partial rate factors corresponding to the substituents (Holleman's product rule).

Consider the two compounds C_6H_5Y and C_6H_5Z with the observed partial rate factors of f_o = a, f_m = b and f_p = c and f_o = p, f_m = q and f_p = r respectively, as shown below.



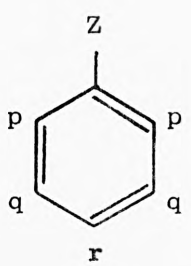


Table 3.9 Partial rate factors for the phenylation of chlorobenzene in the absence and presence of additives

additive	partial rate factors		
	f_o	f_m	f_p
(none)	1.9	0.9	1.2
iron benzoate	2.5	1.1	1.5

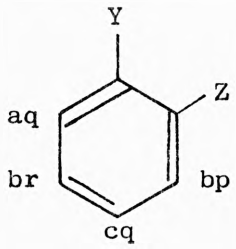
Table 3.10 Partial rate factors and percentage yields for the phenylation of chlorobenzene in the presence and absence of additives

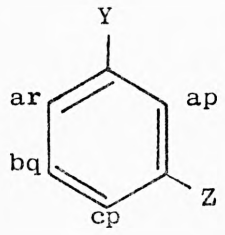
from phenyldehydrogenation :-

additive	yields (mol per mol peroxide)			p.r.f.'s		
	2-chloro-	3-chloro-	4-chloro-	f_o	f_m	f_p
(none)	51.7 %	22.0 %	11.1 %	1.97	0.82	1.07
copper benzoate	55.3 %	23.0 %	12.2 %	2.90	0.90	1.24

each row of results is a mean of four or more figures taken from Tables 3.5 and 3.6

These values can be used to predict the p.r.f.'s of the compounds shown below.





When three or more substituents are involved, exactly the same procedure can be used to assess the amounts of isomeric substitution products in the polysubsituted benzenes.

3.6 EFFECT OF ADDITIVES

The only additive investigated in the competitive sealed tube phenylation of chlorobenzene was copper benzoate. The addition of copper benzoate (0.1 g.) to the phenylation reaction mixture of chlorobenzene and benzene aided the formation of chlorobiphenyls presumably at the expense of dimerisation and possible disproportionation products as shown by the increase in the yields of the isomeric chlorobiphenyls in Table 3.10.

The partial rate factor values for chlorobenzene in the presence of copper benzoate all increased slightly, especially the value for f_o as shown in Table 3.10. This indicated that the effect of the additive favoured the reaction with chlorobenzene compared with the reaction with benzene and favoured attack at the ortho

position in chlorobenzene more than at the <u>meta</u> or <u>para</u> positions.

$$f_o = 2.90 > f_p = 1.24 > f_m = 0.90$$

CHAPTER FOUR

PHENYLATION OF DICHLOROBENZENE

4.1 METHOD OF PHENYLATION OF 1,4-DICHLOROBENZENE

This is the same as the method described in section 3.1. Sections 4.1.1 to 4.1.3 show the chromatograms obtained and their identification, followed by tables listing experimental quantities leading to tables of results tabulating partial rate factors and product yields.

4.1.1 CHROMATOGRAMS

Figures 4.1, 4.2 and 4.3 show actual chromatograms obatined. Figure 4.4 is a reconstructed chromatogram showing the relationship between all the products.

4.1.2 PEAK IDENTIFICATION

The same method was used as has been described in section 3.3.

Figure 4.1

Reaction of p-dichlorobenzene

Chromatogram obtained

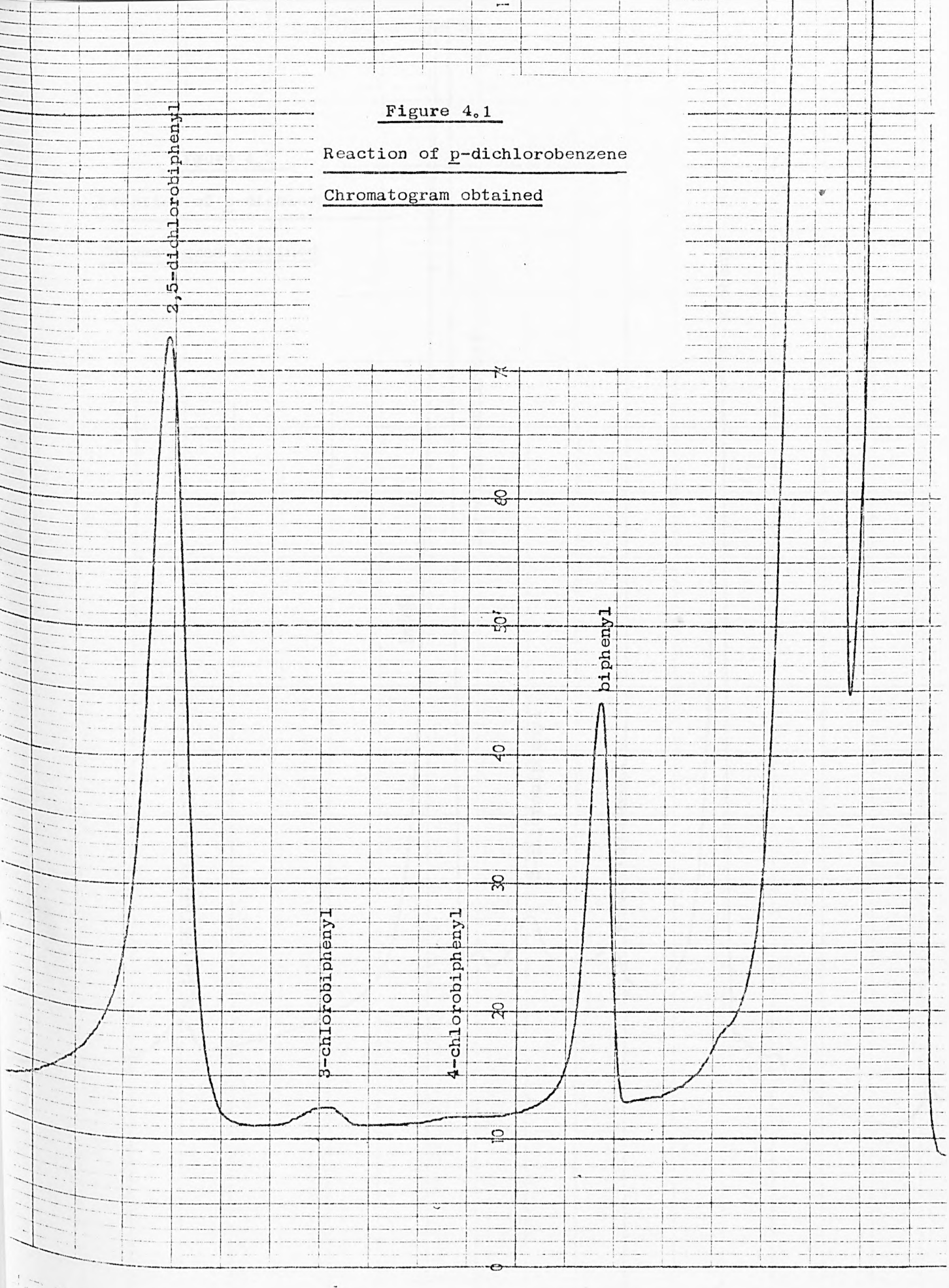


Figure 4.2

Reaction of p-dichlorobenzene

Chromatogram obtained

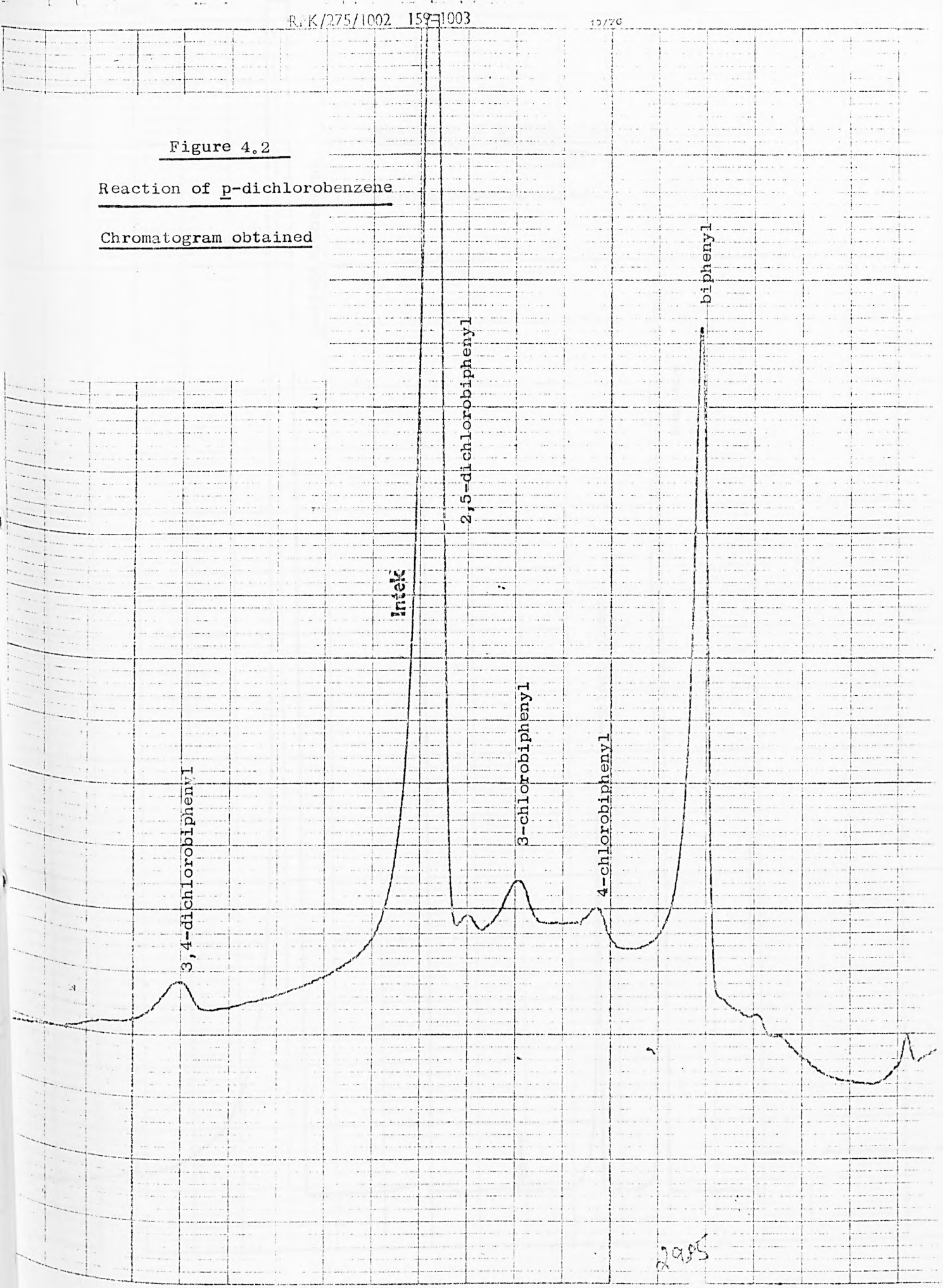


Figure 4.3

Reaction of p-dichloro-benzene

Chromatogram obtained

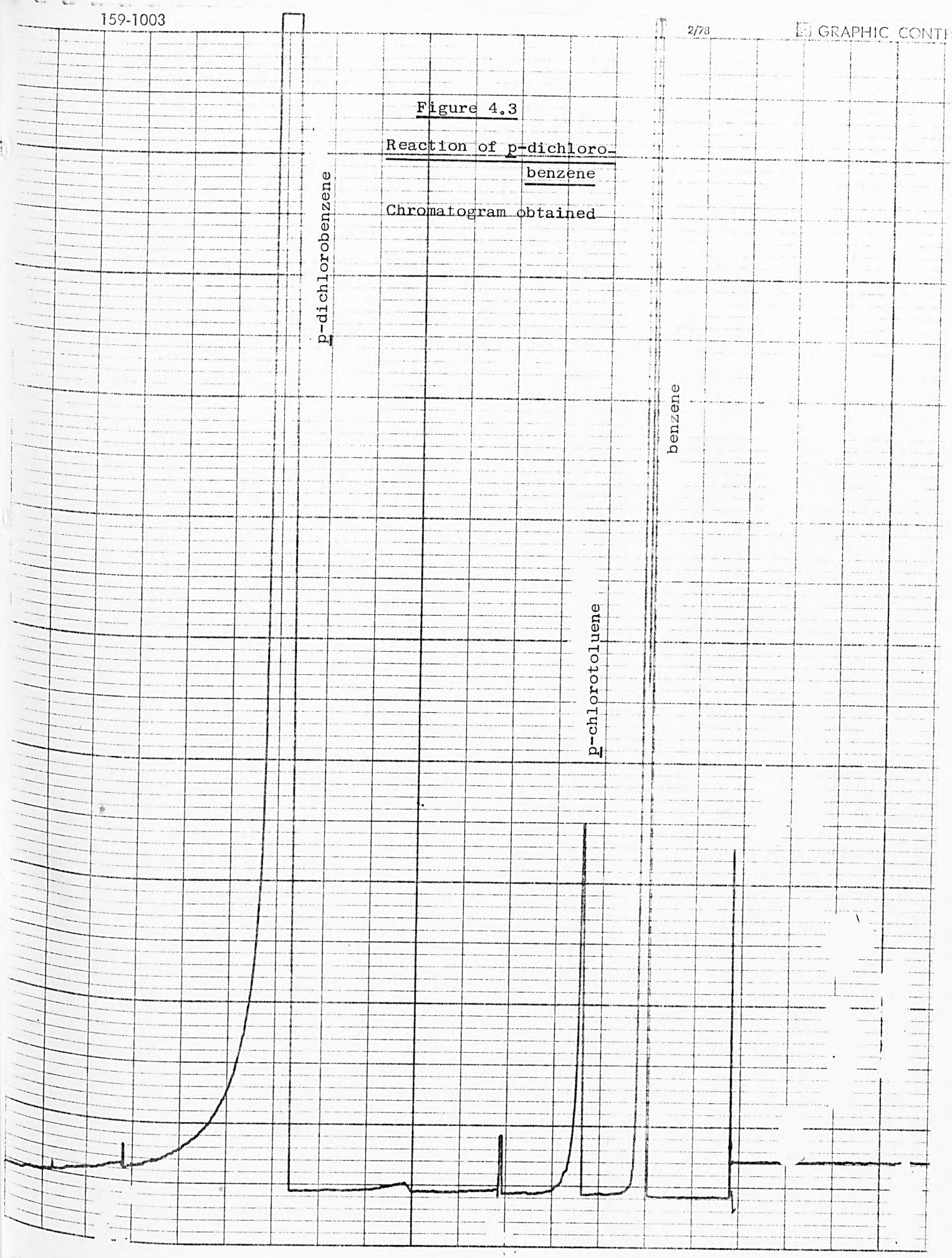


Figure 4.4 Reaction of 1,4-dichlorobenzene, reconstructed chromatogram

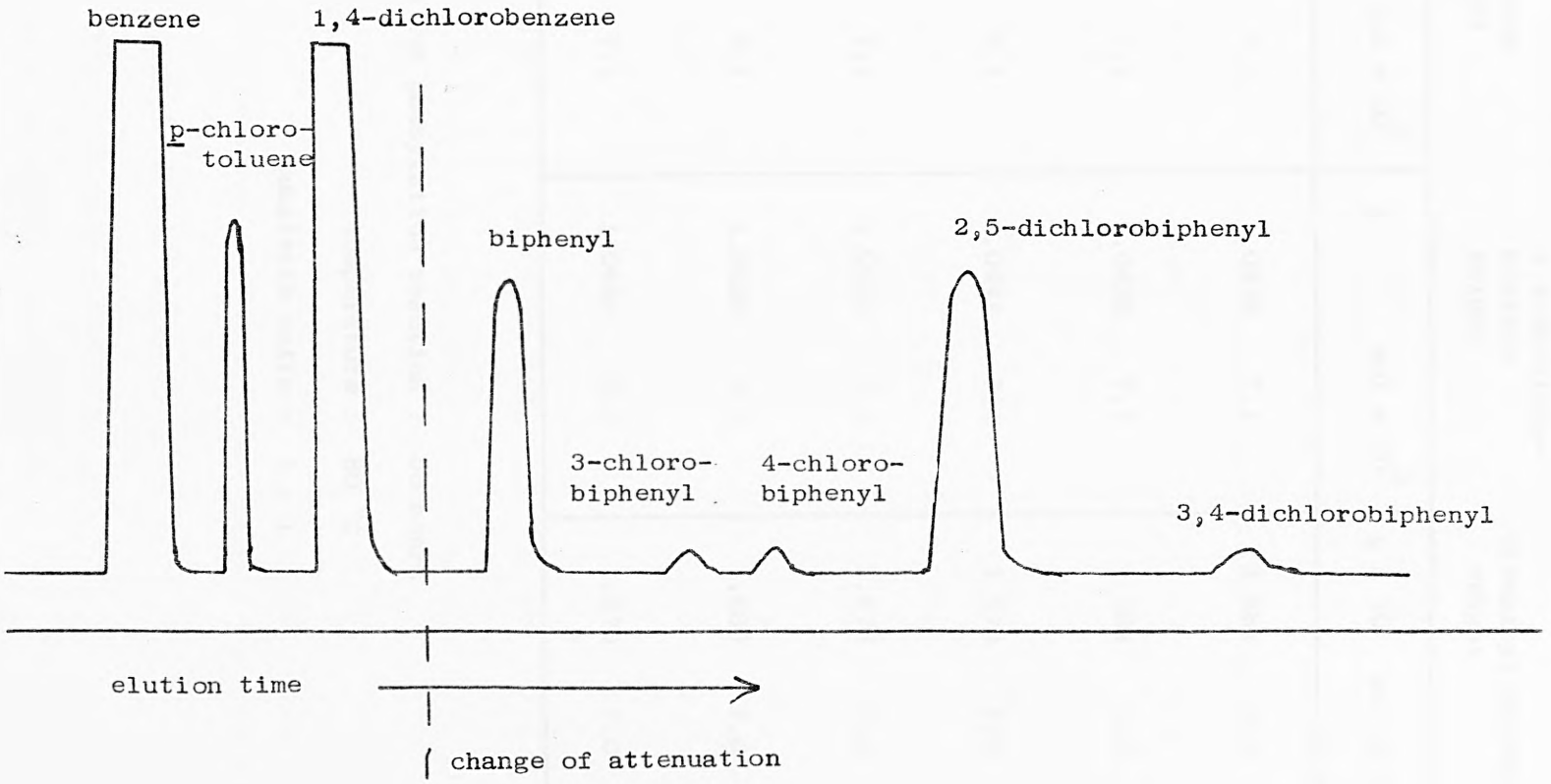


Table 4.1 Sealed tube phenylation reactions of 1,4-dichlorobenzene and benzene with dibenzoyl peroxide - composition of reaction mixtures

experiment number	benzene weight		1,4-dichloro-benzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g	mol x 10^3	g x 10	mol x 10^4
1	5.540	7.1	1.0439	7.1	1.681	7.0
2	5.546	7.1	1.0435	7.1	1.689	7.0
3	5.552	7.1	1.0441	7.1	1.672	7.0
4	5.548	7.1	1.0445	7.1	1.676	7.0
5	5.554	7.1	1.0436	7.1	1.685	7.0
6	5.557	7.1	1.0449	7.1	1.679	7.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

substrate ratio : 1 : 1

Table 4.2 Sealed tube phenylation reactions of 1,4-dichlorobenzene and benzene with dibenzoyl peroxide in the presence of copper additives - composition of reaction mixtures

experiment number	benzene weight		1,4-dichlorobenzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	5.265	6.8	0.9987	6.8	1.755	7.0
2[a]	5.326	6.8	1.0052	6.8	1.800	7.0
3[a]	5.269	6.8	1.0046	6.8	1.768	7.0
4[a]	5.342	6.8	1.0049	6.8	1.779	7.0
5[b]	5.310	6.8	1.0009	6.8	1.756	7.0
6[b]	5.302	6.8	1.0149	6.8	1.774	7.0
7[b]	5.279	6.8	1.0147	6.8	1.772	7.0
8[b]	5.287	6.8	1.0058	6.8	1.752	7.0
9[c]	5.322	6.8	1.0048	6.8	1.749	7.0
10[c]	5.299	6.8	1.0096	6.8	1.783	7.0
11[c]	5.306	6.8	1.0063	6.8	1.765	7.0
12[c]	5.295	6.8	1.0052	6.8	1.788	7.0

a = additive copper benzoate, 0.1 g.

b = additive copper acetate, 0.1 g.

c = additive cupric chloride, 0.1 g.

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

substrate ratio : 1 : 1

Table 4.3 Sealed tube phenylation reactions of 1,4-dichlorobenzene and benzene with dibenzoyl peroxide in the presence of iron powder and trichloroacetic acid - composition of reaction mixtures

experiment number	benzene weight		1,4-dichloro-benzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	5.538	7.1	1.0583	7.2	1.705	7.0
2[a]	5.545	7.1	1.0575	7.2	1.693	7.0
3[a]	5.542	7.1	1.0570	7.2	1.691	7.0
4[a]	5.551	7.1	1.0581	7.2	1.698	7.0
5[b]	5.547	7.1	1.0566	7.2	1.684	7.0
6[b]	5.558	7.1	1.0572	7.2	1.692	7.0
7[b]	5.559	7.1	1.0580	7.2	1.694	7.0
8[b]	5.544	7.1	1.0569	7.2	1.688	7.0
9[b]	5.539	7.1	1.0565	7.2	1.696	7.0

a = additive iron powder, 0.1 g.

b = additive trichloroacetic acid, 0.1 g.

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

substrate ratio : 1 : 1

Table 4.4 Analysis of the phenylation products of 1,4-dichlorobenzene and benzene (Table 4.1 gives compositions)

experiment number	dichlorobiphenyl products				chlorobiphenyl products				biphenyl		p-chlorotoluene	
	2,5-dichloro-		3,4-dichloro-		4-chloro-		3-chloro-				internal standard	
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1	0.0292	0.0412	0.0017	0.0030	0.0027	0.0035	0.0016	0.0021	0.0187	0.0237	0.1443	0.1592
2	0.0276	0.0389	0.0020	0.0034	0.0026	0.0033	0.0013	0.0017	0.0180	0.0228	0.1411	0.1556
3	0.0255	0.0360	0.0015	0.0026	0.0026	0.0033	0.0018	0.0023	0.0183	0.0232	0.1430	0.1579
4	0.0269	0.0380	0.0018	0.0031	0.0028	0.0036	0.0019	0.0025	0.0188	0.0239	0.1433	0.1581
5	0.0263	0.0372	0.0017	0.0029	0.0026	0.0033	0.0014	0.0018	0.0177	0.0225	0.1416	0.1563
6	0.0287	0.0405	0.0015	0.0025	0.0027	0.0034	0.0012	0.0016	0.0185	0.0235	0.1432	0.1578
response factor	1.28		1.56		1.16		1.19		1.01		1.00	

Table 4.5 Analysis of the phenylation products of 1,4-dichlorobenzene and benzene (Table 4.2 gives compositions) in the presence of copper additives

experiment number	dichlorobiphenyl products				chlorobiphenyl products				biphenyl		p-chlorotoluene internal standard	
	2,5-dichloro-		3,4-dichloro-		4-chloro-		3-chloro-					
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1[a]	0.0491	0.0693	0.0020	0.0035	0.0040	0.0051	0.0021	0.0028	0.0234	0.0261	0.1385	0.1528
2[a]	0.0492	0.0696	0.0023	0.0041	0.0039	0.0051	0.0024	0.0031	0.0240	0.0268	0.1400	0.1546
3[a]	0.0488	0.0689	0.0022	0.0038	0.0038	0.0049	0.0022	0.0029	0.0233	0.0260	0.1395	0.1539
4[a]	0.0485	0.0683	0.0019	0.0033	0.0041	0.0052	0.0019	0.0025	0.0241	0.0268	0.1368	0.1505
5[b]	0.0510	0.0719	0.0023	0.0039	0.0039	0.0050	0.0026	0.0034	0.0216	0.0241	0.1416	0.1561
6[b]	0.0519	0.0711	0.0024	0.0040	0.0039	0.0048	0.0025	0.0032	0.0225	0.0243	0.1445	0.1546
7[b]	0.0528	0.0723	0.0026	0.0044	0.0039	0.0048	0.0030	0.0038	0.0226	0.0244	0.1450	0.1552
8[b]	0.0509	0.0716	0.0024	0.0042	0.0039	0.0050	0.0027	0.0035	0.0220	0.0244	0.1401	0.1541
9[c]	0.0482	0.0667	0.0021	0.0035	0.0040	0.0050	0.0024	0.0031	0.0024	0.0031	0.1498	0.1618
10[c]	0.0472	0.0659	0.0016	0.0028	0.0041	0.0052	0.0020	0.0026	0.0259	0.0285	0.1490	0.1625
11[c]	0.0464	0.0653	0.0017	0.0030	0.0038	0.0049	0.0015	0.0020	0.0247	0.0274	0.1458	0.1604
12[c]	0.0492	0.0662	0.0018	0.0029	0.0041	0.0050	0.0018	0.0022	0.0267	0.0283	0.1569	0.1648

a = additive copper benzoate, 0.1 g. b = additive copper acetate, 0.1 g. c = additive cupric chloride, 0.1 g.

Table 4.6 Analysis of the phenylation products of 1,4-dichlorobenzene and benzene (Table 4.3 gives compositions) in the presence of iron powder and trichloroacetic acid

experiment number	dichlorobiphenyl products				chlorobiphenyl products				biphenyl		p-chlorotoluene internal standard	
	2,5-dichloro-		3,4-dichloro-		4-chloro-		3-chloro-					
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1[a]	0.0563	0.0757	0.0027	0.0044	0.0039	0.0047	0.0032	0.0040	0.0234	0.0248	0.1580	0.1659
2[a]	0.0571	0.0765	0.0031	0.0051	0.0045	0.0054	0.0037	0.0046	0.0245	0.0259	0.1571	0.1643
3[a]	0.0539	0.0761	0.0031	0.0053	0.0038	0.0049	0.0030	0.0038	0.0220	0.0245	0.1504	0.1660
4[a]	0.0540	0.0753	0.0028	0.0048	0.0042	0.0053	0.0037	0.0048	0.0230	0.0253	0.1516	0.1652
5[b]	0.0579	0.0786	0.0029	0.0048	0.0045	0.0055	0.0038	0.0048	0.0225	0.0241	0.1499	0.1589
6[b]	0.0557	0.0778	0.0032	0.0056	0.0043	0.0055	0.0034	0.0044	0.0222	0.0245	0.1462	0.1594
7[b]	0.0560	0.0790	0.0034	0.0059	0.0042	0.0054	0.0037	0.0049	0.0218	0.0243	0.1460	0.1609
8[b]	0.0570	0.0781	0.0032	0.0053	0.0044	0.0056	0.0039	0.0050	0.0230	0.0249	0.1510	0.1616
9[b]	0.0590	0.0793	0.0047	0.0050	0.0047	0.0058	0.0042	0.0053	0.0239	0.0253	0.1525	0.1601

a = additive iron powder, 0.1 g. b = additive trichloroacetic acid, 0.1 g.

Table 4.7 Partial rate factors and percentage yields of the products of phenylation of 1,4-dichlorobenzene and benzene

(Table 4.1 gives compositions, Table 4.4 gives results)

experiment number	biphenyl yield %	2,5-dichlorobiphenyl p.r.f. (2-position) f_2	2,5-dichlorobiphenyl yield %	4-chlorobiphenyl p.r.f. (1-position) f_1	4-chlorobiphenyl yield %
1	22.0	1.80	26.4	0.36	2.7
2	21.2	1.77	24.9	0.35	2.5
3	21.5	1.61	23.1	0.35	2.5
4	22.2	1.65	24.3	0.37	2.7
5	20.9	1.71	23.8	0.36	2.5
6	21.8	1.78	25.9	0.36	2.6
(mean value)	21.6	1.72	24.8	0.36	2.6

yields are in mole per mole peroxide x 100

Table 4.8 Partial rate factors and percentage yields of products of phenylation of 1,4-dichlorobenzene and benzene (Table 4.2 gives compositions, Table 4.5 gives results) in the presence of copper additives

experiment number	biphenyl yield %	2,5-dichlorobiphenyl p.r.f. (2-position) f_2	2,5-dichlorobiphenyl yield %	4-chlorobiphenyl p.r.f. (1-position) f_1	4-chlorobiphenyl yield %
1[a]	24.2	2.75	44.4	0.48	3.9
2[a]	24.9	2.69	45.0	0.47	3.9
3[a]	24.1	2.75	44.1	0.46	3.7
4[a]	24.9	2.64	43.8	0.47	3.9
(mean value)[a]	24.5	2.71	44.2	0.47	3.9
5[b]	22.4	3.09	46.1	0.50	3.8
6[b]	22.5	3.03	45.6	0.49	3.6
7[b]	22.6	3.07	46.3	0.49	3.6
8[b]	22.6	3.04	45.9	0.50	3.8
(mean value)[b]	22.5	3.06	46.0	0.50	3.7
9[c]	26.4	2.44	42.7	0.43	3.8
10[c]	26.4	2.39	42.2	0.45	3.9
11[c]	25.4	2.47	41.8	0.44	3.7
12[c]	26.3	2.42	42.4	0.44	3.8
(mean value)[c]	26.1	2.43	42.3	0.44	3.8

yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g.

b = additive copper acetate, 0.1 g.

c = additive cupric chloride, 0.1 g.

Table 4.9 Partial rate factors and percentage yields of products of phenylation of 1,4-dichlorobenzene and benzene (Table 4.3 gives compositions, Table 4.6 gives results) in the presence of iron powder and trichloroacetic acid

experiment number	biphenyl yield %	2,5-dichlorobiphenyl p.r.f. (2-position) f_2	yield %	4-chlorobiphenyl p.r.f. (1-position) f_1	yield %
1[a]	23.0	3.16	48.5	0.47	3.6
2[a]	24.0	3.06	49.0	0.51	4.1
3[a]	22.7	3.21	48.8	0.49	3.7
4[a]	23.5	3.09	48.2	0.51	4.0
(mean value)[a]	23.3	3.13	48.6	0.49	3.9
5[b]	22.4	3.58	50.4	0.56	4.2
6[b]	22.7	3.29	49.8	0.55	4.2
7[b]	22.5	3.37	50.6	0.55	4.1
8[b]	23.0	3.25	50.0	0.55	4.2
9[b]	23.5	3.24	50.8	0.55	4.4
(mean value)[b]	22.8	3.31	50.3	0.55	4.2

yields are in mole per mole of peroxide x 100

a = additive iron powder, 0.1 g.

b = additive trichloroacetic acid, 0.1 g.

Table 4.10 Percentage yields of some by-products of the phenylation reaction of 1,4-dichlorobenzene in the absence and presence of various additives (Tables 4.1 and 4.2 give compositions)

experiment number	0.1 g. additive	3,4-dichlorobiphenyl % yield	3-chlorobiphenyl % yield
1	none	1.9	1.6
2	none	2.2	1.3
3	none	1.7	1.7
4	none	2.0	1.9
5	none	1.8	1.4
6	none	1.6	1.2
(mean value)		1.9	1.5
1	copper benzoate	2.2	2.1
2	copper benzoate	2.6	2.4
3	copper benzoate	2.4	2.2
4	copper benzoate	2.1	1.9
(mean value)		2.4	2.1
1	copper acetate	2.5	2.6
2	copper acetate	2.6	2.4
3	copper acetate	2.8	2.9
(mean value)		2.6	2.6

yields are in mole per mole peroxide x 100

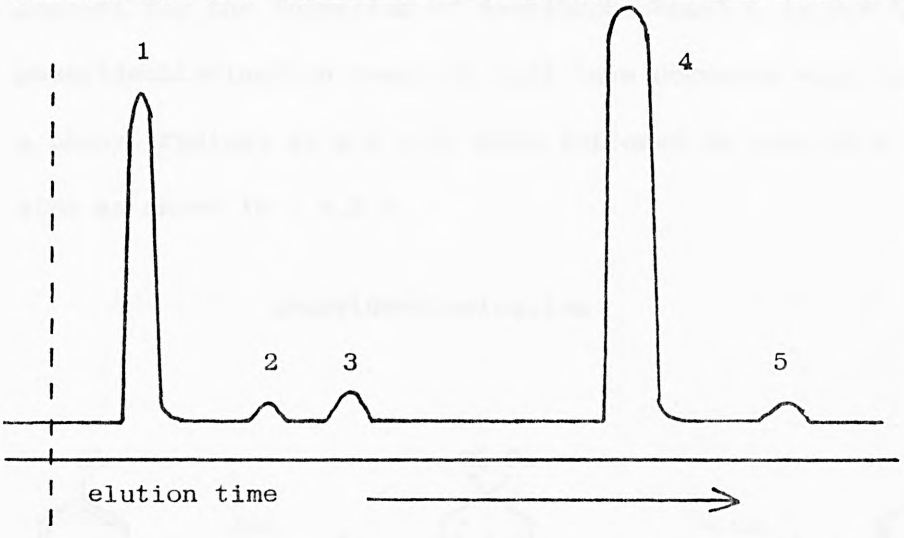
Table 4.11 Percentage yields of some by-products of the phenylation reaction of 1,4-dichlorobenzene in the presence of various additives (Tables 4.2 and 4.3 give compositions)

experiment number	0.1 g. additive	3,4-dichlorobiphenyl % yield	3-chlorobiphenyl % yield
1	cupric chloride	2.2	2.4
2	cupric chloride	1.8	1.9
3	cupric chloride	1.9	1.5
4	cupric chloride	1.9	1.7
(mean value)		2.0	1.9
1	iron powder	2.8	3.0
2	iron powder	3.3	3.5
3	iron powder	3.4	2.9
4	iron powder	3.1	3.6
(mean value)		3.1	3.3
1	trichloroacetic acid	3.1	3.6
2	trichloroacetic acid	3.6	3.3
3	trichloroacetic acid	3.8	3.7
4	trichloroacetic acid	3.4	3.8
5	trichloroacetic acid	3.8	4.0
(mean value)		3.5	3.7

yields are in mole per mole oeroxide x 100

4.1.4 DISCUSSION OF THE PHENYLATION OF 1,4-DICHLOROBENZENE

Figure 4.5 Reconstructed chromatogram showing only products of the phenylation reaction of 1,4-dichlorobenzene and benzene



peak 1 = biphenyl

peak 2 = 3-chlorobiphenyl

peak 3 = 4-chlorobiphenyl

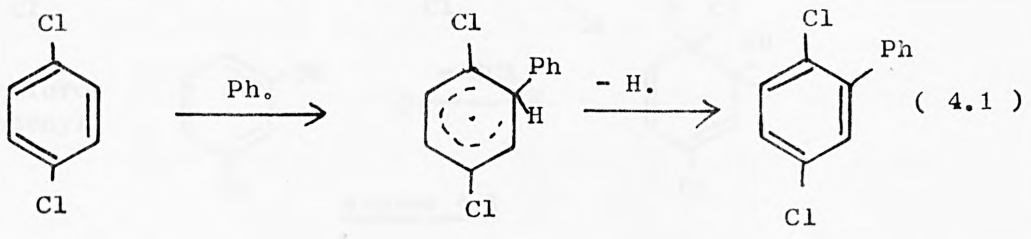
peak 4 = 2,5-dichlorobiphenyl

peak 5 = 3,4-dichlorobiphenyl

The phenylation of 1,4-dichlorobenzene has been reported in the literature. (15, 42) However, the only product of phenylation reported has been that of phenyldehydrogenation, namely 2,5-dichlorobiphenyl. On phenylation of 1,4-dichlorobenzene in sealed tubes, three other products were identified apart from 2,5-dichlorobiphenyl, namely 3- and 4-chlorobiphenyl and 3,4-dichlorobiphenyl.

Attack by a phenyl radical at any of the four C - H sites in 1,4-dichlorobenzene yields 2,5-dichlorobiphenyl as the final, major product (25 % yield), as shown in (4.1).

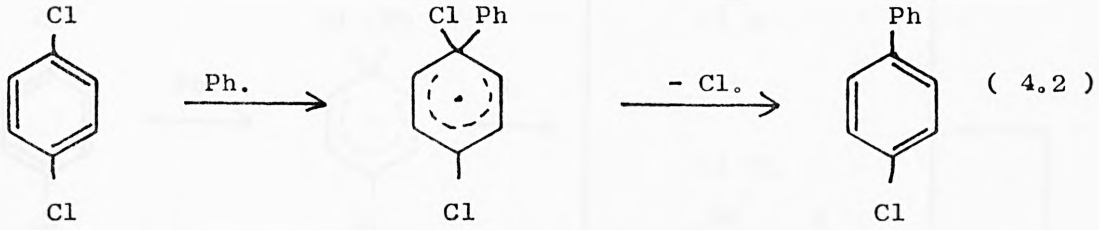
phenyldehydrogenation



(4.1)

The phenylation reaction products were found to also contain 3- and 4-chlorobiphenyls which were confirmed by the g.l.c. retention data and by g.l.c.-mass spectrometry (see Appendix). To account for the formation of 4-chlorobiphenyl (in 2.6 % yield) a phenyldechlorination reaction must have occurred with the attack by a phenyl radical at a C - Cl site followed by loss of a chlorine atom as shown in (4.2).

phenyldechlorination



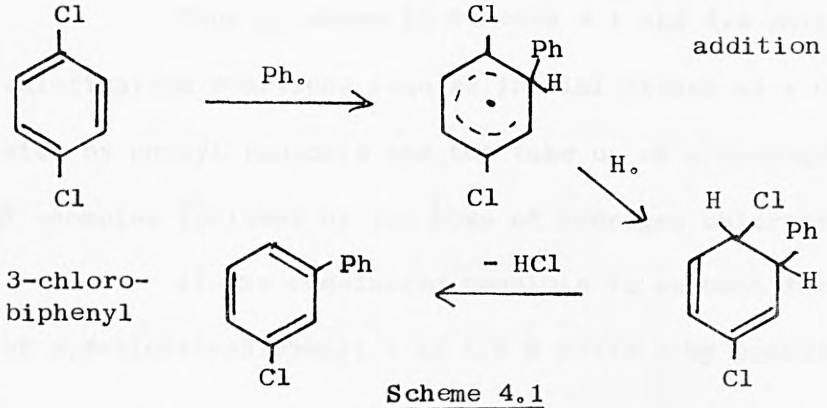
(4.2)

4-chlorobiphenyl

Similarly in the phenylation of 1,4-difluorobenzene (65) the reactions of phenyldehydrogenation (yielding 2,5-difluorobiohenyl) and phenyldefluorination (yielding 4-fluorobiphenyl) were observed.

However, to account for the presence of 3-chlorobiphenyl (in 1.5 % yield) it was considered that an addition - elimination reaction occurred with phenyl and hydrogen radical uptake followed by the elimination of hydrogen chloride as shown in Scheme 4.1.

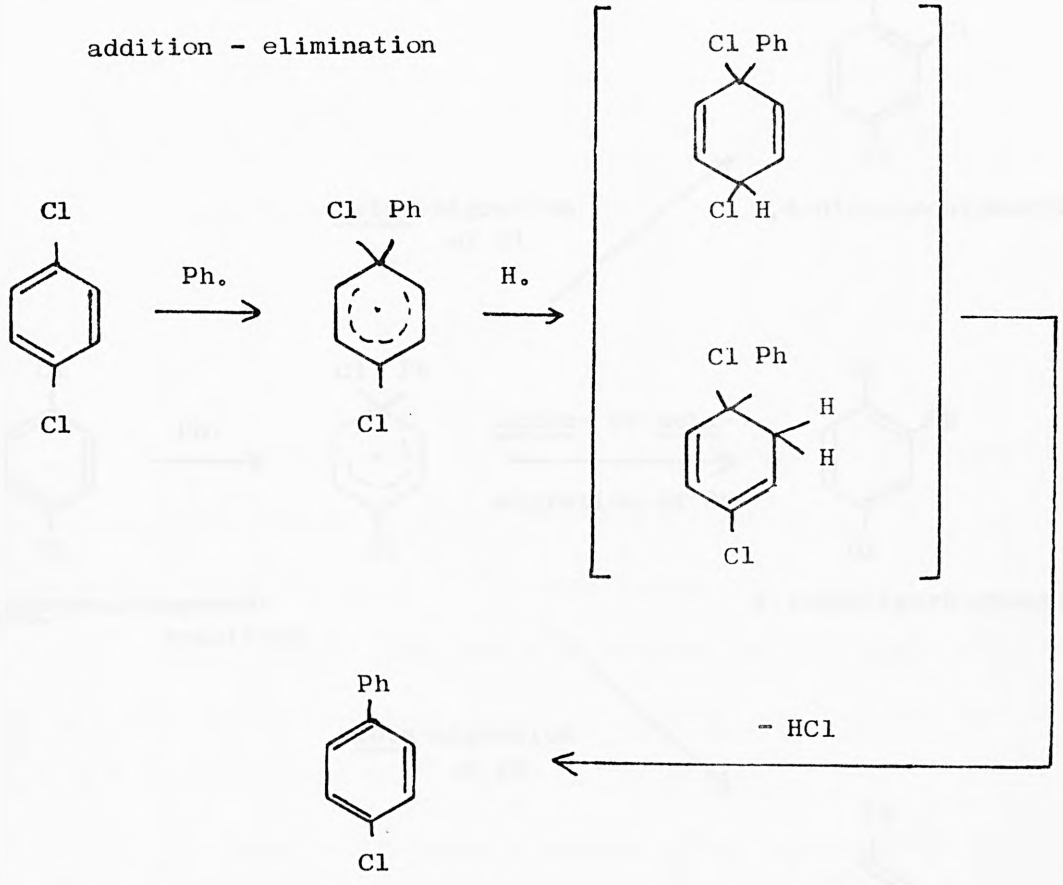
addition - elimination



3-chloro-biphenyl

Scheme 4.1

Besides forming 2,5-dichlorobiphenyl as shown in (4.1), it is possible for the intermediate to pick up a hydrogen radical at the chlorine site next to the phenyl group and subsequently to lose hydrogen chloride form the molecule yielding 3-chlorobiphenyl (Scheme 4.1). Similar trapping of the 3-complex from ipso substitution might lead to 4-chlorobiphenyl as shown in Scheme 4.2.

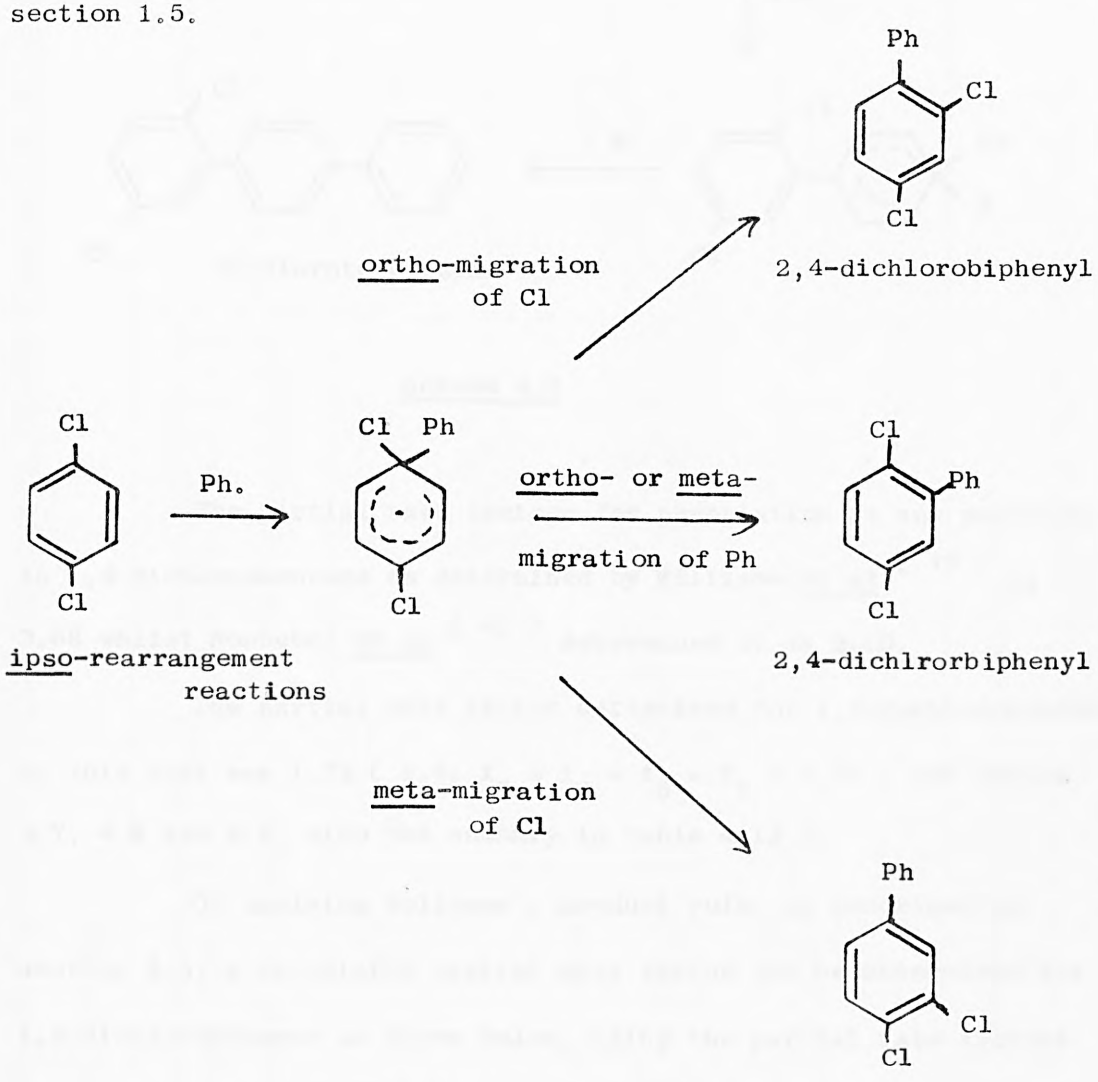


Scheme 4.2

Thus as shown in Schemes 4.1 and 4.2 phenyldehydrochlorination reactions require initial attack at a C - H or C - Cl site by phenyl radicals and the take up of a hydrogen atom by the σ-complex followed by the loss of hydrogen chloride.

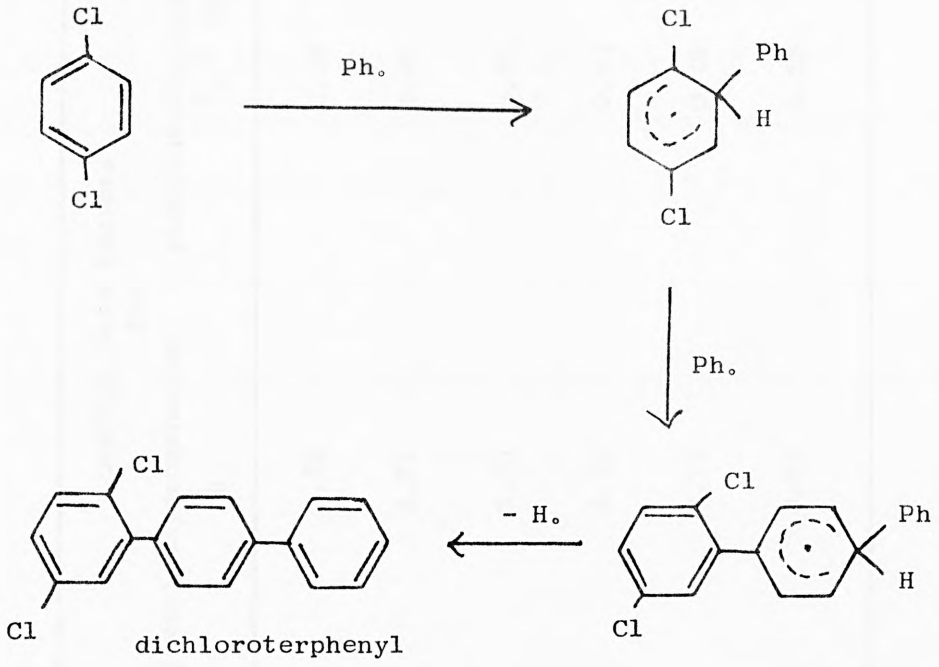
It was considered possible to account for the presence of 3,4-dichlorobiphenyl (in 1.8 % yield) by postulating the

occurrence of an ipso-rearrangement reaction. The ipso-rearrangement would involve initial attack by a phenyl radical at a C - Cl site (as in phenyldechlorination reactions) followed by an ortho- or meta- migration of either phenyl or chlorine group as shown in Scheme 4.3. These types of ipso-rearrangement reactions have been reported in the literature [54] and have been discussed in section 1.5.



Scheme 4.3

G.l.c.-mass spectrometry results showed the presence of dichloroterphenyl (m^+ = 298, see Appendix) in the phenylation reaction mixture in small amounts. A possible mechanism for the formation of the terphenyl is shown in Scheme 4.4



Scheme 4.4

The partial rate factors for phenylation at any position in 1,4-dichlorobenzene as determined by Williams et al [15] is 3.68 whilst Nonhebel et al [42] determined it as 2.60.

The partial rate factor determined for 1,4-dichlorobenzene in this work was 1.72 (i.e. $f_2 = f_3 = f_5 = f_6 = 1.72$, see Tables 4.7, 4.8 and 4.9, also the summary in Table 4.12).

On applying Holleman's product rule, as described in section 3.5, a calculated partial rate factor can be determined for 1,4-dichlorobenzene as shown below, using the partial rate factors determined in the chlorobenzene phenylation reaction, i.e. $f_o = 1.97$, $f_m = 0.82$, $f_p = 1.07$

for reaction at the 2-position,

$$f_2 = \underline{o}\text{-Cl} \times \underline{m}\text{-Cl}$$
$$= 1.97 \times 0.82$$
$$= 1.62$$

Table 4.12 Partial rate factors and percentage yields for the phenylation of 1,4-dichlorobenzene in the presence of additives

row number	additive (0.1 g.)	phenyldehydrogenation product yield (%) 2,5-dichlorobiphenyl	phenyldechlorination product yield (%) 4-chlorobiphenyl	partial rate factors for phenyldehydrogenation f_2	partial rate factors for phenyldechlorination f_1 (ipso)
1	none	24.8	2.6	1.72	0.36
2	copper benzoate	44.2	3.9	2.71	0.47
3	copper acetate	46.0	3.7	3.06	0.50
4	cupric chloride	42.3	3.8	2.43	0.44
5	iron powder	48.6	3.9	3.13	0.49
6	trichloro-acetic acid	50.3	4.2	3.31	0.55

yields are in moles per mole of peroxide x 100

each row of results is a mean of four or more figures derived from Tables 4.7, 4.8 and 4.8

Similarly, in the presence of copper benzoate, the partial rate factor f_2 was found to be 2.71 (see Table 4.8) and using the partial rate factors determined in the phenylation of chlorobenzene in the presence of copper benzoate, i.e. $f_o = 2.90$, $f_m = 0.9$ and $f_p = 1.24$

for reaction at the 2-position in the presence of copper benzoate,

$$f_2 = \underline{o}\text{-Cl} \times \underline{m}\text{-Cl}$$
$$= 2.90 \times 0.9$$
$$= 2.61$$

There appears to be reasonable agreement with the calculated and determined partial rate factor values with the presence of the various additives increasing the partial rate factor by varying amounts as shown in Table 4.12.

4.1.5 EFFECT OF ADDITIVES

The presence of additives in the phenylation reactions increased the biaryl yields as summarised in Table 4.12. The additive with the largest effect was trichloroacetic acid whilst cupric chloride was the least efficient additive. The additives promoted the efficient oxidation of the cyclohexadienyl radical and helped to divert it from reactions of dimerisation and disproportionation as discussed in section 1.9.

As discussed in the preceding section, the presence of additives increased the partial rate factor values as shown Table 4.12. Once again, the different additives increased the partial rate

factors by varying amounts with trichloroacetic acid being one of the most efficient additives. Thus, the partial rate factor f_2 was 1.72 in the absence of additive and 3.31 in the presence of trichloroacetic acid.

4.2 METHOD OF PHENYLATION OF 1,2-DICHLOROBENZENE

This is the same as the method described in section 3.1. Sections 4.2.1 to 4.2.3 show the chromatograms obtained and their identification followed by tables listing experimental quantities leading to tables of results tabulating partial rate factors, yields and calculated isomer ratios.

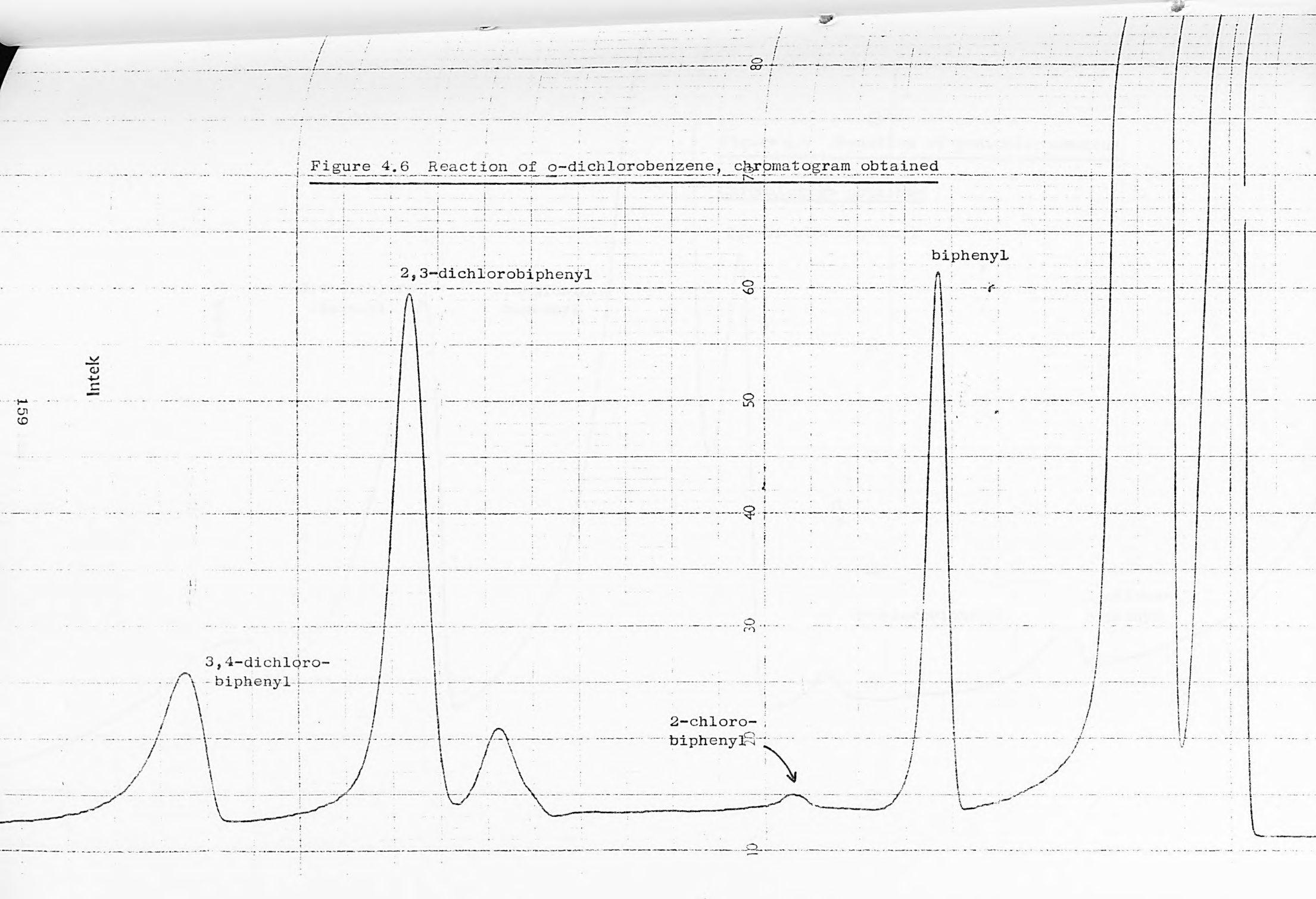
4.2.1 CHROMATOGRAMS

Figures 4.6, 4.7, 4.8, 4.9 and 4.10 show actual chromatograms obtained. Figure 4.11 is a reconstructed chromatogram showing the relationship between all the products.

4.2.2 PEAK IDENTIFICATION

The same method was used as has been described in section 3.3.

Figure 4.6 Reaction of o-dichlorobenzene, chromatogram obtained



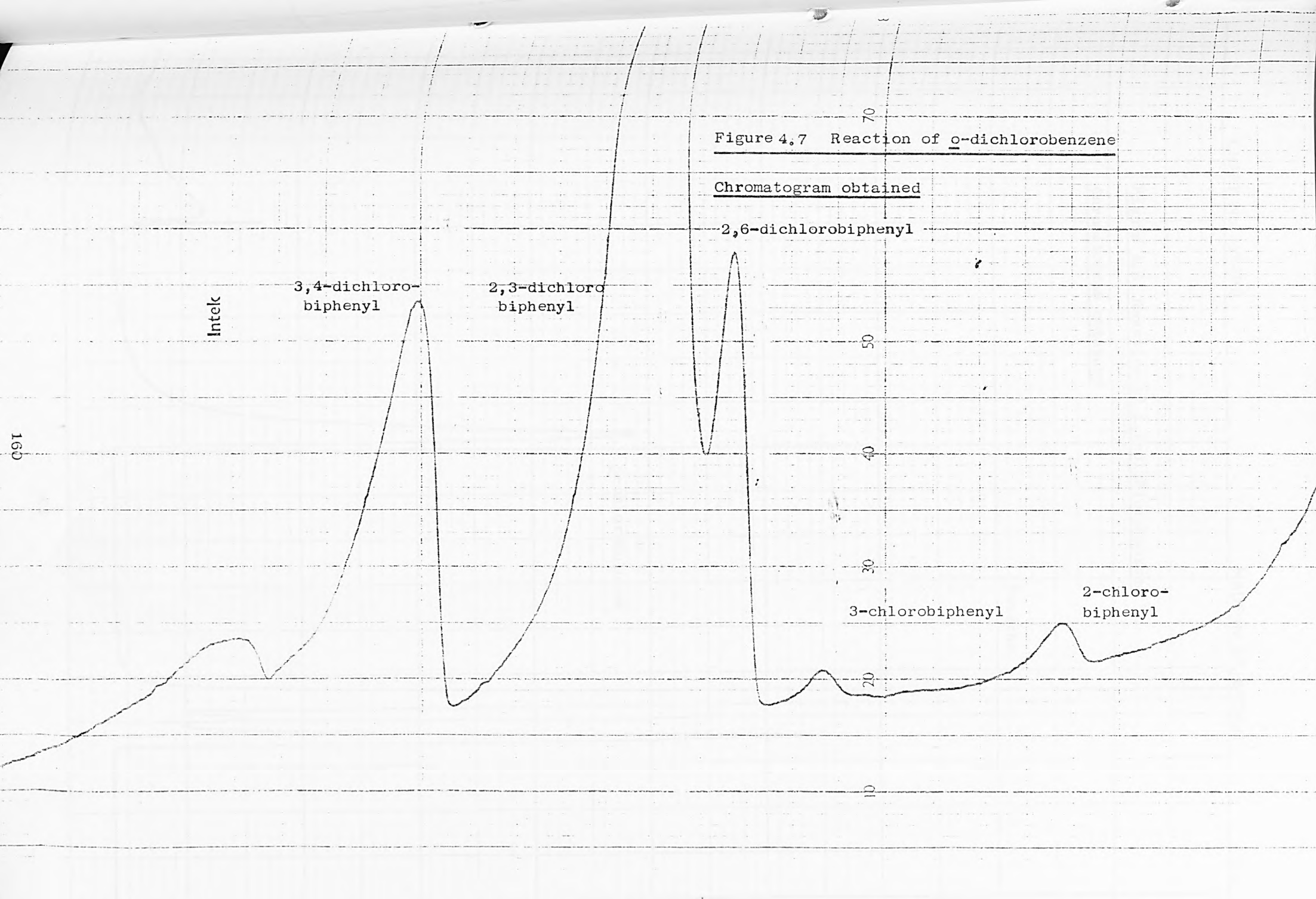
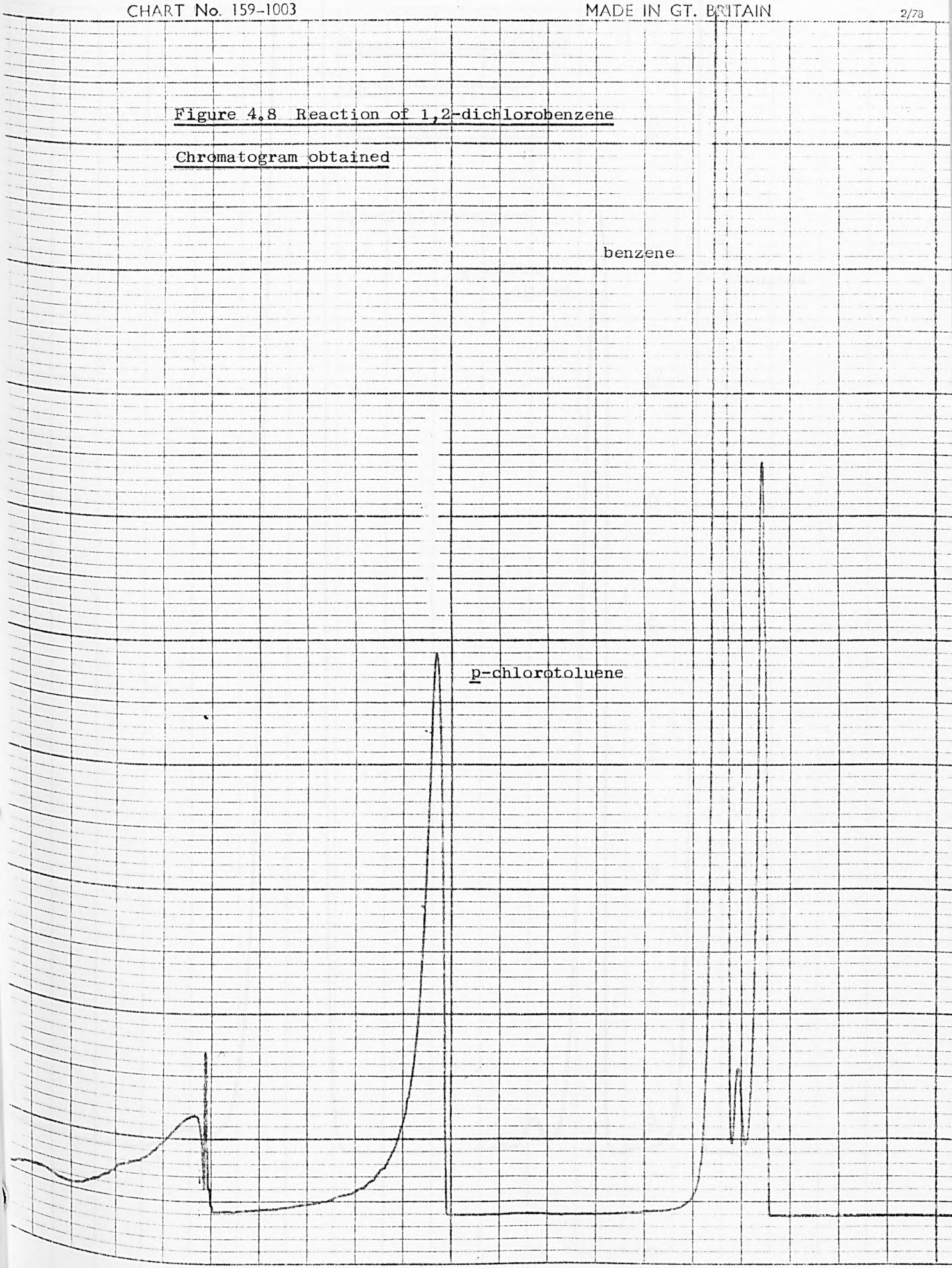


Figure 4.7 Reaction of o-dichlorobenzene

Chromatogram obtained

Figure 4.8 Reaction of 1,2-dichlorobenzene

Chromatogram obtained



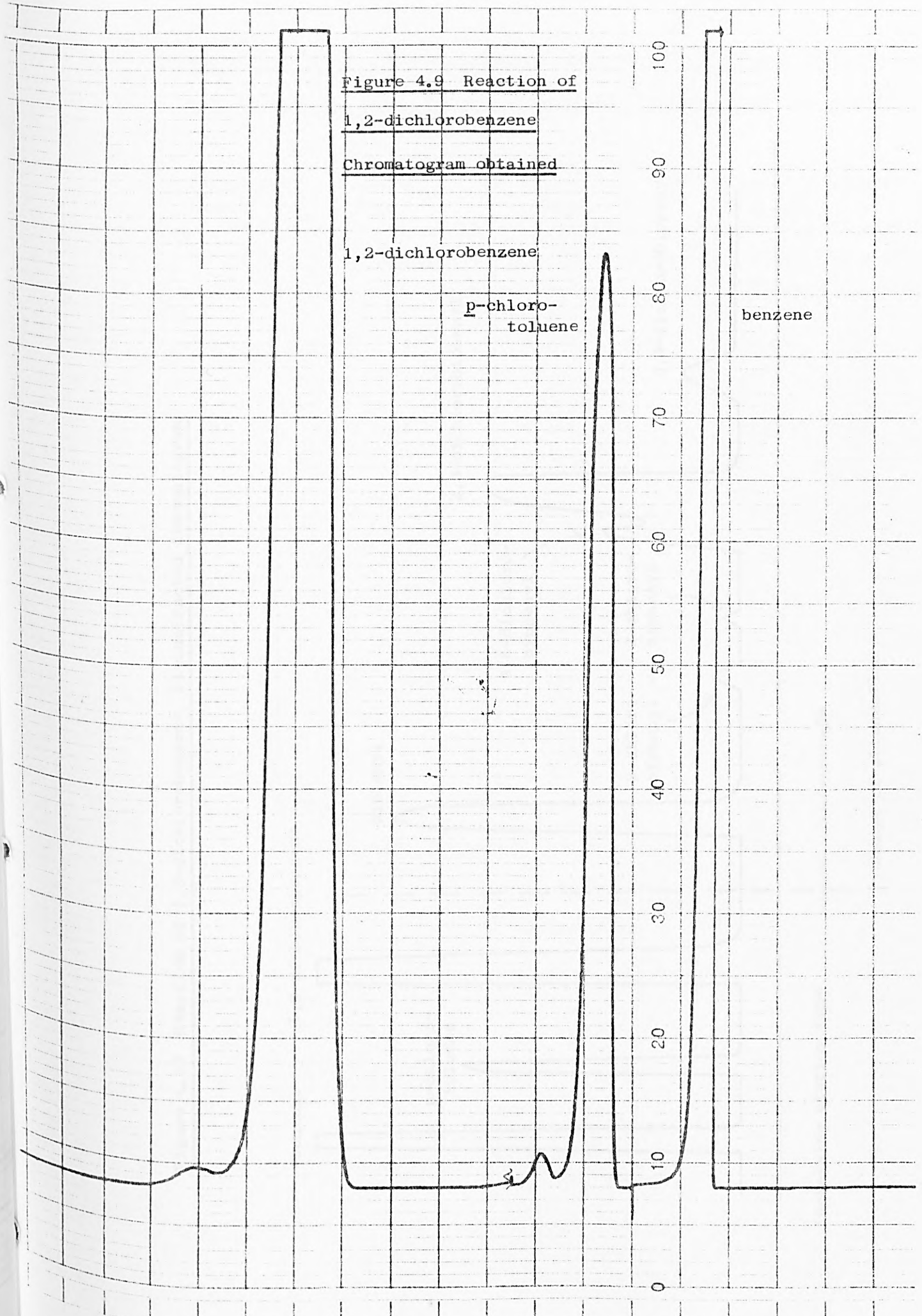


Figure 4.9 Reaction of 1,2-dichlorobenzene Chromatogram obtained

Figure 4.10 Reaction of 1,2-dichlorobenzene, reconstructed chromatogram

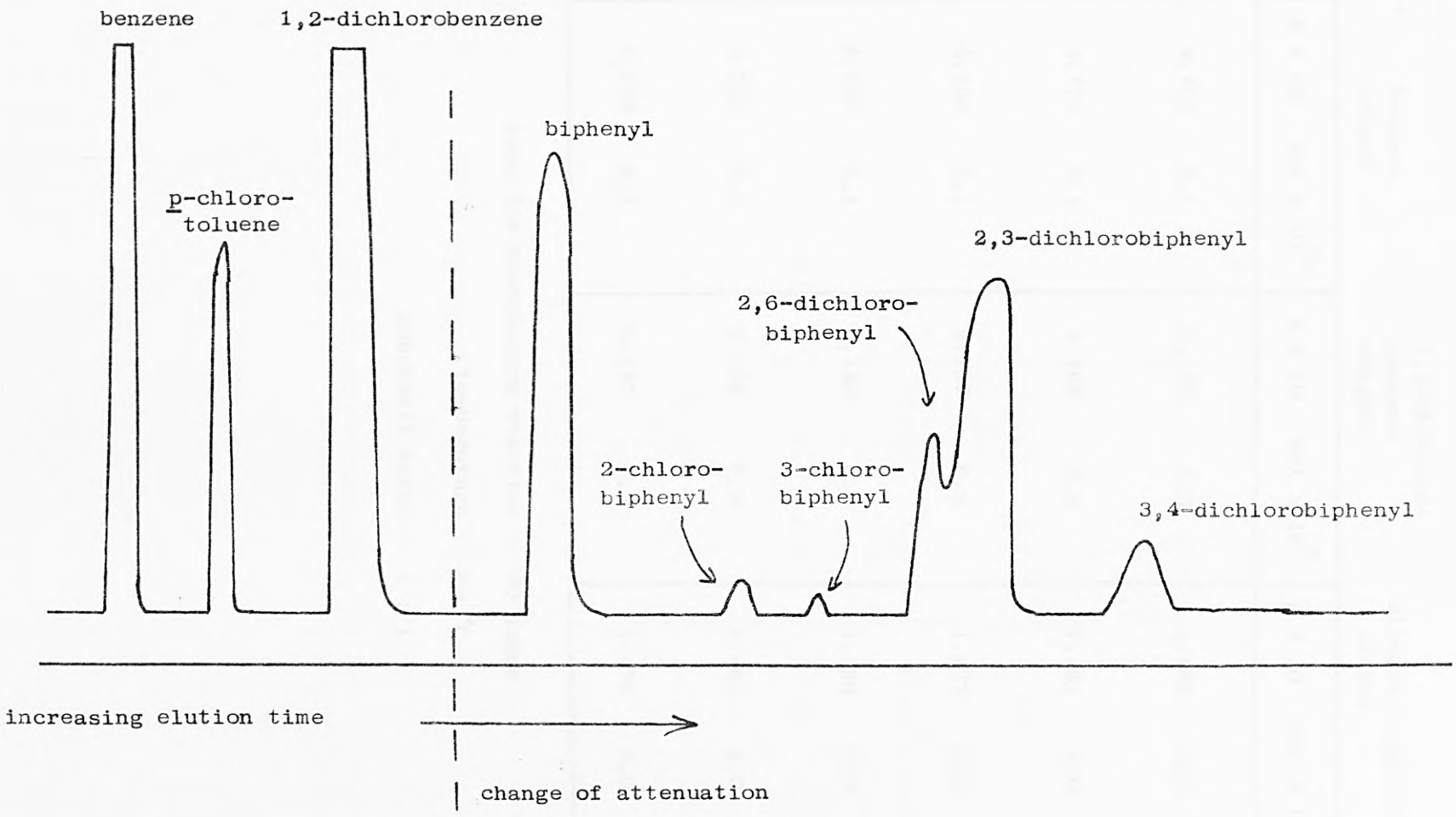


Table 4.13 Sealed tube phenylation reactions of 1,2-dichlorobenzene and benzene with dibenzoyl peroxide - compositions of reaction mixtures

experiment number	benzene weight		1,2-dichloro-benzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1	4.762	6.1	9.153	6.2	1.485	6.0
2	4.771	6.1	9.162	6.2	1.481	6.0
3	4.768	6.1	9.157	6.2	1.477	6.0
4	4.777	6.1	9.149	6.2	1.486	6.0
5	4.765	6.1	9.158	6.2	1.489	6.0
6	4.774	6.1	9.147	6.2	1.479	6.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

substrate ratio : 1 : 1

Table 4.14 Sealed tube phenylation reactions of 1,2-dichlorobenzene and benzene in the presence of copper benzoate - compositions of reaction mixtures

experiment number	temperature	benzene weight		1,2-dichloro-benzene weight		dibenzoyl peroxide weight	
	°C	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1	80	4.784	6.1	9.083	6.2	1.451	6.0
2	80	4.776	6.1	9.087	6.2	1.456	6.0
3	80	4.771	6.1	9.095	6.2	1.462	6.0
4	120	4.733	6.1	9.132	6.2	1.465	6.0
5	120	4.739	6.1	9.138	6.2	1.454	6.0
6	120	4.742	6.1	9.141	6.2	1.467	6.0

time for phenylation reaction : 50 hours

substrate ratio : 1 : 1

weight of copper benzoate : 0.1 g. in each reaction mixture

Table 4.15 Sealed tube phenylation reactions of 1,2-dichlorobenzene and benzene with dibenzoyl peroxide in the presence of various additives - composition of reaction mixtures

experiment number	benzene weight		1,2-dichlorobenzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	4.665	6.0	8.946	6.2	1.475	6.0
2[a]	4.669	6.0	8.951	6.2	1.470	6.0
3[a]	4.673	6.0	8.954	6.2	1.479	6.0
4[a]	4.670	6.0	8.948	6.2	1.481	6.0
5[b]	4.675	6.0	8.955	6.2	1.476	6.0
6[b]	4.678	6.0	8.956	6.2	1.483	6.0
7[b]	4.761	6.0	8.961	6.2	1.480	6.0
8[b]	4.674	6.0	8.965	6.2	1.472	6.0
9[c]	4.679	6.0	8.967	6.2	1.486	6.0
10[c]	4.681	6.0	8.972	6.2	1.488	6.0
11[c]	4.683	6.0	8.964	6.2	1.477	6.0
12[d]	4.686	6.0	8.971	6.2	1.471	6.0
13[d]	4.680	6.0	8.976	6.2	1.468	6.0
14[d]	4.689	6.0	8.968	6.2	1.476	6.0
15[d]	4.684	6.0	8.979	6.2	1.478	6.0

time for phenylation reaction : 50 hours

temperature : 80 °C

substrate ratio : 1 : 1

a = additive copper acetate, 0.1 g.

b = additive cupric chloride, 0.1 g.

c = additive iron powder, 0.1 g.

d = additive trichloroacetic acid, 0.1 g.

Table 4.16 Analysis of the phenylation products of 1,2-dichlorobenzene and benzene (Table 4.13 gives compositions)

experiment number	dichlorobiphenyl products						chlorobiphenyl products				biphenyl		p-chlorotoluene internal standard	
	2,3-dichloro-		3,4-dichloro-		2,6-dichloro-		2-chloro-		3-chloro-					
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1	0.0185	0.0276	0.0093	0.0160	0.0036	0.0048	0.0080	0.0094	0.0022	0.0029	0.0337	0.0427	0.1413	0.1559
2	0.0194	0.0289	0.0094	0.0162	0.0038	0.0051	0.0081	0.0095	0.0020	0.0026	0.0340	0.0431	0.1416	0.1563
3	0.0201	0.0299	0.0090	0.0155	0.0035	0.0047	0.0080	0.0094	0.0024	0.0031	0.0343	0.0435	0.1397	0.1542
4	0.0191	0.0284	0.0091	0.0157	0.0034	0.0045	0.0080	0.0094	0.0025	0.0033	0.0338	0.0429	0.1409	0.1555
5	0.0185	0.0276	0.0095	0.0164	0.0040	0.0053	0.0084	0.0098	0.0021	0.0027	0.0345	0.0438	0.1383	0.1526
6	0.0187	0.0279	0.0092	0.0159	0.0037	0.0050	0.0079	0.0092	0.0019	0.0025	0.0335	0.0425	0.1373	0.1515
response factor	1.35		1.56		1.21		1.06		1.19		1.15		1.00	

Table 4.17 Analysis of phenylation products of 1,2-dichlorobenzene and benzene (Table 4.14 gives compositions) at various temperatures in the presence of copper benzoate (0.1 g.)

experiment number	dichlorobiphenyl products						chlorobiphenyl products				biphenyl		p-chlorotoluene internal standard	
	2,3-dichloro-		3,4-dichloro-		2,6-dichloro-		2-chloro-		3-chloro-					
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1[a]	0.0311	0.0463	0.0192	0.0331	0.0041	0.0055	0.0105	0.0123	0.0027	0.0035	0.0457	0.0510	0.1522	0.1680
2[a]	0.0305	0.0455	0.0192	0.0331	0.0043	0.0058	0.0107	0.0125	0.0024	0.0032	0.0453	0.0505	0.1411	0.1557
3[a]	0.0312	0.0466	0.0196	0.0338	0.0040	0.0054	0.0108	0.0126	0.0027	0.0036	0.0465	0.0518	0.1439	0.1588
4[b]	0.0269	0.0402	0.0183	0.0317	0.0034	0.0045	0.0095	0.0111	0.0023	0.0030	0.0458	0.0512	0.1458	0.1615
5[b]	0.0274	0.0409	0.0179	0.0309	0.0031	0.0042	0.0092	0.0108	0.0021	0.0028	0.0451	0.0503	0.1481	0.1635
6[b]	0.0264	0.0393	0.0166	0.0286	0.0040	0.0054	0.0085	0.0100	0.0027	0.0036	0.0455	0.0496	0.1503	0.1659

a = reaction temperature 80 °C b = reaction temperature 120 °C

Table 4.18 Analysis of the phenylation products of 1,2-dichlorobenzene and benzene (Table 4.15 gives compositions) in the presence of various additives

experiment number	dichlorobiphenyl products						chlorobiphenyl products				biphenyl		p-chlorotoluene internal standard	
	2,3-dichloro-		3,4-dichloro-		2,6-dichloro-		2-chloro-		3-chloro-					
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1[a]	0.0325	0.0485	0.0214	0.0368	0.0038	0.0052	0.0108	0.0127	0.0033	0.0044	0.0434	0.0486	0.1399	0.1545
2[a]	0.0322	0.0480	0.0205	0.0353	0.0039	0.0053	0.0104	0.0122	0.0030	0.0040	0.0425	0.0474	0.1404	0.1550
3[a]	0.0321	0.0478	0.0202	0.0347	0.0037	0.0049	0.0102	0.0119	0.0029	0.0039	0.0422	0.0470	0.1408	0.1554
4[a]	0.0319	0.0476	0.0205	0.0353	0.0036	0.0047	0.0104	0.0122	0.0032	0.0042	0.0432	0.0482	0.1397	0.1542
5[b]	0.0291	0.0434	0.0153	0.0264	0.0034	0.0046	0.0108	0.0126	0.0024	0.032	0.0485	0.0541	0.1412	0.1558
6[b]	0.0293	0.0437	0.0159	0.0273	0.0031	0.0041	0.0110	0.0129	0.0027	0.0035	0.0512	0.0571	0.1395	0.1540
7[b]	0.0289	0.0432	0.0147	0.0253	0.0032	0.0043	0.0109	0.0128	0.0024	0.0031	0.0489	0.0545	0.1415	0.1562
8[b]	0.0295	0.0439	0.0155	0.0267	0.0030	0.0040	0.0114	0.0133	0.0023	0.0030	0.0494	0.0551	0.1421	0.1568
9[c]	0.0330	0.0492	0.0206	0.0355	0.0040	0.0054	0.0111	0.0130	0.0037	0.0048	0.0415	0.0462	0.1401	0.1546
10[c]	0.0305	0.0455	0.0190	0.0327	0.0037	0.0050	0.0103	0.0120	0.0035	0.0046	0.0387	0.0432	0.1381	0.1525
11[c]	0.0329	0.0490	0.0205	0.0353	0.0039	0.0052	0.0109	0.0128	0.0038	0.0050	0.0415	0.0463	0.1393	0.1538
12[d]	0.0338	0.0503	0.0204	0.0351	0.0044	0.0059	0.0113	0.0132	0.0040	0.0053	0.0396	0.0442	0.1396	0.1541
13[d]	0.0334	0.0498	0.0203	0.0349	0.0035	0.0047	0.0110	0.0129	0.0043	0.0057	0.0399	0.0445	0.1403	0.1549
14[d]	0.0333	0.0496	0.0197	0.0340	0.0042	0.0056	0.0113	0.0132	0.0045	0.0059	0.0399	0.0455	0.1406	0.1552
15[d]	0.0340	0.0506	0.0215	0.0369	0.0040	0.0054	0.0117	0.0137	0.0042	0.0055	0.0415	0.0462	0.1408	0.1552

a = additive copper acetate, 0.1 g. b = additive cupric chloride, 0.1 g. c = additive iron powder, 0.1 g.
d = additive trichloroacetic acid, 0.1 g.

Table 4.19 Partial rate factors and percentage yields of the products of the phenylation of 1,2-dichlrorbenzene and benzene

Table 4.13 gives compositions, Table 4.16 gives results

experiment number	biphenyl yield %	2,3-dichloro-biphenyl		3,4-dichloro-biphenyl		2-chloro-biphenyl	
		f_3	yield (%)	f_4	yield (%)	f_1	yield (%)
1	46.2	1.34	20.6	0.78	12.0	0.54	8.3
2	46.7	1.39	21.6	0.78	12.1	0.53	8.4
3	47.1	1.42	22.4	0.74	11.6	0.53	8.3
4	46.4	1.37	21.2	0.76	11.7	0.53	8.3
5	47.4	1.31	20.6	0.77	12.3	0.54	8.7
6	46.0	1.35	20.9	0.77	11.9	0.53	8.1
(mean value)	46.6	1.36	21.3	0.77	11.9	0.53	8.4

yields are in mole per mole peroxide x 100

Table 4.20 Partial rate factors and percentage yields of products for the phenylation of 1,2-dichlorobenzene and benzene in the presence of copper benzoate at various temperatures (Table 4.14 gives compositions, Table 4.17 gives results)

experiment number	biphenyl yield %	2,3 -dichloro-biphenyl f_3	yield (%)	3,4-dichloro-biphenyl f_4	yield (%)	2-chloro-biphenyl f_1	yield (%)
1[a]	55.2	1.88	34.6	1.34	24.7	0.60	10.9
2[a]	54.7	1.87	34.0	1.36	24.7	0.60	11.1
3[a]	56.1	1.86	34.8	1.35	25.3	0.59	11.1
(mean value)[a]	55.3	1.87	34.5	1.35	24.9	0.60	11.0
4[b]	55.4	1.63	30.0	1.28	23.7	0.53	9.8
5[b]	54.4	1.69	30.6	1.27	23.1	0.53	9.6
6[b]	53.7	1.64	29.4	1.19	21.4	0.49	8.8
(mean value)[b]	54.5	1.65	30.0	1.25	22.7	0.52	9.4

a = reaction temperature 80 °C

b = reaction temperature 120 °C

additive = copper benzoate, 0.1 g.

yields are in mole per mole peroxide x 100

Table 4.21 Partial rate factors and percentage yields of products of the phenylation of 1,2-dichlorobenzene and benzene in the presence of various additives (Table 4.15 gives compositions, Table 4.18 gives results)

experiment number	biphenyl yield %	2,3 -dichloro-biphenyl		3,4-dichloro-biphenyl		2-chloro-biphenyl	
		f_3	yield (%)	f_4	yield (%)	f_1	yield (%)
1[a]	52.6	2.07	36.2	1.57	27.5	0.64	11.2
2[a]	51.3	2.10	35.9	1.54	26.4	0.63	10.8
3[a]	50.9	2.11	35.7	1.53	25.9	0.62	10.5
4[a]	52.2	2.05	35.6	1.52	26.4	0.62	10.8
(mean value)[a]	51.7	2.08	35.9	1.54	26.6	0.63	10.8
5[b]	58.6	1.66	32.4	1.01	19.7	0.57	11.1
6[b]	61.8	1.59	32.7	0.99	20.4	0.55	11.4
7[b]	59.0	1.64	32.3	0.96	18.9	0.58	11.3
8[b]	59.6	1.65	32.8	1.00	20.0	0.59	11.8
(mean value)[b]	59.7	1.63	32.6	0.99	19.8	0.57	11.4
9[c]	50.0	2.21	36.8	1.59	26.5	0.69	11.5
10[c]	46.8	2.18	37.0	1.57	24.4	0.68	10.6
11[c]	50.1	2.19	36.6	1.58	26.4	0.68	11.3
(mean value)[c]	49.0	2.19	36.8	1.58	25.8	0.68	11.1
12[d]	47.8	2.36	37.6	1.65	26.2	0.73	11.7
13[d]	48.2	2.32	37.22	1.62	26.1	0.71	11.4
14[d]	48.2	2.31	37.1	1.58	25.4	0.73	11.7
15[d]	50.0	2.37	37.8	1.66	27.6	0.73	12.1
(mean value)[d]	48.5	2.31	37.4	1.63	26.3	0.72	11.7

yields are in mole per mole peroxide x 100

a = additive copper acetate, 0.1 g.

b = additive cupric chloride, 0.1 g.

c = additive iron powder, 0.1 g.

d = additive trichloro-acetic acid, 0.1 g.

Table 4.22 Percentage yields of some by-products of the phenylation reaction of 1,2-dichlorobenzene in the absence and presence of additives

(Tables 4.13 and 4.14 give compositions)

experiment number	0.1 g. additive	2,6-dichlorobiphenyl % yield	3-chlorobiphenyl % yield
1	none	3.6	2.6
2	none	3.8	2.3
3	none	3.5	2.7
4	none	3.4	2.9
5	none	4.0	2.4
6	none	3.7	2.2
(mean value)		3.7	2.5
1[a]	copper benzoate	4.1	3.1
2[a]	copper benzoate	4.3	2.8
3[a]	copper benzoate	4.0	3.2
(mean value)		4.2	3.0
1[b]	copper benzoate	3.4	2.7
2[b]	copper benzoate	3.1	2.5
3[b]	copper benzoate	4.0	3.2
(mean value)		3.5	2.7
1	copper acetate	3.9	3.9
2	copper acetate	4.0	3.5
3	copper acetate	3.7	3.4
4	copper acetate	3.5	3.7

yields are in mole per mole peroxide x 100

a = reaction temperature 80 ^{o}C b = reaction temperature 120 ^{o}C

Table 4.23 Percentage yields of some by-products of the phenylation reaction of 1,2-dichloeobenzene in the presence of additives

(Table 4.15 gives compositions)

experiment number	0.1 g. additive	2,6-dichlorobiphenyl % yield	3-chlorobiphenyl % yield
1	cupric chloride	3.4	2.8
2	cupric chloride	3.1	3.1
3	cupric chloride	3.2	2.7
4	cupric chloride	2.9	2.6
(mean value)		3.2	2.8
1	iron powder	4.0	4.2
2	iron powder	3.7	4.0
3	iron powder	3.9	4.4
(mean value)		3.9	4.2
1	trichloroacetic acid	4.4	4.7
2	trichloroacetic acid	3.5	5.0
3	trichloroacetic acid	4.1	5.2
4	trichloroacetic acid	4.0	4.9
(mean value)		4.0	5.0

yields are in moler per mole peroxide x 100

Table 4.24 Calculated product isomer ratios for the phenylation reaction of 1,2-dichlorobenzene in the absence of additives (Table 4.13 gives compositions)

experiment number	2,3-dichlorobiphenyl %	3,4-dichlorobiphenyl %
1	63.2	36.8
2	64.1	35.9
3	65.7	34.3
4	64.3	35.7
5	63.0	37.0
6	63.7	36.3
(mean value)	64.0	36.0

Table 4.25 Calculated product isomer ratios for the phenylation reaction of 1,2-dichlorobenzene in the presence of copper benzoate (Table 4.14 gives compositions)

experiment number	2,3-dichlorobiphenyl %	3,4-dichlorobiphenyl %
1[a]	58.4	41.6
2[a]	57.9	42.1
3[a]	57.9	42.1
(mean value)[a]	58.1	41.9
4[b]	56.0	44.0
5[b]	57.1	42.9
6[b]	58.0	42.0
(mean value)[b]	57.0	43.0

a = reaction temperature 80 ^{o}C

b = reaction temperature 120 ^{o}C

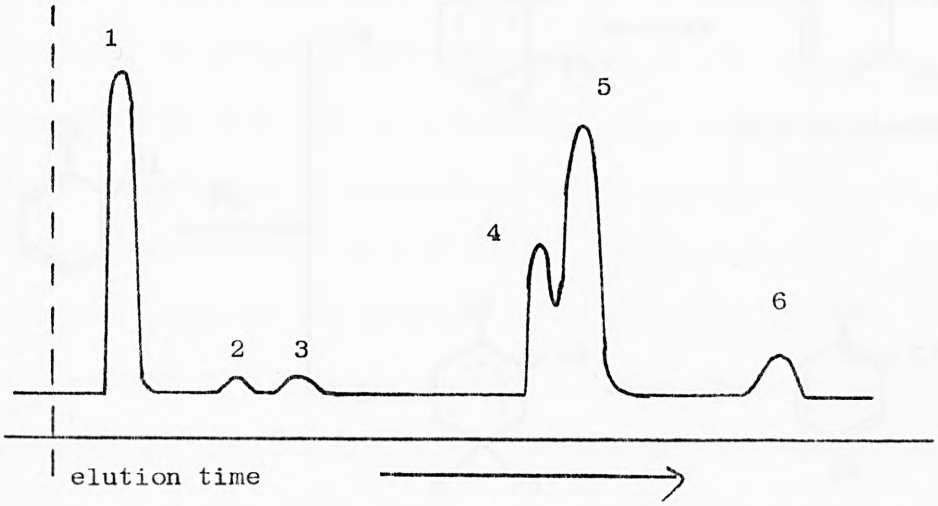
additive, copper benzoate, 0.1 g.

