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# PHOTOCHEMISTRY OF SOME HETEROCYCLIC COMPOUNDS

A thesis, submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Oxford.

by

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It is a great pleasure to acknowledge the debt owed to Dr. A.C. Day for his help and encouragement throughout the work described in this Thesis. Thanks are also due to Dr. J.A. Barltrop and other members of the Oxford photochemistry group for many useful discussions and suggestions.

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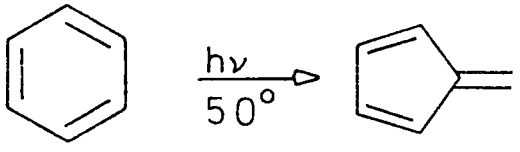
# INTRODUCTION

Aromatic compounds, both homocyclic and heterocyclic, undergo a wide variety of photochemical reactions. Photoaddition with olefinic systems,[1-5] hydroxylic compounds,[6] and oxygen[7] are well known. Similarly, photocyclisation,[8] photosubstitution,[9] lateral nuclear rearrangements[10] and photoreduction[11] are well reported. Another class of light-induced reactions observed for aromatic systems is transposition reactions, i.e. isomerisations that permute the atoms of an aromatic ring. It is these transposition reactions, particularly as they occur in pyrylium ions and thiophene compounds, that are the main concern of this thesis.

Much research has already been carried out in the field of photo-transposition reactions, in order to elucidate both the nature of the photoproducts, and the mechanism of these formally rather simple reactions. It will be useful, initially, to look at the literature concerning photoisomerisations of aromatic compounds in general, since one needs this kind of basis to serve as a framework for thinking about phototranspositions of specific classes of compounds.

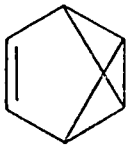
## A. PHOTOISOMERISATIONS OF SIX-MEMBERED AROMATIC COMPOUNDS

The best studied class of compounds are the benzenes, where the first photoisomerisation was discovered quite by chance over twenty years ago.[12] Isopropylbenzene was being used as a trap for radicals produced by ultra-violet irradiation of lead and mercury alkyls. A highly unsaturated yellow product, an isomer of isopropylbenzene itself was produced and identified as a fulvene. Soon afterwards, benzene itself was found to photoisomerise to fulvene (1.1).[13] The photoprocess was found to be temperature dependant.

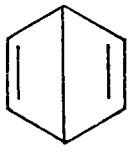



(1·1)

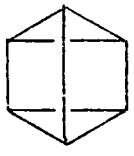
More recent work has shown that irradiation of liquid benzene with 254nm light populates the $S_1$ state, which then gives a mixture of fulvene and benzvalene (tricyclo[3·1·0·$0^{2,6}$] hex-3-ene), (1·2), but no Dewar benzene (1·3).[14-17] The formation of both



(1·2)



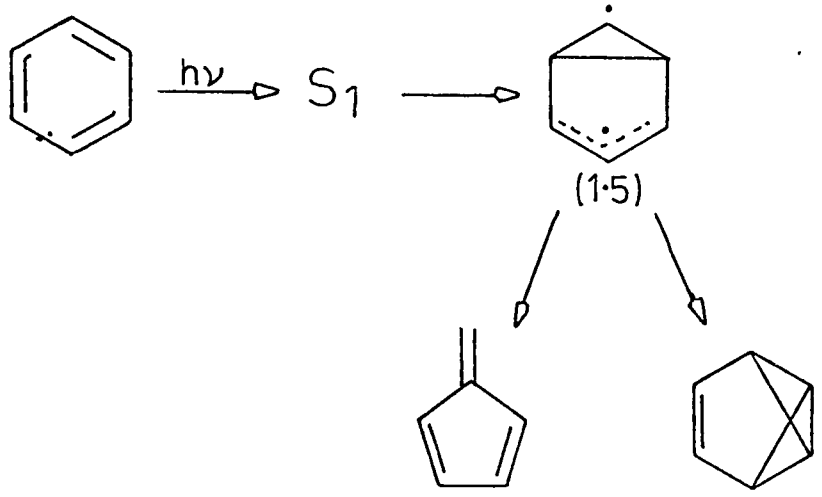
(1·3)



(1·4)

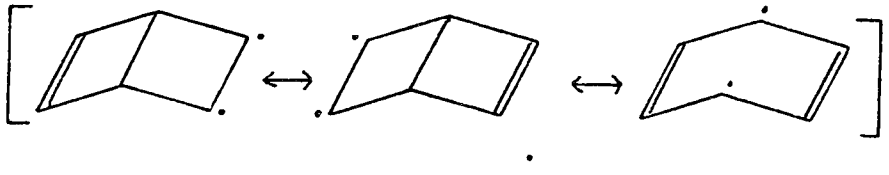
isomers is promoted by increase in temperature. Irradiation of benzene at shorter wavelengths (165-200nm) gives in addition to benzvalene and fulvene, both Dewar benzene and biphenyl.[18] It has been shown that $S_2$ benzene is the precursor of Dewar benzene.[19]

Orbital symmetry considerations suggest that $S_1$ benzene gives rise to a 1,3-bonded biradical species, the so-called prefulvene (1·5);




(1·5)

Both $S_2$ and $T_1$ benzene are thought to transform into the biradical (1·6). This can then collapse to Dewar benzene, from which prismane (1·4) may be obtained by further irradiation ($\pi^2s + \pi^2s$ cycloaddition).

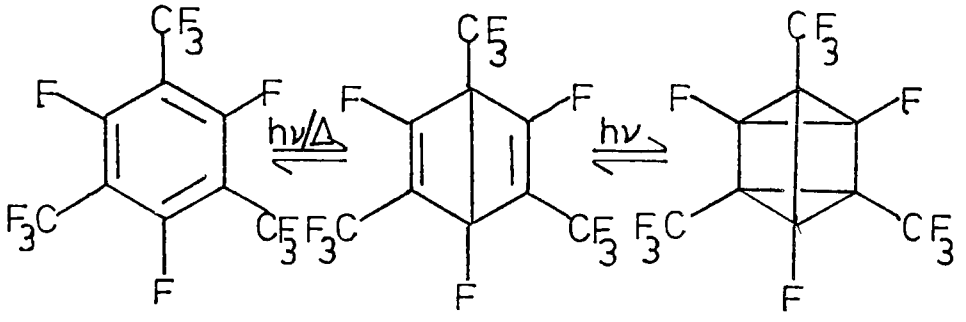


(1·6)

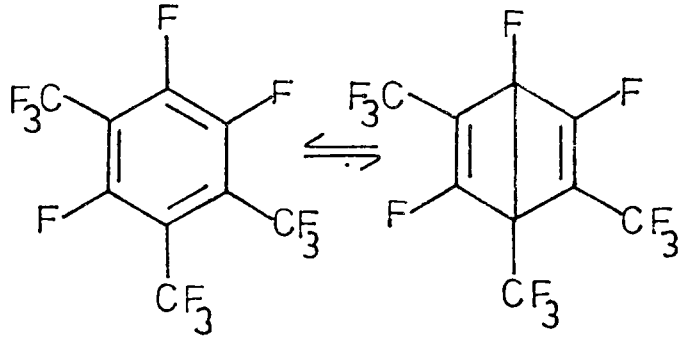
In marked contrast with benzene, hexafluorobenzene forms exclusively hexafluoroDewar benzene (hexafluorobicyclo[ 2·2·0] hexa-2,5-diene) on irradiation in the liquid or vapour phase at wavelengths over the range 212-265nm.[22-24] This rearomatises smoothly in the vapour at 80°. The $S_1$ and $S_2$ states are much closer together in the case of the perfluoro compound and the corresponding absorption envelopes

overlap to a much greater extent than in benzene itself. Thus excitation is within the $S_o \rightarrow S_2$ band rather than $S_o \rightarrow S_1$. The tendency, apparent in hexafluorobenzene, for para-bonding rather than meta-bonding, is also observed in a number of lower fluoro-derivatives.[25]

Haszeldine et al. have described the photoisomerisation of perfluoroalkylbenzenes. The isomer (1.7), for example, is thermally converted into the Dewar isomer (1·8) at 400°.[27] Photoisomerisation leads to the corresponding benzvalene, Dewar benzene and prismane derivatives, which are photointerconvertible.[28] Similar results have been found with the corresponding perfluoroethyl compounds.[29]



(1·7) (1·8) (1·9)



(1·11) (1·10)

Evidently the introduction of perfluoroalkyl substituents greatly increases both the ease of formation and the thermal stability of

Dewar and prismane isomers of aromatic rings.

The interconversion between Dewar isomers *via* prismanes, as illustrated above (1·8)→(1·10), is relevant to the mechanistic problem of photochemical 1,2-shifts of alkyl groups in alkylbenzenes. On irradiation at 254nm in the liquid or gas phase, one or both of the following reactions occur with alkylbenzenes:

(1) ring isomerisation to fulvenes, benzvalanes, Dewar benzenes, prismanes or ring-opened dienynes.

(2) positional isomerisation of the alkyl substituents, e.g. *ortho*- to *meta*-xylene.

It is generally held that positional isomerisation takes place *via* the intermediate formation of a rearomatisation of valence-bond ring isomers. Although such intermediates are not usually detected, their involvement has been inferred, though not established, from isotopic labelling studies. 1,3,5-tri $^{14}C_3$ trimethybenzene on irradiation gives the 1,2,4-isomer derived exclusively by ring-transposition.[30]

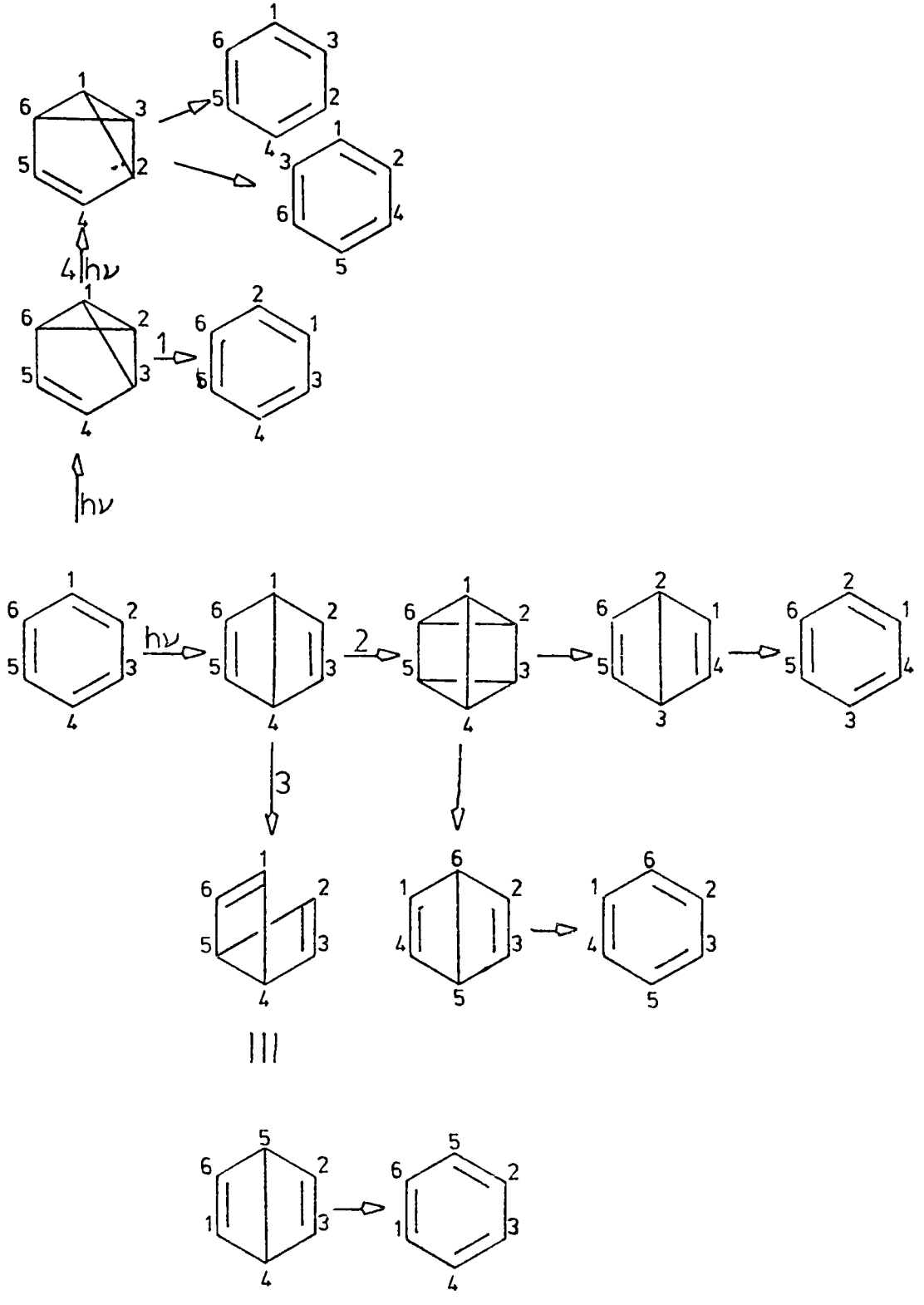
The ring transpositions which give rise to apparent 1,2- shifts of alkyl substituents can in principle go in many ways, though often benzvalene or prismane intermediates are invoked. Those giving rise to apparent 1,3- shifts may involve either prismanes, an isomerisation between Dewar forms, or photoisomerisation between benzvalenes. The processes are illustrated in scheme 1·1.

Path (1) gives rise only to a 1,2- shift, but photoisomerisation of the initially formed benzvalene can provide an apparent 1,3- shift as in path (4).

Path (2) involves two 1,2- transpositions and so can give rise to apparent 1,2- or 1,3- shifts depending on the modes of bond cleavage in the prismane.

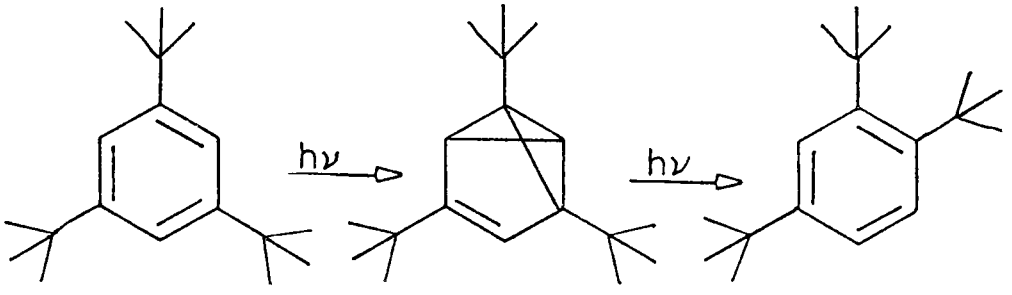
Path (3) can give rise to 1,3-transpositions only.

In addition, Dunlop and Lemal have reported the photoisomerisation of hexamethylbenzvalene to its Dewar isomer.[150]

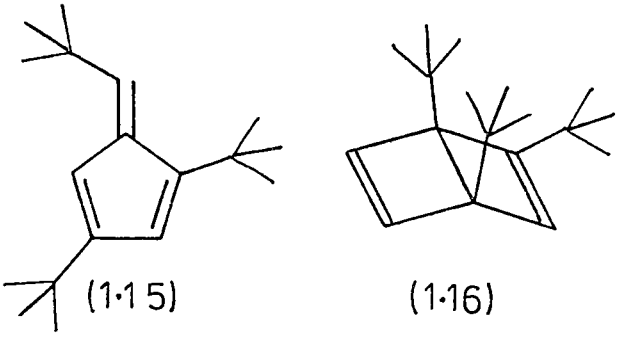


Scheme 1-1

The photoisomerisation reactions of tri-tert-butylbenzenes can serve to illustrate, how, in reality, these paths can lead to a multitude of products. Wilzbach and Kaplan irradiated the 1,3,5-isomer at 254nm and reported that in isohexane solution it gives 1,2,4-tri-tert-butylbenzvalene (1·13) as the only initial product (1·13).[32] Continued irradiation leads to rearomatisation of the benzvalene to give 1,2,4-tri-tert-butylbenzene (1.14). The fulvene (1·15), the Dewar benzene (1·16), the prismane (1·17) and the isomeric benzvalene (1·18) are also formed.



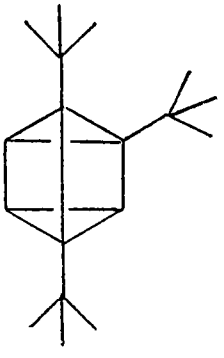

(1·12) (1·13) (1·14)



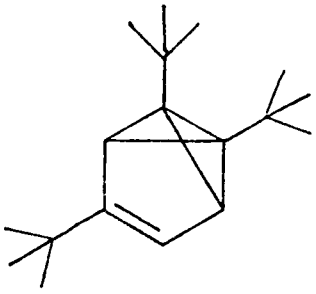
(1·15)



(1·16)



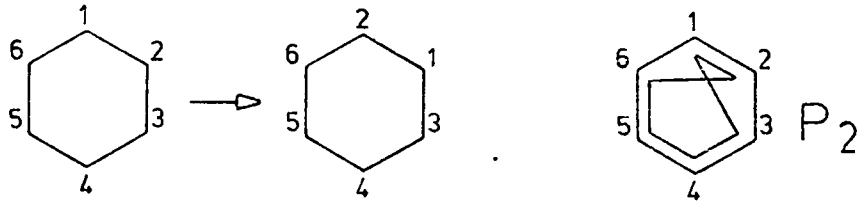
(1·17)



(1·18)

Irradiation of the 1,2,4-isomer gives the Dewar isomer (1·16) together with 1,3,6-tri-tert-butylbenzvalene (1·18), both as primary products.[33] The mechanism for the photochemical interconversion of benzvalenes (1·13) and (1·18) is not known, but is thought to be direct rather than via an intermediate aromatisation stage.

It will be useful at this point to refer to proposals by Barltrop and Day on the analysis of transposition reactions.[34] The authors show that the transposition of atoms in a six-membered ring can be analysed in terms of a set of twelve permutation patterns, as well as by way of benzvalanes, Dewar benzenes and prismane intermediates etc., which although are often proposed as intermediates, are only infrequently observed. Their approach is to concentrate on the pattern of transposition rather than on the various chemical intermediates that are possible. Thus, whereas the transposition (1·19) to (1·20) might be classified conventionally as, for example, a benzvalene type, permutation pattern analysis terms it as a $P_2$ type (1·21).

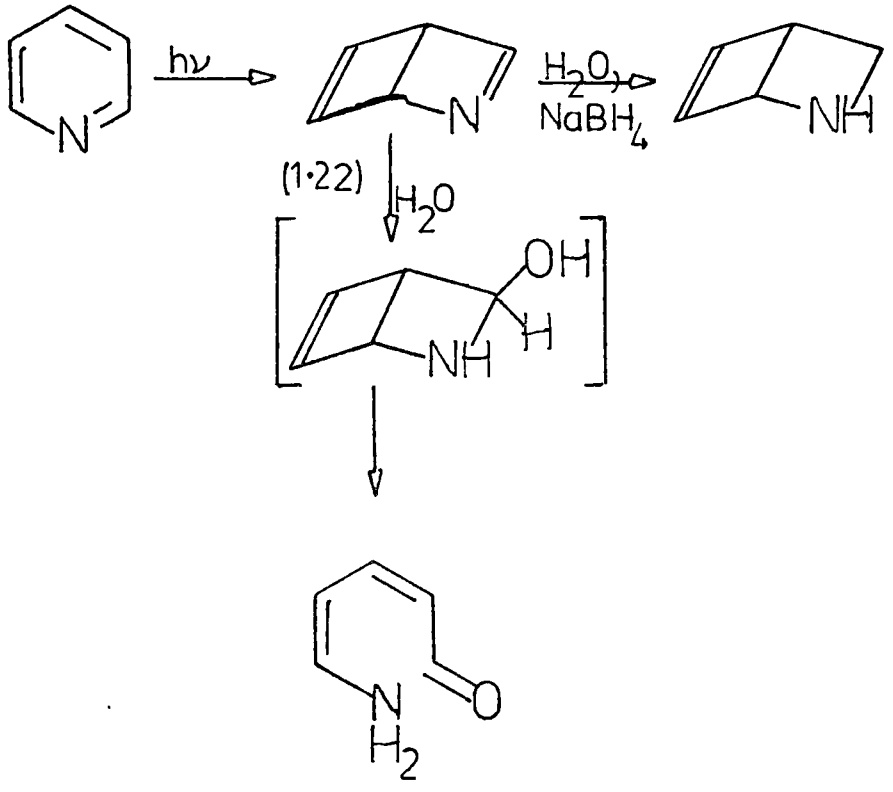



(1·19) (1·20) (1·21)

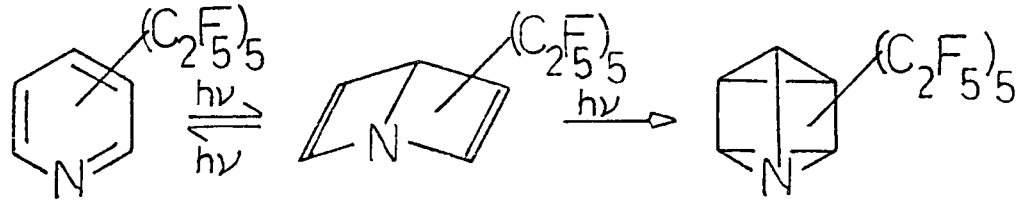
Classification as a $P_2$ type implies that the position of all the ring atoms are known.

Ultra-violet irradiation of aromatic six-membered heterocyclics leads to transpositions of the ring atoms analogous to those observed

in the benzene series. For example, when pyridine is irradiated in butane at -15°, it is converted to Dewar pyridine (1·22). This has been identified by nmr spectroscopy, and has been trapped by sodium borohydride and by water.[35-37] By irradiating pyridine in an argon matrix at 8k, the initially generated Dewar isomer can

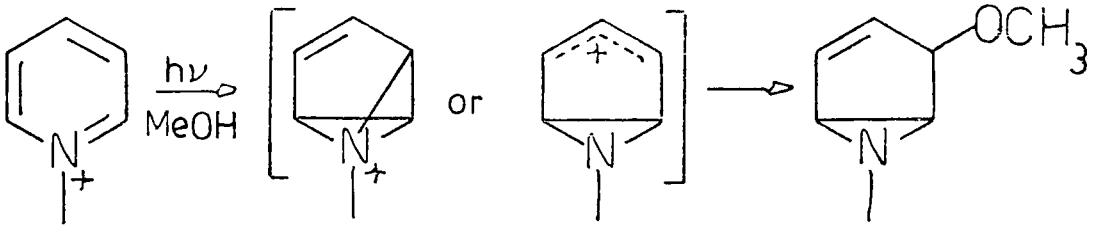



be decomposed photochemically to hydrogen cyanide and cyclobutadiene, which itself further decomposes to acetylene.[38] Other examples of Dewar pyridine formation are reported, and in some cases, irradiation of the Dewar pyridine leads to the generation of an azaprismane.[39]



Alkylpyridines are isomerised upon irradiation in the vapour phase. 2-Methylpyridine at 1 to 1·5 torr, for example, leads to a mixture of 3- and 4-methylpyridine.[40] Irradiation of various dimethylpyridines at 10 torr results in isomerisations which are believed to occur through intermediate azaprismanes, although other mechanisms are also possible.[41-43] The transpositions also occur in acetonitrile solution, where a temperature effect is observed.[44] Alkyl radicals have been detected by e.s.r. spectroscopy on irradiation at 93k.[45]

It seems possible that these processes occur through the $(n,\pi^*)$ excited state of the pyridine,[47] since irradiation of quaternary pyridinium compounds, which can only undergo $\pi\rightarrow\pi^*$ transitions, gives rise to products which apparently derive from azoniabenzvalenes (1·23) or 2,6-bonded bicyclic cations (1·24).[46]



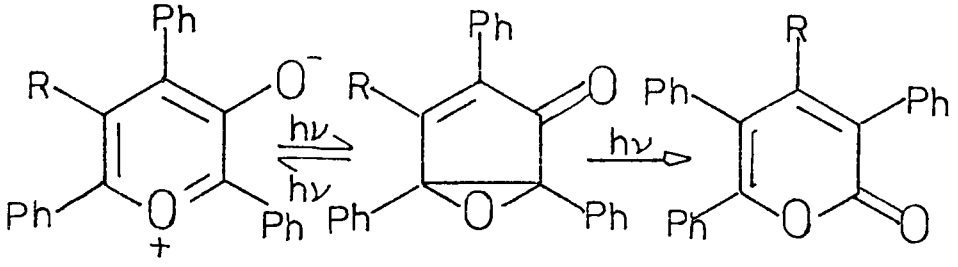

(1·23) (1·24)

Ring scrambling processes occuring in heterocyclic compounds containing two heteroatoms can give rise to new ring-systems. For example, pyrazine reversibly photoisomerises to pyrimidine in the vapour phase.[48-50] The product pyrimidines obtained from irradiation of methyl and dimethylpyrazines were taken as evidence for the intermediacy of diazabenzvalenes. It has been proposed from a study of quantum yields for isomerisation at various wavelengths,

and from sensitisation studies that an upper triplet, or a vibrationally excited $S_1$ state is involved in the photoisomerisation.[51,5] Since the rearrangements occur upon irradiation at 254nm, but not at 313nm, they seem to involve a $(\pi,\pi^*)$ state rather than an $(n,\pi^*)$ state. There are, however, several complicating aspects of these rearrangements. Thus it has recently been shown that the course of the rearrangements is very sensitive to both pressure and temperature; indeed, a new process, conversion to pyridazines, has been observed at very low pressures.[53,54] Pyridazines themselves photoisomerise in the vapour phase to give mixtures of pyrazines and pyrimidines.[48]

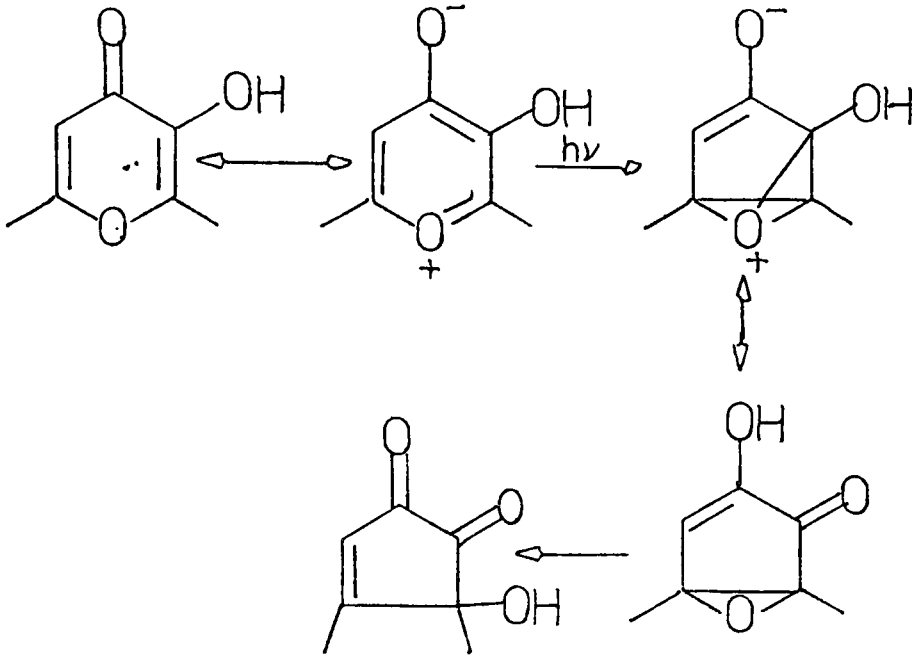
Perfluoropyridazines photoisomerises to perfluoropyrazines, which in turn can undergo transposition to perfluoropyrimidine.[55] Diaza Dewar benzenes have also been isolated in these systems.[56,57] These reactions are thought to take place from $(n,\pi^*)$ excited singlet states. As in the benzene case, the fluorine atoms here seem to have a considerable stabilising effect on the valence-bond isomers,[150] and may also cause a change in energy ordering of the various diazine molecular orbitals.[26]

Transposition reactions are also observed upon u.v. excitation of pyrylium ions. One of the earliest reports was on the reversible photoreaction of the pyrylium-3-oxide (1·25). The epoxide (1·26) can also isomerise to the 2-pyrone (1·27).



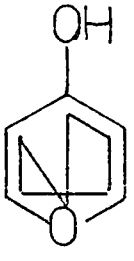

(1·25) (1·26) (1·27)

Scheme 1·2 shows how the light-induced reactions of some 4-pyrones can be interpreted as proceeding <u>via</u> pyrylium ion species.[60] Transposition reactions of 4-pyrones to 2-pyrones under acidic



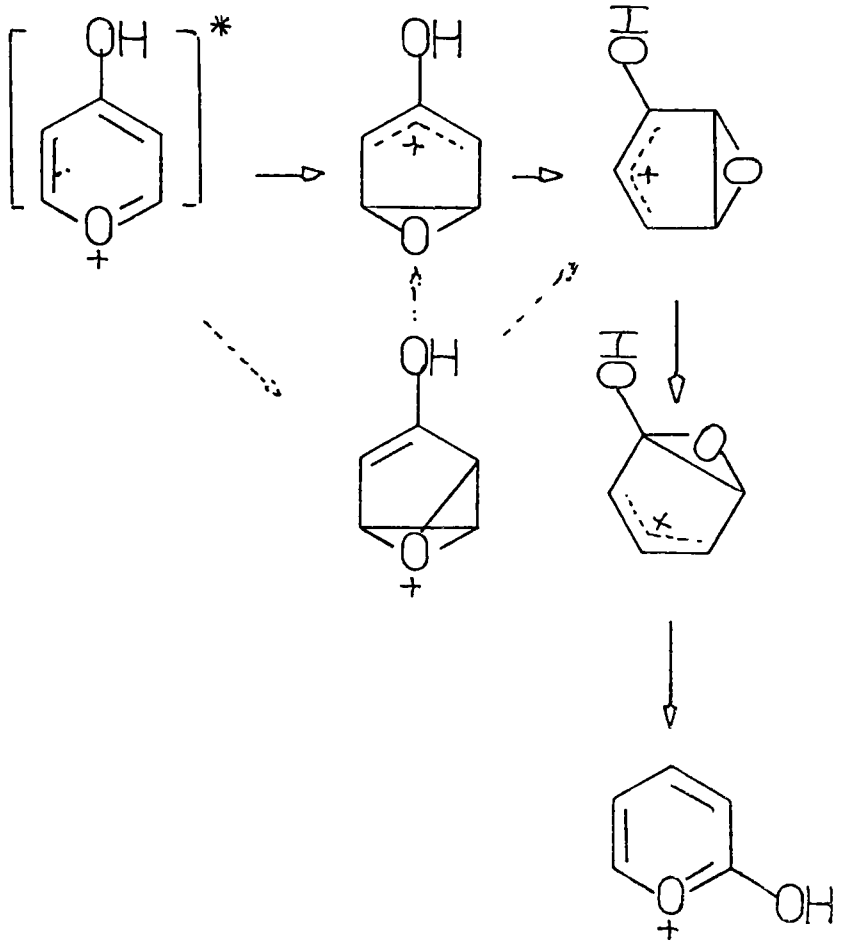

Scheme 1·2

condition are also pyrylium ion reactions.[61-64] Barltrop and Day have recently applied their permutation pattern method of analysis to the light-induced transpositions of some 2- and 4-hydroxypyrylium cations.[65-68] The characteristic permutation pattern for the transposition of the 4-hydroxypyrylium cation into the 2-isomer is found to be $P_4$, orientated as shown. The authors consider the most



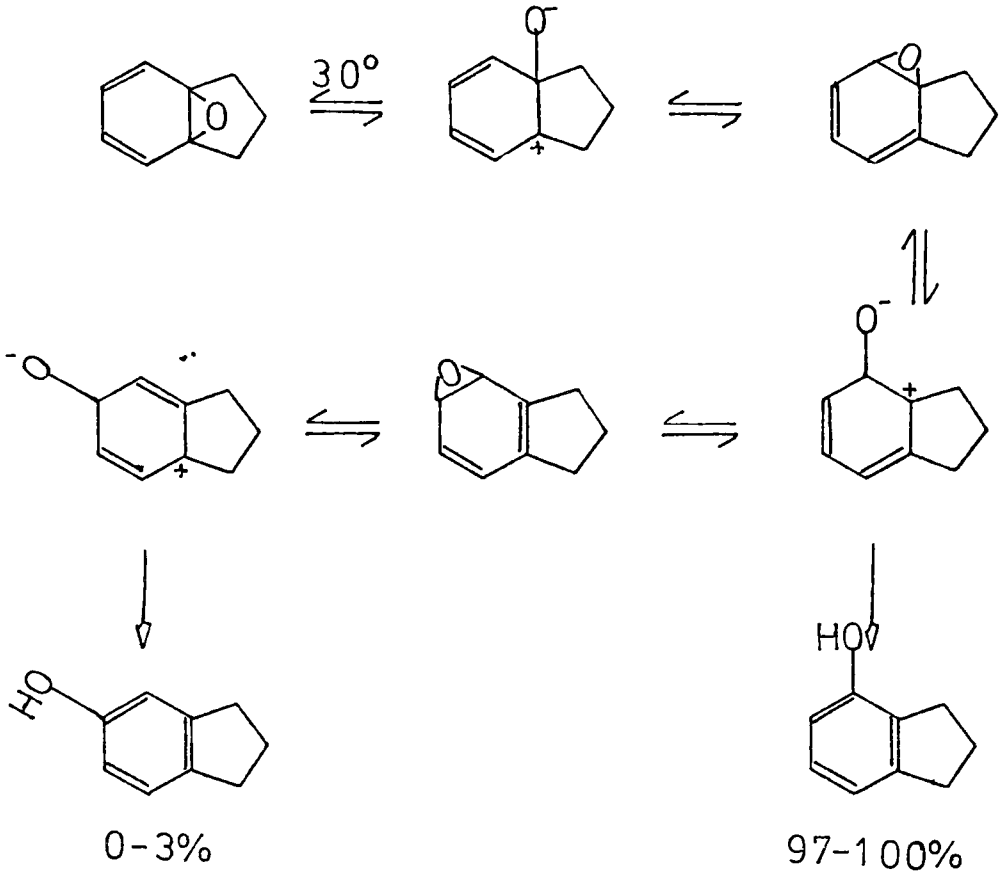

$P_4$

attractive mechanism consistant with the permutation to be of the type involving rearrangement of an oxabicyclohexenyl cation (scheme 1·3) Thus, initial excitation of the pyrylium cation, probably to a ($\pi,\pi^*$)



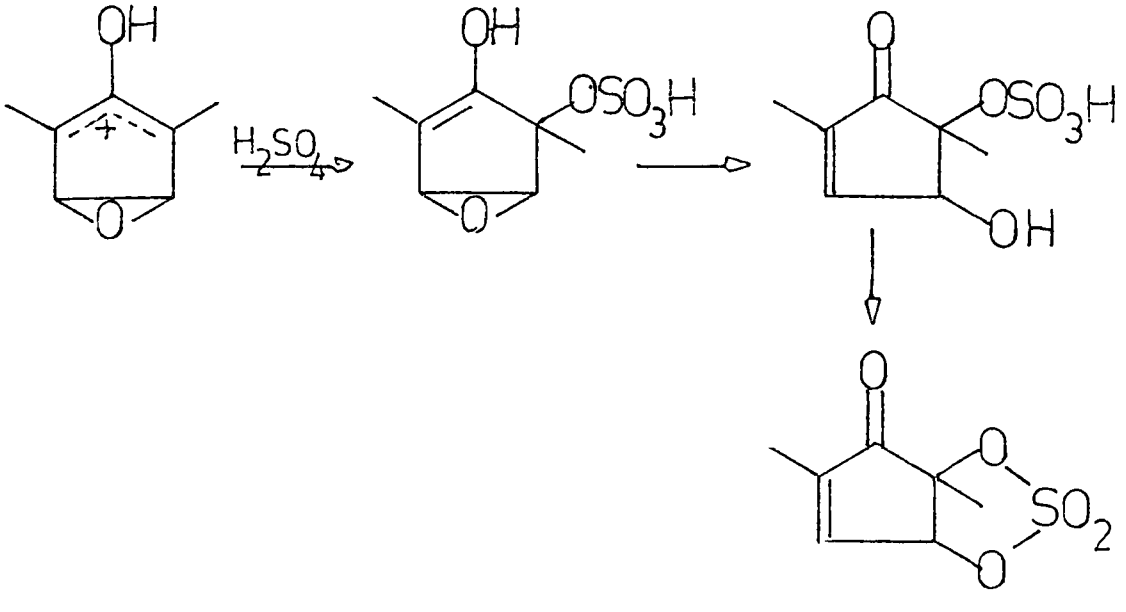
Scheme 1·3

excited state, gives rise to the bicyclohexenyl cation or the oxonia-benzvalene.[69] Once the cation is formed, then the chemistry is essentially ground-state. Oxygen-walk steps as proposed are observed in many thermal rearrangements; for example, with indane oxides (scheme 1·4).[70] Further support for the 4-hydroxypyrylium transposition



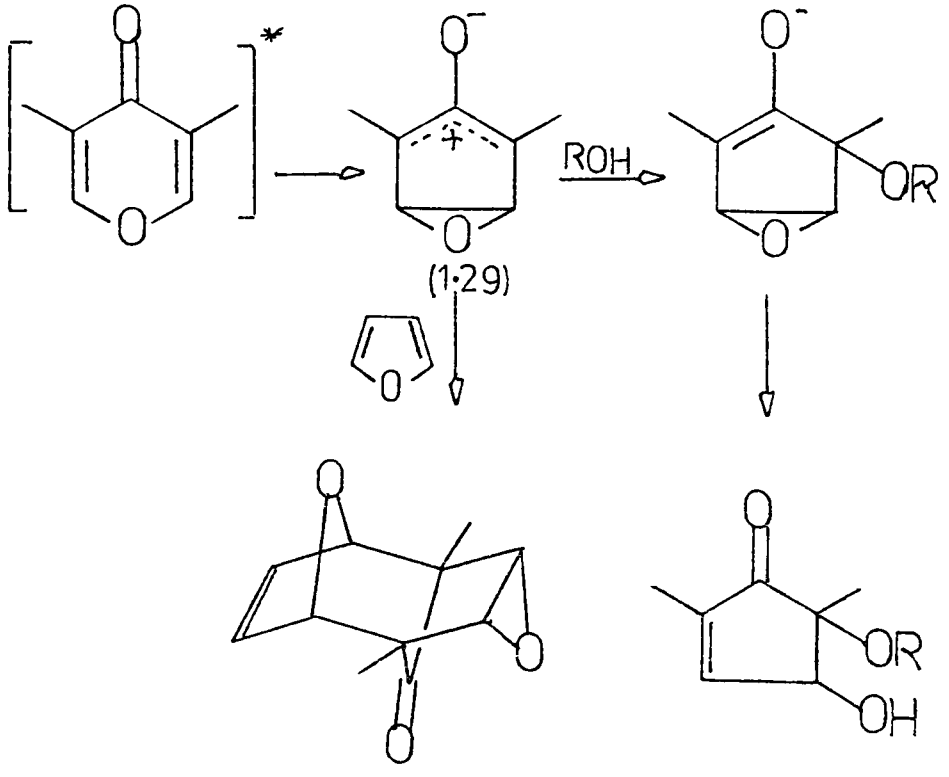

Scheme 1·4

mechanism has been obtained by the isolation of a cyclic sulphate, derived by nucleophilic attack on the initially formed 2,6-bonded cation, from the irradiation of 3,5-dimethyl-4-pyrone in sulphuric acid (scheme 1·5).

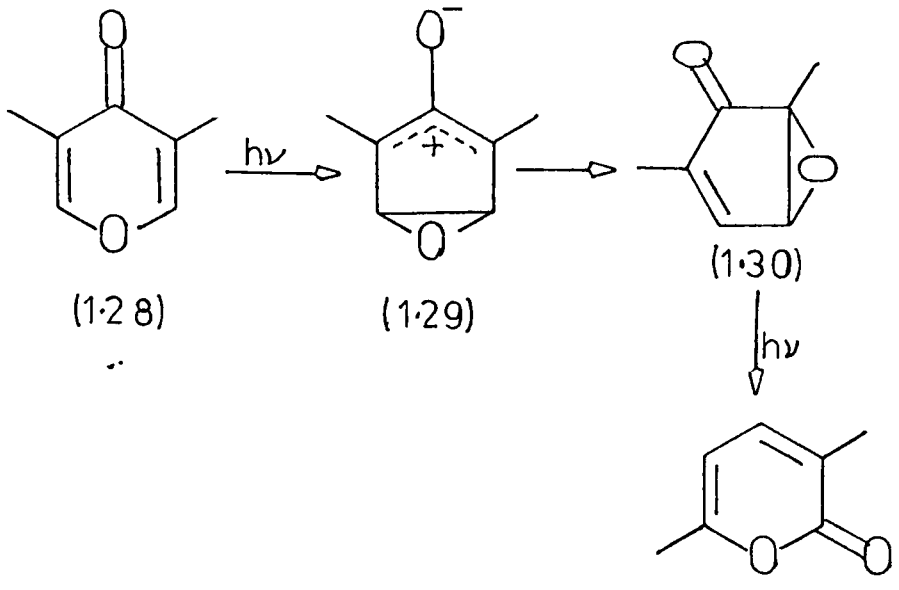



Scheme 1·5

The neutral 3,5-dimethyl-4-pyrone (1·28) itself yields interesting adducts upon irradiation in certain solvents.[66,68] The intermediate zwitterionic species (1·29), analogous to the cation proposed in the case of the 4-hydroxypyrylium cation, can be trapped by nucleophiles, for example 2,2,2-trifluoroethanol, and by furan (scheme 1·6). The pyrone (1·28) also transposes to 3,6-dimethyl-2-pyrone <u>via</u> the epoxide (1·30) in scheme 1·7. The epoxide (1·30) has been isolated and is rapidly converted to the 2-pyrone on irradiation.



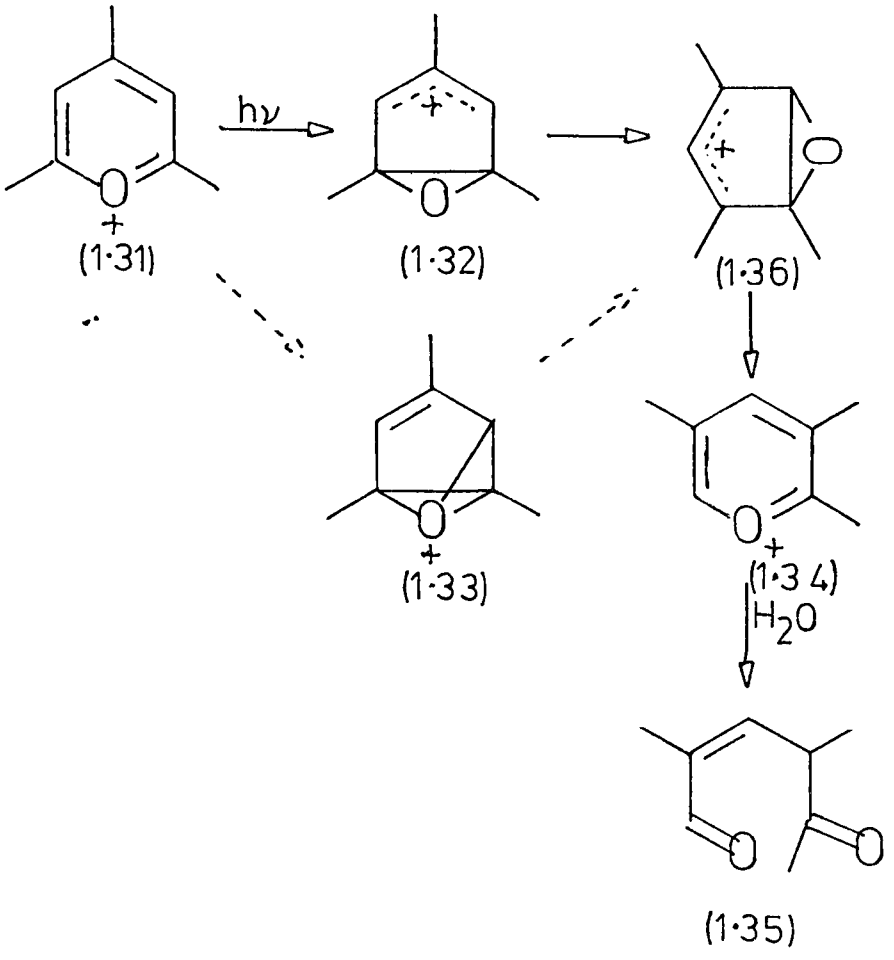

Scheme 1·6




(1·28) (1·29) (1·30)

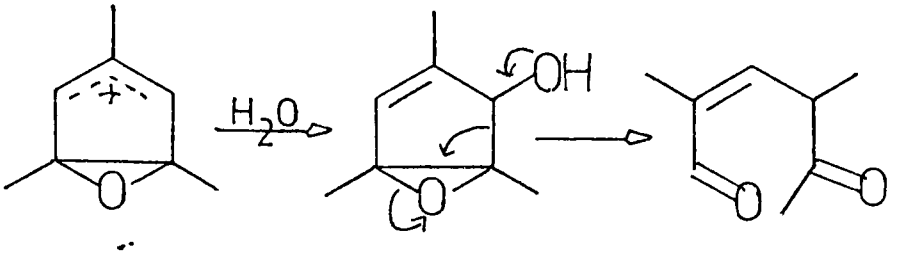
Scheme 1·7

Pyrylium cations without hydroxy substituents also show interesting photochemical reactions. Upon irradiation in water, 2,4,6-trimethypyrylium perchlorate (1·31) undergoes a photohydrolysis reaction to give trans-2,4-dimethyl-5-oxohex-2-enal.[71] It is suggested, by analogy with the photochemical behaviour of benzene and pyridinium salts, that initial $\pi,\pi^*$ excitation gives rise to the oxoniabenzvalene intermediate (1·33) or the bicyclohexenyl cation (1·32).




An oxygen-walk step in (1·32) to the more stable cation (1·36), followed by rearomatisation, gives the transposed pyrylium cation (1·34). This cation, having a free α-position would be expected to rapidly hydrolyse to the cis-form of the keto-aldehyde (1·35).[72,73] This can then isomerise photochemically or thermally to the trans-isomer.[204] It is not possible to rule out other mechanisms not involving a rearomatisation or oxygen-walk step. For example, one could envisage the cation (1·32) being trapped by water to give the bicyclic hydroxy compound (1·37), c.f. pyridinium photochemistry

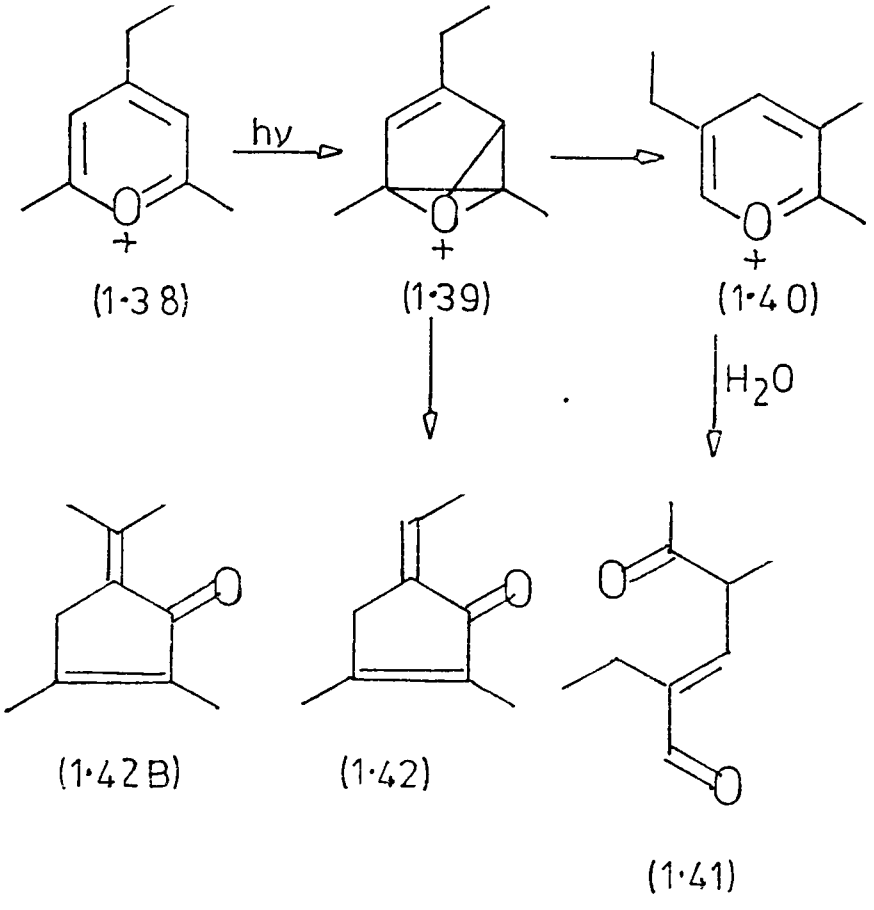
in methanol[46] (1·37) might then undergo a concerted Grob-type



(1·32) (1·37) (1·35)

fragmentation to give the keto-aldehyde (1·35).[74]

4-Ethyl-2,6-dimethylpyrylium perchlorate (1·38) undergoes a similar photohydrolysis reaction.[75] In addition to the expected trans-2-ethyl-4-methyl-5-oxohex-2-enal (1·41), both syn- and anti-5-ethylidine-2,3-dimethylcyclopent-2-enome (1·42) are formed. An oxoniabenzvalene (1·39) is again proposed as an intermediate.

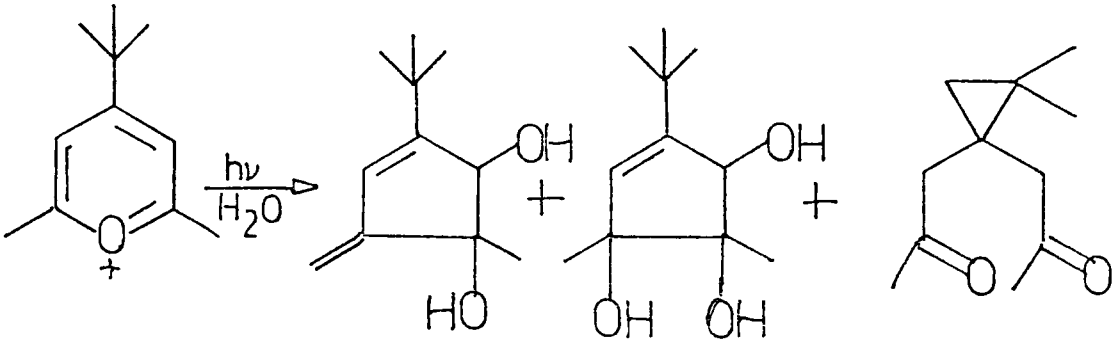


(1·38) (1·39) (1·40)

(1·42B) (1·42) (1·41)

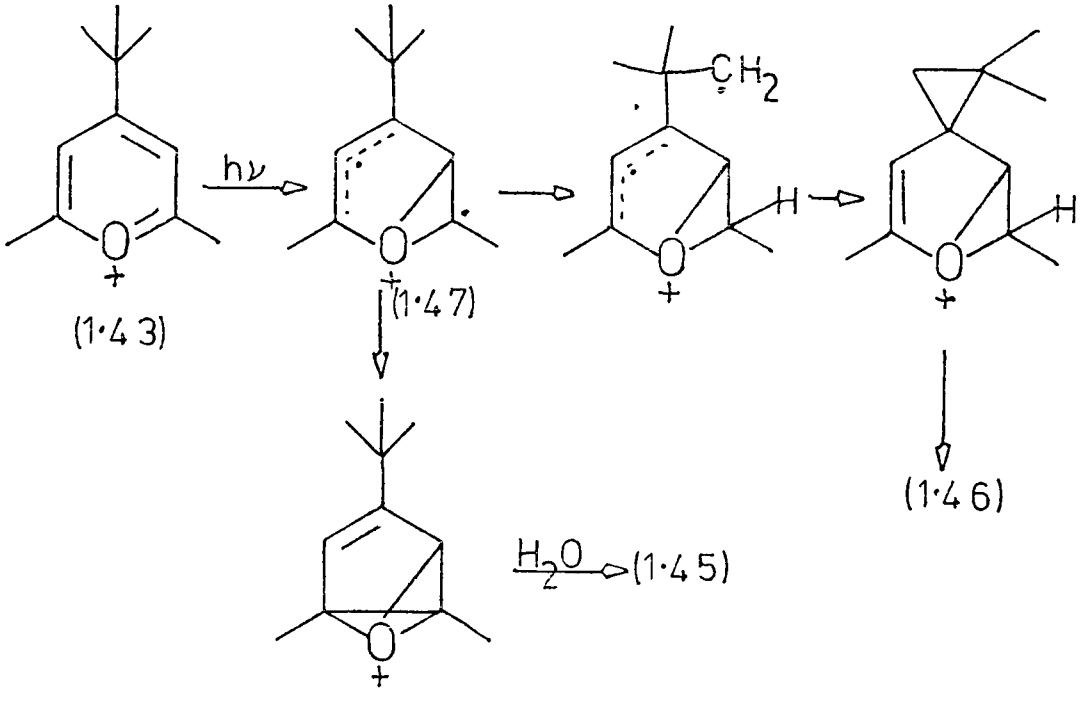
The cyclopentenones are readily derivable from the oxoniabenzvalene or the simple 2,6-bonded cation in non-photochemical heterolytic steps. When irradiated under the same conditions, 4-isopropyl-2,6-dimethylpyrylium perchlorate likewise gave (1·42B)

Evidence for an oxoniabenzvalene intermediate is also obtained from the irradiation of 4-tert-butyl-2,6-dimethylpyrylium perchlorate in water.[60] Four products are obtained. The diol and the two triols




(1·43) (1·44) (1·45) (1·46)

are derivable by hydroxlytic reactions of the proposed oxoniabenzvalene. It was proposed that the novel 1,1-diacetonyl-2,2-dimethylcyclopropane (1·46) was formed via intramolecular hydrogen abstraction of a tert-butyl hydrogen atom in the prevalene (1·47).



No ring-opened keto-aldehydes of the type found in the photohydrolysis of 2,4,6-trimethyl and 4-ethyl-2,6-dimethylpyrylium perchlorate were observed.

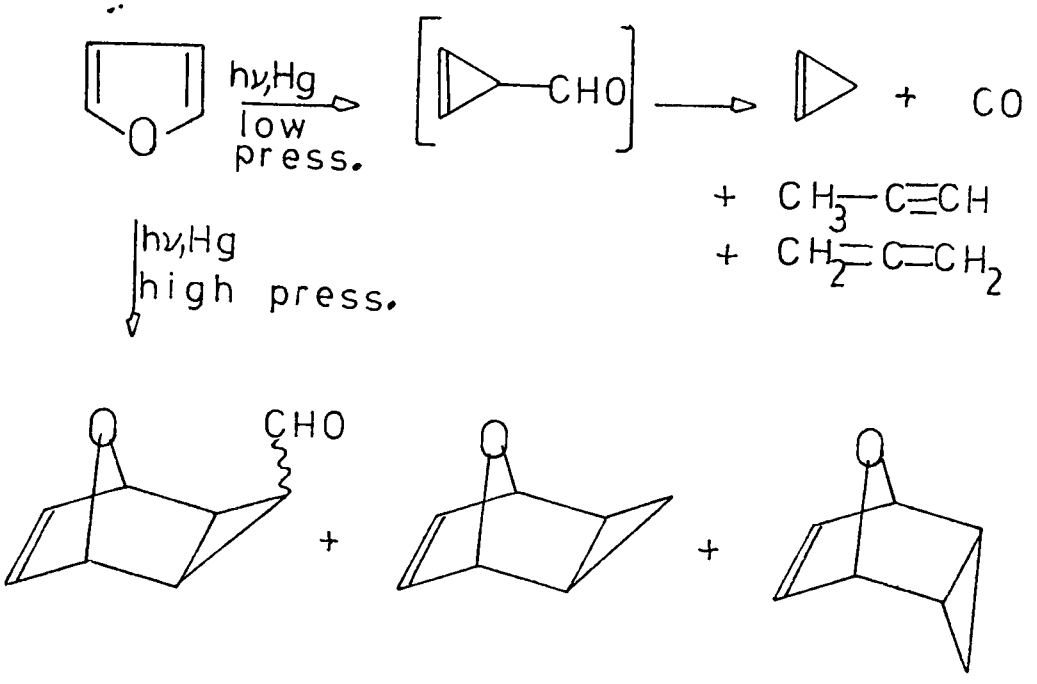
The major aims of the author in this area are centred around the fact that in no case has a solely alkylsubstituted pyrylium cation been shown to photoisomerise to another pyrylium cation. In this respect, irradiations of 2,4,6-trialkylpyrylium cations have been preformed in solvents which should not cause hydrolysis of the proposed transposed cations such as (1·34) and (1·40). Also a variety of 2,3,4,6- and 2,3,5,6-tetraalkylpyrylium cations have been synthesised and irradiated, since these are predicted to give more stable intermediates, and products less susceptible to hydrolysis. Various experiments designed to trap the intermediate bicyclohexenyl cations have also been attempted. The photochemistry of the 4-tert-butyl compound (1·43) has also been reinvestigated since the formation of the diketone (1·46) is much more easily rationalised in terms of an intramolecular hydrogen abstraction in the excited state of ring-opened (1·43).

## B. PHOTOISOMERISATION OF FIVE-MEMBERED HETEROCYCLIC COMPOUNDS

Photochemical transformation of five-membered ring aromatic compounds are well known and are at least as diverse as those occurring in six-membered ring heterocycles.[134-7] Photoisomerisation reactions resulting in scrambling of ring-atoms are known for most classes of five-membered heterocycles, and, for some, the mechanisms are quite well established.

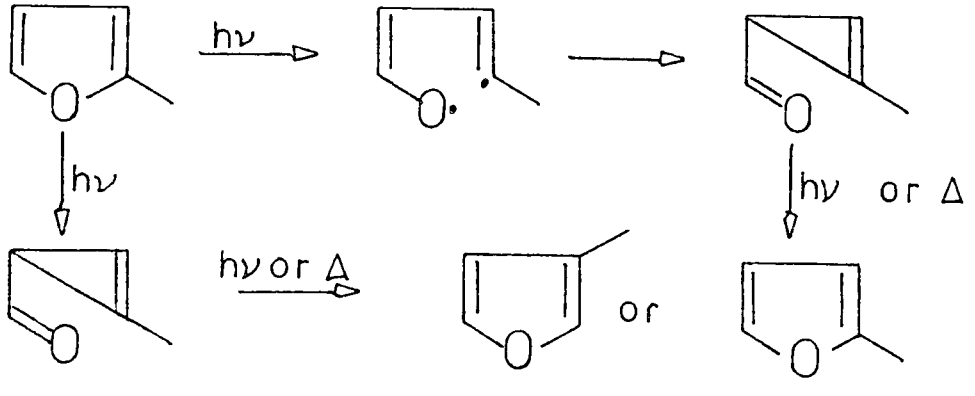
Furan phototranspositions have received much attention over

the last fifteen years. Thus, Srinivasan has shown that mercury sensitisation of furan and some methylfurans[76] results in dissociation at low furan pressures, whilst at higher pressures, various adducts between furan and the primary products are formed, as shown in scheme 1·8.

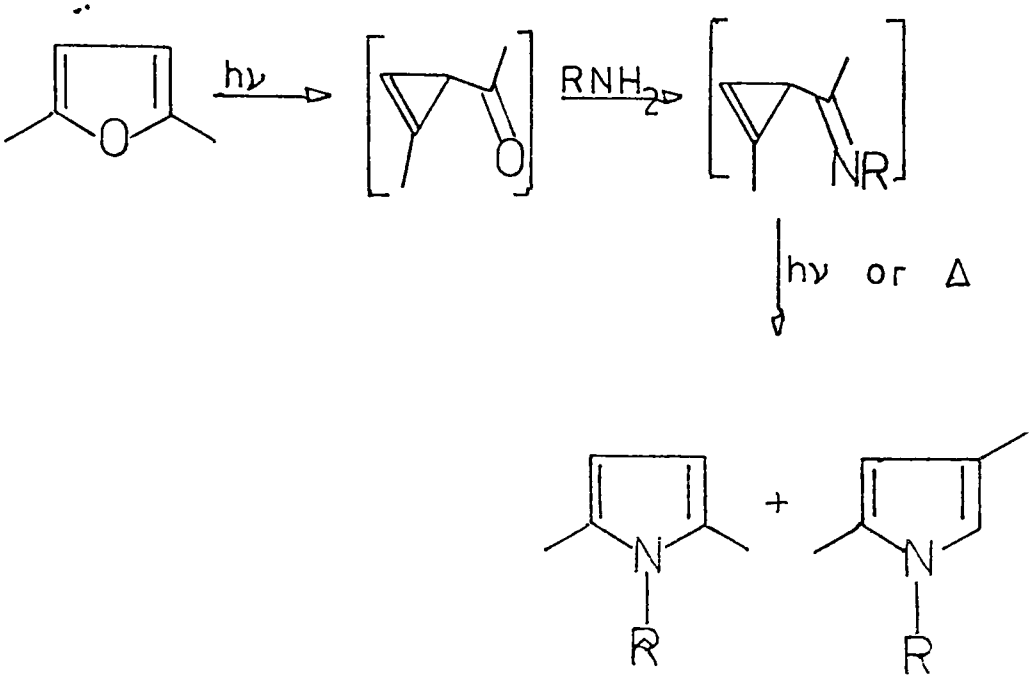



Scheme 1·8

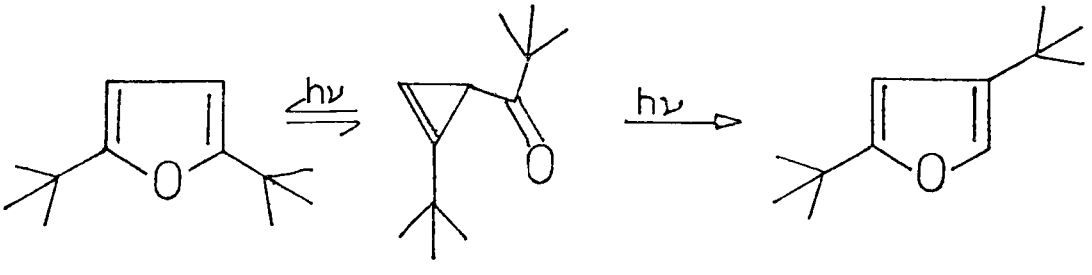
These results suggest that the excited state of furan undergoes rearrangement, either homolytically or by a 1,3-sigmatropic shift, to an acylcyclopropene. The observed transposition of 2-methylfuran



to 3-methylfuran (scheme 1·9), can arise through a subsequent ring-expansion of the acylcyclopropene either via another 1,3-sigmatropic shift, or a cycloaddition of the carbonyl group to a sigma-bond of the cyclopropene. The isolation of various N-propylpyrroles following the irradiation of some furans in the presence of propylamine has been taken as evidence for the inter-



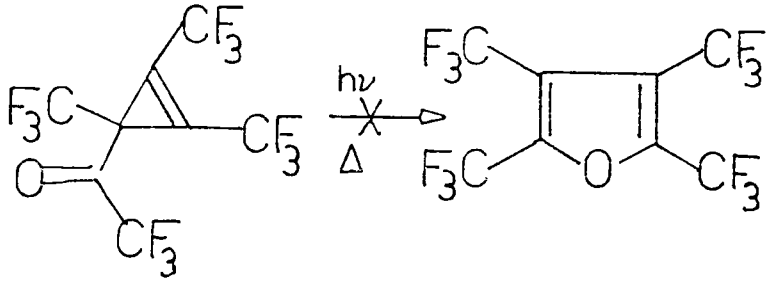

mediacy of acylcyclopropenes.[77,78] In favourable cases the proposed intermediates are isolated.[79] For example, 2,5-di-tert-butylfuran gives reversibly a stable cyclopropene. Irradiation of the cyclopropene gives both the 2,5- and the 2,4-di-tert-butylfurans, scheme 1·10.




Scheme 1·10

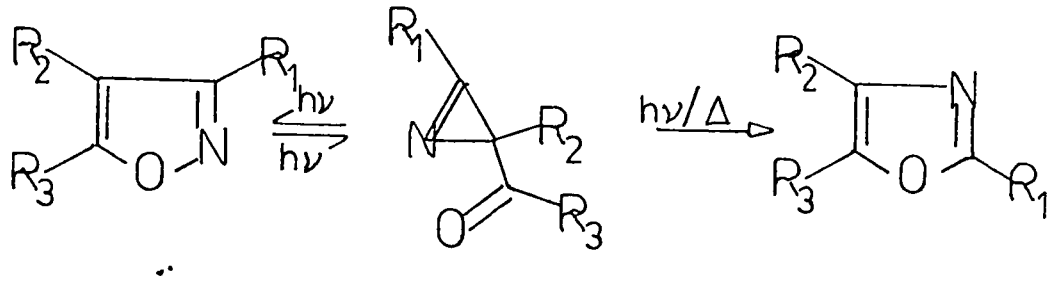
Various other substituted furans have been irradiated.[80,81] Furan-2 carbonitrile has been shown to undergo decarbonylation in the gas-phase, whereas irradiation as a solution in furan or alcohols leads to the formation of adducts of the intermediate cyclopropene. Both furan-2-carboxaldehyde and 2-vinylfuran upon irradiation lead to mixtures of degradation products which can be rationalised in terms of a primary ring-contraction reaction.

Interestingly, tetrakis(trifluoromethyl)furan is stable to irradiation under any conditions.[82] This is in marked contrast to the results obtained with the analogous pyrrole and thiophene compounds from which valence-bond isomers may be obtained. These are described later in this introduction. The tetrakis(trifluoromethyl) cyclopropenylketone (1·48) has been synthesised,[83] and shown not to revert to the furan either photochemically or thermally.



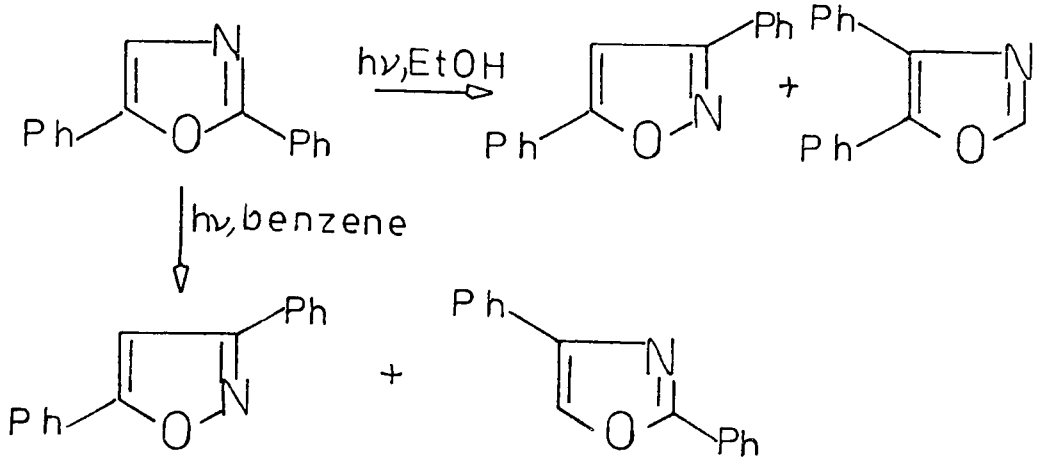

(1·48)

The substitution of a nitrogen atom for an α-carbon in a furan ring does not lead to a drastic change in photochemical behaviour. With few exceptions, irradiation of isoxazoles leads to the formation of azirines. These are often stable enough to be isolated.[84-86] Frequently the azirine will react further, either thermally or photochemically to yield an oxazole (scheme 1·11).



