TO MY PARENTS

THE PHOTOCHEMISTRY
OF SOME
DONOR-ACCEPTOR SYSTEMS

by

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Declaration

I, the undersigned, declare that this thesis represents the sole work of the author.

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INDEX

INTRODUCTION

Chapter One.

Chapter Two.

DISCUSSION

Chapter Three.

Chapter Four.

Experimental

Chapter Five.

ABSTRACT

Irradiation of Donor-Acceptor systems often leads to the formation of radical cation-radical anion pairs (via photoinduced electron transfer) and subsequent ground state reactions of these ion pairs can give rise to reaction products. We have been particlarly interested in two electron deficient aryl halides 3,4,5,6-tetrachlorophthalonitrile (TCPN) and 3,4,5,6-tetrachloro-N-methylphthalimide (Cl_4NMP) as possible electron acceptors in such photoinduced electron transfer reactions. Their photochemical reactions with various potential donor molecules (including several aromatic hydrocarbons and a range of alkenes) have been studied. Several different modes of reactivity were observed and these have been discussed in relation to a possible electron transfer mechanism being operative.

Abbreviations used in this thesis.

TCPN	3,4,5,6-Tetrachlorophthalonitrile
Cl$_4$NMP	3,4,5,6-Tetrachloro-N-methylphthalimide
2-Me-THF	2-Methyltetrahydrofuran
Cl$_4$NEP	3,4,5,6-Tetrachloro-N-methylphthalimide
THF	Tetrahydrofuran
NMP	N-Methylphthalimide
TFPN	3,4,5,6-Tetrafluorophthalonitrile
TCTN	2,3,5,6-Tetrachloroterephthalonitrile

CHAPTER ONE

INTRODUCTION

The vast majority of photochemical reactions occur when a molecule is raised to either the first excited singlet state (S_1) or the first excited triplet state (T_1). Molecules in these states possess a large excess of energy and they tend to revert to the ground state (S_0) as soon as possible. A chemical species can degrade itself to the ground state by one of several general pathways[1,2]:

(a)Fluorescence

(b)Internal Conversion

(c)Intersystem Crossing

(d)Phosphorescence

(e)Vibrational Relaxation

(f)Photochemical Reaction

Fluorescence

In fluorescence an excited species passes from a higher excited state to a lower one of the same multiplicity, with the emission of a photon. It is a rapid process ($K_f \sim 10^6 - 10^9 s^{-1}$) and for the polyatomic molecules encountered in organic chemistry, the transition is usually $S_1 - S_0$.

Internal Conversion

Internal conversion is a radiationless transition between isoenergetic states of the same multiplicity. Such transitions are extremely rapid and account for the negligible emission from upper states. However internal conversion from the first excited singlet state ($S_1 - S_0$) is so much slower that fluorescence can compete.

Intersystem Crossing

Intersystem Crossing is a radiationless transition between states of different multiplicity. The radiationless deactivation of the lowest triplet state ($T_1 - S_0$) competes with normal phosphorescence. The intersystem crossing ($S_1 - T_1$) or ($S_1 - T_n$) which is competitive with fluorescence, is the process by which the triplet manifolds are usually populated.

Phosphorescence

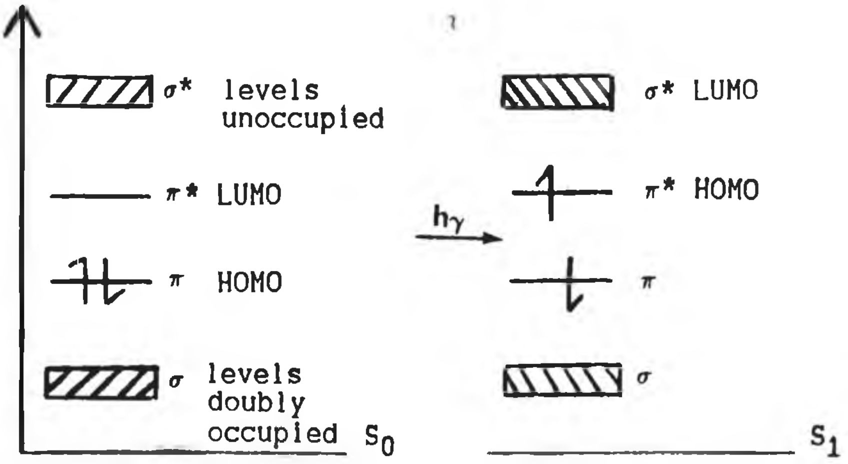
In phosphorescence an excited species passes from a higher excited state to a lower one , of different multiplicity, with the emission of a photon. This process being spin forbidden, has a much smaller rate constant ($K_p \sim 10^{-1}-10^4 s^{-1}$) than that for fluorescence.The transition is typically T_1-S_0.

Vibrational Relaxation

Unless formed by a 0-0 transition (a transition between the zero point vibrational levels of the ground and excited states) an excited species has, at the moment of its creation, an excess vibrational (and rotational) energy. The loss of this vibrational energy (called vibrational relaxation) is largely dependent upon collisions, as a result of which vibrational energy is converted into kinetic energy which is distributed between the partners in the collision.

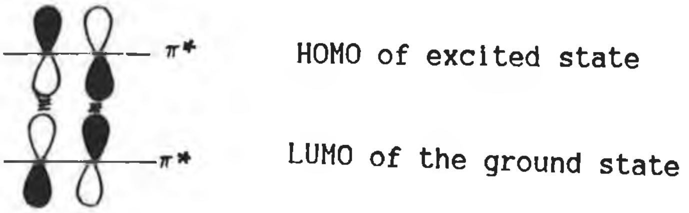
Photochemical Reaction

Photochemical reactions are reactions brought about by the use of visible or ultraviolet radiation as an energy source. In principle the electronic state of any compound can give rise to a number of different excited electronic states, each with its own characteristic properties and electron distribution and, each might have a chemistry as varied as that of the ground state. In practice the range of observed chemical reactions of excited states is restricted by the existence of rapid physical processes by which one excited state of a molecule is converted to another of lower energy. One of the major causes of the differences in thermal chemistry and photochemistry lies in the differences in electron distribution in the ground and excited states of a molecule. This can lead to a major alteration of chemical behaviour. For example, direct irradiation of ethene, (Scheme 1), leads to the



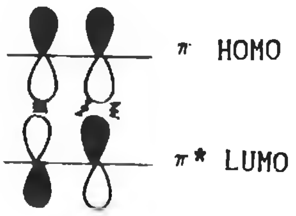
Scheme 1

promotion of an electron from a π-bonding orbital to a π* antibonding orbital. As a result of this electronic rearrangement, the concerted photochemical cyclodimerisation of ethene is symmetry allowed, (Scheme 2).



Scheme 2

The reaction involves overlap of the highest occupied molecular orbital (HOMO) of an excited molecule with the lowest unoccupied molecular orbital of a ground state molecule. The interaction is bonding and therefore symmetry allowed. This is in contrast to the concerted thermal dimerization of ethene. Reaction here would involve overlap of the HOMO (π) of one molecule with the LUMO (π*) of the other molecule. But as π and π* are of opposite symmetry, (Scheme 3), lobes of opposite symmetry



Scheme 3

would approach each other. Interaction is antibonding and repulsive, and a concerted reaction does not occur. A change in the electronic distribution of a molecule upon excitation can also lead to a change in its nuclear geometry. For example, the excited state derived from the planar ground state of ethene has the same geometry as the ground state, but in both singlet and triplet (π,π^*) manifolds the lowest energy conformation is one in which the central bond is rotated through 90° from the ground state geometry, (Scheme 4).

(1) (2)

Scheme 4

In the excited state the two CH_2 groups are joined by what is essentially a single bond with two electrons occupying p-orbitals on the carbon atoms. These two electrons experience electrostatic repulsion and this is minimized by rotation about the C-C single bond, so that the molecule is no longer planar. The rotations following excitation of the ethene molecule also occur in substituted alkenes and are believed to constitute the underlying basis for cis-trans isomerization.

A second major difference between thermal chemistry and photochemistry is that an electronically excited state of a molecule has higher (often a much higher) internal energy than the ground state. As a result, there exists a much greater choice of reaction product for the excited state on thermodynamic grounds. In particular, an excited species can give rise to high energy products such as radicals, biradicals or strained ring compounds which are not readily formed (if they can be formed at all) from the ground state.

Photochemical reactions can be classified into three overall types:

(1) Direct Photoreactions

$M \xrightarrow{h\gamma} M^* \longrightarrow P$

M^* = an excited singlet or triplet state molecule

P = product

(2) Photosensitized Reactions

$D \xrightarrow{h\gamma} D^*$

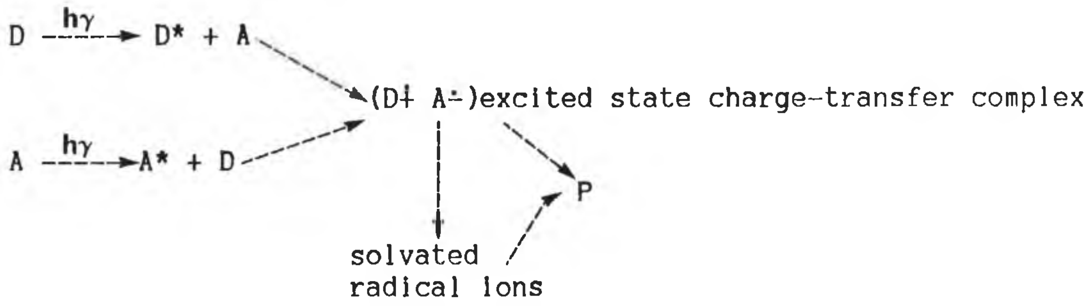
$D^* + A \longrightarrow D + A^* \longrightarrow D + P$

D = donor molecule

A = acceptor molecule

* = excited state

(3) Electron-Transfer Photoreactions



The synthetic potential of the latter type of reaction has only been understood relatively recently and is based on the fact that excited states are both better oxidizers and better reducers than the corresponding ground states. Irradiation of an electron donor (D)-electron acceptor (A) system can lead to the formation of radical cation-radical anion pairs and subsequent ground state processes may lead to reaction products. In general the feasibility of producing radical ions via photoinduced electron transfer can be predicted using Weller's equation[2]:

$$\Delta G = (E_D^{ox} - E_A^{red}) - E_{excit}$$

If the energy stored in the excited species is higher than the energy stored in the radical ion pair (calculated from the oxidation and reduction potentials of the donor and acceptor respectively), the electron transfer becomes exothermic and proceeds at a diffusion controlled rate. Such electron transfer reactions may be induced by excitation of either the donor or the acceptor. Since the energy content of a radical ion pair solvated by a polar solvent is substantially lower than that in a non-polar solvent, photoreactions via separated radical ions are generally observed in polar solvents. Reverse electron transfer between radical ion pairs leading to the ground state of both molecules is an unfortunate energy wasting step responsible for the low quantum yields in many electron transfer reactions.

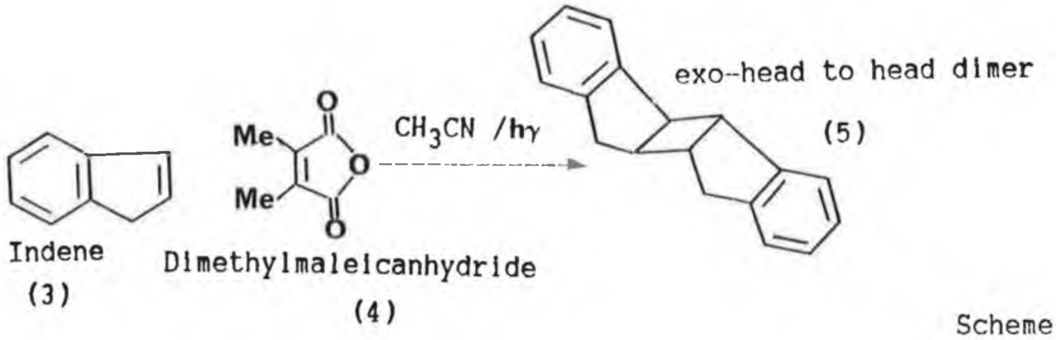
The work reported in this thesis concerns several photosystems which were investigated because of their potential for electron donor-acceptor photochemistry. The remainder of chapter one is concerned with a review of such processes in general.

Electron-Transfer Photoreactions

Numerous photoreactions of A-D pairs have been reported to proceed via ion radicals. These can be classified as follows:

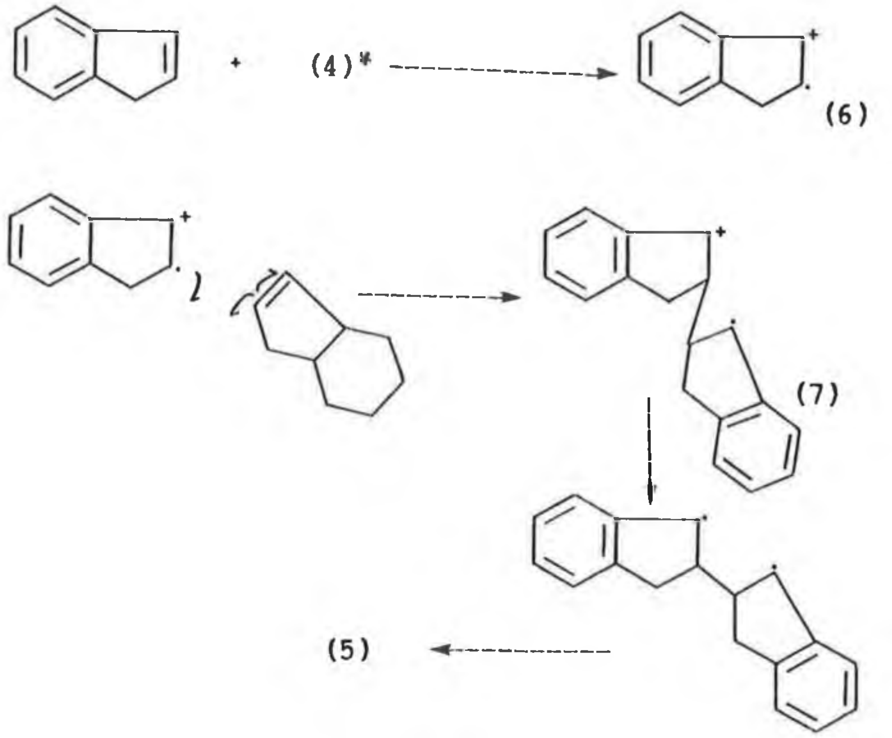
(1)Cyclodimerization of Alkenes

Only a few examples of the photosensitized dimerization of alkenes (or alkynes) via radical cations are known. These dimerizations are believed to be non-concerted i.e. stepwise bond formation produces the thermodynamically more stable exo products derived from the more stable (head to head) 1,4-radical cation intermediate. For example, the dimerization of indene in the presence of dimethylmaleicanhydride[3], (Scheme 5), gives exclusively the less sterically hindered exo head-to-head dimer.



Scheme 5

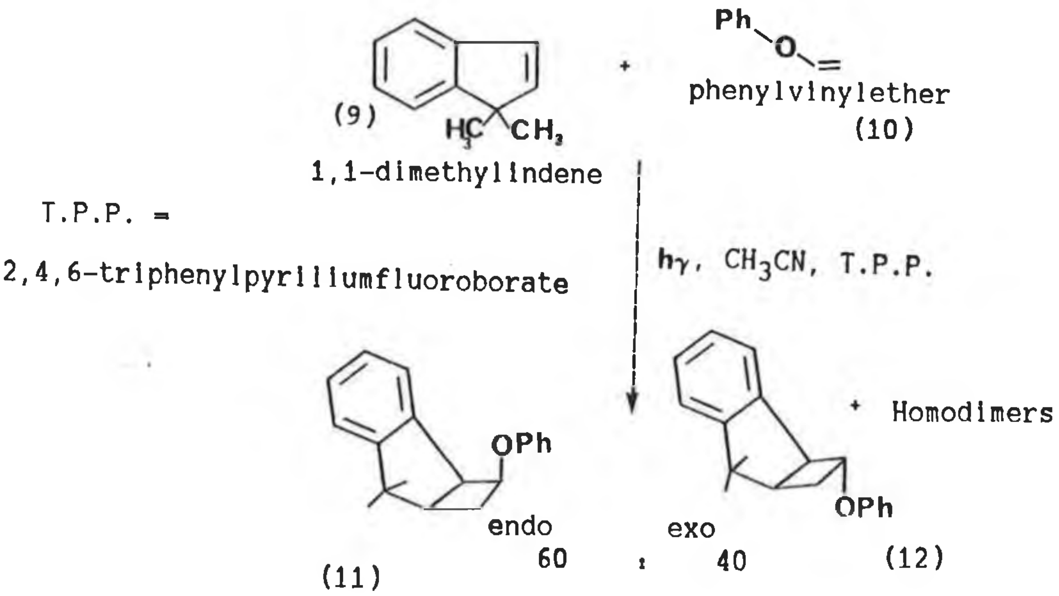
The reaction is believed to proceed via transfer of an electron from a ground state indene molecule, (Scheme 6), to the photoexcited acceptor (dimethylmaleicanhydride). The resultant radical cation (6) then adds electrophilically to another molecule of indene to give the dimeric radical cation (7). This is followed by electron transfer (either from $4^{\cdot-}$ or another indene molecule) and ring closure to yield the observed cyclobutane dimer (5).



Scheme 6

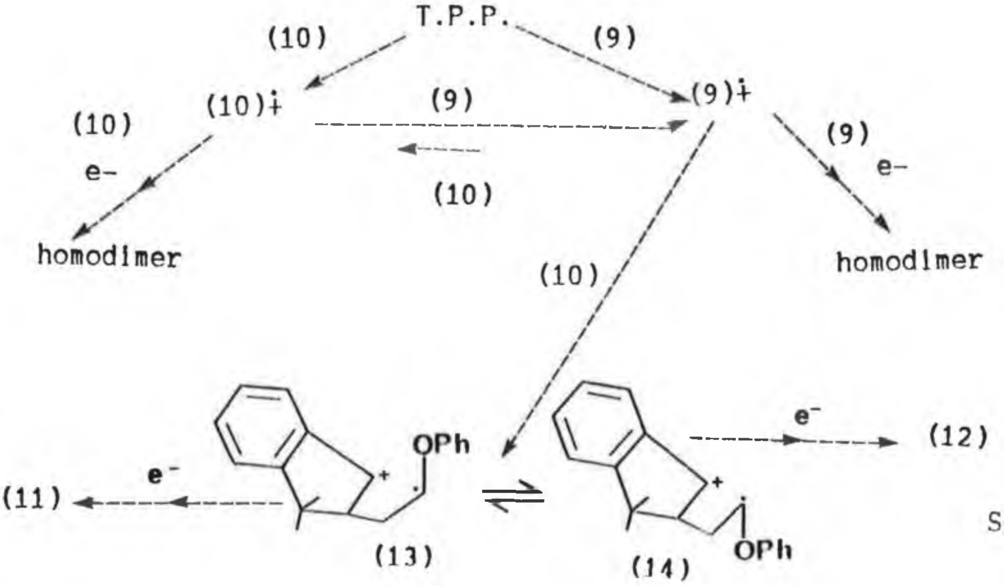
(2)Cross-Addition between Alkenes

Again relatively few examples of cross-addition of alkenes (i.e. addition of the radical cation of an alkene to a different neutral one) have been reported. The (2+2) cycloaddition of dimethylindene and phenylvinylether[4] was the first reported example of such a reaction. Irradiation of an equimolar solution of these alkenes in the presence of triphenylpyrilium fluoroborate yields a 60:40 mixture of the endo and exo mixed photoadducts (11 and 12, Scheme 7), the dimer of dimethylindene, and the dimer of phenylvinylether in the ratio of @ 91:1:8.



Scheme 7

The radical cations of both alkenes (9 and 10) are formed competively via electron transfer to T.P.P. ,(Scheme 8). However the mixed adduct is formed predominantly via the addition of the radical cation of the alkene of lowest oxidation potential (in this case 9) to the ground state of the other alkene (10) to give the radical cation intermediate (13) or (14) . Ring closure following back electron transfer gives the observed photoproducts (8) and (9).



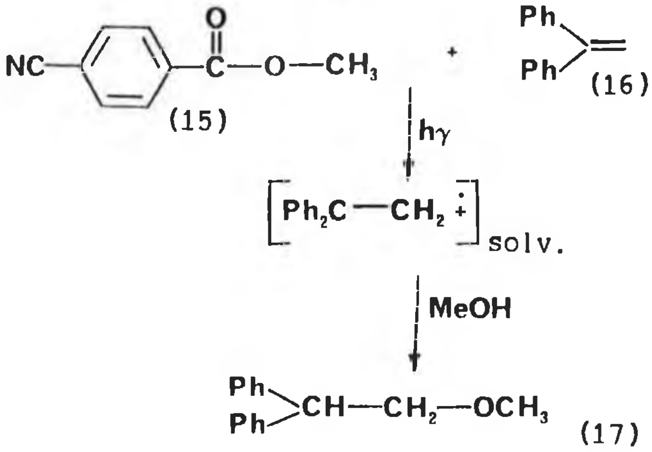
Scheme 8

In the alternative reaction of the radical cation of phenylvinylether (10$^{\dot{+}}$), the exothermic electron transfer giving (10) and (9$^{\dot{+}}$) is expected to be considerably faster than covalent bond formation to give the dimeric radical cation (13 or 14).

(3)<u>Addition of Nucleophiles to Alkenes</u> via

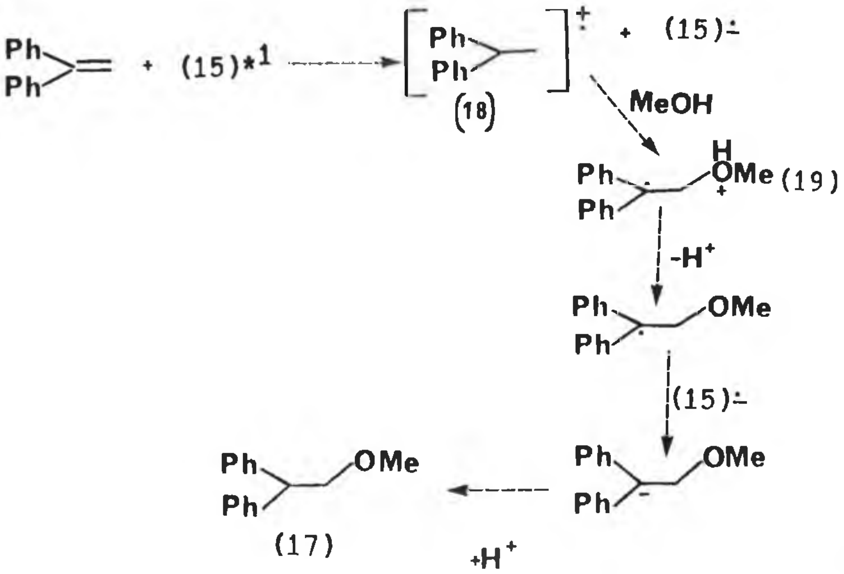
(a)Radical cations

When electron transfer sensitized photoreactions are carried out in nucleophilic solvents (water, alcohols, carboxylic acids, hydrogen-cyanide etc.) the major products are usually those formally derived from anti-Markownikov addition of the nucleophile to the alkene. For example, irradiation of a mixture of methyl-p-cyanobenzoate (15) and 1,1-diphenylethene (16) in methanol gives an ether^{5} (17) and dimerization of the alkene is completely suppressed, (Scheme 9). The reaction is believed to proceed via electron transfer from 1,1-diphenylethene to the ester to give the alkene radical cation (18,



Scheme 9

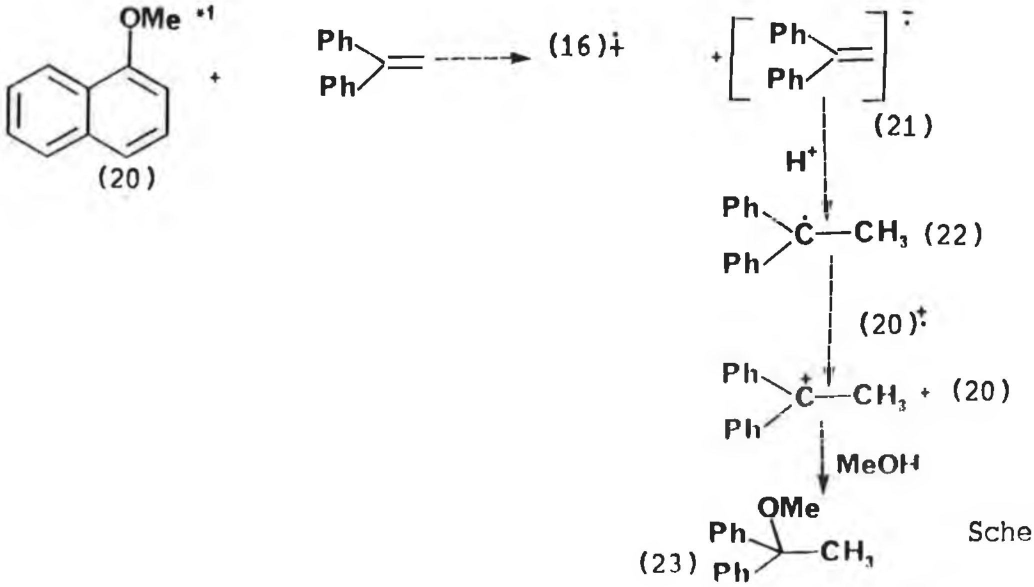
Scheme 10). The nucleophile then adds to the alkene radical cation, forming the more stable intermediate free radical (19). And finally, back electron-transfer from the ester radical anion followed by protonation gives the observed ether (17).



Scheme 10

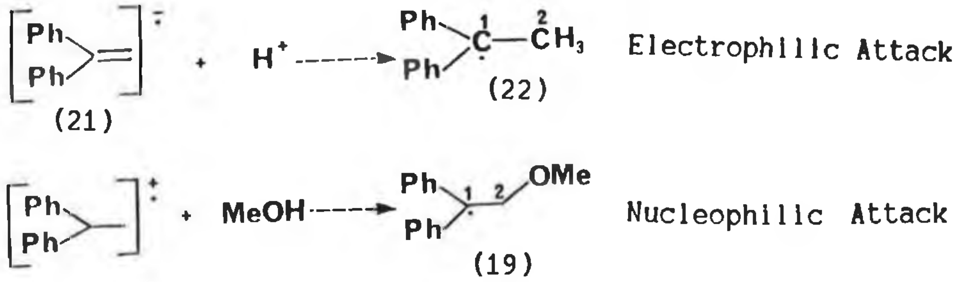
(b)Radical anions

In contrast to the latter reaction, Markownikov addition of alcohols to an alkene can be achieved photochemically under conditions which form, initially, the alkene radical anion. For example, irradiation of 1,1-diphenylethene and 1-methoxynaphthalene in methanol gives 1-methoxy-1,1-diphenylethane,(Scheme 11). The 1-methoxynaphthalene (20) acts as an electron-donating sensitizer and forms the alkene radical anion (21). It is proposed that the radical anion is then protonated, oxidized, and trapped by the nucleophile to give the Markownikov addition product.^{6} Thus the direction of addition of the nucleophile to the alkene



Scheme 11

is determined by the second step in both reactions (Scheme 12). Formation of the radical cation (18) leads to nucleophilic attack of the methanol at the 2-position to give the more stable radical and hence an anti-Markownikov product. On the other hand, formation of the radical anion (21) leads to electrophilic attack by a proton, again at the 2-position, to give the more stable radical and hence the Markownikov product. Nucleophilic attack by methanol on the radical anion formed initially is very unlikely and so attack takes place at the 1-position following protonation.



Scheme 12

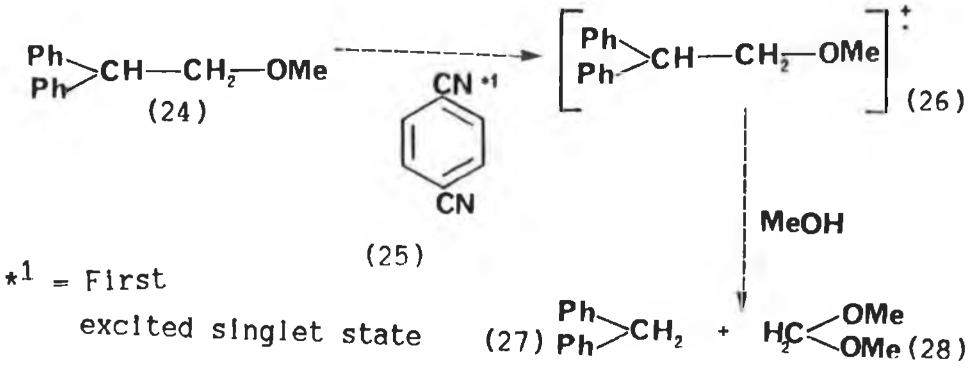
(4)Bond Cleavage Reactions

A variety of bond cleavage reactions can occur following electron transfer. The radical ions so formed may easily fragment if this results in greater stabilization.

(a)Cleavage of non-cyclic σ bonds

A clean fragmentation via a radical cation is observed when β-phenylethyl

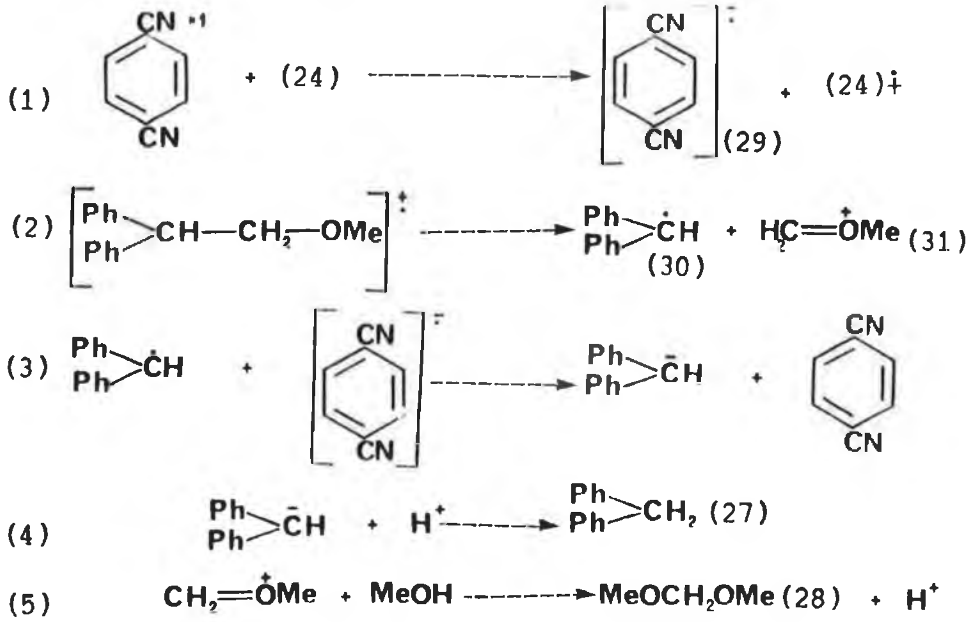
-ethers are irradiated in the presence of aromatic nitriles,[7] (Scheme 13)



*1 = First excited singlet state

Scheme 13

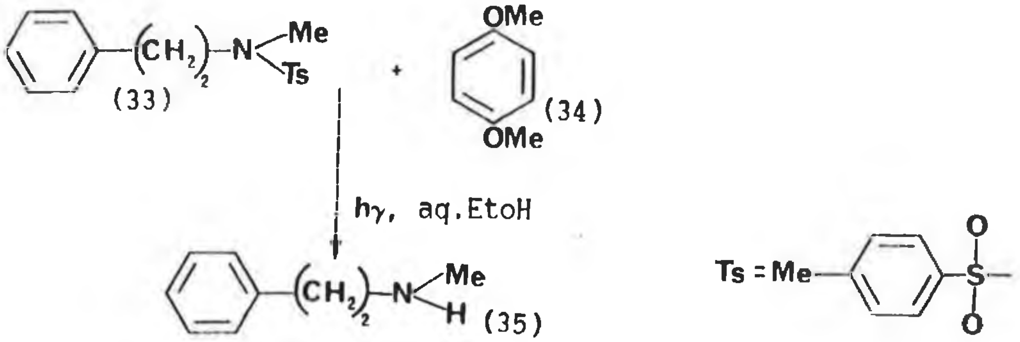
The reaction is believed to proceed via excitation of the nitrile, followed by transfer of an electron from the ether (24) to the excited nitrile, (Scheme 14, step 1).



Scheme 14

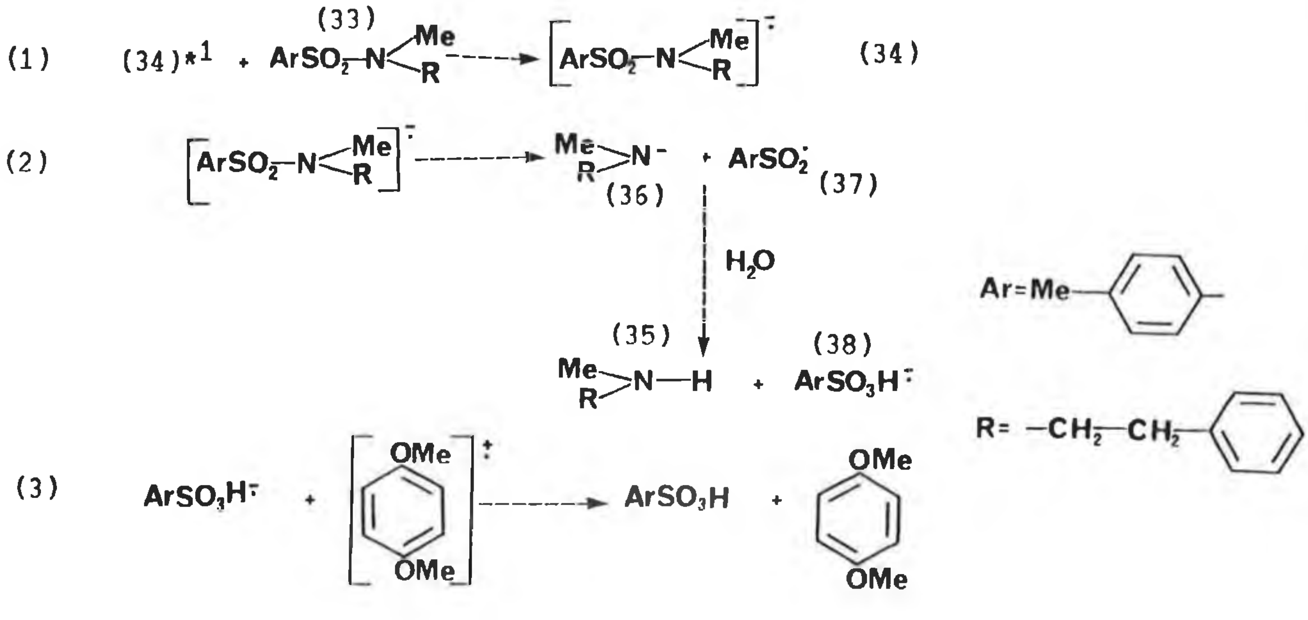
The ether radical cation then cleaves (step 2) in the direction which gives the more stable fragments, in this case the diphenylmethyl radical and the oxycarbonium ion. The diphenylmethyl radical is then reduced to the corresponding anion (step 3) and then protonated (step 4). Finally the α-oxycarbonium ion reacts with the solvent to yield the formaldehyde acetal (28).

These fragmentation reactions are not limited to radical cations. However fewer examples of cleavage via radical anions have been reported. One example is the cleavage of N-tosyl-N-methylphenethylamine (33) to give methylphenethylamine[8], (35, Scheme 15). The reaction is believed to proceed via transfer of an electron from the excited



Scheme 15

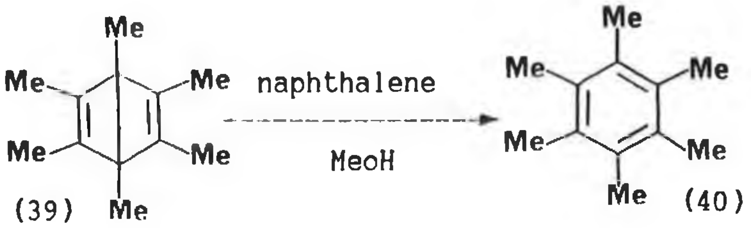
dimethoxybenzene (34) to the N-tosyl-N-methylphenethylamine (step 1, Scheme 16). This is followed by cleavage of the S-N bond and hydrolysis of the resulting fragments to give methylphenethylamine (step 2). Finally the reaction is completed by transfer of an electron from the toluenesulphonic acid radical anion (38) to the dimethoxybenzene radical cation to give toluenesulphonic acid and dimethoxybenzene.



Scheme 16

(b)Cleavage of cyclic σ bonds

Cleavage of cyclic σ bonds may also occur following electron transfer. For example, irradiation of the cyclohexa-2,5-diene (39) and naphthalene in methanol gives hexamethylbenzene[9], (Scheme 17).The reaction is believed to proceed via electron transfer from the diene (39) to naphthalene,(41). This is followed by bond cleavage of the diene radical cation to give the hexamethylbenzene radical cation $(40)^{+\cdot}$ The



Scheme 17

latter then accepts an electron from the diene to give hexamethylbenzene (40) and the diene radical cation. Bond cleavage of the diene radical cation again gives the hexamethylbenzene radical cation and thus sets up a chain reaction, (Scheme 18).

$$(39) + (41) \longrightarrow (39)^{\cdot+}$$

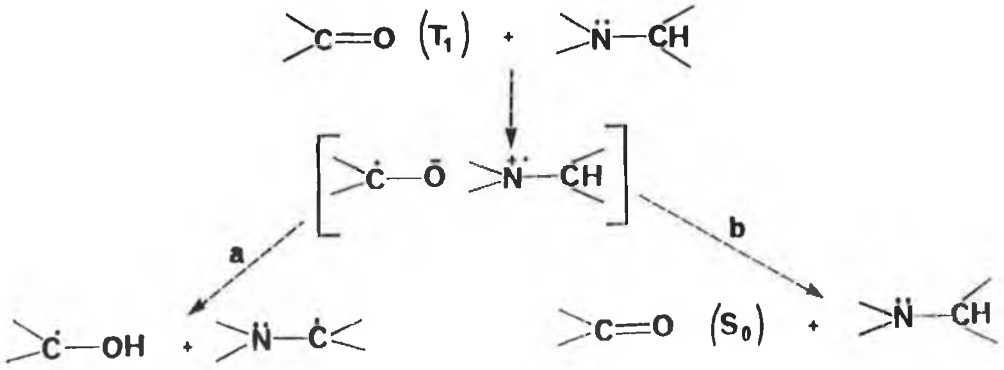
$$(39)^{\cdot+} \longrightarrow (40)^{\cdot+}$$

$$(40)^{\cdot+} + (39) \longrightarrow (40) + (39)^{\cdot+}$$

Scheme 18

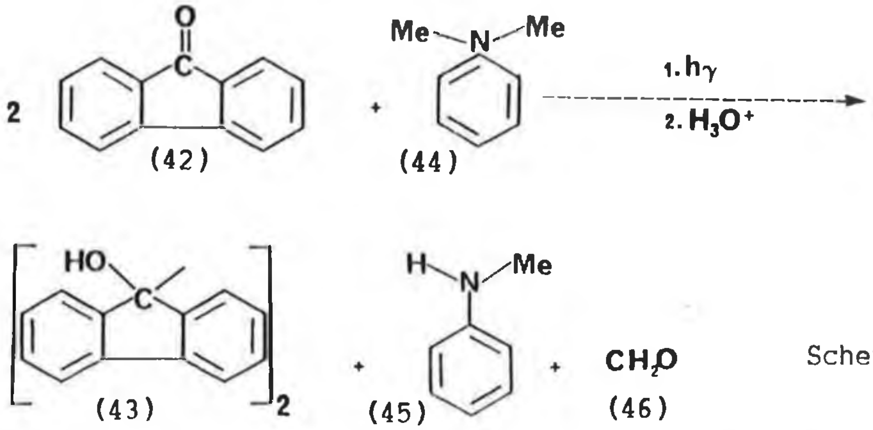
(5)<u>Reduction of Arenes and Aromatic Carbonyl compounds by Amines</u>[10]

Nearly all aromatic carbonyl compounds may be photoreduced by amines which contain α-hydrogen and, in general, most efficiently by such tertiary amines. Reduction appears to proceed by rapid initial interaction at the non-bonding electrons of the heteroatom, leading to a radical cation-radical anion pair, (Scheme 19). This is followed either by transfer of α-hydrogen and formation of radicals (path a) or by back electron transfer to regenerate the starting materials, (path b).



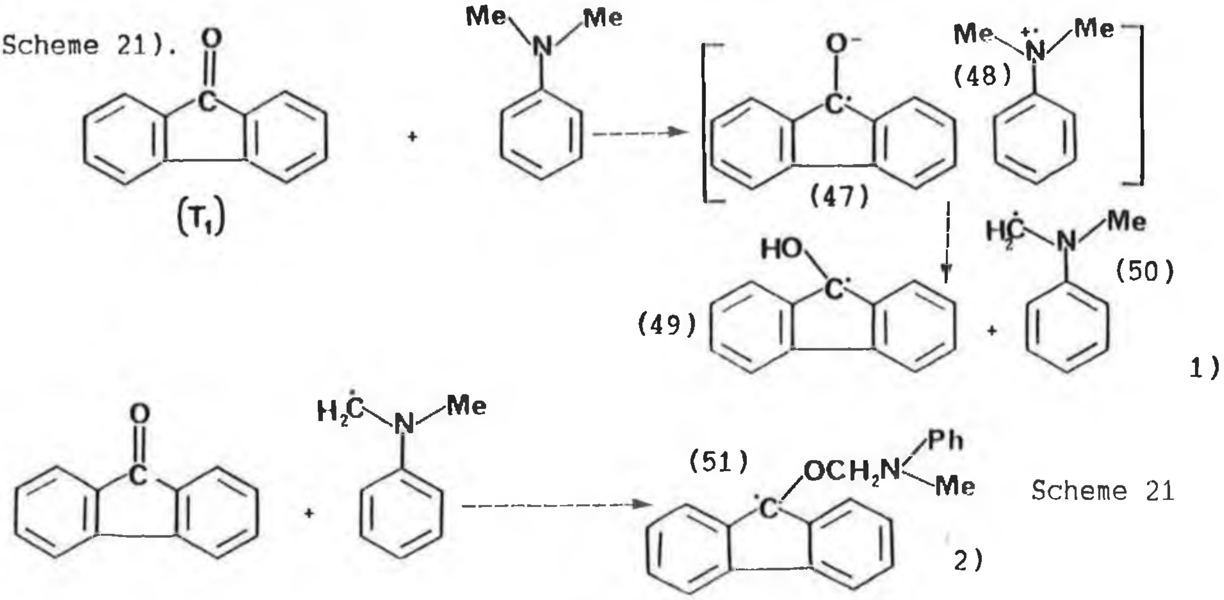
Scheme 19

For example, the reduction of fluorenone (42) by dimethylaniline in benzene, followed by hydrolysis, gives pinacol (43), N-methylaniline and formaldehyde[11], (Scheme 20).



Scheme 20

The reaction is believed to proceed via initial electron transfer from the amine to the fluorenone (42) followed by hydrogen abstraction, (step 1, Scheme 21). This is followed by reduction of a second fluorenone by addition of amine derived radical to give (51), (step 2, Scheme 21).



49, 51 ——► 49-49 + 49-51 + 51-51 3)

49-51, 51-51 $\xrightarrow{H_3O^+}$ 49-49 + (45) + CH_2O 4)

Scheme 21

This is followed by combination and cross combination of radicals (step 3) and finally hydrolysis (step 4) to yield pinacol (43), N-methylaniline and formaldehyde. An examination of the reaction by i.r and n.m.r has indicated that a substantial part of the pinacol and all the N-methylaniline are formed in the hydrolysis step, (step 4).

(6) Oxidation of Alkenes, Alkynes and Dienes[12]

Photosensitized electron transfer reactions carried out in the presence of oxygen occasionally yield oxygenated products. In most such cases, photo-oxygenation has been carried out under conditions in which the oxygenated products are formed by the combination of superoxide and the radical cation of the donor.

The proposed mechanism involves electron transfer from the donor (D) to excited acceptor (A^{*1}) followed by secondary electron transfer from $A^{\cdot -}$ to O_2 forming superoxide and then combination of the superoxide and the radical cation of the donor to give the oxygenated product.

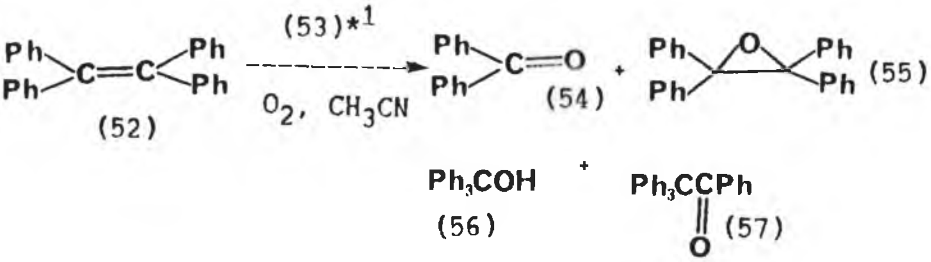
$$A^{*1} + D \longrightarrow A^{\cdot -} + D^{\cdot +}$$

$$A^{\cdot -} + O_2 \longrightarrow A + O_2^{\cdot -}$$

$$O_2^{\cdot -} + D^{\cdot +} \longrightarrow DO_2$$

When D is an alkene, this product is a dioxetane, which may be cleaved under the reaction conditions to give ketone products. When D is an alkyne, the product DO_2 is a dioxete, which isomerizes to a diketone. When D is a diene DO_2 is a peroxide, the isolated product.

