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The Synthesis and Photochemical Studies of Some 1,4-Disubstituted Bicyclo [2,2,2] Octane Compounds

By

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A Thesis submitted for the Degree of Doctor of Philosophy

of

The City University, London

The Department of Chemistry December 1984

DEDICATION

To my parents, for their continuous encouragement and support.

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I wish to give my most sincere thanks to Professor R.S. Davidson for his continuous supervision and his valuable help and guidance throughout this work.

I would also like to thank the following people for their help during this project: [redacted] [redacted] [redacted]
[redacted]

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Many thanks also to [redacted]

Peter Cooper
December 1984

ABSTRACT

In order to elucidate the mechanism of important reactions (photosynthesis, biomimetic methods for harnessing solar energy) it is imperative to understand the principles concerning electron transfer reactions. It is known that compounds in which the redox partners are connected by a flexible chain exhibit intramolecular exciplex formation, intramolecular energy transfer and intramolecular electron transfer. With the intramolecular electron transfer process, the formation of radical ions by electron transfer can and does occur, but the back reaction to produce non-excited species competes. This means that the absorbed electronic energy is completely wasted. This non-productive back electron transfer is due to the radical ions being geminately produced and are not able to diffuse away because of the linking chain. In addition, on linking the two redox groups, it is very difficult to determine the conformational requirements for electron transfer and associated processes such as exciplex fluorescence.

To try to reduce these problems, in this work, the two redox groups were linked via a rigid molecular framework — the bicyclo[2,2,2]-octane framework. A series of 1,4-disubstituted bicyclo[2,2,2]-octane compounds were synthesised and photochemically investigated. These compounds had an aromatic ring (and some also had an amino and substituted amino group on the aromatic nucleus) and a halogen group separated by the rigid insulating bicyclo[2,2,2]octane framework. Photochemical investigation revealed that for those halo-substituted bicyclo[2,2,2]octane compounds that do dehalogenate, the rate of dehalogenation is enhanced if an amine is present during photolysis.

The rigid bicyclo[2,2,2]octane group slows down the back thermal electron transfer. Using a rigid molecular group to separate the redox partners is probably the only way to effectively study conformational effects upon electron transfer reactions.

It would also be interesting to increase the distance between the two redox groups and produce a fairly stable intramolecular radical ion pair.

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CHAPTER 1 - INTRODUCTION

1.1 Electronic Absorption Spectroscopy

Electronmagnetic radiation is considered to be an oscillating electric field and an oscillating magnetic field operating in planes which are perpendicular to each other and to the direction of propagation. De Broglie[1] envisages light as having both wave and particulate properties. Light is a quantised source of energy and is emitted, transmitted and absorbed in discrete units called photons whose energy (E) is directly related to the frequency (ν) of the radiation by the equation,

$$E = h\nu = hc/\lambda \qquad \text{- Eqn. 1.(1)}$$

(h = Planck's constant, c = velocity of light, ν = frequency and λ = wavelength of the radiation).

1.2 Creation of Excited States

In the ground state, the total energy (E_t) of a molecule consists of its electronic (E_{el}) vibrational (E_v) and rotational (E_{rot}) energies. Peturbation of these energies occurs upon the interaction of a molecule with a photon. Far-IR radiation causes transitions affecting E_{rot}, near-IR radiation affects E_{rot} and E_v, and visible and ultraviolet radiation is responsible for E_{el} and E_v transitions.

In the singlet electronic ground state (S_0) of an unexcited aromatic molecule, the electron spins are paired in agreement with the Pauli exclusion principle. On excitation of a π electron without change of spin, the resulting excited electronic state of the molecule is still a singlet state (S_i), where i = 1,2,3...n. A triplet state (T_i), i = 1,2,3...n arises when the π electron spin inverts during excitation. The multiplicity of the electronic state is described by the terms singlet and triplet.

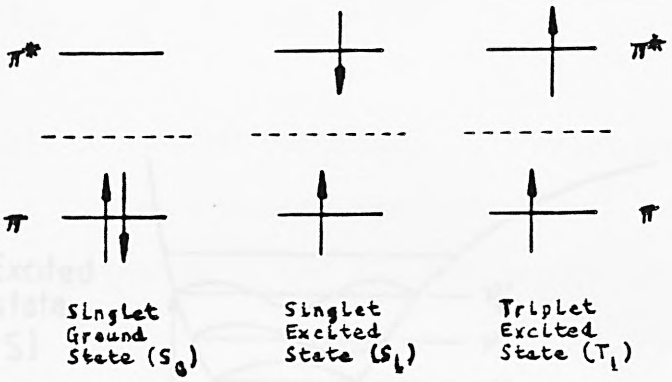


FIGURE 1.(1). Electronic Spins in the S_0, S_i and T_i States.

Transitions causing a change in the total electronic spin quantum number (S) are spin forbidden by selection rules.

Figure 1(2) shows the relative positions of the energy levels and transitions between them in a simple diatomic molecule using Morse Potential[2] energy curves. The electronic ground state and excited state are represented by the curves G and S respectively, while each point on the curve represents the net energy of nuclear-nuclear, nuclear-electronic and electronic-electronic interactions for a certain bond distance R. Re* and Re represent equilibrium bond lengths in the excited state and ground state respectively. . According to the Franck-Condon Principle, electronic transitions occur almost instantaneously (10^{-16} s) so that there is no change in nuclear position or nuclear kinetic energy during the transition - which will be initially to a vibrationally excited level with an identical internuclear distance. The transition may be represented by a vertical line in Figure 1(2). The nuclei assume a new equilibrium internuclear separation Re* after the occurence of the electronic transition.

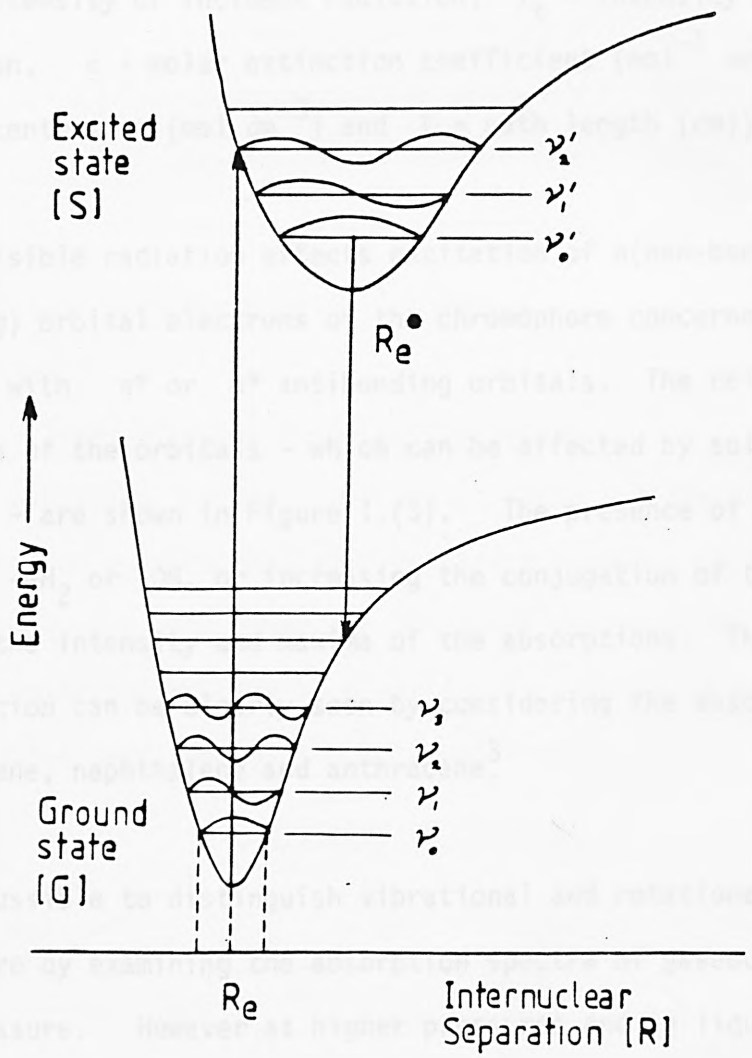


FIGURE 1.(2). Morse Potential Energy Curves for a Simple Diatomic Molecule.

The amount of radiation absorbed from that falling on the sample can be calculated in most cases by the Beer-Lambert Law (Equation 1.(2), thus enabling spectroscopic studies to be quantified.

$$\mathrm{Log}_{10} \frac{I_0}{I_t} = \varepsilon C\ell = O\,D \qquad - \text{Eqn.1.(2).}$$

(I_0 = intensity of incident radiation, I_t = intensity of transmitted radiation, ε = molar extinction coefficient ($\mathrm{mol^{-1}\ dm^{3}\ cm^{-1}}$), C = concentration ($\mathrm{mol\ dm^{-3}}$) and ℓ = path length (cm)).

UV or visible radiation effects excitation of n(non-bonding) and (bonding) orbital electrons of the chromophore concerned, transitions usually with π^* or α^* antibonding orbitals. The relative energies of the orbitals - which can be affected by solvent interactions - are shown in Figure 1.(3). The presence of auxochromes such as $-NH_2$ or -OH, or increasing the conjugation of the chromophore alters the intensity and maxima of the absorptions. The effect of conjugation can be clearly seen by considering the absorption spectra of benzene, naphthalene and anthracene.[3]

It is possible to distinguish vibrational and rotational fine structure by examining the absorption spectra of gaseous samples at low pressure. However at higher pressures and in liquids and solids the spectra tend to be more diffuse making the observation of fine structure more difficult. Temperature and the nature of the solvent affect the spectra. If there is an increased permanent dipole in the excited state, a bathochromic or red-shift is observed on change from a non polar to a polar solvent. A hypsochromic or blue-shift is observed when a change from a non polar to a polar solvent stabilises the ground state more than the excited state.

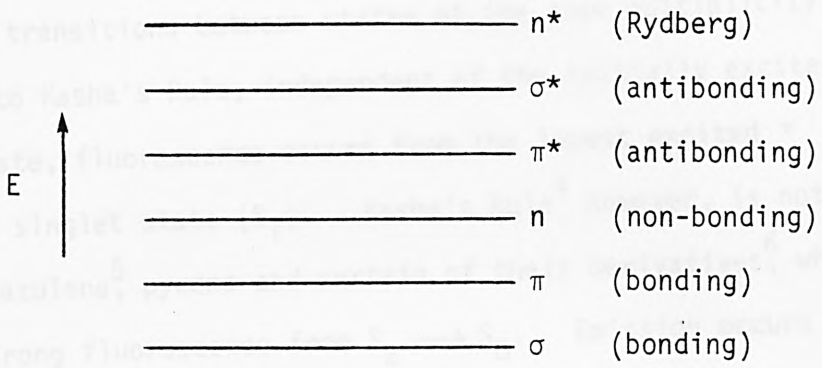


Figure 1.(3) Relative Orbital Energies.

1.3 Types of Decay From Excited States

Several processes (Figure 1.(4) are possible for the dissipation of the energy of a photochemically excited molecule. These processes can compete with each other for the deactivation of an excited state, and the contribution made by a particular pathway is determined by the relative magnitude of the rate constants.

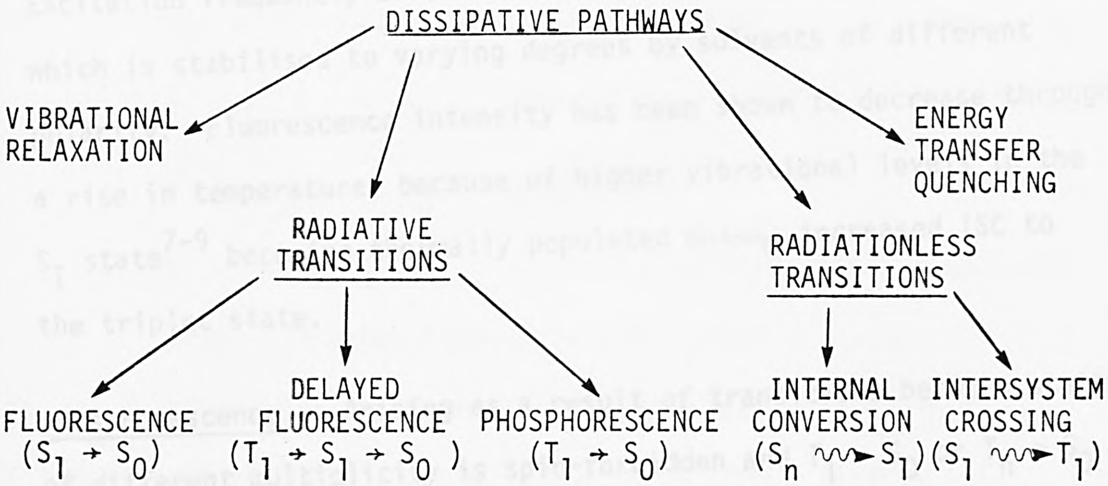


Figure 1.(4) Physical pathways for the dissipation of electronic energy.

1.3.1. Radiative Transitions

In radiative transitions, a photon is emitted due to an excited species passing from a higher excited state to a lower one.

Fluorescence - This is a very rapid process ($k_f \sim 10^6$-10^9 s^{-1}), concerning transitions between states of the same multiplicity. According to Kasha's Rule, independent of the initially excited reached state, fluorescence occurs from the lowest excited π electronic singlet state (S_1). Kasha's Rule[4] however, is not obeyed by azulene[5], pyrene and certain of their derivatives[6], which exhibit strong fluorescence from $S_2 \longrightarrow S_0$. Emission occurs before molecular rearrangement (Franck-Condon Principle), resulting in a ground state molecule in a vibrationally excited state ν_i, where $i > 0$. Emission bands frequently structureless and broad are the result of a whole array of transitions. The maximum wavelength represents the most favourable electronic transition, and usually the absorption and fluorescence spectra are mirror images of each other. The presence of quenching species, temperature, and solvent interactions influence the fluorescence spectra. Excitation frequently affects the dipole moment of the species which is stabilised to varying degrees by solvents of different polarity. Fluorescence intensity has been shown to decrease through a rise in temperature, because of higher vibrational levels in the S_1 state[7-9] becoming thermally populated resulting in increased ISC to the triplet state.

Phosphorescence - Arising as a result of transitions between states of different multiplicity is spin-forbidden and $T_1 \rightarrow S_0$ or $T_n \rightarrow S_0$

is rare, rate constants being $K_p \sim 10^{-2} - 10^{-4}$ s^{-1}. Triplet states are susceptible to impurity quenching because of their long radiative lifetime. Typically, phosphorescence is measured in solutions in rigid glasses at 77 K, but phosphorescence has been observed in solution using perfluorocarbon[10] solvents. Utilising aqueous micellar solutions[11] or protecting the triplet state by a protein[12] enables phosphorescence to be detected at ambient temperatures. High-powered lasers enable the production of significant concentrations of the triplet state species, and are thus of use in phosphorescence studies.

Delayed fluorescence - So-called because the rate of decay of emission measured is smaller than that expected from the transition causing the emission. Two mechanisms are responsible for delayed fluorescence, (a) triplet-triplet annihilation (see Eqns. 1.(3)-1.(6)).and (b) thermal activation. Triplet-triplet annihilation is the result of two excited triplet species colliding to form an intermediate species X, which breaks down to give an S_1 species that causes the delayed fluorescence.

$$T_1 + T_1 \longrightarrow X \qquad \text{Triplet-Triplet} \qquad \text{-Eqn.1.(3)}$$

$$X \longrightarrow S_0 + S_1 \qquad \text{Annihilation} \qquad \text{-Eqn.1.(4)}$$

$$X \longrightarrow S_0 + S_0 \qquad \text{Deactivation} \qquad \text{-Eqn.1.(5)}$$

$$S_1 \longrightarrow S_0 + h\nu \qquad \text{Delayed Fluorescence} \qquad \text{-Eqn.1.(6)}$$

Triplet-Triplet Annihilation Mechanism.

Figure 1.(5) depicts the thermal activation mechanism of the T_1 state through ΔE, the S_1 state then arising from a reverse ISC.

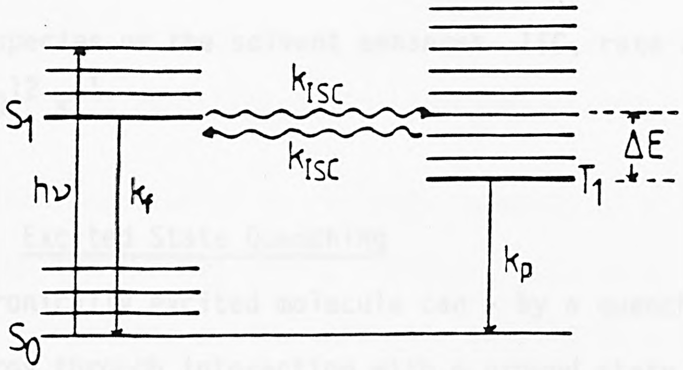


FIGURE 1.(5). Diagram Showing the Energy Levels for the Thermally Activated Delayed Fluorescence.

1.3.2 Radionless Transitions

These arise between isoenergetic (degenerate) vibrational-rotational levels of different electronic states, and involve no change in the total energy of the system. Vibrational relaxation gives the lowest vibrational level (ν_0') electronically excited species through molecular collisions, causing the loss of excess vibrational energy. Rate constants are $10^{13}\ s^{-1}$.

Internal conversion occurs very rapidly between isoenergetic vibrational levels of different states of the same multiplicity (e.g. $S_h \rightsquigarrow S_m$ or $T_n \rightsquigarrow T_m$), accounting for the negligible emission from upper excited states, $k \sim 10^{11} - 10^{14}\ s^{-1}$.

Intersystem crossing occurring between states of different multiplicity is responsible for the population of the triplet manifolds $S_1 \rightsquigarrow T_1$, and is competitive with radiative transitions from S_1.

The heavy atom effect,[13,14] the presence of halogen atoms in the excited species or the solvent enhances ISC, rate constants being $\sim 10^4 - 10^{12}\ s^{-1}$.

1.3.3 Excited State Quenching

An electronically excited molecule can - by a quenching process, lose energy through interaction with a ground state atom or molecule.

Self-quenching (or concentration quenching) - so called by the fact that the intensity (quantum yield) of fluorescence intensity decreases by increasing the concentration of a solute (A). It was shown by Foster and Kasper (while examining fluorescence of pyrene in solution)[15,16] that a new fluorescence band to the red of the monomer appeared as a result of the quenching, this being attributed to the formation of an excited state dimer or excimer, as shown below (Eqn.1.(7)).

$$A_{S_0} \underset{\text{monomer fluorescence}}{\overset{h\nu}{\rightleftharpoons}} A^*_{S_1} \overset{A}{\rightleftharpoons} (AA)^*_{S_1} \overset{\text{Excimer fluorescence}}{\rightleftharpoons}$$

$$A_{S_0} + A_{S_0} + h\nu' \qquad \text{-Eqn.1.(7)}$$

Aromatic hydrocarbons exhibit excimer formation quite commonly, but lower temperatures and higher concentrations than those necessary for pyrene are required for benzene, naphthalene and their methyl derivatives.

Impurity quenching is due to another molecule (Q) quenching an excited species A* and can be caused by (i) exciplex formation, (ii) heavy atom quenching or (iii) energy transfer quenching.

(i) The formation of an exciplex commonly of a 1:1 stoichiometry - by two species coming together, results in the quenching of the fluorescence of A*, which is replaced by a broad new structureless emission at longer wavelengths. The exciplex which exhibits some charge transfer character - varies in its stability and thus in its emission with different solvent polarity. In acetonitrile and other solvents having a high dielectric constant, the emission completely disappears. According to flash photolysis studies, radical ion pairs[17] are formed, derived from the exciplex as well as the initially formed encounter complex. Rehm and Weller[18] have carried out kinetic measurements on the encounter complex and its role in electron transfer quenching. The precise nature of the involved entities is not understood; they have been shown to be an important part in the quenching process of the singlet excited state - see Sections 1.6 and 1.7.

(ii) The presence of heavy atoms (i.e. halogens), causes the molecular fluorescence of the species to be quenched, due to a singlet exciplex being initially produced, which undergoes enhanced ISC to the triplet exciplex, and as shown in Equation 1.(8) subsequently dissociate.

Eqn.1.(8)

$$A_{S_1}^* + Q_{S_0} \longrightarrow (AQ)_S^* \xrightarrow{ISC} (AQ)_{T_1}^* \longrightarrow A_{T_1}^* + Q_{S_0}$$

Wilkinson et al.[19,20,21] have investigated this field and the quenching effect of xenon and halogen derivatives on aromatic hydrocarbons. Excited states are also effectively quenched,[22] at diffusion controlled rates - by oxygen. It is believed that the quenching occurs via triplet exciplexes (Eqn.1.(9)), generating singlet oxygen (Eqn.1.(10)).

$$A_{S_1}^* + {}^3O_2 \longrightarrow (AO_2)T_n^* \longrightarrow (AO_2)T_1^* \longrightarrow A_{T_1}^* + {}^3O_2 \qquad \text{-Eqn.1.(9)}$$

$$A_{T_1}^* + {}^3O_2 \longrightarrow A_{S_0} + {}^1\Delta g O_2 \qquad \text{-Eqn.1.(10)}$$

Singlet excited states are also quenched by the free radical species nitric oxide, probably enhancing ISC.

(iii) In electronic energy transfer quenching, an excited donor molecule (D*) returns to the ground state, the excitation energy being simultaneously transferred to an acceptor molecule A,

$$D_{S_1}^* + A_{S_0} \longrightarrow D_{S_0} + A_{S_1}^* \qquad \text{-Eqn.1.(11)}$$

1.4 Quantum Yields and Lifetimes of Excited States

1.4.1 Quantum Yield of Fluorescence (ϕ_f)

Figure 1.(6) shows a general kinetic scheme for the excitation of a ground state molecule and its decay.

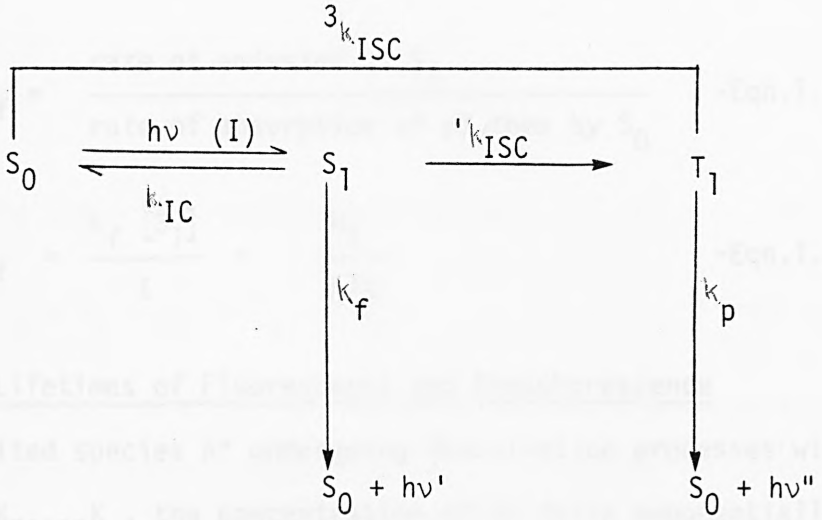


Figure 1.(6) Photophysical pathways associated with an S_1 excited species.

I = rate of absorption of photons

K_f = rate of fluorescence

K_p = rate of phosphorescence

K_{ISC} = rate of intersystem crossing

K_{IC} = rate of internal conversion

Application of the steady-state approximation shows the rates of formation and destruction of the S_1 state to be equal. If the rate of absorption (I) is given by Equation 1.(12),

$$I = [S_1]\ \Sigma\ 'K \qquad \text{-Eqn.1.(12)}$$

(where $'K = K_{IC} + K_f + K_{ISC}$), the quantum yield of fluorescence (ϕ_f) is given by Equations 1.(13) and 1.(14)

$$\phi_f = \frac{\text{rate of emission of } S_1}{\text{rate of absorption of photons by } S_0} \qquad \text{-Eqn.1.(13)}$$

or $$\phi_f = \frac{k_f\,[S_1]}{I} = \frac{k_f}{\Sigma^1 k} \qquad \text{-Eqn.1.(14)}$$

1.4.2 Lifetimes of Fluorescence and Phosphorescence

For an excited species A* undergoing deactivation processes with rates K_1, $K_2 \ldots K_n$, the concentration of A* falls exponentially with a rate constant ΣK. Defining the lifetime (τ) of A* as the [A*] time taken for $[A^*]$ to fall by $^1/e$ of its initial value, then the lifetimes of fluorescence (τ_f) and phosphorescence (τ_p) are given by the expressions in Equation 1.(15)

$$\tau_f = \frac{1}{\Sigma^1 k}\,, \quad \tau_p = \frac{1}{\Sigma^3 k} \qquad \text{-Eqn.1.(15)}$$

The combination of Equations 1.(14) and 1.(15) gives

$$k_f = \frac{\phi_f}{\tau_f} \qquad \text{-Eqn.1.(16)}$$

1.4.3 Quantum Yield of Phosphorescence (ϕ_p)

Assuming the rates of formation and destruction of the T_1 state to be equal, thus

$$^1k_{ISC}\,[S_1] = \Sigma^3 k\,[T_1] \qquad \text{-Eqn.1.(17)}$$

(where $\Sigma^3 k = k_p + {}^3k_{ISC}$)

As ϕ_p is defined by Eqn.1.(18)

$$\phi_p = \frac{K_p [T_1]}{I} \qquad \text{-Eqn.1.(18)}$$

Substituting for I and rearrangement gives

$$\phi_p = \theta_p \, \theta_{ISC} = K_p \, \tau_p \, \phi_t \qquad \text{-Eqn.1.(19)}$$

(where θ_p and θ_{ISC} are the quantum efficiencies of phosphorescence and intersystem crossing respectively). A molecule, on returning to the ground state, must lose all the energy which has been supplied to it during excitation, and combining the efficiencies of the various radiationless processes in a term (ϕ_R) gives

$$\phi_f + \phi_p + \phi_R = 1 \qquad \text{Eqn.1.(20)}$$

1.5 Methods for Examining the Creation and Decay of Excited States

1.5.1 Electrical Discharges

Application of a high potential across an inert gas in the presence of mercury vapour, causes the few stray electrons present to be accelerated to energies which are high enough to ionize the gas. Excited inert gas atoms are formed through recombination of ions and electrons. The gas may also be excited directly

$$Ne + e^- \longrightarrow Ne^+ + 2e^-$$
$$Ne^+ + e^- \longrightarrow Ne^*$$

The Hg atoms are excited through collision of the excited atoms with the former (energy transfer), which then emit radiation.

$$Ne^* + Hg \longrightarrow Ne + Hg^*$$

$$HG^* \longrightarrow Hg + h\nu$$

This forms the basis of mercury arc lamps widely used in photochemistry and illuminating streets. Pressure distinctly influences the spectral distribution of the emission of mercury arcs.

(a) Low pressure arcs, containing Hg at $\sim 10^{-3}$ mm pressure, emit mainly (95%) in the resonance line at 253.7 nm $[Hg('P_1) \rightarrow Hg('S_0)]$ and to a much lesser extent at 184.9 nm $[Hg('P_1) \rightarrow Hg('S_0)]$.

(b) Medium pressure arcs utilise Hg pressures of around 1 atmosphere and greater currents, thereby increasing the electron, ion, and excited species concentration, thus promoting the metastable (relatively long lived) $Hg(^3P_1)$ atoms to many higher levels. A multiplicity of lines characteristic of this type of arc is obtained by emission from these other states.

(c) High pressure arcs, operating at pressures up to several hundred atmospheres, consist of electrodes close together thus restricting the discharge to a small volume, and their near point source of brilliance is comparable with that of the sun. The emission from these arcs is practically continuous, partly due to pressure and temperature (Doppler effect) broading of the numerous lines which consequently tend to overlap.

Also, excited Hg* atoms and Hg atoms in their ground state produce excited dimers:

$$Hg^* + Hg \longrightarrow Hg_2^* \longrightarrow Hg + Hg + h\nu$$

The emission will be continuous because the dimers are dissociated in their ground state, which therefore has no quantized levels.

1.5.2 Lasers

These consist of an emitting material set in a tuned optical cavity (two parallel mirrors, one being partially transparent. Separation of the mirrors by an integral number of $\frac{1}{2}\lambda$ (where $E_u - E_1 = hc/\lambda$), causes the light reflected from a mirror to be in phase with the incident wave (constructive interference). After production of a population inversion in the emitting material, some photons are obtained via spontaneous emission, which on collision with molecules of the excited lasing material stimulate it to emit in phase with the incident photons. On travelling back and forth between the mirrors, the intensity of the wave increases. A chain reaction occurs which destroys the population inversion in a very short interval of time (∿ 1 μs), generating a burst of radiation which escapes through the partially transmitting mirror.

Laser radiation has the following properties:

(i) Coherence - the light waves emitted being all in phase.

(ii) Very high monochromaticity - since the cavity is tuned to one particular frequency, destructive interference occurs for light having other frequencies.

(iii) Accurate parallelism, since the cavity is not tuned for off-axis radiation, which, in any case, would escape after only a few reflections. It is possible to focus the beam to a spot of very small dimensions (of the order of a wavelength) due to the beam's lack of divergence, producing very high density radiation ($> 10^9$ W cm^{-2}) for short laser pulses.

(iv) A laser pulse possesses enormous brilliance - a 'long' pulse of 1 μs containing 1J of energy has a power output of 1 MW. This can be increased by orders of magnitude by shortening the duration of the laser pulse.

1.5.3 Fluorescence Spectra

Fluorescence spectra are recorded by means of a spectrofluorimeter, in which the specimen contained in a cell is excited by a beam of monochromatic light, the emission being observed and analysed at right angles to the incident beam. An XY recorded plots the emission spectrum which represents the output.

Apart from a few exceptions, organic molecules do not phosphoresce in common solvents at ambient temperatures, the system described will only record the fluorescence spectrum. There is also the possibility of recording two types of spectra, because either the excitation or the emission monochromator can be coupled to the XY recorder.

(i) A fluorescence emission spectrum is obtained by setting the excitation monochromator to a certain wavelength absorbed by the sample and scanning the emitted light with the emission monochromator.

(ii) A fluorescence excitation spectrum is obtained by setting the emission monochromator to a certain wavelength contained in the fluorescence output and then scanning the excited wavelengths by means of the exciting monochromator.

In sufficiently dilute solution, a fluorescence excitation spectrum commonly shows a close resemblance to an absorption spectrum.

The identification and quantitative estimation of fluorescence molecules is possible through fluorescence excitation spectroscopy.

1.5.4 Phosphorescence Spectra

Phosphorescence spectra are recorded with spectrophosphorimeters, which differ from spectrofluorimeters only in that they have a mechanical or optical shutter which respectively chops the exciting and emitted light beams in a way that excitation occurs on cutting off the detector and emission is not observed until a definite period after excitation has stopped. The delay between excitation and observation enables fluorescence ($\tau_f < 10^{-6}$ s) to decay to zero before the phosphorescent emission (longer lives) is recorded. Phosphorescence is most easily detected in rigid matrices which inhibit the quenching collisions between impurities and the excited triplets, and consequently, investigation of the sample is commonly in mixed organic solvents which on cooling in liquid nitrogen set to form rigid glasses. Triplet species, formed indirectly via intersystem crossing from the singlet manifold, account for the observed phosphorescence. The phosphorescence excitation spectrum thus corresponds to the ordinary singlet ⟶ singlet absorption spectrum. The observation of triplets formed directly via forbidden S ⟶ T transition is feasible because of the high sensitivity of emission spectroscopy. In phosphorescence excitation spectroscopy, which is based on this, excitation of the S ⟶ T transition is by means of an intense light source. If the absorption intensity has to be increased, ethyl iodide (or another heavy atom solvent) is employed, the formation of excited triplets being monitored by observing their phosphorescence at a certain set wavelength. A plot ofphosphorescence intensity against the wavelength of the exciting light (at constant intensity) gives the S ⟶ T absorption spectrum, since phosphorescence intensity is directly proportional to the extinction coefficient for the S ⟶ T transition at the particular exciting frequency used. Even if the compound itself is non-phosphorescent, this method is still applicable by incorporating a phosphorescent molecule of lower triplet energy which is excited by energy transfer.

1.6 Intermolecular Exciplexes

1.6.1 Factors Affecting Intermolecular Exciplex Formation and Stability

1.6.1.1 Introduction

An electronically excited molecular complex - commonly of a 1:1 stoichiometry - is called an EXCIPLEX (or excited complex). Included in this wide category are various complexes:

(1) Excimers - (excited dimers) formed between two identical atoms or molecules.

(2) Heteroexcimers - formed between two non-identical atoms or molecules.

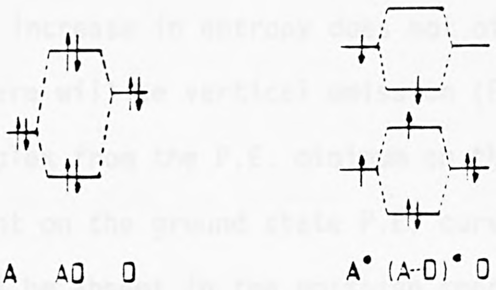
(3) Excited Charge-Transfer (CT) Complexes - formed by excitation of ground state associated molecular complexes. Exciplex will be the term used to describe a hetero excimer and the specialised term used when applicable for the remainder of this report.

A wave function (see Equation 1.(21))[23] can be used to describe the electronic structure of an exciplex formed between two chromophores A and D.

$$\psi = C_1\ \phi(A^*D) + C_2\ \phi(AD^*) + C_3\ \phi(A^-D^+) + C_4\ \phi(A^+D^-) + C_5\ \phi(AD)$$

-Eqn.1.(21)

The C_5 term is of significance for an excited CT complex and accounts for its stability in the ground state. But if the ground state interactions are of no importance, then the weighting of C_1 and C_2 relative to C_3 and C_4 determines the extent to which the exciton resonance contributes to the stability of the exciplex relative to charge transfer interactions. The S_1 exciplexes should fluoresce, but there will be emission to a a weakly bound or dissociative ground state due to the ground state collision complex AD being less tightly bound than (AD*) or (A---D)*.



(a) AD collision pair (Net stabilisation = 0)

(b) (A--D)* exciplex (Net stabilisation = 2 electrons)

FIGURE 1.(7). Electronic Stabilisation in the Collision Pair (AD) and the Exciplex (A--D)*.

The enhanced stability of the (A---D)* exciplex relative to the ground state collision pair (AD) (see Figure 1.(7)) is elucidated by interactions in molecular orbitals (M_0) in exciplexes.

As shown in Figure 1.(8), it is also possible to consider the potential energy surface for the emission of an exciplex (A---D)*, stabilised primarily by charge-transfer interactions. When the distance between the two groups is small enough for collision to occur - assuming the ground state attractions of the donor (D) and acceptor (A) are negligible - the energy of the system is increased due to the instability of the ground state collision complexes. The minimum in the P.E. curve is explained by charge transfer or exciton resonance interactions caused by an increase in the binding energy, arising from the interaction on the excited P.E. surface of A* and D, however at large separation, the emission is that of

A*, as the groups approach. Exciplex formation will occur between A and D if an increase in entropy does not offset the decrease in enthalpy. There will be vertical emission (Franck-Condon Principle) from the exciplex from the P.E. minimum on the excited state to a repulsive point on the ground state P.E. curve. Vibrational fine structure will be absent in the emission spectra of exciplexes and excimers due to the collision pair flying rapidly apart and thus having a very short lifetime. The energy difference between A* and D and (A---D)* represents the exciplex stability (A---D)* and is designated by ΔH_{ex} in Figure 1.(8).

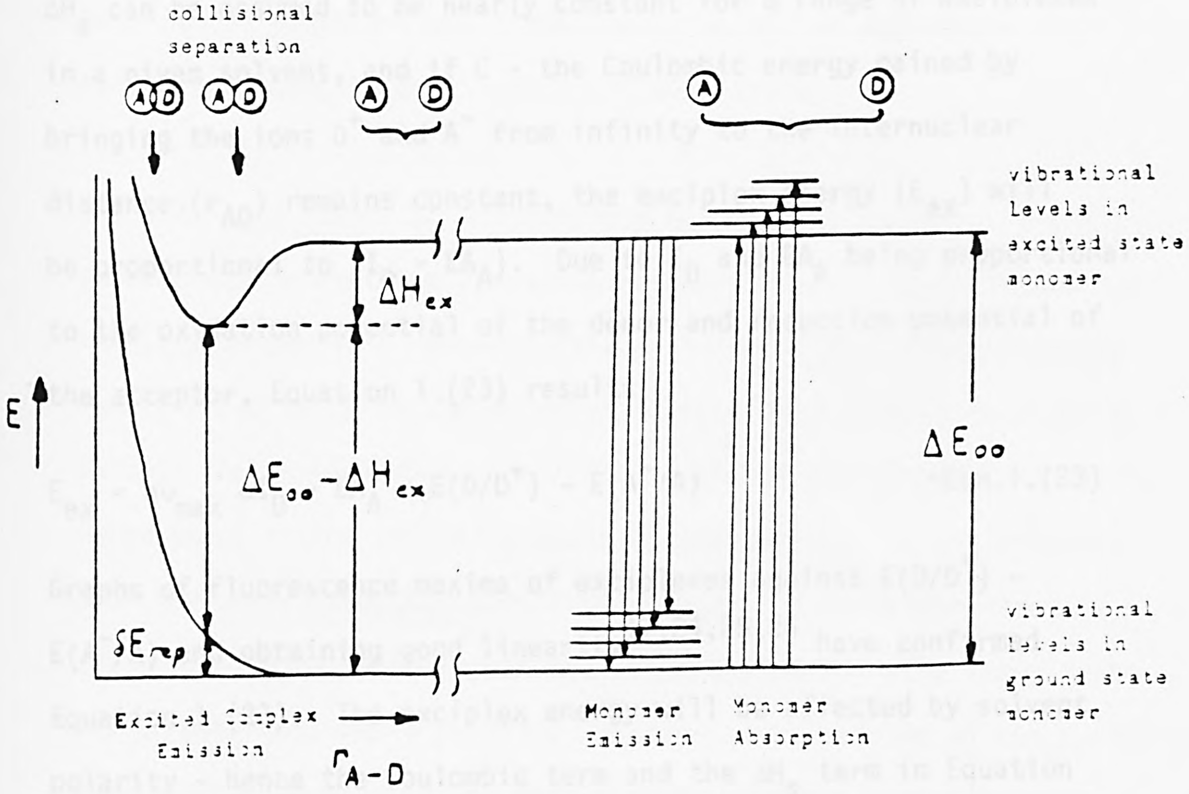


FIGURE 1.(8). Potential Energy Surface for Exciplex Emission in a Donor-Acceptor Exciplex.

1.6.1.2 Thermodynamic Factors Affecting Exciplex Stability

If charge-transfer interactions between the donor and acceptor moieties were solely responsible for exciplex stabilisation, then Equation 1.(22) would give the energetics of exciplex formation

$$E_{(D^+A^-)} = I_D - EA_A - C - \Delta H_s \qquad \text{-Eqn.1.(22)}$$

where $E_{(D^+A^-)}$ = energy of the pure CT state relative to the ground state energy of A and D.

I_D = ionisation potential of donor species

EA_A = electron affinity of acceptor species

C = Coulombic interaction energy between D^+ and A^-.

ΔH_S = solvation energy of the exciplex.

ΔH_s can be assumed to be nearly constant for a range of exciplexes in a given solvent, and if C - the Coulombic energy gained by bringing the ions D^+ and A^- from infinity to the internuclear distance (r_{AD}) remains constant, the exciplex energy (E_{ex}) will be proportional to (I_D - EA_A). Due to I_D and EA_A being proportional to the oxidation potential of the donor and reduction potential of the acceptor, Equation 1.(23) results

$$E_{ex} = h\nu_{max} \alpha I_D - EA_A \propto E(D/D^+) - E(A^-/A) \qquad \text{-Eqn.1.(23)}$$

Graphs of fluorescence maxima of exciplexes against $E(D/D^+)$ - $E(A^-/A)$ and obtaining good linearity[17,24,25,26] have confirmed Equation 1.(23). The exciplex energy will be affected by solvent polarity - hence the Coulombic term and the ΔH_s term in Equation 1.(22) - and this effect can be observed in several hydrocarbon-amine exciplexes.[24,27,28]

1.6.1.3 Steric Factors and the Nature of The Participating Groups

The efficiency of quenching and exciplex formation is reduced due to the close approach of the donor and acceptor species being hindered through steric congestion. Confirmation of this has been given by the quenching of 1-cyano-naphthalene by several dialkyl sulphides[29] as well as exciplex formation between pyrene and N,N-dimethylaniline and its 3,5-ditertiarybutyl derivatives.[30]

Exciplex formation of certain aromatic hydrocarbons with amines is also affected by the nature of the amine group. Exciplex formation occurs more readily with tertiary amines than with secondary and primary amines, the magnitudes of the ionisation potentials accounting for this. With N-H or O-H containing compounds, hydrogen abstraction reactions and formation of molecular aggregates by hydrogen bonding interactions could also arise.

1.6.1.4 The Effect of Solvent Upon Equilibrium Exciplex Formation

Intermolecular exciplex formation between aromatic hydrocarbons and tertiary amines have revealed that an increase in solvent polarity causes a red shift in the exciplex fluorescence as well as a decrease in both the quantum yield and lifetime of the exciplex. Despite the improvement in the solvating power of the solvent, it was proposed that the exciplex dissociates into radical ion pairs more readily by increasing the polarity of the solvent. It was also shown that an increase in solvent polarity decreases the lifetime of the pyrene-dimethylaniline much slower than the fluorescence intensity, and this was thought to be due to the production of radical ion pairs from both the initially formed encounter complex and the fluorescent exciplex as shown in Figure 1.(9).

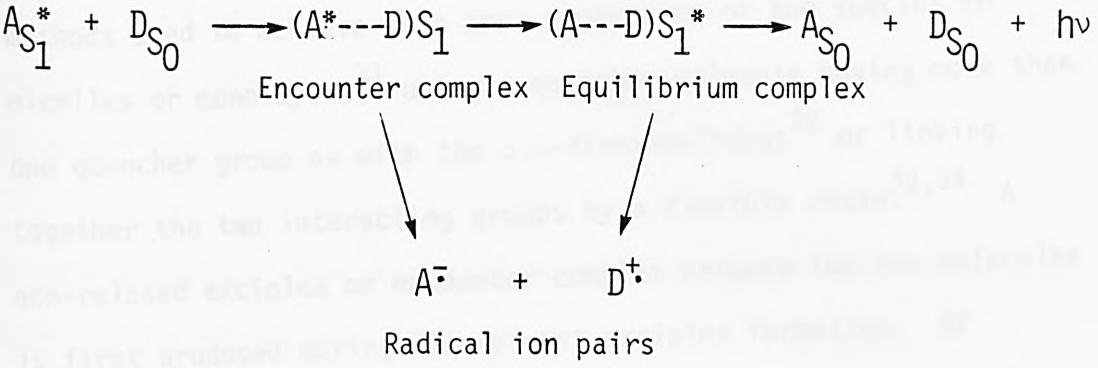


Figure 1.(9) Generation of solvated radical-ion pairs from the encounter complex and fluorescent complex.

The dipole moments of a range of exciplexes[27] have been calculated by taking into account the effect of solvent polarity on the exciplex emission. In most cases the exciplexes have dipole moments which indicate almost complete electron transfer between the donor and acceptor groups. CT interactions contribute little stability on excimeric emission as their independency upon solvent polarity reveals.