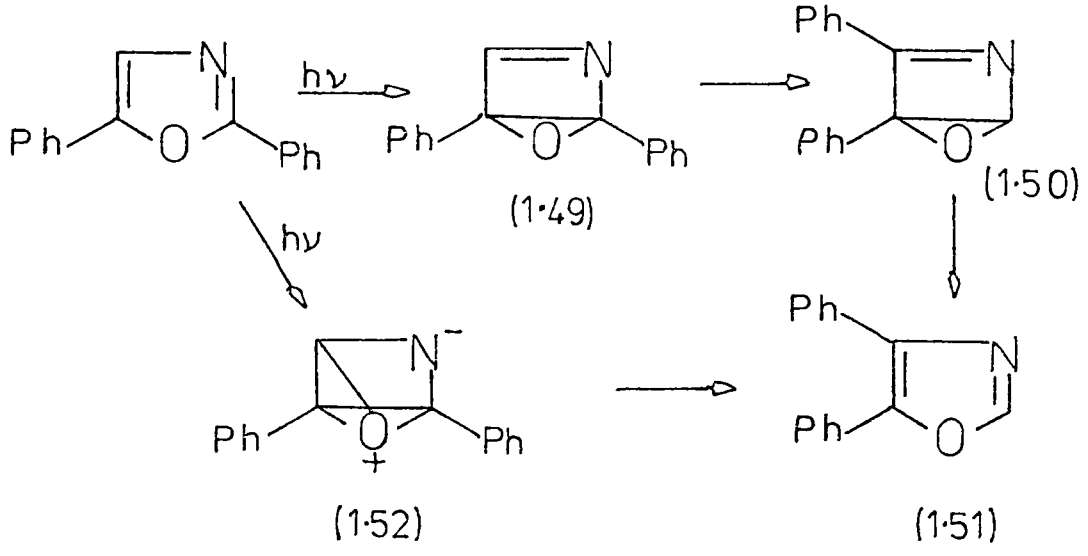
Scheme 1·11

The photochemistry of oxazoles themselves is less easily understood. Consider, for example, the phototransposition reactions of 2,5-diphenyloxazole,[87] scheme 1·12. It is suggested that with benzene

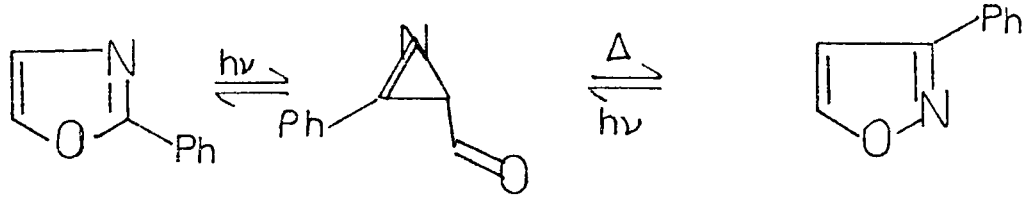


Scheme 1.12

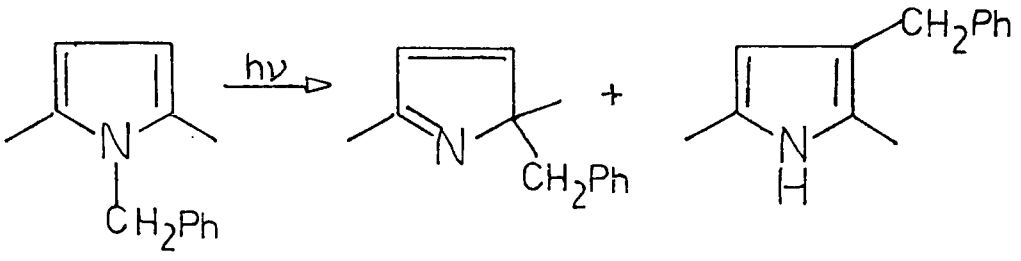
as solvent, the transpositions occur only via a ring-contracted azirine intermediate, but that in ethanol, two mechanisms operate. The additional mechanism proposes the intermediacy of a 2,5 bonded bicyclic compound (1·49). This is presumed to be able to undergo a thermal or photochemical 'walk' of the oxygen atom to give the bicyclic compound (1·50), where a phenyl group is conjugated with the double-bond. This can then rearomatise to give the oxazole (1·51). On the other hand, the formation and subsequent rearrangement of a zwitterionic intermediate such as (1·52) may be favoured in the polar solvent, ethanol.




In one case, 2-phenyloxazole, irradiation has led to the formation of an azirine (1·53) which was thermally converted to 3-phenyisoxazole.[8]



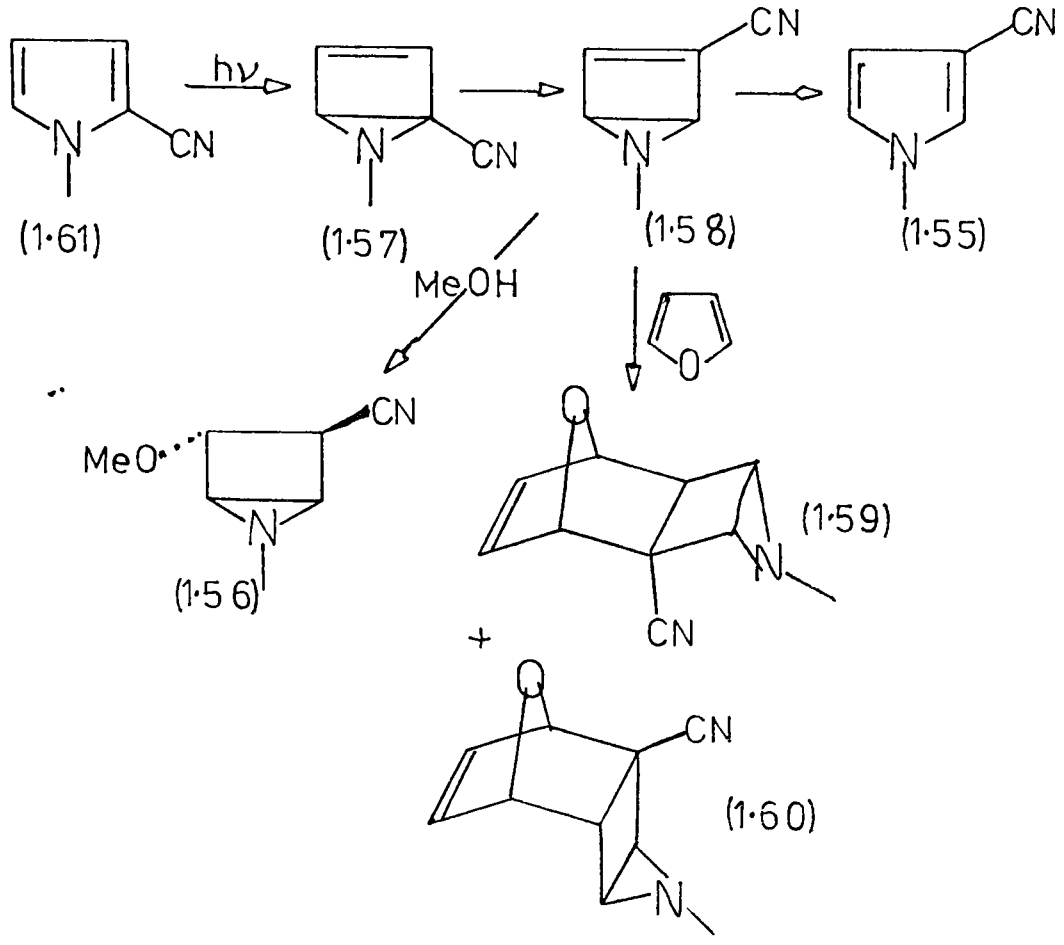
Pyrrole, and both 2,4- and 2,5-dimethylpyrrole give only degradation products upon irradiation in the gas phase.[93,94] In the condensed phase, rearrangements of the 1,2- and 1,3-types are observed. For example, irradiation of N-benzylpyrrole leads to a mixture of 2- and 3-benzylpyrrole.[95] If both the C-2 and C-5 positions are blocked then 2-H-pyrroles such as (1·54) are obtained.[96] In the case of N-substituted 2,4-diphenylpyrroles, clear evidence




(1·54)

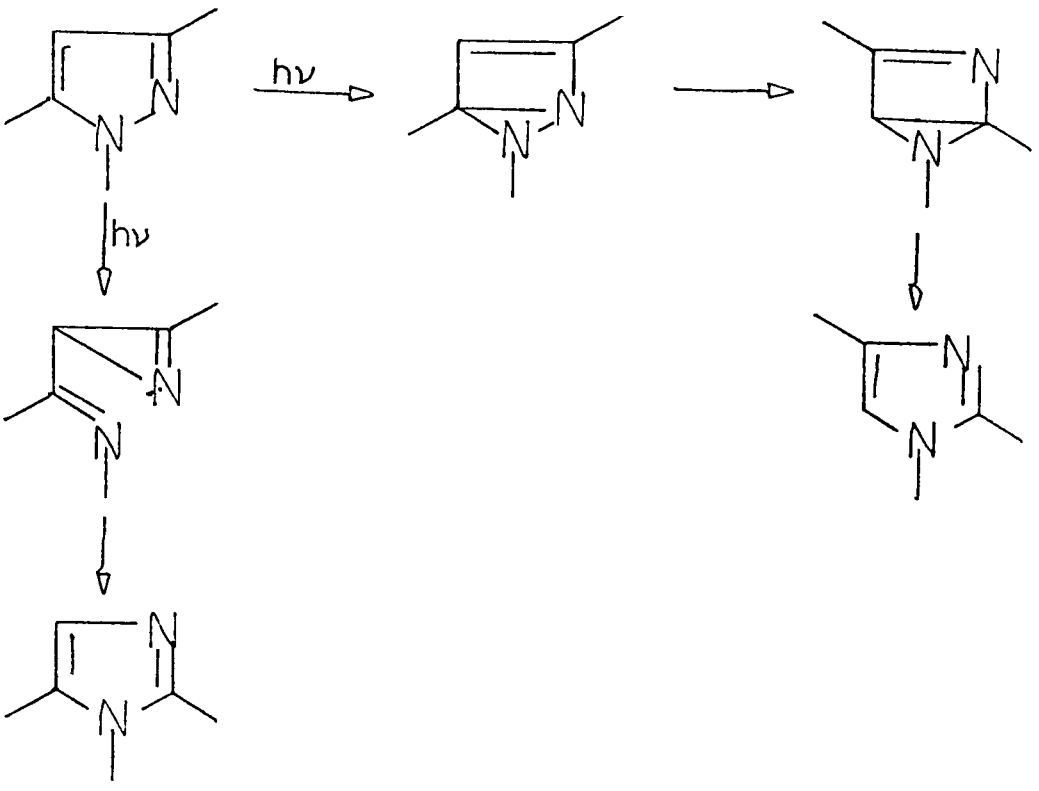
that products are formed by a free-radical mechanism has been obtained.[97]

Irradiation of pyrrole-2-carbonitriles in methanol leads to the 3-isomers.[89,90] Clear evidence that the transposition proceeds via 5-azabicyclo[2·1·0] pentene intermediates is provided by the isolation of methanol adducts and furan adducts of these intermediates.[91] Thus irradiation of N-methylpyrrole-2-carbonitrile (1.61) in methanol gives the 3-cyano isomer (1·55) and the methanol adduct (1·56), whilst (1·55), (1·59) and (1·60) are formed in furan solution. Excitation of (1·61) is presumed to give the 2,5-bonded bicyclic



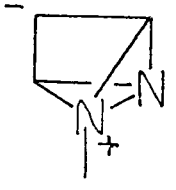

compound (1·57) which rapidly undergoes a nitrogen-walk step to give the conjugatively stabilised (1·58). This can react with the solvent to give adducts, or it can rearomatise to give the transposed pyrrole (1·55). These isomerisations are not reversible; the 3-carbonitriles are decomposed by ultra-violet irradiation.[255]

Pyrazoles and imidazoles are photochemically labile and can isomerise. Irradiation of imidazoles generally leads to scrambling of substituents, whilst pyrazoles are isomerised to imidazoles.[99-101] These rearrangements are often explained in terms of isomerisations of intermediate bicyclic compounds or ring-contracted compounds




Scheme 1·13

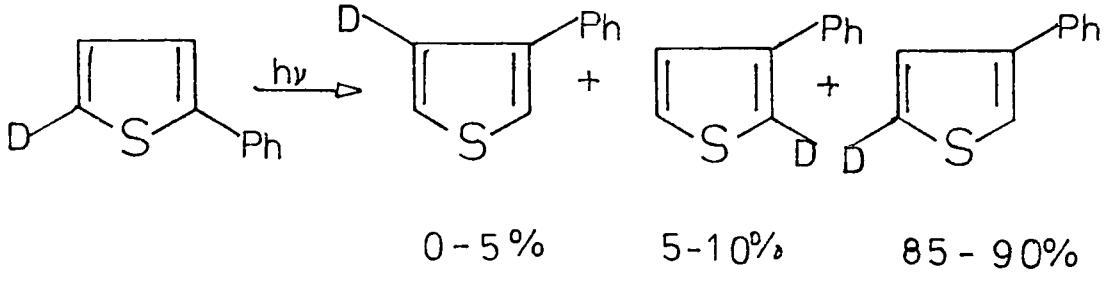
as shown in scheme 1·13. A theoretical paper by Labhart[102] illustrates that CNDO calculations favour a dipolar species such as (1·62) rather than the related bicyclic compound.



(1·62)

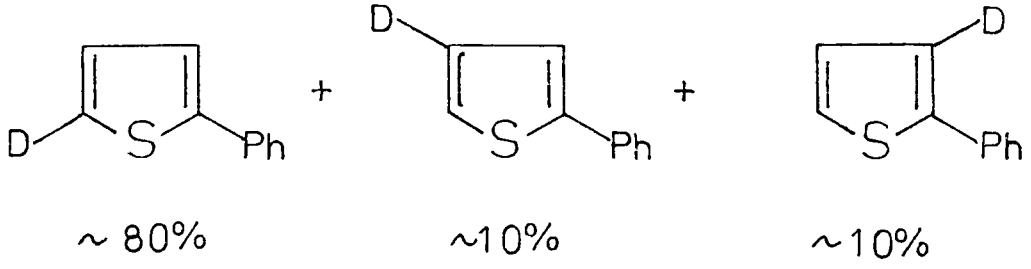
Isothiazole and thiazole photochemistry is extremely diverse and intriguing.[103-112] Many of the isomerisations and mechanisms are closely related to those observed in thiophene photochemistry, so they will not be discussed here separately.

The photoisomerisation reactions of thiophenes have been studied in great detail, particularly by Kellogg and Wynberg. It has been found that for a wide variety of substituents, although by no means all, that 2-substituted thiophenes transpose into 3-substituted thiophenes. Thus 2-phenylthiophene upon irradiation gives 3-phenylthiophene.[114] The reaction is not as simple as it seems however. Deuterium labelled 2-phenylthiophene has also been irradiated and the results are shown below, scheme 1·14.[115]




Scheme 1·14

The residual 2-phenylthiophene was found to contain the deuterium distribution shown in scheme 1·15. All six possible methylphenylthiophenes have been synthesised, and, upon irradiation, each gives




Scheme 1·15

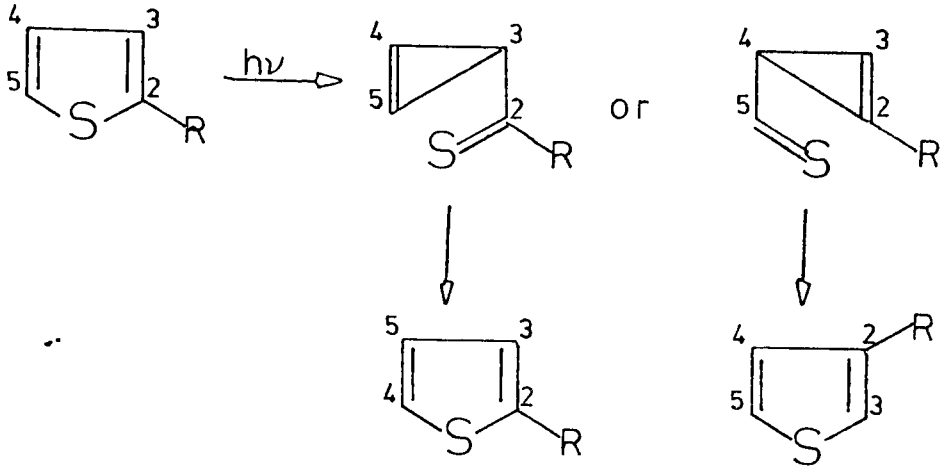
the other five isomers, all as primary products.[116] Labelling

experiments with $^{14}C$ have shown that the phenyl group remains attached to its original carbon atom throughout the rearrangement and thus the reactions are intramolecular.[117] It has also been shown that the reaction takes place, for the 2-phenythiophene case at least, from the first excited singlet state.[118]

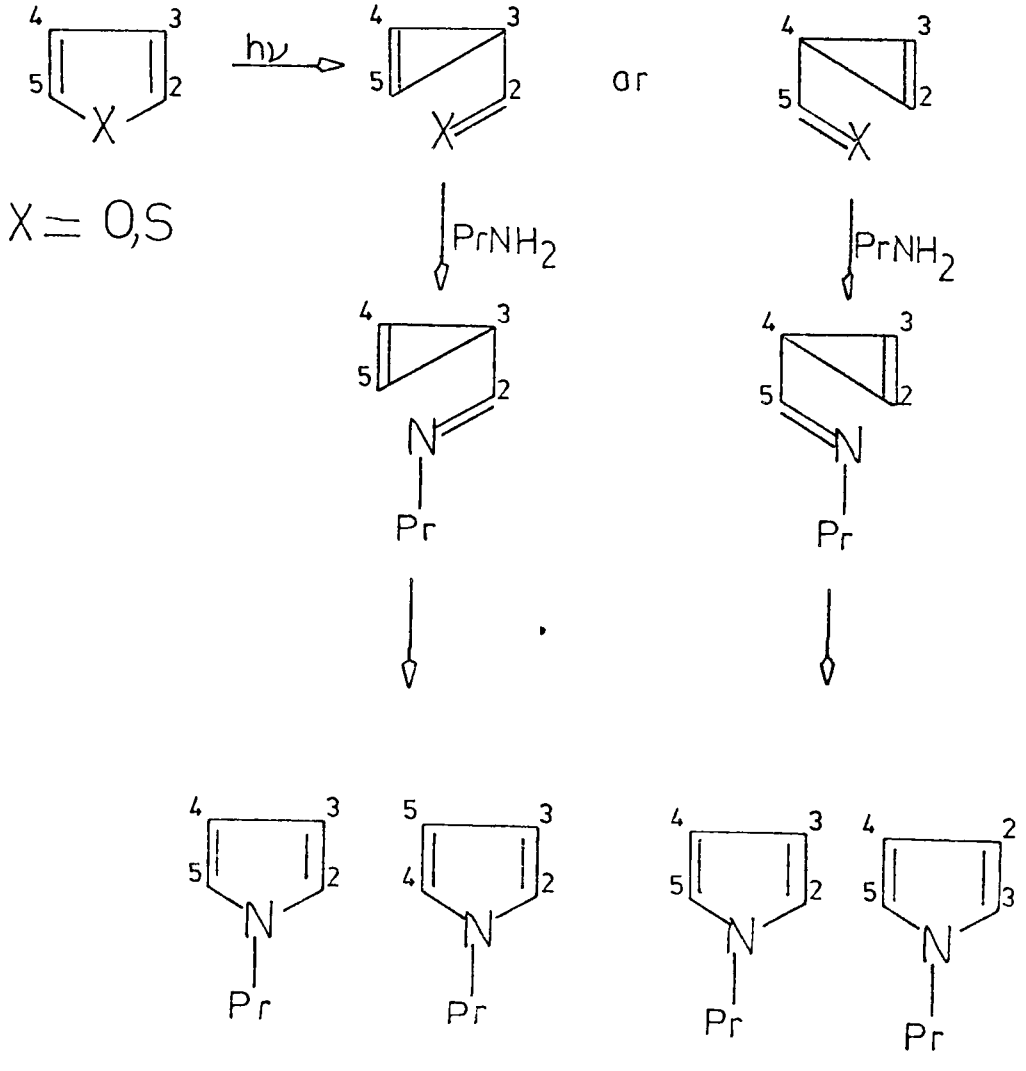
Many mechanisms have been proposed to account for these isomerisations. The type of mechanism described in scheme 1·16 involving ring-contracted species can only account for either C2-C3 or C4-C5 interchange.[119] This clearly falls some way short of explaining the isomerisations of methylphenylthiophenes, where total scrambling is observed. However, support for this mechanism has come from Couture and Lablache-Combier who observed the formation of pyrroles when a series of alkylthiophenes were irradiated in the presence of amines.[120] The products were analogous to those formed under similar conditions in the irradiation of furans,[78] scheme 1·17.

Wynberg et. al.[119] favoured a mechanism involving zwitterionic species as shown in scheme 1·18. Concerted rearrangement of (1·63) could lead to inversion of the C2-C3 or C4-C5 carbon atoms. This scheme fails to predict the observed rearrangements of 3-phenylthiophenes, in particular it cannot lead to a simple C3-C4 inversion.

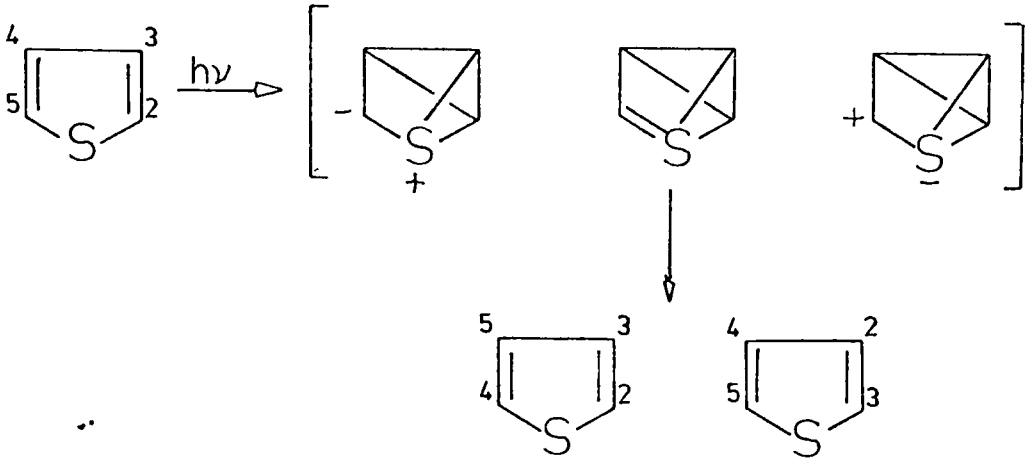
Van Tamelen and Whitesides have proposed a third mechanism to account for the rearrangements which involves an equilibration between cyclopropenylthiocarbonyl compounds and 5-thiabicyclo[2·1·0]pent-2-enes.[79] Their scheme is reproduced here as scheme 1·19.



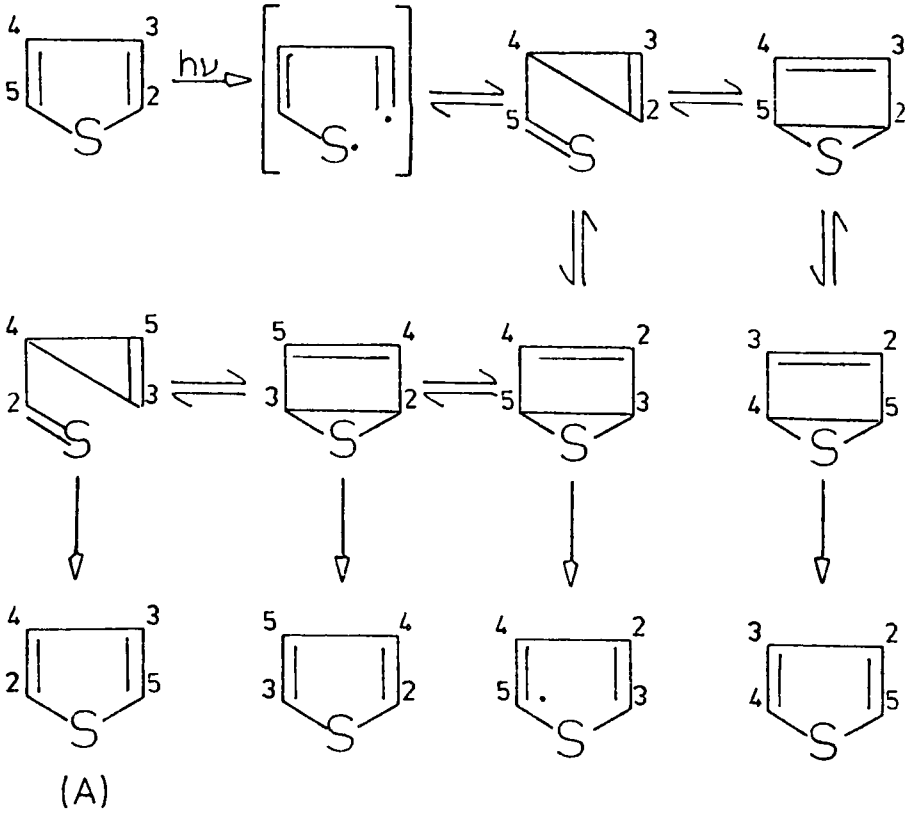

Scheme 1·16




Scheme 1·17

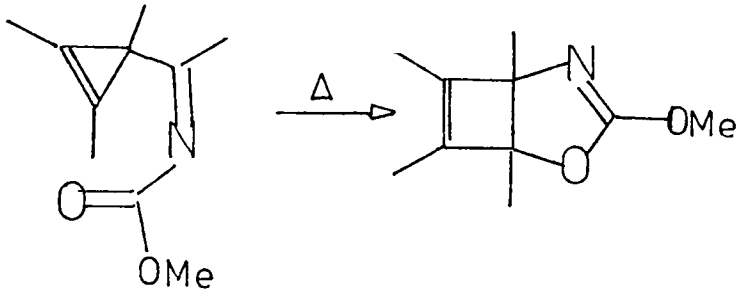


Scheme 1·18



Scheme 1·19

The equilibration between cyclopropenyl intermediates and Dewar intermediates allows for a C3-C4 interchange as shown (A). Equilibration between cyclopropene rings and cyclobutene rings are not unknown in ground-state organic chemistry. For example, gentle heating converts (1·64) to (1·65).[257]



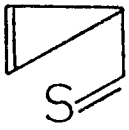

(1·64) (1·65)

A fourth mechanism has been proposed by Kellogg which also allows for a C3-C4 interchange.[121] He suggests that excitation of the thiophene chromophore produces a drastic distortion of the ring geometry to give species in which a two atom fragment is wrenched 90° out of the plane formed by the remaining three atoms. The excited state could have one of three arrangements by 90°

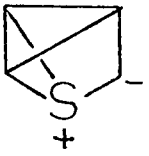
rotation out of the plane of S-C2 (≡S-C5), C2-C3(=C4-C5), or C3-C4(=C4-C3). Which arrangement would actually occur, or indeed what distribution of possible arrangements there might be in the excited state, would depend heavily on the nature and on the position of substituents. Isomerisation would be achieved by "turning over" of the two atom fragments and subsequent rearomatisation. This scheme has a notable advantage over the Van Tamelen-Whitesides mechanism in that it predicts correctly 2-methyl-4-phenylthiophene as a major product from 2-methyl-3-phenylthiophene. However, clearly this mechanism cannot lead to all of the observed products. Thus it cannot directly interconvert 2,5- to 3,4- isomers.

The formation of all six possible isomers, all as primary products, in the photolysis of any methylphenylthiophene emphasises the complexity of thiophene transposition reactions. It is evident that all of the possible valence-bond isomers may be involved, or variations of the same intermediate may be responsible for the diversity. Other paths involving completely unpredicted intermediates might be taken, or, in some cases there may even be direct paths from excited state to ground state surfaces not involving valence-bond intermediates. The nature and positions of substituents must also be an important factor in directing the mechanism one way or another.

It is important when discussing the various possible intermediates to be aware of the relationships between some of them.



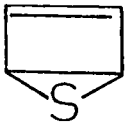
(1·66)



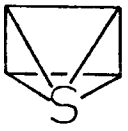
(1·67)



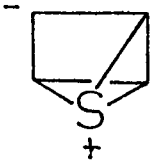
(1·68)



(1·69)



(1·70)

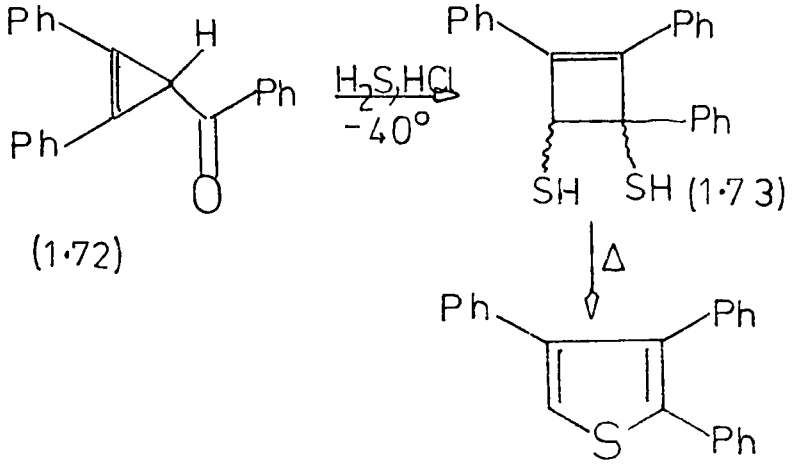


(1·71)

The reported interconversion of cyclopropenes and cyclobutenes has already been mentioned. One could envisage participation of the sulphur 3d orbitals of (1·66) with the carbon-carbon double-bond to give resonance structure (1·67). Alternatively, concerted cycloaddition across the double bond could give rise to an intermediate such as (1·68). Similarly by the use of sulphur 3d orbitals, the Dewar thiophene (1·69), the prismane (1·70) and the benzvalene type (1·71) may be interconverted.

A further point of mechanistic interest in thiophene photochemistry is revealed by the gas-phase irradiation of thiophene itself.[122] Both direct and mercury-sensitised irradiation gives acetylene, methylacetylene, vinylacetylene, allene, and carbon disulphide. Cyclopropene, a likely product from thiodecarbonylation

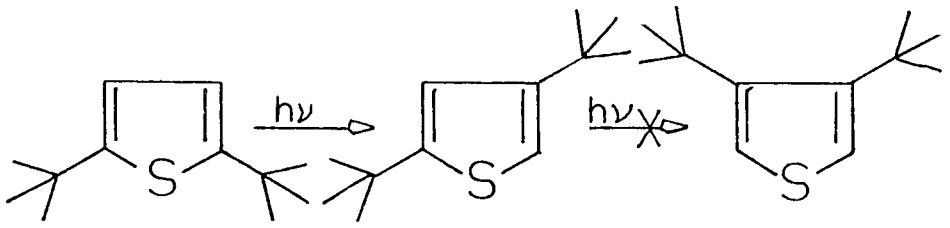
of cyclopropenylthioaldehyde is conspicuously absent. Cyclopropene is of course found in the gas-phase irradiation of furans, and as stated earlier, stable cyclopropenylketones are isolated in the photolysis of di-tert-butylfurans. In this connection, Groen (in ref. 113) attempted to convert the cyclopropenylketone (1·72)




(1·72) (1·73) (1·74)

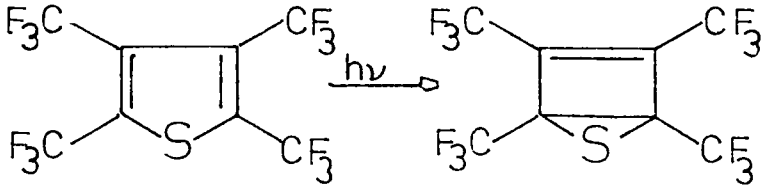
to the thiocarbonyl derivative with $H_2S$ and HCl in ethanol at -40°. No thiocarbonyl compound was detected, and instead, an unstable orange oil thought to be (1·73) was isolated. This gave the triphenylthiophene (1·74) readily on warming.

Attempts to isolate thiocarbonyl compounds from irradiation of di-tert-butylthiophenes have been unsuccessful.[125] The 2,5-isomer gives the 2,4-isomer, but this does not go on to give the 3,4-isomer. It is photostable. It has been assumed that a sufficiently




high barrier is met in passing to this strained ring system causing the intermediate simply to collapse back to starting material.[127] The rearrangement to the respective 3,4-disubstituted thiophenes proceeds with 2,4-diphenylthiophene and 4-methyl-2-phenylthiophene, although here smaller groups are involved.[116,126]

The only photochemically produced valence-bond isomer of a thiophene reported to date in the literature is the Dewar isomer (1·76) obtained by vapour phase irradiation of tetrakis(trifluoromethyl)thiophene (1·75).[123] This is yet another example of the




(1·75) (1·76)

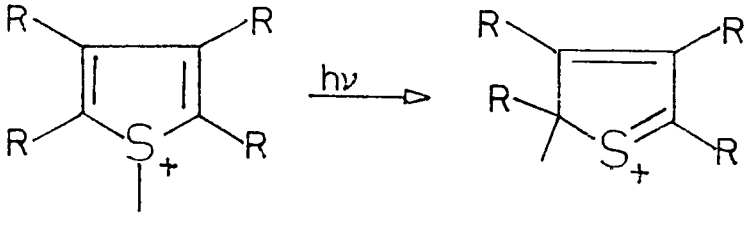
stabilisation of strained intermediates by trifluoromethyl groups. Although this is a special case, it does establish the existance of a valence-bond isomer other than ring-contracted species in the photochemistry of five-membered heterocyclic molecules.

The Dewar isomer (1·76) reverts quantitatively to the thiophene at 160°. In addition, the Dewar isomer undergoes Diels-Alder

reactions with acyclic and cyclic dienes, and can also be converted into Dewar pyrrole compounds.[129,130,137] Conversion of the episulphide into the eipsulphoxide with peroxytrifluoroacetic acid leads to very facile isomerisation.[131] The $^{19}F$ nmr spectrum shows only a narrow singlet down to temperatures as low as -95°. This is thought to be due to rapid 'walking' of the sulphoxide around the four-membered ring, and will be discussed fully later.

Many thiophenes other than alkyl, aryl and perfluoroalkyl substituted types have been irradiated,[113,132,133] e.g. aldehyde, ketone, vinyl and benzoyl substituted compounds. All of these, and electron-withdrawing groups in general, seem to quench thiophene transposition reactions.

A much more drastic perturbation of the thiophene nucleus is achieved by S-alkylation. Kellogg et al. have prepared and irradiated S-alkylthiophenium fluorosulphates and have observed isomerisation.[124] The authors favour a mechanism involving homolysis




of the S-alkyl bond.

The major aim of the author in the area of thiophene photochemistry has been to isolate or trap, photochemically produced valence-bond isomers which might be involved in transposition pathways. Variously substituted thiophenes have been synthesised and irradiated, both over a wide temperature range, and also in the presence of

a variety of chemical reagents designed to react with specific types of intermediates, in an attempt to fulfill this aim. Where isolated, the excited state and thermal chemistry of the valence-bond intermediates has been investigated.

# Chapter Two

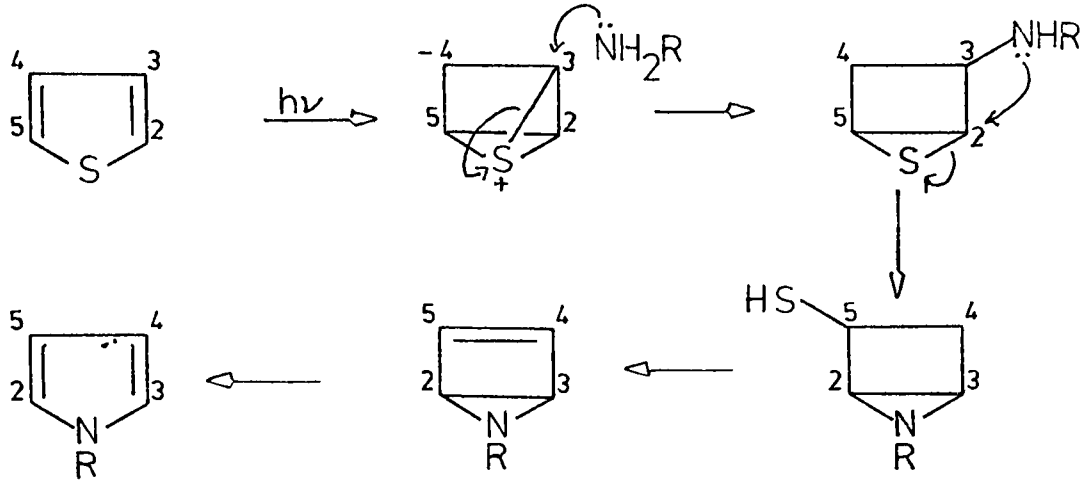
# PHOTOCHEMISTRY OF THIOPHENES

## 2·1 Introduction

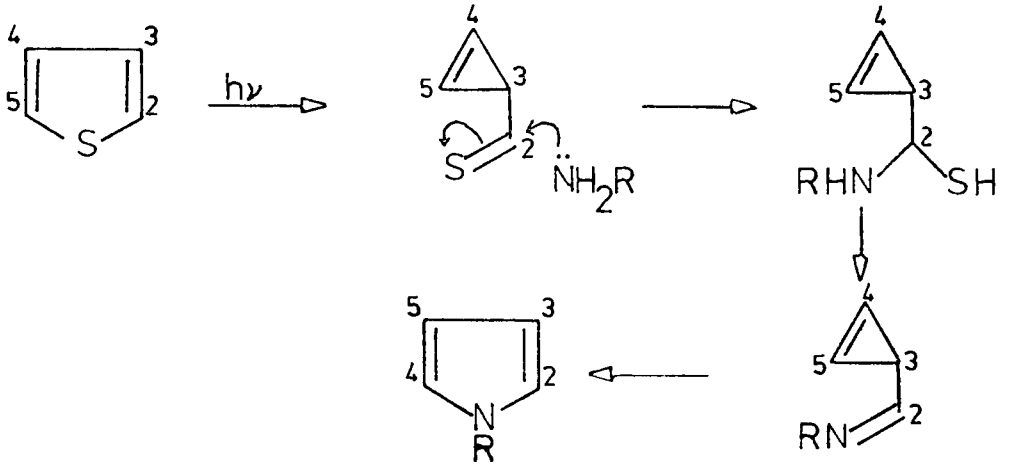
The striking isomerisations of alkyl and aryl substituted thiophenes that occur upon irradiation with ultra-violet light have been described in the main introduction to this thesis. It was shown that no single mechanism had been proposed which could account for all of the rearrangements of thiophenes, but that several were able to predict correctly the major products. This suggests that more than one mechanism can operate, and that which one actually does, depends very much upon the position and nature of the substituents. In finely balanced systems such as the methylphenylthiophenes, the large numbers of products may indicate that more than one mechanism can operate simultaneously.

The literature to date does not contain many references to the isolation or trapping of reactive intermediates or valence-bond isomers in thiophene photochemistry. The single valence-bond isomer obtained has been the tetrakis(trifluoromethyl) Dewar thiophene, described in the introduction. The only other major contribution has been from Lablache-Combier who has irradiated various alkylthiophenes in the presence of propylamine and obtained *N*-propylpyrroles.[78] These interesting experiments have not, however, shed very much light upon the question of transposition mechanisms, since most of the intermediates commonly thought of as leading to transposition products are, in principle, capable of reacting with amines to give pyrroles. This can be seen from the schemes below.

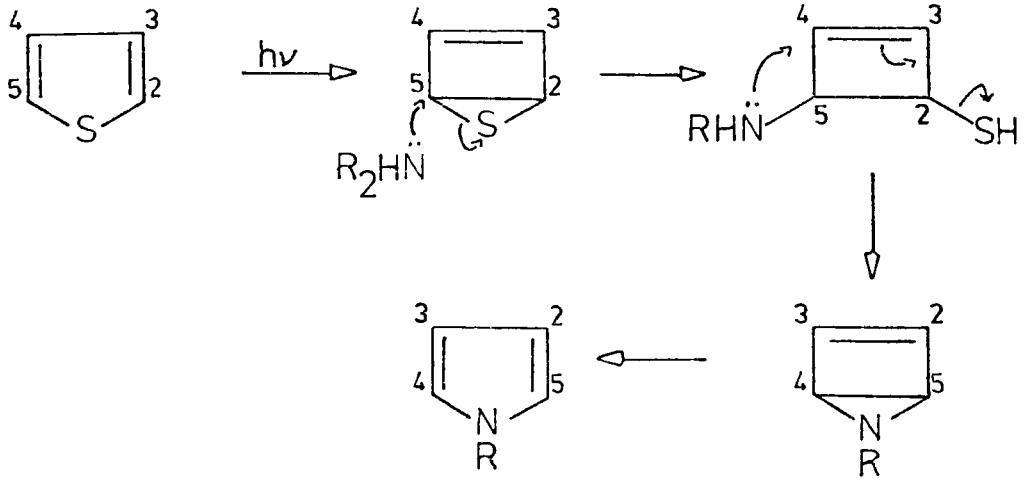
zwitterionic intermediate;



thiocarbonyl intermediate;

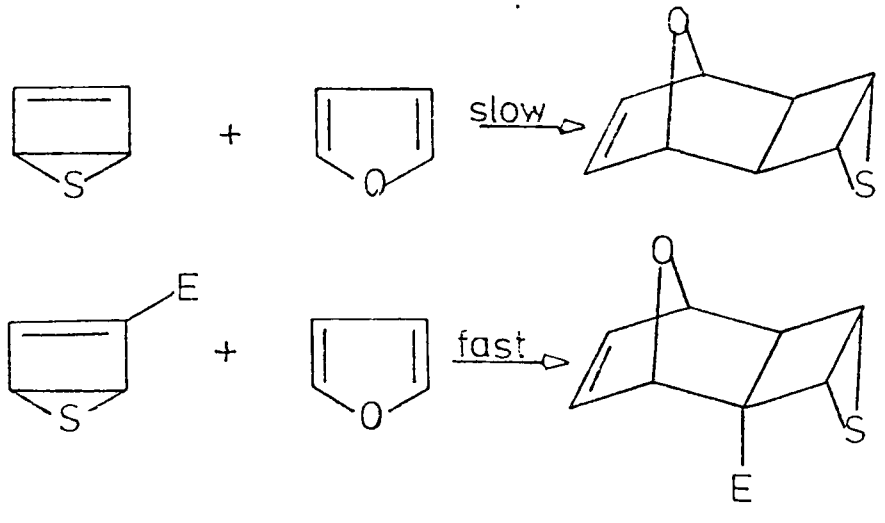


bicyclic intermediate;



The approach to the problem by this author has been three-fold. Firstly attempts have been made to trap and to isolate intermediates in thiophene photochemistry by methods which have not been described in the literature as having been applied to the thiophene field. These include such techniques as irradiation in low-temperature matrices and solutions, and also irradiation in the presence of chemical reagents designed to react rapidly with specific types of intermediates. It should be mentioned at this point that the physical or chemical trapping of a valence-bond isomer that has been formed from an electronically excited thiophene species is not in itself any proof that the species is actually encountered along the transposition path. It must be shown that the intermediate will react, at an appropriate rate, under the conditions of an irradiation to give transposed products.

The second approach by this author has been to put substituents into the thiophene ring, designed to make subsequent intermediates more susceptable to chemical reactions and also more thermodynamically stable. Thus for example, intermediates with double-bonds will be expected to undergo thermal 4+2 Diels-Alder reactions if electron-withdrawing groups are in conjugation with the double-bond, Scheme 2·1.




E = electron-withdrawing group

Scheme 2·1

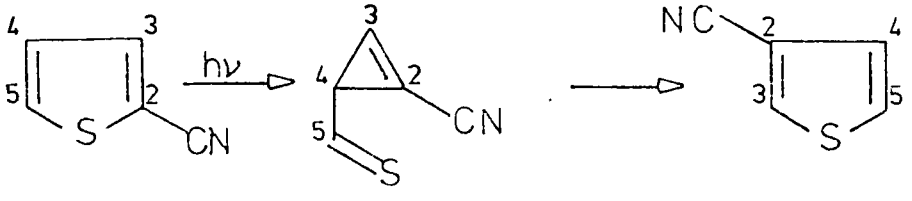
Thirdly, substituents have been placed in the thiophene ring in an attempt to perturb the molecule electronically and so perhaps direct the transposition reaction to a single pathway. For example, in alkylpyrrole photochemistry, the transposition reaction is thought to occur partly through a free-radical mechanism, and partly by a concerted intramolecular process.[255] However, alkylpyrrole-carbonitriles transpose exclusively by a pathway involving bicyclic Dewar intermediates.[91,92]

## 2.2 PHOTOCHEMISTRY OF THIOPHENE-MONOCARBONITRILES

### 2.2.1 Irradiation of thiophene-2-carbonitrile

Irradiation of thiophene-2-carbonitrile in inert solvents gave thiophene-3-carbonitrile in low yield. Identification of the transposed isomer was based upon comparison of its g.c. retention time, mass spectral fragmentation pattern and its nmr spectrum with an authentic sample of the 3-isomer. The fact that no thiophene or thiophene-dicarbonitriles were observed suggests that the rearrangements does not proceed *via* a radical pathway involving homolysis of the C-CN bond since subsequent capture of ·CN by other thiophene-carbonitrile molecules would be expected to occur.

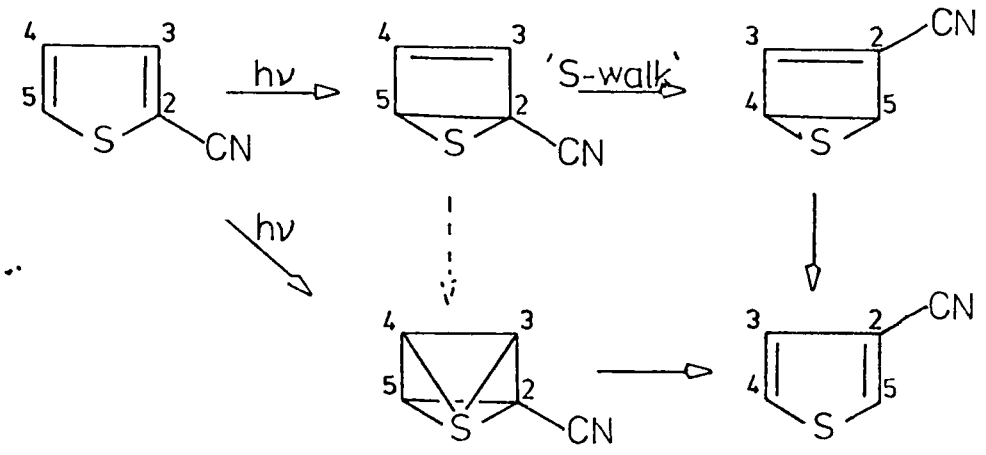
The transposition reaction observed may involve a simple $C_2$-$C_3$ interchange or it may be considerably more complex. The former type of reaction is compatible with a photorearrangement mechanism involving an initial ring-opening reaction to give a cyclopropenyl-thioaldehyde and subsequent photochemical or thermal ring-closure to give the transposed isomer. Such processes are well-known,




particularly in furan and isoxazole photochemistry.[79,84]

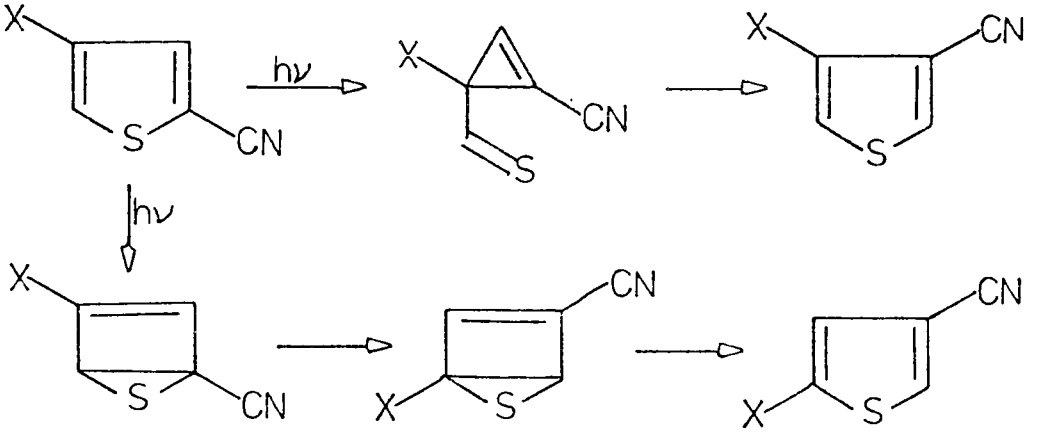
Intermediate Dewar and prismane structures, which predict rearrangements where the carbon atom sequential order will not change, but only a relative change in the position of the sulphur

atom occurs, can also account for the 2- to 3-transposition as shown in Scheme 2·2.




Scheme 2·2

These latter two mechanisms are in principle distinguishable from the ring-contraction, ring-expansion mechanism involving the cyclopropenylthioaldehyde intermediate, since in this case an alteration in the sequential order of carbon atoms in the thiophene ring occurs. Thus by putting a single additional label in an appropriate position in the ring and defining its position in the products, the two mechanisms can be distinguished, Scheme 2·3.

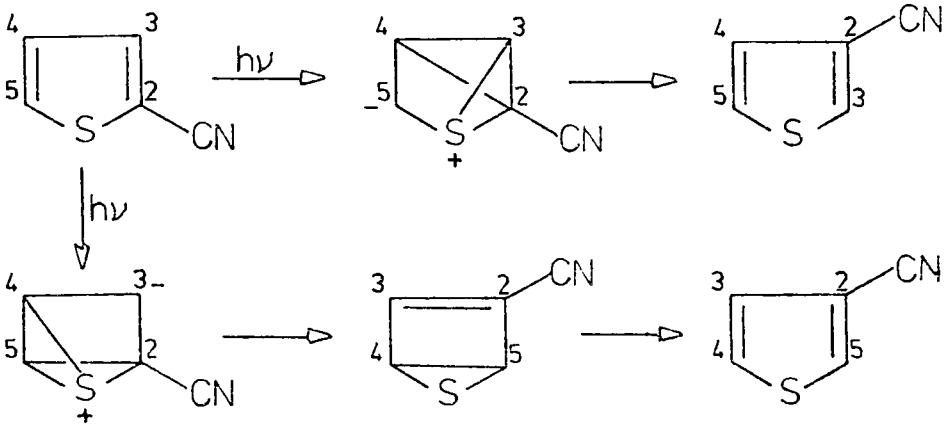



Scheme 2·3

It is always possible that altering the substitution pattern in the thiophene may cause some change in the reaction mechanism. With this in mind, 4-methylthiophene-2-carbonitrile was synthesised *via* the reaction of t-butyl lithium on 3-methylthiophene. The nitrile was found to transpose and give, exclusively, 5-methylthiophene-3-carbonitrile in low yield.

Assuming that the methyl group has not altered the transposition mechanism, it may be reasonable to discount the ring-contraction, ring-expansion mechanism involving the thiocarbonyl intermediate. Further experiments described below will show that the methyl group has no significant effect on the reaction pathway.

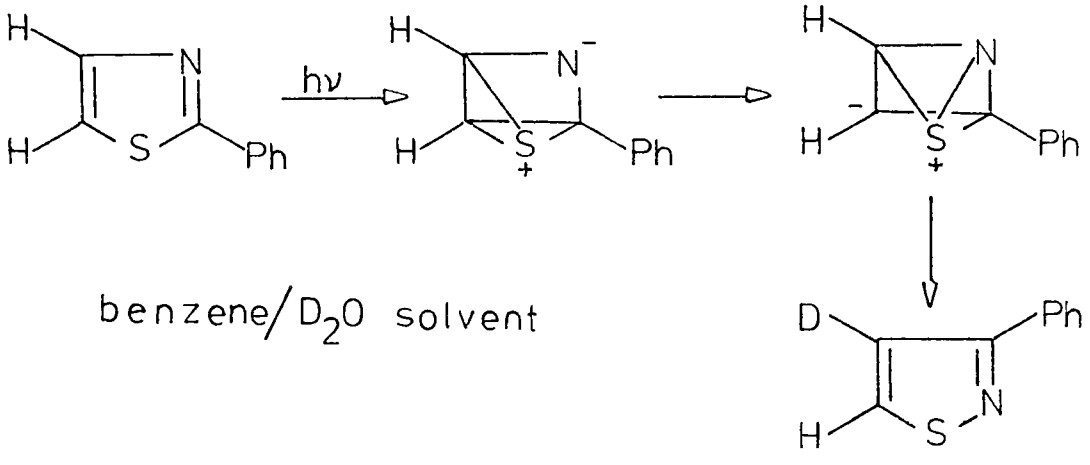
It may also be possible to discount zwitterionic mechanisms of the type shown in Scheme 2·4. Irradiation of the nitrile in




Scheme 2·4

deuteriomethanol showed no incorporation of deuterium. Had such zwitterionic mechanisms been responsible for the transposition reaction, one would have expected some exchange of deuterium.[166]

For example, in the transposition reactions of phenylthiazoles, irradiation in benzene solution containing deuterium oxide leads to deuterium incorporation in the transposition products, Scheme 2·5. The incorporation of deuterium is taken in this case as indicating the intermediacy of carbanionic carbon in the transformation.

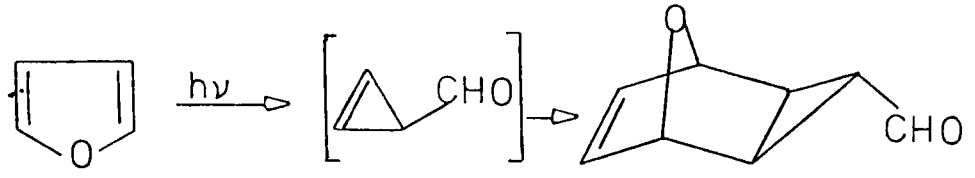



Scheme 2·5

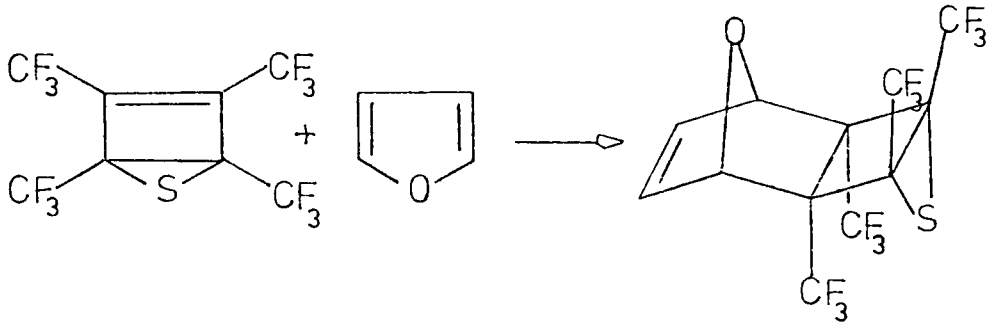
However, although mechanisms involving zwitterionic species with carbanionic carbons may be discounted, those mechanisms involving the sulphur atom accommodating the negative charge cannot, since here no exchange of deuterium would be expected.

## 2.2.2 Trapping experiments with thiophene-2-carbonitrile

The studies by Srinivasan et al. of the photochemistry of furan have shown that relatively short-lived cyclopropenyl compounds can be trapped as Diels-Alder adducts with furan itself.[76]




Tetrakis(trifluoromethyl)Dewar thiophene also reacts rapidly with furan to give a 4+2 adduct.[128] In this case the perfluoroalkyl

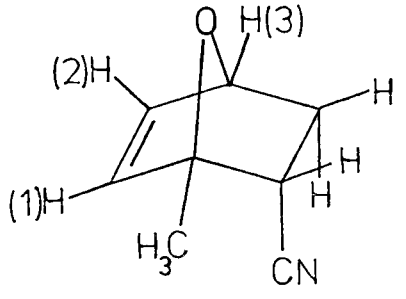



groups are probably a considerable activating force since unsubstituted cyclobutenes do not react with furan. With these results in mind, thiophene-2-carbonitrile was irradiated in the presence of furan - the idea being that, if the reaction proceeded by way of a long-enough lived intermediate, particularly one with an acrylonitrile-type moiety, then the furan might thermally trap it.

This type of experiment was feasible in an RPR using 254nm light since furan only absorbs light below about 230nm and the nitrile absorbs most strongly in the 230-270nm region. Work-up

of the solution following irradiation of the nitrile in furan yielded two crystalline compounds. Mass spectral analysis of these two products showed them both to be 1:1 adducts of the nitrile and furan. The structure of the two compounds was deduced mainly from interpretation of their nmr spectra in the following manner.

Furan 4+2 adducts are well known and give characteristic nmr spectra. The olefinic hydrogens normally resonate around 6·4 and the oxygen bridge-head hydrogens at around 5·0.[138-140] For example, in an adduct of 2-methylfuran and acrylonitrile the resonances are at 5·1, 6·3 and 6·5. In the major adduct obtained

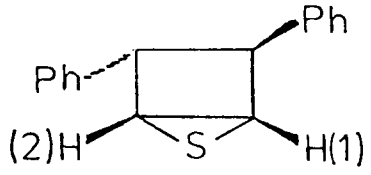



| | |
|---|---|
| H(1) | 6·3 |
| H(2) | 6·5 |
| H(3) | 5·1 |

by this author, signals appeared in the nmr at 5·07, 5·13 and 6·53 (2H), all expected from the furan part of a 4+2 adduct.

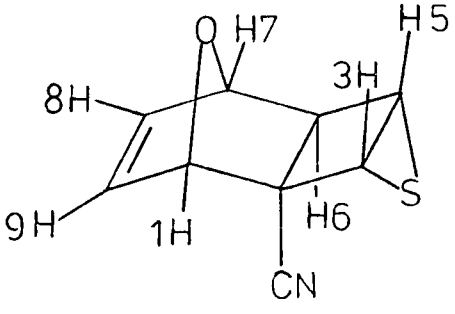
The remaining signals were at 2·76, 3·43 and 3·66. These were coupled to each other, but not to the furan part of the adduct. Signals for cyclopropyl rings would be expected to resonate at much higher field than these three hydrogens. In the furan adduct obtained by the gas phase irradiation of furan, the cyclopropyl hydrogens resonate between 0·6 and 1·6.[76] On the other hand, in the 5-thiabicyclo[2·1·0] pentane obtained by Block and Corey from the photolysis of a divinyl sulphide, the

episulphide hydrogens resonate at 3·96 and 3·69, with J = 4Hz.[141]

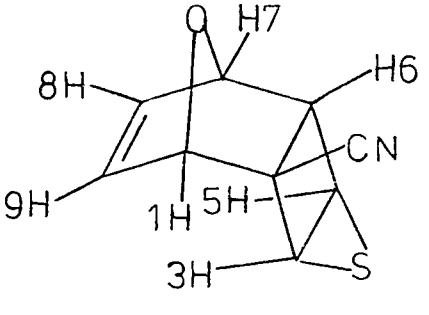



| | |
|---|---|
| H(1) | 3·69 |
| H(2) | 3·96 |

The infra-red spectrum of the major adduct showed the presence of a cyano group at 2235cm$^{-1}$, and the ultra-violet spectrum showed that there was no extensive conjugation. These spectroscopic data suggest that the adduct has the structure shown below (2·1). The stereochemistry and position of the cyano group are deduced as follows:




(2·1)




(2·2)

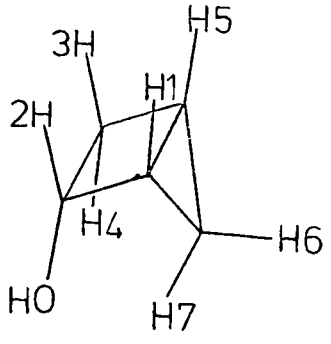
If the adduct had the endo-structure (2·2), then the bridge-head hydrogens would be expected to couple with the adjacent exo-hydrogens on the thiophene part of the adduct, with J = 5Hz.[138-140] Since H(1) and H(7) are singlets at 5·07 and 5·13, the adduct must have the exo-stereochemistry of (2·1). With regard to the position of the cyano group, if it was on the episulphide ring,

then what would be H(2) would be expected to couple with H(6) with J about 8Hz. The only coupling observed on H(6) is 1·3Hz, therefore there cannot be a hydrogen at the 2-position.

The coupling pattern observed on the thiophene part of the adduct is given below;

| | | |
|---|---|---|
| H(3) | 3·66 | J3,5 = 3·8, J3,6 = 1·3 |
| H(5) | 3·43 | J3,5 = 3·8 |
| H(6) | 2·76 | J3,6 = 1·3 |

The fact that H(5) and H(6) do not couple strongly to one another compared to the coupling between H(3) and H(6) is to be expected in bicyclo[2·1·0] systems. For example, in endo-bicyclo[2·1·0] pentan-2-ol, J4,5 = 0·48 whereas J1,4 = 1·0.[142]




That H(3) and H(6) do couple was confirmed (see later) by replacing H(5) by a methyl group. The only coupling then observed was J3,6 = 1·2Hz.

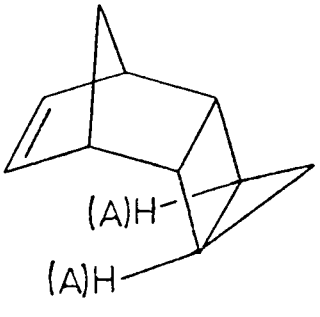
The minor of the two furan adducts obtained had a significantly different nmr spectrum from the major adduct - notably one of the hydrogens at the oxygen bridge-head had a large coupling of 5·5Hz to a hydrogen in the thiophene part of the adduct. This suggests structure (2·2) as a likely description since H(6) is predicted to couple to H(7) with J about 5Hz. The complete coupling pattern on this adduct is;

| | | |
|---|---|---|
| H(1) | 5·20 | J1,9 = 1·5 |
| H(3) | 3·30 | J3,5 = 3·5; J3,6 = 1·0 |
| H(5) | 3·08 | J3,5 = 3·5 |
| H(6) | 3·25 | J3,6 = 1·0; J6,7 = 5·5 |
| H(7) | 5·08 | J6,7 = 5·5; J7,8 = 1·5 |
| H(8) | 6·72 | J7,8 = 1·5; J8,9 = 6·0 |
| H(9) | 6·60 | J1,9 = 1·5; J8,9 = 6·0 |

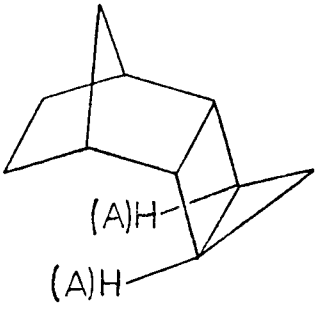
The large difference in chemical shifts of H(3) and H(5) in the exo-adduct compared to the endo-adduct, i.e.

| | | | |
|---|---|---|---|
| exo - H(3) | 3·66 | endo - H(3) | 3·30 |
| H(5) | 3·43 | H(5) | 3·08 |

is due to a shielding effect of the double-bond in the endo-stereochemistry. This is observed in the Diels-Alder adduct of bicyclo[2·1·0]pent-2-ene and cyclopentadiene.[145] In the adduct (2·5), H(A) are at 1·13, whereas in the dihydro compound (2·6), they are at 1·63.

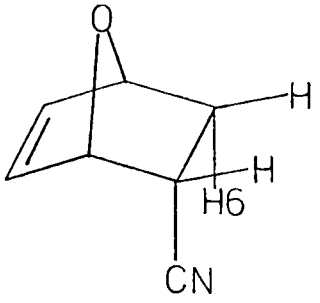



(2·5)

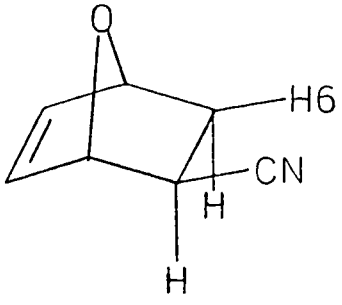



(2·6)

The large difference in chemical shift in H(6), i.e. 2·76 when it has an endo-stereochemistry and 3·25 when it is exo, is the same as that observed with the equivalent hydrogen in exo and endo-adducts of furan with acrylonitrile;[138]

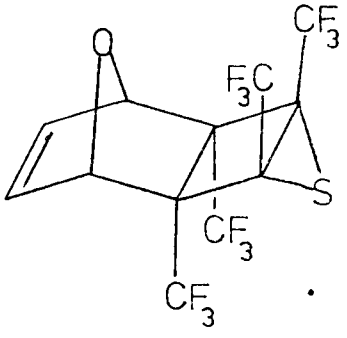



H(6) = 1·6




H(6) = 2·2

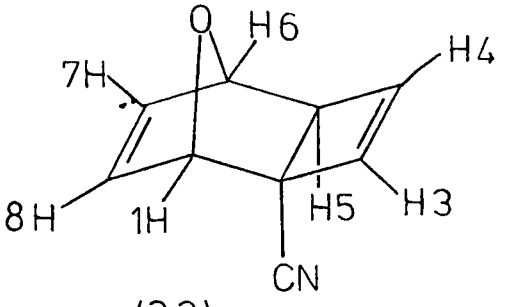
The stereochemistry of the furan adduct of tetrakis(trifluoro methyl)Dewar thiophene has been shown by X-ray analysis to be exo.[12]




Approach to the endo-face of the sulphur is sterically hindered in this case and hence only the exo-adduct is obtained. The stereochemistry of the episulphide ring in the two thiophene carbonitrile adducts must be as shown in (2·1) and (2·2), otherwise H(5) and H(6) would couple strongly.

Further structural proof of the adducts was obtained from their reaction with trimethyl phosphite. This is a reagent known

to give cis-elimination of sulphur with episulphides.[143,144] The major adduct gave the exo-tricyclic diene (2·3).