Table 4.26 Calculated product isomer ratios for the phenylation reaction of 1,2-dichlorobenzene in the presence of additives

(Table 4.15 gives compositions)

experiment number	0.1 g. additive	2,3-dichlorobiphenyl %	3,4-dichlorobiphenyl %
1	copper acetate	56.9	43.1
2	copper acetate	57.7	42.3
3	copper acetate	58.0	42.0
4	copper acetate	57.4	42.6
(mean value)		57.5	42.5
5	cupric chloride	62.2	37.8
6	cupric chloride	61.6	38.4
7	cupric chloride	63.1	36.9
8	cupric chloride	62.3	37.7
(mean value)		62.3	37.7
9	iron powder	58.2	41.8
10	iron powder	58.1	41.9
11	iron powder	58.1	41.9
(mean value)		58.1	41.9
12	trichloroacetic acid	58.9	41.1
13	trichloroacetic acid	58.9	41.1
14	trichloroacetic acid	59.4	40.6
15	trichloroacetic acid	58.8	41.2
(mean value)		59.0	41.0

Figure 4.11 Reconstructed chromatogram showing only products of the phenylation reaction of 1,2-dichlorobenzene and benzene



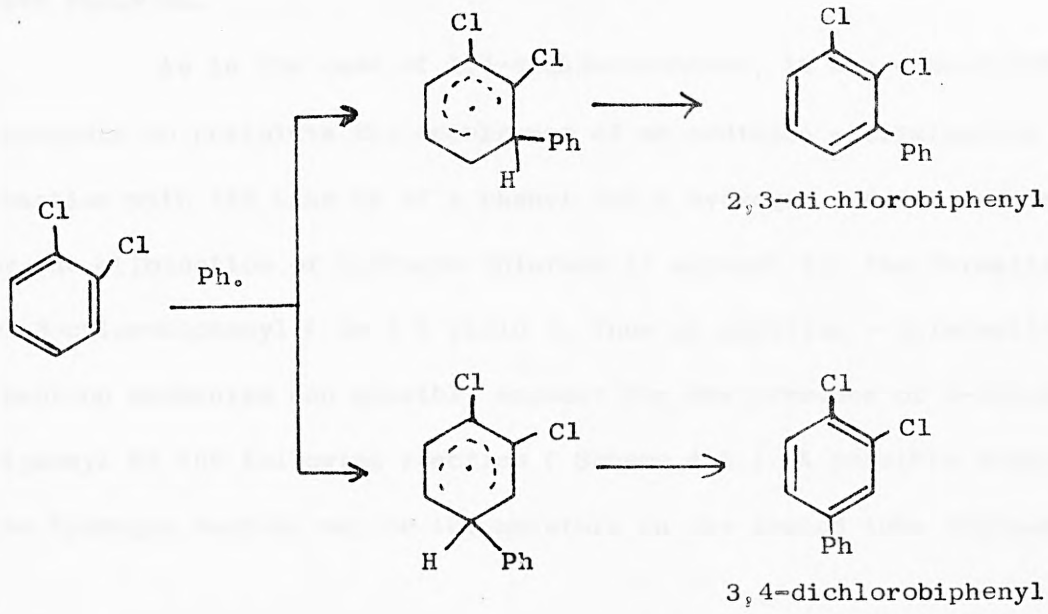
peak 1 = biphenyl

peak 2 = 2-chlorobiphenyl
peak 3 = 3-chlorobiphenyl
peak 4 = 2,6-dichlorobiphenyl
peak 5 = 2,3-dichlorobiphenyl
peak 6 = 3,4-dichlorobiphenyl

The only reports on the phenylation of 1,2-dichlorobenzene in the literature have been by Henriquez and Nonhebel [41] in connection with establishing the reversibility of homolytic aromatic substitution. The products of the phenylation of 1,2-dichlorobenzene reported by the above autours were 2,3- and 3,4-dichlorobiphenyl. In the sealed tube phenylation reactions of 1,2-dichlorobenzene, these dichlorobiphenyls (2,3- and 3,4-) formed the major products, however there were 3 other products of phenylation, namely 2- and 3-chlorobiphenyl and 2,6-dichlorobiphenyl as shown in Figure 4.11.

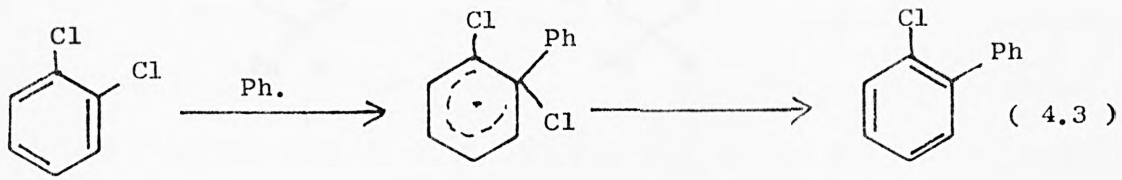
The attack by a phenyl radical at position 3 of 1,2-dichlorobenzene yielded 2,3-dichlorobiphenyl (in 21 % yield), whilst attack at position 4 yielded 3,4-dichlorobiphenyl (in 12 % yield) by

phenyldehydrogenation reactions. The mechanism of these phenyl-dehydrogenation reactions is shown in Scheme 4.4.



Scheme 4.4

To account for the presence of 2-chlorobiphenyl in the phenylation reaction mixture a phenyldechlorination reaction must have occurred. Once again, the presence of monochlorobiphenyls (2- and 3-) was confirmed by g.l.c. retention data as well as g.l.c.-mass spectrometry results (see Appendix). By attack of the phenyl radical at a carbon - chlorine site, it is possible for a phenyldechlorination reaction to occur producing 2-chlorobiphenyl (in 8 % yield) as shown in (4.3).



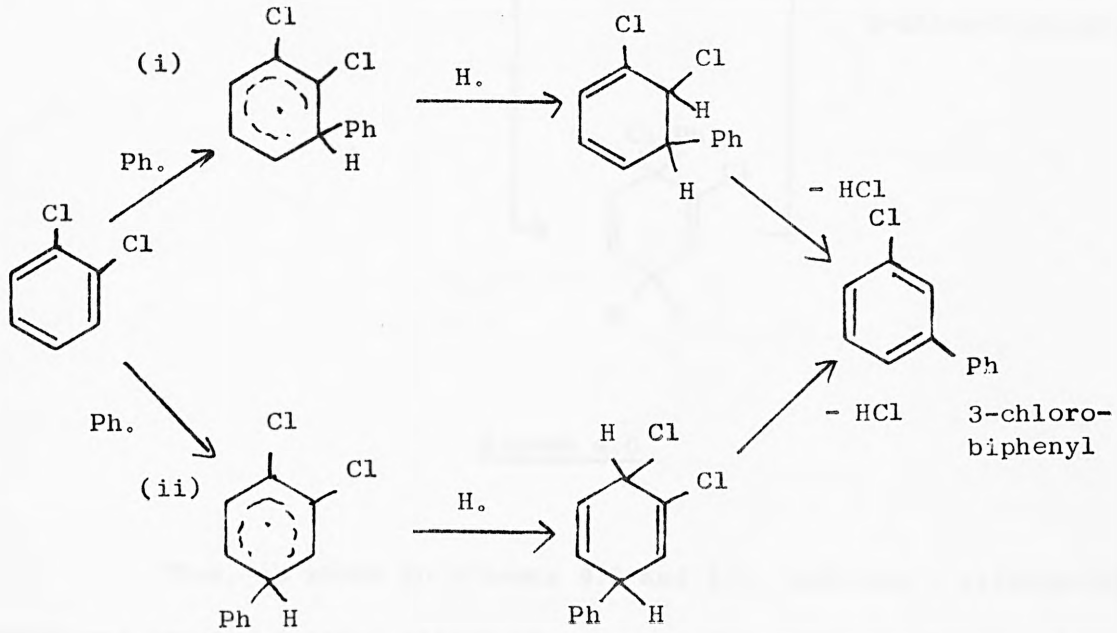
(4.3)

phenyldechlorination

Similarly, in the phenylation of 1,2-difluorobenzene (65) the reactions of phenyldehygrogenation (yielding 2,3- and 3,4-difluorobiphenyls) and phenyldefluorination (yielding 2-fluorobiphenyl) were reported.

As in the case of 1,4-dichlorobenzene, it was considered necessary to postulate the occurrence of an addition - elimination reaction with the take up of a phenyl and a hydrogen radical followed by the elimination of hydrogen chloride to account for the formation of 3-chlorobiphenyl (in 3 % yield). Thus an addition - elimination reaction mechanism can possibly account for the presence of 3-chlorobiphenyl by the following reaction (Scheme 4.5). A possible source of the hydrogen radical may be the moisture in the sealed tube reactants.

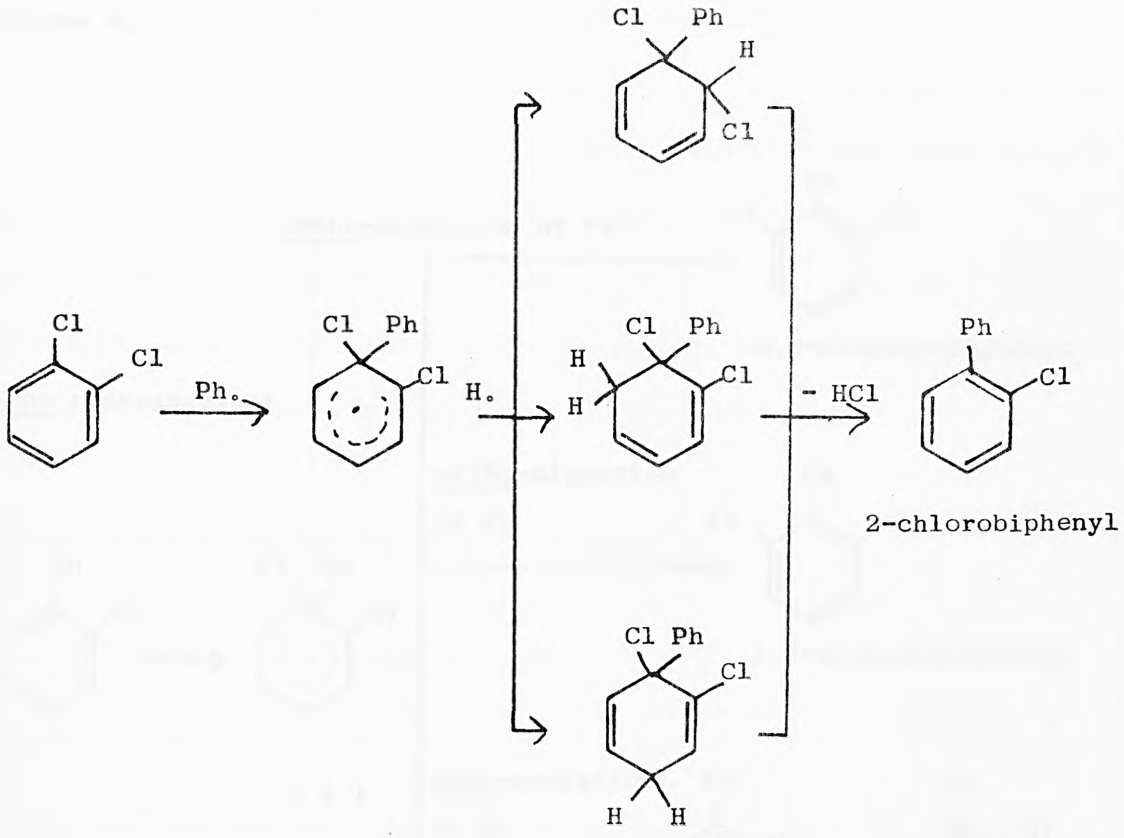
addition - elimination reaction, attack by Ph. at C-3 and C-4



Scheme 4.5

Thus the intermediates (i) and (ii) (Scheme 4.5) besides forming 2,3- and 3,4-dichlorobiphenyls respectively (as shown in Scheme 4.4) can take up a hydrogen radical followed by the elimination of hydrogen chloride as shown in Scheme 4.5.

addition - elimination reaction, attack by Ph. at C-1 and C-2



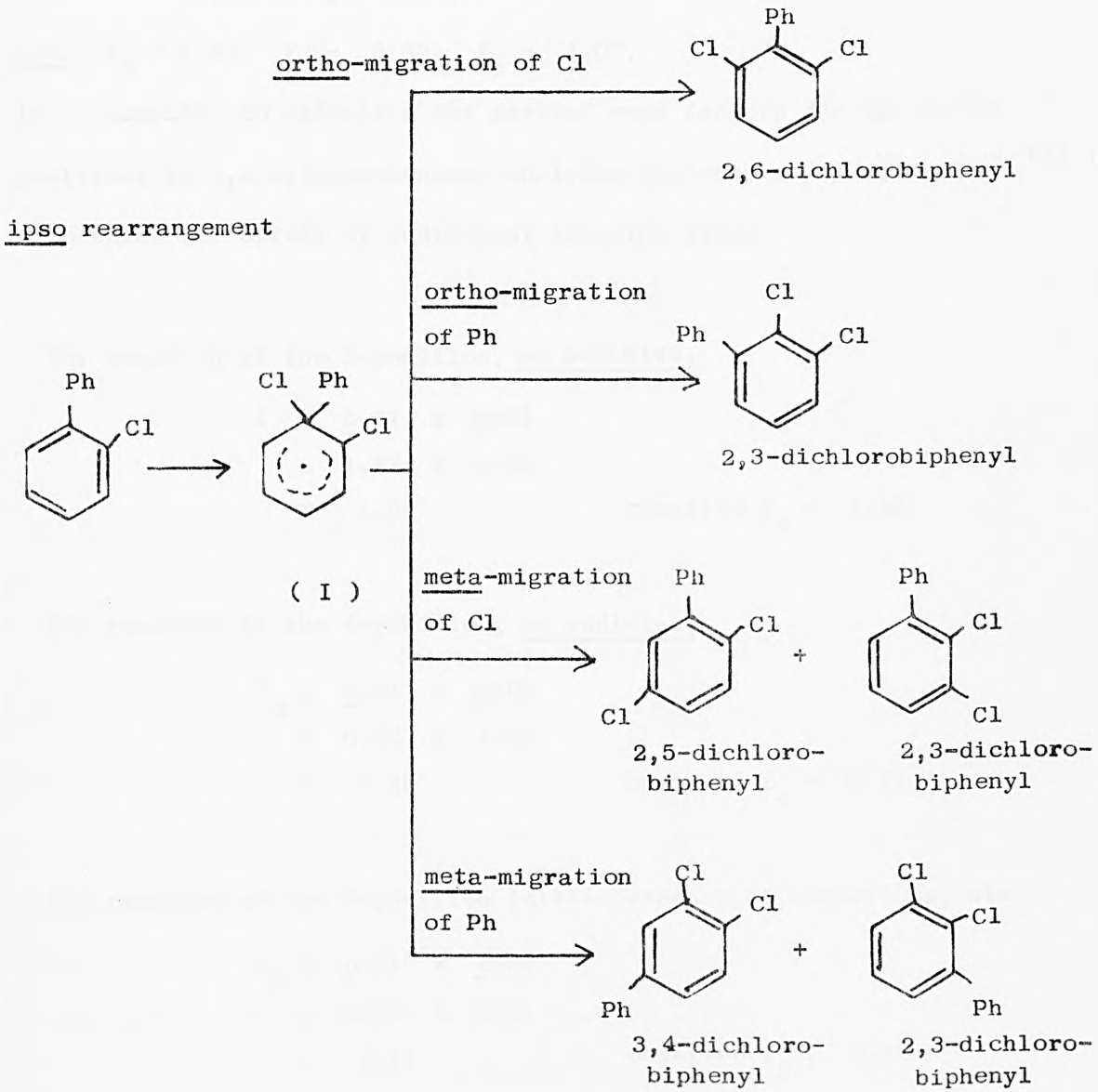
Scheme 4.6

Thus, as shown in Schemes 4.5 and 4.6, addition - elimination reactions require initial attack at a C - H or C - Cl site by phenyl radicals and the take up of a hydrogen atom by the σ-complex followed by the loss of hydrogen chloride.

Scheme 4.6 shows an alternative pathway for the formation of 2-chlorobiphenyl by ipso attack. This type of reaction did not occur

in the phenylation of 1,2-difluorobenzene.

Apart from the expected phenyldehydrogenation dichlorobiphenyl products, (2,3- and 3,4-) there was a third dichlorobiphenyl isomer present in the phenylation reaction mixture, namely 2,6-dichlorobiphenyl (in 4 % yield). The presence of 2,6-dichlorobiphenyl can possibly be explained by postulating the occurrence of an ipso rearrangement reaction, as explained in section 4.1.4 and shown in Scheme 4.7.



Scheme 4.7

Thus it is possible for structure (I), Scheme 4.7, to rearrange by ortho or meta migrations of either chlorine or phenyl groups. It is possible that meta migration of chlorine is unfavourable, thus explaining the absence of any detectable amounts of 2,5-dichlorobiphenyl. The reactions in Scheme 4.7 also provide alternative paths for the formation of 2,3- and 3,4-dichlorobiphenyls, which may occur alongside the phenyldehydrogenation reactions.

The partial rate factors determined for position 3 and 4 in 1,2-dichlorobenzene were $f_3 = 1.36$ and $f_4 = 0.77$ without additives.

Using the partial rate factors determined for chlorobenzene, i.e. $f_o = 1.97$, $f_m = 0.82$, $f_p = 1.07$, it is possible to calculate the partial rate factors for the C - H positions in 1,2-dichlorobenzene applying Holleman's product rule (132) to predict the effect of additional chlorine atoms.

for reaction at the 3-position, no additive,

$$f_3 = \underline{o}\text{-Cl} \times \underline{m}\text{-Cl}$$
$$= 1.97 \times 0.82$$
$$= 1.62 \qquad \text{observed } f_3 = 1.36$$

for reaction at the 4-position, no additive,

$$f_4 = \underline{m}\text{-Cl} \times \underline{p}\text{-Cl}$$
$$= 0.82 \times 1.07$$
$$= 0.88 \qquad \text{observed } f_4 = 0.77$$

for reaction at the 3-position in the presence of copper benzoate,

$$f_3 = \underline{o}\text{-Cl} \times \underline{m}\text{-Cl}$$
$$= 2.90 \times 0.9$$
$$= 2.61 \qquad \text{observed } f_3 = 1.87$$

for reaction at the 4-position in the presence of copper benzoate,

$$f_4 = \underline{m}\text{-Cl} \times \underline{p}\text{-Cl}$$

$$= 0.9 \times 1.24$$

$$= 1.12 \qquad \text{observed } f_4 = 1.35$$

Thus it can be observed that there is a small discrepancy between the calculated and observed partial rate factors for the positions 3 and 4 in 1,2-dichlorobenzene.

The partial rate factor value for position 3 in 1,2-dichlorobenzene was $f_3 = 1.36$, reflecting the effect of one ortho- and one meta-chlorine atom, whilst that for position 4 was $f_4 = 0.77$, reflecting the effect of one meta- and one para- chlorine atom, in the absence of any additive.

The lower value of $f_4 = 0.77$ compared to the calculated value of $f_4 = 0.88$ could possibly be caused by steric hindrance by the adjacent chlorine atoms.

4.2.5 EFFECTS OF ADDITIVES

As shown in Table 4.27, various additives were used in the phenylation reaction. In the presence of these additives the yields of all the biaryls generally increased with little change in isomer ratios.

Biaryl yields were increased in the presence of additives as these promoted the efficient oxidation of the phenylcyclohexadienyl complexes and diverted the reactions of dimerisation and disproportionation as discussed in section 4.1.5.

As can be seen from Table 4.27, the additive with the least effect was cupric chloride and that with the greatest effect was trichloroacetic acid.

Table 4.27 Partial rate factors and percentage yields for the phenylation of 1,2-dichlorobenzene in the presence of additives

row number	additive	phenyldehydrogenation product yields (%)		phenyldechlorination product yield (%)	partial rate factors for phenyldehydrogenation		for phenyldechlorination
		2,3-dichloro-biphenyl	3,4-dichloro-biphenyl	2-chlorobiphenyl	f_3	f_4	f_1 (ipso)
1	none	21.3	11.9	5.4	1.36	0.77	0.53
2	copper benzoate	34.5	24.9	11.0	1.87	1.35	0.60
3	copper acetate	35.9	26.6	10.8	2.08	1.54	0.63
4	cupric chloride	32.6	19.8	11.4	1.63	0.99	0.57
5	iron powder	36.8	25.8	11.1	2.19	1.58	0.68
6	trichloro-acetic acid	37.4	26.3	11.7	2.31	1.63	0.72

yields are in moles per mole peroxide x 100 : each row of results is a mean of four or more figures

Several reactions were carried out with pairs of additives however, due to poor reproducibility and various side reactions, these reactions were discontinued.

The additives had a dramatic effect on the p.r.f. values increasing them substantially as shown in Table 4.27.

4.3 METHOD OF PHENYLATION OF 1,3-DICHLOROBENZENE

This is the same as the method described in section 3.1. Sections 4.3.1 to 4.3.3 show the chromatograms obtained and their identification followed by tables listing experimental quantities leading to tables of results tabulating partial rate factors, yields and calculated isomer ratios.

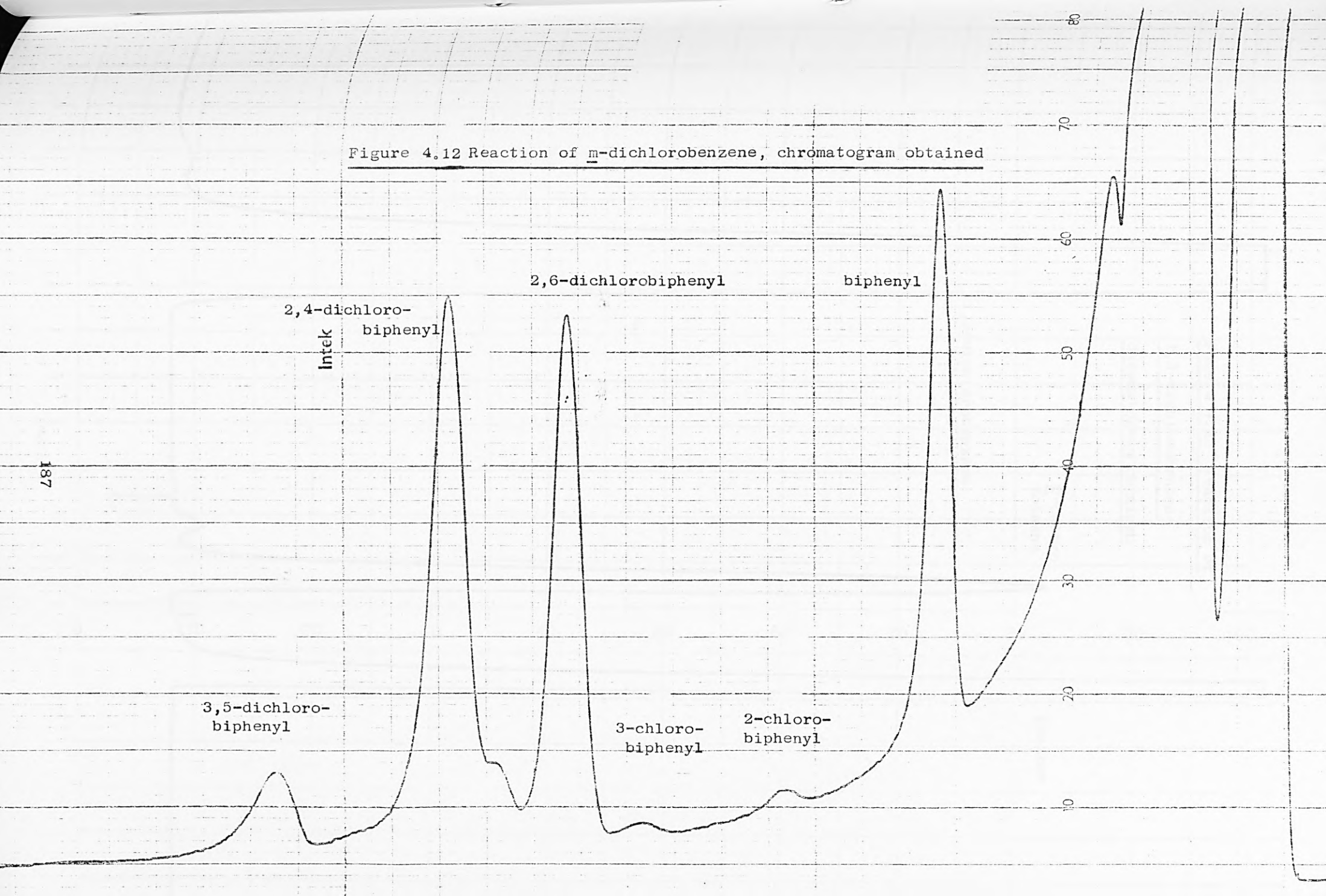
4.3.1 CHROMATOGRAMS

Figures 4.12 and 4.13 show actual chromatograms obtained. Figure 4.14 shows a reconstructed chromatogram showing the relationship of all the products.

4.3.2 PEAK IDENTIFICATION

The same method was used as has been described in section 3.3

Figure 4.12 Reaction of m-dichlorobenzene, chromatogram obtained



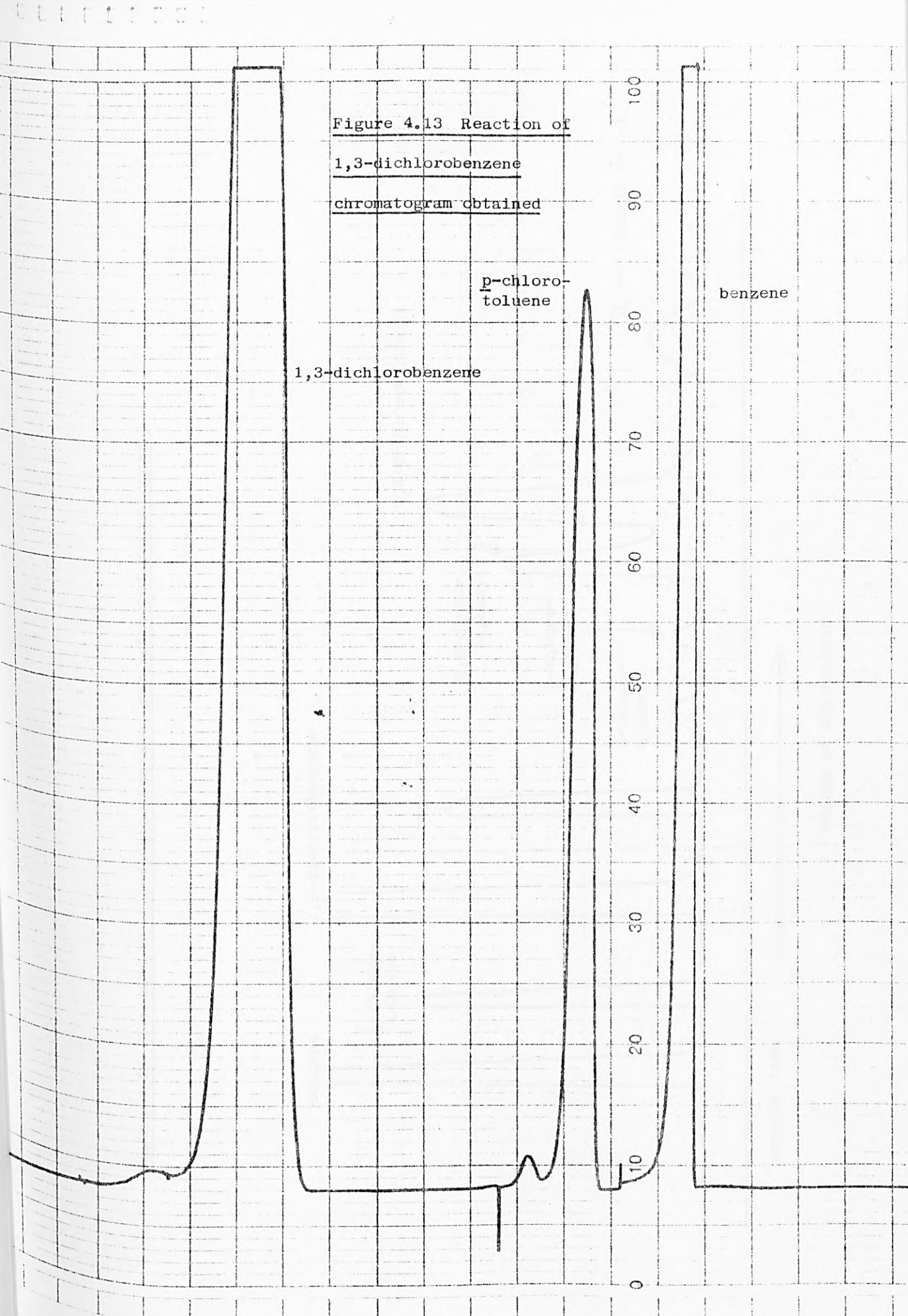


Figure 4.13 Reaction of 1,3-dichlorobenzene chromatogram obtained

Figure 4.14 Reaction of 1,3-dichlorobenzene, reconstructed chromatogram

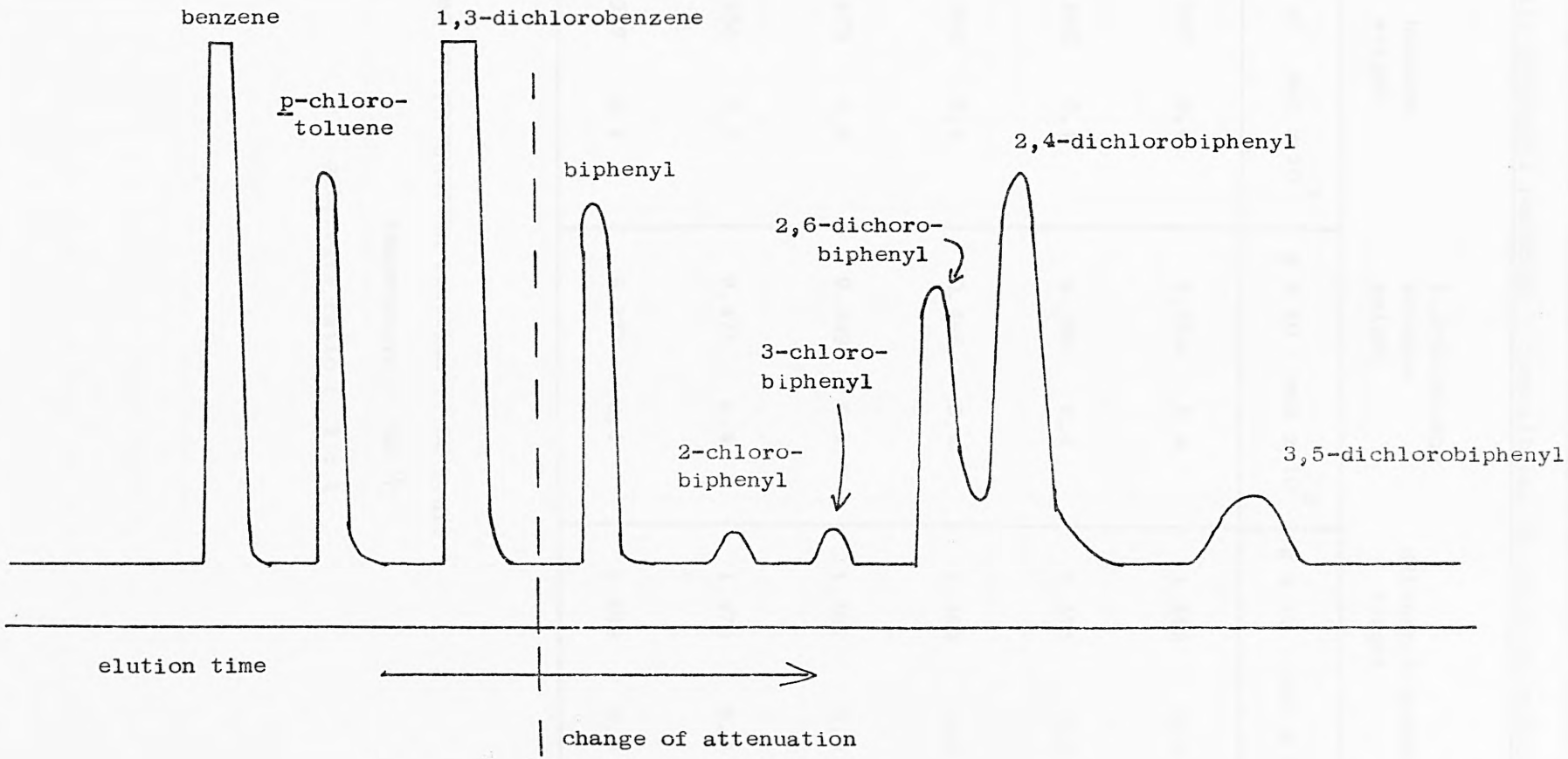


Table 4.28 Sealed tube phenylation reactions of 1,3-dichlorobenzene and benzene with dibenzoyl peroxide - compositions of reaction mixtures

experiment number	benzene weight		1,3-dichloro-benzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1	4.987	6.4	9.354	6.4	1.452	6.0
2.	4.962	6.4	9.368	6.4	1.475	6.0
3	4.992	6.4	9.446	6.4	1.499	6.0
4	4.973	6.4	9.439	6.4	1.481	6.0
5	4.956	6.4	9.471	6.4	1.472	6.0
6	4.997	6.4	9.377	6.4	1.469	6.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

substrate ratio : 1 : 1

Table 4.29 Sealed tube phenylation reactions of 1,3-dichlorobenzene and benzene in the presence of copper additives - compositions of reaction mixtures

experiment number	benzene weight		1,3-dichlorobenzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	4.914	6.3	9.261	6.3	1.452	6.0
2[a]	4.999	6.4	9.350	6.4	1.499	6.0
3[a]	4.901	6.3	9.311	6.3	1.440	6.0
4[a]	4.980	6.4	9.278	6.3	1.483	6.0
5[b]	4.951	6.3	9.299	6.3	1.446	6.0
6[b]	4.948	6.3	9.271	6.3	1.472	6.0
7[b]	4.936	6.3	9.283	6.3	1.455	6.0
8[b]	4.949	6.3	9.256	6.3	1.451	6.0
9[c]	4.925	6.3	9.261	6.3	1.496	6.0
10[c]	4.919	6.3	9.269	6.3	1.472	6.0
11[c]	4.929	6.3	9.309	6.3	1.480	6.0
12[c]	4.943	6.3	9.300	6.3	1.459	6.0

time for phenylation reaction : 50 hours

temperature : 80 °C

substrate ratio : 1 : 1

a = additive copper benzoate, 0.1 g.

b = additive copper acetate, 0.1 g.

c = additive cupric chloride, 0.1 g.

Table 4.30 Sealed tube phenylation reactions of 1,3-dichlorobenzene and benzene with dibenzoyl peroxide in the presence of additives - compositions of reaction mixtures

experiment number	benzene weight		1,3-dichloro-benzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	4.758	6.1	9.114	6.2	1.423	6.0
2[a]	4.751	6.1	9.105	6.2	1.429	6.0
3[a]	4.748	6.1	9.119	6.2	1.433	6.0
4[a]	4.755	6.1	9.122	6.2	1.426	6.0
5[b]	4.739	6.1	9.124	6.2	1.430	6.0
6[b]	4.744	6.1	9.128	6.2	1.435	6.0
7[b]	4.746	6.1	9.120	6.2	1.428	6.0
8[b]	4.741	6.1	9.127	6.2	1.436	6.0

time for phenylation reaction : 50 hours

temperature : 80 °C

substrate ratio : 1 : 1

a = additive iron powder, 0.1 g.

b = additive trichloroacetic acid, 0.1 g.

Table 4.31 Analysis of the phenylation products of 1,3-dichlorobenzene and benzene (Table 4.28 gives compositions

experiment number	dichlorobiphenyl products 2,6-dichloro- peak weight (g.)	2,6-dichloro- cpd. weight (g.)	2,4-dichloro- peak weight (g.)	2,4-dichloro- cpd. weight (g.)	3,5-dichloro- peak weight (g.)	3,5-dichloro- cpd. weight (g.)	chlorobiphenyl products 3-chloro- peak weight (g.)	3-chloro- cpd. weight (g.)	2-chloro- peak weight (g.)	2-chloro- cpd. weight (g.)	biphenyl peak weight (g.)	biphenyl cpd. weight (g.)	p-chlorotoluene internal standard peak weight (g.)	p-chlorotoluene internal standard std. weight (g.)
1	0.0269	0.0359	0.0275	0.0401	0.0060	0.0107	0.0040	0.0053	0.0016	0.0019	0.0385	0.0429	0.1478	0.1631
2	0.0272	0.0364	0.0287	0.0418	0.0059	0.0106	0.0040	0.0053	0.0013	0.0015	0.0404	0.0451	0.1487	0.1642
3	0.0266	0.0355	0.0266	0.0387	0.0055	0.0099	0.0038	0.0050	0.0015	0.0017	0.0389	0.0434	0.1529	0.1688
4	0.0264	0.0353	0.0267	0.0389	0.0057	0.0102	0.0038	0.0050	0.0018	0.0021	0.0380	0.0423	0.1520	0.1677
5	0.0268	0.0358	0.0280	0.0408	0.0051	0.0092	0.0039	0.0051	0.0014	0.0016	0.0392	0.0437	0.1505	0.1661
6	0.0270	0.0360	0.0290	0.0423	0.0060	0.0108	0.0040	0.0053	0.0020	0.0017	0.0398	0.0444	0.1503	0.1659
response factor	1.21		1.32		1.62		1.19		1.06		1.15		1.00	

Table 4.32 Analysis of phenylation products of 1,3-dichlorobenzene and benzene (Table 4.29 gives compositions) in the presence of copper additives

experiment number	dichlorobiphenyl products 2,6-dichloro- peak weight (g.)	2,6-dichloro- cpd. weight (g.)	2,4-dichloro- peak weight (g.)	2,4-dichloro- cpd. weight (g.)	3,5-dichloro- peak weight (g.)	3,5-dichloro- cpd. weight (g.)	chlorobiphenyl products 3-chloro- peak weight (g.)	3-chloro- cpd. weight (g.)	2-chloro- peak weight (g.)	2-chloro- cpd. weight (g.)	biphenyl peak weight (g.)	biphenyl cpd. weight (g.)	p-chlorotoluene internal standard peak weight (g.)	p-chlorotoluene internal standard std. weight (g.)
1[a]	0.0285	0.0380	0.0351	0.0511	0.0086	0.0153	0.0042	0.0055	0.0021	0.0025	0.0306	0.0341	0.1515	0.1671
2[a]	0.0282	0.0376	0.0369	0.0537	0.0085	0.0152	0.0043	0.0056	0.0020	0.0023	0.0315	0.0351	0.1535	0.1694
3[a]	0.0289	0.0386	0.0373	0.0544	0.0086	0.0154	0.0045	0.0054	0.0023	0.0027	0.0317	0.0353	0.1526	0.1684
4[a]	0.0343	0.0379	0.0352	0.0513	0.0083	0.0149	0.0041	0.0054	0.0021	0.0024	0.0309	0.0344	0.1520	0.1678
5[b]	0.0304	0.0406	0.0394	0.0574	0.0102	0.0183	0.0046	0.0061	0.0024	0.0028	0.0308	0.0343	0.1493	0.1648
6[b]	0.0310	0.0414	0.0411	0.0599	0.0101	0.0181	0.0046	0.0061	0.0027	0.0031	0.0314	0.0350	0.1525	0.1682
7[b]	0.0307	0.0409	0.0399	0.0581	0.0101	0.0181	0.0046	0.0061	0.0022	0.0026	0.0312	0.0348	0.1508	0.1663
8[b]	0.0313	0.0418	0.0405	0.0591	0.0104	0.0186	0.0046	0.0061	0.0029	0.0034	0.0323	0.0360	0.1516	0.1674
9[c]	0.0288	0.0385	0.0346	0.0504	0.0083	0.0149	0.0044	0.0058	0.0019	0.0022	0.0318	0.0354	0.1458	0.1609
10[c]	0.0295	0.0394	0.0367	0.0535	0.0082	0.0147	0.0041	0.0054	0.0017	0.0020	0.0328	0.0366	0.1481	0.1634
11[c]	0.0285	0.0380	0.0357	0.0520	0.0081	0.0145	0.0041	0.0054	0.0015	0.0018	0.0320	0.0357	0.1497	0.1652
12[c]	0.0290	0.0387	0.0358	0.0522	0.0084	0.0151	0.0040	0.0053	0.0015	0.0017	0.0330	0.0368	0.1514	0.1671

a = additive copper benzoate, 0.1 g. b = additive copper acetate, 0.1 g. c = additive cupric chloride, 0.1 g.

Table 4.33 Analysis of the phenylation products of 1,3-dichlorobenzene and benzene (Table 4.30 gives compositions) in the presence of additives

experiment number	dichlorobiphenyl products						chlorobiphenyl products				biphenyl		p-chlorotoluene internal standard	
	2,6-dichloro-		2,4-dichloro-		3,5-dichloro-		3-chloro-		2-chloro-					
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1[a]	0.0298	0.0398	0.0312	0.0454	0.0081	0.0144	0.0048	0.0063	0.0027	0.0032	0.0311	0.0347	0.1510	0.1666
2[a]	0.0303	0.0404	0.0330	0.0481	0.0086	0.0154	0.0048	0.0063	0.0029	0.0034	0.0323	0.0360	0.1463	0.1614
3[a]	0.0293	0.0391	0.0309	0.0450	0.0081	0.0144	0.0046	0.0061	0.0031	0.0036	0.0310	0.0345	0.1525	0.1682
4[a]	0.0308	0.0411	0.0324	0.0472	0.0083	0.0149	0.0049	0.0064	0.0027	0.0031	0.0325	0.0362	0.1481	0.1633
5[b]	0.0314	0.0419	0.0413	0.0602	0.0101	0.0181	0.0052	0.0068	0.0030	0.0035	0.0311	0.0347	0.1518	0.1675
6[b]	0.0316	0.0422	0.0454	0.0607	0.0101	0.0181	0.0051	0.0067	0.0035	0.0041	0.0319	0.0356	0.1501	0.1656
7[b]	0.0321	0.0428	0.0420	0.0611	0.0101	0.0180	0.0052	0.0068	0.0032	0.0038	0.0322	0.0359	0.1501	0.1656
8[b]	0.0311	0.0415	0.0399	0.0582	0.0098	0.0176	0.0050	0.0066	0.0031	0.0036	0.0308	0.0343	0.1521	0.1678

a = additive iron powder, 0.1 g. b = additive trichloroacetic acid, 0.1 g.

Table 4.34 Partial rate factors and percentage yields of the products of the phenylation of 1,3-dichlorobenzene and benzene

Table 4.28 gives compositions, Table 4.31 gives results

experiment number	biphenyl yield %	2,6-dichloro-biphenyl f_2	yield (%)	2,4-dichloro-biphenyl f_4	yield (%)	3,5-dichloro-biphenyl f_5	yield (%)	3-chloro-biphenyl f_1	yield %
1	46.4	3.47	26.8	1.94	30.0	1.03	8.0	0.30	4.7
2	48.8	3.34	27.2	1.92	31.2	0.97	7.9	0.29	4.7
3	47.0	3.39	26.5	1.85	28.9	0.94	7.4	0.28	4.4
4	45.8	3.46	26.4	1.91	25.3	1.00	7.6	0.29	4.4
5	47.3	3.39	26.7	1.93	30.5	0.88	6.9	0.29	4.5
6	48.1	3.36	26.9	1.98	31.6	1.01	8.1	0.29	4.7
(mean values)	47.2	3.40	26.8	1.92	29.6	0.97	7.7	0.29	4.6

yields are in mole per mole peroxide x 100

Table 4.35 Partial rate factors and percentage yields of the products of the phenylation of 1,3-dichlorobenzene and benzene in the presence of copper additives - Table 4.29 gives compositions, Table 4.32 gives results

experiment number	biphenyl yield %	2,6-dichloro-biphenyl f_2	yield (%)	2,4-dichloro-biphenyl f_4	yield (%)	3,5-dichloro-biphenyl f_5	yield (%)	3-chloro-biphenyl f_1	yield %
1[a]	36.9	4.62	28.4	3.11	38.2	1.86	11.4	0.39	4.9
2[a]	37.9	4.44	28.1	3.17	40.1	1.80	11.4	0.39	5.0
3[a]	38.2	4.54	28.9	3.20	40.7	1.81	11.5	0.41	5.2
4[a]	37.2	4.56	28.3	3.09	38.3	1.80	11.1	0.38	4.8
(mean values)[a]	37.6	4.54	28.4	3.14	39.3	1.82	11.4	0.39	5.0
5[b]	37.1	4.91	30.3	3.47	42.9	2.22	13.7	0.44	5.4
6[b]	37.9	4.89	30.9	3.54	44.8	2.14	13.5	0.42	5.3
7[b]	38.0	4.87	30.6	3.46	43.4	2.15	13.5	0.43	5.4
8[b]	39.0	4.81	31.2	3.40	44.2	2.13	13.9	0.42	5.4
(mean values)[b]	37.9	4.87	30.8	3.47	43.8	2.16	13.6	0.42	5.4
9[c]	38.3	4.50	28.8	2.95	37.7	1.75	11.1	0.38	5.1
10[c]	39.6	4.46	29.5	3.02	40.0	1.66	11.0	0.36	5.0
11[c]	38.6	4.41	28.4	3.02	38.9	1.69	10.8	0.56	5.0
12[c]	39.8	4.35	28.9	2.94	39.0	1.70	11.3	0.36	4.7
(mean values)[c]	39.1	4.43	28.9	2.98	38.9	1.70	11.1	0.37	4.9

yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g.

b = additive copper acetate, 0.1 g.

c = additive cupric chloride, 0.1 g.

Table 4.36 Partial rate factors and percentage yields of the products of the phenylation of 1,3-dichlorobenzene and benzene in the presence of additives - Table 4.30 gives compositions, Table 4.33 gives results

experiment number	biphenyl yield %	2,6-dichloro-biphenyl f_2	yield (%)	2,4-dichloro-biphenyl f_4	yield (%)	3,5-dichloro-biphenyl f_5	yield (%)	3-chloro-biphenyl f_1	yield %
1[a]	37.6	4.75	29.7	2.71	33.9	1.72	10.8	0.45	5.6
2[a]	38.9	4.65	30.2	2.76	36.0	1.77	11.5	0.43	5.6
3[a]	37.3	4.69	29.2	2.70	33.6	1.73	10.8	0.44	5.4
4[a]	39.2	4.70	30.7	2.70	35.3	1.71	11.1	0.43	5.7
(mean value)[a]	38.3	4.70	30.0	2.72	34.7	1.73	11.0	0.44	5.6
5[b]	37.6	5.00	31.3	3.59	45.0	2.16	13.5	0.48	6.0
6[b]	38.5	4.91	31.5	3.53	45.4	2.11	13.5	0.46	5.9
7[b]	39.0	4.94	32.0	3.53	45.7	2.08	13.5	0.47	6.0
8[b]	37.1	5.02	31.0	3.52	43.5	2.13	13.2	0.47	5.8
(mean value)[b]	38.0	4.97	31.5	3.54	44.9	2.12	13.4	0.47	6.0

yields are in mole per mole peroxide x 100

a = additive iron powder, 0.1 g.

b = additive trichloroacetic acid, 0.1 g.

Table 4.37 Percentage yields of 2-chlorobiphenyl, a by-product of the phenylation of 1,3-dichlorobenzene and benzene in the presence of various additives

experiment number	additves					
	no additive yield %	copper benzoate yield %	copper acetate yield %	cupric chloride yield %	iron powder yield %	trichloro-acetic acid yield %
1	1.7	2.2	2.5	2.0	2.8	3,1
2	1.3	2.0	2.7	1.8	3.0	3,6
3	1.5	2.4	2.3	1.6	3.2	3.4
4	1.9	2.1	3.0	1.5	2.7	3.2
5	1.4	-	-	-	-	-
6	1.5	-	-	-	-	-
(mean values)	1.6	2.2	2.6	1.7	2.9	3.3

yields are in mole per pole peroxide x 100

Table 4.38 Calculated product isomer ratios for the phenylation reaction of 1,3-dichlorobenzene in the absence of additives

(Table 4.28 gives compositions)

experiment number	2,6-dichlorobiphenyl %	2,4-dichlorobiphenyl %	3,5dichlorobiphenyl %
1	53.9	30.1	16.0
2	53.6	30.8	15.6
3	54.9	29.9	15.2
4	54.3	30.0	15.7
5	54.7	31.1	14.2
6	52.9	31.2	15.9

Table 4.39 Calculated product isomer ratios for the phenylation reaction of 1,3-dichlorobenzene in the presence of copper additives (Table 4.29 gives compositions)

experiment number	2,6-dichlorobiphenyl %	2,4-dichlorobiphenyl %	3,5-dichlorobiphenyl %
1[a]	48.2	32.4	19.4
2[a]	47.2	33.7	19.1
3[a]	47.5	33.5	19.0
4[a]	48.3	32.7	19.1
(mean values)[a]	47.8	33.1	19.1
5[b]	46.3	32.7	20.9
6[b]	46.3	33.5	20.3
7[b]	46.5	33.0	20.5
8[b]	46.5	32.9	20.3
(mean values)[b]	46.4	33.0	20.5
9[c]	48.9	31.7	19.0
10[c]	48.8	33.0	18.2
11[c]	48.4	33.1	18.5
12[c]	48.4	32.7	18.9
(mean values)[c]	48.6	32.7	18.7

a = additive copper benzoate, 0.1 g., b = additive copper acetate, 0.1 g.
c = additive cupric chloride, 0.1 g.

Table 4.40 Calculated product isomer ratios for the phenylation reaction of 1,3-dichlorobenzene in the presence of additives

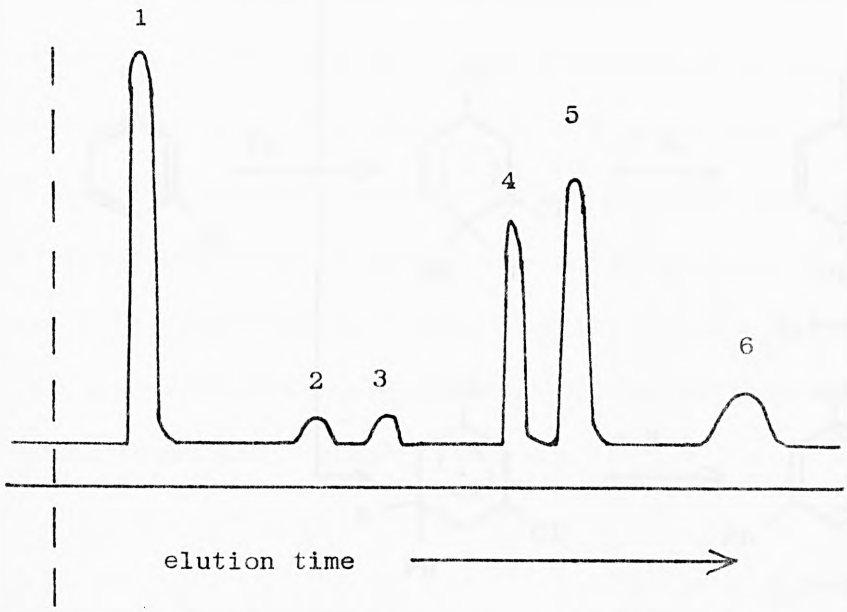
(Table 4.30 gives compositions)

experiment number	2,6-dichlorobiphenyl %	2,4-dichlorobiphenyl %	3,5-dichlorobiphenyl %
1[a]	51.7	29.5	18.7
2[a]	50.7	30.1	19.3
3[a]	51.4	29.6	19.0
4[a]	51.6	29.6	18.8
(mean values)[a]	51.4	29.7	18.9
5[b]	46.5	33.4	20.1
6[b]	46.5	33.5	20.0
7[b]	46.8	33.5	19.7
8[b]	47.1	33.0	20.0
(mean values)[b]	46.7	33.3	19.9

a = additive iron powder, 0.1 g.

b = additive trichloroacetic acid, 0.1 g.

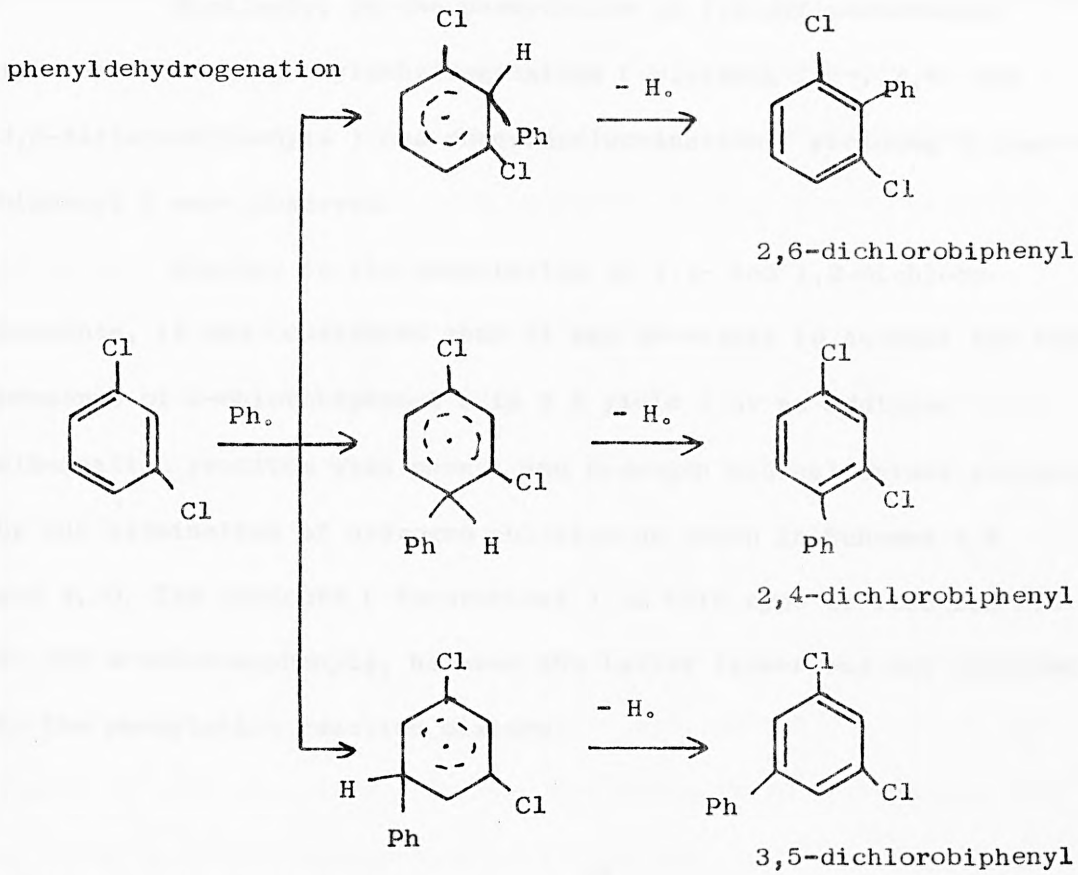
Figure 4.15 Reconstructed chromatogram showing only products of the phenylation reaction of 1,3-dichlorobenzene and benzene



peak 1 = biphenyl

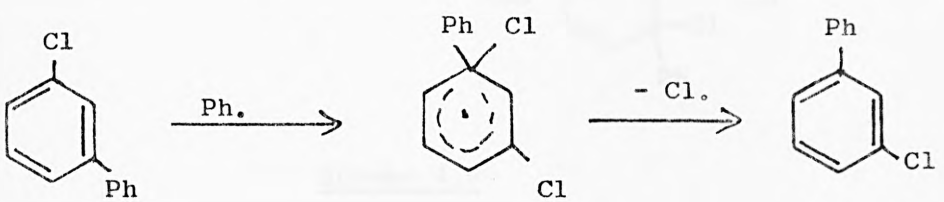
peak 2 = 2-chlorobiphenyl
peak 3 = 3-chlorobiphenyl
peak 4 = 2,6-dichlorobiphenyl
peak 5 = 2,4-dichlorobiphenyl
peak 6 = 3,5-dichlorobiphenyl

The phenylation of 1,3-dichlorobenzene has not been reported in the literature unlike the ortho- and para- isomers. There are three possible products of phenyldehydrogenation formed by displacement of different C - H sites at positions 2, 4 and 5 producing respectively 2,6-, 2,4- and 3,5-dichlorobiphenyls. Scheme 4.8 shows the mechanism of the formation of the phenyldehydrogenation products of isomeric dichlorobiphenyls. Attack by a phenyl radical at position 2 produced 2,6-dichlorobiphenyl (in 27 % yield), whilst attack at positions 4 or 6 yielded 2,4-dichlorobiphenyl (in 30 % yield) and attack at position 5 produced 3,5-dichlorobiphenyl (in 8 % yield).



Scheme 4.8

The phenylation reaction products were found to also contain 3- and 2-chlorobiphenyls which were confirmed by g.l.c. retention time data and by g.l.c.-mass spectrometry results (see Appendix). To account for the formation of 3-chlorobiphenyl (in 4 % yield) a phenyldechlorination reacrion must have taken place with the direct attack by a phenyl radical at a C - Cl site followed by the loss of a chlorine atom as shown in (4.4)

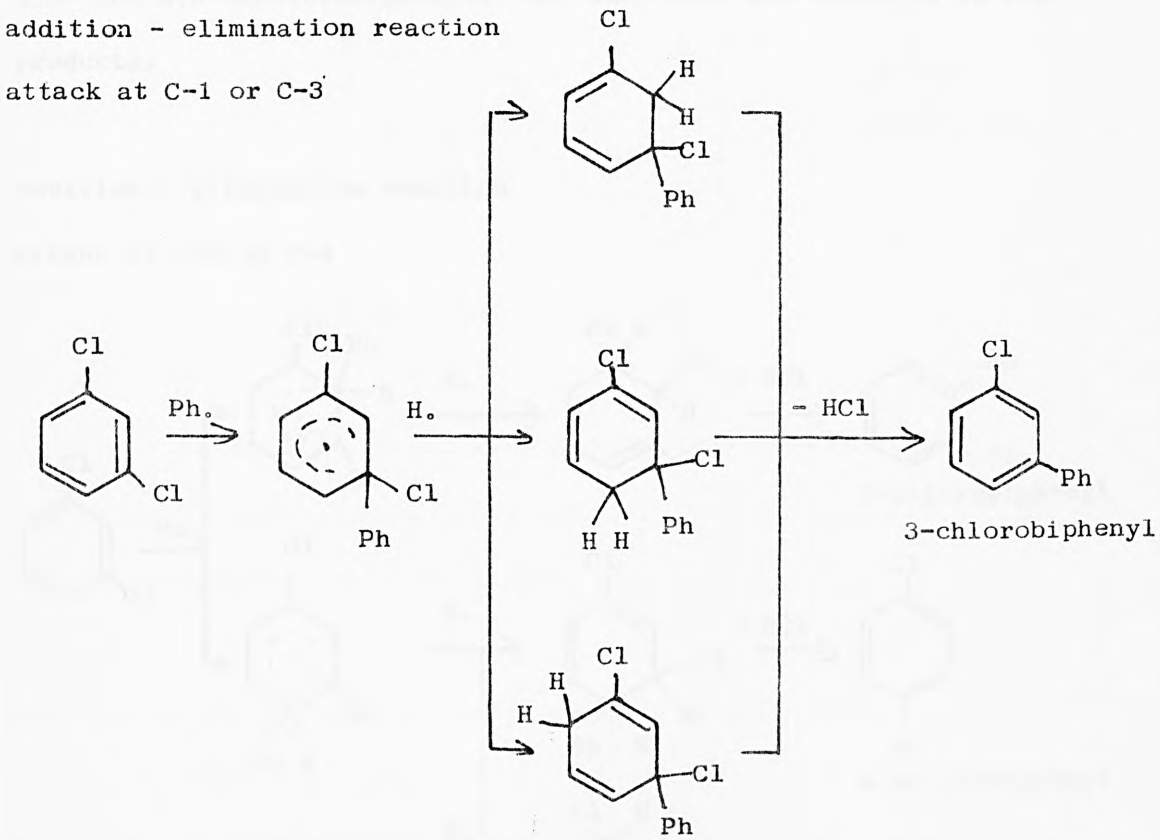


(4.4)

3-chlorobiphenyl

Similarly, in the phenylation of 1,3-difluorobenzene (65) the reactions of phenyldehydrogenation (yielding 2,6-, 2,4- and 3,5-difluorobiphenyls) and phenyldefluorination (yielding 3-fluorobiphenyl) were observed.

Similar to the phenylation of 1,4- and 1,2-dichlorobenzenes, it was considered that it was necessary to account for the presence of 2-chlorobiphenyl (in 2 % yield) by an addition - elimination reaction with phenyl and hydrogen radical uptake followed by the elimination of hydrogen chloride as shown in Schemes 4.9 and 4.10. The products (theoretical) of this type of reaction are 2- and 4-chlorobiphenyls, however the latter isomer was not detected in the phenylation reaction mixture.



Scheme 4.9

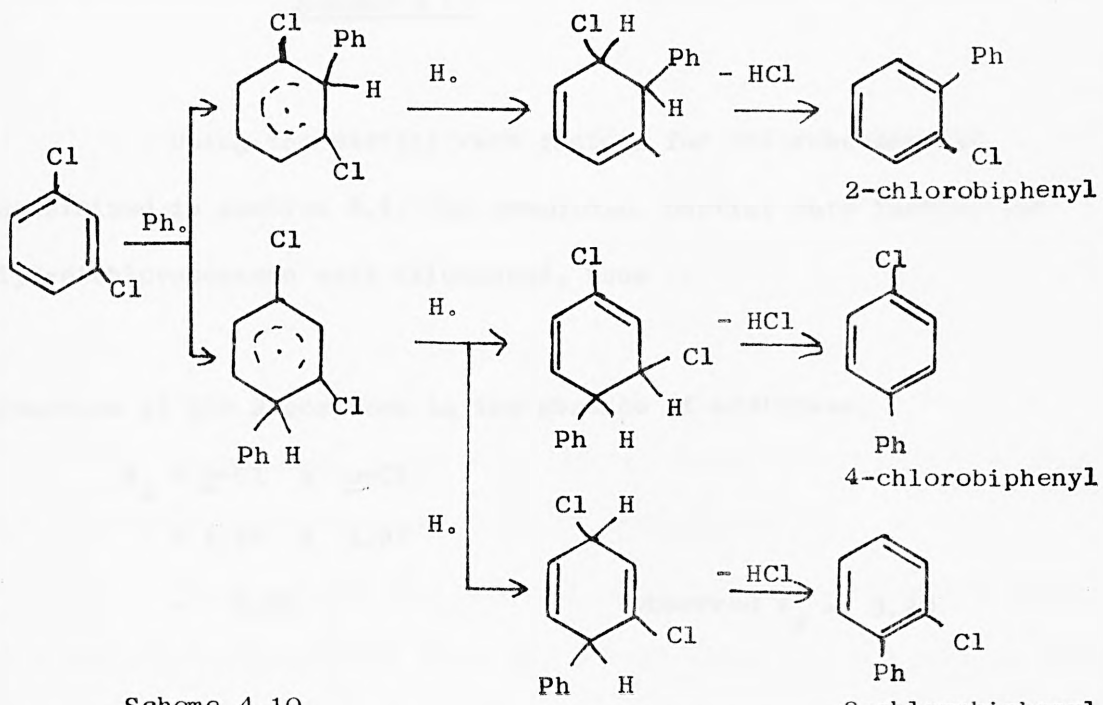
Therefore, as shown in Schemes 4.9 and 4.10, the addition - elimination reaction pathway requires initial attack at a C - H or C - Cl site by phenyl radicals, followed by the take up of a hydrogen atom by the σ-complex, followed by the loss of hydrogen chloride.

Scheme 4.9 shows an alternative pathway for the formation of 3-chlorobiphenyl by the addition - elimination reaction pathway. This type of reaction was not found to occur in the phenylation of 1,3-difluorobenzene.

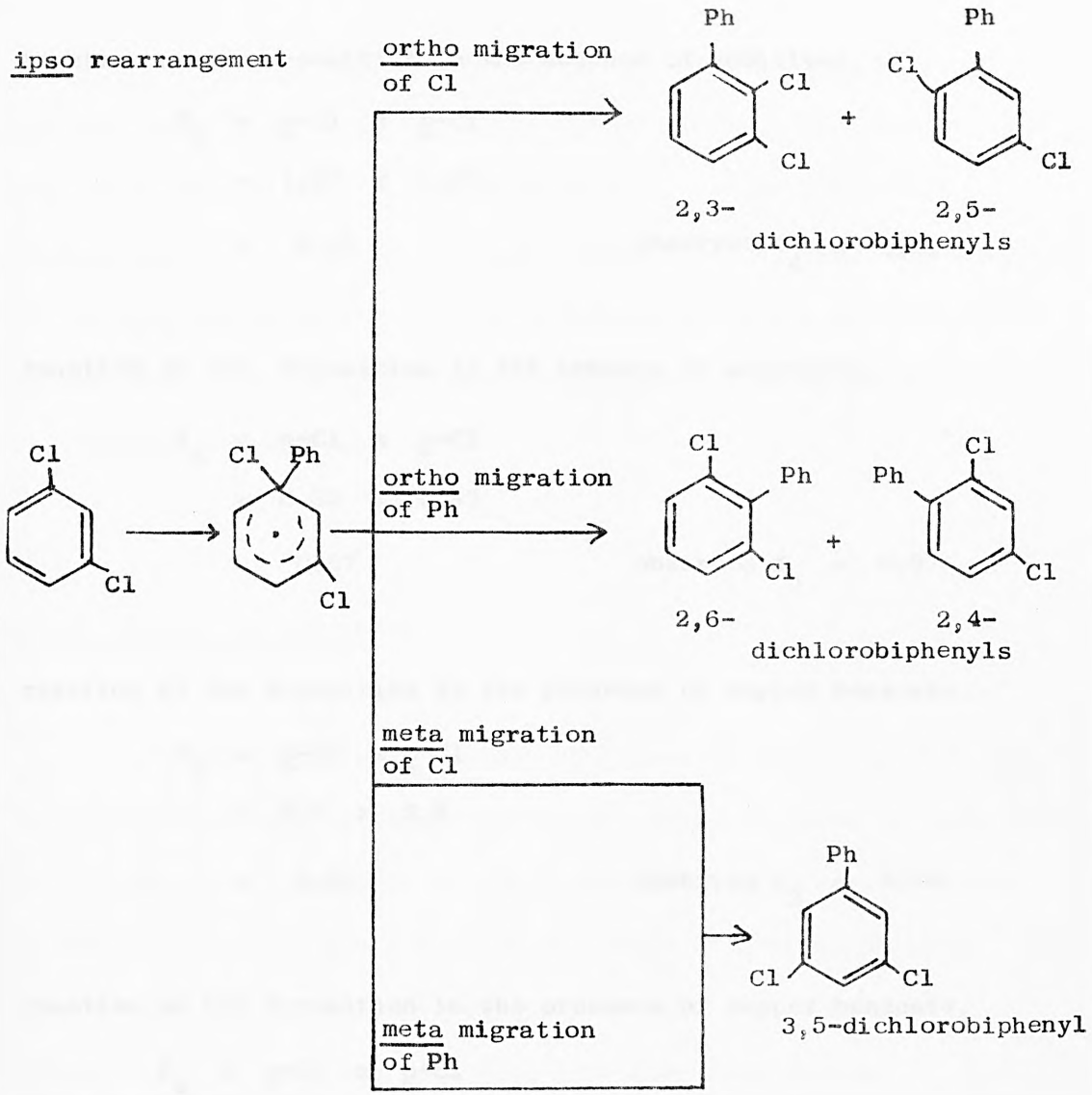
As what has been presumed to be ipso rearrangement products were observed in the phenylation of 1,4- and 1,2-dichlorobenzenes, Scheme 4.11 shows the theoretical products likely to be formed in such reactions. The only new products in this Scheme were 2,3- and 2,5-dichlorobiphenyls, but they were not detected in the products.

addition - elimination reaction

attack at C-2 or C-4



Scheme 4.10



Scheme 4.11

Using the partial rate factors for chlorobenzene as determined in section 3.4, the predicted partial rate factors for 1,3-dichlorobenzene were calculated, thus :-

reaction at the 2-position in the absence of additives,

$$f_2 = \underline{o}\text{-Cl} \times \underline{o}\text{-Cl}$$

$$= 1.97 \times 1.97$$

$$= 3.88 \qquad \text{observed } f_2 = 3.40$$

reaction at the 4-position in the absence of additives,

$$f_4 = \underline{o}\text{-Cl} \times \underline{p}\text{-Cl}$$
$$= 1.97 \times 1.07$$
$$= 2.11 \qquad \text{observed } f_4 = 1.92$$

reaction at the 5-position in the absence of additives,

$$f_5 = \underline{m}\text{-Cl} \times \underline{m}\text{-Cl}$$
$$= 0.82 \times 0.82$$
$$= 0.67 \qquad \text{observed } f_5 = 0.97$$

reaction at the 2-position in the presence of copper benzoate,

$$f_2 = \underline{o}\text{-Cl} \times \underline{o}\text{-Cl}$$
$$= 2.9 \times 2.9$$
$$= 8.41 \qquad \text{observed } f_2 = 4.54$$

reaction at the 4-position in the presence of copper benzoate,

$$f_4 = \underline{o}\text{-Cl} \times \underline{p}\text{-Cl}$$
$$= 2.9 \times 1.24$$
$$= 3.60 \qquad \text{observrd } f_4 = 3.14$$

reaction at the 5-position in the presence of copper benzoate,

$$f_5 = \underline{m}\text{-Cl} \times \underline{m}\text{-Cl}$$
$$= 0.9 \times 0.9$$
$$= 0.81 \qquad \text{observed } f_5 = 1.82$$

Once again, there were several small discrepancies between the observed and calculated values as shown above.

It was found that position 2 in 1,3-dichlorobenzene with its two adjacent chlorine atoms had a high value for its partial rate factor, $f_2 = 3.40$. This appears to be due to the close proximity of the

two ortho chlorine atoms. Position 4 (equivalent to position 6) was affected by one ortho chlorine and by one para chlorine atom and had a partial rate factor value of f_4 = 1.92. The lowest partial rate factor value was that for position 5, which was affected by two meta chlorine atoms, f_5 = 0.97, which have a deactivating effect. This position is slightly deactivated towards phenylation on comparison with benzene.

4.3.5 EFFECT OF ADDITIVES

The presence of various additives in the phenylation of 1,3-dichlorobenzene increased the biaryl yield as shown in Table 4.41, at the expense of products of dimerisation and disproportionation, as discussed in section 1.9. From the range of copper additives, copper acetate was the most efficient in this case, whilst trichloroacetic acid was more efficient than iron powder.

As shown in Table 4.41, the partial rate factors without additive, f_2 = 3.40, f_4 = 1.92, f_5 = 0.97, increased to

f_2 = 4.97, f_4 = 3.54, f_5 = 2.12 in the presence of trichloroacetic acid (0.1 g.).

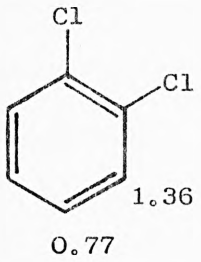
There was also a small increase in the partial rate factor for phenyldechlorination from $f_{1\text{-Cl}}$ = 0.29 without additive, throught $f_{1\text{-Cl}}$ = 0.39 in the presence of copper benzoate to $f_{1\text{-Cl}}$ = 0.47 in the presence of trichloroacetic acid.

Table 4.41 Partial rate factors and percentage yields for the phenylation of 1,3-dichlorobenzene in the presence of additives

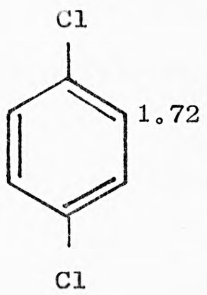
row number	additive (0.1 g.)	phenyldehydrogenation products			phenyldechlorination product	partial rate factor for :-			
		2,6-dichloro-biphenyl yield (%)	2,4-dichloro-biphenyl yield (%)	3,5-dichloro-biphneyl yield (%)	3-chlorobiphenyl yield (%)	phenyldehydrogenation f_2	f_4	f_5	phenyldechlorination f_1
1	(none)	26.8	29.6	7.7	4.6	3.40	1.92	0.97	0.29
2	copper benzoate	28.4	39.3	11.4	5.0	4.54	3.14	1.82	0.39
3	copper acetate	30.8	43.8	13.6	5.4	4.87	3.47	2.16	0.42
4	cuprous chloride	28.9	38.9	11.1	4.9	4.43	2.98	1.70	0.37
5	iron powder	30.0	34.7	11.0	5.6	4.70	2.72	1.73	0.44
6	trichloro-acetic acid	31.5	44.9	13.4	6.0	4.97	3.54	2.12	0.47

yields are in mole per mole peroxide x 100 each row of results is a mean of four or more figures

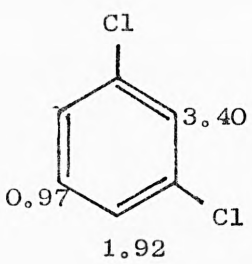
4.3.6 PARTIAL RATE FACTORS FOR THE PHENYLATION OF DICHLOROBENZENES



1,2-dichlorobenzene



1,4-dichlorobenzene



1,3-dichlorobenzene

On comparison of the partial rate factor values as shown above, it can be seen that certain patterns emerge from the isomeric dichlorobenzenes.

The partial rate factor values of positions which have no ortho chlorine atoms are generally low values and show a deactivation towards phenylation. Thus, for example, position 4 in 1,2-dichlorobenzene ($f_4 = 0.77$) and position 5 in 1,3-dichlorobenzene ($f_5 = 0.97$) both have low partial rate factors in comparison to the p.r.f. values of the other positions in 1,2- and 1,3-dichlorobenzenes.

Similarly, a common feature of position 3 in 1,2-dichlorobenzene, position 2 in 1,4-dichlorobenzene and position 4 in 1,3-dichlorobenzene is the presence of an ortho chlorine atom in each case, with the following partial rate factor values :-

$f_3 = 1.36$, $f_2 = 1.72$, $f_4 = 1.92$, respectively.

The highest value for the partial rate factor was found for position 2 in 1,3-dichlorobenzene, which is influenced by two ortho chlorine atoms, which are activating towards phenylation, $f_2 = 3.40$.

CHAPTER FIVE

PHENYLATION REACTIONS OF TRICHLOROBENZENES

5.1 METHOD OF PHENYLATION OF 1,3,5-TRICHLOROBENZENE

This was the same as has been described in section 3.1. Sections 5.1.1 to 5.1.3 show the chromatograms obtained and their identification, followed by tables listing experimental quantities leading to tables of results tabulating partial rate factors and the yields.

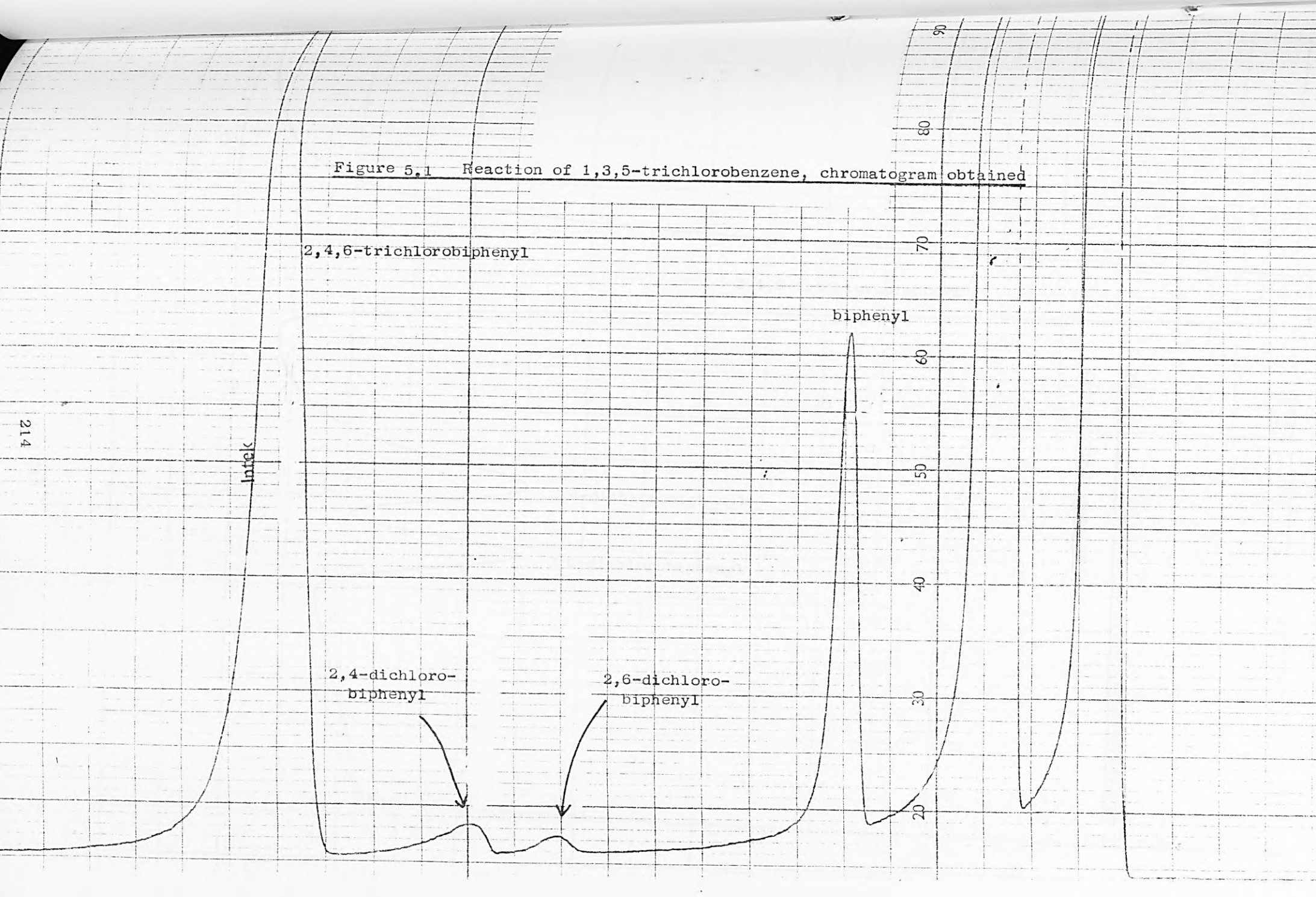
5.1.1 CHROMATOGRAMS

Figures 5.1 to 5.5 inclusive show actual chromatograms obtained. Figure 5.6 shows a reconstructed chromatogram demonstrating the relationship between the products obtained.