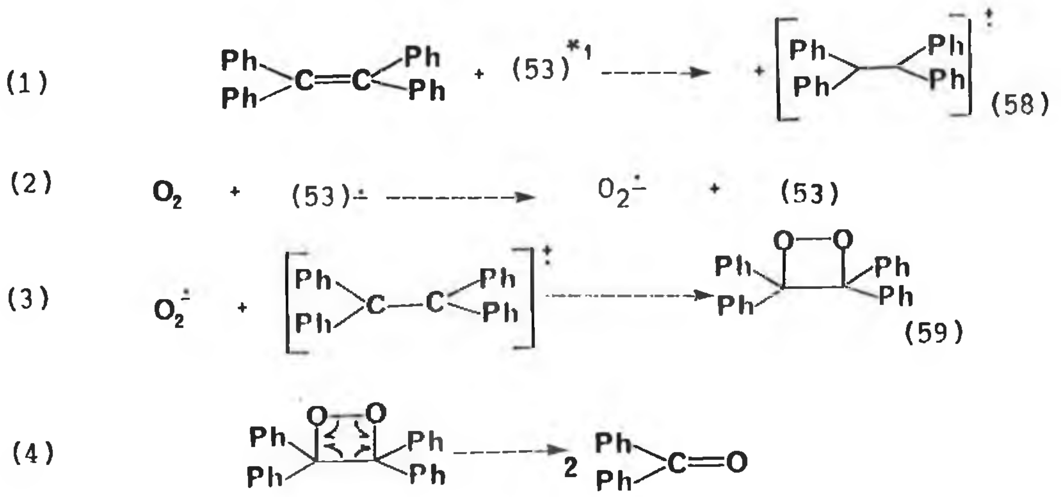
For example, irradiation of tetraphenylethene (52) and dicyanoanthracene (53) in oxygen saturated acetonitrile gives benzophenone, triphenylmethanol, benzopineacolone and tetraphenyloxirane together with small amounts of benzoic acid and benzaldehyde[13], (Scheme22).



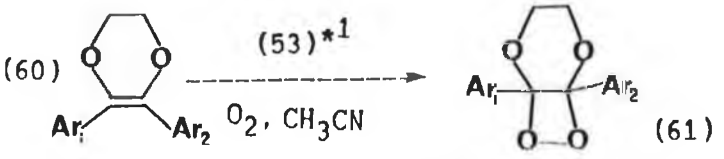
Scheme 22

The reaction is believed to proceed via electron transfer from the alkene to dicyanoanthracene to give the alkene radical cation (58,Scheme 23).This is followed by formation of superoxide (step 2) and then combination of the latter with the radical cation (step 3) to give the dioxetane. Cleavage of this dioxetane (step 4) gives benzophenone as major product.

Occasionally,oxidation of alkenes can lead to isolation of substantial amounts of the 1,2-dioxetanes[14],(Scheme 24). For example, irradiation of (60) and dicyanoanthracene in oxygen saturated acetonitrile gives (61)



Scheme 23

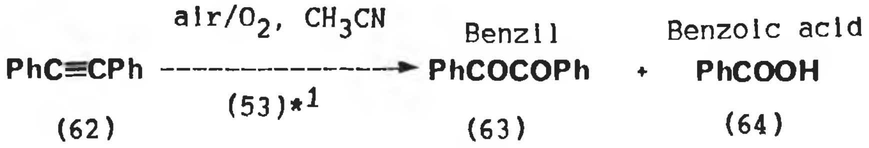


Ar_1, Ar_2 = phenyl, tolyl

Scheme 24

as major product. Again the reaction is believed to proceed via attack of superoxide on the alkene radical cation.

The photooxygenation of various alkynes is also efficiently sensitized by dicyanoanthracene. For example, the electron-transfer photosensitized reaction of 1,2-diphenylethyne[15] (62, Scheme 25) gives benzil and benzoic acid.



$$\underset{(62)}{PhC{\equiv}CPh} \xrightarrow[(53)^{*1}]{air/O_2,\ CH_3CN} \underset{(63)}{\overset{Benzil}{PhCOCOPh}} + \underset{(64)}{\overset{Benzoic\ acid}{PhCOOH}}$$

Scheme 25

Again, reaction is believed to proceed via attack of superoxide on the alkyne radical cation $(62)^{+\cdot}$. Experiment has shown that the alkyne radical cation reacts rapidly with $O_2^{-\cdot}$ but only slowly with O_2. When tetracyanoanthracene (65) is used as sensitizer (instead of 53) no $O_2^{-\cdot}$ can be formed because electron transfer from $(65)^{-\cdot}$ to O_2 is highly endothermic (Scheme 26). Instead, reverse electron transfer from $(65)^{-\cdot}$

to $(62)^{\cdot+}$ competes favorably with the reaction of $(62)^{\cdot+}$ and O_2.

$$(65) + (62) \longrightarrow (65)^{\cdot-} + (62)^{\cdot+} \qquad (1)$$

$$(65)^{\cdot-} + O_2 \not\longrightarrow O_2^{\cdot-} + (65) \qquad (2)$$

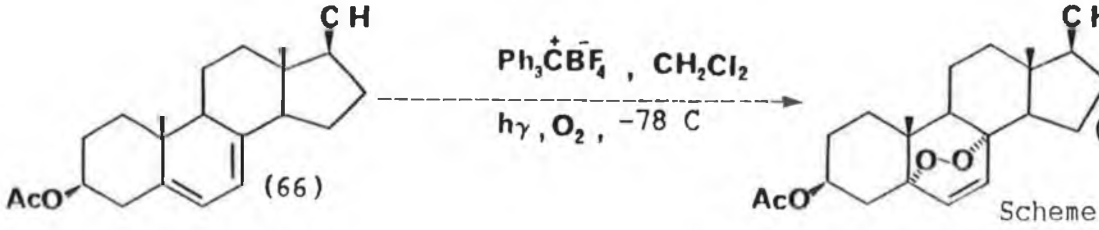
$$(65)^{\cdot-} + (62)^{\cdot+} \longrightarrow (65) + (62) \qquad (3)$$

$$(62)^{\cdot+} \overset{O_2}{\not\searrow}$$

(Scheme 26)

The reaction of the alkyne radical cation with O_2 can however be catalysed by the addition of CF_3CO_2H. The latter protonates the $(65)^{\cdot-}$, suppresses the reverse electron transfer and allows $(62)^{\cdot+}$ to react slowly with O_2 to give benzil and benzoic acid.

Several examples of electron transfer sensitized photooxygenation of dienes have been reported.[16] The reactions are carried out at low temperature in the presence of Lewis acid catalysts. For example, irradiation of ergosterylacetate (66) and trityltetrafluoroborate (Scheme 27) in dichloromethane in the presence of oxygen at -78 C produces the 5α,8α-peroxide[17] (67) in quantitative yield.



(66) (67)

Scheme 27

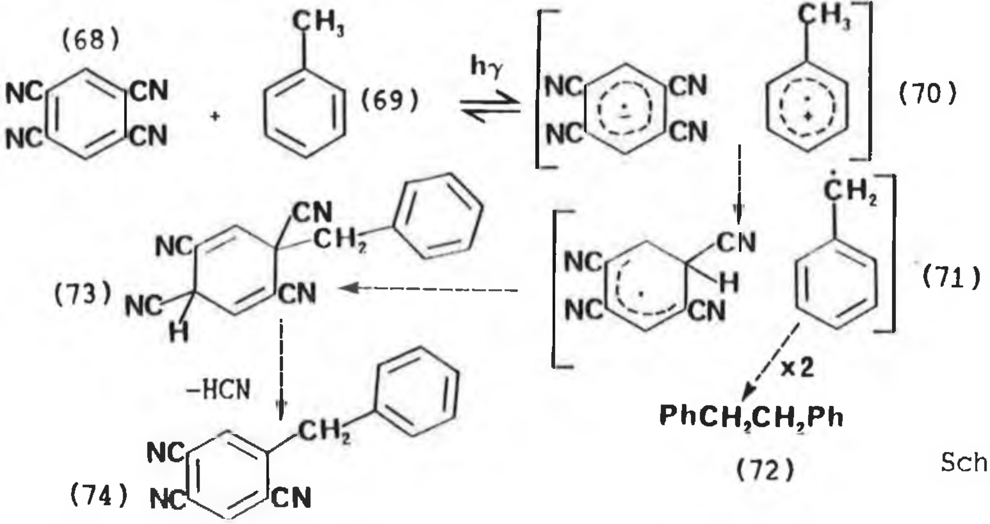
Again reaction is believed to take place via attack of superoxide on the diene radical cation.

(7)<u>Reactions Involving Adduct Formation Between A and D</u>

Irradiation of electron deficient aromatic compounds in the presence of potential electron donating compounds often leads to products derived from both the donor and acceptor molecules. In many cases these products are not formed by direct coupling of the radical ion intermediates but, instead they proceed by proton transfer from the donor radical cation to the acceptor radical anion. This is then followed by coupling of the donor radical to the acceptor radical (or radical anion).

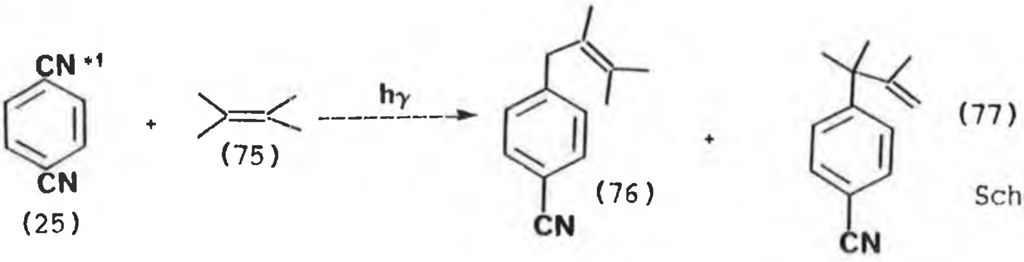
(1) Irradiation of 1,2,4,5,-tetracyanobenzene in toluene gives

1-benzyl-2,4,5-tricyanobenzene (74) plus a small amount of bibenzyl,[18] (Scheme 28). The reaction is believed to take place via electron transfer from toluene to the tetracyanobenzene, to give a radical cation-radical anion pair. This is followed by proton transfer, radical coupling and elimination of HCN to give the observed product (74).



Scheme 28

(2) The photoinitiated reaction of 1,4-dicyanobenzene with 2,3-dimethyl-but-2-ene in acetonitrile gives the substitution products 2,3-dimethyl-1-(4-cyanophenyl)-but-2-ene (76) and 2,3-dimethyl-3-(4 -cyanophenyl)-but-1-ene[19] (77, Scheme 29). The

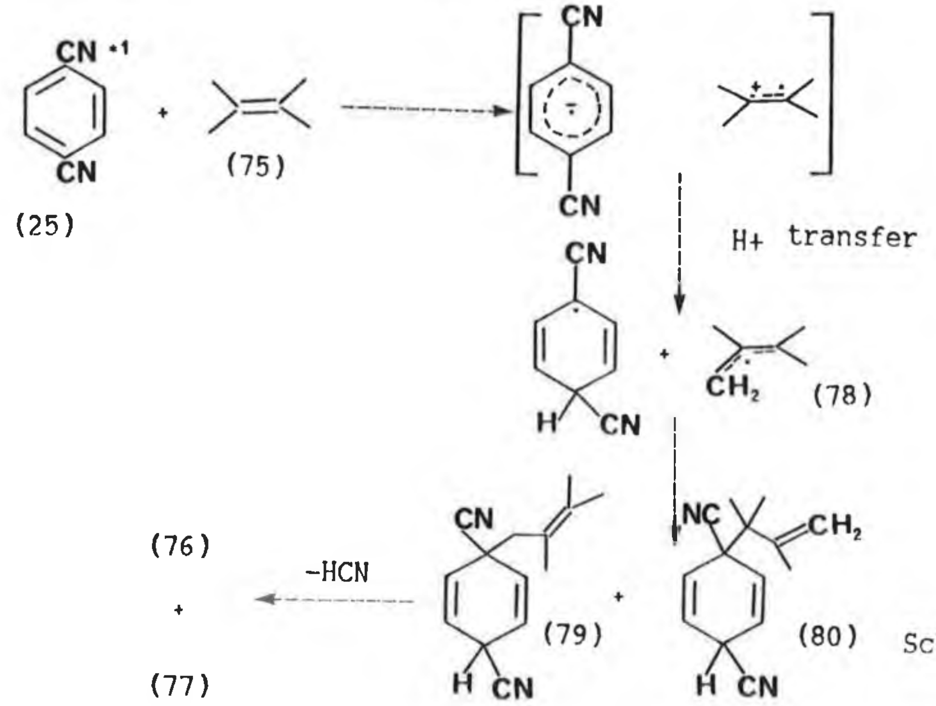


Scheme 29

reaction is believed to proceed via electron transfer from the alkene to the dicyanobenzene. This is followed by proton transfer between the radical ions (Scheme 30) to give the allylic radical (78). Coupling of the latter with the acceptor radical gives adducts (79) and (80) which aromatize by loss of HCN to give the observed products. Similar electron transfer reactions are observed with other electron-deficient aromatic compounds. The photochemical reactions of

(1) 3,4,5,6,-Tetrachlorophthalonitrile (TCPN)

(2) 3,4,5,6,-Tetrafluorophthalonitrile (TFPN)



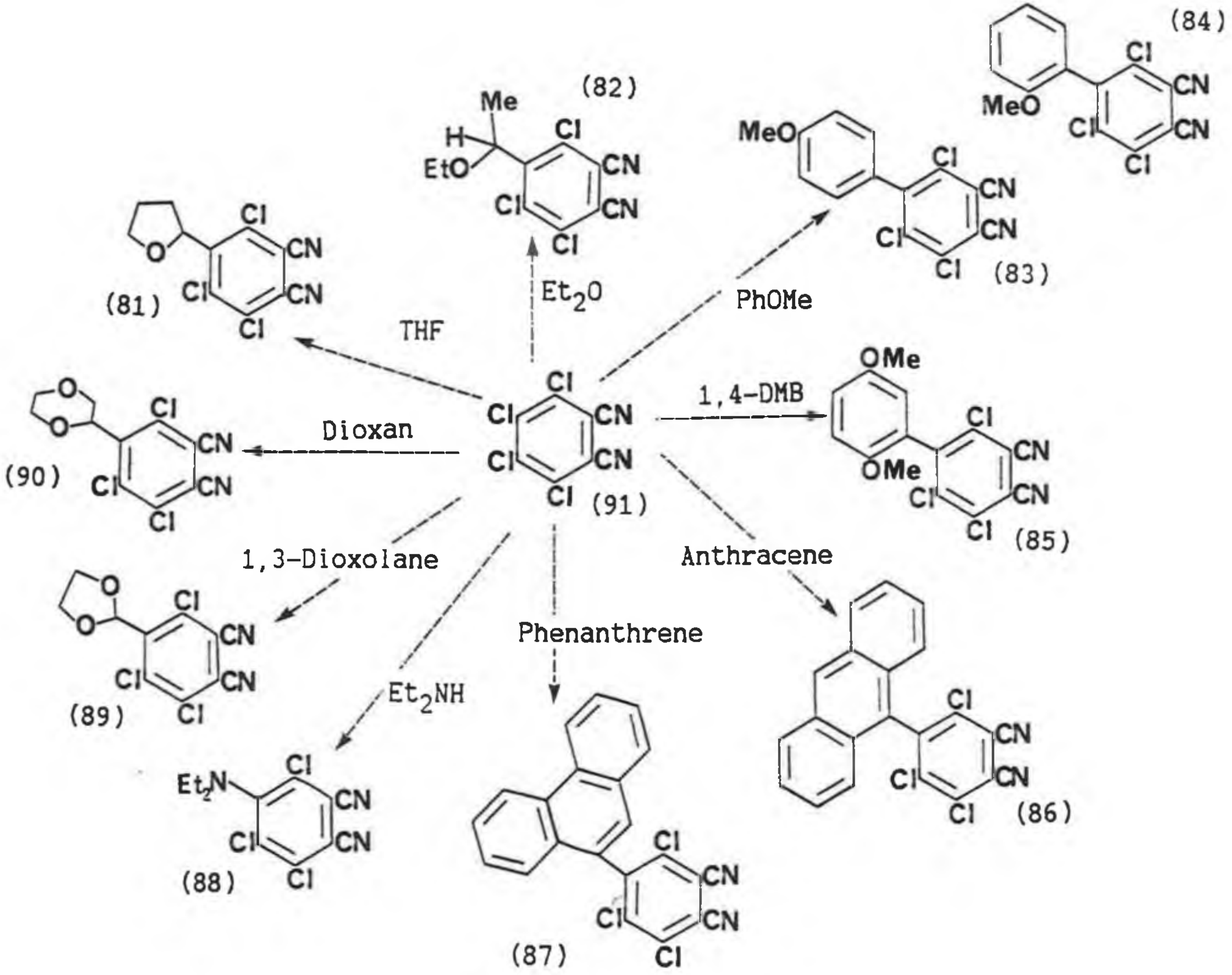
Scheme 30

(3) 2,3,5,6,-Tetrachloroterephthalonitrile (TCTN) and

(4) N-alkyl-3,4,5,6,-tetrachlorophthalimide in the presence of potential electron donating compounds often yield products in which the donor molecule has been incorporated in the aryl halide. These compounds, as well as being electron acceptors, also contain a good leaving group in the chlorine (or fluorine) substituents. It might therefore be expected that, after initial electron transfer from a donor molecule, a chlorine can be replaced by the donor moiety. All four have, in fact, been shown to undergo such photosubstitution reactions and these are outlined in detail in the following section.

The Photochemical Reactions of TCPN

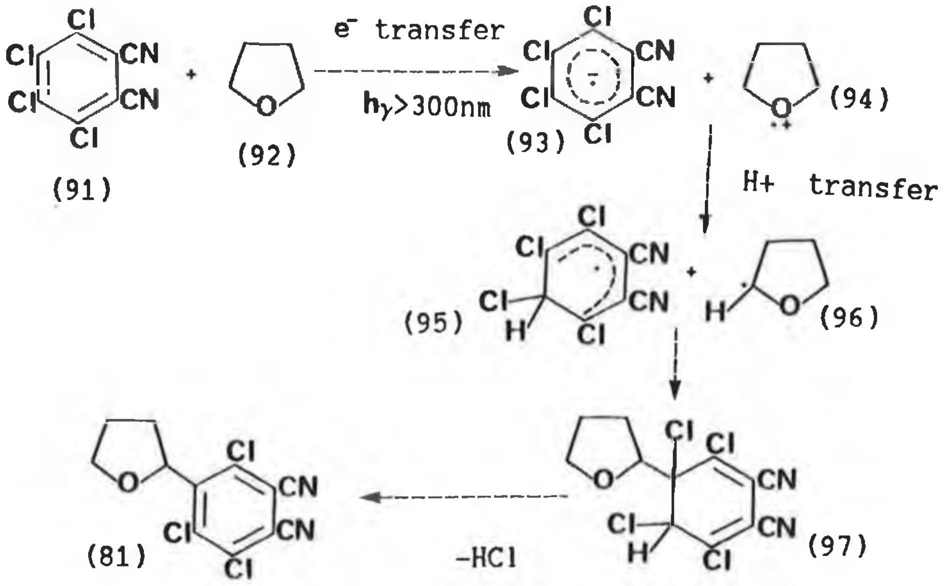
TCPN undergoes a variety of substitution reactions when irradiated in the presence of ethers, aromatic hydrocarbons and amines^{20,21} to give products in which a chlorine has been replaced by the donor moiety. As shown in Scheme 31 TCPN undergoes photochemical reaction with the hydrogen donating ether solvents such as diethylether,^{22} THF, 1,4-dioxan and 1,3-dioxolane. Photosubstitution also occurs with the aromatic ethers methoxybenzene and 1,4-dimethoxybenzene^{23} and with the polycyclic aromatic hydrocarbons anthracene and phenanthrene.^{24} In all these cases a mechanism involving initial electron transfer from the



Scheme 31

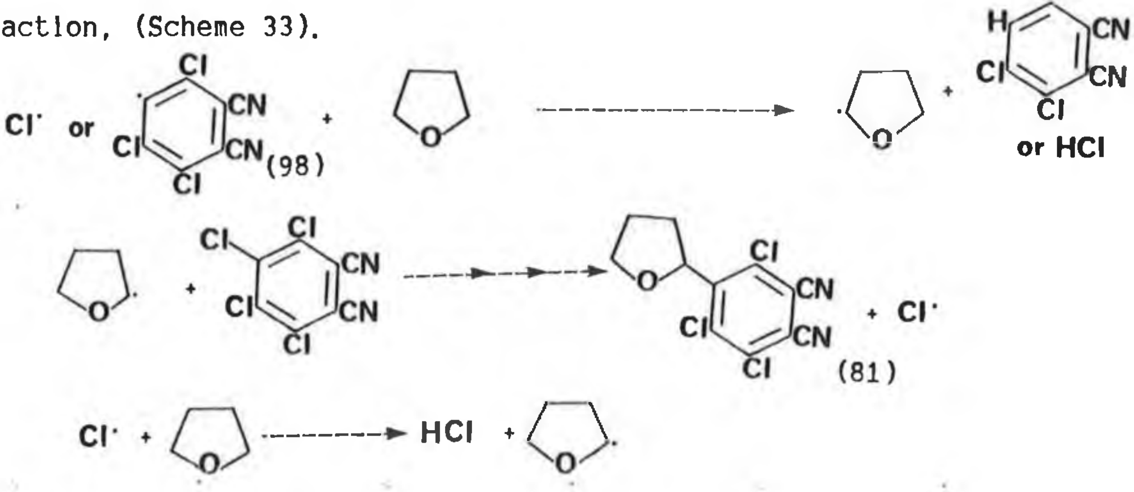
1,4-DMB = 1,4-Dimethoxybenzene

donor molecule to the TCPN has been suggested to account for the observed reaction. For example, it has been proposed that the photochemical reaction of THF with TCPN proceeds via initial electron transfer from THF to TCPN[20] to give a radical cation-radical anion pair (Scheme 32).

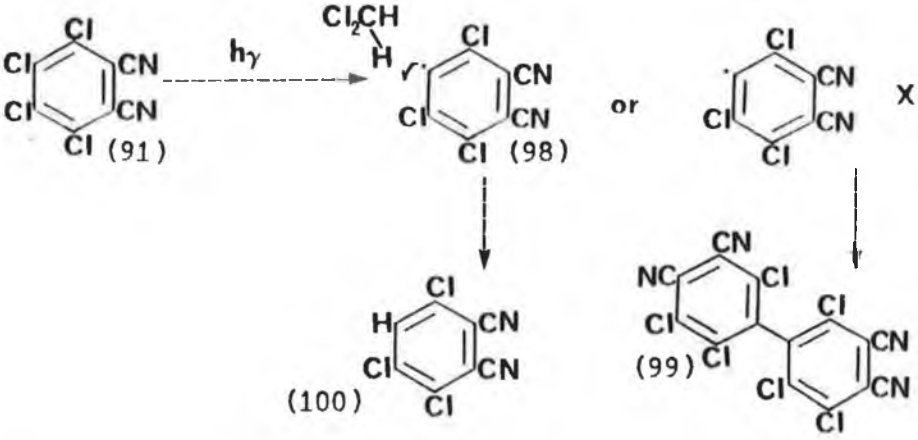


Scheme 32

This is followed by proton transfer from the radical cation to the radical anion, radical coupling and then elimination of HCL to give the observed product (81). An alternative mechanism might involve carbon-chlorine bond homolysis to give (98) and a chlorine radical. Abstraction of a hydrogen from THF by either of these radicals would give a THF radical which could then attack another molecule of TCPN to give the observed product (81) and a chlorine radical. The latter could then abstract hydrogen from another molecule of THF and thus set up a chain reaction, (Scheme 33).



Such a process of simple bond homolysis is well established for the relatively weak carbon-iodine and carbon-bromine bonds. Several facts point to an electron transfer mechanism being operative, rather than a homolytic mechanism, (Scheme 33). Firstly, TCPN is recovered unchanged when irradiated by itself in dichloromethane, ethanol or toluene. If carbon-chlorine bond homolysis were occuring in these solvents, irradiation would be expected to result in loss of TCPN and to be accompanied by product formation, possibly yielding trihalogenophthalonitriles (through H-abstraction from the solvent) and/or biaryls, (Scheme 34).



Scheme 34

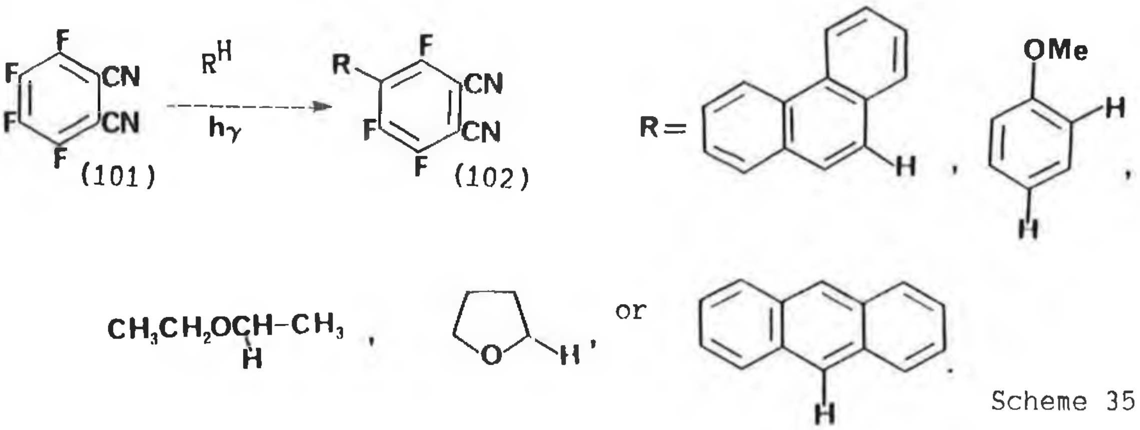
Secondly, even in hydrogen-donating ether solvents (such as diethylether or THF) with which TCPN does react, irradiation does not lead to replacement of halogen by hydrogen. If the aryl radical (98) was present, it would be expected to give the reduced product (100). Instead photoreaction leads to replacement of the chlorine by the ether moiety- a fact which can be more readily explained by the electron transfer mechanism rather than the homolytic mechanism. Thirdly, addition of the hydrogen transfer agent 2,6-di-t-butyl-4-methylphenol has no effect on the photochemical reaction of TCPN with THF. The same photosubstitution product (81), obtained in its absence, is again formed in equal quantity. This photosubstitution product (81) can also be formed by the thermal decomposition of dibenzoylperoxide in a solution of TCPN in THF.[20]

This free radical substitution reaction is inhibited by the addition of 2,6-di-t-butyl-4-methylphenol. A similar homolytic mechanism for the photosubstitution reaction can therefore be ruled out because the latter is unaffected by the addition of the hydrogen transfer agent. These facts are all consistent with an electron transfer mechanism (Scheme 32) being operative.

Other electron-deficient aryl halides form products analogous to those of TCPN with several of the same donor molecules i.e. products in which a halogen has been replaced by the donor moiety.

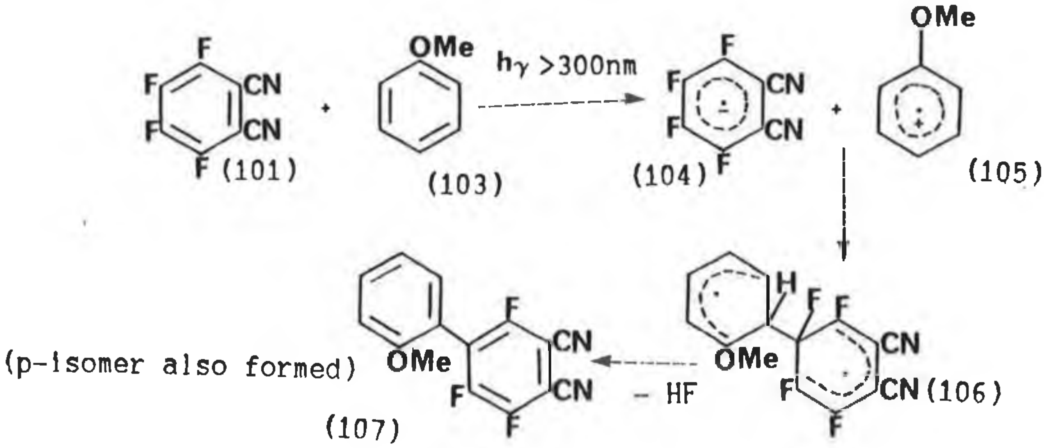
Photochemical Substitution Reactions of TFPN

For example, TFPN undergoes photosubstitution reactions with the hydrogen donating ether solvents diethylether and THF,[20] (Scheme 35).

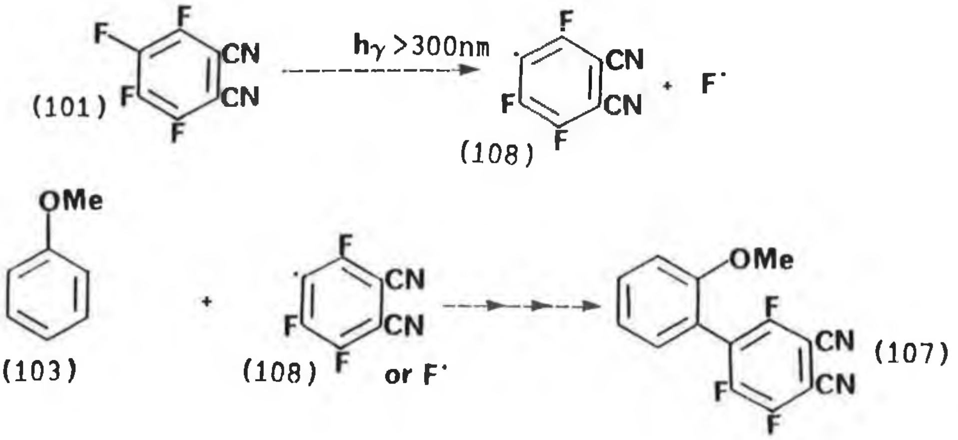


Scheme 35

Photosubstitution also occurs with the polycyclic aromatic hydrocarbons anthracene and phenanthrene[24] and with the aromatic ether, methoxybenzene.[21] In all these cases the products formed are exactly analogous to those of TCPN and a similar electron transfer mechanism has been proposed. For example, the photochemical reaction of TFPN with methoxybenzene is believed to proceed via electron transfer from the aromatic ether to TFPN to give a radical cation-radical anion pair, (Scheme 36).



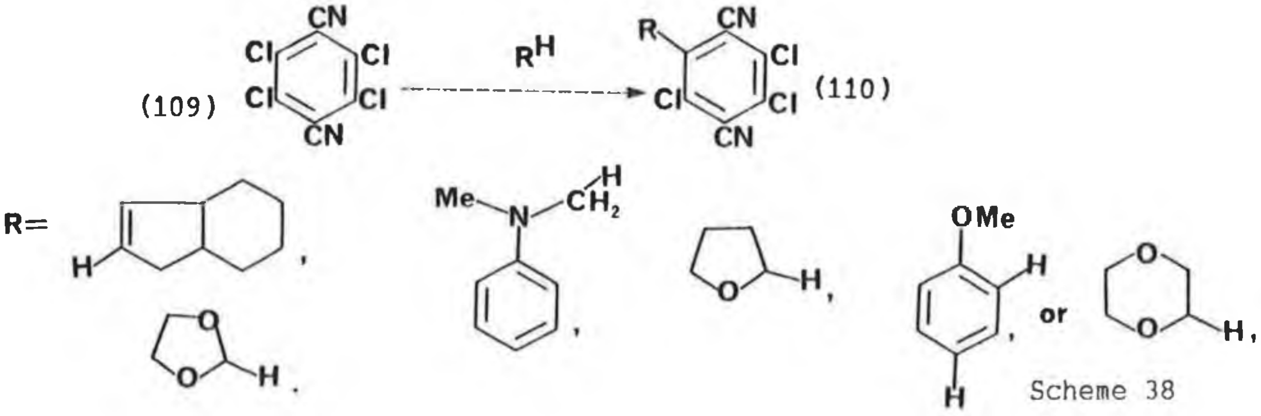
This is followed by radical coupling and elimination of HF to give the photosubstitution product (107). A mechanism involving simple homolysis of the carbon-halogen bond (Scheme 37) ,followed by attack of the aryl radical (or the fluorine radical) on the donor molecule is even more unlikely with TFPN (as compared to TCPN) because of the greater strength of the carbon-fluorine bond.



Scheme 37

Photochemical Substitution Reactions of TCTN

Tetrachloroterephthalonitrile also forms products analogous to those of TCPN when irradiated in the presence of several of the same donor molecules,[25] (Scheme 38).

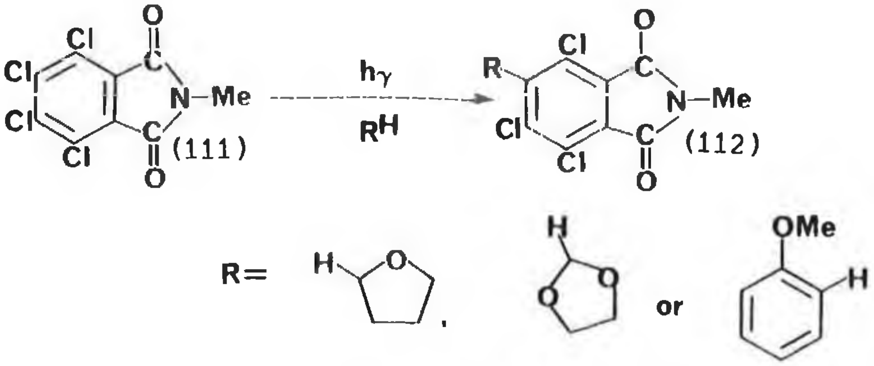


Scheme 38

Again a mechanism involving initial electron transfer from the donor molecule, followed by radical coupling and elimination of HCl has been proposed to account for the observed photosubstitution products.

Photochemical Reactions of N-Methyl-3.4.5.6-Tetrachlorophthalimide

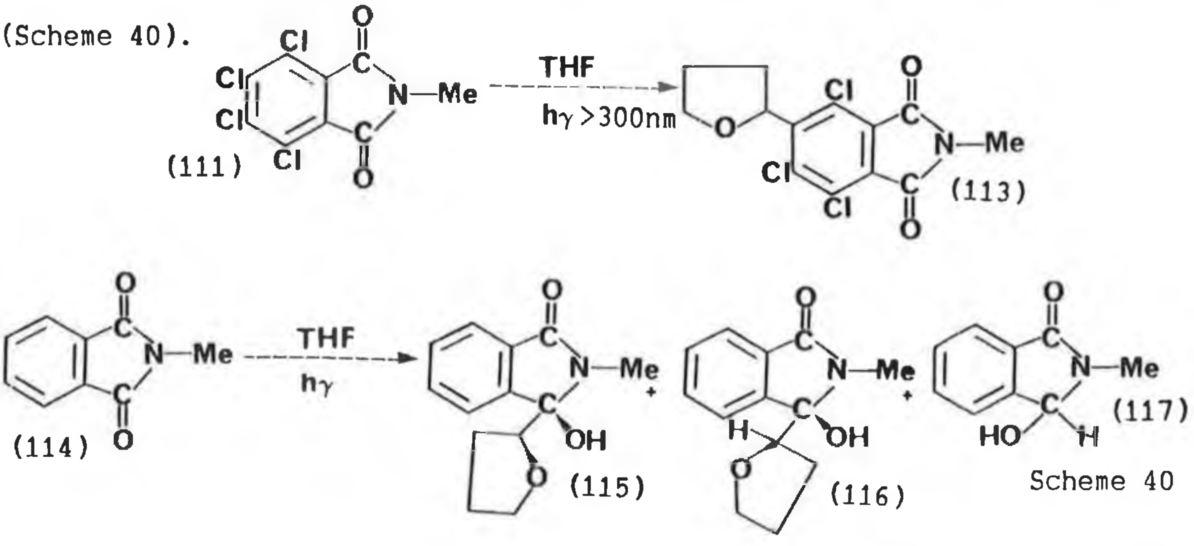
A similar pattern of reactivity to TCPN is also seen in the photochemical reactions of Cl_4NMP with various donor molecules,[26] (Scheme 39). It undergoes photochemical reaction with THF, 1,3-dioxan and methoxybenzene to give products in which a chlorine atom has been replaced by the ether moiety. A mechanism involving initial electron transfer from the donor



Scheme 39

molecule to the electron deficient arylhalide, followed by radical coupling and elimination of HCl has again been proposed to account for the observed reactivity.

The photochemistry of the chlorinated-N-Methylphthalimide (Scheme 39) is in direct contrast to that of the corresponding non-chlorinated phthalimide. For example, photoreaction of Cl_4NMP with THF gives a product (113) in which a chlorine has been replaced by the ether moiety, (Scheme 40).

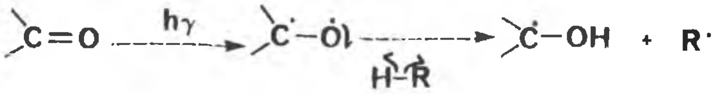


Scheme 40

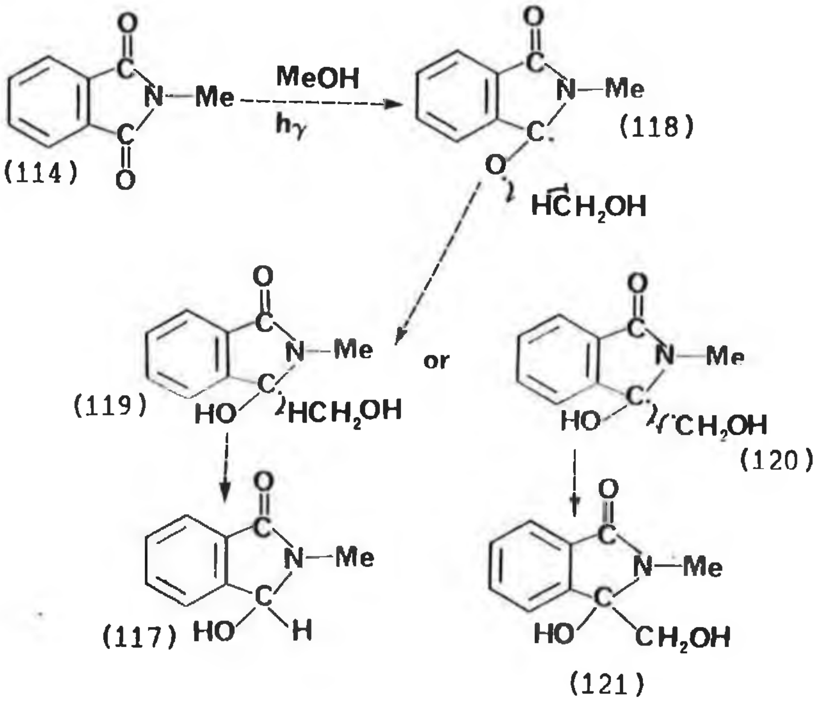
However, irradiation of N-methylphthalimide (NMP) in THF gives the photo addition products, (115) and (116), together with the photo-reduced product[27] (117). In fact the photochemical behaviour of the non-chlorinated phthalimides parallels, to a large extent, that of simpler ketones. They undergo (1) photoreduction (Scheme 40) in solvents having readily available hydrogen, (2) photoaddition in the presence of compounds which contain an activated methylene group and (3) Norrish Type 2 reactions.

Photoreduction and Photoaddition

Compounds which contain a carbonyl chromophore, upon irradiation in solvents having readily abstractable hydrogen, undergo photoreduction as one of their most common reactions:-

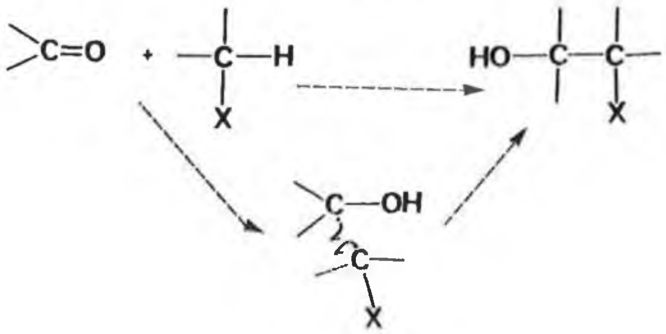


When NMP is photolysed in methanol the corresponding reduced product (117, Scheme 41) is obtained along with the addition product (121).[28]



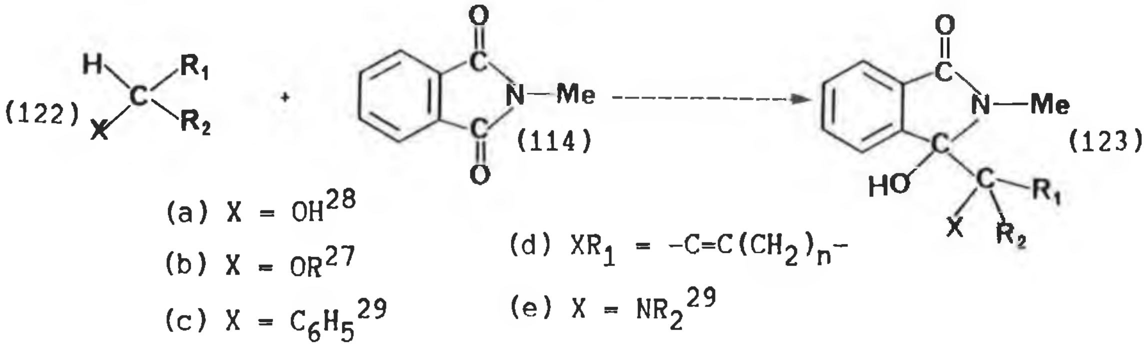
Scheme 41

The reaction proceeds via initial hydrogen abstraction to give the semi-pinacol radical (119). This is followed, either by a second hydrogen abstraction to give the photoreduced product (117) or, by coupling with the solvent derived radical ($\cdot CH_2OH$) to give the photoaddition product (121). Such a photoaddition reaction is another typical reaction of simple carbonyl compounds. The reaction is referred to as a 'photo-aldol condensation'. In general, compounds which contain a methylene group activated by adjacent groups such as double bonds or hetero atoms will be capable of addition leading to carbinols, (Scheme 42).



Scheme 42

Again the photochemistry of NMP parallels that of simpler ketones and irradiation in the presence of a series of hydrogen donors (122) gives rise to the corresponding carbinol (123).



(a) $X = OH^{28}$

(b) $X = OR^{27}$

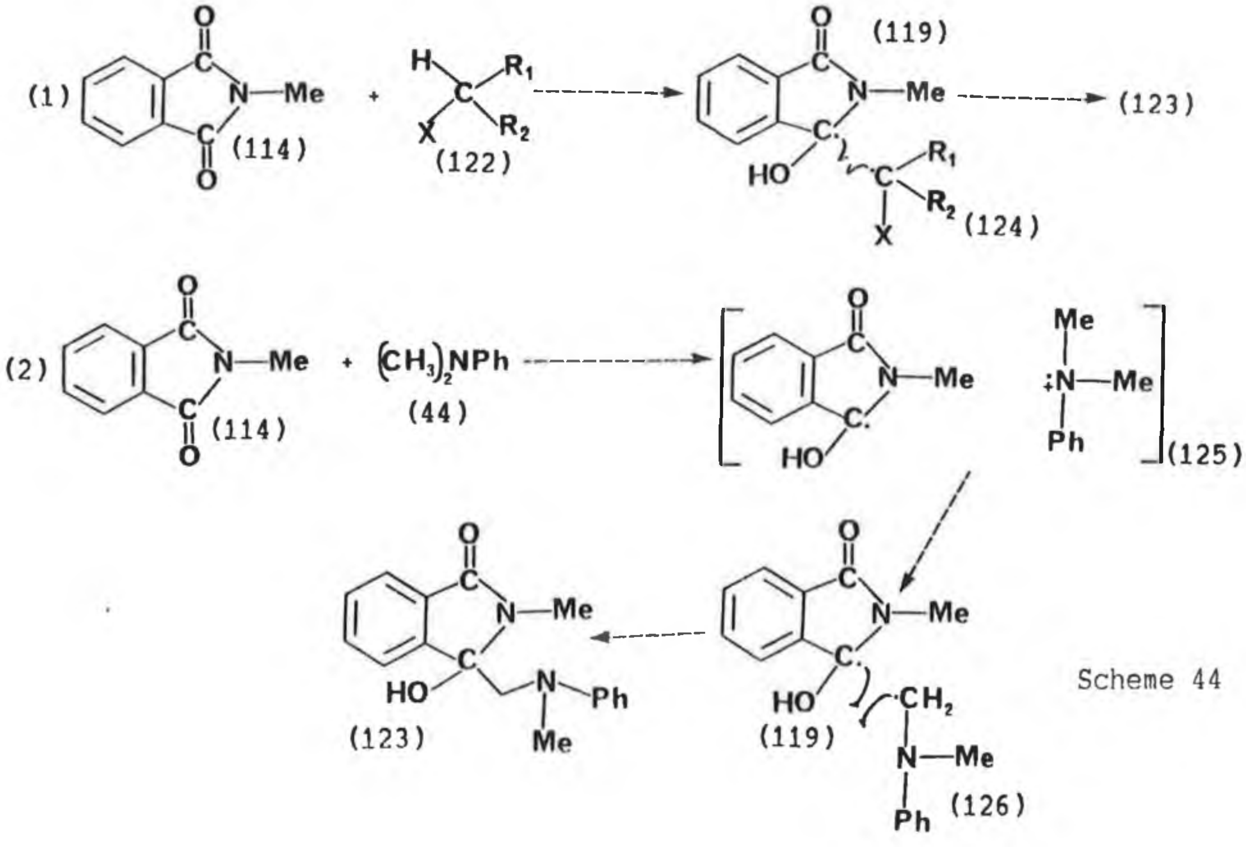
(c) $X = C_6H_5{}^{29}$

(d) $XR_1 = -C{=}C(CH_2)_n-$

(e) $X = NR_2{}^{29}$

Scheme 43

Two different mechanisms have been proposed to account for the formation of (123), (Scheme 44). In some cases it is suggested that direct hydrogen abstraction takes place[30] to give the semi-pinacol radical (119) and a solvent derived radical (124). Coupling of these radicals then gives the photoaddition product (123).

