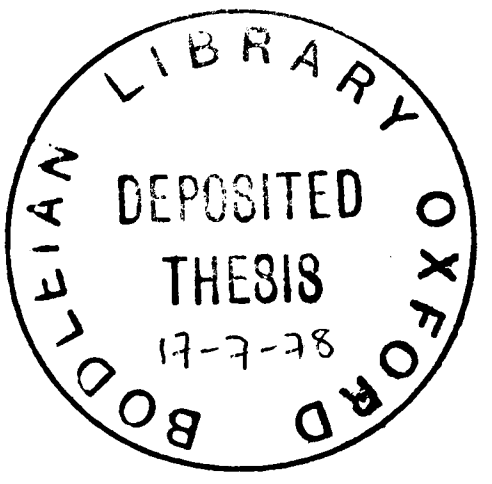
ORGANIC PHOTOCHEMISTRY

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

by

Michael Thompson.



Brasenose College
Trinity Term, 1978.

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ABSTRACT

Organic Photochemistry

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Doctor of Philosophy, Trinity Term 1978.

The photochemistry of a number of aromatic systems has been studied:-

(i) Irradiation of 1, 3, 5-tri-t-butylbenzene in neutral methanol yielded 4-methoxy-2, 4, 6-exo -tri-t-butylbicyclo [3. 1. 0] hex-2-ene, together with a previously unreported compound, tentatively identified as a stereoisomer of 4-methoxy-2, 4, 6-exo -tri-t-butylbicyclo [3. 1. 0] hex-2-ene.

(ii) Irradiation of 1, 3, 5-tri-t-butylbenzene in acidic methanol yielded 1, 2, 4-tri-t-butylbenzene and 1, 2, 5-tri-t-butyl-Dewarbenzene only, as primary and secondary photoproducts respectively. The primary rearrangement process is considered in detail and is shown to be intramolecular by ^{13}C-labelling techniques; a mechanism involving the protonation of a benzvalene is proposed.

(iii) The photorearrangement in the gas phase of the six dimethylpyridine isomers has also been investigated. It is shown that the six isomers may be divided into two groups of three, 2, 5-, 2, 4- and 3, 5-dimethylpyridine and 2, 6-, 2, 3-, and 3, 4-dimethylpyridine. Within each group, photolysis of one isomer leads to the formation of the other two isomers as major products. The rearrangement is shown to be intramolecular and a mechanism is proposed in which the nitrogen atom effectively inserts itself between any two carbon atoms in the aromatic nucleus.

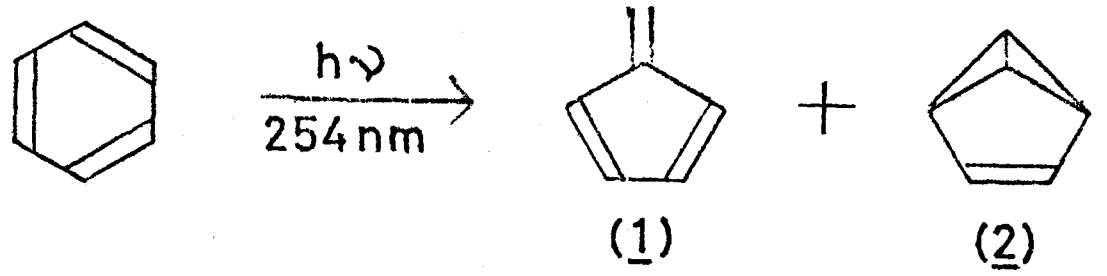
(iv) The photochemistry of the six N-methyl-dimethylpyridinium chlorides is also considered. Preliminary data suggests that photorearrangement of these compounds may occur by a mechanism analogous to that for the dimethylpyridines.

CONTENTS

CHAPTER I.

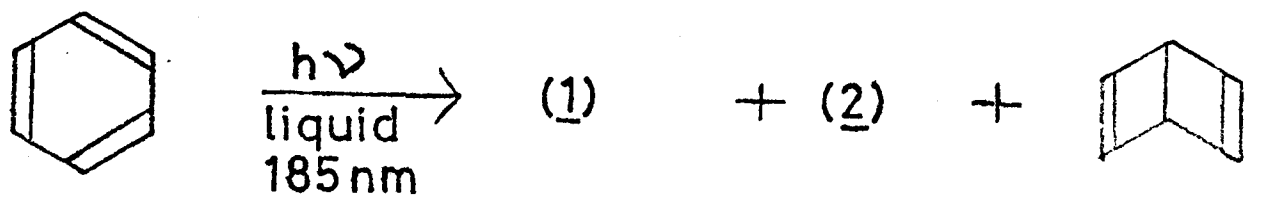
AN INTRODUCTION TO AROMATIC PHOTOTRANSPOSITION REACTIONS.

The photochemistry of benzene and related aromatic compounds has been extensively studied since the first observation that benzene was photolabile.[1] Studies have been carried out in both liquid and vapour phases, and at different excitation wavelengths. Irradiation of benzene as a vapour, as a neat liquid or in alkane solution[2-4] at 254nm yields a mixture of fulvene (1) and benzvalene (tricyclo-[3.1.0.0^{2,6}] hex-3-ene) (2), the yield of benzvalene and fulvene increasing with temperature[3-5] and with decreasing wavelength of excitation.[6]



(1) (2)

Irradiation in the vacuum U.V. range (165-200nm) of liquid benzene produces both (1) and (2) together with a third valence isomer, Dewar benzene (bicyclo [2.2.0] hexa-2,5- diene) (3), the product ratio being 2:5:1,[7]