5.1.2 PEAK IDENTIFICATION

The same method was used as has been explained in section 3.3

Figure 5.1 Reaction of 1,3,5-trichlorobenzene, chromatogram obtained



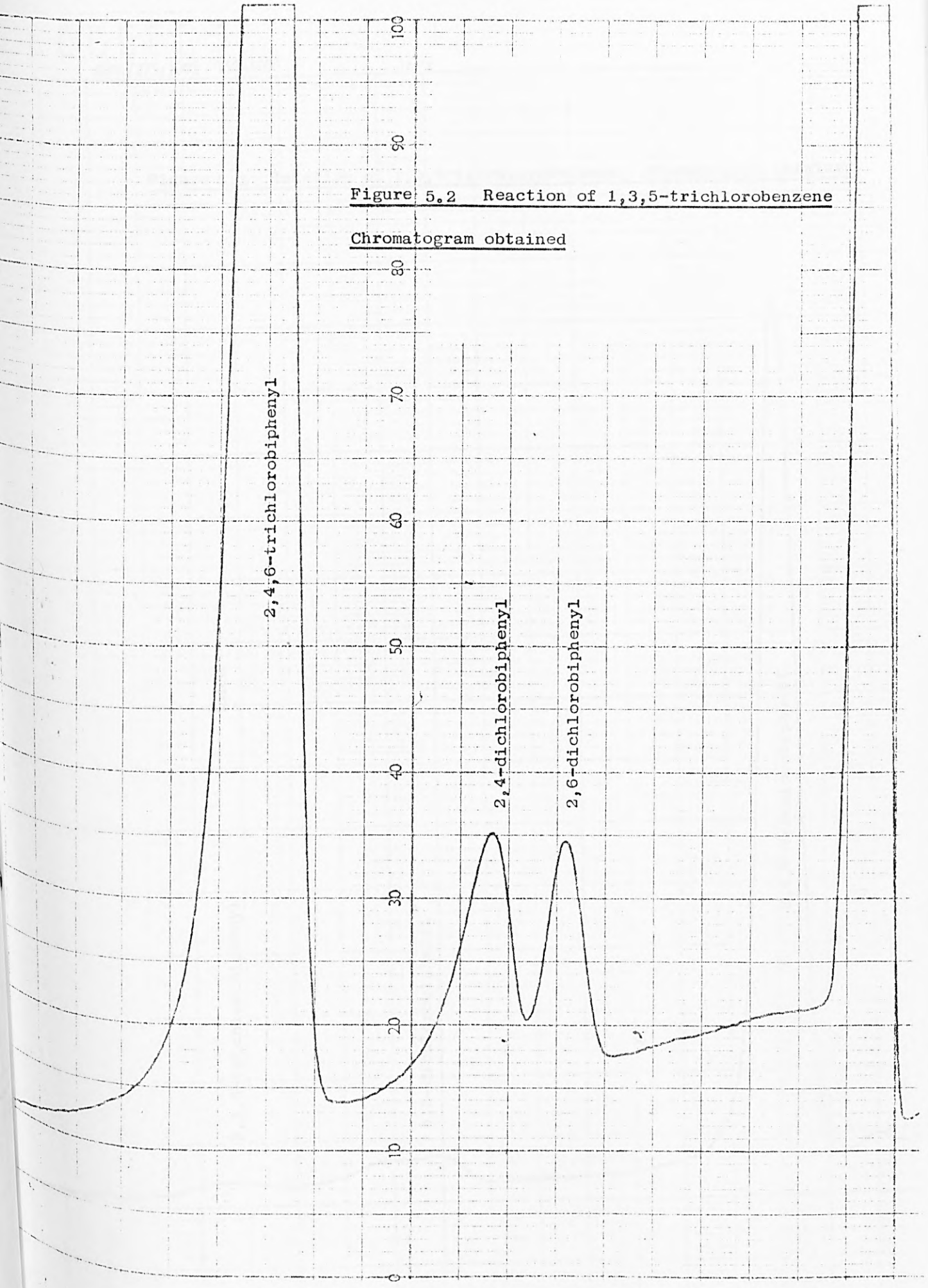
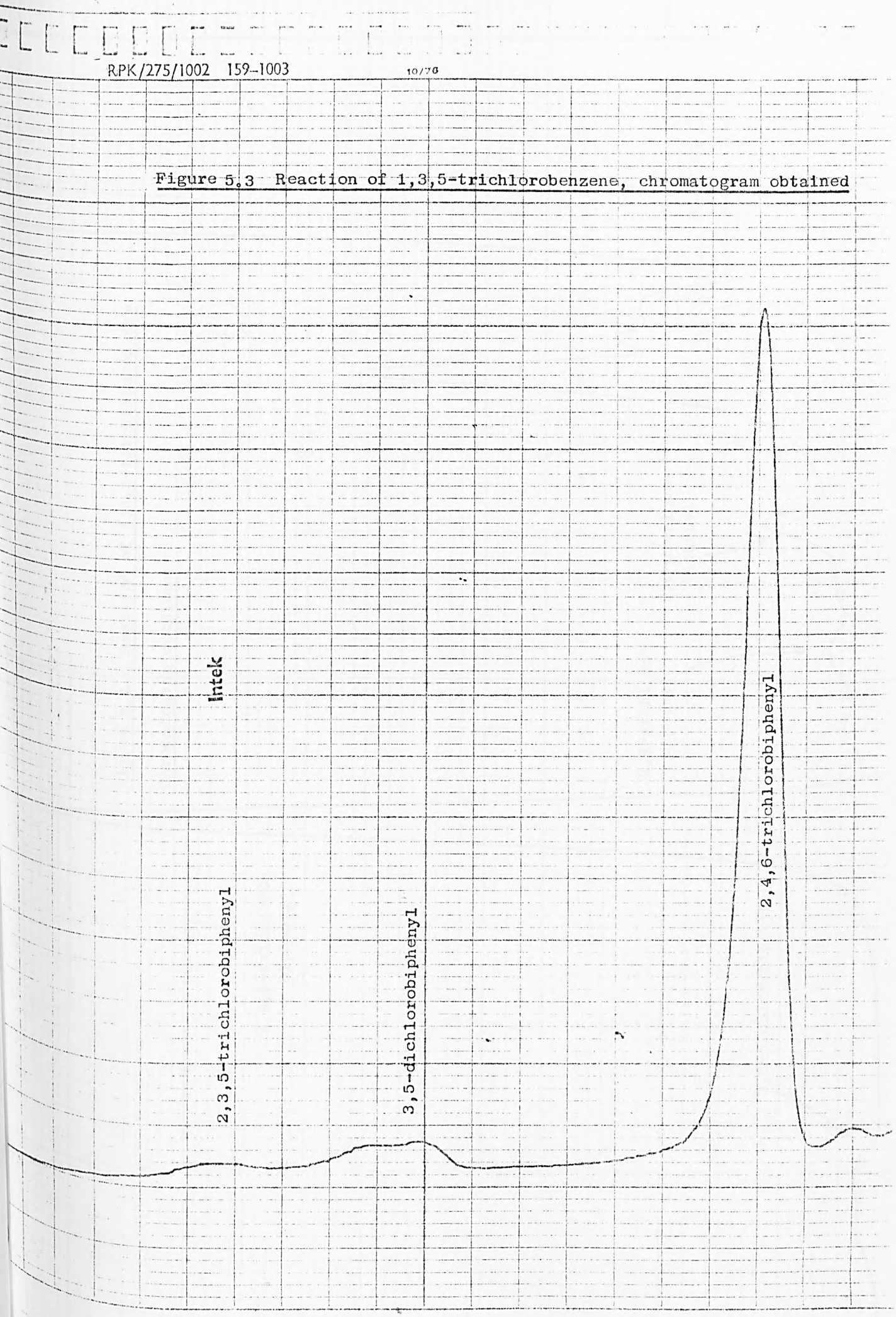


Figure 5.2 Reaction of 1,3,5-trichlorobenzene

Chromatogram obtained

Figure 5.3 Reaction of 1,3,5-trichlorobenzene, chromatogram obtained



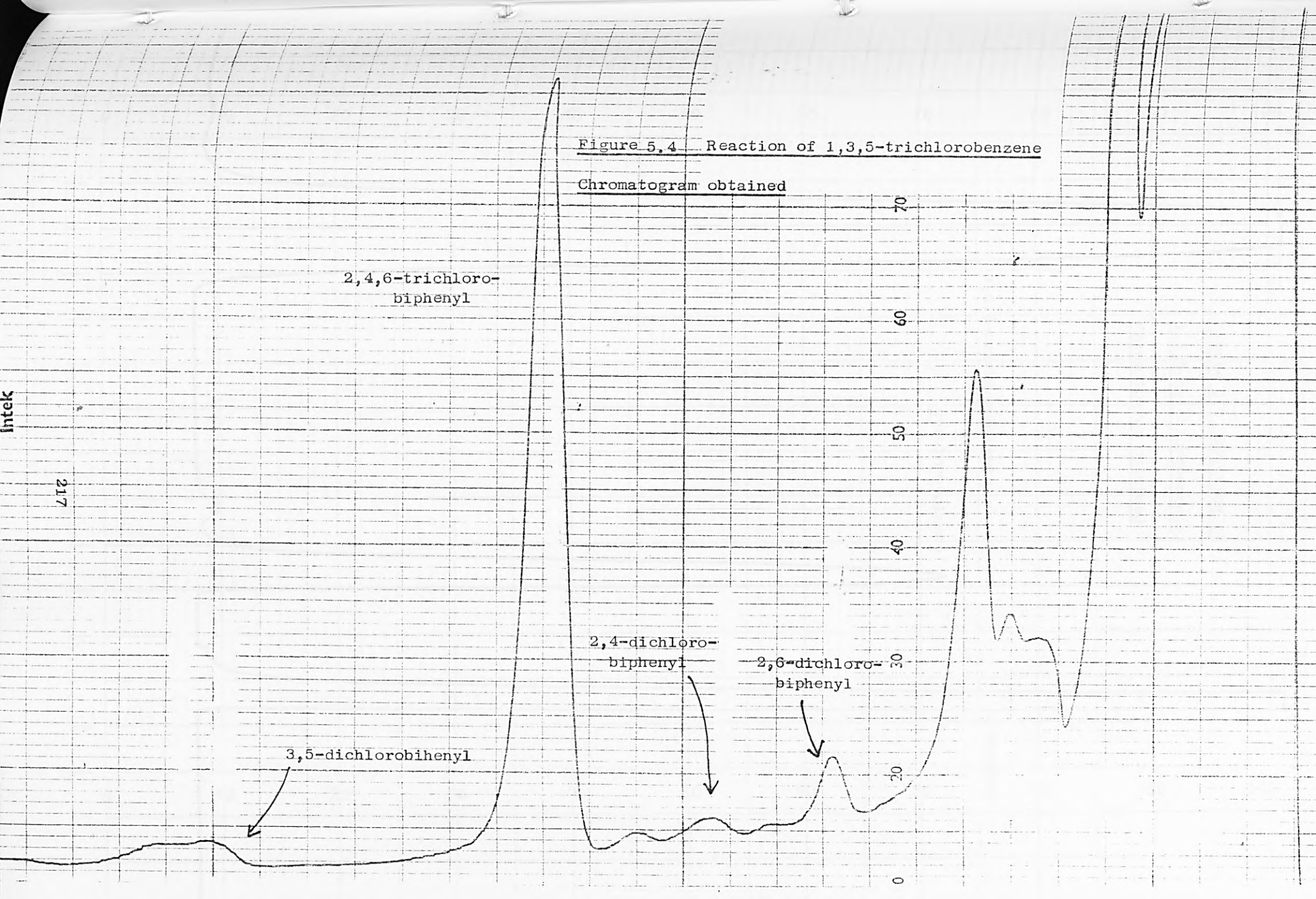


Figure 5.4 Reaction of 1,3,5-trichlorobenzene
Chromatogram obtained
2,4,6-trichloro-
biphenyl
2,4-dichloro-
biphenyl
2,6-dichloro-
biphenyl
3,5-dichlorobihenyl
70
60
50
40
30
20
0
intek
217

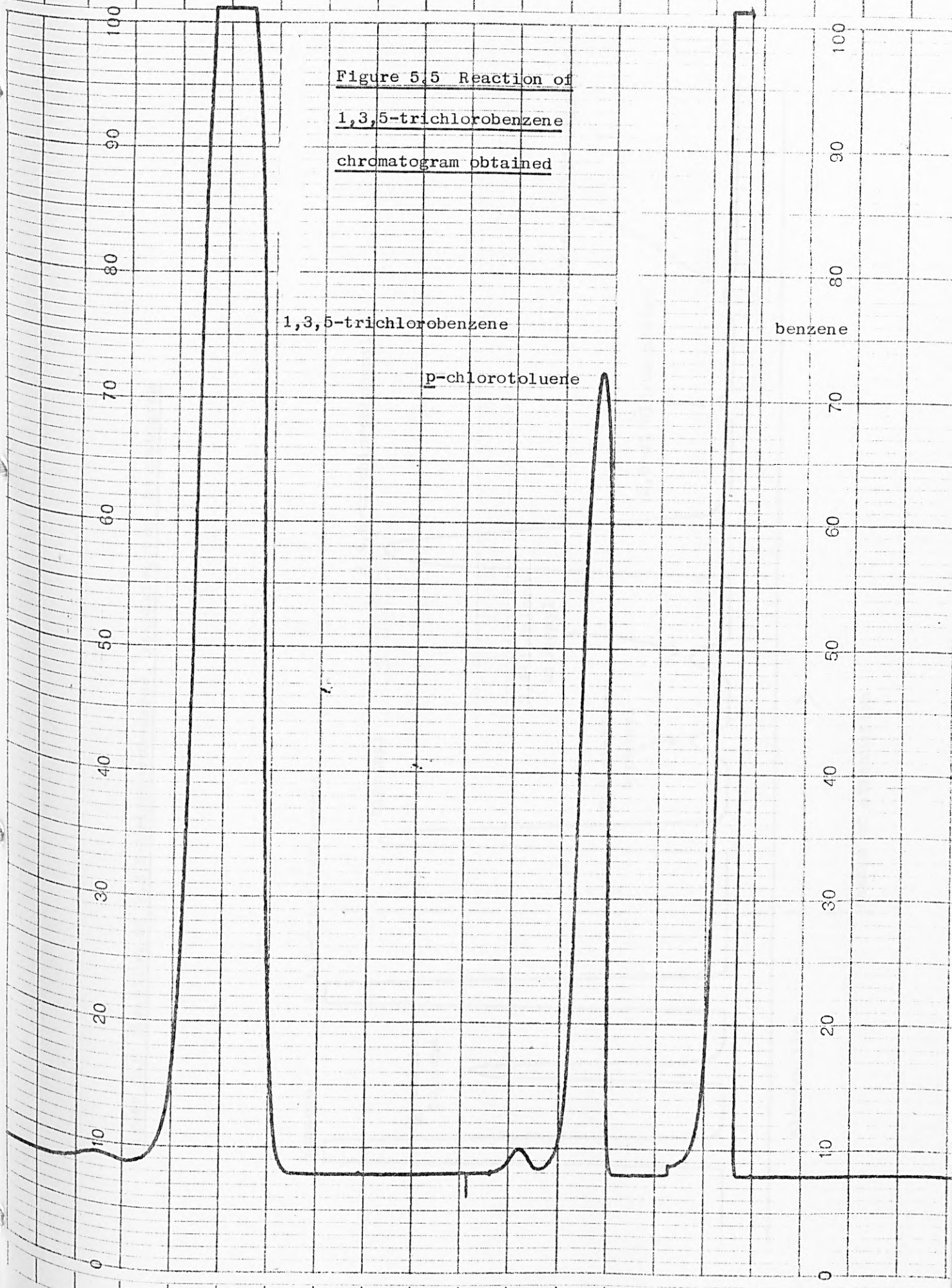


Figure 5.5 Reaction of 1,3,5-trichlorobenzene chromatogram obtained

Figure 5.6 Reaction of 1,3,5-trichlorobenzene, reconstructed chromatogram

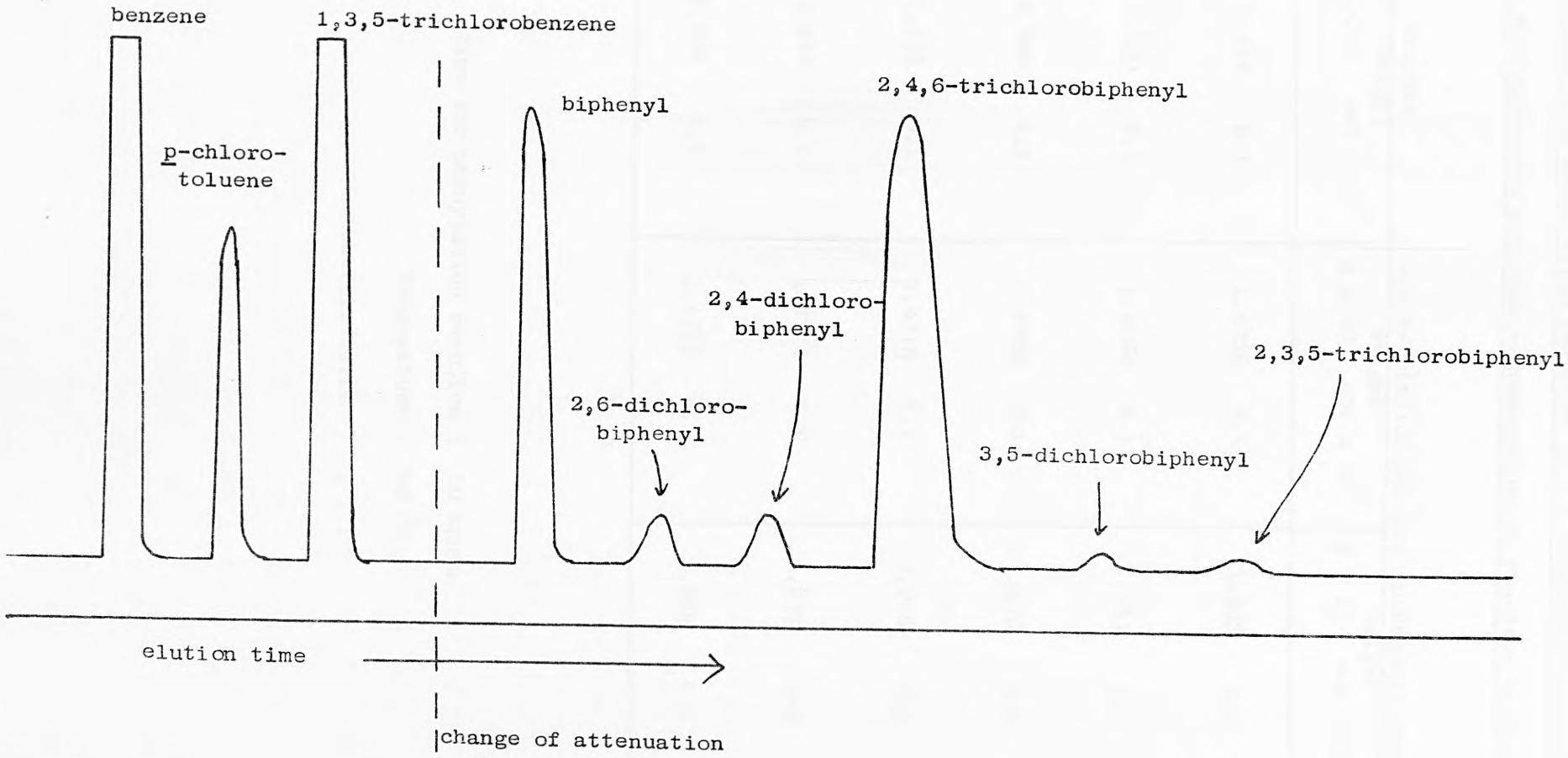


Table 5.1 Sealed tube phenylation reaction of 1,3,5-trichlorobenzene and benzene with dibenzoyl peroxide - composition of reaction mixtures

experiment number	benzene		1,3,5-trichlorobenzene		dibenzoyl peroxide	
	weight g x 10	mol x 10^3	weight g x 10	mol x 10^3	weight g x 10	mol x 10^4
1	6.324	8.1	1.4736	8.1	1.963	8.0
2	6.320	8.1	1.4748	8.1	1.951	8.0
3	6.366	8.1	1.4702	8.1	1.975	8.0
4	6.318	8.1	1.4718	8.1	1.959	8.0
5	6.344	8.1	1.4724	8.1	1.977	8.0
6	6.337	8.1	1.4733	8.1	1.968	8.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

substrate ratio : 1 : 1

Table 5.2 Sealed tube phenylation reaction of 1,3,5-trichlorobenzene and benzene in the presence of additives - compositions of reaction mixtures

experiment number	benzene		1,3,5-trichlorobenzene		dibenzoyl peroxide	
	weight		weight		weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	5.871	7.5	1.3765	7.6	1.966	8.0
2[a]	5.888	7.5	1.3784	7.6	1.976	8.0
3[a]	5.863	7.5	1.3751	7.6	1.980	8.0
4[a]	5.854	7.5	1.3792	7.6	1.984	8.0
5[a]	5.879	7.5	1.3766	7.6	1.962	8.0
6[b]	6.169	7.9	1.4267	7.9	1.954	8.0
7[b]	6.175	7.9	1.4291	7.9	1.945	8.0
8[b]	6.154	7.9	1.4255	7.9	1.942	8.0
9[b]	6.162	7.9	1.4287	7.9	1.957	8.0
10[c]	6.246	8.0	1.4581	8.0	1.962	8.0
11[c]	6.233	8.0	1.4566	8.0	1.955	8.0
12[c]	6.249	8.0	1.4572	8.0	1.951	8.0
13[c]	6.230	8.0	1.4570	8.0	1.964	8.0
14[c]	6.252	8.0	1.4562	8.0	1.950	8.0

time for phenylation reaction : 50 hours

temperature : 80 °C

substrate ratio : 1 : 1

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 5.3 Analysis of the phenylation reaction products of 1,3,5-trichlorobenzene and benzene in the absence of additives (Table 5.1 gives compositions)

experiment number	trichlorobiphenyl products				dichlorobiphenyl products						biphenyl		p-chlorotoluene internal standard	
	2,4,6-		2,3,5-		3,5-dichloro-		2,6-dichloro		2,4-dichloro-					
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1	0.0362	0.0622	0.0006	0.0011	0.0038	0.0064	0.0055	0.0069	0.0042	0.0057	0.0191	0.0226	0.1591	0.1645
2	0.0354	0.0646	0.0005	0.0009	0.0036	0.0065	0.0049	0.0065	0.0042	0.0061	0.0186	0.0235	0.1483	0.1631
3	0.0372	0.0655	0.0004	0.0007	0.0037	0.0063	0.0052	0.0067	0.0042	0.0059	0.0194	0.0237	0.1558	0.1652
4	0.0357	0.0617	0.0006	0.0010	0.0039	0.0065	0.0056	0.0066	0.0043	0.0056	0.0192	0.0230	0.1575	0.1638
5	0.0353	0.0621	0.0005	0.0008	0.0039	0.0065	0.0047	0.0062	0.0036	0.0051	0.0187	0.0228	0.1551	0.1644
6	0.0356	0.0620	0.0005	0.0009	0.0036	0.0062	0.0057	0.0072	0.0040	0.0055	0.0193	0.0233	0.1571	0.1650
response factor	1.66		1.65		1.62		1.21		1.32		1.15		1.00	

Table 5.4 Analysis of the phenylation reaction products of 1,3,5-trichlorobenzene and benzene in the presence of additives (Table 5.2 gives compositions)

experiment number	trichlorobiphenyl products 2,4,6- peak weight (g.)	2,4,6- cpd. weight (g.)	2,3,5- peak weight (g.)	2,3,5- cpd. weight (g.)	dichlorobiphenyl products 3,5-dichloro- peak weight (g.)	3,5-dichloro- cpd. weight (g.)	2,6-dichloro- peak weight (g.)	2,6-dichloro- cpd. weight (g.)	2,4-dichloro- peak weight (g.)	2,4-dichloro- cpd. weight (g.)	biphenyl peak weight (g.)	biphenyl cpd. weight (g.)	p-chlorotoluene internal standard peak weight (g.)	p-chlorotoluene internal standard std. weight (g.)
1[a]	0.0570	0.0993	0.0009	0.0015	0.0043	0.0073	0.0060	0.0079	0.0049	0.0068	0.0225	0.0239	0.1586	0.1665
2[a]	0.0537	0.0980	0.0007	0.0013	0.0040	0.0072	0.0053	0.0071	0.0043	0.0062	0.0214	0.0238	0.1508	0.1659
3[a]	0.0545	0.0986	0.0007	0.0012	0.0042	0.0074	0.0057	0.0075	0.0044	0.0064	0.0219	0.0241	0.1515	0.1651
4[a]	0.0542	0.0989	0.0008	0.0014	0.0040	0.0072	0.0059	0.0080	0.0046	0.0070	0.0217	0.0241	0.1519	0.1669
5[a]	0.0549	0.0984	0.0007	0.0012	0.0042	0.0070	0.0060	0.0078	0.0045	0.0064	0.0220	0.0240	0.1526	0.1648
6[b]	0.0573	0.1009	0.0008	0.0014	0.0044	0.0076	0.0058	0.0075	0.0047	0.0066	0.0225	0.0241	0.1547	0.1640
7[b]	0.0576	0.1015	0.0009	0.0016	0.0045	0.0079	0.0062	0.0079	0.0049	0.0069	0.0225	0.0241	0.1558	0.1653
8[b]	0.0574	0.1013	0.0010	0.0018	0.0045	0.0078	0.0064	0.0082	0.0046	0.0065	0.0226	0.0243	0.1550	0.1649
9[b]	0.0568	0.1001	0.0009	0.0015	0.0044	0.0077	0.0062	0.0080	0.0051	0.0071	0.0223	0.0239	0.1561	0.1656
10[c]	0.0602	0.1088	0.0008	0.0014	0.0048	0.0084	0.0059	0.0078	0.0047	0.0068	0.0224	0.0246	0.1527	0.1663
11[c]	0.0599	0.1091	0.0008	0.0015	0.0047	0.0084	0.0065	0.0086	0.0050	0.0073	0.0221	0.0245	0.1508	0.1655
12[c]	0.0590	0.1081	0.0008	0.0016	0.0046	0.0082	0.0058	0.0077	0.0052	0.0075	0.0219	0.0244	0.1512	0.1668
13[c]	0.0601	0.1096	0.0008	0.0015	0.0047	0.0083	0.0064	0.0085	0.0049	0.0071	0.0223	0.0247	0.1510	0.1658
14[c]	0.0589	0.1081	0.0009	0.0016	0.0046	0.0082	0.0059	0.0079	0.0047	0.0069	0.0218	0.0243	0.1513	0.1672

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 5.5 Partial rate factors and percentage yields of the phenylation reaction products of 1,3,5-trichlorobenzene and benzene in the absence of additives (Table 5.1 gives compositions)

experiment number	biphenyl yield (%)	2,4,6-trichloro-biphenyl f_2	2,4,6-trichloro-biphenyl yield (%)	3,5-dichloro-biphenyl f_1	3,5-dichloro-biphenyl yield (%)
1	18.3	3.29	30.2	0.39	3.6
2	19.1	3.29	31.4	0.38	3.6
3	19.2	3.14	31.8	0.37	3.5
4	18.7	3.21	30.0	0.39	3.6
5	18.5	3.26	30.2	0.38	3.6
6	18.9	3.18	30.1	0.39	3.5
(mean values)	18.8	3.26	30.6	0.38	3.6

yields are in mole per mole peroxide x 100

Table 5.6 Partial rate factors and percentage yields of the phenylation reaction products of 1,3,5-trichlorobenzene and benzene in the presence of additives (Table 5.2 gives compositions)

experiment number	biphenyl yield (%)	2,4,6-trichloro-biphenyl f_2	yield (%)	3,5-dichloro-biphenyl f_1	yield (%)
1[a]	19.4	4.97	48.2	0.42	4.1
2[a]	19.3	4.92	47.6	0.42	4.0
3[a]	20.0	4.89	47.9	0.43	4.2
4[a]	19.6	4.90	48.0	0.41	4.0
5[a]	19.4	4.90	47.8	0.42	3.9
(mean values)[a]	19.5	4.91	47.9	0.42	4.1
6[b]	19.6	5.00	49.0	0.44	4.3
7[b]	19.5	5.03	49.3	0.45	4.4
8[b]	19.7	4.98	49.2	0.44	4.4
9[b]	19.4	4.99	48.6	0.44	4.3
(mean values)[b]	19.6	5.00	49.0	0.44	4.4
10[c]	19.9	5.30	52.8	0.47	4.7
11[c]	19.8	5.33	53.0	0.47	4.7
12[c]	20.0	5.30	52.5	0.46	4.6
13[c]	20.0	5.31	53.2	0.46	4.7
14[c]	19.7	5.31	52.5	0.47	4.6
(mean values)[c]	19.9	5.31	52.8	0.47	4.7

yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 5.7 Percentage yields of some by-products of the phenylation reaction of 1,3,5-trichlorobenzene (Table 5.1 gives compositions)

experiment number	trichlorobiphenyl product 2,3,5-trichloro- yield (%)	dichlorobiphenyl products 2,6-dichloro- yield (%)	2,4-dichloro- yield (%)
1	0.5	3.9	3.2
2	0.4	3.6	3.4
3	0.3	3.8	3.3
4	0.5	3.7	3.1
5	0.4	3.5	2.9
6	0.4	4.0	3.1
(mean values)	0.4	3.8	3.2

yields are in mole per mole peroxide x 100

Table 5.8 Percentage yields of some by-products of the phenylation reaction of 1,3,5-trichlorobenzene in the presence of additives

(Table 5.2 gives compositions)

experiment number	trichlorobiphenyl product 2,3,5-trichloro- yield (%)	dichlorobiphenyl products 2,6-dichloro- yield (%)	2,4-dichloro- yield (%)
1[a]	0.7	4.3	3.8
2[a]	0.6	3.9	3.4
3[a]	0.6	4.2	3.6
4[a]	0.7	4.5	3.9
5[a]	0.6	4.3	3.6
(mean values)[a]	0.5	4.3	3.7
6[b]	0.7	4.2	3.7
7[b]	0.8	4.4	3.9
8[b]	0.9	4.6	3.6
9[b]	0.7	4.5	4.0
(mean values)[b]	0.8	4.4	3.8
10[c]	0.7	4.4	3.8
11[c]	0.7	5.0	4.1
12[c]	0.8	4.3	4.2
13[c]	0.7	4.8	3.9
14[c]	0.8	4.4	3.8
(mean values)[c]	0.7	4.5	4.0

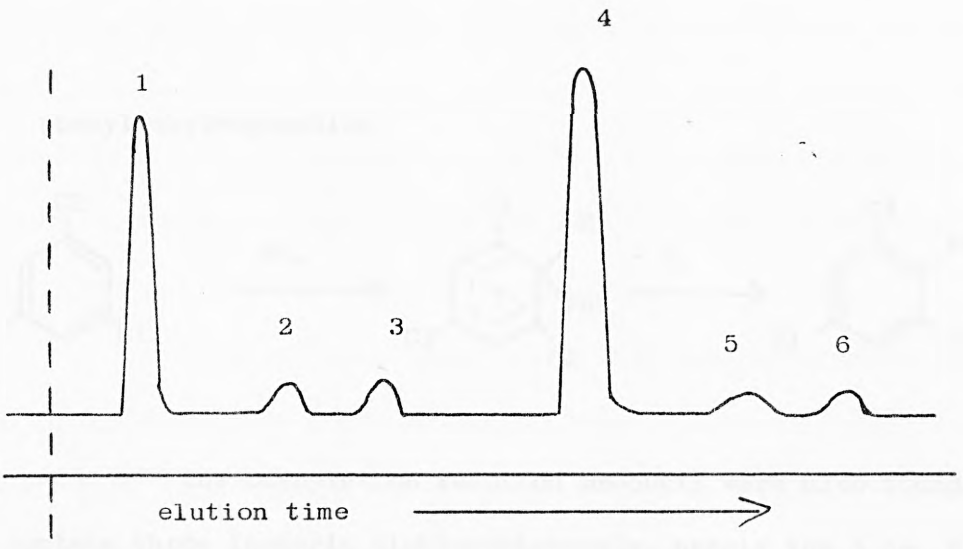
yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Figure 5.7 Reconstructed chromatogram showing only products of the phenylation reaction of 1,3,5-trichlorobenzene and benzene



peak 1 = biphenyl

peak 2 = 2,6-dichlorobiphenyl

peak 3 = 2,4-dichlorobiphenyl

peak 4 = 2,4,6-trichlorobiphenyl

peak 5 = 3,5-dichlorobiphenyl

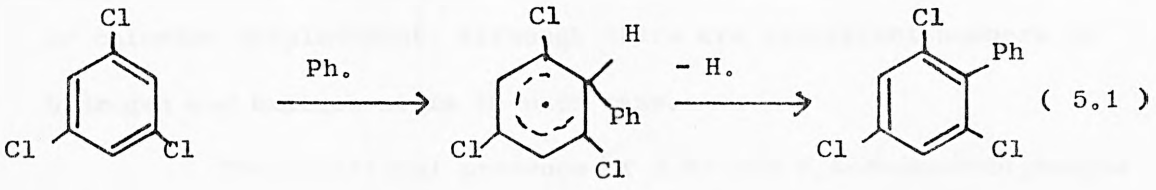
peak 6 = 2,3,5-trichlorobiphenyl

The phenylation of 1,3,5-trichlorobenzene has been reported in the literature by Augood and Williams.[15] However, the only product of phenylation reported has been that of phenyl-dehydrogenation, namely 2,4,6-trichlorobiphenyl. On the phenylation of 1,3,5-trichlorobenzene in sealed tubes, four other products were detected apart from 2.4.6-trichlorobiphenyl, namely 2,6-, 2,4- and 3,5-dichlorobiphenyls and 2,3,5-trichlorobiphenyl.

In 1,3,5-trichlorobenzene, the hydrogen and chlorine atoms alternate in position around the benzene ring and there are equal numbers of hydrogen and chlorine atoms which may be displaced. Thus the chemical environment of the three hydrogen atoms are

equivalent and attack by a phenyl radical at any of the three C - H sites leads to the formation of the main product of phenyldehydrogenation, 2,4,6-trichlorobiphenyl (in 31 % yield).

phenyldehydrogenation

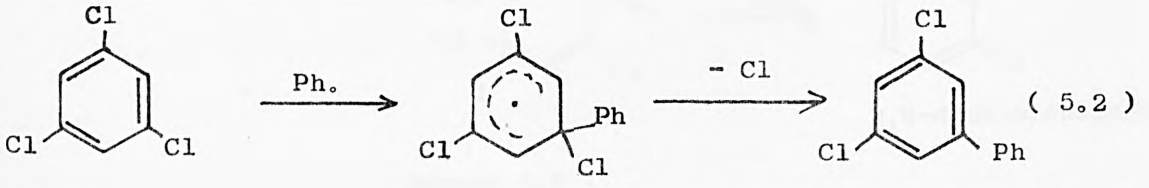


(5.1)

The phenylation reaction products were also found to contain three isomeric dichlorobiphenyls, namely the 3,5-, 2,6- and 2,4- isomers. The presence of these dichlorobiphenyls was confirmed by g.l.c. retention data by comparison with known authentic standards and by g.l.c.-mass spectrometry results (see Appendix). There was also some g.l.c.-mass spectrometry evidence for the presence of trichloroterphenyl in very small amounts whilst no evidence was found for the presence of dichlorobenzene, dichloroterphenyl, chloroterphenyl or tetrachlorobiphenyl.

To account for the formation of 3,5-dichlorobiphenyl (in 4 % yield) a phenyldechlorination reaction must have occurred, with the attack by a phenyl radical at a C - Cl site followed by the loss of a chlorine atom, as shown in (5.2).

phenyldechlorination



(5.2)

3,5-dichlorobiphenyl

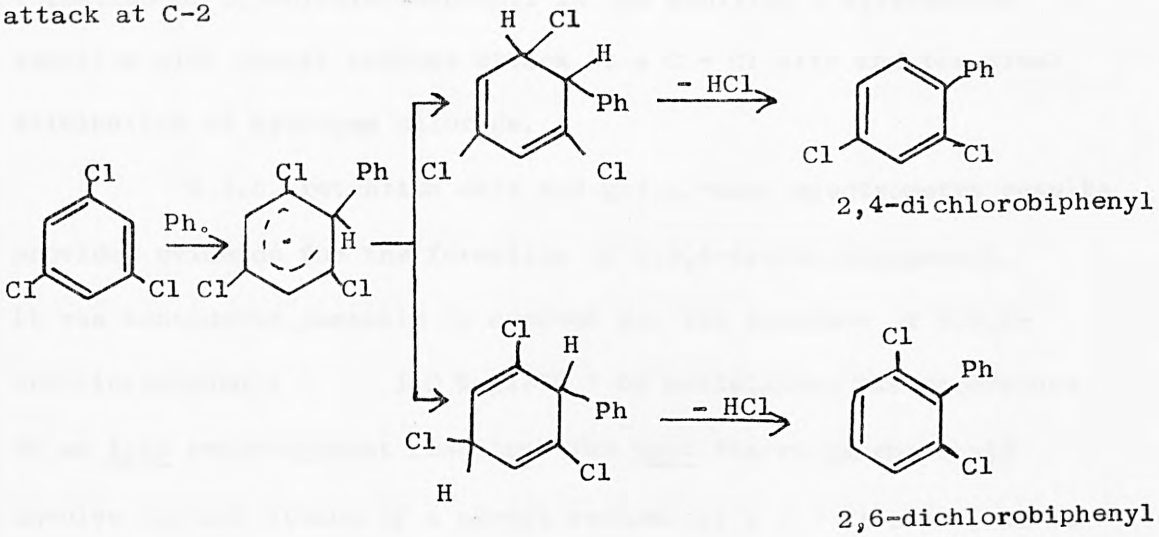
Due to the symmetry of the 1,3,5-trichlorobenzene molecule there is only one product of phenyldechlorination.

Similarly in the phenylation of 1,3,5-trifluorobenzene (65) the dominant reaction was of phenyldehydrogenation (yielding 2,4,6-trifluorobiphenyl) and also of phenyldefluorination (yielding 3,5-difluorobiphenyl) were reported. Thus in 1,3,5-trifluoro- and trichlorobenzenes, hydrogen displacement is preferred to fluorine or chlorine displacement, although there are equivalent numbers of hydrogen and halogen atoms in each case.

The additional presence of 2,6- and 2,4-dichlorobiphenyls (in 3.9 % and 3.2 % yields respectively) was novel and to account for their formation it was considered that an addition - elimination reaction occurred. This type of reaction required initial attack at a C - H or C - Cl site by phenyl radicals and the take up of a hydrogen atom by the phenylcyclohexadienyl intermediate followed by the subsequent loss of hydrogen chloride (see Scheme 5.1). This type of reaction was not reported in the phenylation of 1,3,5-trifluorobenzene.

addition - elimination reaction

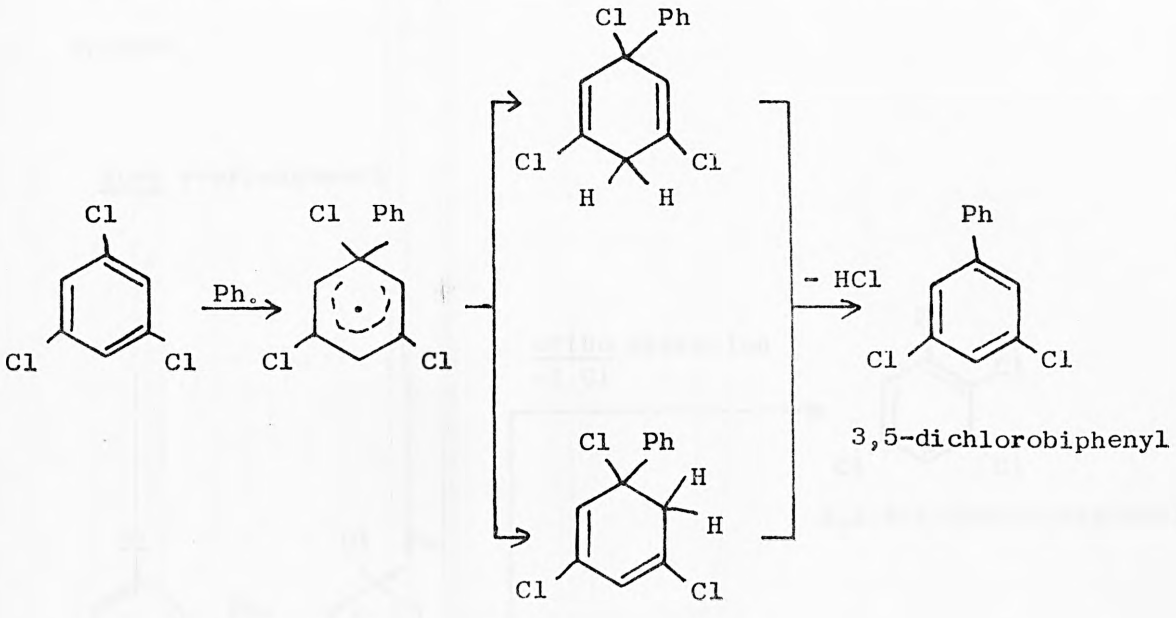
attack at C-2



Scheme 5.1

The total yields of the products 2,6- and 2,4-dichlorobiphenyl (3.9 % and 3.2 %) exceed the yield of 3,5-dichlorobiphenyl (3.6 % yield), the product of the phenyldechlorination reaction.

addition - elimination reaction
attack at C-1



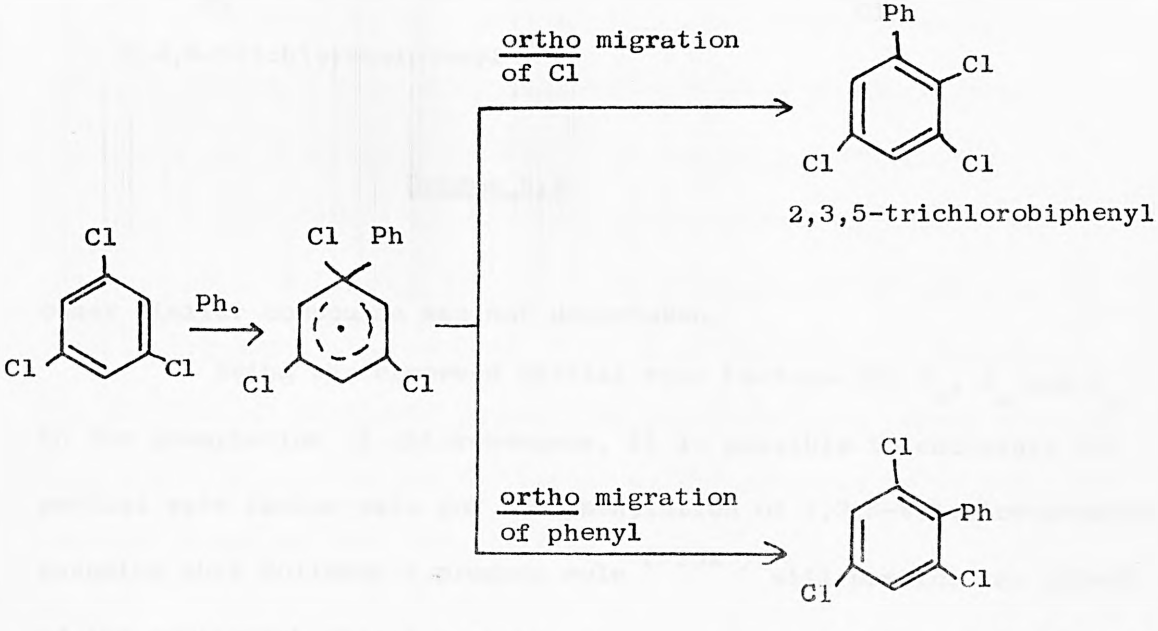
Scheme 5.2

As shown in Scheme 5.2 an alternative pathway for the formation of 3,5-dichlorobiphenyl is the addition - elimination reaction with phenyl radical attack at a C - Cl site and the final elimination of hydrogen chloride.

G.l.c. retention data and g.l.c.-mass spectrometry results provided evidence for the formation of 2,3,5-trichlorobiphenyl. It was considered possible to account for the presence of 2,3,5-trichlorobiphenyl (1.0 % yield) by postulating the occurrence of an ipso rearrangement reaction. The ipso rearrangement would involve initial attack by a phenyl radical at a C - Cl site (as in phenyldechlorination reactions) followed by an ortho or meta migration

of either phenyl or chlorine group as shown in Scheme 5.3. In this case meta migration of either group is not possible as the meta positions are blocked by chlorine atoms. The only ipso rearrangement product found in the phenylation reaction mixture was 2,3,5-trichlorobiphenyl which could have been formed by an ortho migration of a chlorine atom. Ortho migration of a phenyl group would produce 2,4,6-trichlorobiphenyl, which would enhance the yield of the main product.

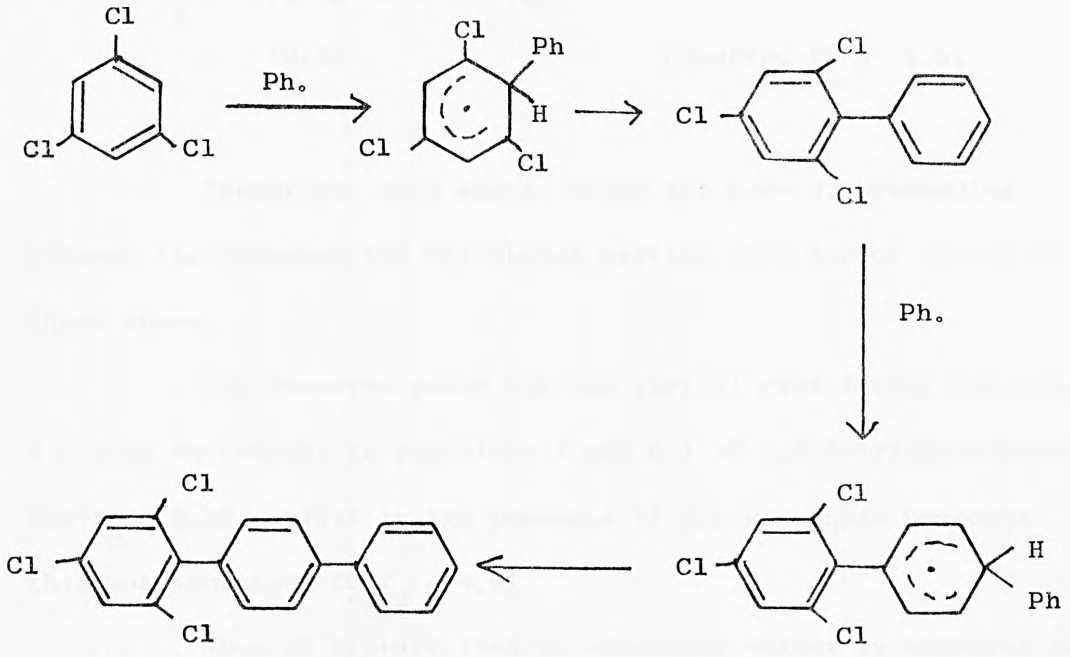
ipso rearrangement



Scheme 5.3

G.l.c.-mass spectrometry results indicated the presence in very small quantities of trichloroterphenyls (see Appendix). The further phenylation of 2,4,6-trichlorobiphenyl is a possible pathway for the formation of trichloroterphenyls (see Scheme 5.4). As the primary aim of this investigation was the determination of the relative rates of attack at the various positions of polychlorobenzenes, work on the formation of terphenyls, quaterphenyls and

pathway for the formation of trichloroterphenyls



2,4,6-trichloroterphenyl

Scheme 5.4

other similar compounds was not undertaken.

Using the observed partial rate factors for f_o, f_m and f_p in the phenylation of chlorobenzene, it is possible to calculate the partial rate factor valu for the phenylation of 1,3,5-trichlorobenzene, assuming that Holleman's product rule (132) will predict the effect of the additional chlorine atoms.

phenylation reaction in the absence of additives,

$$f_2 = \underline{o}\text{-Cl} \times \underline{o}\text{-Cl} \times \underline{p}\text{-Cl}$$

$$= 1.97 \times 1.97 \times 1.07$$

$$= 4.15 \qquad \text{observed } f_2 = 3.26$$

phenylation reaction in the presence of copper benzoate,

$$f_2 = 2.9 \times 2.9 \times 1.24$$

$$= 10.43 \qquad \text{observed } f_2 = 4.91$$

Therefore, once again, there are some discrepancies between the observed and calculated partial rate factor values as shown above.

The observed value for the partial rate factor for position 2 (also equivalent to positions 4 and 6) of 1,3,5-trichlorobenzene was $f_2 = 3.26$, whilst in the presence of 0.1 g. copper benzoate this was increased to $f_2 = 4.91$

Thus it appears that an enhancing effect is observed when position 2 in 1,3,5-trichlorobenzene is flanked by two chlorine atoms and has another chlorine atom in the *para* position.

The partial rate factor in the absence of additives obtained by r. Bolton *et al* [13] was 9.98 and in the presence of iron(III) benzoate it was 9.72. Both these figures are unexpected. The first as it is higher rather than lower than the figure calculated from the Product Rule and the second as the presence of an additive usually increases the rate factor.

5.1.5 THE EFFECT OF ADDITIVES

The presence of various additives (namely copper benzoate, iron powder and trichloroacetic acid) in the phenylation of 1,3,5-trichlorobenzene increased the yields of 2,4,6-trichlorobiphenyl and of 3,5-dichlorobiphenyl as shown in Table 5.9, at the expense of products of dimerisation and disproportionation. Once again, the greatest effect was achieved with the use of trichloroacetic acid as

Table 5.9 Partial rate factors and percentage yields for the phenylation of 1,3,5-trichlorobenzene in the absence and presence of additives

row number	phenyldehydrogenation product 2,4,6-trichlorobiphenyl yield (%)	phenyldechlorination product 3,5-dichlorobiphenyl yield (%)	partial rate factors for :- phenyldehydrogenation f_2	partial rate factors for :- phenyldechlorination f_1
1[a]	30.6	3.6	3.26	0.38
2[b]	47.9	4.1	4.91	0.42
3[c]	49.0	4.4	5.00	0.44
4[d]	52.8	4.7	5.31	0.47

yields are in mole per mole peroxide x 100

each row is a mean of four or more results

a = no additive b = additive copper benzoate, 0.1 g. c = additive iron powder, 0.1 g.

d = additive trichloroacetic acid, 0.1 g.

the additive, with the yields of 2,4,6-trichlorobiphenyl rising from 30.6 % without additive to 52.8 % with trichloroacetic acid (0.1 g.).

As shown in Table 5.9, the partial rate factor value for the phenylation of 1,3,5-trichlorobenzene for phenydehydrogenation without additive was $f_2 = 3.26$, which was inceased to $f_2 = 5.31$ in the presence of trichloroacetic acid.

A small increase was also observed in the partial rate factor value for the phenyldechlorination of 1,3,5-trichlorobenzene form $f_1 = 0.38$ without additive to $f_1 = 0.47$ in the presence of trichloroacetic acid.

5.2 METHOD OF PHENYLATION OF 1,2,3-TRICHLOROBENZENE

This was the same as has been described in section 3.1 Sections 5.2.1 to 5.2.3 show the chromatograms obtained and their identification followed by tables listing experimental quantities leading to tables of results tabulating partial rate factors and the yields.

5.2.1 CHROMATOGRAMS

Figures 5.7 to 5.9 show actual chromatograms obtained. Figure 5.10 shows a reconstructed chromatogram demonstrating the relationship between the products obtained.

5.2.2 PEAK IDENTIFICATION

The same method was used as has been explained in section 3.3

Figure 5.7 Reaction of 1,2,3-trichlorobenzene, chromatogram obtained

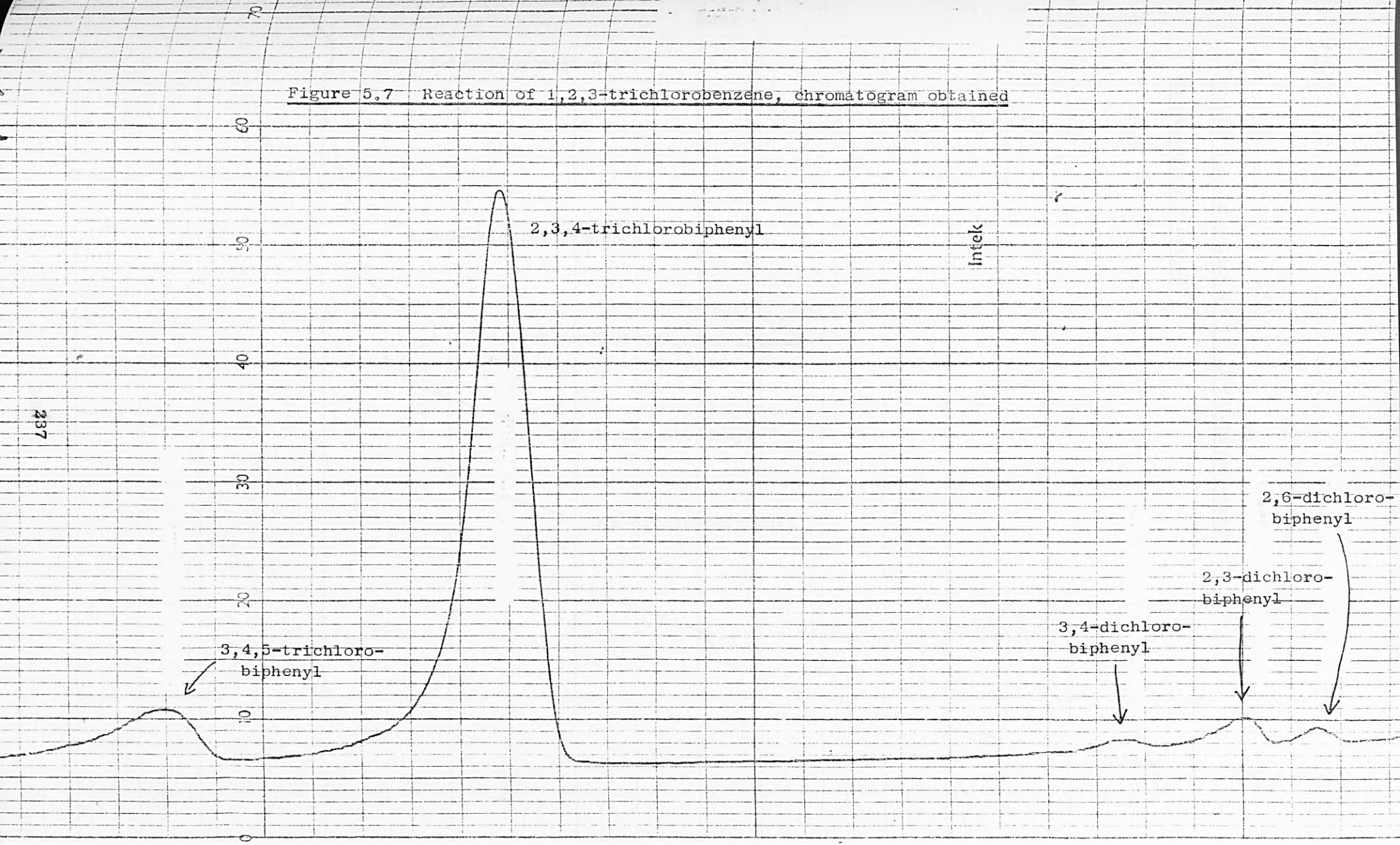
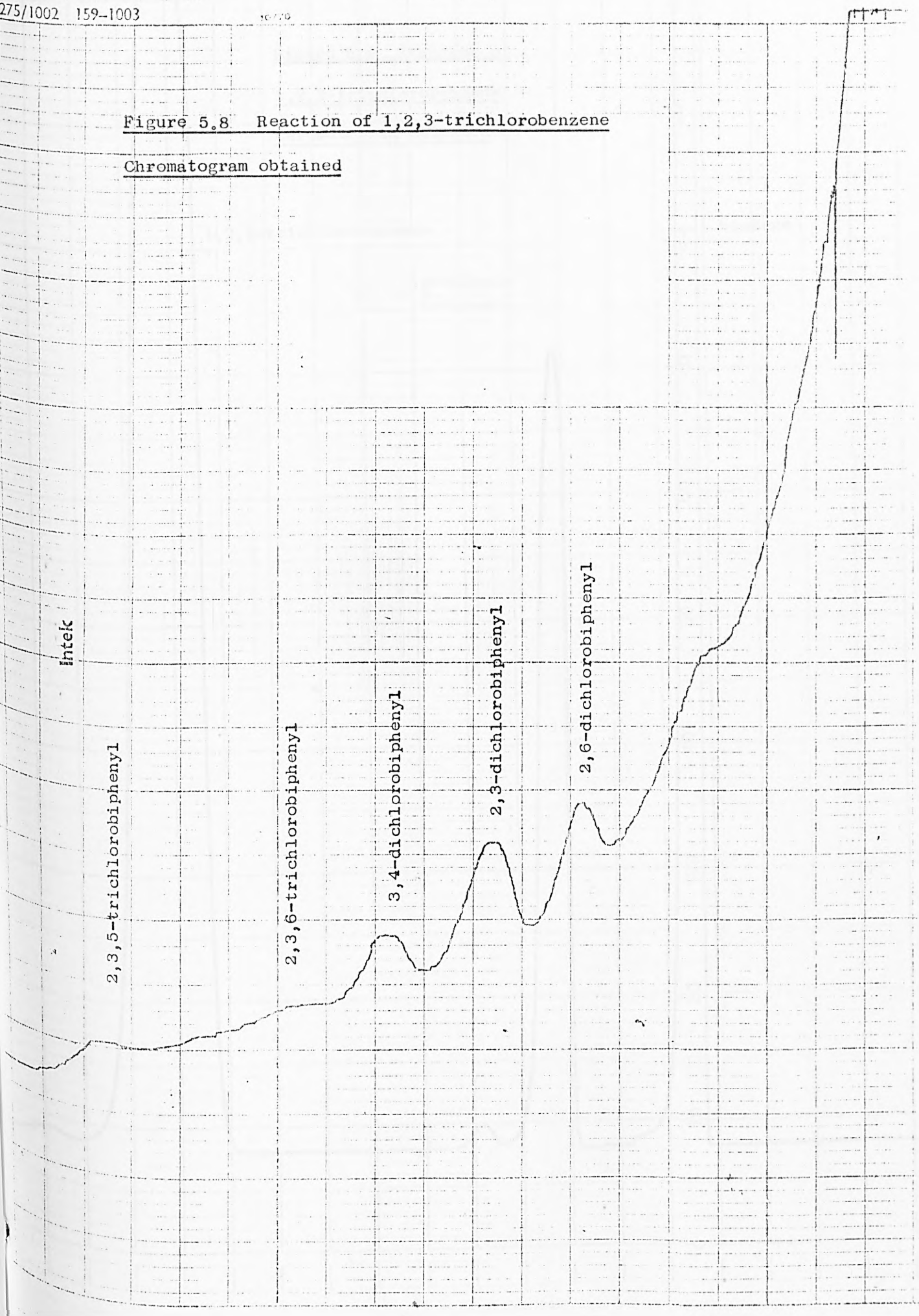


Figure 5.8 Reaction of 1,2,3-trichlorobenzene

Chromatogram obtained



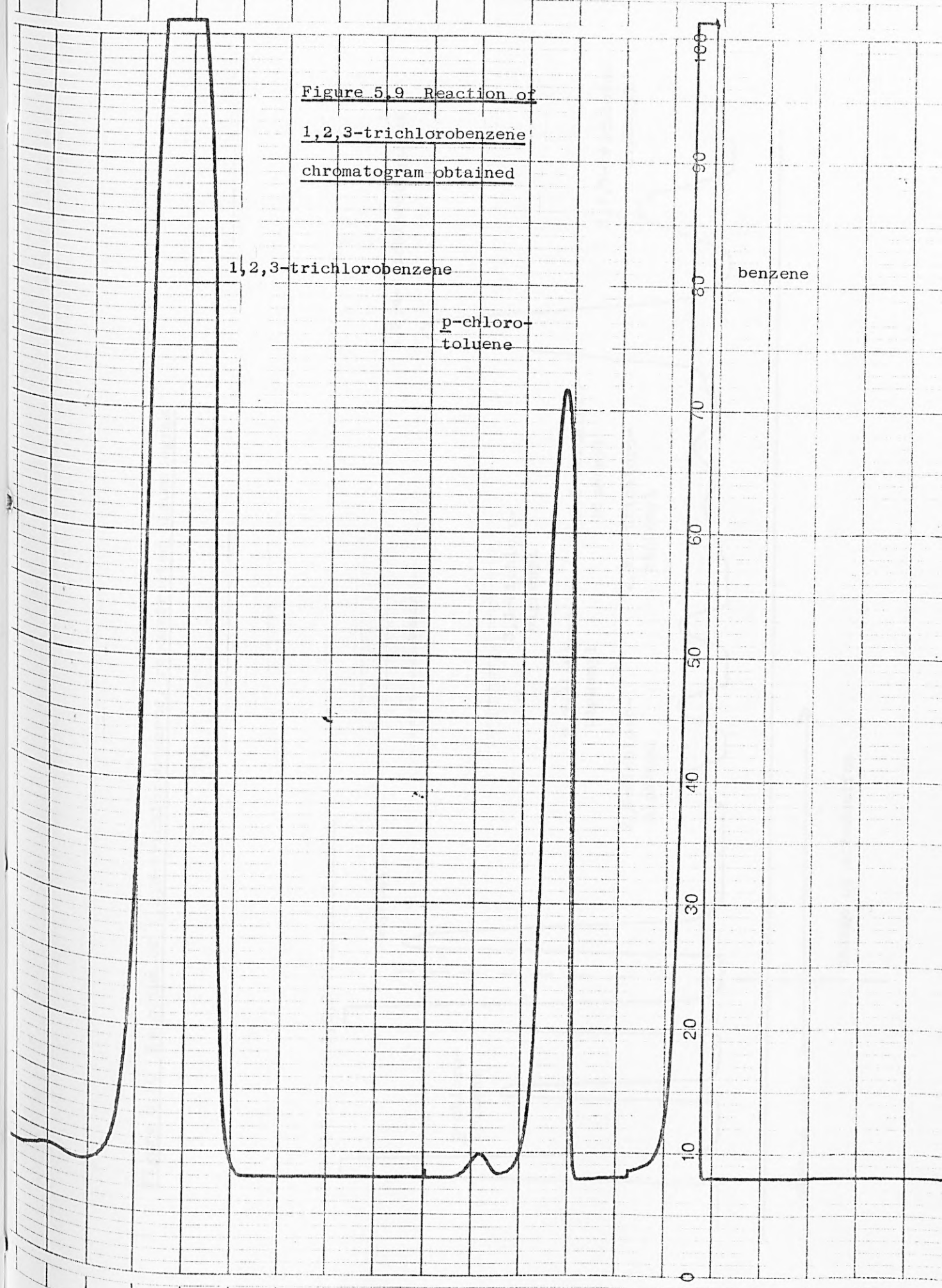


Figure 5.9 Reaction of 1,2,3-trichlorobenzene chromatogram obtained

Figure 5.10 Reaction of 1,2,3-trichlorobenzene, reconstructed chromatogram

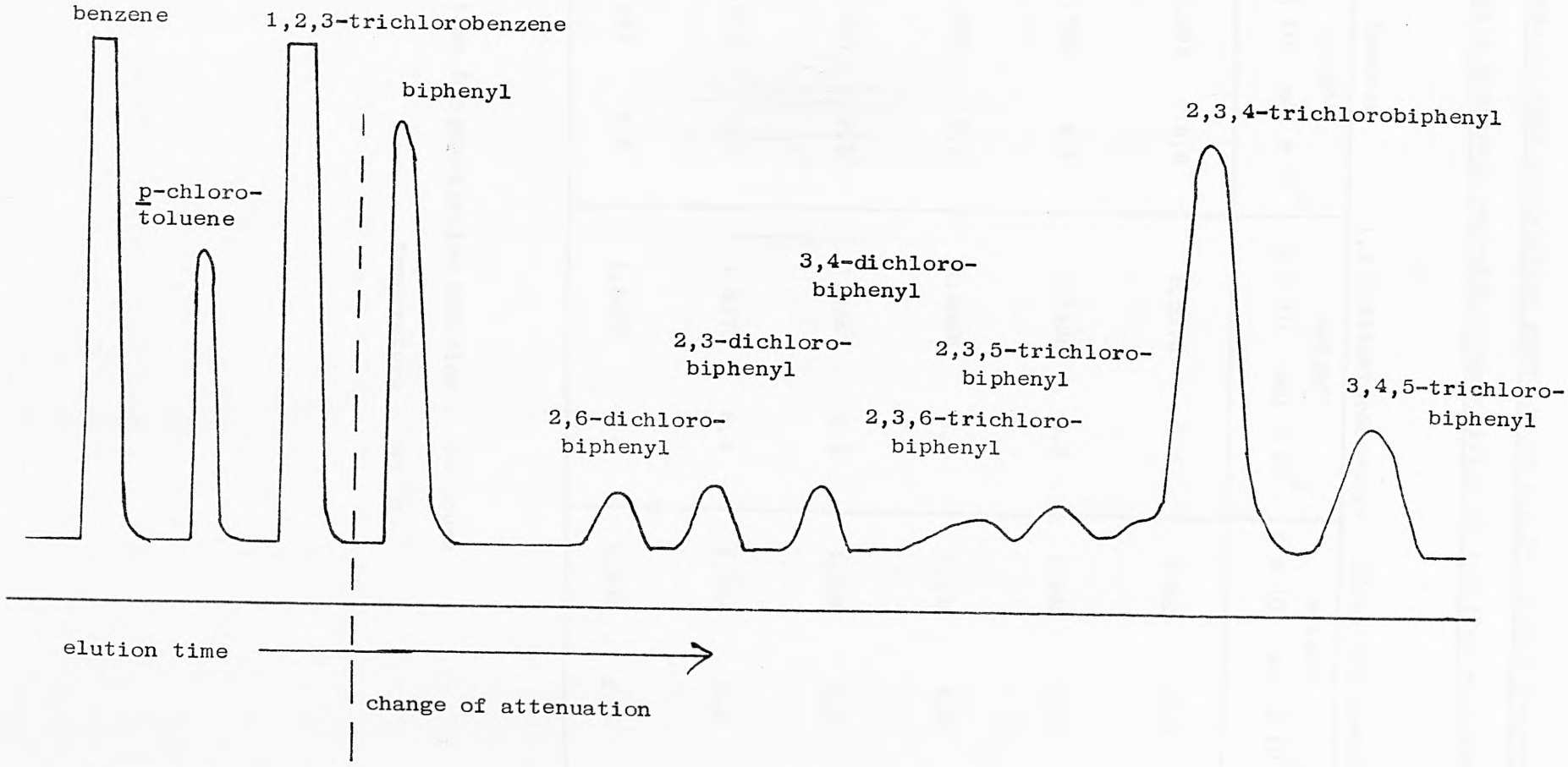


Table 5.10 Sealed tube phenylation reaction of 1,2,3-trichlorobenzene and benzene with dibenzoyl peroxide - composition of reaction mixtures

experiment number	benzene		1,2,3-trichlorobenzene		dibenzoyl peroxide	
	weight		weight		weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1	6.894	8.8	1.5276	8.4	1.939	8.0
2	6.786	8.7	1.5428	8.5	1.943	8.0
3	6.675	8.5	1.5486	8.5	1.952	8.0
4	6.670	8.5	1.5887	8.4	1.936	8.0
5	6.634	8.5	1.5375	8.4	1.954	8.0
6	6.647	8.5	1.5479	8.4	1.949	8.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

Table 5.11 Sealed tube phenylation reactions of 1,2,3-trichlorobenzene and benzene in the presence of additives - composition of reaction mixtures

experiment	benzene		1,2,3-trichlorobenzene		dibenzoyl peroxide	
	weight g x 10	mol x 10^3	weight g x 10	mol x 10^3	weight g x 10	mol x 10^4
1[a]	6.147	7.9	1.5097	8.3	1.922	8.0
2[a]	6.253	8.0	1.5136	8.3	1.904	8.0
3[a]	6.166	7.9	1.5148	8.3	1.917	8.0
4[a]	6.255	8.0	1.5061	8.2	1.941	8.0
5[b]	6.462	8.2	1.5296	8.4	1.932	8.0
6[b]	6.478	8.3	1.5278	8.4	1.940	8.0
7[b]	6.447	8.2	1.5267	8.4	1.953	8.0
8[b]	6.459	8.2	1.5284	8.4	1.951	8.0
9[c]	6.449	8.3	1.5327	8.4	1.946	8.0
10[c]	6.460	8.3	1.5356	8.4	1.941	8.0
11[c]	6.456	8.3	1.5348	8.4	1.938	8.0
12[c]	6.477	8.3	1.5360	8.4	1.933	8.0

temperature for phenylation reaction : 80 °C

time for phenylation reaction : 50 hours

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 5.12 Analysis of the phenylation reaction products of 1,2,3-trichlorobenzene and benzene in the absence of additives (Table 5.10 gives compositions)

experiment number	trichlorobiphenyl products 2,3,4- peak weight (g.)	2,3,4- cpd. weight (g.)	3,4,5- peak weight (g.)	3,4,5- cpd. weight (g.)	dichlorobiphenyl products 2,3-dichloro- peak weight (g.)	2,3-dichloro- cpd. weight (g.)	2,6-dichloro- peak weight (g.)	2,6-dichloro- cpd. weight (g.)	3,4-dichloro- peak weight (g.)	3,4-dichloro- cpd. weight (g.)	biphenyl peak weight (g.)	biphenyl cpd. weight (g.)	p-chlorotolene internal standard peak weight (g.)	p-chlorotolene internal standard std. weight (g.)
1	0.0464	0.0862	0.0064	0.0122	0.0058	0.0085	0.0048	0.0063	0.0031	0.0052	0.0520	0.0567	0.1428	0.1542
2	0.0459	0.0854	0.0068	0.0129	0.0062	0.0090	0.0046	0.0060	0.0030	0.0051	0.0536	0.0585	0.1447	0.1563
3	0.0458	0.0851	0.0070	0.0130	0.0055	0.0080	0.0046	0.0060	0.0028	0.0048	0.0516	0.0564	0.1439	0.1556
4	0.0465	0.0860	0.0068	0.0129	0.0060	0.0087	0.0050	0.0065	0.0032	0.0053	0.0532	0.0578	0.1438	0.1547
5	0.0463	0.0866	0.0066	0.0126	0.0059	0.0087	0.0049	0.0065	0.0027	0.0046	0.0491	0.0583	0.1430	0.1551
6	0.0458	0.0855	0.0064	0.0123	0.0061	0.0089	0.0047	0.0063	0.0027	0.0045	0.0525	0.0576	0.1445	0.1569
response factor	1.72		1.76		1.35		1.21		1.56		1.15		1.00	

Table 5.13 Analysis of the phenylation reaction products of 1,2,3-trichlorobenzene and benzene in the presence of additives (Table 5.11 gives compositions)

experiment number	trichlorobiphenyl products 2,3,4- peak weight (g.)	trichlorobiphenyl products 2,3,4- cpd. weight (g.)	trichlorobiphenyl products 3,4,5- peak weight (g.)	trichlorobiphenyl products 3,4,5- cpd. weight (g.)	dichlorobiphenyl products 2,3-dichloro- peak weight (g.)	dichlorobiphenyl products 2,3-dichloro- cpd. weight (g.)	dichlorobiphenyl products 2,6-dichloro- peak weight (g.)	dichlorobiphenyl products 2,6-dichloro- cpd. weight (g.)	dichlorobiphenyl products 3,4-dichloro- peak weight (g.)	dichlorobiphenyl products 3,4-dichloro- cpd. weight (g.)	biphenyl peak weight (g.)	biphenyl cpd. weight (g.)	p-chlorotoluene internal standard peak weight (g.)	p-chlorotoluene internal standard std. weight (g.)
1[a]	0.0598	0.1128	0.0094	0.0181	0.0068	0.0101	0.0049	0.0066	0.0036	0.0061	0.0473	0.0524	0.1429	0.1567
2[a]	0.0591	0.1116	0.0095	0.0184	0.0063	0.0093	0.0047	0.0063	0.0034	0.0059	0.0470	0.0521	0.1417	0.1555
3[a]	0.0594	0.1123	0.0091	0.0176	0.0067	0.0099	0.0050	0.0067	0.0038	0.0065	0.0475	0.0527	0.1410	0.1549
4[a]	0.0600	0.1132	0.0090	0.0174	0.0063	0.0094	0.0048	0.0065	0.0040	0.0068	0.0473	0.0524	0.1422	0.1561
5[b]	0.0523	0.0986	0.0081	0.0157	0.0059	0.0087	0.0041	0.0055	0.0035	0.0060	0.0420	0.0465	0.1431	0.1569
6[b]	0.0512	0.0968	0.0083	0.0160	0.0054	0.0080	0.0039	0.0053	0.0034	0.0058	0.0416	0.0462	0.1413	0.1554
7[b]	0.0513	0.0974	0.0086	0.0166	0.0055	0.0082	0.0042	0.0056	0.0032	0.0056	0.0425	0.0473	0.1426	0.1573
8[b]	0.0520	0.0980	0.0081	0.0156	0.0059	0.0087	0.0044	0.0058	0.0031	0.0053	0.0431	0.0477	0.1429	0.1561
9[c]	0.0641	0.1214	0.0109	0.0213	0.0077	0.0115	0.0056	0.0075	0.0038	0.0065	0.0474	0.0527	0.1405	0.1548
10[c]	0.0634	0.1197	0.0107	0.0206	0.0076	0.0112	0.0054	0.0072	0.0036	0.0061	0.0472	0.0524	0.1417	0.1556
11[c]	0.0646	0.1222	0.0108	0.0209	0.0078	0.0116	0.0056	0.0075	0.0035	0.0060	0.0484	0.0537	0.1422	0.1563
12[c]	0.0642	0.1219	0.0104	0.0203	0.0077	0.0115	0.0056	0.0075	0.0040	0.0069	0.0474	0.0529	0.1406	0.1552

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 5.14 Partial rate factors and percentage yields of the phenylation reaction products of 1,2,3-trichlorobenzene and benzene in the absence of additives (Table 5.11 gives compositions)

experiment number	biphenyl yield (%)	2,3,4-trichlorobiphenyl f_4	2,3,4-trichlorobiphenyl yield (%)	3,4,5-trichlorobiphenyl f_5	3,4,5-trichlorobiphenyl yield (%)	2,3-dichlorobiphenyl f_1	2,3-dichlorobiphenyl yield (%)	2,6-dichlorobiphenyl f_2	2,6-dichlorobiphenyl yield (%)
1	46.0	2.73	41.8	0.77	5.9	0.31	4.8	0.46	3.5
2	47.5	2.62	41.5	0.79	6.3	0.32	5.0	0.45	3.4
3	45.8	2.71	41.3	0.83	6.3	0.29	4.5	0.44	3.4
4	46.9	2.67	41.8	0.77	6.3	0.31	4.9	0.47	3.6
5	47.3	2.67	41.8	0.77	6.1	0.31	4.9	0.46	3.6
6	46.8	2.66	41.5	0.77	6.0	0.32	5.0	0.45	3.5
(mean values)	46.7	2.67	41.6	0.79	6.2	0.31	4.8	0.46	3.5

yields are in mole per mole peroxide x 100

Table 5.15 Partial rate factors and percentage yields of the phenylation reaction products of 1,2,3-trichlorobenzene and benzene in the presence of additives (Table 5.12 gives compositions)

experiment number	biphenyl yield (%)	2,3,4-trichloro biphenyl f_4	2,3,4-trichloro biphenyl yield (%)	3,4,5-trichloro-biphenyl f_5	3,4,5-trichloro-biphenyl yield (%)	2,3-dichloro-biphenyl f_1	2,3-dichloro-biphenyl yield (%)	2,6-dichloro-biphenyl f_2	2,6-dichloro-biphenyl yield (%)
1[a]	42.5	3.87	54.8	1.24	8.8	0.40	5.7	0.52	3.7
2[a]	42.3	3.84	54.2	1.27	8.9	0.37	5.2	0.50	3.5
3[a]	42.8	3.83	54.5	1.20	8.5	0.39	5.5	0.53	3.8
4[a]	42.5	3.88	55.0	1.19	8.5	0.37	5.3	0.52	3.6
(mean values)[a]	42.5	3.85	54.6	1.22	8.7	0.38	5.4	0.52	3.7
5[b]	37.7	3.80	47.9	1.21	7.6	0.39	4.9	0.49	3.1
6[b]	37.5	3.76	47.0	1.25	7.8	0.36	4.5	0.48	3.0
7[b]	38.4	3.69	47.3	1.26	8.1	0.36	4.6	0.49	3.1
8[b]	38.7	3.68	47.6	1.16	7.6	0.38	4.9	0.50	3.3
(mean values)[b]	38.1	3.74	47.4	1.22	7.8	0.37	4.7	0.49	3.1
9[c]	42.8	4.13	58.9	1.45	10.3	0.45	6.5	0.59	4.2
10[c]	42.5	4.10	58.1	1.41	10.0	0.44	6.3	0.56	4.0
11[c]	43.6	4.08	59.3	1.39	10.2	0.45	6.5	0.58	4.2
12[c]	42.9	4.13	59.2	1.38	9.9	0.45	6.5	0.59	4.2
(mean values)[c]	43.0	4.11	58.9	1.41	10.1	0.45	6.4	0.58	4.2

yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 5.16 Percentage yields of 3,4-dichlorobiphenyl, a by-product of the phenylation of 1,2,3-trichlorobenzene

experiment number	additive (0.1 g.)			
	(no additive)	copper benzoate	iron powder	trichloro-acetic acid
	yield (%)	yield (%)	yield (%)	yield (%)
1	2.9	3.4	3.4	3.6
2	3.0	3.1	3.2	3.4
3	2.7	3.6	3.1	3.4
4	3.0	3.8	2.9	3.9
5	2.6	-	-	-
6	2.5	-	-	-
(mean values)	2.8	3.6	3.2	3.6

yields are in mole per mole peroxide x 100

Table 5.17 Calculated isomer ratios for the products of phenylation of 1,2,3-trichlorobenzene in the absence of additives

experiment number	2,3,4-trichlorobiphenyl yield (%)	3,4,5-trichlorobiphenyl yield (%)
1	78.0	22.0
2	76.8	23.2
3	76.6	23.5
4	77.0	23.0
5	77.6	22.4
6	77.6	22.4
(mean values)	77.3	22.7

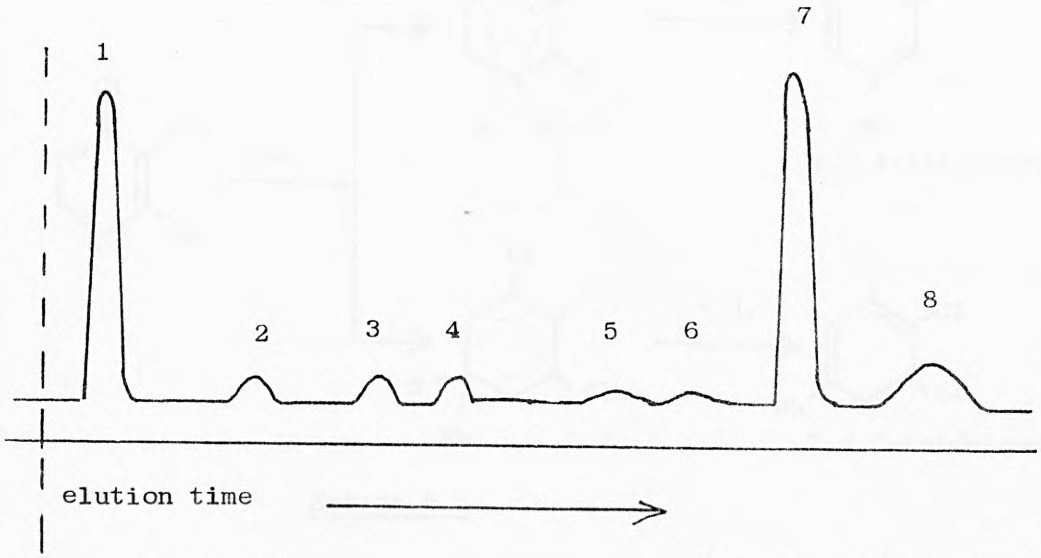
Table 5.18 Calculated isomer ratios for the products of phenylation of 1,2,3-trichlorobenzene in the presence of additives

experiment number	2,3,4-trichlorobiphenyl yield (%)	3,4,5-trichlorobiphenyl yield (%)
1[a]	75.7	24.3
2[a]	75.2	24.8
3[a]	76.1	23.9
4[a]	76.5	23.5
(mean values)[a]	75.9	24.1
5[b]	75.9	24.1
6[b]	75.1	24.1
7[b]	74.6	25.4
8[b]	76.0	24.0
(mean values)[b]	75.4	24.6
9[c]	74.0	26.0
10[c]	74.4	25.6
11[c]	74.6	25.4
12[c]	75.0	25.0
(mean values)[c]	74.5	25.5

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Figure 5.11 Reconstructed chromatogram showing only products of the phenylation reaction of 1,2,3-trichlorobenzene and benzene



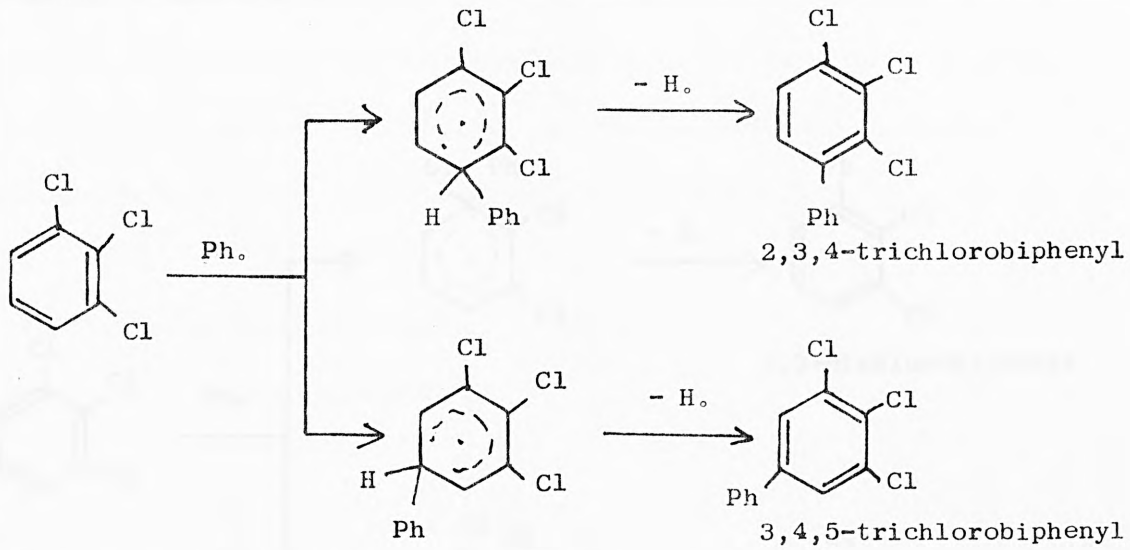
peak 1 = biphenyl

peak 2 = 2,6-dichlorobiphenyl
peak 3 = 2,3-dichlorobiphenyl
peak 4 = 3,4-dichlorobiphenyl
peak 5 = 2,3,6-trichlorobiphenyl
peak 6 = 2,3,5-trichlorobiphenyl
peak 7 = 2,3,4-trichlorobiphenyl
peak 8 = 3,4,5-trichlorobiphenyl

Unlike the 1,3,5-isomer, the phenylation of 1,2,3-trichlorobenzene has not been reported in the literature. In 1,2,3-trichlorobenzene, the hydrogen atom at positions 4 and 6 are equivalent yielding 2,3,4-trichlorobiphenyl (in 42 % yield) on phenylation, whilst attack by phenyl radicals at position 5 yields 3,4,5-trichlorobiphenyl (in 6 % yield). As there are two C - H sites leading to the formation of 2,3,4-trichlorobiphenyl, this product might be expected to predominate.

Thus, phenyldehydrogenation with the attack at C - H sites by phenyl radicals was the major reaction leading to the formation of 2,3,4- and 3,4,5-trichlorobiphenyls, as shown in Scheme 5.5

phenyldehydrogenation



Scheme 5.5

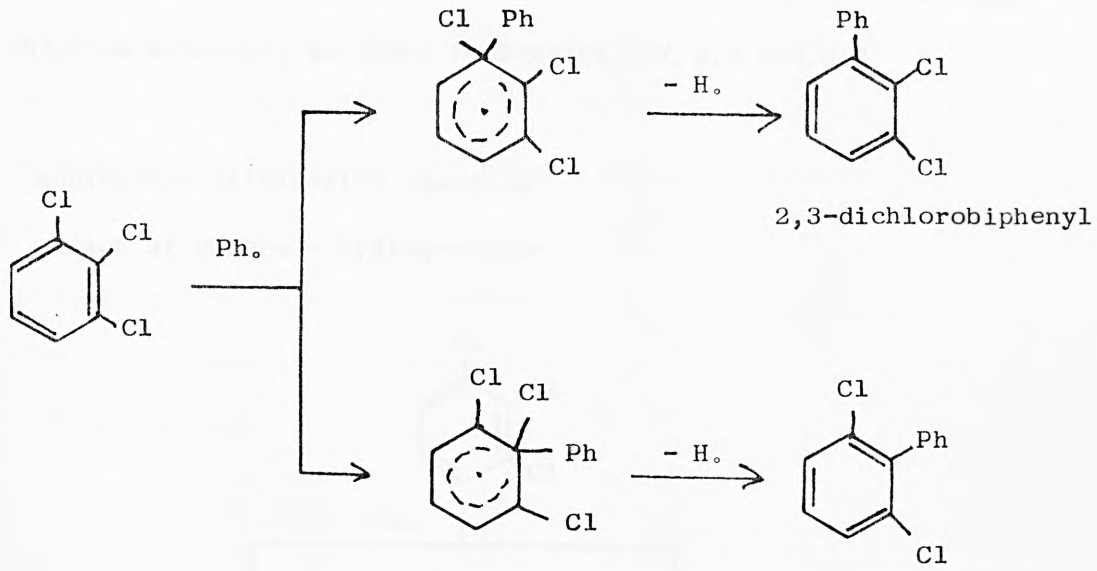
However, on the phenylation of 1,2,3-trichlorobenzene in sealed tubes, five other products were detected, namely 2,6-, 2,3- and 3,4-dichlorobiphenyls (in 3.5 %, 4.8 % and 2.9 % yields respectively) and 2,3,6- and 2,3,5-trichlorobiphenyls (both in $\not>$ 1 % yields).

The presence of these di- and trichlorobiphenyls was confirmed be g.l.c. retention time data by comparison / spiking with known authentic standards and by g.l.c.-mass spectrometry results (see Appendix). However, there was no evidence in the phenylation reaction products for the formation of dichlorobenzene, chlorobiphenyl or chloro, dichloro- or trichloroterphenyls. In this respect the phenylation of 1,2,3-trichlorobenzene differs from that of the 1,3,5-trichloro- isomer in which trichloroterphenyls were present in trace amounts (see section 5.1.4).

The presence of 2,6- and 2,3-dichlorobiphenyls can be accounted for by the occurrence of phenyldechlorination reactions with the attack of phenyl radicals at C - Cl sites followed by

elimination of a chlorine atom.

phenyldechlorination



Scheme 5.6

From the reaction sequence leading to the formation of 2,3-dichlorobiphenyl in Scheme 5.6 it is clear that there are two positions at which chlorine may be substituted by a phenyl radical. Thus it would be reasonable to expect higher yields of 2,3-dichlorobiphenyl, especially as in the formation of 2,6-dichlorobiphenyl there are bulky chlorine atoms ortho to the incoming phenyl radical. However, from the yields of the dichlorobiphenyls it can be seen that they are both of the same order.

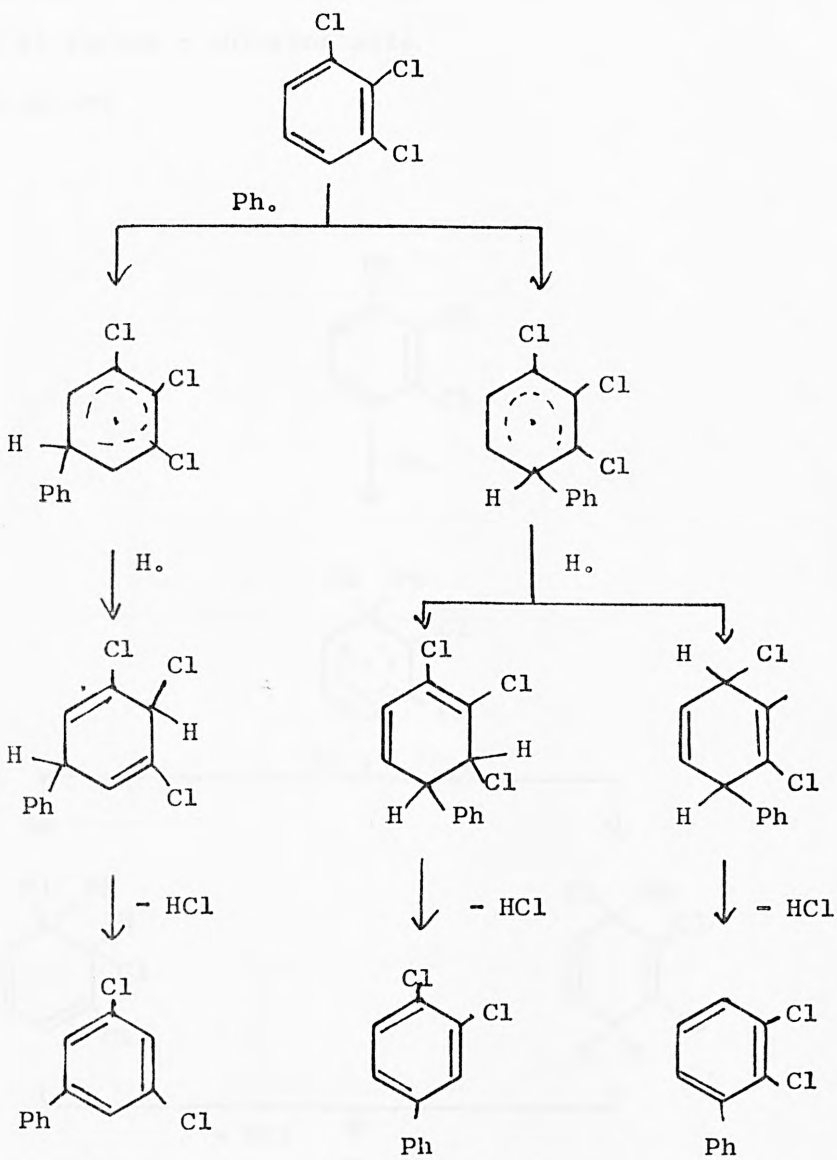
The phenylation of 1,2,3-trifluorobenzene has not been reported in the literature.

Once again, as in the case of the phenylation reaction products of the 1,3,5-isomer, there were more dichlorobiphenyl isomers in the phenylation of 1,2,3-trichlorobenzene than could be

accounted for by the phenyldechlorination reaction alone. The additional presence of 3,4-dichlorobiphenyl (in 2.9 % yield) was novel and to account for its formation it was considered that an addition - elimination reaction occurred with the take up of a phenyl and a hydrogen radical followed by the elimination of a hydrogen chloride molecule, as shown in Schemes 5.7, 5.8 and 5.9

addition - elimination reaction

attack at carbon - hydrogen site



3,5-dichlorobiphenyl 3,4-dichlorobiphenyl 2,3-dichlorobiphenyl

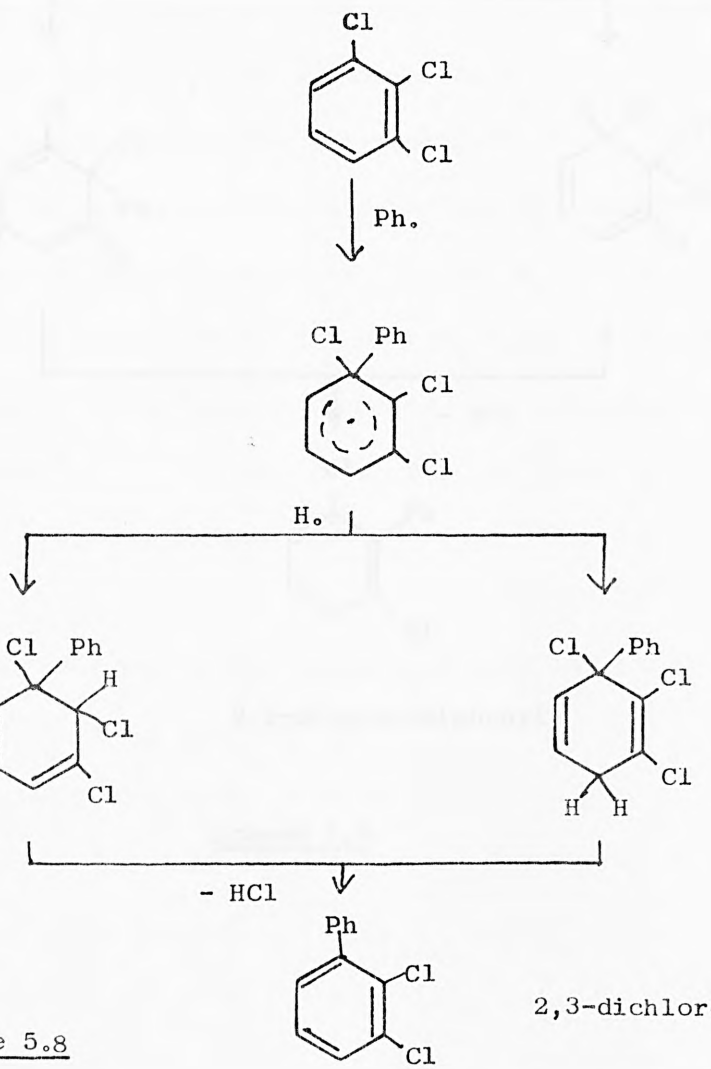
Scheme 5.7

When phenyl radicals attack a C - Cl site, it is possible for the phenylcyclohexadienyl complex to take up a hydrogen atom followed by the subsequent elimination of hydrogen chloride yielding 2,3- and 2,6- dichlorobiphenyls by different pathways then phenyl-dechlorination. Therefore there are two possible pathways for the formation of 2,3- and 2,6- dichlorobiphenyls, namely phenyl-dechlorination and addition - elimination differing in the subsequent elimination of chlorine and hydrogen chloride respectively.

addition - elimination reaction

attack at carbon - chlorine site

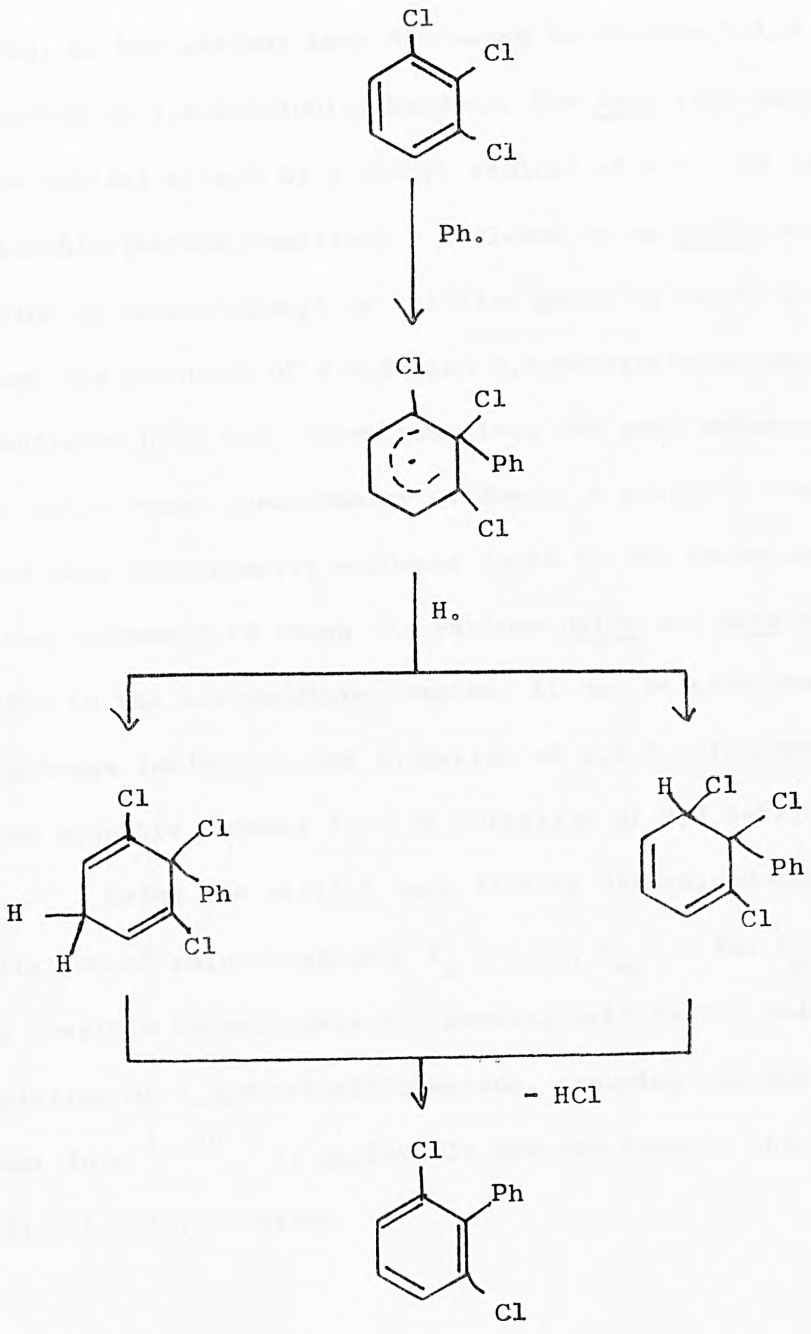
attack at C-1



2,3-dichlorobiphenyl

Scheme 5.8

attack at C-2



2,6-dichlorobiphenyl

Scheme 5.9

The additional trace presence of 2,3,6- and 2,3,5-trichlorobiphenyls ($\not>$ 1 % yield) was novel and to account for their formation it was considered that an ipso rearrangement reaction occurred, as has already been discussed in section 5.1.4 in the phenylation of 1,3,5-trichlorobenzene. The ipso rearrangement would involve initial attack by a phenyl radical at a C - Cl site (as in phenyldechlorination reactions) followed by an ortho or meta migration of either phenyl or chlorine group as shown in Scheme 5.10. Although the presence of 2,3,6- and 2,3,5-trichlorobiphenyls was substantiated by g.l.c. retention times and peak enhancement there was no g.l.c.-mass spectrometry evidence. A possible reason for the lack of mass spectrometry evidence could be the trace amounts involved. Scheme 5.10 shows the various ortho and meta migrations possible in the intermediate complex. It can be seen that there are two pathways leading to the formation of 2,3,6-trichlorobiphenyl and one possible pathway for the formation of 2,3,5-trichlorobiphenyl.