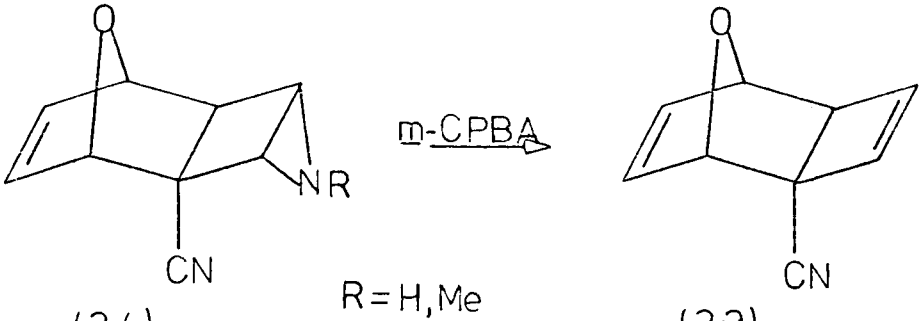



(2·3)

| | | |
|---|---|---|
| H(1) | 4·72 | |
| H(3) | 6·41 | J3,4 = 2·8 |
| H(4) | 6·28 | J3,4 = 2·8 |
| H(5) | 3·04 | |
| H(6) | 4·57 | |
| H(7) | 6·59 | |
| H(8) | 6·59 | |

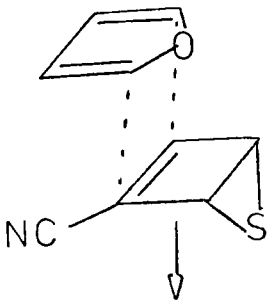
The new vinyl hydrogens H(3) and H(4) have chemical shifts and coupling constants characteristic of cyclobutenes.[146] The mass-spectral fragmentation pattern of this diene was interesting. Whereas the major fragmentation of the episulphide furan adduct was a retro Diels-Alder type of reaction to give furan radical cation, this was not the major process of the diene. This is because the retro Diels-Alder reaction would lead to a cyclobutadiene. Instead, the major fragmentation was loss of HCO.

The diene (2·3) has been obtained by Barltrop et al. following the reaction of M-chloroperoxybenzoic acid on the tetracyclic aziridines (2·4) obtained from the irradiation of pyrrole-2-carbonitriles in furan.[92] The spectroscopic and physical properties of these two dienes were identical.

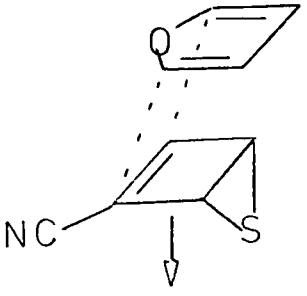



(2·4) (2·3)

The two adducts (2·1) and (2·2) are most easily derivable from addition of furan to 5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile (2·8). The major adduct (2·1) conforms to the endo-addition rule for Diels-Alder addition of furan to the dienophilic acrylonitrile moiety, whereas the minor adduct must come from exo-addition.

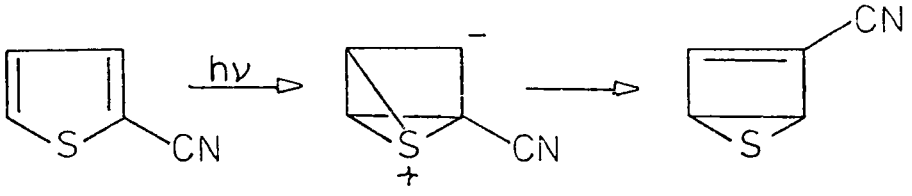



(2·1)



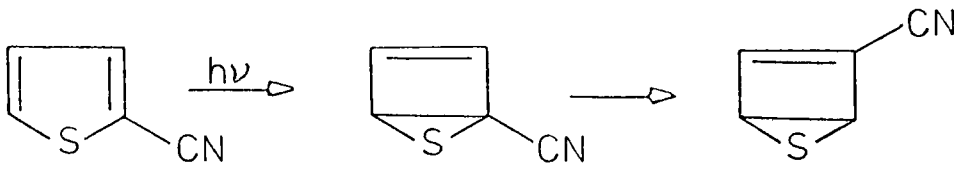

(2·2)

The Dewar thiophene (2·8) could be formed from thiophene-2-carbonitrile via a zwitterionic intermediate of the type (2·9).



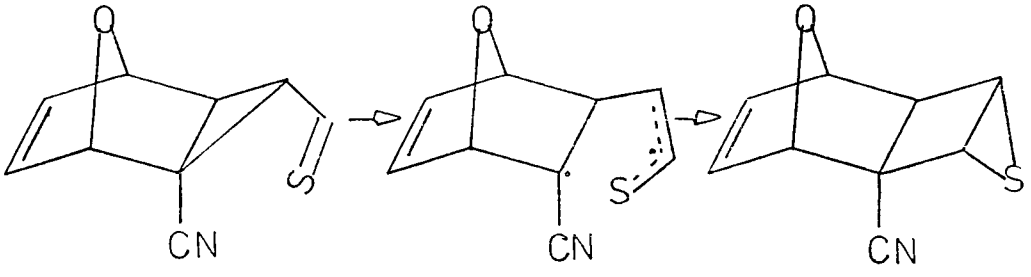

(2·9) (2·8)

Since evidence has already been presented which does not support the intermediacy of carbanionic types such as (2·9), it seems much more likely that (2·8) arises via a 'sulphur-walk' step from the first-formed Dewar isomer (2·7).




(2·7) (2·8)

It is not impossible to rationalise the formation of (2·1) and (2·2) in terms of addition of furan to other types of intermediates and subsequent thermal or photochemical rearrangements giving rise to (2·1) and (2·2). Thus, the adduct derived from addition of furan to a ring-contracted intermediate could rearrange, although this does not seem likely, Scheme 2·6. The analogous

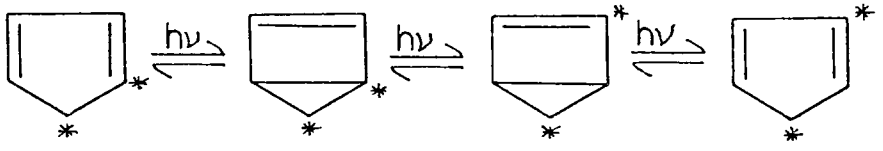



Scheme 2·6

adducts of furan-carbonitriles do not rearrange in this way.

The path by which the two thiabicyclo[2·1·0]pentenes (2·7) and (2·8) might interconvert is an intriguing problem. Clearly the 'walked' bicycle (2·8) is expected to be more stable than (2·7) since the cyano group is conjugated with the double-bond in (2·8). Also, of course (2·8) will be much more dienophilic than (2·7) and will be trapped preferentially by furan.

The process of 1,3- shifts of atoms or groups has often been postulated as occurring in unisolated and undetected heterocyclic[2·1·0] systems to account for phototransposition reactions of some five-membered heteroaromatic compounds. The parent bicyclo[2·1·0]compound, bicyclo[2·1·0]pent-2-ene, has been shown to undergo a photochemical degenerate 1,3-carbon shift.[148] 1,5[$^{13}C_2$]cyclopentadiene gave 2,5-[$^{13}C_2$]cyclopentadiene via the intermediate, isolable, bicyclo[2·1·0]pent-2-enes shown below in Scheme 2·7.




Scheme 2·7

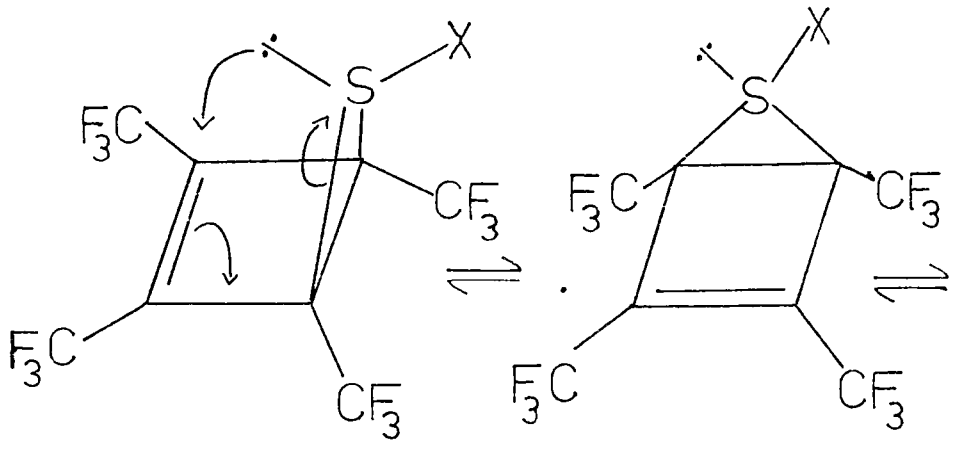
Tetrakis(trifluoromethyl)Dewar thiophene also undergoes a degenerate rearrangement.[131,149] Elevated temperatures are needed (190°) to effect the automerisation, and remarkably, aromatisation of the Dewar isomer to the thiophene is slow at that temperature ($t_{\frac{1}{2}}$ = 5·1h at 160°). The great resistance this molecule offers to opening of the 2,5-bridging bond is in striking contrast to the lability of the parent hydrocarbon, bicyclo[2·1·0]pent-2-ene, where $t_{\frac{1}{2}}$ = 4h at 34°, and ring-opening does not generate an aromatic system. The stability of this Dewar thiophene with regards to aromatisation is another manifestation of the perfluoroalkyl effect.[150]

The exo-sulphoxide derived from the Dewar thiophene isomerises much more rapidly than the episulphide. The process is not stopped until the temperature is lowered to -150°. The activation parameters for the process have been derived from the $^{19}F$ DNMR for both the episulphide and the sulphoxide;

| | EPISULPHIDE (157°) | EPISULPHOXIDE (-136°) |
|---|---|---|
| $\Delta G^{\ddagger}$ | 18·8 kcal/mole | 6·6 kcal/mole |
| $\Delta S^{\ddagger}$ | -7·7 kcal/mole | -0·5 kcal/mole |
| $\Delta H^{\ddagger}$ | 22·1 kcal/mole | 6·7 kcal/mole |

The difference in rates $k_2/k_1 \approx 3 \times 10^{10}$ at 25°.

The mechanism of the exchange in the sulphoxide and episulphide has been proposed to be a pseudopericyclic [1,3] - sigmatropic shift in which bonding and non-bonding orbitals at sulphur simultaneously change roles,[149] Scheme 2·8.




X = lone-pair or oxygen

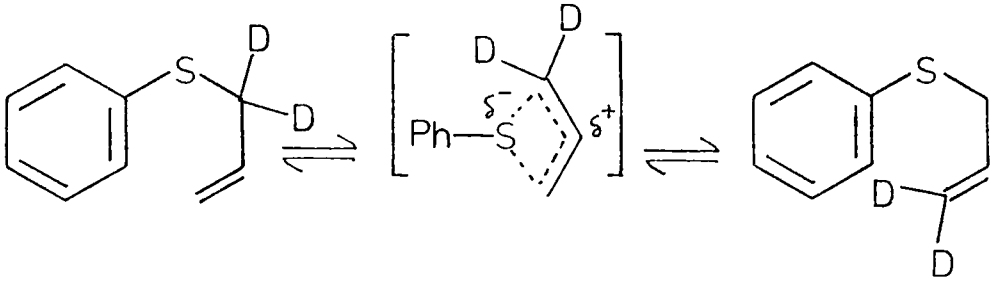
Scheme 2·8

A test for the importance of the lone-pair on the sulphur atom would be to investigate the sulphone derived from the Dewar

isomer, but as yet it has not been prepared. The sulphones of thiabicyclo[2·1·0]pentanes are unstable and undergo elimination reactions to give thiophene-1,1-dioxides, or cyclobutane scission to give divinyl sulphones.[259]

Another possible mechanism for the isomerisation might be *via* a singlet biradical formed by C-S bond homolysis. This, however, seems unlikely since the activation enthalpy should be more than twice the experimental value of 18·8 kcal/mole. From thermochemical data, D(episulphide $\longrightarrow$ ·C-C-S·) = 52 kcal/mole.[151]

There is evidence in the literature that allylic sulphides undergo thermal rearrangement by a dipolar or ionic mechanism,[152,153] Scheme 2·9.



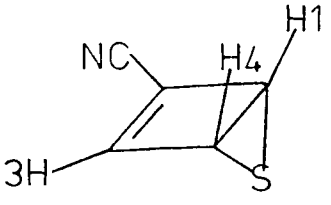

Scheme 2·9

This rearrangement also occurs photochemically, and then the rearrangement is thought to occur *via* a radical chain mechanism.[165]

This type of ionic mechanism does not seem likely to occur in thiophene-2-carbonitrile photochemistry since the irradiation in deuteriomethanol showed no deuterium incorporation nor any methanol adduct formation.

## 2.2.3 Irradiation of thiophene-3-carbonitrile; observation of an unstable intermediate.

It was of considerable mechanistic interest to irradiate thiophene-3-carbonitrile to ascertain whether or not the observed photoisomerisation was reversible. Irradiations of the 3-nitrile in solvents such as acetonitrile and cyclohexane showed that the reverse reaction did take place, and that it was more efficient by a factor of at least 3. An additional bonus was obtained from the irradiations in cyclohexane in that, one of the two bicyclic species proposed as being involved in the phototransposition 5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile (2·8) was formed in about 1% yield.




(2·8)

n.m.r; H(1) 4·15 J1,3 = 4·0, J1,4=4·0

H(3) 7·14 J1,3 = 4·0

H(4) 3·83 J1,4 = 4·0

The chemical shifts of H(1) and H(4) are in the expected region, and J1,4 is of the usual order for cis-episulphide hydrogens.[170] H(3) is similarly correctly placed for a 1-cyanocyclobutene.[154] The large coupling J1,3 and a negligible value for J3,4 are typical for cyclobutene systems.[155] In cyclobutene itself, their values are 2·70 and 0·80 respectively.

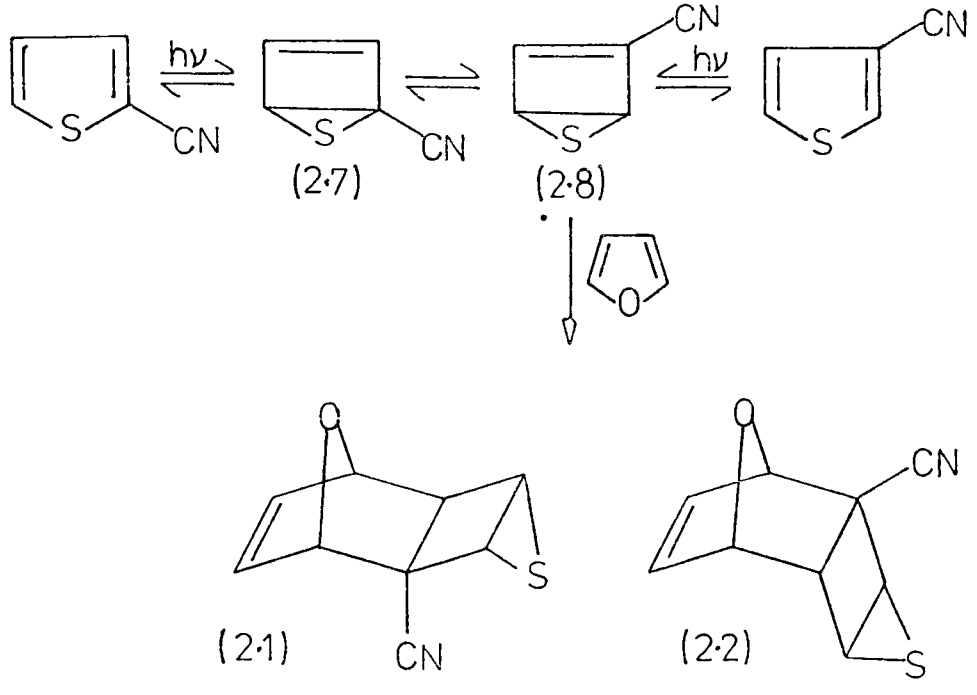
This compound was too sensitive to be obtained in a pure state by layer or column chromatography, but as will be seen below, there can be no doubt as to its identity and role in the phototransposition reaction.

Addition of furan to a sample of the bicycle (2·8) contaminated with thiophene-3-carbonitrile in chloroform resulted in the

quantitative conversion of it to a mixture of the exo- and endo- furan adducts (2·1) and (2·2). Isolation of these two adducts by p.l.c. showed them to be identical in every way to the adducts obtained photochemically from thiophene-2-carbonitrile. Thus, it seems fairly certain that the adducts formed in the photochemical reaction arise from the thermal addition of furan to the sulphur-walked Dewar isomer (2·8).

Irradiation of thiophene-3-carbonitrile in furan gave high yields of the two adducts (2·1) and (2·2). The ratio of exo- and endo- adducts was the same as that obtained by both the thermal reaction of furan with the bicyclic compound (2·8) and by the photochemical reaction with thiophene-2-carbonitrile. The yield of adducts from the 3-cyano compound was at least four times higher than from the 2-cyano compound.

These results strongly suggest that photochemical excitation of either thiophene-2-carbonitrile or 3-carbonitrile leads to the situation depicted in the Scheme 2·10 below. Several points




Scheme 2·10

are not clear about this scheme, however. For example, it is not known whether the isomerisation between (2·7) and (2·8) is a thermal or photochemical step, and also, no direct evidence for the intermediacy of (2·7) exists. The next section will describe experiments designed to detect (2·7), and sections 2·25 and 2·26 will describe experiments showing that the interconversion of (2·7) and (2·8) can occur thermally.

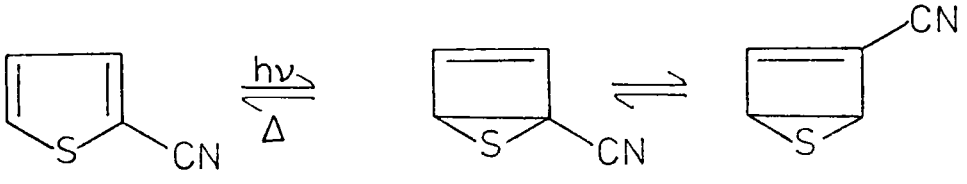
### 2.2.4 Low-temperature irradiation of thiophene-2-carbonitrile.

Up to this time, no direct evidence had been obtained to support the intermediacy of the bicyclic compound (2·7). In an attempt to observe this species before it rearomatised to the thiophene or rearranged to the conjugatively more stable isomer (2·8), some irradiations were carried out at low temperatures. In one experiment thiophene-2-carbonitrile was irradiated in an nmr tube as a solution in tetrahydrofuran at $-68^{\circ}$. After 3h irradiation the nmr tube was rapidly transferred to an nmr spectrometer with the probe cooled to $-70^{\circ}$. The nmr spectrum then recorded did not show the presence of either (2·7) or (2·8), and further, did not show any transposed product. This tends to suggest that there is either a thermal barrier to formation of the 2,5-bond from the excited state thiophene, or, more likely, a thermal barrier to the rearrangement (2·7) to (2·8). Even at $-68^{\circ}$, rearomatisation of (2·7) must be a facile process.

A further attempt to detect the bicyclic compound (2·7) was made by irradiating thiophene-2-carbonitrile at 75K. This was achieved by applying a solution of the nitrile in 2:1 tetrahydrofuran:dichloromethane solvent to a sodium chloride window

at 160K, and then further cooling this with liquid nitrogen in an Oxford Instruments cryostat. Irradiation of this sample for 3h revealed in the infra-red spectrum that the sharp nitrile band at 2225cm$^{-1}$ had decreased in intensity and that a shoulder had appeared on it, on the high wave - number side at 2235cm$^{-1}$. On warming the sample up, the shoulder disappeared between 130 and 138K, while at the same time, the original intensity returned to the band at 2225cm$^{-1}$.

This result is compatable with the idea that irradiation at 75K leads to the formation of the 2,5-bonded bicycle (2·7) with the cyano group at the bridge position, non-conjugated, and hence appearing at higher wavenumber in the infra-red spectrum. On warming to 130K, the compound is able to rearomatise but does not have enough energy to overcome the thermal barrier to the sulphur-walk step. One could argue that in the i.r., the cyano band of (2·8) would not be distinguishable from that of the starting-material, but had (2·7) walked to (2·8), one might have




(2·7) (2·8)

expected to see either (2·8) or thiophene-3-carbinitrile in the low-temperature n.m.r. experiment, since (2·8) is known to be thermally stable at 35°. It seems likely that there is either no, or a very low thermal barrier to 2,5-bonding from the excited-

state, but that the barrier to sulphur-walking of (2·7) is higher at low temperatures than the barrier to rearomatisation.

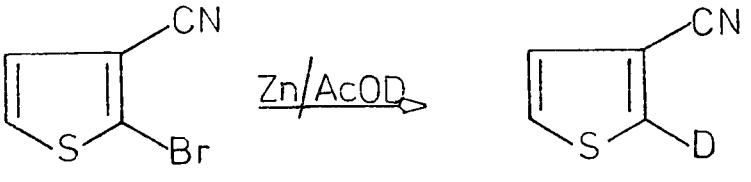
If the infra-red spectrum at 75K is detecting the presence of (2·7), then some explanation as to the relative ease of rearomatisation of the bicycle (2·7) with a bridgehead cyano group compared to (2·8) with a conjugated cyano group is necessary.

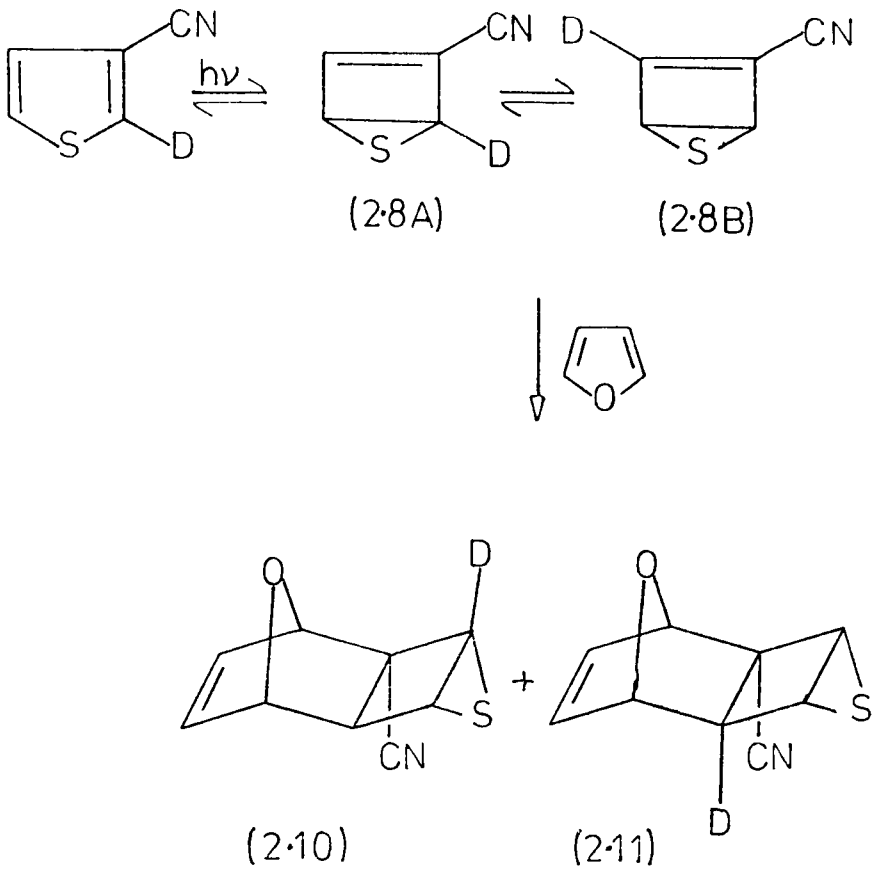
The Woodward-Hoffmann rules predict that rearomatisation of (2·7) should not occur thermally in a concerted manner.[156] However, related systems such as bicyclo[2·1·0]pent-2-ene and Dewar benzene are converted into cyclopentadiene and benzene respectively in solution at room temperature. Calculations have shown that in the case of bicyclo[2·1·0]pent-2-ene, the transition state has a symmetrical structure and that the conversion is a normal concerted electrocyclic process.[157] Thus, all else being equal, the rearomatisation of (2·7) is expected to be easier than that of (2·8) since the latter is stabilised relative to (2·7) by the 1·3 kcals/mole delocalisation energy[261] gained from the conjugated acrylonitrile system. On the other hand, if rearomatisation is not a truly concerted process for these 5-thiabicyclo[2·1·0]pent-2-enes, then the transition state for rearomatisation of (2·7) will be stabilised relative to that of (2·8), since opening of the bridging cyclobutene $\sigma$-bond will involve some charge separation, and the bridgehead cyano group will be able to stabilise negative charge at the adjacent carbon. In this way (2·7) will still be predicted to rearomatise more readily than (2·8). Acceleration of cyclobutene ring-opening reactions in the presence of bridgehead substituents which are either electron-attracting or electron-releasing is a general observation.[158,159]

In sections 2.2.7 and 2.2.8 below, much clearer evidence for the intermediacy of bridgehead cyano bicyclic compounds can be found. Here, the extra stabilisation energy gained by incorporating a methyl group on the double-bond in such compounds is shown not only to enable them to be identified by nmr spectroscopy at low temperatures, but also to enable isomerisation to their more conjugatively stable isomers with the cyano group on the double-bond to be studied.

## 2.2.5 Irradiation of 2-deuteriothiophene-3-carbonitrile in furan.

Returning to the phototransposition reaction of thiophene-3-carbonitrile in furan, it was felt important for two reasons to synthesise and irradiate 2-deuteriothiophene-3-carbonitrile. Firstly to check the structure and coupling assignments in the furan adducts (2·1) and (2·2), and secondly to see if a degenerate rearrangement of the bicyclic intermediate (2·8) would take place. Work up of an irradiation of the deuteriated compound in furan gave an adduct with nmr ($CDCl_3$) 2·76(S-$\frac{1}{2}$H), 3·43(S and overlapping d-1H), 3·66(d-$\frac{1}{2}$H), 5·07(S-1H), 5·13(S-1H), 6·53(S-2H). This nmr is consistant with the presence of a 1:1 mixture of (2·10) and (2·11) shown below, and is most simply rationalised as follows, Scheme 2.11.






Scheme 2·11

Excitation of the thiophene gives rise to the bicycle (2·8A) which rapidly equilibrates with (2·8B) via a sulphur walk step. The rate of furan addition must be slow compared to the rate of isomerisation and so the nett result is isolation of an approximate 1:1 mixture of (2·10) and (2·11). These structures are entirely consistant with the previous analysis of the nmr spectrum of (2·1).

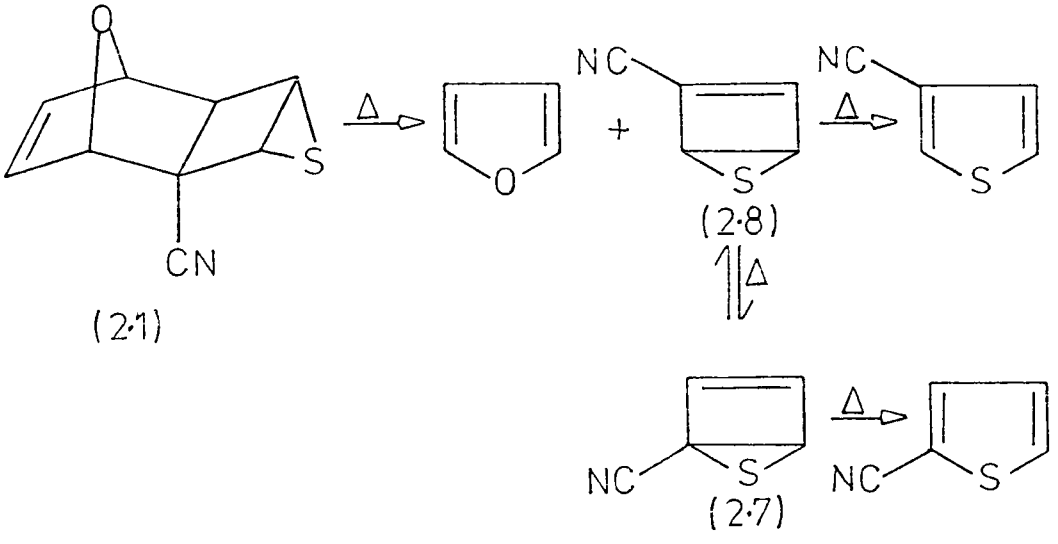
It is most improbable that the position of deuterium in the adducts (2·10) and (2·11) could be the result of some selective radical reaction. The retention of the sequential order of carbon atoms in the thiophene ring is entirely consistant with the proposed mechanism for the isomerisation and adduct formation

reactions. The observed isomerisation here of bicycle (2·8A) and (2·8B) will be shown below to be a thermal reaction. The importance of thermal steps as well as photochemical steps in the isomerisation of thiophenes and their bicyclic intermediates is demonstrated in the experiment described next.

2.2.6 Pyrolysis of furan adducts.

The Diels-Alder reaction is known to be reversible and furan adducts in particular are known to be thermally labile.[160] Thus in principle, one might expect pyrolysis of (2·1) to give both furan and 5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile.

In practice, adduct (2·1) was found to be thermally labile. Pyrolysis in a sealed tube at 170° yielded furan, thiophene-3-carbonitrile and thiophene-2-carbonitrile. These latter two compounds were found to be present in the ratio 1:1, Scheme 2·12.

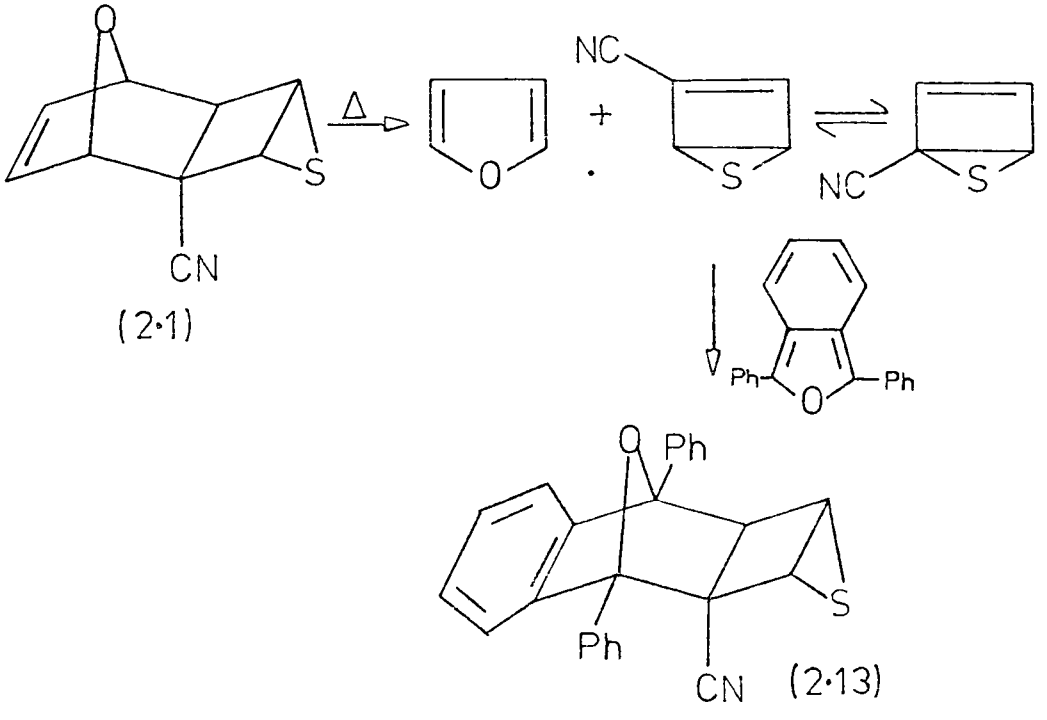



(2·1)

Scheme 2·12

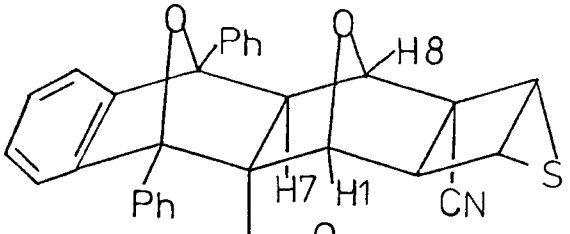
This experiment demonstrates two important points. It shows that rearomatisation of (2·7) and (2·8) can occur thermally as well as photochemically. It also shows that sulphur-walking of the bicyclic compounds becomes increasingly favoured with respect to rearomatisation as the temperature is increased. The irradiations of thiophene-2-carbonitrile at 75K and at -68° show that at extreme temperature limits, thermal sulphur-walking is effectively stopped. The sensitivity of isomerisation to temperature is important and will be pursued when the photochemistry of some other thiophene-carbonitriles is discussed later.

In an attempt to demonstrate the intermediacy of thiabicyclo [2·1·0]pentenes in the pyrolysis of furan adducts, (2·1) was pyrolysed in the presence of some other furans in the hope that some cross-product adducts might be formed in addition to the normal pyrolysis products. The very reactive furan, 2,5-diphenyl-3,4-benzofuran was used in one experiment in the hope of reproducing Scheme 2·13 shown below.

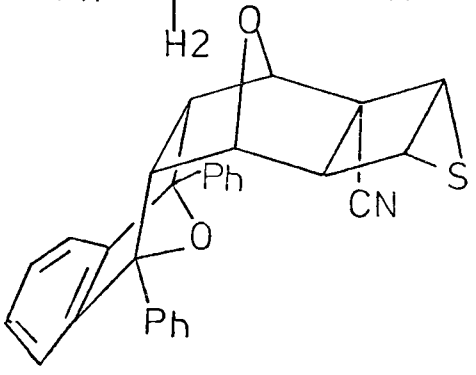



Scheme 2·13

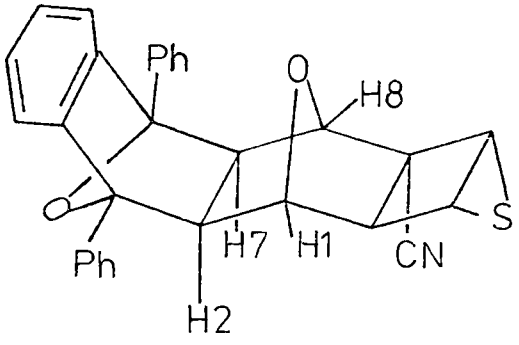
(2·13) might be expected to be more thermally stable than (2·1) since resonance energy is lost in the retro Diels-Alder reaction. However the isobenzofuran proved to be a little too reactive since pyrolysis of (2·1) at 170° in the presence of diphenylisobenzofuran gave mainly the thermally stable adduct exo, exo-3,6-diphenyl-14,15,11-dioxathia-4,5-benzohexacyclo [6·5·$^{1}_{1}$$^{1,8}_{1}$$^{3,6}$. $_{0}$.$^{2,7}$ $_{0}$.$^{9,13}$ $_{0}$.$^{10,12}$] pentadecane-9-carbonitrile (2·12A), derived by addition of the isobenzofuran across the




(2·12A)




(2·12B)



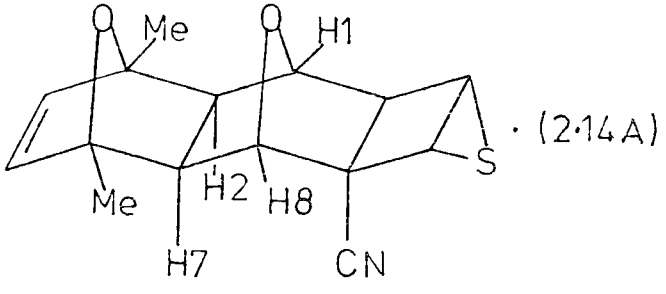

(2·12C)

double bond of (2.1).

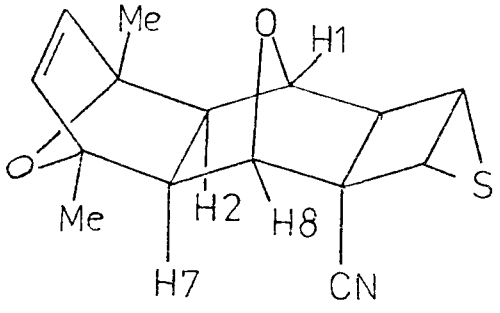
The stereochemistry of this adduct is deduced to be exo, exo-(2·12A) and not (2·12B) from the nmr spectrum. H(1) and H(8) appear as singlets, whereas in the adduct (2·12B) they

should appear as doublets through coupling with (H2) and H(7). The lack of coupling between bridgehead protons and endo-protons has proved general and is to be expected from the Karplus correlation, since the relevant dihedral angles are found from models to be about 90°.[161] The nmr spectrum also distinguishes (2·12A) from the endo, exo-isomer (2·12C). This structure would also show no doupling between the bridgehead and the endo-protons. In these types of isobenzofuran adducts, the phenyl groups orientate themselves so that they are approximately in the plane of the oxygen-bridge to minimise steric interactions.[163] The protons H(2) and H(7) of (2·12A) are just outside the shielding cone of the phenyl groups and are thus deshielded, occurring at 2·56 and 3·05. In adduct (2·14B) where this deshielding is absent, H(2) and H(7) occur at 1·85 and 2·35.

There was no evidence from this experiment for the formation of any adduct of the type (2·13), and so the experiment was repeated with the less reactive 2,5-dimethylfuran. Pyrol ysis of the adduct (2·1) in the presence of 2,5-dimethylfuran gave the two adducts (2·14A) and (2·14B).




· (2·14A)

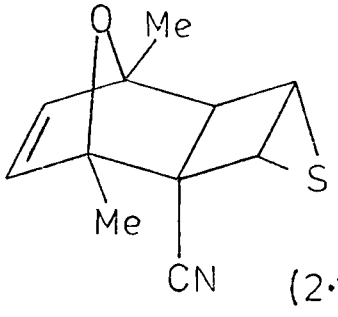



(2·14B)

As before, the stereochemistry of the original furan adduct part of the molecules is unchanged as determined by nmr spectroscopy. In both (2·14A) and (2.14B) there is no coupling between the oxygen-bridgehead hydrogens and H(2) and H(7). In general for these norbornene-type systems, exo-hydrogens resonate at lower field than endo-hydrogens, thus in (2·14A), H(2) and H(7) are endo- with chemical shifts of 1·55 and 2·32, while in (2·14B), where the same two protons are exo, the resonances are at 1·85 and 2·35 respectively.

Similar 2:1 furan adducts have been obtained by treatment of 3,3,4,4-tetrafluorocyclobutene with furan at 100°.[162]

The pyrolysis of (2·1) with 2,5-dimethylfuran did not produce

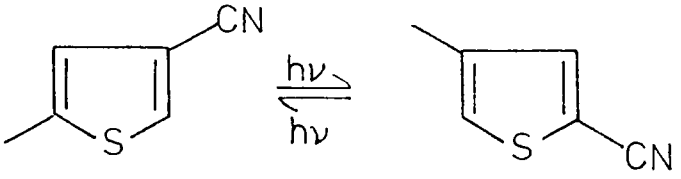



(2·15)

any adduct of the type (2·15). It is probable that the only way to effect an interchange of diene component in these systems would be to start with a more thermally labile adduct, allowing the pyrolysis to be carried out at a lower temperature. In practice however, a reactive diene component is needed to trap the thiabicyclopentene system in reasonable yield, and this precludes the formation of a thermally labile adduct.

## 2.2.7 Irradiation of methylthiophene-3-carbonitriles; isolation of a stable 5-thiabicyclo[2·1·0]pentene.

Since a mechanistic scheme for the transposition reactions of thiophene-carbonitriles was becoming clear, it was felt necessary to test whether the predictions it made would be borne out in practice over a wider range of cyanothiophenes. For example, in the mechanistic scheme illustrated in Scheme 2·10, 5-methylthiophene-3-carbonitrile will reversibly give 4-methylthiophene-2-carbonitrile.




(2·16) (2·17)

The three methylthiophene-3-carbonitriles were synthesised by treatment of the appropriate monoiodo or monobromo compound with copper(I) cyanide in boiling quinoline. They were each irradiated under a variety of conditions and the transposition products are listed in Table 2·1.

Identification of each isomer was not difficult since all of the six possible methylthiophene-carbonitriles could be separated from each other by g.c. using a 50ft carbowax 20M SCOT column at 150-170°. Use could also be made of g.c.m.s. and, in some cases, n.m.r. spectroscopy. The analytical techniques used for the analysis of photolysis mixtures were also capable of detecting dicarbonitriles and simple methylthiophenes.

STARTING MATERIAL

TRANSPOSITION PRODUCTS

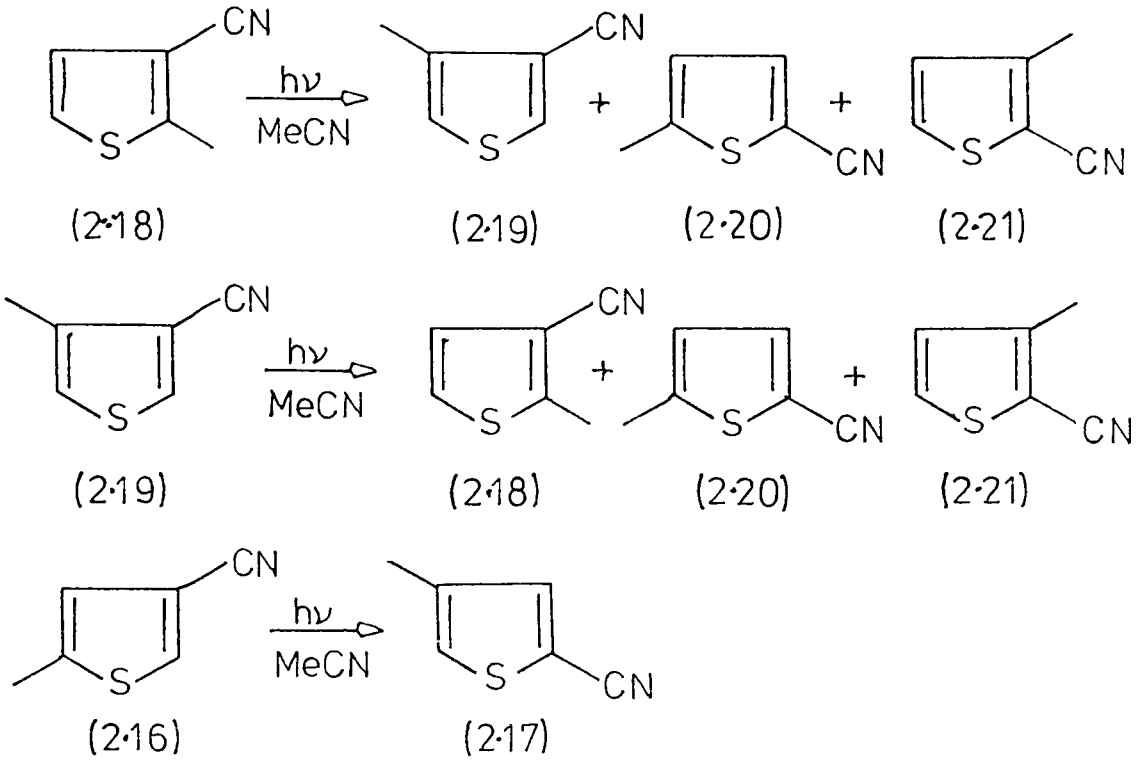


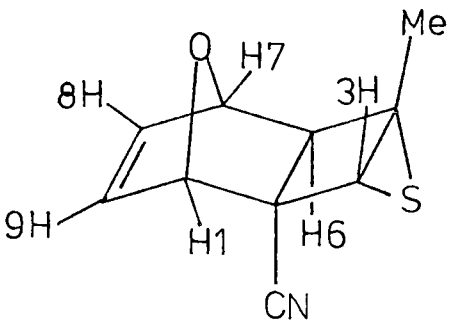

Table 2·1

It may be seen that in each case, only products in which the carbon atom sequential order has not changed are formed. This is in complete agreement with the proposed mechanism of the transposition reactions involving excitation to give a 2,5-bonded 5-thiabicyclo[2·1·0]pent-2-ene which can then undergo one or more sulphur-walk steps to give, subsequent to rearomatisation the transposed thiophene.

However, each thiophene revealed much more of mechanistic interest than can be shown in a Table, and so each will be discussed separately.

5-methylthiophene-3-carbonitrile.

Irradiation of this isomer in cyclohexane gave a 5% conversion to 4-methylthiophene-2-carbonitrile. Evidence that the transposition reaction proceeded via the bicyclic Dewar isomer (2·23) was provided by the isolation of the furan adduct (2·22) after irradiation of the nitrile (2·16) in furan solution.




(2·22)

n.m.r. $CH_3$ 1·64

H(1) 5·00

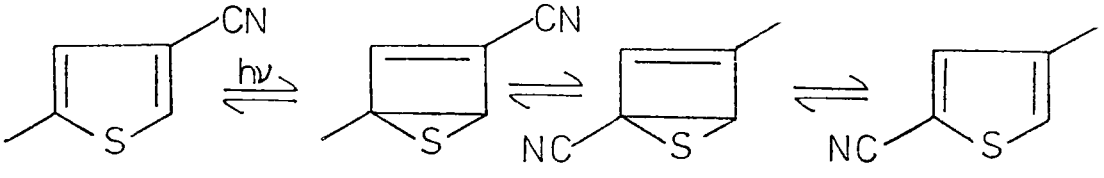
H(3) 3·55; $J_{3,6}$=1·2

H(6) 2·75; $J_{3,6}$=1·2

H(7) 4·93

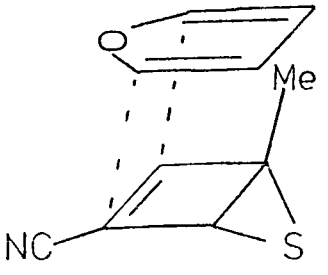
H(8) 6·45

H(9) 6·45



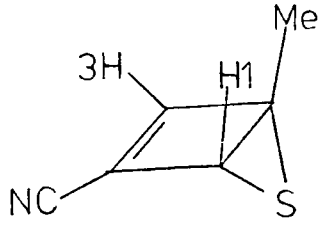

(2·16) (2·23) (2·24) (2·17)

The adduct expected from exo-addition of furan to (2·23) was not observed. This may be due to steric interference in



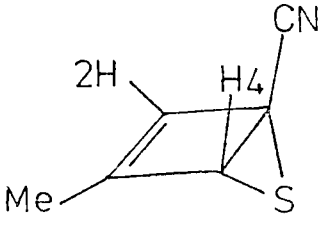
the endo-transition state making it a much less favourable mode of addition than in the case of addition to (2·8).

At the normal temperature of irradiation in the RPR(34°), neither of the two bicyclic compounds (2·23) or (2·24) could be detected. In an attempt to observe these species, an irradiation was performed at -68°in tetrahydrofuran solution. The nmr spectrum of this solution recorded at -70° revealed the presence of mainly starting material, a small amount (<1%) of 4-methylthiophene-2-carbonitrile, 0·65% of 4-methyl-5-thiabicyclo [2·1·0]pent-2-ene-2-carbonitrile (2·23), and 0·3% of 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-1-carbonitrile (2·24).




(2·23)

nmr (THF,-70°) $CH_3$ 2·09
H(1) 4·48; $J_{1,3}$=4·4
H(3) 7·39; $J_{1,3}$=4·4




(2·24)

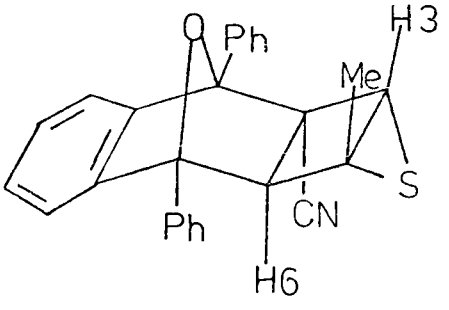
nmr (THF,-70°) $CH_3$ 2·05; $J_{2,CH_3}$=1·8
H(2) 6·31; $J_{2,CH_3}$=1·8, $J_{2,4}$=3·9
H(4) 4·63; $J_{2,4}$ = 3·9

The nmr spectra of these two isomers show the expected cross-ring coupling of about 4Hz. In isomer (2·24), the coupling of the methyl group shows it to be on the double-bond, and H(4), being adjacent to the cyano group as well as being allylic, is at lower field than H(1) in (2·23).

On allowing this nmr sample to warm up to -40°, 80% of the signal intensity of (2·24) disappeared, while the signal intensity of (2·23) increased by about 30%. A corresponding increase in intensity of 10% was observed in the signal intensity of 4-methylthiophene-2-carbonitrile. On further warming to 0°, all of the signals due to (2·24) had disappeared, and in addition, a 50% decrease in the intensity of the signals due to (2·23) was observed. On warming to +25°, all of the signals due to (2·23) had disappeared.

It is probable that no thermal equilibrium is established between (2·23) and (2·24) at low temperatures, but that at -40°, (2·24) is converted irreversibly to (2·23). Since the thermal reaction (2·23) to (2·24) must be an uphill reaction energy-wise, it is likely that at -60°, (2·24) is formed photochemically from (2·23).

An attempt to chemically trap (2·24) was not very successful. 2,5-diphenyl-3,4-benzofuran was added to a mixture of (2·23) and (2·24) at -68°. The major product obtained was the adduct (2·25), derived from Diels-Alder addition to (2·23). The nmr spectrum




| | | |
|---|---|---|
| nmr | $CH_3$ | 1·21 |
| | H(3) | 3.54 |
| | H(6) | 3·48 |

(2·25)

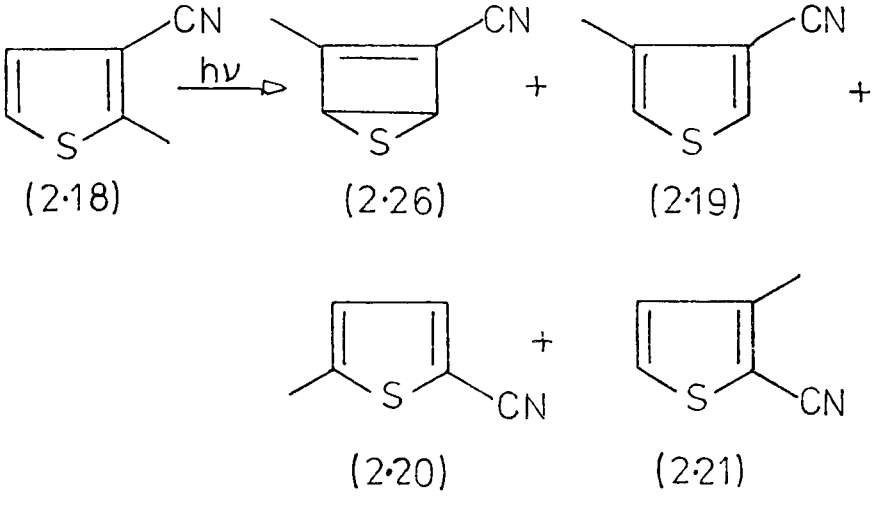
of this adduct is interesting. The methyl group in the 5-position is in the long-range shielding cone of the bridgehead 7-phenyl

substituent and is strongly shielded.[163] Thus it occurs about 0·4 ppm upfield from where it resonates in adduct (2·22) without the phenyl group. On the other hand, H(6) is strongly deshielded at resonates 0·7 ppm to lower field than the equivalent proton in (2·22).

A very small amount of an adduct was formed with a methyl group at 1·43 in the nmr spectrum. This may be due to a small amount of adduct derived from (2·24). The 2,5-diphenylisobenzofuran is expected to react rapidly with (2·23), but probably reacts only sluggishly with (2·24) at -68°.

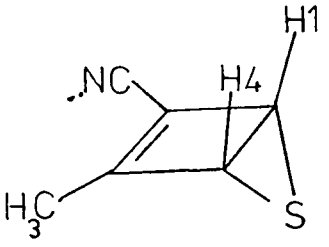
2-methylthiophene-3-carbonitrile

Irradiation of 2-methylthiophene-3-carbonitrile in cyclohexane gave the sulphur-walked bicycle, 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile (2·26) as the primary photochemical product. Further irradiation produced a 15% yield of 4-methylthiophene-3-




carbonitrile (2·19), and small amounts of both 5-methylthiophene-2-carbonitrile (2·20) and 3-methylthiophene-2-carbonitrile (2·21). In this case, the bicyclic compound was stable and could be

isolated and purified by layer chromatography. Full spectroscopic and analytical data for it are given in the Experimental Section and the nmr spectrum is also given below. The nmr data are given for two different temperatures because

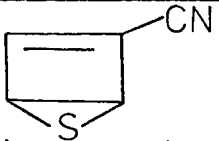
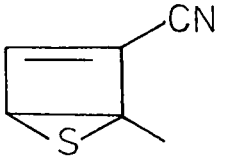
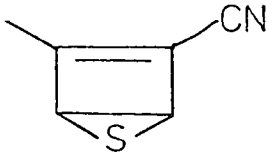
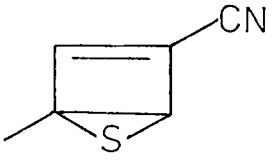
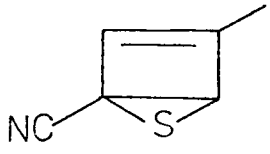
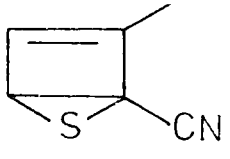



(2·26)

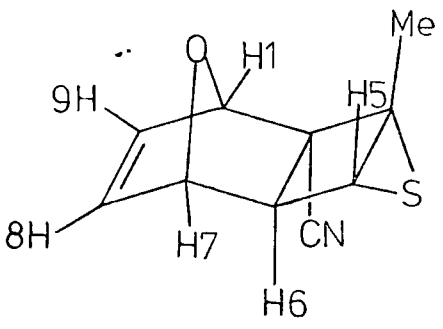
| | | |
|---|---|---|
| nmr (THF, -70°) | $CH_3$ | 2·01; $J_{1,CH_3}$=0·9 |
| | H(1) | 4·42; $J_{1,CH_3}$=0·9, $J_{1,4}$ =3·5 |
| | H(4) | 4·12; $J_{1,4}$ =3·5 |
| nmr ($CDCl_3$, 35°) | $CH_3$ | 2·03 |
| | H(1) | 4·03 |
| | H(4) | 3·76 |

it was only possible to measure the nmr spectra of certain other bicyclic compounds at low temperature. The change in chemical shift of some protons with decrease in temperature is probably due to increased importance of specific solvent interactions.[58] The chemical shifts and coupling constants of this intermediate are all in the expected regions and compare well with other Dewar thiophenes (see Table 2·2).

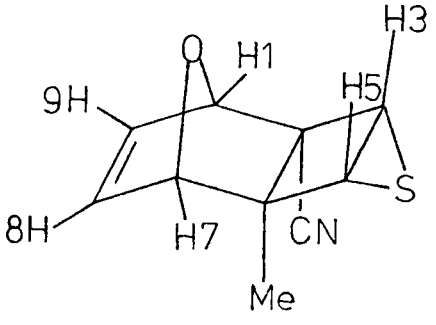
TABLE 2·2

| DEWAR THIOPHENE | CHEMICAL SHIFTS (THF, -70°) | | | | |
|---|---|---|---|---|---|
| | $CH_3$ | H(1) | H(2) | H(3) | H(4) |
|  $J_{1,3}=4·0$; $J_{1,4}=4·0$ | | 4·50 | | 7·49 | 4·18 |
|  no coupling | 2·04 | | | 7·48 | 4·26 |
|  $J_{1,CH_3}=0·9$, $J_{1,4}=3·5$ | 2·01 | 4·42 | | | 4·12 |
|  $J_{1,3}=4·4$ | 2·09 | 4·48 | | 7·39 | |
|  $J_{2,CH_3}=1·8$, $J_{2,4}=3·9$ | 2·05 | | 6·31 | | 4·63 |
|  $J_{3,CH_3}=1·5$ | 2·11 | | | 6·29 | 4·68 |

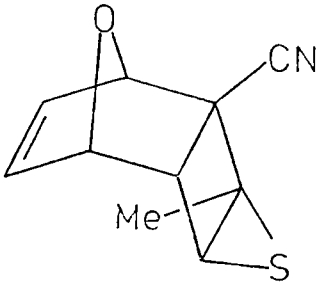
Irradiation of the nitrile (2·18) in furan solution produced four adducts. Two of them, major products in a ratio of 1 to 1, had exo-stereochemistry, and the two minor products had endo-stereochemistry.



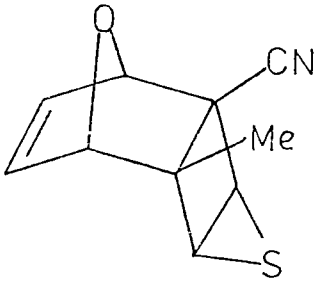

(2·28)




(2·29)




(2·30)



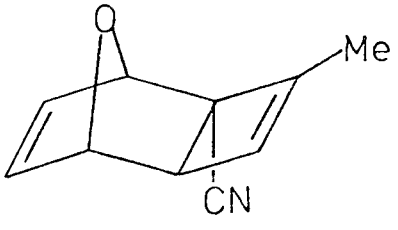

(2·31)

Attempts to separate the two exo-adducts (2·28) and (2·29) by layer chromatography, column chromatography, sublimation and fractional crystallisation were unsuccessful. Under gas chromatographic conditions the adducts gave broad, tailing peaks indicating decomposition. The nmr assignments, particularly of the furan part of the adducts, was made simpler by a further

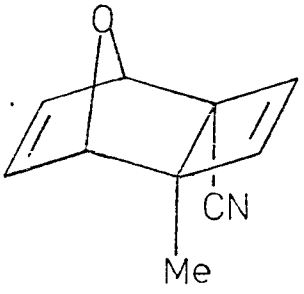
experiment (see below) which produced mainly (2·28) with only a small amount of (2·29).

| n.m.r. | (2·28) | | (2·29) | |
|---|---|---|---|---|
| | $CH_3$ | 1·73 | $CH_3$ | 1·15 |
| | H(1) | 5·07 | H(1) | 5·03 |
| | H(5) | 3·38 | H(3) | 3·62; $J_{3,5}$ = 4·0 |
| | H(6) | 2·26 | H(5) | 3·53; $J_{3,5}$ = 4·0 |
| | H(7) | 4·96 | H(7) | 4·88 |
| | H(8) | 6·53 | H(8) | 6·53 |
| | H(9) | 6·53 | H(9) | 6·53 |

Treatment of the mixture of (2·28 and (2·29) with trimethylphosphite gave, on work up, the two dienes (2·28A) and (2·29A). These were stable to gas chromatographic analysis, the retro Diels-Alder reaction being unfavourable because of the formation of cyclobutadiene, and could be separated with retention times of 16·5 and 17·5 min on Apiezon L at 164°.




(2·28A)




(2·29A)

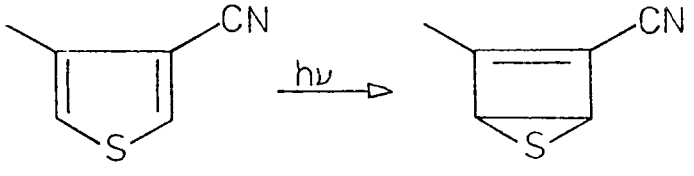
The two minor endo-adducts (2·30) and (2·31) were not present in the ratio 1 to 1, but in the ratio 1 to 3. This again is probably due to steric interference of the 1-methyl

group of (2·27) in the transition state leading to (2·30). It was not possible to separate these two adducts by column or layer chromatography.

| n.m.r. | (2·30) | | (2·31) | |
|---|---|---|---|---|
| | $CH_3$ | 1·58 | $CH_3$ | 1·45 |
| | H(1) | 5·14 | H(1) | 5·15 |
| | H(5) | 3·25 | H(3) | 3·25; $J_{3,5}$ = 3·5 |
| | H(6) | 3·20; $J_{6,7}$ = 5·0 | H(5) | 3·02; $J_{3,5}$ = 3·5 |
| | H(7) | 5·03; $J_{6,7}$ = 5·0 | H(7) | 4·77 |
| | H(8) | 6·68 | H(8) | 6·66 |
| | H(9) | 6·68 | H(9) | 6.66 |

4-methylthiophene-3-carbonitrile

The photochemistry of nitrile (2·19) was found to be very similar to that of 2-methylthiophene-3-carbonitrile. Thus,

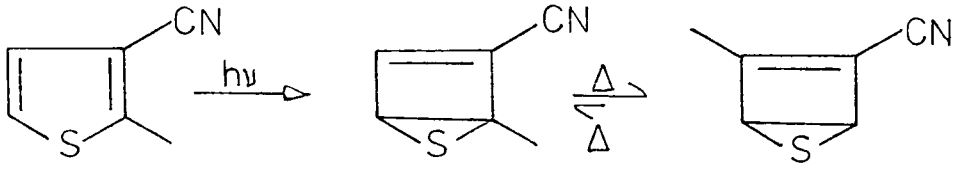



(2·19) (2·26)

irradiation of (2·19) gave the bicyclic compound (2·26) as the primary photochemical product. Further irradiation produced the transposed thiophenes (2·18), (2·20) and (2·21) in the ratio 10:1:1 respectively.

## 2.2.8 Observation of facile thermal isomerisation of 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile.

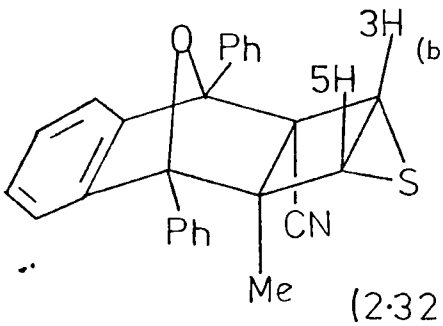
Treatment of the bicyclic intermediate (2·26) with furan gave a very interesting result. Instead of giving a single exo-adduct (2·29), it gave a 1 to 1 mixture of (2·28) and (2·29). This thermal result was identical to that obtained from irradiation of 2-methylthiophene-3-carbonitrile in furan.




(2·18) (2·27) (2·26)

This result indicates that bicyclic intermediates (2·26) and (2·27) must be in thermal equilibrium at ambient temperatures, but since nmr spectroscopy reveals only (2·26), the equilibrium must be mainly in favour of (2·26). However, furan will be expected to add to (2·27) very much more faster than to (2·26). The rates of addition of furan to (2·27) and (2·26) may differ by a factor of over $10^3$ if one compares them to substituted acrylonitriles.[147] Thus the situation has been reached where the difference in rates of addition of furan to (2·26) and (2·27) compensates for their different thermal stabilities, giving an adduct ratio of 1 to 1.

This theory was tested by reacting (2·26) with a very reactive and much less selective diene, 2,5-diphenyl-3,4-benzofuran.

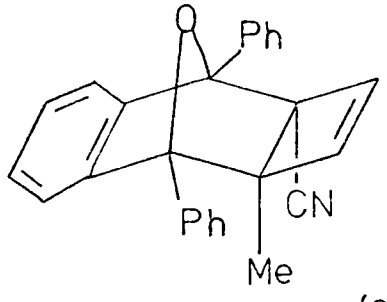



(2·32)

nmr (benzene)

| | |
|---|---|
| $CH_3$ | 1·08 |
| H(3) | 3·24; $J_{3,5}$ = 4·0 |
| H(5) | 3·15; $J_{3,5}$ = 4·0 |

This resulted in the exclusive formation of (2·32). The structure of this adduct was further established by treatment with trimethylphosphite to give the cyclobutene (2·33).



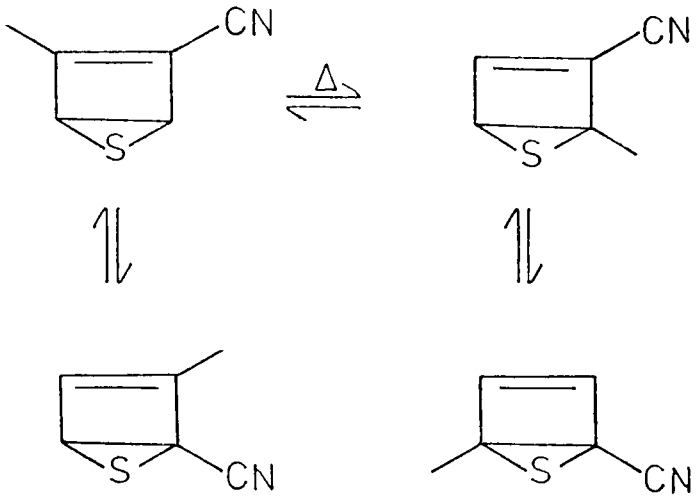

(2·33)

nmr

| | |
|---|---|
| $CH_3$ | 1·40 |
| H(3) | 6·32; $J_{3,4}$ = 3·0 |
| H(4) | 6·06; $J_{3,4}$ = 3·0 |

Thus it appears that the thermal isomerisation of (2·26) and (2·27) is rapid compared to the rate of addition of furan to (2·26), but slow compared to the rate of addition of the isobenzofuran.

It is to be noted that hexachlorocyclopentadiene, a diene that undergoes reverse electron-demand Diels-Alder reactions,[164] i.e. reacts with unactivated or electron-rich double-bonds, did not react with (2·26) over a long period. This suggests that the thermal equilibrium of (2·26) and (2·27) at 25° is limited to those two isomers, and does not include (2·34) and (2·35).



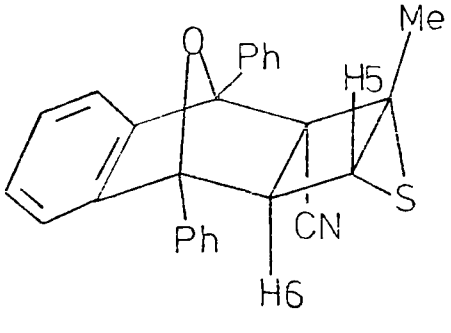
(2·34) (2·35)

Scheme 2·14

These latter two would have been expected to react with hexachlorocyclopentadiene.

The thermal interconversion of the two 5-thiabicyclopentenes (2·26) and (2·27) was further investigated by several low temperature irradiations of 2-methylthiophene-3-carbonitrile (2·18).

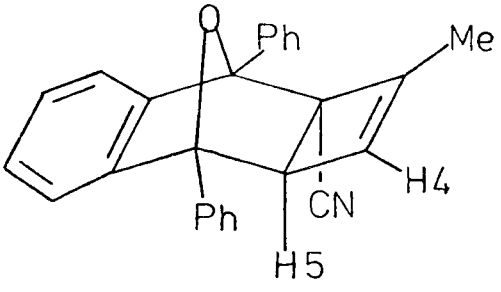
Thus, in one experiment, after 5h irradiation of (2·18) as a solution in tetrahydrofuran at -68°, 2,5-diphenylisobenzofuran was added. In contrast to the 25° experiment, two adducts were obtained, (2·32) and (2·36) in the ratio 1 to 1·2.



(2·36)

| | | |
|---|---|---|
| nmr | $CH_3$ | 1·31 |
| | H(5) | 3·35 |
| | H(6) | 3·30 |

The arguments applied previously about the shielding of bridgehead methyl groups and the deshielding of H(6) by the two phenyl groups apply in (2·36) and account for the unexpected values of chemical shifts for these substituents. Furthur structure proof of (2·36) was obtained by desulphurising the mixture of adducts. Two cyclobutenes were thus obtained,



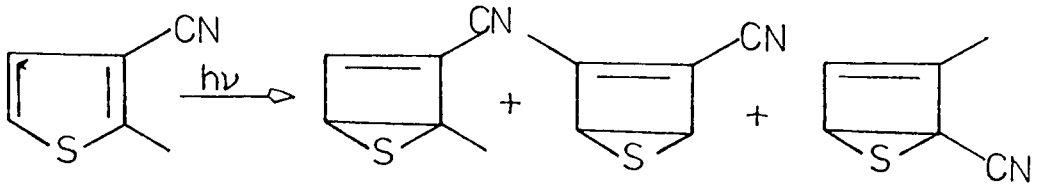

nmr $CH_3$ 1·40; $J_{4,CH_3}$=1·0
H(4) 5·93 (bs)
H(5) 3·60

(2·37)

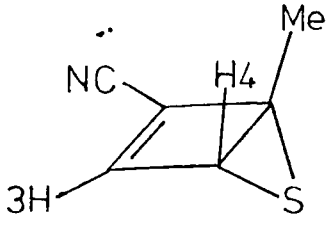
(2·33) as previously, and (2·37), confirming the structure of (2·36).