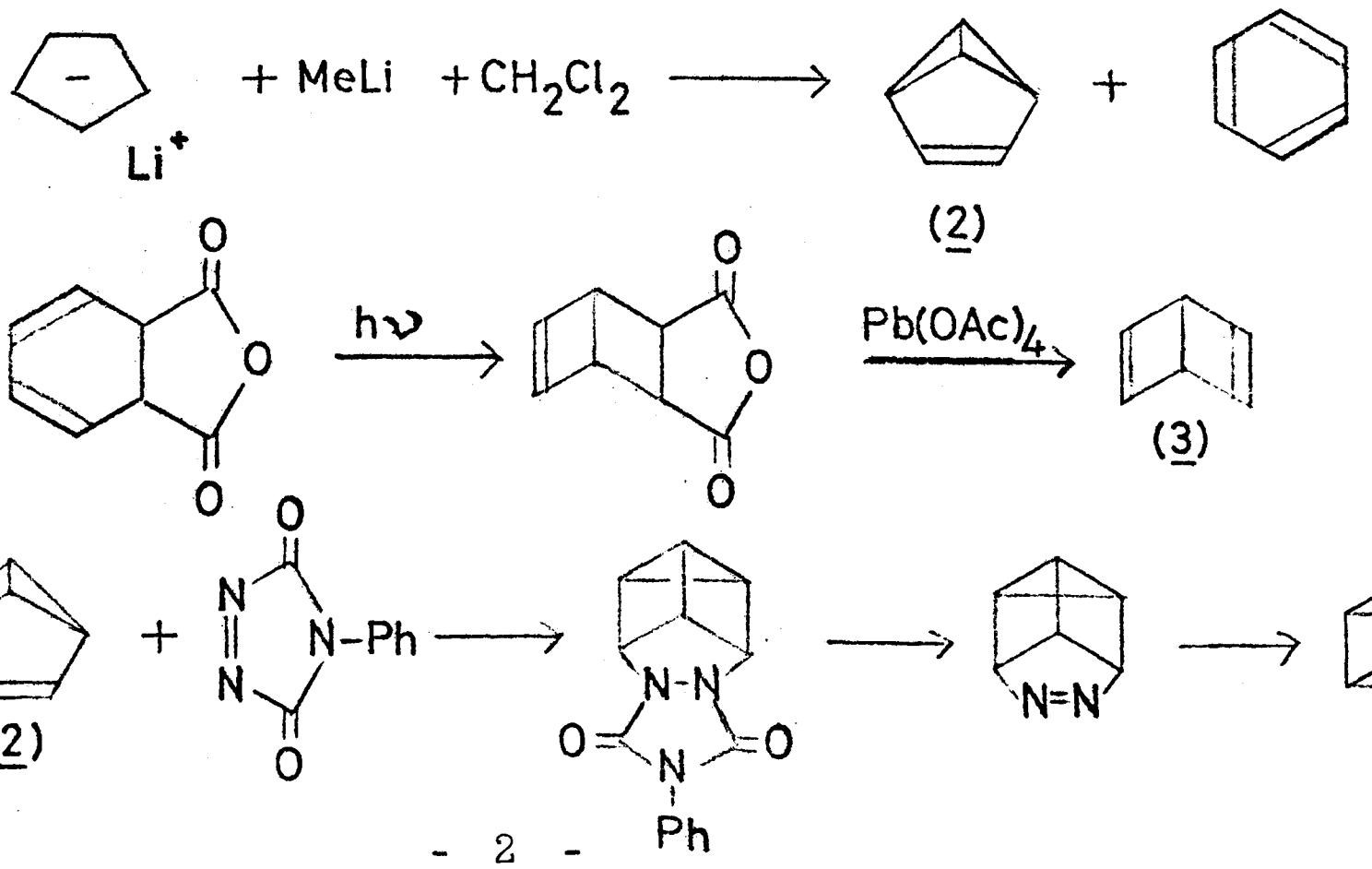


2 : 5 : 1

In the vapour phase, 185nm irradiation gives fulvene and hexa-1,3-dien-5-yne[8-10] as products. These results have been rationalised[6] by suggesting that, at 185nm, the isomers (2) and (3) are initially formed in both vapour and liquid phases; however, in the gas phase they are formed in a vibrationally 'hot' state and,

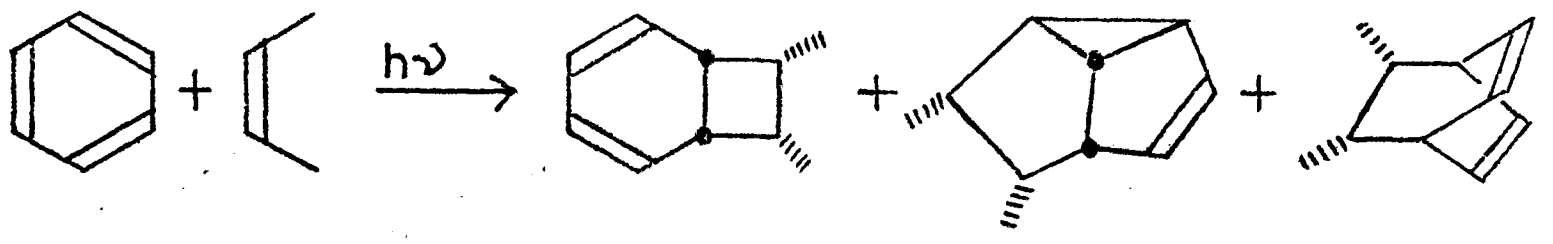
therefore, undergo further reaction thermally. In the liquid phase, excess vibrational energy is lost by collision and thermal equilibrium is rapidly attained. The production of the Dewar isomer at 185nm in the liquid phase has been shown to arise from the S_2 state of benzene by selective excitation within the $S_0 \rightarrow S_2$ band [11]; the temperature dependence [3, 4, 6] of benzvalene formation at 254nm indicates that it is produced from an upper vibrational level of the S_1 state of benzene [5, 6], consistent with the observation that the yield of benzvalene increases with decreasing excitation wavelength within the $S_0 \rightarrow S_1$ band as successively higher vibrational levels are populated. [5] Further evidence in favour of this mechanism comes from a recent study of the effects of xenon on the yields of fluorescence and rearrangement of benzene in oxygen-free cyclohexane. [12] It was found that while xenon reduced the fluorescence yield by a factor of 2.4, the benzvalene yield was not affected. The implication is that xenon quenches the lowest vibrational level of S_1 exclusively, so that photochemistry occurring from upper vibrational levels is unchanged.