Using the partial rate factors determined for the phenylation of chlorobenzene ($f_o = 1.97$, $f_m = 0.82$, $f_p = 1.07$), it is possible to calculate the partial rate factor values for the phenylation of 1,2,3-trichlorobenzene, assuming the Holleman's product rule [132] is applicable and can predict the effect of additional chlorine atoms.

phenylation reaction in the absence of additives,

f_4 = o-Cl x m-Cl x p-Cl

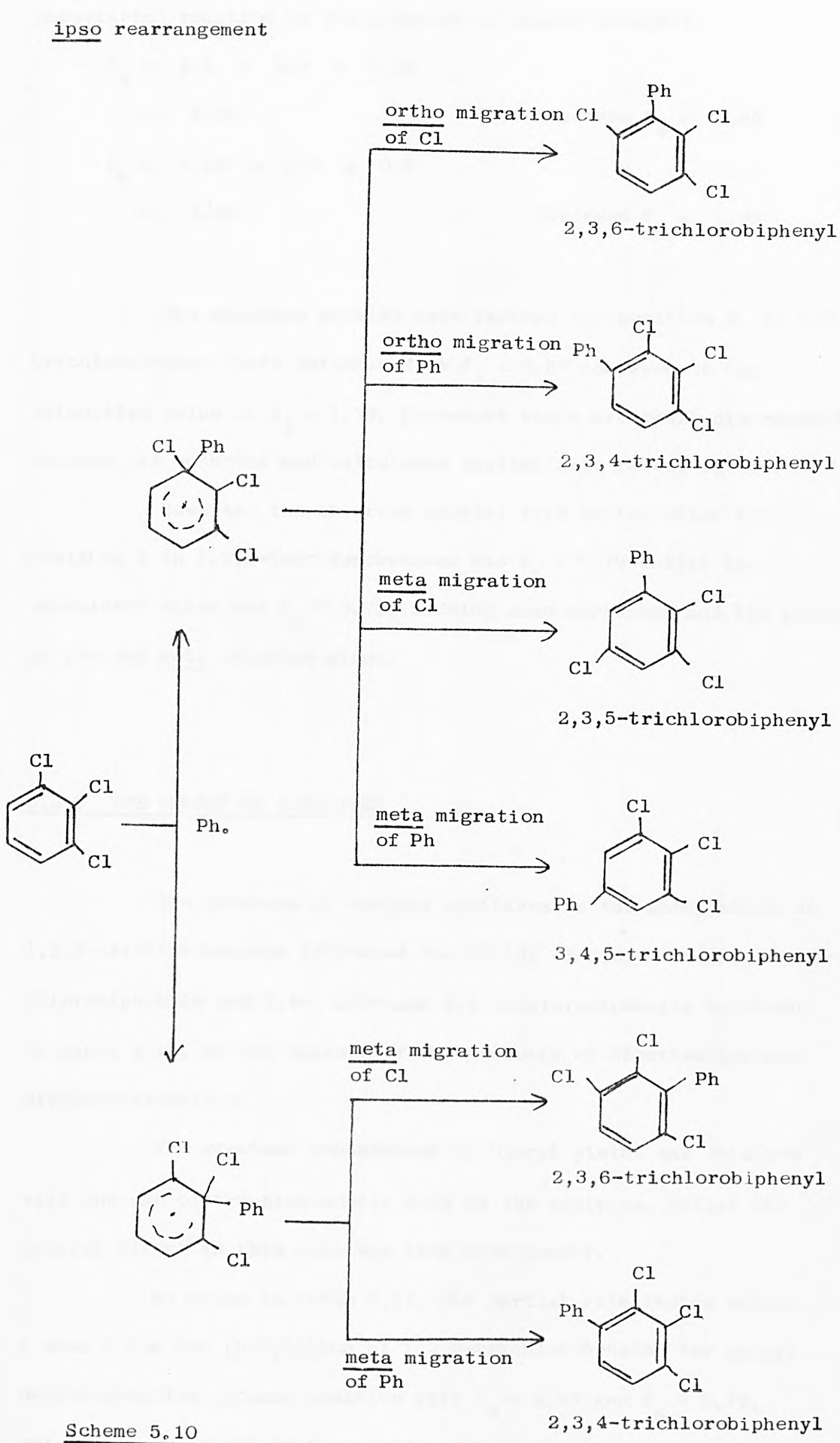
= 1.97 x 0.82 x 1.07

= 1.73 observed f_4 = 2.67

f_5 = p-Cl x m-Cl x m-Cl

= 1.07 x 0.82 x 0.82

= 0.72 observed f_5 = 0.79


ipso rearrangement
ortho migration of Cl
2,3,6-trichlorobiphenyl
ortho migration of Ph
2,3,4-trichlorobiphenyl
meta migration of Cl
2,3,5-trichlorobiphenyl
meta migration of Ph
3,4,5-trichlorobiphenyl
Ph.
meta migration of Cl
2,3,6-trichlorobiphenyl
meta migration of Ph
2,3,4-trichlorobiphenyl

Scheme 5.10

phenylation reaction in the presence of copper benzoate,

$f_4 = 2.9 \times 0.9 \times 1.24$

$= 3.24$ observed $f_4 = 3.85$

$f_5 = 1.24 \times 0.9 \times 0.9$

$= 1.00$ observed $f_5 = 1.22$

The observed partial rate factors for position 4 in 1,2,3-trichlorobenzene were determined as $f_4 = 2.67$ compared to the calculated value of $f_4 = 1.73$. Therefore there are small discrepancies between the observed and calculated partial rate factor values.

However, the observed partial rate factor value for position 5 in 1,2,3-trichlorobenzene was $f_5 = 0.79$ whilst the calculated value was $f_5 = 0.72$, showing some agreement and the effect of the two meta chlorine atoms.

5.2.5 THE EFFECT OF ADDITIVES

The presence of various additives in the phenylation of 1,2,3-trichlorobenzene increased the yields of 2,3,4- and 3,4,5-trichlorobiphenyls and 2,4-, 2,6- and 2,3-dichlorobiphenyls as shown in Table 5.19, at the expense of the products of dimerisation and disproportionation.

The greatest enhancement in biaryl yields was obtained with the use of trichloroacetic acid as the additive, whilst the poorest effect in this case was from iron powder.

As shown in Table 5.19, the partial rate factor values (mean) for the phenylation of 1,2,3-trichlorobenzene for phenyl-dehydrogenation without additive were $f_4 = 2.67$ and $f_5 = 0.79$, which were increased to $f_4 = 3.74$ and $f_5 = 1.22$ in the presence of

Table 5.19 Partial rate factors and percentage yields for the phenylation of 1,2,3-trichlorobenzene in the absence and presence of additives

row number	phenyldehydrogenation products		phenyldechlorination products		partial rate factors for :-			
	2,3,4-trichloro-biphenyl yield (%)	3,4,5-trichloro-biphenyl yield (%)	2,4-dichloro-biphenyl yield (%)	2,6-dichloro-biphenyl yield (%)	phenyldehydrogenation		phenyldechlorination	
					f_4	f_5	f_1	f_2
1[a]	41.6	6.2	4.8	3.5	2.67	0.79	0.31	0.46
2[b]	54.6	8.7	5.4	3.7	3.85	1.22	0.38	0.52
3[c]	47.4	7.8	4.7	3.1	3.74	1.22	0.37	0.49
4[d]	58.9	10.1	6.4	4.2	4.11	1.41	0.45	0.58

yields are in mole per mole peroxide x 100

each row is a mean of four or more figures

a = no additive

b = additive copper benzoate, 0.1 g.

c = additive iron powder, 0.1 g.

d = additive trichloroacetic acid, 0.1 g.

iron powder and f_4 = 4.11 and f_5 = 1.41 in the presence of trichloroacetic acid.

A small increase was also observed in the partial rate factor values for phenyldechlorination 1,2,3-trichlorobenzene as shown in Table 5.19. However, the values for the partia rate factors for phenyldechlorination are less than one, showing the deactivation of these sites and the general difficulty of such reactions.

5.3 METHOD OF PHENYLATION OF 1,2,4-TRICHLOROBENZENE

This was the same as has been described in section 3.1 Sections 5.3.1 to 5.3.3 show the chromatograms obtained and their identification followed by tables listing experimental qunatities leading to tables of results tabulating partial rate factors, yields and calculated isomer ratios.

5.3.1 CHROMATOGRAMS

Figures 5.11 to 5.13 show actual chromatograms obtained. Figure 5.14 shows a reconstructed chromatogram demonstrating the relationship between the products obtained.

5.3.2 PEAK IDENTIFICATION

The same method was used as has been explained in section 3.3

Figure 5.11 Reaction of 1,2,4-trichlorobenzene, chromatogram obtained

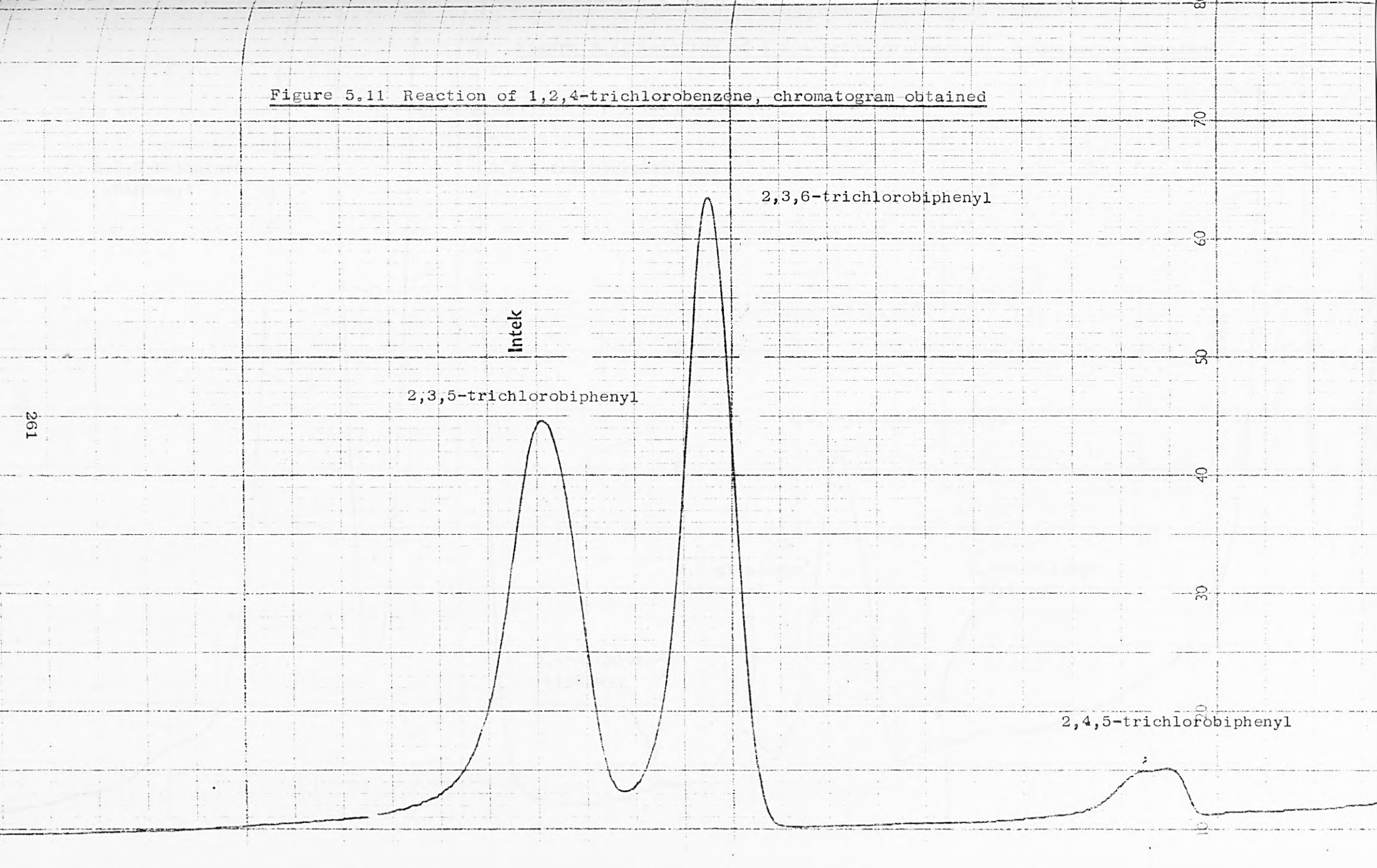
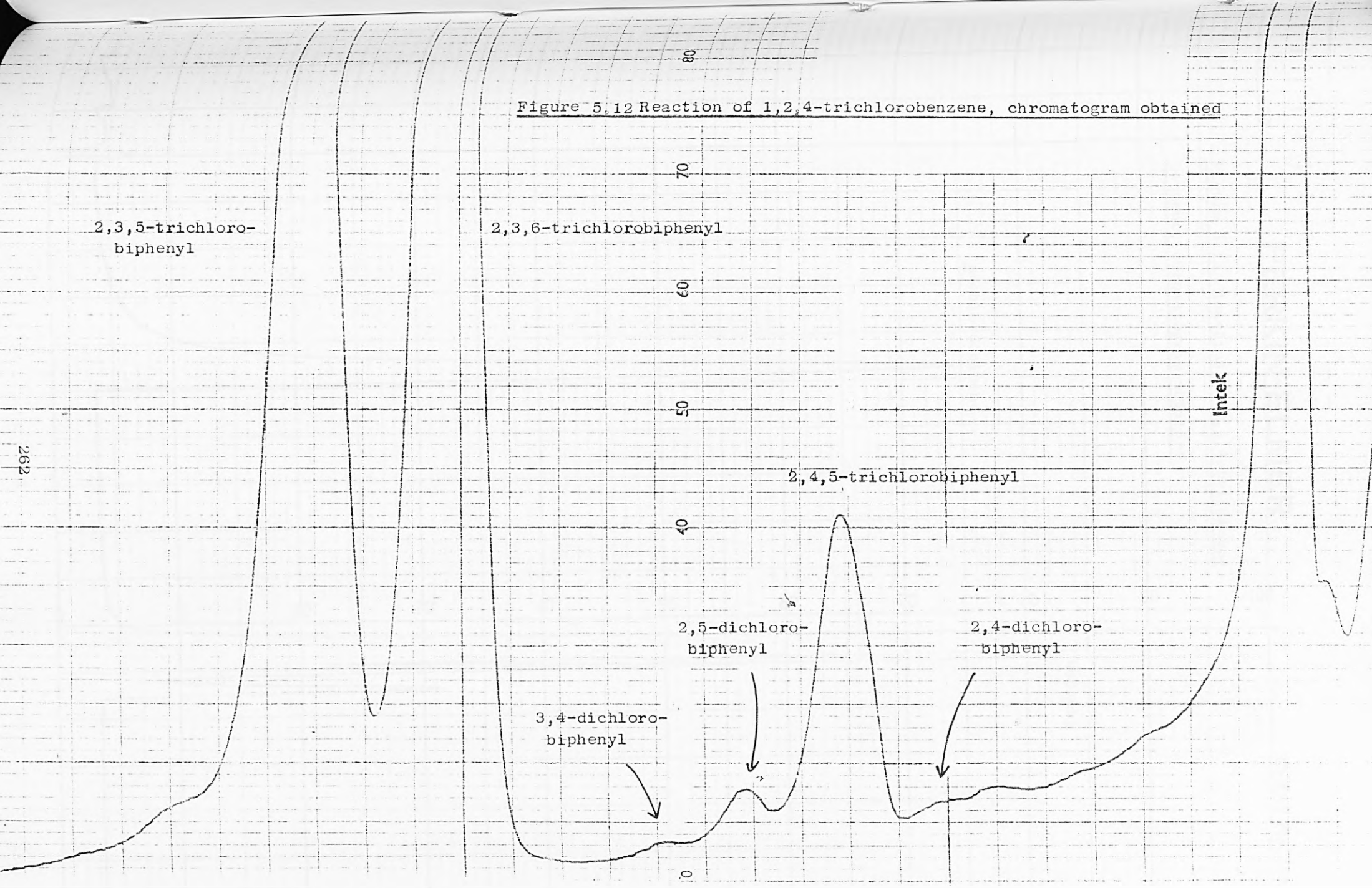


Figure 5.12 Reaction of 1,2,4-trichlorobenzene, chromatogram obtained



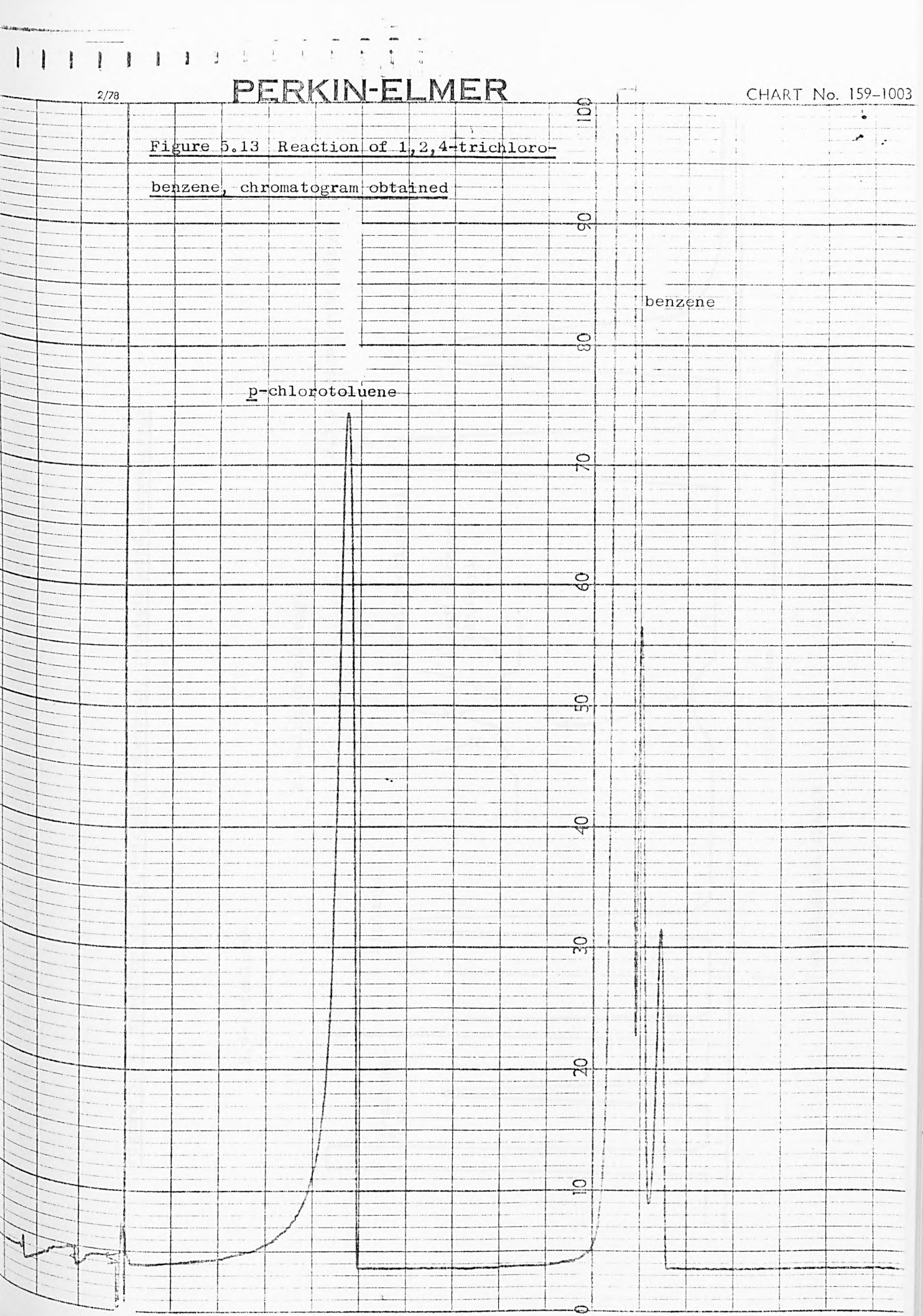


Figure 5.13 Reaction of 1,2,4-trichloro-benzene, chromatogram obtained

Figure 5.14 Reaction of 1,2,4-trichlorobenzene, reconstructed chromatogram

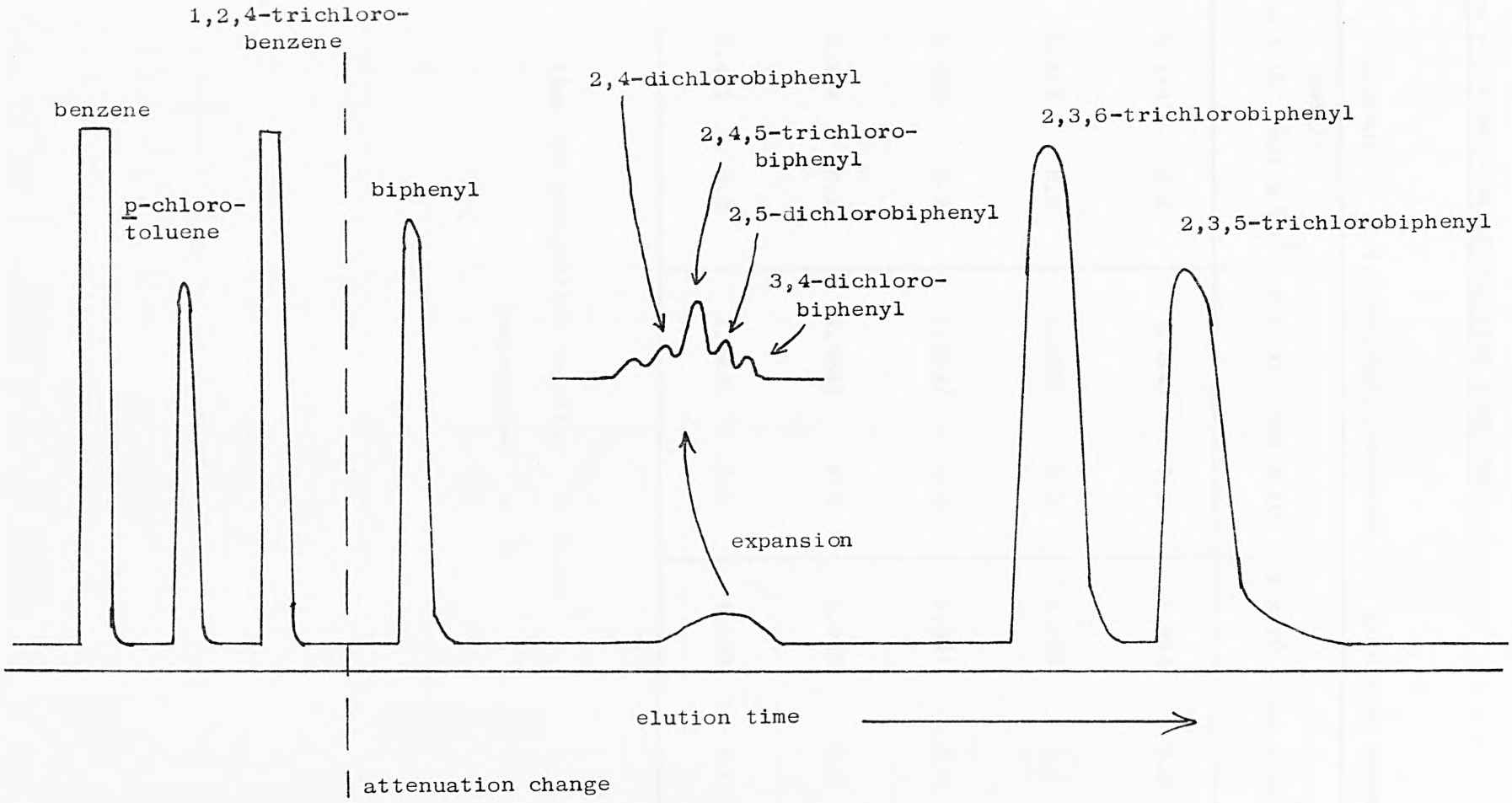


Table 5.20 Sealed tube phenylation reaction of 1,2,4-trichlorobenzene and benzene - composition of reaction mixtures

experiment number	benzene		1,2,4-trichlorobenzene		dibenzoyl peroxide	
	weight					
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1	6.418	8.2	1.4847	8.2	1.954	8.0
2	6.415	8.2	1.4869	8.2	1.943	8.0
3	6.423	8.2	1.4847	8.2	1.951	8.0
4	6.409	8.2	1.4865	8.2	1.955	8.0
5	6.422	8.2	1.4841	8.2	1.947	8.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

Table 5.21 Sealed tube phenylation reaction of 1,2,4-trichlorobenzene and benzene in the presence of additives - composition of reaction mixtures

experiment number	benzene		1,2,4-trichlorobenzene		dibenzoyl peroxide	
	weight		weight		weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	6.241	8.0	1.4523	8.0	1.954	8.0
2[a]	6.256	8.0	1.4486	8.0	1.943	8.0
3[a]	6.251	8.0	1.4518	8.0	1.947	8.0
4[a]	6.236	8.0	1.4509	8.0	1.951	8.0
5[b]	6.318	8.1	1.468	8.1	1.950	8.0
6[b]	6.325	8.1	1.4663	8.1	1.942	8.0
7[b]	6.306	8.1	1.4677	8.1	1.951	8.0
8[b]	6.328	8.1	1.4667	8.1	1.956	8.0
9[c]	6.254	8.0	1.4573	8.0	1.954	8.0
10[c]	6.237	8.0	1.4589	8.0	1.959	8.0
11[c]	6.243	8.0	1.4566	8.0	1.942	8.0
12[c]	6.357	8.0	1.4576	8.0	1.948	8.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 5.22 Analysis of the phenylation reaction products of 1,2,4-trichlorobenzene and benzene in the absence of additives (Table 5.20 gives compositions)

experiment number	trichlorobiphenyl products						dichlorobiphenyl products						biphenyl		p-chlorotoluene internal standard	
	2,3,6-		2,3,5-		2,4,5-		2,4-dichloro-		2,5-dichloro-		3,4-dichloro-					
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1	0.0373	0.0690	0.0167	0.0303	0.0077	0.0138	0.0051	0.0074	0.0033	0.0047	0.0022	0.0038	0.0584	0.0740	0.1394	0.1537
2	0.0378	0.0700	0.0163	0.0297	0.0081	0.0146	0.0051	0.0074	0.0033	0.0046	0.0023	0.0040	0.0589	0.0746	0.1412	0.1556
3	0.0377	0.0694	0.0171	0.0309	0.0078	0.0140	0.0050	0.0073	0.0031	0.0044	0.0023	0.0040	0.0594	0.0749	0.1425	0.1563
4	0.0374	0.0686	0.0164	0.0296	0.0075	0.0134	0.0049	0.0071	0.0033	0.0047	0.0021	0.0036	0.0588	0.0738	0.1418	0.1547
5	0.0374	0.0694	0.0165	0.0301	0.0083	0.0150	0.0049	0.0071	0.0033	0.0046	0.0024	0.0041	0.0585	0.0744	0.1428	0.1578
response factors	1.68		1.65		1.63		1.32		1.28		1.56		1.01		1.00	

Table 5.23 Analysis of the phenylation reaction products of 1,2,4-trichlorobenzene and benzene in the presence of additives (Table 5.21 gives compositions)

experiment number	trichlorobiphenyl products 2,3,6- peak weight (g.)	2,3,6- cpd. weight (g.)	2,3,5- peak weight (g.)	2,3,5- cpd. weight (g.)	2,4,5- peak weight (g.)	2,4,5- cpd. weight (g.)	dichlorobiphenyl products 2,4- peak weight (g.)	2,4- cpd. weight (g.)	2,5- peak weight (g.)	2,5- cpd. weight (g.)	3,4- peak weight (g.)	3,4- cpd. weight (g.)	biphenyl peak weight (g.)	biphenyl cpd. weight (g.)	p-chlorotoluene internal standard peak weight (g.)	p-chlorotoluene internal standard std. weight (g.)
1[a]	0.0514	0.0953	0.0248	0.0451	0.0098	0.0176	0.0065	0.0095	0.0042	0.0060	0.0034	0.0058	0.0695	0.0774	0.1379	0.1521
2[a]	0.0508	0.0944	0.0232	0.0423	0.0085	0.0153	0.0064	0.0090	0.0040	0.0059	0.0033	0.0057	0.0677	0.0756	0.1401	0.1549
3[a]	0.0518	0.0956	0.0237	0.0430	0.0101	0.0180	0.0067	0.0100	0.0043	0.0060	0.0034	0.0060	0.0704	0.0781	0.1396	0.1533
4[a]	0.0511	0.0949	0.0245	0.0448	0.0091	0.0164	0.0064	0.0090	0.0041	0.0058	0.0032	0.0056	0.0695	0.0777	0.1366	0.1511
5[b]	0.0563	0.1038	0.0261	0.0473	0.0110	0.0197	0.0072	0.0105	0.0051	0.0070	0.0037	0.0064	0.0714	0.0792	0.1412	0.1550
6[b]	0.0557	0.1026	0.0254	0.0459	0.0107	0.0192	0.0074	0.0107	0.0048	0.0068	0.0039	0.0067	0.0718	0.0795	0.1434	0.1573
7[b]	0.0555	0.1022	0.0250	0.0452	0.0102	0.0182	0.0070	0.0102	0.0050	0.0070	0.0039	0.0070	0.0719	0.0796	0.1422	0.1559
8[b]	0.0558	0.1034	0.0259	0.0472	0.0099	0.0178	0.0071	0.0104	0.0048	0.0070	0.0041	0.0069	0.0726	0.0809	0.1417	0.1564
9[c]	0.0589	0.1084	0.0276	0.0499	0.0127	0.0226	0.0080	0.0116	0.0055	0.0080	0.0046	0.0078	0.0723	0.0800	0.1409	0.1544
10[c]	0.0594	0.1092	0.0278	0.0502	0.0130	0.0225	0.0079	0.0120	0.0052	0.0073	0.0050	0.0080	0.0735	0.0812	0.1433	0.1567
11[c]	0.0590	0.1098	0.0273	0.0496	0.0117	0.0211	0.0078	0.0113	0.0051	0.0070	0.0047	0.0081	0.0723	0.0805	0.1428	0.1575
12[c]	0.0580	0.1080	0.0269	0.0493	0.0119	0.0215	0.0080	0.0114	0.0052	0.0074	0.0050	0.0079	0.0718	0.0803	0.1405	0.1555

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 5.24 Partial rate factors and percentage yields of the phenylation reaction products of 1,2,4-trichlorobenzene and benzene in the absence of additives (Table 5.20 gives compositions)

experiment number	biphenyl yield (%)	2,3,6-trichloro-biphenyl		2,3,5-trichloro-biphenyl		2,4,5-trichloro-biphenyl		2,4-dichloro-biphenyl		2,5-dichloro-biphenyl		3,4-dichloro-biphenyl	
		f_3	yield (%)	f_6	yield (%)	f_5	yield (%)	f_1	yield (%)	f_2	yield (%)	f_4	yield (%)
1	60.1	3.34	33.5	1.47	14.7	0.67	6.7	0.42	4.2	0.26	2.6	0.21	2.1
2	60.6	3.37	34.0	1.43	14.4	0.70	7.1	0.41	4.2	0.25	2.6	0.22	2.2
3	60.8	3.32	33.7	1.48	15.0	0.67	6.8	0.40	4.1	0.24	2.5	0.22	2.2
4	59.9	3.34	33.3	1.44	14.4	0.63	6.5	0.39	4.0	0.26	2.6	0.20	2.0
5	60.4	3.35	33.7	1.45	14.6	0.72	7.3	0.40	4.0	0.26	2.6	0.23	2.4
(mean values)	60.3	3.34	33.6	1.45	14.6	0.68	6.9	0.41	4.1	0.26	2.6	0.22	2.2

yields are in mole per mole peroxide x 100

Table 5.25 Partial rate factors and percentage yields of the phenylation reaction products of 1,2,4-trichlorobenzene and benzene in the presence of additives (Table 5.21 gives compositions)

experiment number	biphenyl yield (%)	2,3,6-trichloro-biphenyl f_3	yield (%)	2,3,5-trichloro-biphenyl f_6	yield (%)	2,4,5-trichloro-biphenyl f_5	yield (%)	2,4-dichloro-biphenyl f_1	yield (%)	2,5-dichloro-biphenyl f_2	yield (%)	3,4-dichloro-biphenyl f_4	yield (%)
1[a]	62.8	4.42	46.3	2.09	21.9	0.82	8.5	0.51	5.3	0.32	3.4	0.31	3.3
2[a]	61.4	4.48	45.8	2.01	20.5	0.73	7.4	0.51	5.0	0.32	3.3	0.31	3.2
3[a]	63.4	4.39	46.4	1.97	20.9	0.83	8.7	0.52	5.6	0.31	3.4	0.31	3.4
4[a]	63.1	4.38	46.1	2.07	21.8	0.76	8.0	0.50	5.0	0.31	3.3	0.30	3.1
(mean values)[a]	62.7	4.42	46.1	2.04	21.3	0.78	8.2	0.51	5.2	0.32	3.3	0.31	3.2
5[b]	64.3	4.70	50.4	2.14	23.0	0.89	9.6	0.55	5.9	0.37	3.9	0.34	3.6
6[b]	64.5	4.63	49.8	2.07	21.9	0.87	9.3	0.56	6.0	0.35	3.8	0.35	3.8
7[b]	65.0	4.61	49.6	2.04	21.9	0.82	8.8	0.53	5.7	0.36	3.9	0.34	3.9
8[b]	65.7	4.59	50.2	2.09	22.9	0.79	8.6	0.53	5.8	0.35	3.9	0.35	3.9
(mean values)[b]	64.9	4.63	50.0	2.10	22.4	0.84	9.1	0.54	5.9	0.36	3.9	0.34	3.8
9[c]	64.9	4.86	52.6	2.24	24.2	1.01	11.0	0.60	6.5	0.40	4.5	0.40	4.4
10[c]	65.9	4.83	53.0	2.22	24.4	0.99	10.9	0.59	6.7	0.37	4.1	0.41	4.5
11[c]	65.3	4.89	53.3	2.21	24.1	0.94	10.2	0.58	6.3	0.37	3.9	0.42	4.5
12[c]	65.1	4.82	52.4	2.20	23.9	0.96	10.2	0.59	6.4	0.38	4.2	0.41	4.4
(mean values)[c]	65.3	4.84	52.8	2.22	24.2	0.98	10.6	0.59	6.5	0.38	4.2	0.41	4.5

yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 5.26 Calculated isomer ratios for the products of phenylation of 1,2,4-trichlorobenzene in the absence of additives

experiment number	2,3,6-trichloro-biphenyl yield (%)	2,3,5-trichloro-biphenyl yield (%)	2,4,5-trichloro-biphenyl yield (%)
1	61.0	26.8	12.2
2	61.3	26.0	12.7
3	60.7	27.1	12.3
4	61.7	26.6	11.7
5	60.7	26.3	12.3
(mean values)	61.1	26.6	12.4

Table 5.27 Calculated isomer ratios for the products of phenylation of 1,2,4-trichlorobenzene in the presence of additives

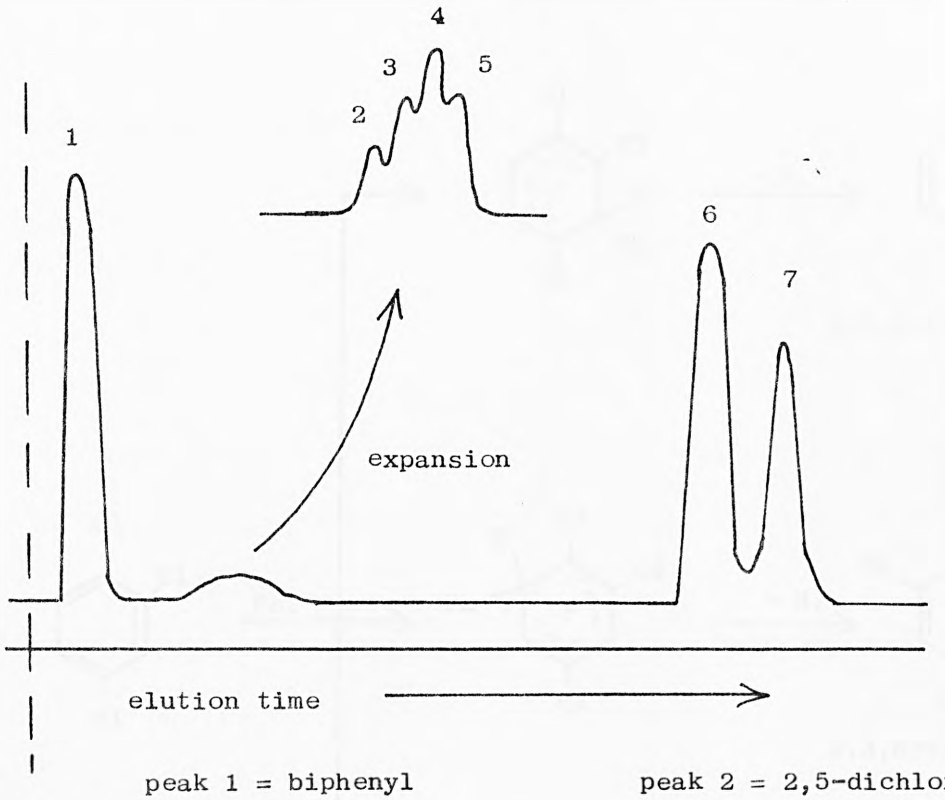
experiment number	2,3,6-trichloro biphenyl yield (%)	2,3,5-trichloro-biphenyl yield (%)	2,4,5-trichloro-biphenyl yield (%)
1[a]	60.3	28.5	11.2
2[a]	62.1	27.8	10.1
3[a]	61.1	27.4	11.5
4[a]	60.8	28.7	10.5
(mean values)[a]	61.0	28.1	10.8
5[b]	60.8	27.7	11.5
6[b]	61.2	27.3	11.5
7[b]	61.7	27.3	11.0
8[b]	61.5	28.0	10.6
(mean values)[b]	61.3	27.6	11.1
9[c]	59.9	27.6	12.5
10[c]	60.1	27.6	12.3
11[c]	60.8	27.5	11.7
12[c]	60.4	27.6	12.0
(mean values)[c]	60.3	27.6	12.1

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Figure 5.15 Reconstructed chromatogram showing phenylation products only



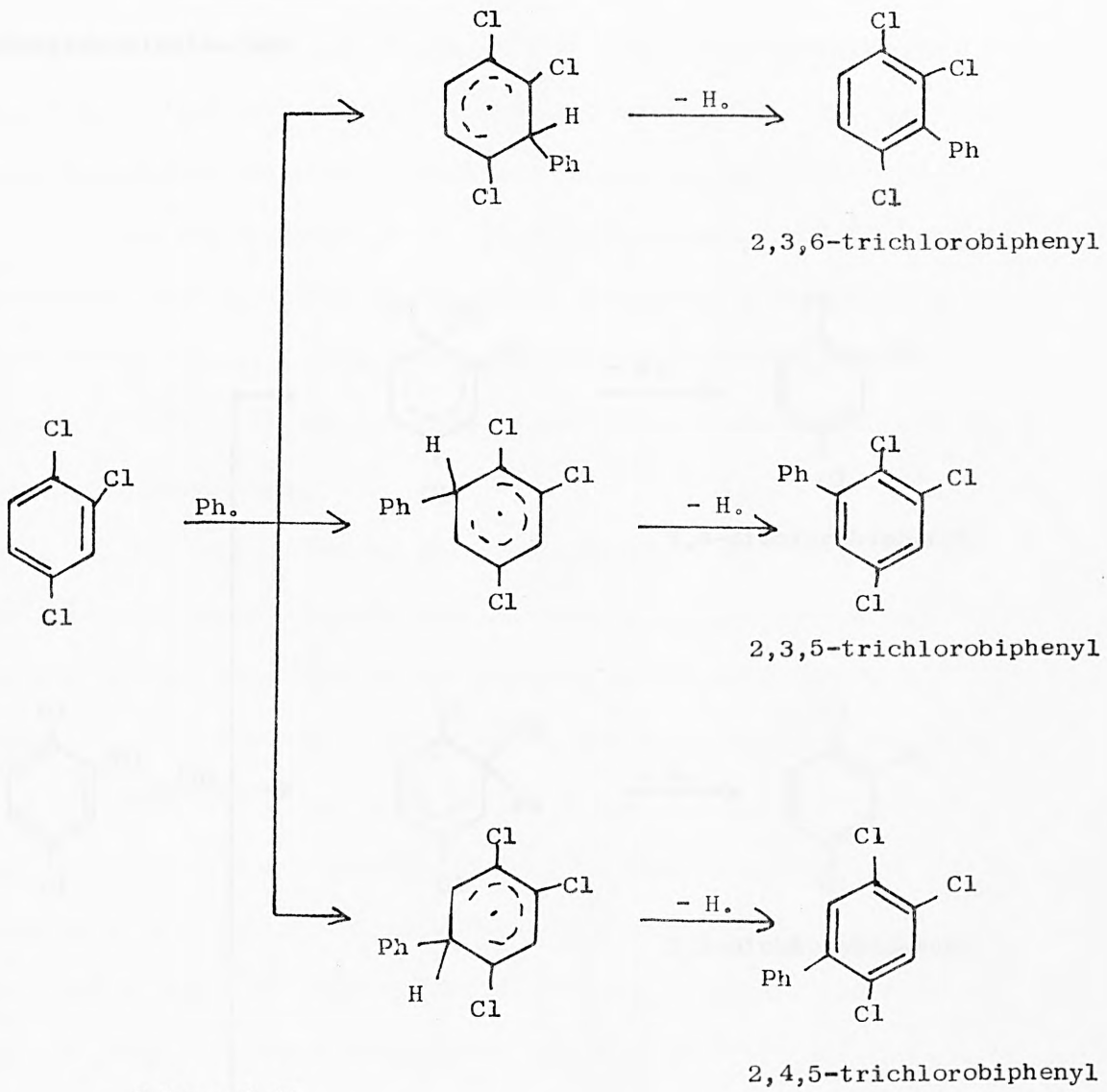
peak 1 = biphenyl

peak 2 = 2,5-dichlorobiphenyl
peak 3 = 2,4-dichlorobiphenyl
peak 4 = 2,4,5-trichlorobiphenyl
peak 5 = 3,4-dichlorobiphenyl
peak 6 = 2,3,6-trichlorobiphenyl
peak 7 = 2,3,5-trichlorobiphenyl

As in the case of the 1,2,3-isomer, the phenylation of 1,2,4-trichlorobenzene has not been reported in the literature. The sealed tube phenylation of 1,2,4-trichlorobenzene produced a complex mixture, with the phenyldehydrogenation reaction yielding three isomeric trichlorobiphenyls as each hydrogen atom had a different chemical environment. The products of phenyldehydrogenation reactions were 2,3,6- (in 34 % yield), 2,3,5- (in 15 % yield) and 2,4,5- (in 7 % yield) trichorobiphenyls. As with the 1,3,5- and 1,2,3- isomers, the reaction of phenyldehydrogenation dominated the

phenylation of 1,2,4-trichlorobenzene (see Scheme 5.11).

phenyldehydrogenation



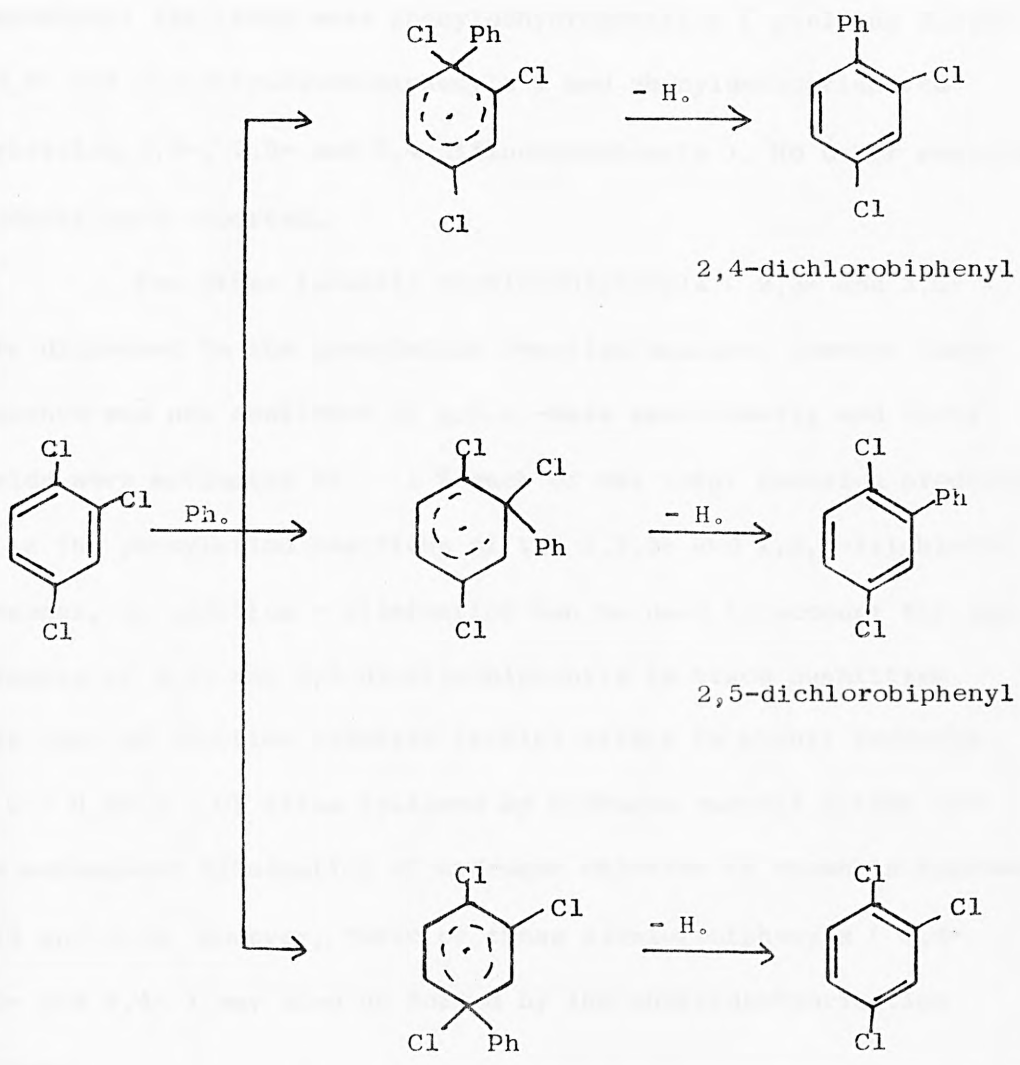
Scheme 5.11

The relatively higher yields of 2,3,6-trichlorobiphenyl can be accounted for by postulating the occurrence of ipso rearrangement reactions.

On the phenylation of 1,2,4-trichlorobenzene, three other products were detected, namely 2,5-, 2,4- and 3,4-dichlorobiphenyls (in 2.6 %, 4.2 % and 2.1 % yields respectively). The presence of

these isomeric dichlorobiphenyls was confirmed by g.l.c. retention data by comparison / spiking with known authentic standards and by g.l.c.-mass spectrometry results (see Appendix). No evidence was found for the presence of terphenyls or quaterphenyls.

phenyldechlorination



Scheme 5.12

The presence of 2,5-, 2,4- and 3,4-dichlorobiphenyls in the phenylation reaction products can be accounted for by the

occurrence of phenyldechlorination reactions with the attack of phenyl radicals at C - Cl sites as shown in Scheme 5.12., followed by elimination of a chlorine atom.

The dichlorobiphenyl peaks were eluted as shoulders on the 2,4,5-trichlorobiphenyl peak as the relative retention times were similar in value. The yields of 2,5- and 3,4-dichlorobiphenyls (2.6 % and 2.2 % respectively) were approximately of the same order, whilst 2,4-dichlorobiphenyl was formed in the highest yield (4 %).

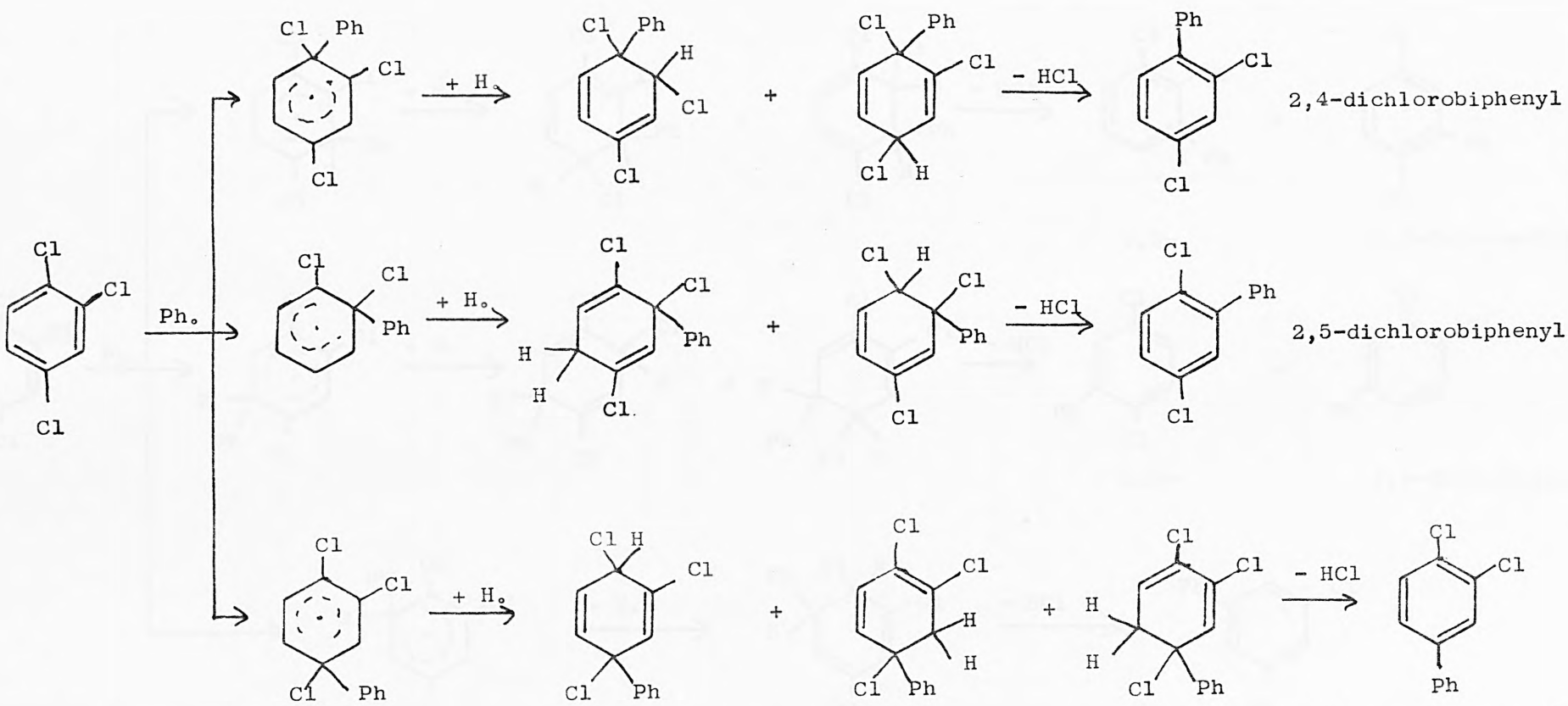
In the phenylation of 1,2,4-trifluorobenzene [65] the predominant reactions were phenyldehydrogenation (yielding 2,3,6-, 2,3,5- and 2,4,5-trifluorobiphenyls) and phenyldefluorination (yielding 2,4-, 2,5- and 3,4-difluorobiphenyls). No other reaction products were reported.

Two other isomeric dichlorobiphenyls (2,3- and 3,5-) were discerned in the phenylation reaction mixture, however their presence was not confirmed by g.l.c.-mass spectrometry and their yields were estimated at 1 % each of the total reaction products. As in the phenylation reactions of the 1,3,5- and 1,2,3-trichlorobenzenes, an addition - elimination can be used to account for the presence of 2,3- and 3,5-dichlorobiphenyls in trace quantities. This type of reaction requires initial attack by phenyl radicals at C - H or C - Cl sites followed by hydrogen radical uptake and the subsequent elimination of hydrogen chloride as shown in Schemes 5.13 and 5.14. However, three of these dichlorobiphenyls (2,4-, 2,5- and 3,4-) may also be formed by the phenyldechlorination pathway.

Unlike the phenylation reactions of the 1,3,5- and 1,2,3-trichlorobenzenes, the phenylation reaction products of 1,2,4-trichlorobenzene showed the absence of any products of <u>ipso</u> rearrangement. Schemes 5.15 and 5.16 show the pathways of various

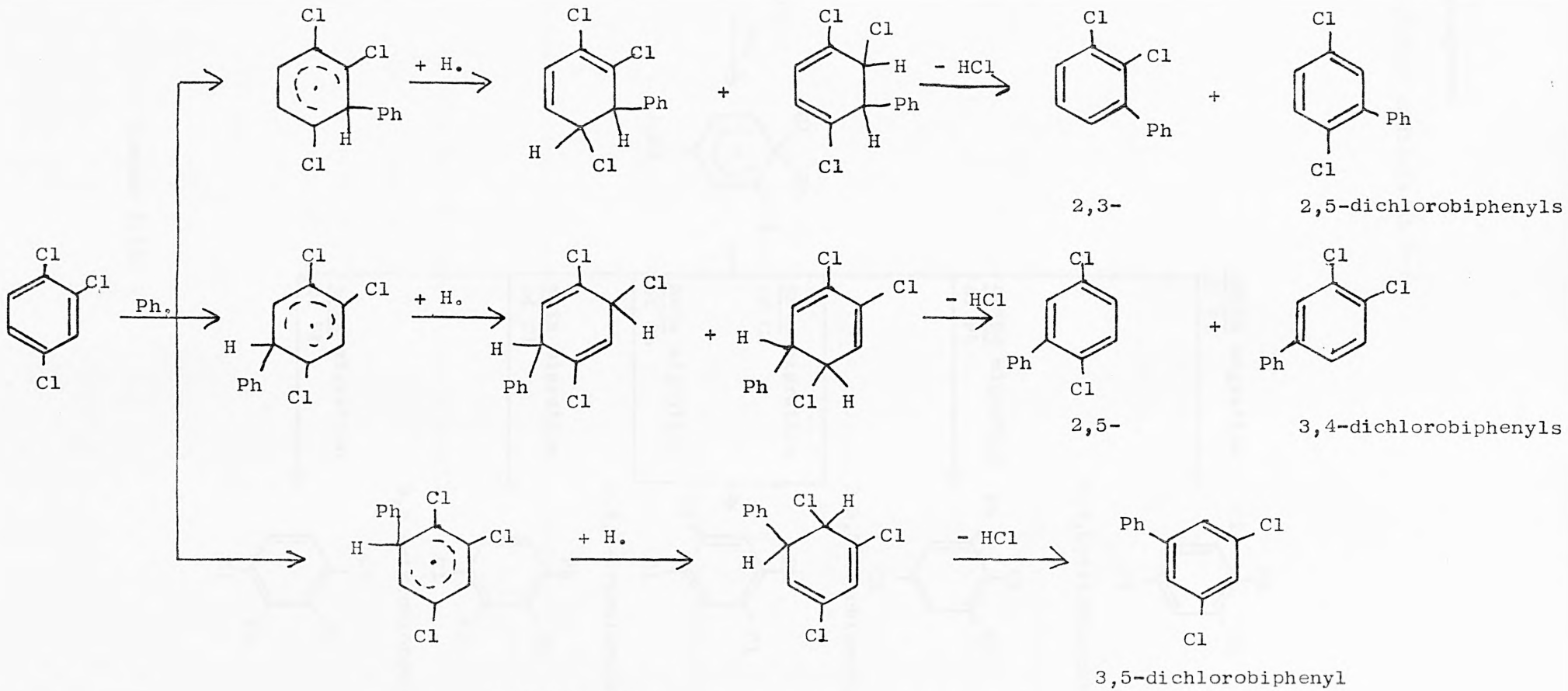
addition - elimination reaction

attack of a C - Cl site by phenyl radicals



Scheme 5.13

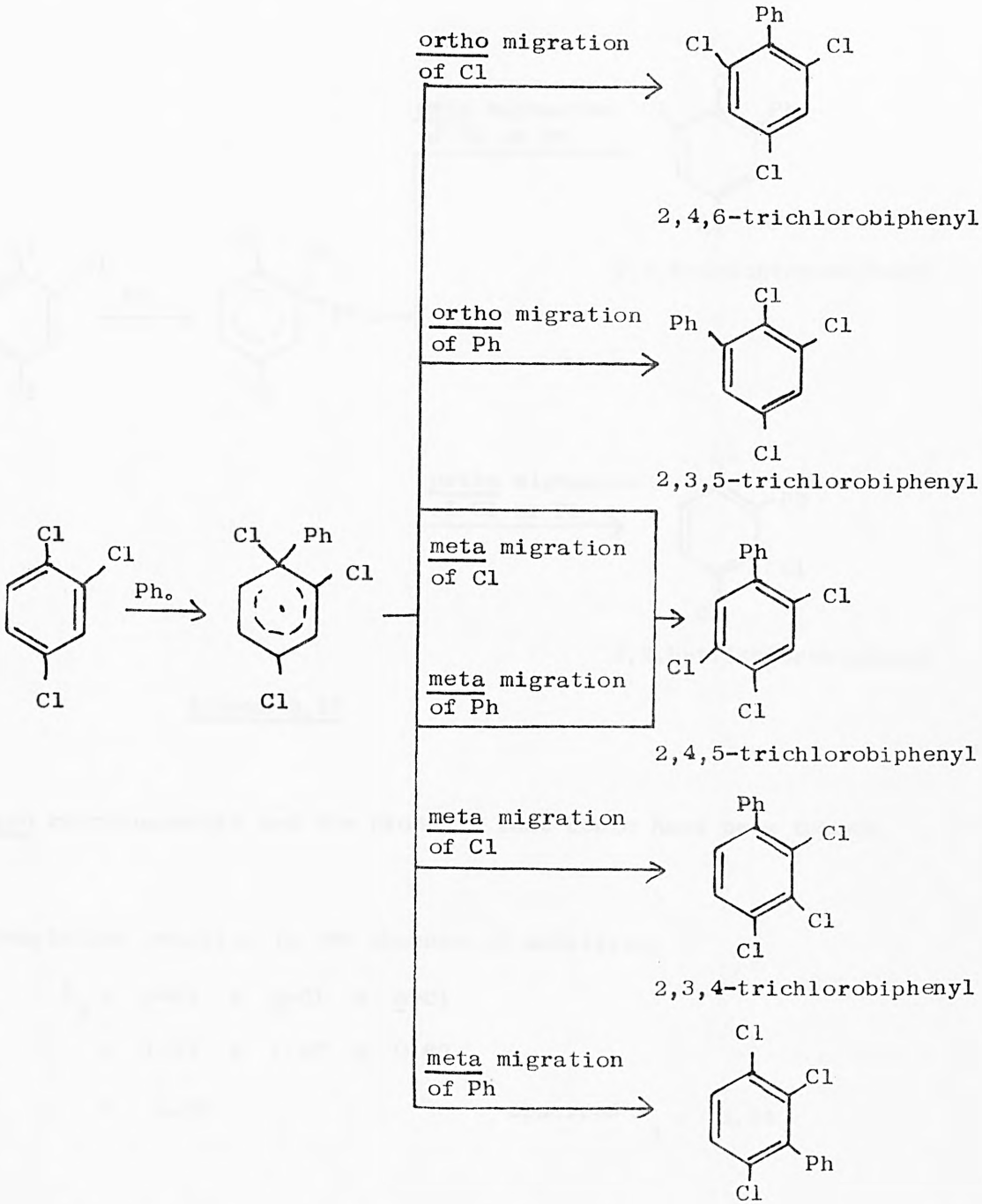
addition - elimination reaction attack at a C - H site by phenyl radicals



Scheme 5.14

ipso rearrangement

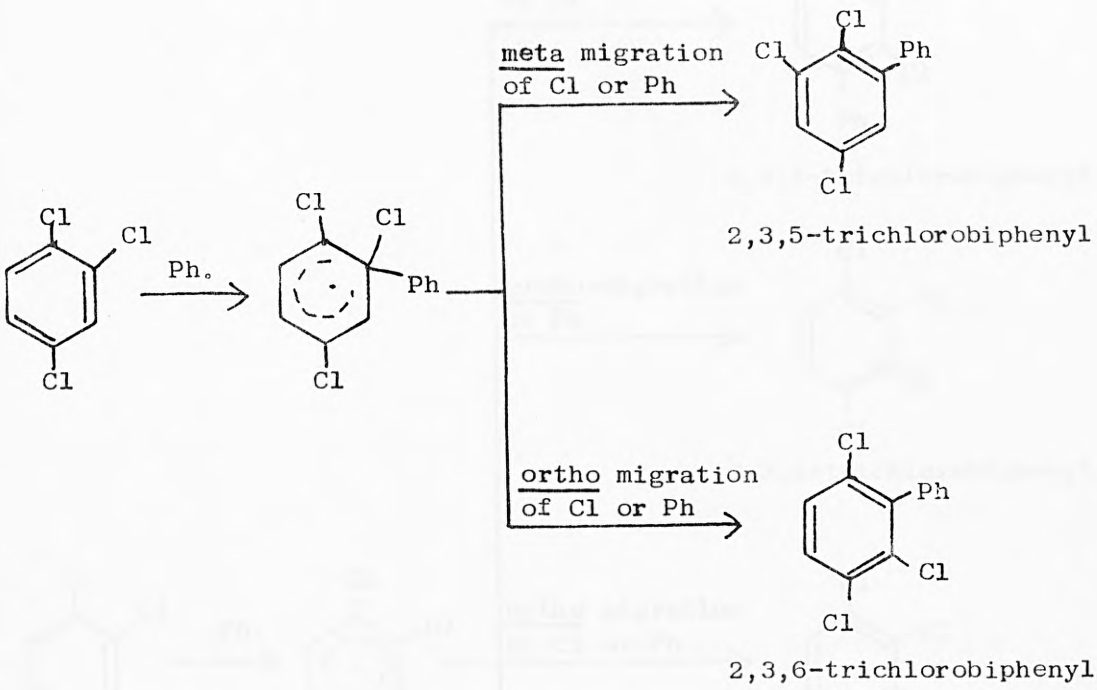
attack by phenyl radicals at C-1



Scheme 5.15

ipso rearrangement

attack by phenyl radicals at C-2



Scheme 5.16

ipso rearrangements and the products that could have been formed.

phenylation reaction in the absence of additives,

f_3 = o-Cl x o-Cl x m-Cl

= 1.97 x 1.97 x 0.82

= 3.18 observed f_3 = 3.34

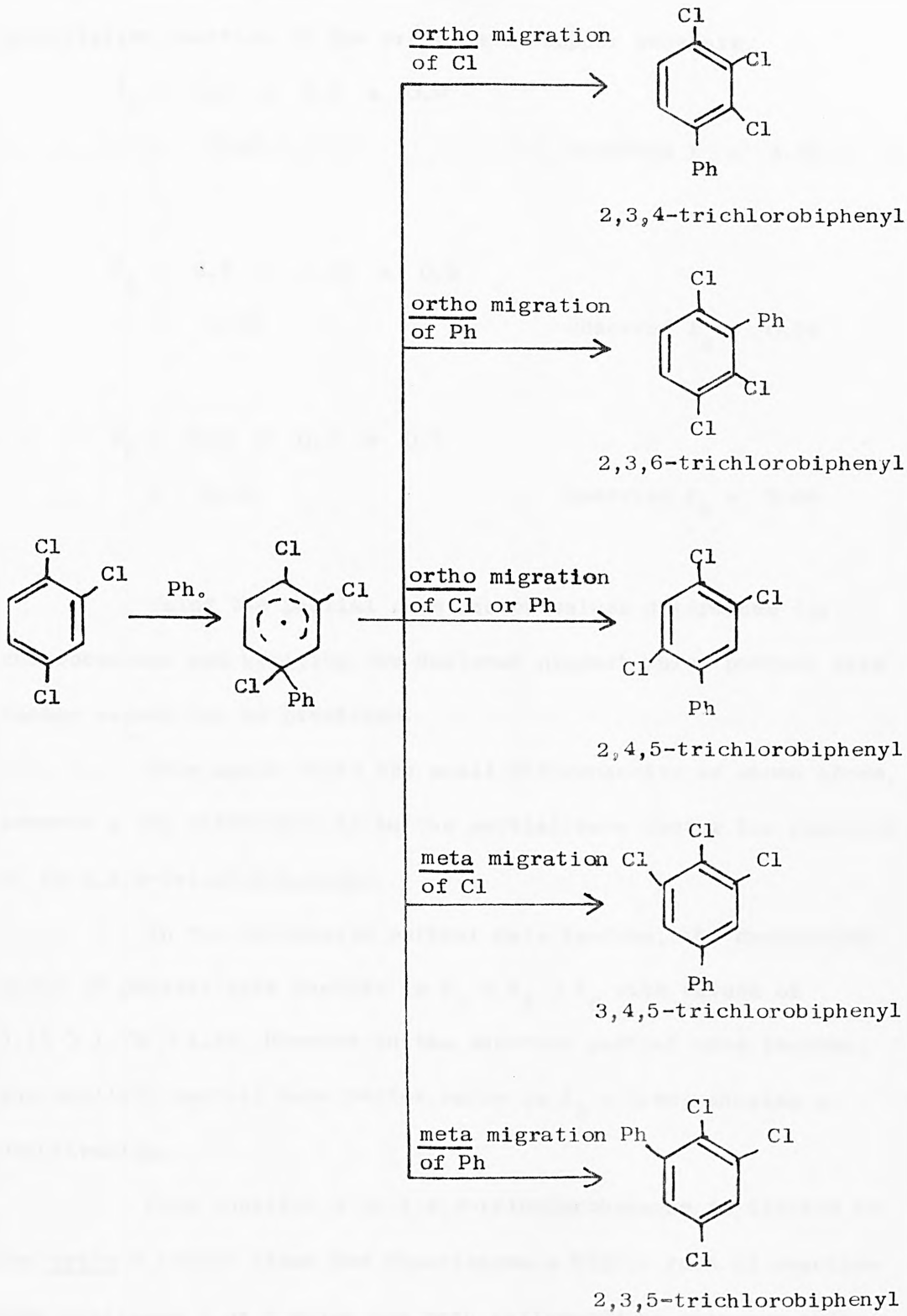
f_5 = o-Cl x p-Cl x m-Cl

= 1.97 x 1.07 x 0.82

= 1.73 observed f_5 = 0.68

ipso rearrangement

attack by phenyl radicals at C-4



Scheme 5.17

f_6 = o-Cl x m-Cl x m-Cl

= 1.97 x 0.82 x 0.82

= 1.32 observed f_6 = 1.45

phenylation reaction in the presence of copper benzoate,

f_3 = 2.9 x 2.9 x 0.9

= 7.57 observed f_3 = 4.42

f_5 = 2.9 x 1.24 x 0.9

= 3.24 observed f_5 = 0.78

f_6 = 2.9 x 0.9 x 0.9

= 2.35 observed f_6 = 2.04

Using the partial rate factor values determined for chlorobenzene and applying the Holleman product rule, partial rate factor values can be predicted.

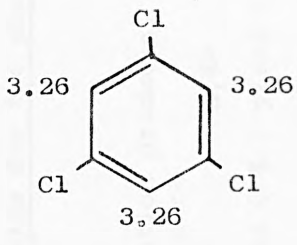
Once again there are small discrepancies as shown above, however a big difference is in the partial rate factor for position 5 in 1,2,4-trichlorobenzene.

In the calculated partial rate factors, the decreasing order of partial rate factors is $f_3 > f_5 > f_6$ with values of $3.18 > 1.73 > 1.32$. However in the observed partial rate factors, the smallest partial rate factor value is $f_5 = 0.68$, showing a deactivation.

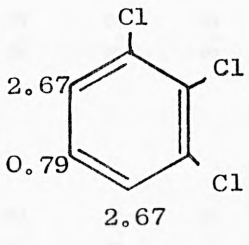
Thus position 3 in 1,2,4-trichlorobenzene is flanked by two ortho c lorine atoms and experiences a higher rate of reaction than positions 5 or 6 which are both influenced by only one ortho chlorine atom.

The difference in the rate of reaction at positions 5 and 6 could be said to reflect the influence of a para chlorine and a meta chlorine atom respectively as both positions are also influenced by one ortho and one meta chlorine atom.

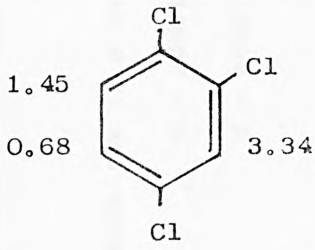
5.3.5 PARTIAL RATE FACTORS FOR THE PHENYLATION OF TRICHLOROBENZENES



1,3,5-



1,2,3-



1,2,4-

On comparing the partial rate factor values of the isomeric trichlorobenzenes, certain patterns can be distinguished, as can be seen from the above.

The partial rate factor values for position 2 in 1,3,5-trichlorobenzene ($f_2 = 3.26$) and position 3 in 1,2,4-trichlorobenzene ($f_3 = 3.34$) both represent the effect of two ortho chlorine atoms on the relative reactivity of those positions.

Positions with two meta chlorine atoms have a low rate of reaction as seen by the partial rate factor value for position 5 in 1,2,3-trichlorobenzene, $f_5 = 0.79$.

However, the presence of even one ortho chlorine atom increases the rate of reaction at that position, as seen from the partial rate factor value for position 4 in 1,2,3-trichlorobenzene, $f_4 = 2.67$ and position 6 in 1,2,4-trichlorobenzene, $f_6 = 1.45$.

Table 5.28 Partial rate factors and percentage yields for the phenylation of 1,2,4-trichlorobenzene in the absence and presence of additives

row number	phenyldehydrogenation products trichlorobiphenyls :-			phenyldechlorination products dichlorobiphenyls :-			partial rate factors for :-					
	2,3,6-	2,3,5-	2,4,5-	2,4-	2,5-	3,4-	phenyldehydrogenation			phenyldechlorination		
	yield (%)	yield (%)	yield (%)	yield (%)	yield (%)	yield (%)	f_3	f_6	f_5	f_1	f_2	f_4
1[a]	33.6	14.6	6.4	4.0	2.6	2.2	3.34	1.45	0.68	0.41	0.26	0.22
2[b]	46.1	21.3	8.2	5.2	3.3	3.2	4.42	2.04	0.78	0.51	0.32	0.31
3[c]	50.0	22.4	9.1	5.9	3.9	3.8	4.63	2.10	0.84	0.54	0.36	0.34
4[d]	52.8	24.2	10.6	6.5	4.2	4.5	4.84	2.22	0.98	0.59	0.38	0.41

yields are in mole per mole peroxide x 100

each row is a mean of four or more figures

a = no additive

b = additive copper benzoate, 0.1 g.

c = additive iron powder, 0.1 g.

d = additive trichloroacetic acid, 0.1 g.

5.3.6 THE EFFECT OF ADDITIVES

The presence of various additives in the phenylation of 1,2,4-trichlorobenzene increased the yield of 2,3,6-, 2,3,5- and 2,4,5-trichlorobiphenyls and of 2,4-, 2,5- and 3,4-dichlorobiphenyls, as shown in Table 5.28, at the expense of products of dimerisation and disproportionation.

The greatest effect was achieved when trichloroacetic acid was used as the additive and the poorest effect was with copper benzoate.

As shown in Table 5.28, the partial rate factors for the phenylation of 1,2,4-trichlorobenzene for phenyldehydrogenation without additive were $f_3 = 3.34$, $f_6 = 1.45$, $f_5 = 0.68$ which were increased to $f_3 = 4.84$, $f_6 = 2.22$, $f_5 = 0.98$ in the presence of trichloroacetic acid.

A small increase was observed in the partial rate factor values for phenyldechlorination of 1,2,4-trichlorobenzene from $f_1 = 0.41$, $f_2 = 0.26$ and $f_4 = 0.22$ without additive to $f_1 = 0.59$, $f_2 = 0.38$ and $f_4 = 0.41$ in the presence of trichloroacetic acid.

CHAPTER SIX

PHENYLATION REACTIONS OF TETRACHLOROBENZENES

6.1 METHOD OF PHENYLATION OF 1,2,3,5-TETRACHLOROBENZENE

This was the same as has been described in section 3.1. Sections 6.1.1 to 6.1.3 show the chromatograms obtained and their identification followed by tables listing experimental quantities leading to tables of results tabulating partial rate factors and yields.

6.1.1 CHROMATOGRAMS

Figures 6.1 to 6.4 show actual chromatograms obtained. Figure 6.5 shows a reconstructed chromatogram demonstrating the relationship between the products obtained.

6.1.2 PEAK IDENTIFICATION

The same method was used as has been explained in section 3.3

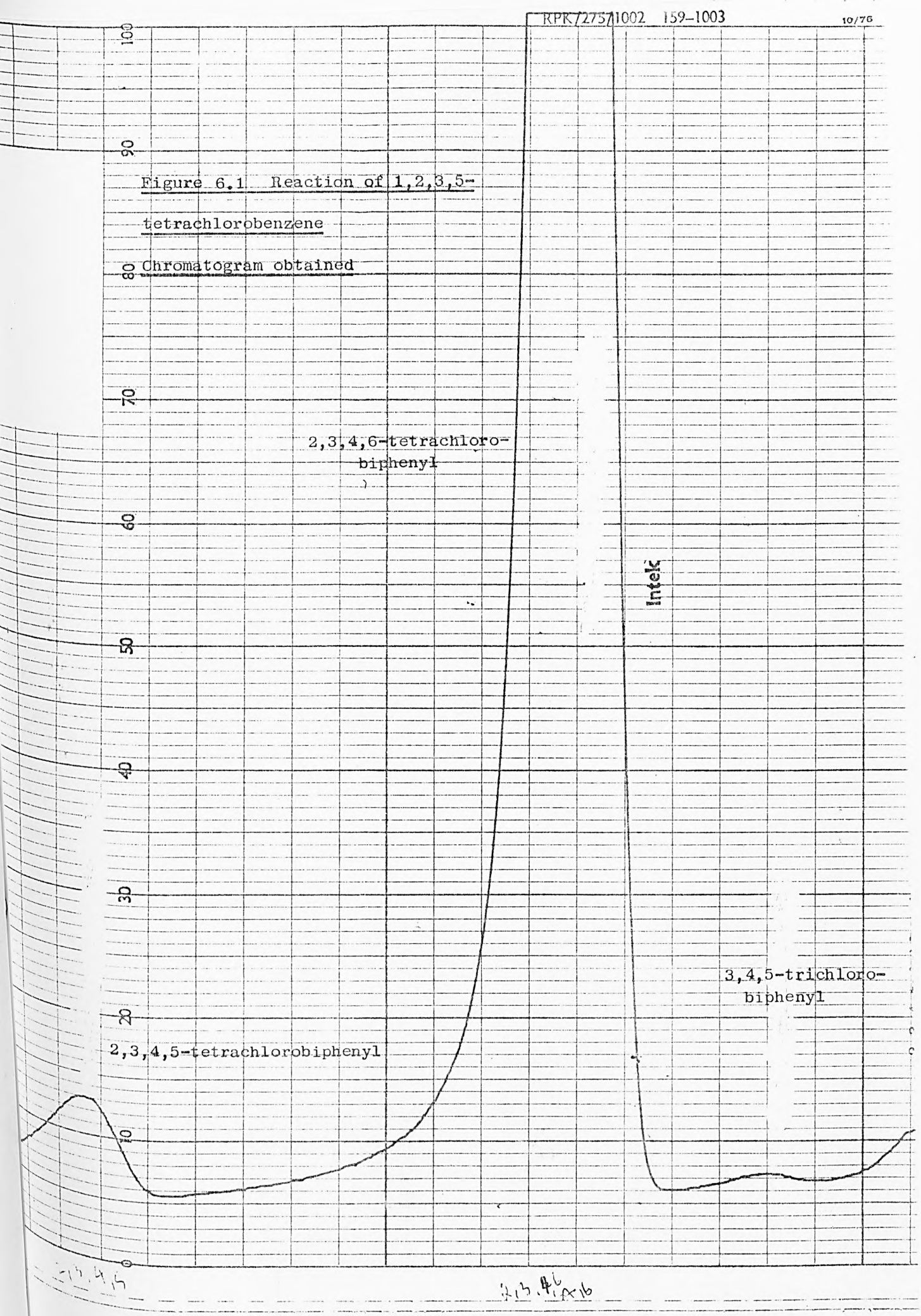


Figure 6.1 Reaction of 1,2,3,5-tetrachlorobenzene

Chromatogram obtained

Figure 6.2 Reaction of 1,2,3,5-tetrachlorobenzene

Chromatogram obtained

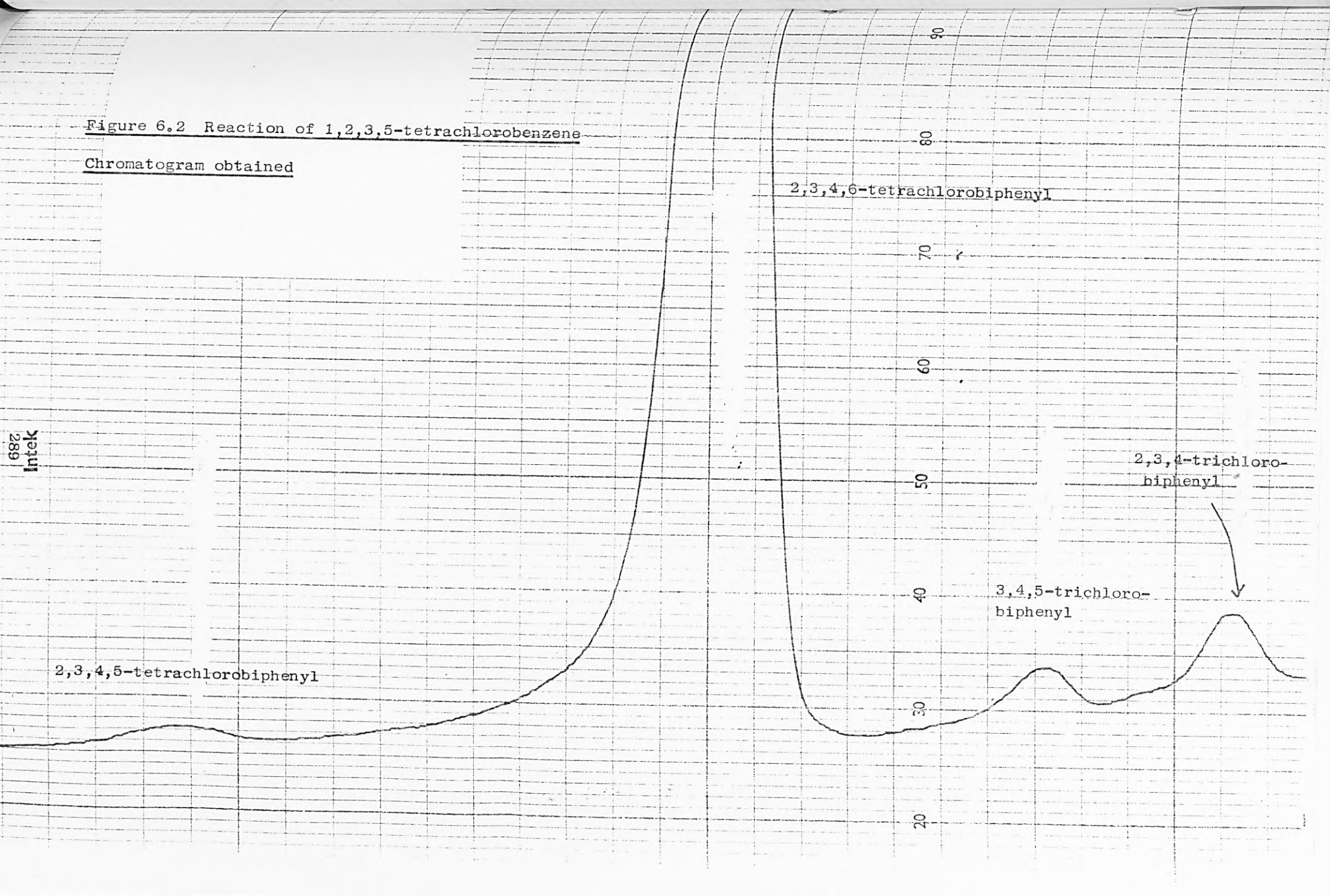
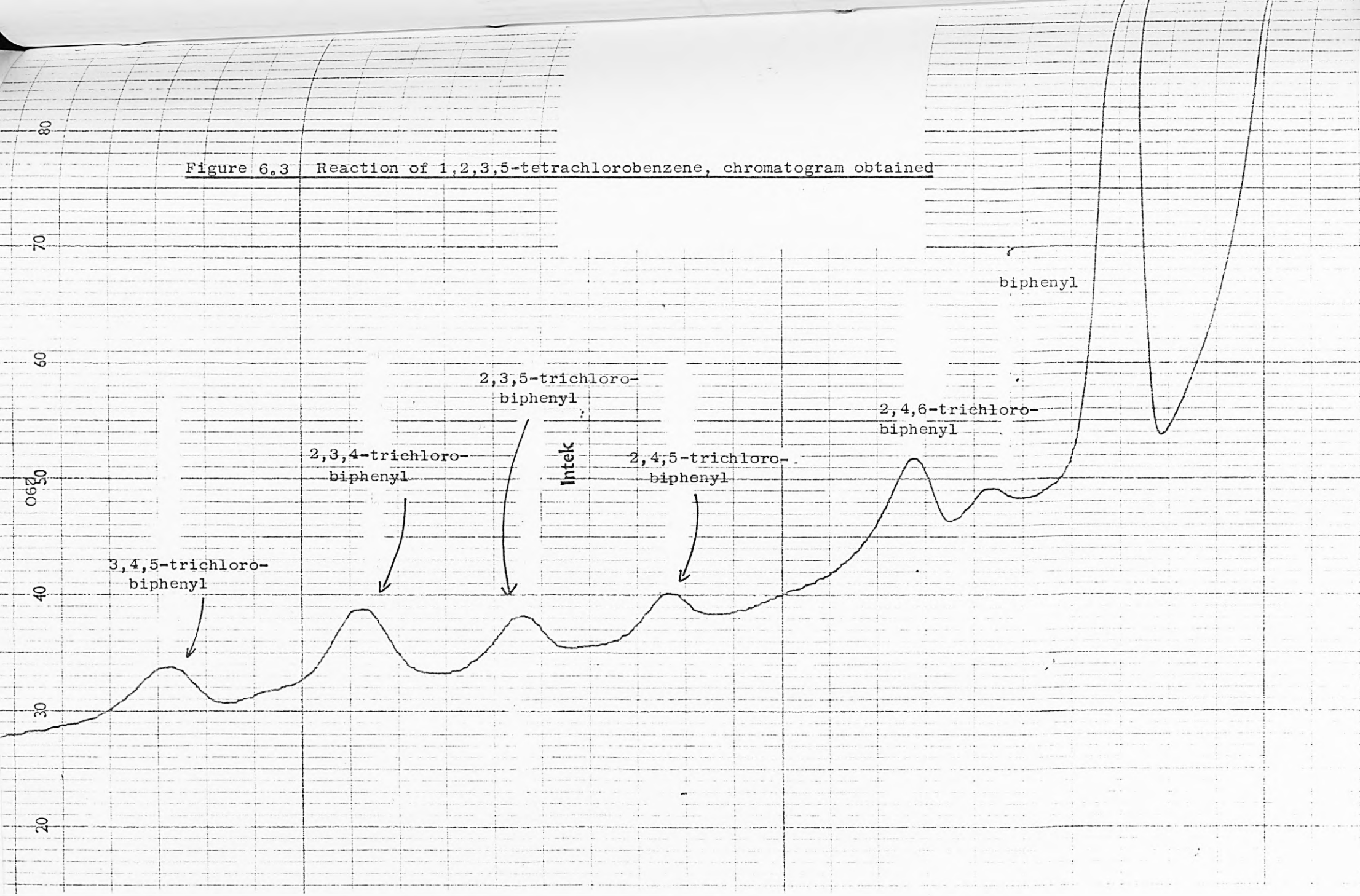