1.6.2 Methods of Formation of Exciplexes

1.6.2.1 Electron Transfer and Solvent Relaxation

It is necessary that if an intermolecular exciplex is to be formed in solution, after one of the reaction partners is excited, it collides with the other partner within the lifetime of the excited state. The diffusion controlled limits for the solvent being used, influences the rate of interaction, and shows that solvent reorganisation is involved. Multiple collisions of the two species are necessary to produce a sufficiently high concentration of the reaction partners to encourage exciplex formation. Among the methods used to achieve this are, production of the species in micelles or monolayers,[31] using a quencher molecule having more than one quencher group as with the α,ω-diaminoalkanes[32] or linking together the two interacting groups by a flexible chain.[33,34] A non-relaxed exciplex or encounter complex between the two molecules is first produced during fluorescent exciplex formation. Of significance for this excited species is the fact that the surrounding solvent molecules have had no time to reorganise to give it maximum stability. Internuclear separation of 7-8 Å[35] could enable electron transfer, but in these encounter complexes the extent of charge transfer is uncertain. Also the non-emissive nature of these complexes suggests that their reaction involvement is through implication. The possibility of encounter complex formation has been suggested to explain triplet species being observed during the quenching of polycyclic aromatic hydrocarbons by added halide ions.[36,37]

Relaxation times - in ordinary solvents, at room temperature are shorter than the lifetime of the emitting species, and emission occurs essentially from the fully solvated equilibrium complex. It is possible to slow down the relaxation rates in which the exciplex fluorescence exhibits a time dependence, by means of time resolved fluorescence spectroscopy and working at low temperatures with solvents of high viscosity. By the use of pyrene (acceptor) and highly viscous supercooled tri-n-butylamine (donor) at 156 K, Nakashima et al.^{38} have observed this effect. Formation of the fluorescent species prevented through involvement of the encounter complex in a non-radiative decay pathway - can also be impaired by bad steric interactions, a lack of conformational mobility and the necessity for rehybridisation of one of the reaction partners during electron transfer.

The main purpose of low or medium polarity solvents is to achieve stabilisation of the excited species, whereas in highly polar solvents such as acetonitrile and methanol, electron transfer to achieve a ground state solvent shared ion pair, competes effectively with exciplex formation. Electron transfer reaction investigations in acetonitrile solutions have been made by Rehm and Weller,^{39} and their results analysed according to a scheme prepared originally by Marcus,^{40} as shown in Figure 1.(10), to derive the overall rate of fluorescence quenching (K_q). Back electron transfer - leading to the neutral ground state (M + Q), with rate constant K_3 - is believed to be the main deactivation process from the solvent shared ion pair.

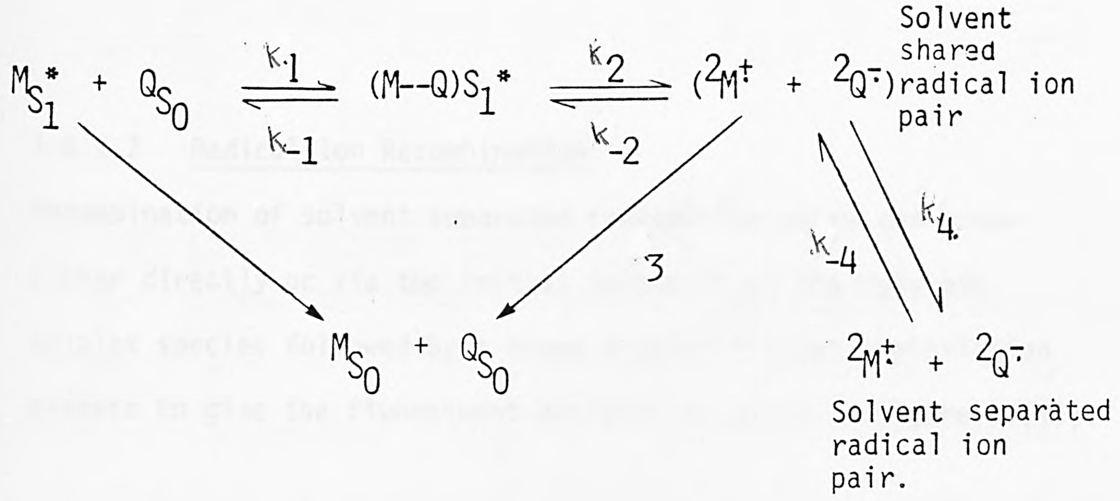


Figure 1.(10) Photophysical processes involved in the formation and decay of solvent shared and solvent separated radical ion pairs.

The relationship between the rate constant k_q and the Gibbs Free Energy change [41,42] have been theoretically investigated. Equation 1.(24)[39] was used to calculate the ΔG^o between the equilibrium exciplex (M--Q)* and the solvent shared radical-ion pair $(^2M^+ + {}^2Q^-)$.

$$\Delta G^o = E^{ox} - E^{red} - \frac{e^2}{\varepsilon' a} - \Delta E_{oo} \qquad \text{-Eqn.1.(24)}$$

(where E^{ox} = oxidation potential of donor, E^{red} = acceptor reduction potential, $e^2/$ 'a = Coulombic interaction energy between two radical ions at encounter distance a in a solvent of dielectric constant ε', ΔE_{oo} = electronic excitation energy of fluorescer). These studies have shown that for $\Delta G^o < -40$ KJ mol^{-1}, the quenching is diffusion controlled and for $\Delta G^o > -40$ KJ mol^{-1}, an activation energy has to be overcome and the rate constants are at least a factor of ten below those for diffusion controlled processes.

1.6.2.2 Radical-Ion Recombination

Recombination of solvent separated radical-ion pairs can occur either directly or via the initial formation of the relevant triplet species followed by a mixed triplet-triplet annihilation process to give the fluorescent exciplex as given in Figure 1.(11).

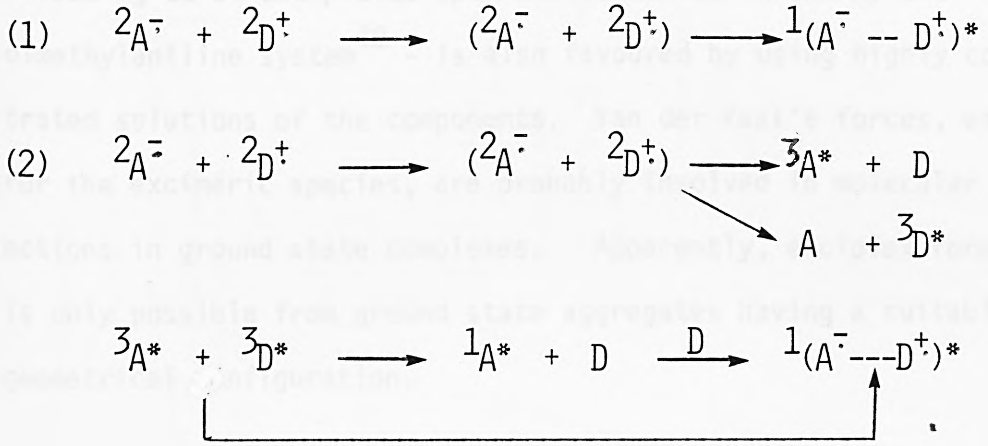


Figure 1.(11) Photophysical processes leading to the formation of fluorescent exciplexes from radical-ion pairs.

The process of radical-ion pair recombination is not only restricted to photochemically generated species. The combination of electrochemically[43] generated radical species as well as mixing solutions of chemically produced radical anions and cations[44-47] have led to fluorescence exciplexes being detected. Monitoring the influence of an applied magnetic field upon the exciplex yield determines triplet state involvement in exciplex formation. A reduction in the triplet lifetime and thus the exciplex yield is caused by an external magnetic field, which perturbs the degeneracy of the triplet state.

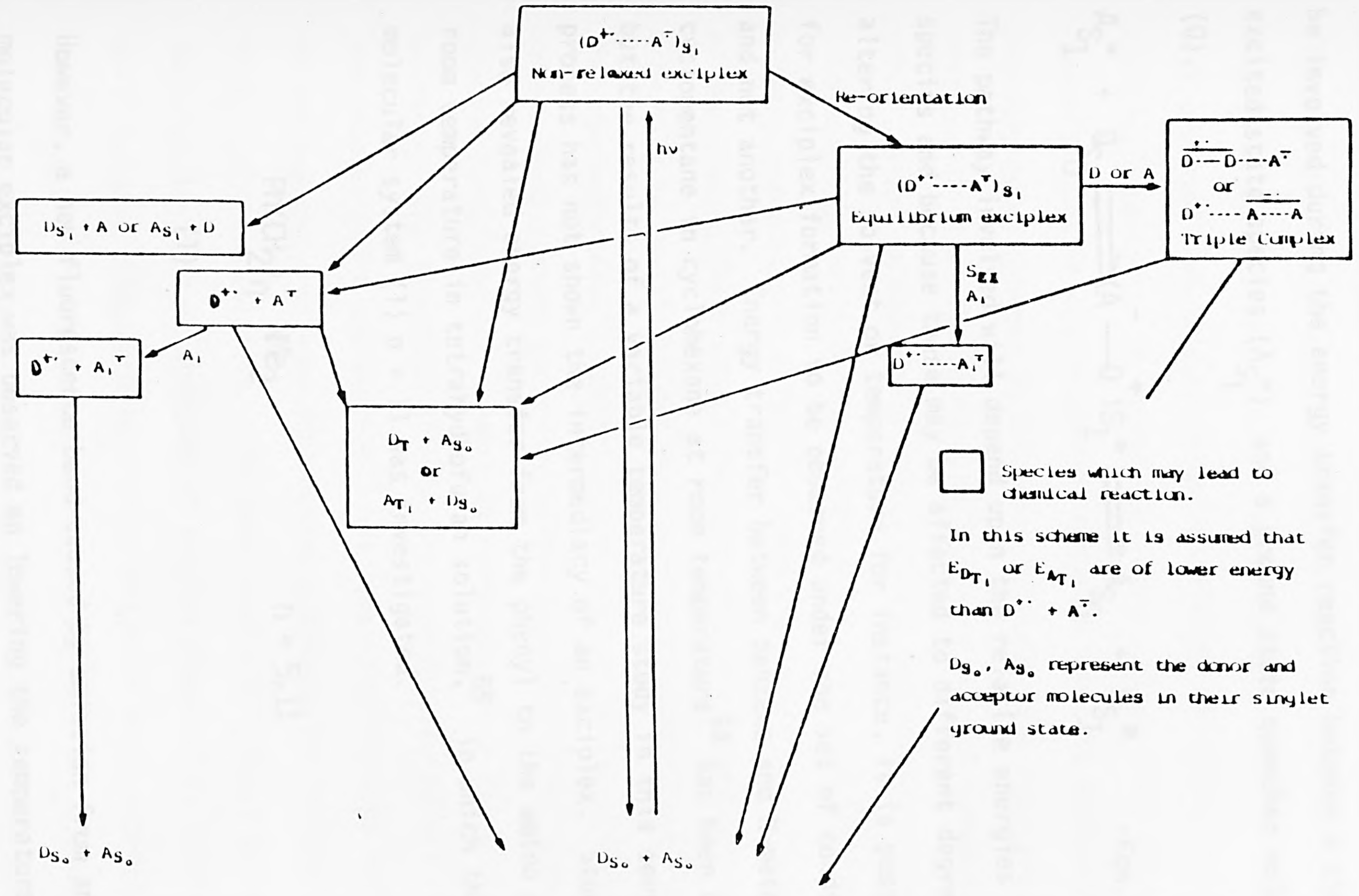
1.6.2.3 Excited Ground State Aggregates

Excimer fluorescence from aromatic hydrocarbons at low temperature (77°K) in rigid matrices arises through excitation of ground state molecular aggregates. Formation of loose ground state complexes - leading to CT exciplexes upon excitation as in the pyrene-dimethylaniline system[48] - is also favoured by using highly concentrated solutions of the components. Van der Vaal's forces, especially for the excimeric species, are probably involved in molecular interactions in ground state complexes. Apparently, exciplex formation is only possible from ground state aggregates having a suitable geometrical configuration.

1.6.3 The Role of the Exciplex in Photochemical Processes

1.6.3.1 The Modes of Decay of Excited Complexes

Several photochemical processes which the encounter complex and solvent relaxed exciplex are capable of undergoing are given in Figure 1.(12). Because it is possible for the non-relaxed exciplex to take part in chemical reactions, a non-radiative and highly efficient pathway for decay is available to the excited species, and this could account for the absence of fluorescence in certain systems. This effect can be seen by considering the interaction of aromatic hydrocarbons with primary and secondary amines. Fluorescent exciplexes are formed between N-methylindole (and related compounds) and aromatic hydrocarbons,[49] but pyrrole forms an addition product with the hydrocarbon.[50,51] Numerous examples of chemical reactions occurring from excited state systems, accompanied by little or no exciplex fluorescence have appeared in the literature.[52,53]



☐ Species which may lead to chemical reaction.

In this scheme it is assumed that $E_{D_{T_1}}$ or $E_{A_{T_1}}$ are of lower energy than $D^{+\cdot} + A^{\overline{\cdot}}$.

D_{S_0}, A_{S_0} represent the donor and acceptor molecules in their singlet ground state.

FIGURE 1.(12). Photophysical Processes which Excited Complexes may undergo.

1.6.3.2 The Role of Exciplexes in Energy Transfer

The intermediate formation of an exciplex, as shown in Equation 1.(25) could be involved during the energy transfer reaction between a singlet excited state species ($A_{S_1}^*$) and a ground state quencher molecule (Q).

$$A_{S_1}^* + Q_{S_0} \rightleftharpoons (\bar{A} --- \overset{+}{Q})S_1^* \rightleftharpoons A_{S_0} + Q_{S_1}^* \qquad \text{-Eqn.1.(25)}$$

The pathway involved will depend upon the relative energies of the species and because these may be affected to different degrees by altering the solvent or temperature for instance, it is possible for exciplex formation to be observed under one set of conditions and not another. Energy transfer between benzene and N-methylazacyclopentane in cyclohexane at room temperature[54] has been detected, but the results of a variable temperature study in this sensitisation process has not shown the intermediacy of an exciplex. Studies have also revealed energy transfer from the phenyl to the amino group at room temperature in tetrahydrofuran solution,[55] in which the intramolecular system (1) n = 11 was investigated.

$Ph(CH_2)_n\ NMe_2$ $\qquad$ n = 5,11

(1)

However, a new fluorescence band caused by emission from an intramolecular exciplex was observed on lowering the temperature.

1.6.3.3 Triplet Formation From Exciplexes

Triplet state species (see Figure 1.(11)) can be formed by recombination of both solvent separated and geminate radical-ion pairs in high polarity solvents which favour radical ions. It has also been proposed that triplet formation via the intermediacy of an exciplex[56] can occur in certain solvents. Laser flash photolysis investigations in the picosecond range on aromatic hydrocarbon-tertiary amine systems in non-polar solvents have revealed the involvement of a relaxed exciplex[57] during triplet formation. For other systems it has been proposed that a non-relaxed exciplex is involved, especially during quenching of aromatic hydrocarbons by primary and secondary amines.[58] Both the length and flexibility of the linking chain affect the influence of the halogeno-group, according to investigations into ω-haloalkylnaphthalene[59] and ω-phenoxyalkylbromide[60] systems. With analogy to the aromatic hydrocarbon-amine systems there may be the possibility for quenching species containing one or more halogeno-groups to favour ISC in the exciplex. The formation of both the naphthalene radical cation and the triplet state hydrocarbon[61] has been shown through investigations on the quenching of some naphthalene compounds by chloroacetonitrile in acetonitrile solution. The involvement of triplet exciplex intermediates during the formation of triplet species has received little verification. But, phosphorescence evidence lends support to the existence of triplet excited CT complexes,[62,63] and cycloaddition reactions of triplets produced via these complexes has been well investigated by Wong and Arnold.[64]

Often, triplet formation[65] is prevented due to the energy of the excited charge-transfer complex being lower than that of the lowest triplet state.

1.6.3.4 Reactions Occurring Via Exciplexes

(a) Intermolecular Cyclo-Addition Reactions

The photochemical reactions of a range of alkenes with benzenes and related compounds has been studied, and Bryce-Smith et al.[66] have proposed certain rules as to their reaction mode. It has been suggested that reactions between components having a large ionisation potential difference will involve an exciplex intermediate, producing the 1,2- and 1,4-cycloadducts. The use of relatively polar solvents has exhibited exciplex fluorescence, and the fluorescence as well as the product formation has been quenched through the addition of triethylamine. A recent review[67] has discussed the photocycloaddition of alkenes and dienes to styrenes and stilbenes. The selectivity of the reactions increases with solvent polarity and it has been proposed that exciplexes are involved. Investigations into the interactions of 9-cyanophenanthrene with a series of styrenes have been carried out,[68,69] and fluorescent exciplexes are produced before the formation of (2 + 2) cycloaddition products and triplet state species.

(b) Reduction Reactions

Davidson[70] has extensively investigated the involvement of exciplexes in several photo-induced reduction reactions. Much of this work has involved the reduction of carbonyl compounds, for example, in the photo reduction of aromatic carbonyl compounds by hydrazines.[71]

1.7 Intramolecular Excited Complexes

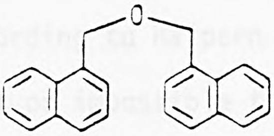
1.7.1 Introduction

It has already been stated (Section 1.b), among the requirements for excited complex formation in fluid solution, is the need for the two reaction partners to collide and interact with each other, within the lifetime of the excited state species. Because the diffusion controlled rate constant for processes in the solvent being used determines the maximum rate of formation, the linking together of the two interacting groups by a flexible polymethylene chain[33,34] enables the diffusional restriction to be eased. This produces high local concentrations of the two species and thus partially offsets unfavourable free energies for excited complex formation, by creating conditions that allow multiple collisions of the partners. The formation and stability factors affecting these intramolecular excited complexes is dealt with in the following sections.

1.7.2 Intramolecular Excimer Formation

1.7.2.1 Conformational Requirements

Forster[72,73] and Birks[74] have recently reviewed intramolecular excimers. Excimer emissions are broad structureless bands to the red of the monomeric emission and have been detected in neat liquids, solutions and solids. Requirements for intramolecular excimer formation are apparently stricter than those for the intramolecular hetero excimers (exciplexes) and most of the solubility of the excimers is derived from excited resonance rather than Coulombic interactions. Because aromatic molecules having parallel molecular planes in the crystal lattice form excimers,[75] it is probable that for intramolecular excimer formation, a sandwich arrangement of the two aromatic rings is required. Hirayama,[76] who found that three methylene groups interposed between the phenyl rings gave the most efficient excimer formation - elucidated certain rules governing intramolecular excimer formation in the α-ω-diphenyl alkanes. The molecule can adopt a strain-free conformation - the aromatic rings overlying each other - because of the flexible propyl linking chain, with no eclipsing interactions occurring in the chain. The binding energy of the excimers is also of significance. The symmetrical α,ω-dinaphthylalkanes exhibit excimer formation only for the propyl system,[77] but the α,ω-dipyrenylalkanes[78] and pyrenyl systems linked by α,ω-dicarboxyalkanes[79] show excimer formation for a variety of chain lengths, because of the increased binding energy of the pyrenyl groups. The use of an oxygen 'spacer' atom - between the CH_2 groups, as for example in the naphthyl ethers (2) and (3) which both exhibit excimer formation[80] - overcomes unfavourable eclipsing interactions between protons in the polymethylene chain. Also the photolysis of (2) yields two products (4) and (5).[81] Assuming that there is a close relationship of the final products to an intermediate excimer, this is indicative of (2) being able to form two excimeric species, according to the overlying of the naphthyl rings.



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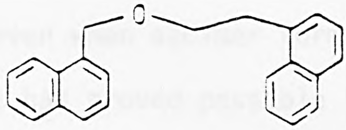

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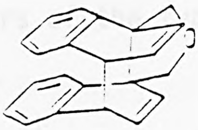

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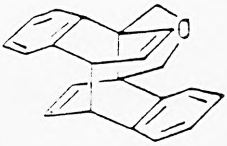
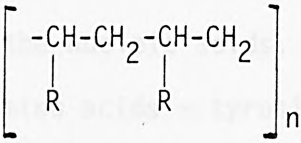


[5]

A good oxygen containing chain for linking aryl groups together[80] is the polyethylenoxy grouping. Fluorescence quenching and excimer formation studies of several anthracene derivatives linked together at the 9-position by such a chain[82] has enabled the dynamics of the flexibility of the chains to be ascertained. Photodimerisation[83,84] processes have been aided through the use of polyethylenoxy chains, in comparison to other anthracene derivatives with a polymethylene chain. It has been found that the fluorescence quantum yields of a series of α,ω-di-(1-naphthyl)alkanes and related compounds in cyclohexane solution[80] show variation, thus suggesting that excimer formation need not occur in the quenching of the monomeric fluorescence. The inability of the rings to adopt the stable sandwich configuration, the non-relaxed exciplex formed, decaying by a radiationless pathway, explain why an excimer is not formed. According to Halpern et al.,[85] even when excimer formation is difficult or impossible to detect, it has proved possible to quench monomeric emission by the use of α,ω-bis-dimethyldiaminoalkanes.

1.7.2.2 Excimer Formation in Polymers

Providing R is an aromatic group such as phenyl, naphthyl, or carbazolyl, intramolecular excimer formation is possible with vinyl polymers of the type shown



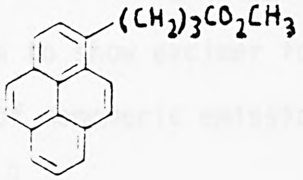
$$\left[\begin{array}{l} -\underset{\displaystyle R}{\underset{|}{CH}}-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-CH_2 \end{array}\right]_n$$

polystyrene being a most important example.[76,86,87] A long wavelength component, due to the excimer, is observed on comparing fluorescence spectra of polystyrene in a range of solvents. As the polymer concentrations at levels $< 0.1\%$ are not dependent on the ratio of excimer to monomer, intramolecular interaction - probably between neighbouring side groups[88] - is the cause of excimeric emission. That the breakdown of the excimer is not responsible merely for the monomeric emission is shown by the differential quenching of the monomer and excimer emissions by oxygen[88,89] and CCl_4.[90] An increase in the excimeric fluorescence intensity, due to intermolecular excimer formation,[91] has been observed at high polystyrene concentrations (< 0.1%).

Bispolymers like DNA, having a double helical structure containing the hydrogen bonded base pairs adenine (A)-thymine T and guanine (G)-cytosine (C), can also form intramolecular excimers. Comparison of the spectral properties of mono-, di- and poly-nucleotides has proven that most dinucleotides exhibit exclusive excimeric fluorescence. Because the fluorescence properties of a copolymer compared of equal amounts of AMP (adenine monophosphate) and TMP (thymine monophosphate) closely resembles that of DNA, it is apparent that (AT) excimers[92] are responsible for DNA fluorescence.

The probability of excimer formation in proteins is much smaller than in the nucleic acids. This is because only three of the common amino acids - tyrosine, tryptophan and phenylalanine - are likely to form excimers. Even though the aromatic amino acid concentration in peptide chains is relatively low, there is still the possibility of local high concentrations being produced from the tertiary folded structure of the proteins, thus favouring excimer formation. In helix supporting solvents like tetrahydrofuran, poly-l-phenylalanine has exhibited intramolecular excimer formation. However, monomeric tyrosine and tryptophan fluorescence is shown by most proteins.

The fluorescence properties of the pyrene ester (6), when incorporated into three polymeric systems[93] relative to the properties in fluid, has been investigated. Results indicate that in various polymeric media there is a blue shift of about 40 nm of the excimer emission relative to that in fluid media.



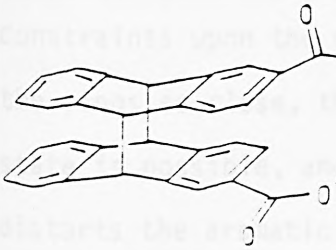
[6]

It is believed that the wavelength shift is caused by the polymeric media preventing the pyrene molecules to adopt the ideal sandwich configuration (possible in fluid media) which was responsible for the characteristic excimer emission at 480 nm. The pyrene molecules, however, adopt a less stable conformation, in which excimeric interaction is still possible.

1.7.2.3 Generation of Excimers in Matrices

It is well established that irradiation of dianthracene or photodimers of other anthracene derivatives at 254 nm, results in the dimers being reverted back to the original molecular pairs. Dissolution of the photodimer and freezing the solution before irradiation, upon photolysis, produces a pair of adjacent parallel anthracene molecules held within a rigid matrix.[94] These molecular pairs (sandwich dimers), have been prepared for several anthracene derivatives.[95,96] One has a pair of molecules situated close enough to each other that excimer fluorescence is shown upon excitation.

Photolytic dissociation[97] of dianthracene is dependent on temperature as well as solvent viscosity, while thermal activation of a benzylic like biradical intermediate (Figure 1.(13)) is involved in excimer formation. Photolytic cleavage of compounds (7) and (8) upon irradiation in ethanol glass yields molecular pairs which are sufficiently close to show excimer formation when suitably excited[98] to the exclusion of monomeric emission.



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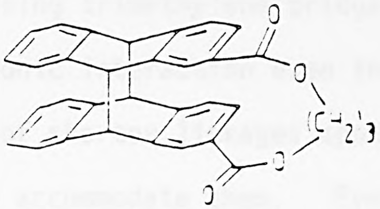

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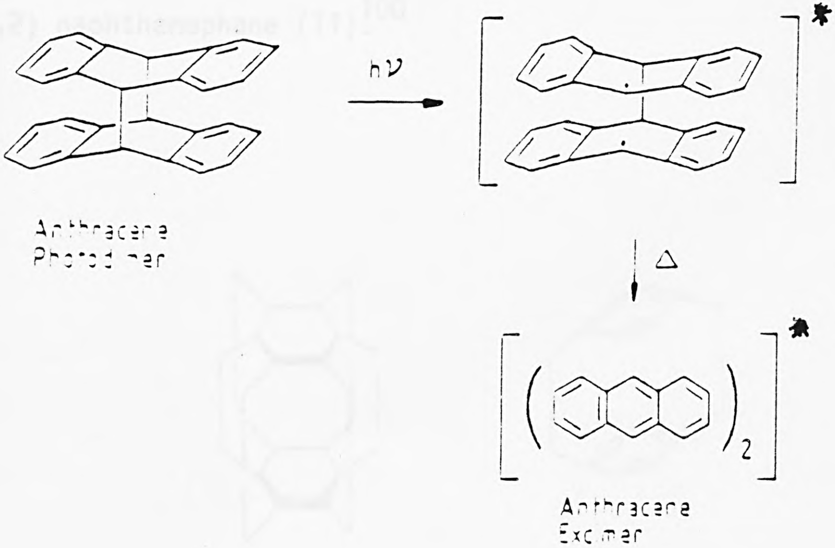
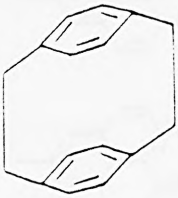


FIGURE 1.(13). Photolytic Breakdown of the Anthracene Photodimer in a Rigid Matrix to Yield the Anthracene Excimer.

1.7.2.4 Intramolecular Excimer Formation in Cyclophanes

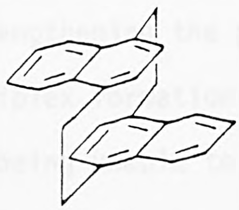
Cyclophanes can also be used to investigate the conformational effects upon excimer formation. Because of the rigid structure of these compounds, the precise investigation of the effect of the relative orientation of the two groups upon excimer fluorescence is possible. A major disadvantage with the cyclophanes, is that the polymethylene bridges between the aromatic rings impose constraints upon the system. Using trimethylene bridges forces the rings so close, that electronic interaction even in the ground state is possible, and the use of shorter linkages apparently distorts the aromatic system to accommodate them. Even with these steric problems, a successful synthesis[99] of the highly strained cyclophane (9) has been carried out. Photochemical and spectroscopic studies of several aromatic cyclophanes have been made, including the benzenoid (2,2) cyclophanes such as (10) and the (2,2) naphthenophane (11).[100]

[9]



[10]

Intramolecular excimer formation was shown by both systems, but for (11) also underwent wavelength and temperature dependent reactions. Investigations on the pyrenophanes (12) and (13)[101] reveal that in (13), a transannular interaction occurs leading to a new absorption band and a structureless excimeric emission at 560 nm, while (12) exhibits characteristic pyrene fluorescence in non-polar solvents and a red-shifted excimer band at 475 nm in more polar media.



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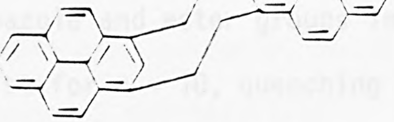

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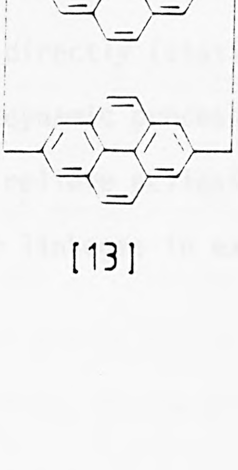


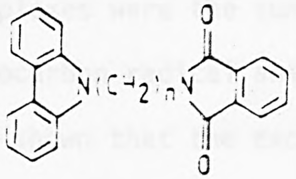
[13]

A CT state is believed to be involved in the isomerisation reaction necessary for (12) to attain the required sandwich configuration. This work shows that although highly ordered structures are possessed by intramolecular excimers, a compound does not necessarily give rise to a unique excimeric species.

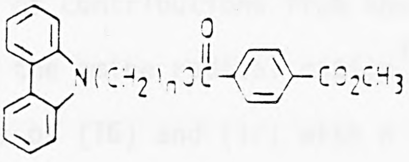
1.7.3 Intramolecular Exciplexes

1.7.3.1 Conformational Requirements for Exciplex Formation

Using naphthylalkyl amines, Chandross and Thomas[102] and Brimage and Davidson[103] have found intramolecular exciplex formation to be very efficient, when the two interacting groups are separated by a methylene group. Lengthening the polymethylene chain reduced the quantum yield of exciplex formation, presumably due to the exciplex binding energy being unable to overcome the energy barriers associated with orientation of the linking chain. However, suitable increase of the binding energy of the exciplex, enables exciplex emission to be observed utilising long chain linkages as in (14)[104] and (15)[105] with h = 1-5 and n = 10. The chain length affects the mode of fluroescence quenching in (15), thus for n = 1 and 2, the exciplex was produced via ground state conformations in which the carbazole and ester groups interacted directly (static-quenching), whilst for n = 10, quenching was by a dynamic process. Oxygen, and other heteroatoms or groups which relieve eclipsing interactions in the chain, permit the use of longer linkages in exciplex formation.[106]

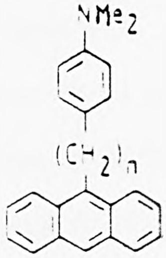


[14]

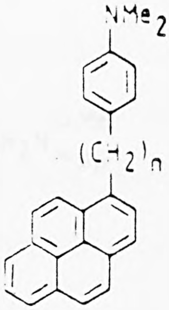


[15]

Okada et al.[107] and Ide et al.[108] using (16) and (17) initially investigated intramolecular exciplex formation between aromatic hydrocarbons and aromatic amines.



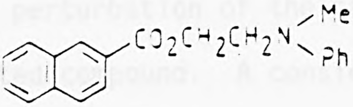
[16]



[17]

In non-polar solvents, and for n = 1, exciplex emission was absent, because of the inability of the amino group to interact directly with the π system of the anthracenyl or pyrenyl unit. However in more polar solvents, and for n = 1,2 and 3, exciplex formation was observed, indicating the invalidity of the 'n = 3 rule' proposed for intramolecular excimers. In addition, nanosecond laser flash photolysis determinations showed that the absorption spectra of the exciplexes were the summation of contributions from the aromatic hydrocarbon radical anion and the amine radical cation.[109] It was also shown that the exciplexes of (16) and (17) with n = 2 and 3 do not necessarily have to adopt the sandwich[110] conformation and that the initially formed complex has a loose structure which undergoes reorientation[111] to give the sandwich structure.

The naphthenoate ester (18) proves an interesting example of exciplex formatin, because the extent of exciplex formation is dependent on whether the amino or naphthoate grouping is excited.[112]



[18]

Time resolved fluorescence investigation showed that after excitation of the amine, fluorescence was observed from both the amine and the exciplex for a few nanoseconds, but that this had changed to naphthalene fluorescence within 10 ns.[113] It was proposed that static quenching produced the exciplex and served as an intermediate in energy transfer from the amine to the naphthoate unit.

Detailed investigations into the fluorescence behaviour of a range of ω-N-,N-diethylaminoalkanes have been carried out by Davidson and

Tretheway.[114] It was found that chain length influences the quantum yield of exciplex formation, but the quenching efficiency of the naphthalene fluorescence remained high throughout. It was suggested that different conformational requirements were necessary for the two processes, with quenching occurring over larger distances.

1.7.3.2 Steric Effects

Intramolecular exciplex formation can be considerably hindered through the presence of bulky groups. Thus, addition of an N-methyl substituent to 3-(n-p-tolyl)amino-1-(9-anthracene)propane, reduced the dipole moment of the exciplex from 15 to 12.2, Debye, indicating a reduction in the charge-transfer character of the excited species.[115] There is the possibility that the extra methyl group results in a perturbation of the sandwich conformation adopted by the non-methylated compound. A consideration of the changes in the entropy of formation of intramolecular excimers[116] is also useful in studying steric influences.

1.7.3.3 Solvent Effects Upon Exciplex Formation

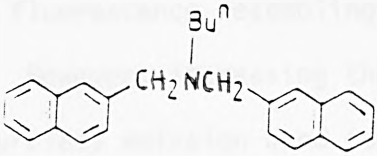
The effects of solvent polarity on exciplex fluorescence have been investigated by Weller et al., who considered intermolecular exciplex formation between aromatic hydrocarbons and tertiary amines. It was proposed that the exciplex dissociates into radical ions in polar solvents, accounting for the observed decrease in quantum yield and lifetime of the exciplex upon increasing the solvent polarity. Exciplex fluorescence in highly polar solvents - in some cases the fluorescence lifetime of the exciplex actually showing an increase - has been observed, through work on a range of aromatic hydrocarbon amine intramolecular exciplexes.[103,106] Apparently dissociation of the solvent-relaxed exciplex into radical ion pairs is not as important here and electron transfer from the non-equilibrium exciplex can occur. The ability of intramolecular exciplexes to fluoresce in such a wide range of solvents and the variation in λ_{max} values of the emission has been used in studying several solvation phenomena. The addition of a polar solvent,[117,118] even in small amounts, can dramatically affect the emission of the naphthylalkyl amines for example, which show quite strong fluorescence in non-polar solvents.

Time resolved fluorescence determinations have revealed that the non-polar environment of the initially produced exciplex is gradually modified during the lifetime of the excited species due to the diffusion of the small polar molecules to the exciplex and subsequent solvation. This modification of the solvation shell results in the wavelength maxima to be red-shifted and changes the shape of the fluorescence band. The dangers of employing mixed solvent systems when investigating exciplex phenomena or when determining reaction mechanisms are thus exemplified. The dipole moments of a variety of excited complexes have been calculated by utilising the fact that exciplex emission is dependent on the solvent. Intramolecular exciplexes which essentially have pure charge transfer character, typically have dipole moments of 12-15 Debye.

However, in comparison, emissions from most inter- and intra-molecular excimers has been shown to be almost completely independent of solvent polarity, suggesting that they derive little if any stabilisation from charge transfer interactions in the excited state.[119]

1.7.4 Competition Between Intramolecular Excimer and Exciplex Formation

An interesting example of a compound showing both intramolecular excimer and exciplex formation[120] is N-(n-butyl)-N,N-di-(2-naphthylmethyl)amine (19).



[19]

In cyclohexane solution, a broad emission was shown by compound (19), due to a mixture of excimer and exciplex fluorescence. However, in degassed solution, the emission closely resembled that of 1,3-di-(2-naphthyl)propane and was therefore attributed mainly to the excimer, in aerated solution the emission underwent a blue-shift of around 20 nm. Under these conditions the emission was mostly ascribed to the exciplex, because the excimeric species will have a longer lifetime and therefore quenched by oxygen to a greater degree. The single broad emission observed in benzene solution was interpreted as being due to a mixture of excimer and benzene solvated exciplex emission. In the polar solvent methanol, emission apparently was due only to the exciplex. Further confirmation that the emissive species in methanol being the exciplex was provided through the addition of small concentrations of ethanoic acid, which quaternised the nitrogen and led to the reappearance of a fluorescent excimer.

1.7.5 Twisted Excited Charge Transfer Complexes

The bonding of two groups to one another by a sigma (σ) bond (as in the case of 9,9'-bianthryl) could also result in intramolecular exciplex formation. The compound is prevented from adopting a structure in which the two rings are coplanar because of bad steric interactions, and a fluorescence resembling anthracene is seen in non-polar solvents. However, increasing the solvent polarity causes a new structureless emission band to be observed.[121] Laser flash photolysis determinations have attributed this as being due to the presence of the anthracene radical anion and cation.[122] Recent picosecond laser flash photolysis experiments[123] reveal a rise time of ∿20 ps of the exciplex fluorescence in acetonitrile solution, possibly reflecting a need for the compound to undergo about the 9,9' bond prior its charge transfer (bringing the two systems nearer to coplanarity). Very early work on twisted CT complexes was carried out on 4-dimethylaminobenzonitrile, a compound in which the amino group is forced to tilt slightly out of the plane of the benzene ring, as shown in Fig. 1.(14). Increasing the polarity of the solvent, results in the appearance of a new structureless emission, probably due to the formation of a twisted intramolecular charge transfer state in the more polar solvents.

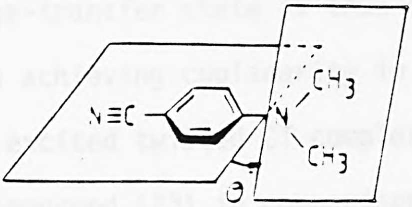
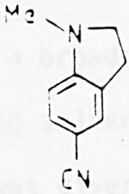
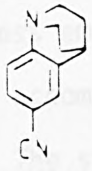


FIGURE 1.(14). Diagrammatic Representation of the Twisted Structure in 4-Dimethylaminobenzonitrile.

Angular distortion effects can also be assessed through comparison of the spectroscopic properties of compounds in which the amino group is held either in the same plane or is forced out of plane of the benzene ring and cannot rotate as in compounds (20) and (21) respectively.[124,125]



[20]



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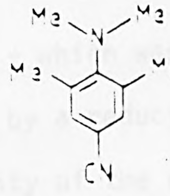
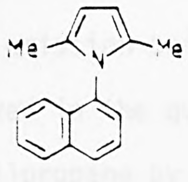
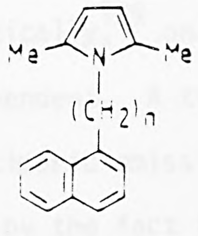


[22]

The conformation in which the benzene ring and the amine are coplanar is prevented in compound (22) by steric interactions between the other methyl groups and the dimethylamino group. Medium polarity solvents result in a red-shifted structureless emission of (21) and (22), whereas (20) failed to fluoresce at all. The production of an excited charge-transfer state is thus dependent upon the benzene and amino groups achieving coplanarity in the excited state. Investigations on excited twisted CT complex formation have been carried out on compound (23) in comparison with compound (24, n = =, 2).[126] (23) is prevented from achieving a coplanar structure because of strong steric hindrance between the methyl groups of the pyrrole ring and the H_1 and H_8 atoms on the naphthalene ring.



[23]



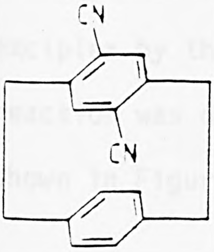
[24]

However, a broad structureless emission - which was red-shifted with increasing solvent polarity accompanied by a reduction in quantum yield - was given by (23). The similarity of the results to those of (24, n = 1, 2) showed excited charge transfer complexes whilst adopting very different conformations in the excited state.

1.8 Multi-Chromophore Excited Complex Formation

Numerous examples of excited complexes involving the interaction of more than two chromophores are recorded. Investigations on the quenching of aromatic hydrocarbon fluorescence by tertiary amines[127] have revealed that an optimal concentration of amine was reached for exciplex formation. Exceeding this level caused a diminution of the exciplex fluorescence intensity and the appearance of a red-shifted band, attributed to the formation of an intermolecular excited ternary complex (exterplex) between two molecules of the amine and one of the hydrocarbon. The interaction of 1,4-dicyanobenzene (DCB) with aromatic hydrocarbons has been well investigated. Beens and Weller[128] proposed that the hydrocarbon caused a quenching of the initially formed 1:1 exciplex between naphthalene and DCB resulting in an exterplex emitting at longer wavelength. It was assigned a DDA structure, proved theoretically,[129] on the basis of the exterplex emission being solvent dependent. A triple complex[130] is also involved in the quenching of excimeric emission from 1,3-di-(2-naphthyl)propane by DCB, favoured by the fact that the two naphthalene units are held together by a polymethylene chain. The interaction of DCB with a series of dinaphthyl derivatives in degassed chloroform solution were investigated by Davidson and Whelan.[131] Exterplex formation occurred in the di-(naphthylmethyl) ethers, but was inefficient for 1,4-di-(2-naphthyl)butane. It was concluded that fluorescent exterplex formation was only efficient when the dinaphthyl compound could itself form an intramolecular fluorescent excimer.

The anthracene concentration has an influence on the efficiency with which N,N-dimethylaniline quenches anthracene photodimerisation. It has been stated[132] that with high anthracene concentrations, interaction of the hydrocarbon with the initially formed anthracene -N,N-dimethylaniline exciplex occurs, resulting in a triple complex, which subsequently collapses to yield the photodimer. Exterplex formation[127] resulted from using high concentrations of amine in the quenching of aromatic hydrocarbon fluorescence. This was investigated further by considering the quenching of naphthalene fluorescence using the α,ω-diaminoalkanes. This showed that for those diamines efficient at fluorescent excimer formation, exterplex emission accompanied the quenching of the hydrocarbon fluorescence. In addition, low fluorescence quantum yields for the exterplexes were found, due to the increased possibility of non-radiative decay from these systems. The involvement of ternary complexes[133] has also been attributed to the efficient quenching of fluorescence from Rose Bengal by the α,ω-diaminoalkanes. The cyclophanes represent another category of compounds that are very useful in investigating bi- and tri- chromophore interactions. Mataga et al.[134] have recently investigated the fluorescence properties of the cyano-substituted aryl cyclophanes (25), (26) and (27).



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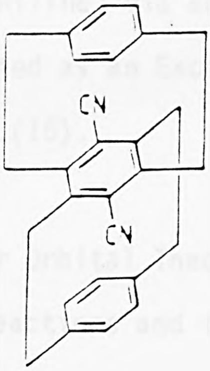
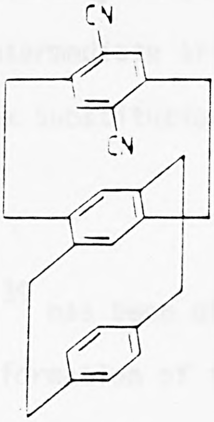
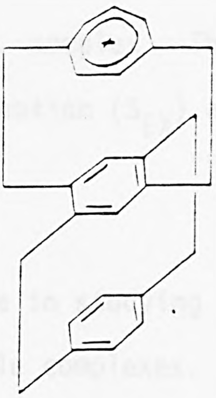


[26]



[27]



[28]

(25) corresponded to a bichromophoric DA complex, while (26) and (27) formed the so-called 'triple-decker' complexes of the DAD and DDA arrangement respectively. Also, the emission was almost independent of solvent polarity in (26), further confirming of the zero dipole moment in symmetrical DAD type exterplexes. Some cyclophanes synthesised exhibited charge transfer absorption bands as in compound (28).[135] Several cycloaddition reactions, including those of phenanthrene with dimethylfumerate[136] and 9-cyanophenanthrene with dimethylacetylenedicarboxylate[137] have been quenched by the addition of either electron donor or electron acceptor species. To explain these findings, it has been proposed that a triple complex is formed between the added electron donor or acceptor and the exciplex resulting in cycloadduct formation.

Investigations by Caldwell, Creed et al.[148] on the reaction between 3,10-dicyanophenanthrene and trans-anethole revealed that exciplex formation between these compounds was quenched by the addition of N,N-diethylaniline, resulting in the formation of a new exciplex between the phenanthrene and the amine. It was suggested that the anethole was displaced from the initially formed anethole-phenanthrene exciplex by the aniline, via an intermediate triple complex. This reaction was denoted as an Exciplex Substitution Reaction (S_{EX}) as shown in Figure 1.(15).

Frontier Molecular Orbital Theory[139] has been of use in studying the role of S_{EX} reactions and the formation of triple complexes.