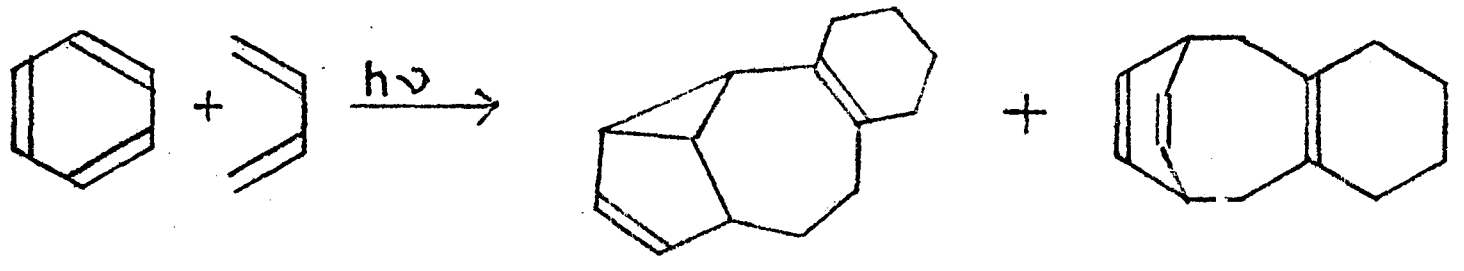
A fourth valence isomer, prismane (4), has not been observed in the photochemistry of benzene itself, although it has been synthesised [13], as have benzvalene [14] and Dewar benzene [15, 16], by alternative routes:-



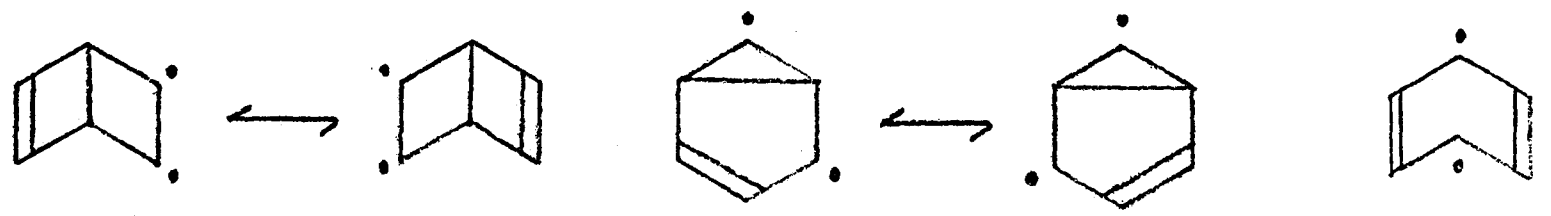
The availability of benzene valence isomers has greatly extended the understanding of benzene photochemistry. (vide infra.).

The photochemistry of benzene is not limited to the formation of valence isomers. It has been found to undergo a very large number of photoaddition reactions with various olefins [17-23] to give 1,2 -, 1,3 - and 1,4 - adducts, examples of which are indicated below:-[19,23]





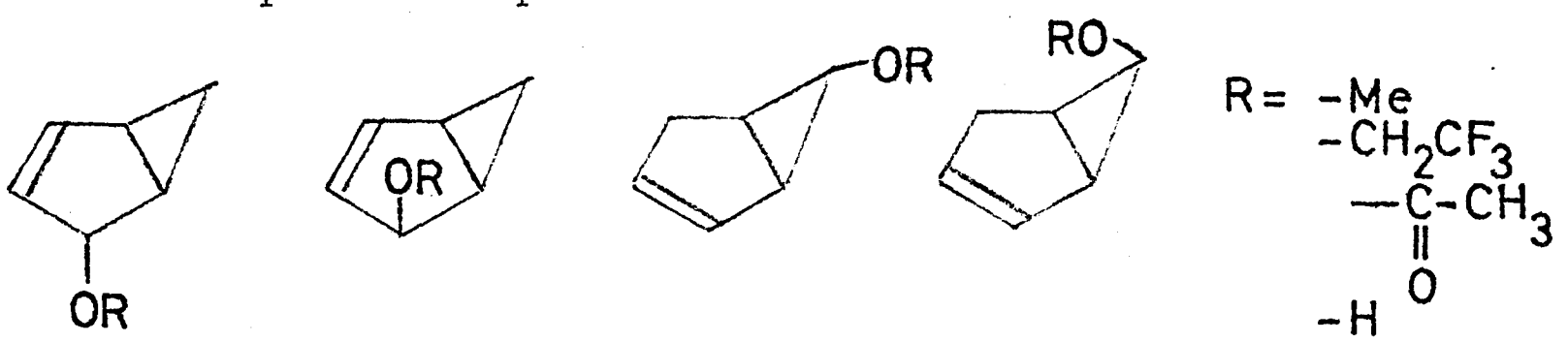
The photochemistry has been rationalised in terms of three biradicals.[24] The pre-Dewar biradical (5) is the precursor of 1,2 - cycloadducts, the prevalene biradical (6) of 1,3 -cycloadducts and the alternative pre-Dewar biradical (7) of 1,4 - cycloadducts.