Figure 6.3 Reaction of 1,2,3,5-tetrachlorobenzene, chromatogram obtained



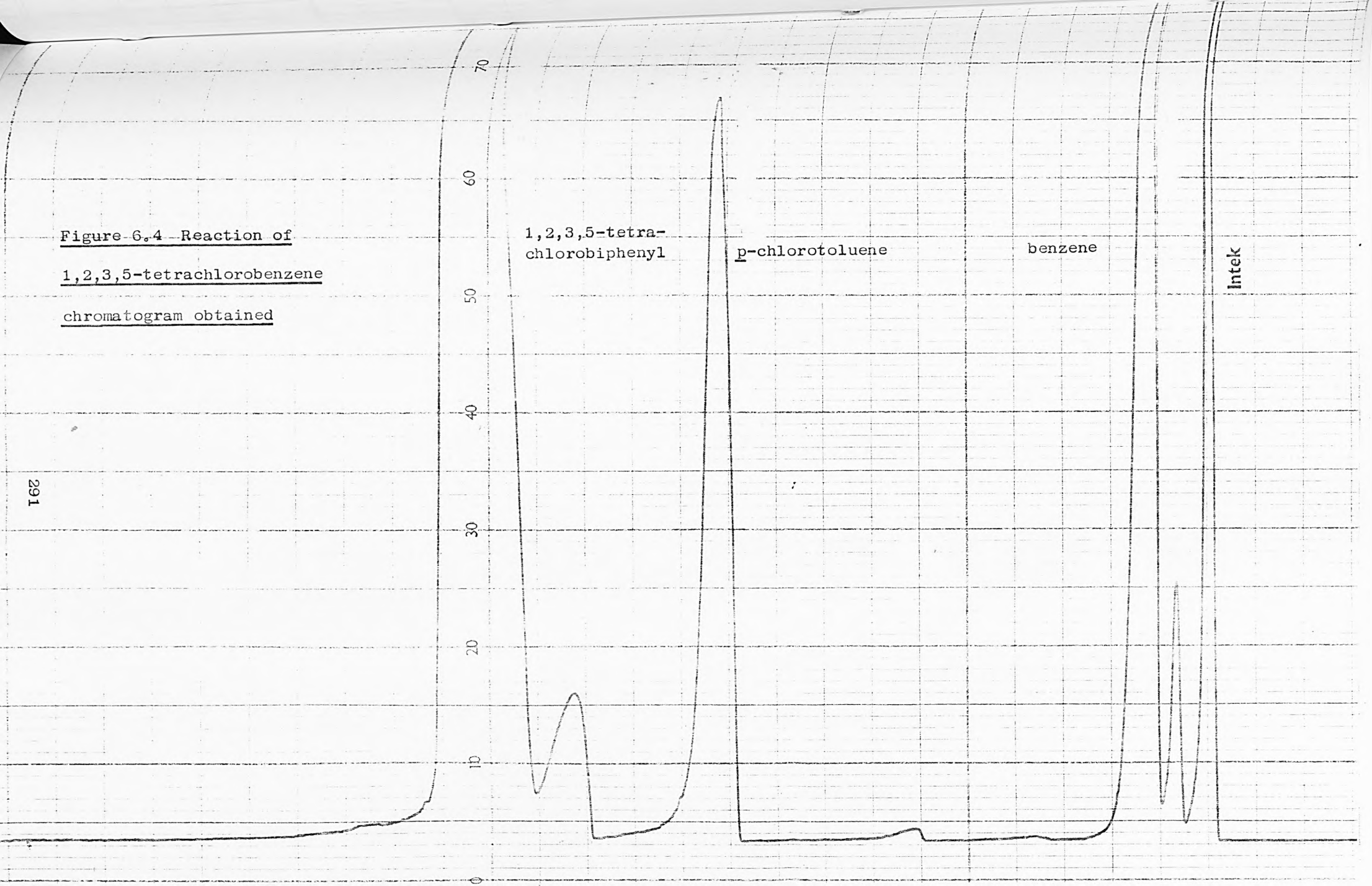


Figure 6.4 Reaction of

1,2,3,5-tetrachlorobenzene

chromatogram obtained

Figure 6.5 Reaction of 1,2,3,5-tetrachlorobenzene, reconstructed chromatogram

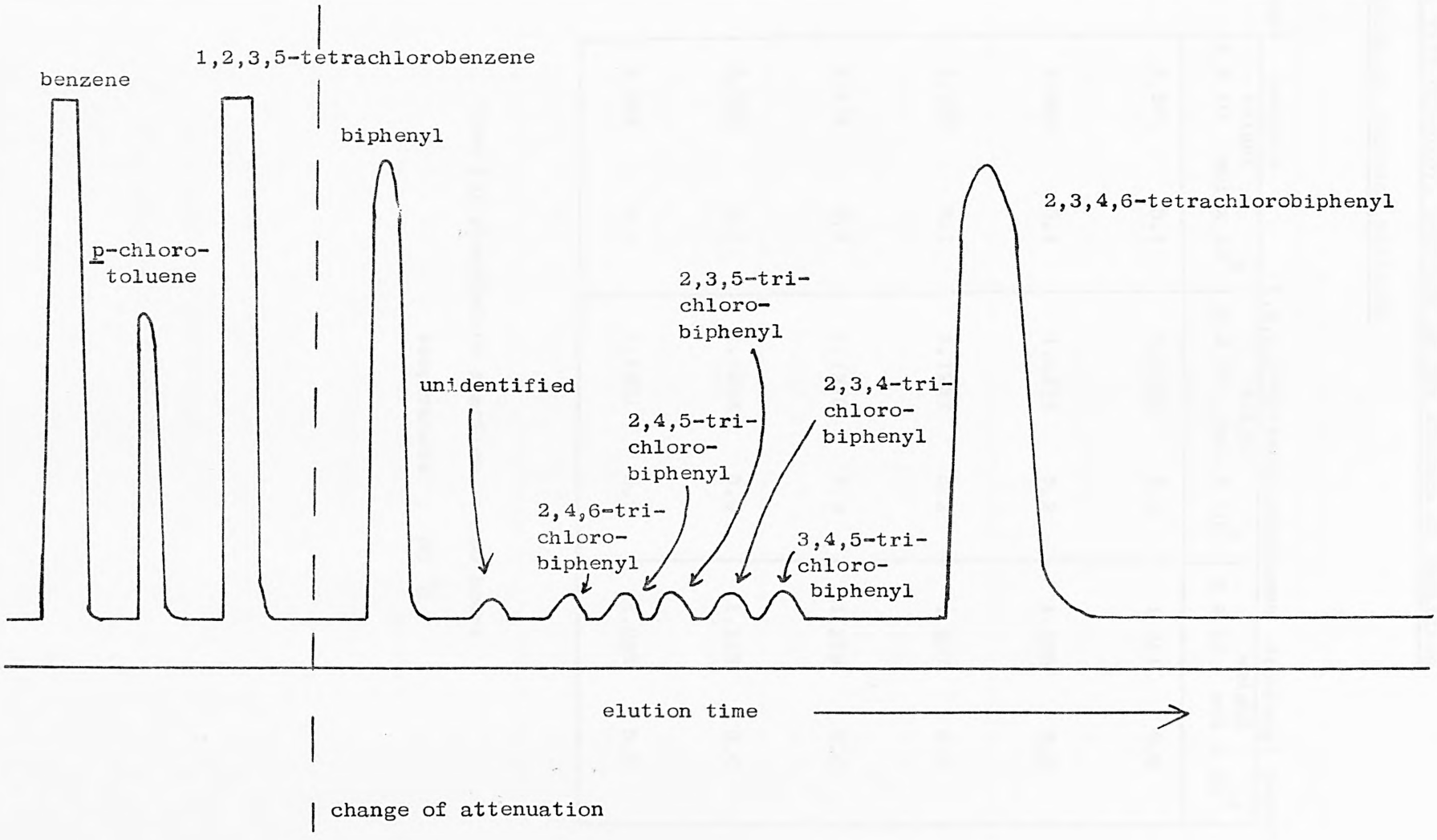


Table 6.1 Sealed tube reactions of 1,2,3,5-tetrachlorobenzene and benzene with dibenzoyl peroxide in the absence of additives composition of reaction mixtures

experiment number	benzene		1,2,3,5-tetrachlorobenzene		dibenzoyl peroxide	
	weight g x 10	mol x 10^3	weight g x 10	mol x 10^3	weight g x 10	mol x 10^4
1	3.971	5.1	1.1266	5.2	1.211	5.0
2	3.964	5.1	1.1274	5.2	1.225	5.0
3	3.996	5.1	1.1257	5.2	1.237	5.0
4	3.978	5.1	1.1270	5.2	1.219	5.0
5	3.985	5.1	1.1263	5.2	1.228	5.0
6	3.969	5.1	1.1271	5.2	1.233	5.0

time for phenylation reaction : 50 hours

temperature : 80 °C

Table 6.2 Sealed tube phenylation reactions of 1,2,3,5-tetrachlorobenzene and benzene in the presence of additives - composition of reaction mixtures

experiment number	benzene		1,2,3,5-tetrachlorobenzene		dibenzoyl peroxide	
	weight		weight		weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	4.125	5.3	1.1448	5.3	1.244	5.0
2[a]	4.139	5.3	1.1425	5.3	1.237	5.0
3[a]	4.143	5.3	1.1416	5.3	1.241	5.0
4[a]	4.130	5.3	1.1433	5.3	1.252	5.0
5[b]	4.145	5.3	1.1453	5.3	1.233	5.0
6[b]	4.156	5.3	1.1456	5.3	1.245	5.0
7[b]	4.168	5.3	1.1461	5.3	1.227	5.0
8[b]	4.153	5.3	1.1459	5.3	1.239	5.0
9[c]	4.150	5.3	1.1442	5.3	1.244	5.0
10[c]	4.142	5.3	1.1450	5.3	1.230	5.0
11[c]	4.127	5.3	1.1437	5.3	1.254	5.0
12[c]	4.136	5.3	1.1445	5.3	1.246	5.0

time for phenylation reaction : 50 hours

temperature : 80 °C

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 6.3 Analysis of the phenylation reaction products of 1,2,3,5-tetrachlorobenzene and benzene in the absence of additives (Table 6.1 gives compositions)

experiment number	2,3,4,6-tetrachlorobiphenyl		trichlorobiphenyls 2,3,5-		2,4,6-		3,4,5		2,3,4-		2,4,5-		biphenyl		p-chlorotoluene internal std.	
	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	std. weight
1	0.0330	0.0681	0.0025	0.0045	0.0020	0.0036	0.0009	0.0017	0.0021	0.0040	0.0011	0.0019	0.0276	0.0350	0.1524	0.1682
2	0.0334	0.0685	0.0026	0.0047	0.0021	0.0039	0.0009	0.0018	0.0019	0.0036	0.0008	0.0015	0.0275	0.0348	0.1522	0.1671
3	0.0324	0.0660	0.0022	0.0040	0.0019	0.0034	0.0009	0.0017	0.0023	0.0044	0.0010	0.0017	0.0272	0.0340	0.1511	0.1644
4	0.0339	0.0698	0.0023	0.0042	0.0020	0.0036	0.0008	0.0016	0.0024	0.0046	0.0012	0.0021	0.0279	0.0354	0.1529	0.1686
5	0.0321	0.0664	0.0022	0.0040	0.0020	0.0037	0.0008	0.0016	0.0021	0.0039	0.0010	0.0018	0.0270	0.0344	0.1501	0.1660
6	0.0326	0.0673	0.0022	0.0040	0.0019	0.0035	0.0008	0.0016	0.0025	0.0048	0.0013	0.0023	0.0273	0.0346	0.1522	0.1678
response factors	1.87		1.65		1.66		1.76		1.72		1.63		1.15		1.00	

Table 6.4 Analysis of the phenylation reaction products of 1,2,3,5-tetrachlorobenzene and benzene in the presence of additives (Table 6.2 gives compositions)

experiment number	2,3,4,6-tetrachlorobiphenyl		trichlorobiphenyls										biphenyl		p-chlorotoluene internal std.	
			2,3,5-		2,4,6-		3,4,5-		2,3,4-		2,4,5-					
	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	cpd. weight	peak weight	std. weight
1[a]	0.0419	0.0865	0.0027	0.0050	0.0023	0.0042	0.0013	0.0025	0.0022	0.0042	0.0010	0.0018	0.0314	0.0350	0.1500	0.1654
2[a]	0.0415	0.0857	0.0028	0.0051	0.0022	0.0040	0.0012	0.0030	0.0024	0.0046	0.0009	0.0016	0.0308	0.0343	0.1516	0.1674
3[a]	0.0425	0.0873	0.0031	0.0056	0.0024	0.0043	0.0016	0.0030	0.0021	0.0040	0.0013	0.0023	0.0322	0.0357	0.1513	0.1662
4[a]	0.0421	0.0861	0.0029	0.0053	0.0023	0.0041	0.0012	0.0024	0.0023	0.0044	0.0011	0.0020	0.0320	0.0354	0.1542	0.1688
5[b]	0.0446	0.0921	0.0032	0.0059	0.0026	0.0047	0.0014	0.0028	0.0025	0.0048	0.0013	0.0024	0.0332	0.0370	0.1445	0.1596
6[b]	0.0453	0.0926	0.0032	0.0058	0.0025	0.0045	0.0014	0.0027	0.0027	0.0050	0.0011	0.0019	0.0332	0.0366	0.1470	0.1623
7[b]	0.0455	0.0933	0.0034	0.0062	0.0025	0.0047	0.0015	0.0029	0.0024	0.0045	0.0012	0.0021	0.0340	0.0376	0.1492	0.1635
8[b]	0.0444	0.0918	0.0032	0.0059	0.0025	0.0046	0.0014	0.0027	0.0027	0.0052	0.0014	0.0026	0.0326	0.0364	0.1461	0.1617
9[c]	0.0472	0.0968	0.0035	0.0063	0.0027	0.0049	0.0016	0.0030	0.0024	0.0045	0.0011	0.0020	0.0333	0.0368	0.1484	0.1626
10[c]	0.0466	0.0974	0.0033	0.0060	0.0026	0.0049	0.0015	0.0029	0.0022	0.0042	0.0009	0.0017	0.0330	0.0372	0.1429	0.1596
11[c]	0.0462	0.0958	0.0032	0.0059	0.0025	0.0046	0.0023	0.0026	0.0026	0.0049	0.0013	0.0023	0.0324	0.0363	0.1449	0.1608
12[c]	0.0470	0.0962	0.0034	0.0061	0.0026	0.0047	0.0025	0.0027	0.0028	0.0053	0.0011	0.0019	0.0331	0.0367	0.1491	0.1633

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 6.5 Partial rate factors and percentage yields for the phenylation of 1,2,3,5-tetrachlorobenzene (Table 6.1 gives compositions)

experiment number	biphenyl	2,3,4,6-tetrachlorobiphenyl		trichlorobiphenyls					
				2,3,5-		2,4,6-		3,4,5-	
	yield (%)	f_4	yield (%)	f_1	yield (%)	f_2	yield (%)	f_5	yield(%)
1	45.5	3.08	46.6	0.23	3.5	0.37	2.8	0.17	1.3
2	45.2	3.11	46.9	0.24	3.7	0.40	3.0	0.18	1.4
3	44.2	3.07	45.2	0.21	3.1	0.36	2.6	0.18	1.3
4	46.0	3.12	47.8	0.21	3.3	0.37	2.8	0.16	1.2
5	44.7	3.06	45.5	0.21	3.1	0.39	2.9	0.17	1.2
6	44.9	3.08	46.1	0.21	3.1	0.37	2.7	0.17	1.2
(mean values)	45.1	3.09	46.0	0.22	3.3	0.38	2.8	0.17	1.3

yields are in mole per mole peroxide x 100

Table 6.6 Partial rate factors and percentage yields for the phenylation of 1,2,3,5-tetrachlorobenzene in the presence of additives

(Table 6.2 gives compositions)

experiment number	biphenyl	2,3,4,6-tetrachlorobiphenyl		trichlorobiphenyls 2,3,5-		2,4,6-		3,4,5-	
	yield (%)	f_4	yield (%)	f_1	yield (%)	f_2	yield (%)	f_5	yield (%)
1[a]	46.5	3.91	59.3	0.26	3.9	0.43	3.3	0.26	1.9
2[a]	44.6	3.95	58.7	0.27	4.0	0.42	3.1	0.26	2.3
3[a]	46.4	3.87	59.8	0.28	4.4	0.43	3.3	0.25	2.3
4[a]	45.9	3.85	59.0	0.27	4.1	0.42	3.2	0.24	1.9
(mean values)[a]	45.6	3.89		0.27		0.43		0.25	
5[b]	48.1	3.94	63.1	0.29	4.6	0.46	3.7	0.27	2.2
6[b]	47.5	4.00	63.4	0.29	4.5	0.45	3.5	0.26	2.1
7[b]	48.8	3.92	63.9	0.30	4.8	0.45	3.7	0.27	2.3
8[b]	47.3	3.99	62.9	0.29	4.6	0.45	3.6	0.27	2.1
(mean values)[b]	47.9	3.96		0.29		0.45		0.27	
9[c]	47.8	4.16	66.3	0.31	4.9	0.48	3.8	0.29	2.3
10[c]	48.3	4.14	66.7	0.29	4.7	0.47	3.8	0.28	2.3
11[c]	47.1	4.17	65.6	0.29	4.6	0.46	3.6	0.26	2.0
12[c]	47.7	4.15	65.9	0.30	4.7	0.46	3.7	0.27	2.1
(mean values)[c]	47.7	4.15		0.30		0.47		0.27	

yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

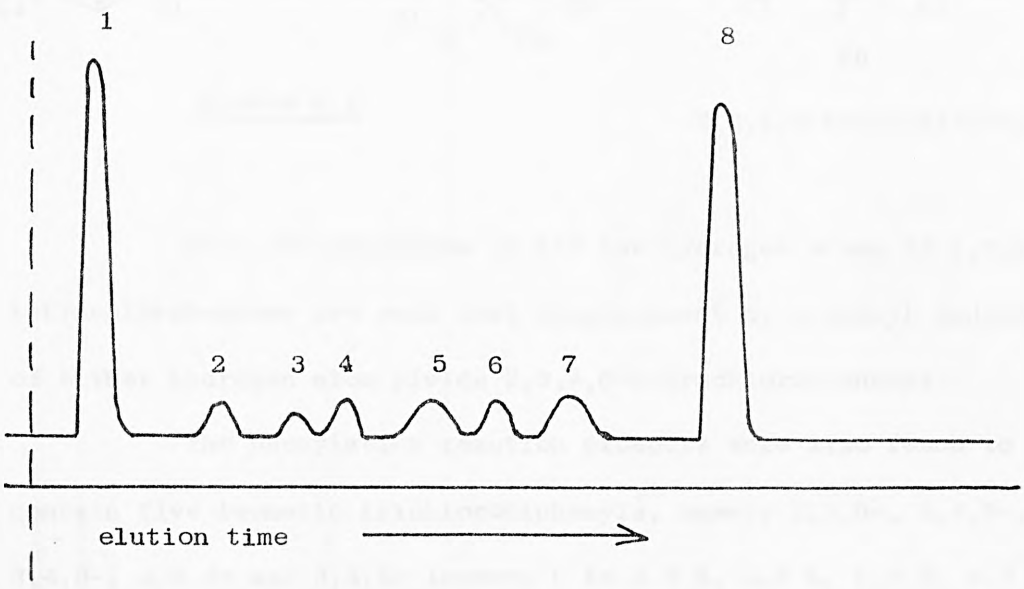
c = additive trichloroacetic acid, 0.1 g.

Table 6.7 Percentage yields of some by-products of the phenylation reaction of 1,2,3,5-tetrachlorobenzene

experiment number	yields of trichlorobiphenyls in the presence of additives :-							
	no additive		copper benzoate		iron powder		trichloroacetic acid	
	2,3,4- (%)	2,4,5- (%)	2,3,4- (%)	2,4,5- (%)	2,3,4- (%)	2,4,5- (%)	2,3,4- (%)	2,4,5- (%)
1	3.1	1.5	3.3	1.4	3.7	1.9	3.5	1.6
2	2.8	1.2	3.6	1.2	3.9	1.5	3.3	1.3
3	3.4	1.3	3.1	1.8	3.5	1.6	3.8	1.8
4	3.6	1.6	3.4	1.6	4.0	2.0	4.1	1.5
5	3.0	1.4	-	-	-	-	-	-
6	3.7	1.8	-	-	-	-	-	-
(mean values)	3.3	1.5	3.3	1.5	3.8	1.8	3.7	1.5

yields are in mole per mole peroxide x 100

Figure 6.6 Reconstructed chromatogram showing only products of the phenylation of 1,2,3,5-tetrachlorobenzene and benzene

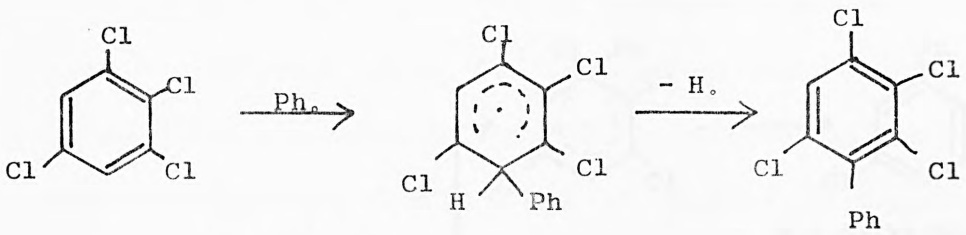


peak 1 = biphenyl

peak 2 = (unidentified)
peak 3 = 2,4,6-trichlorobiphenyl
peak 4 = 2,4,5-trichlorobiphenyl
peak 5 = 2,3,5-trichlorobiphenyl
peak 6 = 2,3,4-trichlorobiphenyl
peak 7 = 3,4,5-trichlorobiphenyl
peak 8 = 2,3,4,6-tetrachlorobiphenyl

The phenylation of 1,2,3,5-tetrachlorobenzene has not been reported in the literature. Sealed tube phenylation of 1,2,3,5-tetrachlorobenzene yielded a complex reaction mixture containing eight products. Phenyldehydrogenation was the dominant reaction with attack by phenyl radicals at C-4 or C-6 in 1,2,3,5-tetrachlorobenzene yielding 2,3,4,6-tetrachlorobiphenyl (in 46 % yield) as shown in Scheme 6.1.

phenyldehydrogenation



Scheme 6.1

2,3,4,6-tetrachlorobiphenyl

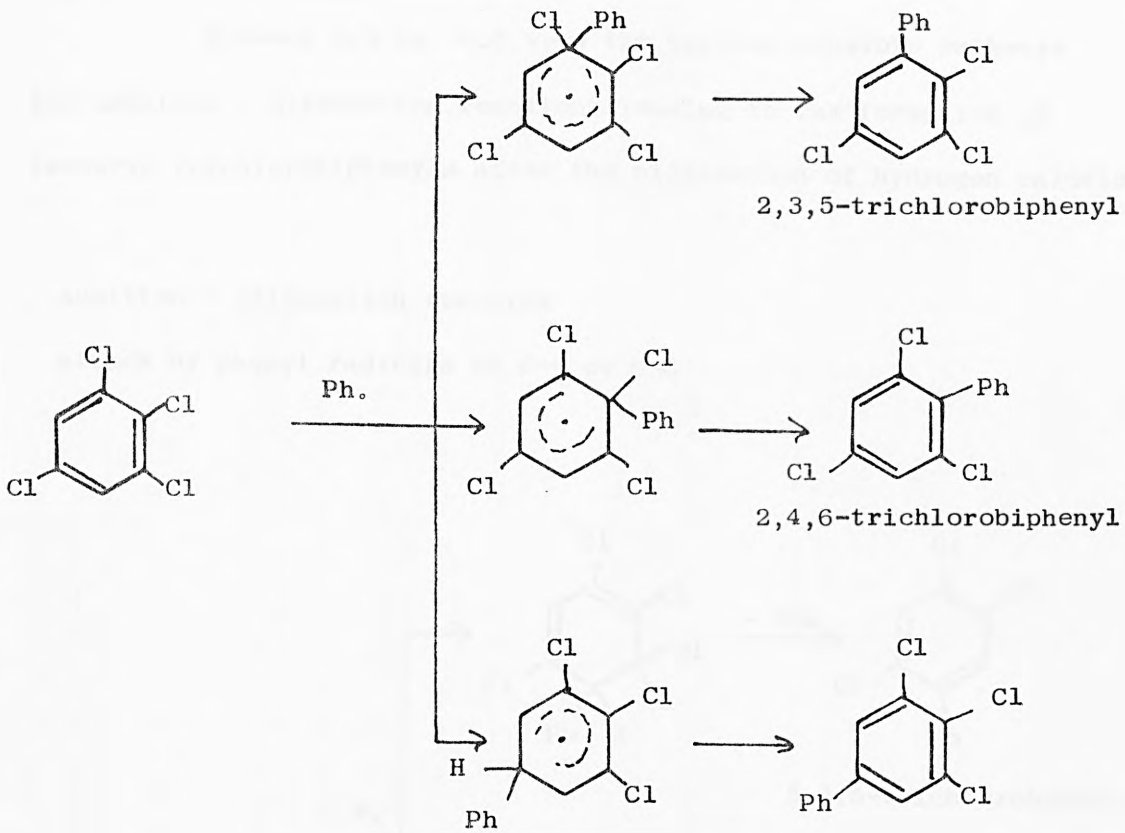
Thus the positions of the two hydrogen atoms in 1,2,3,5-tetrachlorobenzene are such that displacement by a phenyl radical of either hydrogen atom yields 2,3,4,6-tetrachlorobiphenyl.

The phenylation reaction products were also found to contain five isomeric trichlorobiphenyls, namely 2,3,5-, 2,4,6-, 3,4,5-, 2,3,4- and 3,4,5- isomers (in 3.3 %, 2.8 %, 1.3 %, 3.3 % and 1.5 % yields respectively). The presence of these isomeric trichlorobiphenyls was confirmed by g.l.c. retention data by comparison with authentic standards and by g.l.c.-mass spectrometry results (see Appendix). No g.l.c.-mass spectrometry evidence was found, however, for the presence of dichlorobiphenyl, dichloroterphenyl, trichloroterphenyl or tetrachloroterphenyl products.

It appears that as the number of chlorine atoms increase on the benzene ring, reactions such as phenyldechlorination by attack at C - Cl sites become more prevalent. The presence of 2,3,5-, 2,4,6 and 3,4,5-trichlorobiphenyls can be accounted for by phenyl-dechlorination reactions, involving phenyl radical attack at C - Cl sites followed by the elimination of chlorine. Statistically, the attack by a phenyl radical at a C - Cl site is favoured over attack at a C - H site, as there are four C - Cl positions.

Scheme 6.2 shows pathways for phenyldechlorination reactions

phenyldechlorination



Scheme 6.2

leading to the formation of 2,4,6-, 2,3,5- and 3,4,5-trichlorobiphenyls.

The phenylation of 1,2,3,5-tetrafluorobenzene (65) has been reported in the literature, yielding four products of phenylation only. The major reaction of phenyldehydrogenation (yielding 2,3,4,6-tetrafluorobiphenyl) and phenyldefluorination reactions (yielding 2,3,5-, 2,4,6- and 3,4,5-trifluorobiphenyls).

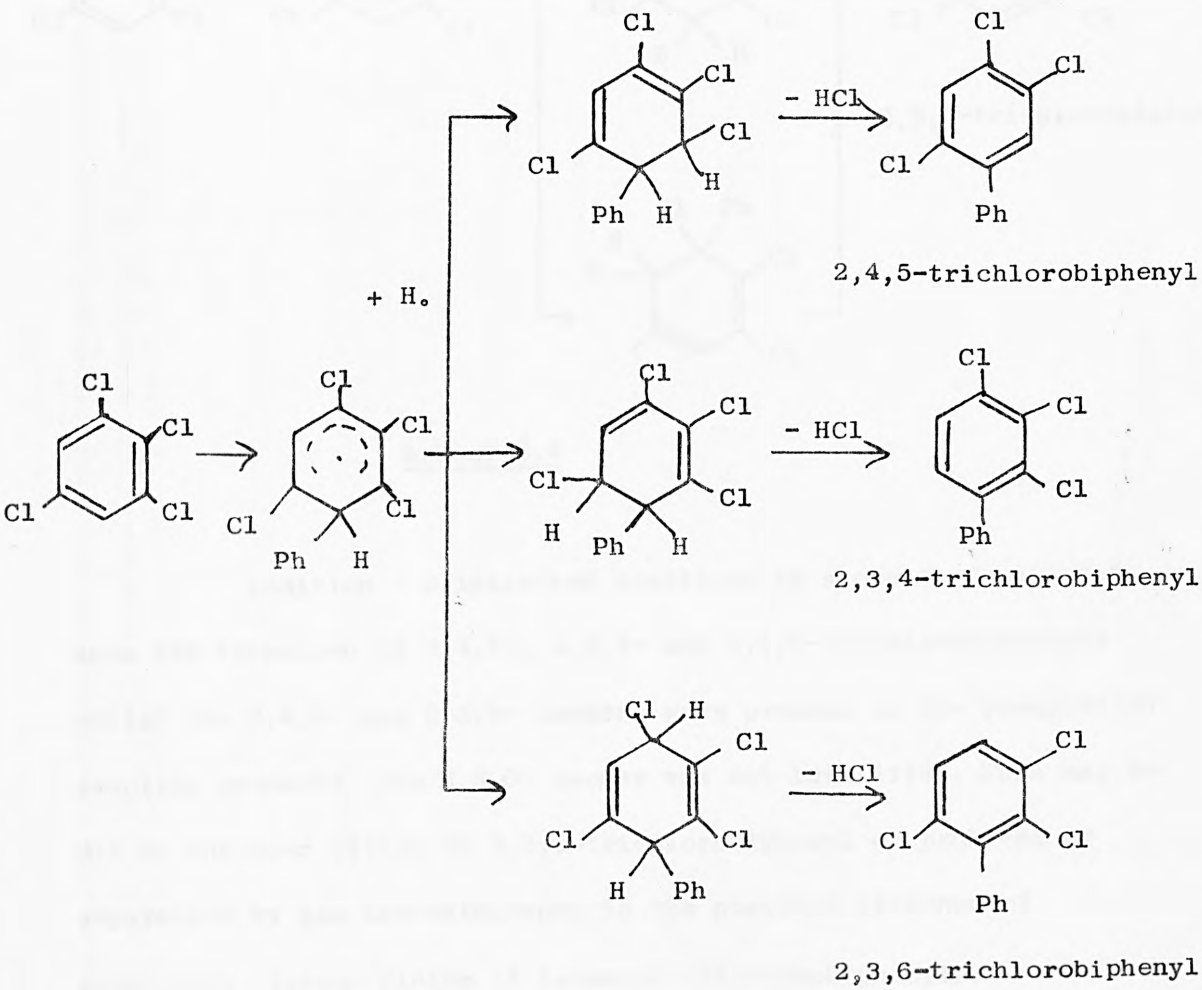
The additional presence of 2,3,4- and 2,4,5-trichlorobiphenyls (in 3.3 % and 1.5 % yields respectively) was novel and to account for their formation, it was considered that an addition - elimination reaction occurred. This type of reaction requires initial

attack at a C - H or C - Cl site by phenyl radicals and the take up of a hydrogen radical by the phenylcyclohexadienyl intermediate followed by the subsequent loss of hydrogen chloride.

Schemes 6.3 to 6.6 show the various possible pathways for addition - elimination reactions leading to the formation of isomeric trichlorobiphenyls after the elimination of hydrogen chloride.

addition - elimination reaction

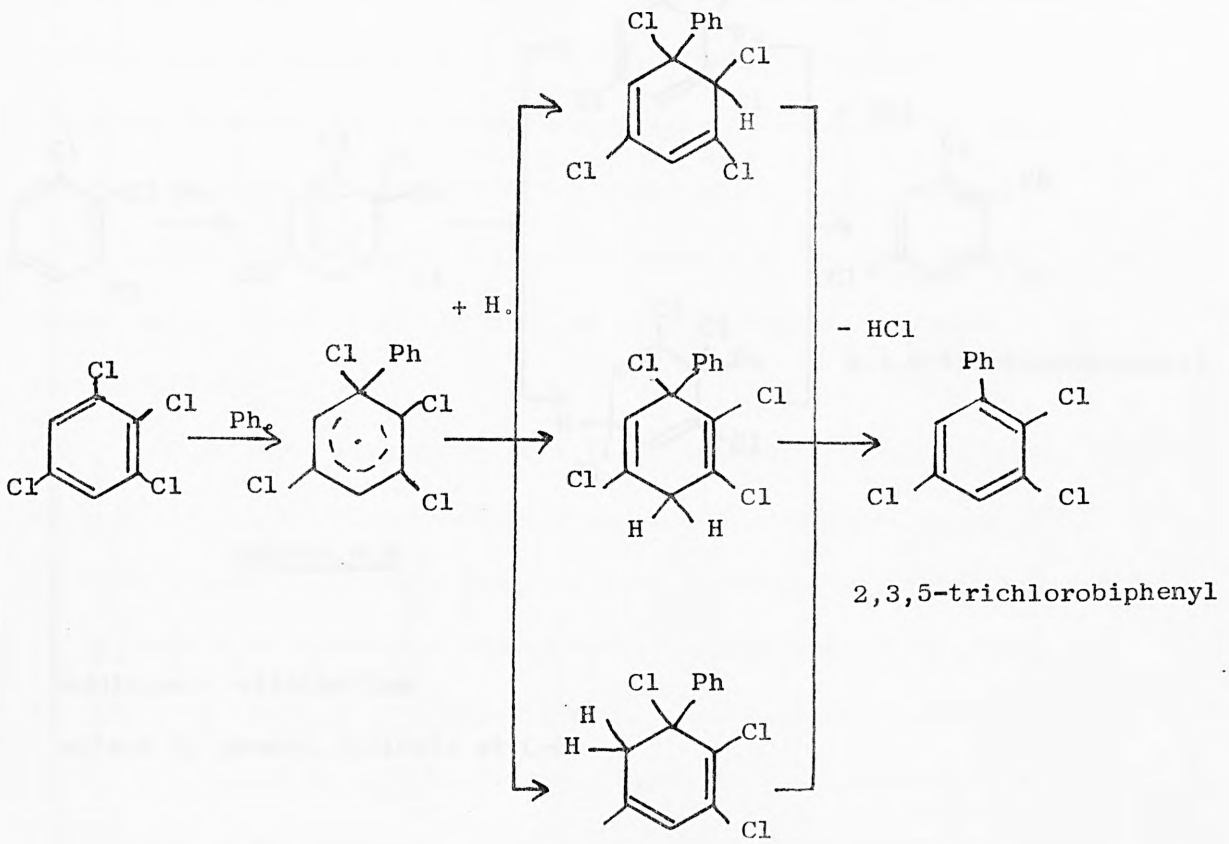
attack by phenyl radicals at C-4 or C-6



Scheme 6.3

addition - elimination

attack by phenyl radicals at C-1 or C-3



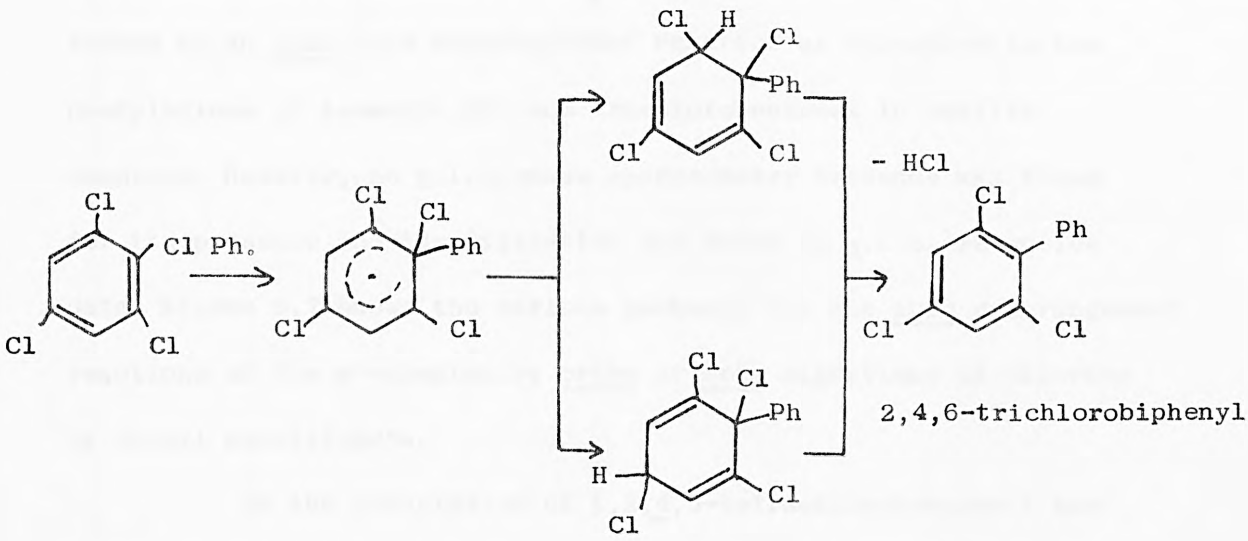
Scheme 6.4

Addition - elimination reactions as shown in Scheme 6.3 show the formation of 2,4,5-, 2,3,4- and 2,3,6-trichlorobiphenyls whilst the 2,4,5- and 2,3,4- isomers were present in the phenylation reaction products, the 2,3,6- isomer was not identified. This may be due to the poor yields of 2,3,6-trichlorobiphenyl or problems of separation by gas chromatography in the possible presence of relatively larger yields of isomeric trichlorobiphenyls.

Thus the reactions shown in Schemes 6.4, 6.5 and 6.6 lead to the formation of 2,3,5-, 2,4,6- and 3,4,5-trichlorobiphenyls by an alternative route to direct phenyldechlorination.

addition - elimination

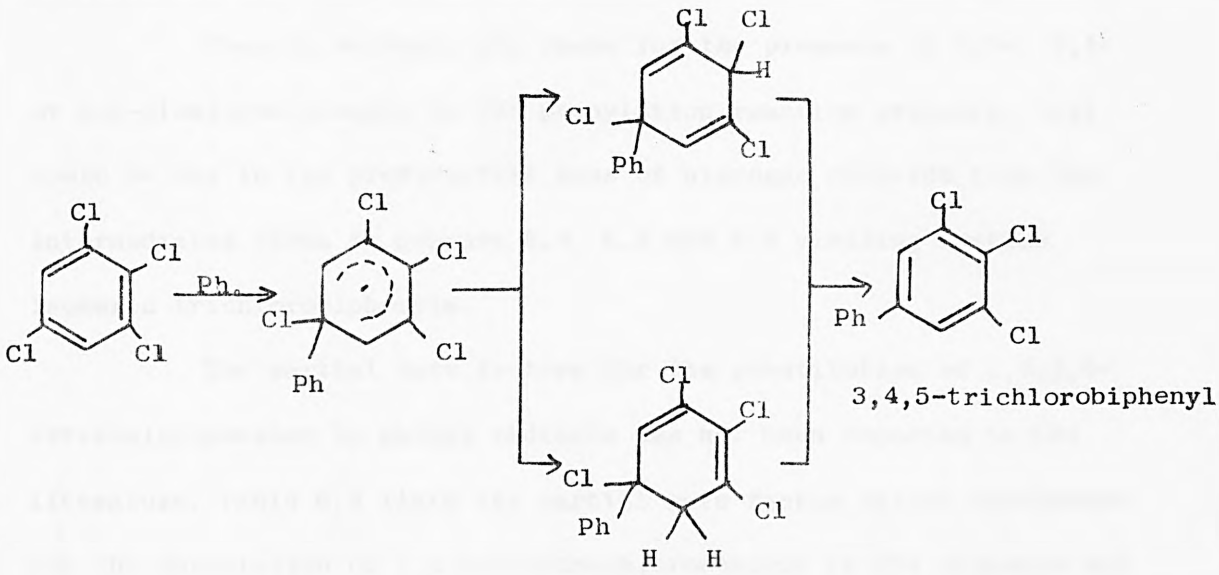
attack by phenyl radicals at C-2



Scheme 6.5

addition - elimination

attack by phenyl radicals at C-5



Scheme 6.6

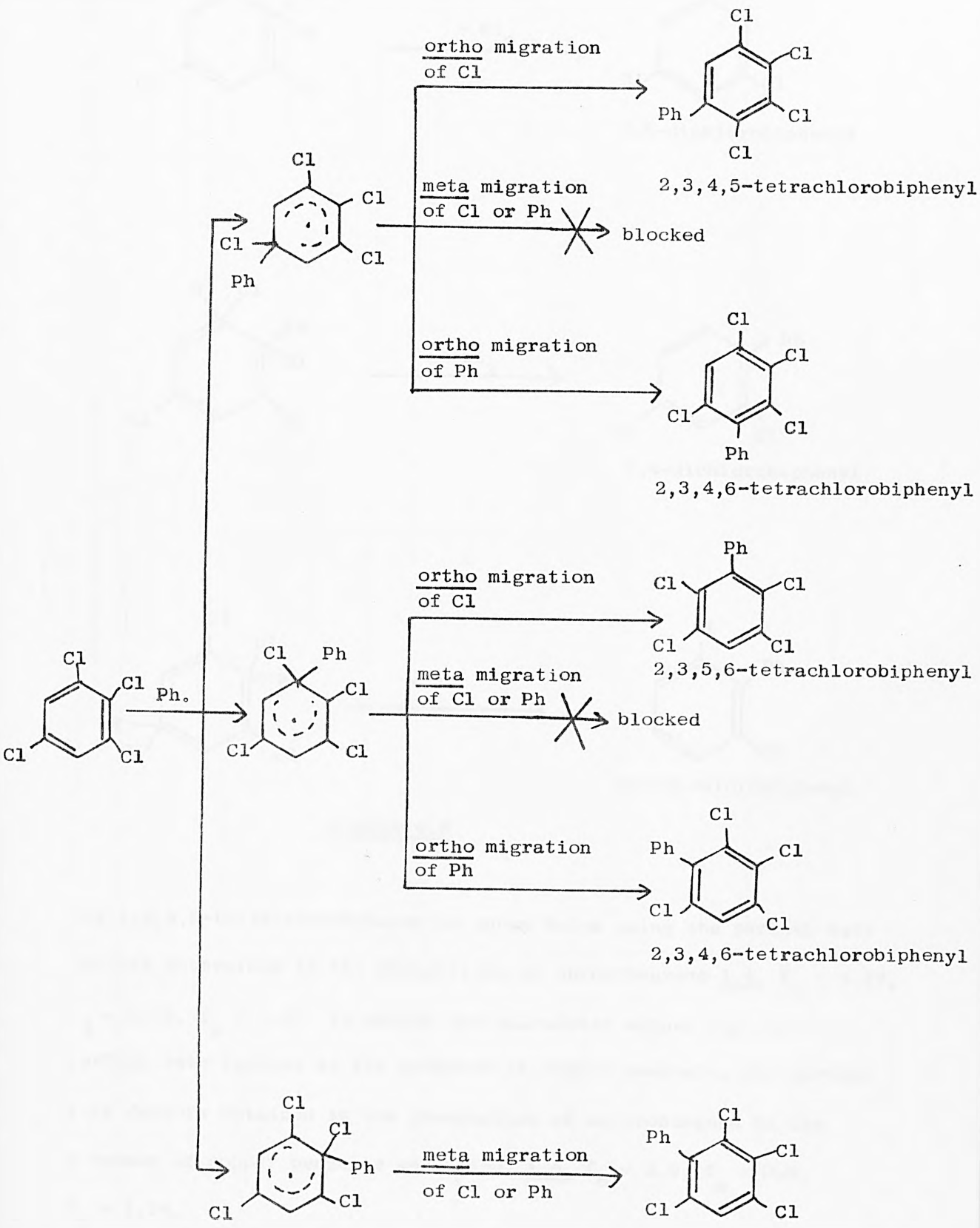
The sealed tube phenylation reaction of 1,2,3,5-tetrachlorobenzene gave rise to products that were also found to contain 2,3,5,6-tetrachlorobiphenyl (in $\not>$ 1 % yield) which could have been formed by an ipso type rearrangement reaction as discussed in the phenylations of isomeric di- and trichlorobenzenes in earlier chapters. However, no g.l.c.-mass spectrometry evidence was found for its presence and identification was based on g.l.c. retention data. Scheme 6.7 shows the various pathways for the ipso rearrangement reactions of the σ-complex by ortho or meta migrations of chlorine or phenyl substituents.

In the phenylation of 1,2,4,5-tetrachlorobenzene (see section 6.3) two isomeric dichlorobiphenyls were detected in the reaction products. No such products were found in the phenylation of 1,2,3,5-tetrachlorobenzene. These dichlorobiphenyls could have been formed by the loss of chlorine from the intermediates shown in Scheme 6.8, after the σ-complex had taken up a hydrogen atom in the course of an addition - elimination reaction as shown in Schemes 6.4, 6.5 and 6.6.

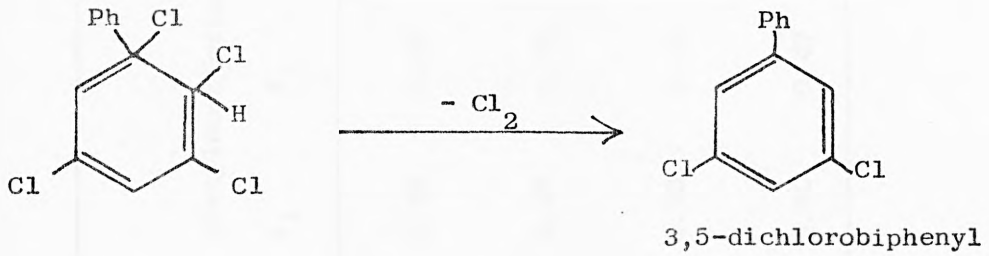
Thus no evidence was found for the presence of 3,5-, 2,4- or 2,6-dichlorobiphenyls in the phenylation reaction products, this could be due to the preferential loss of hydrogen chloride from the intermediates shown in Schemes 6.4, 6.5 and 6.6 yielding instead isomeric trichlorobiphenyls.

The partial rate factors for the substitution of 1,2,3,5-tetrachlorobenzene by phenyl radicals has not been reported in the literature. Table 6.8 lists the partial rate factor values determined for the phenylation of 1,2,3,5-tetrachlorobenzene in the presence and absence of additives. On applying Holleman's product rule as described in section 3.5, a calculated partial rate factor can be determined

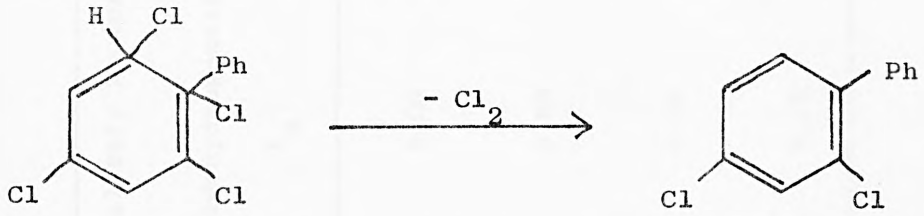
ipso rearrangement



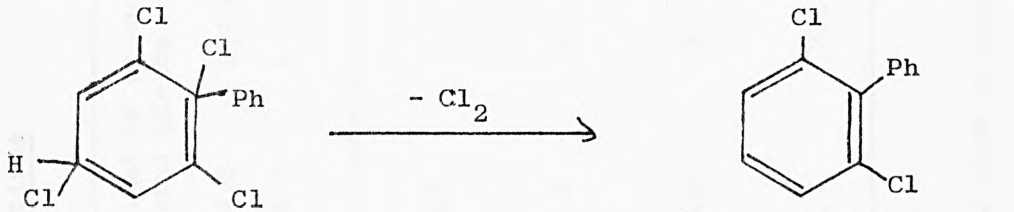
Scheme 6.7



3,5-dichlorobiphenyl



2,4-dichlorobiphenyl



2,6-dichlorobiphenyl

Scheme 6.8

for 1,2,3,5-tetrachlorobenzene as shown below using the partial rate factors determined in the phenylation of chlorobenzene i.e. $f_o = 1.97$, $f_m = 0.82$, $f_p = 1.07$. To obtain the calculated values for the partial rate factors in the presence of copper benzoate, the partial rate factors obtained in the phenylation of chlorobenzene in the presence of copper benzoate were used, i.e. $f_o = 2.9$, $f_m = 0.9$, $f_p = 1.24$.

Table 6.8 Partial rate factors and percentage yields for the phenylation of 1,2,3,5-tetrachlorobenzene in the absence and presence of additives

row number	phenyldehydrogenation product 2,3,4,6-tetrachlorobiphenyl yield (%)	phenyldechlorination products trichlorobiphenyl yields			partial rate factors for :-			
		2,3,5- (%)	2,4,6- (%)	3,4,5- (%)	phenyldehydrogenation f_4	phenyldechlorination f_1	f_2	f_5
1[a]	46.0	3.3	2.8	1.3	3.09	0.22	0.38	0.17
2[b]	59.2	4.1	3.2	2.1	3.89	0.27	0.43	0.25
3[c]	63.3	4.6	3.6	2.2	3.96	0.29	0.45	0.27
4[d]	65.9	4.7	3.7	2.2	4.15	0.30	0.47	0.27

each row of figures is a mean of four or more results

a = no additive

b = additive copper benzoate, 0.1 g.

c = additive iron powder, 0.1 g.

d = additive trichloroacetic acid, 0.1 g.

phenylation in the absence of additives,

f_4 = o-Cl x o-Cl x m-Cl x p-Cl

= 1.97 x 1.97 x 0.82 x 1.07

= 3.41 observed f_4 = 3.09

phenylation in the presence of copper benzoate,

f_4 = 2.9 x 2.9 x 0.9 x 1.24

= 9.29 observed f_4 = 3.89

As shown above, discrepancies exist between the calculated and observed partial rate factors.

Thus the observed partial rate factor value for position 4 without additive (f_4 = 3.09) reflects the effect of the proximity of two ortho, one meta and one para chlorine atom.

6.1.5 THE EFFECT OF ADDITIVES

The presence of various additives (namely copper benzoate, iron powder and trichloroacetic acid) in the phenylation of 1,2,3,5-tetrachlorobenzene increased the yield of 2,3,4,6-tetrachlorobiphenyl and the three isomeric trichlorobiphenyls as shown in Table 6.8 at the expense of higher products of dimerisation or disproportionation.

The largest increase in biaryl yields was achieved with trichloroacetic acid as the additive, whilst the lowest increase was obtained with the use of copper benzoate, as shown in Table 6.8.

Table 6.8 also shows the mean values for the partial rate factors determined for the phenylation of 1,2,3,5-tetrachlorobenzene for phenyldehydrogenation (hydrogen displacement by phenyl) and

phenyldechlorination (chlorine displacement by phenyl). The partial rate factor for phenyldehydrogenation was f_4 = 3.09 without additive, which was increased to f_4 = 4.15 in the presence of trichloroacetic aicd.

Similarly, a small increase was observed in the partial rate factors for phenyldechlorination in the presence of additives as shown in Table 6.8.

6.2 METHOD OF PHENYLATION OF 1,2,3,4-TETRACHLOROBENZENE

This was the same as has been described in section 3.1. Sections 6.2.1 to 6.2.3 show the chromatograms obtained and their identification followed by tables listing experimental quantities leading to tables of results tabulating partial rate factors and yields.

6.2.1 CHROMATOGRAMS

Figures 6.7, 6.8 and 6.9 show actual chromatograms obtained. Figure 6.10 shows a reconstructed chromatogram demonstrating the relationship between the products obtained.

6.2.2 PEAK IDENTIFICATION

The same method was used as has been explained in section 3.3.

Figure 6.7 Reaction of 1,2,3,4-tetrachlorobenzene

Chromatogram obtained

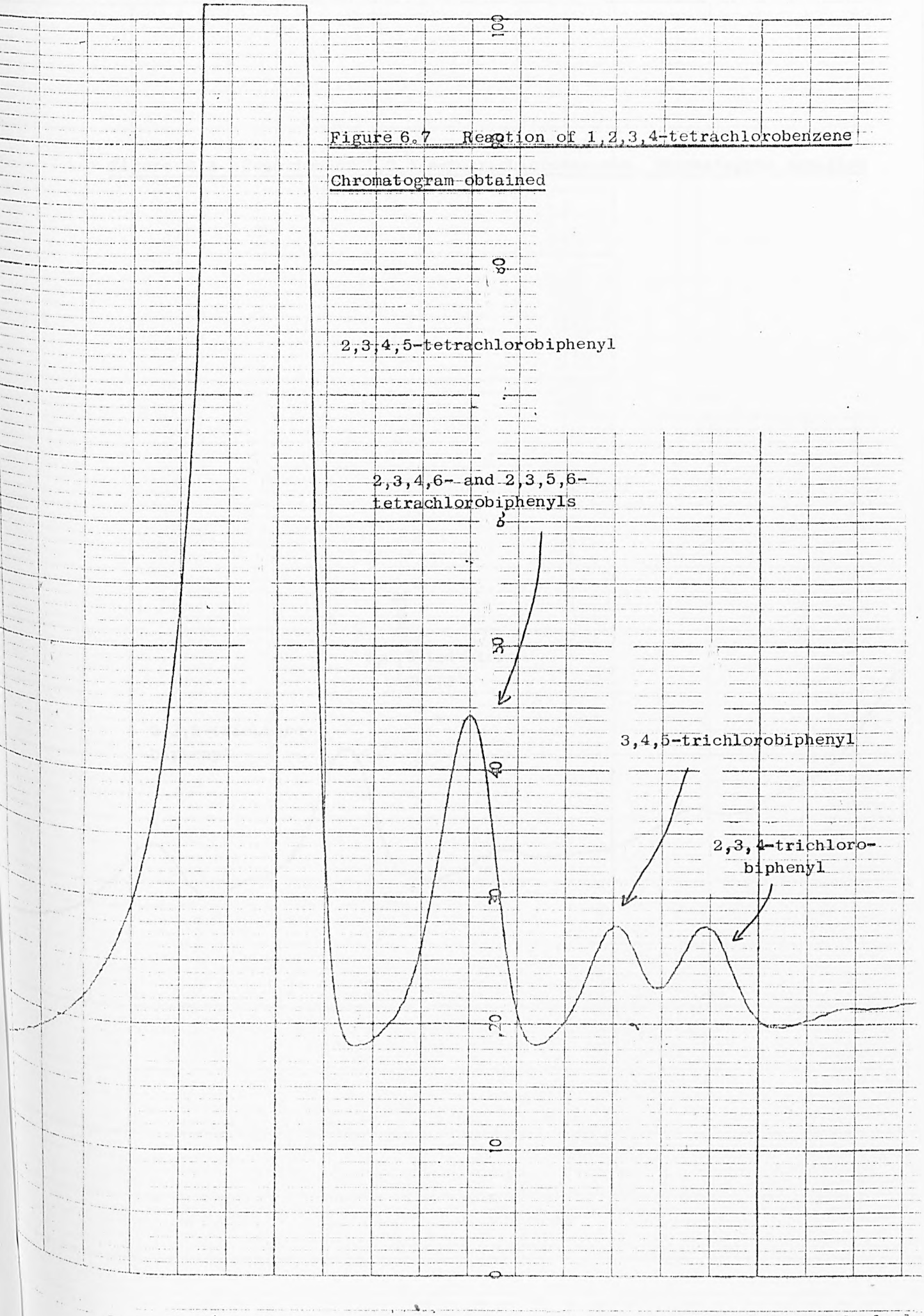


Figure 6.8 Reaction of 1,2,3,4-tetrachlorobenzene, chromatogram obtained

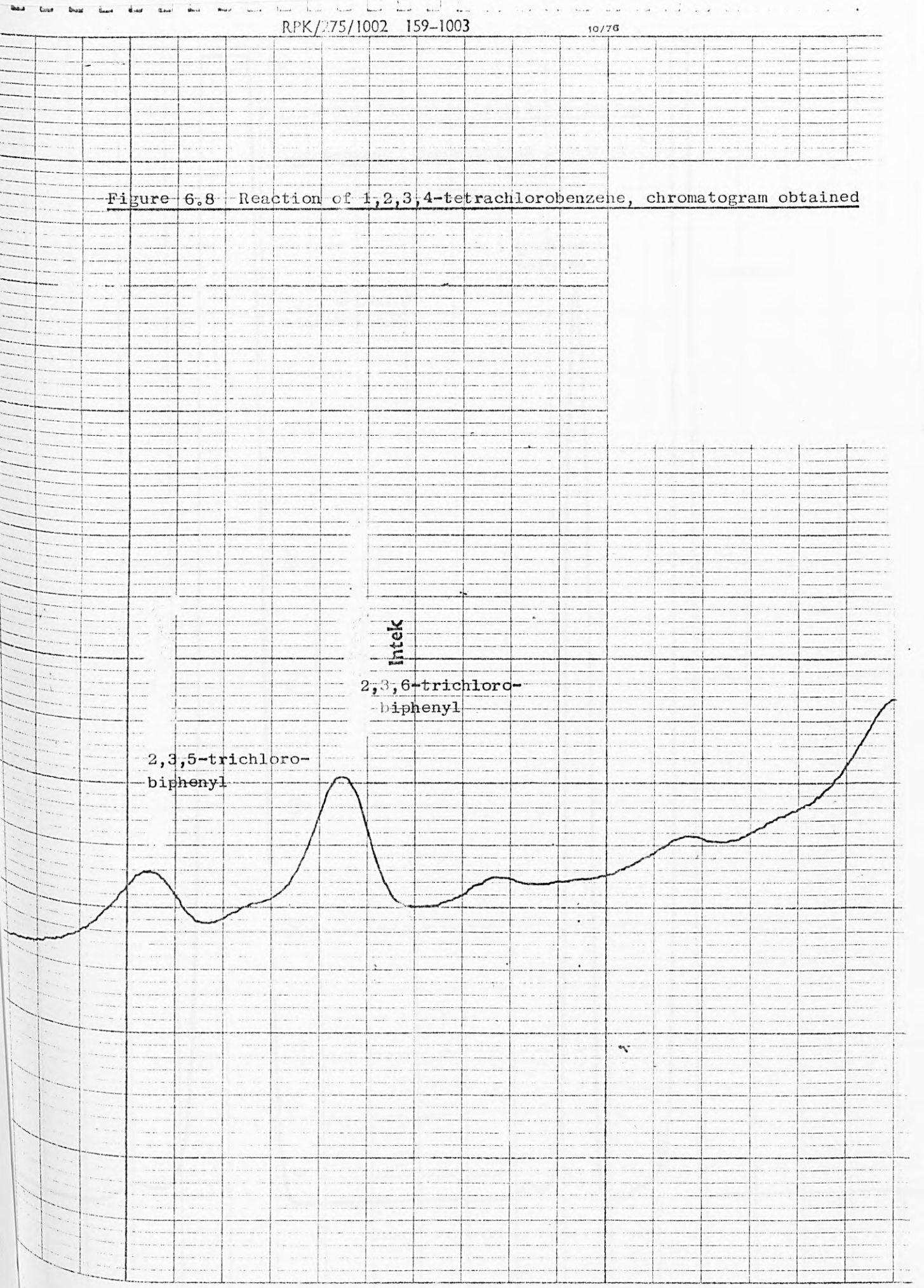


Figure 6.9 Reaction of 1,2,3,4-tetra-chlorobenzene, chromatogram obtained

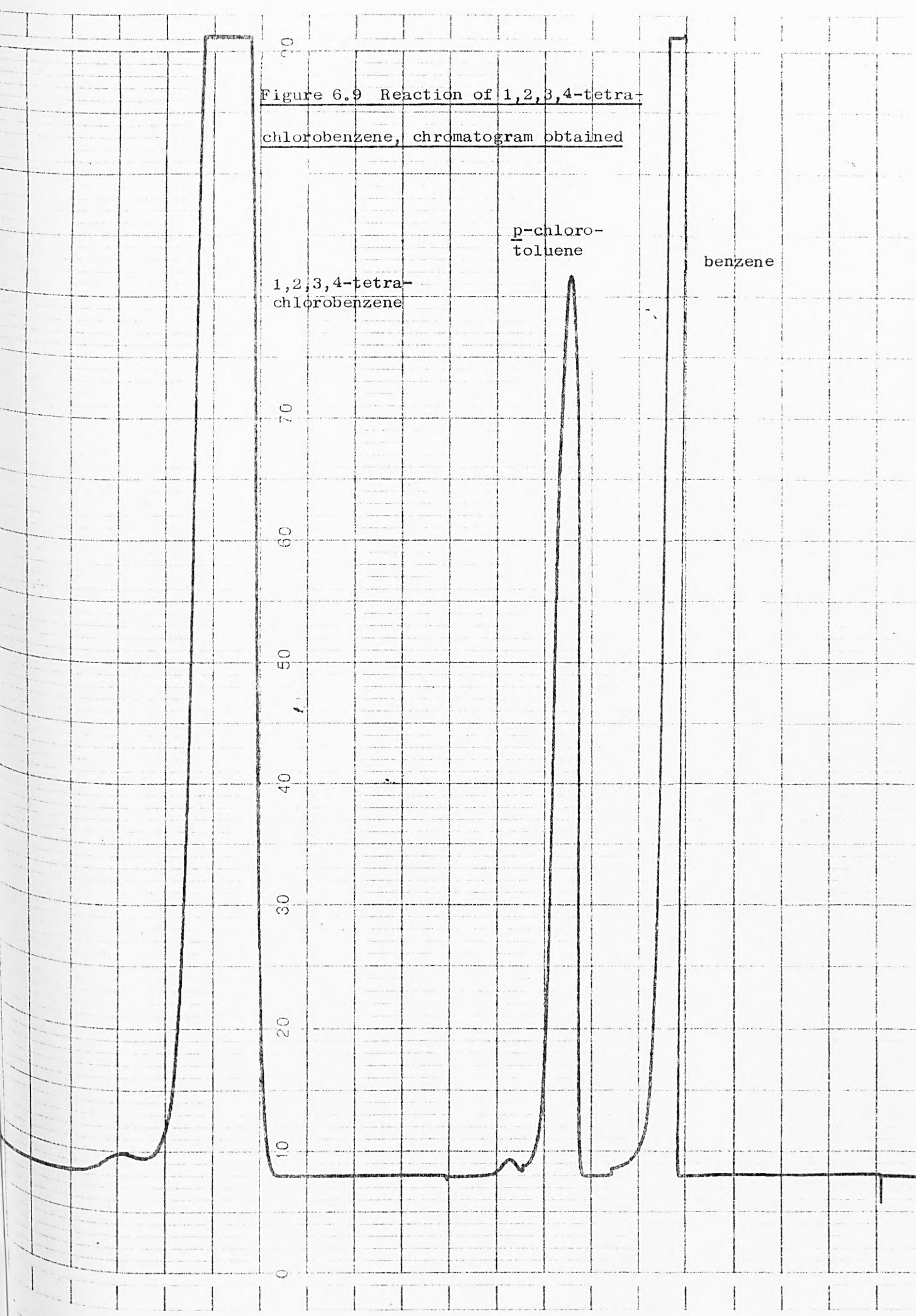


Figure 6.10 Reaction of 1,2,3,4-tetrachlorobenzene, reconstructed chromatogram

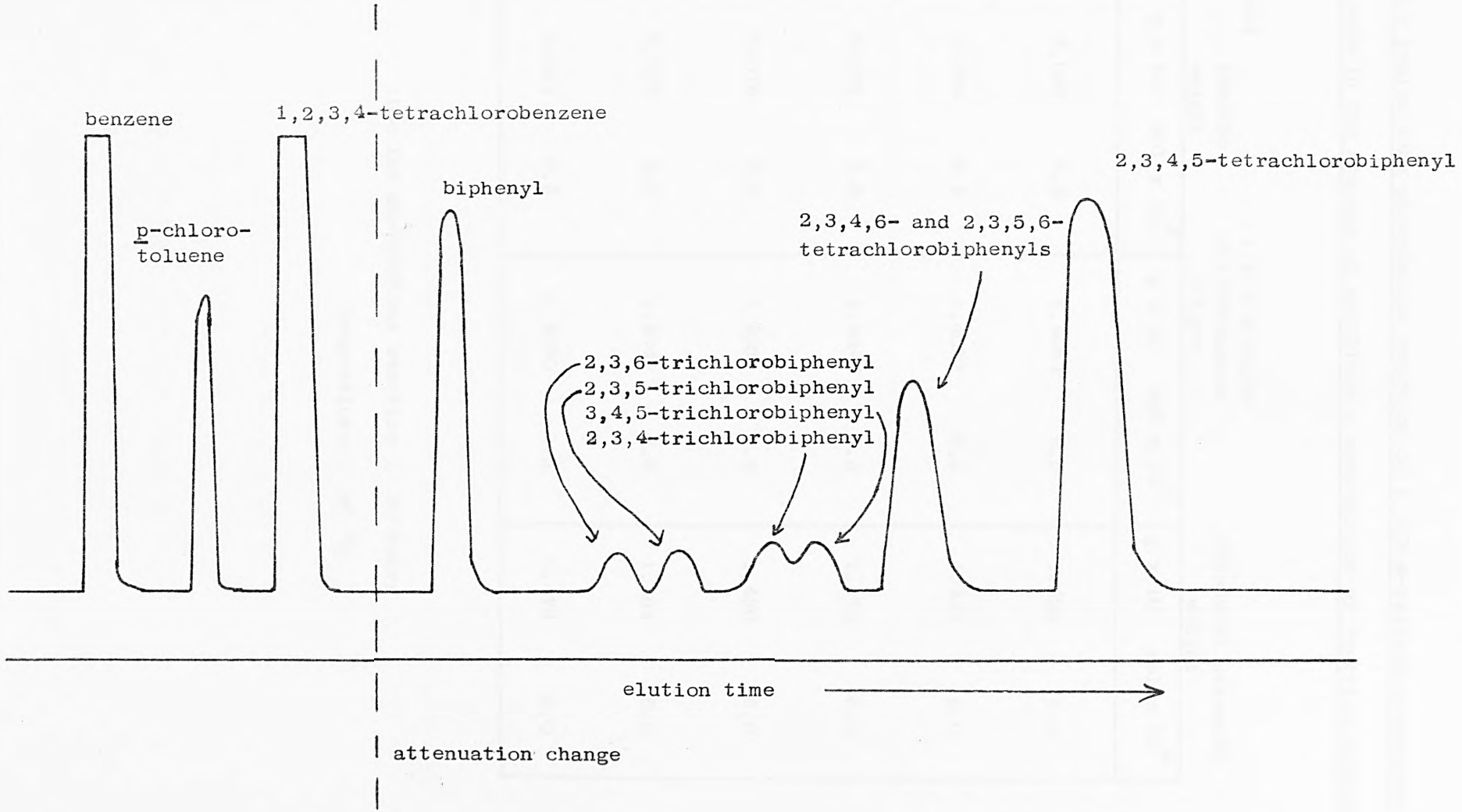


Table 6.9 Sealed tube phenylation reaction of 1,2,3,4-tetrachlorobenzene and benzene in the absence of additives - composition of reaction mixtures

experiment number	benzene weight		1,2,3,4-tetrachlorobenzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1	5.066	6.5	1.4064	6.5	1.425	6.0
2	5.049	6.5	1.4057	6.5	1.467	6.0
3	5.071	6.5	1.4042	6.5	1.473	6.0
4	5.078	6.5	1.4051	6.5	1.450	6.0
5	5.055	6.5	1.4046	6.5	1.464	6.0
6	5.061	6.5	1.4050	6.5	1.478	6.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

Table 6.10 Sealed tube phenylation reaction of 1,2,3,4-tetrachlorobenzene and benzene in the presence of additives - composition of reaction mixtures

experiment number	benzene		1,2,3,4-tetrachlorobenzene		dibenzoyl peroxide	
	weight		weight		weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	5.145	6.6	1.4261	6.6	1.471	6.0
2[a]	5.136	6.6	1.4254	6.6	1.453	6.0
3[a]	5.149	6.6	1.4263	6.6	1.466	6.0
4[a]	5.153	6.6	1.4268	6.6	1.459	6.0
5[b]	5.155	6.6	1.4181	6.6	1.475	6.0
6[b]	5.146	6.6	1.4177	6.6	1.467	6.0
7[b]	5.144	6.6	1.4185	6.6	1.455	6.0
8[b]	5.140	6.6	1.4173	6.6	1.454	6.0
9[c]	5.623	7.2	1.5557	7.2	1.684	6.0
10[c]	5.629	7.2	1.5548	7.2	1.694	6.0
11[c]	5.616	7.2	1.5552	7.2	1.699	6.0
12[c]	5.608	7.2	1.5563	7.2	1.680	6.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 6.11 Analysis of the phenylation reaction products of 1,2,3,4-tetrachlorobenzene and benzene in the absence of additives (Table 6.9 gives compositions)

experiment number	tetrachlorobiphenyls 2,3,4,5-		2,3,4,6- and 2,3,5,6-		trichlorobiphenyls 2,3,4-		2,3,6-		2,3,5-		3,4,5-		biphenyl		p-chloro-toluene internal std.	
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1	0.0296	0.0667	0.0055	0.0113	0.0032	0.0061	0.0043	0.0080	0.0031	0.0057	0.0019	0.0036	0.0359	0.0455	0.1461	0.1612
2	0.0290	0.0653	0.0057	0.0116	0.0032	0.0061	0.0042	0.0077	0.0034	0.0062	0.0017	0.0033	0.0353	0.0448	0.1448	0.1598
3	0.0292	0.0653	0.0054	0.0109	0.0031	0.0059	0.0044	0.0080	0.0030	0.0055	0.0020	0.0039	0.0354	0.0445	0.1483	0.1623
4	0.0293	0.0656	0.0055	0.0111	0.0032	0.0061	0.0045	0.0083	0.0033	0.0060	0.0021	0.0041	0.0357	0.0451	0.1461	0.1605
5	0.0296	0.0666	0.0052	0.0107	0.0032	0.0060	0.0044	0.0080	0.0032	0.0058	0.0019	0.0037	0.0362	0.0459	0.1469	0.1619
6	0.0289	0.0650	0.0051	0.0105	0.0030	0.0058	0.0042	0.0077	0.0030	0.0054	0.0018	0.0035	0.0351	0.0446	0.1445	0.1595
response factors	2.04		1.85		1.72		1.68		1.65		1.76		1.15		1.00	

Table 6.12 Analysis of the phenylation products of 1,2,3,4-tetrachlorobenzene and benzene in the presence of additives (Table 6.10 gives compositions)

experiment number	tetrachlorobiphenyls 2,3,4,5-		2,3,4,6- and 2,3,5,6-		trichlorobiphenyls 2,3,4-		2,3,6-		2,3,5-		3,4,5-		biphenyl		p-chloro-toluene internal std.	
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1[a]	0.0416	0.0940	0.0059	0.0121	0.0048	0.0091	0.0056	0.0105	0.0032	0.0058	0.0021	0.0041	0.0423	0.0474	0.1471	0.1631
2[a]	0.0415	0.0934	0.0057	0.0118	0.0045	0.0086	0.0060	0.0104	0.0036	0.0065	0.0024	0.0046	0.0418	0.0465	0.1463	0.1613
3[a]	0.0423	0.0951	0.0061	0.0124	0.0044	0.0083	0.0059	0.0110	0.0028	0.0061	0.0020	0.0038	0.0419	0.0467	0.1452	0.1601
4[a]	0.0414	0.0937	0.0060	0.0125	0.0047	0.0089	0.0055	0.0102	0.0034	0.0063	0.0023	0.0044	0.0418	0.0469	0.1437	0.1596
5[b]	0.0437	0.0985	0.0065	0.0132	0.0049	0.0093	0.0061	0.0114	0.0036	0.0065	0.0024	0.0046	0.0413	0.0460	0.1446	0.1596
6[b]	0.0444	0.0991	0.0064	0.0129	0.0049	0.0090	0.0060	0.0111	0.0033	0.0060	0.0021	0.0041	0.0422	0.0467	0.1472	0.1612
7[b]	0.0441	0.0995	0.0060	0.0123	0.0047	0.0090	0.0062	0.0116	0.0032	0.0058	0.0022	0.0044	0.0424	0.0473	0.1466	0.1620
8[b]	0.0440	0.0983	0.0066	0.0133	0.0046	0.0088	0.0059	0.0110	0.0034	0.0062	0.0025	0.0049	0.0417	0.0461	0.1483	0.1625
9[c]	0.0458	0.1026	0.0069	0.0141	0.0053	0.0100	0.0065	0.0120	0.0038	0.0069	0.0027	0.0052	0.0408	0.0453	0.1426	0.1567
10[c]	0.0460	0.1034	0.0066	0.0135	0.0052	0.0099	0.0062	0.0116	0.0040	0.0073	0.0029	0.0056	0.0409	0.0455	0.1437	0.1583
11[c]	0.0461	0.1038	0.0071	0.0146	0.0052	0.0098	0.0063	0.0116	0.0036	0.0065	0.0026	0.0050	0.0411	0.0458	0.1425	0.1573
12[c]	0.0466	0.1044	0.0068	0.0139	0.0052	0.0099	0.0063	0.0117	0.0039	0.0071	0.0025	0.0048	0.0414	0.0459	0.1420	0.1559

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 6.13 Partial rate factors and percentage yields for the phenylation of 1,2,3,4-tetrachlorobenzene (Table 6.9 gives compositions)

experiment number	biphenyl	2,3,4,5-tetrachlorobiphenyl		trichlorobiphenyls 2,3,4-		2,3,6-	
	yield (%)	f_5	yield (%)	f_1	yield (%)	f_2	yield (%)
1	49.0	2.32	38.1	0.24	4.0	0.31	5.2
2	48.0	2.31	37.3	0.25	4.0	0.31	5.0
3	48.0	2.32	37.3	0.24	3.8	0.32	5.2
4	49.0	2.30	37.4	0.24	4.0	0.33	5.4
5	50.0	2.29	38.0	0.24	3.9	0.31	5.2
6	48.0	2.31	37.1	0.23	3.8	0.31	5.0
(mean values)	48.8	2.31	37.5	0.24	3.9	0.32	5.2

yields are in mole per mole peroxide x 100

Table 6.14 Partial rate factors and percentage yields for the phenylation of 1,2,3,4-tetrachlorobenzene in the presence of additives

(Table 6.10 gives compositions)

experiment number	biphenyl	2,3,4,5-tetrachlorobiphenyl		trichlorobiphenyls 2,3,4-		2,3,6-	
	yield (%)	f_5	yield (%)	f_1	yield (%)	f_2	yield (%)
1[a]	51.3	3.13	53.7	0.35	5.9	0.40	6.8
2[a]	50.3	3.18	53.3	0.33	5.6	0.40	6.7
3[a]	50.5	3.22	54.3	0.32	5.4	0.42	7.1
4[a]	50.8	3.16	53.5	0.34	5.8	0.39	6.6
(mean values)[a]	50.7	3.17	53.7	0.33	5.7	0.40	6.8
5[b]	49.8	3.38	56.2	0.36	6.0	0.44	7.4
6[b]	50.5	3.36	56.6	0.35	5.8	0.43	7.2
7[b]	51.2	3.33	56.8	0.34	5.8	0.44	7.5
8[b]	50.0	3.38	56.1	0.35	5.7	0.43	7.2
(mean values)[b]	50.3	3.36	56.4	0.35	5.9	0.44	7.3
9[c]	42.0	3.58	58.6	0.40	6.5	0.48	7.8
10[c]	42.2	3.60	59.0	0.39	6.4	0.45	7.5
11[c]	42.5	3.59	59.3	0.38	6.3	0.45	7.5
12[c]	42.6	3.60	59.6	0.39	6.4	0.46	7.6
(mean values)[c]	42.3	3.59	59.1	0.39	6.4	0.46	7.6

yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 6.15 Percentage yields of some by-products of the phenylation reaction of 1,2,3,4-tetrachlorobenzene

experiment number	tetrachlorobiphenyls 2,3,4,6- and 2,3,5,6- yield (%)	trichlorobiphenyls 2,3,5- yield (%)	3,4,5- yield (%)
1	6.5	3.7	2.3
2	6.6	4.0	2.1
3	6.2	3.5	2.5
4	6.3	3.8	2.7
5	6.1	3.7	2.4
6	5.9	3.5	2.3
(mean values)	6.3	3.7	2.4

yields are in mole per mole peroxide x 100

6.16 Percentage yields of some by-products of the phenylation reaction of 1,2,3,4-tetrachlorobenzene in the presence of additives

experiment number	tetrachlorobiphenyls 2,3,4,6- and 2,3,5,6- yield (%)	trichlorobiphenyls 2,3,5- yield (%)	3,4,5- yield (%)
1[a]	6.9	3.8	2.7
2[a]	6.7	4.2	2.9
3[a]	7.1	3.9	2.4
4[a]	7.1	4.1	3.0
(mean values)	7.0	4.0	2.7
5[b]	7.5	4.2	3.0
6[b]	7.3	3.9	2.7
7[b]	7.0	3.8	2.9
8[b]	7.6	4.0	3.2
(mean values)	7.4	4.0	2.9
9[c]	6.9	3.8	2.9
10[c]	6.6	4.1	3.1
11[c]	7.1	3.6	2.7
12[c]	6.8	3.9	2.6

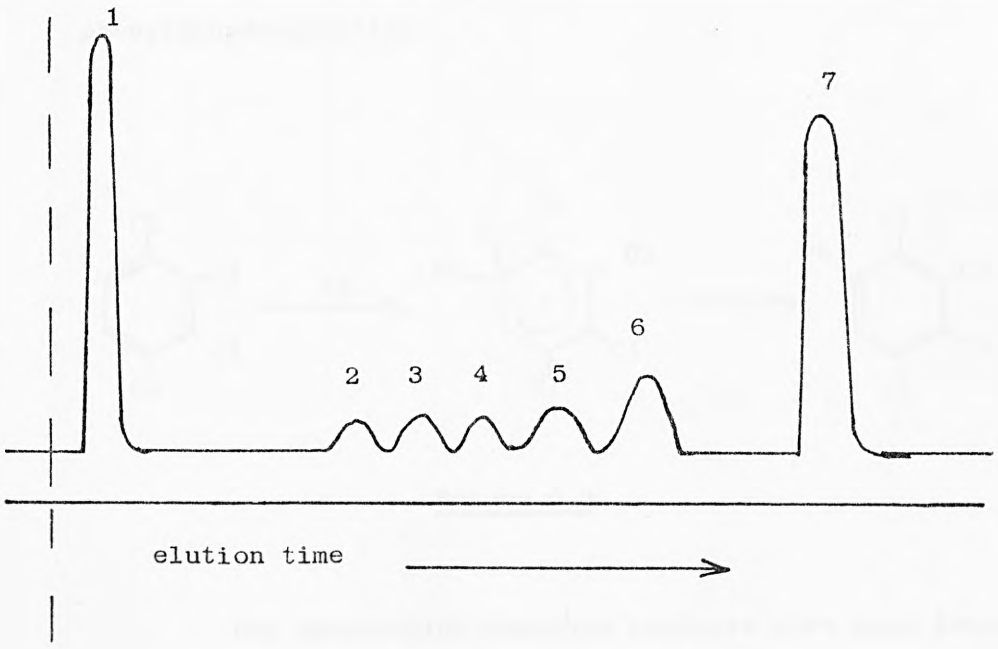
yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Figure 6.11 Reconstructed chromatogram showing only products of the phenylation of 1,2,3,4-tetrachlorobenzene and benzene



peak 1 = biphenyl

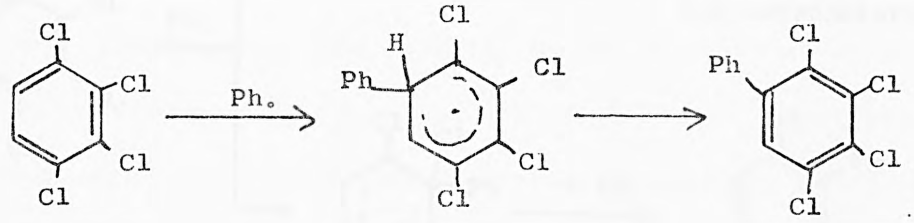
peak 2 = 2,3,6-trichlorobiphenyl
peak 3 = 2,3,5-trichlorobiphenyl
peak 4 = 2,3,4-trichlorobiphenyl
peak 5 = 3,4,5-trichlorobiphenyl
peak 6 = 2,3,4,6- and 2,3,5,6-tetrachlorobiphenyl
peak 7 = 2,3,4,5-tetrachlorobiphenyl

The phenylation of 1,2,3,4-tetrachlorobenzene has not been reported in the literature. Characteristically, the sealed tube phenylation of 1,2,3,4-tetrachlorobenzene yielded a complex reaction mixture containing seven products. Thus, the phenylation of 1,2,3,4-tetrachlorobenzene proceeded in a similar manner to that of the 1,2,3,5- isomer in the formation of several isomeric tri- and tetrachlorobiphenyls by identical reaction pathways.

Phenyldehydrogenation produced the main reaction product (peak 7 in Figure 6.11) of 2,3,4,5-tetrachlorobiphenyl (38 % yield)

as shown in Scheme 6.9. There was only one product of phenyl-dehydrogenation as phenyl radical attack at both C - H sites (i.e. C-5 and C-6) yielded the same isomer of tetrachlorobiphenyl.

phenyldehydrogenation

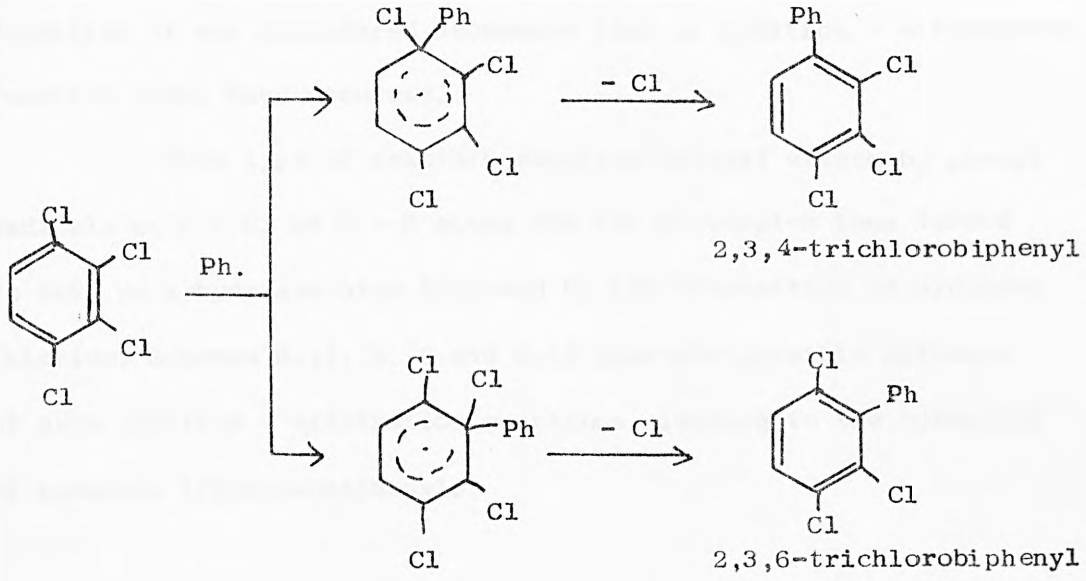


Scheme 6.9

The phenylation reaction products were also found to contain four isomeric trichlorobiphenyls ans isomeric tetrachloro-biphenyls, namely 2,3,6-, 2,3,4-, 2,3,5- and 3,4,5- isomers (in 6 %, 7 %, 4 % and 3 % yields respectively). The presence of these isomeric trichlorobiphenyls was confirmed by g.l.c. retention data and by g.l.c.-mass spectrometry results (see Appendix).

The presence of 2,3,4- and 2,3,6-trichlorobiphenyls can be accounted for by phenyldechlorination reactions, involving phenyl radical attack at C - Cl sites followed by elimination of a chlorine atom as shown in Scheme 6.10. As the number of C - Cl sites (four) is greater than the number of C - H cites (two), statistically the chances of phenyldechlorination reactions occurring are increased. The yields of the products of phenyldechlorination are generally higher in the phenylation of tetrachlorobenzenes as compared to those in the isomeric di- and trichlorobenzenes.

phenyldechlorination



Scheme 6.10

The yields of 2,3,4- (5.7 %) and 2,3,6-trichlorobiphenyls (6.8 %) were similar, which agreed with the fact that there were two positions in each case yielding the same isomeric trichlorobiphenyl.

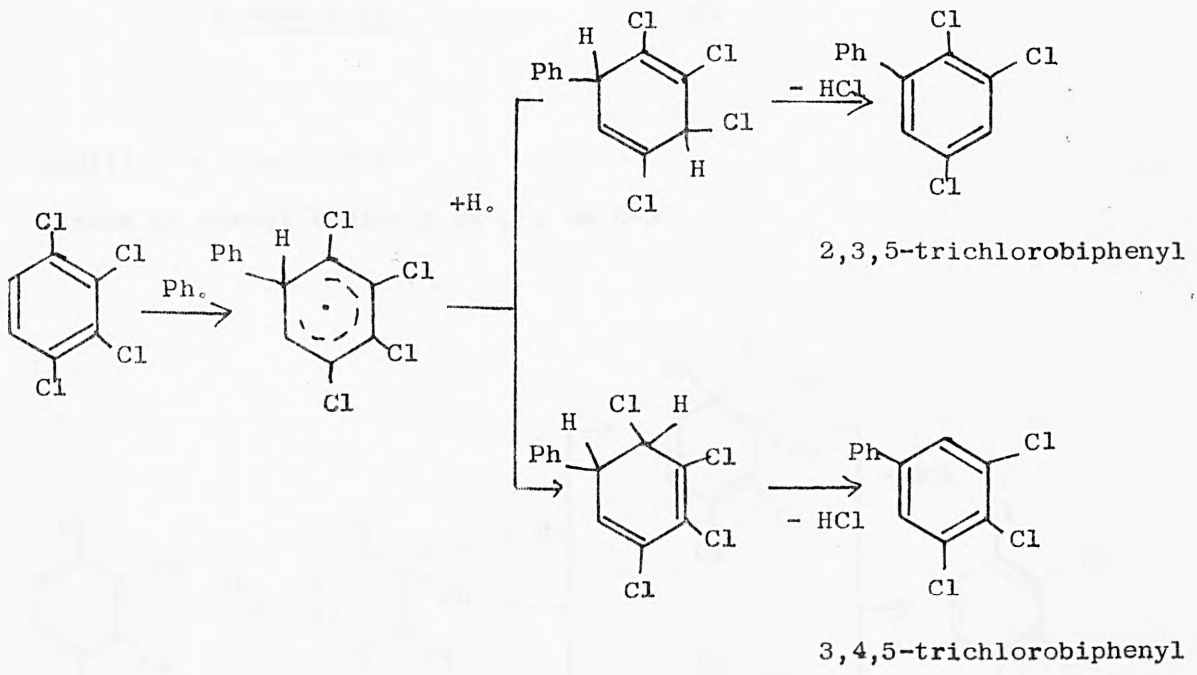
The phenylation of 1,2,3,4-tetrafluorobenzene (65) has been reported in the literature, yielding three products of phenylation only. Phenyldehydrogenation reactions yielded 2,3,4,5-tetrafluorobiphenyl (in 8.3 % yield) whilst phenyldefluorination reactions produced 2,3,4- and 2,3,6-trifluorobiphenyls (in 4.9 % and 13.9 % yields respectively). It was reported that the reaction of phenyldefluorination predominated with the major phenylation product being 2,3,6-trifluorobiphenyl, followed by 2,3,4,5-tetrafluorobiphenyl and the lowest yields were for 2,3,4-trifluorobiphenyl.

The additional presence of 2,3,5- and 3,4,5-trichlorobiphenyls (in 4 % and 3 % yields respectively) amongst the phenylation reaction products was novel and to account for their formation it was considered necessary that an addition - elimination reaction might have occurred.

This type of reaction requires initial attack by phenyl radicals at C - Cl or C - H sites and the σ-complex thus formed to take up a hydrogen atom followed by the elimination of hydrogen chloride. Schemes 6.11, 6.12 and 6.13 show the possible pathways of such addition - elimination reactions, leading to the formation of isomeric trichlorobiphenyls.

addition - elimination

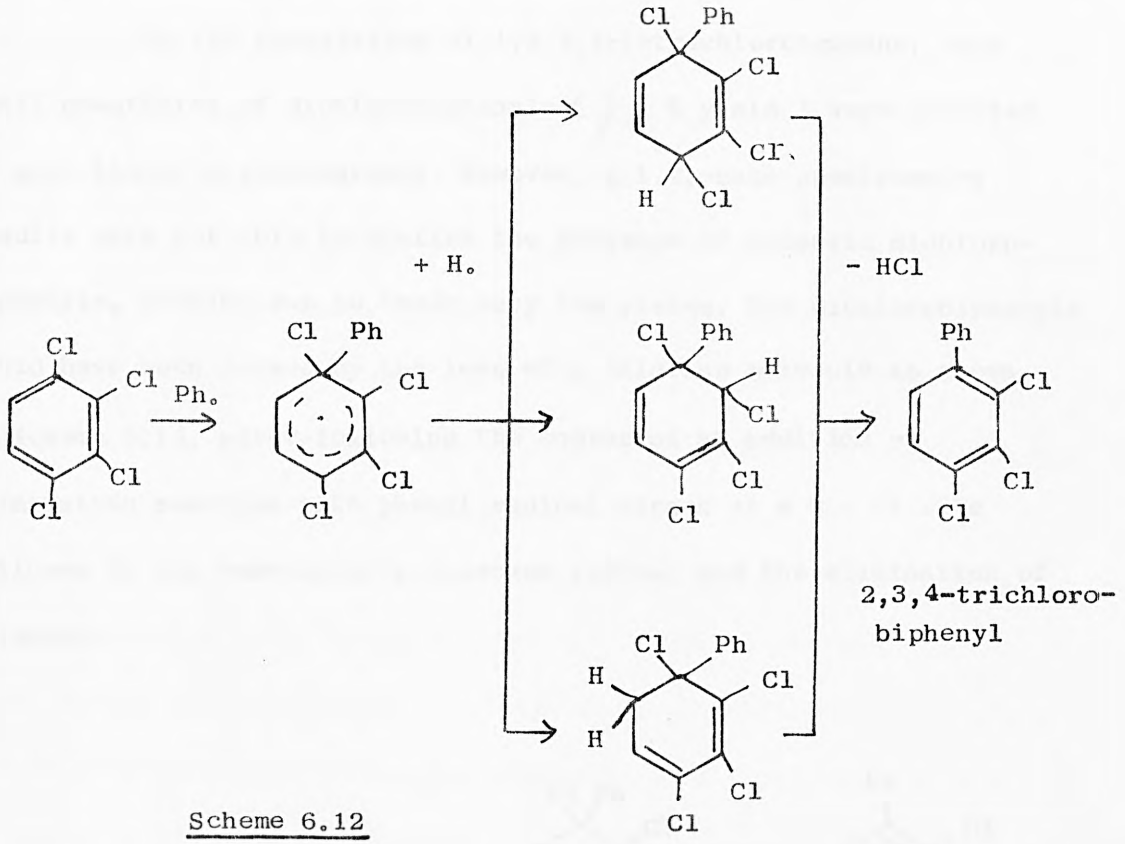
attack by phenyl radicals at C-5



Scheme 6.11

addition - elimination

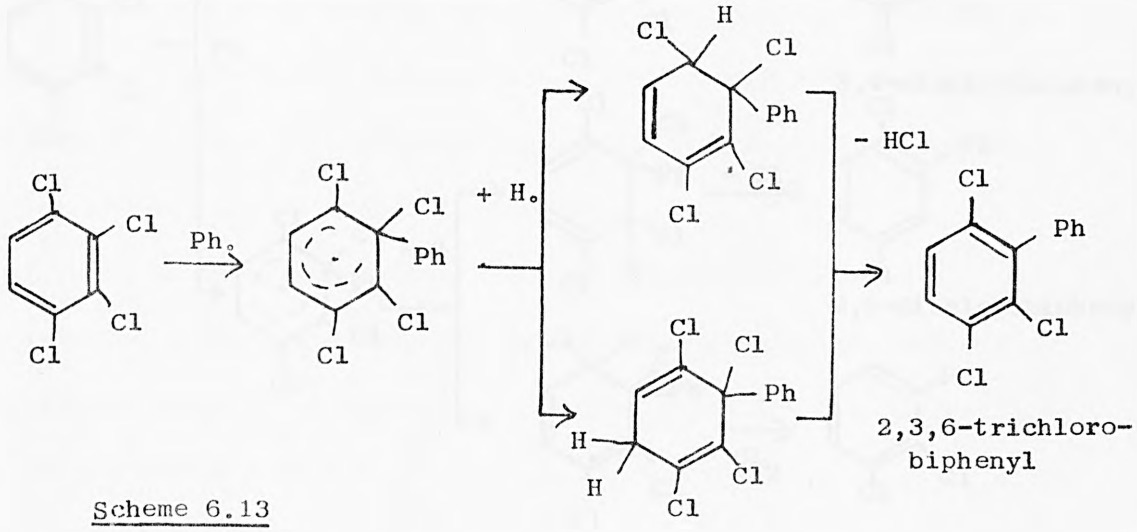
attack by phenyl radicals at C-1 or C-4



Scheme 6.12

addition - elimination

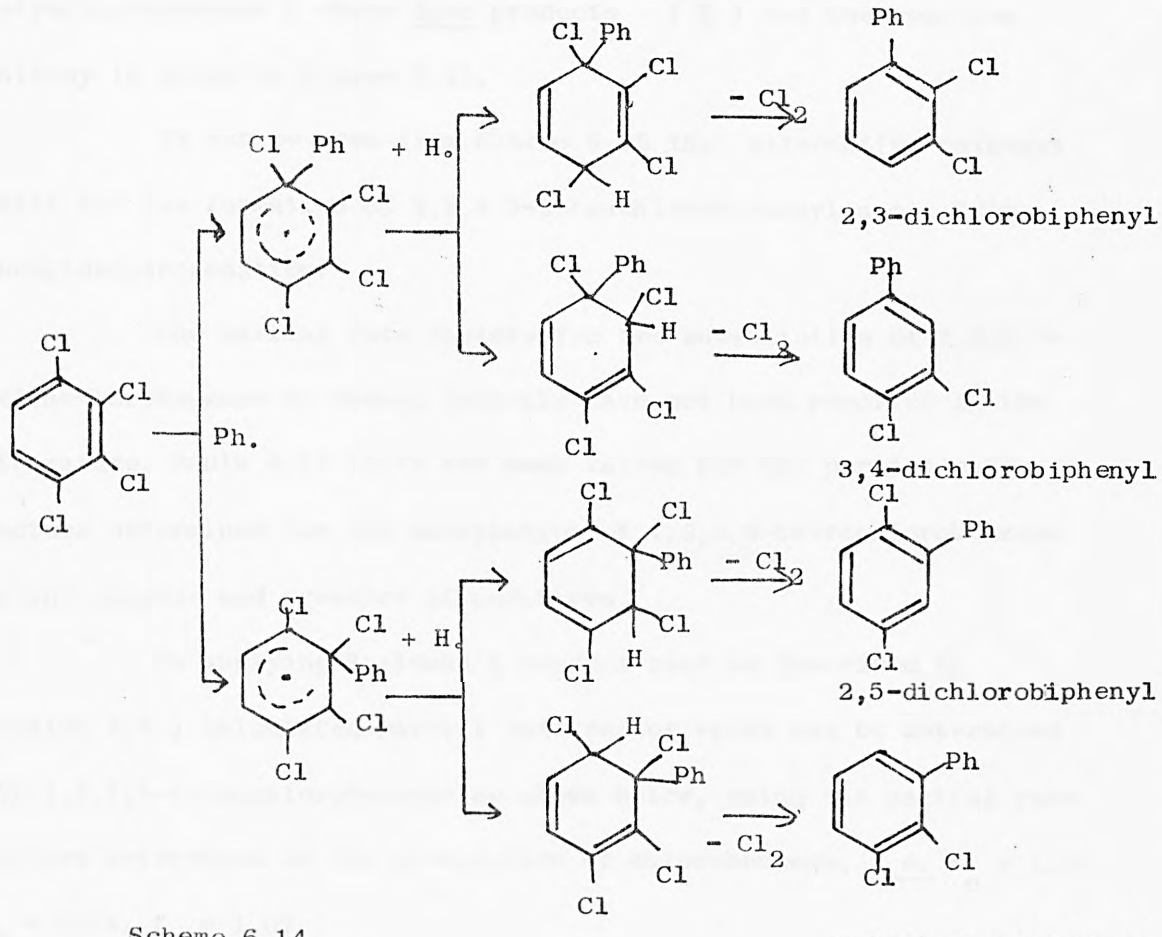
attack by phenyl radicals at C-2 or C-3



Scheme 6.13

Thus the addition - elimination reactions shown in Schemes 6.12 and 6.13 can also lead to the formation of 2,3,4- and 2,3,6-trichlorobiphenyls providing an alternative or additional route for their formation to phenyldechlorination

In the phenylation of 1,2,3,4-tetrachlorobenzene, very small quantities of dichlorobiphenyls ($\not>$ 1 % yield) were detected by gas- liquid chromatography. However, g.l.c.-mass spectrometry results were not able to confirm the presence of isomeric dichlorobiphenyls, perhaps due to their very low yields. The dichlorobiphenyls could have been formed by the loss of a chlorine molecule as shown in Scheme 6.14, after following the course of an addition - elimination reaction with phenyl radical attack at a C - Cl site followed by the take up of a hydrogen radical and the elimination of chlorine.