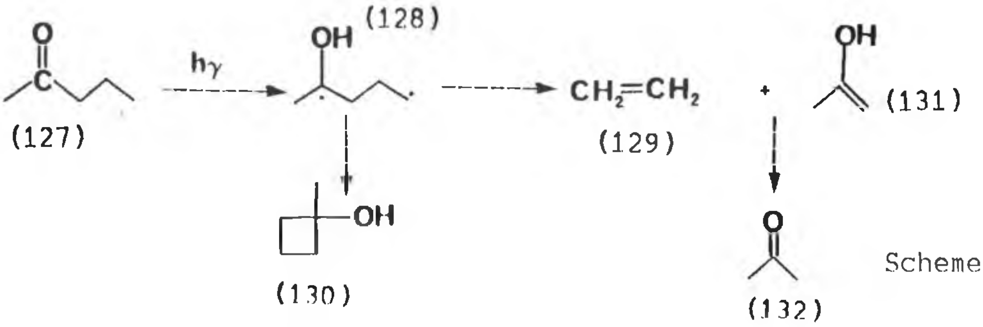


Scheme 44

In other cases it is proposed that reaction takes place via initial electron transfer, followed by proton transfer and radical coupling to give the observed photoaddition product.[29] For example, the photoaddition of dimethylaniline and NMP (2, Scheme 44) is believed to proceed via the latter mechanism.

Norrish Type 2 Reactions

Photolysis of a carbonyl compound (with an accesible hydrogen atom in the γ-position) often gives products derived from intramolecular hydrogen abstraction by the excited carbonyl group from the γ-position, (Scheme 45).

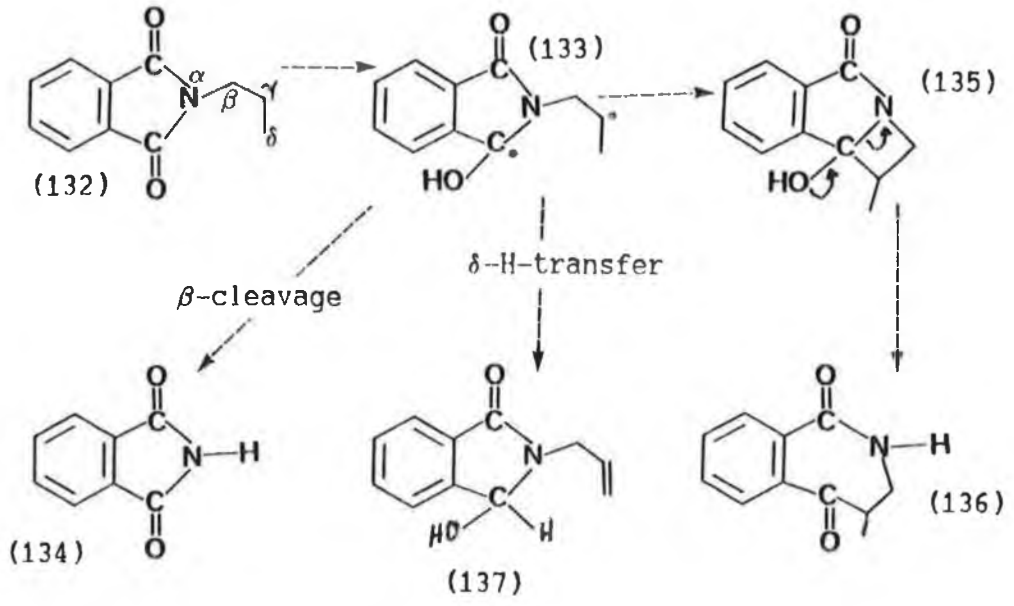


Scheme 45

These products include a shorter chain carbonyl compound (132) and an alkene (129), formed by an elimination mechanism generally referred to as a 'Norrish type 2' process, and a cyclobutanol (130) formed by a ring closure mechanism. The products can be envisaged as arising from an initially formed biradical (128) which can then undergo cyclisation or bond cleavage.

Photolysis of N-alkyl-phthalimides which possess a hydrogen γ to the carbonyl group (132, Scheme 46) gives rise to a series of products which can best be rationalized on the basis of a strictly formal analogy with the 'Norrish type 2' processes which have been well established in simple ketonic systems.[31]

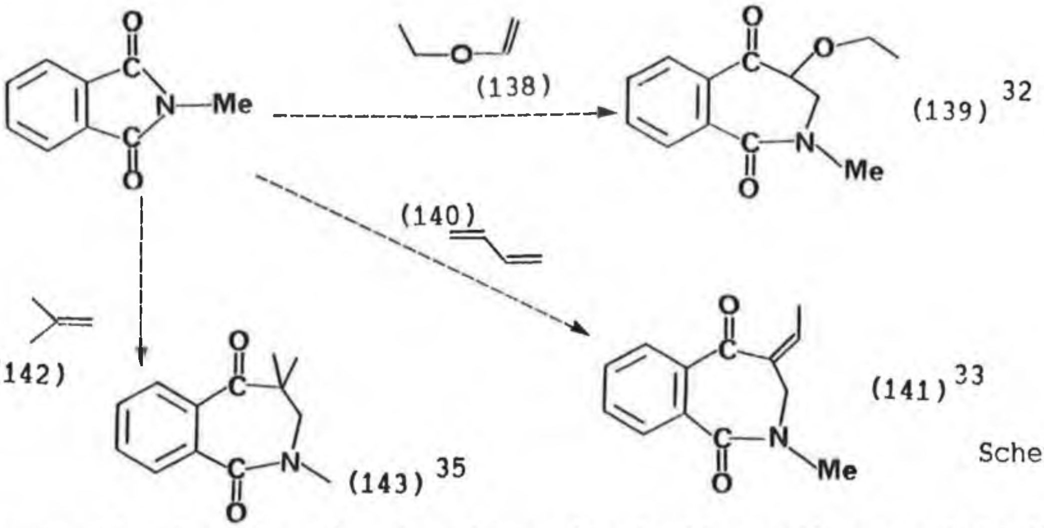
That is the reaction proceeds via initial γ-H abstraction to form a biradical (133). This is followed, either by a 'type-2' elimination to give (134) or by a 'type-2' cyclisation to give an azacyclobutanol (135). This azacyclobutanol, presumably due to ring strain, undergoes a retro-transannular ring opening to give the benzazepinone lactam (136).



Scheme 46

Alternatively, in some of the biradicals with δ-hydrogens, a competing δ-hydrogen abstraction takes place with concomitant formation of an unsaturated product (137).

Along with these reactions which are typical of simple ketones, N-alkylphthalimides also undergo a few unique reactions. They undergo photoaddition reactions with a wide variety of unsaturated molecules to give products derived from insertion into the C(O)-N bond, (Scheme 47).



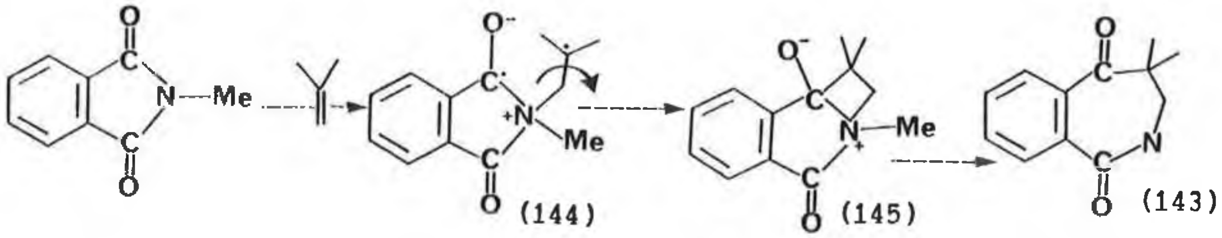
Scheme 47

This reaction has been found to be regioselective with respect to the direction of addition of the alkene component, the most substituted carbon of the origional alkene appearing adjacent to the carbonyl in the final product. The reaction is also selective with respect to the alkene ionization potential i.e. only those alkenes with ionization potentials greater than ~9eV give the benzazepinedione product.[34] It has been suggested that electron transfer quenching of the NMP singlet excited state might be occuring in those cases where the addition reaction did not occur.

$$\begin{tikzcd} \text{Benzazepinedione} & \text{NMP}^* + \text{A} \arrow[l, dashed] \arrow[r, dashed, "\text{electron transfer}"'] & {[\text{NMP}^{\cdot -}] + [\text{A}^{\cdot +}]} \arrow[l, dashed, bend right] \end{tikzcd}$$

That is, electron transfer from the alkene (A) to the excited NMP to give the radical cation-radical anion pair (which subsequently back e^- transfers to regenerate starting material) competes with the addition reaction. This electron transfer competes efficiently when the ionization potential of the alkene is less than ~ 9 eV .

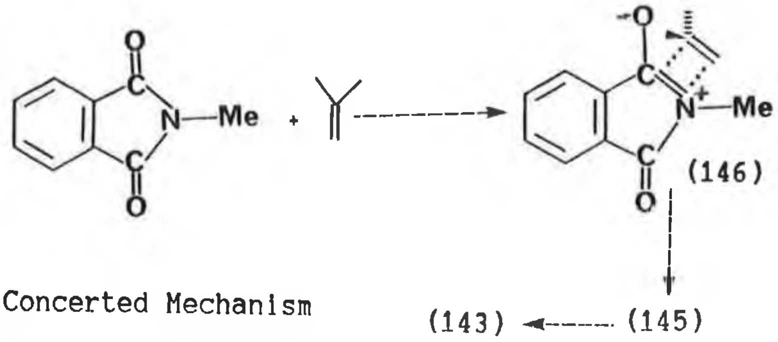
Two possible mechanistic schemes have been considered to account for the observed reactivity.[35] The first involves addition of the alkene (e.g. 2-methylprop-1-ene, Scheme 48) to give a zwitterionic biradical (144) which could then close to give a dipolar bicyclic intermediate (145) and subsequently reopen to give the observed benzazepinedione (143).



Biradical Mechanism

Scheme 48

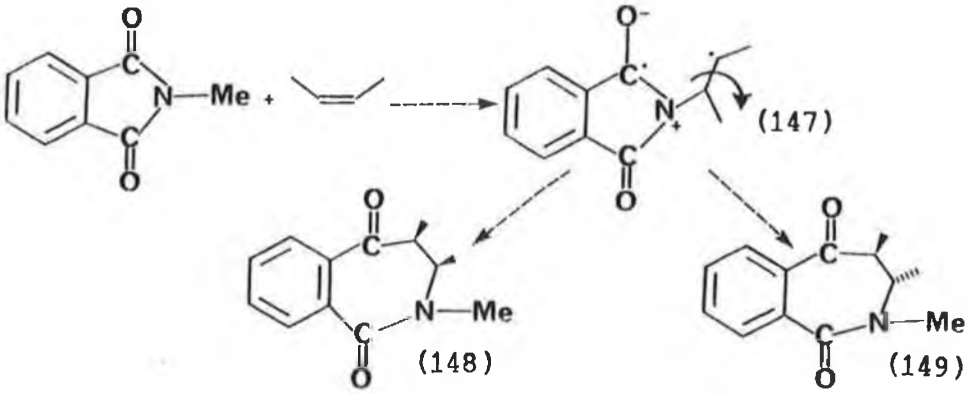
The second mechanism considered is a concerted addition of the alkene to the C(O)-N bond (which has substantial double-bond character) possibly via an oriented exiplex (146) to give the dipolar intermediate (145) directly, (Scheme 49).



Concerted Mechanism

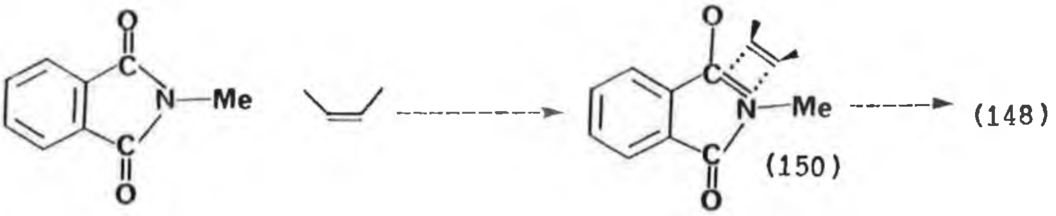
Scheme 49

If the reaction were taking place via the biradical mechanism (Scheme 48) then addition of the alkene would only be stereospecific provided ring closure of the biradical (144) was faster than bond rotation (with subsequent loss of stereochemistry.) For example, if the lifetime of the biradical is long with respect to molecular rotation (about the C-C bond from the alkene) then addition of cis-but-2-ene to NMP would give both the cis- and trans- benzazepinediones, (148) and (149), (Scheme 50).



Scheme 50

However, if reacton were taking place by the concerted mechanism (Scheme 49), addition of cis-but-2-ene would give only the cis-benzazepinedione product.



Experiments at low conversion and with excess alkene (to ensure little cis-trans isomerization of the alkene) suggest that addition of cis-but-2-ene gives only the cis-benzazepinedione and that trans-but-2-ene gives only the trans-benazepinedione i.e. that the reaction is stereospecific as well as regiospecific. The concerted mechanism is therefore the preferred one, although a biradical mechanism in which ring closure is faster than bond rotation cannot be ruled out.

CHAPTER TWO

Photochemical Reactions of Aryl Halides

The photosystems being studied in this thesis include aryl halides (as the possible electron acceptors) in the potential donor-acceptor pairs. Chapter two is therefore concerned with a general review of aryl halide photochemistry.

The major photochemical reactions of aryl halides are photosubstitution and photoaddition reactions. Categorization of these reactions by mechanistic type is difficult because of the variety of interrelated schemes that have been proposed. In general aromatic photosubstitution reactions can be divided into

(a) Nucleophilic
(b) Homolytic and
(c) Electron-Transfer

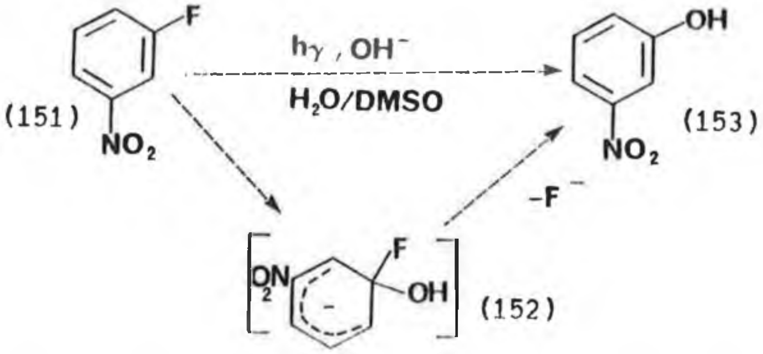
substitution reactions although some reactions (photonucleophilic reactions involving electron-transfer and/or radical chain processes) could be classified under more than one section.

Aromatic Photonucleophilic Substitution Reactions

Aromatic photonucleophilic substitution reactions have been extensively studied by Havinga and co-workers.[36,37] An excited aromatic molecule may undergo nucleophilic substitution via :

(1) Direct Substitution by a Nucleophile, an $S_N2(Ar^*)$ type reaction.

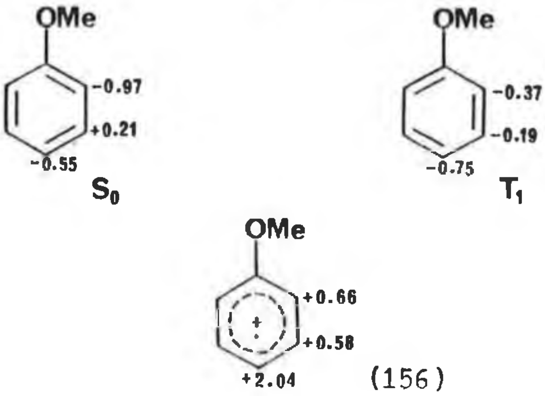
This type of substitution reaction probably only occurs for aromatics substituted with electron-withdrawing groups and is believed to proceed via the formation of a 'σ-complex' of the excited aromatic molecule and the nucleophile. The 'σ-complex' then ejects an origionally bonded group in favour of the incoming nucleophile. The electron-withdrawing group directs the nucleophile to the meta-position. This meta-activation rule finds a simple rationalization in charge density calculations which show that for both $^1\pi,\pi^*$ and $^3\pi,\pi^*$ aromatic states there is a greater charge meta to an electron-withdrawing group, (Scheme 51). Aromatic halides which contain an electron-withdrawing group meta- to the halogen have been reported to undergo this type of reaction. For example, m-fluoronitrobenzene (151) has been reported to undergo this type of photosubstitution[38] in aqueous alkaline solution to give m-nitrophenol (153). The reaction can be considered to proceed via the formation of the σ-complex (152). With aryl halides in general however the presence of the halogen which is a good leaving group will often lead to its substitution no matter what position it is in. Thus o- and p- nitrofluorobenzene give the corresponding nitrophenol when irradiated in alkaline solution.[38]



Scheme 51

Chlorine and fluorine are the most satisfactory leaving groups as bromo- and iodo- arenes often show competition between such nucleophilic substitution and carbon-halogen bond homolysis. Such competition has been reported to occur with some chloro-arenes.[39]

(2) Formation of a radical cation via electron transfer (from the aromatic molecule to the medium) followed by attack of the nucleophile, an $S_{R+N}1$ (Ar*) type reaction. This type of substitution reaction is seen in aromatic molecules substituted with strong electron-donating groups. The latter direct the incoming nucleophile to the ortho- and para- positions. This ortho/para activation cannot be understood on the basis of calculations of the charge densities in either the excited singlet or triplet aromatic molecule. Instead the intermediacy of the radical cation of the aromatic molecule is supported by calculations of its charge density distribution. For example, the calculated charge distributions for anisole in the ground state, in its lowest triplet excited state and as a radical cation are outlined in Scheme 53.

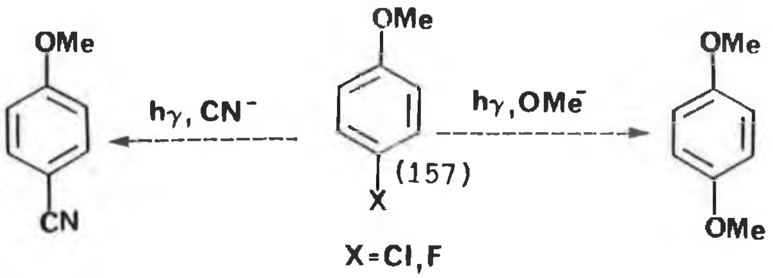


(154) (155) (156)

Scheme 53

These show that attack of an incoming nucleophile on the radical cation is more likely to occur at the ortho- and para- positions. This is in contrast to the S_0 and T_1 states of anisole in which attack is more likely at the meta-position.

Aromatic halides which contain a strong electron-donating group ortho- or para- to the halogen have been reported to undergo this type of reaction. Again, chlorine and fluorine are the most satisfactory leaving groups in this type of reaction as bromo- and iodo- arenes often undergo preferential homolysis of the carbon-halogen bond. For example, in the photosubstitution reaction of p-chloro- or p-fluoro-anisole with cyanide or methoxide, greater than 90% of the photosubstitution products (158) and (159) were isolated,[40] (Scheme 54).

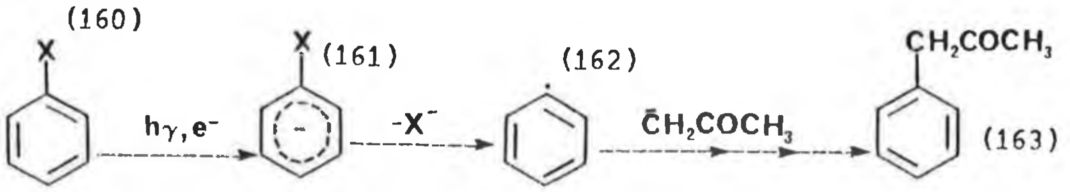


(158) (159)

Scheme 54

(3) <u>Uptake of an electron by the aromatic molecule to form a radical anion,</u> followed by unimolecular expulsion of an anion (usually a halide) to give an aromatic radical which is then attacked by the nucleophile, an $S_{R-N}1$ type reaction. The majority of these reactions involve aryl halides. They have been extensively studied by Bunnett[41] and a number of synthetically useful reactions have been reported. A range of different carbanions has been employed as nucleophiles (ketone,[41] ester[42] and N,N-disubstituted amide[43] enolates) and

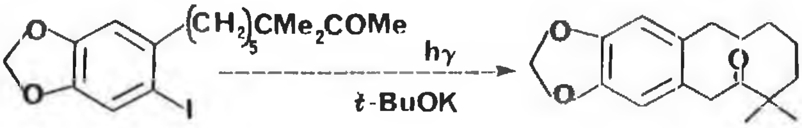
this reaction constitutes a useful method for the attachment of carbon units to aromatic rings.For example, irradiation of halobenzenes in the presence of an electron source and acetone enolate leads to good yields of phenylacetone, (Scheme 55).



$[PhCH_2COCH_3]^{\cdot-}$ + PhX ----→ $Ph^{\cdot-}$ + (163)
(164)

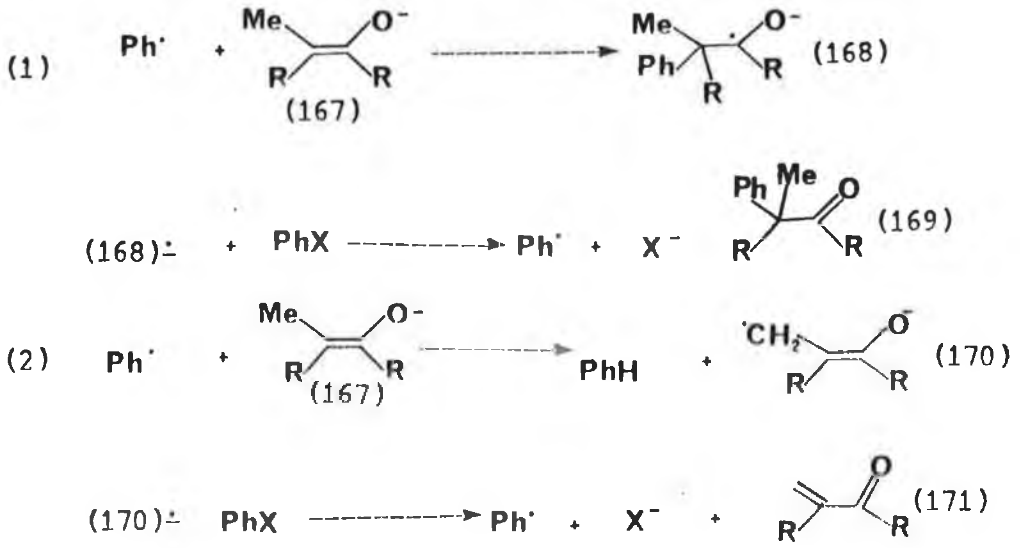
(Scheme 55)

The proposed mechanism involves the formation of the radical ion of the halobenzene (161). This is followed by expulsion of X- to form a phenyl radical. The latter is then attacked by acetone enolate to form $[PhCH_2COCH_3]^{\cdot-}$ which is a good electron donor and transfers an electron to another aryl halide molecule thus setting up a chain reaction and generating the observed product[41] (163). Intramolecular reaction of enolate anions with aryl halides can be efficient and give products with new rings of up to ten atoms. For example, the intramolecular cyclization of the enolate of (165) gives (166),[44] (Scheme 56).



Scheme 56

The efficiency of both the inter- and intra- molecular reactions depends upon competition between the substitution reaction and hydrogen atom transfer from the enolate anion to the transient phenyl radical, (Scheme 57). For example, the enolate anion (167) can react via (1) C-C coupling to give the substitution product (169) or (2) via hydrogen atom transfer to give the α,β-unsaturated ketone (171). In both cases a radical anion (168 or 170) is produced which is formally capable of chain propagation via electron transfer to the aryl halide. Hydrogen atom transfer, resulting in low yields of substitution products can be



Scheme 57

avoided by blocking the α- or β- positions of the enolate anion with carbon substituents instead of hydrogen. These $S_{R-N}1$ reactions and the synthetic use of the intramolecular reactions have been reviewed.[45]

Homolytic Aromatic Photosubstitution Reactions

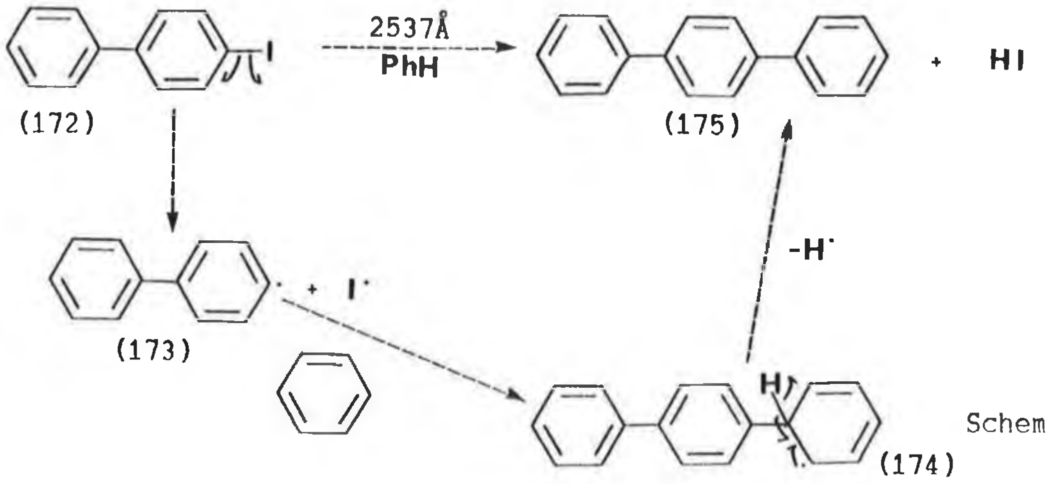
Photosubstitution reactions involving aryl halides often proceed via homolysis of the carbon-halogen bond to give radicals in their ground states, which can then give rise to products by well established thermal pathways, (Scheme 58)

$$\mathrm{Ph{-}X} \xrightarrow[h\nu]{} \mathrm{Ph}^{\cdot} + \mathrm{X}^{\cdot}$$

$$\mathrm{Ph}^{\cdot}\ \mathrm{H{-}R} \longrightarrow \mathrm{Ph{-}H} + \mathrm{R}^{\cdot}$$

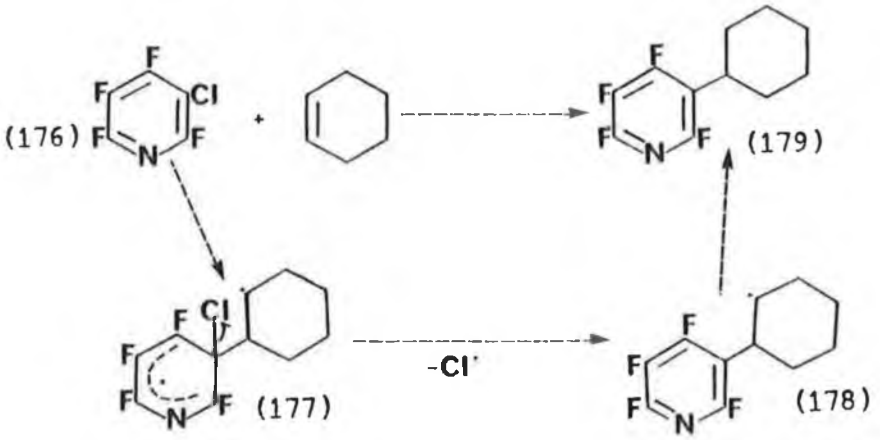
Scheme 58

A phenyl radical (Ph˙) so formed may, in the presence of a hydrogen donating molecule (H-R) abstract hydrogen to give benzene. The light induced homolysis of aryl halogen bonds has important synthetic applications. For example, irradiation of iodinated aromatics in benzene will often give the phenyl-substituted aromatic in high yield,[46] (Scheme 59). The reaction is believed to proceed via initial carbon-iodine bond homolysis to give an aryl radical (173) which then attacks a molecule of benzene to give the radical intermediate (174). The latter then rearomatizes to give the observed product (175).



Scheme 59

Homolytic photosubstitution reactions of aryl halides do not always proceed via initial carbon-halogen bond breaking. Instead reaction may take place via the formation of an intermediate biradical. For example, irradiation of cyclohexene in 3-chloro-tetrafluoropyridine (176) yields 3-cyclohexyl-tetrafluoropyridine[47] (179), (Scheme 60).

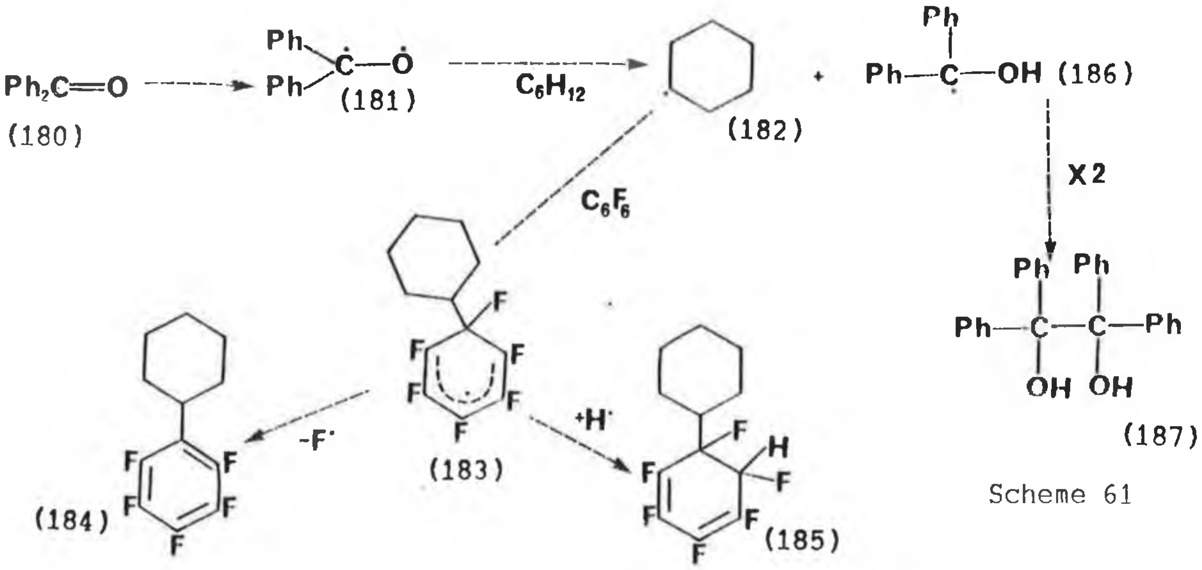


Scheme 60

The reaction is believed to proceed via the formation of biradical (177). This is followed by the loss of Cl˙ to give the radical (178) which then abstracts an allylic hydrogen atom from the cyclohexene. The resulting cycloalkenyl radical then dimerizes. Tetrafluoropyridyl radicals (formed by initial C-Cl bond homolysis) do not appear to be involved. If present they would be expected to abstract hydrogen to give tetrafluoropyridine and none of the latter is observed. In contrast, irradiation of chloro-tetrafluoro-pyridine in diethylether[47] does lead to the replacement of chlorine by hydrogen and the reaction is believed to take place via initial C-Cl bond homolysis to give tetrafluoropyridyl radicals which then abstract hydrogen from the solvent.

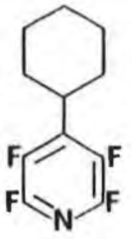
Other reactions that have been reported to proceed via the formation of an intermediate biradical include the photochemical reaction of hexafluorobenzene with benzene to give 2,3,4,5,6,-pentafluorobiphenyl[48] and with toluene to give an analolgous mixture of o-, m-, and p-pentafluorophenyltoluenes.[48]

Homolytic photosubstitution reactions of aryl halides can also be initiated using chemical sensitizers. For example, irradiation of a mixture of benzophenone, hexafluorobenzene and cyclohexane gives the photosubstitution product (184) along with the photoaddition product[49] (185), (Scheme 61).



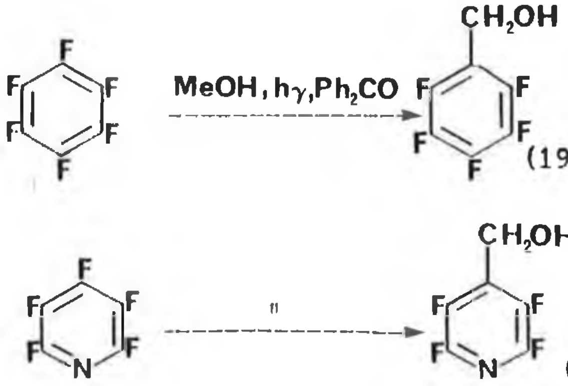
Scheme 61

The proposed mechanism involves the formation of cyclohexyl radicals in the presence of benzophenone. The cyclohexyl radicals (182) then react with hexafluorobenzene to form a radical intermediate (183) which then transforms by two different paths to give the substitution product (184) and the addition product (185). Without benzophenone present a complex mixture of products is formed.[50] Pentafluoropyridine also reacts with cyclohexane in the presence of benzophenone ,in a similar manner, to give the 4-substituted product (188) and no addition product.[51]



(188)

The corresponding reaction of hexafluorobenzene or pentafluoropyridine with other cycloalkanes is much less successful. Both however undergo photosubstitution reactions[52,53] when irradiated in the presence of benzophenone and methanol (Scheme 62).



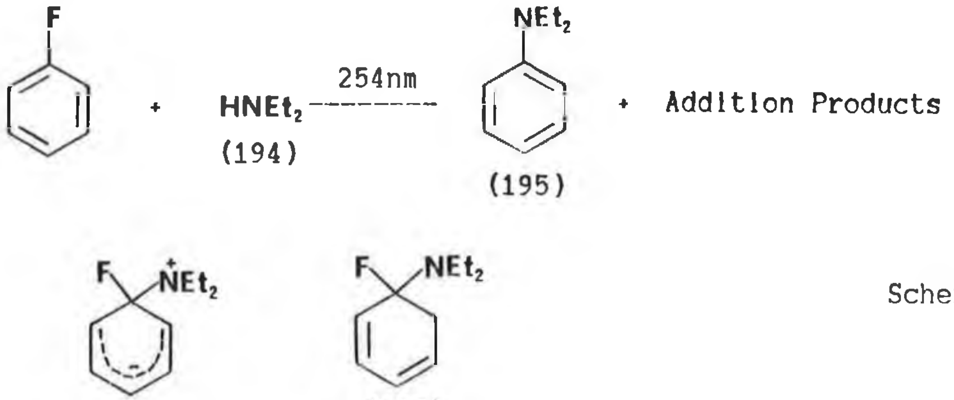
(189) (191) (ref.52)

(190) (192) (ref.53)

Scheme 62

A similar addition-elimination mechanism to that outlined in Scheme 61 for the formation of the substitution product (184) has been proposed to account for the formation of (191)[52] and (192).

A related reaction is seen in the photosubstitution of fluorobenzene by primary and secondary aliphatic amines. The light induced acyclic addition of amines to aromatic hydrocarbons is well known[54] but with some substituted arenes replacement of the substituent also occurs. Thus primary and secondary amines photoreact with fluorobenzene to give a substitution product along with several addition products.[55] An addition-elimination mechanism has been proposed to account for the formation of the substitution products.[55] However, in these reactions sensitization by benzophenone is not required. For example, irradiation of fluorobenzene and diethylamine gives N,N-diethylaniline along with several addition products, (Scheme 63).



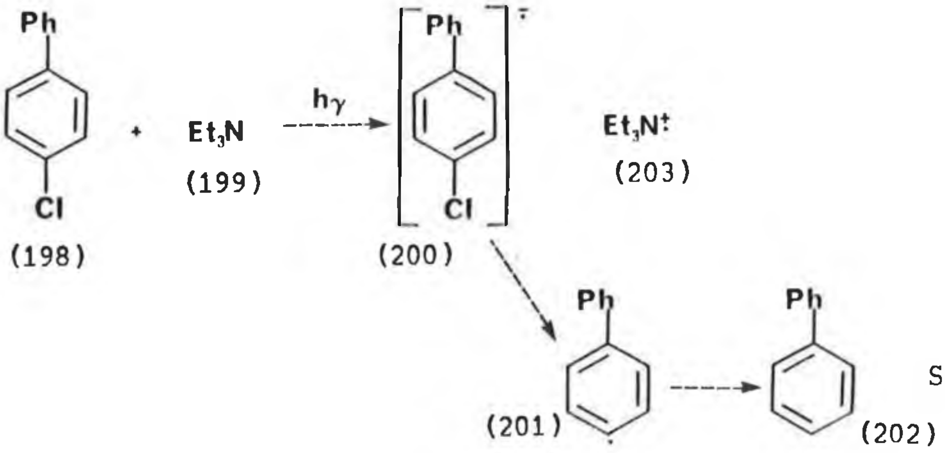
(193) (194) (195)

(196) (197)

Scheme 63

The exact mechanism of this reaction has not been determined but it is believed[55] to proceed via an electron transfer process to give either a Wheland-type intermediate (196) and/or an unstable chemical adduct (197). Overall elimination of hydrogenfluoride from either of these gives the observed photosubstitution product (195). Similar results are obtained using t-butylamine or piperidine[56] instead of diethylamine or replacing fluorobenzene by chlorobenzene,[55] although the product ratios vary considerably. Again the reactions are believed to proceed via initial electron transfer from the amine to the aryl halide.[56,55]

Irradiation of aryl halides in the presence of triethylamine often leads to photoreduction[57] rather than addition or substitution reactions. The photoreduction of chlorinated aromatics has been studied in some detail because of the importance of some of these compounds as environmental pollutants. For example, irradiation of 4-chloro-biphenyl in the presence of triethylamine leads to photoinduced dechlorination.[58] The reaction is believed to proceed via electron transfer from the amine to the aryl halide. This is followed by loss of chloride from the aryl radical anion (200) to give an aryl radical (201) which then abstracts hydrogen from the solvent to give biphenyl (Scheme 64).

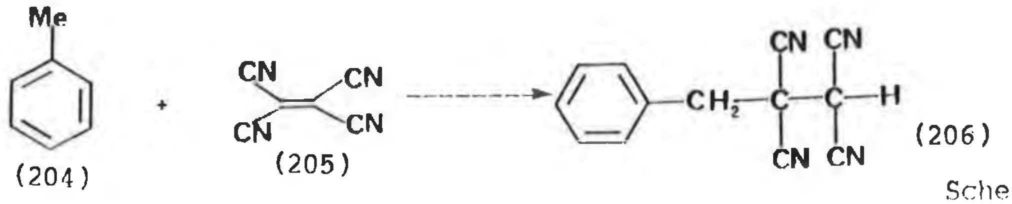


Scheme 64

Other examples of electron-transfer sensitized photosubstitution reactions of aryl halides have been discussed on pages 18-25.

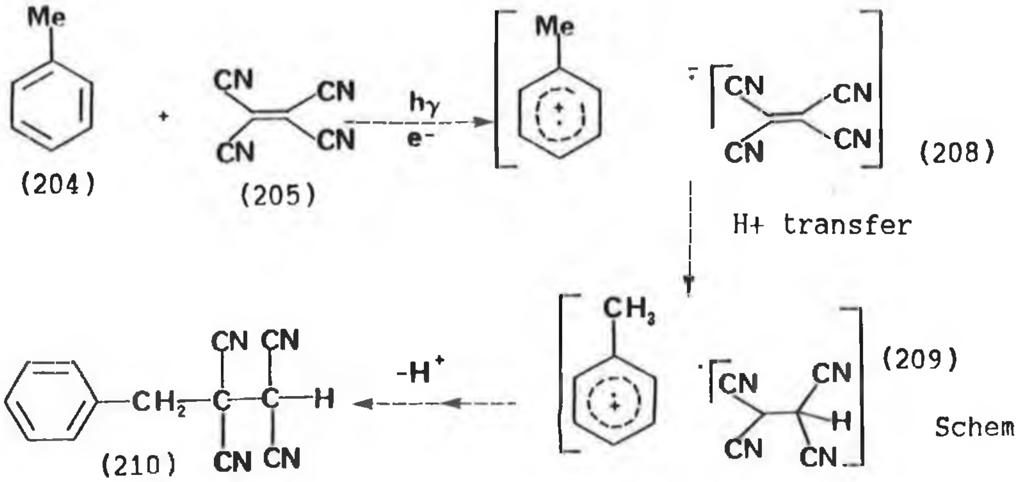
Photoaddition Reactions of Aryl Halides

The irradiation of mixtures of aromatic hydrocarbons and unsaturated systems gives rise to a wide diversity of addition products. It has been suggested that the mode of addition (i.e. whether addition takes place to give a 'substitution'or cycloaddition adduct) depends upon the value of the calculated[2] free energy change for electron transfer (ΔG) between the starting materials.[59] When the calculated ΔG value is negative (or only slightly positive) 'substitution' is preferred whereas when ΔG is positive cycloaddition is preferred. For example, the calculated ΔG value for toluene/tetracyanoethene is negative and irradiation leads, in non-polar solvent, to the 'substitution'-type adduct[60] (206), (Scheme 65), as well as an addition product.



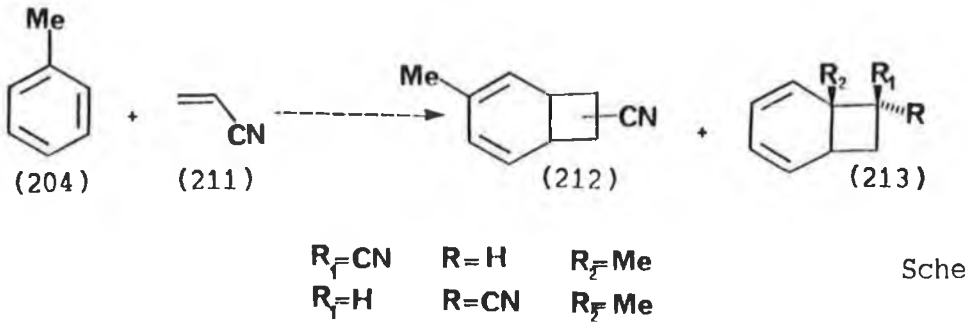
Scheme 65

A mechanism involving initial electron transfer from toluene to the alkene, followed by proton-transfer, radical coupling and deprotonation (Scheme 66) can be proposed to account for the observed product.



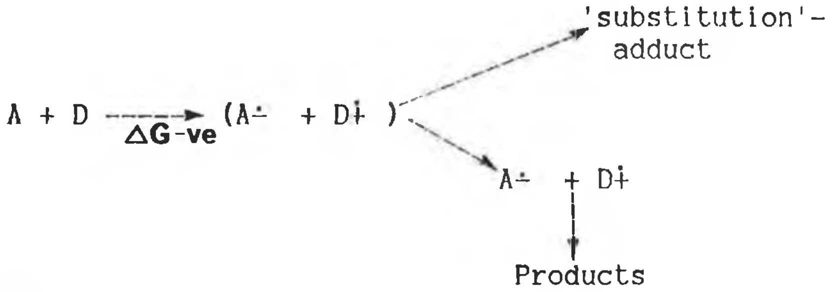
Scheme 66

In contrast the calculated free energy change for toluene/acrylonitrile is positive and the major products are 1,2-cycloaddition products,[61] (Scheme 67).



Scheme 67

When the calculated ΔG value is negative products other than the 'substitution'-adducts can be formed by competing reactions. When irradiations are carried out in polar solvents the initially formed radical cation/radical anion pairs can dissociate into solvent separated radical ions. Ground state reactions of these free radical ions can lead to reaction products, (Scheme 68).