(5) (6) (7)

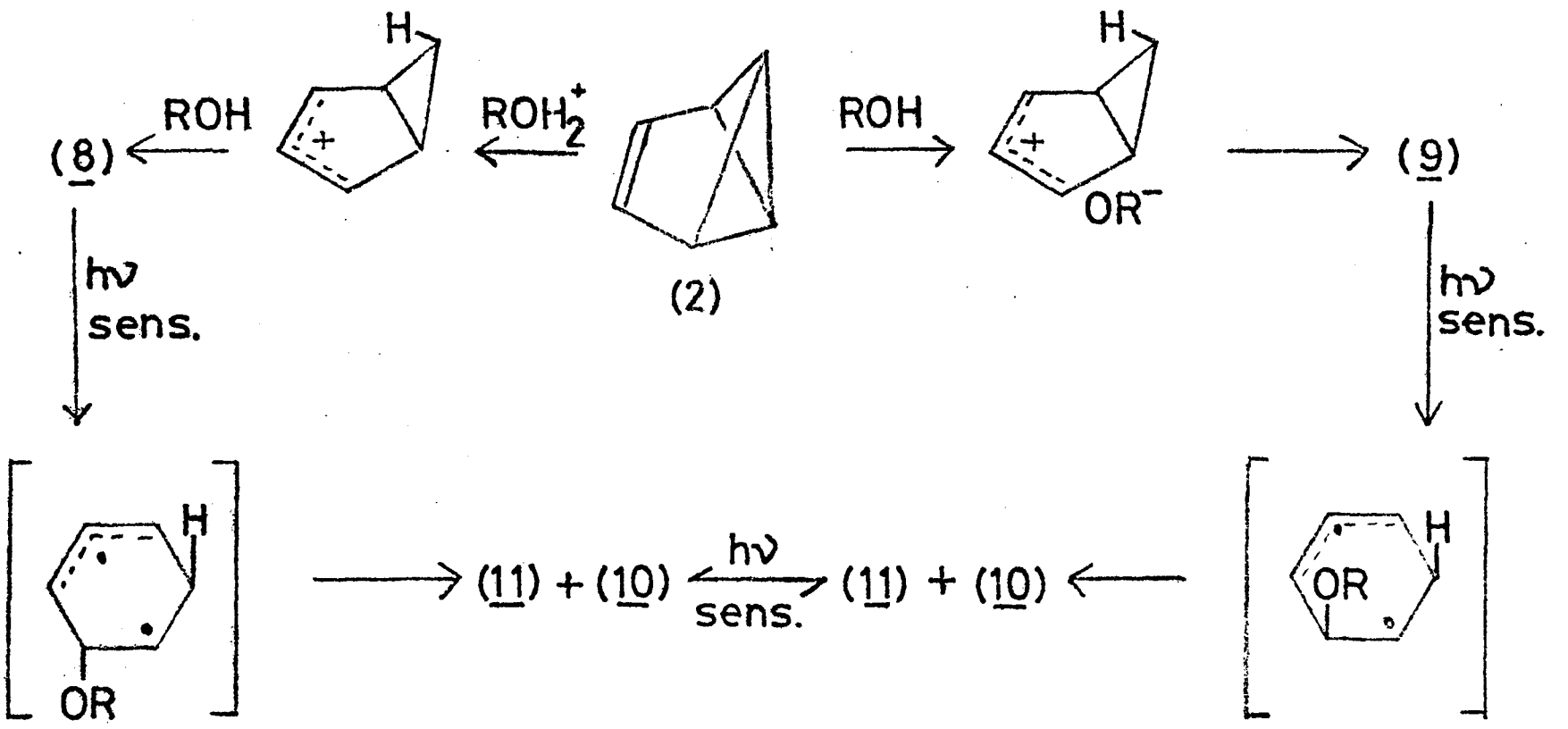
It is readily apparent that such species may lead to valence isomer formation. An analysis in terms of orbital symmetry [5] shows that (6) correlates with the S_1 state of benzene and (7) with the S_2 state, fully consistent with the experimental data that benzvalene arises from S_1 and Dewar benzene from S_2.

Other species can photoadd to benzene; thus acidified methanol, trifluoroethanol, acetic acid and water (as aqueous phosphoric acid) each give all the bicyclo [3. 1. 0.] hexenyl derivatives (8-11) [25] contrary to some earlier published experimental data. [26-29]

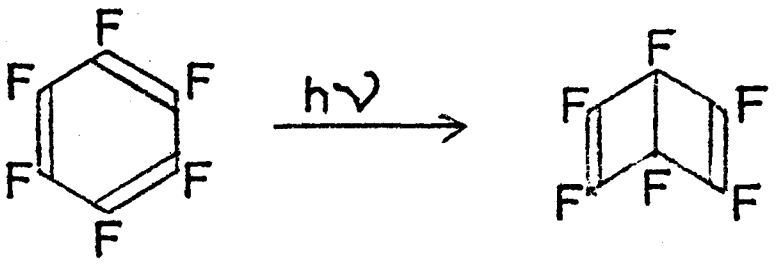


(8) (9) (10) (11)

Evidence that the adducts arise from benzvalene and not the prevalene radicals comes from the observations that acidified methanol readily adds to benzvalene [3, 25] and that the photochemical yields of methanol adduct and benzvalene in the absence of methanol are equal. [28, 29]
In fact, (8) and (9) are the first-formed solvolysis products from benzvalene, while (10) and (11) are formed by sensitised vinylcyclopropane rearrangements of (8) and (9).

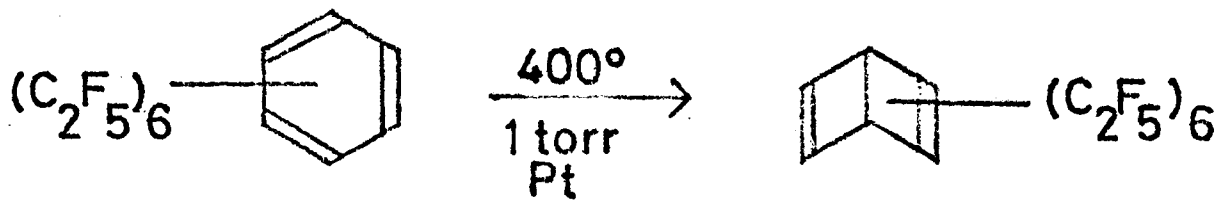


Substituted benzenes also form valence isomers in general. Thus hexafluorobenzene (12) on photolysis in the gas phase yields hexafluorodewar benzene (13) [30, 31].