Scheme 6.14

The sealed tube phenylation reaction products of 1,2,3,4-tetrachlorobenzene were also found to contain other isomeric (2,3,4,6- and 2,3,5,6-) tetrachlorobiphenyls (in 6 % yield). These tetrachlorobiphenyls could have been formed by ipso rearrangement reactions as shown in Scheme 6.15. It can be noted that there are two positions in each case which can yield the isomeric tetrachlorobiphenyl.

As the retention times for 2,3,4,6- and 2,3,5,6-tetrachlorobiphenyls were extrememly close, when both were present in a mixture they were eluted as a single broad peak. This accounted for the larger size of peak 6 in Figure 6.11 as compared to the other products of phenyldechlorination i.e. peaks 2,3,4 and 5.

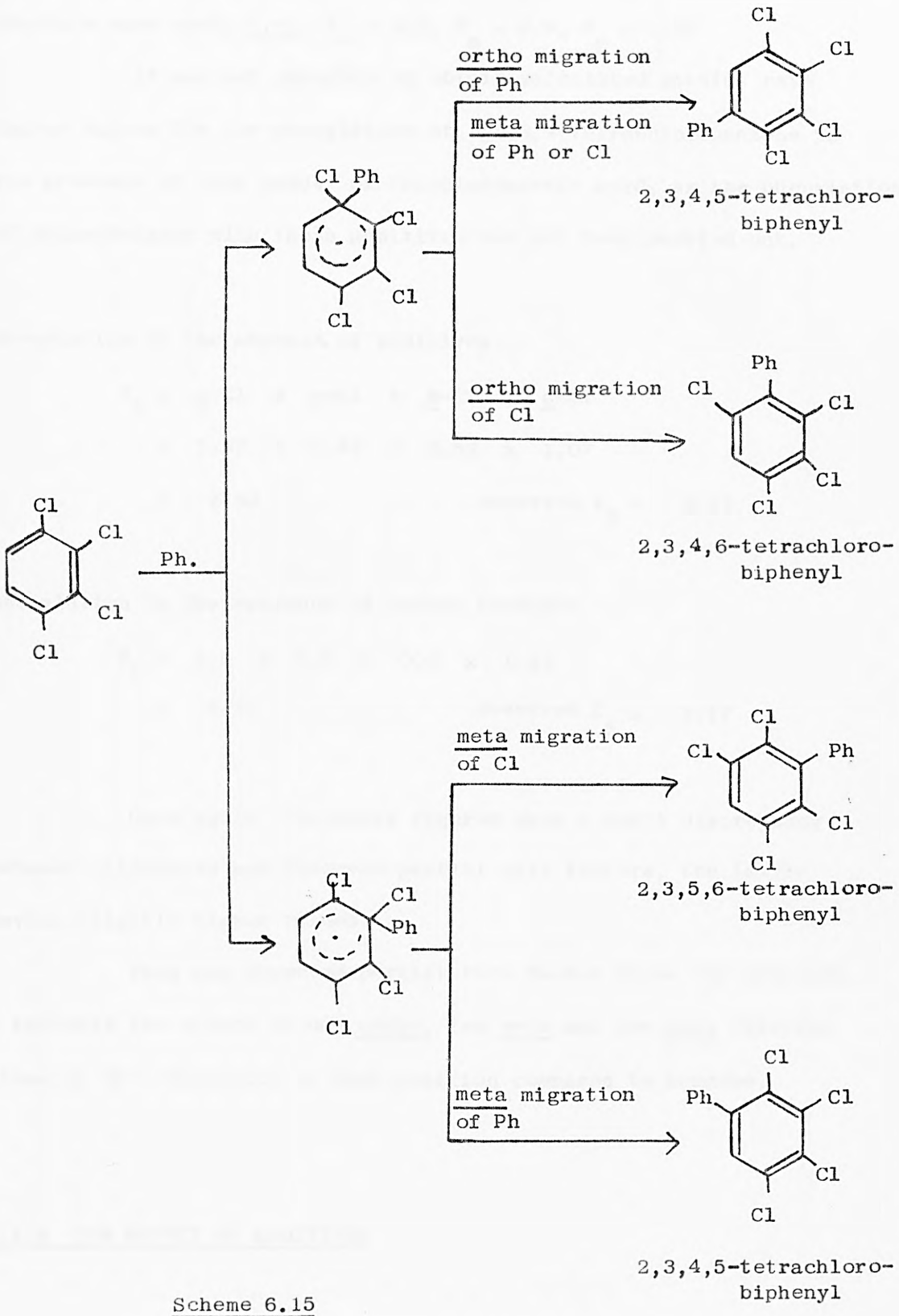
The amount of tetrachlorobiphenyl (6 %) formed by ipso rearrangement in the phenylation of 1,2,3,4-tetrachlorobenzene was much larger than the amount produced in the phenylation of 1,2,3,5-tetrachlorobenzene (where ipso products 1 %) and the reaction pathway is shown in Scheme 6.15.

It can be seen from Scheme 6.15 that alternative pathways exist for the formation of 2,3,4,5-tetrachlorobiphenyl apart from phenyldehydrogenation.

The partial rate factors for the substitution of 1,2,3,4-tetrachlorobenzene by phenyl radicals have not been reported in the literature. Table 6.17 lists the mean values for the partial rate factors determined for the phenylation of 1,2,3,4-tetrachlorobenzene in the absence and presence of additives.

On applying Holleman's product rule as described in section 3.5 a calculated partial rate factor value can be determined for 1,2,3,4-tetrachlorobenzene as shown below, using the partial rate factors determined in the phenylation of chlorobenzene, i.e. $f_o = 1.97$, $f_m = 0.82$, $f_p = 1.07$.

ipso rearrangement



Scheme 6.15

To obtain the calculated partial rate factor values in the presence of additive copper benzoate, the partial rate factors obtained in the phenylation of chlorobenzene in the presence of copper benzoate were used, i.e. $f_o = 2.9$, $f_m = 0.9$, $f_p = 1.24$

It was not possible to obtain calculated partial rate factor values for the phenylation of 1,2,3,4-tetrachlorobenzene in the presence of iron powder or trichloroacetic acid, as the phenylation of chlorobenzene with these additives had not been carried out.

phenylation in the absence of additives,

$$f_5 = \underline{o}\text{-Cl} \times \underline{m}\text{-Cl} \times \underline{m}\text{-Cl} \times \underline{p}\text{-Cl}$$
$$= 1.97 \times 0.82 \times 0.82 \times 1.07$$
$$= 1.42 \qquad \text{observed } f_5 = 2.31$$

phenylation in the presence of copper benzoate,

$$f_5 = 2.9 \times 0.9 \times 0.9 \times 1.24$$
$$= 2.91 \qquad \text{observed } f_5 = 3.17$$

Once again, the above figures show a small discrepancy between calculated and observed partial rate factors, the latter having slightly higher values.

Thus the observed partial rate factor value for position 5 reflects the effect of one ortho, two meta and one para chlorine atoms on the reactivity of that position compared to benzene.

6.2.5 THE EFFECT OF ADDITIVES

The presence of various additives in the phenylation of 1,2,3,4-tetrachlorobenzene increased the yields of 2,3,4,5-tetra-

Table 6.17 Partial rate factors and percentage yields for the phenylation of 1,2,3,4-tetrachlorobenzene in the absence and presence of additives

row number	phenyldehydrogenation product 2,3,4,5-tetrachlorobiphenyl yield (%)	phenyldechlorination products trichlorobiphenyl yields 2,3,4- (%)	2,3,6- (%)	partial rate factors for :- phenyldehydrogenation f_5	phenyldechlorination f_1	f_2
1[a]	37.5	3.9	5.2	2.31	0.24	0.32
2[b]	53.7	5.7	6.8	3.17	0.33	0.40
3[c]	56.4	5.9	7.3	3.36	0.35	0.44
4[d]	59.1	6.4	7.6	3.59	0.39	0.46

each row of figures is a mean of four or more results

a = no additive

b = additive copper benzoate, 0.1 g.

c = additive iron powder, 0.1 g.

d = additive trichloroacetic acid, 0.1 g.

chlorobiphenyl and 2,3,4- and 2,3,6-trichlorobiphenyls as shown in Table 6.17, at the expense of products of dimerisation and disproportionation.

The highest biaryl yields were obtained with the use of trichloroacetic acid as the additive, whilst the lowest increase in biaryl yields was obtained with copper benzoate as shown in Table 6.17.

Table 6.17 also shows the mean values obtained for the partial rate factors of the phenylation of 1,2,3,4-tetrachlorobenzene for hydrogen and chlorine displacement, i.e. phenyldehydrogenation and phenyldechlorination respectively. The partial rate factor for the phenyldehydrogenation reaction was $f_5 = 2.31$ in the absence of additives and in the presence of trichloroacetic acid, $f_5 = 3.59$.

Similarly, a small increase was observed in the partial rate factors for phenyldechlorination in the presence of additives as shown in Table 6.17. Thus the partial rate factors for phnenyl-dechlorination without additive, $f_1 = 0.24$, $f_2 = 0.32$, were increased to $f_1 = 0.39$, $f_2 = 0.46$ in the presence of trichloroacetic acid.

6.3 METHOD OF PHENYLATION OF 1,2,4,5-TETRACHLOROBENZENE

This was the same as has been described in section 3.1. Sections 6.3.1 to 6.3.3 show the chromatograms obtained and their identification followed by tables listing experimental quantities leading to tables of results tabulating partial rate factors and yields.

6.3.1 CHROMATOGRAMS

Figures 6.12, 6.13 and 6.14 show actual chromatograms obtained. Figure 6.15 shows a reconstructed chromatogram demonstrating the relationship between the products of phenylation.

6.3.2 PEAK IDENTIFICATION

This was as has been described in section 3.3.

Figure 6.12 Reaction of 1,2,4,5-tetrachlorobenzene, chromatogram obtained

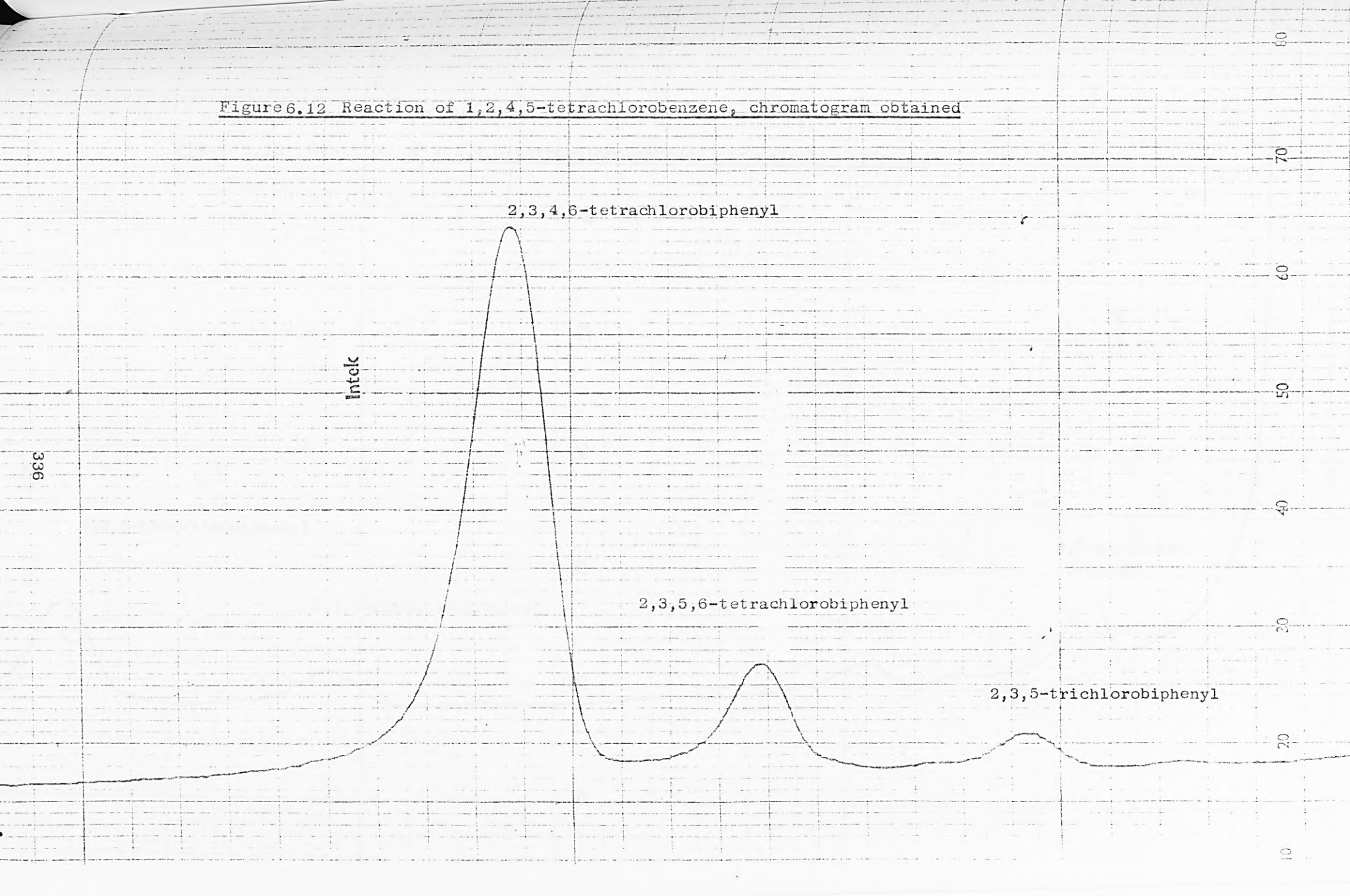
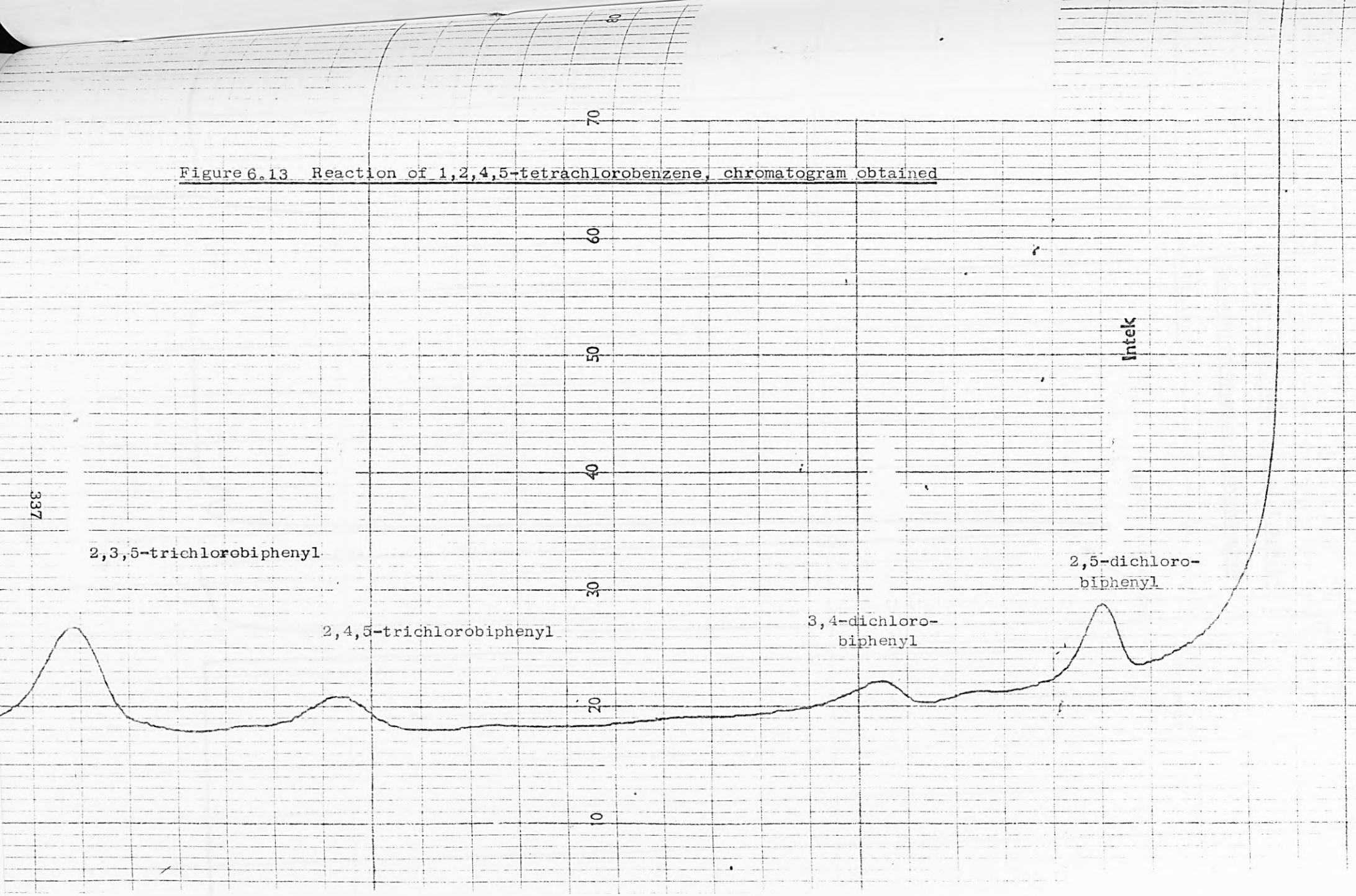


Figure 6.13 Reaction of 1,2,4,5-tetrachlorobenzene, chromatogram obtained



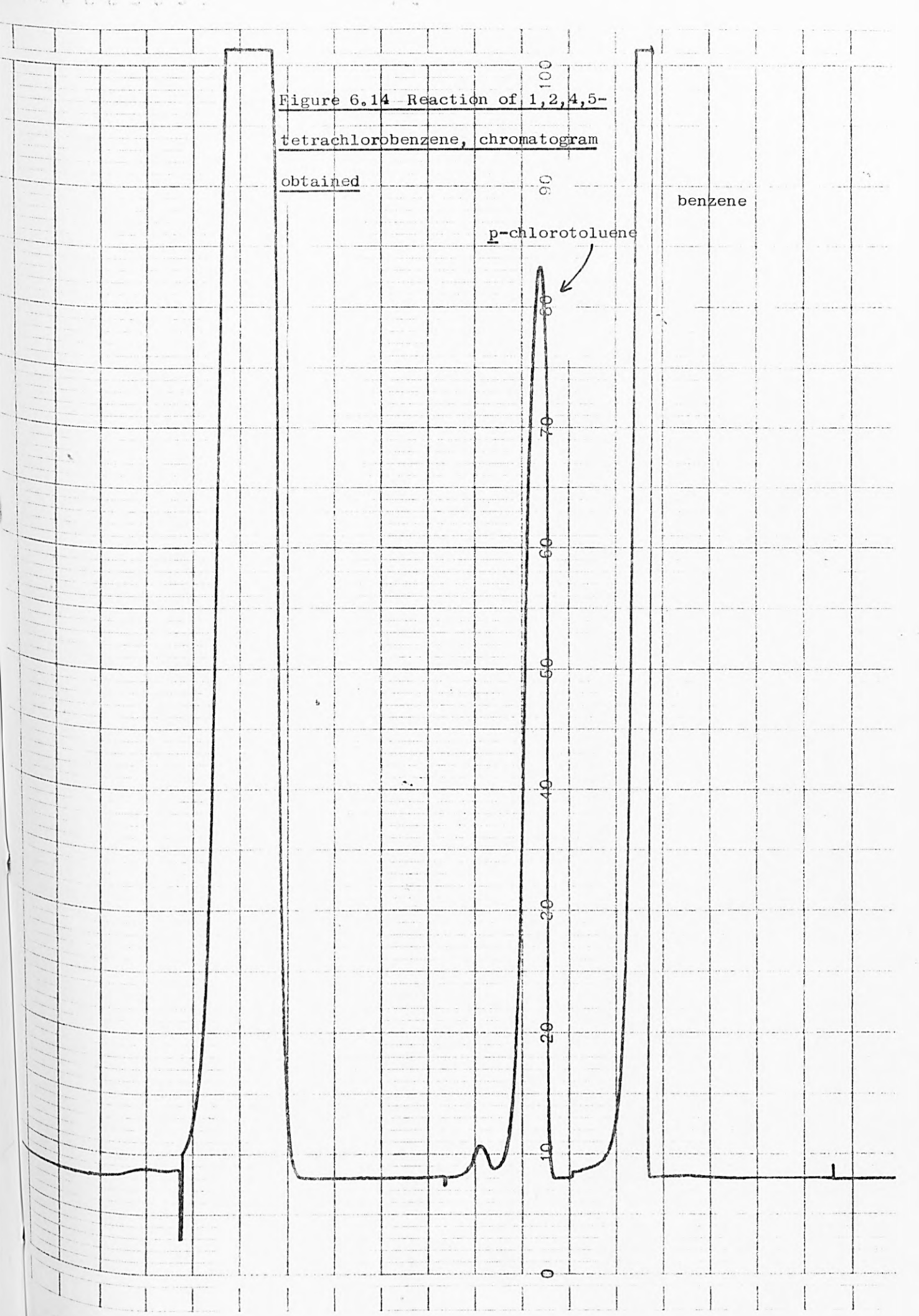


Figure 6.14 Reaction of 1,2,4,5-tetrachlorobenzene, chromatogram obtained

Figure 6.15 Reaction of 1,2,4,5-tetrachlorobenzene, reconstructed chromatogram

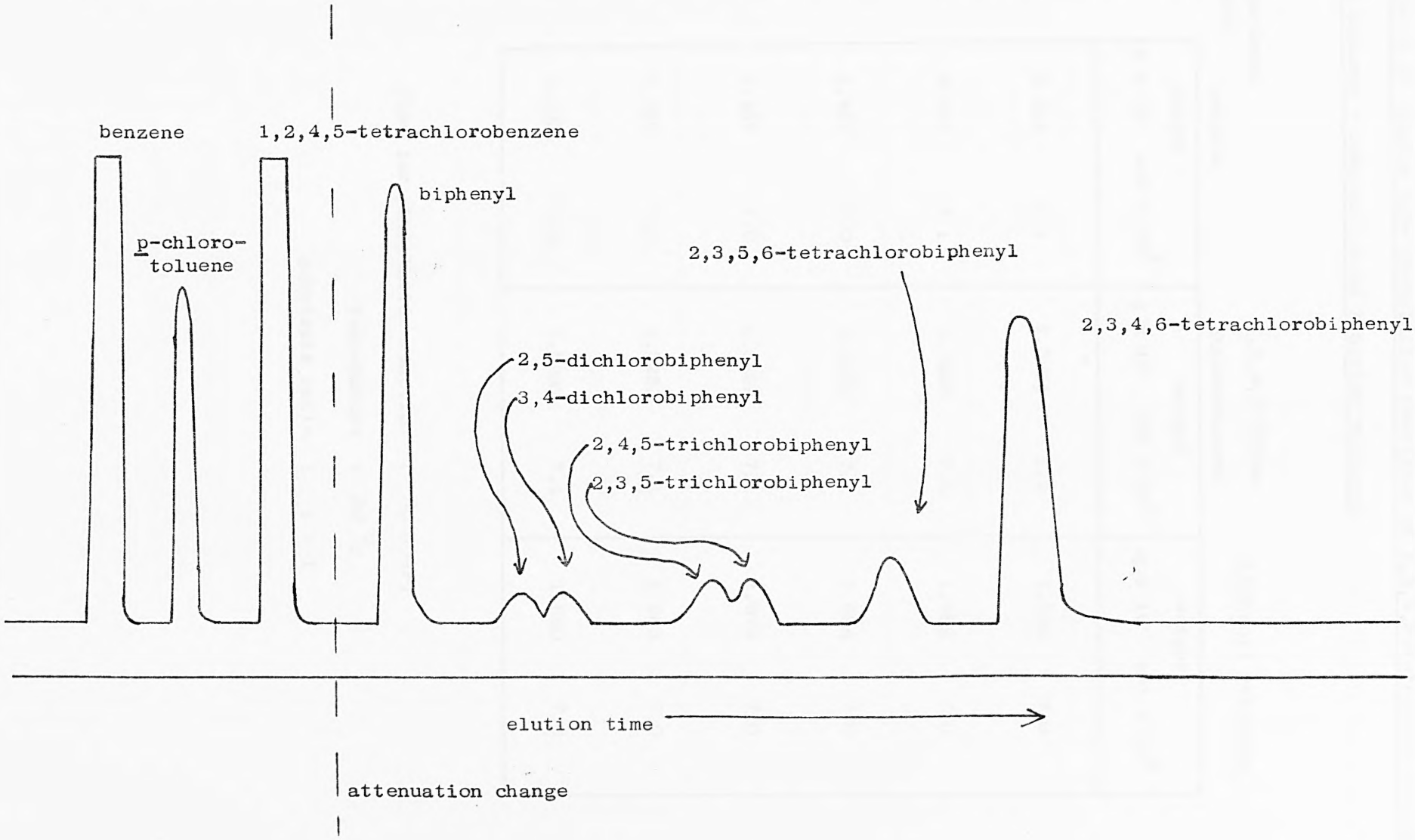


Table 6.18 Sealed tube phenylation reactions of 1,2,4,5-tetrachlorobenzene and benzene - composition of reaction mixtures

experiment number	benzene		1,2,4,5-tetrachlorobenzene		dibenzoyl peroxide	
	weight		weight		weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1	5.538	7.1	1.5251	7.1	1.696	7.0
2	5.526	7.1	1.5265	7.1	1.682	7.0
3	5.467	7.0	1.5258	7.1	1.694	7.0
4	5.462	7.0	1.5269	7.1	1.674	7.0
5	5.489	7.0	1.5253	7.1	1.683	7.0
6	5.475	7.0	1.5267	7.1	1.690	7.0

time for phenylation reaction : 50 hours

temperature : 80 °C

substrate ratio : 1 : 1

Table 6.19 Sealed tube phenylation reactions of 1,2,4,5-tetrachlorobenzene and benzene in the presence of additives - composition of reaction mixtures

experiment number	benzene		1,2,4,5-tetrachlorobenzene		dibenzoyl peroxide	
	weight		weight		weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	5.366	6.8	1.4749	6.8	1.683	7.0
2[a]	5.379	6.8	1.4760	6.8	1.677	7.0
3[a]	5.374	6.8	1.4754	6.8	1.670	7.0
4[a]	5.382	6.8	1.4746	6.8	1.691	7.0
5[b]	5.348	6.8	1.4576	6.8	1.689	7.0
6[b]	5.352	6.8	1.4575	6.8	1.684	7.0
7[b]	5.355	6.9	1.4582	6.8	1.676	7.0
8[b]	5.363	6.9	1.4589	6.8	1.672	7.0
9[c]	5.375	6.9	1.4967	6.9	1.690	7.0
10[c]	5.369	6.9	1.4953	6.9	1.695	7.0
11[c]	5.378	6.9	1.4961	6.9	1.686	7.0
12[c]	5.361	6.9	1.4955	6.9	1.684	7.0

time for phenylation reaction : 50 hours

temperature : 80 °C

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 6.20 Analysis of the phenylation reaction products of 1,2,4,5-tetrachlorobenzene and benzene in the absence of additives (Table 6.18 gives compositions)

experiment number	tetrachlorobiphenyl products 2,3,5,6-		tetrachlorobiphenyl products 2,3,4,6-		trichlorobiphenyl products 2,4,5-		trichlorobiphenyl products 2,3,5-		dichlorobiphenyl products 2,5-		dichlorobiphenyl products 3,4-		biphenyl		p-chlorotoluene internal std.	
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1	0.0330	0.0395	0.0642	0.0768	0.0074	0.0089	0.0082	0.0098	0.0045	0.0054	0.0028	0.0034	0.0249	0.0298	0.1316	0.1574
2	0.0322	0.0388	0.0639	0.0771	0.0077	0.0093	0.0075	0.0091	0.0038	0.0046	0.0023	0.0028	0.0251	0.0303	0.1286	0.1552
3	0.0335	0.0400	0.0640	0.0763	0.0072	0.0086	0.0070	0.0084	0.0043	0.0051	0.0030	0.0036	0.0257	0.0306	0.1314	0.1567
4	0.0327	0.0391	0.0636	0.0761	0.0079	0.0094	0.0079	0.0094	0.0048	0.0057	0.0026	0.0031	0.0259	0.0310	0.1293	0.1546
5	0.0319	0.0382	0.0638	0.0765	0.0074	0.0089	0.0073	0.0088	0.0039	0.0047	0.0022	0.0026	0.0248	0.0297	0.1304	0.1563
6	0.0323	0.0386	0.0647	0.0772	0.0080	0.0096	0.0078	0.0093	0.0043	0.0051	0.0028	0.0033	0.0255	0.0304	0.1322	0.1578
response factors	1.82		1.87		1.63		1.65		1.28		1.56		1.15		1.00	

Table 6.21 Analysis of the phenylation reaction products of 1,2,4,5-tetrachlorobenzene and benzene in the presence of additives (Table 6.19 gives compositions)

experiment number	tetrachlorobiphenyl products 2,3,5,6- peak weight (g.)	tetrachlorobiphenyl products 2,3,5,6- cpd. weight (g.)	tetrachlorobiphenyl products 2,3,4,6- peak weight (g.)	tetrachlorobiphenyl products 2,3,4,6- cpd. weight (g.)	trichlorobiphenyl products 2,4,5- peak weight (g.)	trichlorobiphenyl products 2,4,5- cpd. weight (g.)	trichlorobiphenyl products 2,3,5- peak weight (g.)	trichlorobiphenyl products 2,3,5- cpd. weight (g.)	dichlorobiphenyl products 2,5- peak weight (g.)	dichlorobiphenyl products 2,5- cpd. weight (g.)	dichlorobiphenyl products 3,4- peak weight (g.)	dichlorobiphenyl products 3,4- cpd. weight (g.)	biphenyl peak weight (g.)	biphenyl cpd. weight (g.)	p-chlorotoluene internal std. peak weight (g.)	p-chlorotoluene internal std. std. weight (g.)
1[a]	0.0328	0.0393	0.0649	0.0776	0.0090	0.0108	0.0085	0.0102	0.0044	0.0053	0.0027	0.0032	0.0247	0.0295	0.1292	0.1546
2[a]	0.0322	0.0385	0.0653	0.0781	0.0088	0.0105	0.0090	0.0108	0.0047	0.0056	0.0023	0.0028	0.0244	0.0292	0.1301	0.1557
3[a]	0.0330	0.0396	0.0650	0.0783	0.0080	0.0096	0.0092	0.0110	0.0040	0.0048	0.0028	0.0034	0.0258	0.0309	0.1311	0.1571
4[a]	0.0323	0.0387	0.0641	0.0769	0.0091	0.0109	0.0091	0.0109	0.0043	0.0052	0.0033	0.0040	0.0249	0.0299	0.1302	0.1562
5[b]	0.0339	0.0405	0.0657	0.0786	0.0104	0.0125	0.0089	0.0107	0.0048	0.0057	0.0030	0.0039	0.0263	0.0315	0.1304	0.1560
6[b]	0.0344	0.0414	0.0648	0.0780	0.0099	0.0119	0.0093	0.0112	0.0052	0.0060	0.0031	0.0040	0.0258	0.0311	0.1287	0.1549
7[b]	0.0332	0.0400	0.0644	0.0777	0.0097	0.0117	0.0095	0.0115	0.0043	0.0052	0.0035	0.0042	0.0250	0.0302	0.1290	0.1556
8[b]	0.0339	0.0408	0.0651	0.0783	0.0099	0.0120	0.0087	0.0110	0.0047	0.0056	0.0038	0.0050	0.0260	0.0313	0.1305	0.1569
9[c]	0.0349	0.0418	0.0664	0.0795	0.0105	0.0126	0.0091	0.0109	0.0048	0.0060	0.0040	0.0046	0.0247	0.0295	0.1323	0.1583
10[c]	0.0356	0.0426	0.0673	0.0811	0.0108	0.0129	0.0099	0.0119	0.0050	0.0061	0.0040	0.0050	0.0255	0.0307	0.1312	0.1568
11[c]	0.0341	0.0410	0.0668	0.0804	0.0103	0.0124	0.0088	0.0110	0.0052	0.0063	0.0043	0.0052	0.0244	0.0294	0.1311	0.1577
12[c]	0.0359	0.0431	0.0664	0.0798	0.0107	0.0130	0.0095	0.0114	0.0054	0.0065	0.0046	0.0055	0.0254	0.0305	0.1302	0.1564

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 6.22 Partial rate factors and percentage yields for the phenylation of 1,2,4,5-tetrachlorobenzene in the absence of additives

experiment number	biphenyl yield (%)	2,3,5,6-tetrachlorobiphenyl f_3 yield (%)		2,4,5-trichlorobiphenyl $f_{1'}$ yield (%)	
1	27.6	2.10	19.3	0.27	4.9
2	28.1	2.03	19.0	0.28	5.2
3	28.4	2.07	19.6	0.25	4.8
4	28.8	2.00	19.1	0.27	5.2
5	27.6	2.03	18.7	0.27	4.9
6	28.2	2.01	18.9	0.28	5.3
(mean values)	28.1	2.04	19.1	0.27	5.1

yields are in mole per mole peroxide x 100

Table 6.23 Partial rate factors and percentage yields for the phenylation of 1,2,4,5-tetrachlorobenzene in the presence of additives

experiment number	biphenyl yield (%)	2,3,5,6-tetrachloro-biphenyl f_3	2,3,5,6-tetrachloro-biphenyl yield (%)	2,4,5-trichloro-biphenyl f_1	2,4,5-trichloro-biphenyl yield (%)
1[a]	27.4	2.11	19.2	0.33	6.0
2[a]	27.1	2.09	18.8	0.32	5.8
3[a]	28.7	2.03	19.4	0.32	5.3
4[a]	27.7	2.05	18.9	0.33	6.1
(mean values)[a]	27.7	2.07		0.33	
5[b]	29.2	2.03	19.8	0.36	6.9
6[b]	28.9	2.10	20.3	0.34	6.6
7[b]	28.0	2.09	19.6	0.35	6.5
8[b]	29.0	2.07	20.0	0.35	6.7
(mean values)[b]	28.8	2.07		0.35	
9[c]	27.4	2.24	20.5	0.38	7.0
10[c]	28.5	2.20	20.8	0.38	7.2
11[c]	27.3	2.21	20.1	0.38	6.9
12[c]	28.3	2.23	21.1	0.38	7.2
(mean values)[c]	27.9	2.22		0.38	

yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 6.24 Percentage yields of some by-products of the phenylation reaction of 1,2,4,5-tetrachlorobenzene in the absence of additives

experiment number	2,3,5-trichlorobiphenyl	dichlorobiphenyls	
		2,5-	3,4-
	yield (%)	yield (%)	yield (%)
1	5.4	3.5	2.2
2	5.1	2.9	1.8
3	4.7	3.3	2.3
4	5.2	3.7	1.9
5	4.9	3.0	1.7
6	5.2	3.2	2.1
(mean values)	5.1	3.3	2.0

yields are in mole per mole peroxide x 100

Table 6.25 Percentage yields of some by-products of the phenylation reaction of 1,2,4,5-tetrachlorobenzene in the presence of additives

experiment number	2,3,5-trichlorobiphenyl	dichlorobiphenyls	
		2,5-	3,4-
	yield (%)	yield (%)	yield (%)
1[a]	5.7	3.4	2.1
2[a]	5.9	3.6	1.8
3[a]	6.1	3.1	2.2
4[a]	6.0	3.3	2.6
(mean values)[a]	6.0	3.4	2.2
5[b]	5.9	3.7	2.5
6[b]	6.2	3.8	2.6
7[b]	6.4	3.3	2.7
8[b]	6.1	3.6	3.2
(mean values)[b]	6.2	3.6	2.7
9[c]	6.1	3.8	2.9
10[c]	6.6	4.0	3.2
11[c]	6.1	4.0	3.3
12[c]	6.3	4.2	3.5
(mean values)[c]	6.3	4.0	3.3

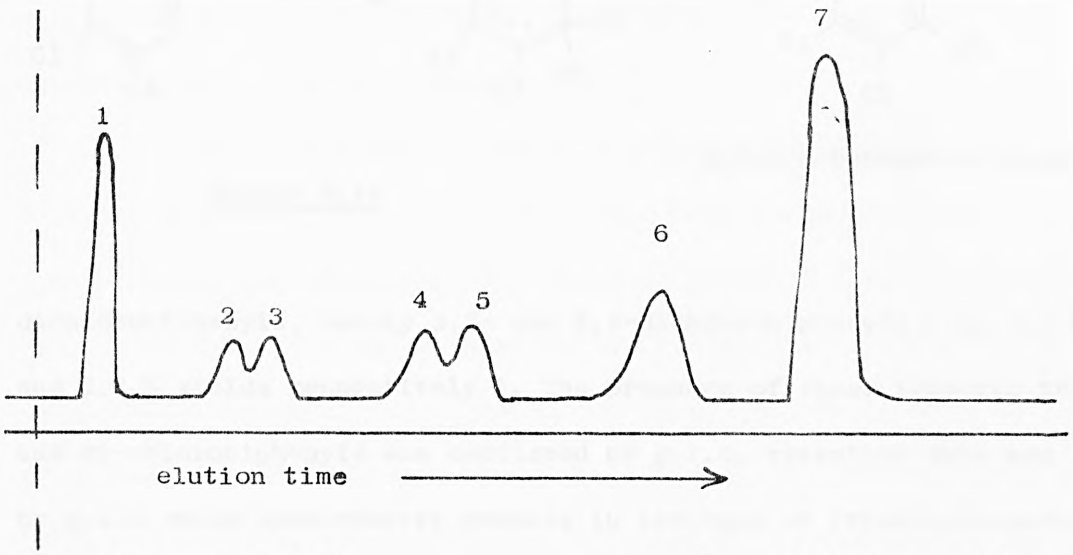
yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Figure 6.16 Reconstructed chromatogram showing only the products of phenylation of 1,2,4,5-tetrachlorobenzene



peak 1 = biphenyl

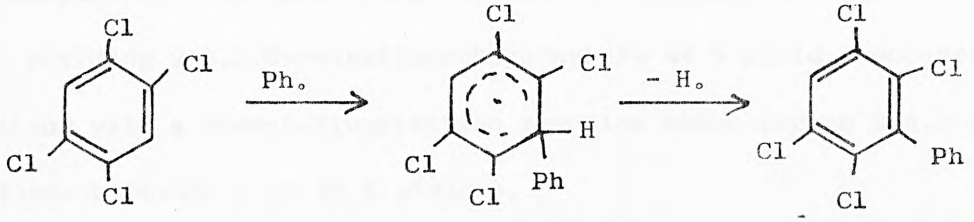
peak 2 = 2,5-dichlorobiphenyl
peak 3 = 3,4-dichlorobiphenyl
peak 4 = 2,4,5-trichlorobiphenyl
peak 5 = 2,3,5-trichlorobiphenyl
peak 6 = 2,3,4,6-tetrachlorobiphenyl
peak 7 = 2,3,5,6-tetrachlorobiphenyl

The phenylation of 1,2,4,5-tetrachlorobenzene has not been reported in the literature. Sealed tube phenylation of 1,2,4,5-tetrachlorobenzene yielded a complex reaction mixture containing seven products.

Phenyldehydrogenation, with phenyl radical attack at the hydrogen sites at C-3 and C-6 lead to the formation of only one products, namely 2,3,5,6-tetrachlorobiphenyl (in 19 % yield), as shown in Scheme 6.16.

The phenylation reaction products were also found to contain two isomeric trichlorobiphenyls, namely 2,4,5- and 2,3,5-trichlorobiphenyls (in 4.9 % and 5.4 % yields respectively and two isomeric

phenyldehydrogenation



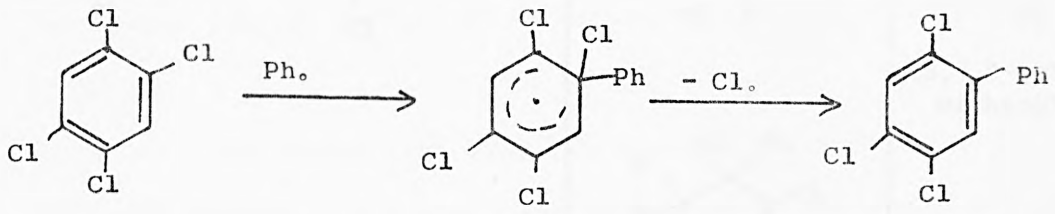
2,3,5,6-tetrachlorobiphenyl

Scheme 6.16

dichlorobiphenyls, namely 2,5- and 3,4-dichlorobiphenyls (in 3.5 % and 2.2 % yields respectively). The presence of these isomeric tri- and di-chlorobiphenyls was confirmed by g.l.c. retention data and by g.l.c.-mass spectrometry results in the case of trichlorobiphenyls only. No g.l.c.-mass spectrometry evidence could be found for the presence of dichlorobiphenyl, dichloroterphenyl or trichloroterphenyl (see Appendix).

The presence of 2,4,5-trichlorobiphenyl (in 5 % yield) can be accounted for by phenyldechlorination reactions, requiring phenyl radical attack at a C - Cl site followed by the elimination of a chlorine atom. As the four chlorine atoms have an equivalent chemical environment and are symmetrically positioned, only one product of phenyldechlorination is produced as shown in Scheme 6.17.

phenyldechlorination



2,3,5,6-tetrachlorobiphenyl

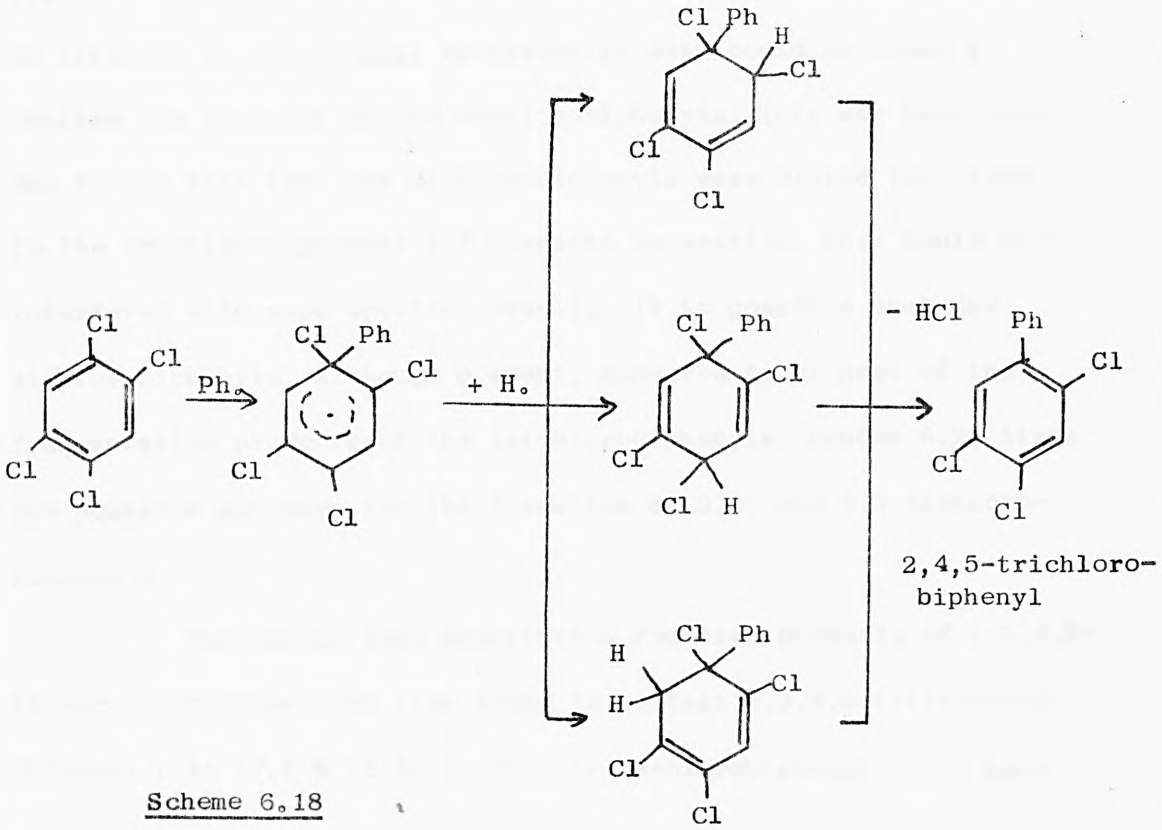
Scheme 6.17

The phenylation of 1,2,4,5-tetrafluorobenzene has been reported in the literature [65] yielding only two products of phenylation. The dominating reaction of phenyldehydrogenation (yielding 2,3,5,6-tetrafluorobiphenyl in 44 % yield) occurred, along with a phenydefluorination reaction which formed 2,4,5-trifluorobiphenyl (in 15 % yield).

The additional presence of 2,3,5-trichlorobiphenyl (in 5.1 % yield) was a novel feature of the phenylation of 1,2,4,5-tetrachlorobenzene. The formation of 2,3,5-trichlorobiphenyl can be accounted for by considering the occurrence of an addition - elimination reaction. This type of reaction requires initial attack by a phenyl radical at a C - H or C - Cl site, the σ-complex formed thus could take up ahydrogen atom followed by the elimination of hydrogen chloride as shown in Schemes 6.18 and 6.19.

addition - elimination reaction

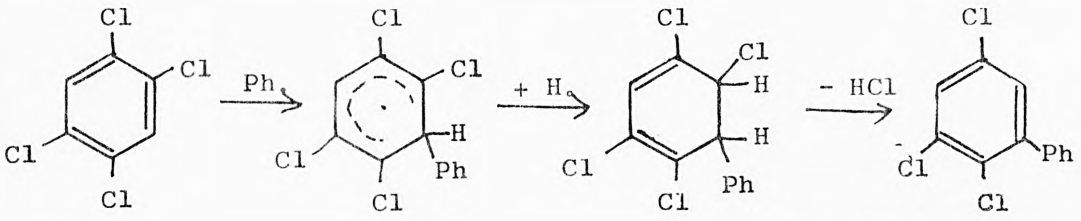
attack by phenyl radicals at C-1



Scheme 6.18

addition - elimination reaction

attack by phenyl radicals at C-3



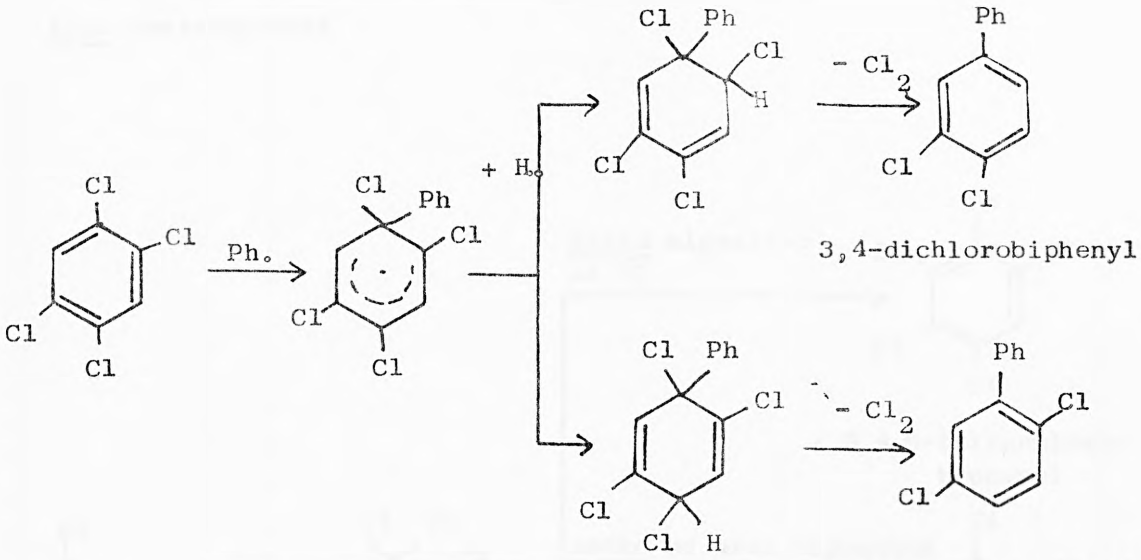
2,3,5-trichlorobiphenyl

Scheme 6.19

Thus the addition - elimination reactions shown in Scheme 6.18 also lead to the formation of 2,4,5-trichlorobiphenyl by an alternative route to direct phenyldechlorination.

Isomeric dichlorobiphenyls were also found to be present in the phenylation reaction mixture of 1,2,4,5-tetrachlorobenzene, namely the 2,5- and 3,4- isomers (in 3.3 % and 2.0 % yields respectively). Relative retention times compared well with the retention times of authentic standard dichlorobiphenyls. However, no evidence by g.l.c.-mass spectrometry data could be found to confirm the presence of the dichlorobiphenyls. This may have been due to the fact that the dichlorobiphenyls were eluted too close to the trichlorobiphenyls for complete separation. This could have interfered with mass spectral results. It is possible that the dichlorobiphenyls, although present, appeared to be part of the fragmentation products of the trichlorobiphenyls. Scheme 6.20 lists the possible pathways for the formation of 3,4- and 2,5-dichlorobiphenyls.

The sealed tube phenylation reaction products of 1,2,4,5-tetrachlorobenzene were also found to contain 2,3,4,6-tetrachlorobiphenyl (in 37.5 % yield). This tetrachlorobiphenyl could have



Scheme 6.20

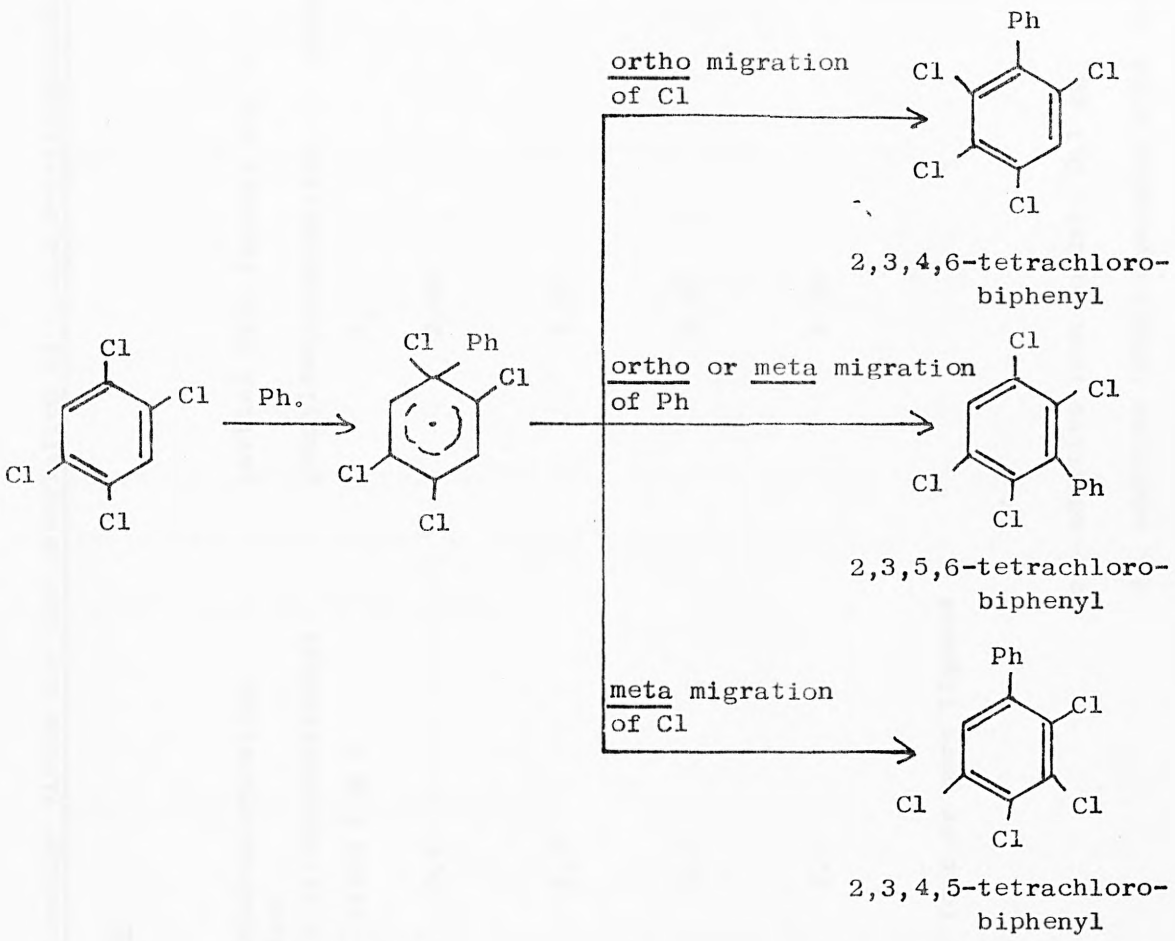
been formed by ipso type rearrangement reactions as discussed in the phenylations of the isomeric di- and trichlorobenzenes in Chapters Four and Five.

Thus it was found that the product of ipso rearrangement exceeded the amount of product formed by phenyldehydrogenation (2,3,5,6-tetrachlorobiphenyl in 19.1 % yield). Such a situation is probable statistically as for the formation of 2,3,5,6-tetrachlorobiphenyl, phenyl radical attack is required at a carbon - hydrogen site of which there are two in 1,2,4,5-tetrachlorobenzene, whilst for the formation of 2,3,4,6-tetrachlorobiphenyl, phenyl radical attack at a C - Cl site is required, of which there are four in 1,2,4,5-tetrachlorobenzene.

Scheme 6.21 shows the various pathways for the ipso rearrangement reactions of 1,2,4,5-tetrachlorobenzene, which require initial radical attack at a C - Cl site followed by ortho or meta migrations of either group in the σ-complex.

As shown in Scheme 6.21, the meta migration of chlorine in the σ-complex could lead to the formation of 2,3,4,5-tetrachlorobiphenyl. However, no evidence was found for the presence of

ipso rearrangement



Scheme 6.21

this isomer of tetrachlorobiphenyl, indicating that the meta migration of Cl was an unfavourable reaction.

The partial rate factors for the substitution of 1,2,4,5-tetrachlorobenzene by phenyl radicals have not been reported in the literature. Table 6.26 lists the mean values for the partial rate factors determined for the phenylation of 1,2,4,5-tetrachlorobenzene both in the presence and absence of additives.

On applying Holleman's product rule as described in section 3.5, calculated partial rate factors may be determined as shown below, using the partial rate factors determined in the phenylation of chlorobenzene.

Table 6.26 Partial rate factors and percentage yields for the phenylation of 1,2,4,5-tetrachlorobenzene in the presence and absence of additives

row number	phenyldehydrogenation product 2,3,5,6-tetrachlorobiphenyl yield (%)	phenyldechlorination product 2,4,5-trichlorobiphenyl yield (%)	partial rate factors for :- phenyldehydrogenation f_3	phenyldechlorination f_1
1[a]	19.1	5.1	2.04	0.27
2[b]	19.1	5.8	2.07	0.33
3[c]	19.9	6.7	2.07	0.35
4[d]	20.6	7.1	2.22	0.38

each row of results is a mean of four or more figures

a = no additive

b = additive copper benzoate, 0.1 g.

c = additive iron powder, 0.1 g.

d = additive trichloroacetic acid, 0.1 g.

phenylation reaction in the absence of additives,

f_3 = o-Cl x o-Cl x m-Cl x m-Cl

= 1.97 x 1.97 x 0.82 x 0.82

= 2.61 observed f_3 = 2.04

phenylation reaction in the presence of copper benzoate,

f_3 = 2.9 x 2.9 x 0.9 x 0.9

= 6.81 observed f_3 = 2.07

From the above figures it can be seen that there is some discrepancy between calculated and observed partial rate factors. Thus the partial rate factor f_3 = 2.04 reflects the effect of two ortho and two meta chlorine atoms.

6.3.5 THE EFFECT OF ADDITIVES

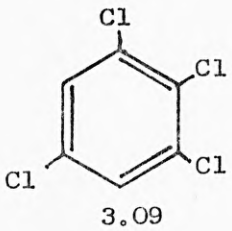
The presence of various additives in the phenylation of 1,2,4,5-tetrachlorobenzene increased the yields of 2,3,4,6- and 2,3,5,6-tetrachlorobiphenyls and 2,4,5-trichlorobiphenyl as shown in Table 6.26, Once again at the expense of the products of dimerisation and disproportionation. It thus follows the similar trend observed in the phenylations of the isomeric di- tri- and tetrachlorobenzenes.

Once again, the highest biaryl yields were achieved with the use of trichloroacetic acid, whilst the lowest increase was with copper benzoate.

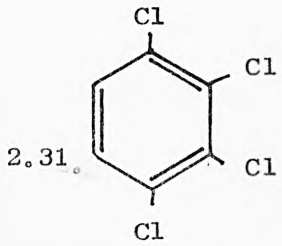
Table 6.26 also shows the mean values obtained for the partial rate factors for the phenylation of 1,2,4,5-tetrachloro-

benzene for both hydrogen and chlorine displacement i.e. phenyldehydrogenation and phenyldechlorination. The partial rate factor for phenyldehydrogenation was f_3 = 2.04 which was increased to f_3 = 2.22 in the presence of trichloroacetic acid. Similarly, a small increase was observed in the partial rate factor value for phenyldechlorination in the presence of additives as shown in Table 6.26. Thus the partial rate factor value without additive f_1 = 0.27 was increased to f_1 = 0.38 in the presence of trichloroacetic acid.

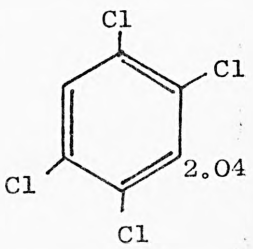
6.3.6 PARTIAL RATE FACTORS FOR THE PHENYLATION OF TETRACHLOROBENZENES



1,2,3,5-tetrachlorobenzene



1,2,3,4-tetrachlorobenzene



1,2,4,5-tetrachlorobenzene

The above shows the partial rate factor values determined for the phenylation reactions of the isomeric tetrachlorobenzenes.

Once again, the enhancing / activating effect of the presence of two ortho chlorine atoms can be seen from the partial rate factor values for position 4 in 1,2,3,5-tetrachlorobenzene (f_4 = 3.09) and position 3 in 1,2,4,5-tetrachlorobenzene (f_3 = 2.04) which is also deactivated by the presence of two meta chlorine atoms.

The partial rate factor value for position 4 in 1,2,3,5-

tetrachlorobenzene is higher than that for 1,2,4,5-tetrachlorobenzene and presumably reflects the difference between the presence of an additional para and meta chlorine atom in 1,2,3,5-tetrachlorobenzene as opposed to the two meta chlorine atoms in 1,2,4,5-tetrachlorobenzene.

Position 5 in 1,2,3,4-tetrachlorobenzene has one ortho chlorine atom and has a lower partial rate factor value of $f_5 = 2.31$ than the partial rate factor value of 1,2,3,5-tetrachlorobenzene with two ortho chlorine atoms.

Therefore the value of the partial rate factor for position 3 in 1,2,4,5-tetrachlorobenzene gives a measure of the effect of two ortho and two meta chlorine atoms on the relative reactivity of that position compared to benzene.

CHAPTER SEVEN

THE PHENYLATION OF PENTACHLOROBENZENE

7.1 METHOD OF PHENYLATION OF PENTACHLOROBENZENE

The same method was used as has been described in section 3.1. The sealed tube phenylation reactions of pentachlorobenzene were carried out at two different temperatures both in the absence and presence of additives. This was due to the fact that the melting point of pentachlorobenzene was 86 ^{o}C. The two temperatures selected for the sealed tube phenylations were 80 ^{o}C and 120 ^{o}C.

Sections 7.1.1 to 7.1.3 show the chromatograms obtained and their identification followed by tables listing experimental quantities leading to tables of results tabulating partial rate factors and yields.

7.1.1 CHROMATOGRAMS

Figures 7.1, 7.2, 7.3, 7.4 and 7.5 show actual chromatograms obtained. Figure 7.6 shows a reconstructed chromatogram demonstrating the relationship between the products of phenylation.

7.1.2 PEAK IDENTIFICATION

This was has been described in Section 3.3.

Figure 7.1 Reaction of pentachlorobenzene

Chromatogram obtained

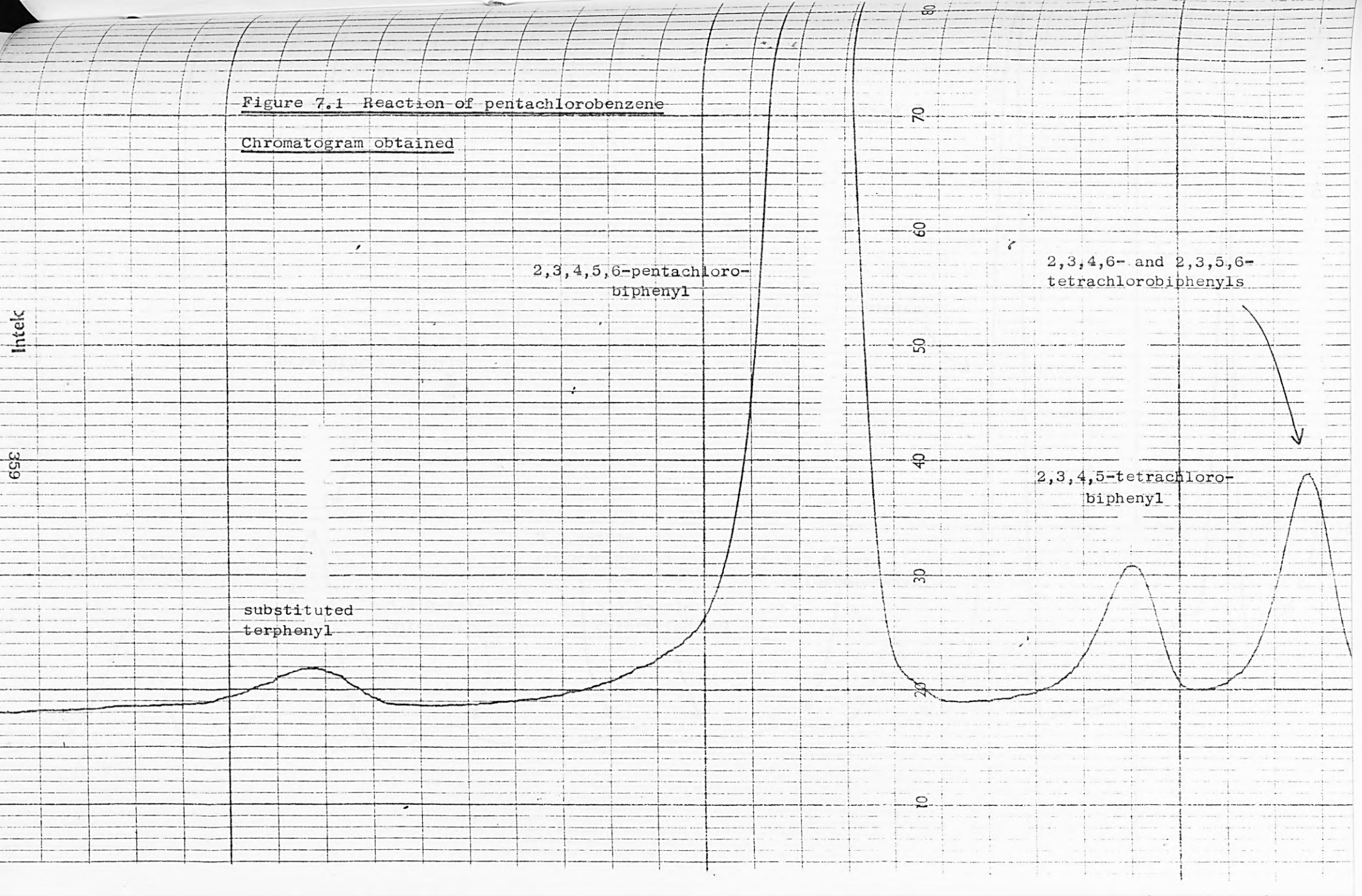


Figure 7.2 Reaction of pentachlorobenzene, chromatogram obtained

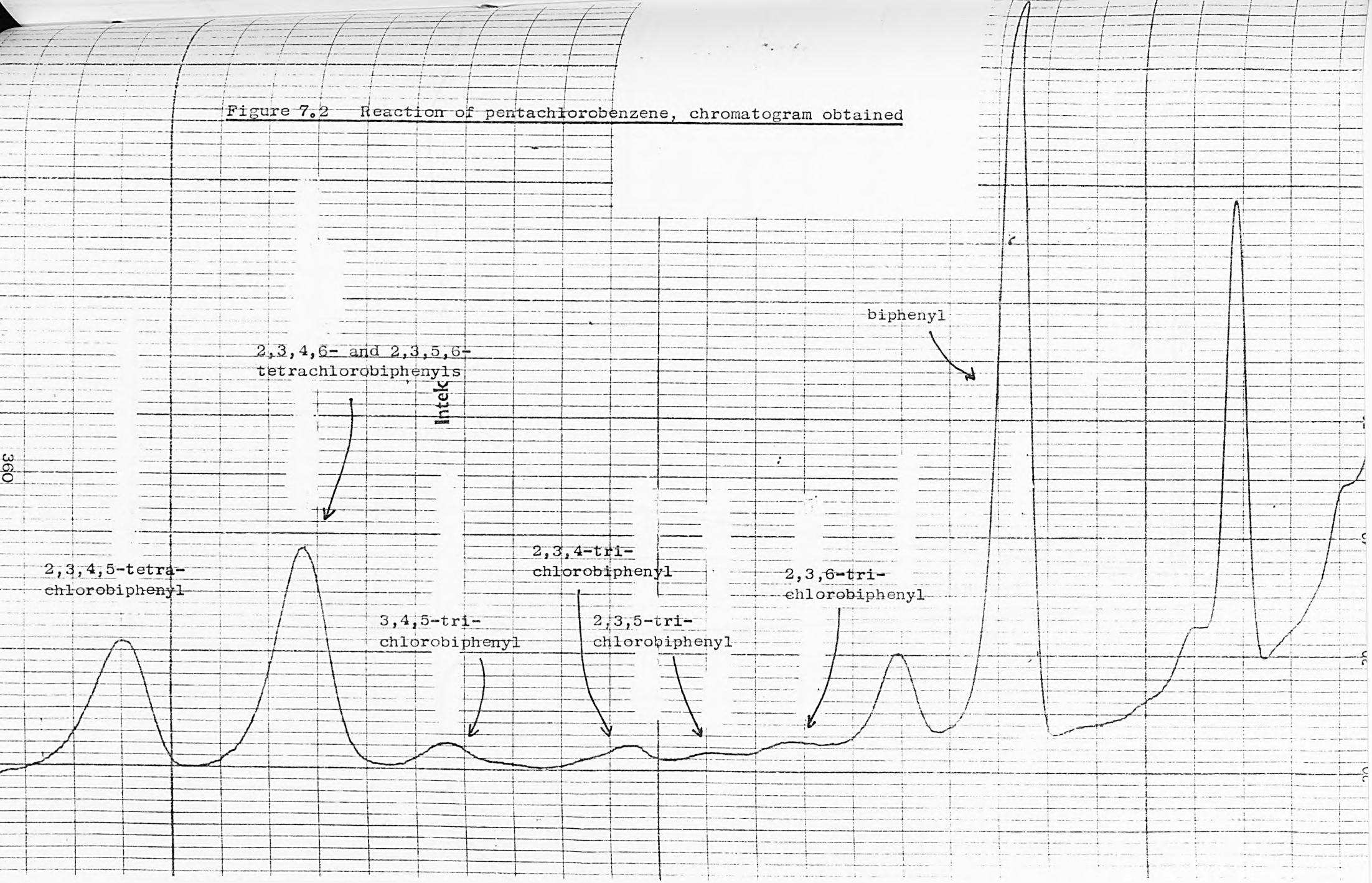
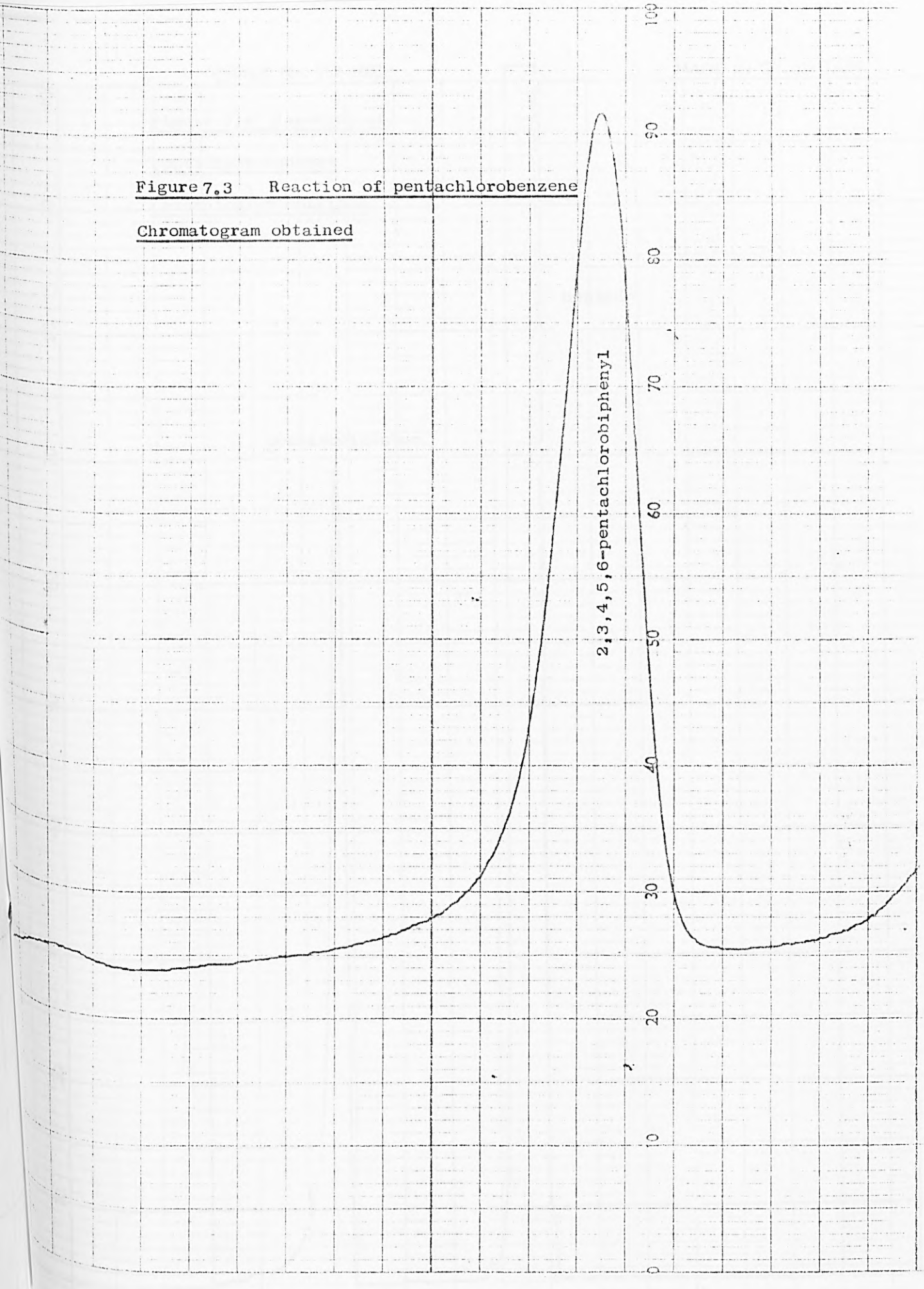


Figure 7,3 Reaction of pentachlorobenzene

Chromatogram obtained



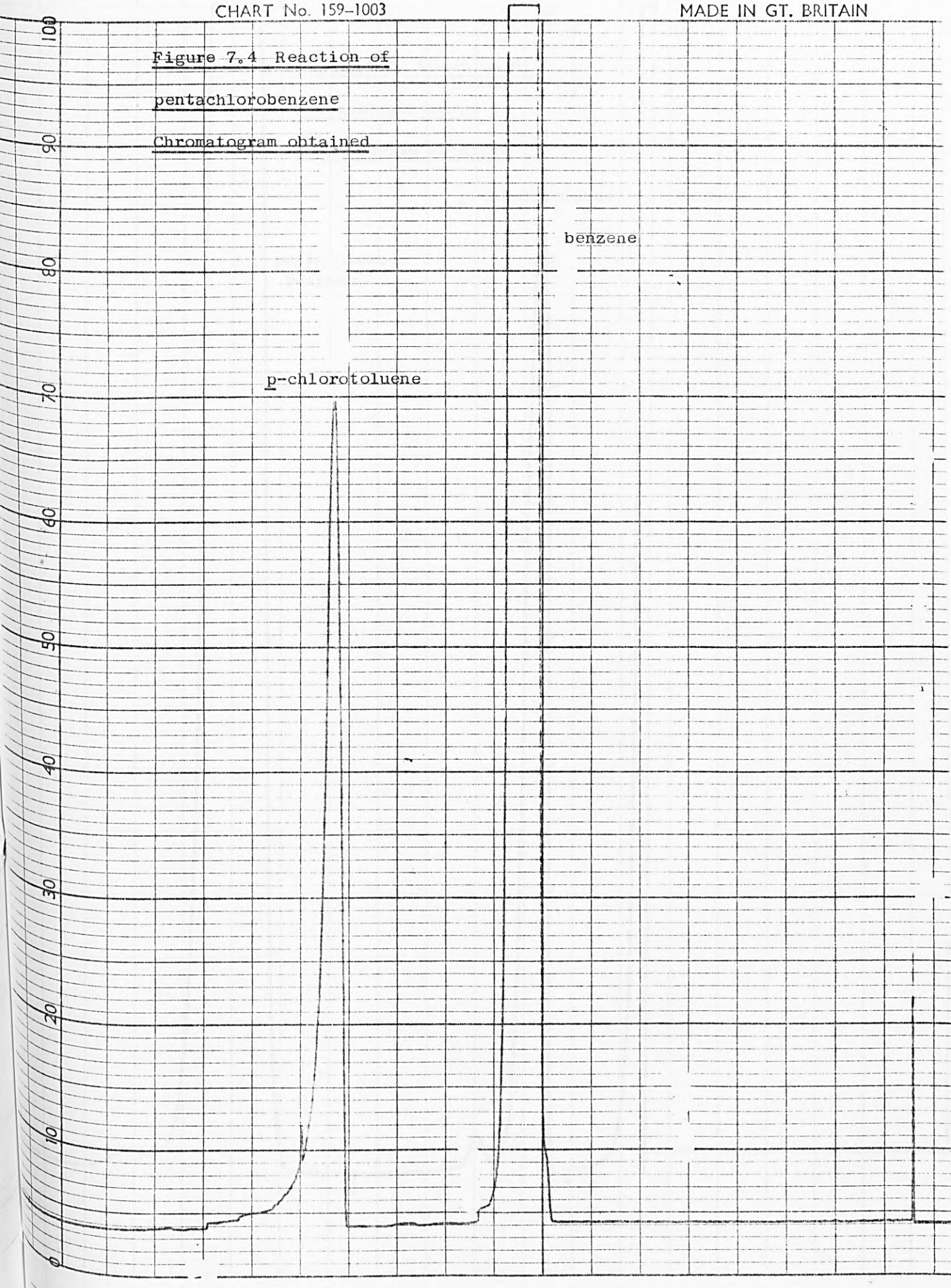


Figure 7.4 Reaction of pentachlorobenzene Chromatogram obtained

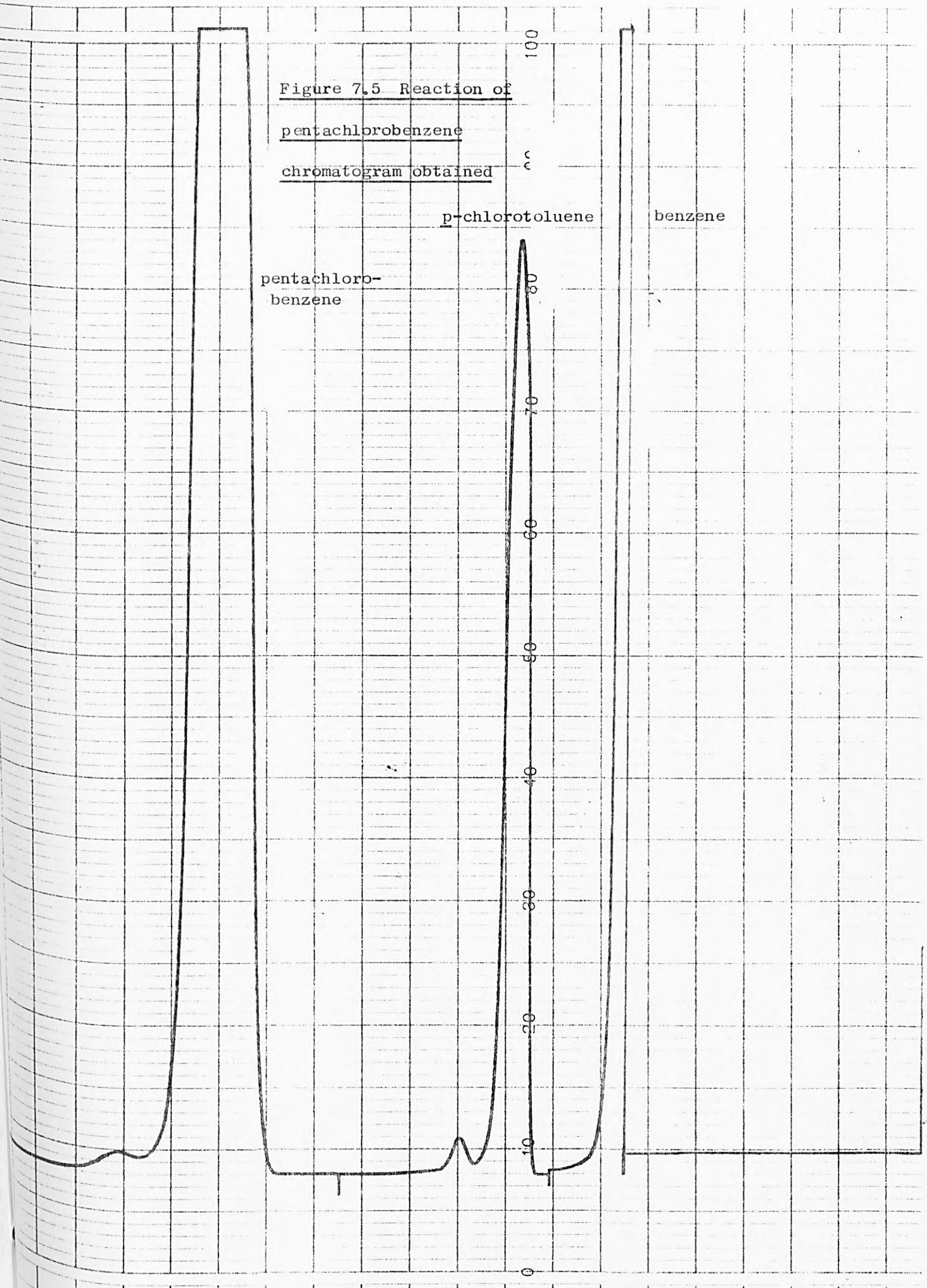


Figure 7.5 Reaction of pentachlorobenzene chromatogram obtained

Figure 7.6 Reaction of pentachlorobenzene, reconstructed chromatogram

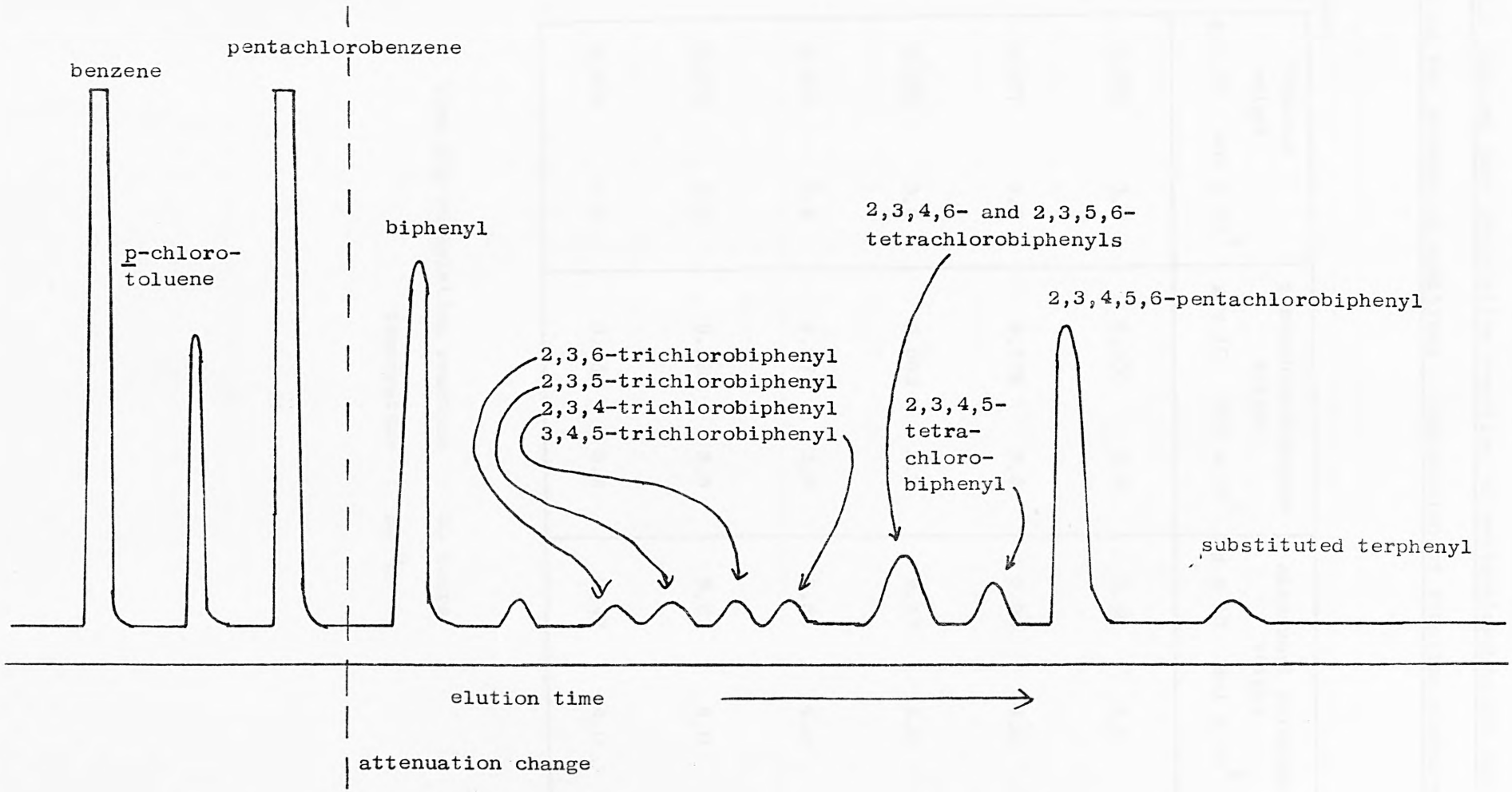


Table 7.1 Sealed tube phenylation reaction of pentachlorobenzene and benzene in the absence of additives - composition of reaction mixtures

experiment number	benzene weight		pentachlorobenzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1	2.986	3.8	9.556	3.8	9.48	4.0
2	2.977	3.8	9.578	3.8	9.54	4.0
3	2.980	3.8	9.562	3.8	9.57	4.0
4	2.975	3.8	9.571	3.8	9.59	4.0
5	2.971	3.8	9.569	3.8	9.61	4.0
6	2.979	3.8	9.557	3.8	9.47	4.0

time for phenylation reaction : 50 hours

temperature : 80 ^{o}C

Table 7.2 Sealed tube phenylation reaction of pentachlorobenzene and benzene in the presence of additives - composition of reaction mixtures

experiment number	benzene weight		pentachlorobenzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	2.989	3.8	9.354	3.7	9.66	4.0
2[a]	2.984	3.8	9.347	3.7	9.57	4.0
3[a]	2.992	3.8	9.340	3.7	9.69	4.0
4[a]	2.996	3.8	9.362	3.7	9.63	4.0
5[b]	2.956	3.8	9.751	3.9	9.50	4.0
6[b]	2.967	3.8	9.746	3.9	9.47	4.0
7[b]	2.953	3.8	9.758	3.9	9.43	4.0
8[b]	2.954	3.8	9.755	3.9	9.49	4.0
9[c]	2.911	3.7	9.406	3.8	9.83	4.0
10[c]	2.923	3.7	9.397	3.8	9.87	4.0
11[c]	2.905	3.7	9.419	3.8	9.91	4.0
12[c]	2.901	3.7	9.424	3.8	9.88	4.0

time for phenylation reaction : 50 hours

temperature : 80 °C

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 7.3 Sealed tube phenylation reaction of pentachlorobenzene and benzene in the absence of additives - composition of reaction mixtures

experiment number	benzene weight		pentachlorobenzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1	3.268	4.2	1.0263	4.1	9.76	4.0
2	3.279	4.2	1.0276	4.1	9.68	4.0
3	3.282	4.2	1.0279	4.1	9.66	4.0
4	3.271	4.2	1.0265	4.1	9.73	4.0
5	3.269	4.2	1.0261	4.1	9.61	4.0
6	3.275	4.2	1.0277	4.1	9.64	4.0

time for phenylation reaction : 50 hours

temperature : 120 °C

Table 7.4 Sealed tube phenylation reaction of pentachlorobenzene and benzene in the presence of additives - composition of reaction mixtures

experiment number	benzene weight		pentachlorobenzene weight		dibenzoyl peroxide weight	
	g x 10	mol x 10^3	g x 10	mol x 10^3	g x 10	mol x 10^4
1[a]	3.273	4.2	1.0273	4.1	9.79	4.0
2[a]	3.266	4.2	1.0275	4.1	9.85	4.0
3[a]	3.275	4.2	1.0266	4.1	9.73	4.0
4[a]	3.261	4.2	1.0269	4.1	9.87	4.0
5[b]	3.278	4.2	1.0278	4.1	9.76	4.0
6[b]	3.269	4.2	1.0272	4.1	9.84	4.0
7[b]	3.272	4.2	1.0263	4.1	9.71	4.0
8[b]	3.270	4.2	1.0276	4.1	9.86	4.0
9[c]	3.264	4.2	1.0265	4.1	9.75	4.0
10[c]	3.271	4.2	1.0270	4.1	9.82	4.0
11[c]	3.267	4.2	1.0269	4.1	9.77	4.0
12[c]	3.272	4.2	1.0274	4.1	9.78	4.0

time for phenylation reaction : 50 hours

temperature : 120 °C

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 7.5 Analysis of the phenylation reaction products of pentachlorobenzene and benzene at 80 °C