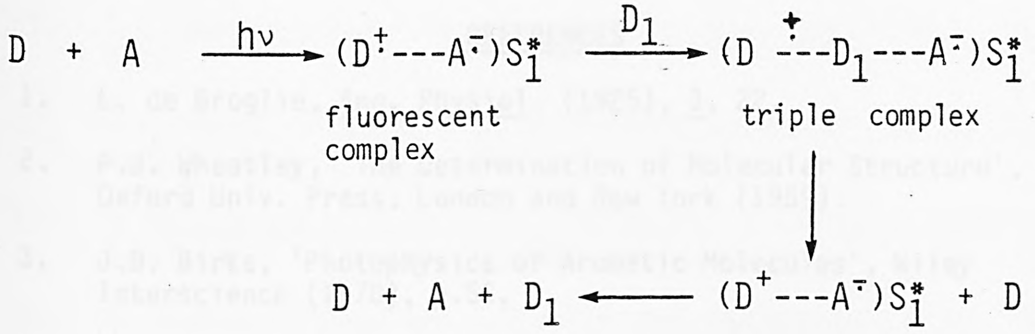


Figure 1.(15) Representation of the Exciplex Substitution Reaction (S_{EX}) involving an intermediate exterplex.

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THE SYNTHESIS OF 1,4-DISUBSTITUTED BICYCLO[2,2,2]OCTANE COMPOUNDS

2.1 Introduction

Functionally substituted bridgehead structures have been of considerable interest in the study of organic reaction mechanisms. Among the numerous methods described for the synthesis of the bicyclo[2,2,2]octane ring system, most are not suitable for the preparation of bridgehead substituted derivatives. In particular, relatively few 1,4-disubstituted bicyclo[2,2,2]octanes have been described and these were prepared by somewhat tedious, multistep syntheses.[1,2]

For the preparation of bridgehead substituted bicyclo[2,2,2]octanes, three approaches have been generally used:

(1) Free-radical attack at the bridgehead hydrogen atom of a bicyclic hydrocarbon.

(2) Wagner-Meerwein rearrangement of an appropriately substituted bicyclic structure.[4]

(3) Introduction of a bridge into a substituted cyclohexane derivative.[1,2,5] This is by far the most important method and will be discussed in detail.

2.2 Introduction of a bridge into a substituted cyclohexane Derivative

Using diethyl 2,5-dioxobicyclo[2,2,2]-1,4-dicarboxylate (1), Roberts et al. have prepared several 4-substituted bicyclo[2,2,2]octane-1-carboxylic acids as shown in Diagram 1. A modification of the method of Guha[1] was employed to prepare I. This involved the condensation of diethyl succinate with sodium ethoxide and reacting the product directly with ethylene dibromide, thus avoiding isolating the intermediate diethyl succinoylsuccinate. Raney nickel desulphurisation[6] of the bis-(trimethylene)-mercaptal (2) - obtained by the condensation of 1 with propane-1,3-dithiol resulted in the reduction of 1 to diethyl bicyclo[2,2,2]octane-1,4-dicarboxylate (3) with a yield of between 50-70%. Poor yields of bicyclo[2,2,2] octane-1,4-dicarboxylic (less than 15%) were the result of attempting to reduce 1 by the Wolff-Kishner and Clemmensen procedures. Hydrolysis of the diester 3 with one equivalent of alkali gave ethyl hydrogen bicyclo[2,2,2]octane-1,4-dicarboxylate, which was the key intermediate for the synthesis of the different unsymmetrically substituted acids and esters. The successive treatment of 4 with triethylamine, ethyl chlorocarbonate (-10^{0}) and anhydrous ammonia produced ethyl 4-carboxamide-bicyclo[2,2,2]octane-1-carboxylate (5). Using this procedure[7] an 88% yield of 5 resulted, as compared to 50-55% yields obtained in the reaction of the acid chloride of 4 with aqueous or anhydrous ammonia. The urethan 6 was obtained in low yield on reacting 5 with bromine and sodium ethoxide in ethanol. Acid hydrolysis of 6 gave 4-aminobicyclo[2,2,2]octane-1-carboxylic acid 7. Dehydration of 5 with phosphorus oxychloride in ethylene dichloride gave ethyl 4-cyanobicyclo[2,2,2]octane-1-carboxylate 8. Alkaline hydrolysis of 8 gave the corresponding cyano acid 9.

4-Bromobicyclo[2,2,2]octane-1-carboxylate 10 was obtained by reacting the silver salt of the monoester (4) with bromine in dichlorodifluoromethane (Freon 12).[8] 48% hydrobromic acid was used to hydrolyse

10 to the corresponding bromo acid 11. Apparently, alkaline hydrolysis of 10 yielded 11 mixed with more or less of 4-hydroxybicyclo [2,2,2]octane-1-carboxylic acid (14). However, refluxing 10 with 1% aqueous alkali for 24 hours gave an 81% yield of 14. The attempted hydrolysis of 10 to the corresponding hydroxy ester (15) with silver oxide or silver nitrate in acetone-water mixtures proved unsuccessful. Possibly, in the basic hydrolysis of 10, the electrostatic effect of the anionic carboxylate group - produced by hydrolysis of the ester group - facilitates expulsion of the bromide ion to a significant extent. A mixture of products containing only about 20% of 14 was obtained on strong alkaline hydrolysis of 10. Reaction of the silver salt of 14 with ethyl iodide in ether yielded the hydroxy ester 15.

Hydrogenolysis of the bromo ester 10 in absolute ethanol containing sodium ethoxide over a Raney nickel catalyst produced ethyl bicyclo [2,2,2]octane-1-carboxylate (12) and the corresponding acid 13.

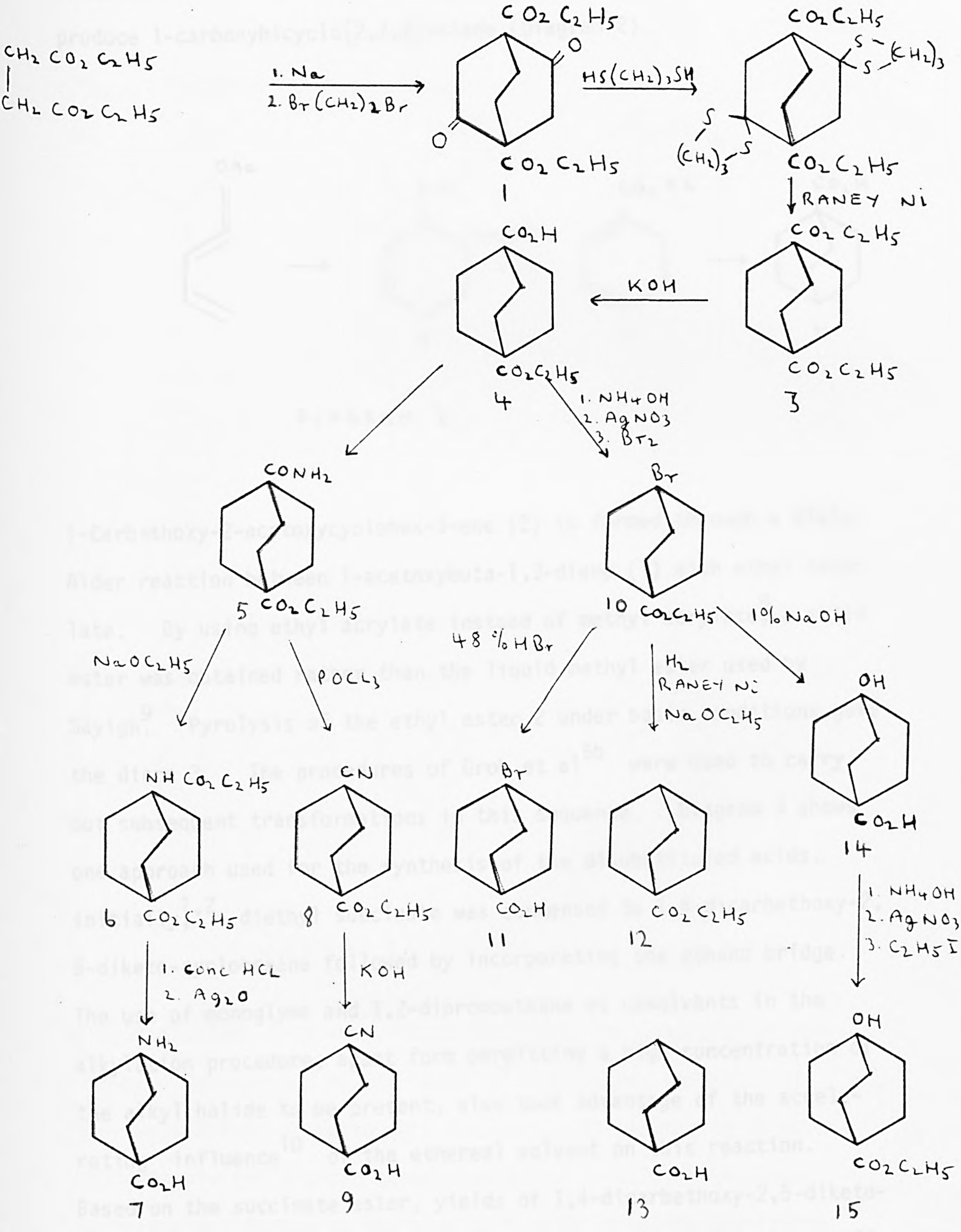

CH2 CO2 C2H5
CH2 CO2 C2H5
1. Na
2. Br(CH2)2Br
CO2 C2H5
O
O
CO2 C2H5
1
HS(CH2)3SH
CO2C2H5
S
(CH2)3
S
S
(CH2)3
S
CO2C2H5
RANEY Ni
CO2 C2H5
CO2 C2H5
3
KOH
CO2H
CO2C2H5
4
1. NH4OH
2. AgNO3
3. Br2
CONH2
5 CO2C2H5
Br
10 CO2C2H5
NaOC2H5
POCl3
48 % HBr
H2
RANEY Ni
NaOC2H5
10% NaOH
NH CO2 C2 H5
6 CO2C2H5
CN
8 CO2C2H5
Br
CO2H
11
CO2 C2H5
12
OH
CO2H
14
1. conc HCl
2. Ag2O
KOH
1. NH4OH
2. AgNO3
3. C2H5I
NH2
CO2H
7
CN
CO2H
9
CO2H
13
OH
CO2C2H5
15

DIAGRAM 1

Holtz and Stock[5b,9] used a composite of two other known routes to produce 1-carboxybicyclo[2,2,2]octane (Diagram 2).

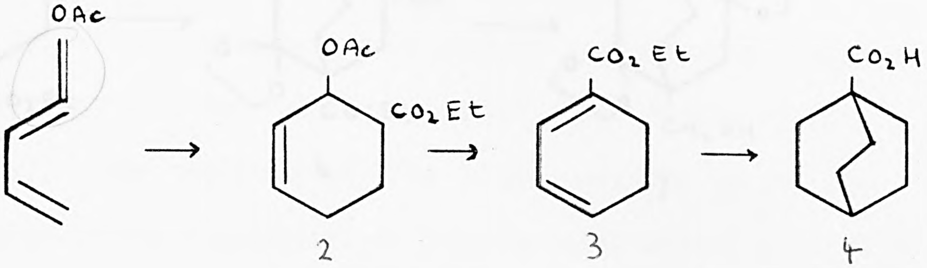


DIAGRAM 2

1-Carbethoxy-2-acetoxycyclohex-3-ene (2) is formed through a Diels-Alder reaction between 1-acetoxybuta-1,3-diene (1) with ethyl acrylate. By using ethyl acrylate instead of methyl acrylate[9], a solid ester was obtained rather than the liquid methyl ester used by Sayigh[9]. Pyrolysis of the ethyl ester 2 under basic conditions gave the diene 3. The procedures of Grob et al[5b] were used to carry out subsequent transformations in this sequence. Diagram 3 shows one approach used for the synthesis of the disubstituted acids. Initially[1,2] diethyl succinate was condensed to 1,4-dicarbethoxy-2,5-diketo-cyclohexane followed by incorporating the ethano bridge. The use of monoglyme and 1,2-dibromoethane as cosolvents in the alkylation procedure, apart form permitting a high concentration of the alkyl halide to be present, also took advantage of the accelerating influence[10] of the ethereal solvent on this reaction. Based on the succinate ester, yields of 1,4-dicarbethoxy-2,5-diketo-bicyclo[2,2,2]octane (5) were nearly 40% of the theoretical quantity.

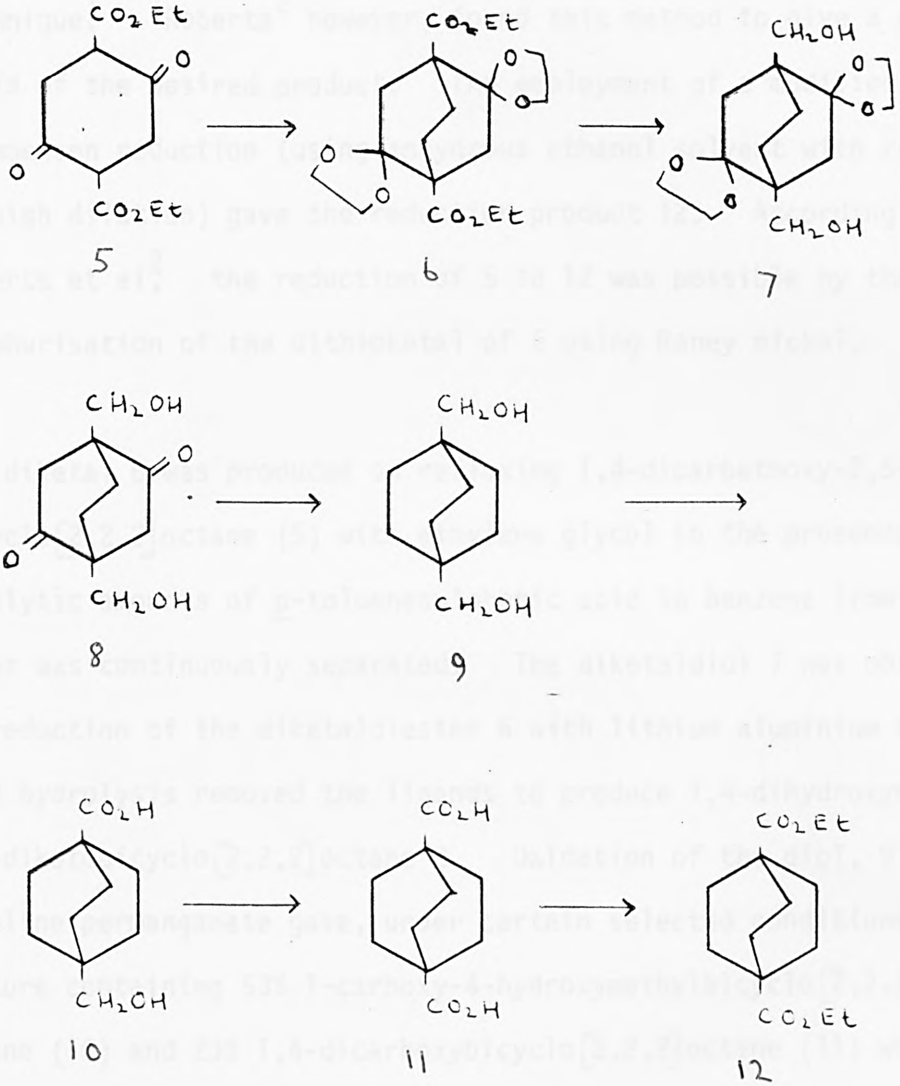


DIAGRAM 3

Serious problems were encountered involving the reduction of the ketone. Destruction of the bicyclic ring and/or formation of other undesirable products were the result of attempting to reduce the diketodiester 5 under basic conditions. 1,3,6,8-tetracarboxyhexane was formed on hydrolysing 6 under alkaline conditions.

Attempted reduction of 6 under Wolff-Kishner conditions gave pyrazolones.[1] Guha, reported success using the Clemmensen reduction technique.[1] Roberts[2] however, found this method to give a poor yield of the desired product. The employment of a modified Clemmensen reduction (using anhydrous ethanol solvent with reagents at high dilution) gave the reduction product 12. According to Roberts et al.[2] the reduction of 5 to 12 was possible by the desulphurisation of the dithioketal of 5 using Raney nickel.

The diketal 6 was produced on refluxing 1,4-dicarbethoxy-2,5-diketobicyclo[2,2,2]octane (5) with ethylene glycol in the presence of catalytic amounts of p-toluenesulphonic acid in benzene from which water was continuously separated. The diketaldiol 7 was obtained on reduction of the diketaldiester 6 with lithium aluminium hydride. Acid hydrolysis removed the ligands to produce 1,4-dihydroxymethyl-2,5-diketobicyclo[2,2,2]octane 8. Oxidation of the diol, 9 using alkaline permanganate gave, under certain selected conditions, a mixture containing 53% 1-carboxy-4-hydroxymethylbicyclo[2,2,2]octane (10) and 23% 1,4-dicarboxybicyclo[2,2,2]octane (11) which was easily separated.

Excess oxidising agent produced the diacid 11. Diagram 3 shows the conversions of the intermediates formed through the reactions shown in Diagram 2 to other substituted acids.

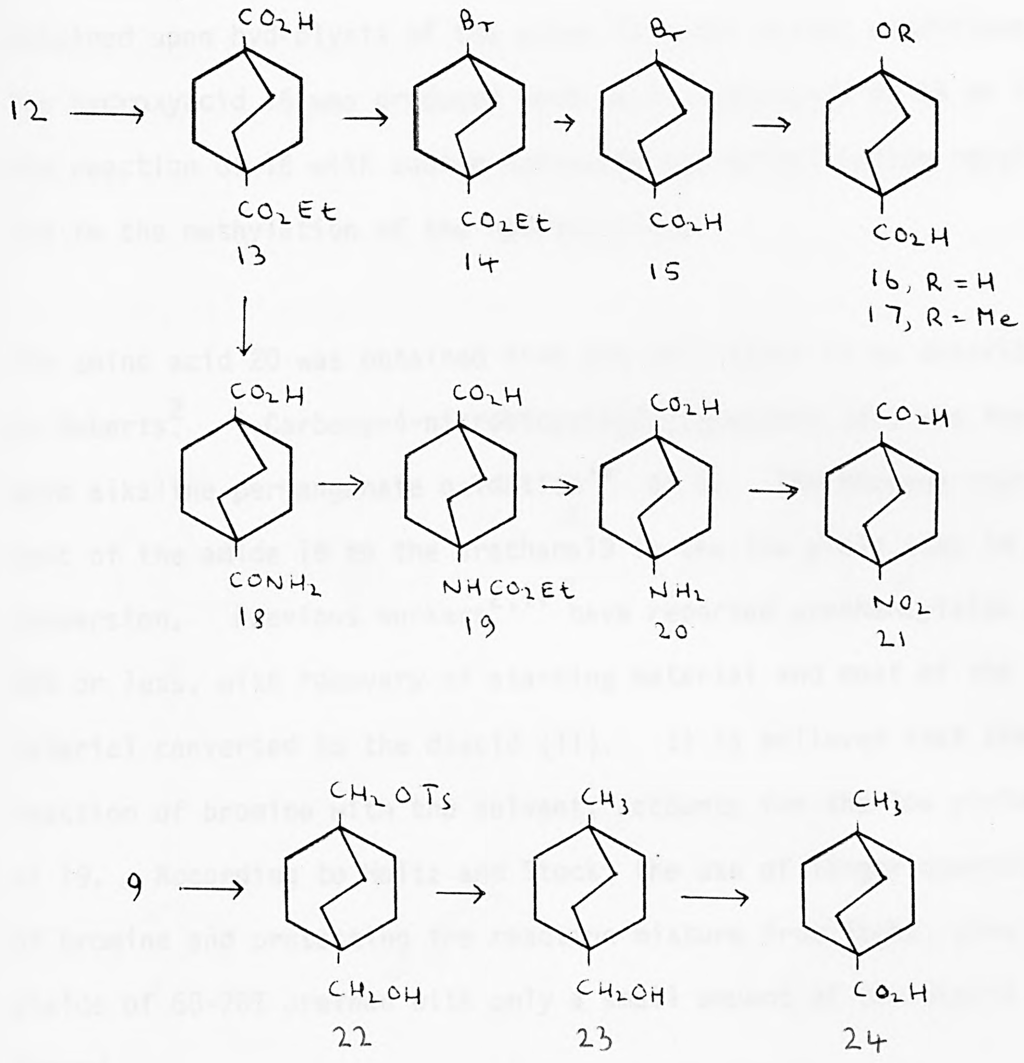


DIAGRAM 3

The procedure described by Roberts[2] was used to carry out the half-hydrolysis of diester 12. The Cristol modification of the Hunsdiecker reaction[12] was used to obtain the bromoester 14 from 13. The bridgehead radical produced during this reaction is non-selective,[13] and thus to avoid contamination of the product, bromotrichloromethane was used as solvent. The bromoacid 15 was obtained upon hydrolysis of the ester 14 under acidic conditions.[2] The hydroxyacid 16 was produced upon basic hydrolysis of 14 or 15. The reaction of 16 with sodium hydroxide and methyl iodide resulted in the methylation of the hydroxy group.

The amino acid 20 was obtained from the half-ester 13 as described by Roberts.[2] 1-Carboxy-4-nitrobicyclo[2,2,2]octane (21) was formed upon alkaline permanganate oxidation[14] of 9. The Hofmann rearrangement of the amide 18 to the urethane 19 is the low yield step in this conversion. Previous workers[2,11] have reported urethane yields of 30% or less, with recovery of starting material and most of the material converted to the diacid (11). It is believed that the reaction of bromine with the solvent, accounts for the low yield of 19. According to Holtz and Stock, the use of larger quantities of bromine and protecting the reaction mixture from light, gave yields of 60-70% urethan with only a small amount of the diacid formed.

Subjection of the diol 9 to tosylation, lithium aluminium hydride reduction of the tosylate, and subsequent alkaline permanganate oxidation of 1-hydroxymethyl-4-methylbicyclo[2,2,2]octane (23), yielded 1-carboxy-4-methylbicyclo[2,2,2]octane (24). In the hydride displacement reaction, the yield of 23 was not adversely affected due to neopentyl character of the tosylate 22.

The synthesis of a series of 1-hydroxy-3-keto-4-substituted bicyclo[2,2,2]octanes (25)[15] from the readily obtainable 3-substituted 3-acetylpimelonitriles[16] have been described by Colange and Viullemet. As shown in Diagram 4, these trisubstituted bicyclo[2,2,2]octanes were converted to 4-methyl- 24, 4-ethyl- 30, and 4-phenyl-1-carboxybicyclo[2,2,2]octane (31).

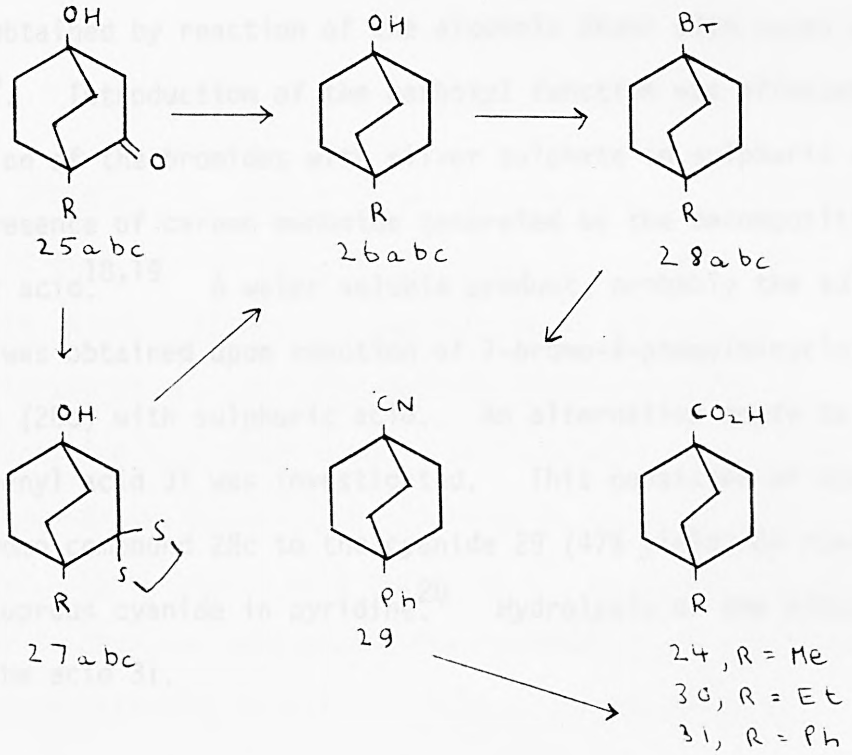
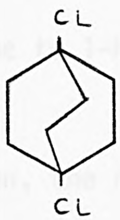


DIAGRAM 4*

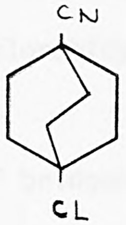
* FOR a, R = Me, b, R = Et, c, R = Ph

Clemmensen reduction of 25a and 25b afforded 4-methyl- (26a) and 4-ethylbicyclo[2,2,2]octanol-1 (26b). Subjection of the isolated products to vapour phase chromatography showed the presence of impurities, which could be removed by chromatography on alumina. A poor yield of 26c was obtained in the Clemmensen reduction. The Wolff-Kishner procedure as described by Georgian[17] et al, was used to reduce the readily obtainable thioketal 27c. Reduction of the thioketals 27ab gave the alcohols 26a and 26b. The bromides 28abc were obtained by reaction of the alcohols 26abc with Lucas reagent at 50°. Introduction of the carboxyl function was effected by reaction of the bromides with silver sulphate in sulphuric acid in the presence of carbon monoxide generated by the decomposition of formic acid.[18,19] A water soluble product, probably the sulphonic acid, was obtained upon reaction of 1-bromo-4-phenylbicyclo[2,2,2]octane (28c) with sulphuric acid. An alternative route to produce the phenyl acid 31 was investigated. This consisted of converting the bromo compound 28c to the cyanide 29 (47% yield) by reaction with cuprous cyanide in pyridine.[20] Hydrolysis of the nitrile 29 gave the acid 31.

Kavers method[21] of forming 1,4-dichlorobicyclo[2,2,2]octane (32) from perchlorocoumalin was exploited by Holtz and Stock to produce 1-carboxy-4-chlorobicyclo[2,2,2]octane (35). The Koch method[18,19] proved unsuccessful with the 1,4-dichloro derivative 32. Before silver chloride precipitation was observed, it was required to heat the sulphuric acid solution to 70°. Following hydrolysis, 1-chloro-4-hydroxybicyclo[2,2,2]octane was isolated in addition to the starting material rather than the acid 35.



32



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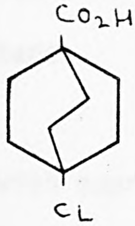


35

A poor yield of the cyanide 34 was obtained on refluxing the dichloride with cuprous cyanide in N-methylpyrrolidone for 3 days.^{22,23} The acid 35 was obtained upon hydrolysis of the cyanide. According to Holtz and Stock, synthetic methods involving bicyclo[2,2,2]octylcarbonium ions often occur with remarkable ease. Ionisation of 1-bromo-4-alkylbicyclo[2,2,2]octanes by reaction with silver ion is easy. In sulphuric acid media, at 0°, precipitation of silver bromide is observed upon mixing the reagents. The ion posesses sufficient stability to allow capture by carbon monoxide. Also, the conversion of 4-substituted bicyclo[2,2,2]octan-1-ols to the corresponding bromides is effected by hydrobromic acid-zinc bromide reagent. The unsubstituted bromides and alcohols react likewise.^{1,13} The velocity of the reactions is significantly affected due to the influence of one halogen substituent on the other in 1,4-dichlorobicyclo[2,2,2]octane. Before the precipitation of silver chloride is detectable, a mixture of the dihalide, silver sulphate, and sulphuric acid must be heated to 70°. The observed substituent effect is very large. However, these reactions can occur as shown by the conversion of 1,4-dichlorobicyclo[2,2,2]octane to 1-hydroxy-4-chlorobicyclo[2,2,2]octane.

In comparison, the reactions of bridgehead halides with cuprous cyanide - probably a reaction having both nucleophilic and electrophilic character - are much slower.

2.2.1 Addition of Ethylene and Other Dienophiles to Cyclohexa-1-3-Diene-1,4-Dicarboxylic Acid Derivatives

According to Kauer, Benson and Parshall,[24] a convenient route to 1,4-disubstituted bicyclo[2,2,2]octanes involves the introduction of a two-carbon bridge via the Diels-Alder reaction of a 1,4-disubstituted 1,3-cyclohexadiene (Diagram 5).

Dimethyl bicyclo[2,2,2]oct-2-ene-1,4-dicarboxylate is obtained when ethylene at 1000 atm. pressure reacts with dimethyl cyclohexa-1,3;diene-1,4-dicarboxylate at 165°.[25] The reaction is rapid and the yields are high. It was observed that the reaction was moderately pressure sensitive. For example, at 1000 atm, it could be carried out satisfactorily overnight at 165°. However, at 300 atm, the reaction was slow, and about one-third of the diene was recovered unchanged after 18 hr. The use of increased temperatures led to isomerisation and aromatisation of the diene, resulting in lower yields. A nearly quantitative conversion occurred in 18 hr at 3000 atm, pressure at 135°. Hydrogenation of the ester, followed by hydrolysis of the saturated ester yielded bicyclo[2,2,2]octane-1,4-dicarboxylic acid, which was identical with a sample prepared by Guha[1] and Roberts[2] procedures.

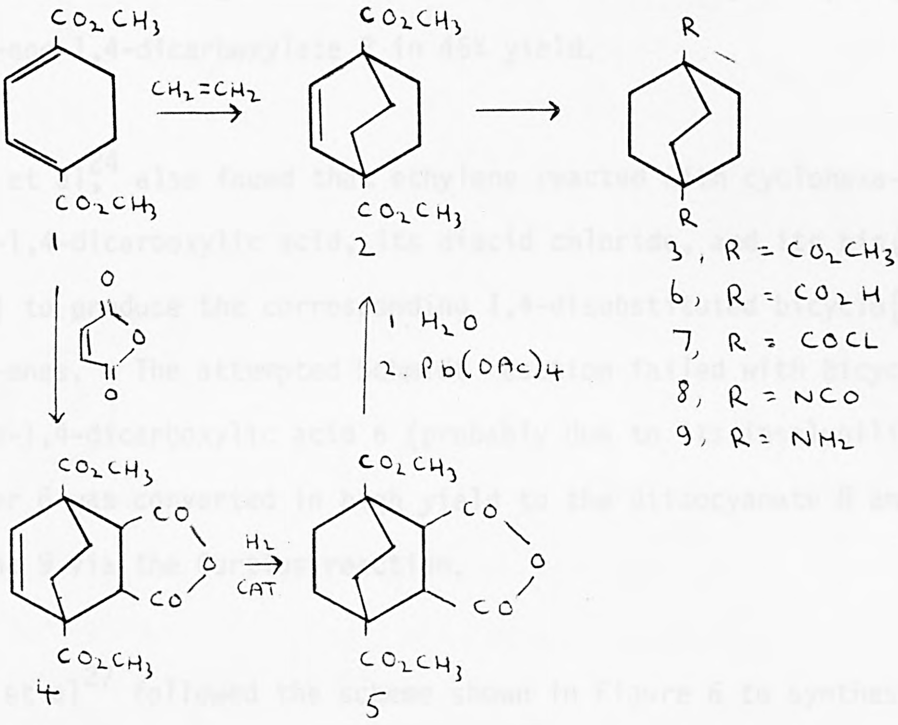


DIAGRAM 5

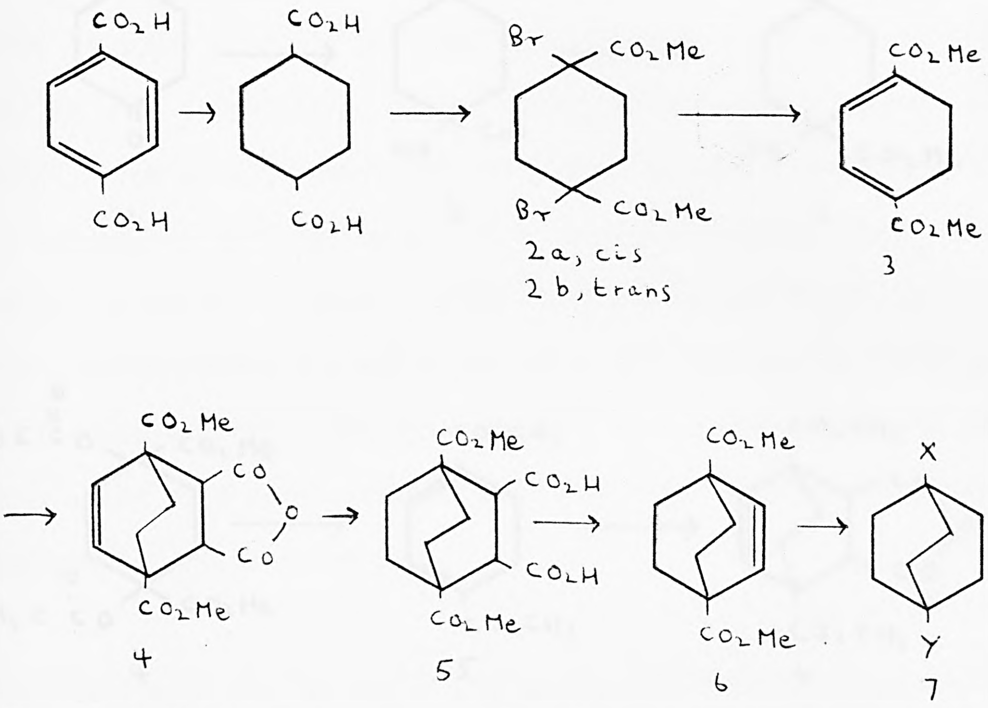
Providing high pressures of ethylene are available, this route is very good for the synthesis of bicyclo[2,2,2]octane-1,4-dicarboxylic acid and its derivatives.

The structure of 2 was checked by preparing[25b,26] an adduct of maleic anhydride with 1. Hydrogenation of this adduct 4, followed by opening of the anhydride ring of the hydrogenation product 5, gave the diester diacid. Oxidative bisdecarboxylation of the diester diacid using Grob's[5b] method yielded dimethyl bicyclo[2,2,2]oct-2-ene-1,4-dicarboxylate 2 in 45% yield.

Kauer et al,[24] also found that ethylene reacted with cyclohexa-1,3-diene-1,4-dicarboxylic acid, its diacid chloride, and its bis(benzylamide) to produce the corresponding 1,4-disubstituted bicyclo[2,2,2]oct-2-enes. The attempted Schmidt reaction failed with bicyclo[2,2,2]octane-1,4-dicarboxylic acid 6 (probably due to its insolubility). However 6 was converted in high yield to the diisocyanate 8 and the diamine 9 via the Curtius reaction.

Toyne et al[27] followed the scheme shown in Figure 6 to synthesise a 1,4-disubstituted bicyclo[2,2,2]octane. The mixed cis- and trans-cyclohexane-1,4-dicarboxylic acid chlorides were brominated followed by conversion into the mixed esters (2).

At this stage, the separation of the cis- and trans-isomer is easy, due to the cis-isomer being more soluble in methanol. The ester 2 was subjected to dehydrobromination under various conditions, but variable yields of the diene 3 were obtained according to Smith et al,[26] and Kauer et al.[24] From the mixed esters 2, a 80% yield of the diene 3 was obtained by employing pyridine as solvent and as a base for the dehydrobromination. In addition, hydrolysis of the ester was avoided and the need to reesterify the product.



7, X = Y = CO_2Me
8, X = CO_2Me, Y = CO_2H
9, X = CO_2Me, Y = Br
10, X = CO_2Me, Y = Ph

11, X = CO_2H, Y = OH
12, X = CO_2Me, Y = OH
13, X = CO_2Me, Y = H

DIAGRAM 6

Starting from hydroquinone, Ainbinder[28] has reported a convenient six stage synthesis of cyclohexa-1,3-diene-1,4-dicarboxylate (Diagram 7). Oxidation of 1,4-cyclohexanediol with chromium trioxide gives the starting material 1,4-cyclohexanedione.

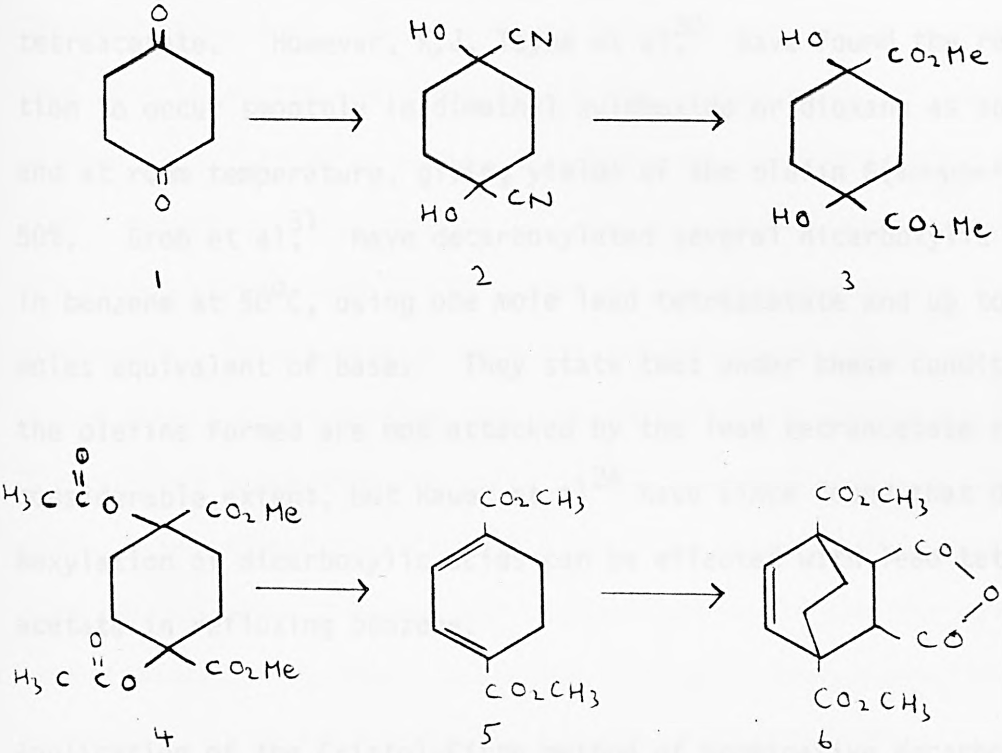


DIAGRAM 7

1,4-Cyclohexanedione reacts readily with acetone cyanohydrin to yield compound 2. Dimethyl 1,4-diacetoxy-1,4-dicarboxylate (4) is formed in two steps from compound 2. The required diene (5) is obtained in 75% yield through pyrolysis of the diacetate (4) at a temperature of 400°. Dimethyl terephthalate, formed in 18% yield, is the other major product obtained. Reaction of the crude pyrolysate with maleic anhydride gives 1,4-bis-(methoxycarbonyl) bicyclo[2,2,2]oct-5-ene-endo-2,3-dicarboxylic anhydride 6.

Humber et al[29] and Smith et al,[26] have unsuccessfully carried out oxidative bis-decarboxylation of compound 5 (Diagram 6) with lead tetraacetate. However, K.J. Toyne et al,[30] have found the reaction to occur smoothly in dimethyl sulphoxide or dioxane as solvent and at room temperature, giving yields of the olefin 6(Diagram 6) of up to 50%. Grob et al,[31] have decarboxylated several dicarboxylic acids in benzene at 50°C, using one mole lead tetraacetate and up to two moles equivalent of base. They state that under these conditions the olefins formed are not attacked by the lead tetraacetate to any considerable extent, but Kauer et al[24] have since found that decarboxylation of dicarboxylic acids can be effected with lead tetraacetate in refluxing benzene.

Application of the Cristol-Firth method of brominative decarboxylation[12,32] to 8 (Diagram 6) using 1,2-dibromoethane as solvent gave yields of 9 (Diagram 6), comparable with those obtained by the Hunsdiecker reaction,[33] but in the latter, unreacted acid was recovered. The Cristol-Firth reaction in petroleum ether (b.p.60-70°) as solvent proved unsuccessful.

Toyne et al,[27] by modifications of the procedures of Bunsen and Riener,[34,35] Colonge and Vuillemey,[5c] and Holtz and Stock,[36] prepared several 1,4-disubstituted bicyclo[2,2,2]octanes via the 4-substituted 1-hydroxy bicyclo[2,2,2]octan-3-ones 4 (Diagram 8). Holtz and Stock[36] reduced the ketones 4a-4c in 30-40% yields. Improved methods were used by Toyne et al[27] to reduce the carbonyl groups in 4a-4e. A 20% yield of 5c was obtained by applying the

Huang-Minlon[37] modification of the Wolff-Kishner for 4c. However, a 40% yield was possible by using Grobs[38] modification of the Wolff-Kishner reduction. The yield was further improved by increasing the time taken for the formation of the hydrazone and by maintaining a slow distillation of hydrazone hydrate during 2 hr. By using these conditions, compound 5c (Diagram 8) was consistently obtained in 65-70% yields, and 70-75% yields of 5 a and 5b (Diagram 8) were achieved. Unfortunately, only 10% and 25% yields of 5d and 5e, respectively were obtained, and the use of acidic conditions,[38] in the hope of increasing the yield of the hydrazone, gave no improvement. Subsequent investigations using 4e (Diagram 8) revealed that the reduction produced satisfactory yields if the hydrazone were isolated, anhydrous conditions were maintained during the decomposition of the hydrazone, and redistilled hydrazine hydrate was added to the mixture of pure hydrazone, potassium hydroxide and diethylene glycol to ensure a gradual rise in temperature as the hydrazine hydrate distilled off. In this manner, a 55% yield of 5e (Diagram 8) was possible. The method of Cagliati and Grasselli[39] involving the tosylhydrazone was also attempted for the reduction of 4e (Diagram 8); a overall yield of 27% was obtained.

Compound 10 was prepared from the corresponding bromide 7c (Diagram 8) by a method described by Reinhardt[20] for biadamantyl dibromide. This consists of heating a mixture of the bromide, cuprous cyanide and pyridine slowly to 210°C as the pyridine distills off. After cooling, the dark coloured residue is extracted with refluxing benzene for 26 hours to give the nitrile.

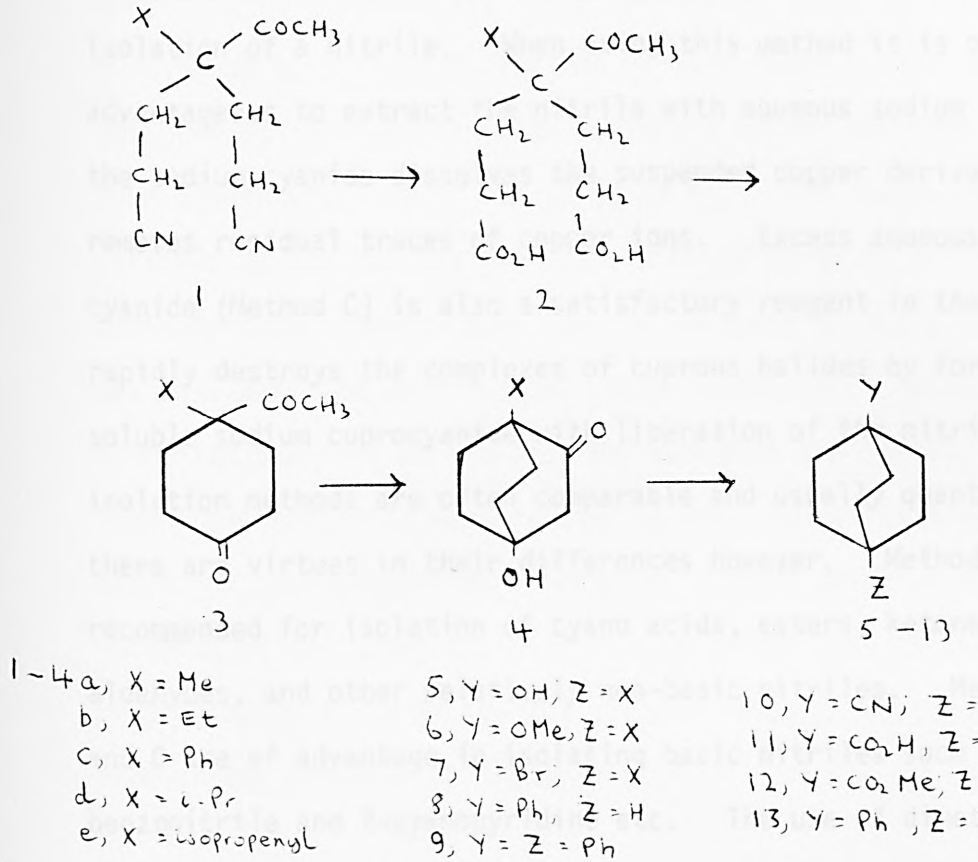


DIAGRAM 8

Dimethylformamide may be used instead of pyridine. However, Toyne et al have used Friedmann and Schechters[23] extraction procedure to isolate the product from the complex reaction mixture. This is based on utilising effective procedures for decomposing the complexes of the nitriles and cuprous halides. Aqueous ferric chloride has been found to be an excellent general reagent for destroying the reaction complexes in dimethylformamide or in pyridine and subsequent isolation of the nitriles (Method A). Ferric chloride rapidly oxidises the adduct of cuprous halide and a nitrile to cupric ion; the nitrile does not complex with cupric ion and separates from the aqueous solution. Aqueous ethylenediamine is also an effective reagent (Method B) because it complexes efficiently with cupric and cuprous ions and allows efficient isolation of a nitrile. When using this method it is often more advantageous to extract the nitrile with aqueous sodium cyanide; the sodium cyanide dissolves the suspended copper derivatives and removes residual traces of copper ions. Excess aqueous sodium cyanide (Method C) is also a satisfactory reagent in that it rapidly destroys the complexes of cuprous halides by formation of soluble sodium cuprocyanide with liberation of the nitrile. The isolation methods are often comparable and usually quantitative; there are virtues in their differences however. Method A is recommended for isolation of cyano acids, esters, ketones and aldehydes, and other relatively non-basic nitriles. Methods B and C are of advantage in isolating basic nitriles such as p-aminobenzonitrile and 2-cyanopyridine etc. The use of dimethylformamide (or pyridine) as a solvent medium and any of the above isolation techniques thus makes the reaction of halides and cuprous cyanide a convenient, efficient and general synthetic method.