The isolation of two adducts in this experiment shows that a much higher proportion of (2·27) is present following irradiation of (2·18) at -68°, than is present following irradiation at 35°, i.e. the isomerisation is not so favourable at -68°.

This was confirmed by repeating the irradiation and then recording the nmr spectrum of the mixture at -70°. After 3h irradiation of (2·18), this showed a 35% conversion to a 3 to 1 mixture of the unwalked bicyclic compound (2·27) and the sulphur-walked isomer (2·26). Additionally, a small amount of the



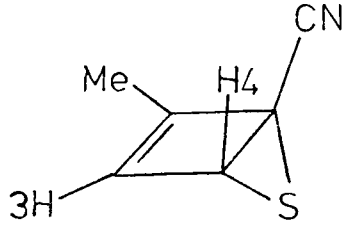

(2·18) (2·27) (2·26) (2·34)




(2·27)

| | | |
|---|---|---|
| nmr (THF, -70°) | $CH_3$ | 2·04 |
| | H(3) | 7·48 |
| | H(4) | 4·26 |

bridgehead cyano bicyclic compound (2·34) was present (~2%). None of the bicyclic compound (2·35) was present. Presumably the stabilisation energy gained by having a methyl group present on the double-bond is sufficient to make a thermal sulphur-walk step to (2·26) an unfavourable process for (2·34) at -70°. The isomer (2.35) would probably need to be formed photochemically from (2·27) at a much lower temperature to prevent a thermal sulphur-walk step from reverting it to (2·27).




(2·34)

| | | |
|---|---|---|
| nmr (THF, -70°) | $CH_3$ | 2·11 |
| | H(3) | 6·29 |
| | H(4) | 4·68 |
| | $J_{3,CH_3}$ = | 1·5Hz |

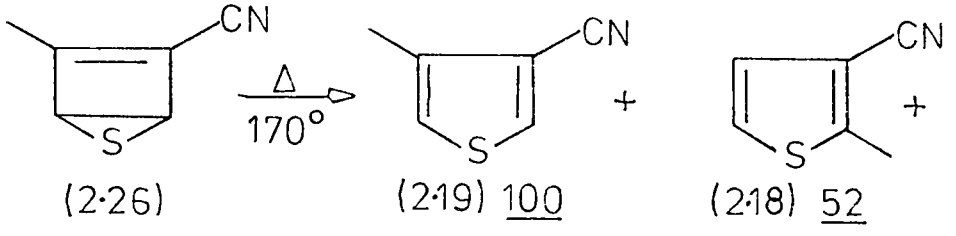
On warming the nmr solution to -35° and waiting five minutes, all of the signals due to isomer (2·34) disappeared. Also 76% of isomer (2·27) was converted into isomer (2·26), which was itself

stable. It is not possible to say which process (2·34) underwent. It would be expected to undergo a sulphur-walk step to give (2·26). The driving force for this reaction would be the 1·3 kcals/mole delocalisation energy[261] that would be gained from the isomerisation. The half-life of (2·27) was calculated to be 2 min ($k = 5{\cdot}4 \times 10^{-3}\ s^{-1}$) at -35°. On holding the temperature at -35°, all of (2·27) was converted into (2·26). As reported earlier, this latter isomer was stable at room temperature.

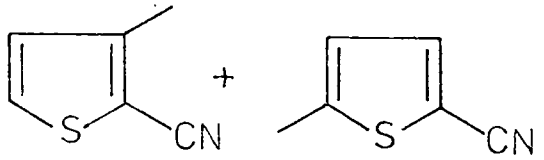
The rapid isomerisation of (2·27) to (2·26) at -35° must be largely due to the stabilisation energy gained from having the methyl group on the double-bond.

This experiment clearly demonstrates the thermal interconversion of 5-thiabicyclo[2·1·0]pent-2-enes.

Although it was shown earlier that at 25°, (2·34) and (2·35) are not formed thermally from (2·26) and (2·27), this is not the case at higher temperatures. Scheme 2·15 shows the four




(2·26) (2·19) 100 (2·18) 52

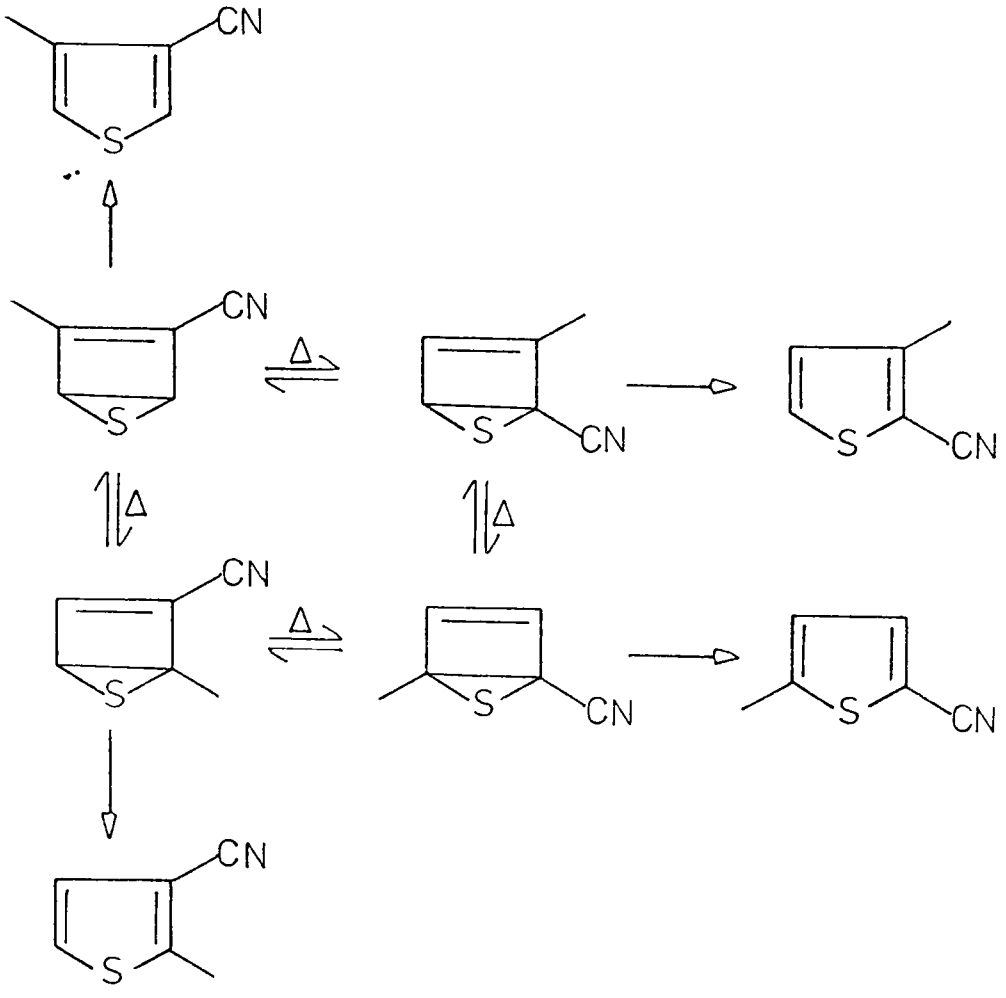



(2·21) 15 (2·20) 5

Scheme 2·15

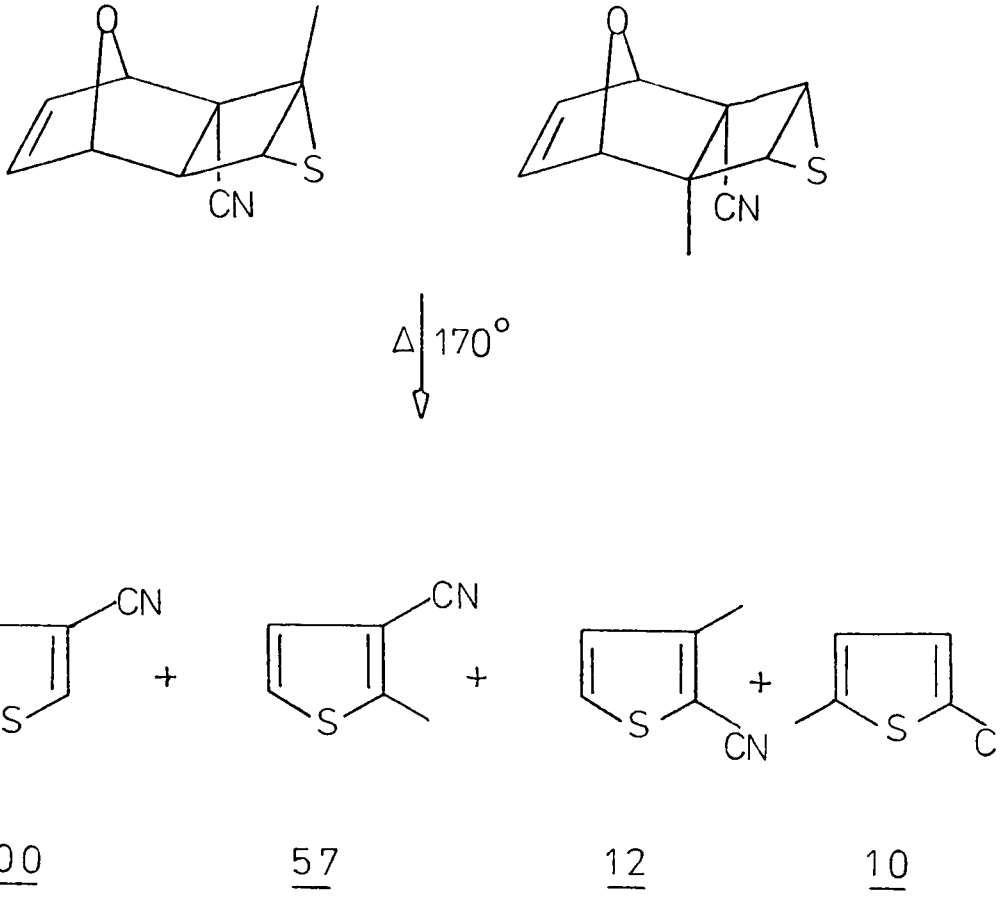
thiophenes, and their ratios, that were formed from pyrolysis of (2·26) at 170°. This result is most easily interpreted by Scheme 2·16. Thus at 170°, the thermal barrier to interconversion

of bicycles with conjugated cyano groups to those with bridgehead cyano groups can be passed. At 170°, the rate of sulphur-walking



Scheme 2·16

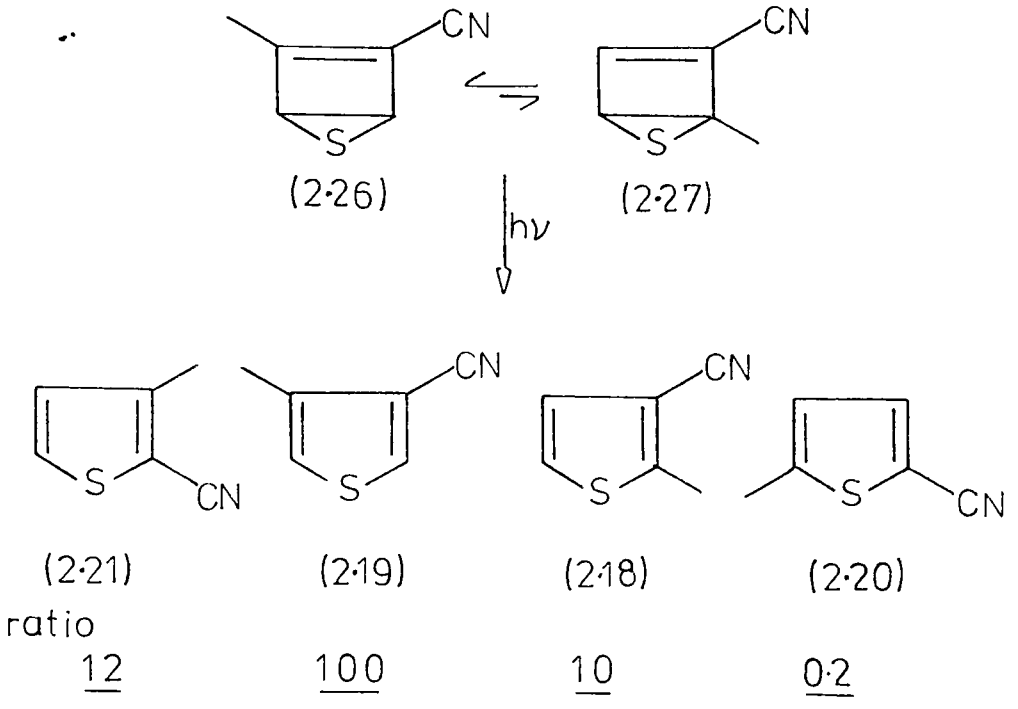
between the intermediates must be competitive with rearomatisation. Interestingly, pyrolysis of the mixture of exo-6 and 3-methyl-10, 4-oxathiatetracyclo[5·2·1·$0^{2,6}$·$0^{3,5}$]dec-8-ene-2-carbonitrile furnished the same four nitriles, in similar ratios, in addition to furan, at 170°. This result is consistant with the assumption made earlier that Diels-Alder retrogression of furan adducts gives furan and bicyclopentenes as primary products.




## 2.2.9 Photochemical aromatisation of 5-thiabicyclo[2·1·0] pent-2-enes

The ultra-violet absorption spectrum of 3-methyl-5-thiabicyclo [2·1·0]pent-2-ene-2-carbonitrile showed that it absorbed light at quite long wavelength ($\lambda$ >340nm) although its $\lambda_{max}$ was at 279nm. This is typical of allyl sulphides.[167] The sulphur 3d orbitals are very diffuse and probably extend far enough to

overlap considerably the $\beta\gamma$-conjugated system. This enabled the bicyclic compound to be irradiated through pyrex ($\lambda$ >290nm). Thus the majority of the light went into the bicyclic compound and virtually none into the product thiophenes. In this way only minimal secondary photolysis would be encountered. The




Scheme 2·17

results of irradiations in ether solution of (2·26) are shown in Scheme 2·17.

The results show that the equilibrium mixture of bicyclic compounds (2·26) and (2·27) can be photochemically aromatised, and that additionally, the intermediates can undergo a photochemical sulphur-walk step to give, subsequent to aromatisation, the 2-cyanothiophenes (2·20) and (2·21).

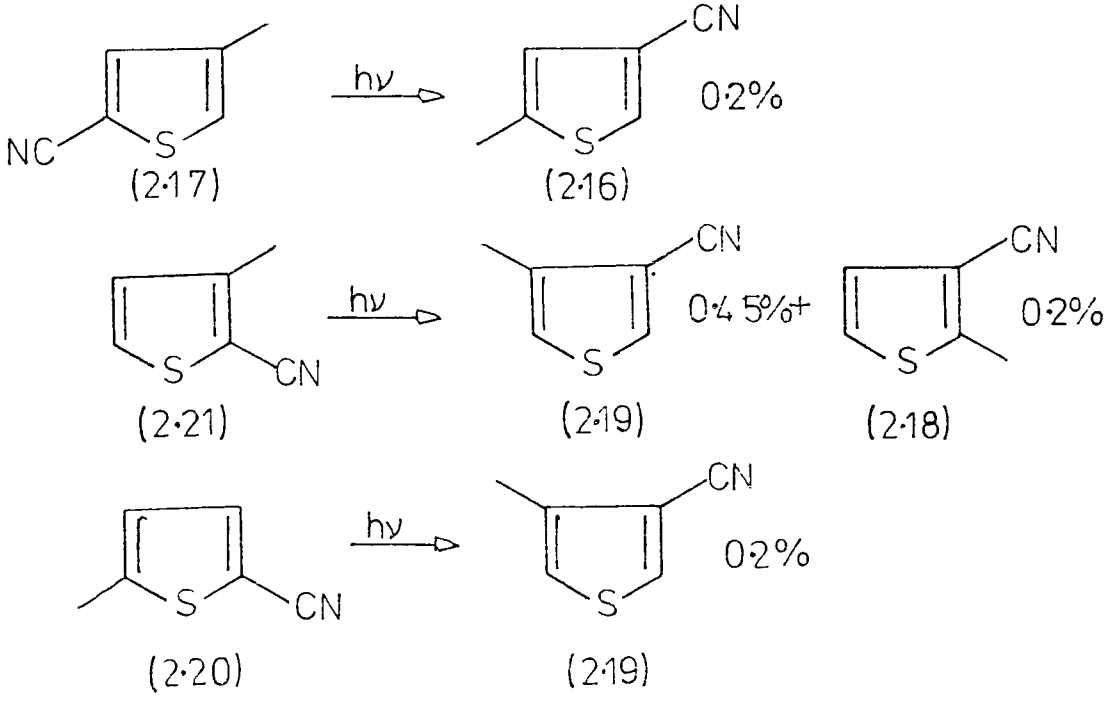
The bicyclic compound (2·26) could also rearomatise upon irradiation with 254nm light, though here, secondary photolysis of the products occurred.

## 2.2.10 Photoisomerisation of methylthiophene-2-carbonitriles.

In section 2.2.7 it was shown that 3-methyl-5-thiabicyclo [2·1·0]pent-2-ene-1-carbonitrile could undergo a thermal sulphur-walk step to give the isomeric 4-methyl-5-thiabicyclo[2·1·0] pent-2-ene-2-carbonitrile. This fully supports the proposed mechanism for the photochemical isomerisation of thiophene-2-carbonitrile to thiophene-3-carbonitrile.

To check that the photochemical isomerisations described here in general were reversible, and also to ensure that no isomerisations not predicted by the bicyclic mechanism occurred, the three possible methylthiophene-2-carbonitriles were investigated

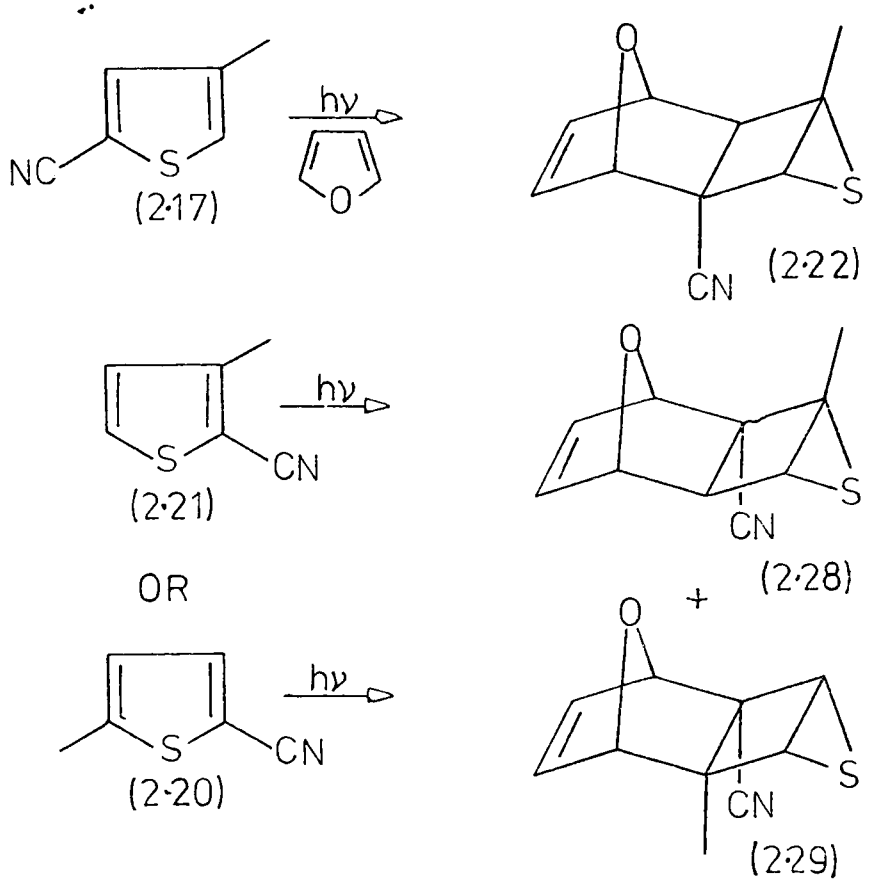
These were synthesised via the appropriate aldehydes, which were all known compounds. Irradiation of all three isomers in hexane showed them all to undergo very inefficient transposition reactions. As can be seen from Scheme 2·18, detection of the




Scheme 2·18

products was difficult. The major reaction in each case was polymer formation.

Prolonged irradiation of each isomer in furan solution produced traces of the adducts expected from furan addition to the corresponding sulphur-walked bicyclic compounds, Scheme 2·19.




Scheme 2·19

Thus, clearly the transposition reactions proceed *via* Dewar thiophene intermediates.

The inefficiency of these reactions compared to the reverse reactions from the analogous 3-cyanothiophenes probably reflects a much more facile 2,5-bonding step from the excited state of the latter compounds. In simple terms, since the excited states

of thiophene-3-carbonitriles are of higher energy than those of the 2-cyano isomers (see Section 2.2.10 below), and since also the bicyclic intermediates derived from the 3-cyanothiophenes are expected to be more stable than those derived from the 2-cyano isomers (because of the delocalisation energy of the conjugated acrylonitrile system in those bicyclic compounds formed from 3-cyano thiophenes), it may follow that 2,5-bonding from an excited state of a 3-cyanothiophene is a much more downhill process, energetically, than from a 2-cyanothiophene. It may also be that other energy dissipating processes are much more favourable for the thiophene-2-carbonitriles, and these may account for the greater proportion of polymeric materials that were formed. None of the simple thiophene-carbonitriles show flourescence.

It was described in the Introduction to this Thesis how the efficiency of photochemical formation of valence-bond isomers of some aromatic compounds was increased with increase in temperatur With this in mind, and since also the pyrolysis of furan adducts and of the bicyclic compound (2·26) had shown that the sulphur-walk step becomes more competitive with rearomatisation at higher temperatures, it was decided to repeat the irradiations of methylthiophene-2-carbonitriles at 80° instead of the usual 30-35°.

A large increase in yield of transposed products was observed from both (2·17) and (2·21). Only a negligible increase was observed for (2·20). Thus the yield of (2·16) from (2·17) had increased from 0.2% to 0.6%; the yield of (2·19) from (2·21) had increased from 0·45% to 3%.

The increase in efficiency of transposition from (2·21) enabled the detection of (2·20) in the photolysis mixture. Similarly from the photolysis of (2·20), in addition to (2·19), traces of (2·21) and (2·18) could be detected. In the limit, one might expect a photolysis at high enough temperatures to give ratios of thiophenes (except excess starting material) similar to those obtained from furan adduct pyrolysis experiments. Sulphur-walking at high temperatures is presumably so rapid that it is not important at which point the bicyclic compound enters Scheme 2·16.

## 2.2.10 Sensitisation and Quenching studies.

At this point it may be useful to consider the experiments carried out to determine the nature of the excited state responsible for 2,5-bonding in thiophene-carbonitriles. The rearrangement of 2-phenylthiophene to 3-phenylthiophene is known to proceed *via* an excited singlet state.[118] This was established by triplet quenching experiments and triplet sensitisation experiments. In a similar manner, sensitisation and quenching experiments were carried out by this author with both thiophene-2 and 3-carbonitrile.

Irradiation of both nitriles in the presence of various concentrations of piperylene ($E_T$ = 59 kcals/mole) showed a small amount of quenching of the transposition reactions, but not a sufficient amount, even at 1·2$\underline{M}$ piperylene and 0·01$\underline{M}$ thiophene-2-carbonitrile to suggest that a triplet state was responsible for the transposition. If the quenching was assumed to be all triplet quenching, then a triplet lifetime of $10^{-10}$s was indicated,

i.e. an extremely short-lived triplet. It seems much more likely that singlet quenching was taking place.

The triplet state of thiophene-2-carbonitrile was then generated by sensitisation with benzophenone ($E_T$ = 69 kcals/mole). No isomerisation was observed. That the triplet level of the nitrile was being populated was shown by the fact that the photoreduction of benzophenone (0·1$\underline{\underline{M}}$) by benzhydrol (0·$\underline{\underline{M}}$) to form benzpinacol was effectively quenched by 0·01$\underline{\underline{M}}$ thiophene-2-carbonitrile. In the case of the 3-carbonitrile, photoreduction experiments showed that the triplet energy of benzophenone could not be transferred. However, similar photoreduction experiments showed that the triplet energy of acetophenone ($E_T$ = 74 kcals/mole) could be transferred. This triplet thiophene did not give transposition products either. The triplet energy of thiophene-3-carbonitrile must lie between 69 and 74 kcals/mole, while that of the 2-carbonitrile must be below 69 kcals/mole.

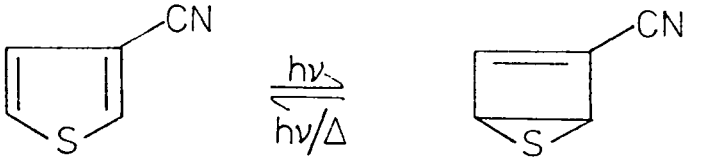
The ultra-violet spectra of the two nitriles shows the 3-isomer to absorb at shorter wavelengths ($\lambda_{max}$ = 238) than the 2-isomer ($\lambda_{max}$ = 259). Small shifts to longer wavelength are observed in the position of both bands when the solvent polarity is increased (cyclohexane to methanol). This observation, and the large extinction coefficients ($\sim 10^4$ l/mol cm) are characteristic of $\pi \rightarrow \pi^*$ transitions. It thus seems certain that $\pi,\pi^*$ singlet states are responsible for the photoisomerisation of thiophene carbonitriles.

## 2.2.11 Mechanistic Conclusions

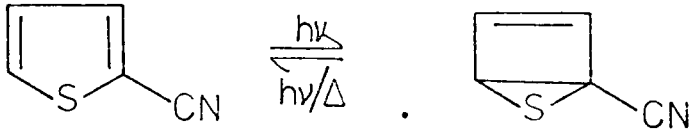
Irradiation of thiophene-carbonitriles with ultra-violet light has been shown to cause photisomerisation to other thiophene-carbonitriles. Products and starting materials are always related in that the sequential order of carbon atoms in the thiophene ring is the same. Only the relative position of the sulphur atom alters.

The photoisomerisations have been shown to occur via initial photochemical formation of bicyclic valence-bond isomers. In the case of thiophene-3-carbonitriles, these are 5-thiabicyclo [2·1·0]pent-2-ene-2-carbonitriles (2·38), and the corresponding 1-carbonitriles (2·39) are formed from thiophene-2-carbonitriles.

The bicyclic compounds can rearomatise, both photochemically




(2·38)



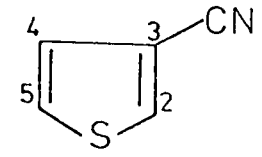

(2·39)

and thermally, or they can undergo a sulphur-walk step to give an isomeric 5-thiabicyclo[2·1·0]pentene, again, either photochemicall or thermally. The thermal isomerisation between bicyclic species with conjugated cyano groups can occur at normal irradiation

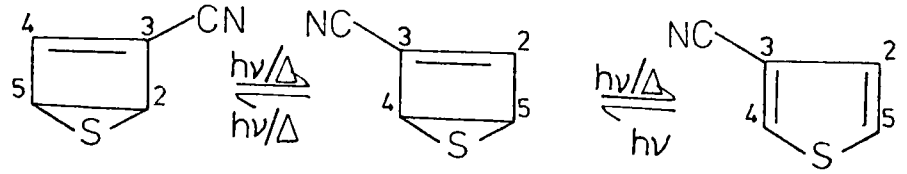
temperatures. Similarly, the isomerisation of a bicyclic compound with a bridgehead cyano group to an isomer with a conjugated cyano group occurs thermally even more readily. From heats of formation of such compounds as allyl cyanide and 1-propenylcyanides, the delocalisation energy of the system R-C=C-C≡N has been experimentally determined as $1{\cdot}3 \pm 0{\cdot}4$ kcal/mole,[261] and this must be the major driving force for such isomerisations. However, the reverse isomerisation is an uphill process and under normal conditions only occurs photochemically, though as the pyrolysis experiments show, it too can occur thermally when sufficient activation energy is available.

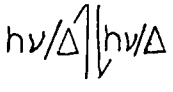
It can be seen that the distribution of products following irradiation of a particular thiophene-carbonitrile will depend upon a number of factors. It will depend upon the relative thermal stabilities of the interconverting bicyclic compounds with respect to one another - the most stable being those with nitrile groups on the double-bond, followed by those with methyl groups on the double-bond, and so on. The ratio will also depend upon the rates of rearomatisation, both thermal, which seems to depend upon bridge-head substituents, and photochemical, which will depend upon extinction coefficients and many other factors.

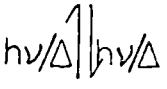
However, because of the basic nature of all of these interconversions, the maximum number of products possible from any particular thiophene-carbonitrile will be four, as shown in Scheme 2·20. This shows that all of the processes, with the exception of initial 2,5-bonding in the thiophene, can be photochemically and thermally reversible under appropriate conditions.

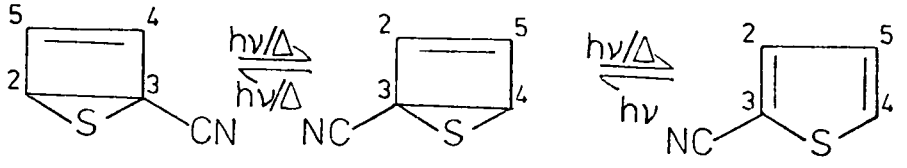

4
3
CN
5
2
S

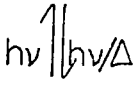

hν/Δ
hν

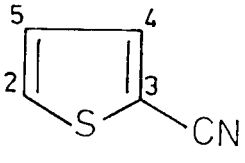

4
3
CN
5
2
S
hν/Δ
hν/Δ
NC
3
2
4
5
S
NC
3
2
hν/Δ
hν
4
5
S


hν/Δ
hν/Δ


hν/Δ
hν/Δ


5
4
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CN
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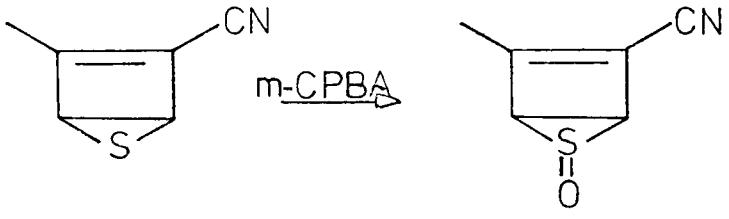

hν
hν/Δ


5
4
2
3
S
CN

Scheme 2·20

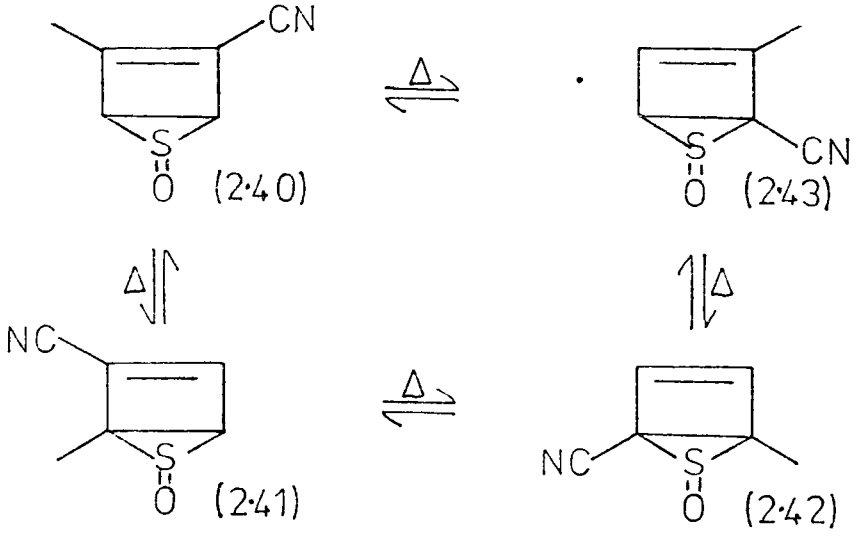
2.2.13 Thermal isomerisation of 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile 5-oxide.

Earlier, (section 2.2.4) reference was made to the facile degenerate rearrangement of tetrakis(trifluoromethyl) Dewar thiophene episulphoxide. Since the conversion here of an episulphide into its oxide had such a dramatic effect on the rate of sulphur-walking, it was decided to convert the bicyclic

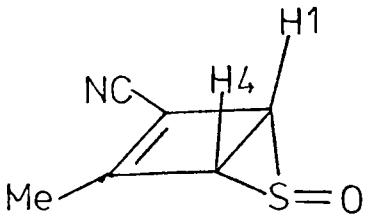



(2·26) (2·40)

episulphide (2·26) to its oxide (2·40). It was hoped that achieving this might lower the energy barrier for the sulphur-walk from bicyclic isomers with conjugated cyano groups to those with bridgehead cyano groups, and thus facilitate the thermal equilibrium depicted in Scheme 2·21 at room temperature.



Treatment of (2·26) with a molar equivalent of m-chloroperoxybenzoic acid gave a quantitative conversion to the sulphoxide (2·40).




(2·40)

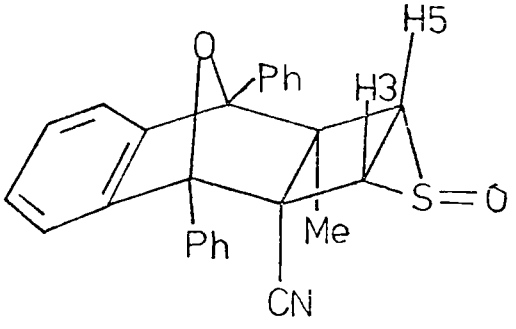
nmr $CH_3$ 1·91; $J1,CH_3$ = 1·0

H(1) 4·68; $J1,CH_3$ = 1·0, $J1,4$ = 2·0.

H(4) 4·05; $J1,4$ = 2·0

The down-field shifts of H(1) and H(4) are typical of some episulphide to episulphoxide conversions, although in the literature, these shifts vary greatly.[168,199] The nmr spectrum of the sulphoxide showed no signals which might be due to other isomers, even on cooling down to -80°. However, the reaction of (2·40) with 2,5-diphenylisobenzofuran gave reason to believe that the thermal equilibrium between at least (2·40) and (2·41) existed at room temperature, and that the rate of isomerisation was considerably more rapid than that between the episulphides (2·26) and 2·27).

Thus treatment of (2·40) with 2,5-diphenylisobenzofuran gave an adduct with signals in the nmr spectrum at 7·2-8·0 due to aromatic groups, two single, uncoupled hydrogens at 2·95 and 3·15, and a methyl group at 1.12. These cannot be due to



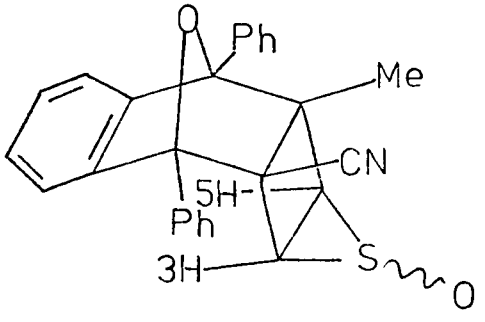

(2·44)

nmr $CH_3$ 1·02

H(3) 3·45

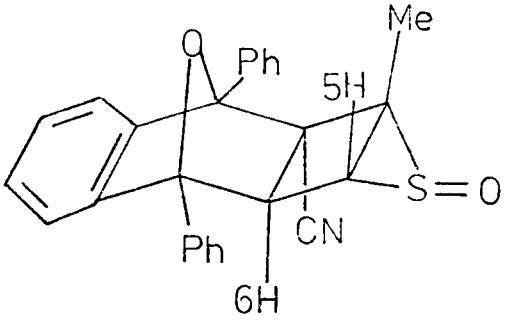
H(5) 3·45

adduct (2·44), since preparation of this by treatment of the analogous episulphide adduct (2·32) with m-chloroperoxybenzoic acid gave a different nmr spectrum. They are also unlikely to




(2·45)

be due to the endo-isomer (2·45), since here H(3) and H(5) would be expected to show some coupling. The nmr signals would be consistant for the isomer (2·46). H(5) and H(6) would be expected

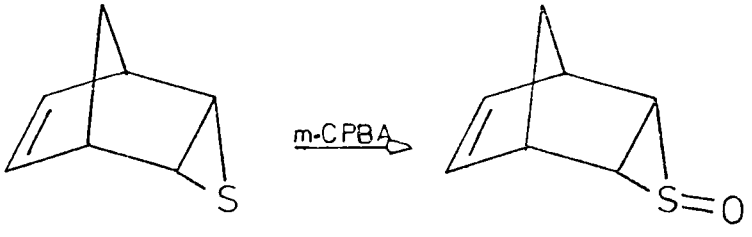



(2·46)

not to couple. The methyl group would be shielded, and H(6) deshielded by the bridgehead phenyl groups as described earlier. If this is true, then one has to rationalise its formation by considering the rate of isomerisation between (2·40) and (2·41) to be much greater than the rate of isomerisation between the analogous episulphides (2·26) and (2·27), and also more rapid than the rate of isobenzofuran addition to (2·40). Alternatively one could consider that the episulphoxides are much less reactive

towards isobenzofuran than the episulphides, and thus the reagent becomes selective, but there is no precedent for this.

The configuration at sulphur in these S-oxide compounds is presumed to be exo. This is clearly the case in (2·44) since approach to the endo-face of the sulphur in (2·32) is sterically hindered. The stereochemistry of tetrakis(trifluoromethyl)Dewar thiophene episulphoxide is also known to be exo at sulphur.[131] Similarly the related tricyclic episulphide (2·47) is known to yield the exo-oxide (2·48) on treatment with m- chloroperoxybenzoic acid.[171]




(2·47) (2·48)

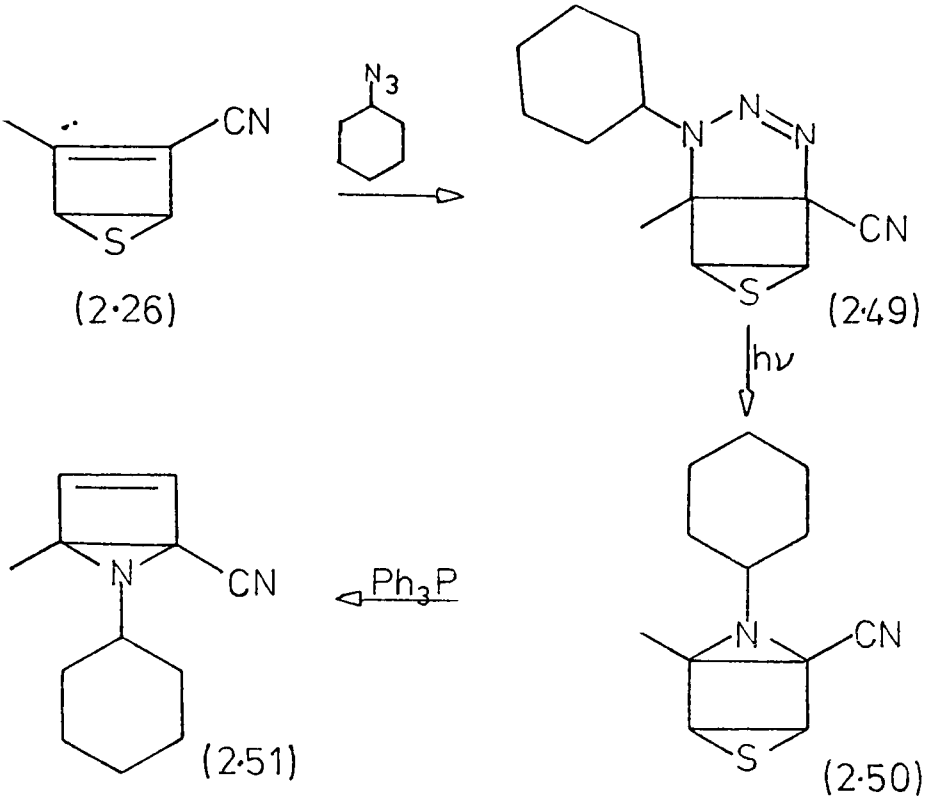
No evidence was obtained in the work with the episulphoxide (2·40) to suggest that it was in thermal equilibrium with the bridgehead cyano bicyclic compounds (2·42) and (2·43) at room temperature.

The bicyclic compound (2·26) was reacted with various other reagents in order to further investigate its thermal chemistry. For example, it was reacted with di-iron nonacarbonyl in an attempt to desulphurise it and obtain an iron-cyclobutadiene complex, but this reaction only led to decomposition products.

In another experiment, an attempt was made to convert (2·26) into the related Dewar pyrrole intermediate (2·51) by the route

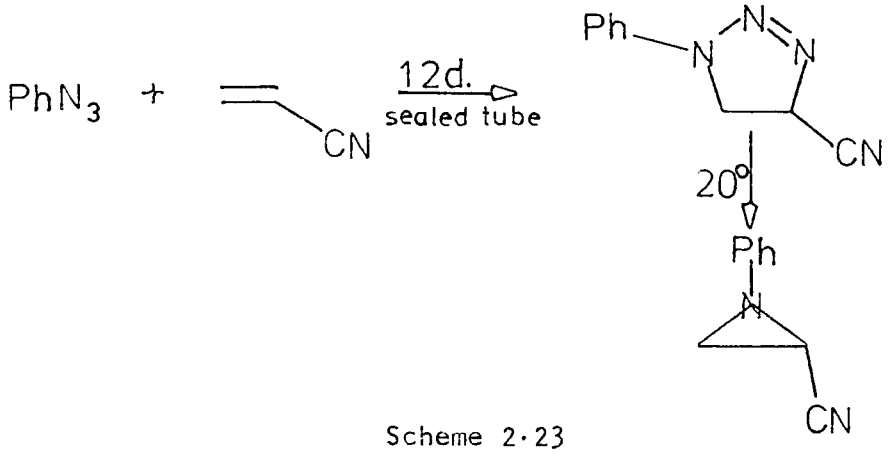
outlined in Scheme 2·22.[130]

The addition of alkyl azides to acrylonitrile moietes is not a rapid reaction.[172]



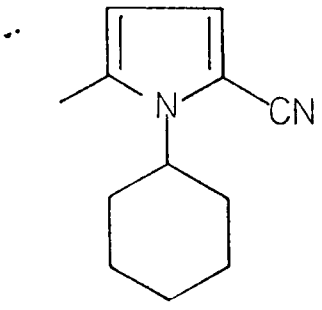

Scheme 2·22

In addition, the adducts formed are unstable and tend to decompose at room temperature,[173] Scheme 2·23.

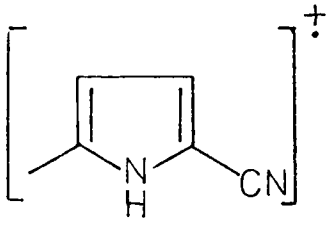



Scheme 2·23

However, in the reaction between (2·26) and cyclohexyl azide neither the triazoline (2·49) nor the 1,4-thiazine (2·50) were obtained. Instead, a low yield of a compound with a molecular weight of 188 was obtained, i.e. correct for a pyrrole of the type (2·52). The fragmentation pattern of the



(2·52)



(2·53)

compound showed a base peak at m/e 106, possibly corresponding to (2·53). The nmr spectrum of this compound contained a methyl group at 2·25, whereas the methyl group in 5-methylpyrrole-2-carbonitrile resonates at 2·28.

The difference in behaviour of (2·26) compared with tetrakis(trifluoromethyl)Dewar thiophene, which is converted to a Dewar pyrrole under these conditions, probably originates in the stabilising effect of the perfluoromethyl groups on the intermediates of the latter compound in the reaction sequence.

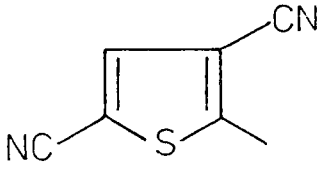
One step conversion of thiophenes to pyrrole carbonitriles is not unknown. For example, treatment of anils derived from 2-nitrothiophene-3-carboxaldehyde, with triethylphosphite gives pyrrole-carbonitriles.[172] The reaction sequence involves the intermediacy of nitrene-azirine species.

## 2.3 PHOTOCHEMISTRY OF THIOPHENE-DICARBONITRILES

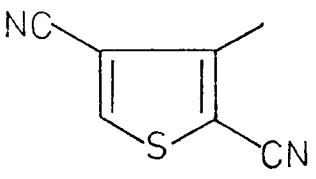
### 2.3.1 Formation of a dihydrothiepin

The photochemistry of some thiophene-dicarbonitriles was investigated in order to see what effect the introduction of a second electron-withdrawing group into the thiophene ring would have on the transposition mechanism and on the stability of any valence-bond isomers that might be formed photochemically.

The two dinitriles (2·54) and (2·55) were readily synthesised from the corresponding, known, dibromo compounds by treatment with copper (I) cyanide in boiling quinoline. The mechanism



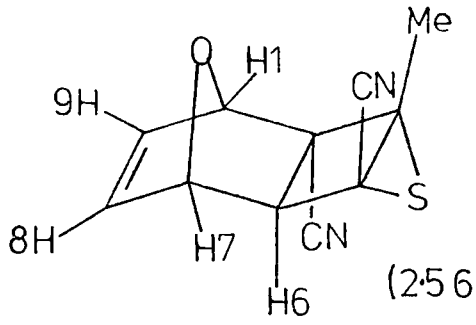

(2·54)




(2·55)

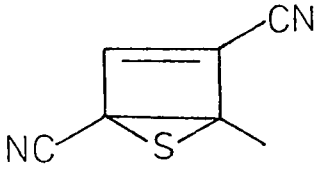
deduced for the transposition reactions of thiophene-monocarbonitriles predicts that these two isomers should photo-interconvert.

Irradiation of (2·54) in acetonitrile gave a low conversion to (2·55), but gave mainly polymeric material. Evidence that the phototransposition reaction occurred *via* a Dewar thiophene valence-bond isomer was obtained by the isolation of the adduct (2·56) from the irradiation of (2·54) in furan solution.




(2·56)

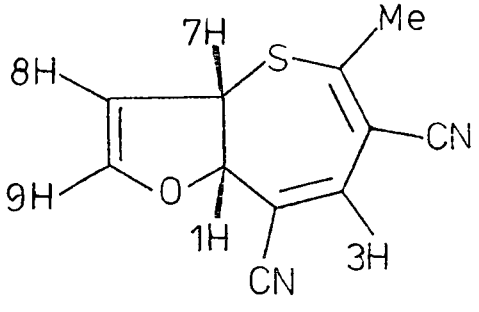
| nmr | | |
|---|---|---|
| | $CH_3$ | 1·90 |
| | H(1) | 5·13 |
| | H(6) | 2·91 |
| | H(7) | 5·18 |
| | H(8) | 6·57 |
| | H(9) | 6·57 |




(2·57)

Clearly, this adduct is most simply derived from Diels-Alder addition of furan to the bicyclic intermediate (2·57) in an exo-fashion.

The irradiation of (2·54) in furan produced an additional adduct, the structure of which was deduced as shown below to be that of the dihydrothiepin (2·58).



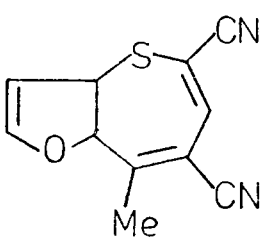

(2·58)

The mass spectrum of (2·58) showed its molecular weight to be 218, ie. furan plus the dinitrile. The ultra-violet spectrum showed absorption out as far as 350nm, indicating considerable conjugation. The infra-red spectrum showed a cyano band, and

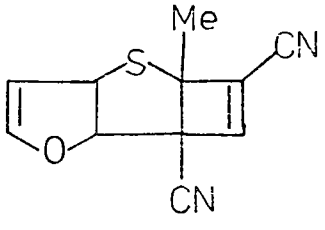
also a strong band at 1610cm$^{-1}$. The nmr spectrum given below contained signals characteristic of furan 2+2 adducts, and not of 4+2 adducts.

| | | | |
|---|---|---|---|
| n.m.r. | $CH_3$ | 1·90 | |
| | H(1) | 4·91 | $J_{1,7}$ = 8·0 |
| | H(3) | 5·87 | |
| | H(7) | 4·28 | $J_{7,9}$ = 1·5, $J_{7,8}$ = 3·0, $J_{1,7}$ = 8·0 |
| | H(8) | 4·87 | $J_{7,8}$ = 3·0, $J_{8,9}$ = 3·0 |
| | H(9) | 6·71 | $J_{7,9}$ = 1·5, $J_{8,9}$ = 3·0 |

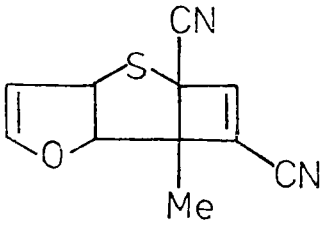
These data suggest structures such as (2·58), (2·59), (2·60) and (2·61).




(2·59)



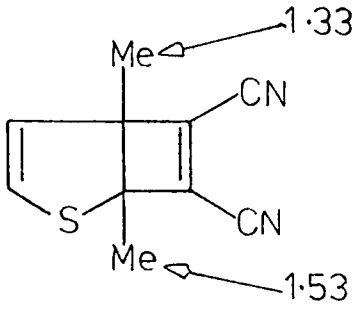

(2·60)




(2·61)

The sulphur atom must be linked to the carbon atom bearing H(7) and not that bearing H(1), since the latter resonates here at too high a field. For example, when oxygen is bonded to C(1), then H(1) resonates at 6·20.[175] When no heteroatom is bonded to C(7), then H(7) resonates between 3 and 4, unless it is part of a small ring.[176]

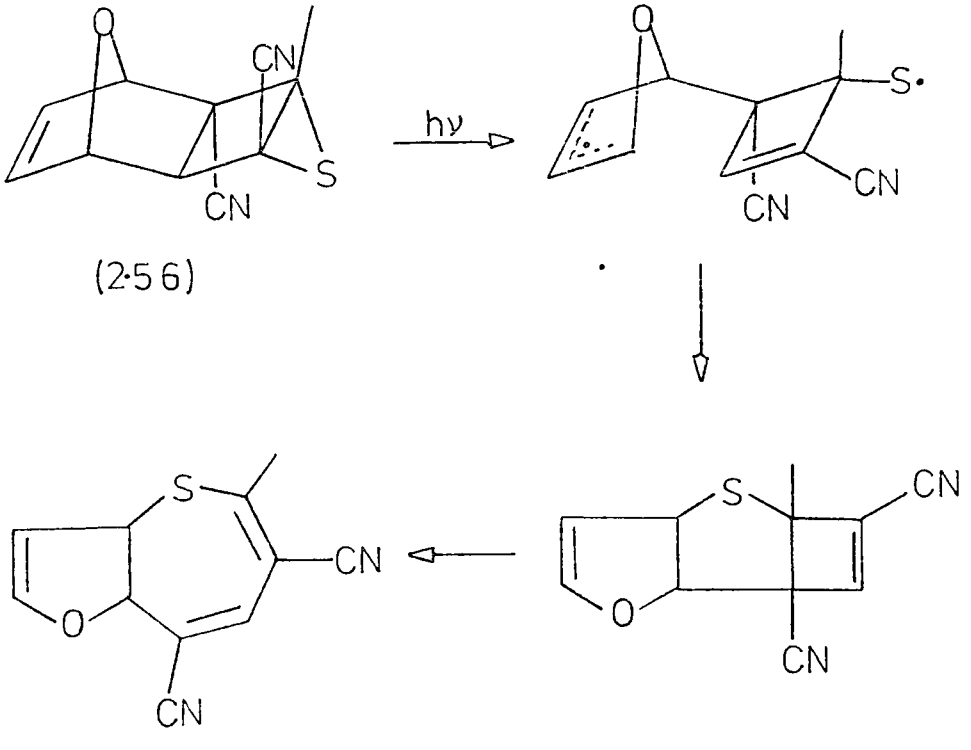
Structures (2·60) and (2·61) can be ruled out, since the methyl group of (2·60) should resonate around 1·53 , and




(2·62)

that of (2·61) around 1·33, cf. (2·62).[159] It is not possible to distinguish (2·58) from (2·59) by nmr spectroscopy, but the former structure is preferred because the mass spectrum shows a significant peak at m/e 59(8) due to $CH_3CS^+$. This would be difficult to obtain from (2·59).

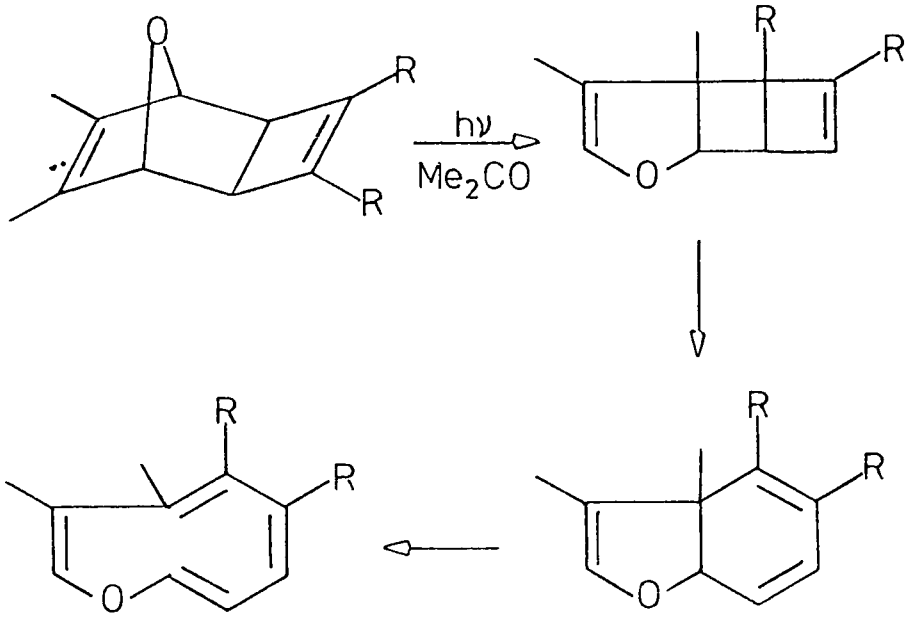
There are several possible routes for the production of (2·58). For example, one could envisage a photochemical rearrangement of the furan adduct (2·56) to give (2·58), as in Scheme 2·24. This type of reaction is well known where




(2·56)

(2·58)

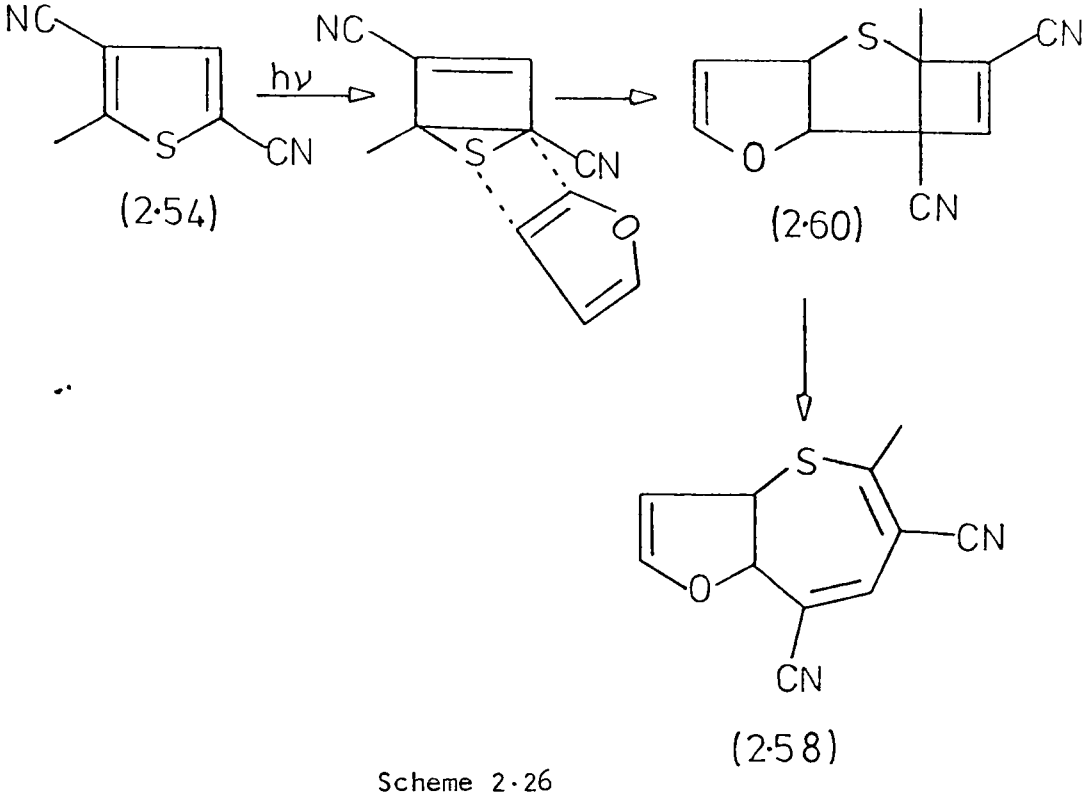
the episulphide system is replaced by a double-bond,[177,178] Scheme 2·25. However, the furan adduct (2·56) was found to




Scheme 2·25

be thermally and photochemically stable under the reaction conditions, and in the presence of acetone sensitiser, thus ruling out the formation of (2·58) from (2·56).

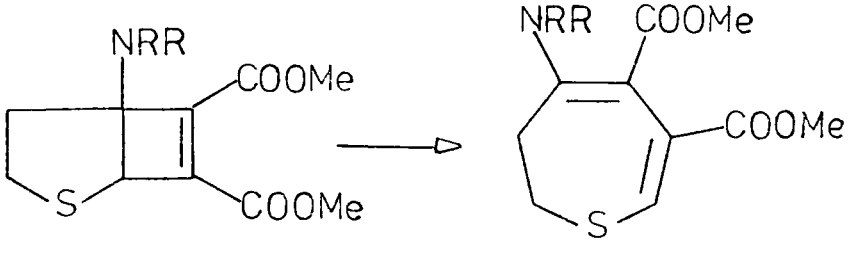
A second possibility is that (2·58) is formed by addition of furan across the S-Cl bond of the bicyclic intermediate (2·57), as shown in Scheme 2·26). Addition of furan to the bicyclic intermediate seems more likely than formation of (2·60)




Scheme 2·26

from an exciplex, since the perfluoroalkyl Dewar thiophene is known to react with some dienes in the normal 4+2 Diels-Alder manner using its cyclobutene double-bond, and with others by reaction across the S-Cl bond.[129]

The 2+2 cycloreversion of 2-thiabicyclo[3·2·0]hept-6-enes of the type (2·60) is a known thermal reaction,[179,180] e.g. (2·63) ⟶ (2·64). The symmetry allowed conrotatory opening

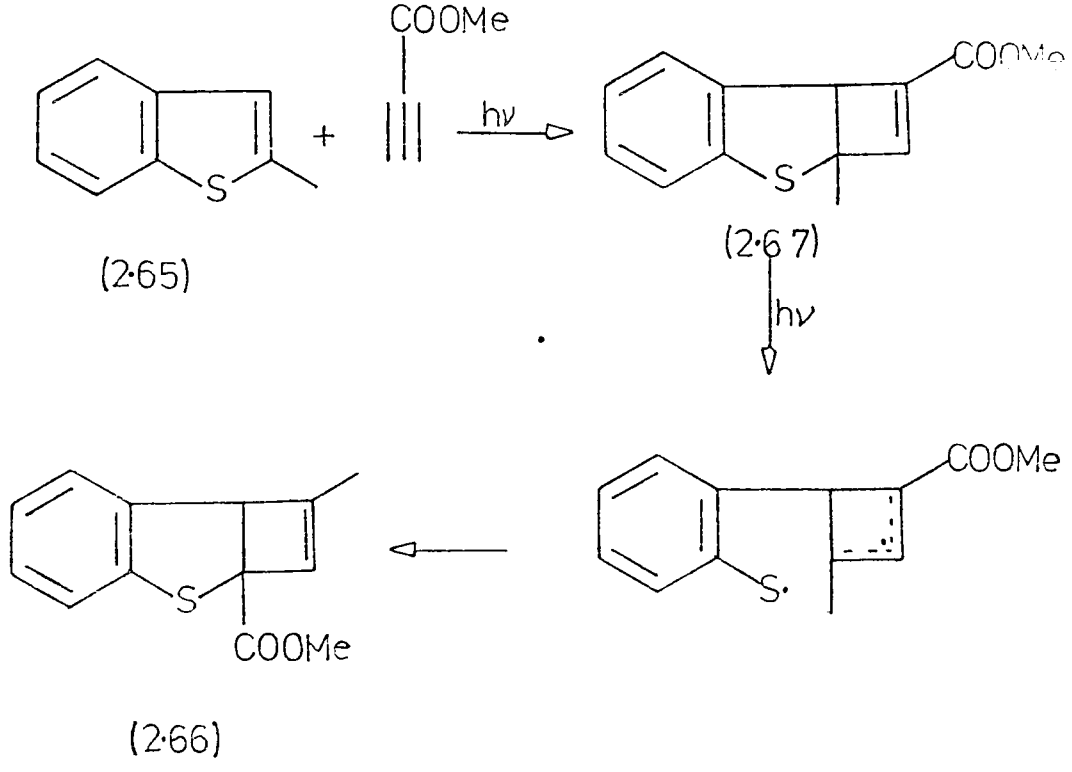



(2·63) (2·64)

of the cyclobutene ring in these compounds would give rise to an energetically unfavourable seven-membered ring with trans

double-bonds. Instead, the opening of the cyclobutene ring is thought to take place by a two-step 'donor-acceptor' mechanism.[159] The rate of isomerisation is enhanced by electron-donating substituents at one of the bridgehead carbon atoms, and by the presence of a heteroatom and substituents that can stabilise negative charge at the adjacent carbon atom.

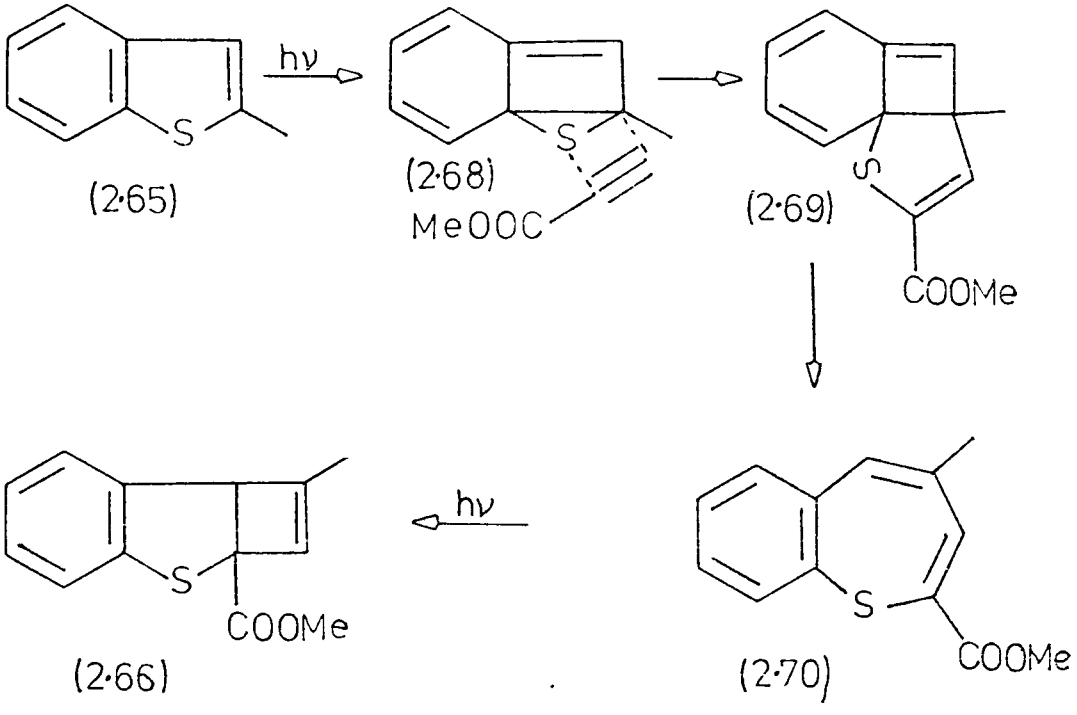
The mechanistic Scheme 2·26 outlined for the formation of (2·58) is also able to account for the formation of several other unexpected addition products formed photochemically between unsaturated compounds and thiophenes.[181-183] For example, addition of various acetylenes to 2,3-benzothiophenes (2·65) leads to the unexpected derivatives (2·66). Experiments suggest that these are formed by photochemical rearrangement of the expected thiabenzo[b]bicyclo[3·2·0]hepta-3,6-dienes




Scheme 2·27

(2·67).[199,260] The product results from ring-closure of the most stabilised resonance structure of the diradical formed by S-Cl bond rupture in (2·67), Scheme 2·27.

These experiments do not completely rule out concerted 1,2-additions which produce the rearranged adducts directly. Thus, the Scheme 2·28 shows how the rearranged products can be obtained by addition of the acetylenes across the S-Cl bond of an intermediate Dewar thiophene (2·68). Anti-aromatic thiepins (2·70) are known to undergo photochemical ring-

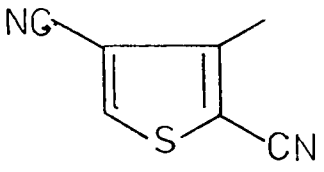



Scheme 2·28

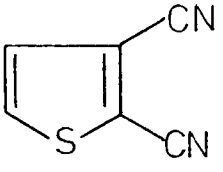
contractions to give cyclobutenes.[200]

## 2.3.2. Electron-transfer reactions

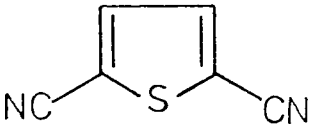
The photochemistry of some other thiophene-dicarbonitriles was investigated in various solvents. Compound (2·55) underwent rapid decomposition to polymeric material upon



(2·55)



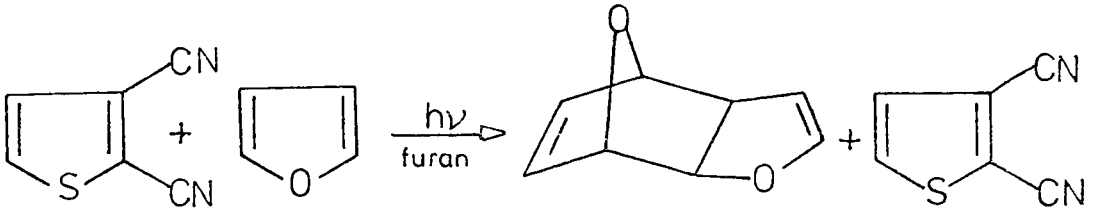
(2·71)



(2·72)

irradiation in acetonitrile. No transposition was observed. The two isomers, (2·71) and (2·72), were photostable in acetonitrile.