(continued overleaf)

experiment number	pentachlorobiphenyl 2,3,4,5,6-		tetrachlorobiphenyl 2,3,4,5-		2,3,4,6- and 2,3,5,6-		biphenyl		p-chlorotoluene internal standard	
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1	0.0221	0.0558	0.0024	0.0055	0.0041	0.0084	0.0304	0.0387	0.1407	0.1559
2	0.0218	0.0550	0.0023	0.0053	0.0038	0.0078	0.0308	0.0392	0.1432	0.1584
3	0.0219	0.0552	0.0022	0.0051	0.0040	0.0081	0.0314	0.0399	0.1395	0.1541
4	0.0223	0.0562	0.0022	0.0050	0.0037	0.0075	0.0317	0.0403	0.1415	0.1563
5	0.0221	0.0548	0.0022	0.0050	0.0039	0.0079	0.0315	0.0395	0.1442	0.1570
6	0.0212	0.0536	0.0022	0.0051	0.0040	0.0082	0.0305	0.0388	0.1400	0.1549
response factors	2.28		2.04		1.85		1.15		1.00	

Table 7.5 continued

experiment number	trichlorobiphenyl products 2,3,6- peak weight (g.)	2,3,6- cpd. weight (g.)	2,3,5- peak weight (g.)	2,3,5- cpd. weight (g.)	2,3,4- peak weight (g.)	2,3,4- cpd. weight (g.)	3,4,5- peak weight (g.)	3,4,5- cpd. weight (g.)
1	0.0024	0.0045	0.0021	0.0038	0.0022	0.0041	0.0017	0.0034
2	0.0026	0.0049	0.0019	0.0034	0.0019	0.0037	0.0020	0.0039
3	0.0027	0.0051	0.0018	0.0033	0.0018	0.0035	0.0018	0.0035
4	0.0025	0.0046	0.0019	0.0035	0.0023	0.0043	0.0016	0.0032
5	0.0024	0.0043	0.0023	0.0041	0.0021	0.0040	0.0020	0.0038
6	0.0028	0.0052	0.0021	0.0039	0.0022	0.0042	0.0018	0.0036
response factors	1.68		1.65		1.72		1.76	

Table 7.6 Analysis of the phenylation reaction products of pentachlorobenzene and benzene at 120 °C

(continued overleaf)

experiment number	pentachlorobiphenyl 2,3,4,5,6-		tetrachlorobiphenyls 2,3,4,5-		2,3,4,6- and 2,3,5,6-		biphenyl		p-chlorotoluene internal standard	
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1	0.0208	0.0524	0.0033	0.0075	0.0051	0.0105	0.0406	0.0515	0.1508	0.1665
2	0.0203	0.0521	0.0037	0.0085	0.0054	0.0112	0.0393	0.0510	0.1461	0.1647
3	0.0204	0.0530	0.0035	0.0081	0.0057	0.0119	0.0400	0.0523	0.1431	0.1629
4	0.0213	0.0542	0.0035	0.0080	0.0059	0.0123	0.0411	0.0528	0.1430	0.1598
5	0.0208	0.0525	0.0034	0.0076	0.0053	0.0109	0.0407	0.0517	0.1425	0.1574
6	0.0214	0.0531	0.0037	0.0085	0.0057	0.0115	0.0416	0.0521	0.1450	0.1580
response factors	2.28		2.04		1.85		1.15		1.00	

Table 7.6 continued

experiment number	trichlorobiphenyl products 2,3,6- peak weight (g.)	2,3,6- cpd. weight (g.)	2,3,5- peak weight (g.)	2,3,5- cpd. weight (g.)	2,3,4- peak weight (g.)	2,3,4- cpd. weight (g.)	3,4,5- peak weight (g.)	3,4,5- cpd. weight (g.)
1	0.0022	0.0040	0.0018	0.0032	0.0019	0.0037	0.0015	0.0030
2	0.0018	0.0035	0.0015	0.0028	0.0017	0.0032	0.0013	0.0026
3	0.0020	0.0038	0.0014	0.0026	0.0020	0.0039	0.0016	0.0033
4	0.0023	0.0043	0.0019	0.0035	0.0020	0.0038	0.0015	0.0029
5	0.0022	0.0041	0.0018	0.0033	0.0021	0.0040	0.0017	0.0034
6	0.0020	0.0036	0.0017	0.0030	0.0023	0.0043	0.0017	0.0032
response factors	1.68		1.65		1.72		1.76	

Table 7.7 Analysis of the phenylation reaction products of pentachlorobenzene and benzene at 80 °C in the presence of additives (continued overleaf)

experiment number	pentachlorobiphenyl 2,3,4,5,6-		tetrachlorobiphenyls 2,3,4,5-		2,3,4,6- and 2,3,5,6-		biphenyl		p-chlorotoluene internal standard	
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1[a]	0.0280	0.0699	0.0038	0.0084	0.0049	0.0099	0.0378	0.0418	0.1464	0.1605
2[a]	0.0275	0.0695	0.0031	0.0071	0.0044	0.0090	0.0368	0.0411	0.1473	0.1629
3[a]	0.0278	0.0688	0.0034	0.0075	0.0048	0.0098	0.0376	0.0412	0.1520	0.1647
4[a]	0.0287	0.0708	0.0037	0.0082	0.0048	0.0095	0.0385	0.0420	0.1535	0.1658
5[b]	0.0287	0.0716	0.0037	0.0082	0.0047	0.0095	0.0373	0.0413	0.1485	0.1626
6[b]	0.0279	0.0708	0.0035	0.0080	0.0046	0.0096	0.0365	0.0410	0.1477	0.1643
7[b]	0.0281	0.0702	0.0034	0.0076	0.0047	0.0096	0.0367	0.0406	0.1513	0.1657
8[b]	0.0285	0.0723	0.0036	0.0082	0.0048	0.0099	0.0372	0.0418	0.1466	0.1631
9[c]	0.0298	0.0743	0.0040	0.0090	0.0051	0.0104	0.0372	0.0411	0.1448	0.1582
10[c]	0.0305	0.0749	0.0038	0.0084	0.0049	0.0097	0.0384	0.0418	0.1420	0.1562
11[c]	0.0310	0.0753	0.0042	0.0091	0.0055	0.0108	0.0389	0.0419	0.1501	0.1601
12[c]	0.0294	0.0738	0.0037	0.0084	0.0049	0.0099	0.0371	0.0412	0.1430	0.1573

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 7.7 continued

experiment number	trichlorobiphenyl products 2,3,6- peak weight (g.)	2,3,6- cpd. weight (g.)	2,3,5- peak weight (g.)	2,3,5- cpd. weight (g.)	2,3,4- peak weight (g.)	2,3,4- cpd. weight (g.)	3,4,5- peak weight (g.)	3,4,5- cpd. weight (g.)
1[a]	0.0027	0.0050	0.0025	0.0045	0.0025	0.0048	0.0020	0.0039
2[a]	0.0026	0.0048	0.0023	0.0042	0.0026	0.0050	0.0021	0.0041
3[a]	0.0030	0.0054	0.0029	0.0051	0.0028	0.0053	0.0023	0.0044
4[a]	0.0028	0.0052	0.0025	0.0044	0.0025	0.0046	0.0019	0.0036
5[b]	0.0030	0.0055	0.0027	0.0048	0.0025	0.0047	0.0020	0.0038
6[b]	0.0031	0.0058	0.0029	0.0053	0.0025	0.0048	0.0022	0.0044
7[b]	0.0033	0.0060	0.0031	0.0056	0.0029	0.0054	0.0024	0.0046
8[b]	0.0033	0.0062	0.0028	0.0051	0.0029	0.0056	0.0021	0.0041
9[c]	0.0036	0.0066	0.0029	0.0053	0.0027	0.0050	0.0022	0.0042
10[c]	0.0039	0.0070	0.0033	0.0059	0.0030	0.0056	0.0024	0.0046
11[c]	0.0035	0.0063	0.0031	0.0055	0.0032	0.0059	0.0026	0.0049
12[c]	0.0037	0.0068	0.0031	0.0057	0.0029	0.0054	0.0027	0.0052

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 7.8 Analysis of the phenylation reaction products of pentachlorobenzene and benzene at 120 °C in the presence of additives (continued overleaf)

experiment number	pentachlorobiphenyl 2,3,4,5,6-		tetrachlorobiphenyls 2,3,4,5-		2,3,4,6- and 2,3,5,6-		biphenyl		p-chlorotoluene internal standard	
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1[a]	0.0271	0.0677	0.0040	0.0090	0.0061	0.0124	0.0479	0.0529	0.1504	0.1645
2[a]	0.0267	0.0671	0.0037	0.0084	0.0059	0.0120	0.0480	0.0533	0.1515	0.1667
3[a]	0.0262	0.0680	0.0034	0.0080	0.0055	0.0116	0.0461	0.0530	0.1417	0.1613
4[a]	0.0257	0.0674	0.0038	0.0090	0.0059	0.0126	0.0452	0.0525	0.1425	0.1639
5[b]	0.0278	0.0702	0.0042	0.0094	0.0062	0.0127	0.0478	0.0534	0.1473	0.1629
6[b]	0.0275	0.0698	0.0040	0.0090	0.0060	0.0123	0.0482	0.0524	0.1485	0.1653
7[b]	0.0281	0.0694	0.0040	0.0089	0.0060	0.0120	0.0485	0.0531	0.1552	0.1681
8[b]	0.0285	0.0706	0.0042	0.0093	0.0059	0.0118	0.0496	0.0544	0.1537	0.1670
9[c]	0.0286	0.0718	0.0050	0.0112	0.0066	0.0135	0.0490	0.0544	0.1515	0.1666
10[c]	0.0289	0.0723	0.0043	0.0097	0.0068	0.0139	0.0488	0.0541	0.1544	0.1694
11[c]	0.0292	0.0727	0.0047	0.0104	0.0070	0.0141	0.0497	0.0548	0.1506	0.1644
12[c]	0.0295	0.0713	0.0044	0.0096	0.0067	0.0131	0.0497	0.0532	0.1587	0.1682

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 7.8 continued

experiment number	trichlorobiphenyl products 2,3,6- peak weight (g.)	2,3,6- cpd. weight (g.)	2,3,5- peak weight (g.)	2,3,5- cpd. weight (g.)	2,3,4- peak weight (g.)	2,3,4- cpd. weight (g.)	3,4,5- peak weight (g.)	3,4,5- cpd. weight (g.)
1[a]	0.0025	0.0046	0.0020	0.0035	0.0022	0.0041	0.0019	0.0036
2[a]	0.0022	0.0041	0.0020	0.0037	0.0023	0.0043	0.0020	0.0038
3[a]	0.0026	0.0049	0.0018	0.0034	0.0023	0.0045	0.0017	0.0035
4[a]	0.0023	0.0044	0.0016	0.0031	0.0020	0.0040	0.0018	0.0037
5[b]	0.0026	0.0048	0.0021	0.0039	0.0024	0.0045	0.0020	0.0039
6[b]	0.0027	0.0051	0.0020	0.0037	0.0022	0.0043	0.0022	0.0044
7[b]	0.0024	0.0044	0.0024	0.0042	0.0026	0.0049	0.0022	0.0041
8[b]	0.0025	0.0046	0.0022	0.0040	0.0027	0.0051	0.0019	0.0037
9[c]	0.0025	0.0047	0.0024	0.0044	0.0024	0.0046	0.0021	0.0040
10[c]	0.0028	0.0052	0.0026	0.0047	0.0028	0.0053	0.0023	0.0045
11[c]	0.0028	0.0051	0.0029	0.0053	0.0029	0.0056	0.0029	0.0048
12[c]	0.0028	0.0049	0.0029	0.0051	0.0027	0.0050	0.0022	0.0041

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 7.9 Partial rate factors and percentage yields for the phenylation of pentachlorobenzene in the absence of additives

experiment number	biphenyl yield (%)	2,3,4,5,6-pentachlorobiphenyl f_6	yield (%)	2,3,4,5-tetrachlorobiphenyl f_1	yield (%)
1[a]	62.8	3.93	42.7	0.22	4.7
2[a]	63.6	3.97	42.1	0.21	4.5
3[a]	64.8	3.92	42.3	0.20	4.4
4[a]	65.4	3.95	43.0	0.19	4.3
5[a]	64.1	3.93	42.0	0.20	4.3
6[a]	63.0	3.91	41.0	0.21	4.4
(mean values)[a]	63.9	3.93	42.2	0.21	4.4
7[b]	83.6	2.88	40.1	0.23	6.4
8[b]	82.8	2.89	39.9	0.26	7.3
9[b]	84.9	2.87	40.6	0.25	6.9
10[b]	85.7	2.90	41.5	0.24	6.9
11[b]	83.9	2.87	40.2	0.23	6.5
12[b]	84.6	2.88	40.7	0.26	7.3
(mean values)[b]	84.3	2.90	40.5	0.25	6.9

a = temperature of phenylation : 80 °C

b = temperature of phenylation : 120 °C

yields are in mole per mole peroxide x 100

Table 7.10 Partial rate factors and percentage yields for the phenylation of pentachlorobenzene in the presence of copper benzoate

experiment number	biphenyl yield (%)	2,3,4,5,6-pentachlorobiphenyl f_6	yield (%)	2,3,4,5-tetrachlorobiphenyl f_1	yield (%)
1[a]	67.9	4.74	53.5	0.32	7.2
2[a]	66.7	4.79	53.2	0.27	5.4
3[a]	66.9	4.72	52.7	0.29	5.7
4[a]	68.2	4.77	54.2	0.31	6.3
(mean values)[a]	67.4	4.75	53.4	0.30	6.2
5[b]	85.9	3.62	51.8	0.27	7.7
6[b]	86.5	3.57	51.4	0.25	7.2
7[b]	86.0	3.63	52.1	0.24	6.9
8[b]	85.2	3.63	51.6	0.27	7.7
(mean values)[b]	85.9	3.61	51.7	0.26	7.4

a = temperature of phenylation : 80 °C

b = temperature of phenylation : 120 °C

additive weight of copper benzoate = 0.1 g.

yields are in mole per mole peroxide x 100

Table 7.11 Partial rate factors and percentage yields for the phenylation of pentachlorobenzene in the presence of iron powder

experiment number	biphenyl yield (%)	2,3,4,5,6-pentachlorobiphenyl f_6	yield (%)	2,3,4,5-tetrachlorobiphenyl f_1	yield (%)
1[a]	67.1	4.91	54.8	0.32	7.0
2[a]	66.6	4.88	54.2	0.31	6.9
3[a]	65.9	4.90	53.8	0.31	6.5
4[a]	67.9	4.89	55.4	0.30	7.0
(mean values)[a]	66.9	4.90	54.5	0.31	6.9
5[b]	86.7	3.72	53.8	0.28	8.1
6[b]	85.1	3.64	53.5	0.26	7.7
7[b]	86.2	3.70	53.1	0.27	7.6
8[b]	88.3	3.67	54.1	0.27	8.0
(mean values)[b]	86.6	3.68	57.1	0.27	7.5

a = temperature of phenylation : 80 °C

b = temperature of phenylation : 120 °C

additive weight of iron powder = 0.1 g.

yields are in mole per mole peroxide x 100

Table 7.12 Partial rate factors and percentage yields for the phenylation of pentachlorobenzene in the presence of trichloroacetic acid

experiment number	biphenyl	2,3,4,5,6-pentachlorobiphenyl		2,3,4,5-tetrachlorobiphenyl	
	yield (%)	f_6	yield (%)	f_1	yield (%)
1[a]	66.7	5.12	56.9	0.34	7.7
2[a]	67.9	5.08	57.4	0.32	7.2
3[a]	68.0	5.09	57.7	0.34	7.8
4[a]	66.9	5.07	56.5	0.32	7.2
(mean values)[a]	67.4	5.09	57.1	0.33	7.5
5[b]	88.3	3.74	55.0	0.33	9.6
6[b]	87.8	3.78	55.4	0.28	8.3
7[b]	89.0	3.75	55.7	0.30	8.9
8[b]	86.4	3.80	54.6	0.29	8.2
(mean values)[b]	87.9	3.77	55.2	0.30	8.8

a = temperature of phenylation : 80 °C

b = temperature of phenylation : 120 °C

additive weight of trichloroacetic acid = 0.1 g.

yields are in mole per mole peroxide x 100

Table 7.13 Percentage yields of some by-products of the phenylation reaction of pentachlorobenzene in the absence of additives

experiment number	tetrachlorobiphenyls 2,3,4,6- and 2,3,5,6- yield (%)	trichlorobiphenyls 2,3,6- yield (%)	2,3,5- yield (%)	2,3,4- yield (%)	3,4,5- yield (%)
1[a]	7.2	4.4	3.7	4.0	3.3
2[a]	6.7	4.8	3.3	3.6	3.8
3[a]	6.9	5.0	3.2	3.4	3.4
4[a]	6.4	4.5	3.4	4.2	3.1
5[a]	6.8	4.2	4.0	3.9	3.7
6[a]	7.0	5.1	3.8	4.1	3.5
(mean values)[a]	6.8	4.6	3.5	3.8	3.4
7[b]	8.9	3.9	3.1	3.6	2.9
8[b]	9.6	3.4	2.7	3.1	2.5
9[b]	10.2	3.7	2.5	3.8	3.2
10[b]	10.5	4.2	3.4	3.7	2.8
11[b]	9.3	4.0	3.2	3.9	3.3
12[b]	9.9	3.5	2.9	4.2	3.1
(mean values)[b]	9.8	3.8	3.0	3.7	4.4

yields are in mole per mole peroxide x 100 a = temperature of phenylation : 80 °C b = temperature : 120 °C

Table 7.14 Percentage yields of some by-products of the phenylation reaction of pentachlorobenzene in the presence of additives at 80 °C

experiment number	tetrachlorobiphenyls 2,3,4,6- and 2,3,5,6- yield (%)	trichlorobiphenyls 2,3,6- yield (%)	2,3,5- yield (%)	2,3,4- yield (%)	3,4,5- yield (%)
1[a]	8.5	4.9	4.4	4.7	3.8
2[a]	7.7	4.7	4.1	5.0	4.0
3[a]	3.4	5.2	5.0	5.2	4.3
4[a]	8.1	5.0	4.3	4.5	3.5
(mean values)[a]	8.2	5.0	4.4	4.8	3.9
5[b]	8.1	5.3	4.7	4.6	3.7
6[b]	8.2	5.6	5.2	4.7	4.3
7[b]	8.2	5.8	5.4	5.2	4.5
8[b]	8.5	6.0	5.0	5.4	4.0
(mean values)[b]	8.3	5.8	5.1	5.0	4.1
9[c]	8.9	6.4	5.2	4.9	4.1
10[c]	8.3	6.8	5.7	5.4	4.5
11[c]	9.3	6.1	5.3	5.7	4.8
12[c]	8.5	6.6	5.5	5.2	5.1
(mean values)[c]	8.7	6.5	5.4	5.4	4.6

yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 7.15 Percentage yields of some by-products of the phenylation reaction of pentachlorobenzene in the presence of additives at 120 °C

experiment number	tetrachlorobiphenyls 2,3,4,6- and 2,3,5,6- yield (%)	trichlorobiphenyls 2,3,6- yield (%)	2,3,5- yield (%)	2,3,4- yield (%)	3,4,5- yield (%)
1[a]	10.6	4.5	3.4	3.9	3.5
2[a]	10.3	3.9	3.6	4.2	3.7
3[a]	9.9	4.8	3.3	4.4	3.4
4[a]	10.8	4.3	3.0	3.9	3.6
(mean values)[a]	10.4	4.4	3.3	4.1	3.6
5[b]	10.9	4.7	3.8	4.4	3.8
6[b]	10.5	5.0	3.6	4.2	4.3
7[b]	10.3	4.3	4.1	4.8	4.0
8[b]	10.1	4.5	3.9	5.0	3.6
(mean values)[b]	10.4	4.6	3.8	4.6	3.9
9[c]	11.6	4.6	4.3	4.5	3.9
10[c]	11.9	5.1	4.6	5.2	4.4
11[c]	12.1	4.9	5.2	5.4	4.7
12[c]	11.2	4.8	4.9	4.9	4.0
(mean values)[c]	11.7	4.8	4.7	5.0	4.2

yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 7.16 Partial rate factors and percentage yields for the phenylation reaction of pentachlorobenzene in the absence and presence of additives at 80 °C and 120 °C

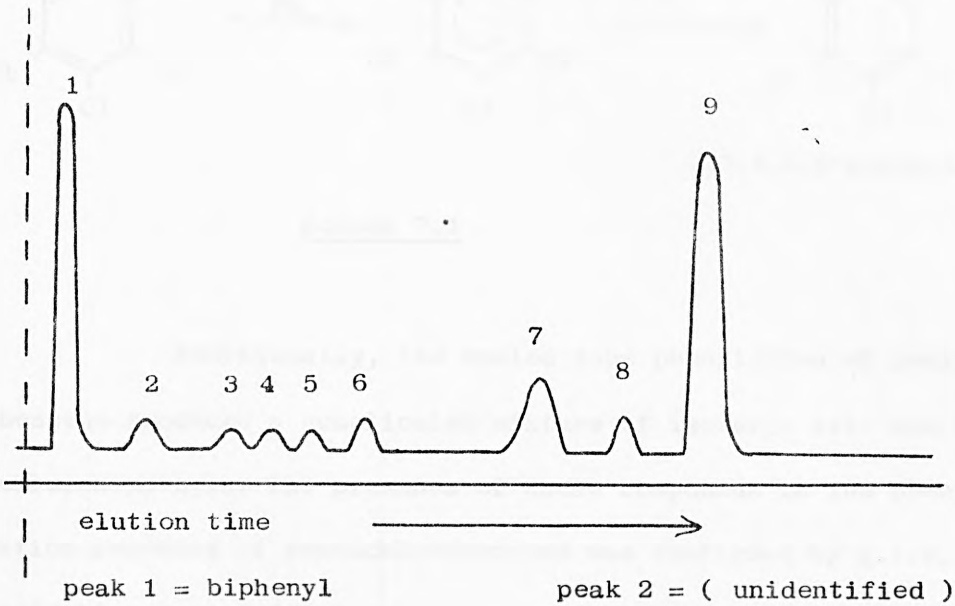
row number	phenyldehydrogenation product 2,3,4,5,6-pentachlorobiphenyl yield (%)	phenyldechlorination product 2,3,4,5-tetrachlorobiphenyl yield (%)	partial rate factors for :- phenyldehydrogenation f_6	partial rate factors for :- phenyldechlorination f_1
1[a,c]	42.2	4.4	3.93	0.21
2[a,d]	53.4	6.2	4.75	0.30
3[a,e]	54.5	6.9	4.90	0.31
4[a,f]	57.1	7.5	5.09	0.33
5[b,c]	40.5	6.9	2.90	0.25
6[b,d]	51.7	7.4	3.61	0.26
7[b,e]	53.6	7.8	3.68	0.27
8[b,f]	55.2	8.8	3.77	0.30

each row of figures is an average of at least four results

a = temperature of phenylation : 80 °C
b = temperature of phenylation : 120 °C
c = no additive
d = additive copper benzoate, 0.1 g.
e = additive iron powder, 0.1 g.
f = additive trichloroacetic acid, 0.1 g.

Note :- the partial rate factors for positions 2 and 3 (f_2 and f_3) could not be determined as the products 2,3,4,6- and 2,3,5,6-tetrachlorobiphenyls were unresolved on the chromatogram, but visual inspection indicated that they were likely to be of the same order as f_1

Figure 7.7 Reconstructed chromatogram showing only the products of phenylation of pentachlorobenzene and benzene



peak 1 = biphenyl

peak 2 = (unidentified)

peak 3 = 2,3,6-trichlorobiphenyl

peak 4 = 2,3,5-trichlorobiphenyl

peak 5 = 2,3,4-trichlorobiphenyl

peak 6 = 3,4,5-trichlorobiphenyl

peak 7 = 2,3,5,6- and 2,3,4,6-tetrachlorobiphenyls (unresolved)

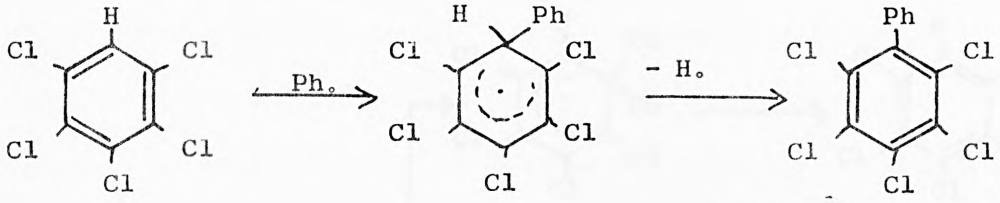
peak 8 = 2,3,4,5-tetrachlorobiphenyl

peak 9 = 2,3,4,5,6-pentachlorobiphenyl

The phenylation of pentachlorobenzene has not been reported in the literature. Analysis of the phenylation reaction mixture showed that the dominant reaction was that of phenyldehydrogenation, with the displacement of hydrogen by phenyl radicals as shown in Scheme 7.1 leading to the formation of 2,3,4,5,6-pentachlorobiphenyl (in 42.2 % yield).

As pentachlorobenzene contains only one hydrogen atom and five chlorine atoms, the fact that phenyldehydrogenation was the dominating reaction was interesting.

phenyldehydrogenation



2,3,4,5,6-pentachlorobiphenyl

Scheme 7.1

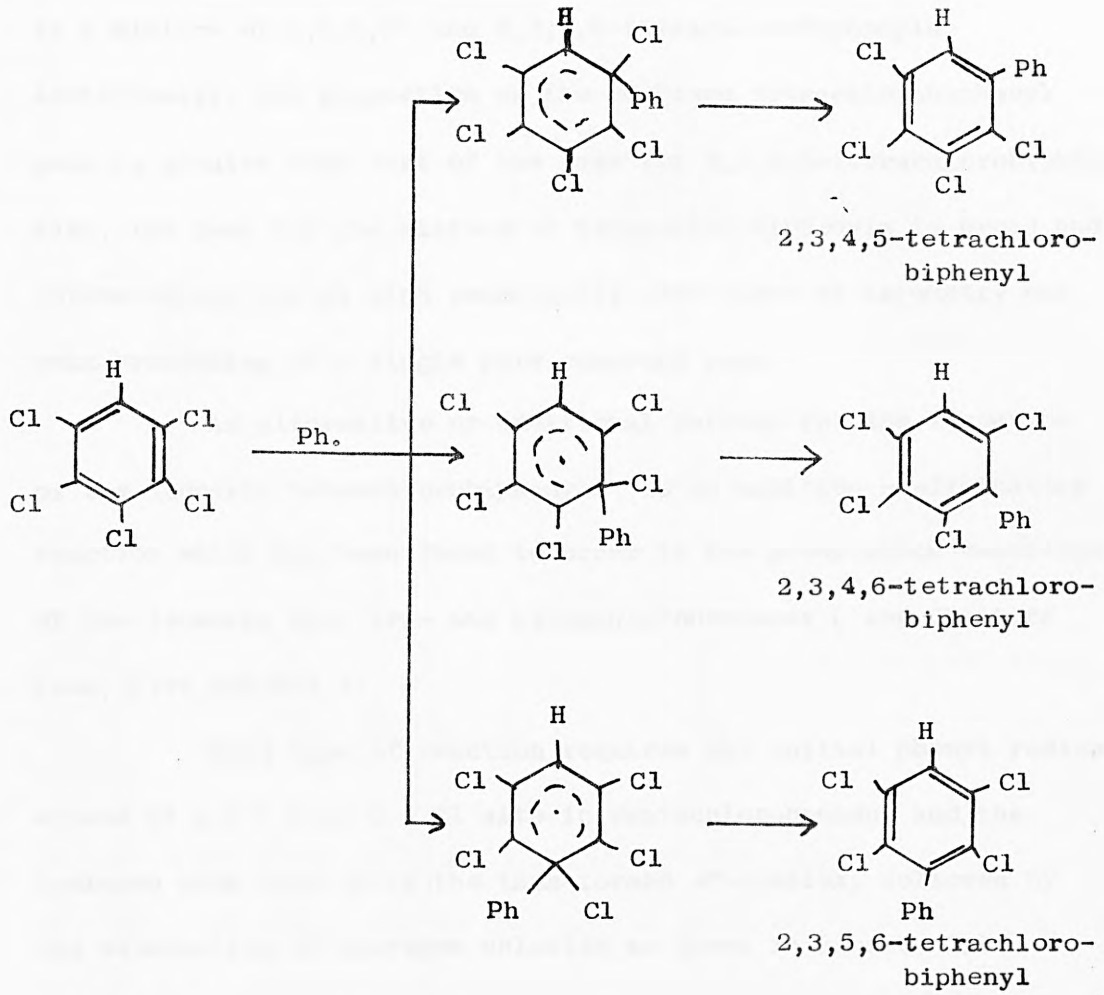
Additionally, the sealed tube phenylation of pentachlorobenzene produced a complicated mixture of isomeric tri- and tetrachlorobiphenyls. The presence of these compounds in the phenylation products of pentachlorobenzene was confirmed by g.l.c. retention data and g.l.c.-mass spectrometry results (see Appendix).

The presence of isomeric tetrachlorobiphenyls in the reaction products can be accounted for by postulating the occurrence of phenyldechlorination reactions. Phenyldechlorination reactions require initial attack of a C - Cl site in pentachlorobenzene followed by the elimination of a chlorine atom as shown in Scheme 7.2 leading to the formation of 2,3,4,6-/2,3,5,6- and 2,3,4,5-tetrachlorobiphenyls (in 6.0 % and 4.4 % yields respectively).

As attack by phenyl radicals at positions 2 and 6 in pentachlorobenzene (Scheme 7.2) both yield 2,3,4,5-tetrachlorobiphenyl, whilst phenyl radical attack at positions 3 and 5 in pentachlorobenzene both yield 2,3,4,6-tetrachlorobiphenyl, higher yields of these isomers were expected than the yield of 2,3,5,6-tetrachlorobiphenyl.

Althought the retention times of 2,3,5,6- and 2,3,4,6-tetrachlorobiphenyls (40.3 and 45.9 minutes respectively) had a difference of 5.6 and synthetic mixtures of the isomers were

phenyldechlorination



Scheme 7.2

distinguishable these two isomers appear to overlap in the chromatogram of the phenylation reaction products, i.e. resolution was difficult and combined yields were reported. However, the peak for 2,3,4,5-tetrachlorobiphenyl was well separated from the 2,3,5,6- and 2,3,4,6-tetrachlorobiphenyl product peak. As 2,3,4,5-tetrachlorobiphenyl's presence has been confirmed (peak 8, Figure 7.1) and peak 7 coincides with the retention times of 2,3,5,6- and 2,3,4,6-tetrachlorobiphenyls, there is no reason why the formation of either tetrachlorobiphenyl isomer should be inhibited or hindered.

Also, g.l.c.-mass spectrometry results show that both peaks 7 and 8 are tetrachlorobiphenyls, m^+ = 292. It can therefore be concluded that the first tetrachlorobiphenyl peak (peak 7, Figure 7.1) is a mixture of 2,3,5,6- and 2,3,4,6-tetrachlorobiphenyls. Additionally, the proportion of the combined tetrachlorobiphenyl peak is greater than that of the peak for 2,3,4,5-tetrachlorobiphenyl. Also, the peak for the mixture of tetrachlorobiphenyls is broad and chromatograms run at high sensitivity show signs of asymmetry and peak broadening of a single pure compound peak.

An alternative or additional pathway for the formation of the isomeric tetrachlorobiphenyls is an addition - elimination reaction which has been found to occur in the phenylation reactions of the isomeric di-, tri- and tetrachlorobenzenes (see Chapters Four, Five and Six).

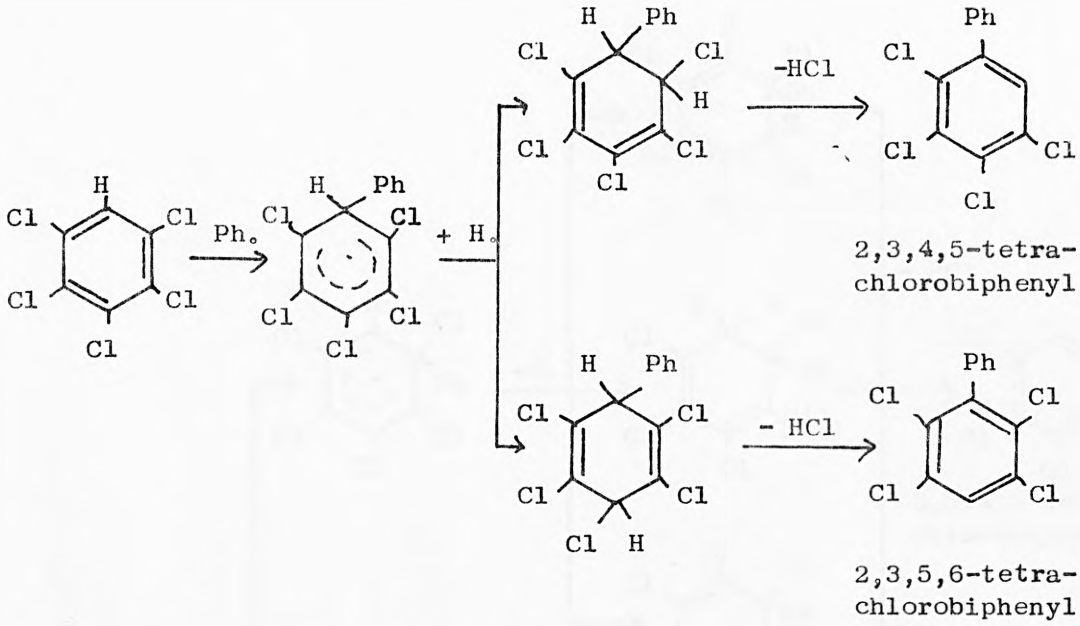
This type of reaction requires the initial phenyl radical attack at a C - H or C - Cl site in pentachlorobenzene and the hydrogen atom take up by the thus formed σ-complex, followed by the elimination of hydrogen chloride as shown in Schemes 7.3 and 7.4.

The additional presence of isomeric trichlorobiphenyls in the phenylation reaction products of pentachlorobenzene was novel and their presence could possibly be accounted for by postulating the occurrence of addition - elimination reactions with the loss of a chlorine molecule as shown in Scheme 7.5.

Thus the pathway for the formation of the isomeric trichlorobiphenyls requires initial ipso type attack by phenyl radicals at a C - Cl site in pentachlorobenzene followed by hydrogen uptake and the final elimination of molecular chlorine. It is, of course, also possible for the intermediate to lose hydrogen chloride instead of chlorine leading to the formation of isomeric tetrachloro-

addition - elimination reaction

phenyl radical attack at C-1



Scheme 7.3

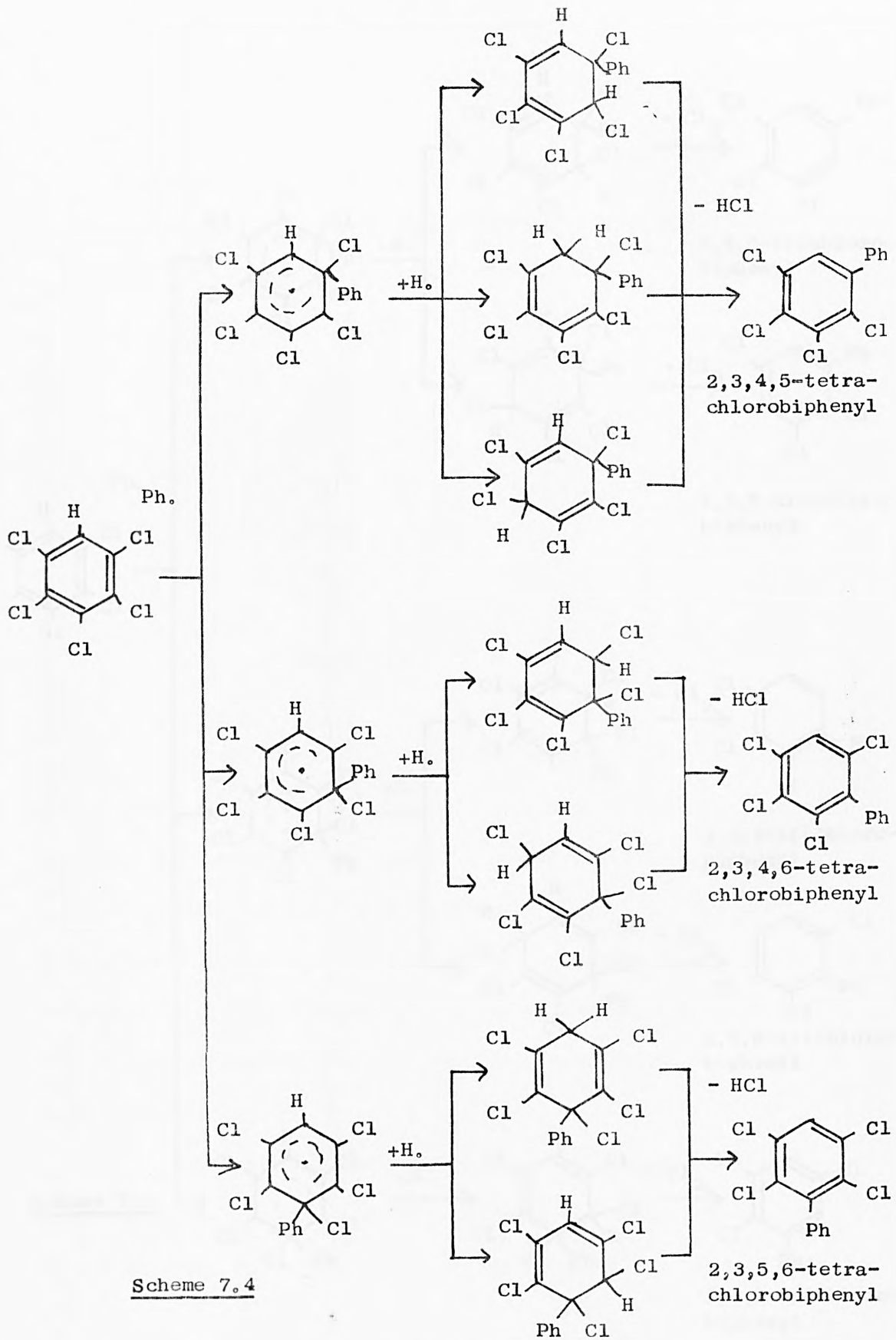
biphenyls as shown in Scheme 7.3 and 7.4. The isomeric trichlorobiphenyls identified in the phenylation products were 2,3,6-, 2,3,5-, 2,3,4- abd 3,4,5-trichlorobiphenyls in the respective yields of 3.8 %, 3.0 %, 3.7 % and 3 % and the reaction pathway is shown as Scheme 7.5.

Any ipso rearrangement reactions which occurres by phenyl radical attack at a C - Cl site in pentachlorobenzene followed by an ortho or meta migration of either group (phenyl or chlorine) would yield 2,3,4,5,6-pentachlorobiphenyl as shown in Scheme 7.6.

As 2,3,4,5,6-pentachlorobiphenyl is already present in the phenylation reaction products as the product of hydrogen displacement (phenyldehydrogenation), it is difficult to decide whether ipso rearrangements occur in the phenylation of pentachlorobenzene.

addition - elimination reaction

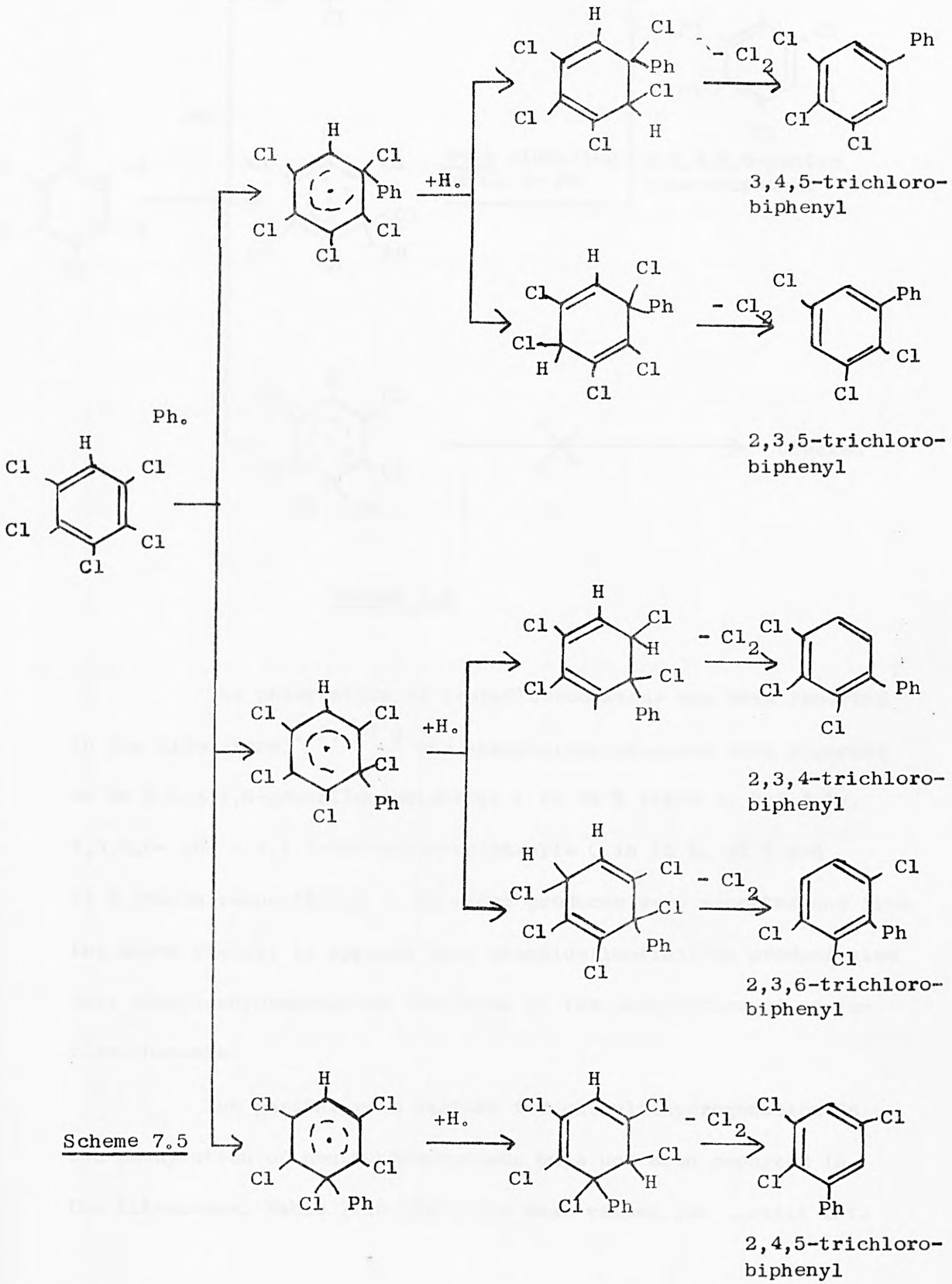
phenyl radical attack at C-2, C-3 and C-4



Scheme 7.4

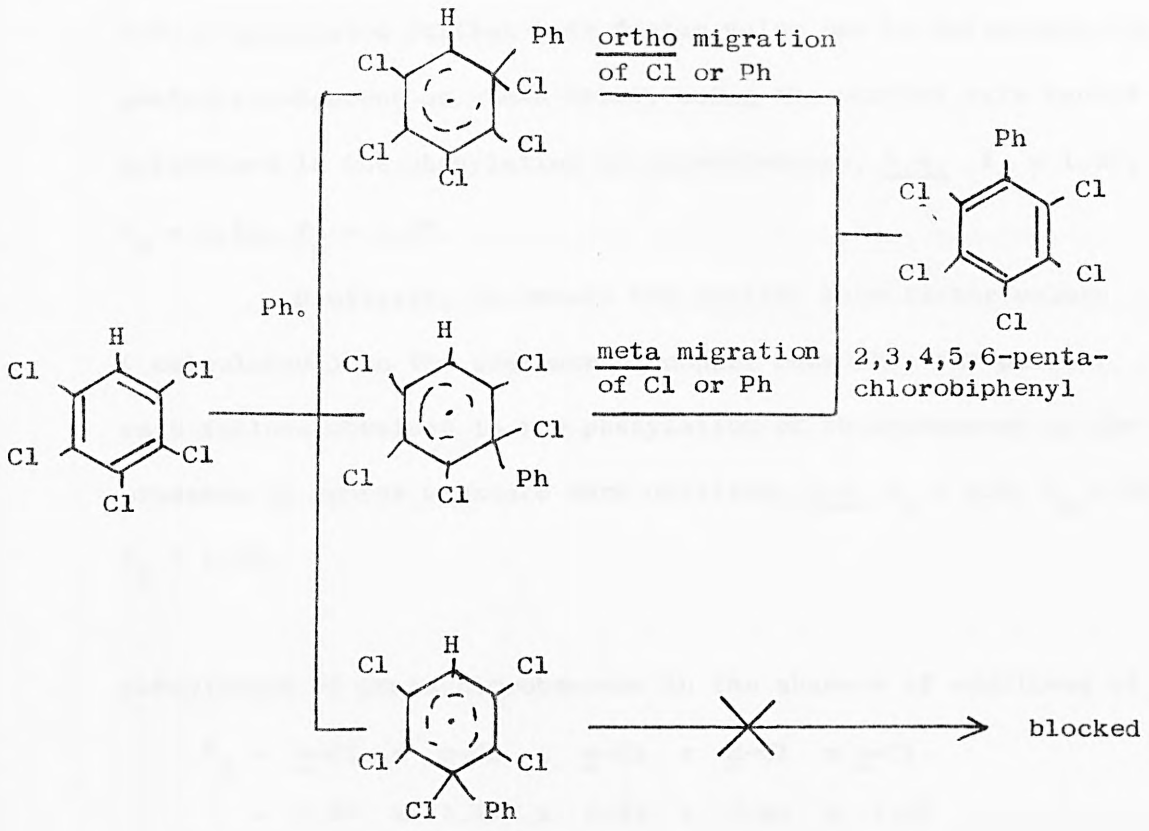
addition - elimination reaction

elimination of molecular chlorine



Scheme 7.5

ipso rearrangements



Scheme 7.6

The phenylation of pentafluorobenzene has been reported in the literature.[2, 77] The phenylation products were reported to be 2,3,4,5,6-pentafluorobiphenyl (in 29 % yield), 2,3,4,5-, 2,3,4,6- and 2,3,5,6-tetrafluorobiphenyls (in 15 %, 45 % and 11 % yields respectively). No other products were reported and from the above yields, it appears that phenyldefluorination predominates over phenyldehydrogenation reactions in the phenylation of pentaflurorbenzene.

The partial rate factors for phenyldehydrogenation in the phenylation of pentachlorobenzene have not been reported in the literature. Table 7.16 lists the mean values for partial rate

factors determined for the phenylation of pentachlorobenzene both in the absence and presence of additives at 80 °C and 120 °C.

On applying Holleman's product rule as described in section 3.5, a calculated partial rate factor value can be determined for pentachlorobenzene as shown below, using the partial rate factor determined in the phenylation of chlorobenzene, i.e. $f_o = 1.97$, $f_m = 0.82$, $f_p = 1.07$.

Similarly, to obtain the partial rate factor values (calculated) in the presence of copper benzoate, the partial rate factors obtained in the phenylation of chlorobenzene in the presence of copper benzoate were utilised, i.e. $f_o = 2.9$, $f_m = 0.9$, $f_p = 1.24$.

phenylation of pentachlorobenzene in the absence of additives at 80 °C

f_6 = o-Cl x o-Cl x m-Cl x m-Cl x p-Cl

= 1.97 x 1.97 x 0.82 x 0.82 x 1.07

= 2.79 observed f_6 = 3.93

phenylation of pentachlorobenzene in the absence of additives at 120 °C

(no available p.r.f.'s for chlorobenzene at 120 °C) observed f_6 = 2.90

phenylation of pentachlorobenzene in the presence of copper benzoate at 80 °C

f_6 = 2.9 x 2.9 x 0.9 x 0.9 x 1.24

= 8.45 observed f_6 = 4.75

phenylation of pentachlorobenzene in the presence of copper benzoate at 120 °C

(no available p.r.f.'s for chlorobenzene at 120 °C) observed f_6 = 3.61

Once again, there are some discrepancies between the calculated and experimental partial rate factor values.

The partial rate factor value for phenyldehydrogenation in the phenylation of pentachlorobenzene at 80 °C without additive was f_6 = 3.9 and at 120 °C it was f_6 = 2.90. Therefore, with an increase in temperature, the partial rate factor for the phenylation of pentachlorobenzene decreased (for hydrogen displacement).

Thus the partial rate factor for phenyldehydrogenation in the phenylation of pentachlorobenzene shows the effect of two ortho chlorine, two meta chlorine and one para chlorine atom on the relative reactivity of that position compared to benzene.

7.1.5 THE EFFECT OF ADDITIVES

The presence of various additives in the phenylation of pentachlorobenzene increased the yield of 2,3,4,5,6-pentachlorobiphenyl and other by-products as shown in Table 7.16, at the expense of products of dimerisation and disproportionation.

The highest biaryl yields were obtained with the use of trichloroacetic acid as the additive, whilst the lowest increase in biaryl yields was obtained with copper benzoate as shown in Table 7.16.

Table 7.16 also shows the mean partial rate factor values obtained for phenyldehydrogenation and phenyldechlorination (hydrogen and chlorine displacement respectively) in the phenylation of pentachlorobenzene at 80 °C and 120 °C.

The presence of additives increased the partial rate factors for the phenyldehydrogenation and for phenyldechlorination as shown in Table 7.16. Thus at 80 °C, without additive, the partial

rate factor for phenyldehydrogenation was f_6 = 3.93, whilst in the presence of trichloroacetic acid the value rose to f_6 = 5.09. Similarly, at 120 ^{o}C without additive, the partial rate factor value for phenyldehydrogenation was f_6 = 2.90, whilst it was f_6 = 3.77 in the presence of trichloroacetic acid.

Similarly, a small increase was observed in the partial rate factors for phenyldechlorination in the presence of additives as shown in Table 7.16. Thus at 80 ^{o}C, without additive, the partial rate factor for phenyldechlorination was f_1 = 0.21 whilst in the presence of trichloroacetic acid, the partial rate factor value rose to f_1 = 0.33. Similarly, at 120 ^{o}C, without additive, the partial rate factor for phenyldechlorination was f_1 = 0.25 which was increased to f_1 = 0.30 in the presence of trichloroacetic acid.

CHAPTER EIGHT

THE PHENYLATION OF HEXACHLOROBENZENE

8.1 METHOD OF PHENYLATION OF HEXACHLOROBENZENE

This was the same as has been described in Section 3.1. Sections 8.1.1 to 8.1.3 show the chromatograms obtained and their identification followed by tables listing experimental quantities leading to tables of results tabulating partial rate factors and yields.

8.1.1 CHROMATOGRAMS

Figures 8.1 and 8.2 show actual chromatograms obtained. Figure 8.3 shows a reconstructed chromatogram demonstrating the relationship between all the products.

8.1.2 PEAK IDENTIFICATION

The same method was used as has been described in section 3.3.

Figure 8.1 Reaction of hexachlorobenzene, chromatogram obtained

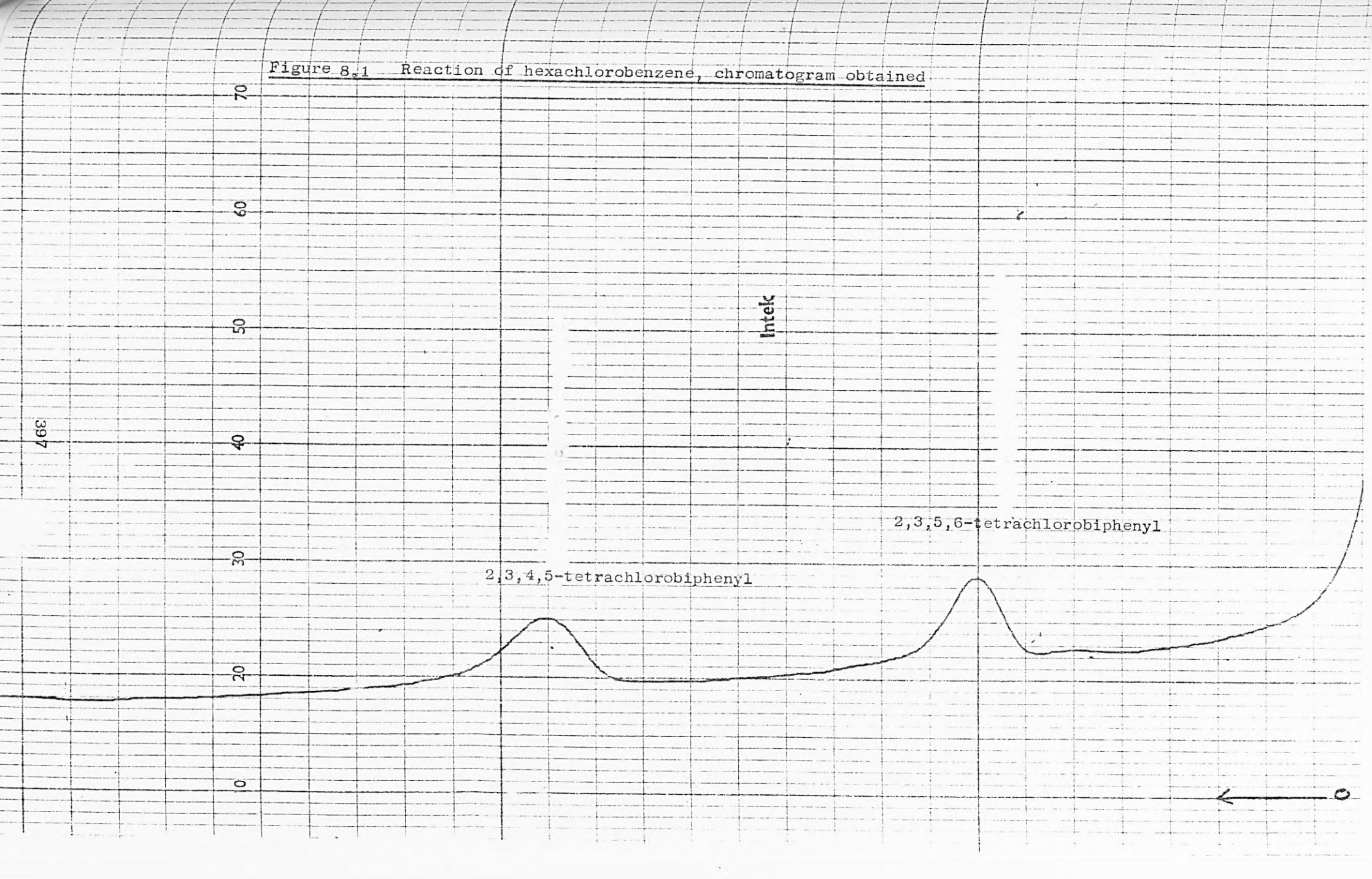


Figure 8.2 Reaction of hexachlorobenzene, chromatogram obtained

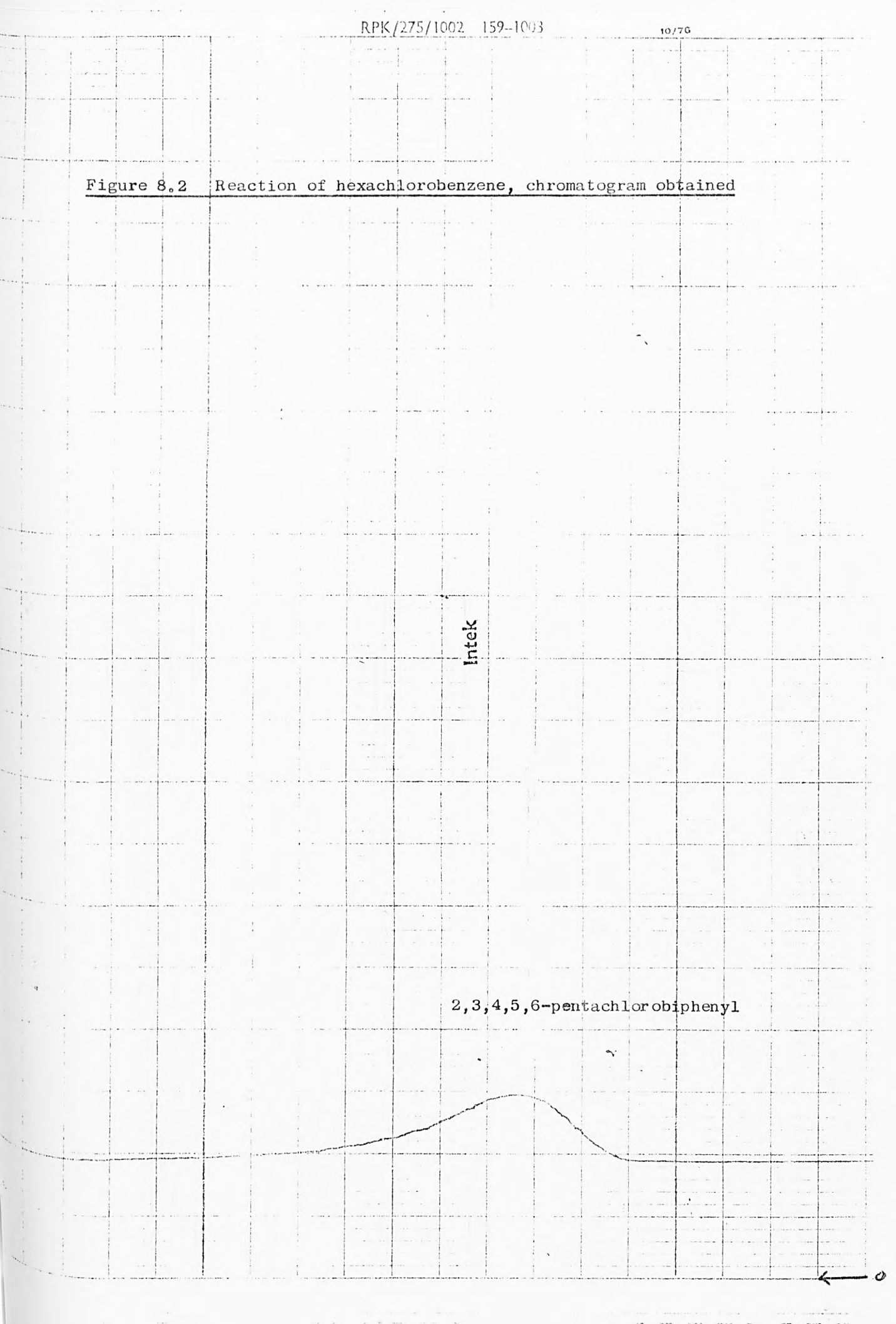


Figure 8.3 Reaction of hexachlorobenzene, reconstructed chromatogram

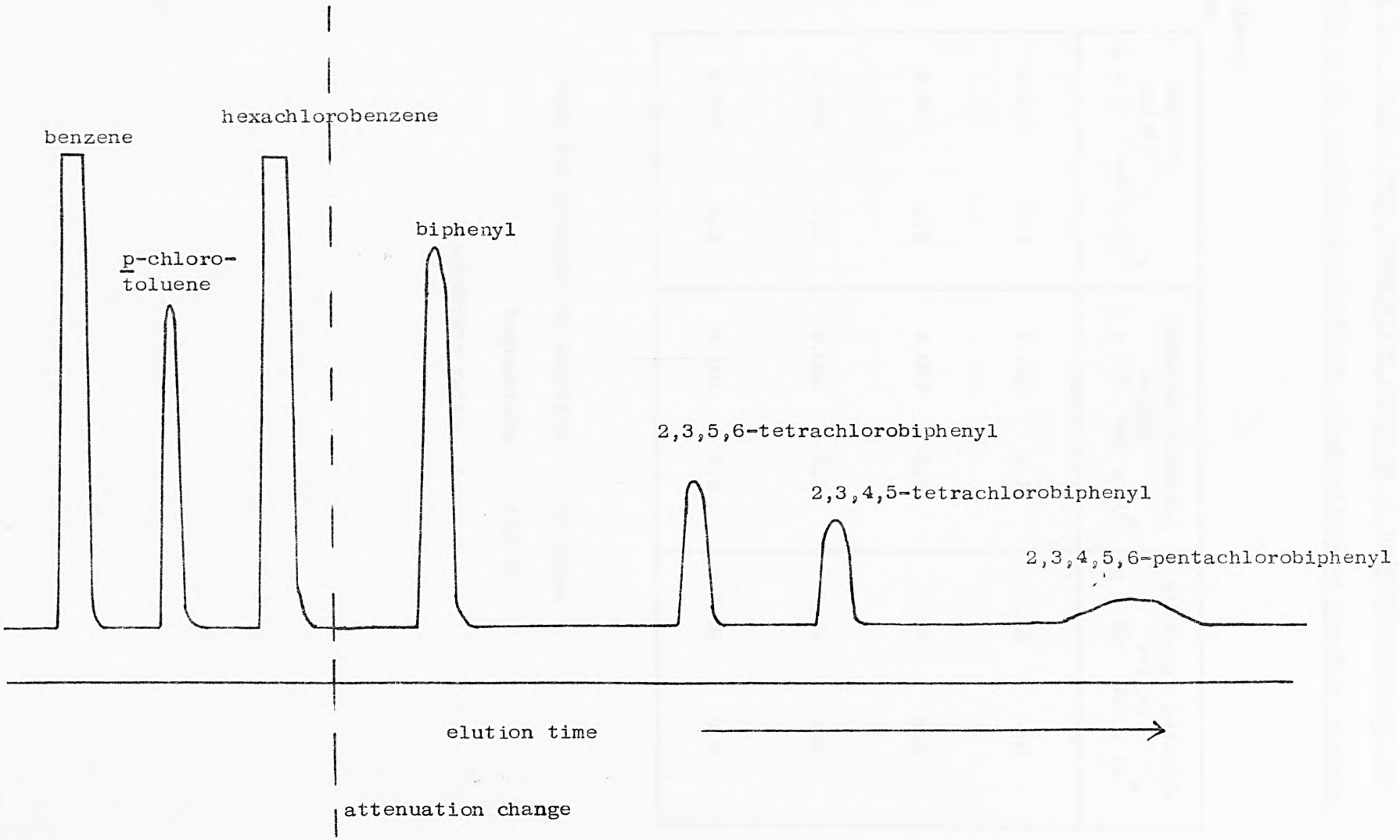


Table 8.1 Sealed tube phenylation reaction of hexachlorobenzene and benzene in the absence of additives - composition of reaction mixtures

experiment number	benzene weight g x 10	benzene mol x 10^3	hexachlorobenzene weight g x 10	hexachlorobenzene mol x 10^3	dibenzoyl peroxide weight g x 10	dibenzoyl peroxide mol x 10^4
1	2.476	3.2	9.106	3.2	7.22	3.0
2	2.455	3.2	9.097	3.2	7.16	3.0
3	2.469	3.2	9.085	3.2	7.29	3.0
4	2.468	3.2	9.101	3.2	7.09	3.0

time for phenylation reaction : 50 hours

temperature : 120 ^{o}C

substrate ratio : 1 : 1

Table 8.2 Sealed tube phenylation reaction of hexachlorobenzene and benzene in the presence of additives - composition of reaction mixtures

experiment number	benzene weight g x 10	benzene mol x 10^3	hexachlorobenzene weight g x 10	hexachlorobenzene mol x 10^3	dibenzoyl peroxide weight g x 10	dibenzoyl peroxide mol x 10^4
1[a]	2.543	3.3	9.495	3.3	7.75	3.0
2[a]	2.559	3.3	9.483	3.3	7.79	3.0
3[a]	2.548	3.3	9.488	3.3	7.66	3.0
4[a]	2.552	3.3	9.492	3.3	7.72	3.0
5[b]	2.494	3.2	9.056	3.2	7.83	3.0
6[b]	2.497	3.2	9.049	3.2	7.79	3.0
7[b]	2.486	3.2	9.044	3.2	7.87	3.0
8[b]	2.495	3.2	9.050	3.2	7.88	3.0
9[c]	2.468	3.2	9.078	3.2	7.52	3.0
10[c]	2.454	3.2	9.071	3.2	7.58	3.0
11[c]	2.463	3.2	9.083	3.2	7.56	3.0
12[c]	2.469	3.2	9.072	3.2	7.57	3.0

time for phenylation reaction : 50 hours

temperature : 120 °C

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 8.3 Analysis of the phenylation reaction products of hexachlorobenzene and benzene in the absence of additives

experiment number	2,3,4,5,6-pentachlorobiphenyl		tetrachlorobiphenyls 2,3,5,6-		2,3,4,5-		biphenyl		p-chlorotoluene internal standard	
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1	0.0015	0.0037	0.0059	0.0118	0.0049	0.0101	0.0044	0.0049	0.1525	0.1681
2	0.0013	0.0032	0.0060	0.0120	0.0052	0.0106	0.0036	0.0040	0.1501	0.1654
3	0.0017	0.0043	0.0056	0.0113	0.0046	0.0094	0.0050	0.0056	0.1518	0.1677
4	0.0014	0.0035	0.0058	0.0116	0.0048	0.0098	0.0038	0.0042	0.1524	0.1669

Table 8.4 Analysis of the phenylation reaction products of hexachlorobenzene and benzene in the presence of additives

experiment number	2,3,4,5,6-pentachlorobiphenyl		tetrachlorobiphenyls 2,3,5,6-		2,3,4,5-		biphenyl		p-chlorotoluene internal standard	
	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	cpd. weight (g.)	peak weight (g.)	std. weight (g.)
1[a]	0.0022	0.0054	0.0067	0.0134	0.0063	0.0128	0.0054	0.0060	0.1503	0.1646
2[a]	0.0019	0.0048	0.0071	0.0142	0.0065	0.0133	0.0047	0.0052	0.1514	0.1660
3[a]	0.0023	0.0057	0.0074	0.0147	0.0059	0.0121	0.0059	0.0065	0.1523	0.1671
4[a]	0.0017	0.0042	0.0076	0.0152	0.0066	0.0135	0.0042	0.0046	0.1511	0.1656
5[b]	0.0023	0.0058	0.0072	0.0145	0.0065	0.0134	0.0057	0.0063	0.1446	0.1596
6[b]	0.0024	0.0061	0.0074	0.0149	0.0067	0.0138	0.0058	0.0065	0.1455	0.1609
7[b]	0.0026	0.0065	0.0075	0.0149	0.0066	0.0136	0.0067	0.0074	0.1473	0.1616
8[b]	0.0021	0.0053	0.0075	0.0150	0.0069	0.0141	0.0055	0.0061	0.1482	0.1624
9[c]	0.0028	0.0069	0.0077	0.0153	0.0071	0.0145	0.0066	0.0073	0.1454	0.1593
10[c]	0.0029	0.0072	0.0073	0.0146	0.0067	0.0138	0.0066	0.0074	0.1426	0.1576
11[c]	0.0026	0.0065	0.0075	0.0150	0.0069	0.0142	0.0059	0.0066	0.1448	0.1598
12[c]	0.0030	0.0076	0.0079	0.0159	0.0072	0.0148	0.0071	0.0079	0.1435	0.1584

a = additive copper benzoate, 0.1 g. b = additive iron powder, 0.1 g. c = additive trichloroacetic acid, 0.1 g.

Table 8.5 Partial rate factors and percentage yields for the phenylation of hexachlorobenzene in the absence of additives

experiment number	biphenyl yield (%)	2,3,4,5,6-pentachlorobiphenyl f_1	yield (%)
1	10.6	0.36	3.8
2	8.7	0.38	3.3
3	12.1	0.36	4.4
4	9.1	0.37	3.8
(mean values)	10.1	0.37	3.8

yields are in mole per mole peroxide x 100

Table 8.6 Partial rate factors and percentage yields for the phenylation of hexachlorobenzene in the presence of additives

experiment number	biphenyl yield (%)	2,3,4,5,6-pentachlorobiphenyl f_1	2,3,4,5,6-pentachlorobiphenyl yield (%)
1[a]	13.0	0.43	5.5
2[a]	11.3	0.43	4.9
3[a]	14.1	0.41	5.8
4[a]	10.0	0.43	4.3
(mean values)[a]	12.0	0.43	5.1
5[b]	13.6	0.44	5.9
6[b]	14.1	0.44	6.2
7[b]	16.0	0.41	6.6
8[b]	13.2	0.41	5.4
(mean values)[b]	14.2	0.43	6.1
9[c]	15.8	0.45	7.0
10[c]	16.0	0.46	7.4
11[c]	14.3	0.47	6.6
12[c]	17.1	0.46	7.8
(mean values)[c]	15.8	0.46	7.2

yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Table 8.7 Percentage yields of some by-products of the phenylation of hexachlorobenzene in the absence of additives

experiment number	tetrachlorobiphenyls	
	2,3,5,6- yield (%)	2,3,4,5- yield (%)
1	13.5	11.5
2	13.7	12.1
3	12.9	10.7
4	13.2	11.2
(mean values)	13.3	11.3

yields are in mole per mole peroxide x 100

Table 8.8 Percentage yields of some by-products of the phenylation of hexachlorobenzene in the presence of additives

experiment number	tetrachlorobiphenyls 2,3,5,6- yield (%)	2,3,4,5- yield (%)
1[a]	15.3	14.6
2[a]	16.2	15.2
3[a]	16.8	13.8
4[a]	17.4	15.4
(mean values)[a]	16.4	14.7
5[b]	16.6	15.3
6[b]	17.0	15.8
7[b]	17.0	15.5
8[b]	17.1	16.1
(mean values)[b]	16.9	15.6
9[c]	17.5	16.6
10[c]	16.7	15.8
11[c]	17.1	16.2
12[c]	18.2	16.9
(mean values)[c]	17.3	16.3

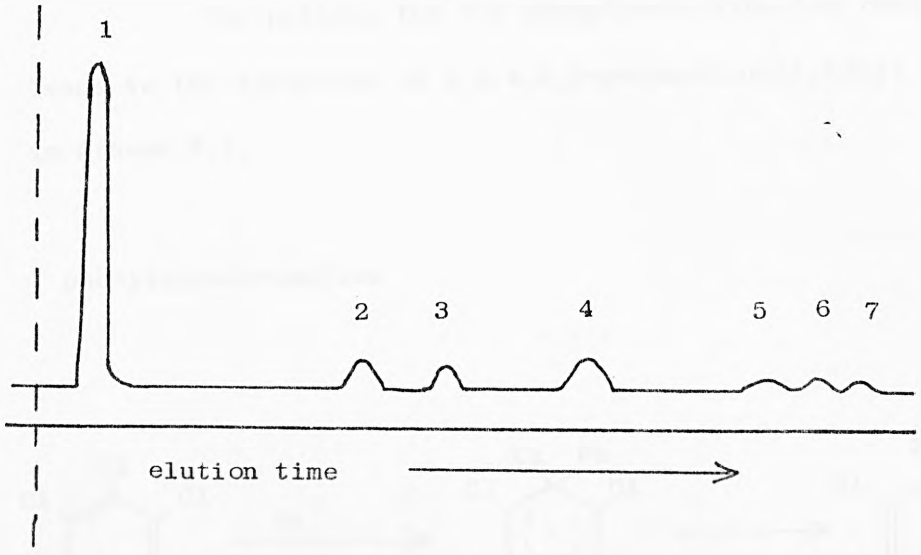
yields are in mole per mole peroxide x 100

a = additive copper benzoate, 0.1 g.

b = additive iron powder, 0.1 g.

c = additive trichloroacetic acid, 0.1 g.

Figure 8.4 Reconstructed chromatogram showing only the products of phenylation of hexachlorobenzene and benzene



peak 1 = biphenyl

peak 2 = 2,3,5,6-tetrachlorobiphenyl

peak 3 = 2,3,4,5-tetrachlorobiphenyl

peak 4 = 2,3,4,5,6-pentachlorobiphenyl

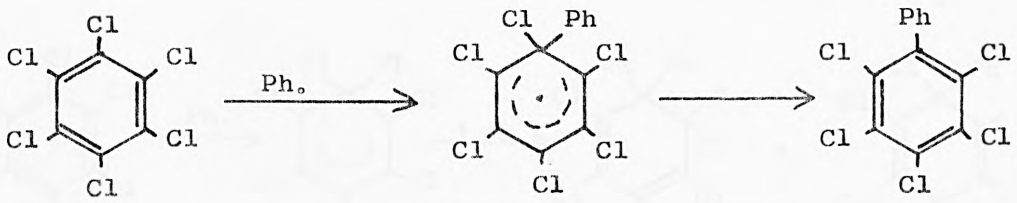
peaks 5,6 and 7 = isomeric tetrachloroterphenyls

The phenylation of hexachlorobenzene has not been reported in the literature. This reaction was particularly interesting as there were no hydrogen atoms present in the molecule. The phenylation of hexafluorobenzene has been well studied and there are several reports in the literature. [2, 48] The main product was 2,3,4,5,6-pentafluorobiphenyl and a range of dimerisation and disproportionation products were also formed. The thermolysis of bis (pentafluoro) benzoyl peroxide in hexafluorobenzene gave small yields of decafluorobiphenyl showing that various factors are involved in determining biaryl yields in aryldefluorination reactions. It was interesting to speculate whether the larger, bulkier chlorine atoms in hexachlorobenzene hindered the approach of phenyl radicals.

On analysis of the reaction products of sealed tube phenylation of hexachlorobenzene, it was discovered that the C - Cl bond was indeed attacked by phenyl radicals, forming 2,3,4,5,6-pentachlorobiphenyl (in 3.8 % yield).

The pathway for the phenyldechlorination reaction which leads to the formation of 2,3,4,5,6-pentachlorobiphenyl is shown in Scheme 8.1.

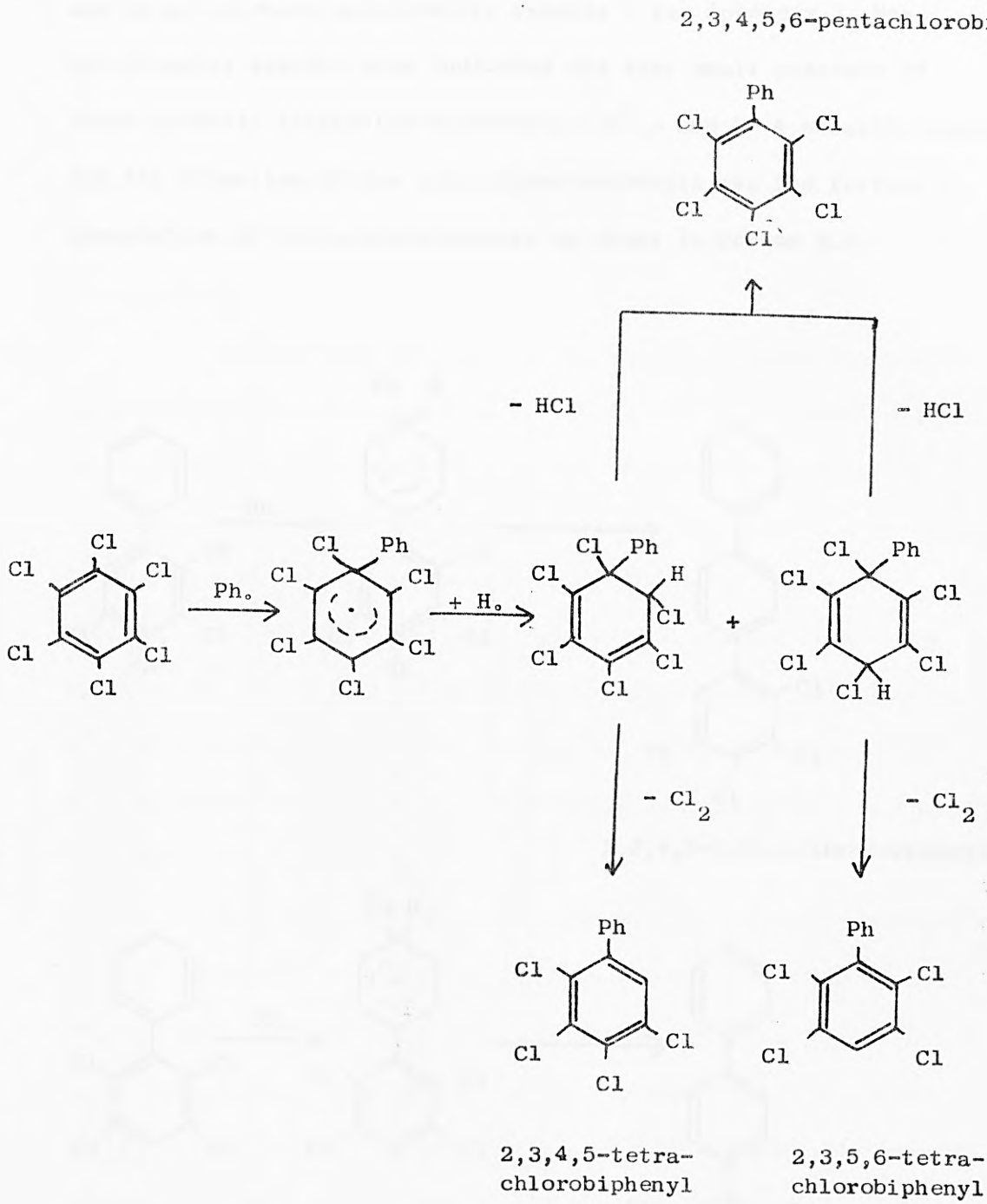
phenyldechlorination



Scheme 8.1

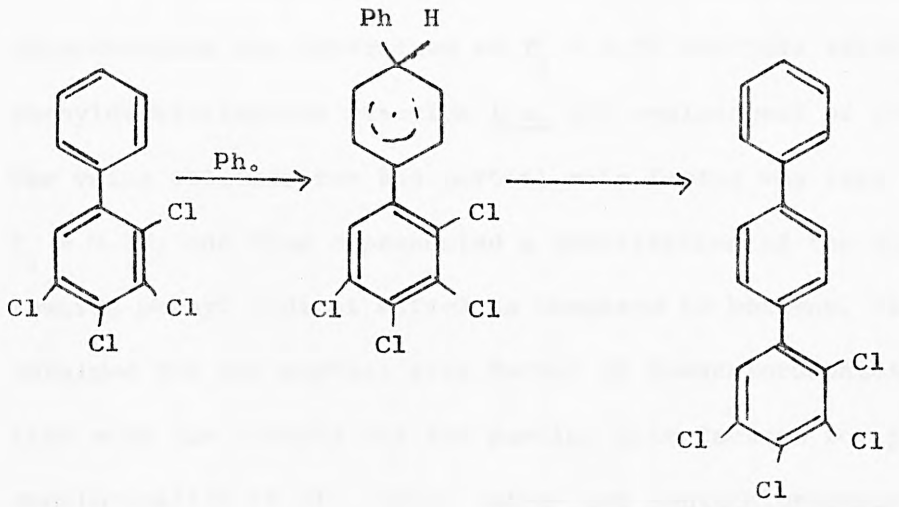
The phenylation reaction products were found to contain two isomeric tetrachlorobiphenyls, namely 2,3,5,6- and 2,3,4,5-tetrachlorobiphenyls (in 13.5 % and 11.5 % yields respectively). The formation of these tetrachlorobiphenyls constitutes a novel reaction and no tetrafluorobiphenyls were reported in the phenylation of hexafluorobenzene. (48) A possible pathway for the formation of these tetrachlorobiphenyls is shown in Scheme 8.2. The mechanism for this reaction involves initial attack by phenyl radicals at a C - Cl site and the take up of a hydrogen atom by the resultant σ-complex followed by the loss of molecular chlorine. If hydrogen chloride was eliminated from the intermediate instead of chlorine, then 2,3,4,5,6-pentachlorobiphenyl would be formed as shown in Scheme 8.2.

addition - elimination reaction

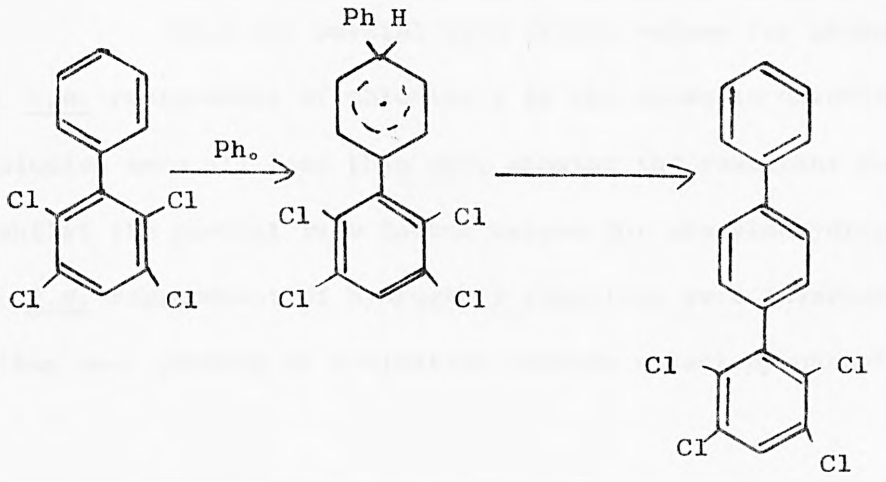


Scheme 8.2

The presence of tetra- and pentachlorobiphenyls in the phenylation reaction products was confimed by g.l.c. retention data and by g.l.c.-mass spectrometry results (see Appendix). Mass spectrometry results also indicated the very small presence of three isomeric tetrachloroterphenyls ($m^+ = 368$). A possible route for the formation of the tetrachloroterphenyls was the further phenylation of tetrachlorobiphenyl as shown in Scheme 8.3.



2,3,4,5-tetrachloroterphenyl



2,3,5,6-tetrachloroterphenyl

Scheme 8.3

However, there was no apparent g.l.c.-mass spectrometry evidence for the presence of pentachloroterphenyl, hexachlorobiphenyl or trichloroterphenyl.

The partial rate factor for the phenylation of hexachlorobenzene has not been reported in the literature. Table 8.9 lists the mean values for the partial rate factors for the phenylation of hexachlorobenzene both in the absence and presence of additives.

The partial rate factor for the phenylation of hexachlorobenzene was determined as $f_1 = 0.37$ and this value was for a phenyldechlorination reaction i.e. the replacement of chlorine. The value obtained for the partial rate factor was less than one, $f_1 = 0.37$, and thus represented a deactivation of the molecule towards phenyl radical attack as compared to benzene. The value obtained for the partial rate factor of hexachlorobenzene was in line with the results for the partial rate factors for phenyldechlorination of di-, tri-, tetra- and pentachlorobenzenes, namely less than one.

Thus the partial rate factor values for phenyldechlorination (i.e. replacement of chlorine) in the isomeric chlorinated benzenes studied were all less than one, showing the resultant deactivation, whilst the partial rate factor values for phenyldehydrogenation (i.e. replacement of hydrogen) reactions were invariably greater than one, showing an activation towards attack by phenyl radicals.

8.1.5 THE EFFECT OF ADDITIVES

The presence of various additives in the phenylation of hexachlorobenzene increased the yields of 2,3,4,5,6-pentachlorobiphenyl

Table 8.9 Partial rate factors and percentage yields for the phenylation of hexachlorobenzene

row number	phenyldechlorination product 2,3,4,5,6-pentachlorobiphenyl yield (%)	partial rate factor for phenyldechlorination f_1
1[a]	3.8	0.37
2[b]	5.1	0.43
3[c]	6.1	0.43
4[d]	7.2	0.46

yields are in mole per mole peroxide x 100

a = no additive

b = additive copper benzoate, 0.1 g.

c = additive iron powder, 0.1 g.

d = additive trichloroacetic acid, 0.1 g.

each row of results is a mean of four or more figures

as shown in Table 8.9, at the expense of products of dimerisation and disproportionation.

Once again, the highest biaryl yields were obtained by using trichloroacetic acid as the additive, whilst the lowest increase in biaryl yields was obtained with copper benzoate as shown in Table 8.9.

The partial rate factor values for the phenyldechlorination (substitution of chlorine) of hexachlorobenzene in the presence of various additives are shown in Table 8.9. Thus the partial rate factor value for phenyldechlorination without additive was $f_1 = 0.37$ which was increased to $f_1 = 0.46$ in the presence of trichloroacetic acid.

8.1.6 CONCLUSION

The homolytic phenylation of chlorinated benzenes was a complex reaction producing products of the displacement of both hydrogen and chlorine i.e. phenyldehydrogenation and phenyldechlorination. In addition to these reactions, it was found that addition - elimination and ipso rearrangement reactions occurred to a significant extent in the phenylation of chlorinated benzenes, which had no parallel in the phenylation reactions of the polyfluorobenzenes thus constituting a major difference.

The presence of additives increased the biaryl yields by diverting the σ-complex from reactions of dimerisation and disproportionation.

It can be seen from the higher p.r.f. value results in Chapters Three to Eight in the presence of additives that the effect

of the additive varies approximately in the following order :-

trichloroacetic acid > iron powder > copper benzoate > copper chloride
copper acetate

most efficient least efficient

The increased partial rate factor values in the presence of trichloroacetic acid may possibly be due to the efficiency of trichloroacetic acid as a hydrogen donor, promoting the removal of chlorine from the intermediate σ_{Cl}-complexes.

Similarly, copper salts act as oxidising agents and remove H. from σ_{H}-complexes preventing dimerisation and disproportionation.

CHAPTER NINE

THE METHYLATION OF CHLORINATED BENZENES

9.0 INTRODUCTION

The methylation of monohalogeno-benzenes has been reported by several workers[136-140] in the literature. However, the methylation of highly chlorinated benzenes has not been reported.

It was interesting to speculate on the course of methylation reactions of chlorinated benzenes, the relative proportions of nuclear/sidechain attack, ease of replacement of chlorine, and formation of mono-, di-methylation products.

Similar to the phenylation reactions, the sigma complex MeArH. is formed on the methylation of ArH which may be dehydrogmated by methyl radicals to form the methylated products and methane.

However, the present work on the methylation of chlorinated benzenes represents qualitative results only and serves as a useful comparison to the phenylation of these compounds.

The methylation reactions were carried out in sealed tubes as described in chapter 2, similar to the phenylation reactions.

The methylation reactions were carried out without additive or solvent, with benzene as the reference compound producing toluene on methylation. Benzene was added to the reaction mixture (as the reference compound producing toluene on methylation) so that partial rate factors could be determined by comparing the yields of toluene and chlorotoluenes.

Di-tertiary butyl peroxide[137] was used as the source of methyl radicals, and the methylation reactions were carried out at 140°C for 40 hours.

As in the phenylation experiments, the methylation reaction products were found to be complex mixtures with the simultaneous occurrence of methyl dehydrogenation and methyl dechlorination. Also it appears from the methylation reaction products of certain chlorinated

benzenes that the novel reactions described in Chapters 3-8 occur to a significant extent, namely reactions involving the take up of a hydrogen atom followed by the elimination of hydrogen chloride or molecular chlorine and the ipso type rearrangement reaction.