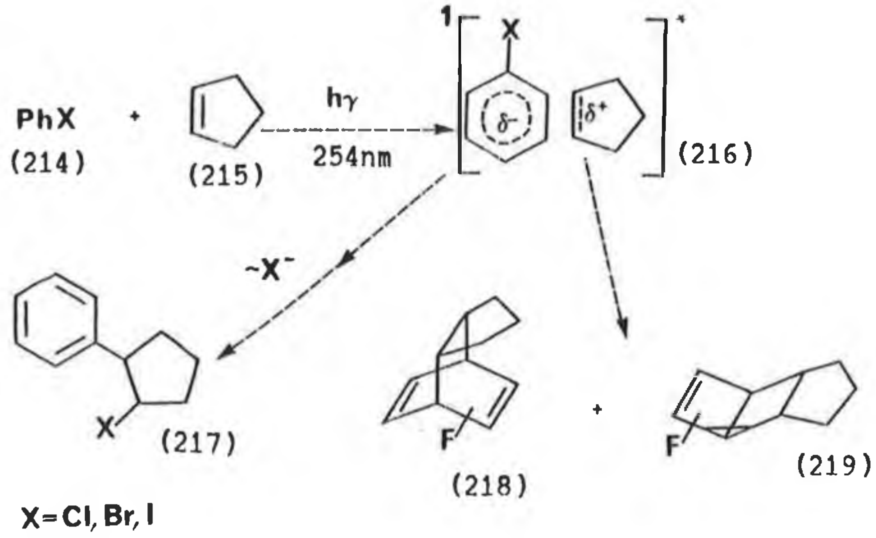


A = Acceptor Arene/Alkene

D = Donor Alkene/Arene

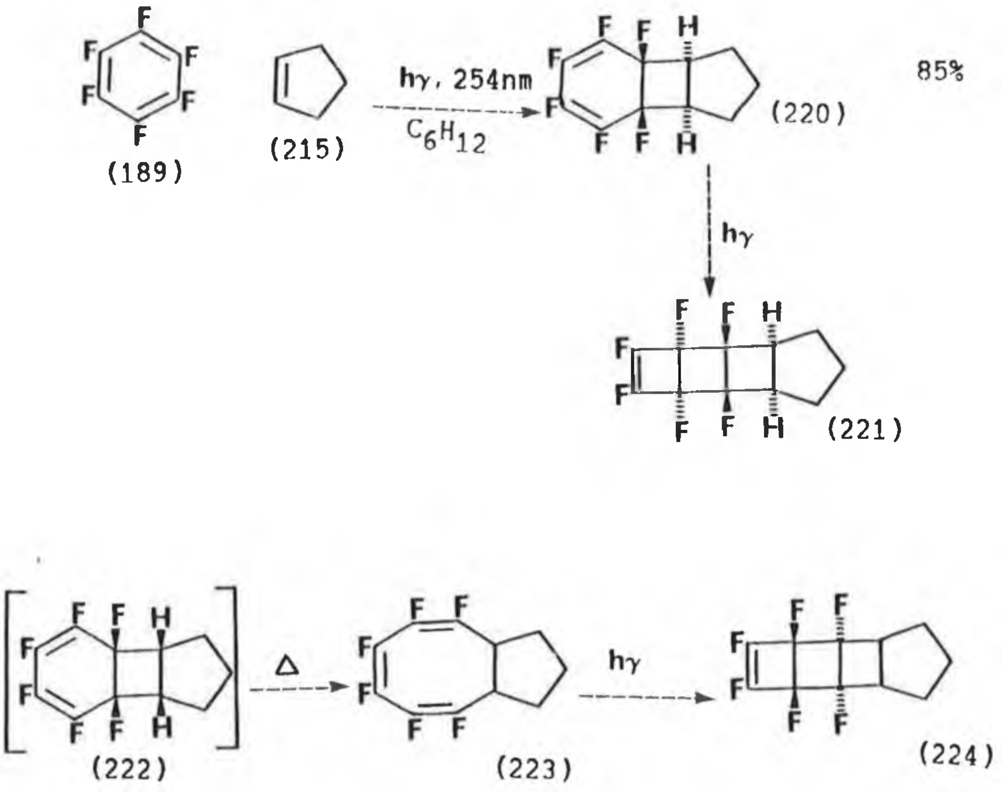
Scheme 68.

The photoreactions of chloro-, bromo-, and iodo-, benzene with cyclopentene appear to be exceptions to the ΔG correlation but again the observed reactivity con be explained on the basis of a competing reaction. All three aryl halides form mainly substitution products with cyclopentene[63] (Scheme 69) but the calculated ΔG values for electron



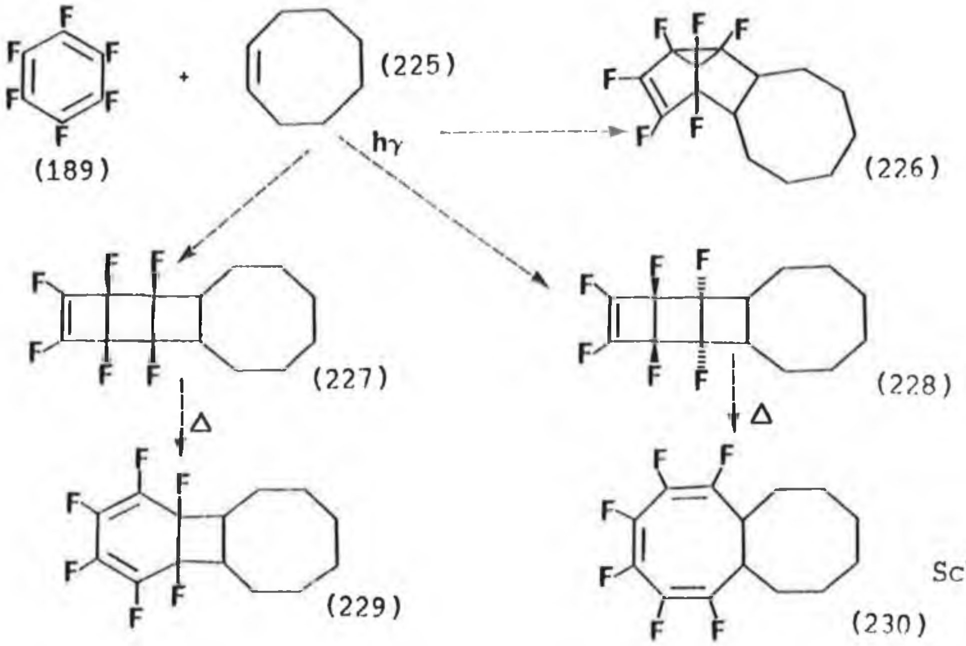
Scheme 69

transfer are positive, though relatively small. It has been suggested that the reaction takes place via a polar exiplex (216) and that migration of halide within such a species leads to the substitution product (217). This mechanism may account for the photoreactions of chloro-, bromo- and iodo- benzene since their carbon-halogen bonds are relatively weak. Indeed the corresponding reaction between fluorobenzene and cyclopentene preferentially yields cycloadducts,[63] the C-F bond strength being of the same order of magnitude as that of the C-H bond. The cycloadducts are formed as a result of 1,3- (219) and 1,4-addition (218) across the aromatic ring. No corresponding 1,2-adducts are formed. This is in marked contrast to the photoreactions of hexafluorobenzene. The latter has been reported to undergo photoaddition with a range of unsaturated systems (cyclopentene[64], cyclooctene[65], indene[66], 1,2-dihydronaphthalene[66], propyne[66], and but-2-yne[66]) to give products derived from a 1,2-addition across the aromatic ring. For example, hexafluorobenzene undergoes 1,2-photoaddition with cyclopentene to give the anti-isomer as major product[64] (Scheme 70) together with (221) and (223). None of the syn-isomer (222) was isolated and it is believed to be very unstable at room temperature and has been postulated

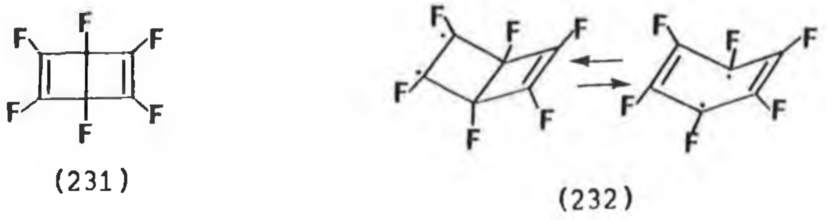


Scheme 70

as the immediate precursor of the observed product (223). Further irradiation of (220) and (223) yields the tetracyclic fluorinated compounds (221) and (224) respectively. The exact mechanism of this reaction has yet to be determined but its selectivity (i.e. only 1,2-addition products are formed) is in marked contrast to the corresponding reaction with cis-cyclooctene[65] in which products derived from both 1,2- (227,228) and 1,3- (226) addition across the aromatic ring are formed, (Scheme 71). The 1,2-adducts undergo thermal isomerization to give (229) and (230). Again the mechanism of this reaction has not been determined. However the 1,2-adducts are believed to be derived, not from the Dewar form of hexafluorobenzene (231), which is formed on irradiation of hexafluorobenzene alone, but from one or more of its precursors such as the biradical (232), (Scheme 72).

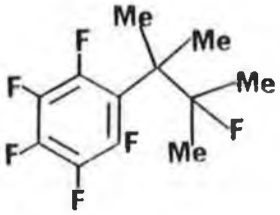


Scheme 71



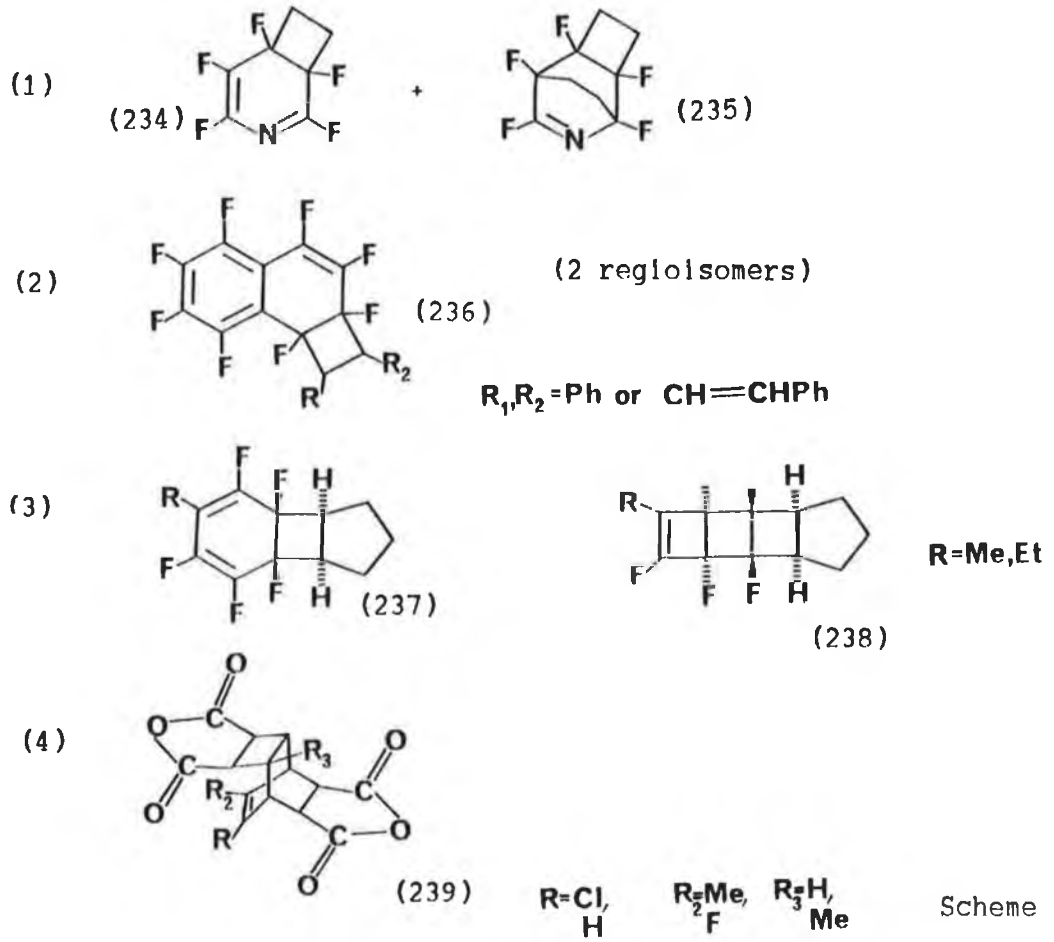
Scheme 72

Only one alkene, tetramethylethene, has been reported to give a 'substitution'-type adduct (233) when irradiated in the presence of hexafluorobenzene.[66] The calculated ΔG value for electron transfer



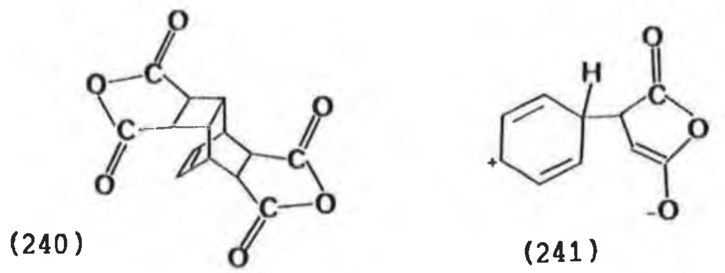
(233)

between tetramethylethene and C_6F_6 is negative. This is in contrast to the corresponding calculations for reaction of cyclopentene or cyclooctene with C_6F_6 both of which give positive ΔG values and is in agreement with the proposal that 'substitution' products are formed when ΔG is negative or only slightly positive. Mattay has also proposed that the mode of cycloaddition (i.e.whether 1,2- or 1,3-addition occurs) between an alkene and aromatic molecule depends upon the actual value of ΔG.[67] He has suggested that within a certain range of ΔG values, the actual values depending upon the aromatic molecule concerned, only 1,2-addition occurs and within another range only 1,3-addition occurs although there will be an area of overlap in which both 1,2- and 1,3- addition will occur. However, with the halogenated aromatic molecules only more systematic studies with a range of alkenes will show whether a similar correlation can be applied to them and, if so, where the ΔG -transition area from 1,2- to 1,3- cycloaddition occurs. A number of 1,2-cycloaddition reactions of other aryl halides with various alkenes have been reported. These include (1) pentafluoropyridine and ethene[68], (2) octafluoronaphthalene and 1,4-diphenylbutadiene[69], (3) alkylpentafluorobenzenes and cyclopentene[70], and (4) o-chlorotoluene (and p-fluorotoluene) and maleicanhydride.[71] The products of these reactions are shown in Scheme 73. The reaction between pentafluoropyridine and ethene also gives a product derived from both 1,2- and 1,4-addition across the ring (235). The 1,2-addition product between alkylpentafluorobenzene and cyclopentene undergoes thermal rearrangement to give the tetracyclic product (238). The product formed in the photoreaction of o-chlorotoluene and maleicanhydride is exactly



Scheme 73

analogous to the one formed (240) between benzene and maleic anhydride[72]. The latter reaction is believed to proceed via the formation of a zwitterionic intermediate (241) which then reacts with another molecule of maleic anhydride before closure of the cyclobutane ring.



Scheme 74

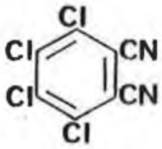
CHAPTER THREE

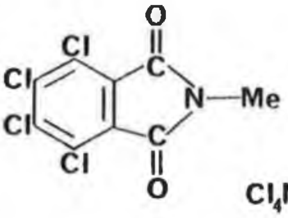
DISCUSSION

Irradiation of Donor-Acceptor systems can often lead to the formation of radical cation-radical anion pairs (via photoinduced electron transfer) and subsequent ground state reactions of these radical ion pairs can give reaction products:-

$$\mathrm{D} + \mathrm{A} \dashrightarrow \mathrm{D}^{+\cdot} + \mathrm{A}^{-\cdot} \dashrightarrow \text{Products (see P.5)}$$

We have been particularly interested in two electron deficient aryl halides, tetrachlorophthalonitrile (TCPN) and N-methyl-tetrachlorophthalimide (Cl_4NMP), as possible electron acceptors in such photoinitiated electron transfer reactions.

(91)

TCPN


(111)
Cl_4NMP

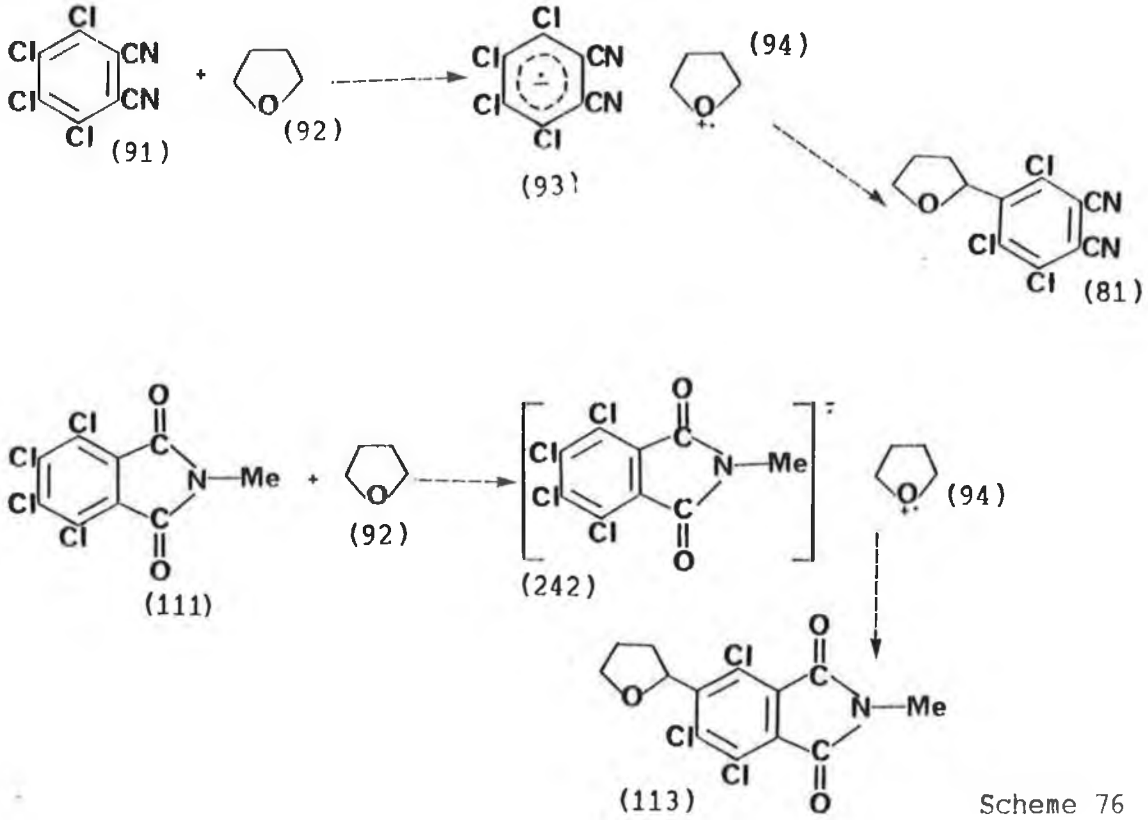
Scheme 75

Both TCPN and Cl_4NMP show strong u.v. absorbance bands above 300nm. Irradiation of reaction mixtures through pyrex (which cuts off light of wavelength < 300nm) should therefore lead to excitation of only the acceptor molecule (TCPN or Cl_4NMP) provided the chosen donor molecules do not also absorb strongly above 300nm :-

$$\mathrm{D} + \mathrm{A} \xrightarrow[\text{Pyrex}]{h\gamma} \mathrm{D} + \mathrm{A}^{*} \dashrightarrow \mathrm{D}^{+\cdot} + \mathrm{A}^{-\cdot} \dashrightarrow \text{Products}$$

$*$ = excited state

i.e. electron transfer should occur from the ground state donor molecule to the excited acceptor molecule. TCPN and Cl_4NMP also possess good leaving groups (the chlorine atoms) so that, after initial electron transfer, it might be expected that the reaction would result in a chlorine atom being replaced. TCPN and Cl_4NMP have, in fact, been shown to undergo photochemical reactions with several potential donor molecules to give products in which a chlorine atom has been replaced by the donor molecule.[73] In all these cases a mechanism involving initial electron transfer from the donor molecule to the excited aryl halide, to give a radical cation-radical anion pair, has been proposed to account for the observed products, (Scheme 76).



Scheme 76

For example, the photochemical reactions of both TCPN and Cl_4NMP with tetrahydrofuran are believed to proceed via initial electron transfer from tetrahydrofuran to the excited aryl halide, (Scheme 76).

In general the feasibility of producing radical ion pairs by photoinduced electron transfer can be predicted using the Weller[2] equation :-

$$\Delta G/kJmol^{-1} = 96.4[E(D/D+)_V - E(A/A-)_V - e^2/\epsilon\alpha] - \Delta E_{o,o}/kJmol^{-1}$$

Where $E(D/D+)_V$ is the oxidation potential of the donor molecule in volts and $E(A/A-)_V$ is the reduction potential of the acceptor molecule in volts. $e^2/\epsilon\alpha$ is an electrostatic term and is the free energy gained on bringing the free ions to equilibrium distance in a solvent of dielectric constant ϵ . If the solvent has a large dielectric constant $e^2/\epsilon\alpha$ is negligible. $\Delta E_{o,o}$ is the singlet excitation energy of either the donor or acceptor depending on which is excited.

The reduction potentials of TCPN, Cl_4NMP and tetrachloro-N-ethylphthalimide (Cl_4NEP) were measured using cyclic voltametry on a platinum electrode (vs. a saturated calomel electrode, S.C.E.). Tetraethylammoniumperchlorate (0.1M in MeCN) was used as supporting electrolyte, (Table 1).

	$-E_{1/2}^{red}/V$	$\Delta E_{o,o}/kjmol^{-1}$
TCPN	1.14	348
Cl_4NMP	1.10	340
Cl_4NEP	1.11	332

Table 1

For TCPN the electron transfer process is irreversible. The half-wave reduction potential ($E_{\frac{1}{2}}^{red}$) was therefore estimated using a $50mVs^{-1}$ sweep rate. For Cl_4NMP the reduction is reversible and the half-wave reduction potential was taken as 0.05V before the anodic peak potential and 0.04V before the cathodic peak potential. For Cl_4NEP the reduction is also reversible and the half-wave reduction was taken as 0.07V before the anodic and cathodic peak potentials. The singlet excitation energies $\Delta E_{o,o}$) of the acceptor molecules were estimated from the intersection of their absorption and emission spectra in acetonitrile. When these values are substituted into the Weller Equation it is found that for ΔG to be negative, the oxidation potential of the donor molecule (E D/D+) must be less than ~2.5V (vs.S.C.E.) i.e. an electron transfer step should be spontaneous (for all three acceptor molecules) when the half-wave oxidation potential of the chosen donor molecules is less than ~2.5V.

Reported values[74] for the oxidation potentials of anthracene, phenanthrene, methoxybenzene, and 1,4-dimethoxybenzene are all less than 2.5V, (Table 2). These compounds have been reported[23,24] to undergo photochemical reaction with TCPN and an electron transfer mechanism has been proposed to account for the observed products. This mechanism is supported by the calculated ΔG values for the electron transfer step which are all negative and which therefore predict that photoinitiated

	$E_{\frac{1}{2}}^{ox}/V$	$\Delta G/kjmol^{-1}$
Anthracene	1.16	-131
Phenanthrene	1.62	-90
Methoxybenzene	1.76	-73
1,4-Dimethoxybenzene	1.34	-113

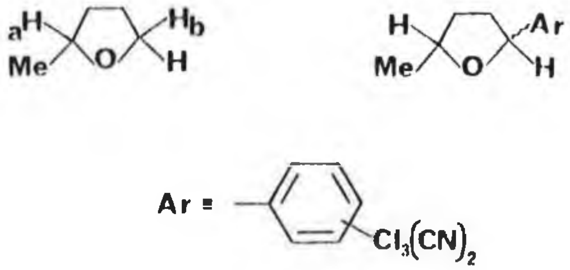
Table 2.

electron transfer should be spontaneous. In contrast the oxidation potentials of tetrahydrofuran (THF), diethylether, 1,4-dioxan, and 1,3-dioxolan will all be much higher than 2.5V. THF is in fact often used as a solvent when measuring the oxidation potentials of organic molecules. All these ethers however also undergo photochemical reaction with TCPN. THF, 1,3-dioxolan and 1,4-dioxan also undergo photochemical reaction with Cl_4NMP. For both the TCPN and the Cl_4NMP reactions with aliphatic ethers an electron transfer mechanism has again been proposed to account for the observed photosubstitution products. Such an electron transfer mechanism may still be valid in cases where the calculated free energy is moderately positive and the life-time of the excited state relatively long. Alternatively these reactions with aliphatic ethers may proceed via a mechanism which involves something other than simply electron transfer from the ground state ether to the excited arylhalide. Perhaps the formation of an exiplex of the aryl halide and ether facilitates the proposed electron transfer. The Weller equation takes no account of structural changes occuring after excitation of the acceptor (or donor) molecules and such a change may well facilitate electron transfer between donor and acceptor molecules.

The Photochemical Reaction of 3.4.5.6-Tetrachlorophthalonitrile with 2-Methyltetrahydrofuran.

TCPN has been reported to undergo a photosubstitution reaction when irradiated in the presence of tetrahydrofuran[20] to give (81), Scheme 32, P.21, in which the hydrogen on the carbon adjacent to oxygen has been replaced by the aryl group. A mechanism involving initial electron transfer, followed by proton transfer, radical coupling and elimination of HCl has been proposed to account for the observed product, (see Scheme 32). 2-Methyltetrahydrofuran (243) might be expected to react in a similar manner to THF when irradiated in the presence of TCPN. With 2-methyltetrahydrofuran however the two hydrogens on the α-carbon atoms (H_a and H_b) are not equivalent. H_b should be more acidic than H_a

(243) (244)

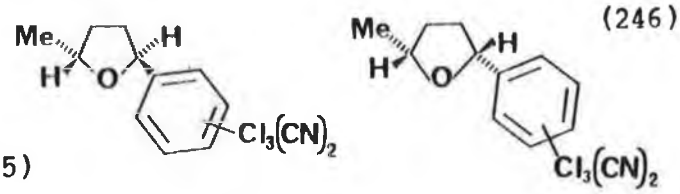


Scheme 77

because of the presence of the methyl group on the carbon bearing H_a. As the proposed mechanism (Scheme 32, P21) involves a proton transfer step from the ether radical cation, the reaction with 2-methyltetrahydrofuran might be expected to lead to the replacement of H_b, the more acidic hydrogen, to give (244). It was therefore decided to irradiate a solution of TCPN and 2-methyltetrahydrofuran in dichloromethane to see whether this did in fact occur.

When a solution of TCPN and 2-methyltetrahydrofuran in dichloromethane was irradiated through pyrex two additional spots were observed on TLC. Chromatographic separation of the reaction mixture led to the isolation of two fractions, (A) and (B). Fraction (B), the major one, eluted marginally behind fraction (A), the minor one. Fraction (B), m.p. 122-

124 °C, showed cyano (2238cm^{-1}) and C-O-C (1078cm^{-1}) absorption bands in the infrared spectrum. The ^{1}H-nmr spectrum suggested that fraction (B) consisted of a mixture of two isomers, possibly, (245) and/or (246), in the ratio ~3:2 (see experimental section for details, P.135). The absence of singlet methyl absorptions from the ^{1}H-nmr spectrum of

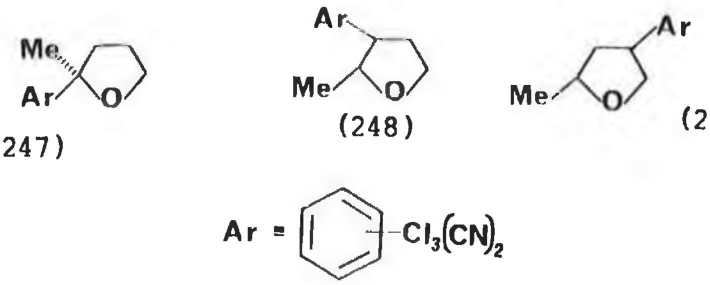


(245)

(246)

Scheme 78

fraction (B) eliminates structure (247) from consideration. In addition, the observation in the ^{1}H-nmr spectrum of the mixture of only two one-proton absorptions below δ2.5 (for each component) eliminates



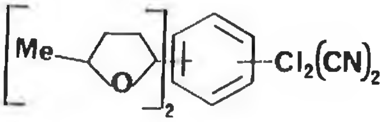
(247)

(248)

(249)

Scheme 79

(248) and (249) from consideration. The ^{1}H-nmr spectrum of fraction (B) is also consistent with a component of the mixture having a structure of the type (250). However the absence of any peaks of m/z >320 in the mass



(250)

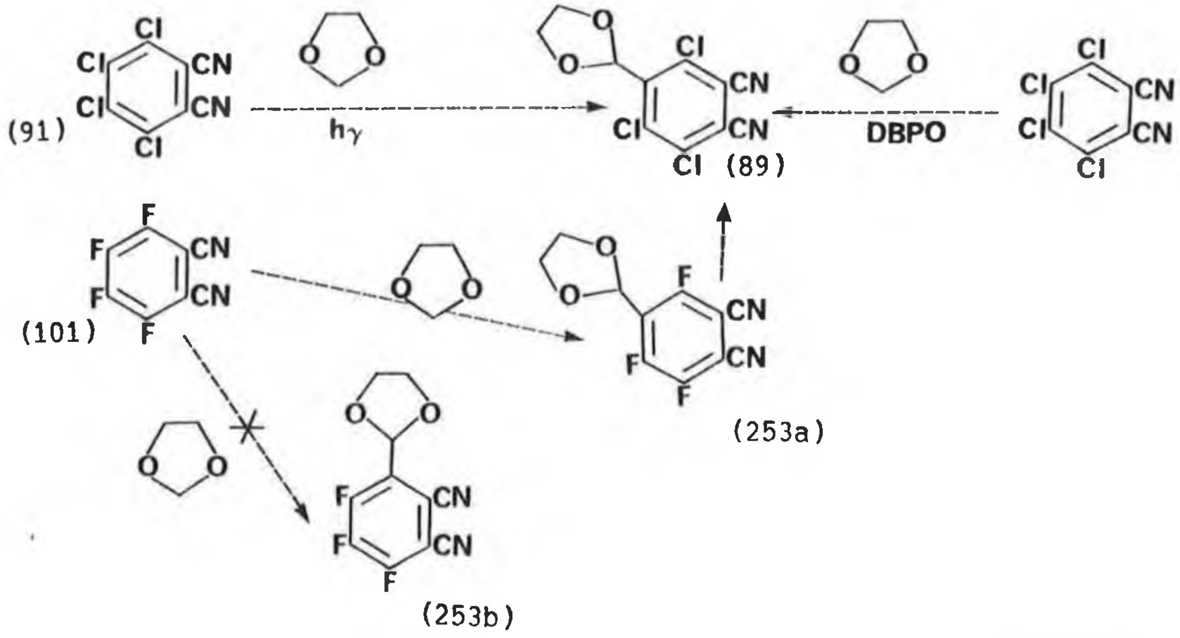
Scheme 80

spectrum of fraction (B) rules out such structures. The molecular ion peak at m/z = 314 is consistent with structures (245) and (246) i.e. with the replacement of one chlorine of TCPN with the ether moiety. This assignment is further supported by the ratio of the peaks at m/z 314:316:318:320 which are very close to those expected for a three chlorine fragment i.e. ~27:27:9:1. The microanalysis data on fraction (B) is also consistent with that expected for a mixture of compounds in which only one chlorine has been replaced by the ether moiety. All the spectral data on fraction (B) therefore suggest that it is a mixture of two isomers of the type (245) and/or (246).

It is presumed that the position of substitution of the aromatic ring is the 4-position rather than the 3-position, yielding (251), as a mixture of two geometrical isomers, rather than (252). This is by analogy with the corresponding reactions[21] of TCPN and TFPN with 1,3-dioxolan, (Scheme 82). Irradiation of TFPN and 1,3-dioxlolan gave a substitution

(252a) and (252b) (251a) and (251b)

Scheme 81

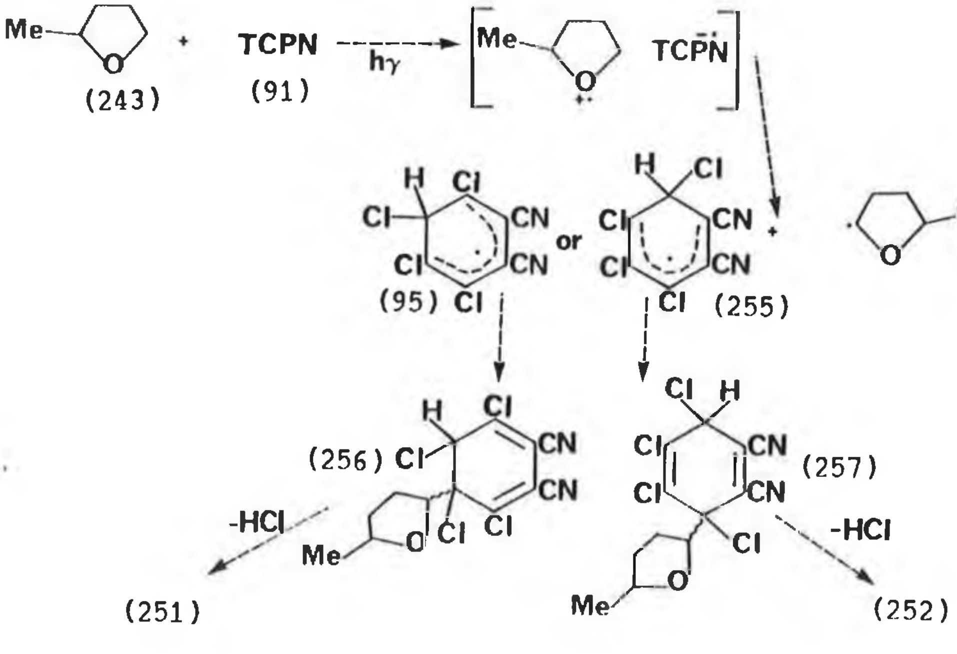


Scheme 82

product whose ^{19}F-nmr spectrum was consistent with structure (253a) rather than (253b), consistent with substitution occurring at the 4-position of the aromatic ring. Irradiation of TCPN in 1,3-dioxolan (or decomposition of DBPO in 1,3-dioxolan containing TCPN) gave an analogous substitution product (89) whose structure was unambiguously confirmed by its direct formation from (253a), (nucleophilic replacement of fluoride by heating with lithium chloride in N-methylpyrrolid-2-one). However the spectral data on fraction (B) is not inconsistent with it being a mixture of any two of the four geometrical isomers (251a, 251b, 252a and 252b). The minor fraction (A), m.p. 112-115 °C, from the photolysis of TCPN and 2-methyltetrahydrofuran has not been fully characterized. It showed two cyano (2225 and 2236cm^{-1}) absorption bands in its infrared spectrum. Its ^{1}H-nmr spectrum suggested that fraction (A) consisted of a mixture of two isomers, possibly (245) and/ or (246) Scheme 78, in the ratio ~1:1 and, in addition, a third compound (see experimental section P.134). As with the major fraction, the absence of singlet methyl absorptions in the ^{1}H-nmr spectrum of fraction (A) eliminates structure (247), Scheme 79, from consideration. In addition, the observation in the ^{1}H-nmr spectrum of the mixture of only two one-proton absorptions below δ2.5 for each isomer eliminates structures (248) and (249), Scheme 79, from consideration. The ^{1}H-nmr spectrum of fraction (A) is also consistent with structures of the type (250). However the absence of peaks of m/e > 320 in its mass spectrum rules out such structures. All the ^{1}H-nmr data of fraction (A) therefore suggests that it is a mixture of two isomers of the type (251) and /or (252), together with a third compound. If it is assumed that the major fraction, (B), consists of the two geometrical isomers (251), (see P.55), this leaves only the two geometrical isomers (252) for fraction (A). The ^{1}H-nmr spectrum of fraction (A) is in fact very similar to that of fraction (B) with the same pattern being repeated at slightly different chemical shifts. This is consistent with fraction (B) containing (251a) and (251b) and fraction

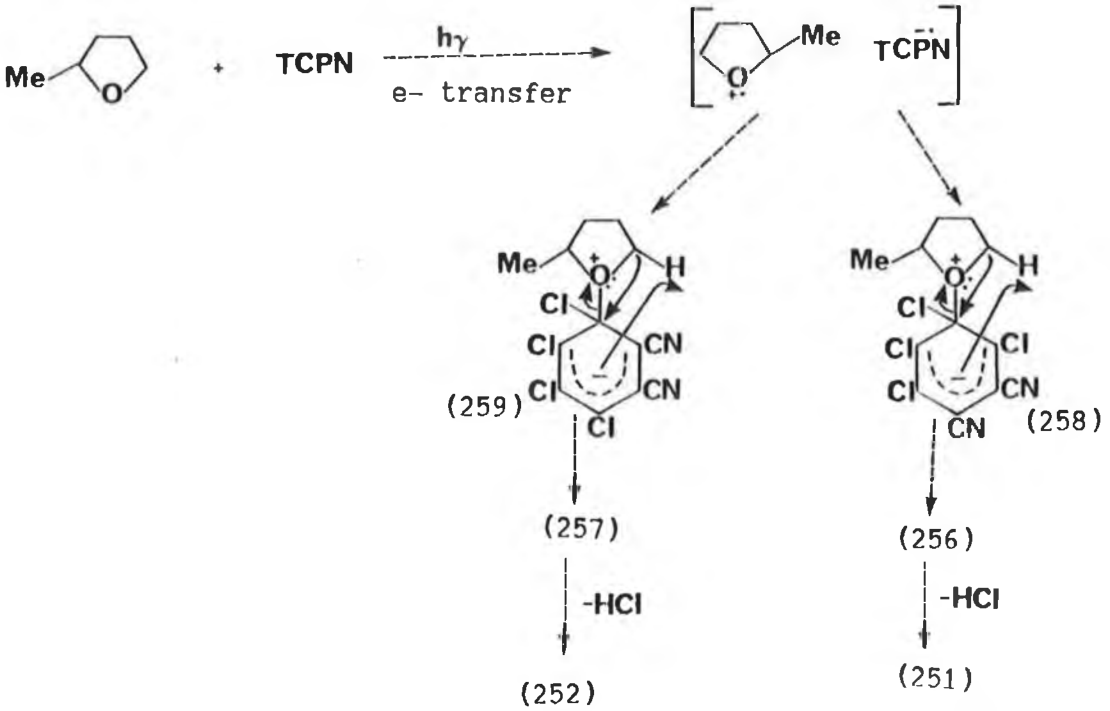
(A) containing (252a) and (252b). The ^{1}H-nmr spectrum of fraction (A) does however show a singlet at δ7.8 which is absent in the ^{1}H-nmr of fraction (B). The chemical shift of the proton in trichlorophthalonitrile (100) is known to be[21] at δ7.8 and trichlorophthalonitrile and fraction (A) have the same R_f value on TLC with a range of solvents. It was therefore suspected that fraction (A) consisted of two isomers together with trichlorophthalonitrile (in the ratio ~3:1, see experimental section P.134 for details). Further characterization of fraction (A) was not carried out because of (a) the difficulty of separating fraction (A) from the major product and (b) the small yield of mixtures involved. However the same four isomers (251-252) formed in this photochemical reaction between TCPN and 2-Me-THF are also formed in a thermal reaction between TCPN and 2-Me-THF. This reaction is discussed in the following section and provides additional evidence to support the belief that fraction (A) contained a mixture of two isomers (probably 252, although 251 or a mixture of both is possible) together with trichlorophthalonitrile, (see P. 61).

A mechanism involving a proton transfer step, (Scheme 83), seems consistent with the formation of the four isomers (251-252), the more acidic α-hydrogen, that at carbon-5 being preferentialy transferred.



Scheme 83

A variation on this mechanism is outlined in Scheme 84, in which radical ion coupling occurs to give (258) or (259) prior to transfer of the more acidic proton during a rearrangement process. This is analogous to the mechanism proposed by Ohashi for the reaction of tetracyanobenzene with THF.[75]



Scheme 84

An estimate[2] of the free energy change for electron transfer from 2-Me-THF to TCPN (the first step in both mechanisms) gives a positive value indicating that the electron transfer will be endothermic (see P. 50) ,a fact which argues against either mechanism. However such an estimate does not take account of any structural changes or any enhanced stabilisation of the radicals formed following excitation. It has been suggested[76,77] that oxygen has an activating influence on the formation of a radical at an adjacent site and, in simple terms, this may be represented as shown in Scheme 85. This stabilizing effect of oxygen on

$$X\text{-}\ddot{O}\text{-}\dot{C}\text{-}(Y) \longleftrightarrow X\text{-}\overset{+}{\dot{O}}\text{-}\overset{-}{\ddot{C}}\text{-}(Y)$$

(260) (261) Scheme 85

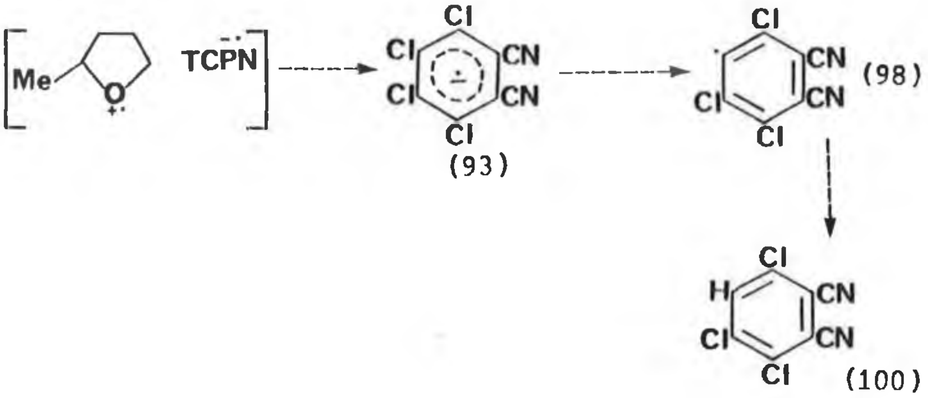
the radical (260) is enhanced, in certain cases, by the presence of electron donor groups (X) attached to oxygen and electron acceptor groups (Y) attached to the radical centre.[76] A similar activating influence on the formation of (254) might well be expected, thus supporting the

(254) (262)

Scheme 86

mechanism outlined in Scheme 83.

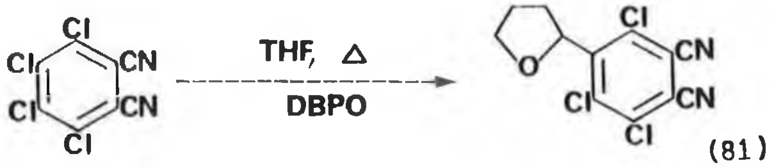
The minor fraction (A) also contained a small amount of the photoreduced product (100). Such a product could have been formed via the escape of some TCPN$^{\cdot-}$ (93) from the radical cation-radical anion pair (Scheme 87), followed by loss of chloride and then H-abstraction from the solvent.



Scheme 87

The Thermal Reaction of 3,4,5,6-Tetrachlorophthalonitrile with 2-Methyltetrahydrofuran.

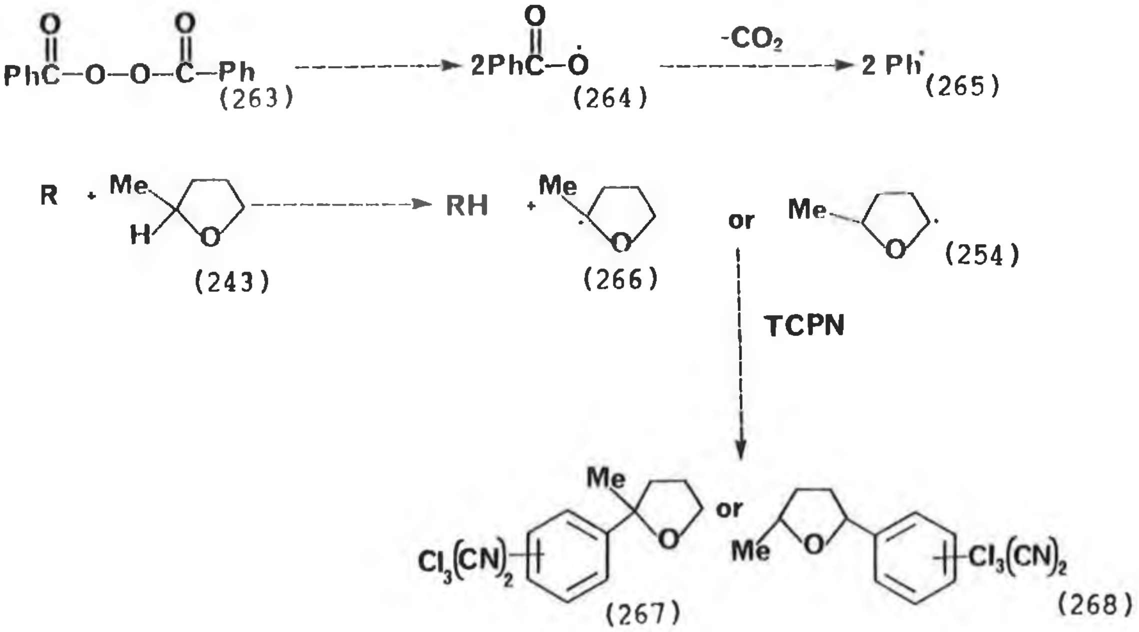
The thermal decomposition of dibenzoylperoxide (DBPO) in THF[20] containing TCPN produces the same product that is obtained on photolysis of TCPN in THF (Scheme 88).