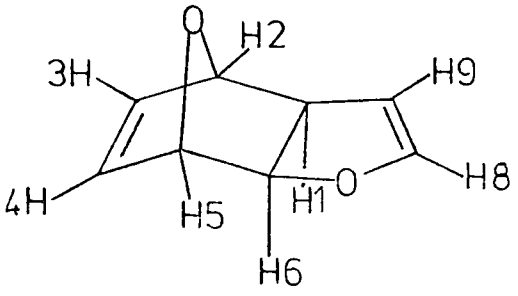
Irradiation of (2·71) in furan in an attempt to trap a Dewar thiophene isomer gave an unexpected result. The only product was the unknown furan dimer (2·73). Its structure




(2·71) (2·73)

was easily deduced since its nmr spectrum consisted solely of signals typical of furan 4+2 and 2+2 adducts. In addition, its mass spectrum showed a weak molecular ion with furan as the base peak. Infra-red spectroscopy showed no cyano bands, but a vinyl ether band at 1625cm$^{-1}$. The ultra-violet spectrum

showed only end-absorption, and pyrolysis of the adduct in a sealed tube with a soft bunsen flame gave only furan. Additionally treatment of the dimer with toluenesulphonic acid in methanol showed hydrolysis of the vinyl ether linkage by nmr spectroscopy.




(2·73)

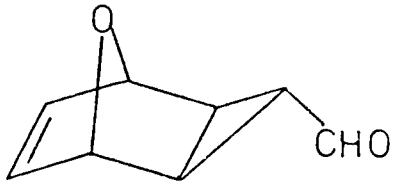
| | | | |
|---|---|---|---|
| nmr | H(1) | 3·22 | $J_{1,8}$=2·0, $J_{1,9}$=2·8, $J_{1,6}$=7·5 |
| | H(2) | 4·73 | b.s. |
| | H(3) | 6·20 | $J_{2,3}$=2·0, $J_{3,4}$=6·0 |
| | H(4) | 6·43 | $J_{4,5}$=2·0, $J_{3,4}$=6·0 |
| | H(5) | 5·02 | b.s. |
| | H(6) | 4·70 | $J_{1,6}$=7·5 |
| | H(8) | 6·39 | $J_{1,8}$=2·0, $J_{8,9}$=2·9 |
| | H(9) | 4·78 | $J_{1,9}$=2·8, $J_{8,9}$=2·9 |

The stereochemistry of the adduct is deduced to be exo- since there is no significant coupling between H(1) and H(2) or between H(5) and H(6).

The dimer (2·73) was not formed in a dark reaction. This apparent 4+2 reaction is photochemically forbidden and thermal 4+2 Diels-Alder reactions only occur between furan and electron-poor olefins such as maleic anhydride and acrylonitrile. It is known that 2,5-diphenylisobenzofuran can undergo a photochemical 4+2 reaction with cyclic 1,3-dienes.[220] However, this reaction is exceptional and proceeds via a biradical mechanism.

It seems clear that the dicyanothiophene is sensitising the reaction is some way. However, it cannot be simple singlet

or triplet senitisation since, as described in the Introduction, neither of these states of furan give rise to such dimers. The only dimers formed are those between furan and its ring-contracted photoisomer, e.g. (2·74).



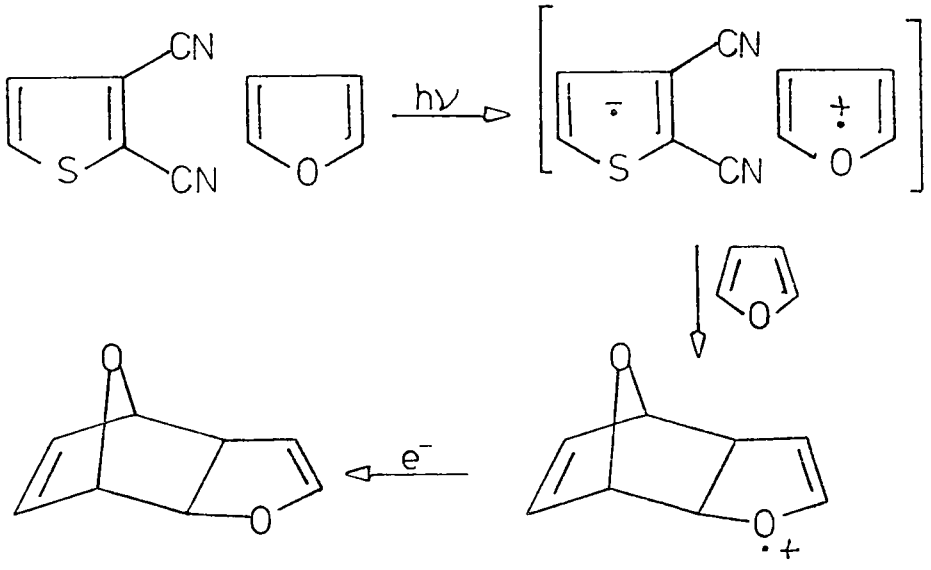

(2·74)

Aromatic compounds containing strongly electron-withdrawing groups are known to behave as electron-acceptors. Thus tetracyanothiophene forms complexes with various $\pi$-bases.[184] Mixtures of electron-donors such as dienes and amines, in solution with electron-acceptors, often exhibit new electronic absorption bands attributed to donor-acceptor complexes. Irradiation into these bands can induce the transfer of an electron from the donor to the acceptor and then further reaction can take place. This type of sensitisation does not occur in the furan-dicyanothiophene system since the ultra-violet absorption spectra of the individual components are unchanged when they are in a mixture.

An excited state molecule is both a better electron-donor and a better electron-acceptor than a ground-state molecule. Thus excited state charge-transfer complexes are more widespread, and evidence will now be presented which shows that the production of the furan dimer is <u>via</u> the intermediate formation of an exciplex.

The Scheme 2·29 depicts the proposed mechanism which involves the following steps. Firstly, excitation of the dicyanothiophene gives a species with a higher electron-

affinity and can form an exciplex with furan. Exciplexes usually stay as such with charge-transfer character or exist as radical ion pairs in non-polar solvents because of the difficulty of separating charge when the dielectric constant is low. Thus in furan free radical ions are unlikely to be formed. Whatever the degree of charge-transfer, the furan will have radical cation character. It can thus subsequently behave as an electron-deficient vinyl ether system and be trapped by solvent furan to give a Diels-Alder adduct. Back electron-transfer will then give the furan dimer and dicyanothiophene.




Scheme 2·29

Evidence in favour of this mechanism is as follows. Dimerisation of furan was affected not only by irradiating 2,3-dicyanothiophene, but also by irradiating 1,2,4,5-tetracyanobenzene, and 1,2-, 1,3-, and 1,4-dicyanobenzenes in the presence of furan. These latter four compounds gave no adducts of themselves with furan, and also did not photoisomerise.

Di- and tetracyanobenzenes are known to form excited state charge-transfer complexes with aromatic compounds, and in some instances, the radical anion of TCNB has been detected by e.s.r. spectroscopy.[185,186,194] The fluorescence of the benzene/TCNB exciplex at 490nm was quenched by the addition of furan which has a much lower ionisation potential (8·89 eV) than benzene (9·38 eV).

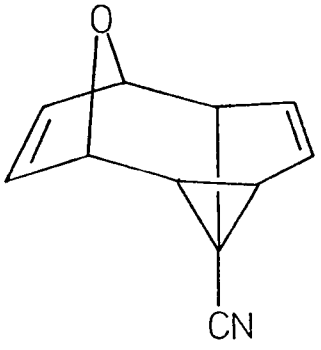
Interestingly, irradiation of benzonitrile in furan does not lead to the furan dimer. This is probably due to the much higher reduction potential of benzonitrile compared to the di- and tetracyanobenzenes,[187] Table 2·3, n.b. although these reduction potentials are ground-state values, the corresponding excited-state reduction potentials will be in a similar order since there is not much difference in the

| | Reduction potential (eV) | L.U.M.O. energy (eV) | Transition energy (eV) |
|---|---|---|---|
| Benzonitrile | -2·74 | -1·657 | 5·58 |
| o - dicyanobenzene | -2·12 | -2·040 | 5·34 |
| m - dicyanobenzene | -2·17 | -1·944 | 5·40 |
| p - dicyanobenzene | -1·97 | -2·146 | 5·27 |
| tetracyanobenzene | -1·02 | -2·673 | 4·85 |

Table 2·3

energy of the 0-0 bands of these compounds.

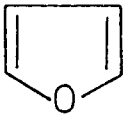
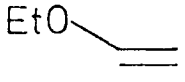
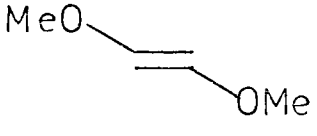
Benzonitrile gives an adduct (2·75) upon irradiation in furan solution.[188] This adduct probably arises from a




(2·75)

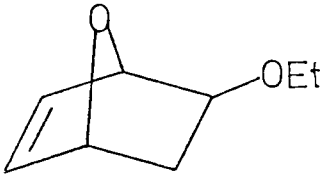
cycloaddition reaction in an exciplex of benzonitrile and furan. Here the degree of charge-transfer may not be great enough to make the exciplex reactive enough to furan solvent.

If the proposed electron-transfer mechanism for the production of the furan dimer is correct, then irradiation of tetracyanobenzene in the presence of furan and a vinyl ether with a lower ionisation potential than furan should lead to ionisation of the vinyl ether and subsequent addition of furan to give a mixed-adduct. The ionisation potentials of furan and some vinyl ethers are shown below.[189] Many electron-rich

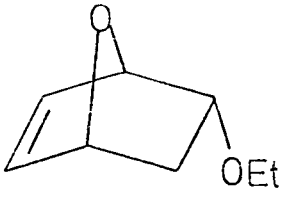
| | I.P. (eV) |
|---|---|
|  | 8·89 |
|  | 8·60 |
|  | 8·04 |

vinyl compounds have been irradiated in the presence of various cyanobenzenes.[190,191] For example, ethyl vinyl ether, which has a lower ionisation potential than furan, can be ionised by an excited state of benzonitrile.[190] Cyclobutanes formed from head to head dimerisation are obtained. Thus, irradiation of tetracyanobenzene in the presence of furan and ethyl vinyl ether should lead to the formation of diethoxycyclobutanes and also 4+2 and/or 2+2 adducts of furan and ethyl vinyl ether. It is to be noted that neither thermally nor photochemically does furan react with ethyl vinyl ether.

Work up of the irradiation of tetracyanobenzene in 50% furan in ethyl vinyl ether produced a number of compounds. The major two were the <u>exo-</u> and <u>endo-</u> adducts (2·76) and (2·77) of furan with ethyl vinyl ether. A compound (2·78) identified

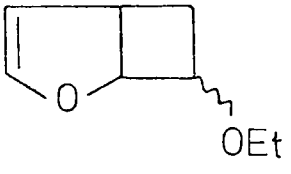



(2·76)




(2·77)

as a 2+2 adduct of furan with ethyl vinyl ether was also



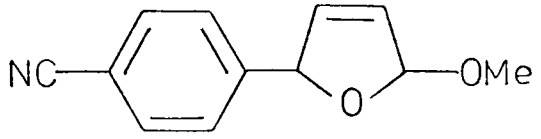

(2·78)

obtained. Additionally, the previously obtained diethoxy-cyclobutanes were observed. None of the furan dimer was formed, supporting the theory that it is the compound with the lowest ionisation potential which gives the reactive radical cation.

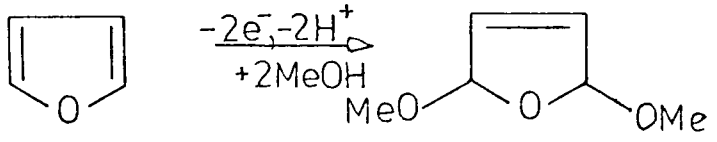
The structures of (2·76) and (2·77) were easily deduced from n.m.r., u.v., i.r., and m.s. data. Identification of (2·78) was based on the facts that mass spectroscopy showed it to be a 1:1 adduct of furan and ethyl vinyl ether, ultra-violet spectroscopy showed it to have no absorption above 220nm, and nmr showed it to contain signals typical of furan 2+2 adducts, an ethoxy group, and a signal due to HC-OEt. It was not possible to deduce the stereochemistry of (2·78).

There is a recent report in the literature of the irradiation of p-dicyanobenzene in furan.[192] Although under the conditions that these experimenters used it would not have been possible to form the furan dimer, their results support the mechanism for the formation of the furan dimer proposed by this author. In essence, the authors irradiated phenanthracene in an acetonitrile-methanol solution containing furan and the dicyanobenzene. Electron-transfer from the excited state phenanthracene (P) to ground-state p-DCNB was observed. They then proposed an electron-transfer from furan (F) to $P^{+\cdot}$ leading to the recovery of P and the formation of $F^{+\cdot}$. Subsequent nucleophilic attack of methanol on $F^{+\cdot}$ and reaction of the intermediate radical with p-$DCNB^{-\cdot}$ gave the observed product (2·79). One can see here the similarity with the anodic oxidation of furan in methanol-acetonitrile to

give dimethoxydihydrofurans,[193] Scheme 2·30.




(2·79)

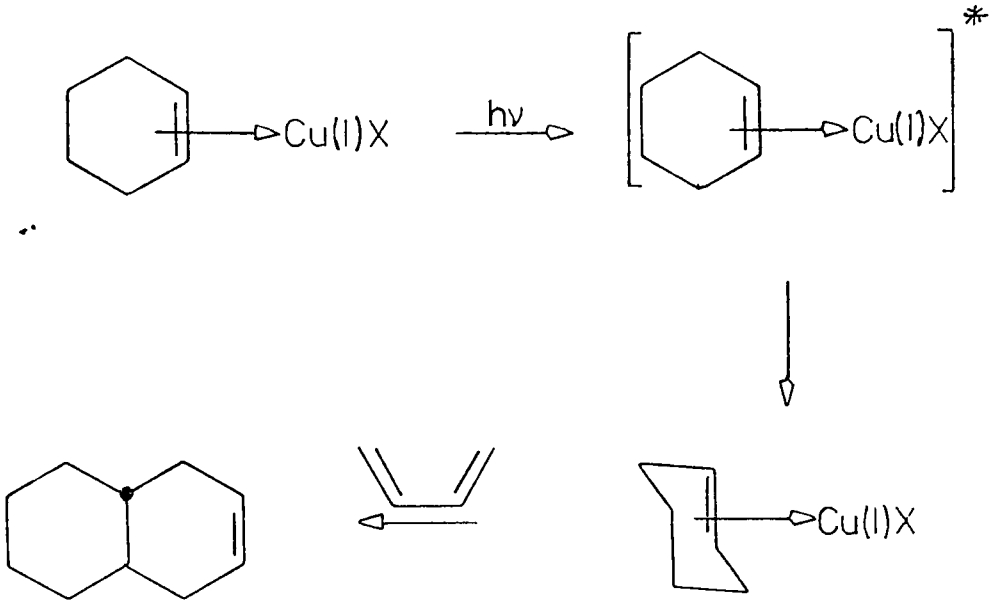



Scheme 2·30

The production of adducts of the type (2·76) and (2·77) is synthetically useful. Diels-Alder reactions between furan and olefins only occur thermally if the double-bond of the olefin is substituted with strongly electron-withdrawing groups. For example, the Diels-Alder reaction of furan with acrylonitrile takes about five weeks at room temperature, or about 4h at 15 kbars pressure.[195] Intramolecular 4+2 reactions are more rapid.[196] However, even under these conditions reactions with unactivated double-bonds take days, and with electron-rich double-bonds, reaction does not take place at all.[197]

In the context of Diels-Alder reactions *via* electron-transfer mechanisms, there have been reports recently of photochemical 4+2 reactions between butadienes and cyclohexene.[198] These reactions occur following irradiation into the charge-transfer absorption band of Cu(I)-cycloalkene complexes as

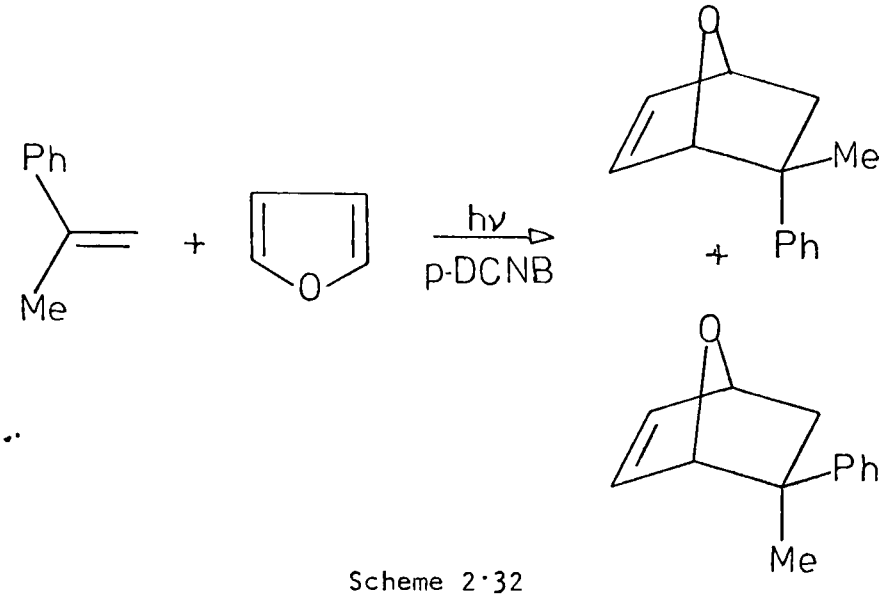
shown in Scheme 2·31. In this case, the electrophilic character




Scheme 2·31

of the olefin is provided by π-donation to empty Cu(I) orbitals. The cis-trans isomerisation is necessary to give products with the correct stereochemistry for a $(\pi^s_4 + \pi^s_2)$ thermal reaction.

Since the completion of the work by this author on the addition of furan to electron-rich olefins through photo-induced electron-transfer in the presence of electron acceptors, a publication has appeared reporting similar work.[256] Here the authors irradiated dicyanobenzene in the presence of furan and aromatic compounds with low ionisation potentials. They observed electron-transfer from the aromatic hydrocarbons to dicyanobenzene, and subsequent reaction of the radical cations with furan. An example is given in Scheme 2·32.



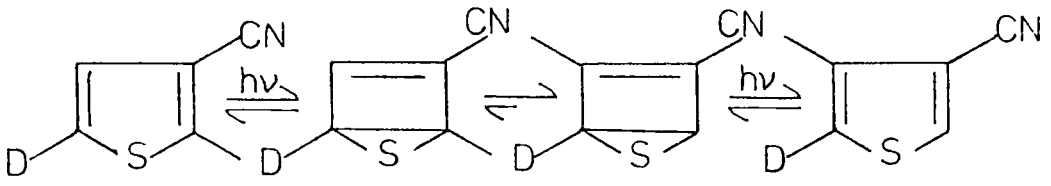

Scheme 2·32

The observation of exciplex formation between thiophene-dicarbonitriles and furan raises the question of whether the adducts formed between furan and the various Dewar thiophenes might derive from exciplexes. The evidence against this is that when the 2,5-bonded bicyclic compounds are generated and then the furan trap is added, the same adducts are formed as are during irradiation in furan solution.

This does illustrate the point that the investigation of phototransposition mechanisms by the chemical trapping of proposed intermediates does not provide any evidence in itself that the trapped intermediates are involved in the phototransposition pathway. Only when the intermediates themselves are isolated and can be shown to further react to the expected products at an appropriate rate under the normal irradiation conditions can their role be firmly established.

## 2.4 PHOTOCHEMISTRY OF VARIOUS OTHER THIOPHENES

The incorporation of a nitrile group into the thiophene nucleus makes 2,5-bonding from an excited singlet state an energetically favourable process. As illustrated in the



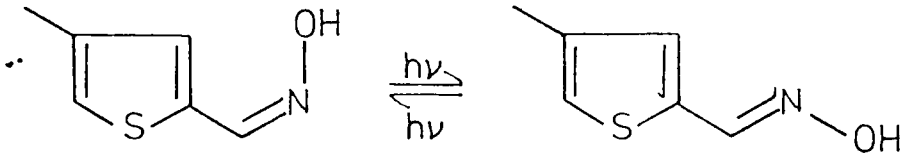

(2·80) (2·81) (2·82) (2·83)

phototransposition reaction of the fully labelled nitrile (2·80), to give as the major products upon irradiation in hexane the nitrile (2·83) and the bicyclic compound (2·82), subsequent reaction leads to products where the sequential order of carbon atoms in starting material and products is the same.

The effect of nitrile groups is much stronger than the effect of methyl groups since methylthiophene-carbonitriles do not behave as methylthiophenes, but as thiophene-carbonitriles. Accessibility to 2,5-bonding may be due, at least in part, to electron-withdrawal by the nitrile group. In order to investigate this further, several compounds containing other electron-withdrawing groups were synthesised and irradiated.

## 2.4.1 Irradiation of thiophene-aldoximes.

Several methylthiophene-aldoximes were irradiated. The main route for energy degradation in these compounds

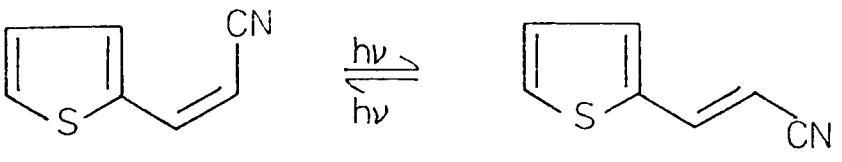



Scheme 2·35

appeared to be syn-anti isomerisation, Scheme 2·35. Thus irradiation of anti-4-methylthiophene-2-aldoxime gave a 1:1 mixture of the syn and anti-isomers. No transposition products were detected. Syn - anti isomerisation has been reported to occur photochemically for various benzaldoximes.[218] Photochemical Beckmann rearrangements were also observed when the irradiations were carried out in acetic acid solution.

## 2.4.2 Irradiation of thiophene-2-acrylonitrile.

A mixture of cis- and trans-thiophene-2-acrylonitrile was irradiated under various conditions. The main reaction




Scheme 2·36

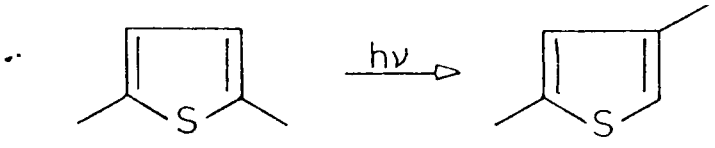
observed was cis - trans-isomerisation, Scheme 2·36. Prolonged irradiation gave small amounts of acrylonitrile 2+2 photodimers. Head to head dimerisation is reported in the literature for acrylonitriles to give mixtures of cis- and trans-cyclobutane-dinitriles.[219] No transposition reaction was detected from thiophene-2-acrylonitrile and irradiation in furan solution produced no furan adducts.

As described in the Introduction, several other thiophenes containing electron-withdrawing groups have been irradiated and were found not to transpose. All of these, like the aldoxime and acrylonitrile just described, had alternative reactions to phototransposition as a means of dissipating excitation energy. The introduction of four perfluoromethyl groups into the thiophene nucleus leads to facile 2,5-bonding upon excitation with ultra-violet light. Perfluoroalkyl groups are photochemically inert and are also electron-withdrawing, but it is difficult to establish how much of the photochemical behaviour of tetrakis(perfluoromethyl) thiophene is due to the peculiar stabilising effect that perfluoroalkyl groups have on strained molecules. In this context it would be interesting to observe the photochemical processes of mono or di-substituted perfluoromethylthiophenes.

The contrast between the phototransposition reactions of thiophene-carbonitriles and alkylthiophenes is clearly illustrated by the photochemical behaviour of 2,5-dimethylthiophene described below.

## 2.4.3 Irradiation of alkylthiophenes.

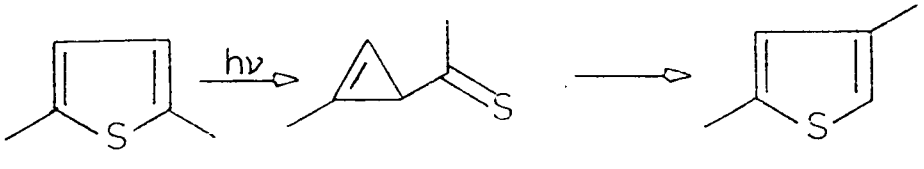
2,5-Dimethylthiophene (2·84) was irradiated in both the gas phase and solution. In both cases 2,4-dimethylthiophene




(2·84) (2·85)

(2·85) was obtained.

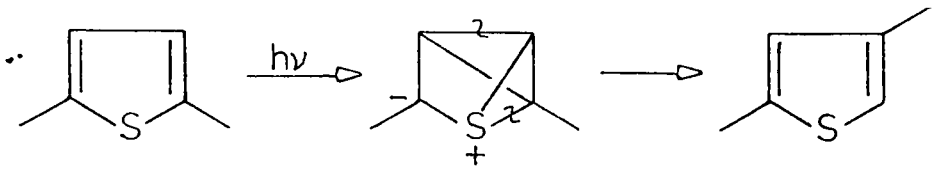
This reaction clearly cannot proceed *via* a pathway involving initial 2,5-bonding to give a 5-thiabicyclo[2·1·0] pent-2-ene and subsequent sulphur-walk, since the sequential order of carbon atoms has altered. The mechanism illustrated in Scheme 2·33 involving primary ring-contraction followed by ring-expansion does account for the observed photoisomerisation. One point against this mechanism is that irradiation of 2,5-




Scheme 2·33

dimethylthiophene in furan solution produced no adducts of any description. The cyclopropenyl system can usually be trapped

by Diels-Alder reaction with furan. However, if the intermediate is very short-lived, it could pass undetected. The transposition could also occur <u>via</u> a zwitterionic mechanism




Scheme 2·34

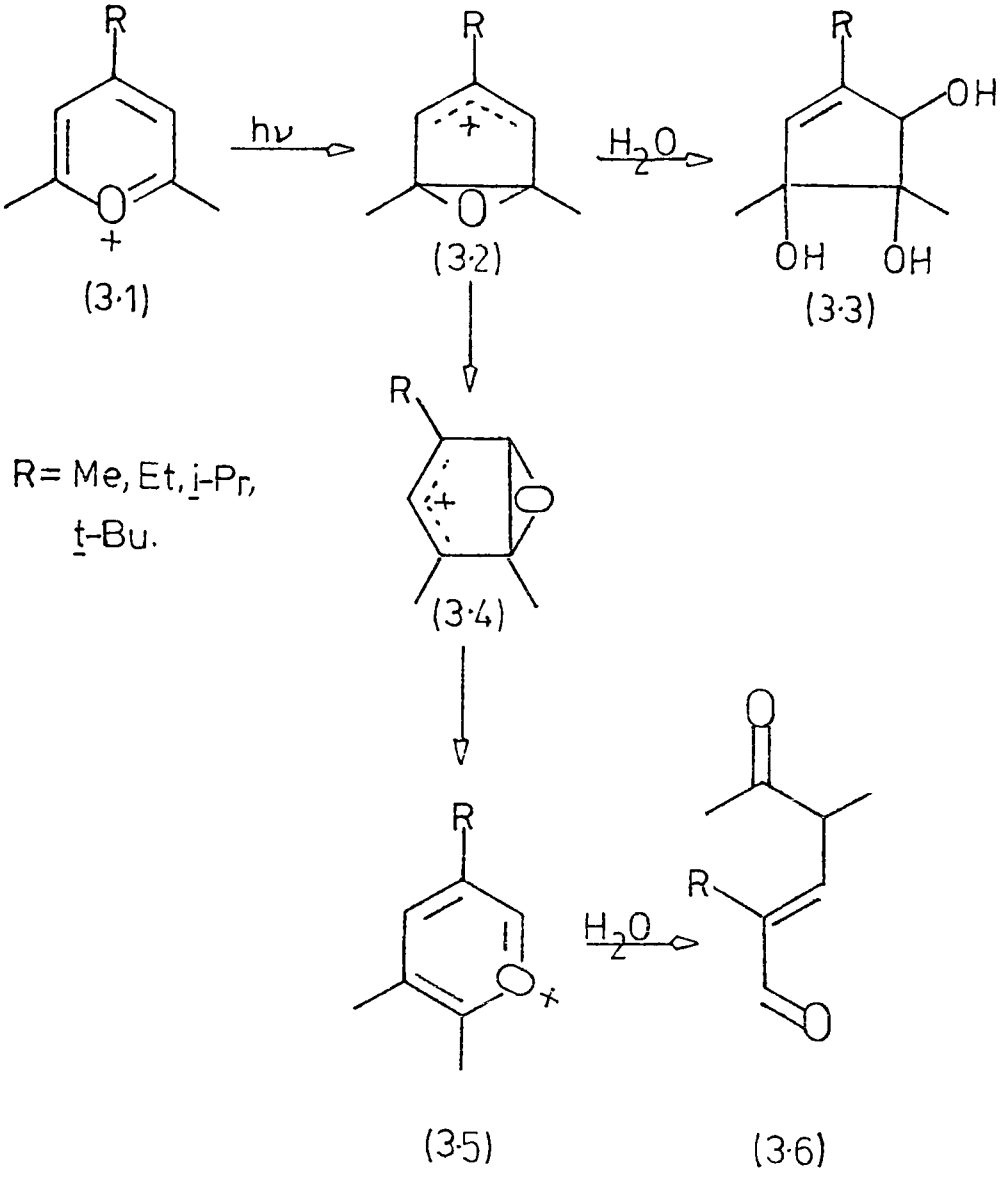
as depicted in Scheme 2·34.

Thiophene itself was irradiated in an argon matrix at 7K for several hours, but monitoring of the irradiation by infra-red spectroscopy showed thiophene to be stable to irradiation at that temperature. No adducts of thiophene could be obtained upon irradiation in the presence of furan at 34°.

## Chapter Three

## PHOTOCHEMISTRY OF PYRYLIUM CATIONS

Barltrop, Day et. al.[60,71,75] found that 2,4,6-trialkylpyrylium cations, when irradiated in water, either underwent an apparent transposition reaction to give a ring-opened keto-aldehyde (3·6) or gave hydrolysis products derived from solvent attack on an intermediate bicyclohexenyl cation as in Scheme 3·1. They proposed




Scheme 3·1

mechanism for the transposition reaction which involved initial 2,6-bonding to give an allylic carbonium ion (3·2) which could then undergo a thermal oxygen-walk step to give a rearranged cation (3·4). Rearomatisation of this was proposed to give a pyrylium cation (3·5) with no alkyl group in one of the α-positions. This was predicted to undergo a ring-opening reaction in water to give the cis-form of (3·6). Alternatively (3·2) could be trapped by solvent to give hydroxycyclopentenes (3·3).

There are several features of the photochemistry of 2,4,6-trialkylpyrylium cations which suggest that the situation depicted in Scheme 3·1 is not accurate. For example, none of these compounds shows any photochemistry in acetonitrile solution.[201] According to Scheme 3·1, one would expect to observe the transposed pyrylium cations. In addition, it is necessary to account for the fact that bulky groups in the 4-position, such as isopropyl and tert-butyl, prevent the apparent phototransposition reaction from occurring in aqueous solution.

The approach to these, and other problems connected with pyrylium cation photochemistry, was outlined in the Introduction. The experiments designed to resolve these questions, their results, and their mechanistic implications will now be described.

## 3.1 Irradiation of 2-ethyl-4,6-dimethyl[5-$^2$H] pyrylium perchlorate

Permutation pattern analysis of the products from the irradiations above shows the results to be interpretable in terms of either a $P_2$ or $P_4$ permutation pattern,[34] Scheme 3·2. The former is consistent with the mechanism involving initial 2,6-bonding and a subsequent oxygen-walk, but the latter is suggestive of a mechanism involving walk of a carbon atom, as well as of other mechanisms.

The difficulty can be resolved by irradiation of an appropriately labelled pyrylium cation which gives different products characteristic of either a $P_2$ or a $P_4$ permutation pattern.

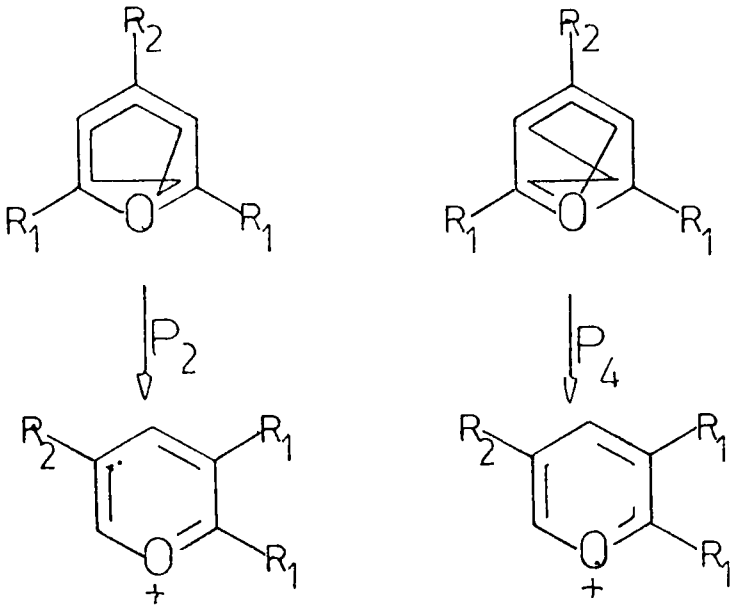
The cation (3·7) was synthesised by treatment of appropriately labelled mesityl oxide with propionyl chloride and aluminium chloride, and then cyclisation of the resulting dicarbonyl compound with perchloric acid. Permutation pattern analysis shows that irradiation of (3·7) should yield a mixture of (3·8) and (3·9) according to the $P_2$ pattern, or (3·10) and (3·11) according to the $P_4$ pattern. (3·8) and (3·10) are the same compound, differing only in the position of the deuterium, and similarly related are (3·9) and (3·11).

Irradiation of (3·7) in water gave a mixture of two compounds. The major product was determined by nmr to be trans-2,4-dimethyl-5-oxo[3-$^2$H]hept-2-enal (3·8), easily distinguished from (3·10) since it contained an aldehydic hydrogen. A smaller amount of the methyl ketone (3·9) was also formed, lacking an aldehydic proton.

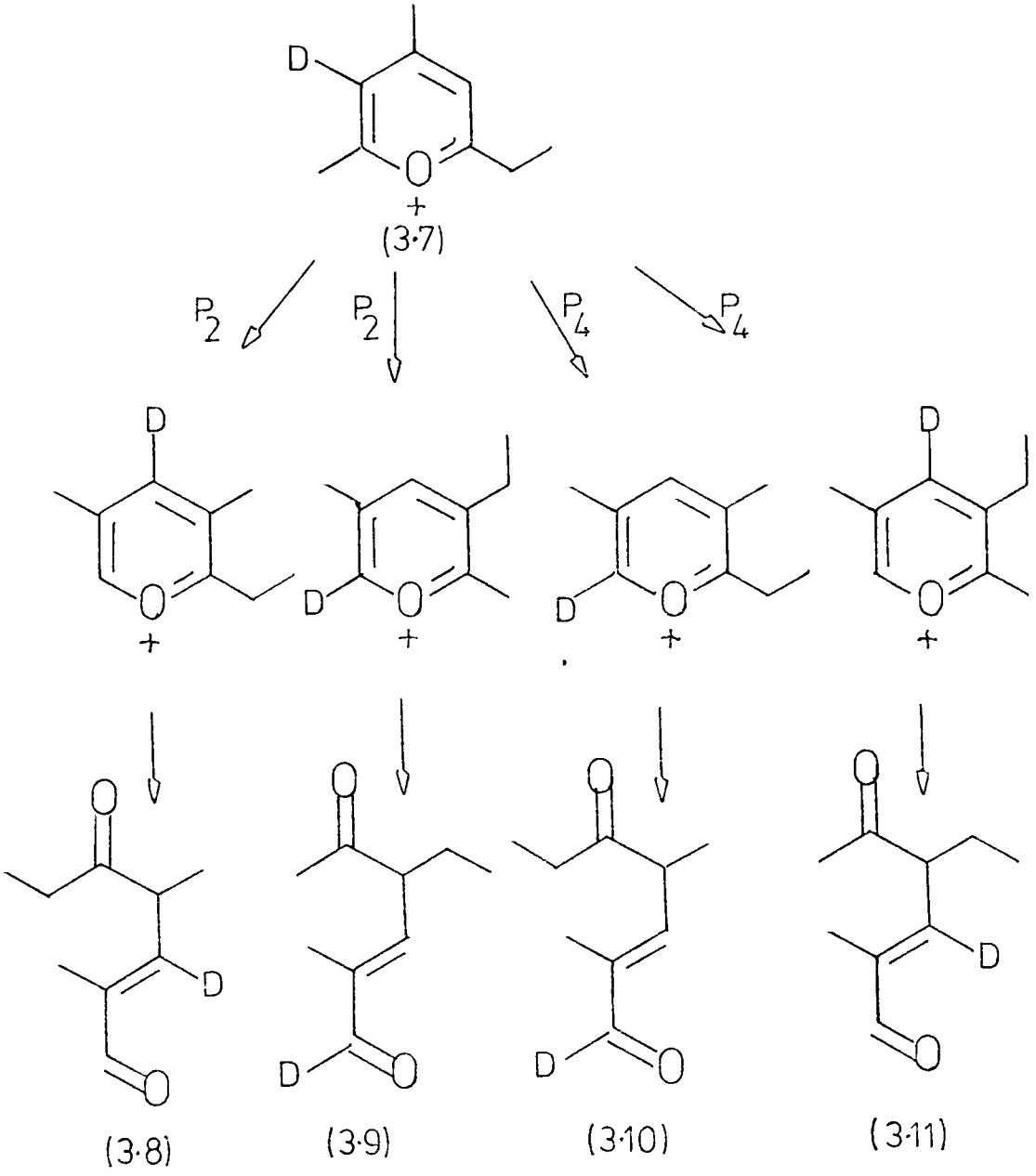
This clearly demonstrates that the $P_2$ pattern is valid and not the $P_4$, for the representation of the photoreaction in water. Thus a mechanism involving migration of carbon atoms can be largely discounted, while a mechanism involving initial 2,6-bonding is supported by the observed $P_2$ pattern for the reaction.

## 3.2 Irradiation of 2,4,6-trialkylpyrylium cations in non-aqueous solvents.

It is apparent that a route to the ring-opened products (3·6) can be postulated which does not involve either a shift of oxygen

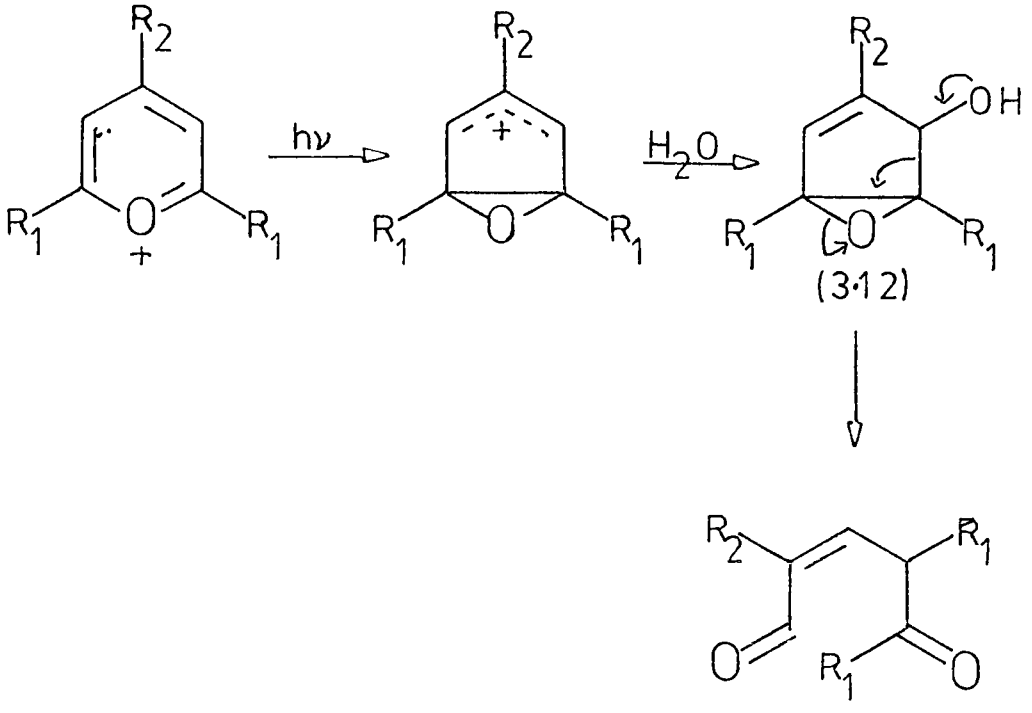


Scheme 3·2



Scheme 3·3

or rearomatisation of the walked oxabicyclohexenyl cation. Thus a Grob-type fragmentation[74] of an intermediate solvent adduct (3·12) can account for all of the observed products, Scheme 3·4.

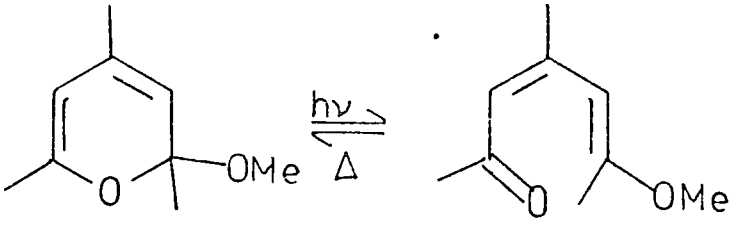



Scheme 3.4

Previous workers had tried to show that this path was not taken by carrying out the irradiations in acetonitrile solution.[201] In this way it was hoped to detect the transposed pyrylium cations with a free α-position. These are known to be stable in acetonitrile solution.[202] However, all of the 2,4,6-trialkylpyryliums (3·1) where $R_1$ = methyl and $R_2$ = methyl, ethyl or tert-butyl, were found to be photostable in acetonitrile solution. Thus either the Grob-type fragmentation route for the formation of the keto-aldehydes is operative in the aqueous photolyses, or acetonitrile does not stabilise the bicyclohexenyl cation sufficiently and so it is either not fully formed or quickly rearomatises.

Since it is known that carbonium ions are more stable in solvents with high dielectric constants, the 2,4,6-trialkylpyrylium pyrylium salts were irradiated by this author in both propylene carbonate ($\varepsilon$ = 65) and N-methylformamide ($\varepsilon$ = 182). These compare with values for acetonitrile and water of 36 and 78·5 respectively. No transposition was observed in these solvents. However it must be pointed out that although these solvents have high dielectric constants, they may not be as good at solvating in these cases as water because of their size.

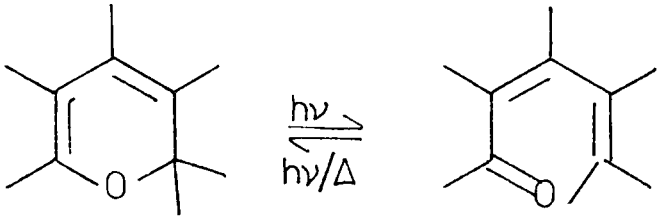
Irradiation of 2,4,6-trimethylpyrylium perchlorate in methanol led to an extremely complex mixture of over twenty products. Analysis of the mixture by g.c.m.s. showed most of the products to contain the pyrylium nucleus with either one, two or three methanol molecules incorporated. The complexity of the mixture prevented identification of any of the components. This complexity may be due to the fact that in methanol solution, pyrylium cations are in equilibrium with 2-methoxypyrans.[203] Treatment of 2,4,6-trimethylpyrylium perchlorate in methanol with sodium methoxide permitted the isolation of 2-methoxy-2,4,6-trimethylpyran (3·13). Upon irradiation in cyclohexane solution, (3·13) was converted to




(3·13) (3·14)

a highly conjugated system containing an $\alpha,\beta$-unsaturated carbonyl band in the infra-red spectrum, and the vinyl hydrogens at 4·83

and 4·93 in the nmr spectrum of (3·13) were replaced by others at 5·45 and 4·15. The reverse reaction occurred thermally. The spectral data suggested that a photoequilibrium was set up between the pyran and its ring-opened vinyl ether isomer (3·14). This behaviour closely parallels that of 2-alkylpyrans.[253,254] These also undergo light-induced ring-opening reactions which are




(3·15) (3·16)

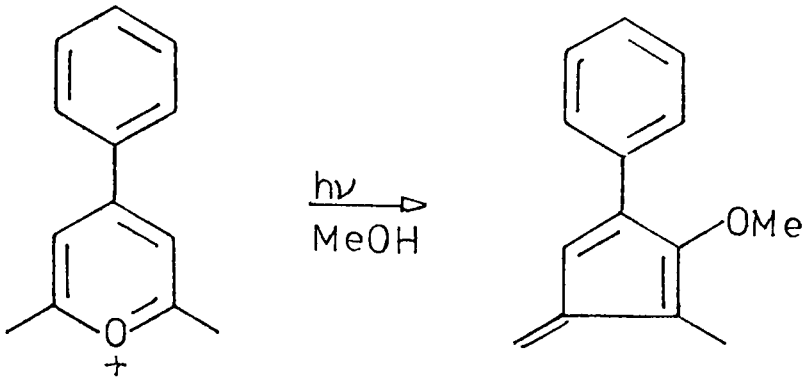
frequently photochemically or thermally reversible as shown in the interconversion of (3·15) and (3·16).

It seems probable that the complexity of the photochemistry of 2,4,6-trimethylpyrylium perchlorate in methanol may be due to the intervention of species such as (3·13) and (3·14) in the reaction system.

## 3.3 Irradiation of 2,6-dimethyl-4-phenylpyrylium perchlorate in methanol.

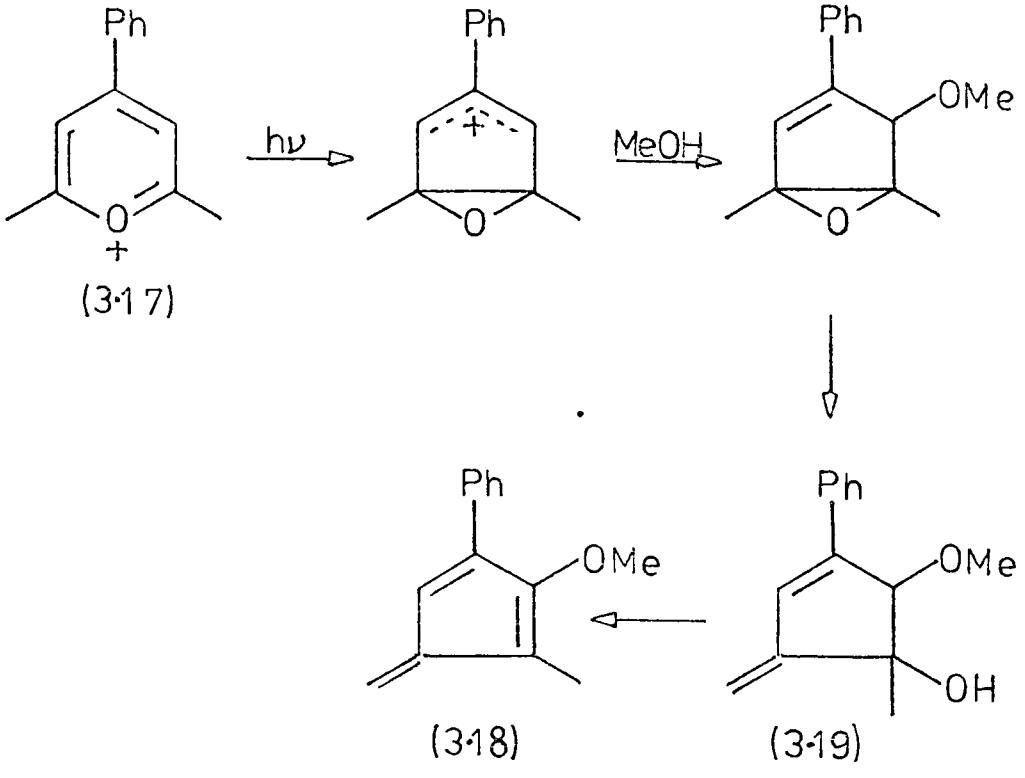
The photochemistry of 2,6-dimethyl-4-phenylpyrylium perchlorate (3·17) in methanol was not as complicated as that of the trimethyl compound. Irradiation led mainly to a compound identified as the fulvene (3·18).

Mass spectral analysis showed the molecular ion of (3·18) at m/e 198. A large metastable ion at 142·5 was probably derived




(3·17) (3·18)

from 198 ⟶ 168(9), a loss of $CH_2O$, highly characteristic of aromatic methyl ethers. The infra-red spectrum showed only bands assignable to (3·18) and the ultra-violet spectrum showed absorption out to long-wavelengths. The nmr spectrum showed a methyl group on a double-bond at 2·38, a methoxy signal at 3·80, three vinyl hydrogens at 6·60, 6·81 and 6·91, and a phenyl group.

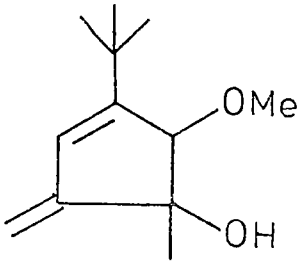



(3·17) (3·18) (3·19)

Scheme 3·5

The fulvene (3·18) is easily derivable from (3·17) as shown in Scheme 3·5. Ultra-violet excitation of the pyrylium cation gives a bicyclohexenyl cation which is trapped by methanol. The acidic conditions thus generated can cause opening of the epoxide and subsequent dehydration to (3·18).

The production of (3·18) *via* (3·19) may be compared with the results of irradiation of 2,6-dimethyl-4-*tert*-butylpyrylium perchlorate in methanol.[201] Among the ten components of the oily photoproduct was a compound tentatively identified as (3·20).

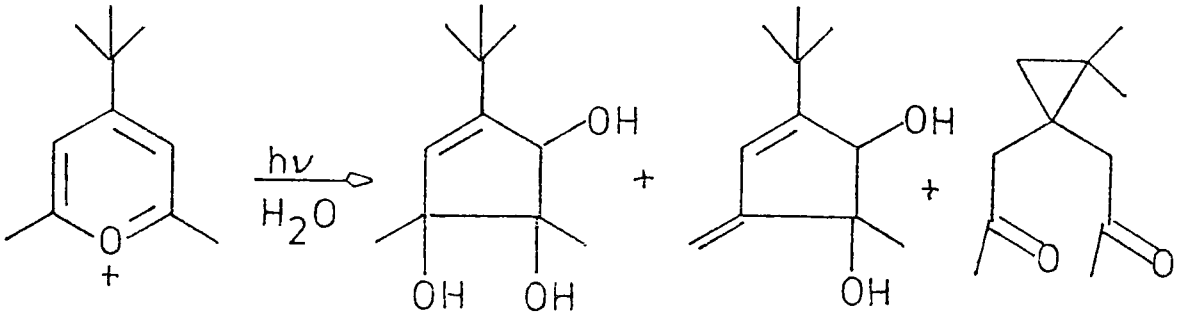



(3·20)

No other components of the mixture were identified.

## 3.4 Irradiation of 2,6-dimethyl-4-tert-butylpyrylium perchlorate and its pseudobase.

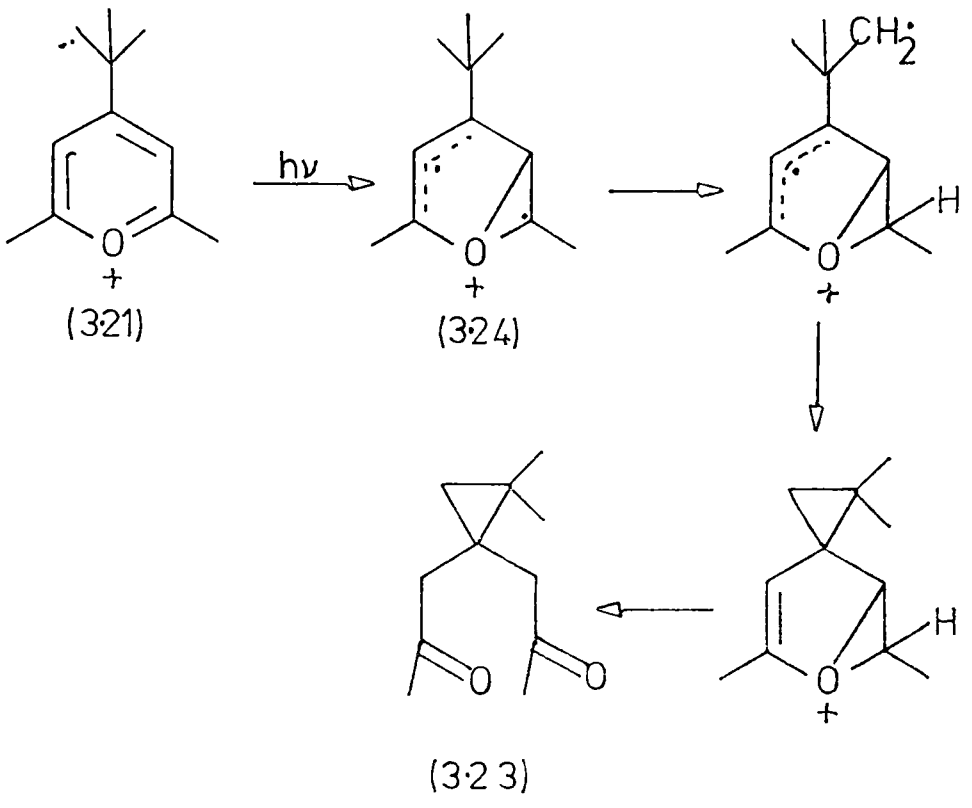
Previous work had shown that irradiation of 2,6-dimethyl-4-*tert*-butylpyrylium perchlorate in aqueous solution gave two isomeric triols, a diol and a cyclopropyl compound,[60] Scheme 3·6.




(3·21) (3·21A+B) (3·22) (3·23)

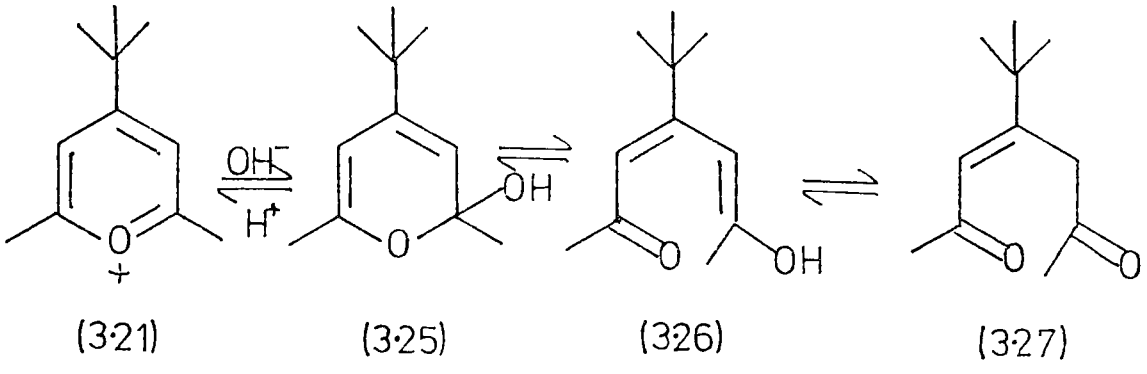
Scheme 3·6

The cyclopropyl compound (3·23) was suggested to have arisen via primary formation of the prevalene (3·24) which then underwent an intramolecular hydrogen abstraction reaction as shown in Scheme 3·7. However, it is known that in aqueous solution,




Scheme 3·7

pyrylium cations are in equilibrium with their pseudobases,[72,204] Scheme 3·8.



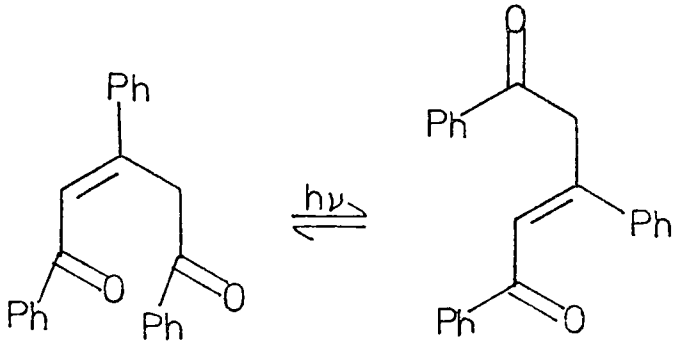

Scheme 3·8

Normally, 2H-pyrans of the type (3·25) readily undergo ring-opening so that only ketones of the type (3·27) are isolated.

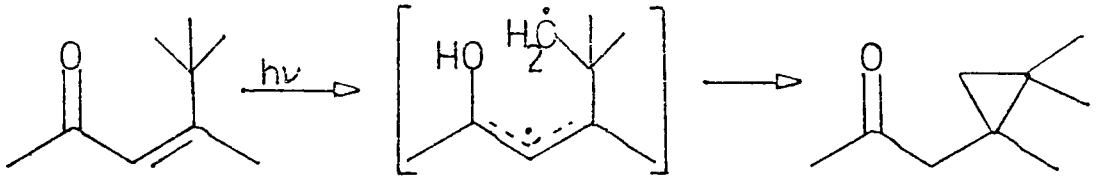
Ultra-violet spectroscopy of $5 \times 10^{-4}$ M solution of (3·21) in water revealed that below pH 1·5 only the pyrylium cation was present ($\lambda_{max}$ = 285nm), above pH 9 only the diketone (3·27) was present ($\lambda_{max}$ = 240nm), and above pH 12·5, the enolate was present ($\lambda_{max}$ = 290nm). Under normal conditions, the pH of the solution of (3·21) being irradiated would be 3·0 - 4·0.

Diketones of the type (3·27) are photoactive. For example, they are known to undergo facile cis to trans isomerisation.[205]

It is also known that α,β - unsaturated carbonyl compounds



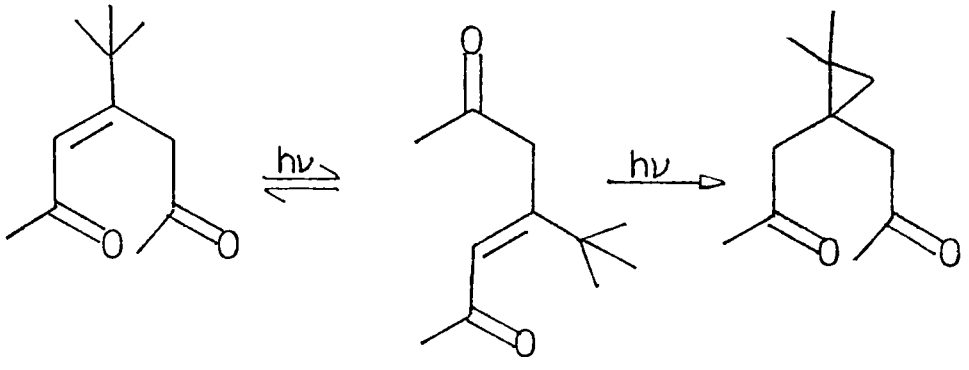

with tert-butyl groups on the β-carbon atom undergo a photochemical intramolecular hydrogen abstraction reaction leading to the formation of cyclopropanes.[207,208] For example, (3·28) is converted upon irradiation in benzene solution to (3·29).




(3·28) (3·29)

Clearly this may be the way in which the cyclopropane (3·27) is formed in the aqueous photolysis of (3·21). This hypothesis was tested in two ways.

Firstly, the ring-opened pseudobase (3·27) of (3·21) was obtained by treatment of the pyrylium salt with aqueous sodium hydroxide. This was irradiated in degassed benzene solution and was observed to undergo facile <u>cis</u> to <u>trans</u> isomerisation giving




(3·27) (3·30) (3·23)

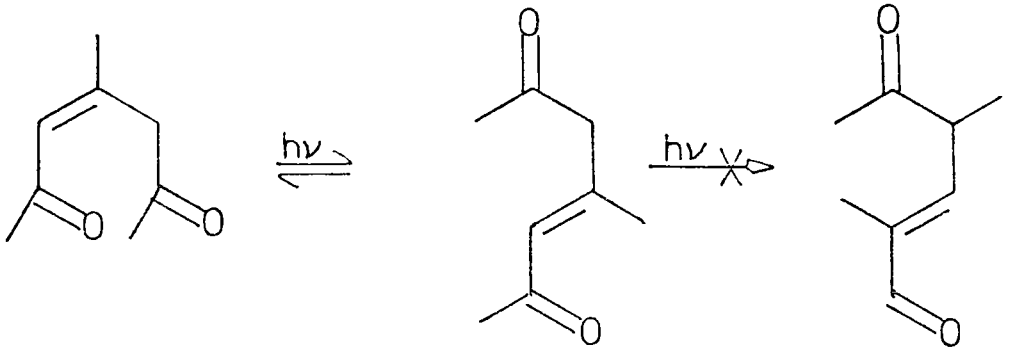
a ratio (3·27) to (3·30) of 1·00 to 1·12, and to yield, upon further irradiation, almost exclusively 1,1-diacetonyl-2,2-dimethylcyclopropane (3·23).

In a second experiment, aqueous solutions of the pyrylium salt were irradiated under various pH conditions, and the various yields of the cyclopropyl compound were determined relative to its yield at the normal irradiation pH of 3·8. Thus, at higher pH, irradiation should give higher yields of the cyclopropane (3·23) since more of the pseudobase (3·27) is present, whilst at pHs of less than 3·8, lower yields should be obtained since less of the pseudobase is present. If the cyclopropyl compound came from the prevalene (3·24), one would expect opposite results since less

of the pyrylium cation is present at high pH values. The experiments showed the yield of (3·23) at various pH values to vary from 0·3 at pH 1·8 to 65 at pH 6·6, compared to a value of 1·0 at the normal irradiation pH of 3·8.

These results clearly show that the cyclopropane (3·23) is derived from ring-opened pyrylium cation and not from the proposed prevalene (3·24).

Ring-opened pyrylium ions are not responsible for the apparent transposition reactions leading to keto-aldehydes.



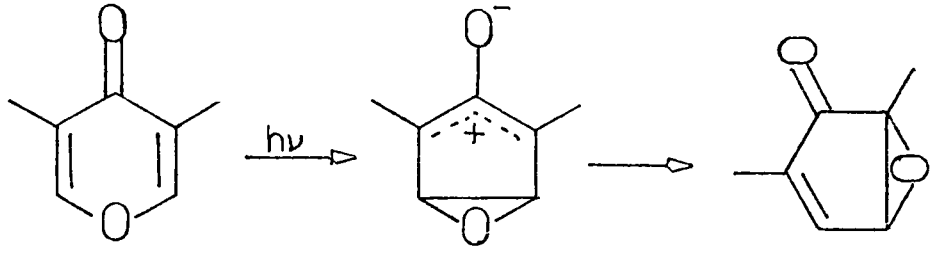

(3·31) (3·32) (3·33)

The diketone (3·31) derived from the action of base on 2,4,6-trimethylpyrylium perchlorate showed only cis to trans isomerisation giving a mixture of (3·31) and (3·32) upon irradiation. No aldehyde of the type (3·33) was formed.

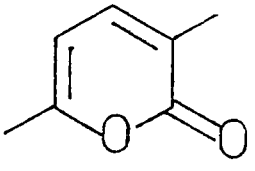
## 3.5 Irradiation of 3- and 5-alkylated pyrylium salts.

In order to answer the basic question of whether or not alkyl substituted pyrylium cations transpose, it was decided to synthesise a number of pyrylium ions with various degrees of substitution at the 3,4 and 5- positions. Since there is evidence that the excited state of the pyrylium cation collapses to a 2,6-bonded allylic carbonium ion, and since it is also known

that tertiary carbonium ions are more stable than secondary, and that there is an increase in stability of carbonium ions with increasing numbers of α-hydrogens,[206,209] it seems likely that increasing 3,4 and 5-substitution will enhance the rate of formation of the allylic cation and may stabilise it to such an extent that transposition reactions may be seen in inert solvents. This has been found to be the case with 4-pyrones.[66,68]



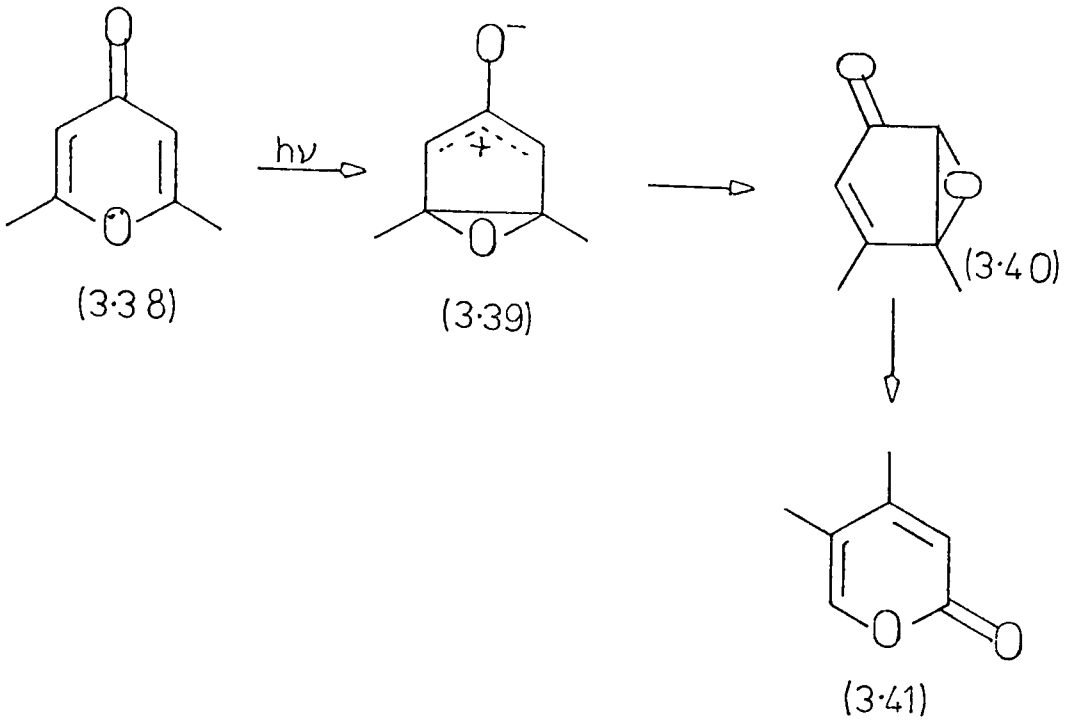

(3·34) (3·35) (3·36)



(3·37)

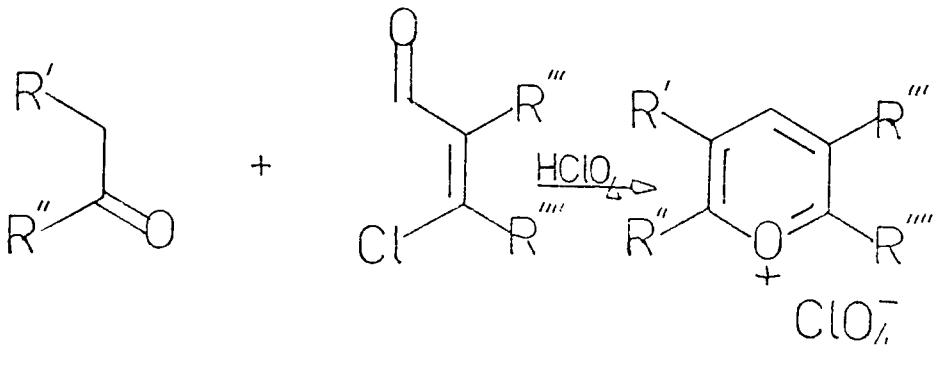
Here, irradiation of 3,5-dimethyl-4-pyrone in 2,2,2-trifluoroethanol gives the 2-pyrone (3·37) via the epoxide (3·36). This epoxide can be isolated and converted photochemically to the 2-pyrone. The analogous 2,6-dimethyl-4-pyrone (3·38) does not rearrange efficiently in this way, but the epoxide (3·40) through which it would pass if the 2,6-bonded allylic carbonium system was formed, has been independantly synthesised and shown to rearrange smoothly to the 2-pyrone (3·41).[247] Only in very dilute solution in 2,2,2-

trifluoroethanol is the dimerisation reaction of (3·38)




retarded enough to allow the formation of a low yield of 4,5-dimethyl-2-pyrone (3·41).[248]

The pyrylium cations (1) to (11) shown in Table 3·1, all with perchlorate as anion, were synthesised. Only (8) and (9) were unknown compounds. These were obtained by the method due to Andrieux et. al.[217] involving the condensation of methylene ketones with β -chlorovinylaldehydes in the presence of anhydrous perchloric acid in acetic acid. Thus the condensation of 2-butanone with 3-chloro-2-methylpent-2-enal gave (8) while the condensation

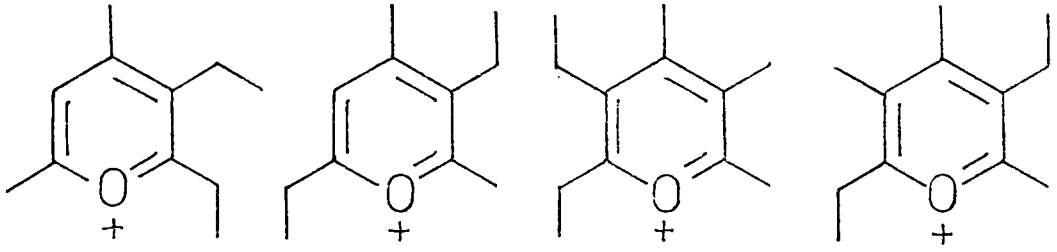


of 3-pentanone with the same aldehyde gave (9).