9.1 LIST OF METHYLATION PRODUCTS CORRESPONDING TO PEAKS IN FIG.9.0 TO 9.11

Fig.9.0

1) Methylation of Chlorobenzene

Peak 1	=	Benzene/Toluene	Peak 3	=	2-chlorotoluene
Peak 2	=	Chlorobenzene	Peak 4	=	3-chlorotoluene
			Peak 5	=	4-chlorotoluene

Fig.9.1

2) Methylation of 1,4-Dichlorobenzene

Peak 1	=	Benzene/Toluene	Peak 6	=	1,4-dichlorobenzene
Peak 2	=	Unknown	Peak 7	=	Unknown
Peak 3	=	3-Chlorotoluene	Peak 8	=	2,4-dichlorotoluene
Peak 4	=	4-Chlorotoluene	Peak 9	=	2,5-dichlorotoluene
Peak 5	=	Unknown	Peak 10	=	3,4-dichlorotoluene

Fig.9.2

3) Methylation of 1,2-Dichlorobenzene

Peak 1	=	Benzene/Toluene	Peak 5	=	Unknown
Peak 2	=	Unknown	Peak 6	=	1,2-dichlorobenzene
Peak 3	=	2-chlorotoluene	Peak 7	=	2,3-dichlorotoluene
Peak 4	=	3-chlorotoluene	Peak 8	=	3,4-dichlorotoluene

Fig.9.3

4) Methylation of 1,3-dichlorobenzene

Peak 1	=	Benzene/Toluene	Peak 5	=	4-chlorotoluene
Peak 2	=	Unknown	Peak 6	=	1,3-dichlorobenzene
Peak 3	=	2-chlorotoluene	Peak 7	=	2,6-dichlorotoluene
Peak 4	=	3-chlorotoluene	Peak 8	=	2,4-dichlorotoluene

Fig.9.4

5) Methylation of 1,3,5-Trichlorobenzene

Peak 1 = Benzene/Toluene

Peak 2 = Unknown

Peak 3 = 2,6-dichlorotoluene

Peak 4 = 2,4-dichlorotoluene

Peak 5 = 3,5-dichlorotoluene

Peak 6 = 1,3,5-Trichlorobenzene

Peak 7 & 8 = Unknown

Peak 9 = 2,4,6-trichlorotoluene

Peak 10= 2,3,4-trichlorotoluene

Peak 11= Unknown

Fig.9.5

6) Methylation of 1,2,3-Trichlorobenzene

Peak 1 = Benzene/Toluene

Peak 2 = Unknown

Peak 3 = 2,6-dichlorotoluene

Peak 4 = 2,3-dichlorotoluene

Peak 5 = 3,5-dichlorotoluene

Peak 6 = 3,4-dichlorotoluene

Peak 7 = 1,2,3-Trichlorobenzene

Peak 8 = 2,3,6/2,3,5-trichlorotoluene

Peak 9 = 2,3,4-trichlorotoluene

Peak 10= 3,4,5-trichlorotoluene

Fig.9.6

7) Methylation of 1,2,4-Trichlorobenzene

Peak 1 = Benzene/Toluene

Peak 2,3,5, 6 & 16 = unknown

Peak 4 = 2,4-dichlorotoluene

Peak 7 = 2,5-dichlorotoluene

Peak 8 = 3,4-dichlorotoluene

Peak 9 = 1,2,4-trichlorobenzene

Peak 10= 2,4,5-trichlorotoluene

Peak 11= 2,4,6-trichlorotoluene

Peak 12= 2,3,6-trichlorotoluene

Peak 13= 2,3,5-trichlorotoluene

Peak 14= 2,3,4-trichlorotoluene

Peak 15= 3,4,5-trichlorotoluene

Fig.9.7

8) Methylation of 1,2,3,5-Tetrachlorobenzene

Peak 1 = Benzene/Toluene

Peak 2-4= Unknown

Peak 5 = 2,4,5-trichlorotoluene

Peak 6 = 2,4,6-trichlorotoluene

Peak 7 = 2,3,6-trichlorotoluene

Peak 8 = 2,3,5-trichlorotoluene

Peak 9 = 2,3,4-trichlorotoluene

Peak 10= 3,4,5-trichlorotoluene

Peak 11 = 1,2,3,5-tetrachlorobenzene

Peak 12,13= Unknown

Peak 14 = 2,3,4,6-tetrachlorotoluene

Peak 15 = 2,3,5,6-tetrachlorotoluene

Peak 16 = 2,3,4.5-tetrachlorotoluene

Fig.9.8

9) Methylation of 1,2,4,5-Tetrachlorobenzene

Peak 1 = Benzene/Toluene

Peak 2-5= Unknown

Peak 6 = 2,4,5-trichlorotoluene

Peak 7 = 2,3,5-trichlorotoluene

Peak 8 = 1,2,4,5-trichlorobenzene

Peak 9, 10 = Unknown

Peak 11 = 2,3,4,6-tetrachlorotoluene

Peak 12 = 2,3,5,6-tetrachlorotoluene

Peak 13 = 2,3,4.5-tetrachlorotoluene

Fig.9.9

10) Methylation of 1,2,3,4-Tetrachlorobenzene

Peak 1 = Benzene/Toluene

Peak 2-9 Unknown

Peak 10 = 2,3,6-trichlorotoluene

Peak 11 = 2,3,4-trichlorotoluene

Peak 12= 3,4,5-trichlorotoluene

Peak 13 = 1,2,3,4-Tetrachlorobenzene

Peak 14 = Unknown

Peak 15 = 2,3,4,6-tetrachlorotoluene

Peak 16 = 2,3,5,6-tetrachlorotoluene

Peak 17 = 2,3,4,5-tetrachlorotoluene

Fig.9.10

11) Methylation of Pentachlorobenzene

Peak 1 = Benzene/Toluene

Peak 2-5 Unknown

Peak 6 = 2,3,4,6-tetrachlorotoluene

Peak 7 = 2,3,5,6-tetrachlorotoluene

Peak 8 = 2,3,4,5-tetrachlorotoluene

Peak 9 = Pentachlorobenzene

Peak 10= Pentachlorotoluene

Fig.9.11

12) Methylation of Hexachlorobenzene

Peak 1 = Benzene/Toluene

Peak 2 = Unknown

Peak 8 = 2,3,4,6-tetrachlorotoluene

Peak 9 = 2,3,5,6-tetrachlorotoluene

Peak 10= 2,3,4,5-tetrachlorotoluene

Peak 11= pentachlorotoluene

Peak 12= Hexachlorobenzene

9.2 DISCUSSION

It can be seen from the chromatograms of the methylation of chlorinated benzenes that the reaction is as complex as that of the phenylation of these compounds.

The conventional products of methyldehydrogenation were the major reaction products in all cases followed by the methyldechlorination products. Similar to the phenylation of chlorinated benzenes (Chapters 3-8) various other isomeric polychlorotoluenes were identified in the reaction mixture, and it is suggested that similar reaction pathways were involved to account for these novel products.

Namely, the take up of a hydrogen atom by the sigma complex followed by the elimination of hydrogen chloride or molecular chlorine and the ipso type rearrangement reactions as described in Chapters 3-8.

9.3 CONCLUSION

COMPARISON OF THE METHYLATION AND PHENYLATION REACTIONS OF CHLORINATED BENZENES

From an examination of the products identified in the methylation reactions of chlorinated benzenes it is clear that the situation is similar to the phenylation of these compounds and that in some instances the reaction products are even more complex perhaps indicating the possibility of higher methylated products or some sort of abstraction reaction.

Fig.9.0 Methylation of Chlorobenzene

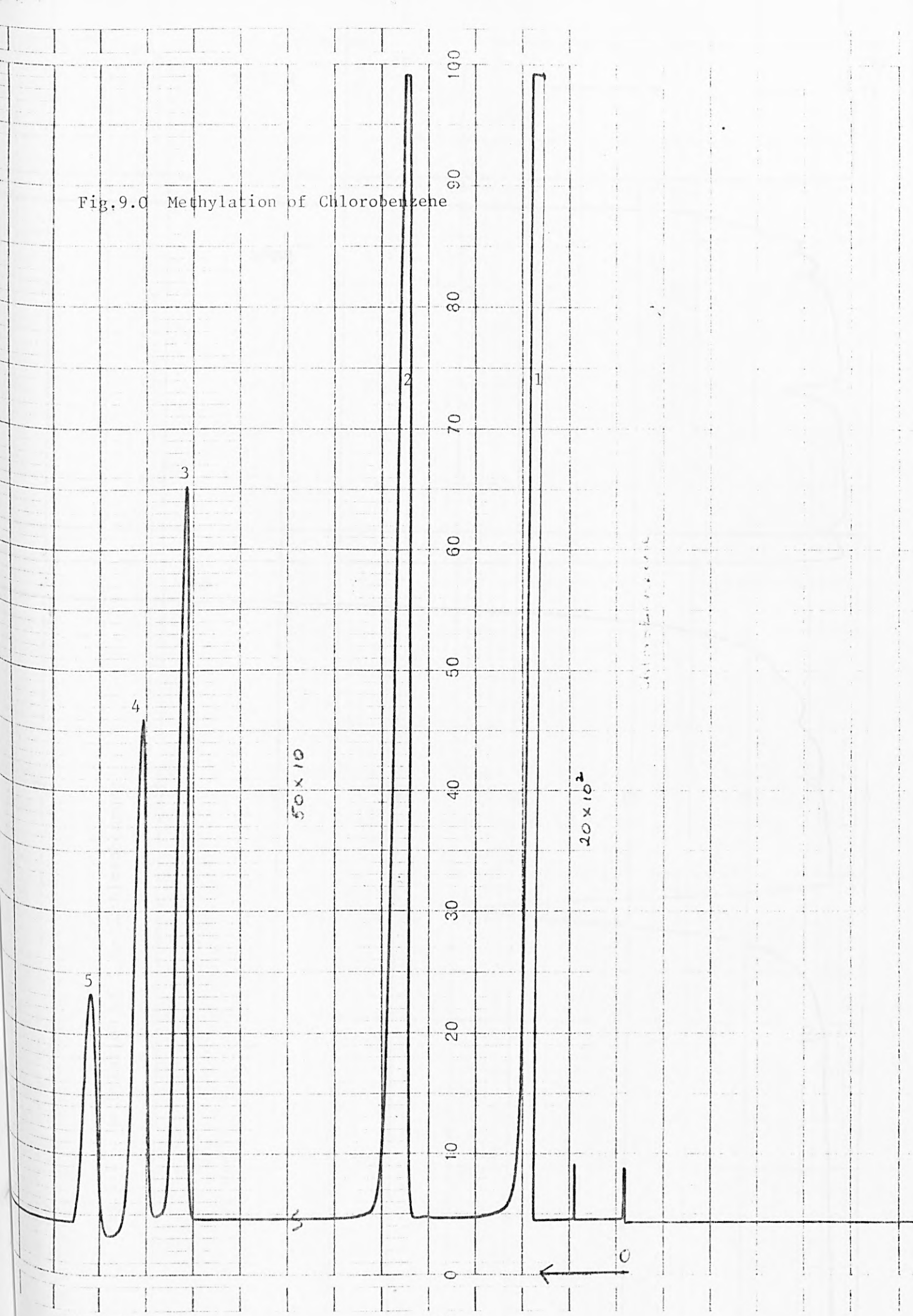


Fig.9.1 Methylation of 1,4-Dichlorobenzene

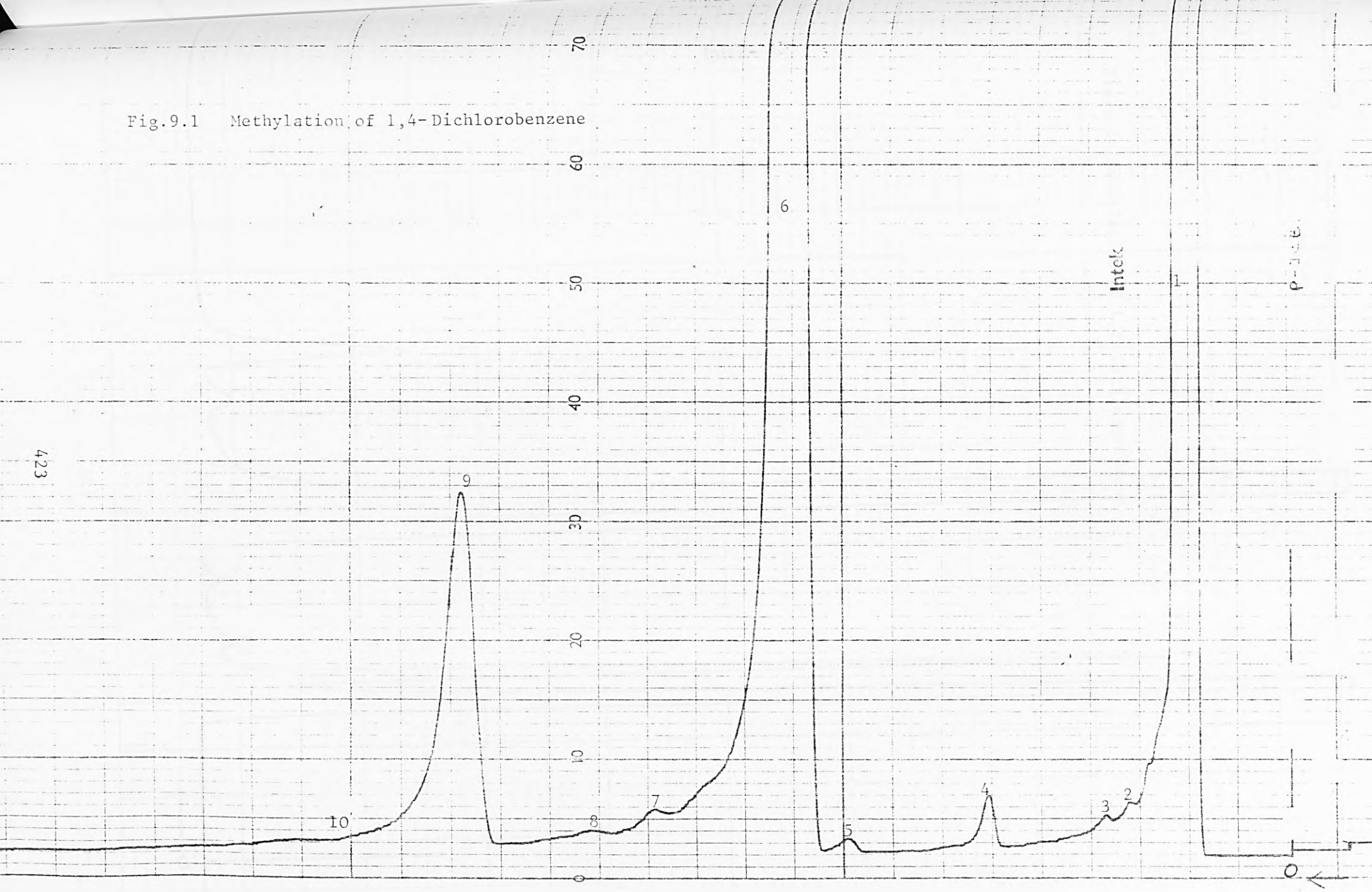
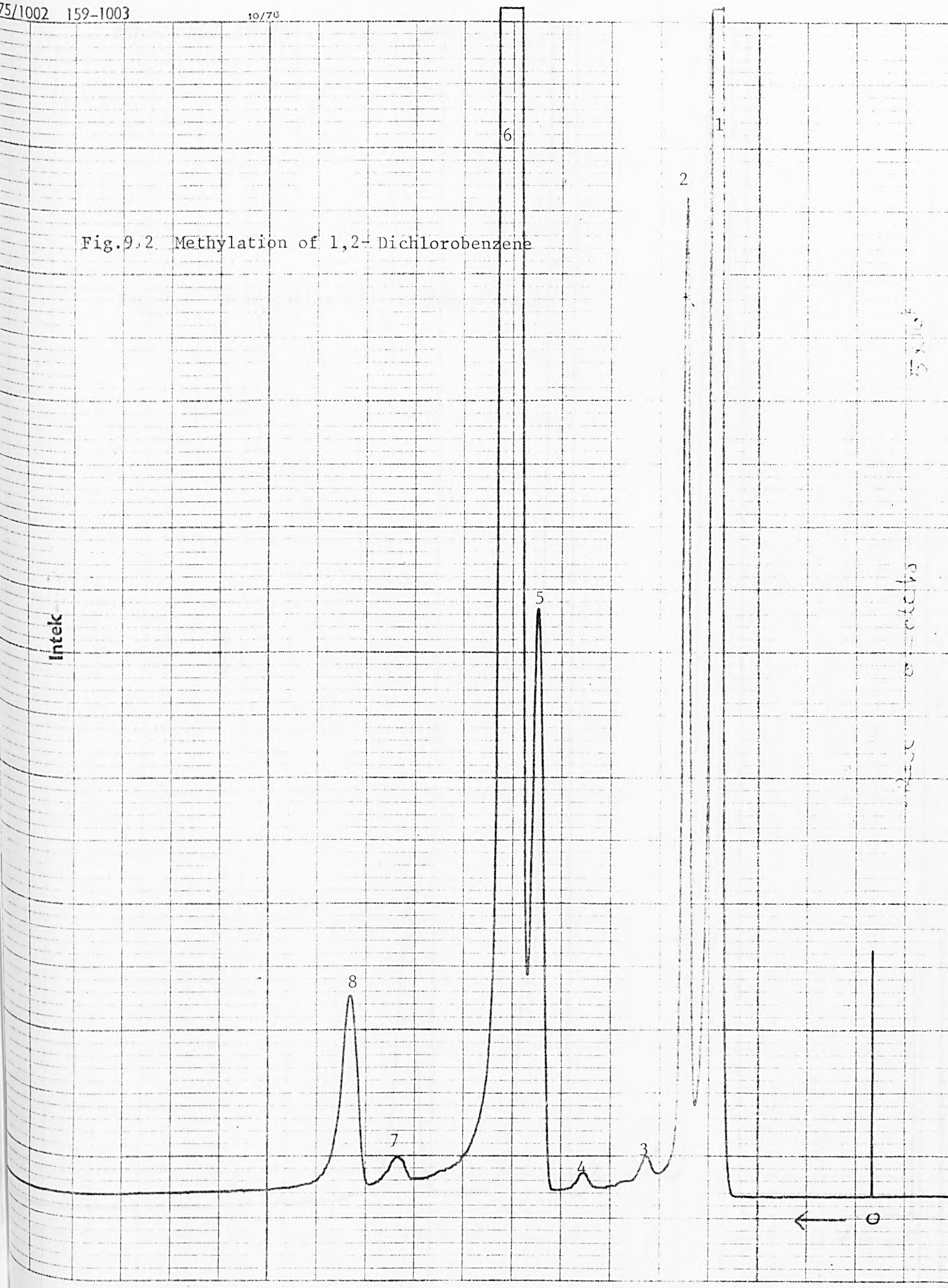


Fig.9.2 Methylation of 1,2- Dichlorobenzene



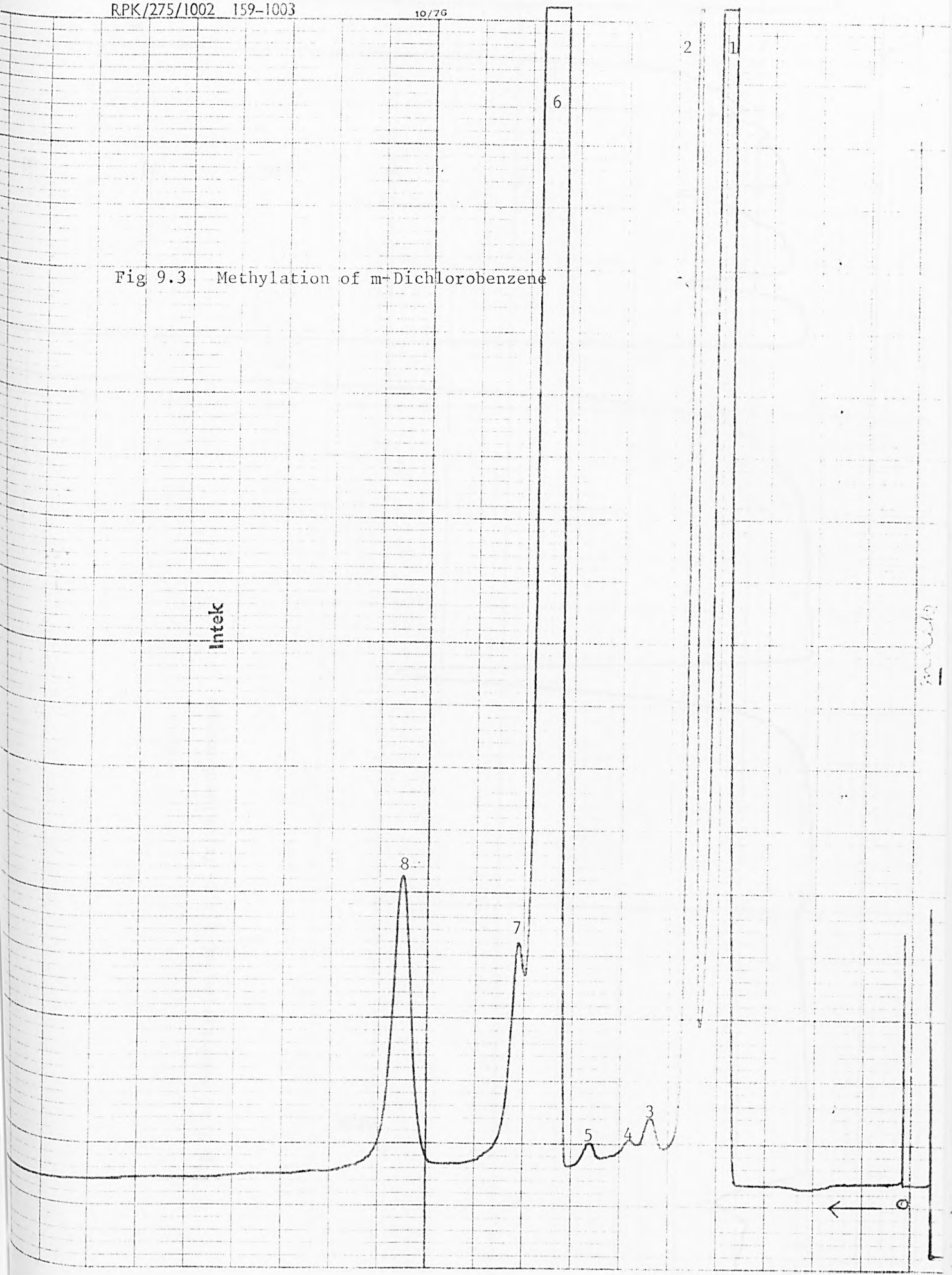
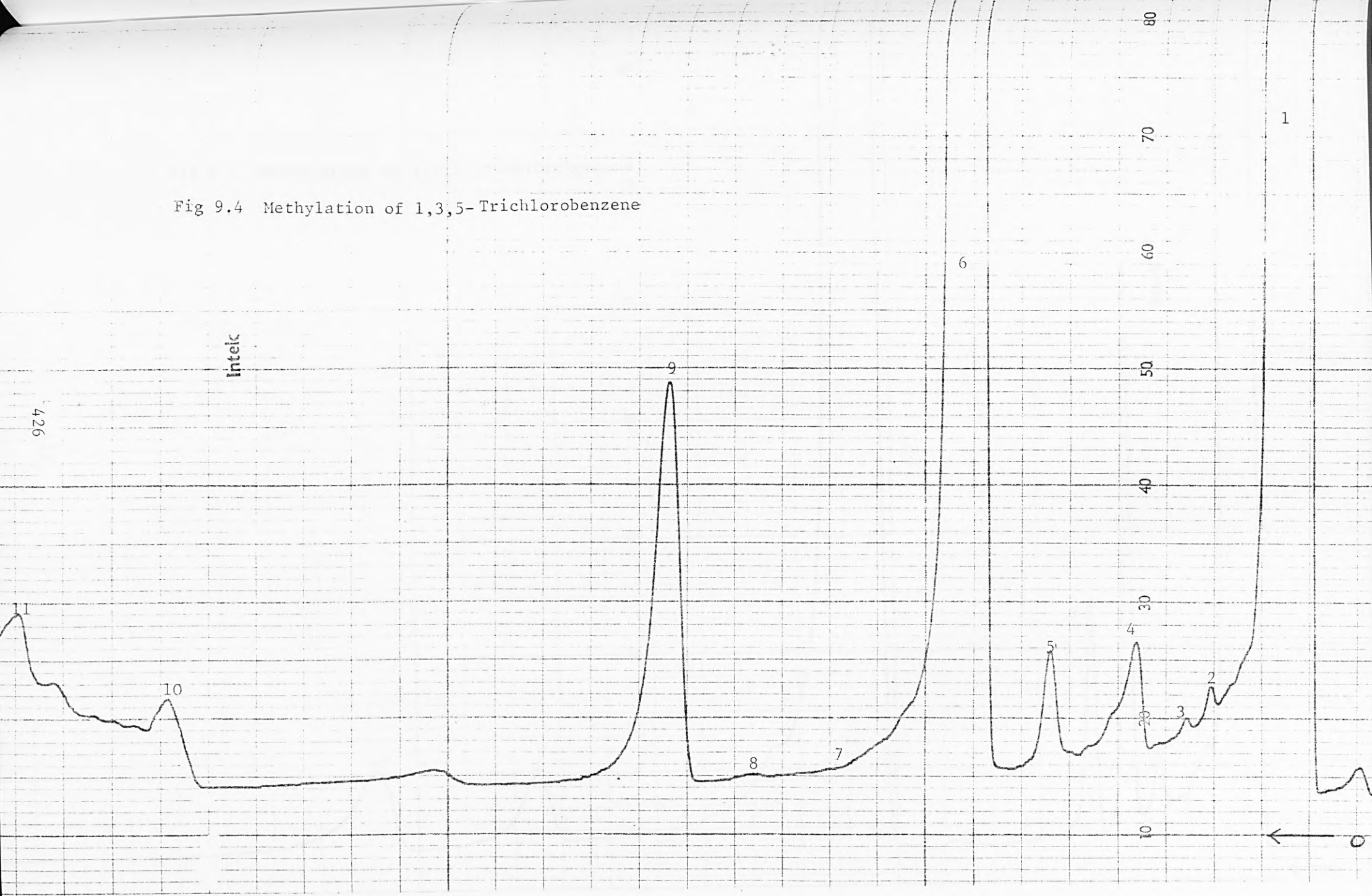


Fig 9.3 Methylation of m-Dichlorobenzene

Fig 9.4 Methylation of 1,3,5-Trichlorobenzene



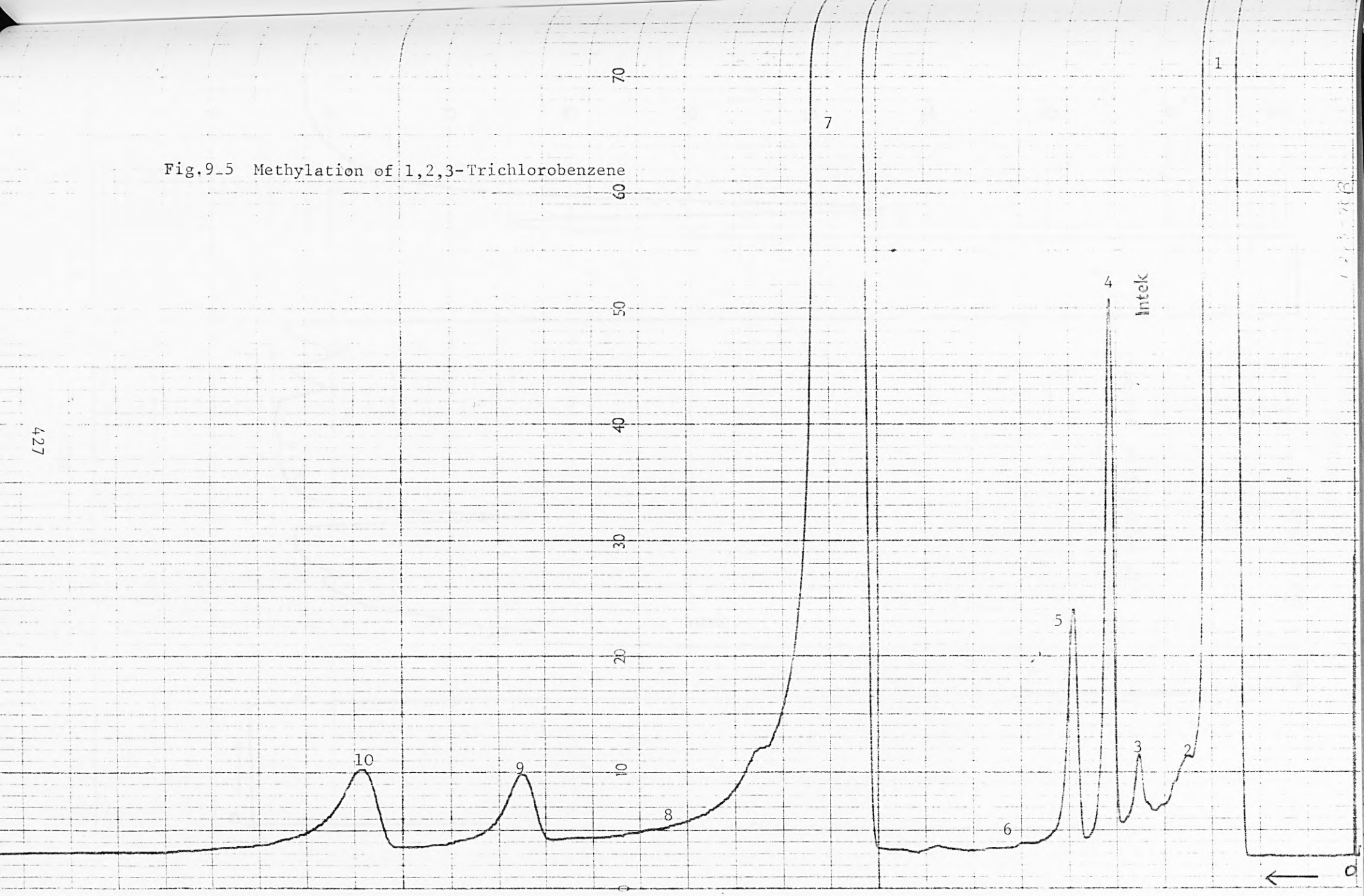


Fig.9_5 Methylation of 1,2,3-Trichlorobenzene

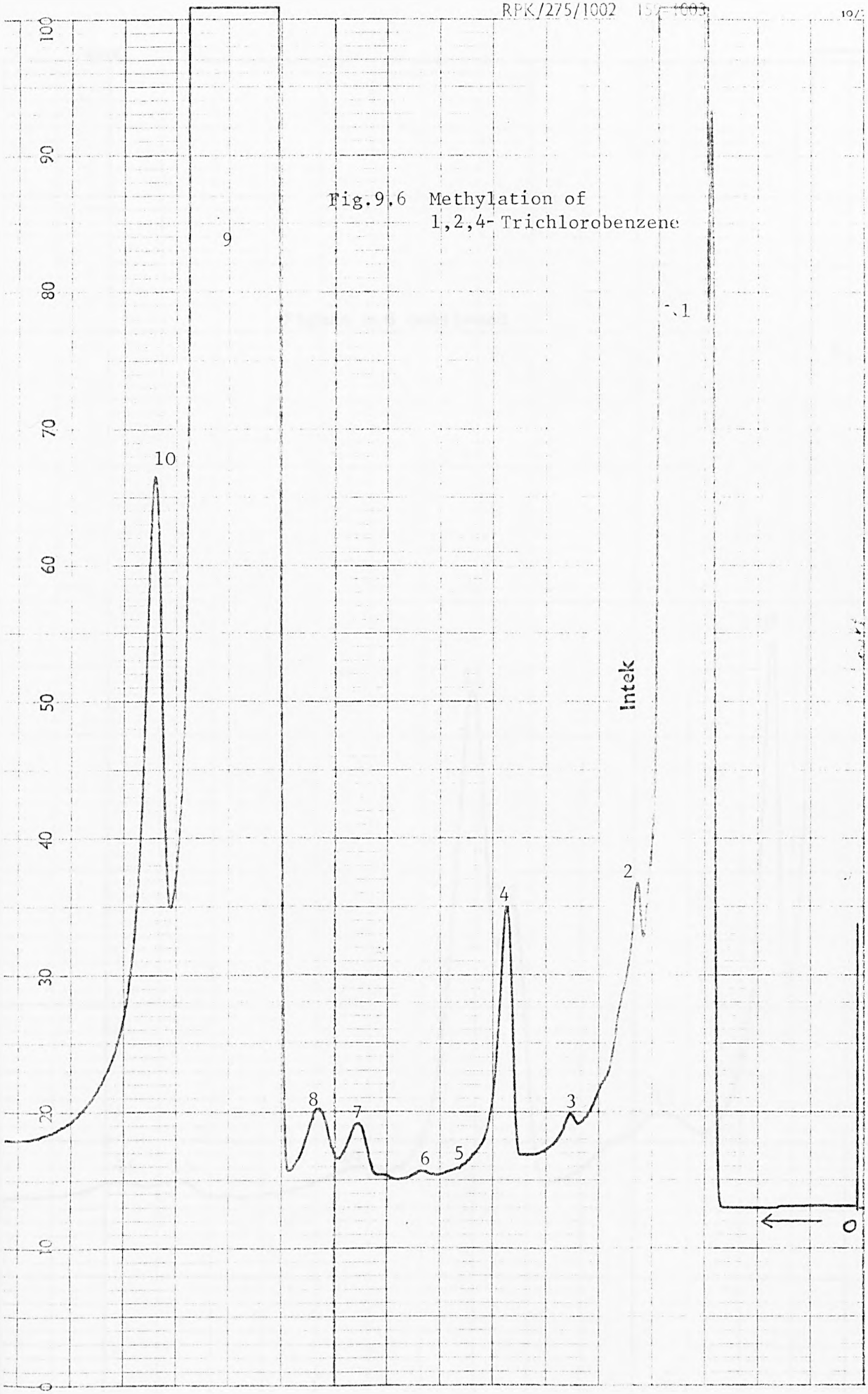


Fig.9.6 Methylation of
1,2,4- Trichlorobenzene

59-1003 10/76

Figure 9.6 continued

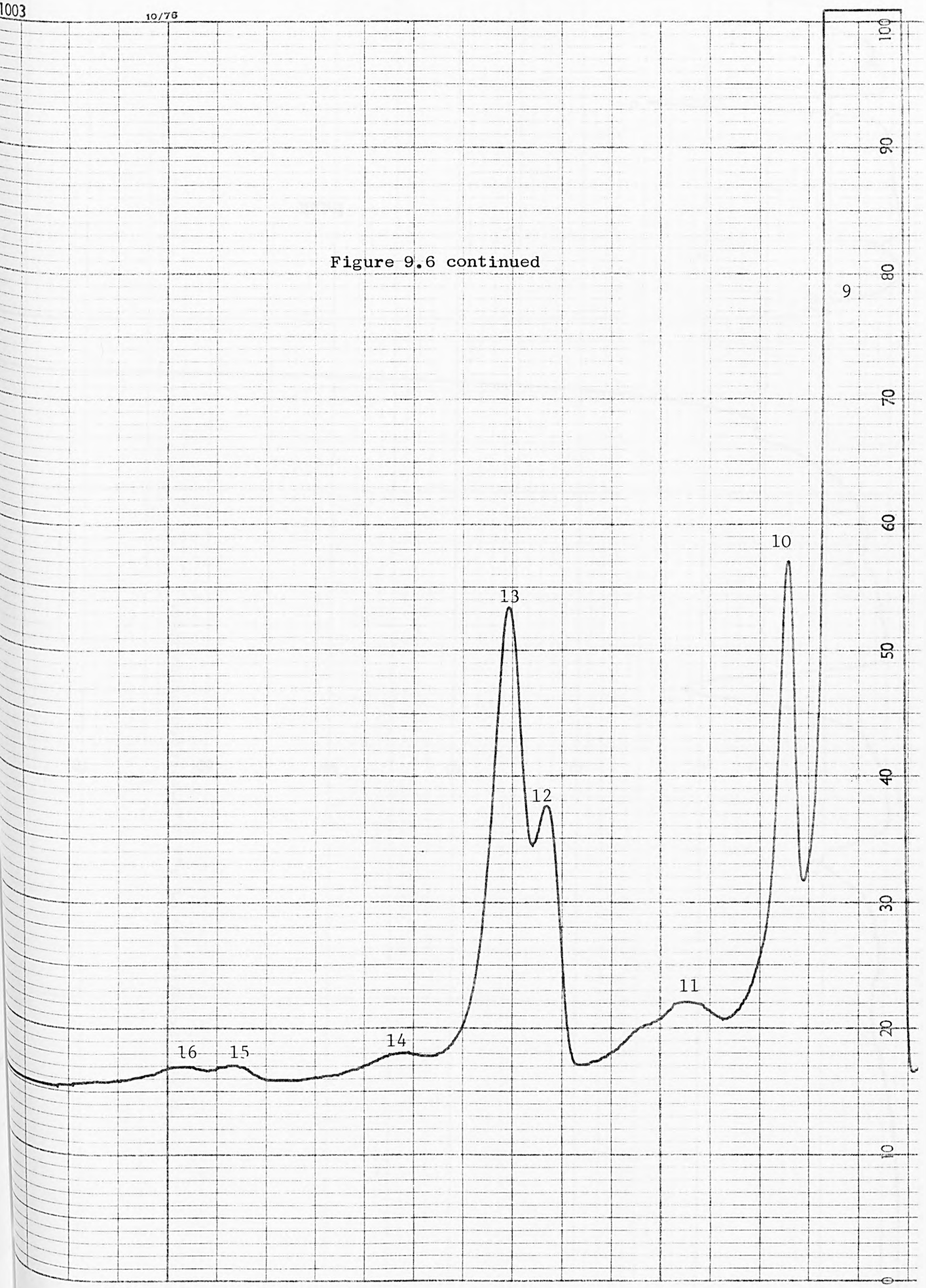


Fig.9.7 Methylation of 1,2,3,5-Tetrachlorobenzene

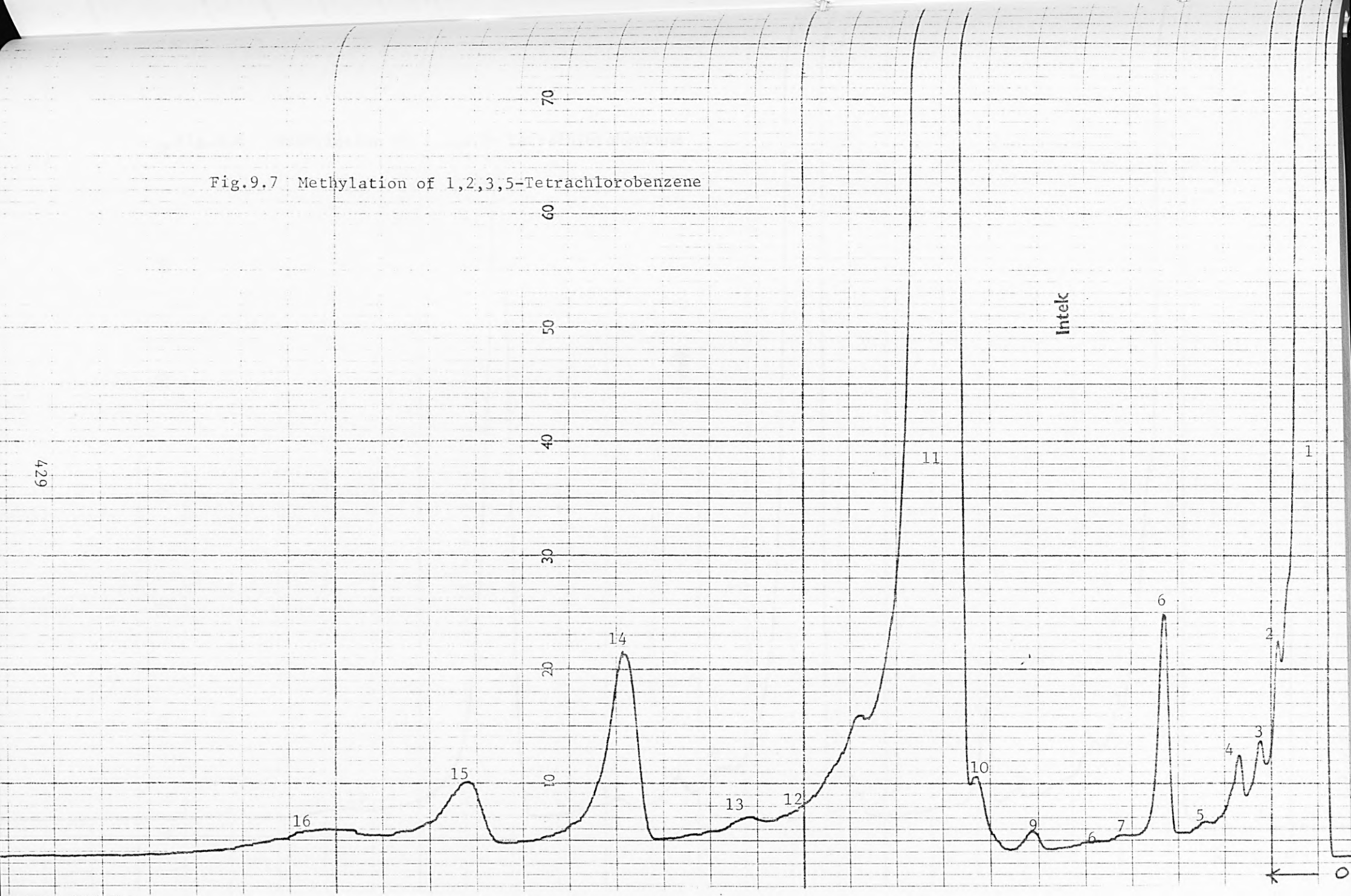


Fig.9.8 Methylation of 1,2,4,5- Tetrachlorobenzene

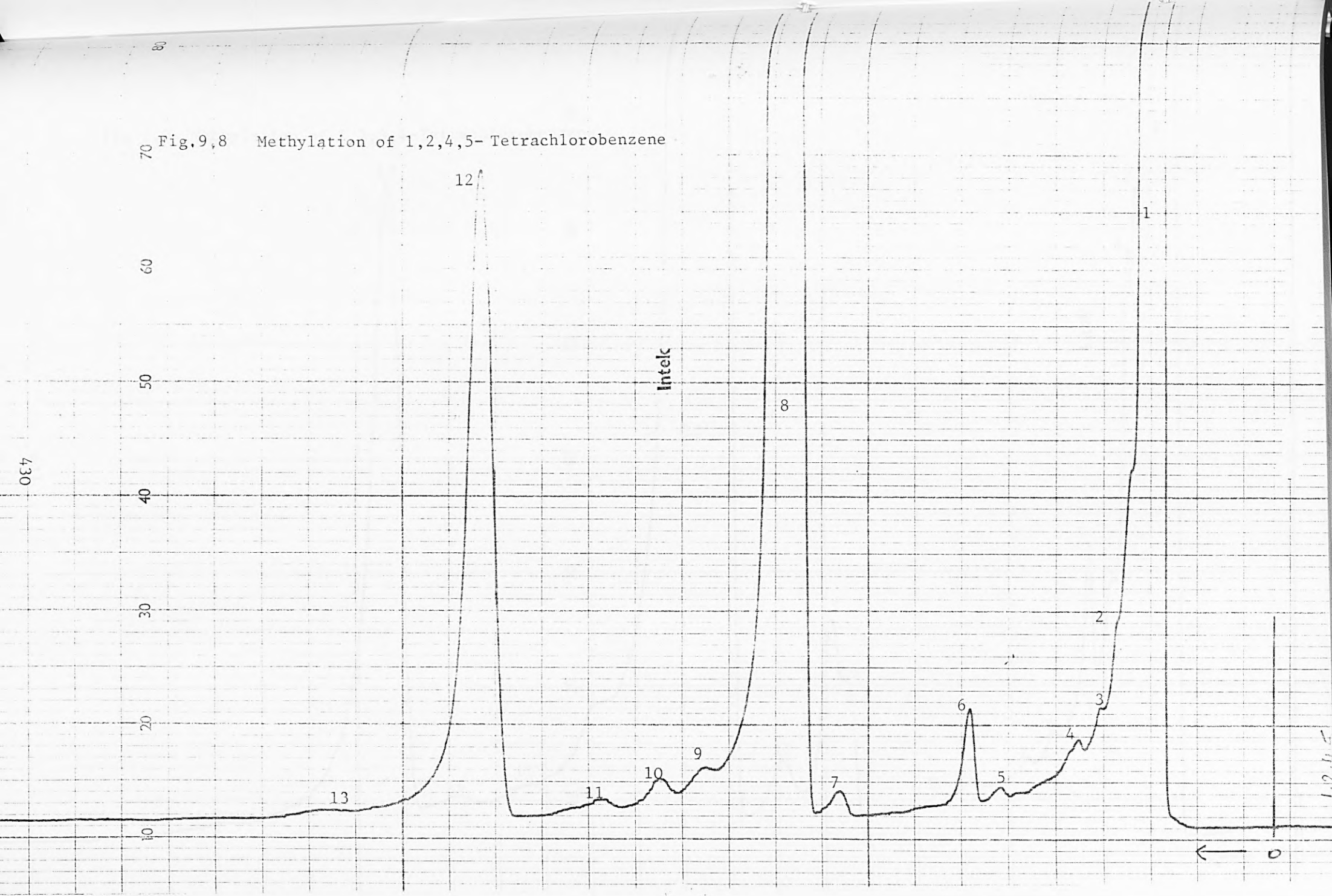
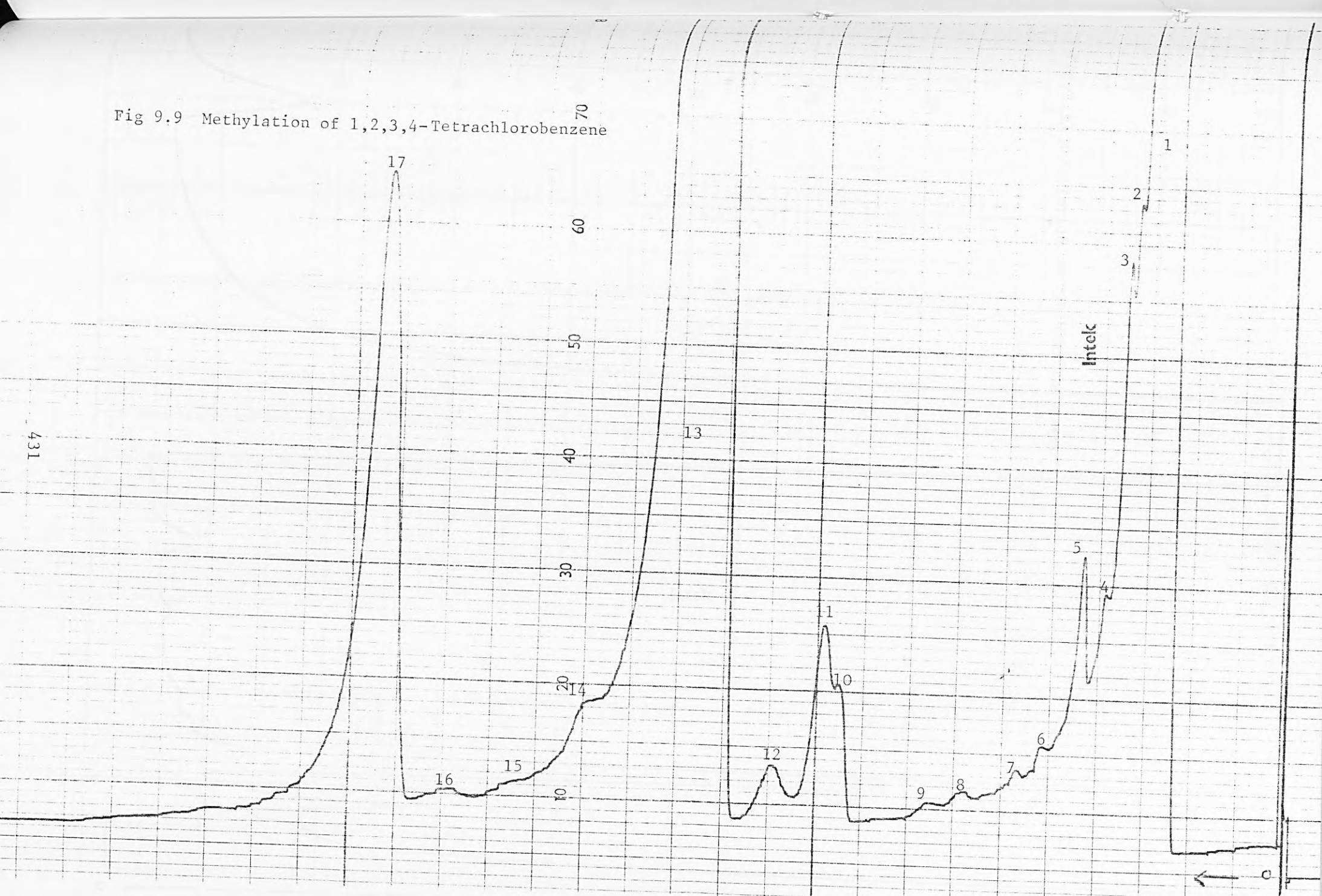


Fig 9.9 Methylation of 1,2,3,4-Tetrachlorobenzene



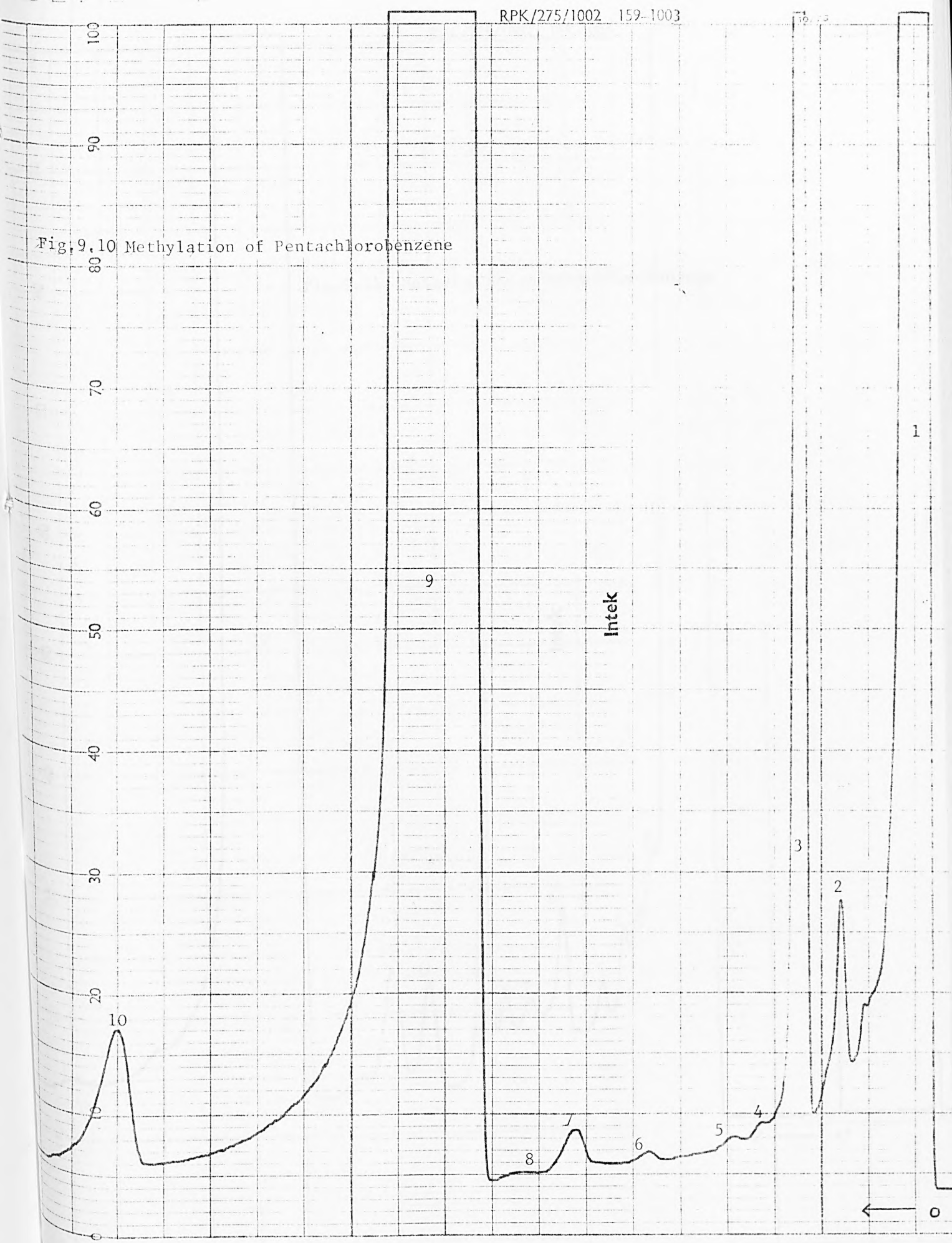


Fig.9.10 Methylation of Pentachlorobenzene

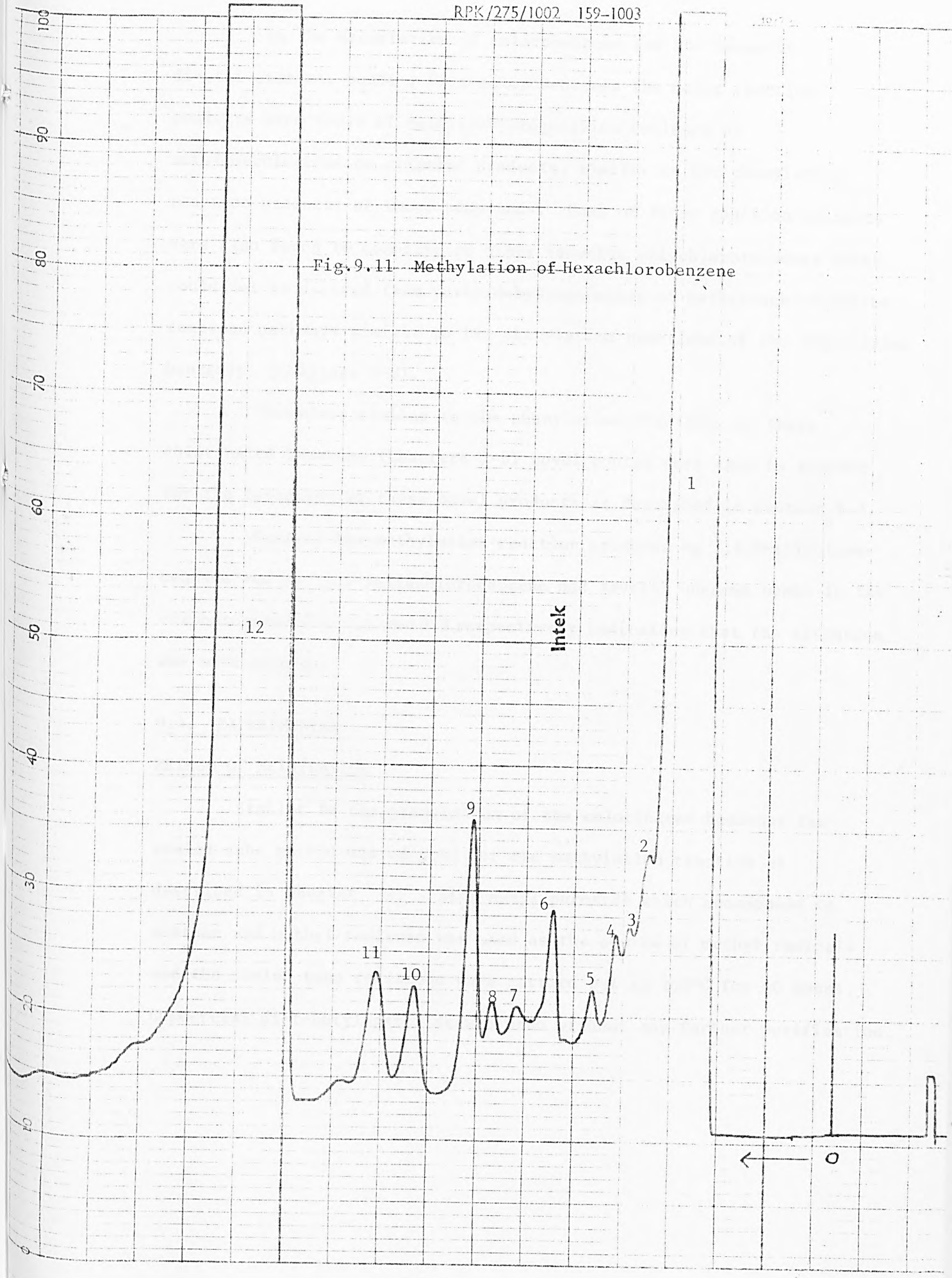


Fig.9.11 Methylation of Hexachlorobenzene

In the methylation of chlorobenzene and the isomeric di-,tri-,tetra-, penta-, hexa-chlorobenzenes the major reaction products were those of methyldehydrogenation followed by methyldechlorination reaction products, similar to the phenylation reaction products of these compounds. Most of these reaction products were also found to comprise of other isomeric polychlorotoluenes which could not be derived from methyldehydrogenation or methyldechlorination reaction pathways similar to the phenylation reactions of the chlorinated benzenes. (Chapters 3-8).

Therefore similar to the phenylation reactions of these chlorinated benzenes (Chapters 3-8) novel routes were used to account for the formation of these novel products as described in section 9.2.

Some of the methylation reaction products eg 1,3,5-trichlorobenzene and 1,2,4,5-tetrachlorobenzene had several unknown peaks in the chromatograms fig.9.4 and 9.8 respectively indicating that the situation was more complex.

9.4. EXPERIMENTAL

METHOD OF METHYLATION

Similar to the phenylation of the chlorinated benzenes the sealed tube method was adopted for the methylation reaction as described in Chapter 2. Di-t-butyl peroxide which decomposes to acetone and methyl radicals was used as the source of methyl radicals and the sealed tube reactions were carried out at 140°C for 40 hours. Commercial di-t-butyl peroxide was used without any further purification.

Table 9.0. Composition of Reaction Mixture

Expt. No.	Chlorinated Benzene	Moles of chlorinated benzene Mol x 10^3	Moles of Benzene Mol x 10^3	Moles of di-t-butyl peroxide Mol x 10^4
1	Chlorobenzene	8.8	8.8	8.0
2	o-dichlorobenzene	6.8	6.8	6.0
3	m-dichlorobenzene	6.8	6.8	6.0
4	p-dichlorobenzene	6.8	6.8	6.0
5	1,3,5-trichlorobenzene	5.5	5.5	5.0
6	1,2,3-trichlorobenzene	5.5	5.5	3.0
7	1,2,4-trichlorobenzene	5.5	5.5	5.0
8	1,2,3,5-tetrachlorobenzene	4.6	4.6	4.0
9	1,2,4,5-tetrachlorobenzene	4.6	4.6	4.0
10	1,2,3,4-tetrachlorobenzene	4.6	4.6	4.0
11	Pentachlorobenzene	4.0	4.0	4.0
12	Hexachlorobenzene	3.5	3.5	3.0

9.4.1 Gas Chromatography Conditions

Column: 5' 10% OV-17 on chromosorb W.

Detector: flame ionisation

Carrier Flow: 50 mls/min.

Initial temp.: 150°C

Rate of heating: 6°C/min.

Final temp.: 240°C

9.5. PREPARATION OF AUTHENTIC COMPOUNDS FOR THE IDENTIFICATION OF PRODUCTS OF THE METHYLATION OF CHLORINATED BENZENES

INTRODUCTION

The isomeric monochlorotoluenes were available commercially along with 2,6-, 2,4-, 2,5-, 3,4-dichlorotoluenes and pentachlorotoluene. Therefore the only dichlorotoluene isomers synthesized were the 2,3- and 3,5-isomers.

Direct chlorination[141] of four of the isomeric dichlorotoluenes yielded only a single trichlorotoluene in each case providing easy routes for the synthesis of the appropriate trichlorotoluene isomers.

Thus		exclusive trichlorotoluene product
2,6-dichlorotoluene	$\xrightarrow{Cl_2}$	2,3,6-trichlorotoluene
3,4-dichlorotoluene	$\xrightarrow{Cl_2}$	2,4,5-trichlorotoluene
3,5-dichlorotoluene	$\xrightarrow{Cl_2}$	2,3,5-trichlorotoluene
2,3-dichlorotoluene	$\xrightarrow{Cl_2}$	2,3,4-trichlorotoluene

Therefore the 2 isomeric trichlorotoluenes that needed to be synthesized by alternative routes were the 3,4,5- and 2,4,6- isomers.

On chlorinating suitable mixtures of isomeric trichlorotoluenes, the tetrachlorotoluenes could be isolated.

2,3,4 - trichlorotoluene
2,4,6 - trichlorotoluene
$\xrightarrow{Cl_2}$ 2,3,4,6-tetrachlorotoluene

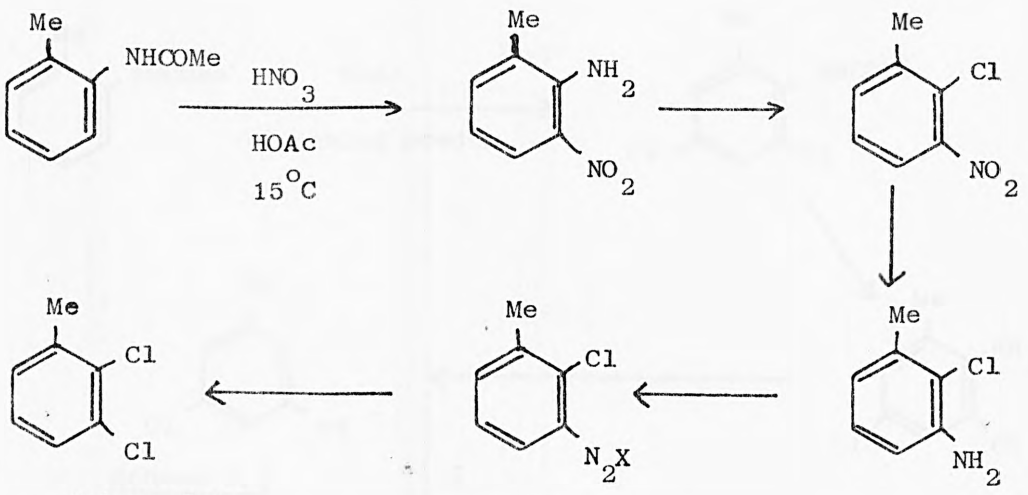
2,3,6-trichlorotoluene
2,3,5-trichlorotoluene
$\xrightarrow{Cl_2}$ 2,3,5,6-tetrachlorotoluene

9.6. METHOD OF DIRECT CHLORINATION

Direct Chlorination[141] was effected by passing chlorine dried by being led through sulphuric acid through the substance to be chlorinated. (5g). The flow of chlorine was regulated and the reaction vessel cooled if the reaction became violent.

It was unnecessary to add any solvent to keep the substance fluid as when crystallisation finally occurred it was usually an indication that the chlorination reaction was complete. It has been found that the fourth chlorine introduced into a trichlorotoluene can occupy ortho and meta positions but not para with respect to the methyl group.

9.7. PREPARATION OF 2,3-DICHLOROTOLUENE



Scheme 9.1

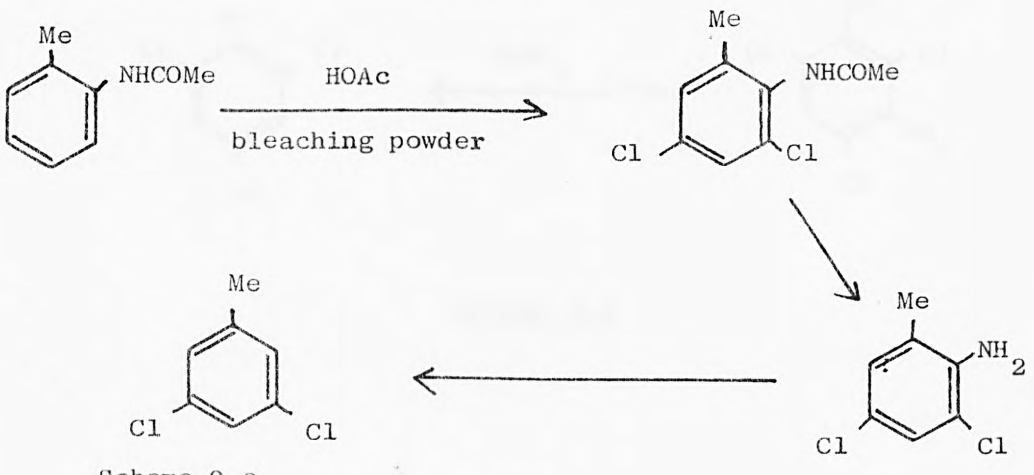
o-Acetotoluidide (15g) was added in small portions to a mixture of fuming nitric acid (60 mls) and glacial acetic acid (20mls) whilst carefully maintaining the temperature at 15°C.[142] The mixture was allowed to stand at room temperature for 4 hours, when distilled water (250mls) was added to precipitate the nitro-compounds. The mixture was filtered and the nitro-compounds washed several times with water. The filtered solid cake was placed in a flask with 40cc. concentrated hydrochloric acid and steam distilled. After 5 hours distillation orange crystals of 3-nitro-2-toluidine was collected in the receiver.

Powdered nitrotoluidine (5g) was suspended in concentrated hydrochloric acid (20mls) and cooled. The cooled solution was diazotised with the addition of solid sodium nitrite (3g). The liquid was added to an ice cold solution of cuprous chloride dissolved in concentrated hydrochloric acid. (Sandmeyers reaction).

When the evolution of nitrogen gas ceased, the liquid was steam distilled when 2-chloro-3-nitro-toluene was collected in the receiver. This nitrotoluene was reduced to 2-chloro-3-toluidine with stannous chloride and concentrated hydrochloric acid.

By diazatisation and a subsequent Sandmeyer reaction the 2-chloro-3-nitrotoluidine was converted to 2,3-dichlorotoluene (bpt 210°, lit bpt 208°C)[122].

9.8. PREPARATION OF 3,5-DICHLOROTOLUENE



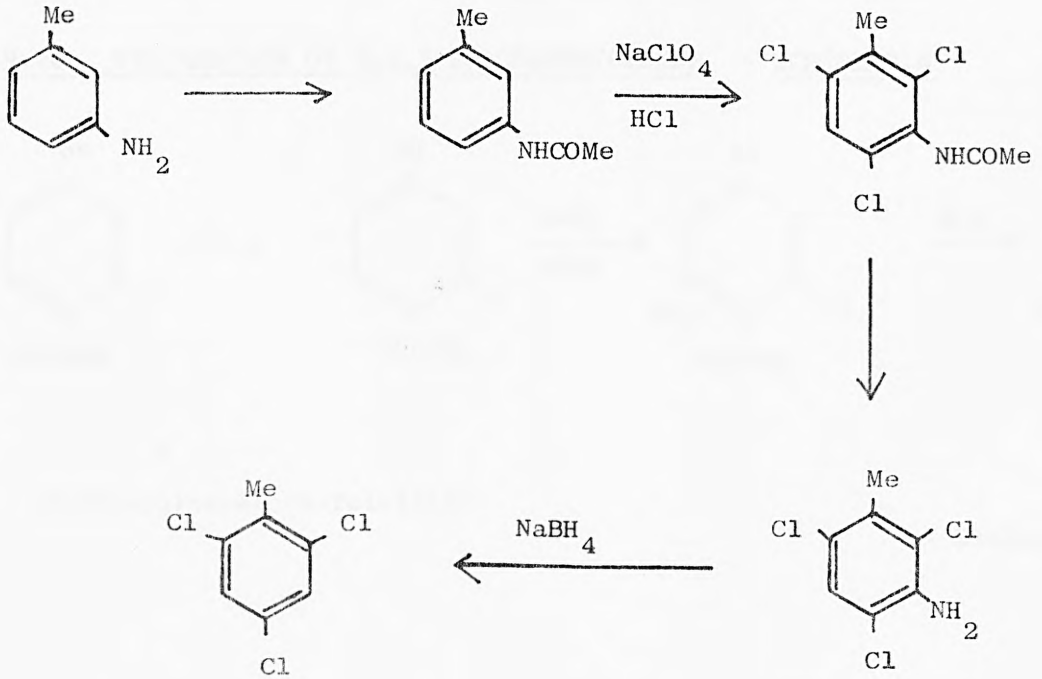
Scheme 9.2

O-Acetoluidine (15g) was dissolved in glacial acetic acid (60mls) and a solution of bleaching powder (50g) in water (1 litre) was slowly added.[141] This mixture was allowed to stand for 15 hours, when the supernatant liquid was decanted from the yellow oil.

An equal volume of glacial acetic acid was added to the yellow oil along with a few drops of concentrated sulphuric acid. This mixture was warmed on a steam bath and then poured into water (200mls) when dichloroacetotoluidide separated out.

The dichloroacetotoluidide was hydrolysed with concentrated hydrochloric acid at 80°C for 3 hours. Deamination was affected with sodium borohydride thus yielding 3,5-dichlorotoluene as the product. (mpt 24, lit mpt 26°C)[122].

9.9. PREPARATION OF 2,4,6-TRICHLOROTOLUENE

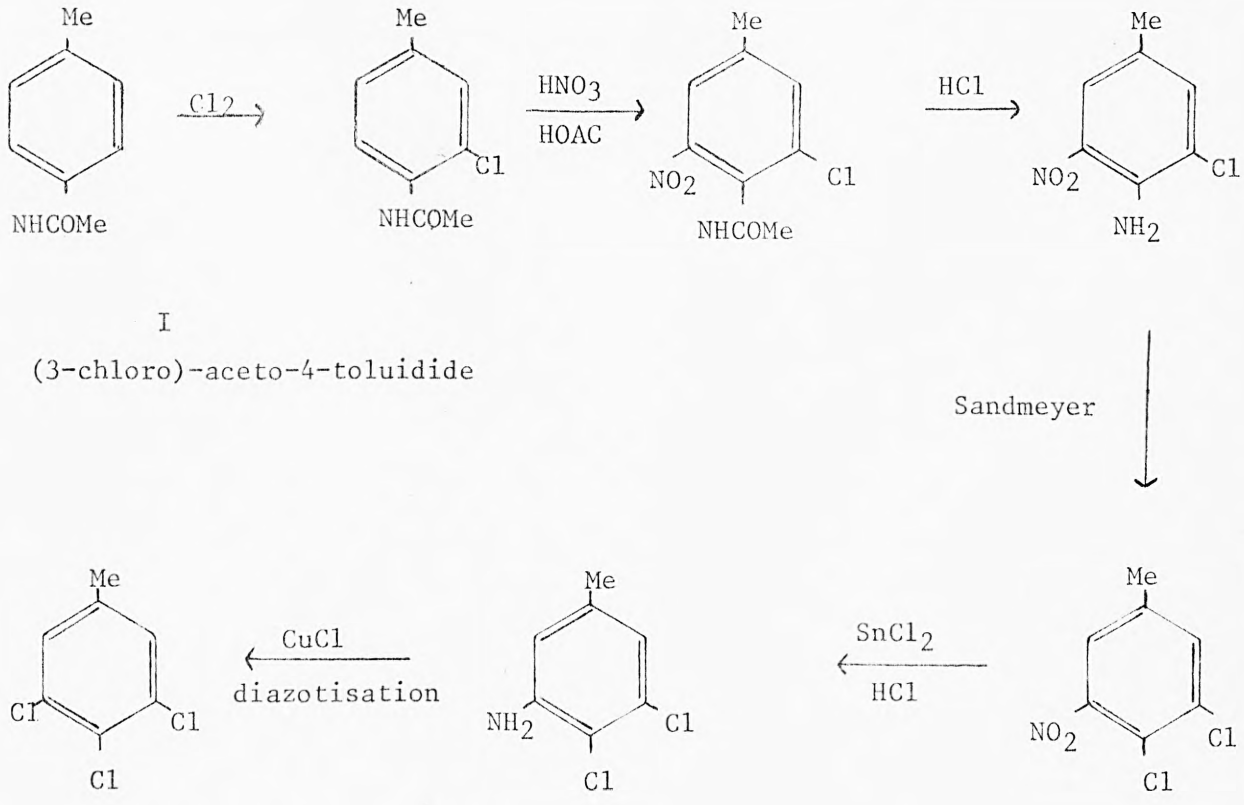


Scheme 9.3

The starting material used in the synthesis of 2,4,6-trichlorotoluene was m-toluidine which was readily available commercially.[143] Upon acetylation, m-toluidine yielded m-Acetotoluidide (5g) which was dissolved in glacial acetic acid (30c.c.). m-acetotoluidide was readily chlorinated by sodium perchlorate and hydrochloric acid to 2,4,6-trichloroacetotoluidide. (See scheme 9.3). Concentrated hydrochloric acid (35c.c) was added to the solution of m-acetotoluidide, and this solution was maintained at 15 - 25°C whilst sodium perchlorate (6g) dissolved in a minimum amount of water was slowly introduced. The solution was allowed to stand for 2 hours, and 2,4,6-trichloroacetotoluidide was precipitated by the addition of water as white needles.

Sulphuric acid (50%) was used to hydrolyse 2,4,6-trichloro-acetotoluidide, and the amino group was removed by sodium borohydride reduction. The resulting 2,4,6-trichlorotoluene is steam volatile and crystallized as white crystals (mpt 33°C lit mpt 34°C) [122].

9.10. PREPARATION OF 3,4,5-TRICHLOROTOLUENE - SCHEME 9.4



As in the preparation of 2,4,6-trichlorotoluene, the starting material in the synthesis of 3,4,5-trichlorotoluene was a substituted toluidide, (3-chloro)-aceto-4-toluidide. I (5g)[143].

Upon nitration with fuming nitric acid (20g) and glacial acetic acid (t = 20°C), (3-chloro)-(3-nitro-)-aceto-4-toluidide was formed. On pouring the solution into water the crystalline nitro compound was obtained in fine needles. Hydrolysis was affected by boiling hydrochloric acid with the formation of 3-chloro, 3-nitro, 4-aminotoluene. II.

The amino group was diazotised and replaced by chlorine in a Sandmeyer type reaction producing the dichloronitrotoluene.

The nitro group was reduced by stannous chloride and hydrochloric acid, after which a Sandmeyer reaction produced the 3,3,5-trichlorotoluene. (mpt 44°C, lit mpt 45.5°C)[122].

Table 9.1 List of Synthesized polychlorotoluenes with their melting points and yields

Compound	Observed mpt °C	Literature mpt[122] °C	Yield*
2,3-dichlorotoluene	210	bpt. 207-8	55
3,5-dichlorotoluene	24	26	49
2,3,6-trichlorotoluene	45	46	68
2,4,5-trichlorotoluene	80	82	61
2,3,5-trichlorotoluene	45	45 - 46	74
2,3,4-trichlorotoluene	40	40 - 41	65
3,4,5-trichlorotoluene	44	45.5	59
2,4,6-trichlorotoluene	33	34	76
2,3,4,6-tetrachlorotoluene	90	91 - 92	60
2,3 5,6-tetrachlorotoluene	94	93 - 94	52
2,3,4,5-tetrachlorotoluene	96	97 - 98	56

*yields based on original starting material

CHAPTER TEN

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APPENDIX

APPENDIX A.1

Gas Chromatography - Mass Spectrometry Results (G.C.-M.S.)

The following appendices show the g.c.-m.s. results obtained from the phenylation reaction mixtures. These results were obtained as described in section 2.11.5.

In general the number of peaks obtained in the scans were approximately N = 250 - 350 and the atomic mass range scanned was MR = 28 - 500 at.mass units.

In reaction mixtures where several isomers of the same compound exist only one table of M/e and R.A. has been shown as the results are practically identical for positional isomers. For example, in the phenylation of 1, 2, 4- trichlorobenzene, three trichlorobiphenyls are possible i.e. 2, 3, 6-, 2, 3, 5- and 2, 4, 5- isomer, however only one table of results has been tabulated.

The peak numbers stated on the fragmentation pattern tables refer to the figure in the discussion of each chapter.

Abbreviations

m/e	Mass by charge ratio
N	Number by peaks
R.A.	Relative abundance
M.R.	Mass range
MW	Molecular Weight

APPENDIX A.2

p- Dichlorobenzene G.C. - M.S. Results

Dichlorobiphenyl M.W. = 223 Peak No. 4 and 5

m/e	231	227	226	225	224	223	222	188	187	186	153	152	151
R.A.	0.7	1.1	10.4	8.1	64.6	13.7	100	2.9	3.0	6.5	6.7	51.7	11.6

m/e	150	148	113	111	105	93	77	75	69	44
R.A.	8.	3.4	1.7	7.3	15.9	13.1	6.9	10.9	16.8	8.3

Monochlorobiphenyl M.W. = 188.5 Peak No. 2 and 3

m/e	193	191	190	189	188	169	153	152	151	150	131	126
R.A.	0.3	3.9	34.7	13.4	100	1.8	21.4	32.3	9.3	3.7	1.1	3.4

m/e	113	112	102	99	98	94	85	71	57	55
R.A.	3.1	1.5	1.6	5.4	2.8	6.5	23.1	37.2	82.8	13.4

Dichloroterphenyl M.W. = 299

m/e	303	302	301	300	299	298	272	270	265	264	263	262	230
R.A.	0.3	7	9.4	47.3	18.6	75.1	2.9	2.6	19.0	18.8	37.5	29.6	53.1

m/e	229	228	227	202	200	151	115	114	113	112	101	100	99	74
R.A.	24.1	100	30.4	4.5	6	4.8	7.1	46.9	80.2	18.7	14	16.7	5.3	3.2

APPENDIX A.3

O-Dichlorobenzene G.C. - M.S. Results

Dichlorobiphenyl M.W. = 223 Peak No. 4, 5, 6

m/e	227	224	223	222	188	186	151	150	126	113	112
R.A.	1.2	59.5	12.8	100	3.0	8.0	50.5	10.1	3.4	1.2	2.3

m/e	111	105	99	98	94	93	75	74	63	51
R.A.	4.4	5.5	3.3	3.1	3.8	11.1	10.7	4.6	4.1	5.4

Monochlorobiphenyl M.W. = 188.5 Peak No. 2 and 3

m/e	191	190	189	188	153	152	151	150	126	113
R.A.	3.1	36.8	10.1	100	20.7	33.3	8.9	3.9	4.0	2.8

m/e	99	77	57	55
R.A.	6.0	39.1	80.1	12.3

APPENDIX A.4

m-Dichlorobenzene G.C. - M.S. Results

Dichlorobiphenyl M.W. = 223 Peak No. 4, 5, 6

m/e	281	269	243	231	227	226	224	223	222	219	188	186	181	169
R.A.	0.8	0.5	0.5	1.3	1.3	10.6	64.1	13.3	100	1.2	2.4	6.6	2.7	2.3
m/e	154	153	152	151	150	146	131	129	119	112	111	105	94	93
R.A.	1.0	6.1	48.4	10.9	7.3	2.0	4.5	3.5	5.7	4.0	6.6	8.1	4.6	13.4
m/e	80	77	76	75	69	50	44							
R.A.	2.6	4.8	10.3	9.9	28.9	3.6	4.9							

Monochlorobiphenyl M.W. = 188.5 Peak No. 2 and 3

m/e	191	190	189	188	153	152	126	99	77	55
R.A.	4.4	36.8	14.9	100	24.1	35.6	5.1	6.7	39.3	9.8

APPENDIX A.5

1, 3, 5 -Trichlorobenzene G.C. - M.S. Results

Dichlorobiphenyl M.W. = 223 Peak No. 2, 3, 5

m/e	226	225	224	223	222	188	187	186	154	153	152
R.A.	6.1	7.5	61.1	11.4	100	4.6	6.6	9.4	2.5	9.7	7.1

m/e	151	150	126	99	98	86	76
R.A.	16.6	9.8	4.1	4.4	4.5	2.6	28.3

Trichlorobiphenyl M.W. = 257.5 Peak No. 4, 6

m/e	262.5	259.5	258.5	256	222	220	193	191	189	186	185
R.A.	0.3	30.4	96.3	100	4.6	5.3	1.5	1.4	2.4	62.4	3.5

m/e	152	151	149	110	93	92	77	55
R.A.	1.5	9.9	3.1	14.3	12.8	7.6	1.3	0.2

Trichloroterphenyl M.W. = 333.5

m/e	338	337	336	335	334	333	332	298	296	264	26.3
R.A.	3.3	5.0	30.6	17.5	94.2	19.1	100	4.2	4.0	10.2	6.3

m/e	262	260	258	256	227	226	224	188	186	151	150
R.A.	32.7	25.5	70.4	70.8	9	30.6	9.3	14.5	41.6	9.4	14.9

m/e	131	130	122	113	112	111	105	93	77	75	51
R.A.	10.5	9.1	22.5	36.1	12	10.8	30	11.6	22.1	14.1	16.0

APPENDIX A.6

1, 2, 3- Trichlorobenzene G.C. - M.S. Results

Dichlorobiphenyl M.W. = 223 Peak No. 2, 3, 4

m/e	232	227	226	225	224	223	222	188	187	186	153	152
R.A.	0.4	1.0	10	7.6	63.5	13.5	100	2.5	4.7	6.0	7.3	7.9
m/e	151	150	126	125	113	112	77	62				
R.A.	11.9	7.4	2.6	1.4	1.5	3.5	11.6	3.7				

Trichlorobiphenyl M.W. = 257.5 Peak No. 7 and 8

m/e	269	263	262	260	259	258	256	224	223	222	220	
R.A.	0.1	0.4	3.0	3.5	28.5	82.1	100	0.7	1.0	3.4	4.9	
m/e	189	188	186	185	184	151	150	149	131	130	129	128
R.A.	1.9	15.6	47.9	3.2	1.8	9.2	13	2.6	1.8	1.6	5	5.7
m/e	111	110	99	98	97	94	93	80	77	75	69	55
R.A.	7.5	11.4	2.5	4.1	27	5.1	16.8	2	2	11.1	10.7	0.1

APPENDIX A.7

1, 2, 4- Trichlorobenzene G.C. - M.S. Results

Dichlorobiphenyl M.W. = 223 Peak 2, 3, 5

m/e	226	225	224	223	222	198	153	152	151	106	105	78
R.A.	3.4	2.6	20.2	4.2	11.6	11.3	1.7	20.1	4.3	21.2	20.0	6.0

m/e	77	65	51	39
R.A.	100	5.6	24.9	10.1

Trichlorobiphenyl M.W. = 257.5 Peak 6, 7, 4

m/e	263	262	260	258	256	222	220	187	186	185	151
R.A.	0.3	2.9	3.5	78.6	100	3.7	5.3	16.3	50.5	3.5	10.1

m/e	150	149	129	111	110	109	99	98	97	93	77
R.A.	15.5	3.3	3.1	6.5	9.3	1.6	3.1	4.6	2.5	12	2.9

m/e	77	75	74	51	39
R.A.	2.9	10.1	5.6	5.9	2.6

APPENDIX A.8

1, 2, 3, 5- Tetrachlorobenzene G.C. - M.S. Results

Trichlorobiphenyl M.W. = 257.5 Peak No. 3, 4, 5, 6, 7

m/e	260	259	258	257	256	230	229	222
R.A.	33.6	10.1	90	12.4	100	8.8	5.1	1.9

m/e	188	186	150	128	77
R.A.	19.8	50.8	13.4	7.1	1.2

Tetrachlorobiphenyl M.W. = 292 Peak No. 8

m/e	294	292	290	254	224	185	184	150	149
R.A.	50.2	14.6	100	4.8	5.5	5.2	3.6	9.9	2.9

m/c	128	110	98	92	77
R.A.	7.9	25.7	4.6	8.8	3.1

APPENDIX A.9

1, 2, 3, 4- Tetrachlorobiphenyl G.C. - M.S. Results

Trichlorobiphenyl M.W. = 257.5 Peak No. 2, 3, 4, 5

m/e	298	270	263	262	261	260	259	258	257	256
R.A.	0.5	0.1	0.6	3.2	2.8	32.2	12.3	99.7	12.3	100
m/e	222	221	188	186	180	152	151	150	129	128
R.A.	3.8	6.6	20.6	57	18.8	6.9	11.9	15.7	5.3	6.3
m/e	110	94	77	51						
R.A.	16.6	5.8	4.5	5.6						

Tetrachlorobiphenyl M.W. = 292 Peak No. 6 and 7

m/e	298	297	296	295	293.5	292	291	290	256	254			
R.A.	0.8	1.3	9.8	6.3	9.1	100	10.8	78.8	3.6	3.3			
m/e	231	224	223	222	220	219	186	185	184	181	150		
R.A.	1.2	4.7	3.5	28	43.7	2.9	3	4.9	6.6	3.1	10.9		
m/e	149	146	131	128	127	119	111	110	98	92	77	69	52
R.A.	3.6	6.3	4	8.2	7.9	5.8	14.1	23.1	3.2	9	2.5	28.8	0.8

APPENDIX A.10

1, 2, 4, 5- Tetrachlorobenzene G.C. - M.S. Results

Trichlorobiphenyl M.W. = 257.5 Peak No. 4 and 5

m/e	281	262	261	260	259	258	257	256	231	222	220	188
R.A.	1.6	2.9	3.4	29	12.1	94.6	14.2	100	2.8	2.0	4.9	16.9
m/e	186	150	131	129	128	110	105	94	77	51		
R.A.	53.2	14.1	9.3	5.6	6.2	13	64.6	7.1	44.5	24.0		

Tetrachlorobiphenyl M.W. = 292 Peak No. 6 and 7

m/e	298	297	296	295	294	293	292	290	256	254	231	224
R.A.	0.7	1.2	10.1	6.1	48.2	13.3	100	78.4	3.7	3.1	0.4	4.8
m/e	222	220	219	186	185	184	181	150	149	146	131	128
R.A.	30.2	47.6	2.1	3.4	5	7.8	1.5	11.5	3.8	5.9	1.5	8.7
m/e	127	122	119	111	110	98	92	77	69	52		
R.A.	8.8	4.9	2.0	10.4	17.4	3.8	8.1	5	8.9	0.8		

APPENDIX A.11

Pentachlorobenzene G.C. - M.S. Results

Pentachlorobiphenyl M.W. = 326.5 Peak No. 9

m/e	330	329	328	326	324	256	255	254	181	169
R.A.	7.3	2.6	23.6	36.7	22.7	18.0	7.6	14.2	25.4	6.4

m/e	153	152	131	127	122	105	77	69	51	44
R.A.	4.5	6.1	8.2	7.6	47.3	100	49.5	52.6	21.3	35.6

Tetrachlorobiphenyl M.W. = 292 Peak No. 7 and 8

m/e	292	290	288	286	284	282	231	219	181	169	153
R.A.	4.8	5.1	4.7	11.1	13.7	7.0	4.7	5.0	21.3	12.3	2.4

m/e	152	131	122	119	105	77	69	51	44	40
R.A.	3.6	17.9	37.9	22.4	59.0	31.4	100	15.4	35.7	54.6

Trichlorobiphenyl M.W. = 257.5 Peak No. 3, 4, 5, 6

m/e	258	256	222	220	187	186	185	151	150	149	129	111	110
R.A.	78.6	100	3.5	4.8	15.1	48.3	4.3	10.9	16.1	3.5	4.1	7.0	8.9

m/e	109	99	98	97	93	77	75	74	51	39
R.A.	2.1	2.8	4.6	2.3	16	3.3	11.1	5.8	6.1	2.4

APPENDIX A.12

Hexachlorobenzene G.C. - M.S. Results

Tetrachlorobiphenyl M.W. 292 Peak No. 3 and 4

m/e	292	290	288	286	284	282	231	219	181	169	153	152
R.A.	4.8	5.1	4.7	11.1	13.7	7.0	4.7	5	21.3	12.3	2.4	3.6

m/e	131	122	119	105	77	69	51	44	40	36
R.A.	17.9	37.9	22.4	59	31.4	100	15.4	35.7	54.6	63.2

Pentachlorobiphenyl M.W. = 326.5 Peak No. 5

m/e	330	329	328	327	326	325	324	290	256	255	254	181
R.A.	7.3	2.6	23.6	4.2	36.7	2.5	22.7	1.7	18.0	7.6	14.2	25.4

m/e	169	153	152	131	127	122	105	77	69	51	44	36
R.A.	6.4	4.5	6.1	8.2	7.6	47.3	100	49.5	52.6	21.3	35.6	40.5

Tetrachloroterphenyl M.W. = 368 Peak No. 6, 7, 8

m/e	373	372	371	370	369	368	367	366	332	298	296
R.A.	1.1	8.1	7.1	38.6	15.5	78.4	13	63.3	5.6	13.1	20.5

m/e	226	198	184	183	181	153	152	149	148	131	130
R.A.	15.2	8.6	10.3	8.1	9.1	3.4	4.2	7.3	11.5	8.9	17.0

m/e	122	113	112	106	105	77	69	51	44	36
R.A.	61.2	13.7	8.5	7.6	100	56.6	23.0	24.5	24.5	36.1