Scheme 88

The thermal process involves a free radical substitution mechanism in which tetrahydrofuryl radicals displace chlorine from TCPN. The corresponding reaction with 2-methyltetrahydrofuran was therefore carried out for comparison with the photochemical reaction.

The thermal decomposition of dibenzoylperoxide (Scheme 89) leads to the formation of benzoyl and phenyl radicals. These radicals (R$^\cdot$) would be expected to abstract hydrogen from the 2- or 5-position of 2-methyltetrahydrofuran to give either (254) or (266). It might be



Scheme 89

expected that the tertiary radical (266) would be formed in preference to the secondary radical (254), thus leading to compounds of the type (267).

When a solution of TCPN in 2-methyltetrahydrofuran (and dichloromethane) containing DBPO was heated under reflux two additional spots were observed on TLC, (C) and (D). Chromatographic separation led to the isolation of two fractions corresponding to (C) and (D). Comparison of the spectral data (^{1}H-nmr, mass spectrum and ir spectrum) obtained for the major fraction (D), m.p. 124-127°C, with that of fraction (B) (the major fraction from the photochemical reaction) shows that the same two isomers constitute the major fraction in both the photochemical and thermal reactions. Fraction (D) and fraction (B) also have the same R_f values on TLC with a range of solvents. Further details of this data are given in the experimental section (see P.135-136).

Similarly, a comparison of the spectral data obtained for the minor fraction (C), with that of fraction (A) (the minor fraction from the photochemical reaction) shows that the same two α-aryl ether isomers are constituents of the minor fractions in both the photochemical and thermal reactions. In addition, trichlorophthalonitrile (100) is formed only in the photochemical process (see P. 56 and P. 57).

Thus the thermal reaction of TCPN and 2-methyltetrahydrofuran produces the same four substituted isomers (251a, 251b, 252a, 252b) as the corresponding photochemical reaction but none of the photoreduced compound (100). A free radical substitution mechanism (Scheme 89) can be proposed to account for the observed products in the thermal reaction. The observed products are not in fact those, (267), expected on thermodynamic grounds i.e. the tertiary radical (266) does not appear to be formed in preference to the secondary radical (254). Instead products of the type (268), equivalent to (251a), (251b), (252a) and (252b), are formed i.e. the presence of a methyl group on the 2-position of (243) appears to have a stabilizing effect on the formation of (254) relative to (266), see P.58 and P.59.

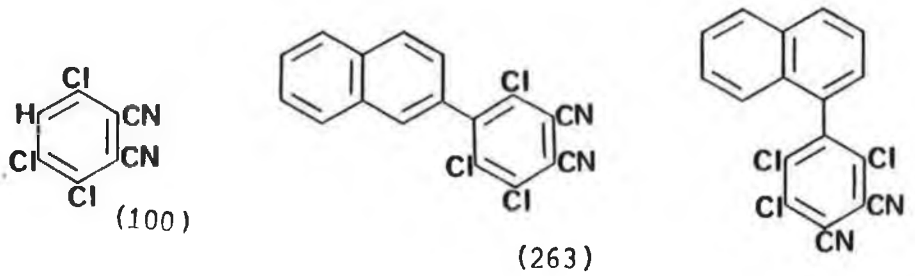
This is in contrast to the reported[77] γ-ray initiated reaction of 2-Me-THF with hexafluoropropene in which products derived from substitution at both the 2- and 5-positions of 2-Me-THF are formed. The major product (ratio ~2:1) in the latter reaction was in fact the one formed via reaction at the 2-position of 2-Me-THF. The discrimination in favour of the tertiary site was surprising and no rationalisation of the result was proposed.[77]

The Photochemical Reaction of 3,4,5,6-Tetrachlorophthalonitrile with Naphthalene in Dichloromethane.

Previously reported photochemical reactions of TCPN have included reactions with the aromatic hydrocarbons anthracene and phenanthrene[24] to give the substitution products (86) and (87) respectively (see P.20). An electron transfer mechanism was proposed to account for these products. Naphthalene, another aromatic hydrocarbon, has previously been reported to undergo photoinitiated electron transfer reactions in the presence of, for example, aliphatic amines.[78] Similarly, 1- and 2-naphthonitriles have been reported to undergo electron transfer sensitized reactions in polar solvents with, for example, tetramethylethene[79] and with acrylonitrile.[80] The photoreaction of naphthalene with excited TCPN was therefore of interest in our exploration of the potential photoinitiated electron transfer processes of TCPN.

When a solution of TCPN and naphthalene in dichloromethane was irradiated through pyrex two products were observed on TLC. The major product was the photoreduced product (100), in which a chlorine of the TCPN had been replaced by hydrogen. Its infrared spectrum and m.p. were identical with those of an authentic sample of compound (100).

The minor product (m.p. 210-211°C) was a mixed photoproduct, $C_{20}H_7Cl_3N_2$, formed by reaction of TCPN with naphthalene and involving loss of hydrogenchloride. Assuming that substitution again takes place at the 4-position of TCPN, (see P.55), this data corresponds to either structure (263) or (264) i.e. a 1- or 2-substituted naphthalene derivative, (Scheme 90). The ^{1}H-nmr spectrum showed seven 1-proton



(100)

(263)

(264)

Scheme 90

absorptions as follows: (1) a doublet at $\delta 8.03$ (J~8Hz) with each arm broadened by an additional small coupling, (2) a doublet at $\delta 7.99$ (J~8Hz) broadened by an additional small coupling, (3) a triplet of doublets at $\delta 7.62$ (J_t~7Hz, J_d<1Hz) slightly overlapping with (4) another triplet of doublets at $\delta 7.58$ (J_t~6Hz,J_d~1.5Hz), (5) a triplet of doublets at $\delta 7.48$ (J_t~8Hz, J_d~1.5Hz), (6) a doublet of doublets at $\delta 7.28$ (J~6Hz and ~1Hz) and (7) a doublet at $\delta 7.16$ with each arm broadened by an additional small coupling.

The reported interproton coupling constants for naphthalene derivatives

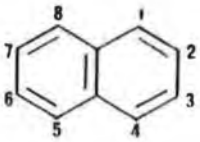
	J ortho/Hz	J meta/Hz	J para/Hz
	1,2: 8.3-9.1 2,3: 6.1-6.9	1,3: 1.2-1.6	1,4: 1Hz

Table 3

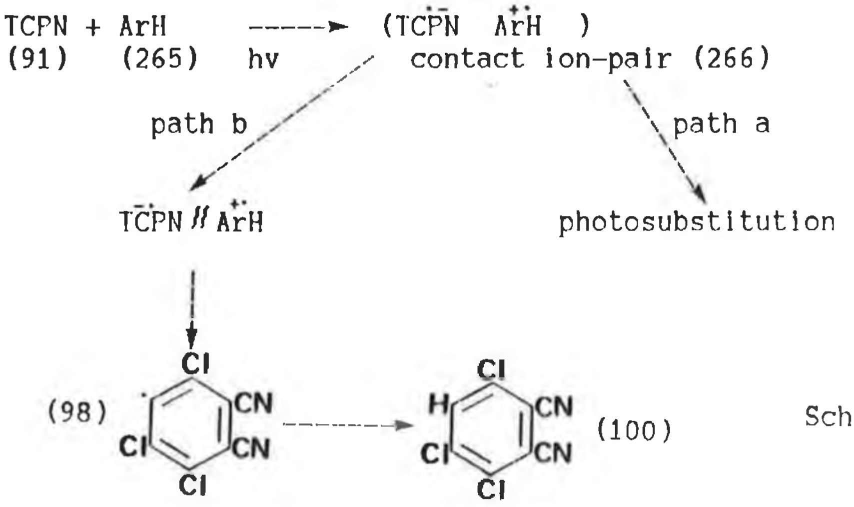
are shown in Table 3. In a 1-substituted naphthalene derivative such as (264) H_2 would be expected to show a large ortho coupling (~6.5Hz) and a small meta coupling (~1.4Hz) i.e. a predominantly doublet pattern. H_3 would be expected to show two large ortho couplings one of ~6.4Hz and the other of ~8.7Hz i.e. a doublet of doublets. However as the values of the two ortho couplings are quite similar overlap of the two central peaks might well occur giving rise to an apparent 'triplet' pattern.(The same can be said for any other proton with two ortho couplings). H_4 would be expected to show a large ortho coupling (~8.7Hz) and a small meta coupling (~1.4Hz) i.e. a 'doublet-like' pattern. H_5 and H_8 would be expected to show large ortho couplings of ~8.7Hz, small meta couplings of ~1.4Hz and very small para couplings of ~1Hz i.e. two 'doublet-like' patterns. H_6 and H_7 would be expected to show two large ortho couplings, one of ~8.7Hz and the other of ~6.4Hz, and small meta couplings of ~1.4Hz i.e. two 'triplet' patterns. The ^{1}H-nmr spectrum of a 1-substituted naphthalene derivative might therefore be expected to show four doublet patterns and three triplet patterns. These can be identified in the ^{1}H-nmr spectrum of for example, 1-bromonaphthalene. The four doublet patterns are at δ8.2, 7.75, and 7.70(two coincident) and the three triplet patterns at δ7.20, 7.45, and 7.55. In a 2-substituted naphthalene derivative such as (263) H_1 would be expected to show a small meta coupling (~1.4Hz) and a small para coupling (~1Hz) i.e. possibly a broad singlet. H_3 would be expected to show a large ortho coupling (~8.7Hz) and a small meta coupling of ~1.4Hz i.e. a slightly split doublet pattern would be expected. H_4 would be expected to show a large ortho coupling of ~8.7Hz and a small para coupling (J~1Hz) i.e. a slightly split doublet pattern. H_5 and H_8 would be expected to show large ortho couplings (J~8.7Hz), small meta couplings of ~1.4Hz and very small para couplings (J~1Hz) i.e. two slightly split doublet patterns. H_6 and H_7 would be expected to show two large ortho couplings, one of ~8.7Hz and the other of ~6.4Hz, and small meta couplings of ~1.4Hz i.e. two 'triplet' patterns. The ^{1}H-nmr spectrum of a 2-substituted naphthalene derivative might therefore be expected to show one broad singlet, four doublet patterns and two triplet patterns. A comparison of these expected spectra for a 1- or 2-substituted naphthalene derivative with the actual spectrum for the isolated product confirmed that it was the 1-substituted naphthalene derivative (264).

The photochemical reaction of TCPN with naphthalene is in marked contrast to its reactions with the other polycyclic aromatic hydrocarbons, anthracene and phenanthrene. Both of these have been reported to undergo photochemical reaction with TCPN to give products in which a chlorine of the TCPN has been replaced by the corresponding 9-aryl group,[24] and none of the dehalogenated product (100),Scheme 91. There does not seem to be any obvious reason why photoreduction of TCPN predominates with naphthalene. An estimate of the free energy change for electron transfer

(86) (87)

Scheme 91

from naphthalene to TCPN (using the Weller equation) gives a value of $\Delta G = -86kjmol^{-1}$ i.e. the electron transfer step is exothermic (c.f. values of $-131kjmol^{-1}$ for anthracene and $-90kjmol^{-1}$ for phenanthrene). However while it has proved possible to isolate charge-transfer complexes between anthracene and TCPN[24], an attempt to make the corresponding complex between naphthalene and TCPN by a similar method failed. Also no charge-transfer absorption band could be detected in the u.v. spectrum of a solution of TCPN and naphthalene in CH_2Cl_2. It has been suggested that the photosubstitution products (86) and (87) might be formed by initial excitation of the corresponding charge-transfer complexes in solution. Alternatively perhaps the difference in reactivity lies in the relative importance of paths (a) and (b), Scheme 92. That is, initial electron-transfer for all three hydrocarbons does occur (as predicted by the Weller equation) to give a contact ion-pair (266). If for anthracene and phenanthrene the substitution reaction (path a) occurs much more rapidly than ion separation (path b) no photoreduction would be seen. With naphthalene however ion pair separation (path b) and consequent photoreduction may compete with the radical coupling process



Scheme 92

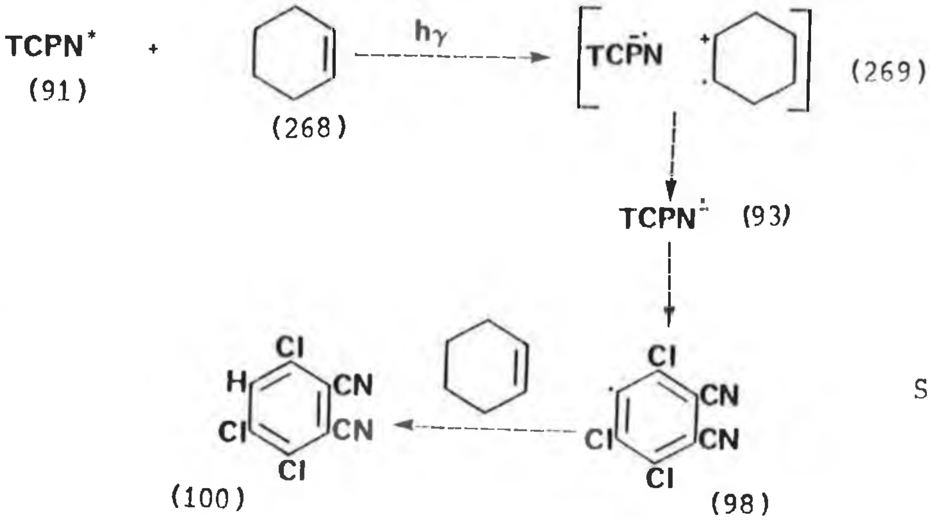
(path a) leading to photosubstitution as well as photoreduction. A factor leading to the observed differences may be that the smaller bulk of the naphthalene radical cation makes for easier escape from the solvated ion pair.

The Photochemical Reactions of TCPN with various Alkenes

When considering other components which might act as electron donors in photosensitized electron transfer reactions involving TCPN alkenes are an obvious choice. With their loosely bound π electrons, typical reactions of alkenes are those in which the double bond acts as a source of electrons i.e. they undergo attack by free radicals and by electrophiles leading to overall addition reactions. Possible reactions of alkenes with TCPN include: (1) substitution of chlorine by an alkenyl group, (2) acyclic addition of the alkene to the C-Cl bond, (3) cycloaddition to the aromatic group, and (4) cycloaddition to the C≡N group. Four alkenes (two conjugated and two non-conjugated) were studied. These were: (1) cyclohexene, (2) hex-1-ene, (3) α-methylstyrene and (4) indene.

The Photochemical Reaction of TCPN with Cyclohexene in acetonitrile.

When a solution of TCPN and cyclohexene (1:5) in dichloromethane was irradiated through Pyrex no major products were observed. However when TCPN was irradiated in the presence of a large excess of alkene (>150:1) in acetonitrile one major product was formed. This was trichlorophthalonitrile (100), which was identified by comparison of its infrared spectrum, m.p. and ^{1}H-nmr spectrum with that of an authentic sample. An electron transfer mechanism can be proposed to account for its formation i.e. the reaction could proceed via initial electron transfer from the cyclohexene to TCPN to give a radical cation/radical anion pair, (Scheme 93).



Scheme 93

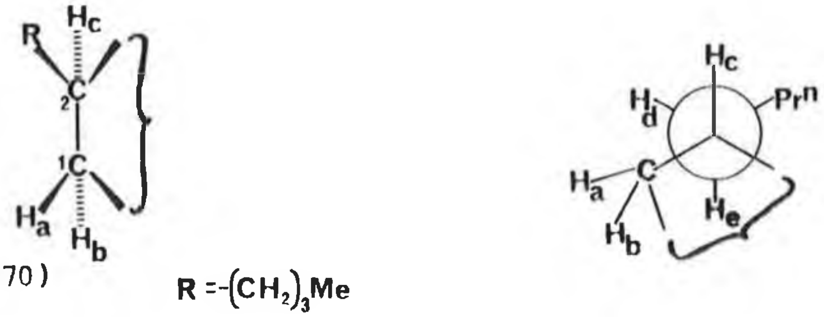
This is followed by radical ion separation, loss of chloride from the TCPN radical anion (93) and then abstraction of hydrogen, possibly from cyclohexene, to give the observed product (100). An estimate of the free energy change for the electron transfer step ($\Delta G = -48 kjmol^{-1}$) gives a large negative value indicating that the electron transfer step is exothermic and supports the proposed mechanism. The photochemical reaction of cyclohexene is in marked contrast to the corresponding reaction with the acyclic alkene hex-1-ene, which is outlined in the next section.

Irradiation of TCPN and Hex-1-ene in Dichloromethane.

Irradition of TCPN and hex-1-ene through pyrex gave two products. The major product (m.p. 89-90 °C) was a photoadduct. The ^{1}H-nmr data was consistent with addition having occurred across the carbon-carbon double bond of hex-1-ene, displaying multiplets only in the δ0.9-2.5 region. An examination of the COSY nmr spectrum of the product also supported such a structure, (see Table 4). This data is consistent with a structure of the type (270) in which the geminal inter-proton coupling constant J_{ab} is 14Hz, the trans vicinal inter-proton coupling constant J_{ac} is 4Hz and the cis vicinal interproton coupling constant J_{bc} is 7.5Hz. The other interproton coupling constants could not be determined because the large number of spin systems involved resulted in complex patterns. The two protons on C_3 (H_d and H_e) are diastereotopic (see 271, Scheme 95) and

carbon atom	group	Chemical Shift/ppm	J/Hz
6	Me	0.9	$J_{6,5}=7$
5	H-C-H	1.4	
4	H-C-H	1.425	
3	H_d-C-H_e	1.7, 1.9	
2	C-H_c	2.5	
1	H_a-C-H_b	2.35, 2.25	$J_{ab}=14$ $J_{ac}=4$ $J_{bc}=7.5$

Table 4



(270)

(271)

Scheme 95

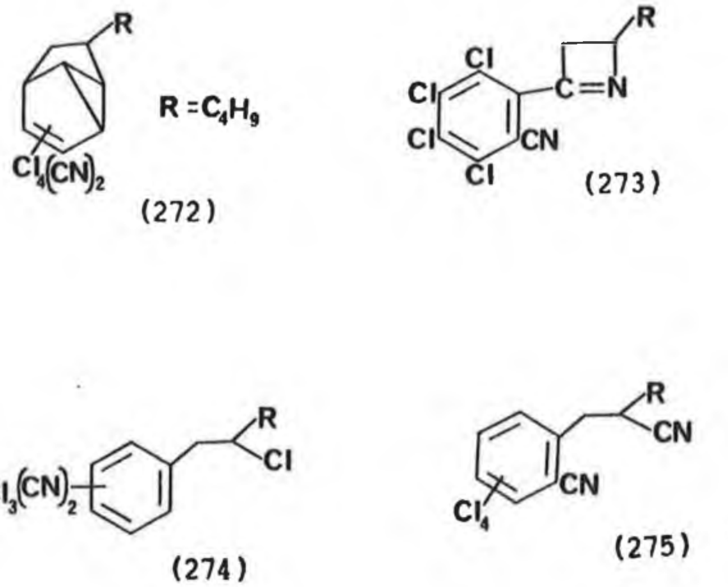
show different chemical shifts(δ1.7 and 1.9) in the COSY spectrum. There are several possible modes of addition of the hex-1-ene to TCPN. These include:

(1) Cyclic addition across the aromatic ring (1,2-, 1,3- or 1,4-addition),

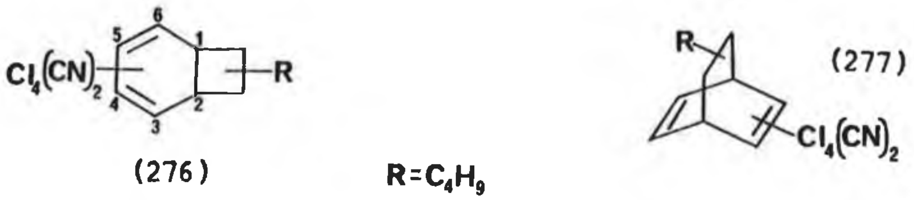
(2) Cyclic addition across the C≡N bond, and

(3) Acyclic addition across the C-Cl or C-CN bonds.

The observed ^{13}C nmr spectrum rules out some of these structures. Besides six aliphatic carbons absorbing in the range δ13-36, it shows: (1) two carbons absorbing at δ56 and δ67, (2) two carbons absorbing at δ114 and δ115 (possibly the two cyano carbons) and (3) four carbons absorbing in the range δ119-142. This data rules out a cycloaddition product (272) involving 1,3-addition across the aromatic ring. It also excludes cycloaddition across a cyano group (273). Insertions into a carbon-chlorine bond (274) or a carbon-cyano bond (275) can also be ruled out. This leaves either a 1,2- or 1,4- cycloaddition product i.e. a compound of the type (276) or (277), Scheme 97. There are, of course, several different isomers of the each type depending upon the exact positions of the chlorine, nitrile and alkyl substituents.



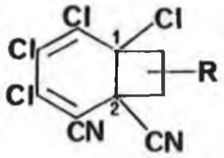
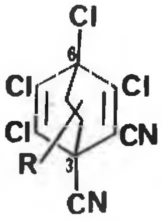
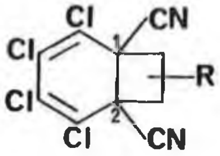
Scheme 96



(276) $R=C_4H_9$ (277)

Scheme 97

Very little ^{13}C nmr data of structures such as these have been reported in the literature. However the observed data does appear to be much more consistent with structures of the type (278) or (279) rather than structures (280) to (283), (Table 5).

	C number, Code, Predicted Value/s.
 (278)	1, CCCX(=CX.CCC,&C/, 72-89. 2, CCCC(%N.=CC.CCC,CCCX&/, 56.
 (279)	6, CCCX(=CC.=CX.C/, 77-84. 3, CCCC(%N=CC.=CX, ,/, 56.
 (280)	1, CCCC(%N.=CX.CCC,& 78.4. 2, CCCC(%N.=CX.CCC,& 78.4.

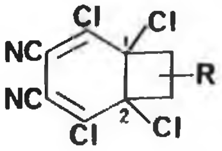
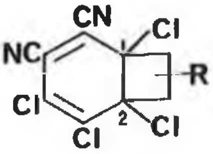
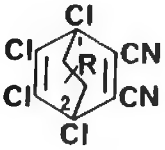
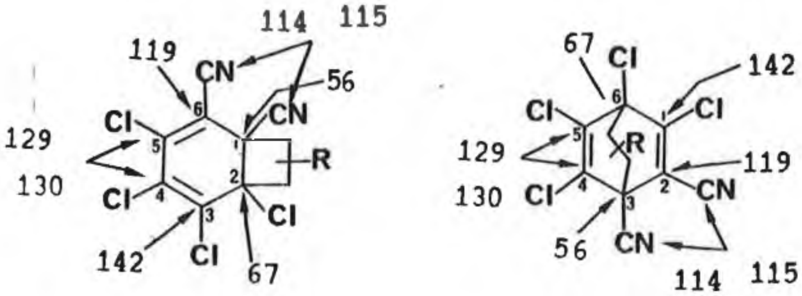
	C number, Code,	Predicted Value/s.
 (281)	1, CCCX(=CX,CCX,& 2, CCCX(=CX,CCX,&	72-89 72-89
 (282)	1, CCCX(=CC,CCX,& 2, CCCX(=CX,CCX,&	73-84 72-89
 (283)	6, CCCX(=CC,=CX,C/ 3, CCCX(=CC,=CX,C/	76-84 76-84

Table 5.

The resonances at δ56 and δ67 are assigned to the two allylic carbons formed on addition of the hex-1-ene to TCPN i.e. C_1 and C_2 in (276) or C_3 and C_6 in (277). They have well separated chemical shifts (δ56 and δ67) consistent with one having a chlorine substituent and the other a cyano substituent. An examination of the possible structures, (278) to (283), according to the method of Bremser et al[82] gives a predicted chemical shift (or more usually a range of chemical shifts) for each carbon atom. The predictions for the allyic carbon atoms are shown in Table 5. Although the code usually breaks down in the third sphere, the actual data fits in much more closely with the predicted data for either

(278) or (279) rather than any of the other structures. The chemical shifts of the remaining sp^2 carbon atoms can then be assigned as shown in Scheme 98, the carbons absorbing at δ 114 and δ115 being assumed to be the cyano carbons. The carbons absorbing at δ 129 and δ130 are assigned to two quite similar chlorine substituted sp^2 carbon atoms (4 and 5). This leaves the resonance at δ119 to be assigned to a cyano-substituted sp^2-carbon atom and that at δ142 to be assigned to a chlorine-substituted sp^2-carbon atom. Attempts to distinguish between possible structures (278) and (279) by comparison of the observed ^{13}C nmr data with that predicted using the method of Bremser et al[82] were unsuccessful. The predicted ranges were often quite large as the code broke down very early for many of the carbon atoms.



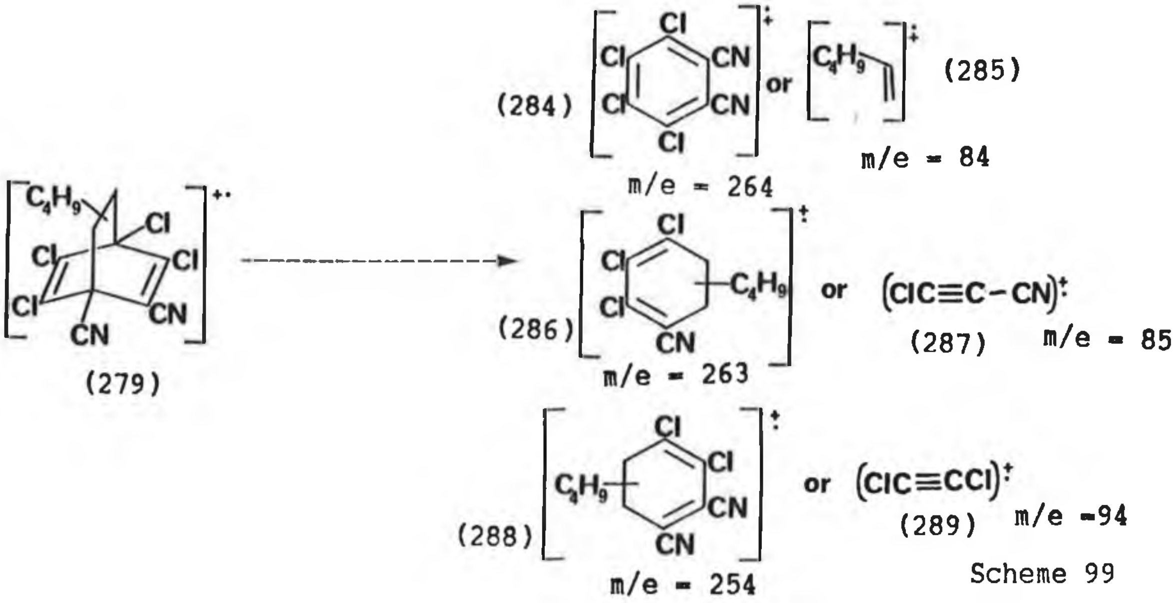
Scheme 98

The mass spectrum of this product shows three major fragmentations. These (together with the molecular ion peak, M+) are outlined in Table 6. The base peak at m/e = 57 corresponds to formation of a $C_4H_9^{\cdot +}$ fragment i.e. to cleavage of the C-R bond in either (278) or (279).

Mass		Relative Abundance (%)
348	$M^{\cdot +}$	<1
317		17
315	$[M-Cl]^{\cdot +}$	53
313		55
261		17
259	$[M-Cl-C_4H_8]^{\cdot +}$	44
257		44
57	$C_4H_9^{\cdot +}$	100

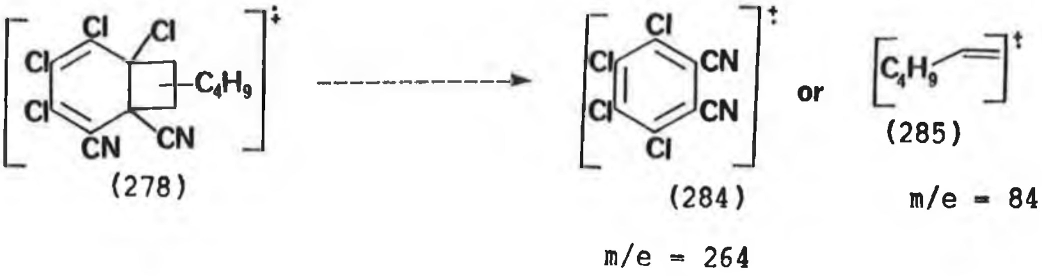
Table 6

For structure (279), formally a 'Diels Alder' type structure, a retro Diels Alder fragmentation process would be expected to be important, Scheme 99. Whilst not all of the fragment ions depicted in the scheme would be expected to be important, inspection of the mass spectral data shows that only low abundances are observed for all of these ions [m/e 84(6.0%), 85(1.3%), 94(1.0%), 254(<1%), 263(3.1%) and 264(7.9%)]. This is in contrast to the mass spectral data of two examples to be discussed later (see P.106 and 118), both of which are 1,4-addition products of cyclohexene and N-alkyltetrachlorophthalimides. These show abundant fragment ions due to retro Diels Alder fragmentation leading to the formation of [cycloadduct-$C_6H_{10}]^{+\cdot}$.



Scheme 99

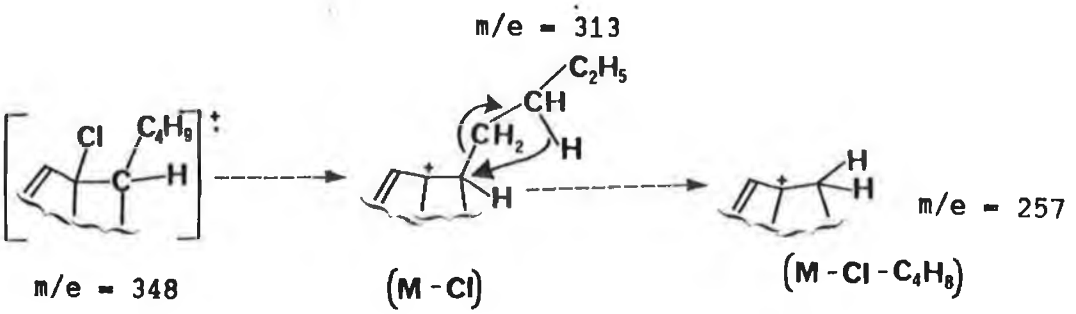
For structure (278), on the other hand, a retro-cleavage process (Scheme 100) might be expected to be less facile since, if concerted, it would be



Scheme 100

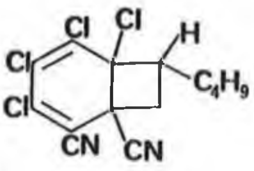
a thermally forbidden process.

On balance therefore the mass spectral data appears to favour structure (278), a 1,2-addition product. The peak at m/e=257 in the product corresponds to the molecular ion peak minus a chlorine atom and a C_4H_8 group ($M^{+\cdot}$ - Cl - C_4H_8). The formation of this fragment may suggest that the chlorine lost is from a carbon adjacent to the one carrying the C_4H_9 group i.e. the following fragmentations occur:



Scheme 101

Assuming that the product is a 1,2-adduct (278) then the peak at m/e=257 argues for structure (290) i.e. one of two possible geometrical isomers.



(290)

Scheme 102

The u.v. spectrum of the product shows absorption maxima at 242 (ε= 10,400 , 235 (11,200) and 206nm (11,000). In general compounds containing isolated double bonds do not show appreciable absorbance above ~200nm. For example ethene, (291, Table 7), shows λ_{max} values at 162.5 and 174.3nm. Replacement of a hydrogen by chlorine (292) leads to a small,~10nm, shift to longer wavelength of the absorption maxima. Substitution of hydrogen by a cyano group (293-297) results in a larger bathochromic shift (~20-30nm for each hydrogen that is substituted by a cyano group). However, conjugation of the double bond with a second double bond not

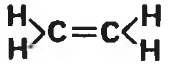
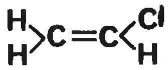
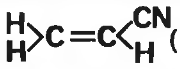
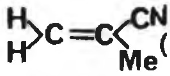
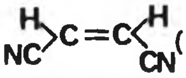
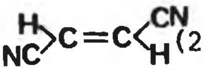
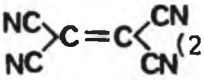
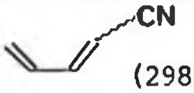
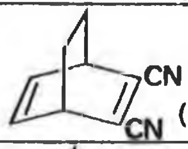
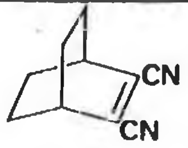
	λ_{max}	ε	Ref.
 $H_2C=CH_2$ (291)	162.5 174.3	15,000 5,500	83
 $H_2C=CHCl$ (292)	185	10,000	84
 $H_2C=CHCN$ (293)	203	6,100	87
 $H_2C=C(CN)Me$ (294)	203		87
 $(H)(NC)C=C(H)(CN)$ (295)	220		85
 $(H)(NC)C=C(CN)(H)$ (296)	218		85
 $(NC)_2C=C(CN)_2$ (297)	265		86
 (298)	240(cis) 239(trans)	21,800 28,000	88 88
 (299)	CN Me 253 cis cis 248 cis trans 257 trans cis 248 trans trans	 23,600 25,600 26,900 30,700	88
 (300)	237 266	8,700 700	89
 (301)	238	12,000	89

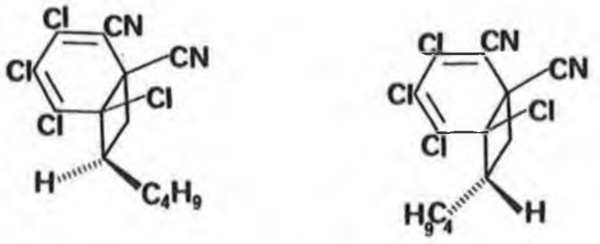
Table 7

only leads to a larger bathochromic shift of the absorption maxima but also to increased extinction coefficients, (c.f. 293 with 298 and 299). The u.v. data of the product (with λ_{max} at 242nm) suggests therefore that the molecule contains appreciable conjugation and argues for a 1,2- (278) rather than a 1,4-adduct (279). Its λ_{max} values and extinction coefficients are not inconsistent with one double bond carrying a cyano and a chlorine substituent in conjugation with another carrying two chlorine substituents. Compounds (300) and (301), model compounds for a 1,4-adduct, do show λ_{max} values in the same region as the product. Both however have two cyano groups on the double bond. Replacement of one by a chlorine (to give a better model compound for 279) would be expected to lead to a shift of the λ_{max} value to a lower wavelength than is observed in the product.[The λ_{max} at 266nm in (300) might well be shifted into the same region as those observed in the product but its extinction coefficient is much smaller than any observed in the product.] The u.v. data is therefore consistent with a 1,2-addition product (278).

An attempt was made to measure the ^{13}C-^{13}C coupling constants in the photoproduct by 2-D nmr spectroscopy (using the 400 MHz F.T. nmr at Cambridge University). With such data available it should prove possible to determine unambiguously whether a 1,2- or 1,4-addition product had been formed. However the attempt was unsuccessful.

An attempt was also made (by Dr. M. Hursthouse, using the S.E.R.C. X-ray diffractometer service at Queen Mary College, University of London) to obtain an X-ray crystal structure of the product. Unfortunately the crystals were unsuitable, failing to show a unit cell but giving rise to a broad mosaic pattern.

Though the structure of the photoadduct cannot be said to be completely and unambiguously decided, the available data is more consistent with it being a 1,2-adduct (302 or 303) rather than a 1,4-adduct.

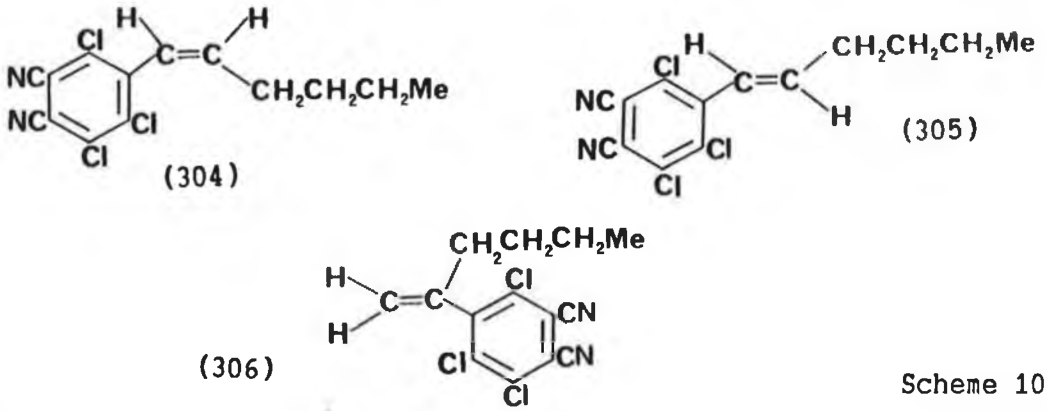


(302)

(303)

Scheme 102

The minor product (m.p. 104-105°C) from the photolysis of TCPN and hex-1-ene in dichloromethane also showed cyano ($2240cm^{-1}$) and carbon-carbon double bond ($1640cm^{-1}$) absorption bands in its infrared spectrum. This product analysed for $C_{14}H_{11}N_2Cl_3$ i.e. for the elimination of HCl from the elements of TCPN and hex-1-ene. Its ^{1}H-nmr spectrum showed a 1-proton triplet of doublets (J_t 1.4Hz, J_d ~1Hz) at δ6.17(C=C-H), a 1-proton triplet of doublets (J_t 11.4Hz, J_d ~1Hz) at δ6.07(C=C-H), a 2-proton 'quartet' (J~7Hz) at δ1.86(C=C-CH_2), a 4-proton multiplet at δ1.27(C=C-C-$(CH_2)_2$-) and a 3-proton triplet (J=7.1Hz) at δ0.85(-Me) These facts lead to initial consideration of three possible structures (304), (305), or (306) i.e. either a cis- , trans- or gem- alkene, (Scheme 103).



Scheme 103

The coupling constant between the two olefinic protons in the photosubstitution product is ~12Hz. Values for the vicinal coupling constants in disubstituted alkenes, X-CH=CH-Y, and for the geminal coupling constants in C=CH_2 are shown in Table 8.[90] A gem-substituted

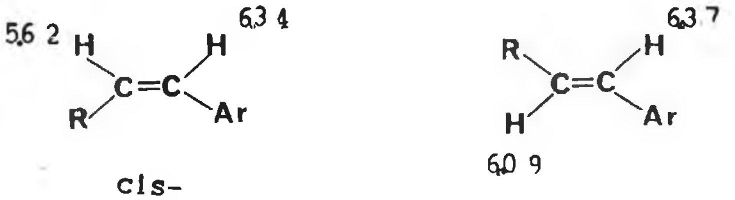
J_{cis} / Hz	2 - 11.7
J_{trans} / Hz	9.5 - 19
J_{gem} / Hz	0 - 2

Table 8

alkene can therefore be ruled out as the observed value in the product is well outside the geminal range. This value does however fall in the overlap region between the cis- and trans- substituted alkenes and an unambiguous assignment of either a cis- or trans- substituted alkene cannot be made on the basis of the observed coupling constant alone. The effect of substituents on the proton chemical shifts of olefinic protons can be calculated using the relationship:[91]

$$\delta_{C=C-H} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$$

where δ5.25 is the chemical shift of the protons in ethene and Z is the substituent shielding constant. The calculated chemical shifts for cis- and trans- 1,2-disubstituted ethenes carrying an aromatic and an alkyl substituent are shown in Scheme 104.



cis-

(307)

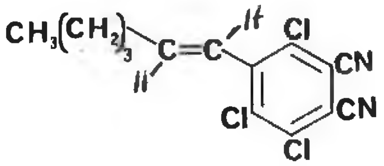
trans-

(308)

Scheme 104

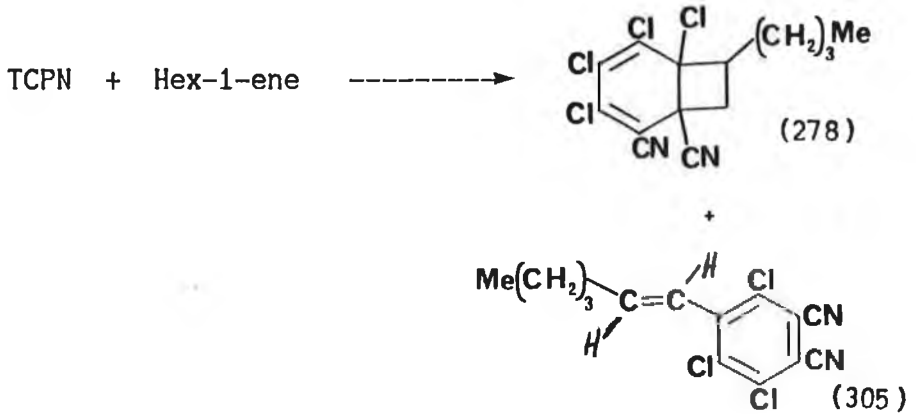
The calculated values for the trans- substituted alkene (308) are closer to the actual observed values (δ6.18 and δ6.08), thus suggesting that the product is a trans-substituted alkene.

A visual comparison of the splitting pattern in the vinyl proton region of the nmr spectrum of the product with the same region in the spectrum of trans-β-methylstyrene shows a remarkable similarity. This comparison, together with the fact that the calculated values for the chemical shifts of the olefinic protons in a trans- substituted alkene are closest to the observed values, supports the trans- structure (305) rather than the cis- structure (304).



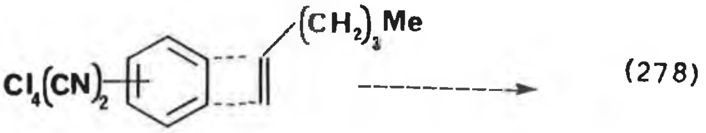
(305)

The position of substitution of the alkene on the aromatic ring is assumed to be the 4- rather than the 3- position. This is based on an analogy with the previously reported photoreactions of TCPN , (see P.55). The photochemical reaction of TCPN with hex-1-ene therefore gives rise to two products, the 1,2-adduct (278) and the substitution product (305), Scheme 105.



Scheme 105

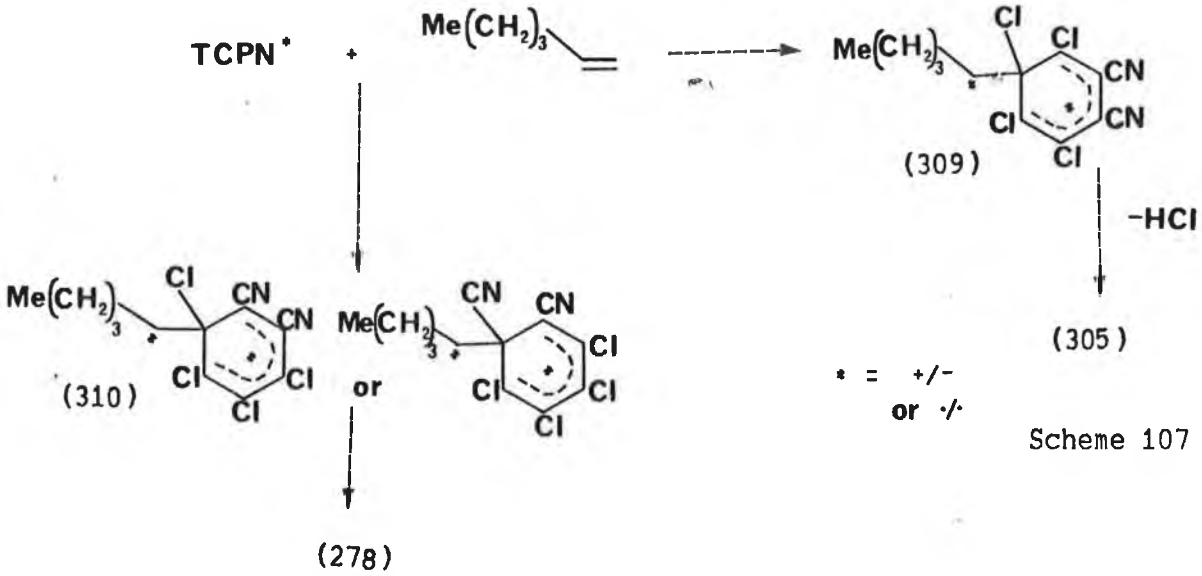
The 1,2-adduct (278) could be formed via direct interaction of the excited TCPN with the ground state alkene, (Scheme 106).