The cations (1) to (9) of Table 3·1 were irradiated in water, acetonitrile and various other solvents. The results are summarised in Table 3·1; fuller details may be found in the Experimental Section.

The pyrylium cations marked "#" were not isolated and characterised, but were identified in mixtures by their nmr spectra. The nmr spectra of pyrylium cations are very indicative of the substitution pattern.[246] For example, in dilute sulphuric acid solution, α-methyl groups appear at 2·87 to 2·96, β-methyl groups at 2·43 to 2·50 and γ-methyl groups at 2·69 to 2·84. Similarly α-hydrogens appear at 9·6, β-hydrogens at 7·70 to 8·00, and γ-hydrogens at 8·50 to 8.90. Ethyl groups also resonate at characteristic frequencies. In acetonitrile solvent, the chemical shift of substituents is equally characteristic of their positions, as Table 3·2 shows.

This method of analysis is conclusive for all of the isomers except (12) and (14). Thus (12) could be confused with (15), and (14) could be confused with (16). However, since (8) gives (13)



(12) (15) (14) (16)

which can be distinguished from (6) by comparison of the nmr spectrum of (13) with authentic (6), it seems clear that unless a drastic change in mechanism has occurred simply on substituting an ethyl group for an α-methyl group, the assignments as shown

TABLE 3·1

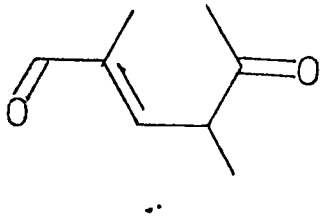
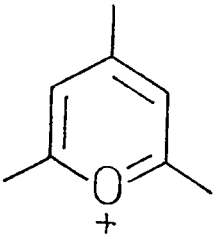
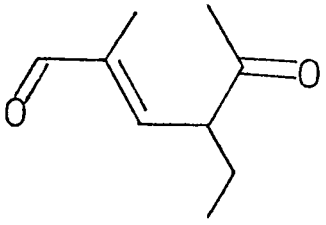
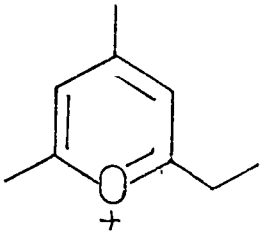
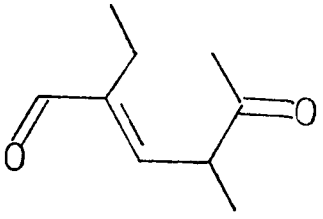
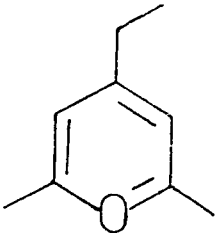
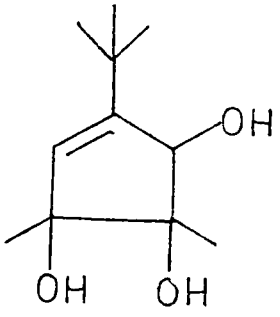
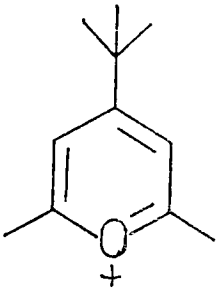
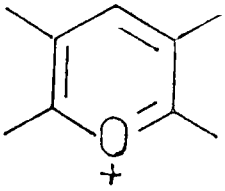
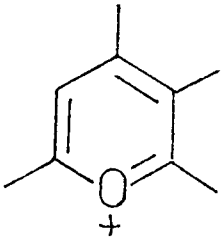
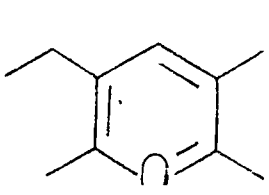
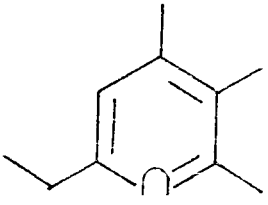
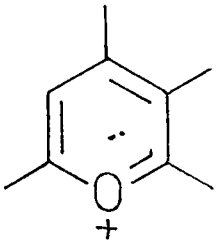
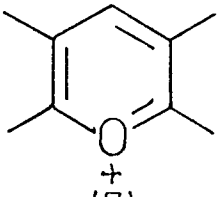
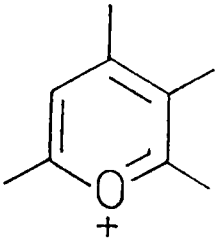
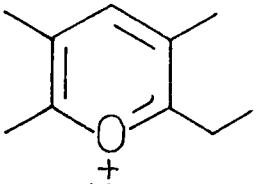
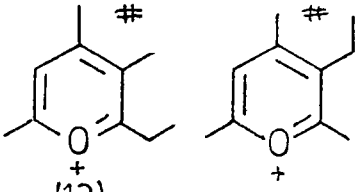
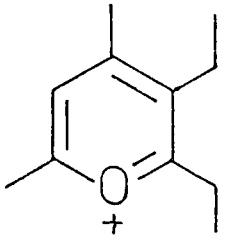
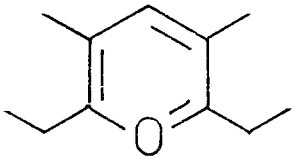
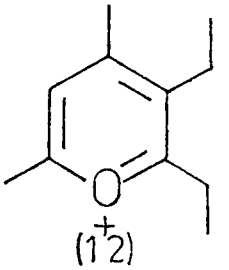
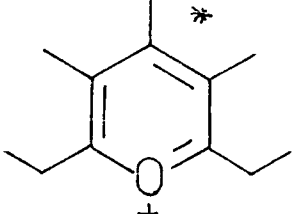
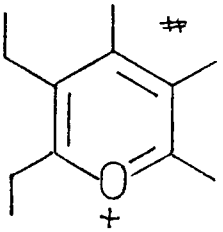
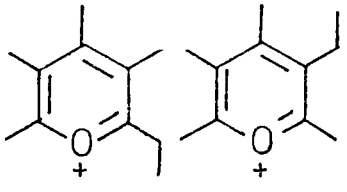
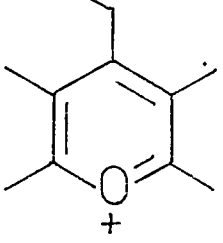
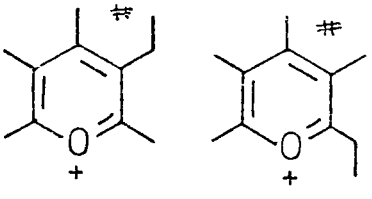
| PRODUCT IN WATER | CATION IRRADIATED | PRODUCT IN ACETONITRILE |
|---|---|---|
|  |  (1) | none |
|  |  (2) | none |
|  |  (3) | none |
|  |  (4) | none |
|  |  (5) | none |
|  |  | none |

TABLE 3·1 contd.

| PRODUCT IN WATER | CATION IRRADIATED | PRODUCT IN ACETONITRILE |
|---|---|---|
|  |  (7) |  |
| not irradiated |  (8) |  (13) |
|  |  (9) |  (12) |
| not irradiated |  (10) |  (14) |
|  |  (11) |  |

* Irradiated in trifluoracetic acid.

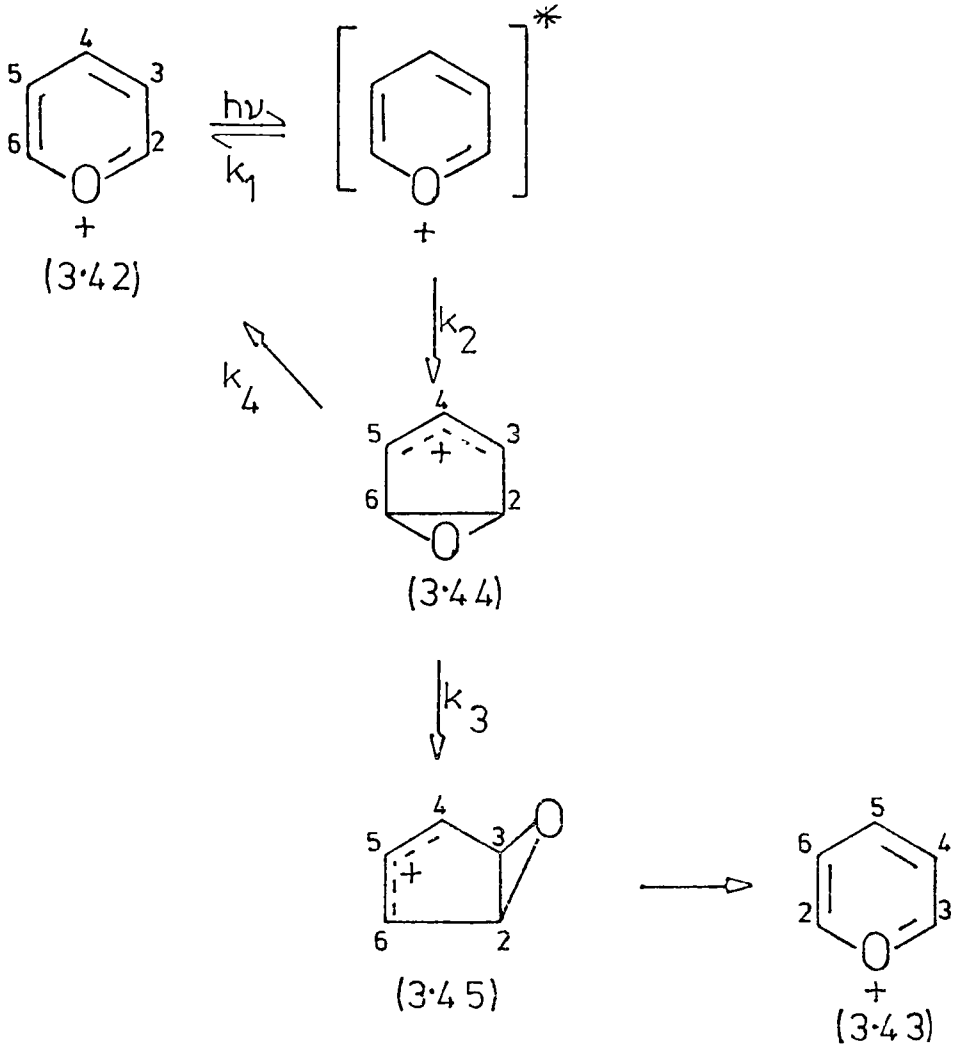
TABLE 3·2

| Pyrylium Cation | Chemical Shift in Acetonitrile | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | β H | γ H | α $CH_3$ | β $CH_3$ | γ $CH_3$ | α Et | β Et | γ Et |
| (1) | 7·71 | | 2·81 | | 2·63 | | | |
| (2) | 7·71 | | 2·81 | | 2·61 | 3·11 | | |
| (3) | 7·74 | | 2·81 | | | | | 2·96 |
| (4) | 7·72 | | 2·79 | | | | | |
| (5) | 7·72 | | 2·78 | 2·34 | 2·60 | | | |
| | | | 2·81 | | | | | |
| (6) | 7·72 | | 2·81 | 2·33 | 2·61 | 3·14 | | |
| (7) | | 8·46 | 2·80 | 2·41 | | | | |
| (8) | | 8·43 | 2·81 | 2·40 | | 3·15 | | |
| (9) | | 8·42 | | 2·40 | | 3·16 | | |
| (11) | | | 2·77 | 2·47 | | | | 2·95 |
| (12) | 7·68 | | 2·76 | | 2·63 | 3·16 | 2·70 | |

for (12) and (14) must be correct.

The results shown in Table 3·1 show that alkyl groups are necessary in both the 3- and 5-positions for photoisomerisation to occur in acetonitrile solution. Alkyl groups in the 4-position are not necessary.

The importance of 3,5-substituents may be explained as follows. If the excited state pyrylium cation transforms into the 2,6-bonded species (3·44), scheme 3·9, then the competition

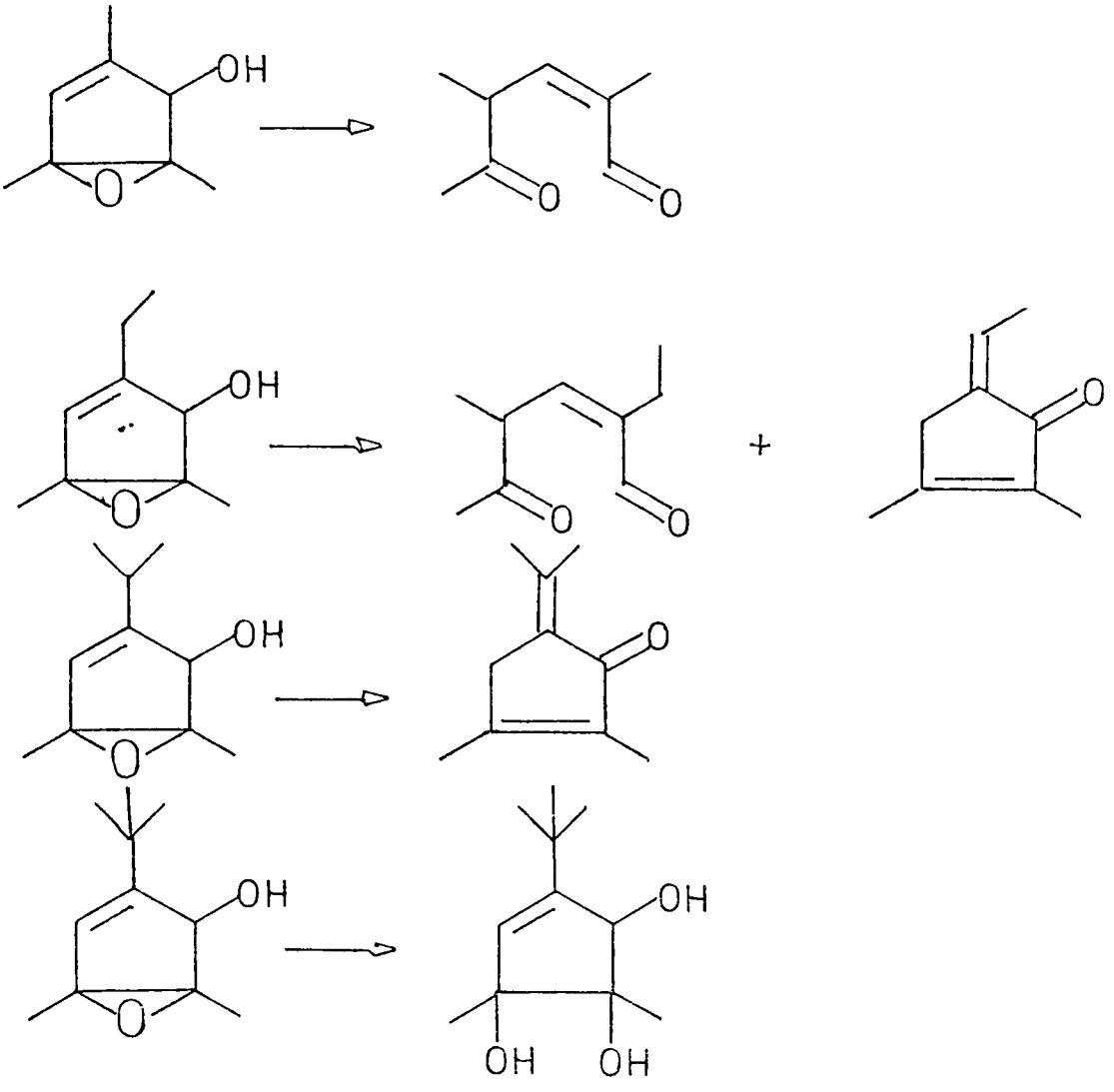



Scheme 3·9

is between rearomatisation to the pyrylium cation (3·42) or oxygen-walk to the rearranged 2,6-bonded species (3·45).

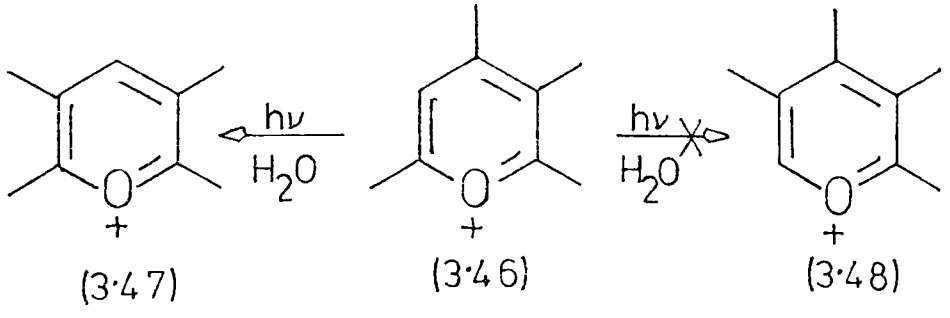
Both of these processes will be favoured by the instability of the allylic carbonium ion. It does not seem likely that the instability of the allylic carbonium ion facilitates the aromatisation but has no effect on the rate of oxygen walk ($k_3$). On the other hand, if the 2,6-bonded species is not formed, then the competition comes earlier, between 2,6-bonding which is disfavoured by the absence of 3,5-alkyl substitution and deactivation of the excited state which might show a smaller dependence on the substitution pattern.

The insensitivity of the photohydrolysis reaction to substitution pattern may be due to nucleophilic attack by water at the C-3/C-5 carbon of the excited state cation. This may facilitate 2,6-bonding by the avoidance of the formation of an unstable allylic carbonium ion. The allylic alcohol thus formed may then undergo a fragmentation reaction as described earlier in Scheme 3·4. Any diketones formed in this way would be expected to cyclise to pyrylium cations under the acidic conditions, while keto-aldehydes would be predicted not to cyclise. Some support for this is gained from the fact that no keto-aldehydes are observed in the aqueous irradiations of 2,6-dimethyl-4-isopropylpyrylium perchlorate and 2,6-dimethyl-4-tert-butylpyrylium perchlorate. Since five atomic centres of one molecule are involved in the transition state for the Grob-type fragmentation, the mechanism has rigorous structural and stereoelectronic requirements. Bulky 4-alkyl groups may prevent the concerted operation of the reaction and favour other types of processes. Thus, whereas the 4-methyl compound readily undergoes the fragmentation, the 4-ethyl compound undergoes it less readily and the 4-isopropyl compound not at all. The 4-t-butyl compound, having no allylic hydrogen on the 4-substituent,



is forced to undergo yet a different reaction.

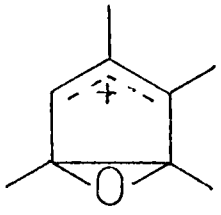
From Table 3·1 it can be seen that unsymmetrically 3,5-substituted pyrylium cations show an interesting regioselectivity in their photohydrolysis reactions. For example, in Scheme 3·10 the cation (3·46) gives (3·47) on irradiation in water, but no (3·48) or its pseudobase. This indicates that there is a marked



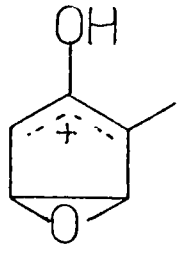

(3·47) (3·46) (3·48)

Scheme 3·10

preference for nucleophilic attack at the more substituted



(3·49)



(3·50)

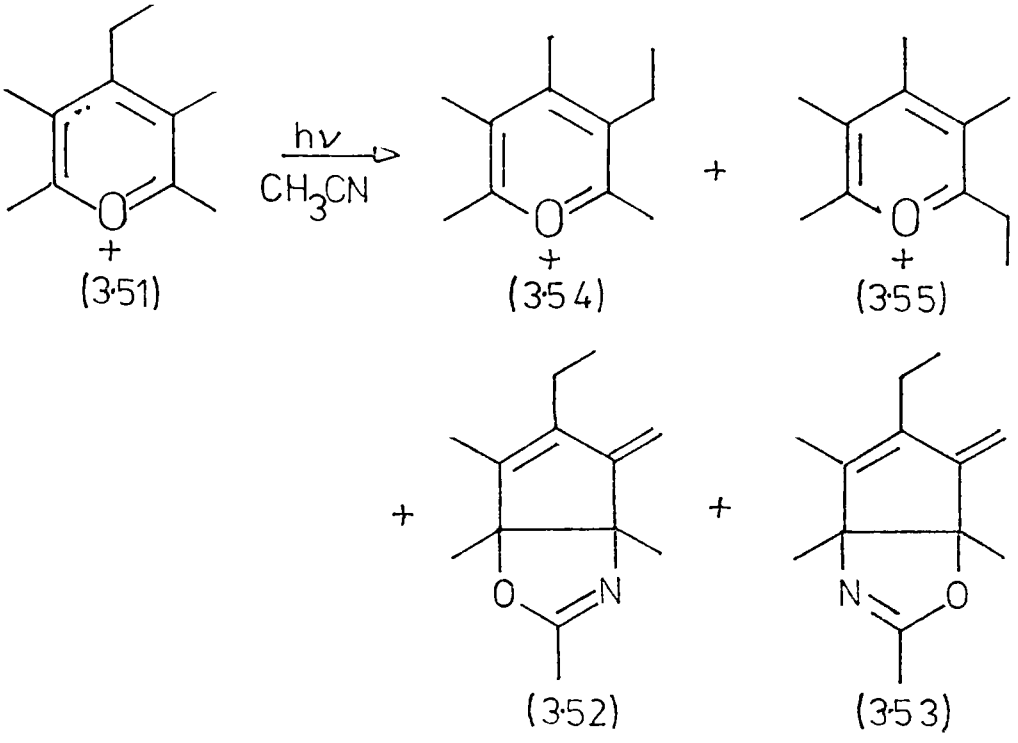
centre of the oxabicyclohexenyl cation (3·49) or its precursor. This corresponds to attack at the position of greater charge density, and has precedents in the known preference for solvolytic attack at the more substituted centre of unsymmetrical allyl cations. A similar regioselectivity is observed in the photo-transposition reactions of 4-hydroxypyrylium cations which are unsymmetrically substituted in the 3- and 5- positions.[258] Thus, irradiation of the 3-methyl-4-hydroxypyrylium cation in sulphuric acid leads to a product distribution of 3 to 1 in favour of those derived by initial nucleophilic attack of bisulphate anion at the 3-position of the bicyclohexenyl cation (3·50).

## 3.6 Formation of Oxazolines

Much evidence has been presented which shows that the photohydrolysis reactions of pyrylium cations can be explained in terms of the intermediacy of a 2,6-bonded species. Calculations on the excited states of pyrylium cations have also shown that 2,6-bonding may correlate with the first excited singlet state.[210]

Evidence that the phototransposition reactions of alkylated pyrylium cations in acetonitrile involves a 2,6-bonded oxabicyclo-

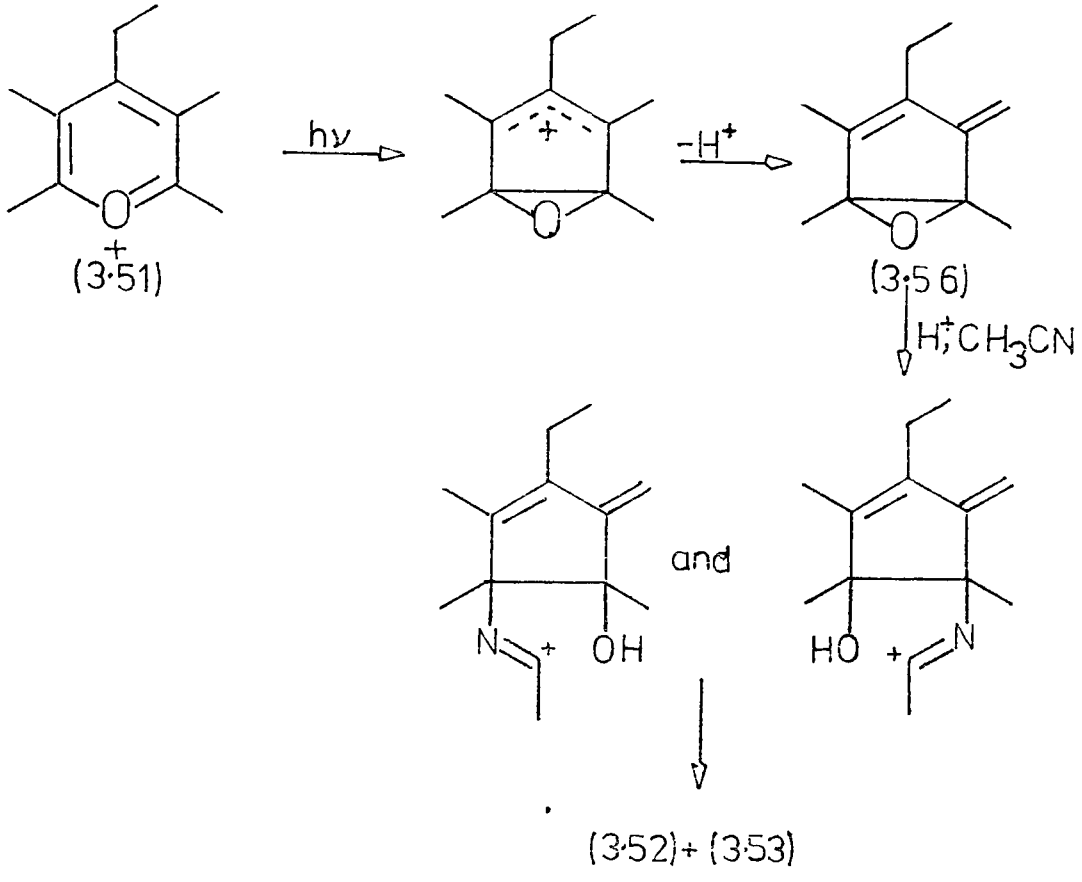
hexenyl cation has been obtained by irradiation of 4-ethyl-2,3,5,6-tetramethylpyrylium perchlorate in dry acetonitrile. Thus, irradiation of (3·51) produced, in addition to the transposed




cations (3·54) and (3·55), two isomeric oxazolines (3·52) and (3·53). These two isomers could not be separated by plc, but could be separated efficiently by g.c. Mass spectral analysis showed them both to have molecular weights of 205, i.e. the pyrylium cation minus $H^+$, and incorporation of acetonitrile. Both isomers showed loss of 41($CH_3CN$), 42($C_2H_2O$), 43($CH_3CO$), 59($CH_2=C(OH)NH_2$) and 70($C_3H_6CO$). The infra-red spectrum showed a strong band at 1645 $cm^{-1}$, characteristic of the C = N of oxazolines[212,213] and also a strong band at 900 $cm^{-1}$ due to = $CH_2$. The ultra-violet spectrum showed $\lambda_{max}$ = 226nm. The nmr spectrum showed singlets at 4·85 and 5·00, characteristic of = $CH_2$.[146] An ethyl group on a double-bond was present at 2·18. A large signal at 1·86 could be assigned as originating from $CH_3$-C(O)=N

since irradiation of the pyrylium ion in deuterioacetonitrile gave an nmr spectrum identical to the normal one, except for the absence of the signal at 1·86. This signal is in the correct region for such a group in an oxazoline.[212] Other singlet resonances were present which were characteristic of the other methyl groups in the molecules.

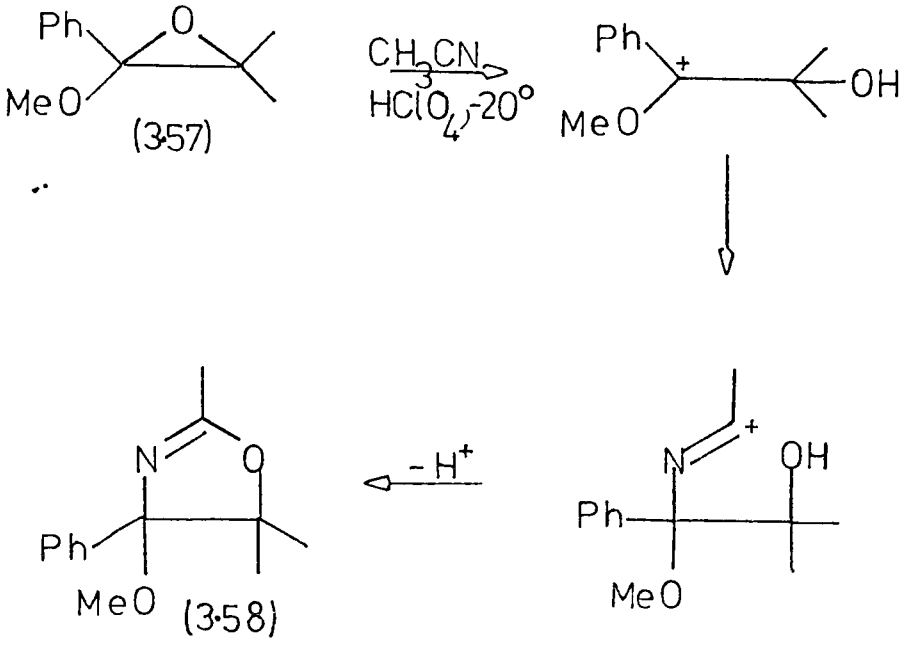
The production of oxazolines (3·52) and (3·53) is most easily rationalised as shown in Scheme 3·11. The production of




Scheme 3·11

oxazolines from epoxides is well-known.[215,216] For example, (3·57) reacts with acetonitrile in the presence of perchloric acid at -20° to give the oxazoline (3·58).[214] In the case of

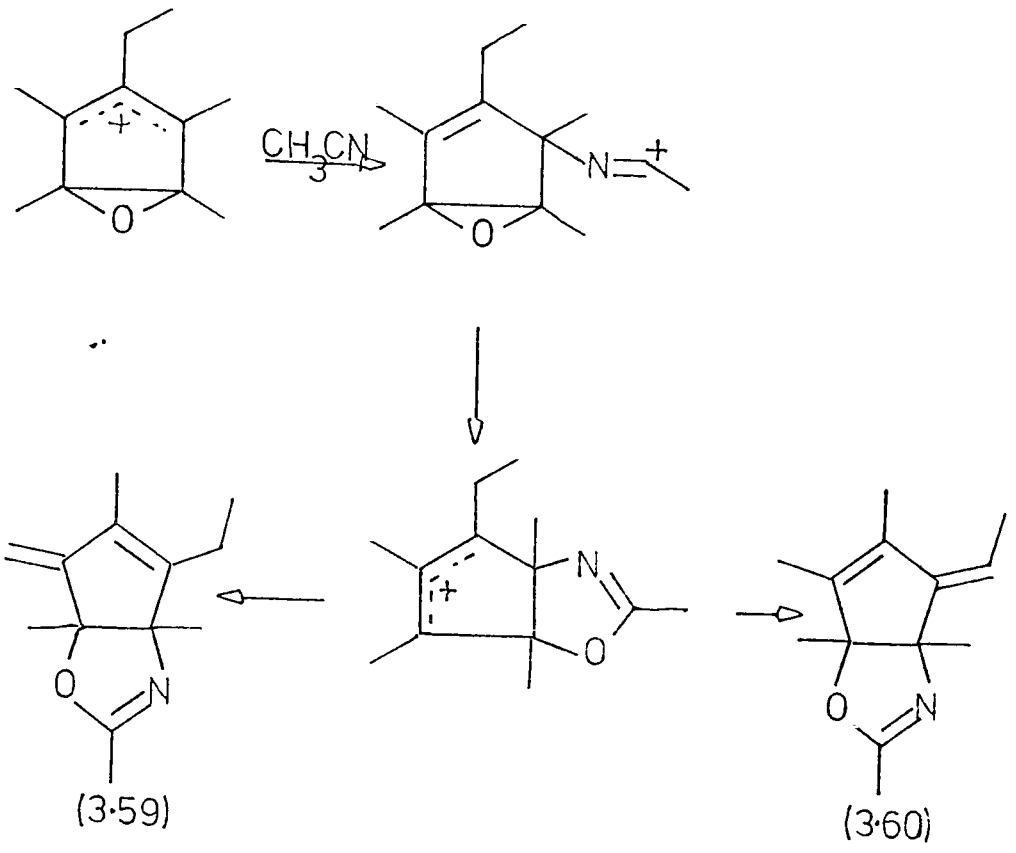
(3·56), there are two ways of opening the epoxide to give two




different carbonium ions of similar stability, and hence two oxazolines are formed. The reaction can be regarded as a type of intramolecular Ritter reaction .

The spectroscopic data presented does not enable one to distinguish (3·52) and (3·53) from (3·59), but since the formation of (3·59) would have to be rationalised in terms of Scheme 3·12, (3·59) can be discounted since (3·60) is predicted to be formed as well, and this was known not to have been formed.

Irradiation of the pyrylium cation (3·51) in solvents such as water and 2,2,2-trifluoroethanol produced only the transposed




Scheme 3·12

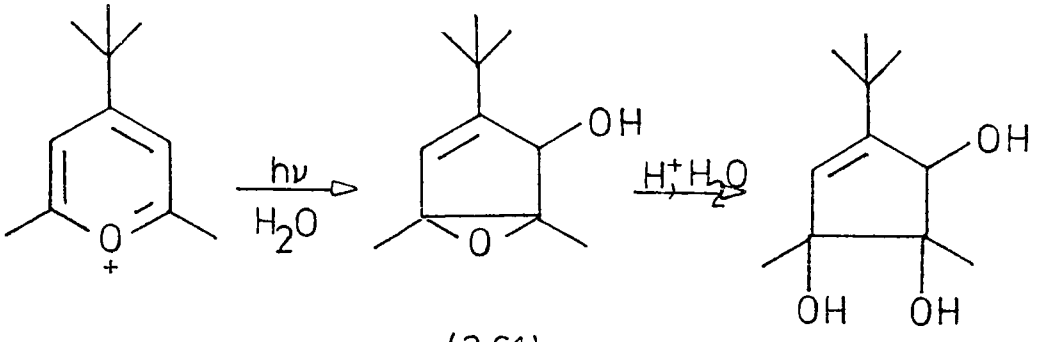
cations (3·54) and (3·55).

The formation of oxazolines was not detected in the irradiation of any other pyrylium cations in acetonitrile. The reason for their formation from (3·51) is probably connected with the fact that (3·51) was totally alkylated. Hence the formation of the 2,6-bonded intermediate from this is highly favourable. This was reflected in the fact that (3·51) transposed at least six times more readily than any other pyrylium cation in acetonitrile.

## 3.7 Attempted Trapping Experiments

Several experiments were carried out in an attempt to trap and to extract epoxides from the photolysis of pyrylium cations.

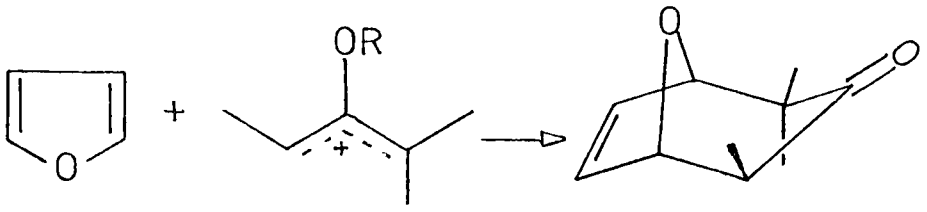
For example, a system was developed which allowed an aqueous solution of a pyrylium cation to be irradiated, and, at the same time, continuously extracted with organic solvents. In this way it was hoped to extract the presumed epoxide intermediates



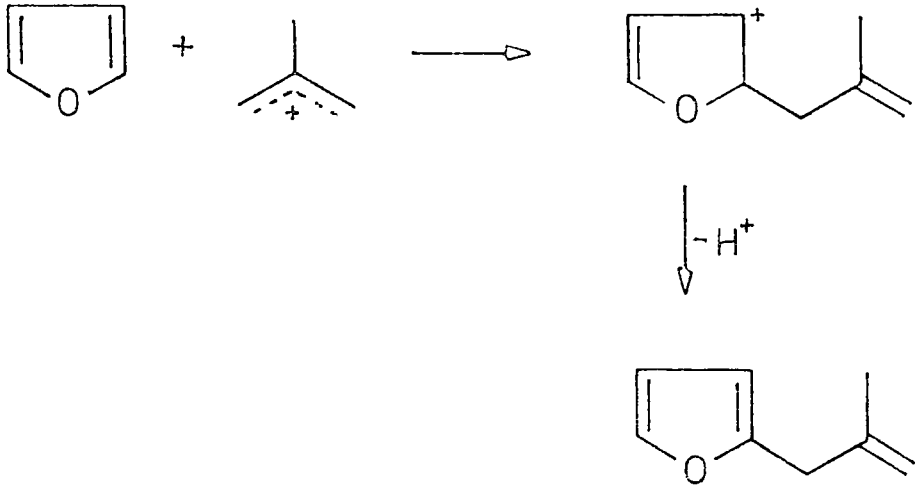

(3·61)

e.g. (3·61) before the ring-opening reaction leading to the two triols or other solvolysis products. This was not successful. Both in the case of the tert-butyl compound (3·21) and 2,4,6-trimethylpyrylium perchlorate, only the normal products were observed. This method did have the advantage of allowing high yields of products to be isolated at the expense of polymer formation.

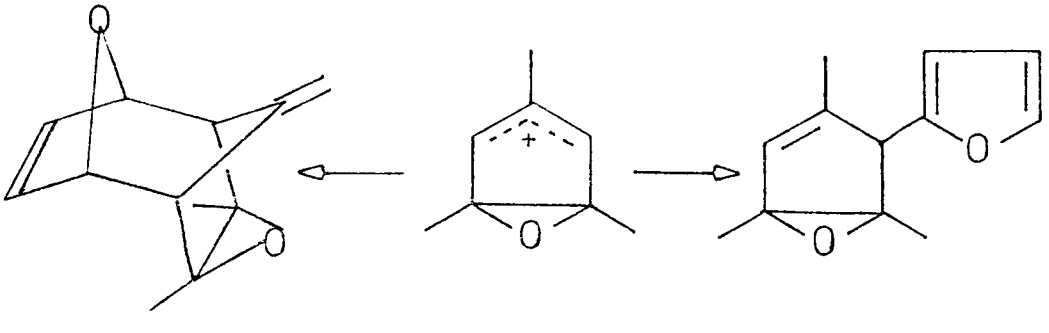
In another series of experiments, several irradiations were carried out under normal conditions in acetonitrile containing furan. This is known to react with 2-methoxyallyl and hydroxyallyl cations to give oxygen-bridged seven membered rings.[249,250]



With 2-methylallyl cation, furan gives an allylfuran, the overall reaction being an electrophilic substitution.[251] Thus products



of the type (3·62) or (3·63) would be expected from reaction of furan with oxabicyclohexenyl cations. Four pyrylium cations were irradiated in this way; 2,4,6-trimethyl; 2,6-dimethyl-4-t-butyl;



(3·62) (3·63)

2,3,5,6-tetramethyl and 2,3,5,6-tetramethyl-4-ethylpyrylium perchlorate. In no case was any adduct obtained. In the latter two cases, the normal transposition reactions were seen. Presumably, the allylic cations proposed as deriving from excitation of pyrylium cations must be too short-lived to react with furan.

## 3.8 Attempted Quencing Experiments

As described earlier, a $\pi,\pi^*$ excited singlet state is thought to be responsible for the photoisomerisation of pyrylium cations.[69] The related pyrones are known to transpose via a $\pi,\pi^*$ singlet state.[252] The photohydrolysis reaction of 2,4,6-trimethylpyrylium perchlorate has been investigated by this author in the presence of various concentrations of biacetyl. This has a much lower triplet energy (56 kcal/mole) than 2,4,6-trimethylpyrylium perchlorate (70·7 kcal/mole)[211] and so the triplet energy of the latter would be expected to be efficiently transferred to biacetyl.

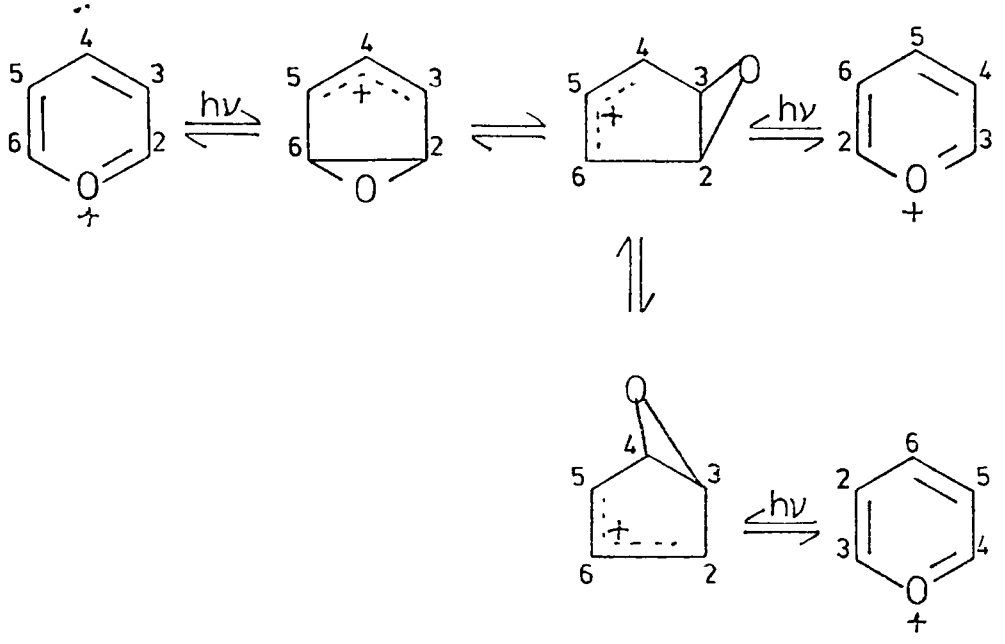
No quenching of the photohydrolysis reaction was observed with biacetyl and so excitation to a singlet state must be responsible for the reaction.

## 3.9 Mechanistic Conclusions

Experiments described in this Chapter show that alkylated pyrylium cations can undergo phototransposition reactions when alkyl groups are present in the 3- and 5-positions.

In all the cases investigated, the transposed isomers are related to starting materials in that the sequential order of the

carbon atoms is the same; only the position of the oxygen atom has altered. The mechanism proposed to account for these results is shown in Scheme 3·13 and involves initial excitation of the pyrylium chromophore to a $\pi,\pi^*$ singlet state to give an oxa-bicyclohexenyl cation. This can rearomatise to give starting material, or can undergo one or more oxygen-walk steps to give,



Scheme 3·13

after rearomatisation, transposed pyrylium cations.

Evidence for initial 2,6-bonding is provided by the isolation, in one case, of oxazolines derived from the reaction of acid and acetonitrile with the first-formed epoxide (3·56).

In aqueous solution, pyrylium cations without 3,5-substituents can undergo a photohydrolysis reaction to give transposed pyrylium cations or ring-opened keto-aldehydes. Their formation is most easily explained in terms of interaction of water with an excited state of the pyrylium cation to give a 2,6-bonded allylic alcohol. Subsequent fragmentation, or, in unfavourable cases, acid-catalysed opening of the epoxide gives the observed products.

# EXPERIMENTAL

## General Procedure

Proton nuclear magnetic resonance spectra (n.m.r.) were recorded on a Perkin-Elmer R-32 (90MHz), R-24 (60MHz) or on a Bruker-WH90 (90MHz) spectrometer. All chemical shifts are quoted in $\delta$ values relative to tetramethylsilane (T.M.S.) as internal standard (0 $\delta$). Following the chemical shift value is information about the signal multiplicity, i.e. s, d, dd... singlet, doublet, double-doublet...., and the signal intensities, i.e. 1H, 2H.... . Coupling constands (J) are recorded in Hertz (Hz) with error limits of $\pm$ 0·2Hz, and follow after the signal intensities.

Infra-red spectra (i.r.) were recorded on either a Unicam SP1000, or a Perkin-Elmer 257 spectrophotometer. Absorptions are reported in wave-numbers ($cm^{-1}$) and intensities are indicated by s, m or w (strong, medium, or weak). Polystyrene was used to calibrate spectra.

Ultra-violet spectra (u.v.) were recorded on a Unicam SP800 or a Cary 14M spectrophotometer. Absorptions ($\lambda_{max}$) are reported in nanometres (nm), followed by the value of the molar extinction coefficient ($\varepsilon$).

Mass spectra (m.s.) were recorded on a Varian CH7, a VG Micromass 16F or a 7070 spectrometer. The molecular ion is indicated by $M^{\cdot+}$ and is followed by its intensity in brackets. The five most intense ions additional to the molecular ion are

then reported with their intensities.

Analytical gas-liquid chromatography (g.l.c.) was performed using a Pye 104 or a Perkin-Elmer F11 gas chromatograph. A Pye 105 preparative chromatograph was used for preparative work.

Melting points (m.pt.) were determined on a Kofler block and are uncorrected.

Microanalyses were carried out by Dr. Strauss and staff.

Analytical thin-layer chromatography (t.l.c.) was carried out on 5 x 20 cm glass plates coated with a 0·3mm layer of Kieselgel HF 254/366 or aluminium oxide F254. Preparative layer chromatography (p.l.c.) was carried out on 20 x 20 cm glass plates coated with 1mm of the above-mentioned absorbents. B.D.H. silica gel (60-120 mesh) was used for column chromatography.

Petrol solvent refers to petroleum ether 40-60, and ether solvent refers to diethyl ether.

Irradiations were carried out in either a Rayonet RPR-100 photochemical reactor (R.P.R.) fitted with 16 low pressure (254nm) mercury arc lamps, a 1l Hanovia reactor fitted with a 125W medium pressure mercury arc lamp (water-cooled) emitting predominantly 254, 265, 297, 313 and 366 nm irradiation, or a 150ml three-sheath reactor fitted with a 450W water-cooled Hanovia medium pressure mercury arc lamp. Other apparatus is described at the appropriate point in the Experimental Section.

## SYNTHESIS

### A. THIOPHENES

#### Thiophene-3-carbonitrile

Thiophene-3-carboxaldehyde was made in 54% yield by the method of Org. Syn.[229] Nmr ($CDCl_3$)[230] 7·25 (dd-1H, J=2·5, 5·0), 7·45 (dd-1H, J=1·5, 5·0), 8·07 (dd-1H, J=1·5, 2·5), 9·85 (s-1H).

2-Bromo-3-bromomethylthiophene (1·4g) was obtained as a by-product from this route.

The oxime was prepared from the aldehyde (3·0g) by refluxing with hydroxylamine hydrochloride (4·2g) in a mixture of ethanol (12ml) and pyridine (36ml) for 4h. The solution was then concentrated by removal of the solvents under reduced pressure, and poured onto water (25ml). The solid was recrystallised from a small amount of methanol to give 2·0g of pale yellow needles of thiophene-3-aldoxime, m.pt. 113-114°.

The oxime (2·0g) was refluxed for 20 min with acetic anhyrdride (25ml). The mixture was cooled, poured onto ice (100g) and neutralised with sodium bicarbonate. The aqueous mixture was extracted with ether (2x50ml), the ethereal extracts dried over magnesium sulphate and concentrated under reduced pressure. Distillation of the residue (90-92°/25mm Hg) afforded 1·0g of thiophene-3-carbonitrile, nmr ($CDCl_3$) 7·30 (dd-1H, J=1·2, 5·0), 7·41 (dd-1H, J=2·9, 5·0), 7·93 (dd-1H, J=1·2, 2·9); u.v. (cyclohexane) $\lambda_{max}$ = 240 (ε = 18250); i.r. (film) 3100(s), 2215(s), 1515(m), 1405(m), 1365(m), 1220(m), 1155(s), 1080(m), 925(s), 870(s), 795(s), 700(s); m.s. $M^+$ 109(100), 45(32), 58(11), 65(7), 110(7), 64(6).

The nitrile was also synthesised as follows. 3-Bromothiophene (16g) and copper (I) cyanide (10g) were refluxed together in dry quinoline (75ml) for 3h. The mixture was distilled under reduced pressure, the distillate diluted with ether (100ml) and poured onto icy water (200ml). The pH of the aqueous phase was adjusted to 3 with 2M hydrochloric acid, and the organic layer separated. The aqueous layer was washed with ether (2x100ml), and the combined ether solutions were dried over magnesium sulphate and concentrated. Distillation of the residue (90-92°/25mm Hg) gave 5·2g (50%) of thiophene-3-carbonitrile.

2-Deuteriothiophene-3-carbonitrile

2-Bromo-3-bromomethylthiophene (1·2g) obtained as a by-product from the side-chain bromination of 3-methylthiophene was subjected to the same reactions as 3-bromomethylthiophene (see synthesis of thiophene-3-carbonitrile) to give 270mg of 2-bromothiophene-3-carbonitrile, b.pt. 112-114°/25mm Hg. This was refluxed for 2h with deuterium oxide (0·4ml), acetic anhydride (0·08ml) and zinc dust (0·13g). The mixture was cooled, poured onto water (50ml) and extracted with ether (2x25ml). The ether solution was washed with aqueous sodium carbonate solution, water, and then dried over magnesium sulphate. Concentration under reduced pressure and plc of the residual oil on silica with 3/1 petrol/ether gave 80mg of pure 2-deuteriothiophene-3-carbonitrile. The deuterium incorporation was found by nmr to be greater than 90%; n.m.r. ($CDCl_3$) 7·30 (d-1H, J=5·0), 7·41 (d-1H, J=5·0); i.r. ($CHCl_3$)[231] C-D at 2320cm$^{-1}$.

3-Methylthiophene-2-carbonitrile

A mixture of 3-methylthiophene-2-carboxaldehyde (16g) sodium acetate trihydrate (22·2g) and hydroxylamine hydrochloride (11·1g) was shaken for 8h in a mixture of water (45ml) and methanol (15ml), then stood at 0° for 16h. The solid was filtered off and recrystallised to give 15·8g (89%) of pale yellow needles of anti-3-methylthiophene-2-aldoxime from aqueous methanol, m.pt. 139-140°; nmr ($CDCl_3$) 2·40 (s-3H), 6·90 (d-1H, J=5·5), 6·45 (d-1H, J=5·5), 7·77 (s-1H); m.s. $M^+$ 141.

The oxime (3·0g) was refluxed with trichloroacetonitrile (15ml) for 2h,[233] the excess trichloroacetonitrile was removed under reduced pressure and the residue was extracted with warm hexane (3x25ml). The hexane solution was washed with water, dried over sodium sulphate and concentrated under reduced pressure. Distillation of the residue afforded 2·2g of 3-methylthiophene-2-carbonitrile in 83% yield, b.pt. 98-100/25mm Hg; n.m.r. ($CDCl_3$)[235] 2·43 (s-3H), 6·85 (d-1H, J=6·0), 7·47 (d-1H, J=6·0); u.v. (cyclohexane) $\lambda_{max}$ = 250 ( $\varepsilon$ = 26500); i.r. (film) 3095(m), 2910(m), 2220(s), 1405(s), 1170(m), 1010(m), 835(s), 735(s); M.S. $M^+$ 123(65), 122(100), 96(19), 124(9), 70(9), 45(9).

4-Methylthiophene-2-carbonitrile

4-Methylthiophene-2-carboxaldehyde was made in 79% yield by the method of Sice[245], b.pt. 82-85°/6mm Hg; n.m.r. ($CDCl_3$)[232] 2·30 (d-3H, J=1·2), 7·32 (m-1H, J=1·2), 7·55 (d-1H, J=1·2), 9·80 (s-1H).

The oxime was then made in 73% yield by the method described for 3-methylthiophene-2-aldoxime. Recrystallisation from chloroform gave a mixture of the syn and anti isomers, m.pt. 148-152°; n.m.r. ($CDCl_3$) anti-isomer, 2·30 (s-3H), 7·20 (s-2H, ring H), 7·63 (s-1H); syn-isomer, 2·30 (s-3H), 6·90 (s-1H), 7·00 (s-1H), 8·20 (s-1H); m.s. $M^+$ 141.

The nitrile was then made by dehydration of the oxime with trichloroacetonitrile in 83% yield as described for 3-methylthiophene-2-carbonitrile, b.pt. 95-97°/25mm Hg; nmr ($CDCl_3$) 2·30 (s-3H), 7·20 (s-1H), 7·42 (s-1H); u.v. (cyclohexane) $\lambda_{max}$ = 242 ( $\varepsilon$ = 18450), 267 ( $\varepsilon$ = 14550); i.r. (film) 3080(s), 2920(m), 2200(s), 1415(s), 1205(s), 1115(s), 860(s), 765(s); m.s. $M^+$ 123(63), 122(100), 45(13), 96(12), 124(9), 44(6).

The nitrile was further purified by preparative g.l.c. on a silicon OV17 column at 180°, and then on a dimethanol-cyclohexane succinate (DMCS) column at 210°.

5-Methylthiophene-2-carbonitrile

The oxime was made from the aldehyde in 78% yield by the method described for 3-methylthiophene-2-aldoxime. Recrystallisation from methanol gave a mixture of syn and anti isomers, m.pt. 118-123°; nmr ($CDCl_3$) syn-isomer, 2·48 (s-3H), 6·68 (d-1H, J=5·0), 6·95 (d-1H, J=5·0), 8·13 (s-1H); anti-isomer, 2·53 (s-3H), 6·73 (d-1H, J=5.0), 7·11 (d-1H, J=5·0), 7·58 (s-1H); m.s. $M^+$ 141.

The nitrile was made from the oxime in 98% yield by dehydration with trichloroacetonitrile in the way described for 3-methylthiophene-2-carbonitrile, b.pt. 93-95°/20mm Hg[234]; nmr ($CDCl_3$) 2·53 (s-3H), 6·77 (d-1H, J=4·5), 7·43 (d-1H, J=4·5); u.v. (cyclohexane) $\lambda_{max}$ = 247·5 ( $\varepsilon$ = 20850), 265 ( $\varepsilon$ = 23150); i.r. (film) 3090(m), 2910(m), 2205(s), 1450(s), 1225(s), 1155(s), 1045(m), 805(s); m.s. $M^+$ 123(65), 122(100), 96(11), 124(9), 70(7), 45(7).

2-Methylthiophene-3-carbonitrile

3,5-Dibromo-2-methylthiophene was prepared by bromination of 2-methylthiophene in 89% yield.[236] B.pt. 48-55°/·4mm Hg; nmr ($CDCl_3$) 2·27 (s-3H), 6·75 (s-1H).

3-Bromo-2-methylthiophene was then prepared by the method of Janda et. al.,[237] b.pt. 40-41°/·8mm Hg; nmr ($CDCl_3$) 2·35 (s-3H), 6·80 (d-1H, J=5·0), 7·00 (d-1H, J=5·0).

The nitrile was then prepared by the method of the same authors (cuprous cyanide in boiling quinoline) in 75% yield, b.pt. 48-50°/·7mm Hg; nmr ($CDCl_3$) 2·63 (s-3H), 7·00 (s-2H); ($CD_3OD$) 2·62 (s-3H), 7·10 (d-1H, J=4·0), 7·30 (d-1H, J=4·0); u.v. (cyclohexane) $\lambda_{max}$ = 241·5 ( $\varepsilon$ = 16950); i.r. (film) 3100(m), 2910(m), 2210(s), 1440(s), 1230(s), 870(s), 720(s); m.s. $M^+$ 123(49), 96(100), 122(59), 53(40), 44(37), 124(16); Analysis, calculated, C 58·53, H 4·09, N 11·38, S 25·99; found, C 58·55, H 3·82, N 11·02, S 26·14.

The material was further purified by preparative g.l.c. on a 10% carbowax 20M column at 180°.

2-Methyl[5-$^{2}$H]thiophene-3-carbonitrile

This was synthesised in exactly the same way as 2-methylthiophene-3-carbonitrile, except that the dibromo compound was treated with zinc and deuterioacetic acid to obtain 3-bromo-2-methyl[5-$^{2}$H]thiophene, which, on treatment with copper (I) cyanide in the usual manner gave the nitrile, with ca 60% deuterium incorporation, exclusively in the 5-position; B.pt. 48·5/50·0°/·7mm Hg; nmr ($CD_3OD$) 2·62 (s-3H), 7·10 (s-1H, and overlapping doublet from residual 5-H), 7·30 (d- residual 5-H).

4-Methylthiophene-3-carbonitrile

3-Methylthiophene (0·98g) was added to a solution containing glacial acetic acid (50ml), mercury (II) acetate (9·6g), and iodine (7·6g). The mixture was heated rapidly until the iodine colour had disappeared and then poured into water (200ml). The solid was filtered off, shaken with 5% aqueous potassium iodide solution (200ml), recrystallised from n-pentanol and dried under vacuum to yield 2·5g (53%) of 3-methyl-2,4,5-triiodothiophene, m.pt. 73-74$^{p}$ (lit.[238] 73-75°); nmr ($CDCl_3$) 2·43(s).

The triiodo compound (4g, 0·008m) and methyl iodide (8g, 0·06m) in dry ether (100ml) were added, in the usual manner for Grignard synthesis, to magnesium turnings (1·6g, 0·067m) in dry ether (25ml). After the reaction had subsided, the mixture was heated on a steam bath for 2h, then cooled and poured slowly onto ice (200g) containing 10% hydrochloric acid (50ml). The mixture was extracted with ether (3x50ml), the etheral extracts

dried over magnesium sulphate and concentrated under reduced pressure. Distillation of the residue gave 0·8g of 3-methyl-4-iodothiophene, b.pt. 85-87°/12mm Hg; nmr ($CDCl_3$) 2·25 (s-3H), 6·90 (m-1H), 7·35 (d-1H, J=3·0), and also 1·2g of 3-methyl-2,4-diiodothiophene, m.pt. 59-60°; nmr ($CDCl_3$) 2·28 (s-3H), 7·50 (s-1H).

3-Methyl-4-iodothiophene was treated with copper (I) cyanide in the manner described previously for 3-bromothiophene to give an 81% yield of 4-methylthiophene-3-carbonitrile, b.pt. 52-54°/0·5mm Hg (lit[244] b.pt. 87°/10mm Hg); nmr ($CDCl_3$) 2·37 (s-3H), 6·98 (m-1H), 7·81 (d-1H, J=3·0); u.v. (cyclohexane) $\lambda_{max}$ = 240 ) ε = 17900), m.s. $M^+$ 123(58), 122(100), 96(82), 45(32), 44(25), 65(10).

The nitrile was further purified by preparative g.l.c. on a 10% Apiezon L column at 190°.

5-Methylthiophene-3-carbonitrile

2-methyl-3,4,5-triiodothiophene was prepared from 2-methylthiophene in 42% yield by the method described above for 3-methylthiophene-2,4,5-triiodothiophene, m.pt. 96-98° (lit.[238] 100-101·5°); n.m.r. ($CDCl_3$) 2·55(s).

The triiodo compound, with excess methyl iodide, was then added to magnesium turnings in the way described for the 3-methyl isomer. In this way a 44% yield of 2-methyl-4-iodothiophene, b.pt. 86-90°/10mm Hg; nmr ($CDCl_3$) 2·42 (s-3H), 6·66 (s-1H), 7·05 (s-1H), was obtained. A small amount of 2-methyl-3,4-diiodothiophene, m.pt. 44-45°; nmr ($CDCl_3$) 2·46 (s-3H), 7·26 (s-1H), was also obtained.

The mono-iodo compound was treated with copper (I) cyanide in quinoline as described previously, to give an 80% yield of 5-methylthiophene-3-carbonitrile, b.pt. 95-98°/10mm Hg; nmr ($CDCl_3$) 2·51 (s-3H), 6·92 (m-1H), 7·65 (d-1H, J=1·0); u.v. (cyclohexane) $\lambda_{max}$ = 241·5 ( $\varepsilon$ = 18450); i.r. (film) 3095(s), 2910(m), 2210(s), 1440(s), 1355(m), 1205(m), 1110(m), 870(m), 830(s); m.s. $M^+$ 123(53), 122(100), 96(60), 44(28), 34(28), 35(22); Analysis, calculated, C 58·53, H 4·09, N 11·38, S 25·99; found, C 58·69, H 4·02, N 11·16, S 26·15.

The nitrile was further purified by preparative g.l.c. on an Apiezon L column at 190°.

Thiophene-2,3-dicarbonitrile

Bromination of 3-bromothiophene by the method of Gronowitz[240] gave a 60% yield of 2,3-dibromothiophene, b.pt. 85-89°/15mm Hg; nmr ($CDCl_3$) 6·80 (d-1H, J=5·5), 7·15 (d-1H, J=5·5).

Treatment of the dibromocompound with copper (I) cyanide in the manner described by MacDowell[239] gave a 20% yield of thiophene-2,3-dicarbonitrile as a white solid after sublimation at 90°/0·1mm Hg; m.pt. 144-145°; nmr ($CDCl_3$) 7·37 (d-1H, J=5·0), 7·72 (d-1H, J=5·0); u.v. ($CH_3OH$) $\lambda_{max}$ = 258 ( $\varepsilon$ = 9400); i.r. ($CHCl_3$) 3110(m), 2220(s), 1405(m), 1160(m), 1080(m), 890(m); m.s. $M^+$ 134(100), 70(23), 64(9), 77(9), 58(9), 107(7).

Thiophene-2,5-dicarbonitrile

This was made from 2,5-dibromothiophene according to the method of Morel et al.,[241] as a white powder after sublimation at 130°/·1mm Hg, m.pt. 200-202°; nmr ($CDCl_3$) 7·60(s); u.v. (ether) $\lambda_{max}$ = 267; m.s. $M^+$ 134(100), 70(34), 64(14), 135(7), 77(5), 58(5).

3-Methylthiophene-2,4-dicarbonitrile

Treatment of 3-methyl-2,4-diiodothiophene obtained above with copper (I) cyanide in the usual manner gave a 25% yield of 3-methylthiophene-2,4-dicarbonitrile as an off-white solid after sublimation at 90°/.2mm Hg; m.pt. 126-127°; nmr ($CDCl_3$) 2·58 (s-3H), 8·03 (s-1H); u.v. ($CH_3CN$) $\lambda_{max}$ = 258 ( $\varepsilon$ = 8500); i.r. (KBr) 3090(m), 2950(w), 2220(s), 1445(s), 1395(s), 1210(s), 885(s), 850(s); m.s. $M^+$ 148(100), 147(95), 121(50), 70(25), 149(15), 120(10); Analysis, calculated, C 56·76, H 2·72, N 18·91, S 21·60; found, C 56·63, H 2·90, N 18·90, S 21·40.

5-Methylthiophene-2,4-dicarbonitrile

Treatment of 3,5-dibromo-2-methylthiophene obtained above with copper (I) cyanide in the usual manner gave, after recrystallisation from petrol, a 32% yield of off-white needles of 5-methylthiophene-2,4-dicarbonitrile, m.pt. 130-130·5°; nmr ($CDCl_3$) 2·72 (s-3H), 7·62 (s-1H); u.v. ($CH_3CN$) $\lambda_{max}$ = 218 ( $\varepsilon$ = 29000), 265 ( $\varepsilon$ = 7800); i.r. (KBr) 3080(s), 2920(w), 2210(s), 1445(s),

1390(s), 1205(m), 1145(s), 865(s); m.s. $M^+$ 148(95), 147(100), 121(45), 70(20), 149(13), 120(11); Analysis; calculated, C 56·76, H 2·72, N 18·91, S 21·60; found, C 56.49, H 2·76, N 19·00 S 21·32.

Cyclohexylazide

Iodocyclohexane was prepared in 90% yield by the method of Org. Syn.,[243] b.pt. 49-51°/3mm Hg; nmr ($CDCl_3$) 1·4-2·2 (m-10H), 4·40( m-1H).

The azide was then prepared from the iodo compound by the method of Rao,[242] b.pt. 70°/3mm Hg; nmr ($CDCl_3$) 1·2-2·2 (m-10H), 3·60 (m-1H); i.r. (film) 2940(s), 2860(s), 2000(s), 1455(m), 1260(s).

## B. PYRYLIUM SALTS

### 2,4,6-Trimethylpyrylium perchlorate

This was prepared by the reaction of perchloric acid with a mixture of t-butanol and acetic anhydride.[221] A 50% yield of colourless needles was obtained with m.pt. 247° after recrystallisation from water containing a few drops of perchloric acid. N.m.r. ($D_2O$) 2·74 (s-3H), 2·90 (s-6H), 7·75 (s-2H); u.v. (0·1M $H_2SO_4$) $\lambda_{max}$ = 230 ( $\varepsilon$ = 4550), 285 ( $\varepsilon$ = 12000).

### 2,6-Dimethyl-4-t-butylpyrylium perchlorate

This was prepared by the reaction of t-butylmagnesium chloride on 2,6-dimethyl-4-pyrone.[222] A 36% yield of colourless needles m.pt. 224-225° (lit.[222] 221°); n.m.r. ($D_2O$) 1·40 (s-9H), 2·90 (s-6H), 7·80 (s-2H); u.v. (0·1M $H_2SO_4$) $\lambda_{max}$ = 281·5 ($\varepsilon$ = 12150).