The Koch-Haaf carboxylation[40] of 7a and 7b (Diagram 8) described by Toyne et al, is an improvement over the one reported by Holtz and Stock. A bridgehead carbonium ion is formed during the reaction, and although the formation of the bicyclo[2,2,2]octyl carbonium ion is more difficult than, for example, the formation of the 1-adamantyl or t-butyl carbonium ion, the formation of a 1 bicyclo[2,2,2]octyl carbonium ion is still conveniently easy.

According to Toyne et al,[27] alkylations of 7a-7d (Diagram 8) or 9 (Diagram 6) proceed easily and in good yield. For 7a or 7b (Diagram 8) the reaction with anhydrous ferric chloride as catalyst gave almost pure 13a or 13b (Diagram 8). The compounds were purified by crystallisation (13a, Diagram 8) or by column chromatography (13b, Diagram 8). For 7d (Diagram 8) the crude product was less pure and purification proved difficult. With anhydrous aluminium chloride as catalyst the reaction was faster, and the impurities (ca. 15%) were removed by one crystallisation from ethanol. The alkylation of benzene using 9 (Diagram 6) or 7c (Diagram 8) and anhydrous aluminium chloride gave 10 (Diagram 6) or 9 (Diagram 8) in 83 and 78% yields, respectively, and no by-product was produced in this reaction.

Bicyclo 2,2,2 octane-1,4-diol[41] is a useful starting material for the preparation of various bridgehead substituted bicyclo[2,2,2] octane derivatives. Diagram 9 is a schematic representation of its synthesis.

Acid-catalysed reaction of isopropenyl acetate with 1,4-cyclohexanedione gives 1,4-diacetoxy-1,3-cyclohexadiene (1) - as well as 1,4-diacetoxy-1,4-cyclohexadiene - which undergoes diene addition with maleic anhydride to give 1,4-diacetoxybicyclo[2,2,2]oct-5-ene-2,3-dicarboxylic acid anhydride (2). Hydrogenation of 2 using a PtO$_2$ catalyst gave 1,4-diacetoxybicyclo[2,2,2]octane-2,3-dicarboxylic acid anhydride (3) which was hydrolysed to the corresponding dicarboxylic acid (4). 4 was subjected to oxidative decarboxylation with lead tetraacetate in pyridine in the presence of oxygen to give 1,4-diacetoxybicyclo[2,2,2]oct-2-ene (5). Hydrogenation of 5 gives 1,4-diacetoxybicyclo[2,2,2]octane which on hydrolysis produces bicyclo[2,2,2]octane-1,4-diol (8).

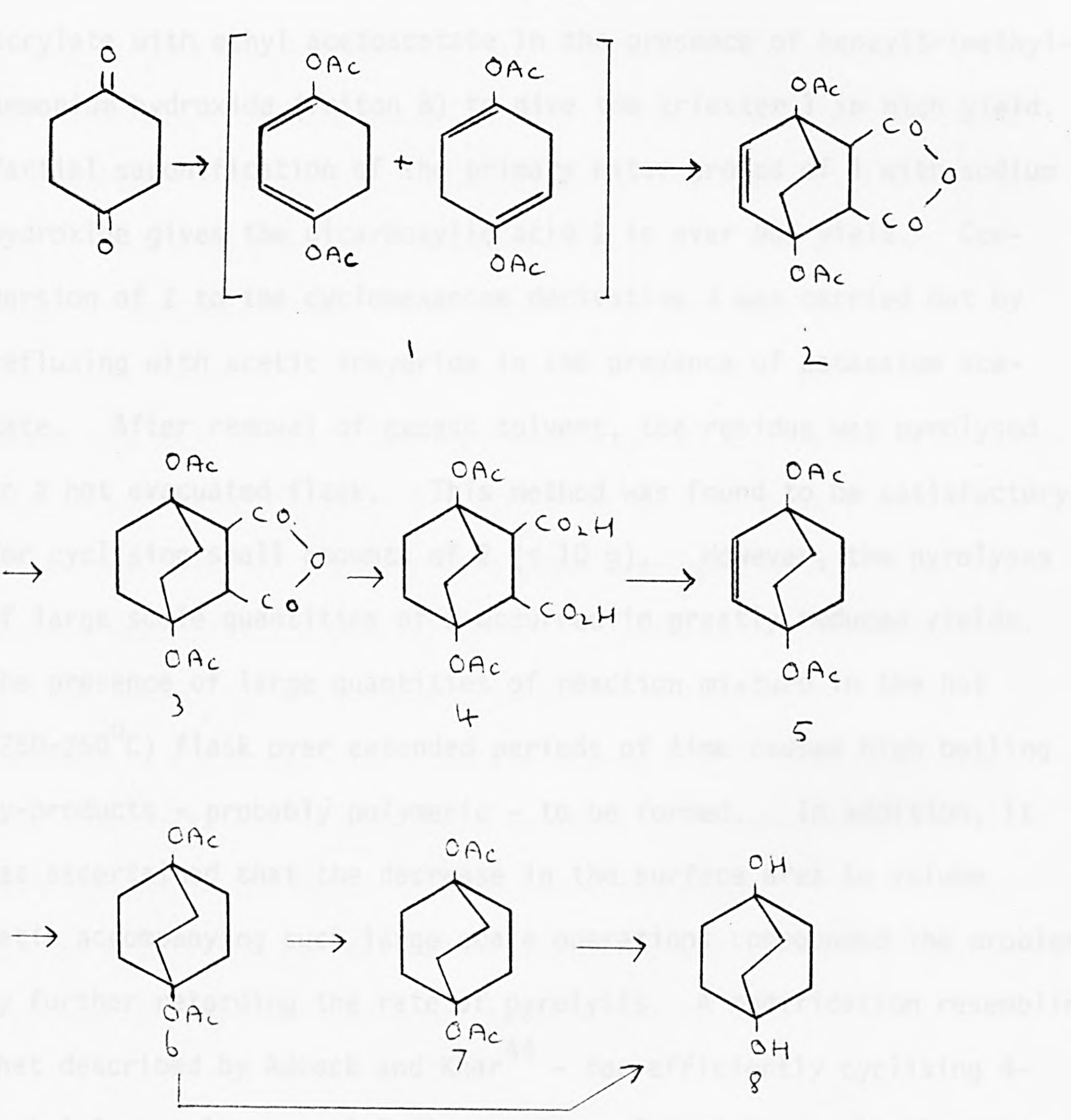
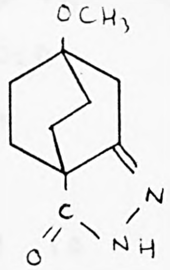


DIAGRAM 9

Adcock and Abeywickrema[42] have recently prepared a series of 4-substituted bicyclo[2,2,2]oct-1-yl fluorides from the dicarboxylic acid (2). A scheme of reactions is depicted in Diagram 10. 2 was prepared by the method described by Grob and Rich.[43] This consists of a Michael Addition of two moles equivalent of ethyl acrylate with ethyl acetoacetate in the presence of benzyltrimethylammonium hydroxide (Triton B) to give the triester 1 in high yield. Partial saponification of the primary ester groups of 1 with sodium hydroxide gives the dicarboxylic acid 2 in over 90% yield. Conversion of 2 to the cyclohexanone derivative 3 was carried out by refluxing with acetic anhydride in the presence of potassium acetate. After removal of excess solvent, the residue was pyrolysed in a hot evacuated flask. This method was found to be satisfactory for cyclising small amounts of 2 (< 10 g). However, the pyrolyses of large scale quantities of 2 occurred in greatly reduced yields. The presence of large quantities of reaction mixture in the hot (250-260^{0}C) flask over extended periods of time caused high boiling by-products - probably polymeric - to be formed. In addition, it was ascertained that the decrease in the surface area to volume ratio accompanying such large scale operations compounded the problem by further retarding the rate of pyrolysis. A modification resembling that described by Adcock and Khar[44] - for efficiently cyclising 4-acetyl-4-phenylheptane-1,7-dioic acid to 4-acetyl-phenylcyclohexanone was used to surmount these difficulties. The reaction mixture was added to a hot evacuated flask at a rate that was approximately equal to the rate of distillation of the resulting pyrolysate. This procedure ensured minimum contact time in the hot vessel, thus preventing the build-up of unpyrolysed material. Scaled up reactions 20-30 times greater than those described by Grob and Rich gave consistently good yields of 3.

A method described by Marita and Kobayashi,[45] involving acid catalysis ($HCl/(CH_3O)_3CH/CH_3OH$) was employed which resulted in the substituted cyclohexanone 3 being cyclised in excellent yield to a mixture of bicyclo[2,2,2]octanone derivatives (4, R = CH_3 and C_2H_5). This acid catalysed procedure leading to the required bicyclic skeletal framework is superior to the base catalysed conditions described by Grob and Rich.[43] The base catalysed conditions gave ethyl-4-hydroxy-2-oxobicyclo[2,2,2]octane-1-carboxylate in approximately only 50% yields as well as significant quantities (ca. 25%) of the base catalysed cleavage product (ethyl-4-oxocyclohexane-1-carboxylate) of 3. Treatment of the esters 4 (R = CH_3 and C_2H_5) with aqueous ethanolic potassium hydroxide resulted in their hydrolysis to the stable β-keto acid 5.[46] The acid 6 was obtained in 80% yield by means of a Huang-Minlon[47] modification of the Wolff-Kishner reduction of 5. The contamination of 6 with the pyrazoline derivative 10 was avoided by employing vigorous stirring and prolonged heating (10 h).



However, should the isolated crude acid 6 be seriously contaminated with 10, a further reflux (6-10 h) of the crude acid under the reaction conditions without hydrazine hydrate readily converts 10 to 6. 4-Methoxybicyclo[2,2,2]octane-1-carboxylic acid (6) possesses appropriate functionality for the synthesis of any number of unsymmetrically substituted bicyclo[2,2,2]octanes by standard procedures. This procedure may thus offer certain advantages for the preparation of 1,4-disubstituted bicyclo[2,2,2]octanes than those procedures that require the synthesis of heavily chlorinated precursors and the necessity for costly high-pressure equipment.[48] In addition, other synthetic procedures[27,36,41] offer only limited access to these important stereochemically well-defined model systems.

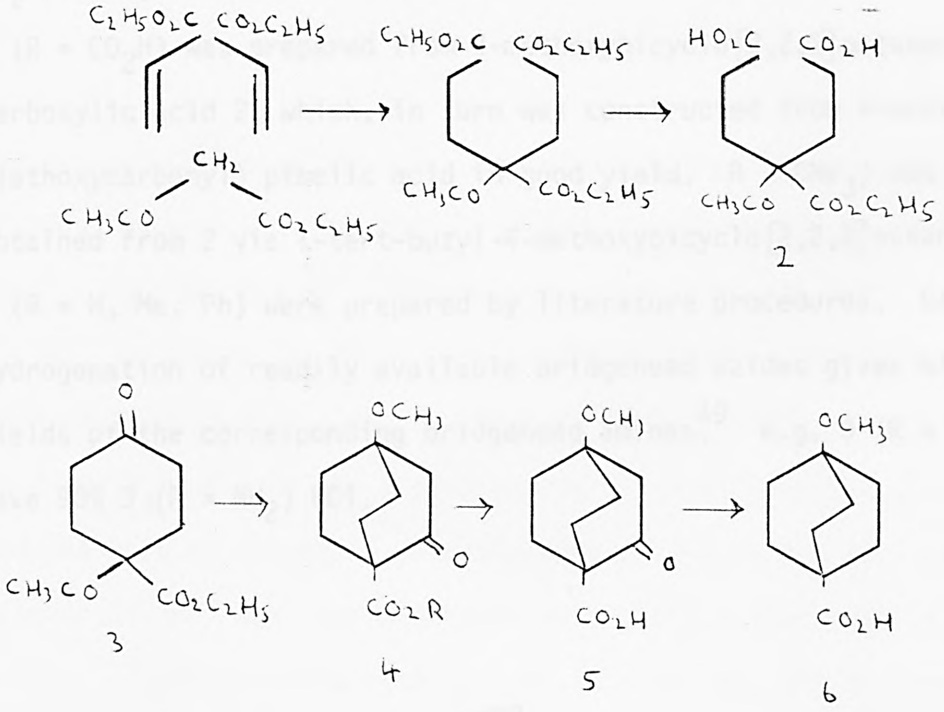
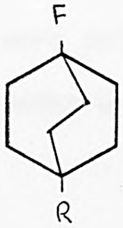


DIAGRAM 10

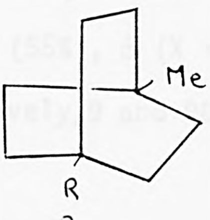
2.3 Miscellaneous Aspects of Bicyclo[2,2,2]Octane Chemistry

Adcock et al[42] have prepared a series of bicyclo[2,2,2]oct-1-yl fluorides I for substituent effect studies.



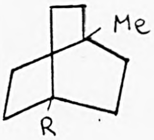
I

I (R = NO_2, cyano, $CONH_2$, Ac, CHO, OMe, OAc, OH, F, Cl, Br, iodo, NH_2, NMe_2, NHAc, Et, $CHMe_2$ and Sn Me_3) were prepared from I (R = CO_2H) using fairly standard functionalisation procedures.
I (R = CO_2H) was prepared from 4-methoxybicyclo[2,2,2]octane-1-carboxylic acid 2, which, in turn was constructed from 4-acetyl-4(ethoxycarbonyl) pimelic acid in good yield. R = CMe_3) was obtained from 2 via 1-tert-butyl-4-methoxybicyclo[2,2,2]octane.
I (R = H, Me, Ph) were prepared by literature procedures. Catalytic hydrogenation of readily available bridgehead azides gives high yields of the corresponding bridgehead amines,[49] e.g. 3 (R = N_3) gave 90% 3 (R = NH_2) HCl.



3

Reaction of 3 (R = tosyloxy) with NaN_3 in boiling PhCl in the presence of ZnI_2 gave the title compound. (3, R = N_3) - Labeled (4)[50] Under the same conditions bicyclooctene 5 (R = tosyloxy) gave only product 6 via solvent addition to the intermediate 7. In hydrocarbon solvents or MeCN, photolysis of 4 gave only oligomeric mixtures. Similar results were obtained on thermolysis of 4 in benzene at 180^{o}, conditions under which decomposition occurred with a half life of 8 h.



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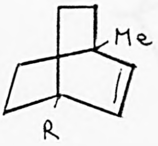

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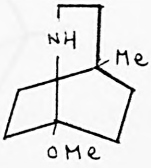

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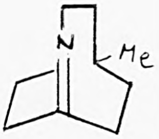
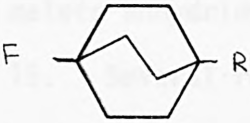


7

Kopecky et al[51] have prepared 1-halobicyclo[2,2,2]octanes 8 (X = Cl, Br, iodo, R = H, Me, Ph) in 59-80% yields from 8 (X = OH, OMe, OAc, R = H, Me, Ph) by treatment with NaCl, KBr, KI, $SOCl_2$, $POCl_2$ or PBr_3 in 100% H_3PO_4 or in polyphosphoric acid at 80-150^{o}C, chlorination of 8 (X = OH, R = Me) (9) with $Cl_2C:CH_2$ also gave 8 (X = CH_2CO_2H, R = Me) as a by-product. 1,4-bicyclo[2,2,2]octanediol and its mono or diacetate gave mixtures of 1,4-dihalo derivatives (yields 20-70%) and 1-halo-4-hydroxybicyclo[2,2,2]octanes (yields 6-28%). Hydrogenation of 8 (X = Br, R = Me, Br, OH) on Raney Ni gave 8 (X = H, R = Me) (55%), 8 (X = R = H) (50.5%) and 8 (X = H, R = OH) (73%), respectively.9 and $POCl_3$, gave, without phosphoric acids, 80% 8 (X = $OPOCl_2$, R = Me)

8

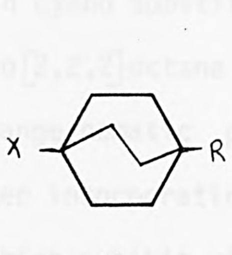
1-Fluoro-4-R-bicyclo[2,2,2]octanes 10 (R = H, Me, Ph, AcO, 4-O_2N-C_6H_4) were prepared[52] in 50-60% yields from 4-R-bicyclo[2,2,2] octan-1-ols and the Yarovenko reagent FCH (Cl) CF_2NEt_2 at 60-140°.



10

Bicyclo[2,2,2]octane-1,4-diols gave 49% 10 (R = F). 10 (R = OH) was prepared by alkaline hydrolysis of 10 (R = oAc) and 10 (R = 4-H_2N-C_6H_4) by reduction of 10 (R = 4-O_2N C_6H_4) with Na BH_4.

Kopecky et al[53] have prepared 1-mercaptobicyclo[2,2,2]octanes 11 (X = SH, R = Me) (12) and 11 (X = SH, R = OH) in 58.5 and 42% yields respectively from 1-hydroxy derivatives 11 (X = SH, n = Me, OH) and thiourea in 100% H_3PO_4.



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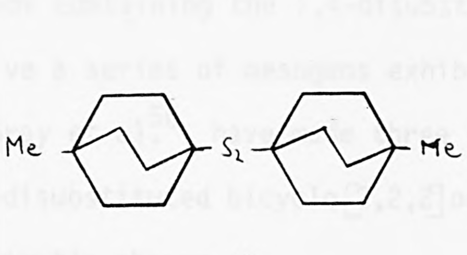
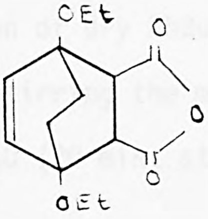


13

12 was methylated to 11 (X = SMe, R = Me) (65%) and further oxidised by $NaIO_4$ to 11 (X = SOMe, R = Me) (65.5%) or by $KMnO_4$ to 11 (X = SO_2 Me, R = Me) (76%). The direct oxidation of 12 by $KMnO_4$ gave 89% disulphide 13.

The synthesis of 1,4-disubstituted bicyclo[2,2,2]octanes by a Diels-Alder reaction has been described by Geivandar and Kashou.[54] 14 (R = OEt, (14a), cyano, Ph) were prepared from 1,4-cyclohexanedione. 14a was treated with maleic anhydride, CH_2:$CHNO_2$, CH_2:CHCN, CH_2:C(OAc)CN, fumaronitrile, and CH_2:CHCHO, and 14 (R = cyano, Ph) were treated with maleic anhydride to give the corresponding bicyclooctenes, e.g. 15. Several reactions of these are described; among the compounds thus prepared were 16 and 17.

14



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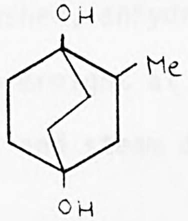
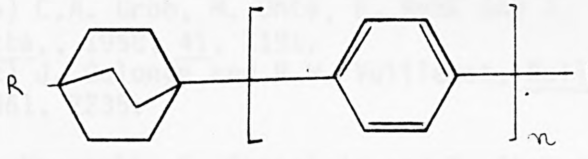


16

17

Using the Holtz and Stock method, Gray and Kelly[55] have prepared certain cyano substituted systems containing the 1,4-disubstituted bicyclo[2,2,2]octane ring to give a series of mesogens exhibiting wide range nematic phases. Gray et al.[56] have made three types of ester incorporating the 1,4-disubstituted bicyclo[2,2,2]octane ring which exhibit wide range nematic phases.

The title compounds 18 (R = alkyl; R' = alkyl, alkoxy, alkanolyloxy, alkoxycarbonyloxy; n > 1) were prepared.[57] 18 are, in general, chemically and photochemically stable, with low dielectric anisotropy and low birefringence. The low dielectric anisotropy makes them useful in multiplaced twisted nematic devices together with materials of positive dielectric anisotropy; the low birefringence makes them useful in cholesteric-to-nematic phase change effect devices.



18

18 (R = R' = Bu, n = 1) was prepared by adding 1-bromo-4-butylbicyclo[2,2,2]octane in dry $PhNO_2$ dropwise during 0.5 h to a well stirred solution of dry PhBu and crushed, anhydrous $AlCl_3$ in dry $PhNO_2$ at 80°, stirring the mixture overnight at 80°, treating it with $HCl/ice/H_2O$ (20 min; stirring), and steam distilling the organic layer.

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PHOTOCHEMICAL STUDIES OF HALOAROMATIC HYDROCARBONS AND RELATED COMPOUNDS

3.1 Introduction

Substituted aryl halides are widely used as pesticides, moth proofing agents and electrical insulators. Aryl halides are photochemically decomposed and this is very important in synthesis.[1]

The various aspects of the photochemistry of haloaromatics are now considered.

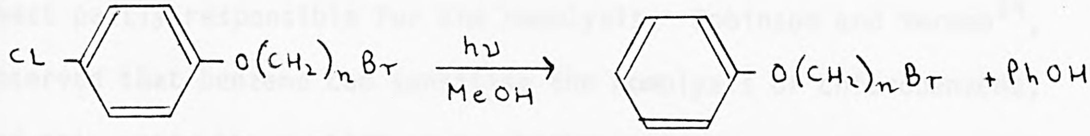
3.2.1 Chloroaromatics

It was shown by Shimoda et al.[2] - from measurements of fluorescence lifetimes of the dichlorobenzenes in the vapour phase, that fast non-radiative decay of the excited singlet state is induced by the chlorine substituents. They also concluded that since the aryl-chlorine bond is of lower energy than the first excited singlet state, this decay must involve bond homolysis as well as intersystem crossing. The fluorescence lifetimes depend upon the pattern of substitution: 1,2-dichlorobenzene, 290 ns, 1,3-dichlorobenzene 280 ns, and 1,4-dichlorobenzene 170 ns. Chlorobenzene has a low fluorescence quantum yield and a high quantum yield for the production of radicals. Freedman et al.[3] have used an excitation source emitting at 193 nm to investigate the mechanism of bond homolysis for chloro-, bromo- and iodobenzene in the vapour phase. There appears to be two reaction pathways. In one pathway, intersystem crossing from a singlet $\pi\pi^*$ state to a triplet $\sigma\sigma^*$ which homolyses is involved. For chlorobenzene intersystem crossing occurs from the $S_1\pi\pi^*$ state whereas for bromo- and iodobenzene S_3 S_2 and S_1 $\pi\pi^*$ states are involved. In the other pathway a distortion of the $S_1\pi\pi^*$ state occurs as takes place in the formation of prefulvene. This distortion allows electronic energy to enter the phenyl ring as vibrational energy thus causing homolysis. This concept of a distorted excited state being responsible for homolysis does not appear to have been considered as a possible reaction pathway for solution phase experiments. Keso et al.[4] have studied the vapour phase dechlorination of chlorotoluenes in the presence of ethene, and they concluded that homolysis occurs from the triplet state.

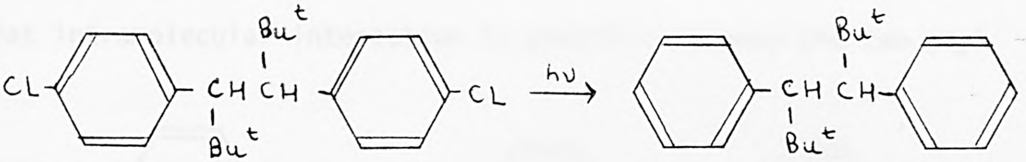
Considerably less precise information is available concerning the photophysical parameters for chlorobenzenes in solution. It is known that chlorobenzene and many of its derivatives homolyse on photolysis. Also, if benzene is used as solvent, the chlorine atom is replaced by a phenyl group, whereas the use of hydrogen-donating solvents such as methanol leads to dehalogenation. Biphenyls are produced upon irradiation of chlorobenzene in benzene and in this system the solvent gathers the light. Benzene can act both as a singlet and a triplet sensitiser (Dubois and Wilkinson[5]). Thus, although the homolysis of chlorobenzenes is sensitised by benzene, one cannot draw any conclusion as to the excited state of chlorobenzene responsible for this reaction. Bunce et al.[6] have carried out sensitisation and quenching experiments to elucidate the mechanism of homolysis of chlorobenzene and other chloroaromatics. The results indicate that the triplet state is responsible for reaction and, in support of this, it was noted that the quantum yield for dechlorination is high (0.54). However, the energy of the triplet state (85 Kcal mol^{-1}) lies well below that of the aryl-chlorine bond strength

(Table 1) and therefore the question arises as to how this energy deficiency is made up. This question has still not been satisfactorily answered. Augustyniak[7], has shown that alkyl ketones can sensitise the homolysis of chlorobenzene. Maharaj and Winnik[8], have recently shown that triplet states of carbonyl compounds will form excited complexes with electron deficient alkanes, and thus one cannot be certain whether the sensitisation observed by Augustyniak is due purely to energy transfer. A variety of substituted chlorobenzenes undergo homolysis on irradiation in benzene solution, e.g. 4-chloroaniline and 2-, and 4-chlorobenzonitriles (Robinson and Vernon[9]). Interestingly, 4-chloroacetophenone and 4-chlorobenzophenone display very low photoreactivity even though their triplet yields are close to unity. This lack of reactivity may be due to the lowest triplet states of these compounds being associated with an n → π* transition rather than a π → π* or σ → σ* transition.

Davidson et al.[10], have irradiated compounds such as (1) in methanol in order to determine the mechanism whereby halobenzenes homolyse. It was found that the compounds dechlorinate rather than the carbon-bromine bond homolysing. This is rather surprising when one considers that the methylene-bromine bond is weaker than the aryl-chlorine bond by ∿ 35 Kcal mol^{-1}. There is effective competition between homolysis of the carbon-chlorine band and energy transfer to the methylene-bromine bond. The triplet state of (1) is of higher energy than the methylene-bromine bond and is of lower energy than that of the aryl-chlorine bond. It was thus concluded that that the excited singlet state of (1) is responsible for homolysis.



1 n = 2,3



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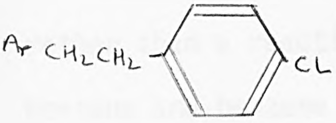
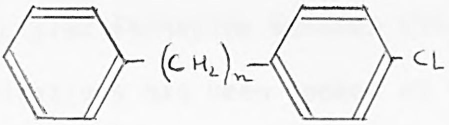
If by any chance the triplet state of chlorobenzenes can homolyse in solution then this process must have a very high rate constant to compete so efficiently with energy transfer.

Compound (2) provides another interesting example of dechlorination competing effectively with other processes (Eichin et al.[11]). Irradiation of meso- (2) in decane gave the meso chlorinated product, dechlorination having competed with homolysis of the benzylic carbon-carbon bond. Homolysis of the benzylic bond should be easy since its energy lies below that of both the excited singlet and triplet states of chlorobenzene.

Robinson and Vernon[12]; Davidson et al.[13] have also investigated the photochemistry of the benzylic compounds (3a) and (3b). It was found that compound (3a) was relatively stable when irradiated in benzene solution but irradiation of (3b) in methanol solution led to dechlorination. Thus in (3b) the dechlorination process competed with both singlet and triplet energy transfer. This result suggests that the excited singlet state of the chloroaromatics must be at least partly responsible for the homolysis. Robinson and Vernen[14], observed that benzene can sensitise the homolysis of chlorobenzene, and this posed the problem as to whether a benzene - chlorobenzene exciplex could be involved. This was investigated by Bunce and Ravanal[15], who found that (4) undergoes dechlorinatiom relatively inefficiently. They found that (4) exhibits exciplex emission showing that intramolecular interaction is possible between the two aryl



3a Ar = 4-Biphenyl
3b Ar = 1-Naphthyl



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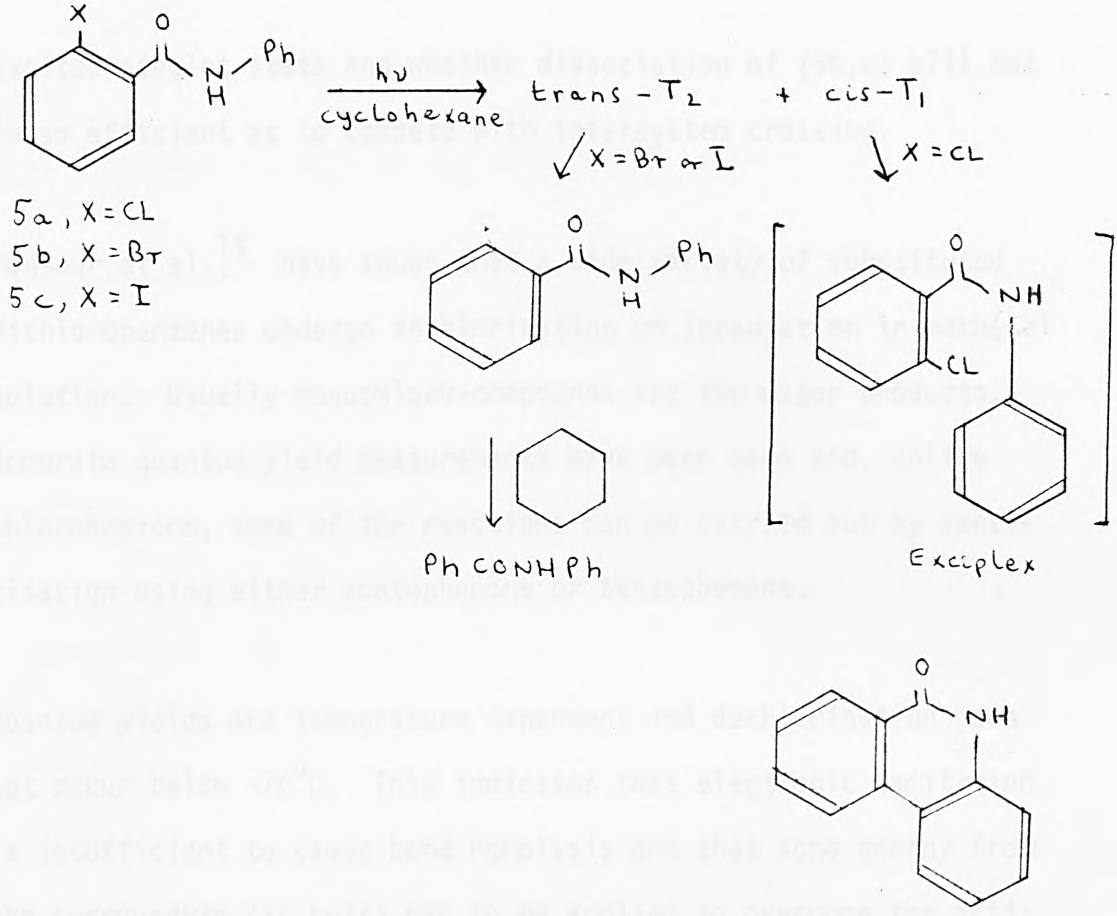
groups. It appears that exciplex formation leads to energy wastage rather than efficient chemical reactions. By extrapolation it seems reasonable to suggest that irradiation of chlorobenzenes in benzene solution leads to intermolecular exciplex formation. If high concentrations of benzene are employed, termolecular complex formation (one molecule of chlorobenzene and two molecules of benzene) is also likely. Before excluding the excited singlet state of the chlorobenzene as being the reactive species, it is necessary to know the extent to which these complexes lead to deactivation. Kajima et al[16], have shown that the relative concentrations of chlorobenzene and benzene plays an important part in determining the product distribution. Thus irradiation of either neat chlorobenzene or concentrated benzene solutions of chlorobenzene gives a different ratio of the o-, m- and p- chlorobiphenyls than when dilute benzene solutions of chlorobenzene are used. The concentration effect was attributed to the participation of chlorobenzene excimers at high chlorobenzene concentrations. It was suggested by Bunce et al.[17] that the excited singlet excimer is an energy-wasting intermediate rather than a reactive one. Exciplex formation between chlorobenzene and benzene and its derivatives has been looked at in other contexts. Grimshaw and de Silva,[18] have shown that the chloro-compound (5a) undergoes photocyclisation in cyclohexane solution whereas the bromo- and iodo-compounds (5b,c) dehalogenate. To rationalise these observations it was suggested that interaction of the chlorine atom in the triplet state of the cis- conformer of (5a) with the other benzenoid groups leads to an exciplex from which carbon-chlorine bond homolysis occurs with resultant cyclisation. If N,N-diethylaniline is added to the reaction mixture only benzanilide is formed, suggesting that the greater electron-donating ability of the amine has negated the rather weak intramolecular complexing ability. For (5b) and (5c) the carbon-halogen bonds are of lower energy than the triplet state and therefore homolysis can occur in the triplet manifold of the trans-conformer, which is the most extensively populated ground-state conformer. For the chloro compound (5a) the trans-conformer is unreactive since the carbon-chlorine bond is of higher energy than the triplet state and the anilino group is not suitably situated spatially to



assist dechlorination. The reactivity of (5a) is reduced to zero by the addition of polar solvents to the cyclohexane solution. This suggests that the initially created excited state has some charge-transfer character and that this can be solvated by polar solvents to such an extent that its energy is lowered below that of the intramolecular exciplex formed between the chlorophenyl and aniline groups. The excited state responsible for the sensitivity of (5a-c) was assigned to the triplet state on the basis of sensitisation and quenching studies. However, it is difficult to tell whether some of the reactivity of (5a) is not due to the excited singlet state and whether dissociation of (5b,c) will not be so efficient as to compete with intersystem crossing.

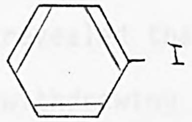
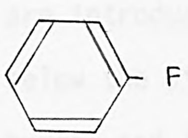
Mansour et al.,[19] have shown that a wide variety of substituted dichlorobenzenes undergo dechlorination on irradiation in methanol solution. Usually monochloro-compounds are the major products. Accurate quantum yield measurements have been made and, unlike chlorobenzene, some of the reactions can be carried out by sensitisation using either acetophenone or benzophenone.

Quantum yields are temperature dependent and dechlorination does not occur below -70°C. This indicates that electronic excitation is insufficient to cause bond homolysis and that some energy from the surroundings (as heat) has to be applied to overcome the activation energy barrier for homolysis.

In the presence of nitrogen oxides, irradiation of 1,4-dichlorobenzene leads to the production of nitro-compounds with little evidence of dechlorination (Najima and Karro). This is rather surprising on considering the relative ease with which chlorobenzenes dechlorinate. No

Table 1

Bond dissociation energies for some carbon-halogen bonds

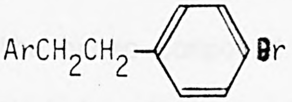
	D(C-X) Kcal mol^{-1}
	94.5
	79.2
	64.4
	123.9
CH_3CH_2-Cl	80.8
CH_3CH_2-Br	67.6
CH_3CH_2-I	53.2

3.2.2. Bromo- and Iodobenzenes

The carbon-halogen bond strength in these compounds is substantially lower than the aryl-chlorine bond strength and falls below the energy of the excited singlet state for benzenoid compounds (see Table 1). Also, the $\sigma \rightarrow \sigma^*$ absorption bands of carbon-bromine bonds have a tail which extends beyond 254 nm. Thus irradiation at short wavelengths such as 254 nm could enable a reaction to occur via direct population of the $\sigma \rightarrow \sigma$ transition as well as via the more classical routes involving the $\pi \rightarrow \pi^*$ transition. It has not been defined which of the two transitions is of lower energy in the singlet manifold. Andrieux et al.,[20] through e.p.r. studies of the radical anions derived from simple halogenobenzenes have revealed that the lowest antibonding orbital is σ^*. If electron-withdrawing groups having -R effects, such as cyano and nitro groups are introduced, the energy of the π^* orbital is reduced bringing it below the σ^* orbital. It is probable that direct irradiation of bromo- and iodobenzenes causes cleavage in the excites singlet state, this process competing with intersystem crossing. With iodo-compounds where the bond-dissociation energy is less than the energy of the triplet state, bond homolysis from this is also possible.

Marchetti and Kearns,[21] have located the $S_0 \rightarrow T_n$ absorption band by examination of the excitation spectrum of phosphorescence for several iodoaromatics. That irradiation into this band leads to homolysis with comparable efficiency to excitation into the $S_0 \rightarrow S_n$ absorption bands suggests that the triplet state is primarily responsible for homolysis in these compounds. Pedersen and Lohse,[22] have revealed that homolysis is due to the triplet state of 1,4-dibromobenzene. Through flash photolysis it is shown that excited 1,4-dibromobenzene reacts in benzene to give a transient which was identified as phenylcyclohexadienyl radical, a species generated by attack of a 4-bromophenyl radical upon benzene. The formation of the cyclohexadienyl radical is quenched by the addition of the classical triplet quencher penta-1,3-diene. The diene quenches the triplet state of the bromo-compound so reducing the amount of 4-bromophenyl radicals available for reaction.

Davidson et al.,[23] by examining the products of photolysis of a series of 4-bromophenoxylalkyl bromides, have shown that the aryl-bromine bond is cleaved preferentially to the weaker methylene-bromine bond. It was revealed that the homolysis reaction competed with success against energy transfer to the weaker bond. For this reason it was stated that homolysis occurred from the singlet manifold. That this mechanism was correct was further justified by the fact that (6) underwent homolysis of the aryl-bromine bond even though a naphthalene group, capable of deactivating the excited singlet and triplet state of the bromophenyl group, is ideally situated within the molecule.



(6) (Ar = 1-Naphthyl)

Is this (6)

$PhO(CH_2)_n\,Hal$

(7) Hal = Br

(8) Hal = I

$PhO(CH_2)_{n-2}CH{=}CH_2$

(9)

The reactions of (7) and (8) (Davey et al.;[24]) show the competition existing between excitation into the $\sigma \rightarrow \sigma^*$ transition of the carbon-iodine bond and the $\pi \rightarrow \pi^*$ transition of the aryl group when using 254 nm light. The reaction of (7) to produce (9) depends upon the value of n, hardly any reaction occurring when $n > 6$. It has been revealed that when n is as large as 6, energy transfer to the carbon-bromine bond becomes inefficient because of the inability of the methylene chain to coil so as to allow the bromine atom to approach close enough to the aryl group to enable energy transfer to occur. In contrast, the efficiency of the reaction of (8) appear to be much less dependent upon the value of n.

Examination of the absorption spectra of (8) have revealed that a measurable percentage of the light absorbed at 254 nm enters the $\sigma \rightarrow \sigma^*$ transition of the carbon-iodine bond.

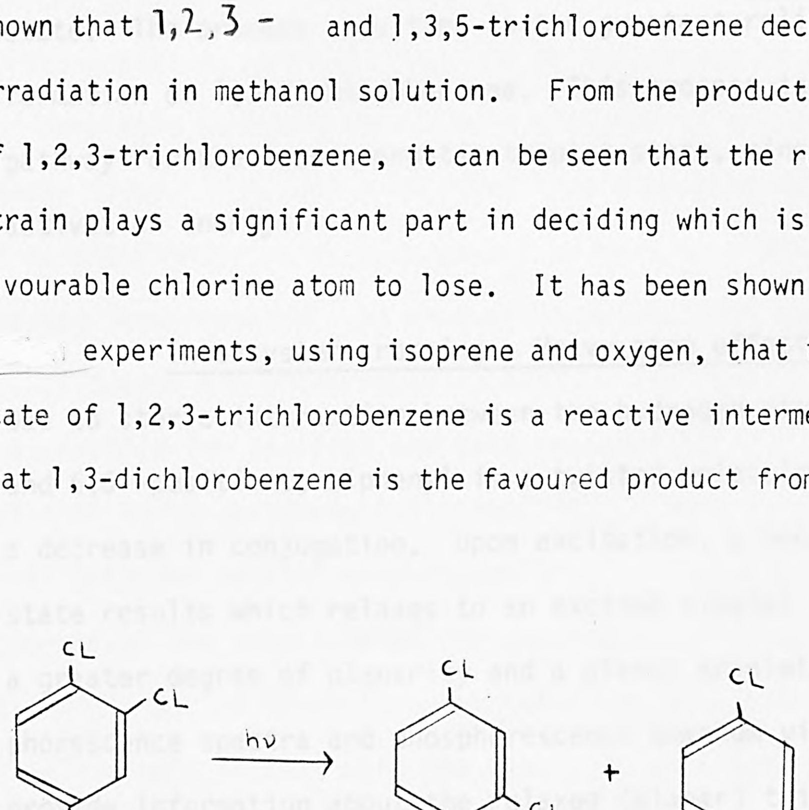
Because the aryl-iodine bond is so much weaker than the aryl-bromine bond (Table 1), it is expected that the quantum yields of products formed via photolytic cleavage of the halo-compounds should be greatest for iodo compounds. This is not found in practice. Irradiation of (11) produces (12) and the quantum yields for reaction of the iodo-compounds are lower than those of the bromo-compound (Grimshaw and de Silva[25]). It has been shown that irradiation of iodo-compounds in neat solvents with which aryl radicals can react often leads to very high yields of products via this process, and these reactions usually occur more readily than those for the corresponding bromocompounds. Because the

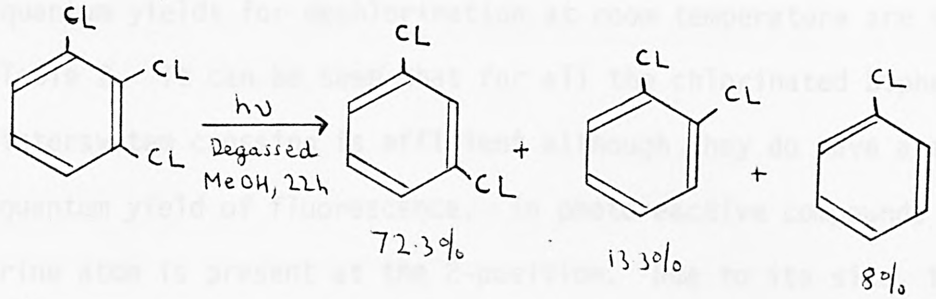
recombination of geminate radicals will reduce the efficiency of the product forming reaction, the quantum yield of product formation is not a true reflection of the efficiency of the photoinduced homolysis. Investigation of the effect of increasing the macroscopic solvent viscosity upon the reaction can enable the extent to which cage recombination occurs to be revealed. Grimshaw and de Silva,[25]
increasing the solvent viscosity
have found that with a decrease in quantum yield of product formation results, e.g. for the iodo-compound in hexane ($n = 0.28$ cp) $Q = 0.35$, whereas in cyclohexane ($n = 0.80$ cp) $Q = 0.21$. The quantum yields are also affected by changing solvent polarity but the fact that within a given type of solvent the quantum yield decreases as the viscosity is increased, indicates that an important energy-wasting process is recombination of geminate aryl radicals and halogen atoms.