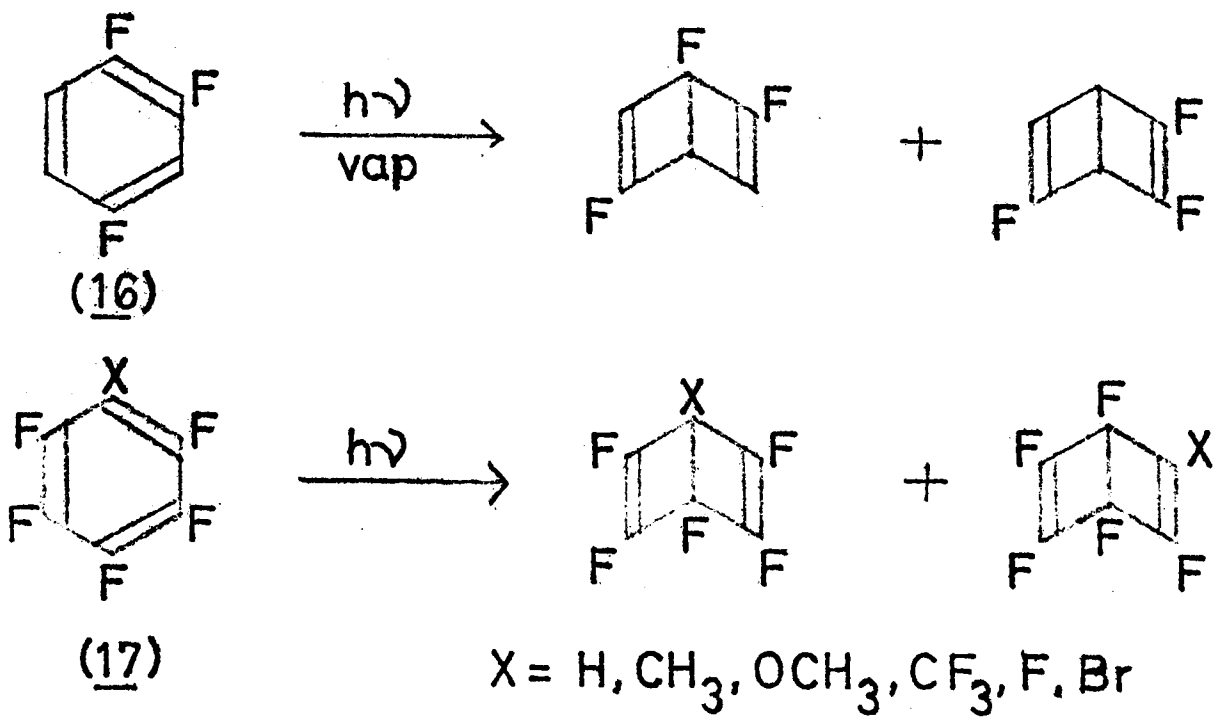
(12) (13)

Hexakis (trifluoromethyl) benzene yields the corresponding fully-fluorinated hexamethyldewarbenzene, , benzvalene and prismane [32-34], although there is disagreement on the relative yields of products; hexakis (pentafluoroethyl) benzene (14) yields Dewar and prismane isomers only, the benzvalene isomer formation, presumably, being unfavourable on steric grounds.[34] The benzene (14) is especially interesting since it is reported to give the Dewar benzene (15) thermally.[35,36]



(14) (15)

The Dewar isomer (15) reverts to (14) on heating at 140° for 65 hours. Other fluorinated benzenes studied include 1, 2, 4-trifluorobenzene (16), which forms two of the three possible Dewar forms[37], and the pentafluorobenzenes (17).[38]

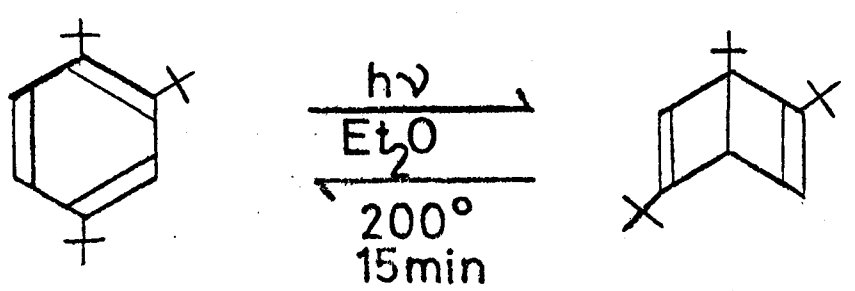


(16)

(17) X = H, CH_3, OCH_3, CF_3, F, Br

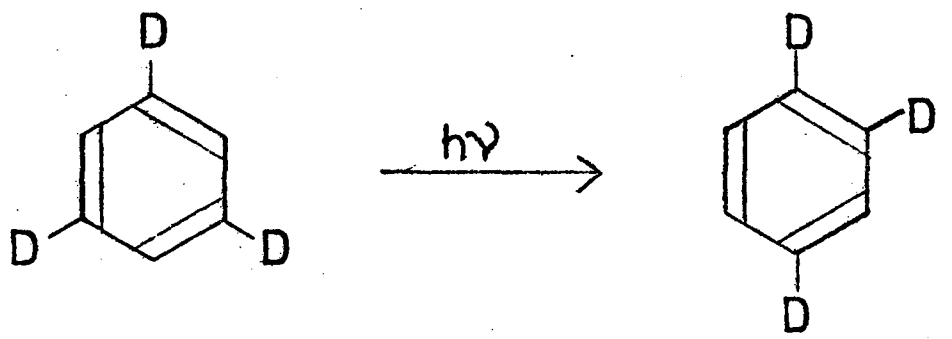
It is possible that the polyfluorinated aromatics undergo photochemistry from states other than S_1 and S_2 owing to a modification of the state energies by introduction of fluorine into the molecule.[5]