### 2-Ethyl-4,6-dimethylpyrylium perchlorate

Propionyl chloride (49ml) was cooled to -5° in an ice-salt bath. Aluminium chloride (66g) was added slowly, with stirring, over 45 min. Mesityl oxide (57ml) was added dropwise, with stirring to the mixture at 0° over 1h. Hydrogen chloride was evolved continuously and the mixture was stirred at 15° for 12h. The dark brown mixture was then poured onto ice (600g) containing conc. hydrochloric acie (15ml). After the ice had melted, the top layer was discarded and the aqueous layer was washed twice with ether (100ml). 60% Perchloric acid (30ml)

was added to the aqueous solution which was then stood at 0°. White crystals separated after 2h. These were filtered off, recrystallised twice from methanol, washed with ether and then air-dried to give 15·7g (13% yield) of needle crystals, m.pt. 200-201° (lit.[223] 198°); nmr ($CD_3CN$) 1·40 (t-3H, J=8), 2·66 (s-3H), 2·81 (s-3H), 3·11 (q-2H, J=8), 7·71 (s-2H); u.v. (0·1M $H_2SO_4$) $\lambda_{max}$ = 285 ($\varepsilon$ = 12100); i.r. (KBr) 3080(s), 3000(m), 2960(w), 2940(w), 1650(s), 1555(s), 1400(m), 1460(m), 1380(m), 1100(s), 875(m), 790(m); Analysis; calculated, C 45·67, H 5·55, Cl 14·97; found, C 45·92, H 5·73, Cl 14·68

2,3,4,6-Tetramethylpyrylium perchlorate

A mixture of t-pentyl alcohol (52ml) and acetic anhydride (250ml) was cooled to -5° in an ice-salt bath. Perchloric acid (84g of the 60% acid) was cautiously added to the stirred mixture over 1h., the temperature being maintained below 10°. After the addition of acid, the temperature of the mixture was allowed to rise to 20° over 2 h, and then to 100° over 2h. The temperature was maintained at 100° for 2h. The mixture was then cooled and water (200ml), followed by ethanol (200ml) and ether (400ml) were added. On standing overnight the homogenous solution deposited a dark oil which was separated, and on treatment with ether gave pale yellow crystals. N.m.r. showed the crystals to be a mixture of the title compound and 2,6-dimethyl-4-ethylpyrylium perchlorate in a ratio of 10 to 1. The latter was obtained pure by repeated recrystallisation from ethanol. The tetramethyl salt was obtained pure by treatment

with iron (III) chloride in conc. hydrochloric acid to obtain the chloroferrate (m.pt. 155° after recrystallisation from conc. hydrochloric acid), which was then converted back to the perchlorate by dissolving in warm 70% perchloric acid, cooling, filtering and then repeating the process once more. 7·5g of white needle crystals m.pt. 190° (decomposition)[224] were obtained in this way. N.m.r. ($CD_3CN$) 2·34 (s-3H), 2·60 (s-3H), 2·78 (s-3H), 2·81 (s-3H), 7·72 (s-1H); u.v. (0·1M $H_2SO_4$) $\lambda_{max}$ = 289 ($\varepsilon$ = 11500); i.r. (KBr) 3080(m), 2920(w), 1645(s), 1555(s), 1510(s), 1460(m), 1100(vs), 950(m), 890(w); Analysis, calculated, C 45·67, H 5·55, Cl 14·97; found, C 45·90, H 5·74, Cl 15·02.

2,3,5,6-Tetramethylpyrylium perchlorate

This was prepared by the reaction of perchloric acid with a mixture of pent-2-ene and acetic anhydride.[225] Recrystallisation from propan-2-ol gave light brown needles, m.pt. 80-82° (lit[225] 82-83°), nmr ($CD_3CN$) 2·41 (s-6H), 2·80 (s-6H), 8·46 (s-1H); u.v. ($CH_3CN$) $\lambda_{max}$ = 302·5 ($\varepsilon$ = 13650); i.r. (KBr) 3040(w), 2940(w), 1620(s), 1500(s), 1450(s), 1100(vs), 705(m).

2,6-Diethyl-3,5-dimethylpyrylium perchlorate

Under a nitrogen atmosphere, Dimethylformamide (116ml) in trichloroethylene (250ml) was cooled to 5° in an ice-salt bath. Phosphoryl chloride (135ml) was added slowly, with stirring over 1h., the temperature of the mixture being maintained below 10°.

The temperature was then allowed to rise to 20° and diethylketone (107ml) in trichloroethylene (250ml) was added at such a rate that the temperature did not rise above 60°. After the addition, the mixture was maintained at 55° for 3h. The mixture was then cooled to 30° and saturated aqueous sodium acetate solution (500ml) was added cautiously over 1h, while the temperature of the mixture was kept below 35° with external cooling. After standing overnight, the mixture was extracted with ether (2x200ml). The ethereal solution was washed with saturated aqueous sodium chloride solution, deoxygenated water, and was dried over sodium sulphate. The ether was removed under reduced pressure and the oily product distilled. The fraction at 80-90°/30mm Hg was collected and consisted of 62g (47% yield) of cis- and trans-3-chloro-2-methylpent-2-enal.[226] N.m.r. ($CDCl_3$); cis-isomer, 1·20 (t-3H, J=7), 1·78 (s-3H), 2·69 (q-2H, J=7), 10·23 (s-1H); trans-isomer, 1·25 (t-3H, J=7), 1·82 (s-3H), 3·01 (q-2H, J=7), 10·08 (s-1H).

Diethylketone (15·8ml) and 3-chloro-2-methylpent-2-enal (14g) were dissolved in glacial acetic acid (100ml). Anhydrous perchloric acid (as a 28% solution of perchloric acid in acetic acid, obtained by the addition of the requisite amount of acetic anhydride to ice-cold 60% aqueous acetic acid) was added and the mixture was refluxed for 1h. The mixture was allowed to cool and ether (500ml) was added to precipitate the pyrylium salt as a brown oil. The oil was washed with dry ether and dried over sodium hydroxide in a vacuum dessicator. The oil gave a tacky solid which was recrystallised from propan-2-ol to give white needles, m.pt. 178-181° (decomposition),

n.m.r. ($CF_3COOH$) 1·40 (t-6H, J=7), 2·42 (s-6H), 3·18 (q-4H, J=7), 8·40 (s-1H): u.v. ($CH_3CN$) $\lambda_{max}$ = 304 ( $\varepsilon$ = 14000); i.r. (KBr) 3020(w), 2975(m), 2940(w), 1605(m), 1495(s), 1410(m), 1330(m), 1180(m), 1090(vs), 795(m), 700(m); Analysis; calculated, C 49·90, H 6·49, Cl 13·38; found, C 49·50, H 6·48, Cl 13·58.

cis-4-t-Butylhept-3-en-2,6-dione

2,6-Dimethyl-4-t-butylpyrylium perchlorate (4.0g) in water (100ml) was treated with aqueous 2M sodium hydroxide solution until the pH of the solution was 11. The mixture was extracted with ether (2x100ml) and the ether extracts were combined and dried over magnesium sulphate. The ether was removed under reduced pressure to yield 2·72g of the pure cis-diketone, n.m.r. ($CDCl_3$) 1·05 (s-9H), 2·05 (s-3H), 2·13 (s-3H), 3·55 (s-2H), 6·20 (s-1H); u.v. ($CH_3OH$) $\lambda_{max}$ = 239; i.r. ($CCl_4$) 3010(w), 2980(s), 2950(m), 2910(m), 2880(m), 1743(s), 1693(s), 1610(s), 1480(m), 1470(m), 1420(m), 1360(s), 1310(m), 1270(m), 1190(m), 1160(s), 960(m), 865(s).

2-Ethyl-4,6-dimethyl[5-$^2$H]pyrylium perchlorate

4-Methyl[3-$^2$H]pent-3-en-2-one was made by the method of Sammes et al.[228] 60% incorporation of deuterium was obtained. This was then acylated with propionyl chloride in the same way as in the preparation of the non-deuteriated pyrylium salt,

except that dry nitrogen was passed through the mixture during and after the addition of 3-deuteriomesityl oxide.

A 13% yield of the pyrylium salt was obtained, m.pt. 201-202° (lit[223] 198° for the non-deuterated salt) after recrystallisation from methanol. N.m.r. ($CD_3CN$) 1·40 (t-3H, J=8·0), 2·66 (s-3H), 2·81 (s-3H), 7·71 (s-1H plus residual H), 60% incorporation of deuterium); u.v. (0·1M $H_2SO_4$) $\lambda_{max}$ = 285 ( $\varepsilon$ = 12100), i.r. (KBr) C-D at 2300$cm^{-1}$.

2-Ethyl-3,5,6-trimethylpyrylium perchlorate

This compound was prepared in exactly the same way as 2,6-diethyl-3,5-dimethylpyrylium perchlorate, except that in the reaction between the $\beta$-chlorovinylaldehyde and the ketone, methylethylketone was substituted for diethylketone. The compound was recrystallised as colourless plates from 2-propanol, m.pt. 130-132°; nmr ($CF_3COOH$) 1·40 (t-3H, J=7·0), 2·45 (s-6H), 2·85 (s-3H), 3·20 (q-2H, J=7·0), 8 43 (s-1H); u.v. ($CH_3CN$) $\lambda_{max}$ = 303 ( $\varepsilon$ = 13900); i.r. (KBr) 3020(w), 2980(w), 2940(w), 1615(s), 1500(s), 1450(m), 1100(vs), 795(m), 700(m); Analysis; calculated, C 47·90, H 6·04, Cl 14·14; found, C 47·71, H 6·24, Cl 13·89.

2,6-Diethyl-3,4,5-trimethylpyrylium perchlorate

Propanoic acid (150ml) was dissolved with vigorous stirring into polyphosphoric acid (200g). Diethylketone (10g) was added and the mixture was heated at 140° for 2 h. The mixture was cooled and poured onto ice (400g). This was extracted with ether (2x400ml), the ethereal extracts were washed with 10% aqueous potassium hydroxide solution (400ml), water (400ml) and then dried over magnesium sulphate. The ether was removed under reduced pressure and the resulting brown oil was passed down a silica column with ether eluant. A colourless oil was obtained which yielded, after recrystallisation from petrol, 8·0g (30%) of 2,6-diethyl-3,5 dimethyl-4-pyrone, m.pt. 39-40° (lit[227] 39°); nmr $CCl_4$) 1·20 9t-6H, J=8·0), 1·82 (s-6H), 2·60 (q-4H, J=8·0); m.s. $M^+$ 180(85), 179(100), 137(18), 113(14), 57(13), 83(11).

2,6-Diethyl-3,5-dimethyl-4-pyrone (4·5g) was dissolved in dry ether (100ml). 1M methyl lithium solution in hexane (25ml) was added dropwise, with stirring over 15 min, and the mixture was stirred for a further 2h. It was then poured onto ice (300g) containing 60% aqueous perchloric acid (60ml). The aqueous layer was washed with ether (2x75ml) and on standing at 4°, yielded light brown crystals of the pyrlium salt. Recrystallation from 4/1 ethyl acetate/acetic acid gave colourless needles, m.pt. 112°; nmr ($CDCl_3$) 1·50 (t-6H, J=8·0), 2·50 (s-6H), 2·65 (s-3H), 3·30 (q-4H, J=8·0); u.v. (0·1M $H_2SO_4$) $\lambda_{max}$ = 298 ( $\varepsilon$ = 13200); i.r. (KBr) 2980(m), 2920(m), 1610(s), 1490(s), 1450(s), 1100(vs), 860(m), 680(m).

4-Ethyl-2,3,5,6-tetramethylpyrylium perchlorate

This was prepared in 53% yield by the method of Balaban and Nenitzescu[224] involving treatment of 3-ethylpent-3-ene in acetic anhydride with perchloric acid in acetic anhydride. Recrystallisation of the product from 4/1 ethyl acetate/acetic acid, followed by recrystallisation from 2-propanol gave off-white needles, m.pt. 107-107·5 (lit[224] 108°); nmr ($CD_3CN$) 1·15 (t-3H, J=8·0), 2·36 (s-6H), 2·77 (s-6H), 2·92 (q-2H, J=8·0); u.v. (0·1M $H_2SO_4$) $\lambda_{max}$ = 298 ($\varepsilon$ = 16400) i.r. (KBr) 2970(m), 2920(m), 1610(s), 1490(s), 1450(s), 1390(m), 1210(m), 1090(vs), 1000(m), 870(m), 780(m), 760(m), 680(m).

3-Ethylpent-2-ene was made in 70% yield by the dehydration of triethylmethanol with 33% sulphuric acid, b.pt. 95-96°, nmr ($CDCl_3$) 0·95 (t-6H, J=8·0), 1·60 (d-3H, J=6·0), 2·08 (q-4H, J=8·0), 5·20 (q-1H, J=6.0).

2-Ethyl-4,5,6-trimethylpyrylium perchlorate

2-Methyl-2-butene, b.pt. 38°, was prepared by dehydration of t-pentanol with 33% sulphuric acid in 71% yield.

3,4-Dimethylpent-3-en-2-one, b.pt. 147-150°, by acylation of 2-methyl-2-butene in 28% yield by the method of Timmons et al.[263]

Treatment of this with propionyl chloride/aluminium chloride in the same manner as described above in the preparation of 2-ethyl 4,6-dimethylpyrylium perchlorate gave, after recrystallisation from methanol, a 15% yield of off-white needles of 2-ethyl-4,5,6-trimethylpyrylium perchlorate, m.pt. 132-137°;

nmr ($CDCl_3$) 1·38 (t-3H, J=8·0), 2·40 (s-3H), 2·65 (s-3H), 2·88 (s-3H), 3·22 (q 2H, J=8·0), 7·73 (s-1H); u.v. (0·1M $H_2SO_4$) $\lambda_{max}$ = 289 ($\epsilon$ = 11900); i.r. (KBr) 3080(m), 3000(m), 2960(m), 2920(m), 1650(s), 1550(s), 1510(s), 1460(m), 1450(m), 1235(m), 1100(s), 895(s), 795(m).

# IRRADIATIONS

## A. THIOPHENES

### Thiophene-2-carbonitrile

1. In ether solution:

$10^{-2}$ M Thiophene-2-carbonitrile in dry ether was degassed with a stream of nitrogen for 30min and then irradiated through quartz in an RPR with 254nm light. The photolysis was continuously monitored by gas chromatographic analysis (50ft carbowax 20M SCOT column at $162^{o}$ with an argon flow rate of 2ml/min). The starting material had a retention time of 9·7 min. After 30 min irradiation a new peak was visible with a retention time of 11·6 min. After 6h irradiation this signal had grown to 1% that of the starting material, whilst the latter had diminished by 5%. Further irradiation did not improve this ratio but resulted in much polymer formation.

The new compound was found by co injection to have a retention time identical to that of thiophene 3-carbonitrile on both the carbowax 20M SCOT column and a 5ft, 10% Apiezon L column. Analysis by g.c.m.s. showed it to give the same molecular ion and fragmentation pattern as that of authentic thiophene-3-carbonitrile. N.m.r. of the crude photosylate showed it to contain only thiophene-2-carbonitrile and thiophene-3-carbonitrile.

Close inspection of the g.c. traces showed there to be no thiophene present, nor any long retention time peaks attributable to thiophene-dicarbonitriles.

2. In acetonitrile solution:

This experiment was carried out in the same manner as the ether solution experiment. The results were essentially the same except the transposition reaction was 30% faster.

3. In cyclohexane solution:

In an experiment carried out in the same manner as that of the ether solution experiment, the transposition reaction was found to be 50% slower and a larger amount of polymeric material was formed.

4. In furan solution:

The nitrile (50mg) was dissolved in redistilled furan (100ml), the solution was degassed with nitrogen for 30min and then irradiated in an RPR for 2h with 254nm light. The furan was removed under reduced pressure. N.m.r. of the oily residue showed it to contain about 70% of thiophene-2-carbonitrile and also many additional signals. T.l.c. of residue on silica gel plates with 1:1 petrol:ether showed three main spots after visualisation with iodine. P.l.c. showed a band at rf 0·7 identified by nmr and g.c. to be mainly thiophene-2-carbonitrile with 0·3% of thiophene-3-carbonitrile. The band at rf 0·5 gave, after recrystallisation from methanol-petrol, 12·0mg of colourless needles of exo-10,4-oxathiatetracyclo[5·2·1·$0^{2,6}$·$0^{3,5}$] dec-8-ene-2-carbonitrile, m.pt. 76·5-77·5°; nmr ($CDCl_3$) 2·76 (d-1H, J=1·3), 3·43 (d-1H, J=3·8), 3·66 (dd-1H, J=1·3,3·8), 5·07 (s-1H), 5·13 (s-1H), 6·53 (s-2H); (pyridine-$d_5$) showed the olefinic protons at 6·53 as a quartet with J=1·5 and 6·0;

u.v. (ether) end-absorption only; i.r. (KBr) 3020(w), 2950(w), 2235(s), 1640(w), 1310(s), 1130(m), 1045(m), 1015(m), 980(m), 930(m), 920(s), 870(m), 820(m), 805(m), 720(s); m.s. $M^+$ 177(16), 68(100), 148(22), 122(12), 121(10), 109(7); Analysis; calculated, C 61·01, H 3·98, N 7·91, S 18·07; found, C 60·79, H 4·16, N 7·79, S 17·88.

The band at rf 0·2 gave, after recrystallisation from ether-petrol, 2·0 mg of endo-10,4-oxathiatetracyclo[$5\cdot2\cdot1\cdot0^{2,6}.0^{3,5}$]dec-8-ene-2-carbonitrile, m.pt. 105-110°; nmr ($CDCl_3$) 3·08 (d-1H, J=3·5), 3·29 (m-2H), 5·08 (dd-1H, J=1·5, 5·5), 5·20 (d-1H, J=1·5), 6·60 (dd-1H, J=1·5, 6·0), 6·72 (dd-1H, J=1·5, 6·0); u.v. (ether) end-absorption only; i.r. (KBr) 3010(m), 2950(w), 2930(w), 2225(s), 1325(s), 1300(m), 1260(m), 1225(s), 1175(m), 1120(m), 1030(s), 1015(s), 940(m), 890(m), 880(m), 870(m), 850(m), 805(m), 740(s); m.s. $M^+$ 177(13), 68(100), 148(40), 122(19), 121(15), 109(11); Analysis; calculated, C 61·01, H 3·98, N 7·91, S 18·07; found, C 61·10, H 4·07, N 7·71, S 18·14.

A dark experiment showed that no transposition or adduct formation took place in the absence of ultra-violet light.

5. In methanol solution:

A $10^{-2}$M solution of the nitrile in dry methanol was degassed with nitrogen for 30 min and then irradiated in an RPR with 254nm light. Monitoring of the reaction by gas-chromatographic analysis showed transposition to the 3-isomer, but no additional peaks. After 6h irradiation, the methanol was removed under reduced pressure. N.m.r. of the residue showed no signals expected for a methanol adduct, notably no methoxy signal.

In a similar experiment, the nitrile (20mg) was dissolved in deuteriomethanol (0·4ml) and irradiated for 15h with 254nm light. N.m.r. analysis of the resulting solution showed no deuterium incorporation in the nitrile.

Thiophene-3-carbonitrile

1. In ether solution:

$10^{-2}$ M Thiophene-3-carbonitrile in dry ether was degassed for 30 min with a stream of nitrogen and then irradiated through quartz in an RPR with 254nm light. The photlysis was monitored by gas chromatographic analysis (50ft carbowax 20M SCOT column at $162^{\circ}$ with an argon flow rate of 2ml/min). The starting material showed a retention time of 11·6 min. After 15 min irradiation, a new peak was visible with a retention time of 9·7 min. After 6h irradiation, the new signal was 2·5% the height of the starting material, while the peak height of the starting material had diminished by 5%. Further irradiation for up to 12h did not significantly improve this ratio but resulted in much polymer formation.

The new compound was found by co-injection on a carbowax 20M and a 10% Apiezon L column to have a retention time identical to that of authentic thiophene-2-carbonitrile. Analysis by g.c.m.s. showed it to give the same molecular ion and fragmentation pattern as that of authentic thiophene-2-carbonitrile. N.m.r. of the crude photosylate after removal of solvent showed it to contain only thiophene-3 and 2-carbonitrile.

Close inspection of the g.c. traces showed no thiophene or thiophene-dicarbonitriles present.

2. In acetonitrile solution:

In an experiment carried out in the same manner as the ether experiment, essentially the same result was obtained, except the reaction was about 30% faster.

3. In cyclohexane solution:

A $10^{-2}$ M solution of the nitrile in redistilled cyclohexane was degassed for 30 min with a stream of nitrogen and then irradiated in an RPR. Monitoring of the reaction by n.m.r. showed the primary photochemical product to be 5-thiabicyclo [2·1·0]pent-2-ene-2-carbonitrile, nmr ($CDCl_3$) 3·83 (d-1H, J=4), 4·15 (dd-1H, J=4, 4), 7·14 (d-1H, J=4). Further irradiation enabled the 2-nitrile to be detected by n.m.r. A maximum conversion to 2% of the bicyclic compound was achieved after 3h irradiation.

4. In furan solution:

The nitrile (50mg) was dissolved in redistilled furan (100ml), degassed with nitrogen for 30 min and then irradiated through quartz in an RPR for 2h. with 254n, light. The furan was removed under reduced pressure to yield 90mg of a pale brown oil. N.m.r. of this revealed that the starting material had disappeared and that the oil consisted mainly of a mixture of exo- and endo-10,4-oxathiatetracyclo[$5·2·1·0^{2,6}·0^{3,5}$]dec-8-ene-2-carbonitrile, as observed after the irradiation of thiophene-2-carbonitrile in furan solution. Only traces of thiophene-2 and 3-carbonitrile could be observed. The two adducts were separated by p.l.c. as before and gave 58mg of the exo-adduct and 6mg of the endo-adduct. These two samples had

identical spectroscopic properties to the previously obtained samples.

A dark experiment revealed that no adduct formation took place in the absence of ultra-violet light.

5. In methanol solution:

In an experiment essentially the same as the ether experiment, the 3 to 2 transposition was observed by g.c. analysis, but it only occurred at about half the rate of the ether experiment. N.m.r. of the residue after removal of the solvent showed no signals additional to the two nitrile isomers.

In a similar experiment, the nitrile (20mg) was dissolved in deuteriomethanol (0·4ml) and irradiated with 254nm light for 15h. N.m.r. of the resulting solution showed no deuterium incorporation in the nitrile.

Reaction of 5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile with furan

$10^{-2}$M Thiophene-3-carbonitrile (150ml) in cyclohexane was degassed with nitrogen and then irradiated for 2h in an RPR with 254nm light. The solvent was then removed under reduced pressure at $15^{o}$. The oily residue was dissolved in deuteriochloroform (0·5ml) and n.m.r. revealed the presence of thiophene-2- and 3-carbonitrile and also 2% of the bicyclic compound. Furan was then added in such a quantity that the solution became 5% in furan. The reaction was then monitored by n.mr. and over a period of 8h, in the dark, the signals due to the bicyclic compound disappeared and the signals due to the two furan adducts

appeared, in a ratio of 10 to 1 exo- to endo- adduct. Isolation of the adducts by p.l.c. showed them to be spectorscopically identical to the previously obtained exo- and endo- 10,4-oxathiatetracyclo[5·2·1·$0^{2,6}$·$0^{3,5}$]dec-8-ene-2-carbonitrile.

Reaction of exo-10,4-oxathiatetracyclo[5 2 1 $0^{2,6}$ $0^{3,5}$] dec-8-ene-2-carbonitrile with trimethyl phosphite.

The title adduct (10mg) and trimethyl phosphite (200mg) were heated together on an oil bath at 100-110°. The reaction was monitored by t.l.c. on silica gel plates using ether eluant. After 8h heating, the furan adduct had been completely converted to a new compound at rf 0·6. P.l.c. of the sample afforded, after recrystallisation from petrol, 6·0mg (73% yield) of white needles of exo-9-oxatricyclo[4·2·1·$0^{2,5}$]nona-3,7-diene-2-carbonitrile, m.pt. 70-72°; nmr ($CDCl_3$) 3·04(s-1H), 4·57 (s-1H), 4·72 (s-1H), 6·28 (d-1H, J=2·8), 6·41 (d-1H, J=2·8), 6·59 (s-2H); u.v. (ether) end-absorption only; i.r. (KBr) 3080(w), 3020(w), 2970(w), 2930(w), 2225(s), 1300(s), 1285(m), 1125(m), 1080(m), 1015(s), 825(m), 800(s), 740(s); m.s. $M^+$ 145(7), 116(100), 68(88), 90(73), 117(60), 77(53).

Pyrolysis of exo-10,4-oxathiatetracyclo[5·2·1·$0^{2,6}$·$0^{3,5}$] dec-8-ene-2-carbonitrile

1. In Air:

The adduct (10mg) was sealed in a glass tube (10x0·3cm) and heated at 170° in an oven for 30 min. The tube was cooled in ice, opened, and the contents dissolved in deuteriochloroform (0·5ml). N.m.r. of this solution showed the adduct to be present (~50%) as well as furan, thiophene-3-carbonitrile and thiophene-2-carbonitrile. The two thiophenes were separated from the adduct by t.l.c. and then analysed by g.c. on a 5ft column containing 7·5% carbowax 20M and 7·5% silicone gum rubber XO-60, at 134°. The ratio of the two nitriles was found to be 1:1.

2. In the presence of 2,5-diphenyl-3,4-benzofuran:

The adduct (50mg) and 2,5-diphenyl-3,4-benzofuran (100mg) were thoroughly mixed together and pyrolysed in a sealed tube at 170° for 3h. The tube was cooled in ice, opened, and the contents washed out with chloroform. After filtration, the solution was subjected to p.l.c. on silica plates with ether eluant. A high rf band was shown by nmr to be 2,5-diphenyl-isobenzofuran containing a small amount of thiophene-2 and 3-carbonitrile. The major component was found to be exo, exo-3,6-diphenyl-14,15,11-dioxathia-4,5-benzohexacyclo[6·5·$1^{1,8}$ $1^{3,6}$·$0^{2,7}$·$0^{9,13}$·$0^{10,12}$] pentadecane-9-carbonitrile, which gave pale brown crystals from chloroform/methanol with m.pt. 249-250°; nmr ($CDCl_3$) 2·56 (d-1H, J=6·6), 2·73 (d-1H, J=1·5), 3·05 (d-1H, J=4·0), 3·05 (d-1H, J=6·6), 3·30 (dd-1H, J=1·5, 4·0), 4·37 (s-1H), 4·44 (s-1H), 7·1-7·8 (m-14H); u.v. (methanol)

$\lambda_{max}$ = 225(sh), 265 ( $\varepsilon$ = 1050), i.r. (KBr) 3080-3020(m), 2960(m), 2930(m), 2870(m), 2235(m), 1605(w), 1505(m), 1460(s), 1450(s), 1355(m), 1310(s), 1020(s), 930(m), 850(m), 800(m), 760(s), 710(s); m.s. $M^+$ 447(0·2), 270(100), 271(23), 241(8), 77(6), 105(5); Analysis; calculated, C 77·84, H 4·73, N 3·13, S 7·15; found, C 77·64, H 4·63, N 3·10, S 7·29.

3. In the presence of 2,5-dimethylfuran:

The adduct (30mg) and 2,5-dimethylfuran (60mg) were mixed, sealed in a glass tube, and heated at 170° for 2h. The tube was cooled in ice, opened, and the contents washed out with chloroform. After filtration, the solution was concentrated to give a complicated nmr spectrum. P.l.c. of the sample with ether on silica gave two bands in the region where furan adducts were expected. The band at rf 0·3 gave 7·0 mg of a white solid which melted over the range 160-180° with n.m.r. ($CDCl_3$) 1·62 (s-3H), 1·64 (s-3H), 1·85 (d-1H, J=6·0), 2·35 (d-1H, J=6·0), 2·72 (d-1H, J=1·3), 3·27 (d-1H, J=3·7), 3·50 (dd-1H, J=1·3, 3·7), 4·64 (s-1H), 4·68 (s-1H), 6·22 (s-2H), consistant with endo, exo-3,6-dimethyl-13,14,11-dioxathiahexacyclo[$6\cdot5\cdot1^{1,8}\cdot1^{3,6}\cdot0^{2,7}0^{9,13}\cdot0^{10,12}$]pentadec-4-ene-9-carbonitrile, m.s. $M^+$ 273(2), 96(100), 43(28), 95(10), 68(8), 81(6).

The band at rf 0·4 gave 6·0 mg of a white solid with nmr ($CDCl_3$) 1·55 (d-1H, J=6·0), 1·62 (s-3H), 1·75 (s-3H), 2·32 (d-1H, J=6·0), 2·75 (d-1H, J=1·3), 3·40 (d-1H, J=3·8), 3·53 (dd-1H, J=1·3, 3·8), 4·57 (s-1H), 4·72 (s-1H), 6·30 (d-1H, J=5·0), 6·43 (d-1H, J=5·0), consistant with exo, exo-3,6-dimethyl-13,14,11-dioxathia[$6\cdot5\cdot1^{1,8}\cdot1^{3,6}\cdot0^{2,7}\cdot0^{9,13}\cdot0^{10,12}$]pentadec-4-ene-9-carbonitrile.

2-Deuteriothiophene-3-carbonitrile

The nitrile (13mg) in redistilled furan (25ml) was degassed for 30 min with a stream of nitrogen and then irradiated through quartz in an RPR with 254n, light for 1h. The furan was removed under reduced pressure and the oily residue (18mg) was subjected to p.l.c. on silica with 1:1 petrol: ether eluant. The band at rf 0·5 was shown by nmr to be exo-10,4-oxathiatetracyclo[5·2·1·$0^{2,6}$.$0^{3,5}$]dec-8-ene-2-carbonitrile with the deuterium distributed equally between the 3- and 6-positions, nmr ($CDCl_3$) 2·76 (s-$\frac{1}{2}$H), 3·43 (s and overlapping d-1H), 3·66 (d-$\frac{1}{2}$H), 5·07 (s-1H), 5·13 (s-1H), 6·53 (s-2H).

Irradiation of thiophene-2 and 3-carbonitrile in the presence of 1,3-pentadiene

Four solutions were made up in dry ether as shown below, degassed with nitrogen for 30 min, and then irradiated under identical conditions for 6h in an RPR with 254nm light.

| CONC. OF 2-CYANOTHIOPHENE | CONC. OF 1,3-PENTADIENE | REL. YIELD OF 3-CYANO THIOPHENE |
|---|---|---|
| $10^{-2}$M | 0 | 1·00 |
| $10^{-2}$M | 0·4M | 0·85 |
| $10^{-2}$M | 0·8M | 0·52 |
| $10^{-2}$M | 1·2M | 0·45 |

The relative yields were determined by g.c. on a carbowax 20M SCOT column. Calculation gives a triplet lifetime of $10^{-10}$ S assuming quenching is diffusion controlled.

The same experiments were carried out with thiophene-3-carbonitrile in place of the 2-isomer. A maximum quenching of 19% was observed with 1·2$\underline{M}$ pentadiene.

Irradiation of thiophene-2 and 3-carbonitrile in the presence of triplet sensitisers.

Three solutions were made up as shown below in benzene solvent, degassed with nitrogen for 30 min, and then irradiated through pyrex with a 450W medium pressure mercury arc lamp for 21h. No transposition was detected in any of the solutions by n.m.r. or g.c. analysis:

1. $10^{-2}\underline{M}$ thiophene-2-carbonitrile
2. $10^{-2}\underline{M}$ thiophene-2-carbonitrile + $10^{-1}\underline{M}$ benzophenone
3. $10^{-2}\underline{M}$ thiophene-2-carbonitrile + $10^{-1}\underline{M}$ acetophenone

Two solutions were made up as shown below in benzene, degassed for 30 min and then irradiated under the conditions above for 2·5h.

1. $10^{-2}\underline{M}$ thiophene-2-carbonitrile
   $10^{-1}\underline{M}$ benzophenone
   $10^{-2}\underline{M}$ benzhydrol
2. $10^{-1}\underline{M}$ benzophenone
   $10^{-1}\underline{M}$ benzhydrol

Analysis of the solutions by n.m.r. after removal of solvent showed that solution no. 2 had been converted to benzopinacol,

m.pt. 189-190°, in a yield of 95%. Solution no.1 showed mainly starting materials and only a 5% yield of benzopinacol.

The same experiments were repeated, substituting thiophene-3-carbonitrile for the 2-nitrile. No transposition was observed upon sensitisation with benzophenone or acetophenone, after 13h. irradiation. In addition no quenching of benzophenone photoreduction in the presence of benzhydrol was observed. However photoreduction of $10^{-1}$M acetophenone by $10^{-1}$M benzhydrol was observed by nmr to be quenched to the extent of 90% by $10^{-2}$M thiophene-3-carbonitrile. This brackets the triplet energy of the 3-nitrile to 69-74 kcal/mole. That of the 2-nitrile must be less than 69 kcal/mole.

5-Methylthiophene-3-carbonitrile.

1. In cyclohexane solution;

The nitrile (20mg) in redistilled cyclohexane (25ml) was degassed with a stream of nitrogen for 30 min and then irradiated through quartz in an RPR with 254nm light. The reaction was monitored by nmr and g.c. (using a 50ft carbowax 20M SCOT column at 160° with an argon flow rate of 2ml/min). After 30 min, a new peak was visible on g.c. with a retention time of 8·3 min. After 14h irradiation it had attained a height of 5% that of the starting material. Further irradiation did not significantly improve the ratio but resulted in much polymer formation. Authentic 4-methylthiophene-2-carbonitrile coinjected with the new peak. G.c.m.s. confirmed that the new peak was an isomer of the starting material by its molecular ion at m/e 123, base peak at m/e 122 and large m/e 96. N.m.r. of

the residue after removal of solvent under reduced pressure showed peaks additional to starting material at ($CDCl_3$) 2·30 (s-3H), 7·20 (s-1H) and 7·42 (s-1H). These are consistant with 4-methylthiophene-2-carbonitrile.

Close inspection of the g.c. traces showed that no methylthiophenes or thiophene-carbonitriles were formed.

2. In furan solution:

The nitrile (100mg) in redistilled furan (150ml) was degassed for 30 min and irradiated in an RPR for 5h with 254nm light. The furan was removed under reduced pressure to give 130mg of light brown oil. N.m.r. showed this to contain two methyl groups, one at 2·50 due to starting material, and another of twice its intensity at 1·64. A smaller methyl signal at 2·3 revealed the presence of a small amount of transposed starting material. P.l.c. of the oil on silica with 1:1 petrol:ether gave a band at high rf due to thiophenes and also a band at rf 0·4. Recrystallisation of the pale yellow solid of this band from petrol-chloroform gave 20mg of needles of exo-5-methyl-10,4-oxathiatetracyclo[$5·2·1·0^{2,6}·0^{3,5}$] dec-8-ene-2-carbonitrile, m.pt. 82-84°; nmr ($CDCl_3$) 1·64 (s-3H), 2·75 (d-1H, J=1·2), 3·55 (d-1H, J=1·2), 4·93 (s-1H), 5·00 (s-1H), 6·45 (s-2H); u.v. (ether) end-absorption only; i.r. (KBr) 3020(w), 2970(m), 2930(m), 2870(w), 2225(s), 1450(m), 1380(m), 1350(m), 1310(s), 1230(m), 1140(m), 1050(m), 1030(m), 1020(m), 980(m), 830(m), 760(s); m.s. $M^+$ 191(22), 68(100), 120(72), 162(39), 121(25), 91(10).

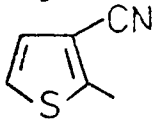
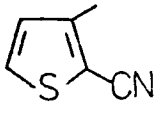
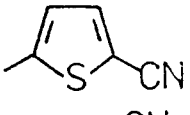
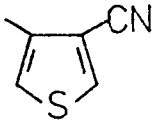
2-Methylthiophene-3-carbonitrile

1. In acetonitrile solution:

The nitrile (24mg) in dry acetonitrile (50ml) was degassed with nitrogen for 30 min and then irradiated through quartz in an RPR with 254nm light. The reaction was monitored by nmr and by g.c. (using a carbowax 20M SCOT column at 153° with an argon flow rate of 2ml/min).

After 10 min irradiation a new peak was visible on g.c. at longer retention time (13·0 min) than starting material (10·7 min). After 1h, this had grown to 15% the height of the starting material peak. In addition, two other small peaks had appeared at retention times of 11·2 and 11·6 min. These two peaks were of equal intensity and were of the order of 0·3% the height of the starting material. Further irradiation increased the height of the two small peaks at the expense of the two larger peaks. Irradiation times of longer than 2·5h resulted in the formation of much polymer.

Shown below are the ratios of products after 1h irradiation (20% destruction of starting material), and the compounds that they co-injected with;

| Retention time (min) | Peak Height | Coinjects with |
|---|---|---|
| 10·7 | 100 |  |
| 11·2 | 0·3 |  |
| 11·6 | 0·3 |  |
| 13·0 | 15·0 |  |

In addition to the coijnection information, g.c.m.s. of a sample irradiated for 2·5h showed the three new peaks to give molecular ions at m/e 123 and large peaks at m/e 122 and 96, characteristic of methylthiophene-carbonitriles. In addition, nmr clearly showed the presence of 4-methyl thiophene-3-carbonitrile, ($CDCl_3$) 2·37 (s-3H), 6·98 (m-1H), 7·81 (d-1H, J=3·0), and also showed methyl groups attributable to the other isomers at 2·53 (for the 5-$CH_3$) and 2·43 (for the 3-$CH_3$).

No peaks were observed on g.c. due to methylthiophenes or thiophene-carbonitriles.

2. In cyclohexane solution:

The nitrile (120mg) in redistilled cyclohexane (180ml) was degassed with nitrogen for 30 min, and then irradiated in an RPR with 254nm light for 1h. The cyclohexane was removed under reduced pressure at 25°. N.m.r. of the residue showed the presence of starting material and transposed products as in the acetonitrile irradiation, but in addition new signals were seen at 2·03, 3·76 and 4·03. P.l.c. of the oil on silica with 5:1 petrol:ether gave a band at 0·4-0·5 containing thiophenes and a band at 0·3 containing the new compound. A second p.l.c. of the rf 0·3 band gave 7·0 mg of a pale yellow oil identified as 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile, n.m.r. ($CDCl_3$) 2·03 (d-3H, J=1·0), 3·76 (d-1H, J=3·5), 4·03 (m-1H, J=1·0, 3·5). An additional coupling of 0·3Hz could be seen between the methyl group and the 4-H; u.v. (ether) $\lambda_{max}$ = 279 ($\varepsilon$ = 3810), 340 ($\varepsilon$ = 708); i.r. (film) 3015(w), 2960(w), 2900(w), 2210(s), 1630(m), 1435(m), 1380(m), 1265(m),

1100(w), 1045(m), 990(w), 810(w), 700(w); m.s. $M^+$ 123(88), 122(100), 97(18), 96(16), 83(12), 45(12); Analysis; calculated, C 58·53, H 4·09, N 11·38, S 25·99; found, C 57·94, H 4·06, N 11·53, S 25·55.

The n.m.r. spectrum of this compound remained unchanged, except for small variations in chemical shifts, over the temperature range -80° to +90°.

3. In furan solution:

The nitrile (240mg) in redistilled furan (150ml) was degassed with nitrogen for 30 min and then irradiated in an RPR with 254nm light for 2h. The furan was removed under reduced pressure to give 350 mg of a dark oil. N.m.r. of the oil showed signals additional to thiophenes at 1·2, 1·8, 2·4-2·7, 4·8-5·0 and 6·5. P.l.c. of the oil on silica with ether eluant gave a broad band at rf 0·55 to 0·85. This broad band was scraped off as three narrow bands at rf 0·85-0·75, rf 0·75-0·65 and rf 0·65-0·55.

The high rf band was shown by g.c. to contain the four methylthiophene-carbonitriles that were observed in the cyclohexane irradiation of 2-methylthiophene-3-carbonitrile.

The medium rf band contained traces of the thiophenes and also two furan adducts.

The low rf band contained the two furan adducts above, and additionally two more.

Column chromatography with silica and ether eluant enabled the two furan adducts of the rf 0·75-0·65 band to be obtained free from thiophenes, but no separation of the two adducts themselves could be achieved. Recrystallisation of the adducts

from carbon tetrachloride followed by vacuum sublimation at 50°/0·2mm Hg failed to alter the 1:1 ratio of the adducts. The mixture melted at 76-78° and was identified as containing exo-3-methyl-10,4-oxathiatetracyclo[5·2·1·$0^{2,6}$·$0^{3,5}$] dec-8-ene-2-carbonitrile, nmr ($CDCl_3$) 1·75 (s-3H), 2·66 (s-1H), 3·38 (s-1H), 4·96 (s-1H), 5·07 (s-1H), 6·53 (s-2H), and also exo-6-methyl-10,4-oxathiatetracyclo[5·2·1·$0^{2,6}$·$0^{3,5}$]dec-8-ene-2-carbonitrile, nmr ($CDCl_3$) 1·15 (s-3H), 3·53 (d-1H, J=4·0), 3·62 (d-1H, J=4·0), 4·88 (s-1H), 5·03 (s-1H), 6·53 (s-2H). The mixture also showed u.v. (ether) end-absorption only: i.r. (KBr) 3030(w), 2980(m), 2940(m), 2240(s), 1450(s), 1385(s), 1315(s), 1035(s), 1025(s), 985(m), 915(s), 730(s), 715(s); m.s. $M^+$ 191(13), 68(100), 122(47), 123(41), 162(25), 40(24); Analysis; calculated, C 62·82, H 4·75, N 7·33, S 16·74; found, C 62·65, H 4·74, N 7·21, S 16·94.

Column chromatography of the low rf band gave a 1:1 mixture of the exo-adducts described above, and also a mixture of two endo-adducts, namely endo-6-methyl-10,4-oxathiatetracyclo [5·2·1·$0^{2,6}$·$0^{3,5}$]dec-8-ene-2-carbonitrile, nmr ($CDCl_3$) 1·45 (s-3H), 3·02 (d-1H, J=3·5), 3·25 (d-1H, J=3·5), 4·77 (s-1H), 5·15 (s-1H), 6·66 (bs-2H), and also endo-3-methyl-10,4-oxathia-tetracyclo[5·2·1·$0^{2,6}$ $0^{3,5}$]dec-8-ene-2-carbonitrile, nmr ($CDCl_3$) 1·58 (s-3H), 3·20 (d-1H, J=5·0). 3·25 (s-1H), 5·03 (d-1H, J=5·0), 5·14 (s-1H), 6·68 (bs-2H). These two adducts were present in the ratio 3:1 respectively and showed, u.v. (ether) end-absorption only, i.r. (KBr) 3030(w), 2980(m), 2940(m), 2240(s), 1455(s), 1385(s), 1325(s), 1240(m), 1030(s), 995(s), 750(s); m.s. $M^+$ 191(7), 68(100), 40(71), 122(71), 123(59), 162(29).

2-Methyl[5-$^2$H]thiophene-3-carbonitrile

A solution of the nitrile (80mg) in redistilled hexane (120ml) was degassed with nitrogen and irradiated for 2h in an RPR with 254nm light.

Work up of the photosylate in the way described for the photolysis of the non-deuterated isomer in cyclohexane gave at rf 0·3, 4·0mg of 3-methyl-4-deutero-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile, nmr ($CDCl_3$) 2·03 (d-3H, J=1·0), 3·76 (d-residual H, J=3·5), 4·03 (q-1H, J=1·0 and overlapping M due to residual 4-H).

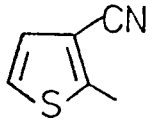
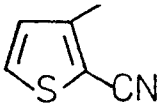
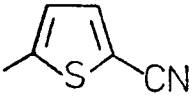
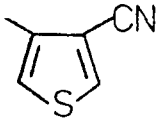
The band at rf 0·4-0·5 contained starting material and 4-methyl[5-$^2$H]thiophene-3-carbonitrile, nmr ($CDCl_3$) 2·37 (s-3H), 6·98 (m-residual H), 7·81 (s-1H, and overlapping doublet due to residual 5-H).

The deuterium incorporation in both of these compounds was ca 60%, the same as in the starting material.

4-Methylthiophene-3-carbonitrile

The nitrile (30mg) in redistilled cyclohexane (60ml) was degassed with nitrogen for 20 min and then irradiated in an RPR with 254nm light for 3·5h. The cyclohexane was removed under reduced pressure at 25° and nmr of the residual oil revealed the presence of 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile and starting material in the ratio 1:8. P.l.c. of the oil on silica with 5:1 petrol:ether gave a broad band due to thiophenes at rf 0·4-0·5, and a band due to the bicyclic compound at rf 0·3. Analysis of the thiophenes band

on a carbowax 20M SCOT column at 153° showed the presence of four nitriles in the ratio shown below;

| Retention time (min) | Peak Height | Coinjects with |
|---|---|---|
| 10·7 | 8 |  |
| 11·2 | 0·8 |  |
| 11·6 | 0·8 |  |
| 13·0 | 100 |  |

The identities of the nitriles were confirmed by coinjection with authentic samples, and their molecular ions were determined as 123 by g.c.m.s. No cyanothiophenes or methylthiophenes were observed either on the p.l.c. plate or on the g.c. trace.

The spectral properties of the bicyclic compound obtained in this experiment were identical to those obtained previously after irradiation of 2-methylthiophene-3-carbonitrile in cyclohexane.

•

Reaction of the mixture of exo-6 and 3-methyl-10,4-oxathiatetracyclo [5·2·1·$0^{2,6}$·$0^{3,5}$]dec-8-ene-2-carbonitrile with trimethyl phosphite

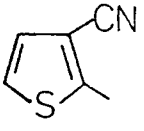
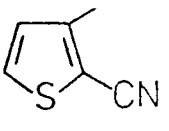
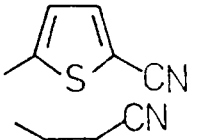
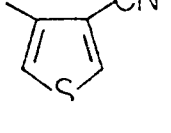
Treatment of the adduct mixture (20mg) with trimethyl phosphite (400mg) in the way described for the non-methylated furan adduct, gave on work up a mixture of the respective olefins; exo-5-methyl-9-oxatricyclo[4·2·1·$0^{2,5}$]nona-2,7-diene-2-carbonitrile,

n.m.r. ($CDCl_3$) 1·00 (s-3H), 4·60 (s-1H), 4·70 (s-1H), 6·10 (d-1H, J=2·0), 6·33 (d-1H, J=2·0), 6·55 (s-2H), and also exo-3-methyl-9-oxatricyclo[4·2·1·$0^{2,5}$]nona-3,7-diene-2-carbonitrile, n.m.r. ($CDCl_3$) 1·85 (d-3H, J=1·0), 2·85 (bs-1H), 4·53 (s-2H), 6·03 (bs-1H), 6.55 (s-2H).

This mixture of olefins could be separated by g.c. on an Apiezon L column at 164° to give two sharp peaks with retention times of 16·5 and 17·5 min.

Pyrolysis of the mixture of exo-6 and 3-methyl-10,4-oxathia tetracyclo[5·2·1·$0^{2,6}$·$0^{3,5}$]dec-8-ene-2-carbonitrile

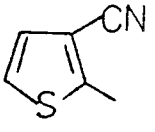
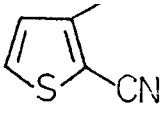
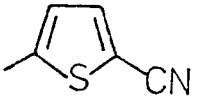
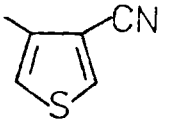
The mixture of furan adducts (10mg) was sealed in a glass tube (10x0·3cm) and heated in an oven at 170° for 30min. The tube was then cooled in ice, opened, and the contents dissolved in deuteriochloroform. N.m.r. revealed the presence of the adduct mixture, furan and both 2- and 4-methylthiophene-3-carbonitrile. The thiophenes were separated from the adducts by p.l.c. on silica using 5:1 petrol:ether as eluant. G.c. of the thiophenes band showed four isomers to be present in the ration shown below:

| Retention time (min) | Peak height | Coinjects with |
|---|---|---|
| 10·7 | 57 |  |
| 11·2 | 12 |  |
| 11·6 | 10 |  |
| 13·0 | 100 |  |

G.c.m.s. confirmed the identity of these compounds as methylthiophene-carbonitriles.

Pyrolysis of 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile

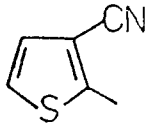
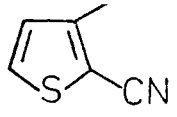
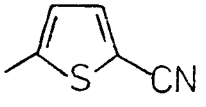
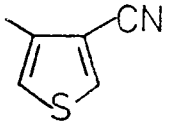
1 $\mu$l of a solution of the nitrile in chloroform (10mg/ml) was injected into the inlet port of a gas chromatograph with the injection port and the column at 170°. Four peaks other than solvent were observed at retention times consistant with the four nitriles shown below:

| Retention time (min) at 170° (SCOT 20M column) | Peak Height | Consistant with |
|---|---|---|
| 7·2 | 52 |  |
| 7·5 | 15 |  |
| 7·8 | 5 |  |
| 8·7 | 100 |  |

Irradiation of 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile.

1. Through pyrex:

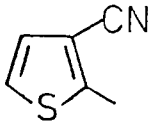
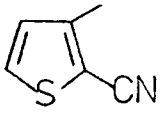
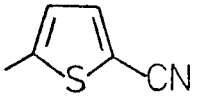
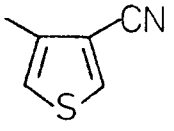
The nitrile (15mg) in dry ether (50ml) was degassed for 30 min with a stream of nitrogen and then irradiated for 3h through pyrex with a 450W medium pressure mercury arc lamp. The ether was removed under reduced pressure and nmr of the oil showed that the bicyclic compound had been destroyed, and that present was mainly 4-methylthiophene-3-carbonitrile. G.c. of this solution on a carbowax 20M SCOT column at 153° showed that four nitriles were present:

| Retention time (min) | Peak Height | Coinjects with |
|---|---|---|
| 10·7 | 10 |  |
| 11·2 | 12 |  |
| 11·6 | 0·2 |  |
| 13·0 | 100 |  |

2. Through quartz;

The nitrile (15mg) in dry ether (50ml) was degassed for 30 min with nitrogen and then irradiated through quartz in an R.P.R. with 254n, light for 45 min. N.m.r. of the residue after removal of solvent showed that the bicyclic compound had been destroyed and that four methylthiophene-carbonitriles

were present. G.c. analysis on a carbowax 20M SCOT column gave the following ratio of products:

| Retention time (min) | Peak Height | Coinjects with |
|---|---|---|
| 10·7 | 10 |  |
| 11·2 | 32 |  |
| 11·6 | 35 |  |
| 13·0 | 100 |  |

G.c.m.s. of the sample confirmed the four products to have molecular ions at m/e 123 and large peaks at m/e 122 and 96.

Reaction of 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile with various dienes.

1. With furan:

The nitrile (10mg) was dissolved in deuteriochloroform containing 5% (V/V) furan (0·3ml). The nmr of the solution was continuously monitored. Over a period of 8h, the bicyclic compound was quantitatively converted into a 1:1 mixture of exo-6 and exo-3-methyl-10,4-oxathiatetracyclo[5·2·1·$0^{2,6}$·$0^{3,5}$] dec-8-ene-2-carbonitrile as obtained previously. A small amount of the endo-adducts was also formed, accounting for 8% of the total yield of adducts.

2. With 2,5-diphenyl-3,4-benzofuran:

The nitrile (10mg) was dissolved in deuteriochloroform (0·3ml) and 2,5-diphenyl-3,4-benzofuran (25mg) was added. N.m.r. showed that the bicyclic compound had been instantly converted to an adduct identified as exo-6-methyl-1,7-diphenyl-10,4-oxathia-8,9-benzotetracyclo[5·2·1·$0^{2,6}$·$0^{3,5}$]decan-2-carbonitrile. Recrystallisation from methanol gave pale brown crystals, m.pt. 188-189° (dec); n.m.r. ($CDCl_3$) 1·23 (s-3H), 3·50 (s-2H), 7·1-8·0 (m-14H); (benzene) 1·08 (s-3H), 3·15 (d-1H, J=4·0), 3·24 (d-1H, J=4·0), 7·0-8·0 (m-14H); u.v. (methanol) $\lambda_{max}$ 220(sh), 265 ($\varepsilon$ = 615); i.r. (KBr) 3060(w), 3015(w), 2960(m), 2930(m), 2225(m), 1605(w), 1500(m), 1450(s), 1385(s), 1345(s), 1300(s), 1180(w), 1020(m), 1005(m), 900(w), 850(w), 775(s), 745(s), 705(s), 695)s); m.s. $M^+$ 393(0·6), 270(100), 271(23), 241(10), 105(9), 77(9); Analysis: calculated, C 79·37, H 4·87, S 8·14, N 3·59; found, C 79·60, H 4·92, S 8·36, N 3·72.

Treatment of this adduct (10mg) with excess trimethyl phosphite (100mg) at 110° for 3h, gave, at rf 0·7 after p.l.c. with benzene on silica, exo-5-methyl-9-oxa-7,8-benzotricyclo[4·2·$1^{1,6}$·$0^{2,5}$]non-3-ene-2-carbonitrile, nmr ($CDCl_3$) 1·40 (s-3H), 6·06 (d-1H, J=3·0), 6·32 (d-1H, J=3·0), 7·1-7·9 (m-14H).

Treatment of the episulphide adduct (10mg) in chloroform (0.4ml) with m-chloroperoxybenzoic acid (4·0mg) gave immediately the sulphoxide adduct, n.m.r. ($CDCl_3$) 1·02 (s-3H), 3·45 (s-2H), 7·2-8·0 (m-14H). This was obtained free from acids by washing the chloroform solution with aqueous sodium bicarbonate solution. The sulphoxide gave i.r. ($CHCl_3$) 3060(w), 2940(w), 2230(m),

1600(m), 1510(m), 1455(m), 1355(s), 1310(s), 1190(s), 1080(vs), 1020(s); m.s. $M^+$ 409(1), 270(100), 139(63), 105(53), 77(48), 122(29).

3. With hexachlorocyclopentadiene;

Hexachlorocyclopentadiene (50mg) was added to a solution of the nitrile (10mg) in deuteriochloroform (0·3ml). The reaction was monitored by nmr for two days but no adduct formation took place.

Reaction of 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile with various reagents.

1. Cyclohexylazide;

The azide (50mg) was added to a solution of the nitrile (10mg) in deuteriochloroform (0·3ml). The reaction was monitored by nmr over two days, during which time the bicyclic compound slowly disappeared. A new methyl signal appeared at 2·25 in the nmr spectrum, but it was very small, about a 5% yield. Analysis of this mixture on a carbowax 20M SCOT column at 171° revealed the presence of several short retention time peaks, and one at long retention time (23 min). G.c.m.s. of this signal showed it to give the fragmentation pattern, $M^+$ 188(31), 106(100), 107(87), 55(64), 149(60), 83(41). The fragmentation pattern of 5-methyl-N-cyclohexylpyrrole-2-carbonitrile, or an isomer, might be expected to be similar to that illustrated.

2. Di-iron nonacarbonyl;

Di-iron nonacarbonyl (30mg) was added to a solution of the nitrile (10mg) in tetrahydrofuran, at -68°. The solution was allowed to warm up to 20° over 30 min, and the reaction was then monitored by nmr. The nitrile slowly disappeared over 24h, but no new signals appeared in the nmr. The reaction was repeated with dichloromethane and chloroform as solvents, but the same results were obtained.

3. m-Chloroperoxybenzoic acid;

The acid (14mg) was added at -68° to a solution of the nitrile (10mg) in tetrahydrofuran. The solution was allowed to warm up to 35°, and nmr showed that the bicyclic compound had been quantitatively converted to the episulphoxide, n.m.r. (THF) 1·91 (d-3H, J=1·0), 4·05 (d-1H, J=2·0), 4·68 (m-1H, J=1·0, 2·0). The nmr spectrum of this compound was unchanged, except for small differences in chemical shift, over the temperature range -80° to +35°.

Addition of 2,5-diphenyl-3,4-benzofuran to this solution converted the sulphoxide into an adduct with n.m.r. (THF) 1·12 (s-3H), 2·95 (s-1H), 3·15 (s-1H), 7·2-8·0 (m-14H). This nmr spectrum is not consistant with the nmr spectrum obtained by treatment of the 6-methyl-2-cyano episulphide adduct with peroxyacid, but it would be consistant with the isomeric 3-methyl-2-cyano episulphoxide adduct.

4-Methylthiophene-2-carbonitrile

1. In hexane solution;

A solution of the nitrile (20mg) in redistilled hexane (25ml) was degassed with nitrogen for 30 min and irradiated in an RPR with 254nm light. The reaction was monitored by g.c. using a carbowax 20M SCOT column at 160°. After 3h irradiation a new peak appeared with a retention time of 9·6 min. Prolonged irradiation (12h) led to an overall conversion to the new compound of 0·2% (60% destruction of starting material). The new peak was found to coinject with 5-methylthiophene-3-carbonitrile.

2. In acetonitrile solution at 80°;

A solution of the nitrile (1·0g) in dry acetonitrile (800ml) was heated to 80° in a Hanovia 11 reactor with the aid of an isomantle. The solution was irradiated through quartz with a 100W medium pressure mercury arc lamp in an immersion well, while the photolysis was monitored by n.m.r. and g.c. After 4h, new signals were visible in the nmr at ($CDCl_3$) 2·51, 6·92 and 7·65. After 19h irradiation, the new peak had a height of 2·5% that of the starting material on g.c. Further irradiation did not improve this ratio but resulted in much polymer formation. Authentic 5-methylthiophene-3-carbonitrile coinjected with the new peak, and g.c.m.s. showed it to have a molecular ion at m/e 123, base peak at m/e 122 and a strong peak at m/e 96.

3. In furan solution;

A solution of the nitrile (200mg) in redistilled furan (100ml) was degassed with nitrogen and irradiated for 60h with 254nm light in an RPR. The furan was removed under reduced pressure to yield 220mg of a light brown oil. P.l.c. of the oil on silica plates with 1:1 petrol:ether gave a thiophene band at high rf, and a band at rf 0·44 (10mg) shown by nmr and i.r. to be identical to exo-5-methyl-10,4-oxathiatetracyclo[5·2·1·$0^{2,6}$·$0^{3,5}$]dec-8-ene-2-carbonitrile obtained previously from irradiation of 5-methylthiophene-3-carbonitrile in furan.

3-Methylthiophene-2-carbonitrile

1. In hexane solution;

A solution of the nitrile (120mg) in redistilled hexane (90ml) was degassed with nitrogen for 30 min and irradiated in an RPR with 254nm light. The reaction was monitored by g.c. using at 50ft carbowax SCOT column at 164°. The main reaction appeared to be polymer formation, but after 15h irradiation (50% destruction of starting material) two new peaks could be seen by g.c. The peak heights corresponded to conversions of 0·45% and 0·25%, and coinjection with authentic samples suggested that they were 4-methylthiophene-3-carbonitrile and 2-methylthiophene-3-carbonitrile respectively. A small shoulder could be seen on the starting material peak at the retention time expected for 5-methylthiophene-2-carbonitrile. Further irradiation did not improve the yields of these new compounds.

2. In acetonitrile solution at 80°;

This irradiation was carried out in the same manner as that of 4-methylthiophene-2-carbonitrile, and the photolysis was monitored by nmr and g.c. After 5h irradiation, new signals were visible in the n.m.r. at 2·37, 2·55, 2·63, 7·00 and 7·84. These signals reached a maximum intensity after 14h. Further irradiation led to much polymer formation. Analysis of the mixture on a carbowax 20M SCOT column showed a large peak due to starting material at 9·5 min, a large peak at 11·2 min (10% the height of starting material), and a smaller peak at 9·2 min (2% the height of starting material). At this time 70% of starting material had been destroyed. A shoulder was present on the long retention side of starting material. 4-Methylthiophene-3-carbonitrile and 2-methylthiophene-3-carbonitrile coinjected with the peaks at 11·2 and 9·2 min respectively. G.c.m.s. showed these two peaks to give molecular ions at m/e 123 and base peaks at m/e 122. The shoulder on the starting material had the same retention time as 5-methylthiophene-2-carbonitrile.

3. In furan solution;

A solution containing the nitrile (150mg) in redistilled furan (90ml) was degassed with nitrogen and irradiated in an RPR for 60h with 254nm light. The furan was removed under reduced pressure to give 170mg of pale brown oil. P.l.c. of the oil on silica plates with ether eluant gave a band at high rf due to thiophenes, and a band at rf 0·65 consisting mainly of a 1:1 mixture of exo-3 and 6-methyl-10,4-oxathia-tetracyclo[$5\cdot2\cdot1\cdot0^{2,6}\cdot0^{3,5}$]dec-8-ene-2-carbonitrile (12mg).

A band at rf 0·55 contained 2mg of the corresponding endo-isomers. These samples had nmr spectra identical to those of the adducts obtained previously from irradiation of 2-methylthiophene-3-carbonitrile in furan solution.

5-Methylthiophene-2-carbonitrile

1. In hexane solution;

A solution of the nitrile (120mg) in redistilled hexane (90ml) was degassed with nitrogen for 30 min and irradiated with 254nm light in an RPR. The reaction was monitored by g.c. using a carbowax 20M SCOT column. The major reaction was polymer formation, but after 15h irradiation, a small peak, corresponding by coinjection with 4-methyl-thiophene-3-carbonitrile could be seen. The overall yield was 0·2% at 50% destruction of starting material. A small bump could be seen on the base-line at the retention time of 2-methylthiophene-3-carbonitrile.

2. In acetonitrile at 80°;

This irradiation was carried out in the same way as that of 4-methylthiophene-2-carbonitrile. After 5h irradiation, nmr revealed the presence of new signals at 2·37, 7·00 and 7·83. G.c. analysis on a carbowax 20M SCOT column showed a peak consistant by coinjection with 4-methylthiophene-3-carbonitrile. This peak accounted for about 0·5% the height of the starting material. The g.c. trace also revealed very small amounts of 2-methylthiophene-3-carbonitrile and 3-methyl

thiophene-2-carbonitrile. Further irradiation did not improve the yield of these compounds but gave rise to much polymeric material.

3. In furan solution;

A solution containing the nitrile (150mg) in redistilled furan (90ml) was degassed with nitrogen and irradiated in an RPR with 254nm light for 60h. The furan was removed under reduced pressure to yield an oil whose nmr spectrum revealed mainly starting material. Additional signals were present due to a 1:1 mixture of exo-3 and 6-methyl-10,4-oxathiatetracyclo [5.2.1.$0^{2,6}$.$0^{3,5}$] dec-8-ene-2-carbonitrile. From the intensity of these signals and the volume of solution, a yield of about 2·0mg of adducts had been obtained.

5-Methylthiophene-2,4-dicarbonitrile

1. In acetonitrile solution;

A solution of the dinitrile (20mg) in dry acetonitrile (25ml) was degassed with nitrogen for 30 min and irradiated in an RPR with 254nm light. The reaction was monitored by nmr and by g.c. (using a carbowax 20M SCOT column at 172°). After 2h irradiation a new peak could be seen on g.c. with a retention time of 45·4 min (starting material came at 39·7 min). After 3·5h, new signals could be seen in the nmr at 2·58 and 8·03, consistant with 3-methylthiophene-2,4-dicarbonitrile. An authentic sample of this compound coinjected perfectly with the new peak on g.c. The overall yield of the new compound was 4·6% after 3·5h (60% destruction of starting material).

2. In furan solution;

A solution of the dinitrile (150mg) in redistilled furan (120ml) was degassed for 30 min and then irradiated in an RPR with 254nm light for 15h. The furan was removed under reduced pressure to yield 200mg of brown oil. N.m.r. showed this to contain 60% starting material. P.l.c. of the oil on silica plates with 3:2 petrol:ether gave three bands. The band at rf 0·5 was shown by nmr to be unreacted starting material. The band at rf 0·4 contained starting material and a new compound. A second p.l.c. of this band under the same conditions yielded 8·0mg of 5-methyl-10,6-oxathiabicyclo [5·2·0$^{1,7}$]dec-2,4-diene-2,4-dicarbonitrile as a colourless oil, nmr ($CDCl_3$) 1·90 (s-3H), 4·28 (m-1H, J=1·5, 3·0, 8·0), 4·87 (t-1H, J=3·0, 3·0), 4·91 (d-1H, J=8·0), 5·87 (s-1H), 6·71 (dd-1H, J=1·5, 3·0); u.v. (methanol) $\lambda_{max}$ = 209 ($\varepsilon$ = 8650), 285 ($\varepsilon$ = 2400), 350 ($\varepsilon$ = 170); i.r. ($CHCl_3$) 2960(w), 2940(w), 2870(w), 2240(s), 1610(s), 1390(m), 1315(s), 1150(s), 985(m), 915(s); m.s. $M^+$ 216(0·7), 68(100), 148(20), 149(19), 39(18), 121(9).

The band at rf 0·3 gave, after recrystallisation from chloroform-petrol, 15·0mg of exo-3-methyl-10,4-oxathiatetracyclo [5·2·1$^{1,7}$·0$^{2,6}$·0$^{3,5}$] dec-8-ene-2,5-dicarbonitrile, m.pt. 148-151°, nmr ($CDCl_3$) 1·90 (s-3H), 2·91 (s-1H), 5·13 (s-1H), 5·18 (s-1H), 6·57 (s-2H); i.r. (KBr) 3010(m), 2980(w), 2930(m), 2235(s), 2225(s), 1450(s), 1390(m), 1310(s), 1150(s), 1090(m), 1015(s), 930(m), 910(s), 800(m), 695(s); m.s. $M^+$ 216(0·6), 68(100), 148(85), 149(83), 155(60), 121(38).

This latter adduct was stable to irradiation both under the reaction conditions and in the presence of acetone.

3-Methylthiophene-2,4-dicarbonitrile

1. In acetonitrile solution;

A solution of the dinitrile (10mg) in dry acetonitrile (25ml) was degassed and irradiated with 254nm light in an RPR. The reaction was monitored by g.c. and nmr. After 2h, all of the starting material had disappeared. Only polymeric material had formed.

2. In furan solution;

A solution of the dinitrile (10mg) in redistilled furan (25ml) was degassed and irradiated for 3h with 254nm light in an RPR. The furan was removed to leave a brown residue which was mainly insoluble in organic solvents.

Thiophene-2,3-dicarbonitrile

1. In acetonitrile solution;

The dinitrile (5mg) in deuterioacetonitrile (0·35ml) was irradiated in an RPR for 21h with 254nm light. Analysis of the solution by g.c. and n.m.r. showed only starting material present.

2. In furan solution;

The dinitrile (15mg) in redistilled furan (25ml) was degassed with nitrogen for 30 min and then irradiated with 254nm light in an RPR for 18h. The furan was removed under reduced pressure to yield 30mg of a pale yellow oil, shown by t.l.c. to be a mixture of only two components. P.l.c. of the

oil on silica plates with 3:2 petrol:ether gave unreacted starting material at rf 0·2. Analysis of this fraction by g.c. showed no transposition to have taken place. The band at rf 0·35 gave 7·0mg of exo-7,10-dioxatricyclo[$4\cdot2\cdot1^{2,5}0^{1,6}$] dec-3,8-diene as a colourless liquid, nmr ($CDCl_3$) 3·22 (m-1H, J=2·0, 2·8, 7·5), 4·70 (d-1H, J=7·5), 4·73 (bs-1H), 4·78 (t-1H, J=2·8, 2·9), 5·02 (bs-1H), 6·20 (dd-1H, J=2·0, 6·0), 6·39 (dd-1H, J=2·0, 2·9), 6·43 (dd-1H, J=2·0, 6·0); u.v. (ether) end-absorption only; i.r. ($CCl_4$) 3080(w), 3010(m), 2960(s), 2930(s), 2880(m), 1625(m), 1470(m), 1280(w), 1210(m), 1200(m), 1165(s), 1140(s), 1070(s), 915(s), 860(m); m.s. $M^{+\cdot}$ 136(0·2), 68(100), 39(33), 29(15), 51(10), 42(6); Analysis; calculated, C 70·57, H 5·92, found, C 70·41, H 5·82.

Pyrolysis of this adduct in a sealed tube with a soft bunsen flame gave exclusively furan.