3.3 Evidence for S_1 and T_1 fluorescence and phosphorescence

Several workers[26] have studied the photochemistry of trichlorobenzenes. 1,3- and 1,4-dichlorobenzene is produced upon irradiation of 1,2,4-trichlorobenzene in either cyclohexane or propan-2-ol; steric compression between the ortho-chlorine atoms is relieved due to the loss of a chlorine atom. The loss of a chlorine atom from the four position could not be seen. There must be some involvement between the relief of steric congestion and the energetics of the homolytic process, and there is proof supporting the fact that both the excited singlet and triplet states are reactive. It was observed that the ratio of the products formed in the reaction is sensitive to the presence of oxygen. In propan-2-ol the ratio of 1,3-dichlorobenzene to 1,4-

dichlorobenzene changes from 0.65 in degassed solution to 0.5 in aerated solution. Also a ratio of 3:1 results by employing acetone as sensitiser. These results support the idea that the triplet state is involved and also that the triplet state leads to a different product distribution to that from the singlet state. Henne and Fischer[27] are investigating the relative reactivity of excited singlet and triplet states. Because substrate concentration does not affect the product distribution indicates that only triplet sensitisation is occurring. It is difficult to interpret the results in a quantitative manner, because there is reaction between the sensitiser and the solvent, and it is likely that some is consumed during the irradiation period. Choudhry et al.,[26b] have shown that 1,2,3 - and 1,3,5-trichlorobenzene dechlorinate on irradiation in methanol solution. From the product distribution of 1,2,3-trichlorobenzene, it can be seen that the relief in strain plays a significant part in deciding which is the most favourable chlorine atom to lose. It has been shown - by quenching experiments, using isoprene and oxygen, that the triplet state of 1,2,3-trichlorobenzene is a reactive intermediate and that 1,3-dichlorobenzene is the favoured product from this species.





These results reveal that reaction of the triplet rather than the excited singlet state favours the formation of 1,3-dichlorobenzene. The excited singlet state should exhibit less regio-selectivity since it possesses about 15 Kcal mol^{-1} more energy than the triplet state. The process resulting in the greatest relief of strain is formation of 1,3-dichlorobenzene. This process is the more favourable pathway for the less energetic triplet state, since it has the lowest activation energy.

3.4 Intersystem crossing - Heavy atom effect

Due to steric interaction between the hydrogen atoms at the 2,2'- and 6,6'-positions, biphenyl is a twisted molecule, which causes a decrease in conjugation. Upon excitation, a non planar singlet state results which relaxes to an excited singlet state possessing a greater degree of planarity and a planar triplet state. Phosphorescence spectra and phosphorescence quantum yield measurements provide information about the relaxed (planar) triplet state. Care must be exercised in interpreting chemical reactivity from phosphorescence data since this relaxed state may not be a reactive state. Photophysical parameters of the chlorinated biphenyls and quantum yields for dechlorination at room temperature are shown in Table 2. It can be seen that for all the chlorinated biphenyls, intersystem crossing is efficient although they do have a measurable quantum yield of fluorescence. In photoreactive compounds a chlorine atom is present at the 2-position. Due to its size, the substituent will increase the energy of activation for the biphenyl system to achieve planarity. On its expulsion, a far larger relief in strain results than if the chlorine had been substituted at either a 3- or 4-position.

Compounds have a shorter triplet lifetime if they contain a 2-chloro group, than those lacking a chlorine substituent in an ortho-position, and this could be an indication of the significance of homolytic carbon-chlorine bond cleavage as a non-radiative decay route. This was determined from quenching data obtained from experiments using cyclohexa-1,3-diene as a triplet quencher. It has been revealed[28] by product investigations that o-chloro substituents are preferentially lost. That the triplet state is responsible for reaction has been revealed through quenching studies using cyclohexa-1,3-diene.[29,30] There is the possibility that both the excited singlet and triplet states are quenched because of the quenching of the excited singlet state of the chlorobiphenyls by the diene.[29] Some curvature in Stern-Volmer plots[30] should result if this were the case. No curvature was seen. Kinetic analysis of the 4-chlorobiphenyl/diene system is difficult[31] because it is not possible to achieve conditions by which the whole

Table 2

Photophysical parameters of chlorinated biphenyls and quantum yields for dechlorination

Positions of substitution	ϕ_F	ϕ_P	$\tau_T/10^{-8}$ s	ϕ_R	
2	0.09	0.46		0.39^x	
3	0.07	0.27		0.0011^x	
4	0.07	0.60		0.0006^x	
2,4	0.02			0.62^x	
2,5	0.06			0.13^x	
2,21	0.005	0.95		0.16^x	
2,4,5	0.11			0.43^x	0.05^z
2,4,6	0.003			0.14^x	0.02^z
2,2',4,4'	0.02	0.94	0.78	0.45	0.10^y
2,2',3,3'			0.77	0.007^x	
2,2',5,5'	0.0007		0.67	0.0053^x	0.01^y
2,2',6,6'			0.70		0.006^y
3,3',4,4'	0.08		2.20	0.005^x	
3,3',5,5'	0.02	0.41	1.91	0.0003^x	0.002^z
2,2',4,4',6,6'	0.003	∿ 1.0			

x Bunce et al., 1978; ϕ_r determined using 245 nm radiation with iso-octane as solvent.

y Ruzo et al., 1974; ϕ_r determined using 300 nm radiation with cyclohexane as solvent.

z Ruzo et al., 1975; ϕ_r determined using 300 nm radiation with cyclohexane as solvent.

of the incident radiation is absorbed by the biphenyl. There is apparent reaction between the chloroaromatic and the excited diene. With 1-chloronaphthalene, cyclo-adducts were isolated. The effect of added dienes on the photochemistry of chloroaromatic compounds cannot be properly explained due to these findings.

The heavy atom effect has been used. This procedure depends upon the ability of an added compound containing a heavy atom (e.g. bromine or iodine) or a heavy atom itself (e.g. xenon) to enhance the rate of intersystem crossing between an excited singlet state and a triplet state. If this happens, the triplet yield being thus increased, and the triplet lifetime is not appreciably shortened, then there should be an increase in the yield of triplet product. These findings[29] give some indication of the involvement of the triplet state in the reaction.

Enhancement of intersystem crossing is observed[32] upon introducing chlorine substituents into terphenyls, which decrease the quantum yield of fluorescence. Dechlorination results by irradiation of chlorinated terphenyls in cyclohexane and methanol. A reaction in methanol consists of replacing the chlorine by a methoxy group; there is competition between dehalogenation and nucleophilic substitution. In compounds containing an o-chloro substituent, the quantum yields for dechlorination are significantly higher than those in which the substituent is in other positions. That the reaction is occurring from the triplet state is further justified by finding that the reaction is slowed down by the presence of oxygen and the addition of xenon (a heavy atom quencher) enhances the quantum yield for reaction. Inconclusive results were obtained on performing sensitisation experiments using benzophenone. Thus, although there is evidence in favour of the participation of the triplet state in dechlorination, it is also possible that some reaction occurs from the excited singlet state.

Ruzo et al.[33] have investigated the effect of the addition of lithium halides to see if the dehalogenation of 1-iodonaphthalene, 4-iodobiphenyl and 1-bromonaphthalene occurs from the singlet or triplet manifold, using methanol as solvent for the reactions. It was found that the retardation efficiency by the ions was $I^- > Br^- > Cl^-$. It is known[34] that the excited singlet states of aromatic hydrocarbons are quenched by halide ions. There is a relation between the ease of oxidation of the ions - not the heavy atom effect - and the quenching efficiency.

Since quenching causes triplet production,[34c] it may be thought from the observed retardation, that the excited singlet state is quenched by the added ions and that reaction occurs from this state. But the efficiency of intersystem crossing between $T \rightarrow S_0$ by the heavy atom effect is well known. Since this process is accelerated by halide ions,[35] it may be thought that the quenching effect of the ions suggests that the reaction occurs from the triplet state. The problems of studying reaction mechanisms using the heavy atom effects are highlighted by this example. Very often, the relative efficiency of $S_1 \rightarrow T_1$ and $T \rightarrow S_0$ are unknown.

With some ω-naphthylalkyl halides, there is an increase in triplet yield if the halogen groups are present, with little effect upon triplet lifetime.[36] Griesce? and Thomas[37] have investigated the lability of triplet bromo- and iodonaphthalenes and biphenyls. The triplet lifetime and yield of these compounds as a function of temperature were studied, thus obtaining activation energies for homolysis from the triplet state. A value of ∿ 5 Kcal mol^{-1} was found for 1- and 2-iodonaphthalenes, and a value of 16 Kcal mol^{-1} was obtained for 4-bromobiphenyl.

It was not possible to determine the activation energy for the homolysis of triplet 1-bromonaphthalene, because of the high temperatures necessary in the homolysis of this species. Nanosecond flash photolysis studies[38] have revealed that there is competition between internal conversion and intersystem crossing with homolysis of the excited singlet state of 2-iodoanthracene. There is little homolysis from the lowest triplet state of this compound. Likewise, there is homolysis from upper triplet states of 9-iodoanthracene - produced by intersystem crossing - but not from the lowest triplet state due to insufficient energy.

3.5 Lifetimes and bimolecular processes

It is possible to estimate the rate constant for reaction in the excited state by measurement of the lifetime of the excited state.

The expression $\tau = (k_r + k_{-1})^{-1}$ defines the lifetime, where k_r = rate constant for chemical reaction and k_{-1} is the sum of rate constants for physical decay processes, phosphorescence and intersystem crossing to ground state for a lowest triplet state, or fluorescence, radiationless decay to ground state and intersystem crossing to triplet state for a lowest excited singlet state. In order to determine rate constants (k_x) for emission and for S → T intersystem crossing, the quantum efficiency (ϕ_x) for a process is measured and the value combined with the measured lifetime (τ) as in the equation $\phi_x = \tau k_x$.

The bimolecular processes can be subdivided into 5 general types:

(1) Perturbation processes - the energy levels of an excited aromatic molecule may be perturbed by interaction with an adjacent molecule.

(2) Excitation migration and transfer processes: If an excited molecule interacts with an unexcited molecule, its excitation energy can be transferred either by a radiative process (emission followed by absorption) or by a radiationless process. Excitation migration is homoplanar excitation transfer between molecules of the same species. Excitation (energy) transfer is heteropolar radiative and radiationless transfer is heteropolar radiative and radiationless transfer between aromatic molecules of different species under certain conditions.

(3) Complex formation between the two unexcited molecules: Usually, aromatic hydrocarbon molecules do not associate

in the ground state, although homopolar molecular complexes are often formed between dye molecules in concentrated solutions.

(4) Complex formation by an excited molecule and an unexcited molecule: Excited dimers ($^{1}D^{*}$) are produced when aromatic hydrocarbon molecules in their first excited singlet state ($^{1}M^{*}$) interact with unexcited molecules(^{1}M) of the same species, $^{1}M^{*} + {}^{1}M \rightarrow {}^{1}D^{*}$. These excited dimers ($^{1}D^{*}$) dissociate in the ground state. Excimers behave as a distinct molecular species, having their own characteristic fluorescence. Exciplexes (heteropolar excited molecular complexes) - which dissociate in the ground state - result from interaction of $^{1}M^{*}$ with unexcited molecules of other aromatic hydrocarbons, or with unexcited molecules (^{1}Q) of other appropriate compounds, $^{1}M^{*} + {}^{1}Q \rightarrow {}^{1}E^{*}$.

(5) Interaction between two excited molecules: Consider the homopolar interaction between two identical molecules in the excited triplet state ($^{3}M^{*}$)

$$^{3}M^{*} + {}^{3}M^{*} \begin{array}{l} \nearrow \; {}^{1}D^{*} \\ \searrow \; {}^{1}M^{*} + {}^{1}M \end{array}$$

In fluid solution, the triplet-triplet association process gives both excited molecules ($^{1}M^{*}$) and excimers ($^{1}D^{*}$), and the fluorescence of these species constitutes the P-type (pyrene-type) delayed fluorescence.

3.6 Chemical reaction

Table 3 shows quantum yield measurements for dechlorination of chloroanisoles and chlorotoluenes made by Mansour et al.[39] On assuming that the quantum yields of formation of the excited singlet and triplet states are similar for all the compounds, it appears that chlorotoluenes are more reactive than chloroanisoles. This is what would be expected on the basis of the influence of OMe vs Me upon the polar contribution to the transition state for the homolytic reaction. It has been observed that dechlorination of 3,5-dichloroanisole occurs more efficiently than with dichloroanisoles possessing a 2-chloro substituent.

From investigatios carried out by Akermark et al.[26a]; Choudhry et al.[26b]; it would be expected that the chlorine atoms in the 2-position would be particularly prone to homolysis. Irradiation of 4-chloroanisole in methanol leads to both homolysis (producing anisole) and nucleophilic substitution (Soumillian and De Wolf[40]). The formation of a radical ion pair has been proposed in the substitution reaction. 1,4-Dimethoxybenzene is formed by the reaction of th radical cation with methanol.

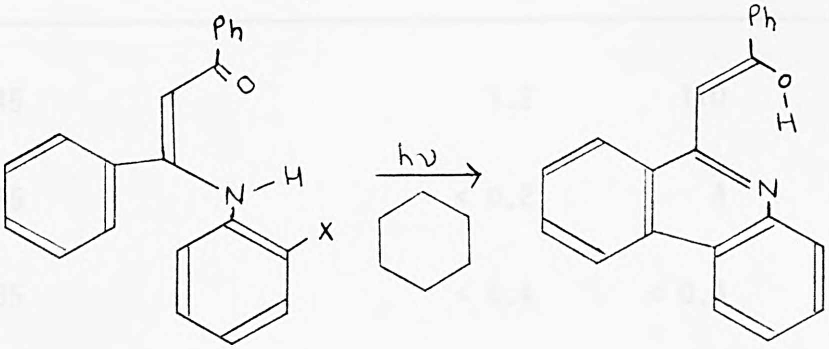
Grimshaw and de Silva,[41] have investigated the relevance of the strength of the carbon-halogen bond relative to the energy of the excited state undergoing reaction using compounds (10a-c). On irradiation in cyclohexane, these compounds undergo photocyclisation and the quantum yields for this process show a strong wavelength dependence (Table 4). This wavelength effect suggests that

Table 3

Quantum yields for dechlorination of chloroanisoles and chlorotoluenes in methanol.

Starting Compound	Products	Quantum Yields
2,6-Dichloroanisole	2-Chloroanisole anisole	5.24×10^{-3}
3,5-Dichloroanisole	3-Chloroanisole anisole	7.18×10^{-2}
2,4-Dichlorotoluene	4-Chlorotoluene toluene	7.59×10^{-3}
2,5-Dichlorotoluene	3-Chlorotoluene toluene	1.44×10^{-1}
3,4-Dichlorotoluene	4-Chlorotoluene	1.10×10^{-1}

dissociation is occurring from either a vibrationally excited first excited singlet state or an upper excited singlet state. The latter could take place if the energy entering the molecule via the $\sigma \rightarrow \sigma^*$ transition of the arylhalo group leads solely to dissociation rather than being channelled into the lower lying $\pi \rightarrow \pi^*$ transition.



10a X = Cl
10b X = Br
10c X = I

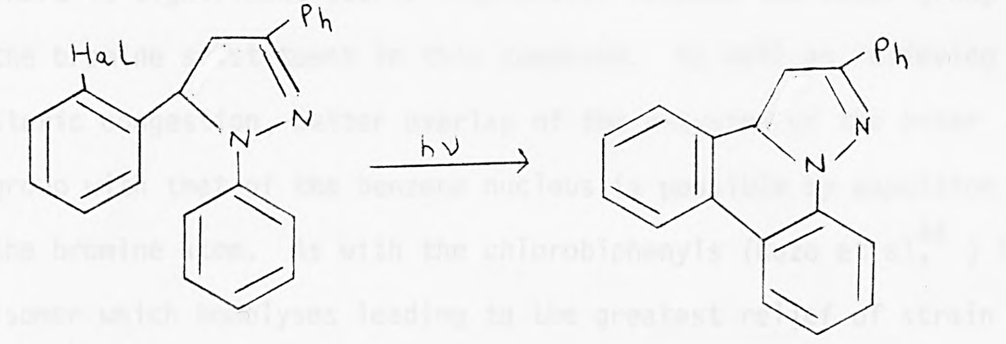
It is also possible to triplet sensitise the cyclisation of compounds such as (11). The chloro compound undergoes reaction and if this occurs from the triplet state, the process is endothermic. To explain the reactivity of the compounds (11) it has been stated that the triplet state of the arylamine portion of the compound forms an excited complex with the haloarene group and it is this complex which undergoes reaction. Grimshaw and de Silva,[42] have used a similar explanation to explain the reactivity of (13) which contrasts with the stability of (14). In the complex formed by (13) there is

Table 4

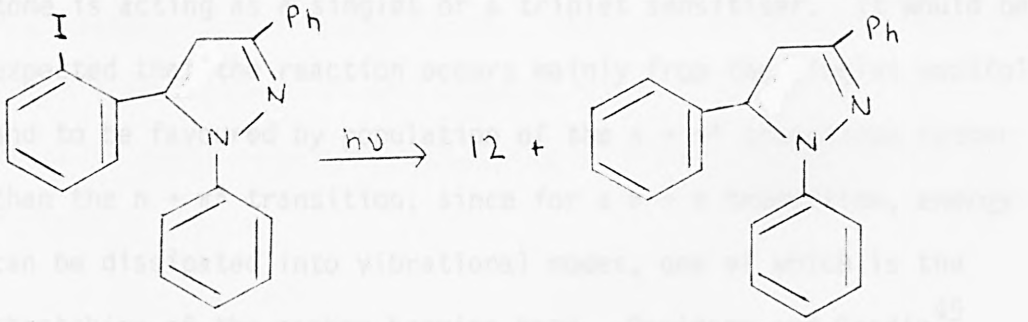
Quantum yields for the photocyclisation of compounds (10a-c).

Irradiation wavelength/nm	Quantum Yield (x 10^2)		
	X = Cl	X = Br	X = I
245	1.2	110	460
315	< 0.2	4	90
335	< 0.4	< 0.4	9
370	< 0.1	< 1	< 4

the possibility of interaction of the aryl-iodine bond with the arylamino group. This is not the case in (14), and it is thought that this is the reason for the stability of this compound. Compound (15) is also photostable. This stability was attributed to light-induced charge transfer occurring as with (13) but with back electron transfer effectively competing with aryl-bromine bond homolysis.



11 12



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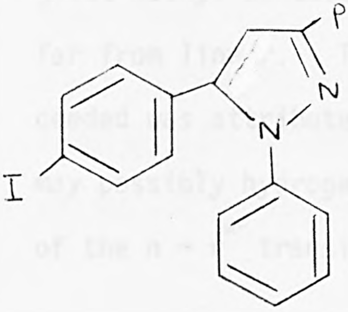

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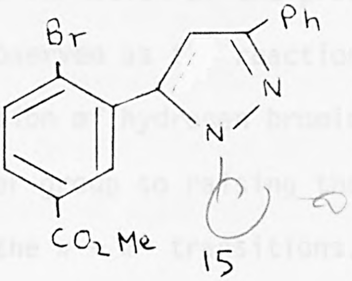
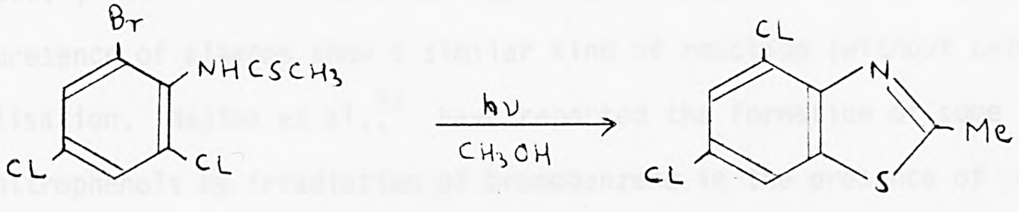


15

According to Nickishin and Chaltsova,[43] with the isomeric methyl bromobenzoates, there is the possibility of reaction from an n → π* excited state. Low yields of methyl benzoate and high yields of phenylated methyl benzoates are obtained by photolysis of the esters in benzene solution containing acetone. Homolysis of the carbon-bromine bond does not occur in these compounds. Methyl-2-bromobenzoate showed the greatest rate of reaction. There is significant steric interaction between the ester group and the bromine substituent in this compound. As well as relieving steric congestion, better overlap of the π-system of the ester group with that of the benzene nucleus is possible by expulsion of the bromine atom. As with the chlorobiphenyls (Ruzo et al,[44]) the isomer which homolyses leading to the greatest relief of strain is the most reactive. The concentration of acetone affects the efficiency of the reaction. It is difficult to establish if the acetone is acting as a singlet or a triplet sensitiser. It would be expected that the reaction occurs mainly from the singlet manifold and to be favoured by population of the π → π* transition rather than the n → π* transition, since for a π → π transition, energy can be dissipated into vibrational modes, one of which is the stretching of the carbon-bromine bond. Davidson and Goodin,[45] have revealed that photolysis of methyl 4-bromobenzoate in methanol gives methyl benzoate, but the rate of formation of the product is far from linear. The acceleration observed as the reaction proceeded was attributed to the accumulation of hydrogen bromide which may possibly hydrogen bond to the ester group so raising the energy of the n → π* transition relative to the π → π* transitions. It is shown that the photolysis of methyl 4-bromo benzoate in methanol containing hydrogen bromide is very much more efficient than in the absence of hydrogen bromide. Also the production of methyl benzoate was found to be almost linear with time.

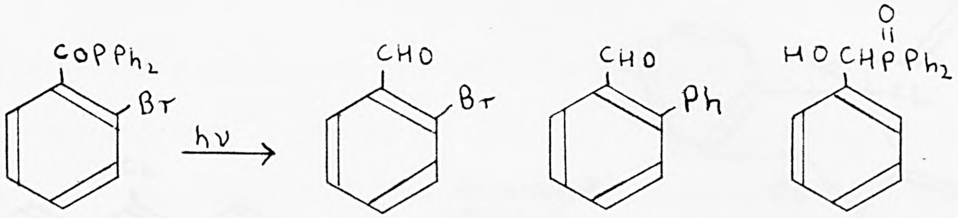
Paramasivem et al.,[46] have shown that in the photocyclisation of (16) to give (17), not only does the thiocarbonate group intramolecularly scavenge the aryl radicals in competition with the reaction of the radicals with solvent methanol but also reaction occurs solely via the homolytic cleavage of the aryl-bromine bond, the weakest carbon-halogen bond. Robinson and Vernon, have also shown that cleavage of aryl-bromine bonds in preference to aryl-chlorine bonds occurs on photolysis of 4-bromo-4'-chlorodiphenylmethane. Ref.



16

17

Dankauski et al.,[48] have shown that when 2-bromobenzoyldiphenylphosphine (18) is irradiated, products are formed which suggest that there is competition between acyl-phosphorus bond cleavage and aryl-bromine bond homolysis. This gives an indication concerning the acyl-phosphorus bond lability and because acylphosphines and related compounds are utilised as photoinitiators for polymerisation, it would be useful to investigate this further. Mitani et al.,[49] using cuprous chloride as catalyst, have achieved the photoaddition of bromobenzene to alkenes possessing electron-

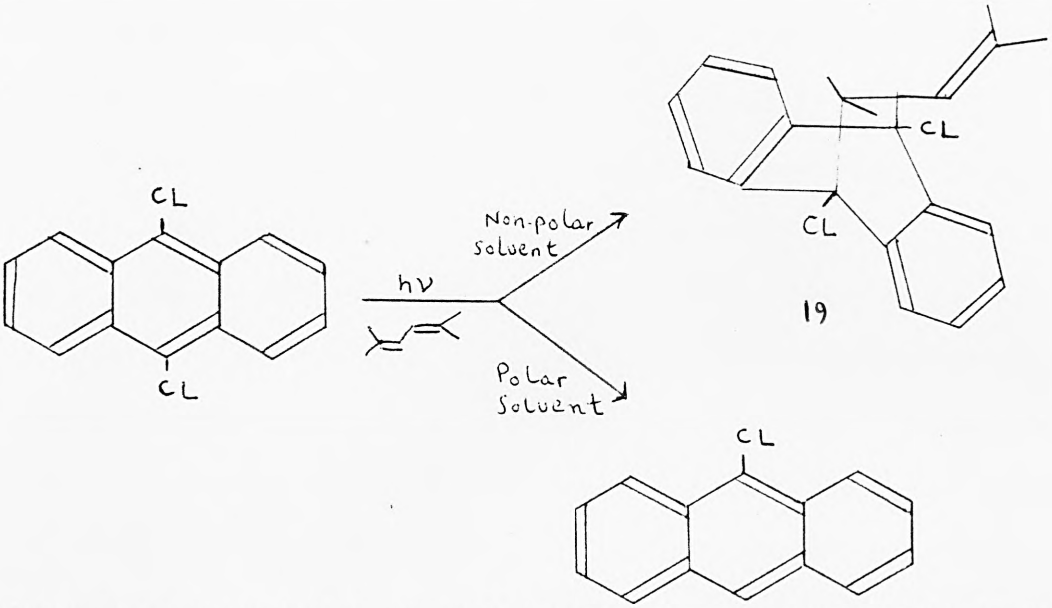


18

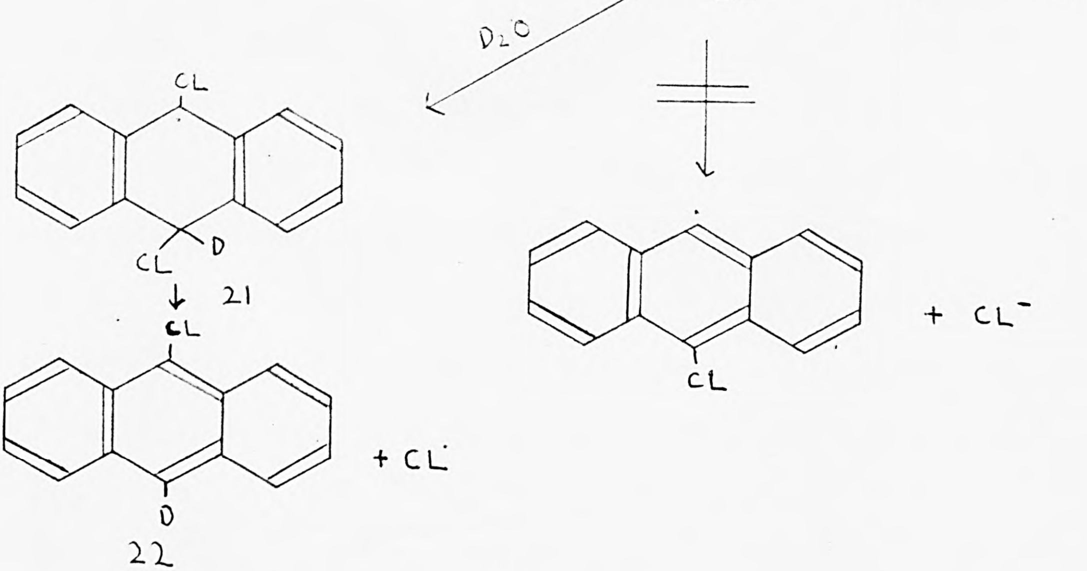
withdrawing groups. Irradiation of chlorobenzene (Bryce-Smith et al.,[50]) and 3-chloroatetrafluoropyridine (Barlow et al.,[51]) in the presence of alkenes show a similar kind of reaction (without catalisation. Najima et al.,[52] have reported the formation of some nitrophenols by irradiation of bromobenzene in the presence of nitrogen oxides. However, there is little evidence as to the mechanism of this reaction.

3.7 Electron transfer reaction of haloaromatics

Dechlorination and the production of 9-chloroanthracene are the result of irradiation of 9,10-dichloroanthracene in acetonitrile solution in the presence of 2,5-dimethylhexa-2,4-diene or cyclohexa-1,3-diene. However, a cycloaddition reaction occurs on utilising benzene as solvent to give (19). An exciplex intermediate is believed to be involved in the formation of (19). Complete electron transfer may occur in polar solvents, by the excited anthracene interacting with conjugated dienes and aromatic hydrocarbons. Deuterated 9-chloroanthracene (22) was produced by using acetonitrile containing deuterium oxide as solvent and 2,5-dimethylhexa-2,4-diene as diene. The formation of (22) suggests that



electron transfer occurs through interaction between the diene and the excited anthracene, and also that chlorine loss occurs from the radical (21) and not from the radical anion (20).



3.8 Assisted dehalogenation of halogenoaromatics

Amine- and sulphide-assisted dehalogenation of halogenoaromatics

The formation of excited complexes between aromatic hydrocarbons and tertiary amines has been well investigated (Davidson[53]; Gordon and Ware[54]; Matage and Ottolenghi[55]). According to Andrieux et al., the reduction potentials of haloaromatic hydrocarbons in many cases is similar to the parent hydrocarbons. Thus excited complexes or radical ions may be formed between the excited singlet state of these compounds and electron donors. Intersystem crossing may be enhanced to such an extent by the presence of a halogen atom, that the excited singlet state has a very short lifetime and thus little chance of taking part in a bimolecular reaction. If there is no reaction between the triplet state and the amine, the addition of amine will have no effect. It is also possible that the singlet lifetime is attenuated due to the photoinduced homolysis having a very large rate constant, and thus reaction with an amine will be inefficient. According to Davidson and Goodin,[56] this seems to be the case for bromobenzene and iodobenzene and related compounds since the presence of tertiary amines does not affect dehalogenation reactions. Upon irradiation in methanol, 4-chlorobenzonitrile does not dechlorinate, the addition of triethylamine results in dechlorination. The inefficiency of the homolytic reaction permits the bimolecular reaction with the amine to compete. Bunce et al.[57]; Ruzo et al.,[58] have reported that the dechlorination of many chlorinated biphenyls is accelerated by the addition of triethylamine, the most marked acceleration being shown by compounds with a low quantum yield for dechlorination. Compounds such as chlorinated terphenyls (Chirtini et al.[32]) undergo triethylamine-assisted dehalogenation. Here again, only the relatively light stable compounds show the enhancement, 1-chloronaphthalene (Ruzo et al.[59]; Bunce et al.[60a]) and bromobiphenyls (Bunce et al.[60b]). In the latter reactions, a much clearer reaction results by the addition of triethylamine and, if the quantum yield of biphenyl formation is being measured, the apparent acceleration by the amine is due to the suppression of side reactions.

To indicate the formation of some type of complex between the haloaromatic and the amine, terms like "amine assisted" and "acceleration" have been used. Bunce et al.[60a], have reported fluorescence from complexes formed between 1-chloronaphthalene and triethylamine. The fluorescence of haloaromatics (Bunce et al.[60a]; Ohashi et al.[61]) and haloheterocycles (Nasielski et al.[62]) is quenched in many cases by triethylamine. As this cannot be a classical energy-transfer process, it may be assumed that the quenching is due to excited complex formation. It is observed that the accelerating effect of added amines is increased by the use of highly polar solvents - this is taken as evidence of complexes or radical ions taking part in these reactions as shown in Scheme 1 (Bunce et al.[60a]; Davidson and Goodin[56]; Ohashi et al.[61]).

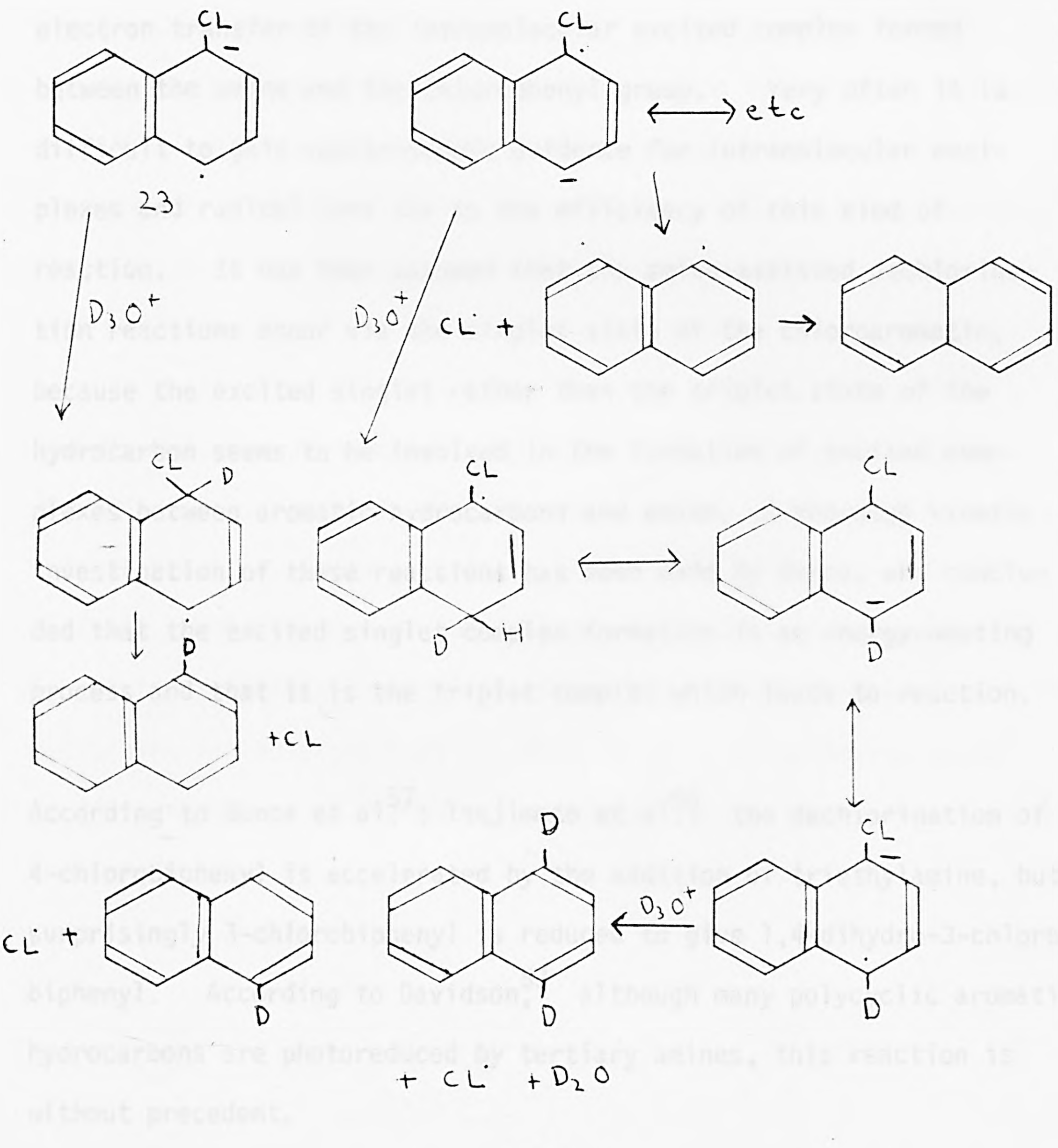
$$\mathrm{Ar\,Hal}_{S_1} + \mathrm{Et_3N} \longrightarrow (\mathrm{ArHal})^{\overline{\cdot}} \quad \mathrm{Et_3N}^{\dot{+}}$$

$$\mathrm{Ar\,Hal}^{\overline{\cdot}} \longrightarrow \mathrm{Ar}^{\cdot} + \mathrm{Hal}^{-}$$

$$\mathrm{Ar}^{\cdot} \xrightarrow[\text{or amine}]{\text{Solvent}} \mathrm{ArH}$$

Scheme 1

Using a mixture of acetonitrile and deuterium oxide as solvent, a series of dehalogenation reactions have been carried out to further elucidate the participation of radical ions. If the radical ions (e.g. (23) possess a reasonably short lifetime, and some of these have been determined (Andrieux et al.[63]), then they may be deuterated which can result in deuterium incorporation into the product. Deuterium incorporation has been observed in many cases, e.g. 1-chloro and 1-bromonaphthalene, 4-chlorobiphenyl and 9-chloroanthracene (Davidson and Goodin[56]; Bunce[64]). Although addition of



triethylamine is necessary for reaction to occur (Davidson and Goodin[56]), deuterium incorporation into benzonitrile produced from 4-chlorobenzonitrile was not observed. In none of the reactions investigated was deuterium incorporation into the starting material observed. Thus in these cases, once the radical ion of the halocarbon has been formed it does not revert to starting material. This is in contrast with the fact that N,N-dimethyl-4-chlorophenylpropylamine dechlorinates more slowly than 4-chlorophenylpropane (Bunce and Ravanol[15]). This indicates that there is efficient back electron transfer of the intramolecular excited complex formed between the amine and the chlorophenyl group. Very often it is difficult to gain spectroscopic evidence for intramolecular exciplexes and radical ions due to the efficiency of this kind of reaction. It has been assumed that the amine-assisted dechlorination reactions occur via the singlet state of the chloroaromatic, because the excited singlet rather than the triplet state of the hydrocarbon seems to be involved in the formation of excited complexes between aromatic hydrocarbons and amine. A thorough kinetic investigation of these reactions has been made by Bunce, who concluded that the excited singlet complex formation is an energy-wasting process and that it is the triplet complex which leads to reaction.

According to Bunce et al.[57]; Tsujimoto et al.[65], the dechlorination of 4-chlorobiphenyl is accelerated by the addition of triethylamine, but surprisingly 3-chlorobiphenyl is reduced to give 1,4-dihydro-3-chlorobiphenyl. According to Davidson,[53] although many polycyclic aromatic hydrocarbons are photoreduced by tertiary amines, this reaction is without precedent.

Nasielski et al.[66]; Parkenyi[67], have reported that the addition of secondary aliphatic amines as well as tertiary amines accelerates the debromination of bromopyrimidines, and radical ions have been postulated as intermediates. There is less possibility of secondary amines to take part in electron-transfer reactions, because of their higher oxidation potential in comparison to tertiary amines.

Tosa et al.[68]; Pac et al.[69]; Grobowski and Latauski[70]; Bunce and Gallacher,[31] have found that haloaromatics such as chloro- and bromobenzene quench the fluorescence of aromatic amines such as N,N-dimethylaniline, and exciplex fluorescence is observed. Benzene, biphenyl, phenylated N,N-dimethylanilines and N-methylaniline is produced by irradiation of the amine in the presence of halobenzenes. These products are produced as a result of the reactions generating aryl radicals.

The fluorescence of aromatic hydrocarbons is quenched by sulphides and this is attributed to the occurrence of a charge-transfer rather than an energy transfer process. Davidson et al.[45] have reported that the dehalogenation of haloaromatic hydrocarbons is accelerated by sulphides such as diethyl sulphide. That either radical ions or exciplexes are intermediates is shown by performing the reactions in the presence of deuterium oxide, whereby deuterium is incorporated into products.

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RESULTS AND DISCUSSION

4.1 The preparation of compounds containing donor and acceptor groups separated by the bicyclo[2,2,2]-octane framework

Synthetic strategy

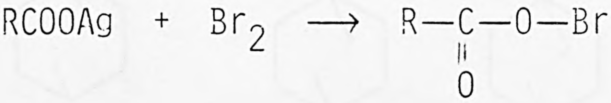
(i) A flowsheet of the proposed synthetic route is depicted in Figure 1. The target molecule in this synthesis was to be a compound in which an aromatic ring and a dialkylamine group were separated by two bicyclo[2,2,2]octane rings. The action of thionyl chloride upon cyclohexane-1,4-dicarboxylic acid would give the acid chloride, which would be converted to the bromo ester compound (2) by a Hell-Volhard-Zelinsky reaction followed by treatment with methanol. Dehydrobromination of dimethyl-1,4-dibromo cyclohexane-1,4-dicarboxylate with pyridine would lead to the formation of dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate (3). A Diels-Alder reaction between 3 and maleic anhydride would be expected to produce 1,4-dimethoxycarbonylbicyclo-[2,2,2]oct-2-ene-5,6-dicarboxylic anhydride (4). Treatment of anhydride (4) with a mild base should produce the dicarboxylic acid (5), which would be decarboxylated to give 1,4-dimethoxycarbonylbicyclo-[2,2,2]oct-2-ene (6). Hydrogenation of (6) would result in the reduction of the double bond giving (7), which upon subjection to partial hydrolysis would yield 1-methoxycarbonyl-bicyclo[2,2,2]-octane-4-carboxylic ester (8).

A Kolbe reaction on compound (8) would be expected to result in decarboxylative dimerization in which two bicyclo[2,2,2]octane units are linked together, i.e. a free-radical mechanism is involved:

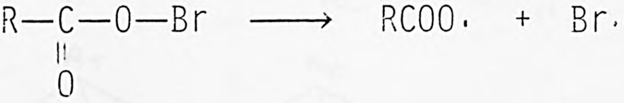
$$RCOO^- \xrightarrow[\text{oxidation}]{\text{electrolytic}} RCOO\cdot \longrightarrow \underset{\displaystyle CO_2}{\overset{}{R\cdot} \atop +} \longrightarrow R{-}R$$

where R = bicyclo 2,2,2 octane

Partial hydrolysis on compound (9) would produce the half ester (10). The conversion of the carbonyl group in compound (10) to a bromine could be achieved by means of a Hunsdiecker reaction. This is a decarboxylative bromination involving the reaction of a silver salt of the carboxylic acid with bromine. A mechanism for this conversion would be:



$$RCOOAg \;+\; Br_2 \longrightarrow R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}O{-}Br$$



$$R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}O{-}Br \longrightarrow RCOO\cdot \;+\; Br\cdot$$

$$RCOO\cdot \longrightarrow R\cdot \;+\; CO_2 \qquad \text{(initiation)}$$

$$R\cdot \;+\; RCOOBr \xrightarrow[\text{etc.}]{} RBr \;+\; RCOO\cdot \qquad \text{(propagation)}$$

The introduction of an aromatic ring in place of the bromine could be achieved by means of a Friedel-Crafts reaction on compound (11). Hydrolysis of compound (12) followed by a Hofmann degradation and alkylation would give the proposed target compound (13).

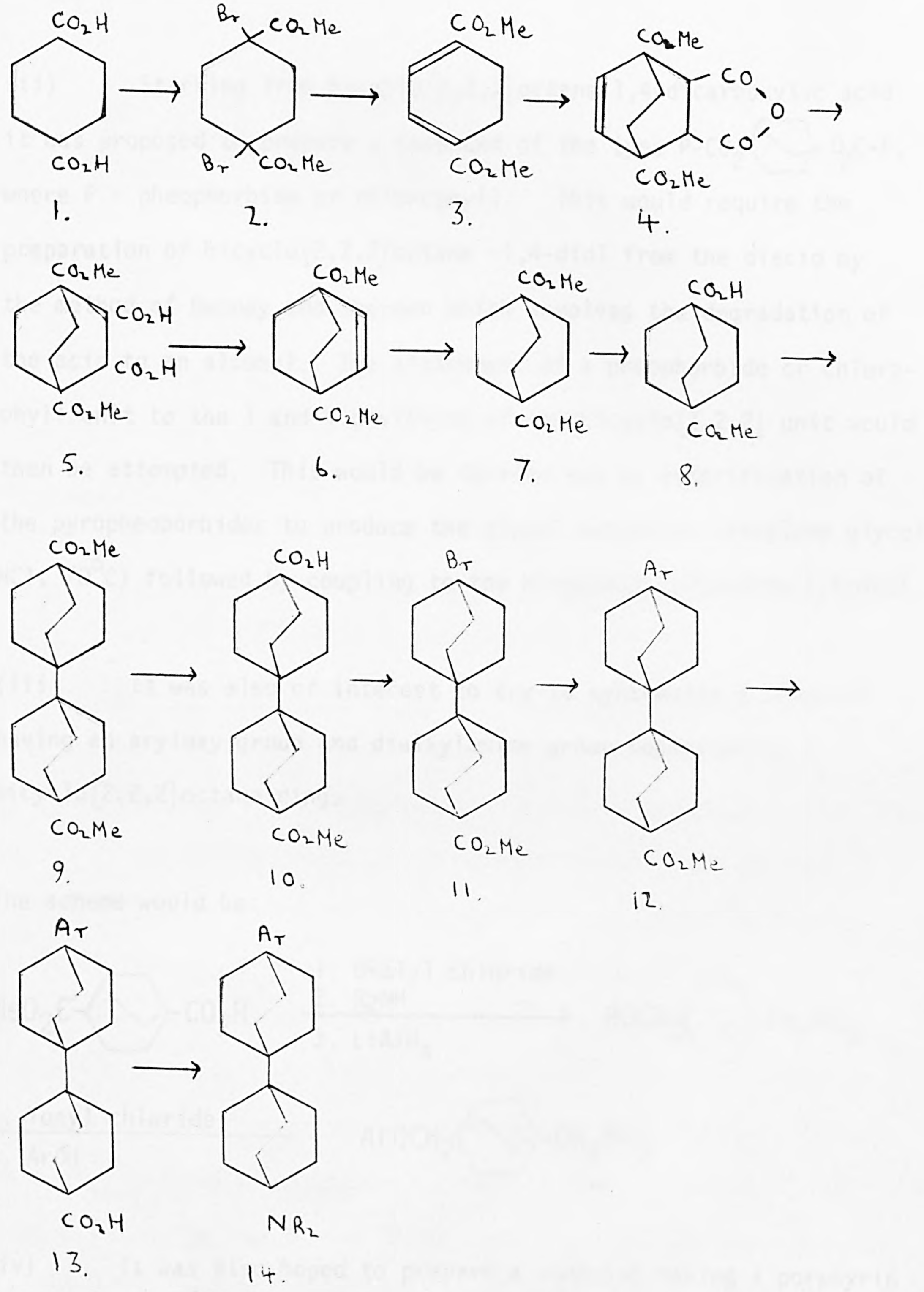
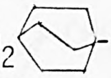
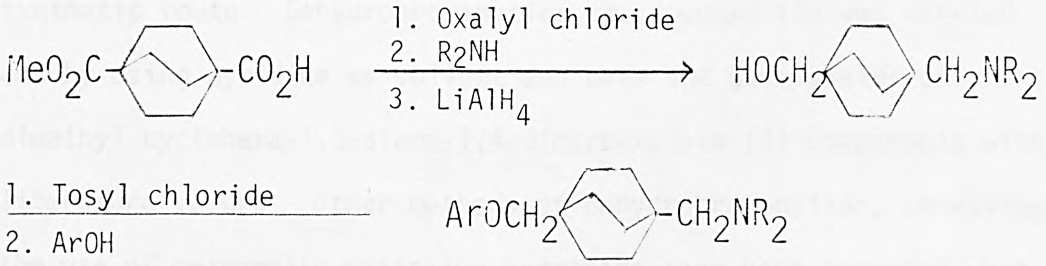


FIGURE 1. PROPOSED ROUTE FOR THE COUPLING OF TWO BICYCLO [2.2.2] OCTANE RINGS

(ii) Starting from bicyclo[2,2,2]octane 1,4-dicarboxylic acid it was proposed to prepare a compound of the type $P-CO_2$$-O_2C-P$, where P = pheophorbide or chlorophyll. This would require the preparation of bicyclo[2,2,2]octane -1,4-diol from the diacid by the method of Denney and Sherman which involves the degradation of the acid to an alcohol. The attachment of a pheophorbide or chlorophyll unit to the 1 and 4 positions of the bicyclo[2,2,2] unit would then be attempted. This would be carried out by esterification of the pyropheoborbides to produce the glycol monoester (ethylene glycol HCl, 70°C) followed by coupling to the bicyclo[2,2,2]octane-1,4-diol.