Scheme 106

Alternatively perhaps both the addition (278) and substitution (305) products are formed via:

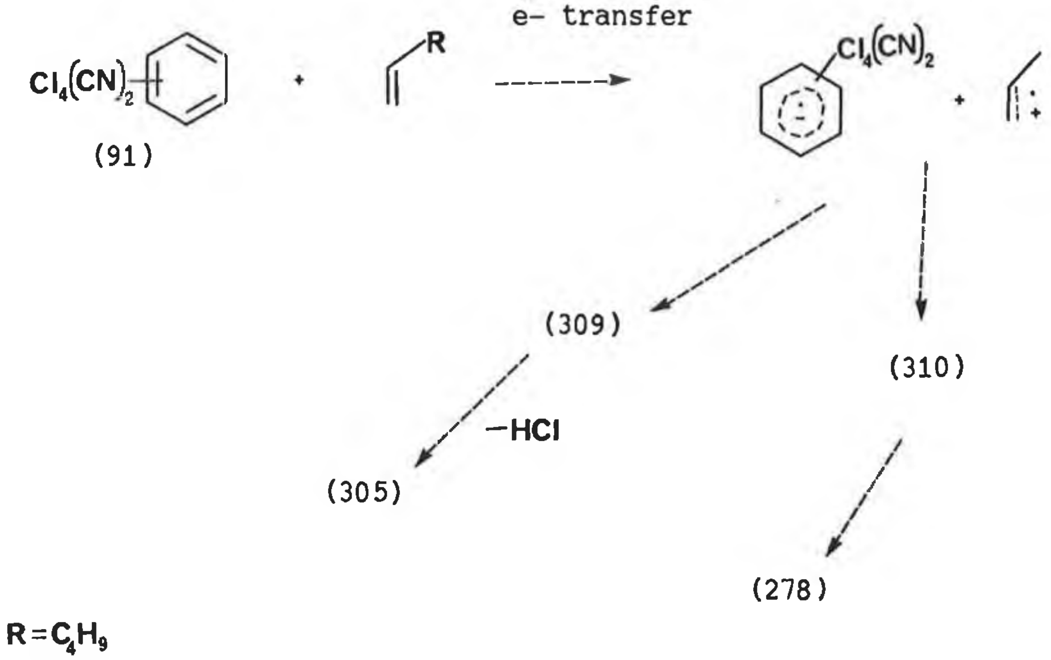
(1) interaction of the excited TCPN with the ground state alkene to give an intermediate (310 or 309), Scheme 107.



Scheme 107

(310) could then ring close to give the observed 1,2-adduct and (309) could undergo elimination of HCl to give the observed substitution product.

(2) Electron transfer from the ground state alkene to the excited TCPN to give a radical cation/ radical anion pair, followed by radical coupling to give (310) or (309), Scheme 108. Again (310) could ring close to give the 1,2-adduct and (309) undergo elimination of HCl to give the substitution product (305).



Scheme 108

An estimate of the free energy change for electron transfer (ΔG_{ET}) from hex-1-ene to TCPN gives a small positive value indicating that the electron transfer step is endothermic. An electron transfer step can still be postulated when ΔG is only slightly positive provided the lifetime of the excited state is long. Mechanism (3), Scheme 108, cannot therefore be entirely ruled out.

Several photoreactions of alkenes with benzonitrile (311) have been reported. These include reactions with 2-methyl-2-butene,[92] ethoxyethene,[92] 2-methylpropene,[93] cyclohexene,[93] cyclopentene,[94] 2-methoxypropene[94] and 1,2-dichloroethene.[94] In all these cases addition takes place to give 1-cyanobicyclo[4.2.0]octadienes i.e. compounds analogous to the 1,2-addition product formed between TCPN and hex-1-ene (278). For example, irradiation of (311) with 2-methylpropene (142) gives the 1,2-adduct (312), Scheme 109, in 49% yield.

(311) (312) Scheme 109

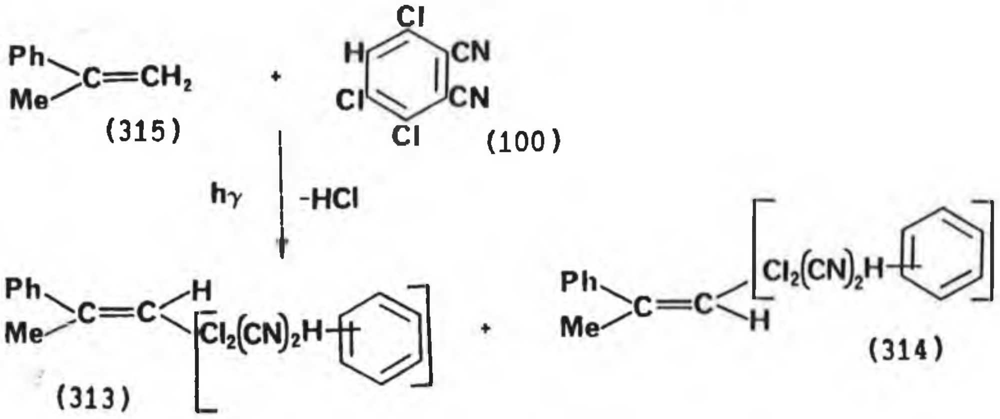
Several photochemical reactions of alkenes with arylhalides have been reported in the literature, (see P.42-47). These reactions include 1,2-, 1,3-, and 1,4-addition reactions, and acyclic addition reactions but no true photosubstitution reactions.

Irradiation of TCPN and Methylstyrene in Dichloromethane.

When a solution of TCPN and α-methylstyrene in dichloromethane was irradiated through pyrex two spots were observed on TLC. Chromatographic separation led to the isolation of: (1) a complex mixture of hydrocarbons, (2) TCPN, (3) a minor fraction and (4) a major fraction.

The major product was the photoreduced product (100), identified by comparison of its m.p., infrared spectrum and nmr spectrum with that of an authentic sample.

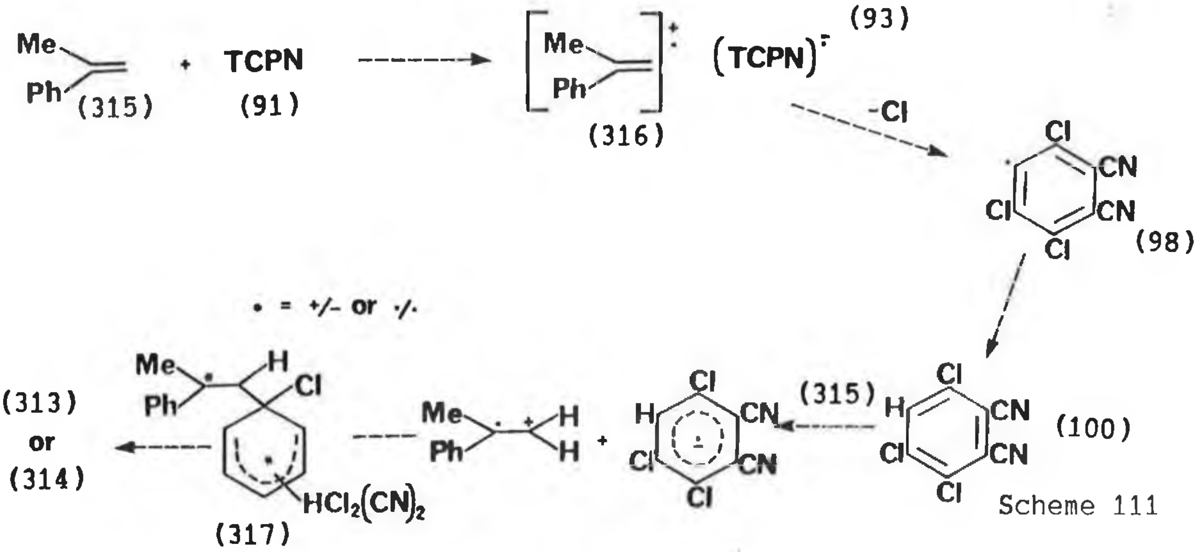
The minor fraction (m.p. 138-142) from the photolysis of TCPN and α-methylstyrene was not fully characterized. It showed cyano (2236cm^{-1}), aromatic or alkene C-H (3035cm^{-1}) and C=C (1614cm^{-1}) absorption bands in its infrared spectrum. The appearance of the ^{1}H-nmr spectrum suggested that this fraction was in fact a mixture of two components in an approximately 2:1 ratio. The major pattern showed a 6-proton multiplet at δ7.38(Ph-), 1-proton singlets at δ6.18(C=C-H) and δ5.40(C=C-H), and a 3-proton singlet at δ2.36(Me-C=C). The minor pattern showed a 6-proton multiplet at δ7.20(Ph-), 1-proton singlets at δ6.17(C=C-H) and δ5.21(C=C-H), and a 3-proton singlet at δ2.40(Me-C=C). The fraction analysed for $C_{17}H_{10}N_2Cl_2$. This corresponded to elimination of HCl from the elements of α-methylstyrene and trichlorophthalonitrile (100) and suggested that this fraction was in fact derived from reaction of α-methylstyrene with the photoreduced product (100) to give possibly (313) and (314), Scheme 110. There are three possible regioisomers of both (313)



Scheme 110

and (314) and as the ^{1}H-nmr of each component in the minor fraction shows two alkenyl protons each probably contains two of the six regioisomers. However as each component only shows one methyl singlet it must be assumed that the methyl groups of the two isomers are coincident.

An electron transfer mechanism can again be postulated to account for the formation of the photoreduced compound (100), and also for the formation of the photosubstitution products (313) and (314), Scheme 111. That is the reaction could proceed via initial electron from α-methylstyrene to TCPN to give a radical cation / radical anion pair. Loss of chlorine from the TCPN radical anion followed by abstraction of hydrogen from the solvent or from α-methylstyrene would give (100). An estimate of the free

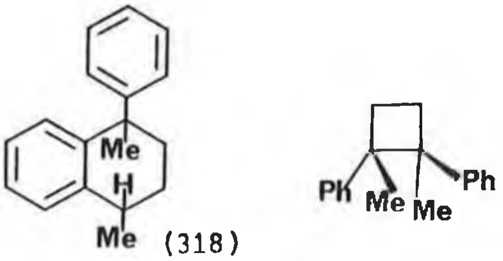


Scheme 111

energy change for electron transfer (ΔG_{ET}) from the α-methylstyrene to TCPN gives a small negative value (-8.7 kjmol^{-1}) i.e. the electron transfer is exothermic, thus supporting the proposed mechanism. Further reaction of (100) with α-methylstyrene, possibly again via an electron transfer mechanism, Scheme 111, gives the substitution products (313) and (314).

α-Methylstyrene has been reported to undergo ionic dimerization[95] when irradiated in acetonitrile with 1,2,4,5-tetracyanobenzene. The major fraction isolated was assigned by nmr and mass spectrometry to be 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (318). The trans-dimer

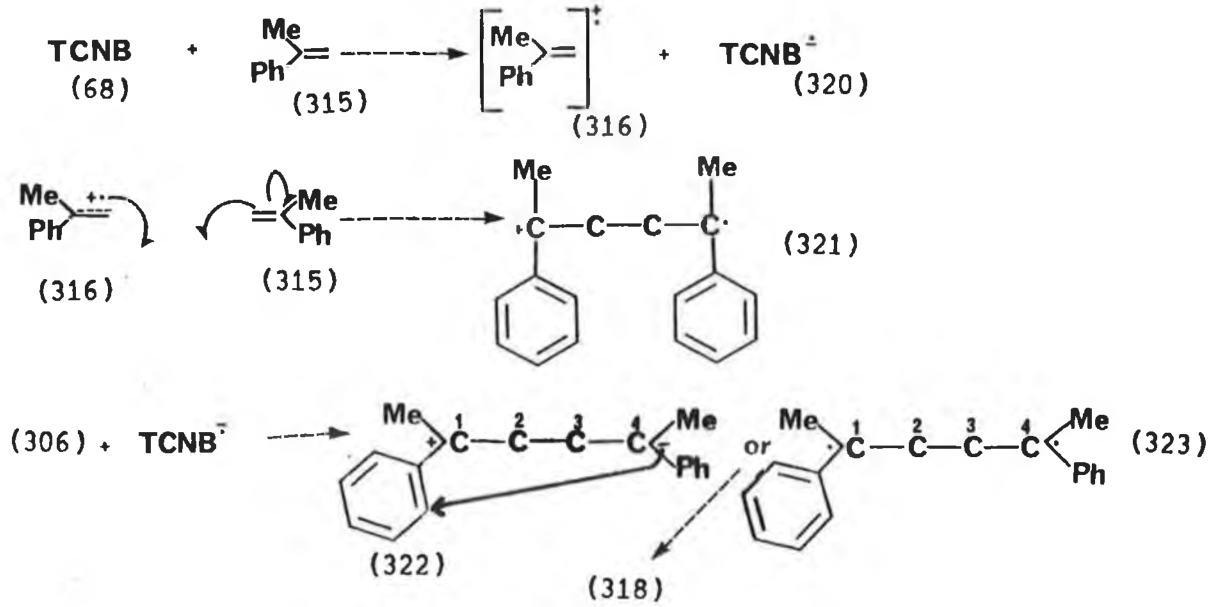
(319) was also formed.



(318) (319)

Scheme 112

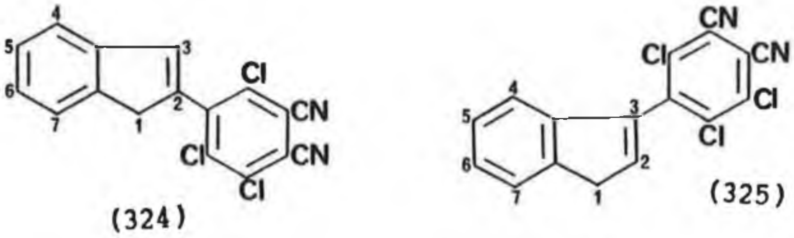
The reaction is believed to proceed via initial electron-transfer from the alkene to the tetracyanobenzene (TCNB) to give a radical cation /radical anion pair, Scheme 113. The β-carbon of the α-methylstyrene radical cation then attacks the β-carbon of another α-methylstyrene molecule to give a dimer cation radical (321). This is followed by back electron transfer from the radical anion (TCNB$^{-\cdot}$) to give either (322) or (323) and theh ring closure to give the observed tetrahydronaphthalene (318). Formation of the trans dimer (319) can be explained by coupling between the 1- and 4- carbon atoms of either (322) or (323). Such reactions may account for the fate of the proposed α-methylstyrene radical cation intermediate in the photochemical reaction of TCPN and α-methylstyrene, (Scheme 111).



Scheme 113

Irradiation of TCPN and Indene in Dichloromethane.

Irradiation of a solution of TCPN and indene in dichloromethane gave one major mixed photoproduct. This product (m.p. 186-187 ℃) showed a cyano ($2234cm^{-1}$) absorption band in its infrared spectrum. It analysed for $C_{17}H_7N_2Cl_3$ which corresponds to the elimination of HCl from the elements of TCPN and indene. Its ^{1}H-nmr spectrum showed a 2- proton multiplet at δ7.55 (Ar-H, H_4, H_7), a 2-proton multiplet at δ7.36 (Ar-H, H_5, H_6), a 1-proton triplet at δ7.0 (C=C-H, J_t~2Hz) and a 2-proton doublet at δ3.8 (CH_2, J_d~2Hz). This data is a priori consistent with either structure (324) or (325) i.e. with a 2- or a 3-substituted



(324) (325)

Scheme **114**

indene. Tetrachloroterephthalonitrile (TCTN) has been reported to undergo photochemical reaction with indene[25] to give a similar product in which a chlorine has been replaced by the alkenyl moiety. The ^{1}H-nmr data of this mixed photosubstitution product are shown in Table 8. The product is

δ / ppm	
3.85	2-proton doublet
7.2	1-proton triplet
7.5	4-proton multiplet

Table 8

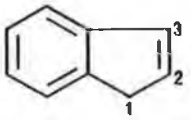
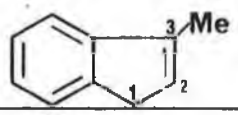
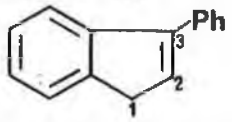
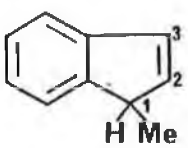
believed to be a 2-substituted rather than a 3-substituted indene. This decision was based on a comparison of its ^{1}H-nmr data with that of 2- and 3-phenyl indene, (and other 2- and 3-substituted indene derivatives- see Table 9).

The observed coupling constants for the olefinic protons in indene and

Substituted Indene	CH_2/ppm	C=C-H/ppm
TCTN photoproduct[25]	3.85	7.2
TCPN photoproduct	3.80	7.0
2-phenylindene[96]	3.87	7.13
3-phenylindene[97]	3.48	6.58
2-methylindene[98]	3.30	6.50
3-methylindene[99]	3.12-3.44	6.2-6.28
2-ethylindene[99]	3.27	6.47
3-ethylindene[99]	3.27	6.16
2-butylindene[99]	3.28	6.48
3-butylindene[99]	3.25-3.32	6.14-6.22
2-propylindene[99]	3.27	6.48
2-bromoindene[99]	3.54	6.88

Table 9

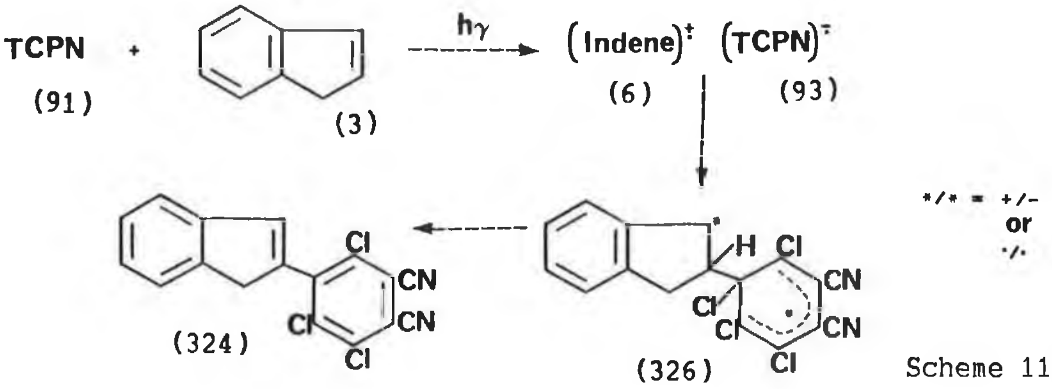
some substituted indenes are shown in Scheme 115.[110,101] Unfortunately the 1,2- and 1,3-couplings are found to be very similar in magnitude and

	$J_{2,3}$ 5.58Hz $J_{1,3}$ 1.98Hz $J_{1,2}$ 2.02Hz
	$J_{1,2}$ 1.8 ∓ 0.2Hz
	$J_{1,2}$ 2.5Hz
	$J_{1,2}$ 1.95 ∓ 0.05Hz $J_{1,3}$ 1.95 ∓ 0.05Hz

Scheme 115

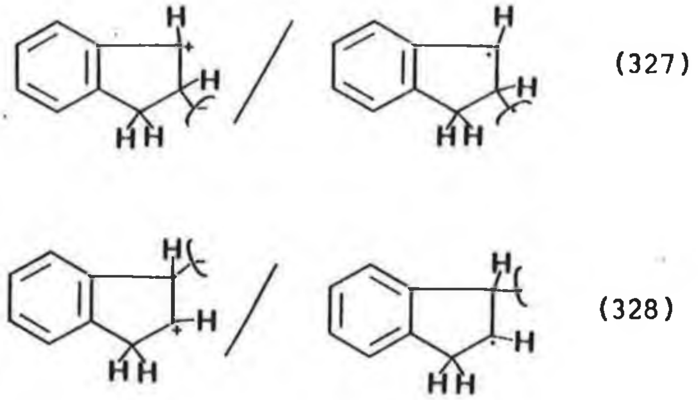
cannot therefore be used to distinguish between 2- and 3-substituted indenes. The olefinic coupling constant in the TCPN/indene photoproduct has the expected magnitude i.e. ~2Hz.

The position of substitution of the aromatic ring is believed to be the 4- rather than the 3-position, by analogy with previously reported photochemical substitution reactions of TCPN, (see P.55). A mechanism similar to the one outlined for (81)[25] can be proposed to account for the formation of this 2-substituted indene (324) i.e. the reaction may proceed via initial electron-transfer from indene to TCPN, (Scheme 116),



Scheme 116

to give a radical cation/radical anion pair, followed by radical coupling and elimination of hydrogenchloride to give the observed product. The attachment at C-2 of the indene molecule (as compared to C-3) would be expected from such a mechanism since structures (327) are stabilised by



Scheme 117

resonance relative to structures (328). The structural assignment is thus consistent with the proposed mechanism. An estimate of the free energy change for electron-transfer from indene to TCPN gives a negative value (ΔG_{ET} =-88kjmol^{-1}) indicating that the electron tranfer step is exothermic and thus supporting the proposed mechanism. Indene has in fact been reported to undergo photosensitised dimerisation when irradiated in the presence of the electron acceptor dimethylmaleicanhydride, (see P.9). This reaction is believed to be initiated via a electron transfer process similar to that outlined for TCPN/indene.

Conclusions.

The electron deficient arylhalide TCPN has been shown to undergo a variety of different reactions when irradiated in the presence of potential donor molecules. These reactions, together with the corresponding calculated free energy changes for electron transfer to TCPN (from the donor molecule) are shown in Scheme 118. Previously reported photochemical reactions of TCPN (along with the corresponding ΔG_{ET} values have also been included).

Donor Molecule	ΔG_{ET}	Mode of Reactivity
(1) 2-Me-THF	+ve*	Substitution
THF[22]	"	"
1,3-Dioxolane[22]	"	"
Dioxane[22]	"	"
Diethylether[22]	"	"
(2) Hex-1-ene	$+12 kJmol^{-1}$	Substitution and Addition
(3) Cyclohexene	$-45 kJmol^{-1}$	Reduction
α-Methylstyrene	$-8.7 kJmol^{-1}$	"
Triethylamine[21]	$-33 kJmol^{-1}$	"
(4) Naphthalene	$-86 kJmol^{-1}$	Reduction (+ some Substitution)
Diethylamine[21]	$-32 kJmol^{-1}$	"
(5) Methoxybenzene[23]	$-88 kJmol^{-1}$	Substitution (+ some Reduction)
1,4-Dimethoxybenzene[23]	$-113 kJmol^{-1}$	"
Indene	$-88 kJmol^{-1}$	Substitution only
Anthracene[24]	$-131 kJmol^{-1}$	"
Phenanthrene[24]	$-90 kJmol^{-1}$	"

Scheme 118

Re: Scheme 118. *The actual E_{ox} values for these ethers have not been reported - all are however strongly positive (>2.5V) and so the calculated ΔG_{ET} values will also be strongly positive.

There does not seem to be any obvious correlation between the observed modes of reactivity and the calculated ΔG_{ET} values. However if the reactivity of the aliphatic ethers (group1) is regarded as anomalous, several general trends in reactivity can be proposed: (1) Photosubstitution predominates when the calculated ΔG_{ET} values are strongly negative, (2) At intermediate values of ΔG_{ET} (though still negative values) photoreduction predominates, and (3) When ΔG_{ET} is positive (as for hex-1-ene) photoaddition occurs. However the photochemical reactions of TCPN with other donor molecules (especially those giving positive ΔG_{ET} values) would be required to further substantiate these proposals. The observed reactivity of the alkenes with TCPN is in fact in agreement with the proposal of Mattay[59] for predicting the reactivity of unsaturated systems with aromatic compounds. He suggested that when the calculated ΔG_{ET} value is positive cycloaddition predominates (as with TCPN / hex-1-ene) whereas when the calculated ΔG_{ET} value is negative substitution is the preferred mode of reactivity.

CHAPTER FOUR

THE PHOTOCHEMICAL REACTIONS OF N-METHYL-3,4,5,6-TETRACHLOROPHTHALIMIDE

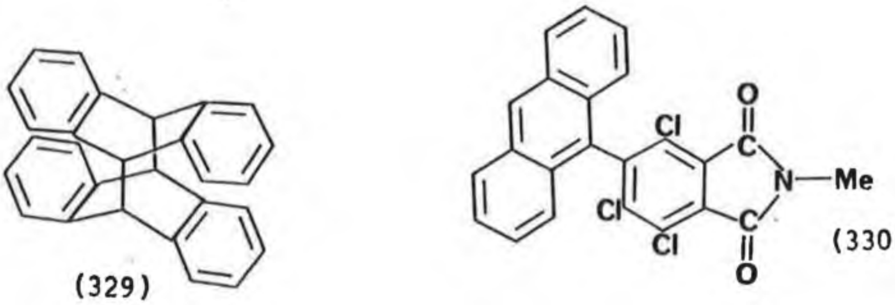
The photochemical reactions of a second electron-deficient arylhalide, N-methyltetrachlorophthalimide, with various donor molecules were also studied and the results are outlined in the following section.

The Photochemical Reactions of N-Methyl-3,4,5,6-tetrachlorophthalimide with Aromatic Hydrocarbons

The polycyclic aromatic hydrocarbons phenanthrene, anthracene and naphthalene undergo photosubstitution reactions when irradiated in the presence of the arylhalide TCPN and an electron-transfer mechanism has been proposed to account for the observed products.[24] The corresponding potential photochemical reactions with N-methyl-3,4,5,6-tetrachlorophthalimide (Cl_4NMP) have been investigated here.

No products were isolated from the photolysis of an equimolar solution of Cl_4NMP and naphthalene in acetonitrile and the starting materials were recovered.

Irradiation of an equimolar solution of Cl_4NMP and Anthracene in acetonitrile led only to the formation of dianthracene (329) and none of the anticipated photosubstitution product, (330).



(329) (330)

Scheme 119

The Cl_4NMP was recovered unchanged. The dianthracene was characterised by comparison of its infrared spectrum and m.p. (267-278 °C) with those of an authentic sample. The latter (m.p. 270-280 °C) was prepared according to the method of Coulson et al.[102] Photolysis of a 1:10 solution of anthracene and Cl_4NMP also led only to the formation of dianthracene.

When an equimolar solution of Cl_4NMP and phenanthrene was irradiated through Pyrex one product was observed on TLC. Chromatographic separation from the starting materials led to the isolation of a yellow crystalline solid (m.p. 286-287 C). Its infrared spectrum showed C=O (1777 and 1720cm^{-1}) and aromatic C-H (3062cm^{-1}) absorption bands. It analysed for $C_{23}H_{12}O_2Cl_3N$ which corresponds to the elimination of HCl from Cl_4NMP and phenanthrene. Its proton nmr spectrum was typical of that expected for a 9-substituted phenanthrene. It showed a 2-proton multiplet at δ8.8 (H-4, H-5), a 1-proton multiplet at δ8.0 (H-8), a 5-proton multiplet at δ7.6 (H-1, H-2, H-3, H-6, H-7), a 1-proton singlet at δ7.4 (H-10) and a 3-proton singlet at δ3.3 (N-Me). A comparison with the reported chemical shifts in the ^{1}H-nmr spectra of 9-(3,5,6-trifluoro-1,2-dicyanophenyl)phenanthrene (331) and 9-(3,5,6-trichloro-1,2-dicyanophenyl)phenanthrene (87) shows a clear similarity, (Table 10).

(331) (87)

Ar = 9-phenanthryl-

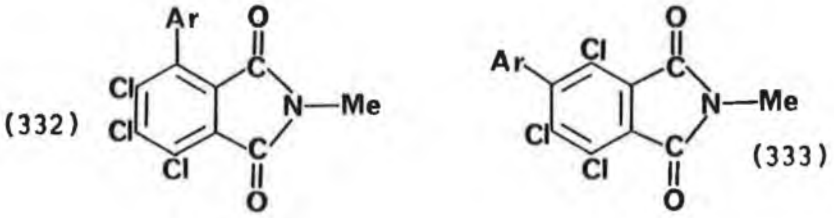
Scheme 120

	(331)	(87)	product
	δ/ppm	δ/ppm	δ/ppm
2-proton multiplet (H-4, H-5)	8.9	8.7	8.8
6-proton multiplet	7.8	7.7	7.8
(H-1, H-2, H-3, H-6, H-7, H-8)			
1-proton singlet (H-10)	7.25	7.20	7.4

Table 10

Its ^{13}C nmr spectrum showed two C=O peaks at δ164.3 and δ164.2, nineteen aromatic carbons between δ142 and 120 and an N-Me carbon at δ24ppm. This data is consistent with either a 3- or 4-substituted N-methylphthalimide

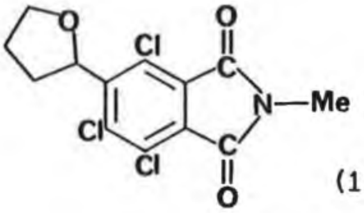
(332 or 333).



(332) (333)

Ar = 9-phenanthryl- Scheme 121

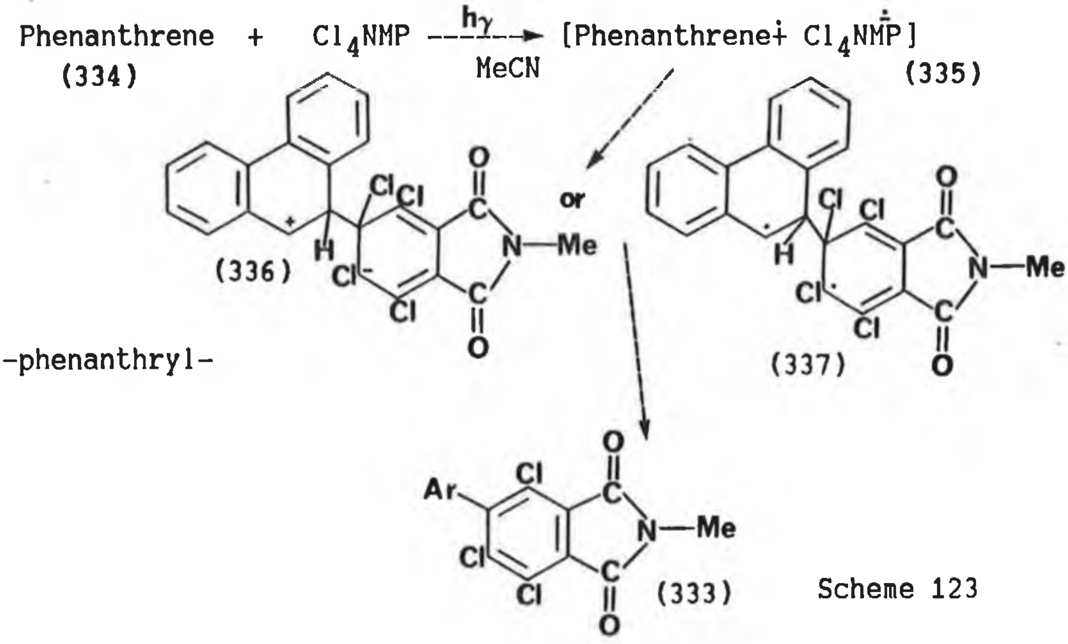
Cl_4NMP has been shown[26] to undergo photosubstitution reactions with various ethers to give products in which the chlorine at position-4 has been replaced by the ether moiety. For example, irradiation of a solution of Cl_4NMP in tetrahydrofuran gives (113). By analogy, it might be



(113) Scheme 122

expected that with phenanthrene substitution would again take place at the 4-position to give (333).

A mechanism involving initial electron-trnsfer from phenanthrene to Cl_4NMP (Scheme 123, shown for a 4-substituted product) can be proposed to account for the observed photosubstitution product. This is followed by coupling to give either a zwitterionic (336) or biradical (337)



Ar = 9-phenanthryl-

Scheme 123

intermediate and then elimination of HCl to give the observed product. A similar mechanism has been proposed to account for the formation of the corresponding photosubstitution product (87) with TCPN. It has been suggested that (87) is formed as a result of excitation of a charge-transfer complex of TCPN and phenanthrene in solution.[24] A solid charge-transfer complex between TCPN and phenanthrene can be isolated. However attempts during the present work to isolate a corresponding complex between Cl_4NMP and phenanthrene failed. Indeed the u.v. spectrum of a mixture of Cl_4NMP and phenanthrene in acetonitrile showed no charge-transfer absorption bands.

Thus the three polycyclic hydrocarbons naphthalene, anthracene and phenanthrene behaved in very different ways when irradiated in the presence of the arylhalide Cl_4NMP. Only phenanthrene underwent the anticipated photosubstitution reaction (to give 333) whilst anthracene only underwent dimerisation and naphthalene did not react at all.

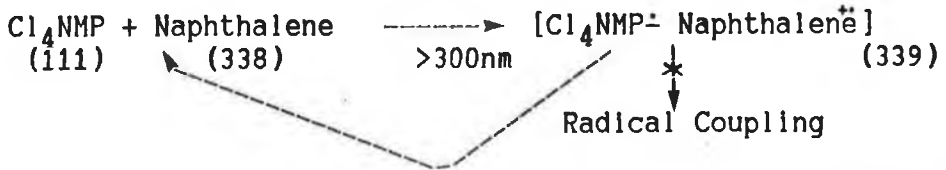
Estimates of the free energy change for electron transfer (from naphthalene, phenanthrene or anthracene) to Cl_4NMP indicate that

Hydrocarbon	ΔG / $kJmol^{-1}$
Naphthalene	-82.6
Anthracene	-126.9
Phenanthrene	-86.5

Table 11

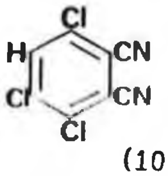
electron transfer from all three hydrocarbons to an excited Cl_4NMP should be exothermic, Table 11. The negative value for phenanthrene/ Cl_4NMP thus supports the proposed mechanism, (see Scheme 123).

The lack of reactivity with Cl_4NMP/naphthalene may perhaps be due to back electron-transfer (from an initially formed radical cation/radical anion pair, 339) to regenerate the starting materials, (Scheme 124),

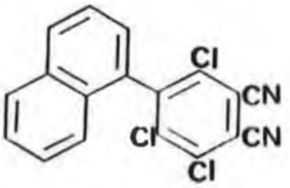


Scheme 124

being more energetically favorable than a radical coupling pathway leading to photosubstitution. This lack of reactivity is in contrast to that of TCPN with naphthalene which reacts to give mainly the photoreduced compound (100) together with the 1-substituted naphthlene (264).



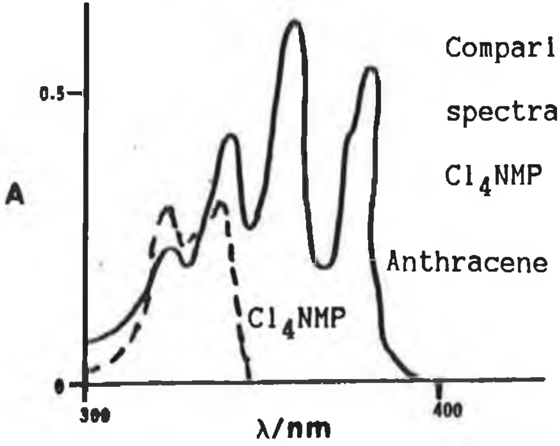
(100)



(264)

Scheme 125

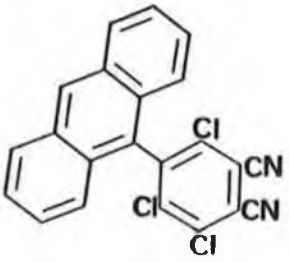
Irradition of a solution of Cl_4NMP and anthracene only leads to the formation of anthracene photodimer (329). Again perhaps back electron-transfer, from an initially formed radical cation/ radical anion pair, is more energetically favorable than radical coupling leading to a substitution product. More likely, anthracene probably competes with Cl_4NMP for the available light. In fact a comparison of the u.v. spectraof equimolar solutions of Cl_4NMP and anthracene above 300nm shows that anthracene does indeed compete favourably.



Comparison of the u.v. absorption spectra of 10^{-4}M solutions of Cl_4NMP and Anthracene in MeCN.

Scheme 126

The photodimeristion of anthracene is well established[102] and takes place at a diffusion controlled rate so it is not surprising that only dimerisation occurs here. However anthracene has been shown to undergo photosubstitution (along with dimerisation), when photolysed in equimolar amounts with TCPN, to give (86). TCPN does not compete with anthracene for the available light (>300nm) any more favorably than Cl_4NMP, (Scheme 126), so a lack of photosubstitution with Cl_4NMP cannot be due entirely to anthracene absorbing most of the available light. It has been suggested that the photosubstitution product (86) is formed as a result of the

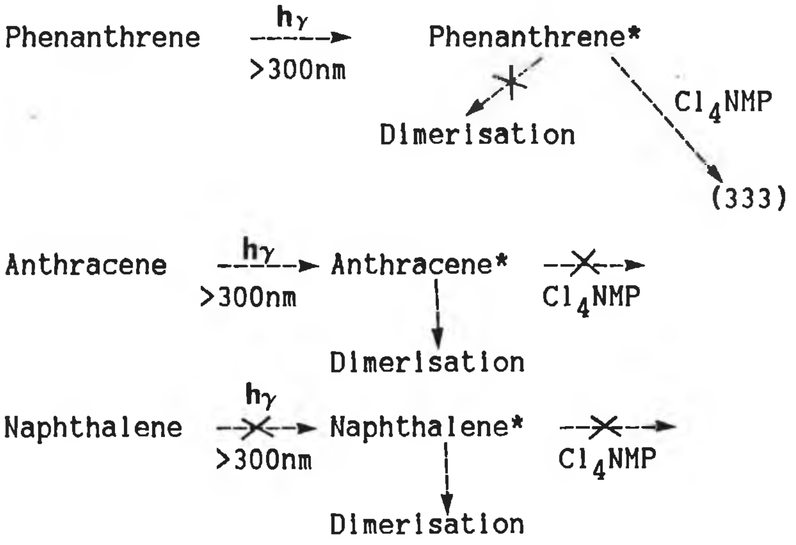


(86)

Scheme 127

excitation of a charge-transfer complex between TCPN and anthracene in solution. It has proved possible to isolate a solid charge-transfer complex between anthracene and TCPN[24] but attempts during the course of this work to isolate a corresponding charge-transfer complex between Cl_4NMP and anthracene failed. Also the u.v. spectrum of a mixture of Cl_4NMP and anthracene showed no charge-transfer absorption bands. Alternatively perhaps the quantum yield for substitution between TCPN/anthracene is much higher than for the Cl_4NMP/anthracene reaction so that, in the former case, product can be formed (i.e. it does manage to compete with anthracene photodimerisation) whereas in the latter case only dianthracene is observed.

Phenanthrene is the only one of the three hydrocarbons which undergoes photoreaction with Cl_4NMP to give a substitution product, (333). Perhaps (333) is formed as a result of reaction between the excited hydrocarbon molecule (i.e. phenanthrene) and the arylhalide, (Scheme 128).

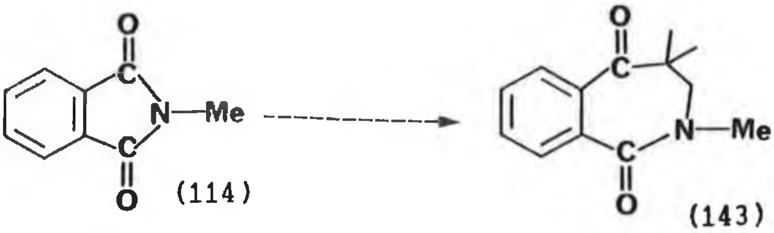


Scheme 128

Excitation of anthracene however leads to photodimerisation in preference to photosubstitution, (presumably because of the high quantum yield for the dimerisation reaction). The photodimerisation of β-substituted naphthalenes[103,104] and various phenanthrene derivatives[105] are known but neither naphthalene nor phenanthrene have been reported to undergo photodimerisation. Competition from such dimerisations with any potential photosubstitution reaction is therefore unlikely. Naphthalene is the only one of the three hydrocarbons which does not compete with Cl_4NMP for the available light and it neither undergoes photosubstitution nor photodimerisation.

The Photochemical Reactions of Tetrachloro-N-Methylphthalimide and Tetrachloro-N-Ethylphthalimide with Alkenes.

A large number of photochemical reactions between non-chlorinated phthalimides (for example, N-methylphthalimide, 114) and unsaturated systems have been reported.[106] In almost all cases the reaction involves photoaddition of the unsaturated molecule across the C-(O)-N bond of the phthalimide. For example, the photochemical reaction of 2-methylprop-2-ene with N-methylphthalimide gives (143), Scheme 129.



Scheme 129

Irradiation of tetrachloro-N-methylphthalimide (111) or tetrachloro-N-ethylphthalimide (322) with alkenes might well be expected to give rise to similar photoaddition products.

Scheme 130

Alternatively, photoreaction of the chlorinated phthalimides with alkenes might possibly lead to:

(a) Acyclic addition of the alkene across the carbon-halogen bond. Several examples of acyclic addition of alkenes across a carbon-halogen bond have been reported, (see P.43) ;

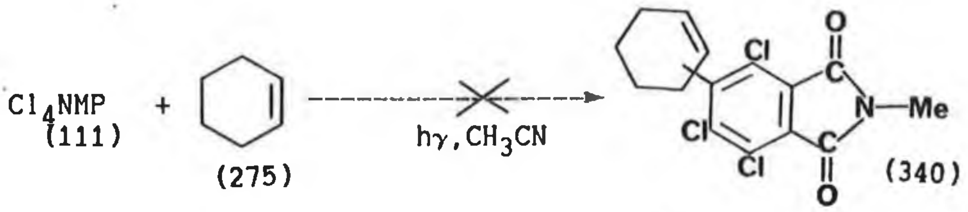
(b) Replacement of a chlorine (from the aromatic halide) by the alkenyl moiety. Previously investigated reactions of Cl_4NMP with various ethers[26] have given rise to products in which a chlorine atom has been replaced by the ether moiety, (see P.25). Irradiation of alkenes with either (111) or (322) might well be expected to lead to analogous reactions. It was therefore decided to irradiate the chlorinated phthalimides, (111) and (322), with an alkene to see whether their photoreactions paralleled those of the non-chlorinated phthalimides or whether reaction took place at the aromatic ring.

Irradiation of tetrachloro-N-methylphthalimide (111) and cyclohexene through Pyrex in acetonitrile gave two products. The major product (m.p. 158-159 °C) showed two carbonyl (1710 and 1777cm^{-1}) and two C=C (1654 and 1579 cm^{-1}) absorption bands in the infrared spectrum. It analysed for $C_{15}H_{13}NCl_4O_2$ i.e. for addition of cyclohexene to N-methyltetrachlorophthalimide (111). This data is consistent with several possibilities :

(1) Addition of the alkene to the aromatic ring, either 1,2-, 1,3- or 1,4- ;

(2) Addition of the alkene across the C(O)-N bond ; and

(3) Acyclic addition across the C-Cl bond, but rules out a substitution reaction, Scheme 131.



Scheme 131

The ^1H nmr spectrum showed a 9-proton multiplet at δ0.9-2.0, a 1-proton multiplet at δ2.3 (10 cyclohexyl protons) and a 3-proton singlet at δ3.1 (N-CH_3). Again this is consistent with any of the three addition modes (1,2 and 3, above).

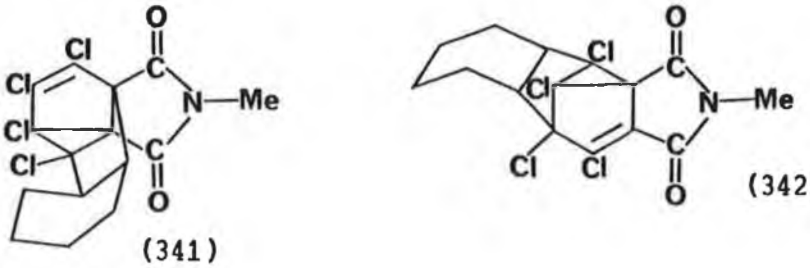
The ^{13}C nmr spectrum of the product, (Table 12), shows a total of fifteen peaks consistent with an unsymmetrical addition of cyclohexene

^{13}C nmr Data of the Major product from the photolysis of Cl_4NMP and Cyclohexene.