3. In ether solution;

The dinitrile (15mg) in dry ether (50ml) was degassed with nitrogen for 30 min and irradiated for 15h in an RPR with 254nm light. N.m.r. and g.c. analysis of the residue showed all of the starting material to have been destroyed. No isomers were observed.

Thiophene-2,5-dicarbonitrile

1. In acetonitrile solution;

The dinitrile (15mg) in deuterioacetonitrile (0·4ml) was irradiated in an RPR for 21h with 254nm light. N.m.r. and g.c. analysis showed slow destruction of starting material but no isomerisation.

Benzene-1,2,4,5-tetracarbonitrile

1. In furan solution;

A solution of the tetranitrile (5mg) in redistilled furan (60ml) was degassed with nitrogen for 30 min and irradiated at 254nm in an RPR. Monitoring of the photolysis by nmr spectroscopy showed the slow formation of exo-7,10-dioxatricyclo[$4\cdot2\cdot1^{2,5}\cdot0^{1,6}$] deca-3,8-diene. After 21h irradiation, work up in the usual manner gave 9·0mg of the adduct after p.l.c. with 3/2 petrol/ether. This had identical spectroscopic properties to the previously obtained material. 2·0mg of the tetranitrile was recovered.

A dark reaction showed no adduct formation on work up.

2. In 50% (V/V) furan in ethyl vinyl ether;

A solution containing the tetranitrile (20mg) in the solvent mixture (100ml) was degassed with nitrogen and irradiated with 254nm light for 15h in an RPR. N.m.r. of the residue after removal of the solvents under reduced pressure showed a complicated pattern of signals, but none due to exo-7,10-dioxatricyclo[$4\cdot2\cdot1^{2,5}\cdot0^{1,6}$]deca-3,8-diene.

P.l.c. of the residue with 3/1 petrol/ether on silica gave bands at rf 0·3, 0·5, 0·7 and 0·8.

The band at rf 0·3 gave 5·0mg of a colourless oil identified as exo-6-ethoxy-7-oxabicyclo[2·2·1$^{1,4}$]hept-2-ene, nmr ($CDCl_3$) 1·20 (t-3H, J=7·0), 1·40 (m-1H, J=3·0, 4·0,12·0), 1·70 (dd-1H, J=6·0, 12·0), 3·50 (dq-2H, J=7·0), 3·65 (dd-1H, J=3·0, 6·0), 4·90 (d-1H, J=2·0), 4·96 (dd-1H, J=2·0, 4·0), 6·30 (dd-1H, J=2·0, 6·0), 6·40 (dd-1H, J=2·0, 6·0); u.v. (ether) end-absorption only; i.r. ($CHCl_3$) 3010(w), 2980(m), 2960(s), 2900(s), 1450(w), 1430(w), 1350(m), 1320(s), 1250(s), 1100(s), 1045(m), 1020(m), 870(s); m.s. $M^+$ 140(0·4), 44(100), 72(90), 68(55), 73(48), 43(39).

The band at rf 0·5 gave as a colourless oil 5·0mg of endo-6-ethoxy-7-oxabicyclo[2·2·1$^{1,4}$]hept-2-ene, nmr ($CDCl_3$) 1·10 (dd-1H, J=2·5, 11·0), 1·22 (t-3H, J=6·0), 2·15 (m-1H, J-5·0, 8·0, 11·0), 3·52 (dq-2H, J=6·0), 4·10 (m-1H, J=2·5, 4·0, 8·0), 4·90-5·00 (m-2H, J=2·0, 5·0; 2·0, 4·0), 6·20 (dd-1H, J=2·0, 6·0), 6·50 (dd-1H, J=2·0, 6·0); u.v. (ether) end-absorption only; m.s. $M^+$ 140(0·4), 72(100), 68(100), 44(100), 39(70), 43(57).

The band at rf 0·7 gave as a colourless oil 3·0mg of a 2+2 adduct of furan with ethyl vinyl ether, nmr ($CDCl_3$) 1·19 (t-3H, J=7·5), 1·30 (m-1H), 2·48 (m-2H), 3·38 (q-2H, J=7·5), 3·85 (m-1H), 5·03 (t-1H, J=3·0, 3·0), 5·10 (dd-1H, J=5·0, 7·0), 6·35 (dd-1H, J=1·5, 3·0); u.v. (ether) end-absorption only; i.r. ($CCl_4$) 3020(w), 2960(m), 2920(m), 2850(m), 1600(w), 1460(m), 1375(m), 1290(m), 1120(m), 1070(m), 960(m); m.s. $M^+$ 140(4), 72(100), 44(97), 68(43), 43(37), 29(30).

The band at rf 0·8 gave 3·0mg of a colourless oil which gave two peaks with retention times of 6·3 and 6·8 min on a 50ft carbowax 20M SCOT column at 100°. G.c.m.s. of these two peaks showed the shorter retention time compound to give a base peak at m/e 18, and large peaks at m/e 44(98), 72(90), 92(60), 58(55), 85(46), 43(45), 100(30). The longer retention time peak gave a mass spectrum consistant with a cyclobutane diethoxy ether, m.s. $M^+$ 144(1), 72(100), 44(75), 60(33), 43(28), 116(21).

N.m.r. of this sample showed two compounds to be present, ($CDCl_3$) 1·18 (t-3H, J=7·0), 1·21 (t-3H, J=7·0), 1·90-2·10 (m-3H based on the two $CH_3$ groups at 6H), 2·25 (m-1H), 3·48 (q-2h, J=7·0), 3·50 (q-2H, J=7·0), 3·75 (m-1H), 4·02 (m-1H). The two ethyl groups were present in the ratio 1:0·75. Irradiation of the multiplet at 4·02 collapsed the multiplet at 2·0 to a broad singlet. Irradiation of the multiplet at 2·0 collapsed the multiplet at 4·02 to a singlet and the multiplet at 3·75 to a simpler three signal pattern.

The ultra-violet spectrum of the mixture showed no absorption. The infra-red spectrum gave 2990(m), 2970(m), 2950(m), 2925(m), 2890(m), 2870(m), 2850(m), 1460(s), 1445(s), 1370(s), 1350(m), 1330(m), 1290(m), 1175(s), 1140(s), 1110(s), 1060(m), 960(w), 860(w).

Benzene-dicarbonitriles

1. In furan solution;

Solutions of the 1,2-, the 1,3- and the 1,4-dicarbonitriles in furan (0·1mg/ml) were degassed and irradiated with 254nm light in an RPR. The sole product in each case was exo-7,10-dioxatricyclo[4·2·1$^{2,5}$·0$^{1,6}$]deca-3,8-diene. The yields after 24h irradiation were similar in each case at 7·0mg. No transposition of starting materials was observed.

2-Bromothiophene-3-carbonitrile

A solution of the nitrile (20mg) in redistilled furan (40ml) was degassed with nitrogen and irradiated in an RPR for 1h with 254nm light. The furan was removed under reduced pressure to yield a black oil. Polymeric material was removed by passing the oil down a short silica column with ether eluant. N.m.r. of the residue after removal of the ether showed only starting material and a small amount of 2-bromofuran, nmr ($CDCl_3$) 6·28 (dd-1H, J=0·8, 3·25), 6·33 (dd-1H, J=2·10, 3·25), 7·37 (dd-1H, J=0·8, 2·10).

Thiophene

Redistilled thiophene (20mg) in furan (40ml) was degassed and irradiated in an RPR with 254nm light. The reaction was monitored by nmr but only polymeric material was formed.

2,5-Dimethylthiophene

1. In ether solution;

The thiophene (15mg) in dry ether (30ml) was degassed and irradiated in an RPR with 254nm light. The photolysis was monitored by g.c. on a carbowax 20M SCOT column at 102°. After 30 min irradiation, a new peak was visible with a retention time of 10·2 min (starting material 9·2 min). After 2·5h irradiation, a 15% conversion to the new compound had been achieved.

N.m.r. of the residue after removal of ether showed starting material at ($CDCl_3$) 2·40 (s-3H) and 6·50 (s-2H), and additional signals at 2·18 and 6·60. G.c.m.s. of the mixture gave the fragmentation pattern of the new compound at $M^{+\cdot}$ 112(66), 111(100), 97(42), 45(12), 39(11), 59(7). All of the four possible dimethylthiophenes have been analysed by mass spectrometry and all give characteristic fragmentation patterns.[98] Of the three possible isomers the new compound could be, (2,3-, 2,4-, or 3,4-), it cannot be the 2,3- isomer since this gives a base peak at m/e 97. It cannot be the 3,4-isomer as this, having no α-methyl groups gives a very small m/e 59 (less than 3%) and a very large m/e 43 (8). The fragmentation pattern of the new compound is in reasonable agreement with that given for the 2,4-isomer; $M^{+\cdot}$ 112(73), 111(100), 97(49), 45(26), 39(19), 59(7).

No peaks due to thiophene, methylthiophenes or trimethylthiophenes were observed by g.c.

2. In furan solution;

This experiment was carried out in exactly the same way as the ether experiment, except furan was used as solvent. After 2h irradiation, the furan was removed under reduced pressure to yield an oily residue, the nmr spectrum of which revealed only 2,5-dimethylthiophene and a small amount of the 2,4-isomer. No furan adducts or cyclopropyl hydrogens were observed by nmr.

Thiophene-2-acrylonitrile

1. In acetonitrile;

The nitrile (15mg) in deuterioacetonitrile (0·4ml) was irradiated at 254nm in an RPR. The photolysis was monitored by nmr. The initial cis/trans ratio of 1·0:1·49 as determined by nmr spectroscopy changed to 1·0:0·84 after 24h. Further irradiation did not affect this ratio. No transposed products were observed by nmr or g.c. analysis.

Prolonged irradiation gave rise to a complicated pattern of signals in the 2·0-3·2 region of the nmr spectrum. These are probably associated with 2+2 acrylonitrile dimers. Dicyanocyclobutanes give rise to signals in this region.[219]

2. In furan;

A solution of the nitrile (100mg) in furan (50ml) was degassed and irradiated at 254nm in an RPR for 72h. Analysis of the residue, after removal of solvent, showed no traces of furan adducts by nmr spectroscopy. The only additional signals to starting material were in the region 2·0-3·2, typical of cyclobutane compounds.

Anti-4-methylthiophene-2-aldoxime

This isomer, obtained from recrystallisation of a mixture of the syn and anti-isomers from aqueous methanol, was irradiated as a solution (35mg/ml) in deuterioacetonitrile. The reaction was monitored by nmr spectroscopy and this showed a rapid conversion to a 1:1 mixture of the syn and anti-isomers. The nmr of the anti-isomer can be found in the synthesis section, that of the syn-isomer was determined as ($CDCl_3$) 2·30 (s-3H), 6·90 (s-1H), 7·00 (s-1H), 8·20 (s-1H). Prolonged irradiation showed no phototransposition to occur.

## Low Temperature Irradiation of Thiophenes

### Thiophene-2-carbonitrile

1. In a 2:1 tetrahydrofuran:dichloromethane glass at 75K:

An Oxford Instruments Cf 5383/CF 100 cryostat and control unit was used to obtain low temperature matrices.

A 2% solution of the nitrile in the solvent mixture was applied to a sodium chloride window at 173K under a stream of dry nitrogen. The sample was cooled to 100K before being evacuated to below $10^{-6}$ torr with further cooling to 75K. The infra-red spectrum of the glass was recorded and showed the nitrile absorption as a sharp symmetrical band at 2225$cm^{-1}$. The sample was irradiated with a 100W high pressure mercury arc lamp for 3h and the infra-red spectrum was recorded again. This showed the intensity of the nitrile band to have decreased by 30% and also that it contained a shoulder at 2235$cm^{-1}$. On warming up, the shoulder began to disappear at 130K and had completely disappeared after 10 min at 138K. At this time the nitrile band had grown to 90% of its original intensity. Further warming produced no changes in the spectrum.

2. At $-68^{o}$ in tetrahydrofuran;

A solution of the nitrile (10mg) in deuteriotetrahydrofuran (0·3ml) contained in a quartz n.m.r. tube was placed into a quartz Dewar containing methanol/dry ice at $-68^{o}$. The Dewar and its contents were irradiated in an RPR with 254nm light for 3h. The n.m.r. tube was then rapidly transferred to a

Bruker WH 90 n.m.r. spectrometer with the probe pre-cooled to -70°. The n.m.r. spectrum was recorded at this temperature and showed only starting material to be present.

This experiment was repeated twice, but after 3h irradiation, to one sample was added 2,5-diphenylisobenzofuran and to the other was added hexachlorocyclopentadiene. The samples were kept at -68° for 2h, and then allowed to warm up to 20° over 4h. In both cases, the n.m.r. spectra of the resulting solutions showed no adduct formation.

4-Methylthiophene-2-carbonitrile

1. At -68° in tetrahydrofuran;

This n.m.r. scale experiment was carried out in exactly the same manner as that with thiophene-2-carbonitrile, except the irradiation time was increased to 6h. N.m.r. of the resulting solution at -70° revealed only unchanged starting material.

2-Methylthiophene-3-carbonitrile

1. At -40° in furan;

A solution of the nitrile (40mg) in furan (50ml) in quartz tubes was degassed with nitrogen and placed in a quartz Dewar holding a bath of acetonitrile and dry ice at -40°. The vessel was irradiated in an RPR with 254nm light for 4h. The solutions were then stood at -40° for a further 1h before the furan was removed under reduced pressure. Work up of the

residue in the same manner as the room temperature irradiation of this nitrile in furan gave the two exo-adducts 3-methyl and 6-methyl-10,4-oxathiatetracyclo[5·2·1·$0^{2,6}$·$0^{3,5}$]dec-8-ene-2-carbonitrile. These were present in the ratio 10:1 compared to the room temperature ratio of 1:1.

G.l.c. of the thiophenes band showed that transposition had also occurred to give mainly 4-methylthiophene-3-carbonitrile.

2. At -68° in tetrahydrofuran;

In the same manner as for thiophene-2-carbonitrile, the nitrile (30mg) in deuterated tetrahydrofuran (0·3ml) was irradiated for 12h at -68°. On allowing the sample to warm up to room temperature, the n.m.r. spectrum showed the solution to contain 36% starting material and 64% 3-methyl-5-thiabicyclo [2·1·0] pent-2-ene-2-carbonitrile. Several very minor signals were also present.

In a similar experiment, after 5h irradiation at -68°, 2,5-diphenylisobenzofuran was added. The mixture was shaken in the bath at -68° for 5 min, and then allowed to warm up to room temperature with vigorous shaking. P.l.c. of this mixture on silica with benzene eluant gave 2-methylthiophene-3-carbonitrile at rf 0·4, 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile at rf 0·45, and at rf 0·5, two adducts in the ratio 1·2:1·0, respectively exo-3-methyl-1,7-diphenyl-10,4-oxathia-8,9-benzotetracyclo[5·2·1·$0^{2,5}$·$0^{3,5}$]decane-2-carbonitrile and the exo-6-methyl isomer. The n.m.r. of the latter was identical to that obtained from treatment of 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile with 2,5-diphenylisobenzofuran. The n.m.r. of the 3-methyl isomer

was determined as ($CDCl_3$) 1·31 (s-3H), 3·30 (s-1H), 3·35 (s-1H), 7·1-8·0 (m-14H).

It was not possible to separate these two adducts by p.l.c., but desulphurisation of this mixture with trimethyl phosphite in the manner previously described afforded two olefins after p.l.c. with benzene. The olefin at rf 0·7 had an nmr spectrum identical to that of the previously obtained exo-5-methyl-9-oxa-7,8-benzotricyclo[$4·2·1^{1,6}·0^{2,5}$]nona-3-ene-2-carbonitrile. The other olefin at rf 0·75 gave nmr ($CDCl_3$) 1·40 (d-3H, J=1·0), 3·60 (s-1H), 5·93 (bs-1H), 7·1-7·9 (m-14H), consistant with the exo-3-methyl isomer.

In a similar experiment, following irradiation of the nitrile (9mg) in deuterated tetrahydrofuran (0·3ml) at -68° for 3h, the nmr tube was rapidly transferred to a Bruker WH 90 nmr spectrometer with the probe precooled to -70°. The nmr spectrum showed a 35% conversion to 1-methyl-5-thiabicyclo [2·1·0]pent-2-ene-2-carbonitrile, nmr 2·04 (s-3H), 4·26 (bs-1H), 7·48 (bs-1H); and also 3-methyl-5-thiabicyclo 2·1·0 pent-2-ene-2-carbonitrile, nmr 2·01 (d-3H, J=0·9), 4·12 (d-1H, J=3·5), 4·42 (m-1H, J=0·9, 3·5), which were present in the ratio 3:1. Additionally, 2% of 2-methyl-5-thiabicyclo[2·1·0]pent-2-ene-1-carbonitrile was present, nmr 2·11 (d-3H, J=1·0), 4·68 (bs-1H), 6·29 (m-1H). The chemical shift values are based on the 2-$CH_2$ of THF at 1·72. On warming the solution to -35° and waiting 5 min, all of the signals due to the 1-cyano bicyclic compound disappeared, and 76% of the 1-methyl isomer was converted to the 3-methyl isomer. On standing at -35° for a further 5 min, 80% of the remainder was converted to the 3-methyl isomer. This gives a half-life of 130 sec for the 1-methyl isomer and a rate constant of $5·37 \times 10^{-3}$ $s^{-1}$ for the sulphur-walk. On further warming, all of the 1-methyl isomer was converted to

the 3-methyl isomer. This latter isomer was stable at 25°.

5-Methylthiophene-3-carbonitrile

1. At -68° in tetrahydrofuran;

In an experiment identical to that with thiophene-2-carbonitrile, the nitrile (10mg) in deuterated tetrahydrofuran (0·3ml) was irradiated for 5h at -68°. N.m.r. of the resulting solution showed a 1% conversion to a mixture of 4-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile, nmr 2·09 (2-3H), 4·48 (d-1H, J=4·4), 7·39 (d-1H, J=4·4); and 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-1-carbonitrile, nmr 2·05 (d-3H, J=1·8), 4·63 (d-1H, J=3·9), 6·31 (m-1H, J=1·8, 3·9), which were present in the ratio 1·00:0·44. A small amount of 4-methylthiophene-2-carbonitrile was also present (1%). On warming the solution to -40° and waiting 10 min, 82% of the bicyclic compound with the bridgehead cyano group had disappeared. The signals due to the bicyclic compound with the conjugated cyano group increased in intensity by 32%, and those due to 4-methylthiophene-2-carbonitrile increased by about 10%. On further warming to 0° and waiting 10 min, all of the signals due to the 3-methyl isomer had disappeared, and in addition, a 47% decrease in the amount of the 4-methyl isomer was observed. On warming to +25°, all of the 4-methyl isomer had disappeared.

In a similar experiment, after 5h irradiation at -68°, 2,5-diphenylisobenzofuran (5mg) was added. The mixture was kept at this temperature for 2h and then allowed to warm up to 20° over a period of 4h. The solvent was then removed and

the residue dissolved in deuteriochloroform. N.m.r. ($CDCl_3$) of this solution showed 1·21 (s-3H), 3·48 (s-1H), 3·54 (s-1H) and phenyl hydrogens consistant with exo-5-methyl-1,7-diphenyl-10,4-oxathia-8,9-benzotetracyclo[$5\cdot2\cdot1\cdot0^{2,6}\cdot0^{3,5}$] decane-2-carbonitrile. In addition to these signals, there was a small singlet at 1·43. This may be due to a trace of the exo-3-cyano-6-methyl isomer.

3-Methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile

1. At -68° in tetrahydrofuran;

In the usual manner, 2-methylthiophene-3-carbonitrile (9mg) was irradiated in an n.m.r. tube at -68° for 3h. The sample was then allowed to warm up to room temperature and n.m.r. revealed a 25% conversion to the title compound. The sample was then recooled to -68° and further irradiated for 2·75h. On allowing the sample to warm up to 25°, n.m.r. spectroscopy revealed the presence of a small amount of 4-methylthiophene-3-carbonitrile. P.l.c. of the sample to remove the bicyclic compounds, followed by g.c. of the thiophenes band confirmed this identification.

Thiophene

1. At 7K in an Argon matrix;

Thiophene was degassed on a vacuum line by three 'freeze-pump-thaw' cycles and then allowed to evaporate into a 250ml double-section vessel to a pressure of 8 torr, and then made

up to 300 torr with argon. This was applied to a sodium chloride window at 30K in a 'pulsed'manner through a 'spray-on' nozzle. The temperature of the sample was reduced to 7K with liquid helium coolant and the sample was irradiated with a 100W Hanovia high pressure mercury arc lamp for several hours. Continuous monitoring by infra-red spectroscopy showed the sample to be stable to irradiation at this temperature.

## B. PYRYLIUM CATIONS

### 2,3,5,6-Tetramethylpyrylium perchlorate

A solution of the perchlorate (250mg) in dry acetonitrile (25ml) was degassed with nitrogen and irradiated in an RPR with 254nm light. The reaction was monitored by n.m.r. spectroscopy and this revealed the appearance after 3h irradiation of signals at ($CD_3CN$) 2·34, 2·60, 2·78 and 7·73. These signals grew in intensity until after 45h the ratio of starting material to product was 1:2. Further irradiation destroyed both compounds until after 80h, only signals due to product were visible. The acetonitrile was removed under reduced pressure to yield a black tar which was dissolved in water (10ml) and extracted with ether (10ml). The water was removed under reduced pressure to leave a black oil. This was treated several times with dry ether and then stood at 4° under ether for 24h. The ether was decanted to yield a black solid. Recrystallisation of this solid from 2-propanol yielded 5·0mg of pale brown crystals, m.pt. 101-104°. This compound had an n.m.r. spectrum, i.r. spectrum and u.v. spectrum identical to that of authentic 2,3,4,6-tetramethylpyrylium perchlorate.

Similar results were obtained upon irradiation in 2,2,2-trifluoroethanol, methanol, trifluoroacetic acid and water.

2,6-Diethyl-3,5-dimethylpyrylium perchlorate

A solution of the perchlorate (20mg) in acetonitrile (0·5ml) was irradiated with 254nm light in an RPR. N.m.r. showed the slow destruction of starting material and the appearance of new signals at ($CD_3CN$) 1·16, 2·63, and 7·68. After 90h irradiation all of the starting material had been destroyed. The acetonitrile was removed under reduced pressure and the residue was recrystallised from 2-propanol to yield 4·2mg of pale brown needles of 2,3-diethyl-4,6-dimethylpyrylium perchlorate, m.pt. 152-156°, nmr ($CD_3CN$) 1·16 (t-3H, J=7·0), 1·38 (t-3H, J=7·0), 2·63 (s-3H), 2·70 (q-2H, J=7·0), 2·76 (s-3H), 3·16 (q-2H, J=7·0), 7·68 (s-1H); u.v. (acetonitrile) $\lambda_{max}$ = 292 ( $\varepsilon$ = 12000); i.r. (KBr) 3080(w), 2980(w), 2940(w), 1645(m), 1480(m), 1390(m), 1230(w), 1100(vs), 900(w).

Similar results were obtained upon irradiation in 2,2,2-trifluoroethanol, trifluoroacetic acid and methanol.

2-Ethyl-3,5,6-trimethylpyrylium perchlorate

The perchlorate (20mg) in dry acetonitrile (0·5ml) was irradiated in an RPR with 254nm light. The starting material was slowly destroyed as new signals appeared in the n.m.r. spectrum at 1·16(t), 1·45(t), 2.47(s), 2·58(s), 2·63(s), 2·70(q), 2·75(s), 2·77(s), 3·13(q) and 7·60(s). The irradiation was stopped after 16h when the ratio was 2:1 starting material to transposed products. The appearance of two new ethyl groups in the regions expected for $\alpha$ and $\gamma$-ethyl groups, the appearance

of a γ-methyl group and the non-appearance of any aromatic H other than in the 7·6 region suggests the two new products to be 2-ethyl-3,4,6-trimethylpyrylium perchlorate and 3-ethyl-2,4,6-trimethylpyrylium perchlorate.

Attempts to separate these salts by fractional crystallisatior was unsuccessful. Reversed phase t.l.c. with paraffin impregnated plates and methanol/acetic acid solvent also failed to give any separation.

Similar results were obtained upon irradiation in trifluoro-acetic acid and methanol.

4-Ethyl-2,3,5,6-tetramethylpyrylium perchlorate

1. In deuterioacetonitrile;

A solution of the perchlorate (20mg) in deuterioacetonitrile (0·5ml) was irradiated in an RPR with 254nm light. After 30 min irradiation, a new methyl group at ($CD_3CN$) 2·55 was visible in the nmr spectrum, characteristic of a 4-methyl group in a pyrylium ion. After 2lh, a second methyl group became visible in this region at 2·53. Similarly new ethyl groups appeared with $CH_2$ groups at 2·80 and 3·12 respectively. This behaviour is consistant with the 4-ethyl isomer transposing to the 3-ethyl isomer, and then the 2-isomer.

A number of signals also appeared in the nmr spectrum after 3h irradiation which were not consistant with pyrylium ions. These were in the region 1·55 to 1·85, and also at 5·26. A repeat of this experiment in non-deuteriated acetonitrile gave the same result except for the appearance of an additional methyl group at 1·90.

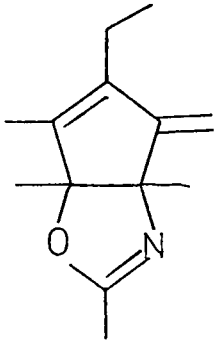
This experiment was repeated on a larger scale using 1·0g of pyrylium salt in 60ml of acetonitrile with 24h irradiation. The solution was then poured onto water (100ml) and extracted twice with ether (25ml). The ethereal solution was dried over magnesium sulphate, the ether removed under reduced pressure and the residue subjected to p.l.c. with ether eluant on silica gel. This gave one major band at rf 0·5, and several very minor bands. G.l.c. of the rf 0·5 band on a 10% Apiezon L column at 188° showed two poorly separated peaks. A column containing 7·5% carbowax 20M and 7·5% silicone XE-60 at 150° gave better resolution with the two peaks at 7·0 and 7·6 min. G.c.m.s. of these two peaks gave the following fragmentation patterns:

| | 7·0 min | 7·6 min |
|---|---|---|
| $M^{+\cdot}$ | 205 (68) | 205 (43) |
| | 146 (100) | 162 (100) |
| | 162 (79) | 163 (90) |
| | 43 (63) | 43 (33) |
| | 163 (58) | 135 (32) |
| | 131 (42) | 146 (20) |
| | 135 (33) | 164 (20) |

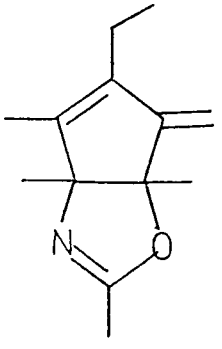
The molecular ions suggest that the pyrylium cation has incorporated one molecule of acetonitrile with the loss of a proton. The appearance of a methyl group in the n.m.r. spectrum when the irradiation is performed in $CH_3CN$ but not in $CD_3CN$ supports this. The infra-red spectrum of this mixture gave ($CH_3CN$) 2990(w), 2980(m), 2940(m), 2880(w), 1645(s),

1490(m), 1390(m), 1350(m), 1245(m), 1150(m), 1060(m), 975(m), 900(m). The strong band at 1645cm$^{-1}$ is typical of C=N, and that at 900cm$^{-1}$ of $=CH_2$. The ultra-violet spectrum showed ($CH_3CN$) $\lambda_{max}$ = 226 ( $\varepsilon$ = 5600 ), and the n.m.r. spectrum gave ($CDCl_3$) 0·98 (t,J=8·0), 1·25(s), 1·30(s), 1·33(s), 1·38(s), 1·76(s), 1·80(s), 1·86(s), 2·18 (q,J=8·0), 4·85(s), 5·00(s). The signal at 1·86 was assigned as originating from acetonitrile.

These data are consistant with the formation of the two isomeric oxazolines shown below (4·1) and (4·2).




(4·1)




(4·2)

2. In 2,2,2-trifluoroethanol;

A solution of the perchlorate (20mg) in 2,2,2-trifluoroethanol (0·5ml) was irradiated at 254nm in an RPR. After 3h irradiation a new methyl group was visible in the nmr spectrum at 2·59 and a new ethyl group at 2·82 ($CH_2$) and 1·21 ($CH_3$). After 8h irradiation a new methyl group appeared at 2·56 and an ethyl group at 3·23 ($CH_2$) and 1·40 ($CH_3$). Irradiation in excess of 72h produced no significant change in the ratio of ethyl groups; 4-ethyl 1·0; 3-ethyl 1·5; 2-ethyl 1·5. No additional signals other than those of the pyrylium cations were seen in the n.m.r. spectrum.

Irradiation of this salt in water produced the same result as with trifluoroethanol.

2,6-Diethyl-3,4,5-trimethylpyrylium perchlorate

Irradiation of a solution of the perchlorate (20mg) in trifluoroacetic acid (0·5ml) with 254nm light in an RPR produced a new methyl group, characteristic of a 2-methyl group at 2·88 after 2h. A new methyl group also appeared at 2·68.

Attempts to separate the products by fractional crystallisation and reversed phase layer chromatography were unsuccessful.

2-Ethyl-4,6-dimethylpyrylium perchlorate

1. In acetonitrile;

Prolonged irradiation (96h) of a solution of the perchlorate (20mg) in acetonitrile (0·5ml) showed only very slow destruction of starting material. No new signals appeared in the n.m.r. spectrum.

2. In water;

The pH of a solution of the pyrylium salt (1·0g) in water (800ml) was adjusted to 2·0 by addition of 60% aqueous perchloric acid. The solution was degassed with nitrogen and irradiated through a 270nm silver bromide filter solution with a 125W medium pressure mercury arc lamp while being continuously

extracted with petrol. After 48h the irradiation was stopped. The petrol solution was dried over magnesium sulphate and concentrated by evaporation under reduced pressure to yield 200mg of light brown oil. T.l.c. of the oil on silica with 3/1 petrol/ether eluant gave spots at rf 0·16 and rf 0·19. These two spots were separated by column chromatography using silica and 3/1 petrol/ether eluant.

The high rf band gave 45mg of trans-2,4-dimethyl-5-oxohept-2-enal, nmr ($CDCl_3$) 1·05 (t-3H, J=7·0), 1·26 (d-3H, J=8·0), 1·81 (d-3H, J=1·0), 2·48 (q-2H, J=7·0), 3·70 (m-1H, J=8·0, 10·0), 6·43 (m-1H, J=1·0, 10·0), 9·42 (s-1H). The low rf band gave 30mg of trans-4-ethyl-2-methyl-5-oxohept-2-enal, nmr ($CDCl_3$) 0·91 (t-3H, J=8·0), 1·43 (m-2H, J=7·0, 8·0), 1·82 (d-3H, J=1·0), 2·17 (s-3H), 3.55 (m-1H, J=7·0, 10·0), 6·40 (m-1H, J=1·0, 10·0), 9·44 (s-1H).

## 2,6-Dimethyl-4-phenylpyrylium perchlorate

A solution of the perchlorate (1·0g) in dry methanol (800ml) was degassed with nitrogen and irradiated through pyrex with a 450W medium pressure mercury arc lamp for 70h. The methanol was removed under reduced pressure to yield 1·0g of a black oil. T.l.c. of the oil with petrol on silica gave spots at rf 0·3 and 0·5. P.l.c. of the oil under the same conditions gave at rf 0·5 a pale yellow oil having nmr ($CCl_4$) 2·38 (s-3H), 3·80 (s-3H), 6·60 (bs-1H), 6·81 (bs-1H), 6·90 (bs-1H), 7·2-7·5 (m-5H); u.v. (methanol) $\lambda_{max}$ =

253, 293(sh); i.r. ($CCl_4$) 3070(m), 3040(m), 3005(m), 2960(s), 2930(s), 2870(m), 2850(m), 1610(s), 1480(s), 1425(m), 1340(s), 1225(m), 1170(s), 1155(s), 1065(m), 1055(s), 910(s), 865(s), 700(s): m.s. $M^{+\cdot}$ 198(100), 199(17), 166(16), 155(16), 153(15), 152(13), 77(6). A metastable ion at 142·5 was derived by 198 $\longrightarrow$ 168(9), loss of $CH_2O$. This is a common fragmentation for aromatic methyl ethers. These data are consistant for 3-methoxy-2-methyl-4-phenylfulvene.

2,4,6-Trimethylpyrylium perchlorate

1. In acetonitrile;

A solution of the perchlorate (20mg) in dry acetonitrile (0·5ml) was stable to 96h irradiation in an RPR with 254nm light.

2. In methanol;

A solution of the perchlorate (0·9g) in dry methanol (170ml) was degassed and irradiated through a 270nm silver bromide filter solution with a 450W medium pressure mercury arc lamp. After 20h irradiation (90% destruction of starting material) the solution was concentrated to 30ml, ether (150ml) was added and the solution was washed with water (2x250ml). The ethereal solution was dried over magnesium sulphate and concentrated to give a brown oil (900mg). G.l.c. of this oil on a 20% carbowax 20M x 5% triethanolamine column at 130° showed it to consist of more than 15 components. N.m.r. of the oil showed the presence of many methoxy signals.

G.c.m.s. of the first six peaks gave the following results;

| RETENTION TIME (MINS) | 5·0 | 7·0 | 8·2 | 9·8 | 11·8 | 15·3 |
|---|---|---|---|---|---|---|
| $M^{+}$ | 154 | 154 | 168 | 186 | 200 | 200 |
| M(100) | 43 | 43 | 43 | 43 | 43 | 43 |
| | 109(57) | 39(51) | 39(66) | 72(39) | 137(36) | 41(41) |
| | 39(43) | 137(48) | 137(64) | 41(30) | 41(36) | 39(36) |
| | 123(27) | 77(24) | 153(46) | 39(24) | 167(32) | 58(33) |
| | 41(27) | 109(23) | 77(33) | 73(18) | 39(32) | 169(31) |

The peaks at 5·0 and 7·0 min correspond to addition of methoxide ion to the pyrylium cation. The peak at 9·8 min corresponds to the further addition of methanol while that at 8·2 min shows addition of further methanol with loss of water. The peaks at 11·8 and 15·3 min correspond to the addition of methoxide and two methanol molecules, and loss of one water molecule per pyrylium cation.

At low concentration in methanol ($10^{-3}$M), it was observed that the ultra-violet absorptions of the pyrylium nucleus at 230 and 285nm had been replaced by a single absorption at 265·5nm. Treatment of the pyrylium salt (0·22g) with sodium methoxide (0·10g) in dry methanol (100ml) gave, reversibly, a quantitative conversion to 2-methoxy-2,4,6-trimethylpyran, which could be extracted with cyclohexane; nmr ($CCl_4$) 1·40 (s-3H), 1·75 (d-3H, J=1·3), 1·83 (s-3H), 3·03 (s-3H), 4·83 (m-1H), 4·93 (m-1H); i.r. ($CCl_4$) 3020(m), 3000(s), 2950(s), 2920(s), 2870(m), 1672(s), 1610(m), 1450(m), 1370(s), 1315(s),

1165(s), 1135(s), 1090(m), 1050(s), 980(m), 845(m).

Irradiation of the methoxy pyran at $10^{-4}$M in cyclohexane with 254nm light showed its $\lambda_{max}$ at 266nm to decrease in intensity by 40% on irradiation for 10 min. New absorption appeared at long wavelength. On standing for 2h, the 266nm band returned to its original intensity. This cycle was repeatable on the same sample. N.m.r. scale irradiation in cyclohexane showed the two vinyl protons of the pyran to diminish in intensity and be replaced by two signals at 5·45 and 4·15. A new methoxy signal appeared at 3·35. The u.v. spectrum showed $\lambda_{max}$ = 270nm and a long wavelength absorption at 420nm. The infra-red spectrum showed a new band at 1685$cm^{-1}$, typical of $\alpha\beta$ -unsaturated ketones.

These data are consistant with the pyran undergoing a photochemical ring-opening reaction to give 6-methoxy-4-methylhept-3,5-diene-2-one.

3. In water;

Two solutions of the pyrylium salt (2·4g) in water were prepared. The pH of one solution was adjusted to 2·0 with perchloric acid and the pH of the other to 9·8 with aqueous sodium hydroxide solution. Both solutions had their final volumes adjusted to 160ml and were irradiated through a 270nm silver bromide filter solution with a 450W medium pressure mercury arc lamp for 69h. The solutions were then extracted with ether, these were dried over magnesium sulphate and concentrated under reduced pressure. Both of the resulting oils were treated with methanolic 2,4-dinitrophenylhydrazine solution (25ml). The precipitates were filtered off and

subjected to t.l.c. with 3/1 petrol/ether on silica. Both gave spots at rf 0·28 due to the bis-2,4-dinitrophenyl hydrazone of ring-opened starting material, but only the pH 2 solution gave a spot at rf 0·18 corresponding to the bis-2,4-dinitrophenylhydrazone of 2,4-dimethyl-5-oxohex-2-enal, nmr ($CDCl_3$) 1·42 (d-3H, J=8·0), 2·10 (s-6H), 3·78 (m-1H, J=8·0, 10·0), 6·00 (d-1H, J=10·0), 7·83 (s-1H), 7·9-9·1 (m-6H), 11·0 (bs-2H).

3-5. In trifluoroethanol, propylene carbonate and N-methyl formamide;

A solution of the pyrylium salt (15mg) in either of the three solvents (0·5ml) was stable to prolonged irradiation.

6. In the presence of biacetyl;

Irradiation of the pyrylium salt ($4\times10^{-2}$M) in the presence of biacetyl ($4\times10^{-2}$M and $4\times10^{-3}$M) in aqueous solution with a 450W medium pressure mercury arc lamp for 23h produced identical results to irradiation of the pyrylium salt in the absence of biacetyl under the same conditions. The solutions were analysed by g.c. using a 10% carbowax 20M column at 125°. The keto-aldehyde product had a retention time of 9·0 min.

2,6-Dimethyl-4-tert-butylpyrylium perchlorate.

1-4. In acetonitrile, trifluoroethanol, propylene carbonate and N-methylformamide;

A solution of the perchlorate (20mg) in either of these solvents (0·5ml) was stable to prolonged irradiation in an

RPR with 254nm light.

5. In water;

The pH of aqueous solutions of the pyrylium salt (1%) were adjusted with aqueous sodium hydroxide or perchloric acie to 1·8, 2·1, 3·8, 5·1 and 6·6. These solutions were irradiated under identical conditions with a 450W medium pressure mercury arc lamp through quartz for 48h. The relative yields of 1,1-diacetonyl-2,2-dimethylcyclopropane were determined by g.c. analysis on a 5% silicone oil column at 135° (retention time 6·0 min) with ethylene glycol (retention time 4·9 min) as internal standard;

| Solution pH | 1·8 | 2·1 | 3·8 | 5·1 | 6·6 |
|---|---|---|---|---|---|
| Relative yield | 0·9 | 1·5 | 3·0 | 48 | 196 |

In a second experiment, a solution of the pyrylium salt (2·5g) in water (900ml) was irradiated through a 270nm silver bromide solution with a 125W medium pressure mercury arc lamp while being continuously extracted with petrol. The initial pH of the aqueous solution was adjusted to pH 1·5 with perchloric acid. After 5h irradiation the petrol was removed under reduced pressure to yield 30mg of oil consisting exclusively of the diol, the two triols and the cyclopropane in the ratio 3:2:2:1 respectively as determined by n.m.r. spectroscopy. The addition of concentrated sulphuric acid to this sample converted the two triols quantitatively to the diol.

This pyrylium cation was very sensitive to pH. Below pH 1·5 it was essentially all in the form of the pyrylium

cation with $\lambda_{max}$ = 285nm. Above pH 9·0 it was all in the form of the ring-opened diketone, with $\lambda_{max}$ = 240nm. Above pH 12·5 it was present as the enolate with $\lambda_{max}$ = 290nm.

Irradiation of cis-4-tert-butylhept-2-ene-2,6-dione.

A solution of the diketone (2·0g) in benzene (150ml) was degassed with nitrogen and irradiated through pyrex with a 450W medium pressure mercury arc lamp. The reaction was monitored by n.m.r. spectroscopy and showed rapid cis-trans isomerisation to take place, giving a ratio of 1 to 1·2 respectively. The cyclopropyl diketone was slowly formed until after 300h, all of the starting material had been destroyed. The benzene was removed under reduced pressure and the oily residue was passed down a short silica column with ether eluant to remove polymeric material. After drying over magnesium sulphate, the ether was removed under reduced pressure to yield 1·7g of a colourless oil. Distillation at 50-55°/0·2mm Hg afforded 1·2g of 1,1-diacetonyl-2,2-dimethyl cyclopropane, nmr ($CDCl_3$) 0·29 (s-2H), 1·06 (s-6H), 2·00 (s-6H), 2·51 (s-4H); u.v. (ether) no absorption; i.r. ($CCl_4$) 3060(m), 2990(s), 2980(s), 2920(s), 2890(s), 1730(s), 1450(s), 1420(s), 1360(s), 1290(m), 1250(m), 1215(m), 1170(s), 1120(m), 1040(m), 960(m), 935(m), 865(m); m.s. $M^+$ 182(0·7), 43(100), 39(15), 41(14), 125(10), 81(4); Analysis, calculated C 72·49, H 9·95; found, C 72·59, H 10·01.

2,6-Dimethyl-4-ethylpyrylium perchlorate

A solution of the perchlorate (20mg) in acetonitrile (0·5ml) was stable to prolonged irradiation with 254nm light in an RPR.

2,3,4,6-Tetramethylpyrylium perchlorate

1. In acetonitrile;

A solution of the perchlorate (20mg) in acetonitrile (0·5ml) was irradiated in an RPR with 254nm light. The salt was slowly destroyed over 48h, but no new signals appeared in the nmr spectrum.

2. In water;

A solution of the perchlorate (20mg) in water (0·5ml) was irradiated in an RPR with 254nm light. After 8h, a new signal appeared in the aromatic region at 8·46, characteristic of the 4-position in the pyrylium cation. A new methyl group also appeared at 2·41. The ratio of the aromatic signals at this time was 10 to 1, 7·72 to 8·46. Further irradiation did not improve this ratio. It was not possible to separate the salts by layer chromatography or fractional crystallisation.

Addition of authentic 2,3,5,6-tetramethylpyrylium perchlorate to the n.m.r. sample caused the new signals to increase in intensity; no new signals appeared.

2-Ethyl-4,5,6-trimethylpyrylium perchlorate

1. In acetonitrile;

A solution of the perchlorate (20mg) in acetonitrile (0·5ml) was irradiated in an RPR with 254nm light. The salt was slowly destroyed over 72h, but no new signals appeared in the n.m.r. spectrum.

2. In water;

A solution of the perchlorate (20mg) in water (0·5ml) was irradiated in an RPR with 254nm light. After 8h, a new signal was visible at 8·40 in the aromatic region, characteris of the 4-position of a pyrylium cation. A new ethyl group also appeared at 2·81, characteristic of a 3-ethyl group. Further irradiation did not improve the ratio of 10:1 starting material to product. The n.m.r. data is consistant with the formation of 3-ethyl-2,5,6-trimethylpyrylium perchlorate.

2-Ethyl-4,6-dimethyl[5-$^{2}$H]pyrylium perchlorate

A solution of the perchlorate (150mg) in water (100ml) was degassed with nitrogen and irradiated through a 270nm silver bromide filter solution with a 450W medium pressure mercury arc lamp for 18h. The solution was extracted with ether (2x50ml), the ethereal solution was dried over magnesium sulphate and the ether was removed under reduced pressure. The residue was shown by n.m.r. spectroscopy to contain two aldehydes, but the lower field aldehyde proton was largely

absent compared to the near 1:1 ratio of aldehyde signals obtained from irradiation of the non-deuteriated title compound in water. P.l.c. on silica with 3/1 petrol/ether gave at rf 0·19, trans-2,4-dimethyl-5-oxo[3-$^2$H]hept-2-enal, nmr ($CDCl_3$) 1·05 (t-3H, J=7·0), 1·26 (d-3H, J=8·0), 1·81 (s-3H), 2·48 (q-2H, J=7·0), 3·70 (q-1H, J=8·0), 9·42 (s-1H); a small amount of the non-deuteriated compound was present and gave rise to additional multiplets at 3·70 and 6·43

Irradiation of pyrylium salts in furan

Two general procedures were used. N.m.r. scale irradiations were performed on solutions of the pyrylium salts (10mg) in 0·5ml of 50% furan in acetonitrile. Other irradiations were performed by dissolving the pyrylium salt (25mg) in 50% furan in acetonitrile (25ml), irradiating, and then working up by addition of ether and water, separation of the ether layer, drying, concentrating, and then investigating the residues by n.m.r. spectroscopy. All of the irradiations were performed in an RPR with 254nm light.

Both 2,4,6-trimethylpyrylium perchlorate and 2,6-dimethyl-4-tert-butylpyrylium perchlorate were photostable under these conditions, no adducts were formed.

Both 2,3,5,6-tetramethylpyrylium perchlorate and 2,3,5,6-tetramethyl-4-ethylpyrylium perchlorate showed their normal phototransposition reactions, no adducts were formed.

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PHOTOCHEMISTRY OF SOME HETEROCYCLIC COMPOUNDS

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The phototransposition reactions of thiophene-carbonitriles were shown to occur via the intermediate formation and isomerisation of 5-thiabicyclo[2·1·0]pent-2-enes. Thus, irradiation of thiophene-3-carbonitrile in cyclohexane gave 5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile as the primary photochemical product. Further irradiation produced thiophene-2-carbonitrile. The reaction was reversible. Addition of furan to 5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile yielded a mixture of exo and endo-10,4-oxa thiatetracyclo[5·2·1·$0^{2,6}$· $0^{3,5}$]dec-8-ene-2-carbonitrile. These two adducts were similarly formed upon irradiation of either thiophene-2 or 3-carbonitrile in furan.

Evidence for the thermal interconversion of 5-thiabicyclo [2·1·0]pent-2-enes was provided by irradiation of 2-methyl thiophene-3-carbonitrile in tetrahydrofuran at -68°. This produced 1-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile which, on warming to -40°, isomerised to 3-methyl-5-thiabicyclo [2·1·0]pent-2-ene-2-carbonitrile. This could be isolated, and, though apparently pure by n.m.r. spectroscopy, was shown to be in thermal equilibrium with the 1-methyl isomer by its reaction with Diels-Alder dienes. Thus, with furan it

produced both exo-3 and 6-methyl-10,4-oxathiatetracyclo [5·2·1·$0^{2,6}$·$0^{3,5}$]dec-8-ene-2-carbonitrile, while with the much more reactive diene, 2,5-diphenylisobenzofuran, only the corresponding 6-methyl adduct was formed. This illustrated that the rate of the sulphur-walk step of 3-methyl-5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile was fast compared to the rate of addition of furan, but slow compared to the rate of addition of 2,5-diphenylisobenzofuran.

Low temperature n.m.r. experiments also revealed the photochemical formation of 5-thiabicyclo[2·1·0]pent-2-ene-1-carbonitriles from the corresponding 2-carbonitrile isomers.

5-Thiabicyclo[2·1·0]pent-2-enes were shown to rearomatise both photochemically and thermally to give thiophenes.

Irradiation of thiophene-2,3-dicarbonitrile in furan produced the novel furan dimer, exo-7,10-dioxatricyclo[4·2·$1^{2,5}$ $0^{1,6}$]dec-3,8-diene by a photochemical electron-transfer mechanism.

Irradiation of various alkyl substituted pyrylium cations in acetonitrile was shown to lead to phototransposition only when alkyl groups were present in both the 3 and 5-positions of the cation. In one case, two isomeric oxazolines were also produced.

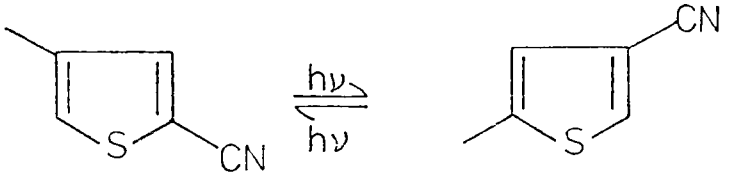
1,1-Diacetonyl-2,2-dimethylcyclopropane appeared not to be formed by irradiation of 2,6-dimethyl-4-t-butylpyrylium perchlorate in water, but rather from its pseudobase, 4-t-butylhept-3-en-2,6-dione.

## ADDITIONAL LONGER ABSTRACT

The Introduction to this Thesis described the diverse and intriguing photoisomerisation reactions of five and six-membered aromatic heterocyclic compounds. Thiophene phototransposition reactions in particular were shown to be extremely complex, since complete scrambling of substituents around the thiophene ring is often observed upon irradiation of a substituted thiophene with ultra-violet light.[1]

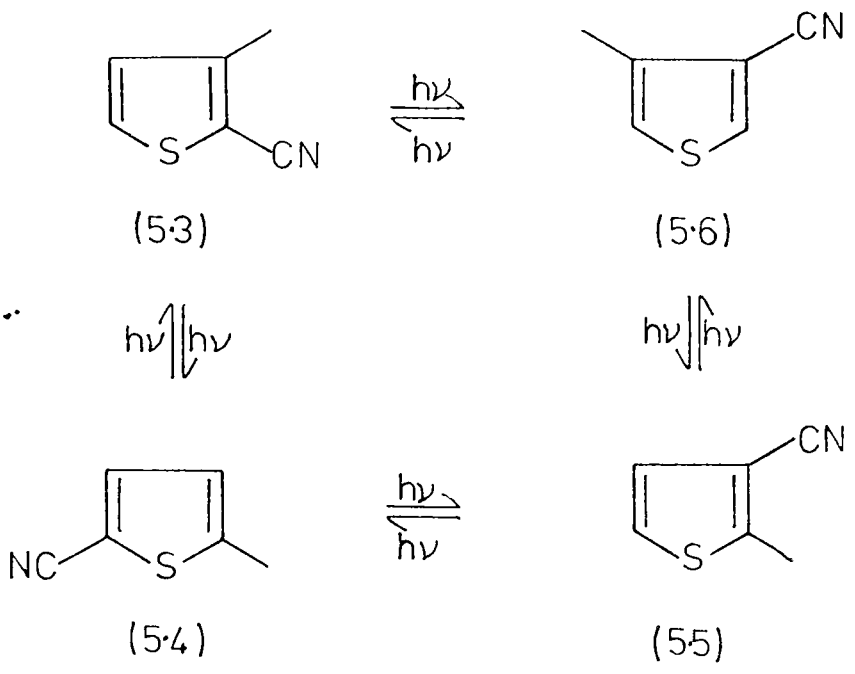
In order to elucidate a mechanistic pathway that could account for the phototransposition reactions of thiophenes, a number of substituted thiophenes were synthesised and then irradiated under various conditions.

Thus, irradiation of thiophene-2-carbonitrile in cyclohexane produced thiophene-3-carbonitrile. The reaction was shown to be reversible, as irradiation of the 3-carbonitrile gave the 2-carbonitrile. The six isomeric methylthiophene-carbonitriles were synthesised and irradiated. Analysis of the transposition products of each isomer showed them to fall into two families. Thus, in Scheme 5·1, irradiation of 4-methylthiophene-2-carbonitrile gave, reversibly, 5-methylthiophene-3-carbonitrile. The other four nitriles, Scheme 5·2, were interconvertable and formed a tetrad.



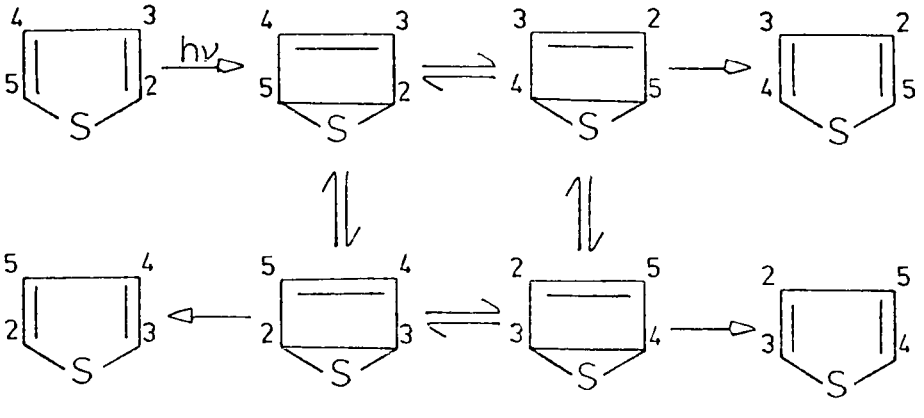

(5·1) (5·2)

Scheme 5·1



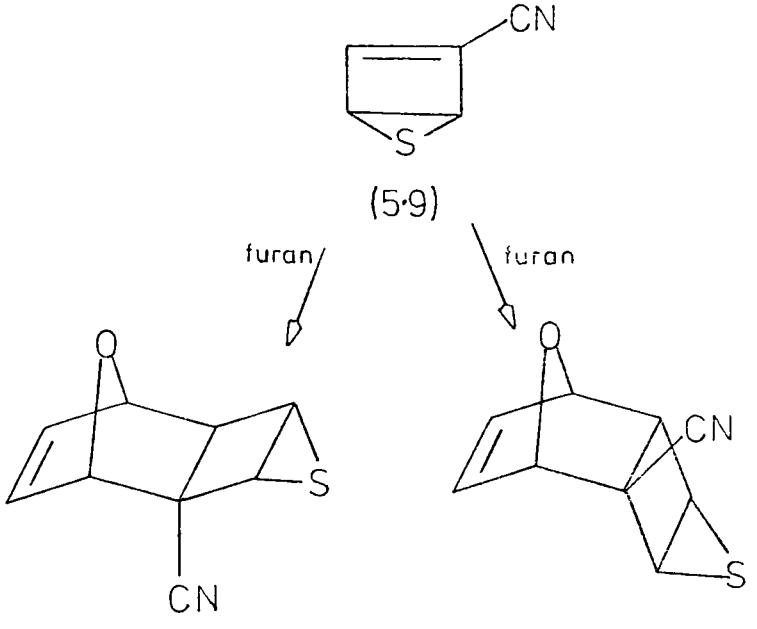

Scheme 5·2

These photoisomerisations are accounted for by the mechanistic Scheme 5·3. Here, excitation of the thiophene chromophore gives a 2,5-bonded species which is able to undergo one or more 'sulphur-walk' steps to produce isomeric 5-thiabicyclo[2·1·0]pent-2-enes. Subsequent rearomatisation leads to the formation of the rearranged thiophenes.




Scheme 5·3

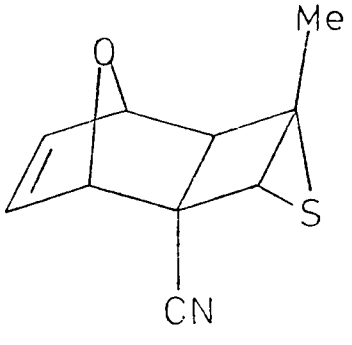
Support for the intermediacy of 2,5-bonded bicyclic compounds was obtained from irradiation of the nitriles in furan. For example, irradiation of either thiophene-2-carbonitrile or thiophene-3-carbonitrile in furan solvent produced a mixture of the exo and endo-furan adducts, (5·7) and (5·8). These are most easily derivable in terms of exo or endo addition of furan to 5-thiabicyclo[2·1·0]pent-2-ene-2-carbonitrile (5·9), Scheme 5·4, in a 4+2 Diels-Alder manner.



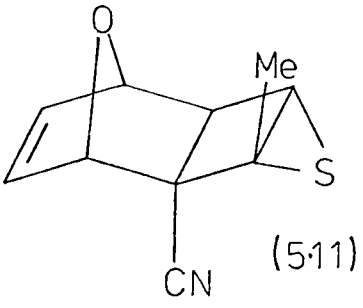

(5·9)

(5·7) (5·8)

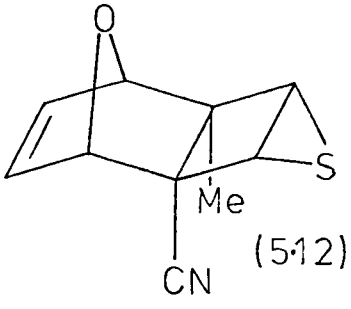
Scheme 5·4




(5·10)



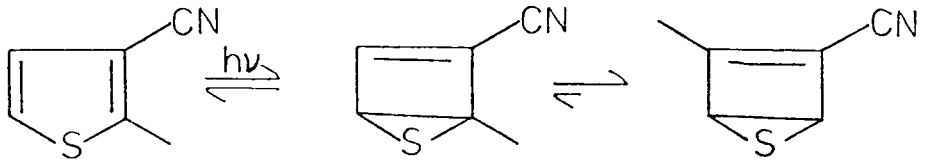

(5·11)




(5·12)

In a similar fashion, irradiation of either of the two nitriles of Scheme 5·1 in furan provided the analogous Diels-Alder adduct (5·10), while irradiation of any of the four nitriles of Scheme 5·2 provided a 1 to 1 ratio of adducts (5·11) and (5·12). Small amounts of the corresponding endo-adducts were also observed.

The proposed intermediate bicyclic compounds were observed by n.m.r. spectroscopy in some cases. Thus, 5-thiabicyclo [2·1·0]pent-2-ene-2-carbonitrile (5·9) was formed in 2% yield from irradiation of thiophene-3-carbonitrile in cyclohexane. Irradiation of 2-methylthiophene-3-carbonitrile in tetrahydro furan at -68° produced a high yield of the bicyclic compound

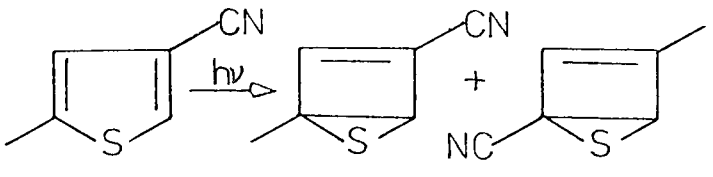



(5·5) (5·13) (5·14)

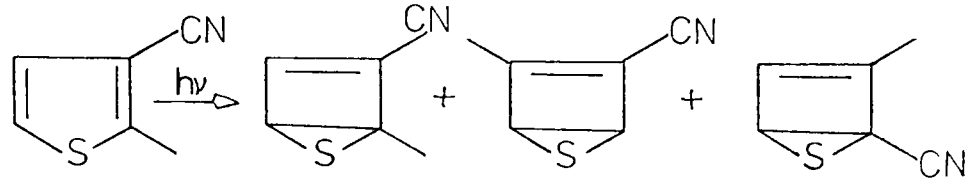
(5·13). On warming to -40°, this underwent a thermal 'sulphur-walk' step to give the isomeric bicyclic compound (5·14). This isomer was stable at room temperature and could be isolated and purified.

Although apparently pure by n.m.r. spectroscopy, the bicyclic compound (5·14) was shown to be in thermal equilibrium with its sulphur-walked isomer (5·13) at room temperature from its reactions with various Diels-Alder dienes. For example, addition of furan to (5·14) produced the two exo-adducts (5·11) and (5·12) in a ratio of 1 to 1, while treatment with the much more reactive diene, 2,5-diphenylisobenzofuran, produced only the adduct corresponding to (5·12). This demonstrated that the rate of addition of 2,5-diphenylisobenzofuran to (5·14) was fast compared to the rate of isomerisation of (5·14) to (5·13), but that the rate of addition of furan was slower.

Evidence for the intermediacy of bicyclic compounds with bridgehead cyano groups in the phototransposition reactions of thiophene-carbonitriles was also obtained from low temperature n.m.r. experiments. Thus, following irradiation of (5·2) and (5·5) at -68°, the bicyclic compounds (5·16) and (5·17) respectively were observed by n.m.r. spectroscopy.




(5·2) (5·15) (5·16)




(5·5) (5·13) (5·14) (5·17)

On warming, these rapidly isomerised to the more stable bicyclic compounds with the conjugated cyano groups.

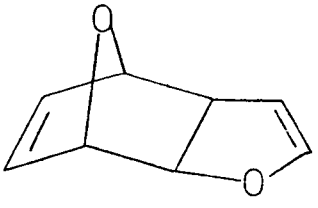
The thermal interconversion of 5-thiabicyclo[2·1·0] pentenes was further demonstrated in pyrolysis experiments. For example, the bicyclic compound (5·14) produced the four nitriles of Scheme 5·2 upon pyrolysis at 170°, showing that rearomatisation becomes less favourable with respect to sulphur-walking at high temperatures. Similar results were obtained from pyrolysis of the furan adducts (5·7), (5·11), and (5·12). Here, the intermediate bicyclic compounds were generated through retro Diels-Alder reactions of the adducts.

Rearomatisation of 5-thiabicyclo[2·1·0]pent-2-enes was also shown to occur photochemically since irradiation of the bicyclic compound (5·14) produced mainly 4-methylthiophene-3-carbonitrile (5·6), and smaller amounts of (5·5), (5·4) and (5·3).

The photoisomerisation reactions of thiophene-carbonitriles were shown to be excited singlet state reactions by sensitisation experiments with benzophenone and acetophenone, and quenching experiments with piperylene.

The photochemistry of some thiophene-dicarbonitriles was also investigated. Thus, irradiation of 5-methylthiophene-2,4-dicarbonitrile in acetonitrile gave the isomeric 3-methyl thiophene-2,4-dicarbonitrile, by way of 5-thiabicyclo[2·1·0] pent-2-ene intermediates.

Irradiation of thiophene-2,3-dicarbonitrile in furan produced the novel furan dimer, exo-7,10-dioxatricyclo[4·2·1$^{2,5}$ 0$^{1,6}$]dec-3,8-diene (5·18).

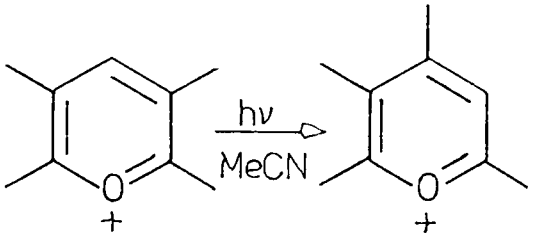


(5·18)

This was shown to be formed via an electron-transfer reaction from furan to photoexcited thiophene-2,3-dicarbonitrile to give furan radical cation.· Subsequent addition of furan in a 4+2 manner and back electron-transfer gives (5·18). Other easily reducible aromatic compounds such as di- and tetracyano benzenes were also shown to effect this dimerisation.

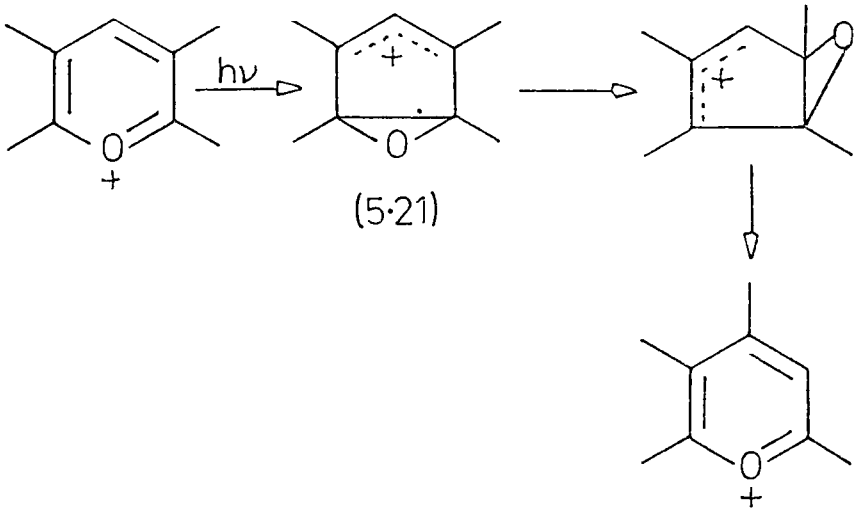
Several other thiophenes, such as carbaldoximes and acrylonitriles, were shown to undergo photochemical cis - trans isomerisation reactions, but not to phototranspose.

The photochemistry of some alkyl substituted pyrylium cations was investigated. Phototransposition reactions giving rise to isomeric pyrylium cations were shown to take place in non-aqueous solvents only when substituents were present in both the 3 and 5-positions, e.g. (5·19) to (5·20).




(5·19) (5·20)

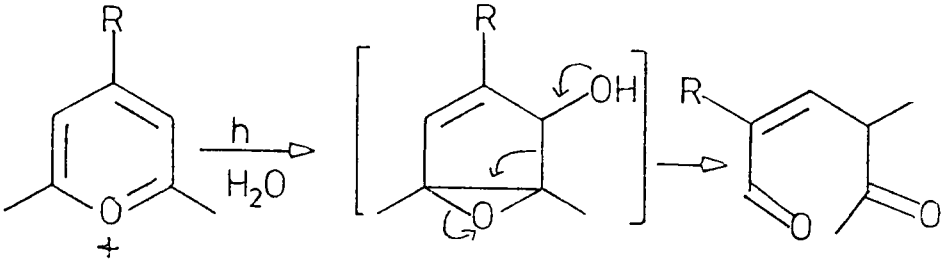
All of the phototranspositions observed in this way were consistant with the mechanistic Scheme 5·5 involving initial excitation to give a 2,6-bonded oxabicyclohexenyl carbonium ion (5·21) which can then undergo one or more thermal oxygen-walk steps to give, subsequent to rearomatisation, the transposed pyrylium cation.




(5·21)

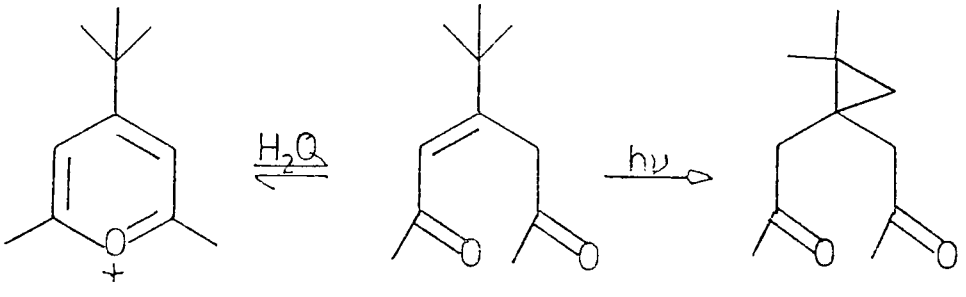
Scheme 5·5

The lack of reactivity of 2,4,6-trialkyl pyrylium cations in solvents such as acetonitrile suggested that their photohydrolysis reactions, reported previously,[2] to give ring-opened keto-aldehydes do not proceed <u>via</u> hydrolysis of intermediate transposed pyrylium cations, but rather by way of fragmentation of a solvent adduct, Scheme 5·6.




Scheme 5·6

The novel 1,1-diacetonyl-2,2-dimethylcyclopropane (5·24) described in the literature[3] as deriving from photolysis of the pyrylium cation (5·22) in water was shown to be formed, not from the cation, but from an intramolecular hydrogen abstraction reaction of its ring-opened pseudobase. (5·23).




(5·22) (5·23) (5·24)

References

1. a) H. Wynberg, R.M. Kellogg, H. Van Driel and G.E. Beekhuis, J. Am. Chem. Soc., 1966, 88, 5047;

b) ibid., 1967, 89, 3498.

2. a) J.A. Barltrop, K. Dawes, A.C. Day and A.J.H. Summers, J.C.S. Chem. Comm., 1972, 1240;

b) J.A. Barltrop, K. Dawes, A.C. Day, S.J. Nuttal and A.J.H. Summers, ibid., 1973, 410.

3. JA. Barltrop, K. Dawes, A.C. Day and A.J.H. Summers, J. Am. Chem. Soc., 1973, 95, 2406.