Bulky substituents might also be expected to stabilise a Dewar benzene relative to the parent by virtue of reduced steric interactions, borne out by the stability of 1, 2, 5-tri-t-butyl-bicyclo [2. 2. 0] hexa-2, 5-diene (18) prepared photochemically from 1, 2, 4 -tri-t-butylbenzene (19).[39]



(19) (18)

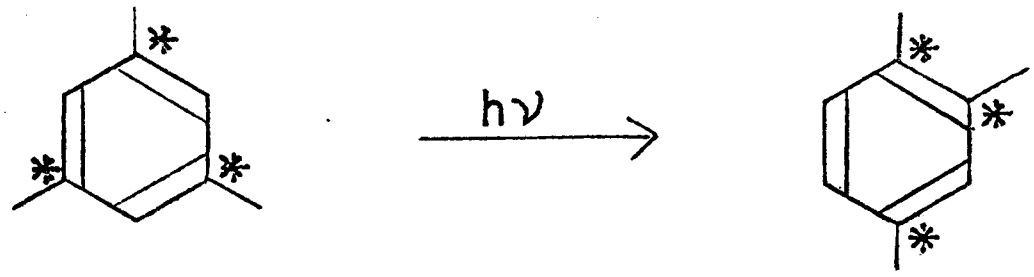
The irradiation of non-symmetrically substituted benzenes has aroused great interest since the recovered aromatic species sometimes show skeletal rearrangement. For example, 1, 3, 5 -benzene-d_3 (20), irradiated in solution, under conditions where intermolecular hydrogen transfer does not occur, undergoes a transposition reaction to give 1, 2, 4-benzene-d_3 (21).[29]



(20) (21)

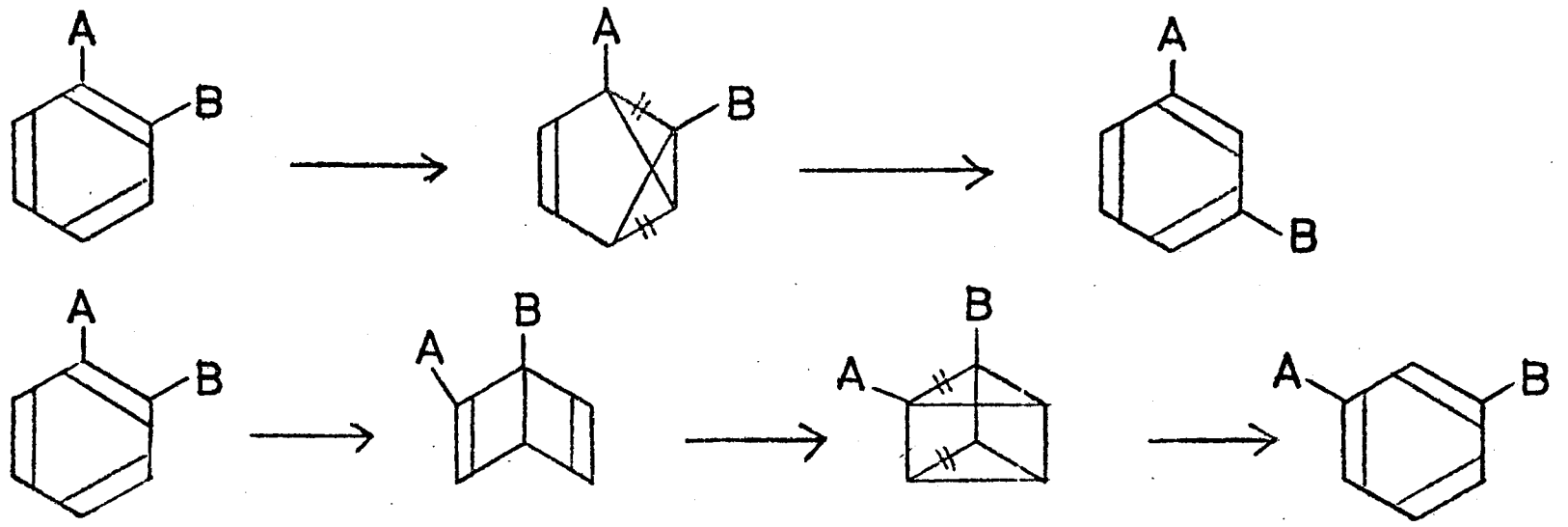
Interestingly, the product of photolysing 1, 4-benzene-d_2 is reported to have unchanged optical properties suggesting that no sketetal rearrangement occurs.[40]