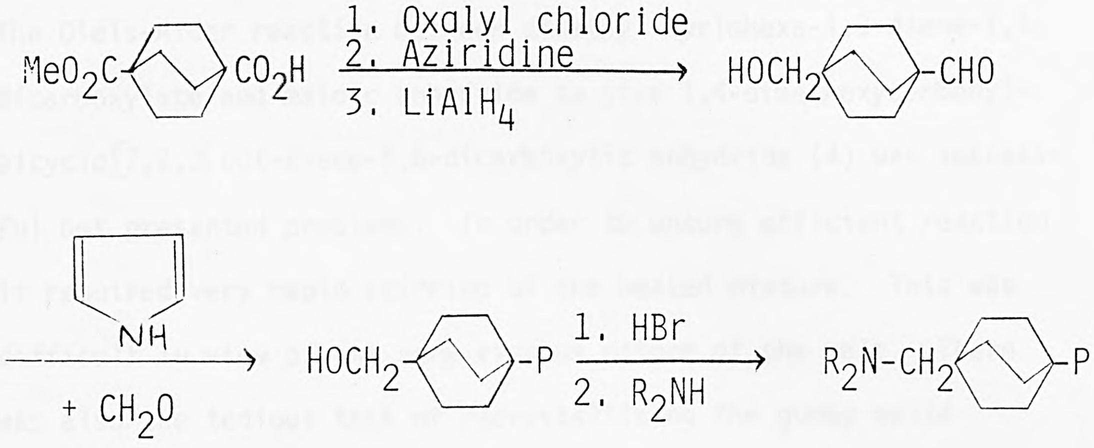
(iii) It was also of interest to try to synthesise a compound having an aryloxy group and dialkylamine group separated by a bicyclo[2,2,2]octane ring.

The scheme would be:



(iv) It was also hoped to prepare a compound having a porphyrin and dialkylamino group on the 1 and 4 positions of the bicyclo[2,2,2]-octane ring.

Reaction scheme suggested:



P = PORPHYRIN

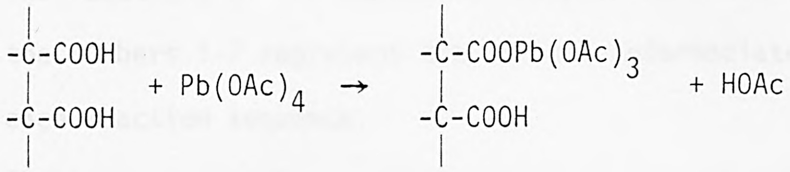
4.2 Outline of synthetic methods for the preparation of 1,4-disubstituted bicyclo[2,2,2]octane compounds

(i) Synthesis of 1,4-dimethoxycarbonylbicyclo[2,2,2]octane

After conversion of cyclohexane-1,4-dicarboxylic acid to the acid chloride, dimethyl-1,4-dibromocyclohexane-1,4-dicarboxylate (2) was successfully obtained by means of bromination (Hell-Volhard-Zelinsky) followed by reaction with methanol. Figure 2 shows the synthetic route. Dehydrobromination of compound (2) was carried out by using pyridine as solvent and base and gave yields of dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate (3) comparable with literature values. Other methods of dehydrobromination, involving the use of methanolic potassium hydroxide have been reported, but these give poor yields of the diene. The use of potassium hydroxide also presents the added problem in which the ester groups could be hydrolysed, thus making it necessary to re-esterify the carboxyl group.

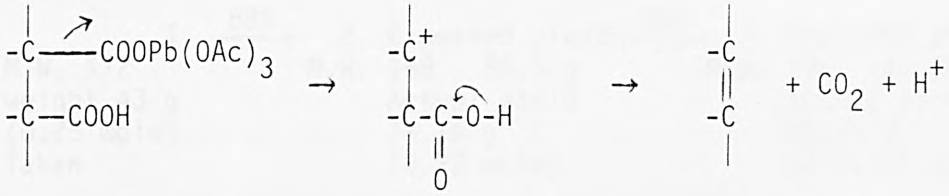
The Diels-Alder reaction between dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate and maleic anhydride to give 1,4-dimethoxycarbonylbicyclo[2,2,2]oct-2-ene-5,6-dicarboxylic anhydride (4) was successful but presented problems. In order to ensure efficient reaction it required very rapid stirring of the heated mixture. This was difficult in view of the very viscous nature of the melt. There was also the tedious task of recrystallising the gummy solid numerous times from petroleum ether in order to extract the Diels-Alder adduct. An improvement of this method was adopted which consisted of refluxing the diene and maleic anhydride in chlorobenzene, and subsequently cooling to give the desired anhydride in good yield.

The anhydride ring of (4) was easily opened by treatment with a mild base (with stronger base there is risk of hydrolysing ester groups), and after hydrogenation, acidification and cooling, 1,4-dimethoxycarbonylbicyclo[2,2,2]octane-2,3-dicarboxylic acid (5) was obtained. Oxidative bisdecarboxylation of the dicarboxylic acid (5) presented more difficulties. The decarboxylation procedure of refluxing the diacid with lead tetraacetate in benzene was attempted several times but gave poor yields (18%) of the decarboxylated product. It was suggested that the lead salts attacked the double bond under the conditions of the experiment, accounting for these low yields. The decarboxylation procedure in benzene was repeated under less drastic conditions in which the mixture was not allowed to reflux, but kept at a temperature of about 45-50°C. Yields of decarboxylated product still did not improve significantly. An improved method was tried which involved sonicating the diacid and lead tetraacetate in dimethyl sulphoxide at room temperature under nitrogen. A 35% yield of 1,4-dimethoxycarbonylbicyclo[2,2,2]oct-2-ene (6) was achieved.



$$\begin{array}{l}|\\ -\mathrm{C}-\mathrm{COOH}\\ |\\ -\mathrm{C}-\mathrm{COOH}\\ |\end{array} + \mathrm{Pb(OAc)_4} \rightarrow \begin{array}{l}|\\ -\mathrm{C}-\mathrm{COOPb(OAc)_3}\\ |\\ -\mathrm{C}-\mathrm{COOH}\\ |\end{array} + \mathrm{HOAc}$$

$$\mathrm{Pb(OAc)_3} \longrightarrow \mathrm{Pb(OAc)_2} + \mathrm{OAc^-} + \mathrm{CO_2}$$



$$\begin{array}{l}|\\ -\mathrm{C}-\mathrm{COOPb(OAc)_3}\\ |\\ -\mathrm{C}-\mathrm{COOH}\\ |\end{array} \rightarrow \begin{array}{l}|\\ -\mathrm{C^+}\\ |\\ -\mathrm{C}-\mathrm{C}-\mathrm{O}-\mathrm{H}\\ |\ \ \ \|\\ \ \ \ \ \mathrm{O}\end{array} \rightarrow \begin{array}{l}|\\ -\mathrm{C}\\ \|\\ -\mathrm{C}\\ |\end{array} + \mathrm{CO_2} + \mathrm{H^+}$$

Hydrogenation of (6) using palladium on carbon catalyst gave a near quantitative yield of 1,4-dimethoxycarbonylbicyclo[2,2,2]octane.

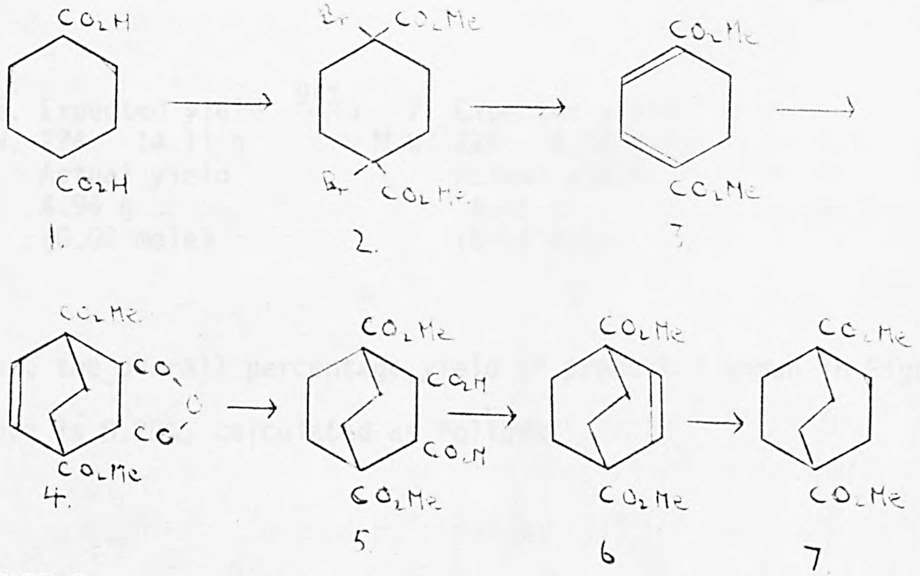


FIGURE 2

Let us consider the six stage reaction scheme as shown in Figure 2. for the synthesis of 1,4-dimethoxycarbonylbicyclo[2,2,2]octane from cyclohexane 1,4-dicarboxylic acid and the various yields (written as percentages over the arrows depicting each sequence of the reaction) of the subsequent steps. As indicated in Figure 3, the numbers 1-7 represent the various intermediates prepared in each reaction sequence.

Thus:

FIGURE 3 Yields of the various synthetic stages

1. $\xrightarrow{88\%}$	2. Expected yield $\xrightarrow{69\%}$	3. Expected yield $\xrightarrow{47.7\%}$
M.W. 172	M.W. 358 89.5 g	M.W. 196 43.12 g
weight 43 g	Actual yield	Actual yield
(0.25 mole)	78.76 g	29.75 g
Taken	(0.22 mole)	(0.15 mole)

4. Expected yield $\xrightarrow{87\%}$	5. Expected yield $\xrightarrow{35\%}$
M.W. 294 44.63 g	M.W. 314 22.74 g
Actual yield	Actual yield
21.29 g	19.78 g
(0.07 mole)	(0.06 mole)

6. Expected yield $\xrightarrow{94\%}$	7. Expected yield
M.W. 224 14.11 g	M.W. 226 4.98 g
Actual yield	Actual yield
4.94 g	4.68 g
(0.02 mole)	(0.02 mole)

Thus, the overall percentage yield of product 7 shown in Figure 3 above is 8.29%, calculated as follows:

$$1.\ \xrightarrow{88\%}\ 2.\ \xrightarrow{69\%}\ \underset{60.72\%}{3.}\ \xrightarrow{47.7\%}\ \underset{28.96\%}{4.}\ \xrightarrow{87\%}\ \underset{25.20\%}{5.}\ \xrightarrow{35\%}$$

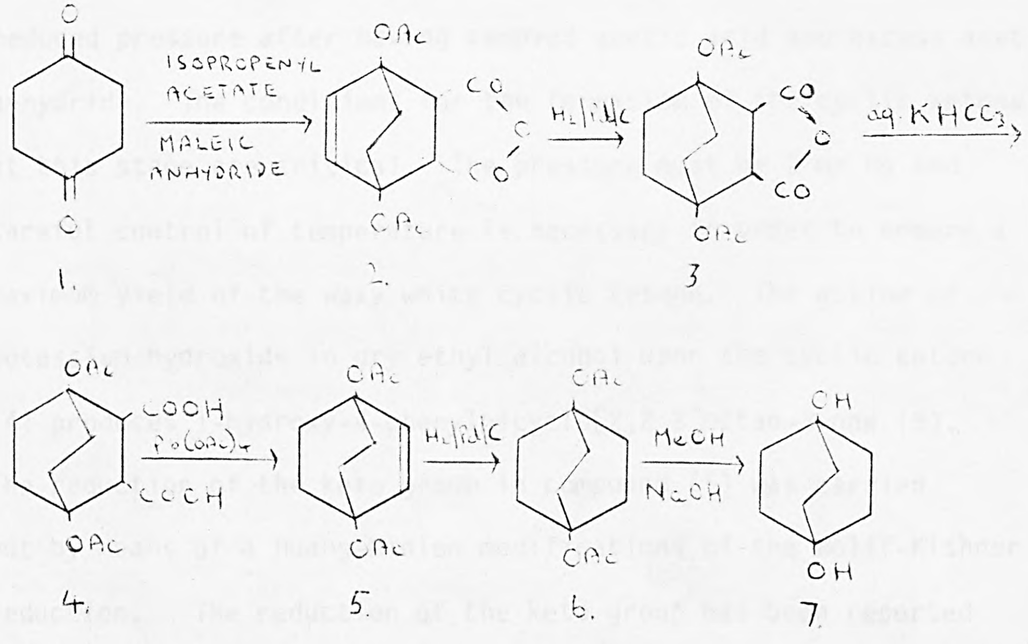
$$\underset{8.82\%}{6.}\ \xrightarrow{94\%}\ \underset{8.29\%}{7.}$$

However, a very poor yield of material (6) was actually obtained in the bis decarboxylation stage 5 → 6, because several decarboxylations using the reflux in benzene method (≃ 18% yield) were attempted before the more successful room temperature sonication method in dimethyl sulphoxide was adopted. From these decarboxylation procedures, a total of about 2 g of 1,4-dimethoxycarbonylbicyclo[2,2,2]-octane (7) was obtained. Although the partial hydrolysis of (7) to give 4-carboxy-1-methoxycarbonylbicyclo[2,2,2]octane was successful, unfortunately less than 1 g of the carboxy compound was obtained. This would not have been enough with which to carry out a successful Kolbe decarboxylative dimerization and other subsequent conversions as shown in Figure 1 of Section 1 in this chapter. Due to the time factor and lack of availability of starting material this approach had to be abandoned and other, more prosperous synthetic routes were embarked upon.

(ii) Synthesis of bicyclo[2,2,2]octane 1,4-diol

Bicyclo[2,2,2]octane 1,4-diol was prepared by the convenient six stage synthesis according to Kapecky et al. The reaction between cyclohexa-1,4-dione, isopropenyl acetate (a powerful acetylating agent), maleic anhydride and the presence of a small amount of p-toluenesulphonic acid as catalyst gave a good yield of 1,4-diacetoxybicyclo[2,2,2]oct-5-ene-2,3-dicarboxylic acid anhydride (2). The scheme of reactions is shown in Figure 4. Hydrogenation of compound (2) produced 1,4-diacetoxybicyclo[2,2,2]octane-2,3-dicarboxylic anhydride (3) quantitatively. Hydrolysis of compound (3) followed by acidification and cooling gave the corresponding dicarboxylic acid (4), which was converted into 1,4-diacetoxybicyclo[2,2,2]oct-2-ene (5) by means of oxidative decarboxylation with lead tetra-acetate in pyridine. Hydrogenation of (5) to give 1,4-diacetoxybicyclo[2,2,2]octane (6) was quantitative. Hydrolysis of (6) with methanolic sodium hydroxide yielded bicyclo[2,2,2]octane-1,4-diol (7).

<u>FIGURE 4</u> Synthesis of bicyclo[2,2,2]octane-1,4-diol



The overall yield of bicyclo[2,2,2]octane-1,4-diol (compound 7) depicted in Figure 4 is 19.54% as follows:

1. $\xrightarrow{43.5\%}$ 2. $\xrightarrow{99\%}$ 3. $\xrightarrow{95\%}$ 4. $\xrightarrow{66\%}$ 5. $\xrightarrow{99\%}$ 6. $\xrightarrow{73.1}$ 7. 19.54

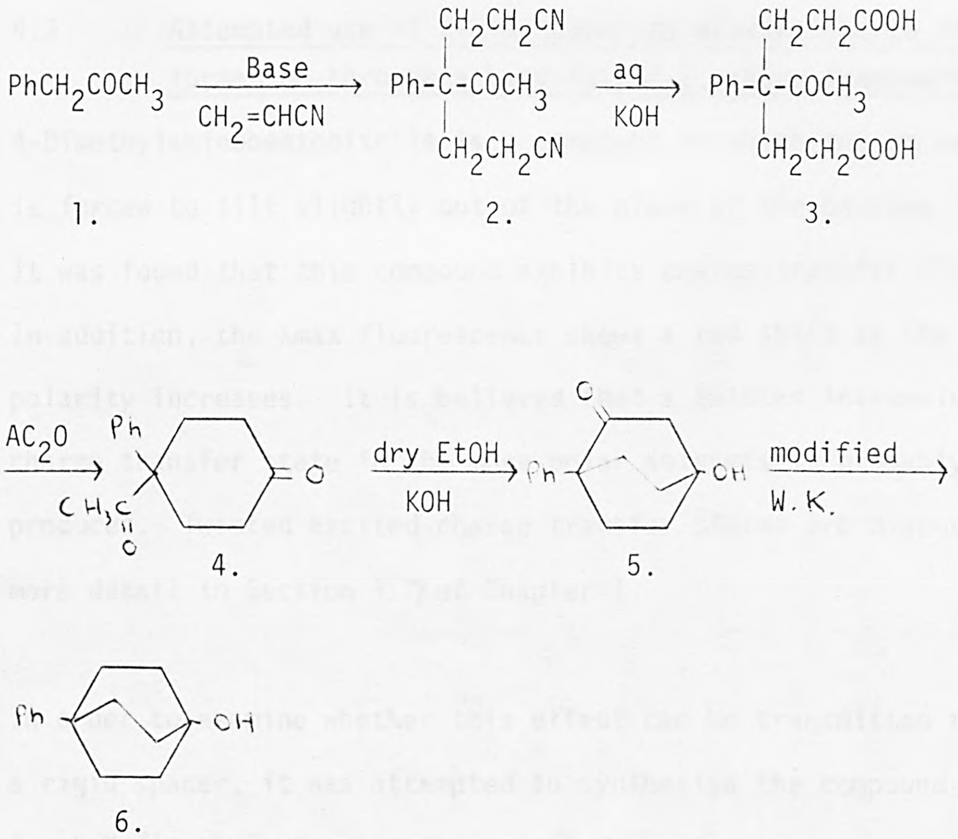
(iii) <u>Synthesis of 1-hydroxy-4-phenylbicyclo[2,2,2]octane</u>

The base catalysed Michael addition between 3-phenylpropan-2-one and acrylonitrile in t-butanol affords 3-acetyl-1,5-dicyano-3-phenyl-pentane (2) in good yield. 3-Acetyl-3-phenylpentane-1,5-dicarboxylic acid (3) was obtained in 80% yield by refluxing the dicyano compound (2) with sodium hydroxide. Figure 5 gives a flowsheet of the reaction sequences.

The cyclic ketone, 4-acetyl-4-phenylcyclohexanone (4) was obtained by heating the dicarboxylic acid (3) with acetic anhydride and NaOAc as catalyst and subsequent distillation of the residue under reduced pressure after having removed acetic acid and excess acetic anhydride. The conditions for the formation of the cyclic ketone at this stage are critical. The pressure must be 2 mm Hg and careful control of temperature is necessary in order to ensure a maximum yield of the waxy white cyclic ketone. The action of potassium hydroxide in dry ethyl alcohol upon the cyclic ketone (4) produces 1-hydroxy-4-phenylbicyclo[2,2,2]octan-3-one (5). The reduction of the keto group in compound (5) was carried out by means of a Huang-Minlon modifications of the Wolff-Kishner reduction. The reduction of the keto group has been reported in yields ranging from 20-75%. In this work, in order to ensure a maximum yield of the reduced carbonyl compound, 1-

hydroxy-4-phenylbicyclo[2,2,2]octan-3-one was first refluxed with aqueous hydrazine hydrate for 5 hours. After cooling, potassium hydroxide, and diethylene glycol were added. After arranging the apparatus for distillation, the temperature was gradually raised to 160°C and maintained at this temperature for 1 hour to remove the majority of the unreacted hydrazine hydrate. Increasing the temperature to 220°C caused nitrogen to evolve and this temperature was maintained until nitrogen evolution had ceased. This procedure yielded 1-hydroxy-4-phenylbicyclo[2,2,2]octane in over 60%.

<u>FIGURE 5</u> Synthesis of 1-hydroxy-4-phenylbicyclo[2,2,2]octane



The overall yield of 1-hydroxy-4-phenylbicyclo[2,2,2]octane in Figure 5 above is 12.48%; i.e.

$$1.\ \xrightarrow{74.7\%}\ 2.\ \xrightarrow{79.4\%}\ 3.\ \xrightarrow{53.5\%}\ 4.\ \xrightarrow{64.7\%}\ 5.\ \xrightarrow{60.8\%}\ 6.$$

59.31%   31.73%   20.53%   12.48%

Bicyclo[2,2,2]octane-1,4-diol was synthesised with a view to preparing some naphthyl esters for the study of excimer formation.

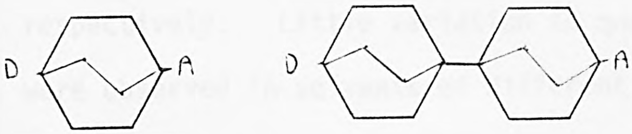
It was hoped to convert 1-hydroxy-4-phenylbicyclo[2,2,2]octane into suitable derivatives (see Sections 4.3, 4.5 and 4.6 of this chapter) with a view to investigating charge transfer reactions.

4.3 Attempted use of rigid spacer to examine charge transfer formation through a bicyclo[2,2,2]octane framework

4-Dimethylaminobenzonitrile is a compound in which the amino group is forced to tilt slightly out of the plane of the benzene ring. It was found that this compound exhibits charge transfer fluorescence. In addition, the λmax fluorescence shows a red shift as the solvent polarity increases. It is believed that a twisted intramolecular charge transfer state in the more polar solvents is probably produced. Twisted excited charge transfer states are discussed in more detail in Section 1.7 of Chapter 1.

In order to examine whether this effect can be transmitted through a rigid spacer, it was attempted to synthesise the compound 1-cyano-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane.

In compounds of the type:

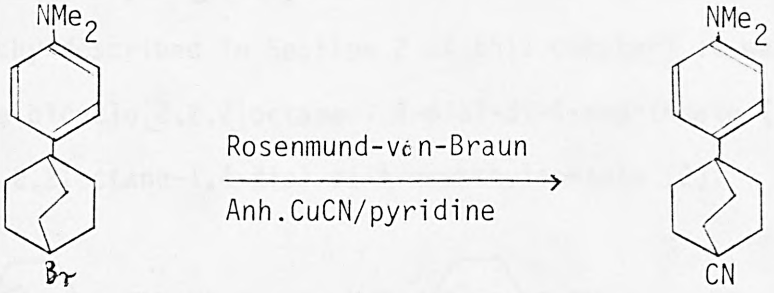


A = ACCEPTOR

D = DONOR

folding cannot occur (i.e. D and A are not able to come near each other) and the Donor and Acceptor moieties are separated by known distances. Thus if charge transfer does arise, it either occurs through space or possibly through bond interaction.

The synthesis of 1-bromo-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane from 1-hydroxy-4-phenylbicyclo[2,2,2]octane is described in Section 6 of this chapter. The replacement of the bromine group by a nitrile group to produce the desired cyano-substituted bicyclo[2,2,2]octane compound was attempted by means of a Rosemund-von-Braun reaction. This consists of heating the bromo compound with anhydrous cuprous cyanide and pyridine. Extraction of the residue with a suitable solvent followed by a subsequent purification utilising preparative thin layer chromatography successfully yielded the desired cyano compound.



Figures 6 and 7 show the fluorescence spectra of 1-cyano-4-p-N,N-dimethylaminobicyclo[2,2,2]octane in acetonitrile and cyclohexane respectively. Little variation in quantum yields of fluorescence were observed in solvents of different polarity (i.e. acetonitrile and cyclohexane). From the spectra it was concluded that the bicyclo[2,2,2]octane framework is not transmitting the charge transfer effect through its sigma bonds. The shift in λmax fluorescence which are seen are due to the perturbation of the localised anilino group ($Ph-NMe_2$).

In theory, it is expected that the efficiency of charge transfer should fall off as the distance between Donor and Acceptor increases. Unfortunately, we were not able to investigate this matter due to the difficulties encountered (see Section 2 of this chapter) in obtaining suitable amounts of starting material to effect a coupling of two bicyclo[2,2,2]octane rings.

4·4 Attempted use of rigid spacers to study excimer formation

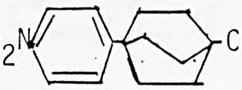
(i) The synthesis of some naphthyl esters to be used in investigating possible excimer formation

Starting with bicyclo[2,2,2]octane-1,4-diol (prepared by the method of Kapenechy described in Section 2 of this chapter) it was attempted to prepare bicyclo[2,2,2]octane-1,4-diol-di-1-naphthoate (1) and bicyclo[2,2,2]octane-1,4-diol-di-1-naphthylacetate (2).

(1)

(2)

FIGURE 6

Fluorescence spectra of Me_2NCN in (1) degassed and (2) aerated acetonitrile solution.

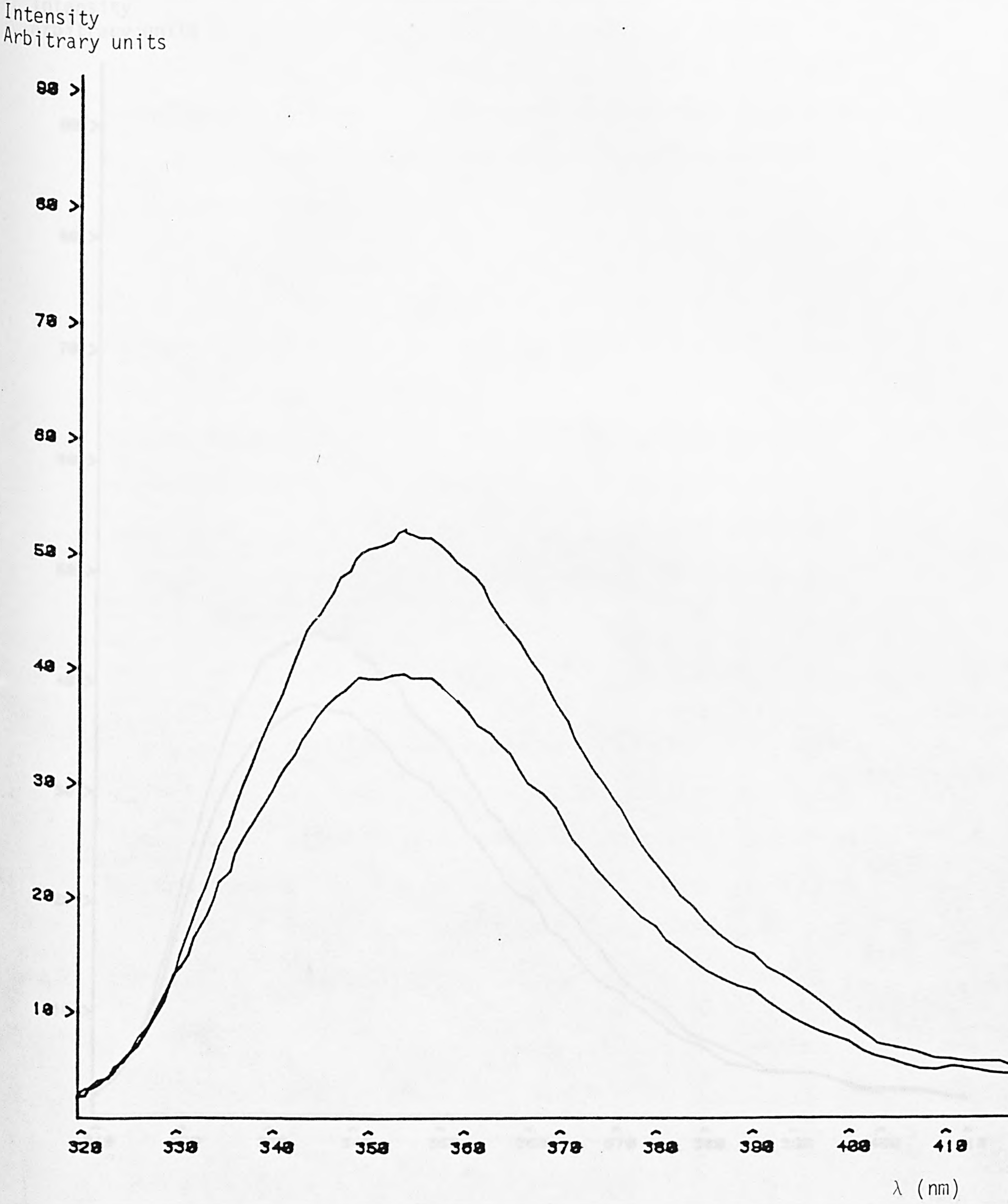
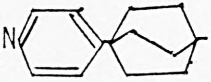
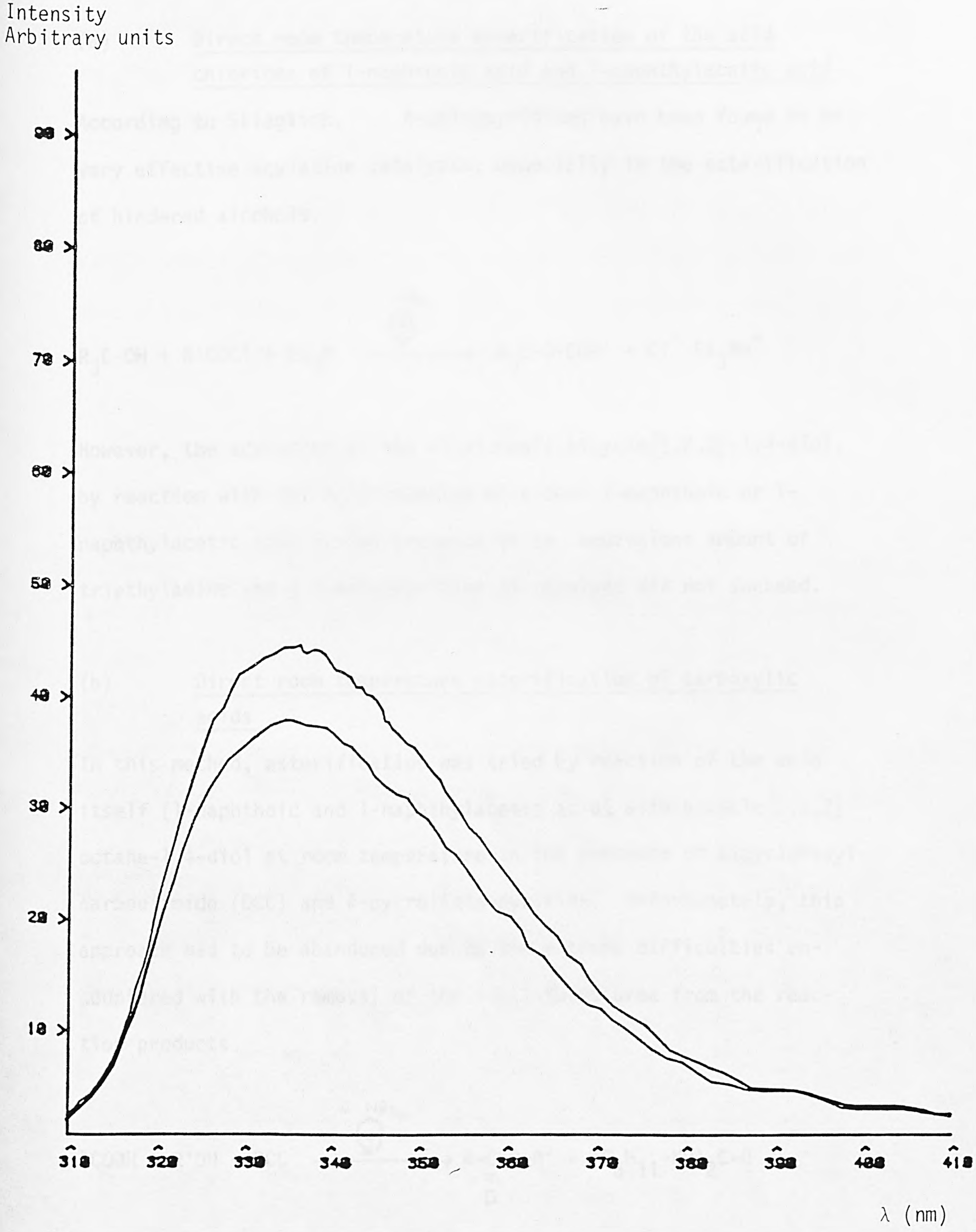


FIGURE 7

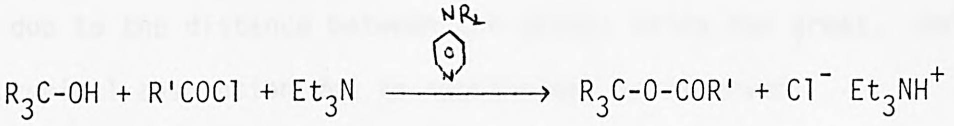
Fluorescence spectra of Me$_2$NCN in (1) degassed and (2) aerated cyclohexane solution.



The synthesis of these naphthyl esters was attempted in three ways:

(a) Direct room temperature esterification of the acid chlorides of 1-naphthoic acid and 1-naphthylacetic acid

According to Stieglich, 4-aminopyridines have been found to be very effective acylation catalysts, especially in the esterification of hindered alcohols.

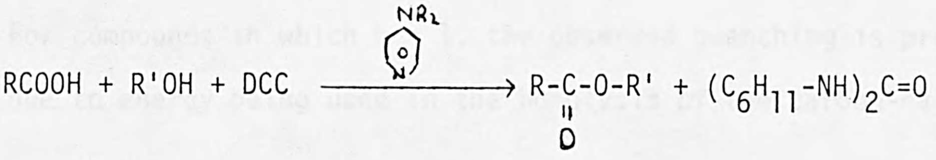


$$R_3C\text{-}OH + R'COCl + Et_3N \xrightarrow{} R_3C\text{-}O\text{-}COR' + Cl^- \; Et_3NH^+$$

However, the acylation of the di-alcohol, bicyclo[2,2,2]-1,4-diol, by reaction with the acid chloride of either 1-naphthoic or 1-naphthylacetic acid in the presence of an equivalent amount of triethylamine and a 4-aminopyridine as catalyst did not succeed.

(b) Direct room temperature esterification of carboxylic acids

In this method, esterification was tried by reaction of the acid itself (1-naphthoic and 1-naphthylacetic acid) with bicyclo[2,2,2] octane-1,4-diol at room temperature in the presence of dicyclohexylcarbodiimide (DCC) and 4-pyrrolidinopyridine. Unfortunately, this approach had to be abandoned due to the extreme difficulties encountered with the removal of the substituted urea from the reaction products.

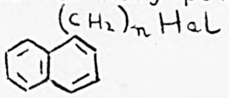


$$RCOOH + R'OH + DCC \xrightarrow{} R\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}R' + (C_6H_{11}\text{-}NH)_2C{=}O$$

(c) Reaction between the acid chloride and alcohol under reflux

This consisted of refluxing the acid chloride of 1-naphthoic acid or 1-naphthylacetic acid with bicyclo[2,2,2]-1,4-diol in the presence of pyridine. This method proved successful and the corresponding naphthyl esters were isolated. The fluorescence spectra of the esters are shown in Figures 8 and 9. From the spectra it can be seen that excimer formation had not taken place and this is due to the distance between the groups being too great. Only the typical absorption due to naphthalene is observed.

4.5 Use of rigid spacer groups to study heavy atom effects

It is known that for many polycyclic aromatic hydrocarbons linked to halogen () severe fluorescence quenching is observed. There is the possibility that triplet formation could be enhanced, via complex formation, as well as radiationless processes such as carbon-halogen bond homolysis. It has been shown that for a given halogen, fluorescence quenching decreases as the chain length increases from n = 1 to n = 3. In addition, for a given chain length, the efficiency of quenching is I > Br > Cl. It is believed that the halogeno group can behave as (i) a heavy atom quencher and (ii) as an electron donor, whereas the carbon-halogen bond can act as (i) an electron acceptor and (ii) an energy sink.

For compounds in which n = 1, the observed quenching is probably due to energy being used in the homolysis of the carbon-halogen

FIGURE 8

Fluorescence spectra of Np-CO_2  -O_2C-Np in degassed acetonitrile solution.

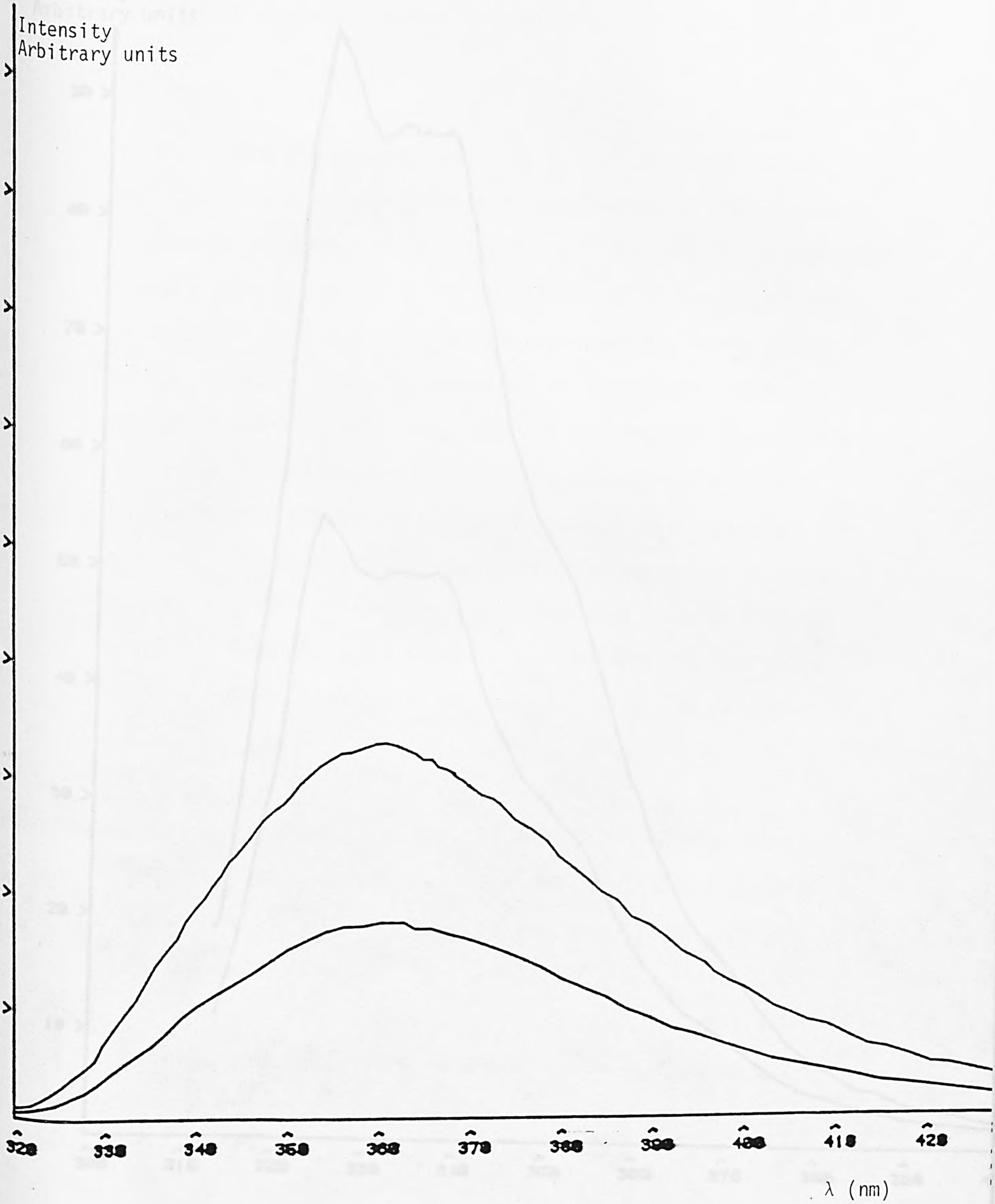
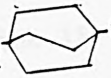
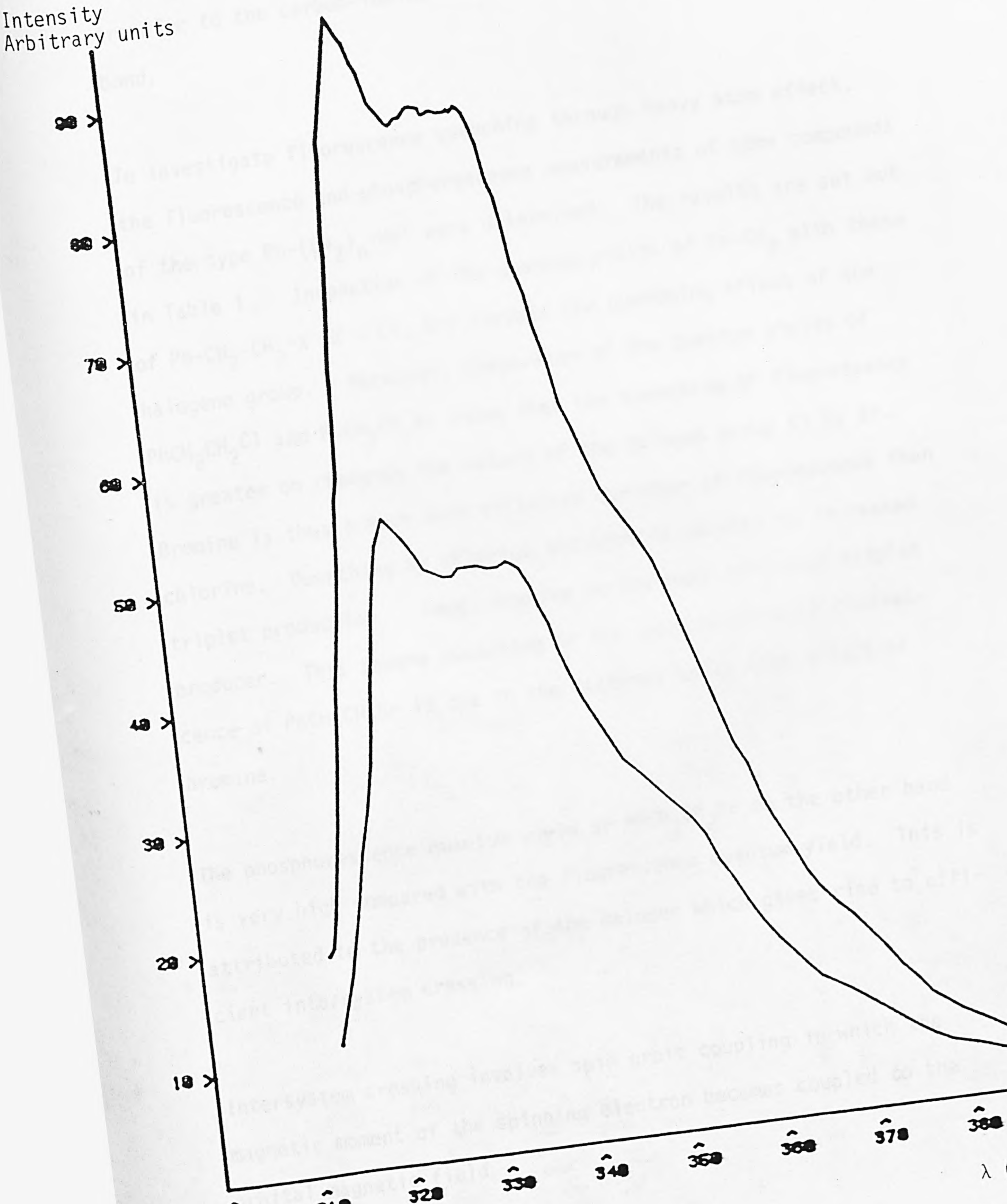


FIGURE 9

Fluorescence spectra of $NpCH_2CO_2$O_2CCH_2-Np in degassed acetonitrile solution.



bond. Triplet production by iodine is very low, and it likely that fluorescence quenching in this case could be due to energy transfer to the carbon-iodine bond resulting in homolysis of the bond.