δ/ppm	Assignment
168.6	C=O
162.5	
147.2	
132.9	alkene carbons
129.1	
125.5	
78.3	3°/4° carbons
58.6	
57.3	
51.8	
29.3	
28.9	C-H cyclohexyl
26.9	CH_3-N
26.6	
25.4	

Table 12

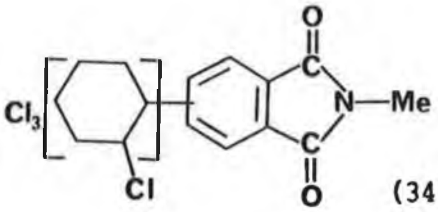
to Cl_4NMP. There are six peaks between δ26.6 and δ57.3. These are relatively intense and can be assigned to the six hydrogen-bearing carbons of the cyclohexyl group. There are two peaks, at δ58.6 and δ78.3 respectively. These are relatively weak and probably arise from tertiary or quaternary carbons. The ^{13}C nmr spectrum shows : (1) four peaks between δ125.5 and δ147.2, assigned to sp^2 alkene carbons, (2) two peaks at δ162.5 and 162.6, respectively, assigned to carbonyl carbons and (3) one peak at δ25.4, assigned to the CH_3-N carbon. This data completely rules out: (1) Any 1,3-addition products of the type (341) or



(341) (342)

Scheme 132

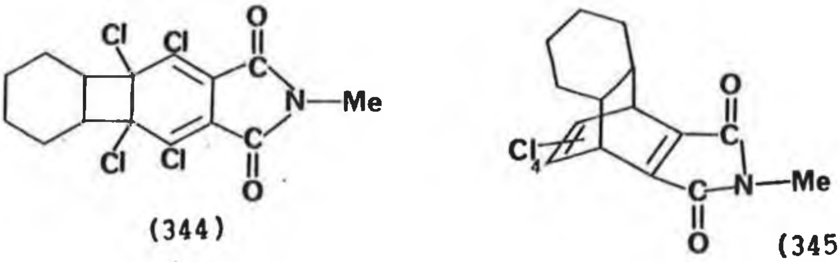
(342); (2) Any acyclic addition products related to (343); (3) Any



(343)

Scheme 133

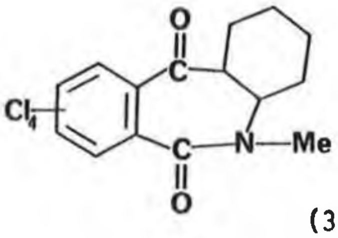
symmetrical 1,2- or 1,4-addition products, (344) or (345); and (4)



(344) (345)

Scheme 134

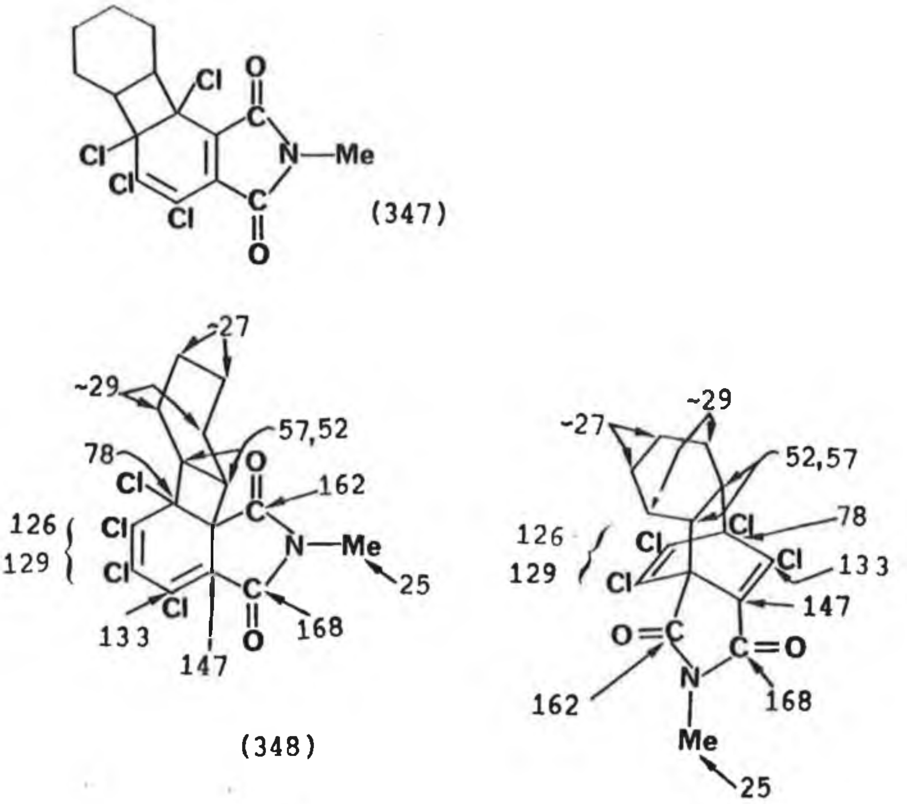
Addition across the C(O)-N bond of the phthalimide to give structures of the type (346).



(346)

Scheme 135

The ^{13}C nmr data is therefore only consistent with structures (347), (348) or (349), Scheme 136. Structure (347) is unlikely as it does not appear to account for the large difference (δ78.3, δ58.6) in the values of the two 3°/4 carbons in the ^{13}C nmr spectrum. The observed peaks in the ^{13}C nmr spectrum may therefore be assigned to isomers (348) and (349) as shown in Scheme 136. However it is not possible to distinguish between them on the basis of this data alone.



(347)

(348)

(349)

Scheme 136

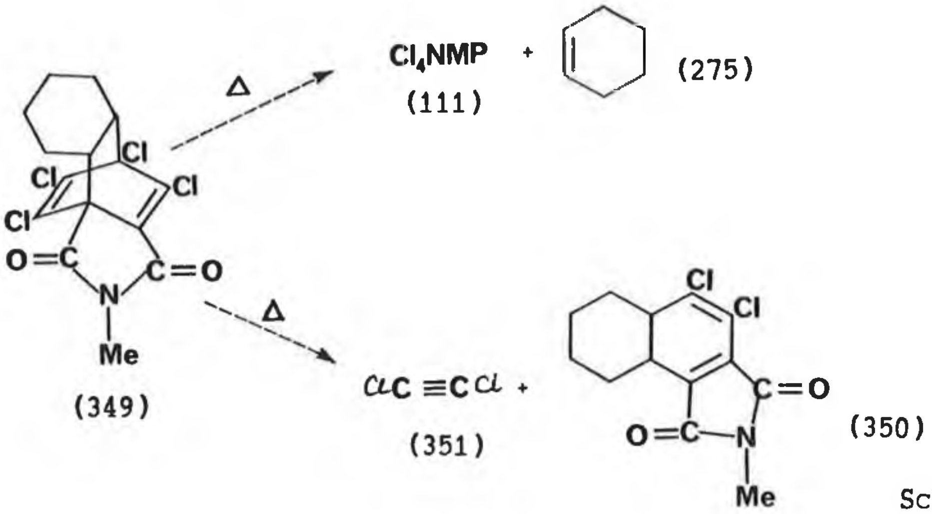
The major peaks in the mass spectrum of the product are shown in Table 13. A compound formed by the addition of cyclohexene to Cl_4NMP should show a molecular ion peak at 379 and this is observed. The percentage relative abundance is very small but this is to be expected in a compound containing several chlorine atoms. The peak at m/e = 344 corresponds to the molecular ion peak minus a chlorine atom (M+ - Cl). The peak at m/e = 298 corresponds to the molecular ion peak minus eightyone i.e. minus a cyclohexene unit plus hydrogen (M+ - 82 + H). The peak at m/e = 311 corresponds to the molecular ion peak minus sixtyeight. Loss of a fragment of m/e = 67 is characteristic of a cyclohexyl compound[107] and this peak at (M+ - 68) can be assigned to a (M+ -67- H) fragment. The

Mass	% R.A	Mass	% R.A.
379	M+, <1	276	38
		278	39
344	56	280	16
346	55		
348	18	82	76
		67	100
311	63	69	23
313	79	54	47
315	38	41	28
298	49		
300	61	R.A. = relative abundance	
302	34		
304	12		

Table 13

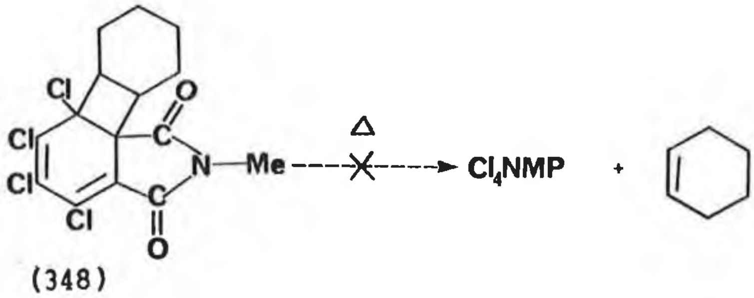
peak at m/e = 276 corresponds to the loss of a chlorine (35) from the fragment at m/e = 311 or loss of a 68 mass unit from the fragment at m/e = 344. The ratio of the peaks at M : M+2 : M+4 etc. for each of the fragmentations listed above are consistent with the assigned number of chlorines. The peak at m/e = 82 corresponds to a cyclohexene ion fragment. The mass spectrum also shows : (1) peaks at m/e = 67 and m/e = 54, both of which are characteristic of a cyclohexene derivative, and (2) a peak at m/e = 41 which is characteristic of alkene or alkyl compounds. All of these fragments are consistent with both the 1,2- (348) and 1,4- (349) addition products. However a 1,4-addition product (349) might be expected to undergo a retro Diels Alder reaction to give either fragments (111) and (275) or, alternatively the fragments (350) and (351), Scheme 137. The 1,2-addition product, on the other hand, would not be expected to undergo such a retro reaction to give (111) and/or (275) because that process is thermally forbidden, Scheme 138.

Expected Fragments for a 1,4-Addition Product



Scheme 137

Expected Fragments for a 1,2-Addition Product



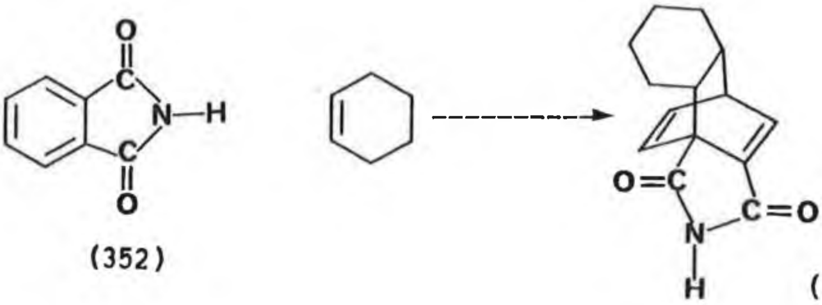
Scheme 138

The molecular weights of all these fragments together with their percentage relative abundance in the mass spectrum of the product are shown in Table 14. The large percentage relative abundance for the cyclohexene fragment points to a 1,4- rather than a 1,2-addition product

Ion Fragment / I^{+} or $I^{+\bullet}$	M.Wt.	Relative Abundance in mass spectrum of product
Cl_4NMP	297	5%
Cyclohexene	82	76%
Cl-≡-Cl	94	<1%
(350)	245	2%

Table 14

but the 1,2-addition cannot be entirely ruled out on this evidence alone. Recently the photochemical reaction of phthalimide (352) with cyclohexene (Scheme 139) has been shown[108] to give the 1,4-addition product (353). The latter structure has been unambiguously assigned on



Scheme 139

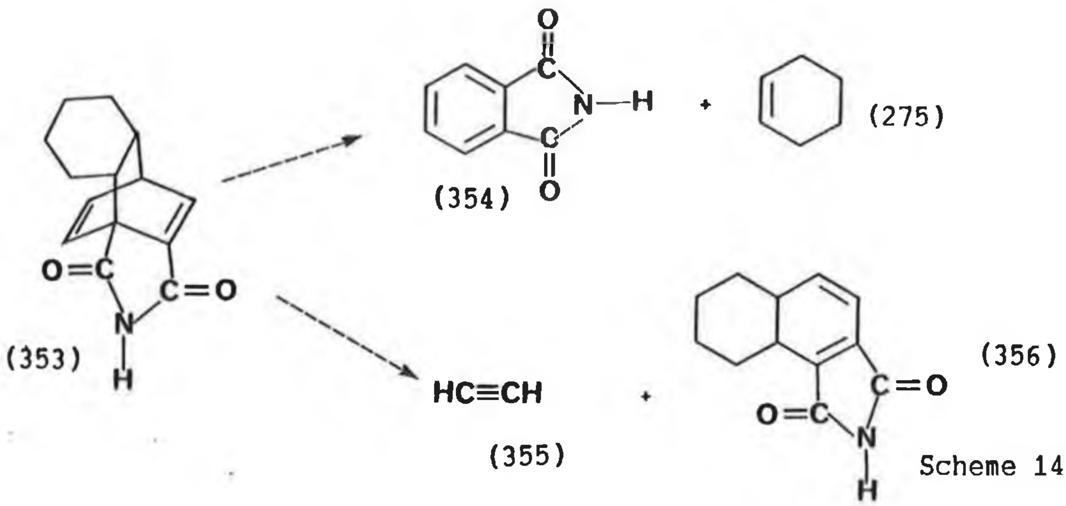
the basis of the compound's ^1H nmr spectrum. It showed : (1) a 9-proton multiplet at δ0.95–1.89, a 1-proton multiplet at δ2.03 (cyclohexyl C-H); (2) a 1-proton multiplet at δ3.67 (C-H) ; (3) three 1-proton multiplets at δ6.08, 6.75 and 6.94 (C=C-H) ; (4) a 1-proton singlet (broad) at δ8.84 (N-H). This data is only consistent with one of the geometrical isomers of structure (353) and no other addition product. This compound is analogous to the 1,4-adduct (349), which has been tentatively assigned to the major product from the photolysis of Cl_4NMP/cyclohexene. A comparison of the mass spectrum, the u.v. spectrum and the nmr data for (353) with the corresponding data for this product further supports the assignment of a 1,4-adduct structure (349) in preference to the 1,2-adduct structure (348).

The major peaks in the mass spectrum of (353) are shown in Table 15, (cf. Table 12, P.113). Both compounds show the same fragmentation pattern due to the presence of the cyclohexyl group, (cf. the % R.A. of the peaks at m/e = 82,69,67,54 and 41). (353) might be expected to undergo a reverse Diels-Alder reaction to give either fragments (354) and (275) or, alternatively (355) and (356), Scheme 139. The 1,4-addition compound (353)

Mass	% R.A.	Mass	% R.A.
228	4	115	13
173	10	82	41
161	100	69	12
148	80	67	82
130	23	54	47
		41	23

Table 15

(353), like the Cl_4NMP adduct, shows a large % R.A. for the cyclohexene fragment (m/e = 82). This further supports the assignment of a 1,4-addition structure (i.e. 349) to the Cl_4NMP adduct.



Scheme 140

The u.v. spectrum of (353) and the Cl_4NMP adduct are also quite similar, (see Table 16), suggesting that both contain similar chromophores i.e. that the Cl_4NMP product is also a 1,4-adduct. The differences observed

	$\lambda_{max}(CH_3CN)/nm$	$\epsilon/mol^{-1}dm^3cm^{-1}$
major product,	208	10,517
Cl_4NMP/cyclohexene	240	12,331
(353)	192	7,186
	224	9,125

Table 16

are best accounted for by the presence of the additional chlorine substituents in the Cl_4NMP adduct.

The ^{13}C nmr data of (353) is outlined in Table 17. The observed peaks

δ/ppm	Assignment
175.9	C=O
165.3	
145.3	Alkene carbons
141.6	
134.9	
123.6	
56.6	4° carbon
51.9	Cyclohexyl C–H, + one 3° C–H
51.0	
45.4	
32.7	
30.3	
27.7	
27.5	

Table 17

correlate well with those obtained for the Cl_4NMP adduct, (cf. Table 12), suggesting that the two molecules contain a similar carbon skelton i.e. that the Cl_4NMP-product is the 1,4-adduct (349).

The cyclohexyl region in the ^1H nmr spectrum of (353) and the Cl_4NMP adduct is also very similar, with both showing one proton at a higher δ value than the other nine (and showing a similar 'doublet-like' pattern). The major product from the photolysis of Cl_4NMP/cyclohexene is therefore believed to be the 1,4-adduct (349) and not the 1,2-adduct (348).

The photochemical reaction of Cl_4NMP with cyclohexene also gave a second, minor, addition product. The ^{13}C nmr data for this product are shown in Table 18. A comparison with the ^{13}C nmr data for the major

δ/ppm	Assignment	δ/ppm	Assignment
169 162.5	C=O	59.5 53.2 30.8	C-H, cyclohexyl + one N-Me
140.0 137.5 135.8 125.5	Alkene Carbons	29.6 27.8 27.6 25.8	
79.6 59.1	3° / 4° Carbons		

Table 18

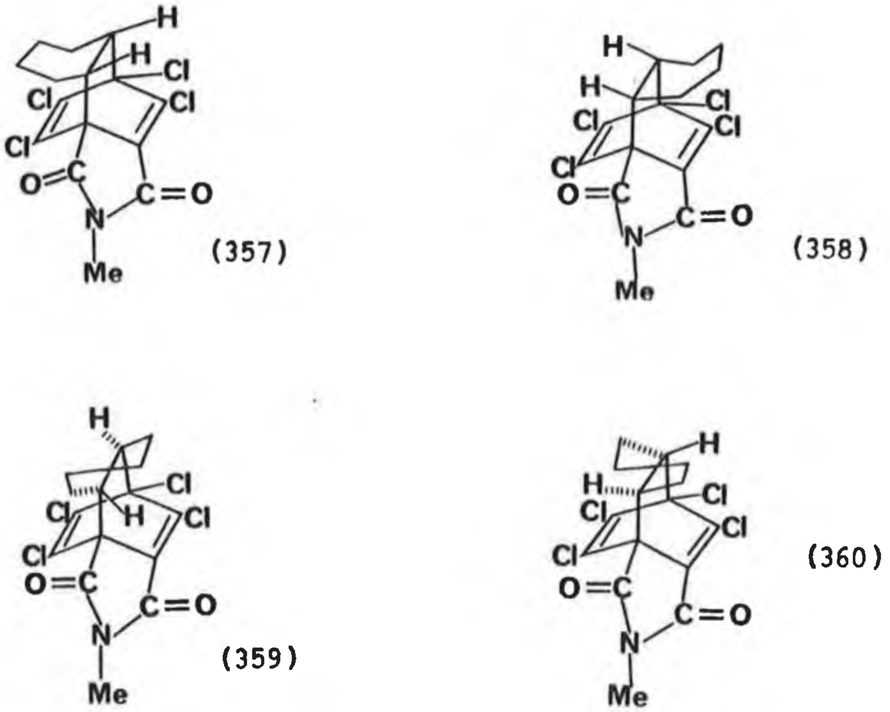
product (see Table 12) suggests that they are geometrical isomers, i.e. that the minor product is also a 1,4-adduct of the type (349).

The u.v. data of the major and minor products (see Table 19) are also very

	λ_{max}/nm	ϵ/mol^{-1}dm^{3}cm^{-1}
major product	208	10,517
	240	12,331
minor product	207	9,437
	240	11,932

Table 19

similar, suggesting that they contain the same chromophore and thus supporting the belief that they are in fact geometrical isomers. There are of course several different stereoisomers of the general structure (349) and these are shown in Scheme 141. The major and minor products could be any two of these four structures. The u.v. ,infrared and ^{13}C



(357) (358) (359) (360)

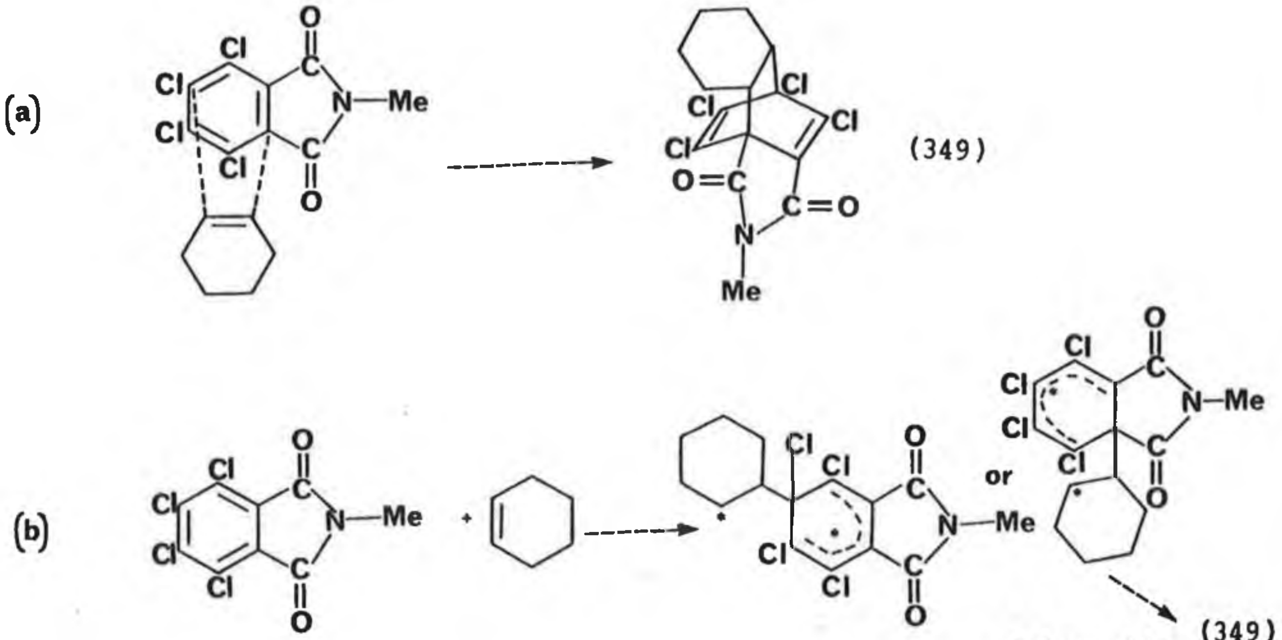
Scheme 141

nmr data of both products correspond closely. The only obvious difference in their respective spectral data lies in the ^1H nmr spectrum viz:- the δ value of one of the bridgehead cyclohexyl protons in the major isomer is significantly higher than the others. This may be due to and interaction of the downfield proton with the carbonyl group of the imide moiety and thus suggests that the major isomer is (357) or (359) in which the carbonyl group is closest to one of the cyclohexyl protons. In contrast the two bridgehead cyclohexyl protons in the minor isomer are similar thus suggesting that the minor isomer is (358) or (360) in which both of these protons are not in the vicinity of a carbonyl group.

These two products could be formed via several different mechanisms:-

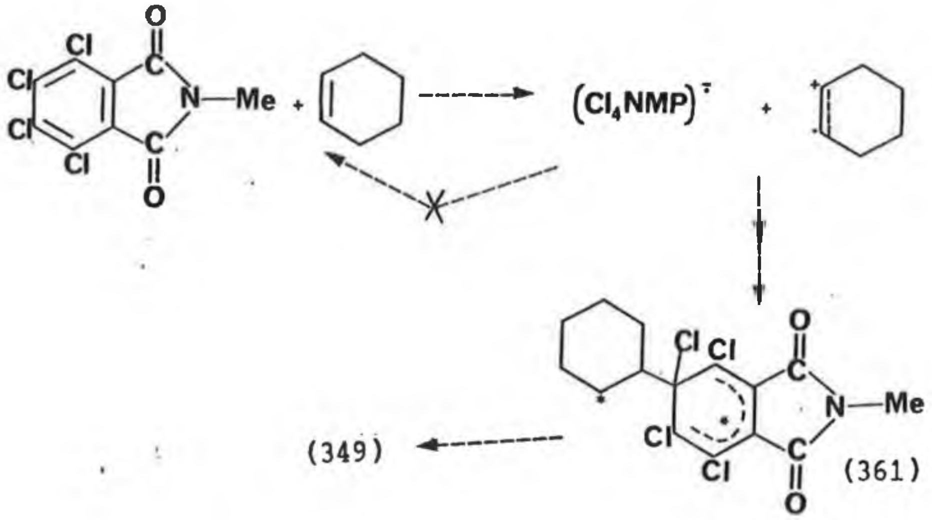
(1) Direct interaction of the excited Cl_4NMP molecule with the ground state alkene to give the product, [see (a), Scheme 142], in a concerted process. If this mechanism operates it will result in cis-addition to the double bond yielding (357) and (358) as the products.

(2) Interaction of the excited Cl_4NMP to give a biradical or zwitterionic intermediate which can then ring close to give the product, [see (b), Scheme 142], or



Scheme 142

(3) Electron transfer from the ground state alkene to the excited Cl_4NMP to give a radical cation / radical anion pair, followed by radical coupling to give (361). Ring closure of this intermediate would then give the observed product, Scheme 143. An estimate of the free energy change

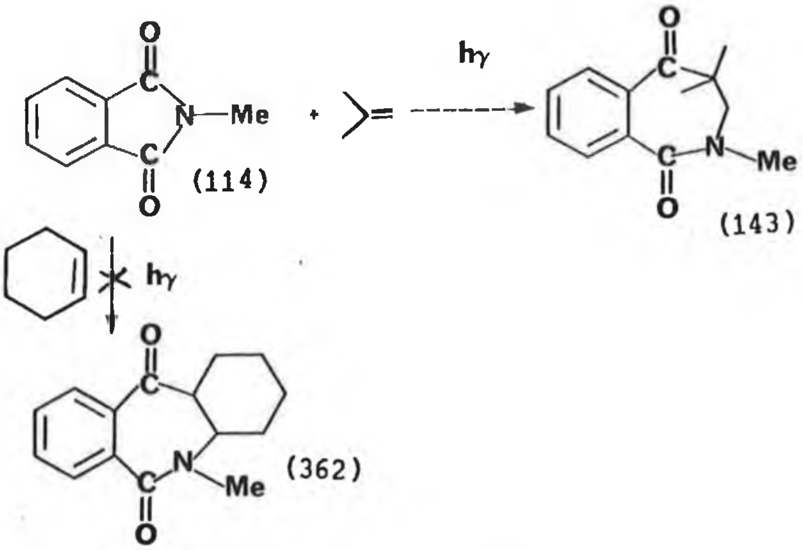


Scheme 143

for electron transfer (ΔG_{ET}) from cyclohexene to Cl_4NMP gives a negative value ($-41 kJmol^{-1}$) indicating that the electron transfer step is exothermic and thus supporting the above mechanism.

A large number of photochemical reactions between the non-chlorinated

N-methylphthalimide (114) and alkenes has been reported. In almost all cases the reaction proceeds via the addition of the alkene (eg.2-methyl-prop-1-ene) to the C(O)-N bond, (see Scheme 144).



Scheme 144

However, the corresponding reaction with cyclohexene does not occur. Mazzocchi has suggested[106] that when the free energy change for electron transfer from the alkene to NMP is negative (as it is with cyclohexene) addition across the C(O)-N bond does not occur because electron transfer quenching of the NMP excited state takes place in preference, (Scheme 145).

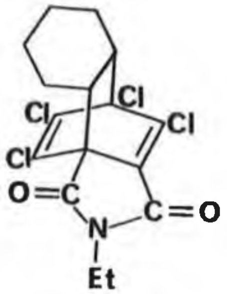
Scheme 145

The radical cation / radical anion pair so formed can subsequently back transfer an electron to regenerate the starting materials. With the chlorinated-N-methylphthalimide and cyclohexene the free energy change for electron transfer is also negative and, in agreement with Mazzocchi's proposal, no addition across the C(O)-N bond occurs. However, in contrast to the non-chlorinated phthalimide, irradiation of Cl_4NMP with cyclohexene does lead to reaction products. Perhaps electron transfer from cyclohexene to Cl_4NMP is occuring (as expected from the ΔG_{ET} value) but then radical coupling to give (361) occurs in preference to back electron transfer to regenerate the starting materials, (Scheme 143).

The Photochemical Reaction of 3,4,5,6-Tetrachloro-N-Ethylphthalimide and Cyclohexene.

Irradiation of a mixture of tetrachloro-N-ethylphthalimide (Cl_4NEP) and cyclohexene through Pyrex in acetonitrile also led to the formation of two products. Both the major and minor products analysed for $C_{16}H_{15}NCl_4O_2$ i.e. for the addition of cyclohexene to Cl_4NEP.

A comparison of the ^1H nmr and ^{13}C nmr data for these two products with that of the two products from the previous reaction (Cl_4NMP / cyclohexene) suggests that the products from the Cl_4NEP reaction are also 1,4-adducts of the type (363).

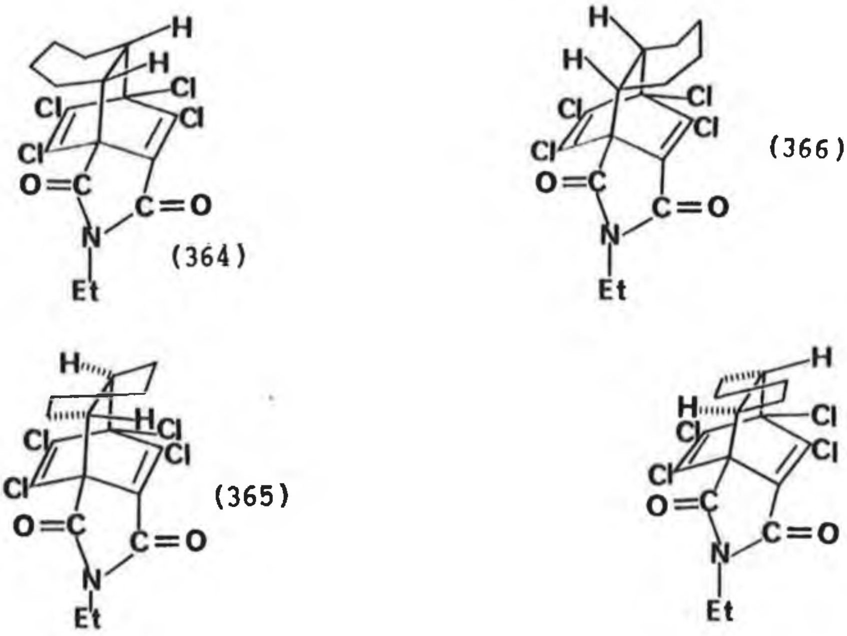


(363)

Scheme 146

The ^1H nmr spectrum of the major isomers (and similarly the two minor isomers) from both reactions are almost identical apart from obvious differences due to substitution of N-Me by N-Et, (see experimental section P.146 and P.145). There is in fact only one clear difference between the ^1H nmr spectra of all four compounds viz :- with the major isomers the δ value of one of the bridgehead cyclohexyl protons is significantly higher than the others. This supports the belief that the major isomers (from both the Cl_4NMP and Cl_4NEP reactions) are members of one series of compounds i.e. possibly (364) or (365) in the Cl_4NEP case, (cf. P.122), and that the minor isomers are members of a second series of compounds i.e. possibly (366) or (367), (Scheme 147).

The ^{13}C nmr data of the two products from the Cl_4NEP / cyclohexene reaction also support the assignment of a 1,4-structure of the type (363) for both major and minor products. In fact the ^{13}C nmr data of (a) the two major products (cf. Table 12 and Table 20) and (b) the two minor


(364)

(366)

(365)

(367)

Scheme 147

isomers (cf. Table 18 and Table 21) are almost identical, again supporting the belief that the two major isomers are members of the same series of compounds and that the two minor isomers are members of another series of compounds. The ^{13}C nmr spectrum of the minor product from the photolysis

The ^{13}C nmr data of the Major product from the photolysis of Cl_4NEP and Cyclohexene.

δ/ppm	Assignmemt	δ/ppm	Assignment
168.3	C=O	57.3	C-H,cyclohexyl + one $N-CH_2-$
162.2		51.7	
		34.3	
147.0	Alkene carbons	29.3	
133.0		28.7	
129.1		27.0	
125.6		26.6	
78.3	3° carbons	13.4	$N-CH_2-$<u>Me</u>
58.4			

Table 20

^{13}C nmr Data of the Minor product from the Photolysis of Cl_4NEP and Cyclohexene.

δ/ppm	Assignment	δ/ppm	Assignment
168.1	C=O	58.7	C-H,cyclohexyl + one N-CH_2
161.5		53.4	
		34.4	
139.0	Alkene carbons	29.2	
138.5		27.0	
135.1		26.9	
123.5			
		13.3	N-C-H_2-Me
78.5	3° carbons		
57.9			

Table 21

of Cl_4NEP has one fewer peak than expected but this peak may in fact be coincident with the peak at δ29.2.

The u.v. data for both products from the photolysis of Cl_4NEP / cyclohexene (Table 22) is also very similar to that from the corresponding Cl_4NMP reaction, (see Table 18). This suggests that all four compounds

major product	λ_{max}/nm	ϵ/$mol^{-1}dm^3cm^{-1}$
	208	13,758
	242	15,539
minor product	207	9,344
	242	11,844

Table 22

contain the same chromophores and further supports the asignment of structure (363) to the products from the Cl_4NEP reaction.

The mass spectrum of the two products from the photolysis of Cl_4NEP / cyclohexene are also consistent with structures of the type (363),Table 23. They show the same fragmentation pattern as the major product from the Cl_4NMP / cyclohexene reaction, (see P.115). Both spectra show fragmentations at : (1) [M+ - Cl],m/e = 358 (for the Cl_4NEP product), (2) [M+ -82+H], m/e = 312, (3) [M+ -68], m/e = 325, (4) [M+ -68-Cl], m/e = 290 and (5) at m/e = 82, 69, 67, 54 and 41, due to the cyclohexyl group,

Mass	% R.A.	Mass	% R.a.
393	M+, 1	290	36
		292	34
358	55	294	12
360	54		
362	18	82	70
		67	100
325	59	69	24
327	77	54	44
329	37	41	26
312	52		
314	65		
316	33		
318	10		

Table 23

see Table 23 (major product) and Table 24 (minor product). The large % relative abundance at m/e = 82 (corresponding to a cyclohexyl ion fragment) in both products is consistent with the 1,4-adduct (363). The latter might be expected to undergo a retro Diels Alder reaction to give such an ion fragment.

Mass	% R.A.	Mass	% R.A.
393	M+, 3	290	43
		292	40
358	44	294	16
360	43		
362	13	82	73

Mass	% R.A.	Mass	% R.A.
325	26	67	100
327	33	69	14
329	18		
		54	38
312	49		
314	62	41	43
316	33		
318	10		

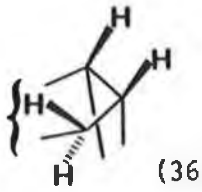
Table 24

Thus the photolysis of Cl_4NEP with cyclohexene produces two products (364 or 365 and 366 or 367) which are in fact members of the same series of compounds as the corresponding products from the Cl_4NMP / cyclohexene reaction. These products could be formed via mechanisms analogous to those outlined in P.122-123 for the Cl_4NMP products. Again an estimate of the free energy change for electron transfer (from cyclohexene to Cl_4NEP) gives a negative value ($\Delta G = -32$ kjmol^{-1}) indicating that an electron transfer step is exothermic and thus supporting mechanism (3), P.123.

The photochemical Reaction of 3,4,5,6-Tetrachloro-N-methylphthalimide, (111), with Indene.

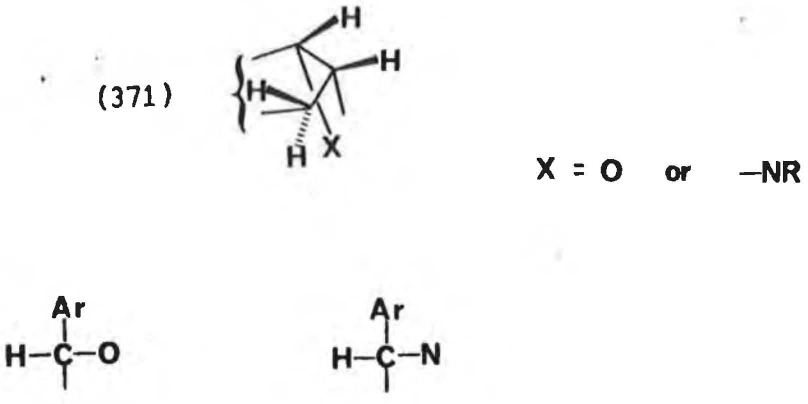
Indene has been reported to undergo a wide range of photochemical reactions including dimerization[110], addition[111,112,113], and substitution[113] (see also P.87and P.24) reactions. In many cases an electron transfer mechanism has been proposed to account for the observed products. Irradiation of a solution of indene and the electron acceptor Cl_4NMP (111) might well be expected to lead to transfer of an electron from indene to Cl_4NMP to give a radical cation/radical anion pair. Further reaction of this radical ion-pair could then lead to reaction products. For example, the reaction could lead to replacement of a chlorine of the phthalimide by an alkenyl group i.e. a product analogous to the one formed between Cl_4NMP and phenanthrene (see P.96).
Alternative reactions between Cl_4NMP and indene might involve :-
(1) Photoaddition of indene across the C(O)-N bond of the phthalimide, a characteristic reaction of the non-chlorinated phthalimides (see P.29),
(2) Cycloaddition of indene across the aromatic ring of the phthalimide, either 1,2-, 1,3- or 1,4-,
(3) Acyclicaddition of indene across the C-Cl bond of the phthalimide.
When a solution of Cl_4NMP and indene in acetonitrile was irradiated through Pyrex two products were observed on TLC. The major product (m.p. 210-212°C) showed two carbonyl absorption bands (1707 and 1767cm^{-1}) in the infrared spectrum. It analysed for $C_{18}H_{10}NO_2Cl_3$ i.e. for the elimination of HCl from the elements of Cl_4NMP and indene. This molecular formula is also supported by the compound's mass spectrum which has a molecular ion peak at m/e = 377.
Its ^{1}H nmr spectrum showed :
(1) a 3-proton singlet at δ 3.00ppm (N-Me); (2) a 1-proton doublet at δ3.30, J 1.6Hz; (3) a 1-proton doublet of doublets, J 1.6Hz, J 1Hz at δ3.43; (4) a 1-proton doublet of doublet of doublets at δ4.42, J 1Hz, J 0.5Hz, J 0.4Hz; (5) a 1-proton doublet at δ5.20, J 0.5Hz; (6) a 3-

proton multiplet at δ7.15, and (7) a 1-proton multiplet at δ7.60. The highfield (>6) part of the spectrum seems at first sight to be consistent with a part-structure of the type (368), Scheme 148, suggesting that indene may have undergone addition to the carbon-chlorine bond. There are however two problems with assigning such a


(368)

Scheme 148

part-structure to the major product. Firstly, such a structure does not account for all the protons expected from the microanalysis and mass spectral data. Secondly, the proton at δ4.42 as well as coupling to the protons at δ3.30 and δ3.43 also shows an additional small coupling (J 0.4Hz) to a fourth hydrogen, a fact which is not readily explained by the above unless long range coupling is involved.
The chemical shift of the proton at δ5.2 is quite high for an alipatic proton, suggesting that it is attached to a carbon of the type (369) or (370) giving (371) as part structure, Scheme 149.

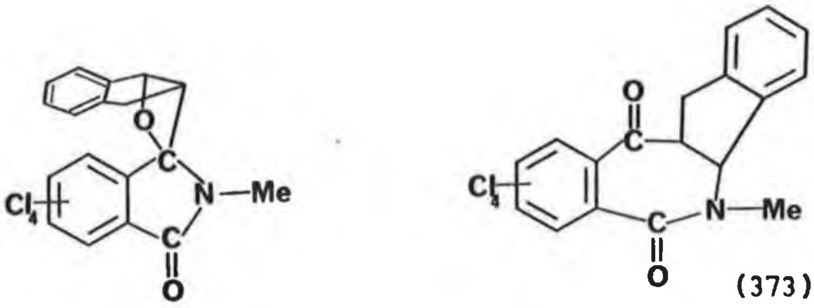


(371)

(369) (370)

Scheme 149

Such a structure could be formed via : (1) addition across the C=O bond of the phthalimide (111) to give, initially, the oxetane (372) or (2) addition across the C(O)-N bond of the phthalimide to give, initially, the benzazepinedione (373), Scheme 150.



(372)

(373)

Scheme 150

However neither of these compounds are consistent with the microanalytical or mass spectral data and it is not obvious how HCl can be lost from either of them to give a reasonable structure consistent with the molecular formula.

The ^{13}C nmr data of the product (Table 25) is not helpful in assigning

δ/ppm	Assignment	δ/ppm	Assignment
165.3	C=O,	53.5	Aliphatic C-H
155.3	Alkene,	43.9	
153.1	Aromatic,	32.8	
142.9	carbons.		
139.2		24.2	N-Me
128.5			
127.4			
126.3			
125.9			
123.9			
122.1			

Table 25

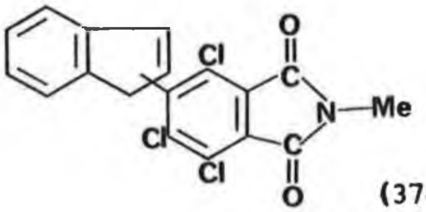
a structure, with only fifteen carbons being observed, (eighteen are expected from the microanalysis and mass spectrum). It does however show the three aliphatic C-H carbons and the N-Me carbon consistent with structure (368) and, in addition, eleven low field carbons between δ 165.3 and 122.1.

The mass spectral data of this product are shown in Table 6 and again this information is not particularly helpful in assigning a structure, with the major fragments being due to loss of chlorines. The fragment at m/e = 343 can be assigned to the molecular ion peak minus chlorine plus hydrogen, (M+ -Cl +H). The fragment at m/e = 308 corresponds to loss of chlorine from the latter fragment, (M+ $-Cl_2$ +H). The fragment at m/e = 258 correspoonds to loss of a fifty mass unit from the latter fragment. The fragment at m/e = 223 corresponds to loss of a chlorine from the latter fragment.

m/e	R.A.%	m/e	R.A.%
377	11, M+	223	5
379	11	225	15
381	4	227	
343	100	187	16
345	72	189	4
347	13		
308	28		
310	6		

Table 26

In conclusion, both the microanalysis and mass spectral data on this compound are consistent with the elimination of HCl from the elements of Cl_4NMP and indene. However the ^{1}H nmr data is not consistent with a straightforward substitution reaction in which one chlorine of Cl_4NMP has been replaced by an indenyl group, (374), Scheme 151. Instead the ^{1}H nmr coupling pattern and the observed ^{13}C nmr chemical shifts



(374)

Scheme 151

suggest an addition reaction at the indene double bond to give a proton arrangement similar to that shown in Scheme 148. Again the observed data is not consistent with a straightforward addition reaction and an X-ray crystal structure of the compound will ultimately be required to determine the actual carbon skeleton.

The photochemical reaction of Cl_4NMP with indene also gave a second minor product (m.p.202-203°C). It showed two carbonyl bands (1767 and 1708cm^{-1}) in the infrared spectrum and analysed for $C_{18}H_{11}NO_2Cl_2$ i.e. for the loss of two chlorine atoms from the elements of Cl_4NMP and indene. This could be accomodated by the loss of HCl together with the replacement of a second chlorine by hydrogen. The product's mass spectrum also supports this molecular formula showing a molecular ion peak at m/e = 343, see Table 27. The mass spectrum of this product is in fact very closely related to that of the major product from the reaction. The same major fragments are present in both (though with different % relative abundances), c.f.Table 26. The only major

m/e	% R.A.	m/e	% R.A.
343	100	258	18
345	68	260	12
347	12		
		223	13
308	18	225	5
310	16		

Table 27

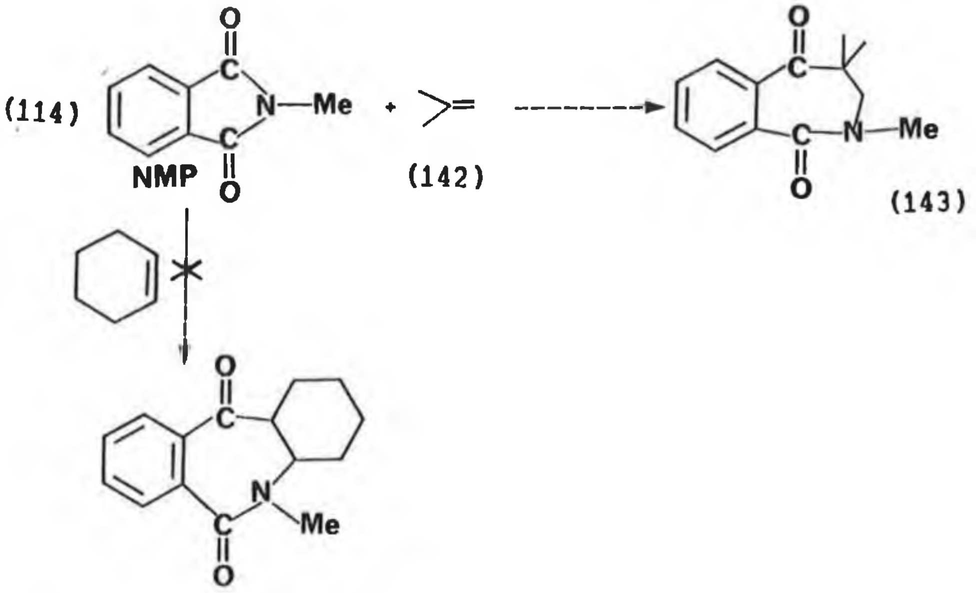
difference is the additional presence of the molecular ion peak in the mass spectrum of the major product. The primary fragmentation of the major product in fact gives rise to fragment (M+ -34) corresponding to the molecular ion of the minor product. It is therefore not surprising that the subsequent fragmentation patterns displayed by the two products are very similar. The molecular ion of the minor product (m/e = 343) corresonds to the elmination of two chlorines (i.e. elimination of HCl and replacement of a chlorine by hydrogen) from the elements of Cl_4NMP and indene. This ion which is in fact the base peak for both products) contains two chlorine atoms and the ratio of the % R.A. of the ion fragments at 343 : 345 : 347 should therefore be 9 : 6 : 1. The observed values mare very close to this ratio and thus support the assignment of this peak to (Cl_4NMP + Indene - 2Cl).

The ^{1}Hnmr of this minor product is also very similar to that of the major product with the same pattern being repeated at slightly different chemical shift values, c.f. P.120. It showed : (1) a 3-proton singlet at δ3.10 (N-Me); (2) a 1-proton doublet at δ3.30, J 1.6Hz; (3) a 1-proton doublet of doublets, J 1.6Hz, J 1Hz, at δ3.44; (4) a 1-proton doublet of doublet of doublets at δ4.60, J 1Hz, J 0.5Hz, J 0.5Hz; (5) a 1-proton doublet at δ5.25, J 0.5; (6) a 3-proton multiplet at δ7.22, alkene/aromatic C-H; (7) a 1-proton multiplet at 7.67 , alkene/aromatic C-H. The similarity of the two proton nmr spectra suggests that the products are closely related i.e. that the proton arrangement in the minor product is similar to that of the major product, (see P.120).