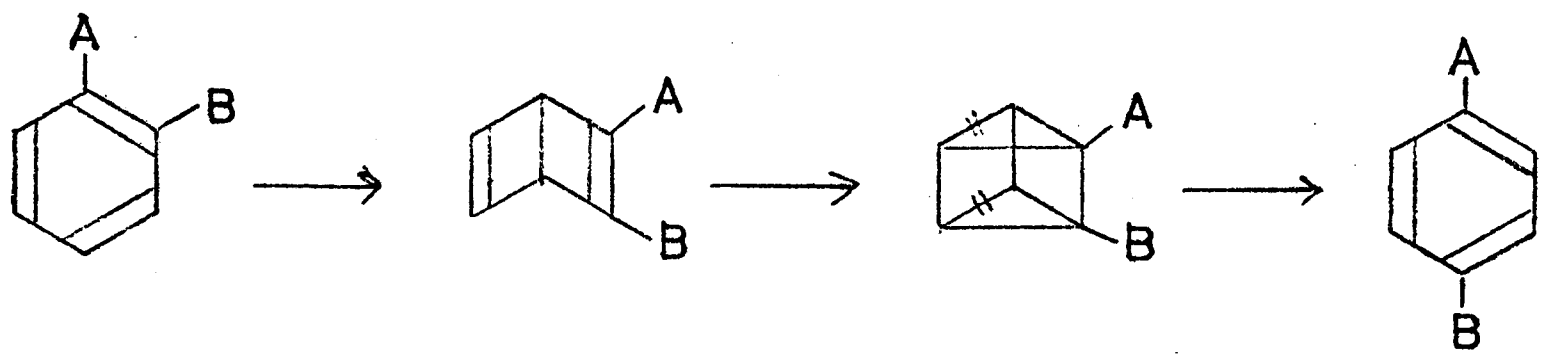
Evidence that phototranspositions are intramolecular is provided by the irradiation of mesitylene (22) labelled with ^{14}C in the 1-, 3- and 5- positions. Ozonolysis of the product, 1, 2, 4-trimethylbenzene (23), showed that the methyl groups remained attached to ^{14}C ring atoms.[41]



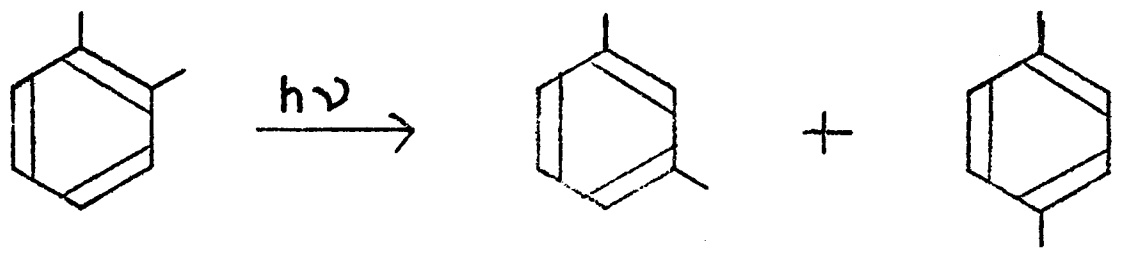
(22) (23)

Since the rearrangements do appear to be intra-molecular, it is generally assumed [41] that transpositions occur via benzvalene or Dewar benzene/prismane intermediates. The scheme indicates how the former might give overall 1,2-shifts and the latter either 1,2- or 1,3 - shifts.





Wilzbach and Kaplan [42] first reported the isomerisation of o-xylene (24) to m- and p-xylenes (25) and (26) in the vapour phase at 254nm.



(24) (25) (26)

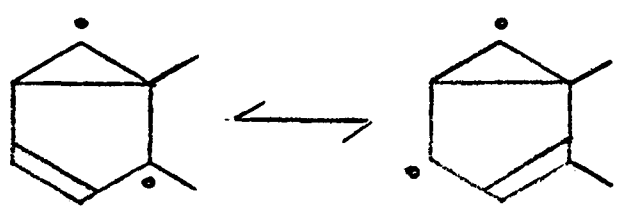
At low conversions no p-isomer was seen and hence was assumed to be formed by secondary photolysis of the m-isomer; consistent with this, was the observation that the major product from m-xylene photolysis was p-xylene with a higher overall quantum yield (ϕ ca 0.03). In solution, however, formation of p-xylene

from o-xylene is apparently, primary. [41]

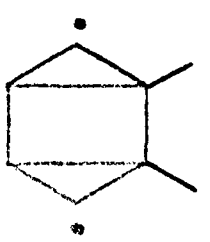
Ward and Barta [43-45] have shown, using a mixture of d_0 and d_6 o-xylene (deuterium in the methyl groups) that the rearrangement is, as expected, intramolecular since the m-xylene produced shows the same isotopic distribution as the recovered o-xylene. [44] They also found that irradiation in the vacuum U.V. region and at 254nm yielded identical products and attributed this to a common set of intermediates. They concluded, that since no light emission was observed from S_1 or T_1 after excitation at the shorter wavelength, these states could not be populated under the vacuum U.V. isomerisation conditions and, hence that rearrangement could not occur from S_1 or T_1. They suggested the participation of a vibrationally excited ground state as intermediate. Barta [45] has since reported that at 185nm both m- and p- isomers are primary products while at 254nm m-xylene only is primary.

Cundall and Voss, however, reach a different conclusion. [46-48] Their results confirm that triplet states are not involved in the isomerisation (trans-but-2-ene, a triplet quencher, has no effect on the formation of m-isomer) and indicate that a vibrationally excited singlet state is involved; xenon quenches formation of m-xylene (heavy atom effect) and increasing the temperature increases the extent of isomerisation (cf benzene → benzvalene formation). The temperature dependency was confirmed by a study of xylene isomerisation in solution. [49]

Plausible mechanisms have been proposed in terms of benzvalenes or prismanes and prevalene-type species (27) and (28). [50]



(27)



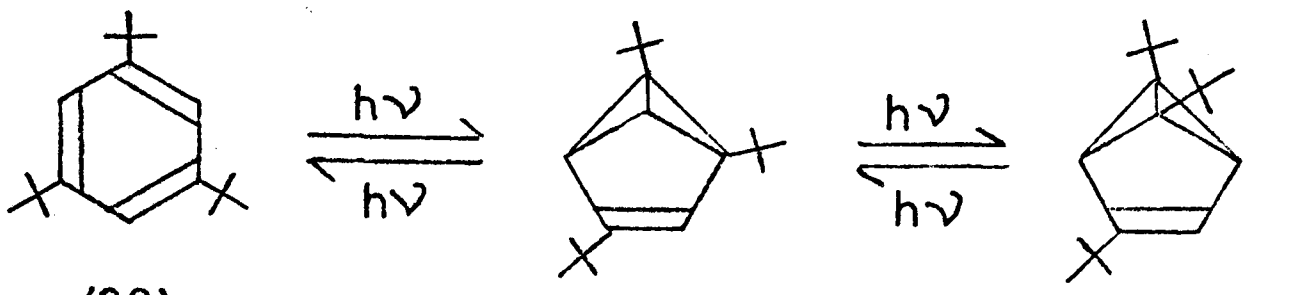
(28)

However, as Noyes and Harter point out,[51] it is likely that the intermediates themselves may be photolysed directly or undergo decomposition sensitised by the aromatic species present. Examples of both processes are known.[52, 53]

It is apparent that the xylene system is extremely complex and far from understood.