To investigate fluorescence quenching through heavy atom effect, the fluorescence and phosphorescence measurements of some compounds of the type Ph-$(CH_2)_n$-Hal were determined. The results are set out in Table 1. Inspection of the quantum yields of Ph-CH_3 with those of Ph-CH_2-CH_2-X (X = Cl, Br) reveals the quenching effect of the halogeno group. Moreover, comparison of the quantum yields of $PhCH_2CH_2Cl$ and $PhCH_2CH_2Br$ shows that the quenching of fluorescence is greater on changing the nature of the halogen group Cl by Br. Bromine is thus a much more efficient quencher of fluorescence than chlorine. Quenching by chlorine and bromine results in increased triplet production. Here, bromine is the most efficient triplet producer. This severe quenching of the quantum yield of fluorescence of $PhCH_2CH_2Br$ is due to the external heavy atom effect of bromine.

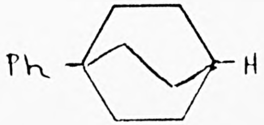
The phosphorescence quantum yield of $PhCH_2CH_2Br$ on the other hand is very high compared with the fluorescence quantum yield. This is attributed to the presence of the halogen which gives rise to efficient intersystem crossing.

Intersystem crossing involves spin orbit coupling in which the magnetic moment of the spinning electron becomes coupled to the orbital magnetic field

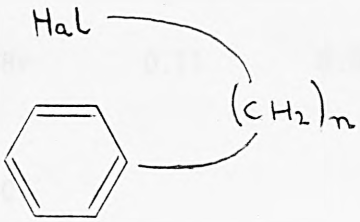
TABLE 1

QUANTUM YIELDS OF FLUORESCENCE AND PHOSPHORESCENCE

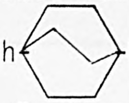
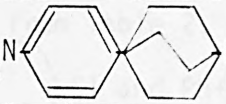
FOR $Ph(CH_2)_n$ Hal

Compound	ϕF at RT	$\phi P/\phi F$ Methylcyclohexane, $T\phi\,^oK$	ϕF	ϕP	τP sec
1. $PhCH_3$	0.14	1.09	0.31	0.34	7.0
2. $PhCH_2CH_2Cl$	0.09	3.29	0.24	0.8	2.4
3. $PhCH_2CH_2Br$	0.01	27.78	0.03	0.92	0.16
4. $PhCH_2CH_2CH_2Cl$	0.11	1.19	0.35	0.42	
5. $PhCH_2CH_2CH_2Br$	0.01	5.2	0.07(5)	0.39	1.5
6. $PhCH_2CH_2CH_2CH_2Cl$	0.12	1.16	0.3	0.35	8.0
7. $PhCH_2CH_2CH_2CH_2Br$	0.04(4)	1.59	0.18	0.29	4.0
8. 	0.045	0.36	0.25	0.09	5.2
9. 	0.044	0.35	0.20	0.07	4.8
10. 	0.035	0.43	0.20	0.09	3.2

The quantum yield of phosphorescence is reduced as the number of methylene groups is increased from 2 to 4. It can also be observed from the table that the magnitude of fluorescence quenching is decreased as the chain length is increased from n = 2 to 4 in compounds (1)-(7). With compounds of the type $Ph(CH_2)_n$-Hal the halogen can interact with the phenyl through space, i.e.



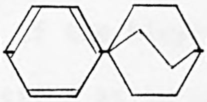
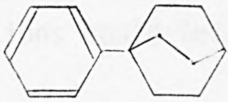
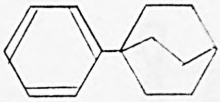
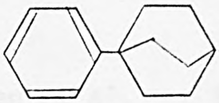
However, as the chain length increases the molecule can adopt more random conformations. This means that there will be less chance of obtaining an interaction between halogen and the chromophore.

To investigate if the above described effect could be killed, compounds of the kind PhHal (Hal = Cl and Br) were synthesised in which the phenyl ring and the halogen group are separated by the intervening rigid bicyclo[2,2,2]octane spacer unit. The synthesis of these halogeno substituted bicyclo[2,2,2]octane compounds is discussed in Section 6 of this chapter. Also a compound of the type Me_2NBr was synthesised as described in Section 6 of this chapter.

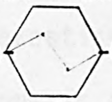
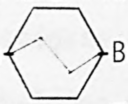
The fluorescence data of the above synthesised compounds in acetronitrile and cyclohexane are set out below (Table 2).

TABLE 2

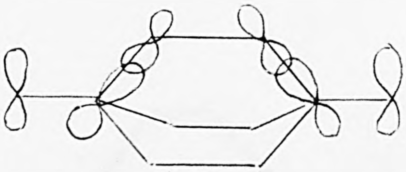
Fluorescence quantum yields of some 1,4-disubstituted bicyclo[2,2,2] octane compounds

	ϕ_F Acetonitrile		ϕ_F Cyclohexane	
	Degassed	Aerated	Degassed	Aerated
1. Me$_2$NBr	0.11	0.08	0.10	0.08
2. -Cl			0.03	0.02
3. -Br			0.03	0.02
4. -H			0.04	

The fluorescence spectra of compounds (1) to (4) in Table 2 above are shown in Figures 10 to 14.

As can be seen from Table 2, the fluorescence quantum yield of compounds PhCl and PhBr were very similar to the value obtained for PhH. The presence of the halogeno group does not increase the efficiency of intersystem crossing in the phenyl group, indicating a lack of the heavy atom effect. Also fluorescence and phosphorescence measurements for compounds (8) to (10) in Table 1 reveal no significant heavy atom effect. Thus electronic effects are not transmitted through the bicyclo[2,2,2] octane framework. This means that there is no interaction between the aromatic ring and the halogen, due to the rigid nature of the intervening bicyclo[2,2,2]octane ring. This clearly shows that the heavy atom effect is determined by the proximity of halogen to the aromatic nucleus.

The use of the bicyclo[2,2,2]octane framework as a separater poses the question as to whether the substituents at the bridgehead positions could interact by a through bond process as shown below:



Passmen et al. have shown that charge transfer by through bond interaction can occur through a study of adamantane and other suitable compounds. These results show an absence of through bond effects.

4.6 Photoinduced dehalogenation of 1-halo-4-phenylbicyclo-[2,2,2]octane compounds

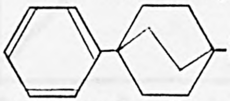
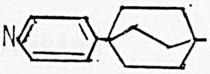
The photochemistry of aryl halides has been well studied but it would be interesting to investigate the photochemistry of compounds having an aromatic ring and halogen group separated by a rigid insulating spacer group, i.e. the bicyclo[2,2,2]octane framework. A series of 1,4-disubstituted bicyclo[2,2,2]octanes of the type -X (where X = Cl, Br, I) were synthesised. The precursor for these 1-phenyl-4-halogeno bicyclo[2,2,2]octanes is

FIGURE 10

Fluorescence spectra of Me$_2$N-Br in (1) degassed and (2) aerated acetonitrile solution.

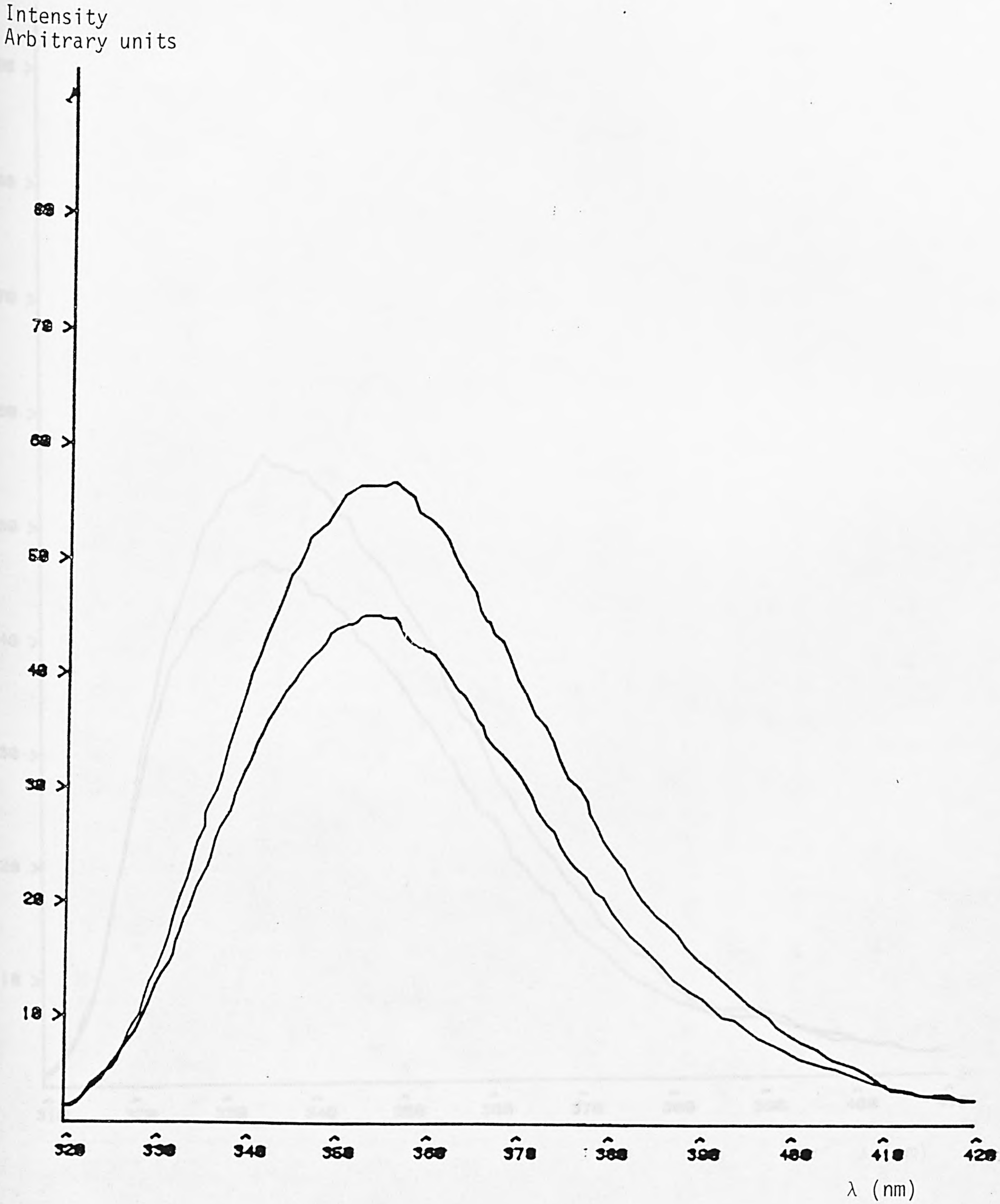
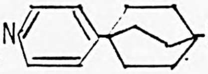


FIGURE 11

Fluorescence spectra of Me$_2$NBr in (1) degassed and (2) aerated cyclohexane solution

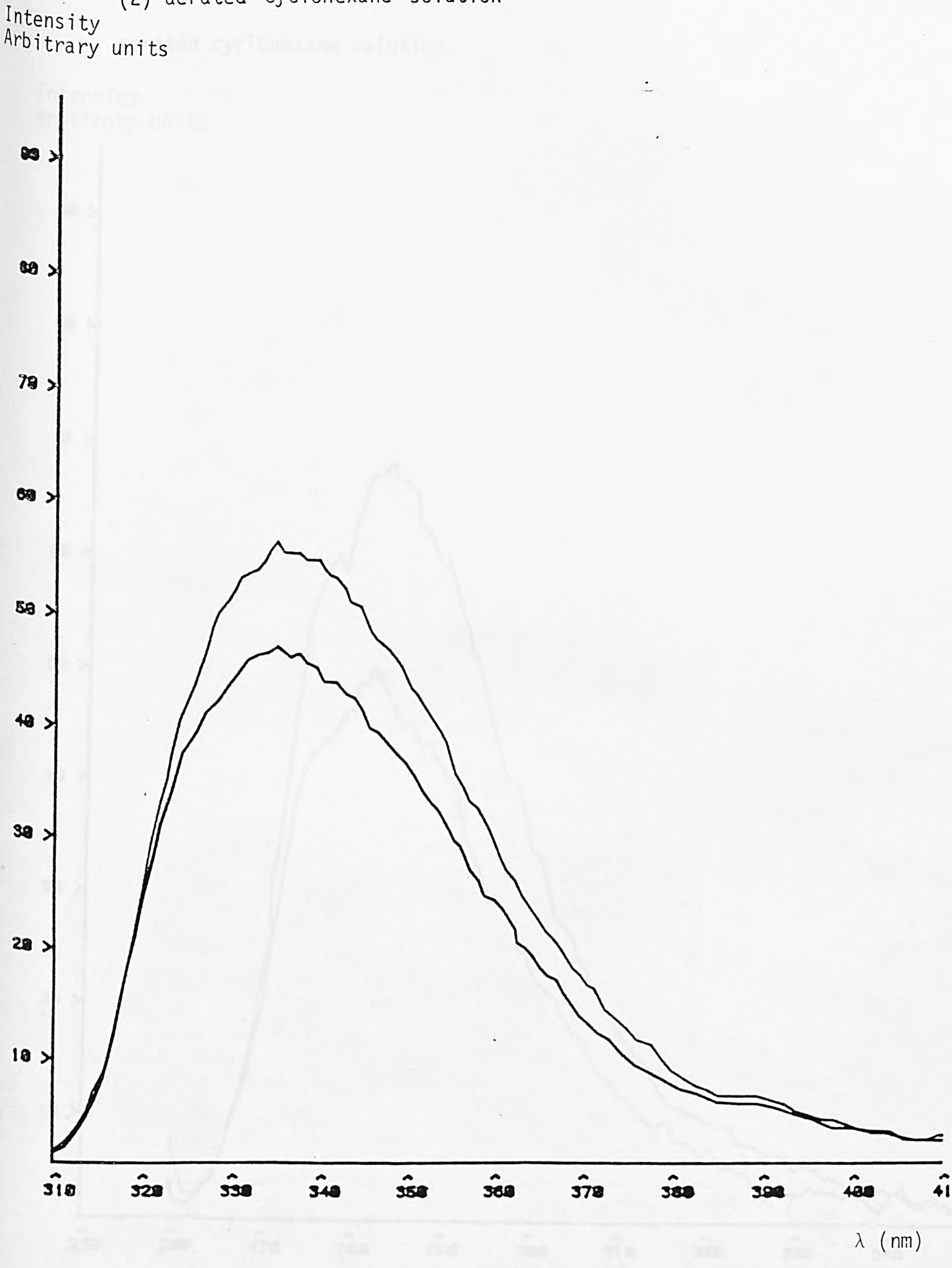
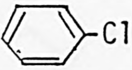


FIGURE 12

Fluorescence spectra of Ph-Cl in (1) degassed and (2) aerated cyclohexane solution.

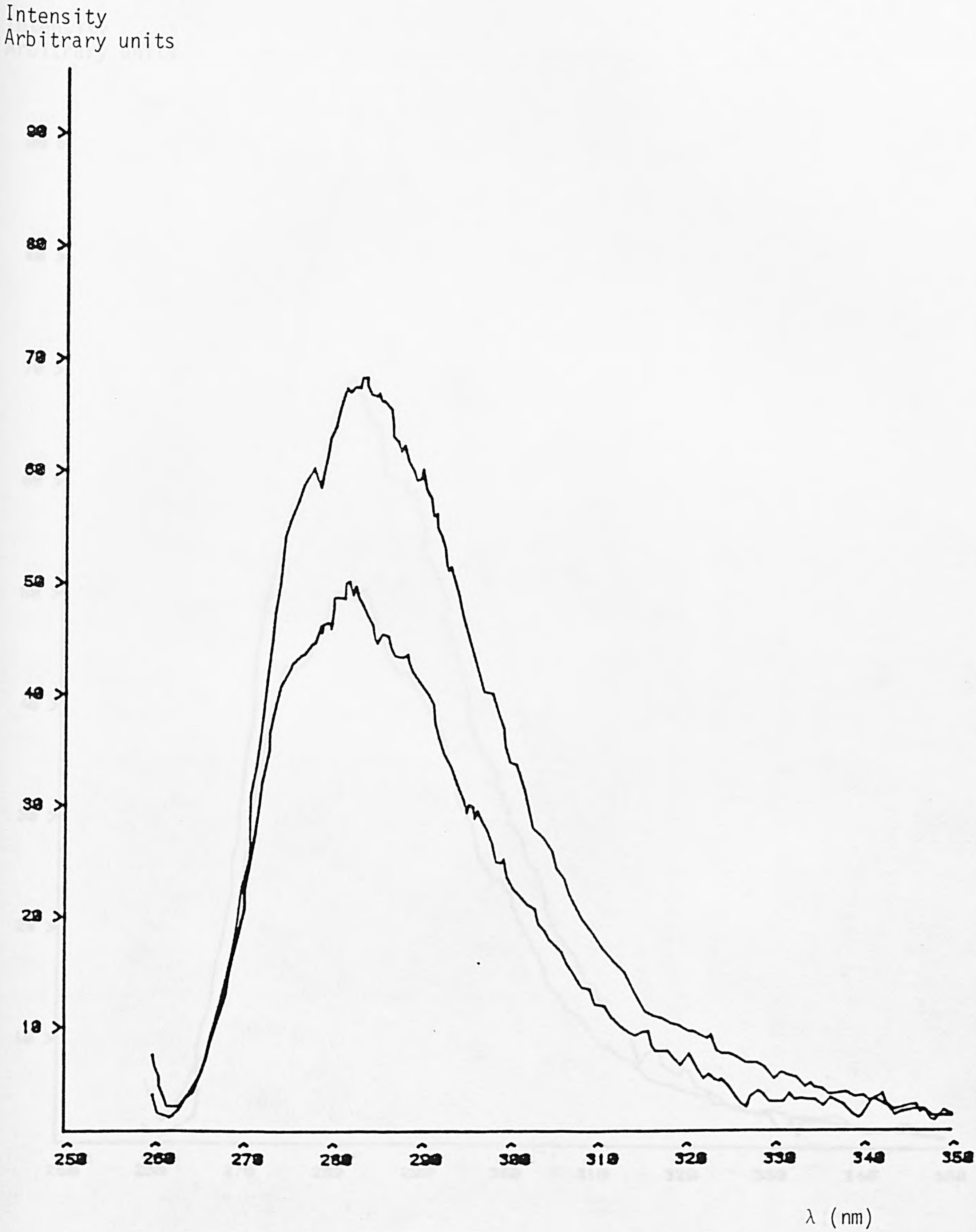


FIGURE 13

Fluorescence spectra of Ph-Br in (1) degassed and (2) aerated cyclohexane solution.

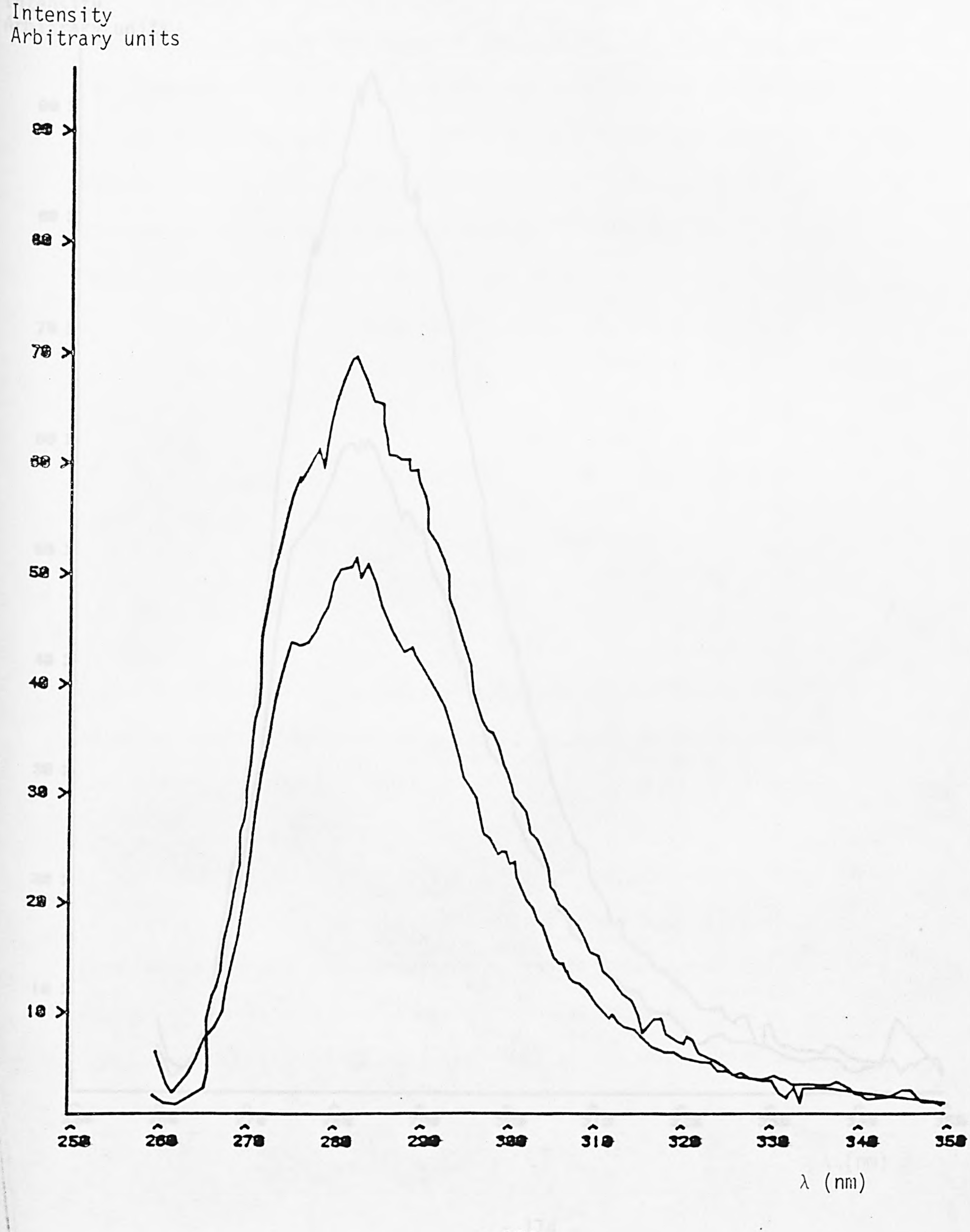
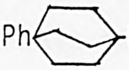
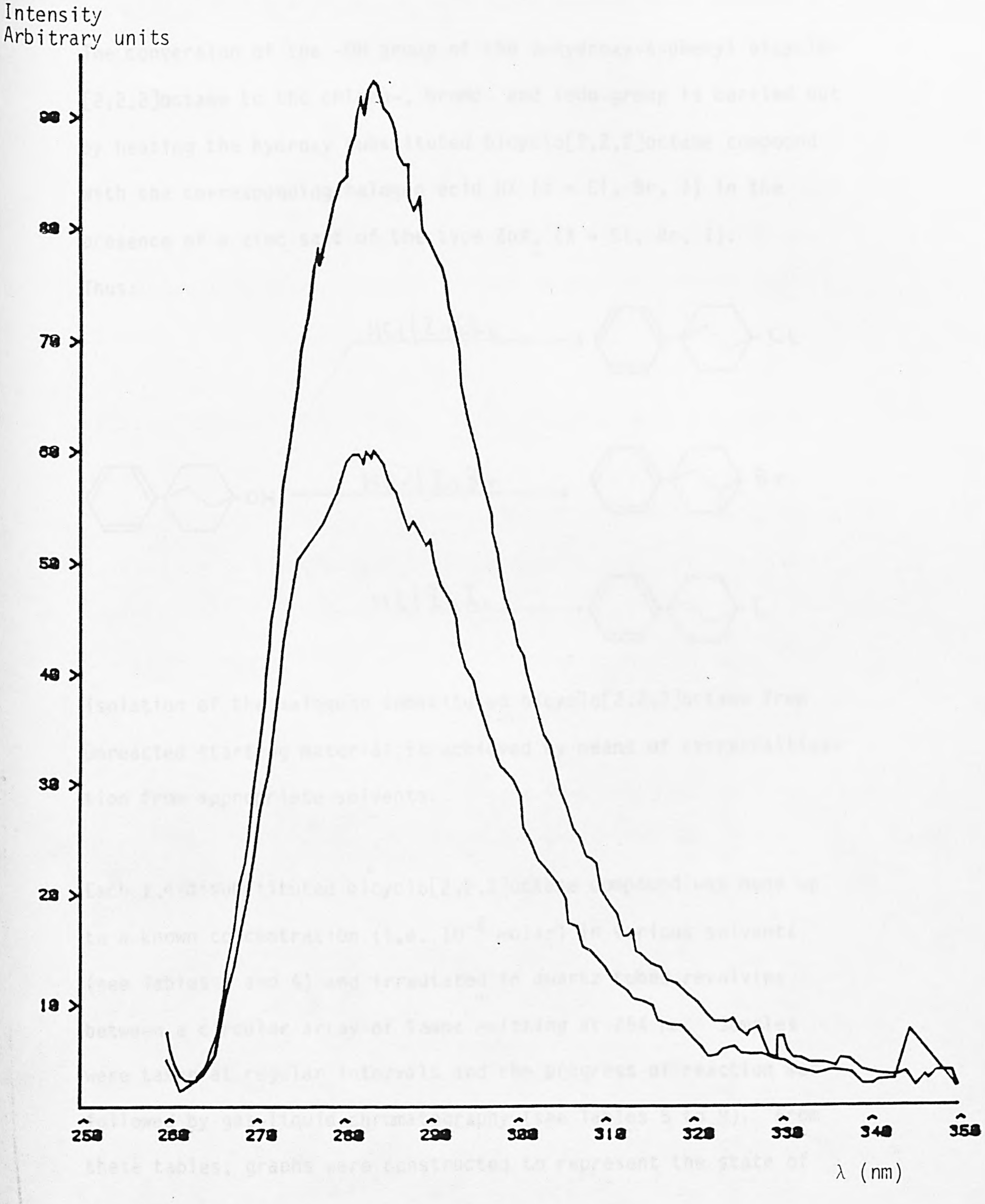


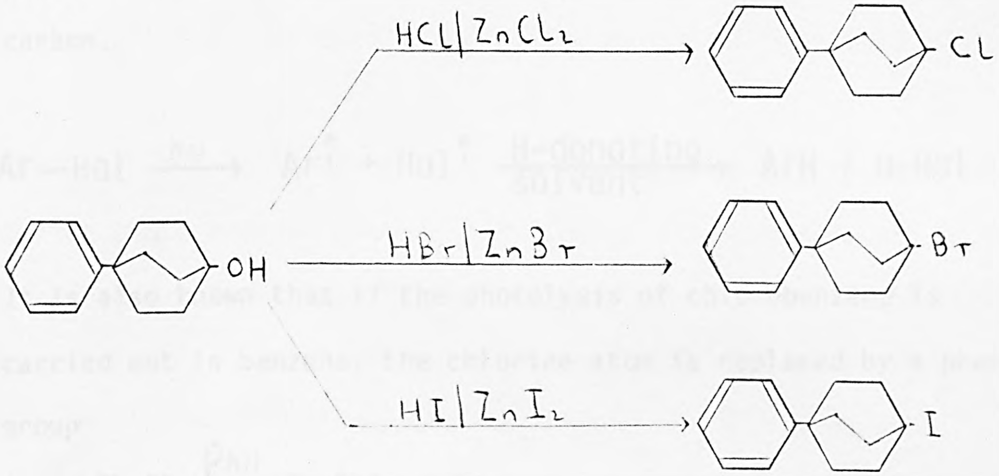
FIGURE 14

Fluorescence spectra of PhH in (1) degassed and (2) aerated cyclohexane solution.



1-phenyl-4-hydroxy bicyclo[2,2,2]octane which, as already described in Section 2 of this chapter is obtained by a relatively convenient six stage route starting from 3-phenylpropan-2-one.

The conversion of the -OH group of the 1-hydroxy-4-phenyl bicyclo-[2,2,2]octane to the chloro-, bromo- and iodo-group is carried out by heating the hydroxy substituted bicyclo[2,2,2]octane compound with the corresponding halogen acid HX (X = Cl, Br, I) in the presence of a zinc salt of the type ZnX_2 (X = Cl, Br, I). Thus:



Isolation of the halogeno substituted bicyclo[2,2,2]octane from unreacted starting material is achieved by means of recrystallisation from appropriate solvents.

Each 1,4-disubstituted bicyclo[2,2,2]octane compound was made up to a known concentration (i.e. 10^{-2} molar) in various solvents (see Tables 3 and 4) and irradiated in quartz tubes revolving between a circular array of lamps emitting at 254 nm. Samples were taken at regular intervals and the progress of reaction was followed by gas-liquid chromatography (see Tables 5 to 9). From these tables, graphs were constructed to represent the state of the reaction (see Figures 15 and 16), i.e. the progress of photochemical decomposition, if any occurring. Tables 3 and 4 indicate the times taken, without amine and in the presence of amine respectively, for some halogeno-substituted bicyclo[2,2,2]octane compounds to photolyse (dehalogenate) upon irradiation in various solvents.

Many halo-aromatic compounds homolyse upon irradiation in hydrogen donating solvents to produce aryl radicals. These aryl radicals can abstract hydrogen from the solvent to give an aromatic hydrocarbon.

$$\mathrm{Ar{-}Hal} \xrightarrow{h\nu} \mathrm{Ar}^{\dot{*}} + \mathrm{Hal}^{\dot{*}} \xrightarrow[\text{solvent}]{\text{H-donating}} \mathrm{ArH} + \text{H-Hal}$$

It is also known that if the photolysis of chlorobenzene is carried out in benzene, the chlorine atom is replaced by a phenyl group
(i.e. $\text{Ph-Cl} \xrightarrow[h\nu]{\text{PhH}} \text{Ph-Ph}$).

The irradiation of these halogeno-substituted bicyclo[2,2,2]octanes were carried out because it was thought that there may be some energy transfer from the excited phenyl group into the carbon-halogen bond.

Inspection of Table 3 reveals that the chloro compound was stable towards photolysis, i.e. dehalogenation of 1-phenyl-4-chlorobicyclo-[2,2,2]octane in acetonitrile, cyclohexane, benzene and methanol had not taken place.

From Table 3 it can be seen that there is photoreactivity upon irradiation of 1-phenyl-4-bromobicyclo[2,2,2]octane and 1-phenyl-4-iodobicyclo[2,2,2]octane. Both of the bromo and iodo compounds undergo dehalogenation in acetonitrile, cyclohexane and methanol. The iodo compound also dehalogenates in benzene, but the bromo compound shows no dehalogenation.

Because these photolysis reactions were carried out with light of 254 nm wavelength it is possible that the observed reactions were due to a significant amount of the energy absorbed at 254 nm entering the $\sigma \rightarrow \sigma^*$ transition of the carbon-halogen bond.

The lack of reactivity of 1-chloro-4-phenylbicyclo[2,2,2]octanes is due to the energy of the excited singlet and triplet state of the phenyl group being insufficient to homolyse the carbon-chlorine bond. In the case of benzene as solvent the excited singlet and triplet states of benzene and the benzene excimer also seem to be incapable of sensitizing the carbon-chlorine bond fission.

In the case of 1-bromo-4-phenylbicyclo[2,2,2]octane the observation of dehalogenation in cyclohexane, methanol and acetonitrile indicates either that light is being absorbed by the orbitals associated with the carbon-bromine bond, or else an excited state of the phenyl group is being produced which sensitizes carbon-bromine homolysis by energy transfer.

The fact that the bromo compound is unreactive when irradiated in benzene solution suggests that either the benzene is acting as a light filter and preventing excitation of the carbon-bromine bond, or else that the benzene excimer and the triplet excited state of benzene are of insufficient energy to cause homolysis. Since neat benzene is used, singlet energy transfer from the benzene to the carbon-bromine bond is precluded because of the much higher probability of benzene excimer formation.

It is surprising that triplet benzene appears to be unable to sensitize the homolysis of the carbon-bromine bond in view of the fact that triplet benzene has an energy of 83.4 Kcal mole and tert-butyl bromide has a carbon-bond strength of 63 Kcal mole. It could be that the carbon-bromine bond in the 1-bromo-4-phenylbicyclo-[2,2,2]octane is of higher energy than that in tert-butyl bromide since the fission of the carbon-bromine bond in the bicyclo[2,2,2] octane does not lead to any relief of strain.

The 1-iodo-4-phenylbicyclo[2,2,2]octane was found to dehalogenate in benzene, acetonitrile, cyclohexane and methanol. This latter result is particularly important since at the irradiation wavelength of 254 nm the benzene will absorb all the radiation and therefore the observed reaction must be resulting by energy transfer from either triplet benzene or benzene excimer to the carbon-iodine bond.

In contrast to the bromo compound the iodo compound reacts to give a near quantitative yield of 1-phenyl-4-methoxybicyclo[2,2,2] octane compound and less than 5% of hydrocarbon. This solvolysis reaction occurs via a non-planar carbonium reaction.

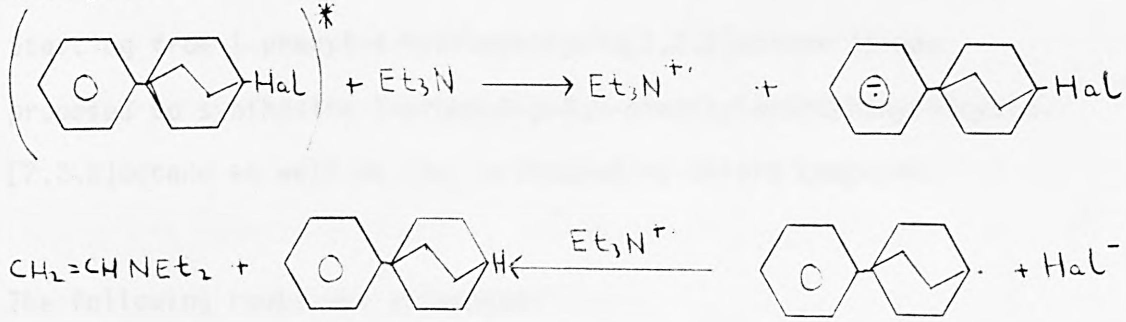
4.6.1 Amine assisted dehalogenation

The rate of dechlorination of many chloroaromatics in polar solvents is enhanced in the presence of a tertiary amine i.e.

$$\mathrm{ArCl^{*} + Et_3N \longrightarrow (ArCl)^{\bar{\cdot}}\ \ (Et_3N)^{+*} \longrightarrow Ar^{\cdot} + Cl^{-} + Et_3N^{\cdot}}$$

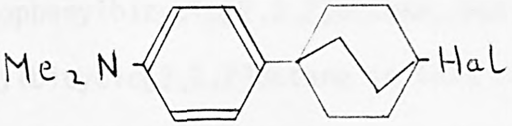
$$\mathrm{ArH + HCl + CH_2{=}CHNEt_2}$$

Because of the accelerating effect of amines on the photoinduced homolysis of carbon-halogen bonds the following reaction was attempted.



The photolysis times for some halogeno substituted bicyclo[2,2,2]-octanes in various solvents in the presence of amine are shown in Table 4. Comparison of Tables 3 and 4 reveal that for those halo compounds that dehalogenate, the rate of dehalogenation is enhanced if an amine is present during the photolysis. Thus in both cyclohexane and acetonitrile, decomposition of the bromo and iodo compounds, to produce the hydrocarbon, was accelerated by the addition of triethylamine. The chloro-compound however did not show any reactivity. Amine assisted dehalogenation reactions probably involve excited complex formation. The excited singlet states of these compounds could result in the production of excited complexes or radical ions with electron donors. Amine assisted dehalogenation reactions were also attempted intramolecularly, i.e. by having the amino group on the molecule itself, namely on the para position of the aromatic ring.

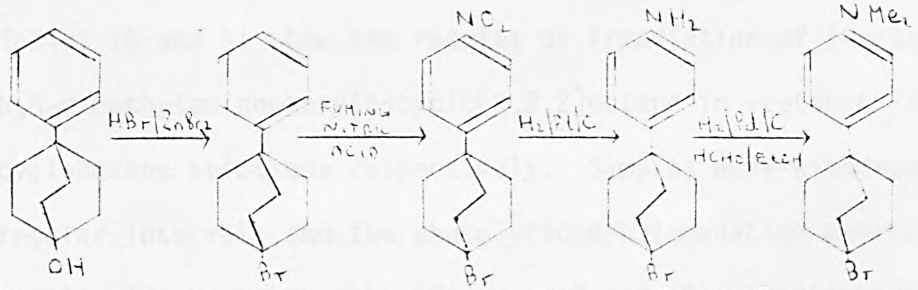
In order to carry out intramolecular amine assisted dehalogenation studies it was attempted to synthesise compounds of the type



Hal = Br and Cl

Starting from 1-phenyl-4-hydroxybicyclo[2,2,2]octane it was proposed to synthesise 1-bromo-4-p-N,N-dimethylaminophenylbicyclo-[2,2,2]octane as well as the corresponding chloro compound.

The following route was attempted:



The preparation of 1-bromo-4-phenylbicyclo[2,2,2]octane from the hydroxy compound has already been discussed at the beginning of this section. The nitration of the aromatic ring to give 1-bromo-4-p-nitrophenylbicyclo[2,2,2]octane was carried out by means of fuming nitric acid in a medium of acetic anhydride. Because of the risk of unwanted side products formed from substitution on other positions on the ring, several recrystallisations were necessary in order to obtain the desired para compound. 1-Bromo-4-p-amino-phenylbicyclo[2,2,2]octane was obtained by hydrogenation of the nitro compound using a palladium on carbon catalyst. 1-Bromo-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane was successfully isolated by hydrogenation of the amino compound with a palladium on carbon catalyst in ethanol in the presence of formaldehyde.

The preparation of the corresponding 1-chloro-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane, but starting from 1-chloro-4-phenylbicyclo[2,2,2]octane in this case was also successfully carried out utilising the above described technique.

It is interesting to note that the conversion of the nitro group to the dimethylamino group ($-NO_2 > NMe_2$) may be performed in one step by hydrogenating the nitro compound in ethanol using a Pd/C catalyst in the presence of formaldehyde.

Tables 10 and 11 show the results of irradiation of 1-bromo-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane in acetonitrile and cyclohexane solutions respectively. Samples were withdrawn at regular intervals and the photolytic dehalogenation monitored by gas liquid chromatography (Figures 17 and 18). Rapid homolysis of the carbon-halogen bond was observed due to the presence of the dimethylamino group. The dehalogenation of the bromo compound was faster in the more polar solvent (i.e. acetonitrile) than in cyclohexane. The reactivity of the chloro-compound is probably due to the dimethylanilino group having a low ionisation potential.

The results clearly show that the amines enhance the rate of dehalogenation. In the case of 1-halo-4-phenylbicyclo[2,2,2]octanes there is the possibility that the electron either enters the excited carbon-halogen bond or else it enters the aryl group to generate the aryl radical anion. There is also the possibility that the amine is excited in these reactions. It is the excited amine which donates the electron. However, excited amines are non-fluorescent in non-polar solvents and their ability to denote electrons from their excited states in these solvents has not been proven. Since the electron transfer processes are bimolecular it is more likely that the electron is transferred from the amine to the aryl group since the excited state of the aryl group has a much longer lifetime than the excited state of the carbon-halogen bond. Thus one may classify these reactions as mediated electron transfer reactions. In the case of 1-halo-4-dimethylaminophenylbicyclo-[2,2,2]octanes, electron transfer reaction is likely to be intramolecular. The greater ease of oxidation of the dimethylamino group compared with triethylamine favours the reaction.

Summary:

Certain 1-halo-4-phenylbicyclo[2,2,2]octanes dehalogenate upon irradiation in various solvents. Irradiation in cyclohexane or acetonitrile affords the hydrocarbon (i.e. the halogeno group is replaced by a hydrogen). For those halo bicyclo[2,2,2]octanes that dehalogenate in benzene solution, the halogen group is replaced by a phenyl group.

The bicyclo[2,2,2]octane unit is not transferring electronic effects through its rigid structure. The case for electron transfer through space could possibly be occurring on the basis of the amine accelerated dehalogenation of the halo biphenyls. Recently two papers have appeared in which bicyclo[2,2,2]octane frameworks have been used to separate a porphyrin group from a quinone. The efficiency of electron transfer between the groups is highly dependent upon the porphyrin structure and in the case of the tetraaryl porphyrin, electron transfer is ineffficient.

TABLE 3

The photolysis of halo-substituted bicyclo[2,2,2]octane compounds in the absence of amine, in various solvents.

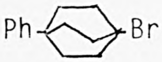
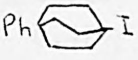
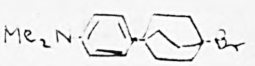
Bicyclo[2,2,2]octane			
Concentration	10^{-2} M	10^{-2} M	10^{-2} M
Acetonitrile	2 hours*		No reaction
Cyclohexane	4 hours	8 hours	No reaction
Benzene	75 minutes	No reaction	No reaction
Methanol	6 hours	6 hours	No reaction

TABLE 4

The photolysis of halo-substituted bicyclo[2,2,2]octane compounds in various solvents, in the presence of amine (2 x 10^{-2} M trimethylamine

Bicyclo[2,2,2]-octane				
Concentration	10^{-2} M	10^{-2} M	10^{-2} M	10^{-2} M
Acetonitrile	30 minutes	2.5 hours	No reaction	110 minutes
Cyclohexane	80 minutes	3 hours	No reaction	3.5 hours

*The times given in Tables 3 and 4 are the times taken for the total disappearance of starting material.

TABLE 5

Photolysis of 1-phenyl-4-iodobicyclo[2,2,2]octane in acetonitrile, in the presence of triethylamine.

Time (Minutes)	Area of product peak	Internal standard 1-Bromonaphthalene	Area of product peak corrected
10	0.375	1.5	0.477
20	0.42	1.34	0.598
30	0.675	1.72	0.749
40	0.75	1.91	0.75
50	0.68	1.68	0.77
60	0.675	1.73	0.79
70	0.63	1.46	0.82
80	0.645	1.44	0.85
100	0.6	1.32	0.86

TABLE 6

Photolysis of 1-phenyl-4-iodobicyclo[2,2,2]octane in cyclohexane, in the presence of triethylamine.

Time (Minutes)	Area of product peak	Internal standard 1-Bromonaphthalene	Area of product peak corrected
20	0.308	2.22	0.39
40	0.42	2.24	0.52
60	0.65	2.5	0.73
80	0.57	2.11	0.76
100	0.65	2.82	
120	0:.675	2.64	

TABLE 7

Photolysis of 1-phenyl-4-iodobicyclo[2,2,2]octane in benzene.