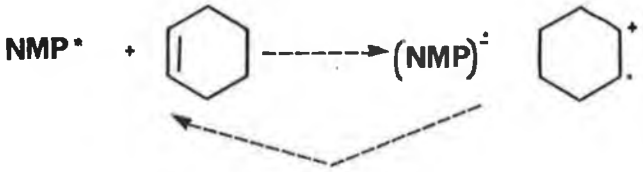
Thus both the mass spectrm and ^{1}H nmr spectrum of the minor product suggests that it has a structure closely related to the major product, with perhaps the difference between them being the replacement of one chlorine by hydrogen in the minor product. Again however the observed data is not consistent with a straightforward addition reaction, (followed perhaps by elimination of HCl and then replacement of chlorine by hydrogen) and an X-ray structure of the minor product will also be required to determine its actual carbon skeleton.

Conclusion

The photochemical reactions of the chlorinated phthalimides (Cl_4NMP and Cl_4NEP) outlined here are in marked contrast to those of the corresponding non-chlorinated phthalimides. A large number of photochemical reactions of non-chlorinated phthalimides has been reported and in almost all cases the reactions involve photoaddition of an unsaturated system e.g. 2-methylprop-1-ene across the C(O)-N bond of the phthalimide,[87] (Scheme 152). However not all alkenes (for example cyclohexene) undergo this addition reaction. Mazzocchi[87] has suggested that when the free energy for electron transfer from the alkene is negative i.e. the electron transfer is exothermic (as it is with cyclohexene) addition across the C(O)-N bond does not occur because electron transfer quenching of the NMP excited state takes place in preference, (Scheme 153).



Scheme 152



Scheme 153

The radical cation / radical anion pair so formed can sbseqently back transfer an electron to regenerate the starting materials. The calculated values for the free energy for electron transfer between the chlorinated phthalimide and the various donor molecules studied here are shown in

Donor-Acceptor Pair	ΔG_{ET}/kJmol^{-1}	Mode of Reactivity
Cl_4NMP/Phenanthrene	-86.5	Substitution
Cl_4NMP/Cyclohexene	-41	Addition across the aromatic ring
Cl_4NEP/Cyclohexene	-32	Addition across the aromatic ring

Table 28

Table 28 together with the observed mode of reaction. In all cases the calculated value for ΔG_{ET} is negative i.e. the electron transfer is exothermic and no addition across the C(O)-N bond of the phthalimide is observed. These results are therefore in agreement with Mazzocchi's proposal that addition accross the C(O)-N bond in phthalimides occurs when ΔG_{ET} is positive. However with the chlorinated phthalimides electron transfer from the donor molecules does not lead to quenching of the phthalimide excited state. Instead reaction (probably following electron transfer) occurs at the aromatic ring of the phthalimide. Calculation of ΔG_{ET} for Cl_4NMP/Phenanthrene gives a large negative value and irradiation leads to substitution of a chlorine on Cl_4NMP by the phenanthrenyl moiety. This reaction is exactly analogous to the corresponding reaction between TCPN and phenanthrene and an electron transfer mechanism has been proposed to account for its formation, (see P.96). Calclation of ΔG_{ET} for Cl_4NMP and cyclohexene (and similarly Cl_4NEP/cyclohexene) gives an intermediate negative value and irratiation leads to addition of the cyclohexene across the aromatic ring of the phthalimide. Several mechanisms (including an electron transfer mechanism) can be proposed to account for the addition products formed, (see P.112).

Irradiation of all the donor/acceptor pairs shown in Table 28 therefore gives rise to products formed by reaction at the aromatic ring of the phthalimide. In all cases an electron transfer can be proposed to account for the observed reactivity and the negative ΔG_{ET} values support this proposal.

CHAPTER FIVE

EXPERIMENTAL SECTION

General Techniques.

Photochemical reactions were carried out in a cylindrical vessel approximately 300mm in length and 75mm in diameter. The vessel was fitted with a water cooled quartz immersion well containing a 400W medium pressure mercury vapour lamp and a pyrex filter. All solutions were first degassed by bubbling nitrogen rapidly through them for fifteen minutes. A very slow stream of nitrogen was then employed throughout the subsequent reaction period. All general purpose grade solvents used for photochemical reactions were previously distilled ; dichloromethane from anhydrous calciumchloride and acetonitrile from anhydrous calciumsulphate.

Flash Chromatography of crude reaction mixtures was carried out using columns packed with silica gel of particle size 32-63μm (Riedel-de-Haien, No.31607, Kieselgel S). Preparative scale radial centrifugal thin layer chromatography was also carried out using a Chromatotron (Model 7924T, Harrison Research, Palo Alto, California). Circular glass plates, 240mm in diameter were coated with silica gel (Merck No.7749, silica gel 60 PF 254 containing $CaSO_4$. H_2O) of layer thickness 1, 2 or 4 mm. The plate was spun at a constant rate and the crude reaction mixture and the solvent applied at the centre. The series of concentric bands so formed on the silica were observed using an ultraviolet lamp operating at 254nm. The polarity of the solvent was increased stepwise over approximately one hour.

Thin layer chromatography was carried out on strips of aluminium coated with a fluorescent indicator (Riedel-de-Haein, D.C.Karten SIF, layer thickness 0.2mm). After development the plates were examined under an ultraviolet lamp operating at 254nm.

Infrared absorption spectra were recorded using a Perkin Elmer 983G infrared spectrometer. Solids were examined as nujol mulls or sodiumchloride discs.

Ultraviolet absorption spectra were recorded on a Shimadzu UV240 spectrophotometer.

^1H nmr spectra (60 MHz) were recorded on a Perkin Elmer R12B instrument using tetramethylsilane as reference standard. ^1H nmr (270 MHz) and ^{13}C nmr (67.80MHz) were recorded by the NMR section, Department of Chemistry, University College, Galway, Ireland, on a Joel GX270 S.C.M. nmr spectrometer. $CDCl_3$ was used as the solvent and tetramethylsilane as the reference standard unless otherwise stated.

Microanalyses were carried out by the Microanalysis Department, University College, Belfield, Dublin 4, Ireland.

Mass spectra were recorded by the Department of Agricultural Chemistry and Soil Science, University College, Belfield, Dublin 4, Ireland, on a V.G. Analytical 70E double focusing mass spectrometer and a Finnigan Super Incos 2400 data system.

Fluorescence spectra were recorded on a Perkin Elmer LS-5 Luminescence spectrometer.

Reduction potentials were measured using cyclic voltametry on platinum electrode with an E.G. and G. P.A.R. model 174A polarographic analyser. Tetraethylammoniumchloride (0.1M in acetonitrile) was used as supporting electrolyte and the reference electrode was a saturated calomel electrode.

Synthesis of N-Methyl-3,4,5,6-tetrachlorophthalimide. (111).

Tetrachlorophthalicanhydride (12.5g, 0.044mol) was placed in a 250ml round-bottom flask. A 33% solution of methylamine in ethanol (10ml, 0.083 mol) was cautiously added, with intermittent shaking and cooling. Water and ethanol were removed by slowly heating to 100 C. The residual yellow material was then heated to 250 C. The resulting hot liquid was poured into a mortar and allowed to cool, with stirring. The solid was then crushed to a fine granular powder and the crude product (12.52g, m.p. 203-206°C) was recrystallised twice from chloroform to give N-methyl-tetrachlorophthalimide (111), (8.5g, 6.5%), m.p. 210-212°C; λ_{max} (CH_3CN) 332 ($2050 dm^3 mol^{-1} cm^{-1}$), 320 (2050), 235 (24,565) and 217 (17,754); ν_{max} $1714 cm^{-1}$ and $1775 cm^{-1}$, δ_H (60)MHz), 3.23ppm (s, -Me).

Synthesis of N-Ethyl-3,4,5,6-tetrachlorophthalimide. (322).

Tetrachlorophthalic anhydride (12.5g, 0.044mol) was placed in a 250ml round-bottom flask and ethylamine (70% solution in water, 7g, 0.16mol) was added slowly with intermittent cooling (ice-bath) and shaking. Water was removed by heating slowly to 100 C and the residual yellow material was heated to 250 C. The hot liquid was poured into a mortar and allowed to cool, with stirring. The resulting solid was then crushed to a fine granular powder. The crude product (13.12g, m.p.168-176°C) was recrystallised twice from chloroform to give N-ethyl-3,4,5,6-tetrachlorophthalimide (322), (4.4g, 3.2%), m.p.181-184°C ; $\lambda_{max.}$ (CH_3CN) 332 ($2,160 dm^3 mol^{-1} cm^{-1}$), 320 (2,100), ~235 br (24,600) and 217nm (17,760) ; $\nu_{max.}$ 1725 and $1785 cm^{-1}$ (C=O) ; δ_H (60 MHz ; solvent CCl_4) 1.25 (3H, t, J 7Hz, -Me) and 3.75 (2H, q, J 7Hz, $-CH_2$).

Photolysis of TCPN and 2-Methyltetrahydrofuran in dichloromethane.

TCPN (1.0g, 3.8mmol) and 2-methyltetrahydrofuran (11.0g, 0.13mol) in dichloromethane (310ml) were irradiated through Pyrex for 35h. TLC showed the formation of two additional spots. The dichloromethane and 2-methyltetrahydrofuran were removed under vacuum. The resulting crude mixture was separated using a Chromatotron with, initially, a 4mm silica plate and then subsequent 2mm plates. The eluent was a mixture of dichloromethane / light petroleum (b.p. 40-60°C) (10:90, increased stepwise to 60:40). This gave, in order of recovery from the plate :-

(1) 2-Methyltetrahydrofuran (7mg, 0.082mol) identified by comparison of its infrared spectrum with that of an authentic sample,

(2) TCPN (0.133g, 0.5mmol) identified by comparison of its infrared spectrum with that of an authentic sample,

(3) An unidentified white solid, (4mg),

(4) Fraction (A), (the minor fraction), possibly a mixture of the cis and trans isomers of 2-methyl-5-(trichloro-1,2-dicyanophenyl)tetrahydrofuran (252a and 252b) and trichlorophthalonitrile (100) ; a white crystalline solid, (33mg), m.p.112-115°C (from light petroleum b.p.80-100°C) ; (Found : C, 49.3; H, 1.7; N, 9.7%) ; $v_{max.}$ 2236 and 2225 (C=N), and 1079cm^{-1} (C-O-C) ; The ^1H nmr spectrum of fraction (A) showed a mixture of two isomers (252a and 252b) in the ratio ~1:1 (after recrystallisation) and, in addition the photoreduced compound, trichlorophthalonitrile, (100). The ratio of the two isomers to (100) was ~3:1, based on the combined integrations of the two methyl doublets (δ1.45 and 1.3) to that of the aromatic singlet, (δ7.8). One isomer showed : δ_H 1.3 (3H, d, J 6Hz, Me) ; 5.5 (1H, m, C(5)-H) ; 4.7 (1H, m, C(2)-H) ; 2.25 (m) and 1.8 (m), $C(3)H_2$-$C(4)H_2$. The other isomer showed : δ_H 1.4 (3H, d, J 6Hz, Me) ; 5.3 (1H, m, C(2)-H) ; 4.1 (1H, m, C(5)-H) ; 2.2 (m) and 1.8 (m), $C(3)H_2$-$C(4)H_2$. The aromatic singlet at δ7.8 is assigned to trichlorophthalonitrile, (100).

(5) Fraction (B), (the major fraction), a mixture of the cis and trans isomers of 2-methyl-5-(3,5,6-trichloro-1,2-dicyanophenyl)-tetrahydrofuran, (251a and 251b) ; a white crystalline solid, (431mg, 42%), m.p.122-124°C (light petroleum b.p.80-100°C), (Found : C, 49.2 ; H, 2.8 ; Cl, 33.3. $C_{13}H_9N_2Cl_3O$ requires C, 49.5; H, 2.9; N, 8.9; Cl, 33.7%); $v_{max.}$ 2233 (C≡N) and 1078 (C-O-C); $\lambda_{max.}(CH_3CN)$ 325 ($3639 dm^3 mol^{-1} cm^{-1}$) , 313 (2,729), 230 (58,219) and 205 (24,925) ;

The ^1H nmr spectrum of fraction (B) showed a mixture of two isomers (251a and 251b) in the ratio ~3:2 (based on the relative integrations of the two methyl doublets after recrystallisation). The major isomer showed : δ_H 1.45 (3H, d, J 6Hz, Me) ; 5.6 (1H, m, C(5)-H) ; 4.2 (1H, m, C(2)-H) ; 2.35 (m) and 1.8 (m), $C(3)H_2$-$C(4)H_2$. The minor isomer showed : δ_H 1.3 (3H, d, J 6Hz, Me) ; 5.8 (1H, m, C(5)-H) ; 4.6 (1H, m, C(2)-H) ; 2.15 (m) and 1.8 (m), $C(3)H_2$-$C(4)H_2$.

Repeated attempts to separate the two isomers chromatographically failed but led instead to the isolation of a mixture of two isomers in a different ratio (~1:1, m.p.124-126°C).

Thermal Reaction of TCPN with 2-Methyltetrahydrofuran in the presence of Dibenzoylperoxide.

TCPN (1.0g, 3.8mmol) and dibenzoylperoxide (205mg, 0.85mmol) in 2-methyltetrahydrofuran (20ml) and dichloromethane (25ml) were heated under reflux for 6h. TLC of the reaction mixture showed two additional spots after ~30min. The mixture was concentrated under vacuum. The resulting crude product was separated using a Chromatatron with initially, a 4mm silica plate and then subsequent 2mm plates. The eluent was a mixture of dichloromethane-light petroleum (b.p. 40-60°C) (5:95 increased stepwise to 40:60). This gave, in order of recovery from the plate :-

(1) TCPN (701mg, 2.6mmol) identified by comparison of its infrared spectrum with that of a known sample.

(2) Fraction (C), a mixture of the cis and trans isomers of 2-methyl-5-(4,5,6-trichloro-1,2-dicyanophenyl)tetrahydrofuran, (252a and 252b) ; a white crystalline solid, (31mg, 8.8%), m.p.159-160°C (light petroleum b.p. 80-100°C), (Found C, 50.8; H, 2.9; N, 8.6; Cl, 31.92. $C_{13}H_9N_2Cl_3O$ requires C, 49.5; H, 2.9; N, 8.9; Cl, 33.3); $\nu_{max.}$ 2239 and 2225cm^{-1} (C≡N), and 1079cm^{-1} (C-O-C); m/e 314 (M+,5%), 272 (50), 259 (35), 235 (35), 208 (26), 58 (100) and 41 (42). The ^{1}H nmr of fraction (C) showed a mixture of two isomers in the ratio ~1.5:1 (based on the relative integrations of the two methyl doublets after recrystallisation). The major isomer showed : δ_H 1.4 (3H, d, J 6Hz, Me); 5.5 (1H, m, C(5)-H); 4.7 (1H, m, C(2)-H); 2.5 (m) and 1.8 (m), C(3)H_2-C(4)-H_2. The minor isomer showed : δ_H 1.5 (3H, d, J 6Hz, Me) ; 5.3 (1H, m, C(5)-H); 4.1 (1H, m, C(2)-H); 2.25 (m) and 1.8 (m), C(3)H_2-C(4)-H_2.

(3) Fraction (D), a mixture of the cis and trans isomers of 2-methyl-5-(3,5,6-trichloro-1,2-dicyanophenyl)tetrahydrofuran, (251a and 251b); a white crystalline solid, (130mg, 36%), m.p.124-127°C (light petroleum, b.p.80-100°C), (Found C, 49.2; H, 2.7; N, 8.8; Cl, 33.4%. $C_{13}H_9N_2Cl_3O$ requires C, 49.5; H, 2.9; N, 8.9; Cl, 33.7%); $\nu_{max.}$2237 (C≡N) and 1078cm^{-1} (C-O-C); $\lambda_{max.}$(CH_3CN) 325 (ϵ 3,935 dm^{3}mol^{-1}cm^{-1}), 313 (2,856), 230 (63,293) and 205 (25,347);

The ^{1}H nmr spectrum of (D) showed a mixture of two isomers (251a and 251b) in the ratio ~2:1 (based on the ratio of the two methyl doublets after recrystallisation). The major isomer showed : δ_H 1.35 (3H, d, J 6Hz, Me); 5.8 (1H, m, C(5)-H); 4.6 (1H, m, C(2)-H); 2.25 (m) and 1.8 (m), C(3)H_2-C(4)H_2. The minor isomer showed : δ_H 1.45 (3H, d, J 6Hz, Me); 5.6 (1H, m, C(5)-H); 4.2 (1H, m, C(2)-H); 2.25 (m) and 1.8 (m), C(3)H_2-C(4)H_2.

Photolysis of TCPN and Naphthalene in dichloromethane.

TCPN (1.0g, 3.8mmol) and naphthalene (0.6g, 4.7mmol) in dichloromethane (310ml) were irradiated through Pyrex for 16h. TLC showed the formation of two products. The solvent was removed under vacuum and the mixture filtered through a silica column (15cm 4cm) using diethyl ether-light petroleum (50:50) in order to remove baseline impurities. Again the solvent was removed under vacuum and the crude mixture was then separated using a Chromatotron with a 2mm silica plate. The eluent was a mixture of dichloromethane-light petroleum (b.p.40-60°C) (10:90 increased stepwise to 30:70). This gave, in order of recovery from the plate :-

(1) Naphthalene (224mg, 1.8mmol) identified by comparison of its infrared spectrum with that of an authentic sample;

(2) TCPN (552mg, 2.1mmol) identified by comparison of its infrared spectrum with that of an authentic sample;

(3) 3,5,6-Trichloro-4-(1-naphthyl)-1,2-dicyanobenzene; a pale yellow solid (120mg, 18%) m.p.210-212°C (Found : C, 60.14; H, 1.81; N, 7.73; Cl, 30.16. $C_{18}H_7N_2Cl_3$ requires C, 60.40; H, 1.96; N, 7.83, Cl, 29.81%); $\nu_{max.}$ 2235cm^{-1} (C=N); $\lambda_{max.}$(CH_3CN) 205 (ϵ82,500$dm^3mol^{-1}cm^{-1}$), 220 (18,1130), 226 sh (14,500), 253 (25,500). 260 sh (22,500), 280 (15,000), 290 sh (11,250), 312 (5,250) and 325nm (6,375); δ_H (270 MHz) 8.03 (1H, d, J~8Hz, each arm broadened by a small additional coupling), 7.62 (1H, t of d, J_t~7Hz, J_d<1Hz), 7.58 (1H, t of d, J_t~6Hz, J_d~1.5Hz), 7.48 (1H, t of d, J_t~8Hz, J_d~1.5Hz), 7.28 (1H, d of d, J~6Hz, J~1Hz), 7.16 (1H, d, J~8Hz, each arm is broadened by an additional small coupling); δC (67.8 MHz, standard $CDCl_3$) 146.1, 141.4, 138.3, 136.5, 133.7, 132.3, 129.6, 112.4 and 112.3 (aromatic quaternary carbons), 130.5, 129.1, 127.7, 127.0, 126.6, 125.5 and 123.5 (aromatic C-Hs), and 118.3 and 116.6 (C≡N);

(4) Trichlorophthalonitrile (100) (85mg, 22%) identified by comparison of its infrared spectrum with that of an authentic sample.

Photolysis of TCPN and Cyclohexene in dichloromethane.

TCPN (250mg, 0.94mmol) and cyclohexene (400mg, 4.9mmol) in dichloromethane (300ml) were irradiated through Pyrex for 26h. The solution turned dark brown in colour afer a few hours but no products were observed on TLC. The solvent was removed under vacuum to give a black viscous tar. The crude reaction mixture was filtered throngh a silica column (15cm×4cm) using diethyl ether (to remove baseline impurities) and then separated using a Chromatotron with a 2mm plate. The eluent was a mixture of ethylacetate-light petroleum, b.p.40-60°C, (0:100 increased stepwise to 10:90). This gave, in order of recovery from the plate :-

(1) Cyclohexene (47mg) identified by comparison of its infrared spectrum with that of a known sample.;

(2) An unidentified yellow oil (7mg);

(3) TCPN (187mg, 0.7mmol) identified by comparison of its infrared spectrum with that of a known sample;

(4) An unidentified yellow oil (9mg).

Photolysis of TCPN and Cyclohexene in acetonitrile.

TCPN (1.0g, 3.8mmol) and cyclohexene (50g, 0.6mol) in acetonitrile (260ml) were irradiated through Pyrex for 16h. TLC showed the formation of one product. The reaction mixture was concentrated under vacuum and the crude reaction mixture separated using a Chromatotron with a 4mm silica plate. The eluent was a mixture of dichloromethane-petroleum ether, b.p.40-60°C, (3:97 increased stepwise to 20:80). This gave, in order of recovery from the plate :-

(1) Cyclohexene (2g, 0.02mol) identified by comparison of its infrared spectrum with that of a known sample ;

(2) TCPN (77mg, 0.3mol) identified by comparison of its infrared spectrum with that of an authentic sample.

(3) Trichlorophthalonitrile (100); (651mg, 81%) identified by comparison of its infrared spectrum with that of an authentic sample.

Photolysis of TCPN and Hex-1-ene in dichloromethane.

TCPN (1.0g, 3.8mmol) and hex-1-ene (4.1g, 0.48mol) in dichloromethane (320ml) were irradiated through Pyrex for 20h. TLC showed the formation of two products. The dichloromethane and hex-1-ene were removed under vacuum to give a black viscous oil. This crude reaction mixture was separated using a silica column (40cm 5cm). The eluent was a mixture of diethyl ether-light petroleum, b.p.40-60°C, (3:97 increased stepwise to 10:90). This gave, in order of recovery from the column :-

(1) A mixture of two minor products as a yellow oil (22mg);

(2) 2,5,6-Trichloro-1-(trans-hex-1-enyl)-3,4-dicyanobenzene (305) as a light brown oil (180mg, 18%). The oil was mixed with light petroleum b.p. 80-100°C (3ml) and placed in the freezer overnight. An off-white solid (30mg) precipitated from solution. This was recrystallised twice from light petroleum b.p.60-80 C to give a white crystalline solid (7mg) m.p. 104-105°C; (Found: C, 53.4, H, 3.4; N, 8.9; Cl, 34.05. $C_{14}H_{11}N_2Cl_3$ requires C, 53.6; H, 3.5; N, 8.9; Cl, 33.9%); $v_{max.}$ 2240 (C=N) and 1640cm^{-1} (C=C); δ_H (270 MHz, standard $CDCl_3$) 6.18 (1H, t of d, J_t 11.4 Hz and J_d~1 Hz), 6.08 (1H, t of d, J_t 11.4 Hz and J_d~1 Hz), 1.86 (2H, 'quartet', J~7 Hz), 1.27 (4H, m) and 0.85 (3H, t, J 7.1 Hz).

(3) A light brown oil (230mg, 21%). The oil was mixed with light petroleum, b.p.60-80°C (4ml) and placed in the freezer overnight. An off-white solid (104mg) precipitated from solution. This was then recrystallised three times from petroleun ether b.p.80-100°C to give 1,2,3,4-tetrachloro-5,6-dicyano-8-butylbicyclo[4.2.0]octa-2,4-diene, (302 or 303), a white crystalline solid (14mg) m.p.89-90°C; (Found : C, 47.8; H, 3.4; N, 7.9; Cl, 40.3. $C_{14}H_{12}N_2Cl_4$ requires C, 48.0; H, 3.4; N, 8.0; Cl, 40.5%); $v_{max.}$ 2220 and 2200 (C=N), 1635 (s) and 1610 (w) cm^{-1} (C=C); $\lambda_{max.}$(cyclohexane) 242 (11,205dm^{3}mol^{-1}cm^{-1}), 235 (11,205), 206nm (10,471); $_H$(270 MHz) 2.5 (1H, m, CH_2-$\underline{C}$H-CH_2), 2.3 (2H, m, $\underline{C}H_2$-CH), 1.9 (1H, m, CH_2-CH-$\underline{C}H_2$), 1.7 (1H, m, CH_2-CH-$\underline{C}H_2$), 1.4

(4H, m, $-C(CH_2)_2Me$) and 1.0 (3H, t, J 7 Hz, Me); δ_C (67.8 MHz, standard $CDCl_3$) 141.4, 130.7, 129.8, 119.3 (alkene Cs), 115.1, 114.2 (C=N), 67.3 (3 C), 55.6 (4 C), 36.3 [$-C(7)H_2-$], 31.9 [$-C(8)H-$], 31.7, 28.6, 22.2 [$-C(9)H_2-C(10)H_2-C(11)H_2-$], 13.7 (Me); m/e 348 (M+,<1%), 317 (17), 315 (53), 313 (55), 267 (11), 261 (17), 260 (10), 259 (44), 258 (16), 257 (44), 232 (17), 231 (10), 230 (16), 223 (17), 221 (21), 186 (180, 69 (15), 57 (100), 56 (28) and 55 (22).

Photolysis of TCPN and α-Methylstyrene in dichloromethane.

TCPN (1.0g, 3.8mmol) and α-methylstyrene (2.5g, 21mmol) in dichloromethane (320ml) were irradiated through Pyrex for 22h. The solution began to darken after ~ 30min. TLC showed the formation of two products. The solvent was removed under vacuum to yield a black viscous oil. Baseline impurities were removed using Flash Chromatography on a silica column (40cm 5cm, eluent : diethyl ether-light petroleum, 3:97 increased stepwise to 10:90). The products were then separated using a Chromatotron with a 2mm silica plate (eluent : ethyl acetate-light petroleum, b.p. 40-60°C, 0:100 increased stepwise to 7:93). This gave, in order of recovery from the plate :-

(1) A complex mixture of hydrocarbons as a yellow oily liquid (990mg); $\nu_{max.}$ 3083, 3053, 3018, 2959, 2925, 2865, 1596, 760, 739 and 700cm^{-1} (no C≡N stretching in the region 2000-2300cm^{-1}); δ_H (60 MHz, solvent CCl_4) 7.1 (m, 5H), 2.8 (m, 1H) and 1.7 (m, 5H);

(2) TCPN (414mg, 1.6mmol) identified by comparison of its infrared spectrum with that of an authentic sample;

(3) An unidentified white solid, (23mg, 2%), m.p.138-142°C) (from light petroleum b.p.80-100°C), Found : C, 65.4; H, 3.2; N, 8.9; Cl, 24.2. $C_{17}H_{10}Cl_2N_2$ requires C, 65.2; H, 3.2; N, 9.0 and Cl, 22.7% ; $\nu_{max.}$ 2236 (C≡N) and 1614cm^{-1} (C=C). The appearance of the ^{1}H nmr spectrum, [δ_H(270 MHz)], suggested that (3) contained a mixture of several isomers. It showed two patterns : the major pattern showed a 6-proton multiplet at δ 7.38 (Ph-), 1-proton singlets at 6.18 and 5.40

(C=C-H), and a 3-proton singlet at 2.37 (Me-). This pattern was then repeated at slightly different chemical shifts and with a different intensity (~2:1). The minor pattern showed 6-proton multiplet at δ7.20 (Ph-), a 1-proton singlet at 6.17 (C=C-H), a 1-proton singlet at 5.21 (C=C-H) and a 3-proton singlet at 2.40 (Me-);

(4) Trichlorophthalonitrile, (100), (280mg, 55%) identified by comparison of its infrared spectrum with that of an authentic sample.

Photolysis of TCPN and Indene in dichloromethane.

TCPN (1.0g, 3.8mmol) and indene (0.38g, 3.3mmol) in dichloromethane (310ml) were irradiated through Pyrex for 10h. TLC showed the formation of two products. The solvent was removed under vacuum to give a black tar. This crude mixture was passed through a silica column (10cm×5cm), using diethyl ether as eluent, in order to remove baseline impurities. The solvent was removed under vacuum and the resulting mixture separated using a Chromatotron with a 2mm silica plate. The eluent was a mixture of dichloromethane-petroleum ether, b.p.40-60°C, (5:95 increased stepwise to 30:70). This gave, in order of recovery from the plate :-

(1) A mixture of three minor products as a yellow oil (36mg);

(2) TCPN (487mg, 1.8mmol) identified by comparison of its infrared spectrum with that of a known sample;

(3) 2-(3,5,6-trichloro-1,2-dicyanophenyl)indene, (324), a yellow crystalline solid (134mg, 20%) m.p.186-187°C ($CHCl_3$-light petroleum, b.p.80-100 °C); (Found : C, 58.3; H, 1.9; N, 8.1; Cl, 29.7 . $C_{17}H_7N_2Cl_3$ requires C, 59.1; H, 2.0; N, 8.1; Cl, 30.8%); $\nu_{max.}$ 2234cm^{-1} (C≡N); $\lambda_{max.}$ 345 (sh) (ϵ 2,210dm^{3}mol^{-1}cm^{-1}), 325 (3,454), 316 (sh) (2,977), 285 (sh) (3,011), 254 (21,124), 228 (60,564); δ_H (60 MHz) 7.5 (4H, m, Ar-H), 7.0 (1H, t, J~2Hz), and 3.8 (2H, d, J~2Hz);

(4) A mixture of four minor products as a yellow oil (74mg).

Photolysis of N-Methyl-3,4,5,6-tetrachlorophthalimide (111) and Naphthalene in acetonitrile.

N-Methyltetrachlorophthalimide (111), (1.0g, 3.4mmol) and naphthalene (0.43g, 3.4mmol) in acetonitrile (310ml) were irradiated through Pyrex for 40h. TLC showed the formation of one product in trace amounts. The acetonitrile was removed under vacuum and the mixture filtered through a silica column (10cm X 4cm), using dichloromethane as eluent, in order to remove baseline impurities. The dichloromethane was removed under vacuum and the resulting crude mixture separated using a Chromatotron with, initially, a 4mm plate and then a 2mm plate. The eluent was a mixture of ethyl acetate-light petroleum (b.p.40-60°C) (3:97 increased stepwise to 20:80). This gave, in order of recovery from the plate :-

(1) Naphthalene (0.32g, 2.5mmol), identified by comparison of its infrared spectrum with that of a known sample.

(2) N-Methyltetrachlorophthalimide (111), (0.67g, 2.3mmol), identified by comparison of its infrared spectrum with that of a known sample.

(3) An unidentified off-white solid (0.002g).

Photoylsis of N-Methyl-3,4,5,6-tetrachlorohpthalimide and Anthracene in acetonitrile.

N-Methyltetrachlorophthalimide (111), (1.0g, 3.4mmol) and anthracene (0.6g, 3.4mmol) in acetonitrile (310mm) were irradiated through Pyrex for 22h. A white solid started to precipitate from solution after a few minutes. TLC showed the formation of one product. The white solid was identified as dianthracene (329), (0.36g, 1.0mmol) by comparison of its infrared spectrum and m.p.(267-278°C, lit.,[109] 270-280°C), with that of an authentic sample.[102] The acetonitrile was then removed under vacuum and the resulting mixture separated using a Chromatotron with a 4mm plate silica plate. The eluent was a mixture of ethyl acetate-light petroleum (b.p.40-60°C),(0:100 increased stepwise to 20:80). This gave, in order of recovery from the plate :-

(1) Anthracene (0.042g, 0.24mmol) identified by comparison of its infrared spectrum with that of a known sample.

(2) Dianthracene (329), (0.147g, 0.41mmol), identified by comparison of its infrared spectrum and m.p. (268-278 C, lit.,[109] 270-280 C) with that of an authentic sample.[102]

(3) N-Methyltetrachlorophthalimide (111), (0.883g, 3.0mmol) identified by comparison of its infrared spectrun with that of an authentic sample.

N-Methyltetrachlorohpthalimide (111), (1.0g, 0.34mmol) and anthracene (6.0g, 34mmol), in acetonitrile (310ml) were irradiated through Pyrex for 40h. A white solid started to precipitate from solution after a few minutes and TLC showed the formation of dianthracene (329). Anthracene (0.060g) was added at 10h intervals. TLC showed only the formation of dianthracene (329).

Preparation of Dianthracene (329).[102]

A solution of anthracene (0.6g, 3.4mmol) in acetonitrile was irradiated through Pyrex for 7h. A white solid started to precipitate from solution after ~fifteen minutes. This solid (410mg, 70%) was filtered from solution at the end of the reaction and recrystallised from benzene to give dianthracene (329), m.p.270-278 C.

Photolysis of N-Methyl-3,4,5,6-tetrachlorophthalimide, (111), and Phenanthrene in acetonitrile.

N-Methyltetrachlorophthalimide, (111), (1.0g, 3.4mmol) and phenanthrene (0.69g, 3.9mmol) in acetonitrile (310ml) were irradiated through Pyrex for 20h. TLC showed the formation of one product. The solvent was removed under vacuum and the crude reaction mixture filtered through a silica column (12cm X 4cm), using ethyl acetate as eluent, in order to remove baseline impurities. The ethyl acetate was removed under vacuum and the resulting mixture separated using a Chromatotron with initialy a 4mm dichloromethane-light petroleum (b.p.40-60 °C), (20:80, increased stepwise to 60:40). This gave, in order of recovery from the plate :-

(1) Phenanthrene (0.223g, 1.3mmol), identified by comparison of its infrared spectrum with that of a known sample.

(2) N-Methyltetrachlorophthalimide, (111), (0.54g, 1.8mmol) identified by comparison of its infrared spectrum with that of a known sample.

(3) 3,5,6-Trichloro-4-[9-phenanthryl]-N-methylphthalimide, (333), (0.190g, 26%), a yellow crystalline solid, m.p.286-7 °C (Found C, 62.3; H, 2.6; Cl, 25.5; N, 3.03. $C_{23}H_{12}O_2Cl_3N$ requires C, 62.7; H, 2.7; Cl, 24.2; N, 3.2%); $\nu_{max.}$ 3062 (aromatic C-H), 1777 and 1720cm^{-1} (C=O); $\lambda_{max.}$ (CH_3CN) 210 (33,467dm^{3}mol^{-1}cm^{-1}), 240 (72,805), 252 (71,239), 272 (sh, 14,982), 285 (12,526), 297 (13,308) and 330nm (br, 3,502); δ_H(270 MHz) 8.8 (2H, m, H-4, H-5), 7.7 (6H, m, H-1, H-2, H-3, H-6, H-7, H-8), 7.4 (1H, s, H-10) and 3.3 (3H, s, N-Me); δ_C (67.8 MHz, standard $CDCl_3$) 164.3 and 164.2 (C=O), 141.9, 132.0, 131.3, 131.0, 130.7, 130.6, 129.2, 129.1, 129.0, 128.2, 128.2, 128.1, 127.8, 127.6, 127.3, 127.2, 124.7, 123.5, 122.8, 122.7, (aromatic carbons) and 24.7 (N-Me).

Photolysis of N-Methyl-3,4,5,6-tetrachlorophthalimide (111) and Cyclohexene.

N-Methyltetrachlorophthalimide (2.2g, 7.4mmol) and cyclohexene (57.5g, 0.7mol) in acetonitrile (300ml) were irradiated through Pyrex for 35h. TLC showed the formation of two products. The acetonitrile and cyclohexene were removed under vacuum to give a yellow solid. This crude reaction mixture was then separated on a silica column (40cm X 5cm). The eluent was a mixture of diethyl ether-light petroleum b.p.40-60 °C (7:93 increased stepwise to 30:70). This gave, in order of recovery from the column :-

(1) N-Methyltetrachlorophthalimide (650mg, 2.2mmol) identified by comparison of its infrared spectrum with that of a known sample.

(2) an isomer of N-Methyl-3,4,5,6-tetrachloro-2,5-cyclo[1,2]-hexane-[1,2-cyclohexa-1,4-diene-1,2-dicarboximide], (349), a white crystalline solid (729mg, 37%), m.p.158-9°C (from MeOH), (Found : C, 46.8; H, 3.4; N, 3.7; Cl, 37.8; O, 8.4. $C_{15}H_{13}NCl_4O_2$ requires C, 47.3; H,3.4; N,3.7; Cl, 37.3; O, 8.4%; $\lambda_{max.}$ (CH_3CN) 208(ϵ 10,517$dm^3mol^{-1}cm^{-1}$) and 240nm (12,331); $\nu_{max.}$ 1777 (s) and 1710 (vs) (C=O), 1654 (s) and 1579cm^{-1} (C=C); δ_H(270 MHz) 0.9-2.0 (9H, m), 2.3 (1H, m) and 3.1 (3H, s, N-Me); δ_C (67.8 MHz; standard $CDCl_3$) 168.6, 162.5, 147.2, 132.9, 129.1, 125.5, 78.3, 58.6, 57.3, 51.8, 29.3, 28.9, 26.9, 26.6, and 25.4; m/e 379 (M+, <1%), 348 (18), 346 (55), 344 (56), 315, (38), 313 (79), 311 (63), 304 (13), 302 (34), 300 (61), 298 (49), 280 (16), 278 (39), 276 (38), 82 (76), 69 (23), 67 (100), 54 (47), and 41 (28).

(3) another isomer of N-Methyl-3,4,5,6-tetrachloro-2,5-cyclo[1,2]-hexane-[1,2-cyclohexa-1,4-diene-1,2-dicarboximide], (349), a white crystalline solid, m.p.169-170°C (from MeOH), (Found : C, 47.5; H, 3.3; N, 3.5; Cl, 37.7%. $C_{15}H_{13}NCl_4O_2$ requires C, 47.3; H, 3.4; N, 3.7; Cl, 37.3%); $\lambda_{max.}$ (CH_3CN) 207 (9,437$dm^3mol^{-1}cm^{-1}$) and 240nm (11,932); $\nu_{max.}$ 1780 (s) and 1715cm^{-1} (vs) (C=O); 1665 and 1580cm^{-1} (C=C); δ_H (220 MHz) 3.1 (3H, s, N-Me), 2.15 (2H, m), 1.9 (2H, m), 1.55 (1H, m), 1.3 (4H, m), and 1.05 (1H, m); δ_C (68 MHz; solvent CD_3CO; standard CD_3CO) 169.0, 162.5, 140.0, 137.5, 135.8, 125.5, 79.6, 59.5, 59.1, 53.2, 30.8, 29.6, 27.8, 27.6, and 25.8.

Photolysis of N-Ethyl-3,4,5,6-tetrachlorophthalimide (322) and Cyclohexene in acetonitrile.

N-Ethyltetrachlorophthalimide (2.0g, 6.4mmol) and cyclohexene (27.2g, 0.33mol) in acetonitrile (300ml) were irradiated through Pyrex for 15h. TLC showed the formation of two products. The cyclohexene and acetonitrile were removed under vacuun. Flash Chromatography on silica gel, with diethyl ether-light petroleum b.p.40-60°C (3:97 increased stepwise to 7:93) as eluent, yielded (in order of recovery from the column) :-

(1) N-Ethyltetrachlorophthalimide (576mg, 1.8mmol) identified by comparison of its infrared spectrum with that of a known sample.

(2) an isomer of N-Ethyl,3,4,5,6-tetrachloro,2,5-cyclo[1,2]hexane--[1,2-cyclohexa-1,4-diene-1,2-dicarboximide], (363), a white crystalline solid (510mg, 28%), m.p.170-172°C (from light petroleum b.p.60-80°C), (Found : C, 48.1; H, 3.7; N, 3.2; Cl, 36.2. $C_{16}H_{15}NCl_4O_2$ requires C, 48.6; H,3.8; N, 3.5; Cl, 35.9%); $\lambda_{max.}$(CH_3CN) 208 (13,758dm^3 mol^{-1}cm^{-1}) and 242nm (15,539); $\nu_{max.}$1768 (vs) and 1709cm^{-1} (vs) (C=O); δ_H(270 MHz) 3.7 (2H, q, N-CH_2-), 2.25 (1H, m), 0.8-2.1 (9H, complex multiplets) and 1.2 (3H, t, N-CH_2-$\underline{CH_3}$); δ_C (67.8 MHz; standard $CDCl_3$) 168.3, 162.2, 147.0, 133.0, 129.1, 125.6, 78.3, 58.4, 57.3, 51.7, 34.3, 29.3, 28.7, 27.0, 26.6, and 13.4; m/e 393 (M+, 1%), 362 (18), 360 (54), 358 (55), 329 (37), 327 (77), 325 (59), 318 (10), 316 (33), 314 (65), 312 (52), 294 (12), 292 (340, 290 (36), 82 (70), 67 (100), 69 (24), 54 (44) and 41 (26).

(3) another isomer of N-Ethyl,3,4,5,6-tetrachloro,2,5-cyclo[1,2]-hexane--[1,2-cyclohexa-1,4-diene-1,2-dicarboximide,(363), a white crystalline solid (277mg, 15%), m.p.158-159°C (from petroleum b.p.60-80°C), (Found : C, 49.3; H, 3.9; N, 3.3; Cl, 33.4. $C_{16}H_{15}NCl_4O_2$ requires C, 48.6; H, 3.8; N, 3.5; Cl, 35.9); $\lambda_{max.}$ 207 (ϵ 9,344dm^{3}mol^{-1}cm^{-1}) and 242nm (11,844); $\nu_{max.}$1769 (s) and 1708cm^{-1}(vs) (C=O), 1664 and 1587cm^{-1} (C=C); δ_H (270 MHz) 3.7 (2H, q, J 6Hz, N-CH_2-), 2.2 (2H, m), 1.9 (2H, m), 1.6 (2H, m), 1.0-1.5 (4H, m), and 1.2 (3H, t, J 7Hz, Me); δ_C (67.8 MHz; standard $CDCl_3$) 168.1, 161.5, 139.0, 138.5, 135.1, 123.5, 78.5, 58.9, 58.8, 57.9, 53.4, 34.4, 29.2, 27.0, 26.9, 13.3; m/e 393 (3%), 362 (13), 360 (43), 358 (44), 329 (18), 327 (33), 325 (26), 318 (10), 316 (33), 314 (62), 312 (49), 294 (16), 292 (40), 290 (43), 82 (73), 69 (14), 67 (100), 54 (38) and 41 (43).

Photolysis of N-Methyl-3,4,5,6-tetrachlorophthalimide and Indene in acetonitrile.

N-Methyltetrachlorophthalimide (1.0g, 3.4mmol) and indene (0.38g, 3.3mmol) in acetonitrile (300ml) were irradiated through Pyrex for 19h. TLC showed the formation of two major products. The acetonitrile was removed under vacuum and the resulting brown tar filtered through a silica column (30cm X 5cm) using diethyl ether as eluent. The ether was then removed under vacuum and the resulting mixture separated using a Chromatotron with a 2mm silica plate. The eluent was a mixture of diethyl ether-light petroleum (b.p.40-60°C) (5:95, increased stepwise to 20:80). This gave, in order of recovery from the plate :-

(1) Indene (17mg, 0.15mmol), identified by comparison of its infrared spectrum with that of an authentic sample.

(2) N-Methyltetrachlorophthalimide (346mg, 1.2mmol) identified by comparison of its infrared spectrum with that of an authentic sample.

(3) An unidentified white crystalline solid (75mg, 10%), m.p.202-203°C (from light petroleum, b.p.80-100°C), (Found : C, 63.2; H, 3.0; N, 3.9; Cl, 20.7. $C_{18}H_{11}NO_2Cl_2$ requires C, 62.8; H, 3.2; N, 4.06; Cl,20.6; $\lambda_{max.}$ (CH_3CN) 320 (ϵ 6448$dm^3mol^{-1}cm^{-1}$), 230 (50940), 248 (15046) and 192 (75228); $\nu_{max.}$ 3063 and 3018 (aromatic C-H), 2953, 2917, 2845 (aliphatic C-H), 1767 s and 1708 vs (C=O), 1622cm^{-1} (C=C); δ_H (270MHz) 7.67 (1H, m,alkene/aromatic C-H), 7.22 (3H, m, alkene/aromatic C-H), 5.25 (1H, d, J 0.5Hz,), 4.60 (1H, d of d of d, J 1Hz, J 0.5Hz, J 0.4Hz, 3.44 (1H, d of d, J 1.6Hz, J 1Hz, 3.30 (1H, d, J 1.6Hz, and 3.10 (3H, s, N-Me; m/e 343 (M+, 100%), 345 (68), 328 (6), 310 (6), 308 (18), 260 (12), 258 (18), 225 (5), 223 (13) and 187 (15).

(2) An unidentified pale yellow needle-like solid (144mg, 17.4%); m.p.210-212°C (from $CHCl_3$-light petroleum, b.p.80-100°C) (Found : C, 57.6; H, 2.6; N, 3.3; Cl, 27.4. $C_{18}H_{10}NO_2Cl_3$ requires C, 57.0; H, 2.6; N, 3.7; Cl, 28.1); $\lambda_{max.}$ (CH_3CN) 327 (ϵ 4,540$dm^3mol^{-1}cm^{-1}$),

250, (29,512), 232 (55,392) and 193nm (2,6901); $v_{max.}$ 3014 (aromatic C-H), 2946 (aliphatic C-H), 1767 s and 1707 vs (C=O); δ_H (270MHz) 7.6 (1H, m, alkene/aromatic C-H), 7.15 (3H, m, aromatic/alkene C-H), 5.2 (1H, d, J 0.5Hz), 4.42 (1H, d of d of d, J 1Hz, J 0.5Hz, J 0.4Hz), 3.43 (1H, d of d, J 1.6Hz, J 1Hz), 3.3 (1H, d, J 1.6Hz) and 3.0 (3H, s, N-Me); δ_C (67.6MHz)165.3, 155.3, 153.1, 142.9, 139.2, 128.5, 127.4, 126.3, 125.9, 123.9, 122.1, 53.5, 43.9, 32.8, 24.2; m/e 377 (M+, 11%), 381 (4), 379 (11) 347 (13), 345 (72), 343 (100), 310 (28), 308 (28), 258 (19), 225 (5), 223 (15), 189 (4) and 187 (16).

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