Time (Minutes)	Area of product peak	Internal standard 1-Bromonaphthalene	Area of product peak corrected
45	0.36	2.67	
75	0.24	1.495	0.42
90	0.325	2.04	

TABLE 8

Photolysis of 1-phenyl-4-bromobicyclo[2,2,2]octane in acetonitrile in the presence of triethylamine

Time (Minutes)	Area of product peak	Internal standard 1-Bromonaphthalene	Area of product peak corrected
45	0.99	3.33	1.11
90	1.78	3.76	1.78
135	1.70	3.36	1.90
180	1.87	3.75	1.87
225	1.26	2.52	1.87

TABLE 9

Photolysis of 1-phenyl-4-bromobicyclo[2,2,2]octane in cyclohexane in the presence of triethylamine

Time (Minutes)	Area of product peak	Internal standard 1-Bromonaphthalene	Area of product peak corrected
1	0.36	3.18	0.44
2	0.432	3.737	0.46
3	0.6	3.48	0.68
4	0.621	3.48	0.70
5	0.625	3.465	0.71
6	0.78	3.95	0.78

TABLE 10

Photolysis of 1-bromo-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]-octane in acetonitrile in the presence of propylamine

Time (Minutes)	Area of product peak	Internal standard 1-Bromonaphthalene	Area of product peak corrected
0	7.11	12.1	9.99
10	5.85	11.45	8.68
20	5.75	13.1	7.46
50	3.18	15.3	3.53
70	2.45	17	2.45
90	1.55	15.45	1.70
110	0.90	15.9	0.96

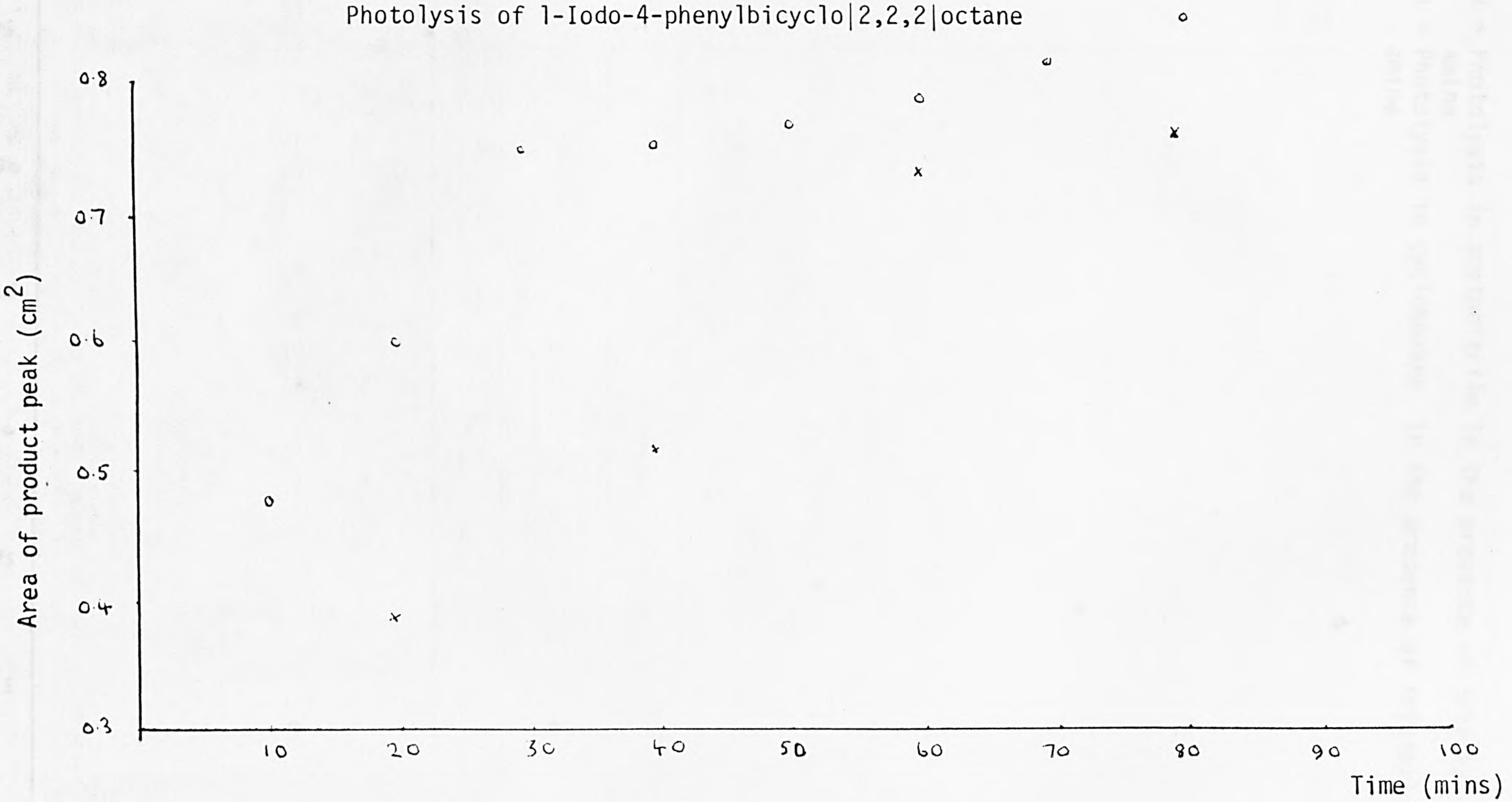
TABLE 11

Photolysis of 1-bromo-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]-octane in cyclohexane in the presence of triethylamine

Time (Minutes)	Area of product peak	Internal standard 1-Bromonaphthalene	Area of product peak corrected
0	3.3	5.9	5.93
30	3.0	9.8	3.24
60	2.09	4.35	5.09
90	1.417	4.3	3.49
120	1.365	5.85	2.47
150	1.48	6.7	2.34
180	1.49	10.6	1.49
210	0.9	4.9	1.94 (6)
240	1.1	6.25	1.86
300	0.95	6.25	1.61

FIGURE 15

Photolysis of 1-Iodo-4-phenylbicyclo|2,2,2|octane



o = Photolysis in acetonitrile in the presence of triethylamine

x = Photolysis in cyclohexane in the presence of triethlamine

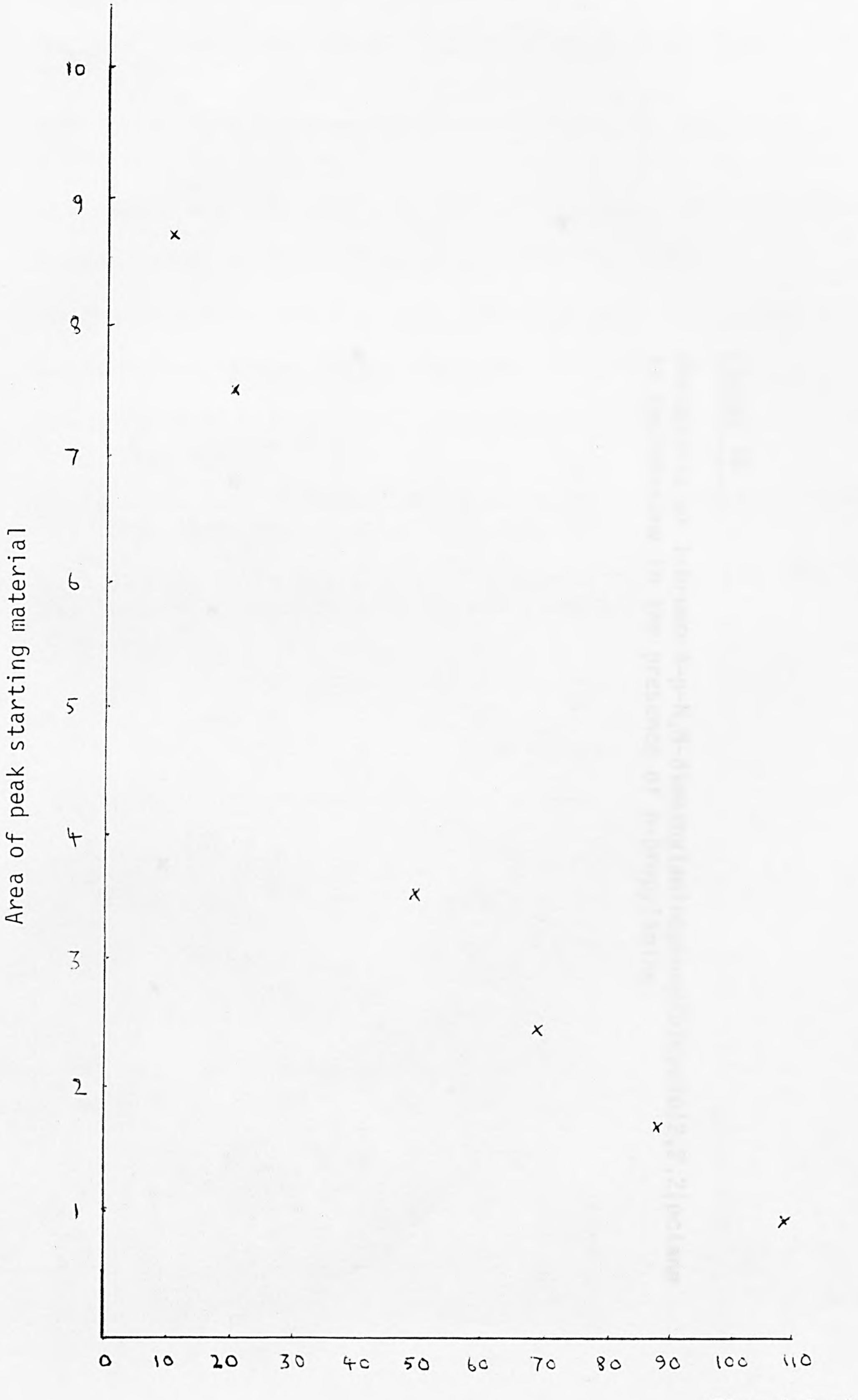
FIGURE 16

Photolysis of 1-bromo-4-phenylbicyclo|2,2,2|octane

x = Photolysis in acetonitrile in the presence of triethylamine
o = Photolysis in cyclohexane in the presence of triethylamine

FIGURE 17

Photolysis of 1-bromo-4-p-N,N-dimethylaminophenylbicyclo|2,2,2|-octane in acetonitrile in the presence of n-propylamine



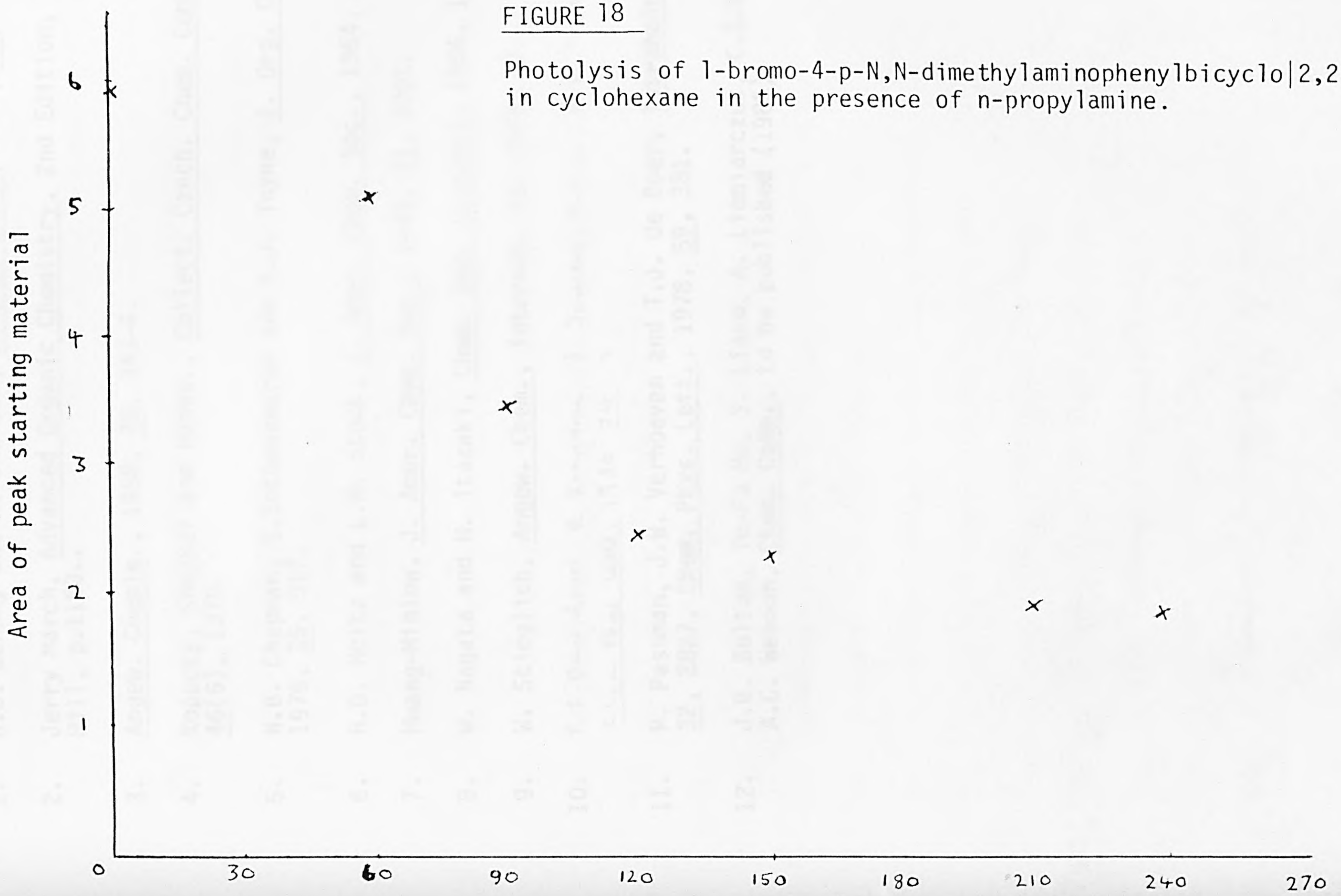


FIGURE 18

Photolysis of 1-bromo-4-p-N,N-dimethylaminophenylbicyclo|2,2,2|octane in cyclohexane in the presence of n-propylamine.

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List of Compounds Synthesised

1. Dimethyl-1,4-dibromocyclohexane-1,4-dicarboxylate.
2. Dimethylcyclohexa-1,3-diene-1,4-dicarboxylate.
3. 1,4-Dimethoxycarbonylbicyclo[2,2,2]oct-2-ene-5,6-dicarboxylic anhydride.
4. 1,4-Dimethoxycarbonylbicyclo[2,2,2]octane-2,3-dicarboxylic acid.
5. 1,4-Dimethoxycarbonylbicyclo[2,2,2]oct-2-ene.
6. 1,4-Dimethoxycarbonylbicyclo[2,2,2]octane.
7. 1,4-Diacetoxybicyclo[2,2,2]oct-5-ene-2,3-dicarboxylic acid anhydride.
8. 1,4-Diacetoxybicyclo[2,2,2]octane-2,3-dicarboxylic anhydride.
9. 1,4-diacetoxybicyclo[2,2,2]octane-2,3-dicarboxylic acid.
10. 1,4-Diacetoxybicyclo[2,2,2]oct-2-ene.
11. 1,4-Diacetoxybicyclo[2,2,2]octane.
12. Bicyclo[2,2,2]-1,4-diol.
13. 3-Acetyl-1,5-dicyano-3-phenylpentane.
14. 3-Acetyl-3-phenylpentane-1,5-dicarboxylic acid.
15. 4-Acetyl-4-phenylcyclohexane.
16. 1-Hydroxy-4-phenylbicyclo[2,2,2]octan-3-one.
17. 1-Hydroxy-4-phenylbicyclo[2,2,2]octane.
18. 1-Bromo-4-phenylbicyclo[2,2,2]octane.
19. 1-Chloro-4-phenylbicyclo[2,2,2]octane.
20. 1-Iodo-4-phenylbicyclo[2,2,2]octane.
21. 1-Cyano-4-phenylbicyclo[2,2,2]octane.
22. 1-Bromo-4-p-nitrophenylbicyclo[2,2,2]octane.

23. 1-Bromo-4-p-aminophenylbicyclo[2,2,2]octane.

24. 1-Bromo-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane.

25. 1-Chloro-4-p-nitrophenylbicyclo[2,2,2]octane.

26. 1-Chloro-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane.

27. 1-Cyano-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane.

28. Bicyclo[2,2,2]octane-1,4-diol-di-1-naphthoate.

29. Bicyclo[2,2,2]octane-1,4-diol-di-1-naphthyl acetate.

30. 4-Carboxy-1-methoxycarbonylbicyclo[2,2,2]octane.

Dimethyl 1,4-dibromocyclohexane-1,4-dicarboxylate

A mixture of cis- and trans-cyclohexane-1,4-dicarboxylic acids (148 g, 0.86 mole) - prepared by hydrogenating terephthalic acid with a Raney nickel catalyst in 2N-aqueous sodium hydroxide[1], were refluxed with redistilled thionyl chloride (390 ml, 5.33 mole) until the solution clarified (5 hours). Anhydrous conditions were observed by performing the experiment under dry nitrogen. At this stage, bromine (94.7 mls, 1.84 moles) was added dropwise during 6 hours, and the mixture was refluxed for 2 days. The mixture was irradiated with a 100 W tungsten lamp for the final 24 hr. The excess of bromine and thionyl chloride were removed on a rotavapor and anhydrous methyl alcohol (345 ml) was slowly added to the residue cooled in ice. The mixture was then refluxed for 3 hours. After adding methyl alcohol (172 ml) to dissolve the dimethyl cis-1,4-dibromocyclohexane-cis-1,4-dicarboxylate, the residual solid was filtered off and recrystallised from methanol-acetone (1:1) to give dimethyl trans-1,4-dibromocyclohexane-trans, 1,4-dicarboxylate (148.4 g, 146-147°C (lit. 148-150°C, 48.1%).

A yellow waxy solid (125 g, 40.6%) was obtained after removing the methyl alcohol from the filtrate which consisted chiefly of dimethyl cis-1,4-dibromocyclohexane-cis-1,4-dicarboxylate, but also containing a small amount of the trans isomer.

The total yield of cis/trans-dimethyl-1,4-dibromo-cyclohexane-1,4-dicarboxylates was 273.4 g (88.7%).
NMR ($CDCl_3$) δ, 2.68 (s, 8H, $-CH_2$), 3.84 (s, 6H, $-CH_3$).

Dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate

Dimethyl 1,4-dibromocyclohexane-1,4-dicarboxylate (148.4 g, 0.414 mole) was refluxed with excess pure dry (KOH) pyridine (190 ml) for 16 hr. After cooling, the mixture was diluted with water (1.25 litres). The precipitated solid was filtered off, dried in a vacuum desiccator ($CaCl_2$) and recrystallised from light petroleum (b.p. 60-80°C) to give dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate, m.p. 82-84°C (lit. 83-85°C). cite

Yield of diene from trans-bromo ester = 34.8 g (43%)
cis- bromo ester = 17.6 g (25.7%)

NMR ($CDCl_3$) δ, 2.65 (s, 4H, $-CH_2$), 3.75 (s, 6H, $-CH_3$), 7.1 (s, 2H, -CH=).

IR (nujol mull) 3020, 2950, 2890, 2830, 1705 (C=O), 1645, 1582 (C=C), 1430, 1380, 1255, 1190, 1090, 955, 920, 880, 805, 765, 720 cm^{-1}.

1,4-Dimethoxycarbonylbicyclo[2,2,2]oct-2-ene-5,6-dicarboxylic anhydride

Dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate (52.4 g, 0.267 mole) and maleic anhydride (78.6 g, 0.80 mole) in chlorobenzene (450 ml) were heated under vigorous reflux (temperature of oil bath maintained at 160°C) for 18 hours. The solution was then allowed to cool and placed in a refrigerator for 24 hours. The solid was filtered off to give 1,4-dimethoxy carbonyl bicyclo[2,2,2]oct-2-ene-5,6-dicarboxylic anhydride (37.5 g, 47.7%), m.p. 179-181°C (lit. 181-183°C).

NMR ($CDCl_3$) δ, 1,6-1,8 (m, 2H), 2.0-2.25 (m, 2H), 3.9 (s, 6H, CH_3), 6.9 (2H, CH=).

IR (nujol mull), 1865, 1780 (anhydride), 1745 (ester), 1620 (C=C) cm^{-1}.

1,4-Dimethoxycarbonylbicyclo[2,2,2]octane-2,3-dicarboxylic acid

1,4-Dimethoxycarbonylbicyclo[2,2,2]oct-2-ene-5,6-dicarboxylic anhydride (41.3 g, 0.14 mole) was heated with a solution of potassium bicarbonate (28.1 g, 0.28 mole) in distilled water (150 ml) on a steam bath for 20 minutes. 10% Palladium-on-carbon catalyst (1 g) was added to the cold product, and the mixture was hydrogenated. The calculated amount of hydrogen was absorbed in about 2 hours. After filtering off the catalyst, the mixture was oxidated to Congo Red with concentrated hydrochloric acid and cooled. The white solid which was precipitated was recrystallised from hot water to give 1,4-dimethoxycarbonylbicyclo[2,2,2]octane-2,3-dicarboxylic acid (38.14 g, 87.1%), m.p. 166°C (lit 166-168°C).

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1,4-Dimethoxycarbonylbicyclo[2,2,2]oct-2-ene

1,4-Dimethoxycarbonylbicyclo[2,2,2]octane-2,3-dicarboxylic acid (19.8 g, 0.064 mole) was dissolved in 200 ml dry dimethyl sulphoxide. Dry pyridine (11.4 ml, 0.14 mole) was added and the apparatus was kept under an atmosphere of dry nitrogen. After adding lead-tetraacetate (31.4 g, 0.0708 mole), the mixture was sonicated for 1 hour. The mixture was poured into water and extracted with benzene (4 x 100 ml). The benzene layer was washed with sodium carbonate solution (2N), hydrochloric acid (2N), water (2 x to remove acid), dried ($HgSO_4$). The benzene was removed on a rotavapor and the residue was recrystallised from petroleum ether (40/60) to give 5 g, 1,4-dimethoxycarbonylbicyclo[2,2,2]oct-2-ene (35% yield).

solid or liquid,

NMR ($CDCl_3$) δ, 1.75 (sym. m, 8H, $-CH_2$), 3.85 (6H, $-OCH_3$), 6.65 (2H, CH=).

IR (nujol mull) 2970, 1735, 1625 (weak), 1450, 1340, 1268, 1145, 1090, 855, 740 cm^{-1}.

1,4-Dimethoxycarbonylbicyclo[2,2,2]octane

5 g, 1,4-dimethoxycarbonylbicyclo[2,2,2]oct-2-ene was dissolved in ethanol and hydrogenated using 10% palladium-on-carbon catalyst. The theoretical amount of hydrogen was absorbed within 75 minutes. The catalyst was removed by filtration, and evaporation of the filtrate gave a residue which, on recrystallisation from petroleum spirir (40/60) yielded 1,4-dimethoxycarbonylbicyclo[2,2,2]octane (4.7 g, 94%) m.p. 97-99° (lit^{a} 98-100, 100-101°C). cite

NMR ($CDCl_3$) δ, 1.85 (s, 12H, $-CH_2-$), 3.75 (s, 6H, $-OCH_3-$).

IR (nujol) 1725, 1250, 1190, 1075, 990, 940, 855, 830, 790, 740 cm^{-1}.

Preparation of 1,4-Diacetoxybicyclo[2,2,2]oct-5-ene-2,3-dicarboxylic acid anhydride

A mixture of 1,4-cyclohexanedione (5.6 g, 0.05 mole), isopropenyl acetate (15 g, 0.15 mole), and maleic anhydride (4.9 g, 0.05 mole) with a small amount of p-toluene sulphonic acid were refluxed for 1½ hours. The apparatus was then set up for distillation, and after all the acetone had distilled off the product, a dark brown very viscous liquid - was allowed to stand overnight to form a mass of crystals. These were washed with cold ethanol and collected by suction. After recrystallisation from benzene 3.24 g (43.5%) of pure 1,4-diacetoxybicyclo[2,2,2]oct-5-ene-2,3-dicarboxylic acid anhydride was obtained.

NMR δ ($CDCl_3$), 1.7-1.95 (m, 4H, $-CH_2-$), 2.1 (s, 6H, CH_3), 4.2 (s, 2H, -CH), 6.3 (s, 2H, -CH=).

IR (nujol), 1790, 1780, 1755, 1735, 1370, 1230, 1080, 920 cm^{-1}.

1,4-Diacetoxybicyclo[2,2,2]octane-2,3-dicarboxylic anhydride

5 g, of 1,4-diacetoxybicyclo[2,2,2]oct-5-ene-2,3-dicarboxylic acid anhydride was hydrogenated in 40 ml THF using Pd/C catalyst. Yield 5 g (99%).

NMR ($CDCl_3$) δ, 1.98 (s, 8H, $-CH_2-$), 4.45 (d, 2H, -CH).

IR (nujol mull) 1785, 1735, 1370, 1235, 1070, 915 cm^{-1}.

1,4-Diacetoxybicyclo[2,2,2]octane-2,3-dicarboxylic acid

5 g of 1,4-diacetoxybicyclo[2,2,2]octane -2,3-dicarboxylic anhydride in 21 ml potassium bicarbonate (15%) was heated on a water bath with stirring until dissolution. After cooling and acidification with conc. HCl, a pale yellow solid was precipitated which on recrystallisation from 50% acetic acid gave 4.9 g of pure 1,4-diacetoxybicyclo[2,2,2]octane-2,3-dicarboxylic acid.

NMR $(CD_3)_2SO$ δ, 2.0 (s, 8H, $-CH_2-$), 4.45 (d, 2H, -C-H).

IR (nujol mull) 1785, 1735, 1375, 1235, 1065, 910 cm^{-1}.

1,4-Diacetoxybicyclo[2,2,2]oct-2-ene

Oxygen was bubbled through 32 ml pyridine for 15 min. 4g 1,4-Diacetoxybicyclo[2,2,2]octane-2,3-dicarboxylic acid and 8.5 g lead tetra-acetate were added and the mixture was heated at 65-70°C, oxygen still being bubbled through the mixture. After cooling, the mixture was decomposed with excess dilute nitric acid (1:2) and extracted with ether. The combined ether extracts were washed with potassium bicarbonate solution, saturated sodium chloride, and dried ($HgSO_4$). Subsequent removal of ether, recrystallisation of residue from 50% acetic acid, gave a yellow waxy solid. Yield 1.9 g (66%).

NMR ($CDCl_3$) δ, 1.83 (s, 8H, $-CH_2$), 2.0 (s, 6H, CH_3), 6.23 (s, 2H, -C-H).

IR (nujol mull) 2880, 1730, 1375, 1245, 1085 cm^{-1}.

1,4-Diacetoxybicyclo[2,2,2]octane

4.9 g of 1,4-Diacetoxybicyclo[2,2,2]oct-2-ene in 40 ml THF was hydrogenated using Pd/C catalyst. Yield 4.9 g (99%).

NMR ($CDCl_3$) δ, 1.91 (s, 6H, CH_3), 2.06 (s, 12H, $-CH_2-$).

IR (nujol mull) 2880, 1730, 1380, 1360, 1260, 1245, 1055, 925 cm^{-1}.

Bicyclo[2,2,2]octane-1,4-diol

1.6 g, of 1,4-Diacetoxybicyclo[2,2,2]octane in 25 ml methanol containing 2 g sodium hydroxide and 2 ml water was refluxed for 2 hours. The mixture was cooled, acidified with dilute hydrochloric acid, and evaporated in vacuum. After extracting the residue with boiling anhydrous acetone, evaporation of solvent gave a solid m.p. 189-190°C (lit. 187°C).

NMR ($CDCl_3$) δ, 1.58 (s, 12H, $-CH_2-$), 3.95 (s, 2H, HO-).

IR (nujol mull) 3300, 2945, 2870, 1465, 1350, 1115, 1095, 920, 825, 650 cm^{-1}.

C.H.N. analysis, $C_8H_{14}O_2$. Found C, 67.62%, H, 9.74%
Calc. C, 67.57%, H, 9.92%.

3-Acetyl-1,5-dicyano-3-phenylpentane

3-Phenylpropan-2-one (53.6 g, 0.4 mole) was added to t-butanol (30 ml) with stirring (apparatus under nitrogen). Triton B - Benzyltrimethyl ammonium hydroxide (40% in methanol), (4 g, 10 ml) was added, causing an orange colouration, and soon after acrylonitrile (42.4 g, 0.8 mole) was added dropwise with vigorous stirring and maintaining the temperature at 20-25°C. After stirring the mixture for 2 hours, the pale green paste was washed with ethanol and the white solid collected by suction filtration. Recrystallisation from ethanol gave 3-acetyl-1,5-dicyano-3-phenylpentane 71.7 g (74.7% yield).

3-Acetyl-3-phenylpentane-1,5-dicarboxylic acid

139 g, 0.58 mole, 3-acetyl-1,5-dicyano-3-phenylpentane was refluxed with sodium hydroxide (92.6 g, 2.31 mole) in 280 ml water for 8 hours. The reaction mixture was heated with decolourising charcoal for a further ½ hour, filtered, acidified and placed in a refrigerator overnight. The precipitated solid was recrystallised from hot water to give 127.9 g, 3-acetyl-3-phenylpentane-1,5-dicarboxylic acid (79.4% yield). m.p. 167-168°C (lit. 168-170°C).

4-Acetyl-4-phenylcyclohexanone

3-Acetyl-3-phenylpentane-1,5-dicarboxylic acid (44.5 g, 0.16 mole) and 112 ml acetic anhydride were heated in a distillation apparatus, the apparatus being arranged in order to allow the acetic acid produced during the reaction to slowly distill off. Raising the temperature of the oil bath to 250°C and maintaining it at this temperature ensured complete removal of acetic acid and excess acetic anhydride. After cooling, the residue was distilled under reduced pressure (b.p. 164-167, 2 mm Hg) to give a white waxy solid. Yield of 4-acetyl-4-phenylcyclohexanone 18.5 g (53.5%). m.p. 76-77°C (lit.^{e} 76-77°C, 78°C), b.p. 164-167°C/2 mm (lit 163-166°C/2 mm, 163-165°C/2 mm). ab

1-Hydroxy-4-phenylbicyclo[2,2,2]octan-3-one

4-Acetyl-4-phenylcyclohexanone (25 g, 0.11 mole) was added portionwise to a solution of potassium hydroxide (38.8 g, 0.69 mole) in dry ethyl alcohol (137 ml). After vigorously shaking the mixture for about 5 hours in order to dissolve the solid lumps, a pale yellow solid had precipitated. 175 ml water was added and the precipitated product was filtered off and recrystallised from ethanol-water (2:1) to give 1-hydroxyl-4-phenylbicyclo[2,2,2]octan-3-one (16.2 g, 64.7%). m p ?

1-Hydroxy-4-phenylbicyclo[2,2,2]octane

1-Hydroxy-4-phenylbicyclo[2,2,2]octan-3-one (16 g, 0.07 mole) was refluxed with aqueous hydrazine hydride (92.6 ml of 98-100% w/w) hydrate for 5 hours. After cooling the mixture, potassium hydroxide (20.8 g, 0.37 mole) and diethylene glycol (130 ml) was added, the apparatus was arranged for distillation, and the mixture was slowly heated in an oil bath maintaining the temperature at 160°C for 1 hour to ensure removal of most of the unreacted hydrazine hydrate. Raising the temperature of the reaction mixture slowly to 220°C resulted in evolution of nitrogen, and this temperature was maintained for about 2 hours until the evolution of nitrogen ceased. The reaction mixture was cooled, poured into water and washed with ether. The whole apparatus was washed out with ether, and the distillate was neutralised with 2N hydrochloric acid and shaken with ether. The ether extracts were combined, washed with 2N hydrochloric acid, water and dried (Mg SO_4). Removal of solvent left a solid which, on recrystallisation from cyclohexane gave 1-hydroxy-4-phenylbicyclo[2,2,2]octane (9.1 g, 60.8%). m.p. 115-116°C (lit.? 115-117°C, 122-123°C).

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1-Bromo-4-phenylbicyclo[2,2,2]octane

1-Hydroxy-4-phenylbicyclo[2,2,2]octane (5 g, 0.025 mole) was added to zinc bromide (25 g, 0.11 mole) in 48% hydrobromic acid (50 ml). The temperature of the mixture was maintained at 60-70°C for 7 hours with stirring. The mixture was cooled, poured into water and shaken with ether. The ether layer was washed with water and dried (Mg SO_4). The solid remaining after evaporation of solvent, was recrystallised from ethanol to give 1-bromo-4-phenylbicyclo[2,2,2]-octane. Yield 5.3 g, 81%. m.p. 107-108°C (lit.[2] 107-108°C, 109-110°C).

cite

NMR (CDCl$_3$) δ, 1.85-2.30 (12H, m), 7.12-7.33 (5H, m).

CHN analysis, $C_{14}H_{17}Br$: Found C, 63.41%, H, 6.46%, Br, 30.13%
Calc. C, 63.45%, H, 6.41%, Br, 30.03%.

1-Chloro-4-phenylbicyclo[2,2,2]octane

A mixture of 1-hydroxy-4-phenylbicyclo[2,2,2]octane (0.5 g, 0.0025 mole), 5 ml, Lucas reagent (68 g, $ZnCl_2$ dissolved in 45 ml concentrated hydrochloric acid) was heated with stirring at 130-140°C overnight. The mixture was allowed to cool and poured into ice-water (100 ml). The solid was filtered off, dried and recrystallised from petroleum ether (60-80°C), ethanol (1:1) to give 1-chloro-4-phenylbicyclo[2,2,2]octane. Yield 0.34 g (63%), m.p. 88-89°C (lit. 90-91°C). cite

NMR ($CDCl_3$) δ, 1.85-2.30 (12H, m), 7.10-7.35 (5H, m).
IR 985, 880, 761, 697, 540 cm^{-1}.

1-Iodo-4-phenylbicyclo[2,2,2]octane

1-Hydroxy-4-phenylbicyclo[2,2,2]octane (0.5 g, 0.0025 mole), 2 ml glacial acetic acid, 2.5 ml hydriodic acid (55%) and zinc oxide (0.6 g) were heated together to 110°C ovenight. The mixture was cooled, poured into water and extracted with ether. The organic layer was washed with water, dilute sodium bicarbonate solution, dilute sodium thiosulphate solution, water, dried ($MgSO_4$). Removal of the solvent left a white powder, which on recrystallisation from ethanol gave 0.65 g, 1-iodo-4-phenylbicyclo[2,2,2]octane. Yield 83.3%. m.p. 123-125°C (lit. 126-126°C). cite

NMR ($CDCl_3$) δ, 1.85-2.15 (6H, m), 2.45-2.75 (6H, m), 7,10-7.35 (5H, m).
IR 1495, 970, 760, 705, 698, 538 cm^{-1}.

1-Cyano-4-phenylbicyclo[2,2,2]octane

A mixture of 1-bromo-4-phenylbicyclo[2,2,2]octane (1 g, 0.00375 mole), cuprous cyanide (1.25 g, 0.014 mole), and pyridine (6.5 ml) were slowly heated to 210°C in a distillation apparatus. After the pyridine had distilled, the apparatus was allowed to cool and the residue was extracted with benzene for 24 hours. Removal of benzene left a solid which was recrystallised from methanol to give 1-cyano-4-phenylbicyclo[2,2,2]octane (0.37 g, 48.28%).

NMR ($CDCl_3$) δ, 1.90-2.36 (12H, m), 7.4-7.6 (5H, m).

1-Bromo-4-p-nitrophenylbicyclo[2,2,2]octane

1.2 g (0.0045 mole) 4-bromo-1-phenylbicyclo[2,2,2]octane was dissolved in 24 ml acetic anhydride, with stirring at 25°C. Fuming nitric acid (600 µℓ, 0.0136 mole) was added slowly during 30 minutes from a micrometer syringe. The mxiture was stirred for 3 hours, poured into water and extracted with ether. The organic layer was washed with dilute sodium carbonate solution, water and dried (Mg SO_4). The solvent was removed to give a residue which on recrystallisation from ethanol (three times) yielded 1-bromo-4-p-nitrophenylbicyclo[2,2,2]octane, 0.6 g, 42.8%, m.p. 147-148°C (lit. 150-153°C).

NMR ($CDCl_3$) δ, 1.85-2.30 (12H, m), 7.43 (2H, d), 8.13 (2H, d).

IR 2950, 2875 (CH_2), 1520, 1350, 855, 755 (NO_2), 3090, 1600 (aromatic), 825 (1,4-disubstitued benzene), 695 cm^{-1}.

1-Bromo-4-p-aminophenylbicyclo[2,2,2]octane

1-Bromo-4-p-nitrophenylbicyclo[2,2,2]octane (0.3 g, 0.009 mole) was hydrogenated in 25 ml ethanol using a Pd/C catalyst. After filtration the solvent was removed and the product recrystallised from petroleum ether (40/60) to give 0.22 g, 1-bromo-4-p-aminophenylbicyclo[2,2,2]octane (88%), m.p.

NMR ($CDCl_3$) δ, 1.78-2.42 (12H, m), 3.44-3.58 (2H, s), 6.48-7.10 (4H, m).

IR, 3450, 3390, 2840, 2910, 1615, 1470, 1280 cm^{-1}.

CHN analysis $C_{14}H_{18}NBr$. Found C, 59.97%, H, 6.53%, N, 4.81%
Calc. C, 60.01%, H, 6.47%, N, 5.00%

1-Bromo-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane

1-Bromo-4-p-nitrophenylbicyclo[2,2,2]octane (0.3 g, 0.009 mole) was hydrogenated in 40 ml ethanol, containing 1 ml formaldehyde, using Pd/C catalyst. On removal of the catalyst by filtration and subsequent removal of solvent on a rotavapor, the product was recrystallised from petroleum ether (40/60) to give 0.23 g, 1-bromo-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane (85.2%). m.p. 168.5-170.5°C.

NMR ($CDCl_3$) δ, 1.96-2.50 (12H, m), 2.95 (6H, S), 6.68-7.32 (4H, m),

IR 3600, 3125, 2910, 2830, 1615, 1520, 1310, 1100, 815 cm^{-1}.

CHN analysis, $C_{16}H_{22}NBr$, Found C, 62.47% H, 7.21%, N, 4.30%.
Calc. C, 62.34%, H, 7.19%, N, 4.54%

1-Chloro-4-p-nitrophenylbicyclo[2,2,2]octane

0.25 g, 0.0011 mole, 1-chloro-4-phenylbicyclo[2,2,2]octane was dissolved in 5 ml acetic anhydride, with stirring at 25°C. Fuming nitric acid (150 μℓ, 0.0033 mole) was slowly added during 30 minutes from a micrometer syringe. After stirring for 4½ hours, the mixture was poured into water and extracted with ether. The ethereal layer was washed with dilute sodium carbonate solution, water and dried (Mg SO_4). Removal of solvent gave a residue which was recrystallised three times from ethanol to give 0.18 g, 61.4% 1-chloro-4-p-nitrophenylbicyclo[2,2,2]octane, m.p. 130-132°C (lit. 128-130°C).

NMR ($CDCl_3$) δ, 1.89-2.33 (12H, m), 7.43 (2H, d), 8.13 (2H, d).

IR 1595, 1515, 1350, 980, 850 cm^{-1}.

1-Chloro-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane

1-Chloro-4-p-nitrophenylbicyclo[2,2,2]octane (0.1 g) 0.0037 was hydrogenated in 25 ml ethanol - containing 1 ml formaldehyde, using Pd/C catalyst. After removal of the catalyst by filtration, the solvent was removed on a rotavapor, the residue was recrystallised from petroleum ether (40/60) to give a white solid, 1-chloro-4-p-N,N-dimethylaminobicyclo[2,2,2]octane. Yield 0.04 g, 41%.

NMR ($CDCl_3$) δ, 1.78-2.44 (12H, m), 2.90 (6H, s), 6.58-7.24 (4H, m).

IR 3635, 3540, 2910, 2830, 1710, 1610, 1510, 1350, 810 cm^{-1}.

1-Cyano-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane

1-Bromo-4-p-N,N-dimethylaminophenylbicyclo[2,2,2]octane (0.1g, 0.00032 mole), cuprous cyanide (0.12 g, 0.00128 mole) and pyridine (0.6 ml) were slowly heated to 210°C in a distillation apparatus. After the pyridine had distilled off, the apparatus was allowed to cool and the residue was extracted with refluxing benzene for 24 hours. Removal of benzene left a solid which was recrystallised from methanol to give 1-cyano-4-p-N,N-dimethylaminobicyclo[2,2,2]octane.

This was further purified by preparative thin layer chromatography (10% ethyl acetate, 90% methyl dichloride) to give a white solid 0.04 g, 48.2%.

NMR ($CDCl_3$) δ, 1.60-2.08 (12H, m), 2.88 (6H, s), 6.36-7.08 (4H, m).

IR 2910, 2215, 2215, 1620, 1610, 1510, 1340, 810.

CHN analysis $C_{17}H_{22}N_2$, Found C, 80.27%, H, 8.72%, N, 11.01%
Calc. C, 78.50%, H, 8.43%, N, 10.69%

Mass spectrum: m/e (relative intensity) 254 (M^+, 16), 239 (M^+, $-CH_3$, 3), 227 (M^+, -CN, 3), 226 (M^+, HCN, 9).

M, 16 ?

Bicyclo|2,2,2|octane-1,4-diol-di-1-naphthoate

0.35 g (0.002 mole) of 1-naphthoic acid was refluxed with 0.5 ml (0.004 mole) oxalyl chloride in sodium dried benzene for 2 hours to form the acid chloride. The acid chloride was added dropwise to a solution of bicyclo|2,2,2|octane 1,4-diol (0.142 g, 0.001 mole) and pyridine (0.003 mole, 0.24 g) in benzene for 5 days. The whole procedure was performed under dry nitrogen. The solution was coded, water was added and extracted with chloroform. The chloroform layer was washed with sodium carbonate solution, water, and dried. Subsequent removal of solvent and recrystallisation of the residue from benzene yielded a solid (0.141 g).

NMR ($CDCl_3$) δ, 1.85-2.30 (12H, m), 7.2-8.1 (14H, m).

CHN analysis Found C, 79.69%, H, 5.81%
Calc. C, 79.98%, H, 5.815%

Bicyclo|2,2,2|octane-1,4-diol-di-1-naphthylacetate

1.5 ml oxalyl chloride (0.01 mole) was added to 0.93 g (0.005 mole) of 1-naphthylacetic acid in sodium dried benzene and refluxed for

2 hours, under nitrogen to give the corresponding acid chloride. The acid chloride in benzene was then added dropwise to bicyclo-[2,2,2]octane-1,4-diol (0.142 g, 0.001 mole) and pyridine (0.237 g, 0.003 mole) in sodium dried benzene and refluxed for 3 days. After this period, the reaction mixture was cooled and water was added. This was followed by extraction with chloroform, washing with sodium carbonate solution, water and dried ($Mg\ SO_4$). After removal of the solvent the residue was recrystallised from benzene to give a solid (0.13 g).

NMR ($CDCl_3$) δ, 1.85-2.30 (12H, m), 4.1 (2H, s), 4.3 (2H, s), 7.2-8.1 (14H, m).

CHN analysis	Found C, 80.05%,	H, 6.40%
	Calc. C, 80.31%,	H, 6.317%

4-Carboxy-1-methoxycarbonylbicyclo[2,2,2]octane

1,4-Dimethoxycarbonylbicyclo[2,2,2]octane (3.5 g) was refluxed with a mixture of potassium hydroxide (0.9 g), methanol (16.5 ml) and water (1.6 ml) for 7 hours. The mixture was cooled, poured into water and extracted with ether. The organic phase was washed with water and dried ($Mg\ SO_4$). Subsequent removal of the solvent gave recovered di-ester. The aqueous phase was heated to drive off any dissolved ether, and acidified to Congo-Red. The precipitated acids were washed with chloroform (3 x 50 ml), and the aqueous phase was filtered to remove any insoluble dicarboxylic acid. The chloroform layer was chilled and any dicarboxylic acid which had precipitated was filtered off. The filtrate was dried ($Mg\ SO_4$) and the solvent removed. The residue was recrystallised from benzene to give 0.95 g (28.96% yield) of 4-carboxy-1-methoxycarbonylbicyclo[2,2,2]octane.

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