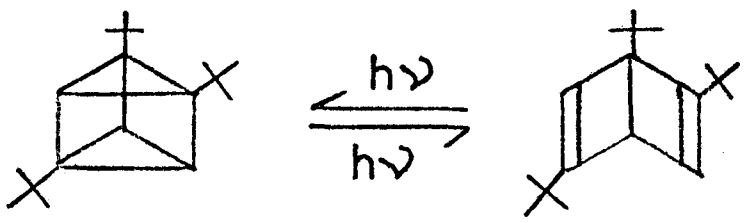
The di-t-butylbenzene system is analogous to the xylene system[54, 55]. Thus o-di-t-butylbenzene, on photolysis, yields a 1:4 photostationary mixture of m-and p-di-t-butylbenzenes. The same photostationary mixture results from either the m- or p-isomers. The apparent 1,3 -shift to form the p-isomer from the o-isomer is, in fact, comprised of two 1,2 -shifts, the p-isomer being a secondary photolysis product. Since no di-t-butylbenzene forms on photolysing a mixture of t-butylbenzene and tri-t-butylbenzene, it is assumed that photochemical reactions of t-butylated benzenes do not involve dealkylation/realkylation mechanisms.

Among the alkyl benzenes, the tri-t-butyl- system is the only example where the valence isomers have been isolated and the photochemical mechanism defined.[26, 39, 52, 56] Irradiation of 1,3,5-tri-t-butylbenzene (29) in isohexane at 254nm results in the formation of a photostationary mixture of 1,3,6-tri-t-butylbenzvalene (30), 1,2,4-tri-t-butylbenzene (31), the Dewar benzene (32) and the prismane (33), in which (33) is the principal component. In fact, a second benzvalene (34) is the first-formed product from (29), but is unstable, with half life 17 mins at 25°, and yields, on photolysis, a 1:1:3 mixture of (30), (31) and (29).[52] In methanol, the unstable benzvalene (34) is completely quenched by methanol to yield an adduct (35) so that in this solvent no isomerisation is observed.



(29) (34) (30)

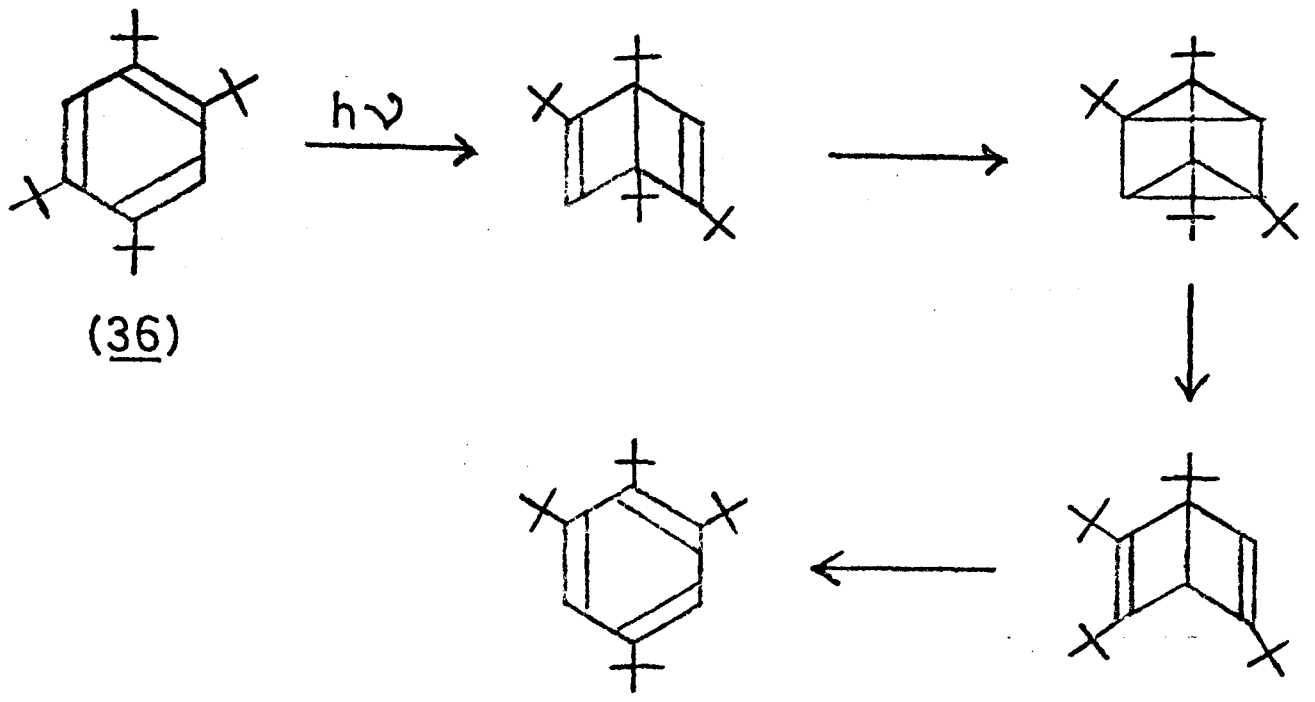
(35) (31)



(33) (32)

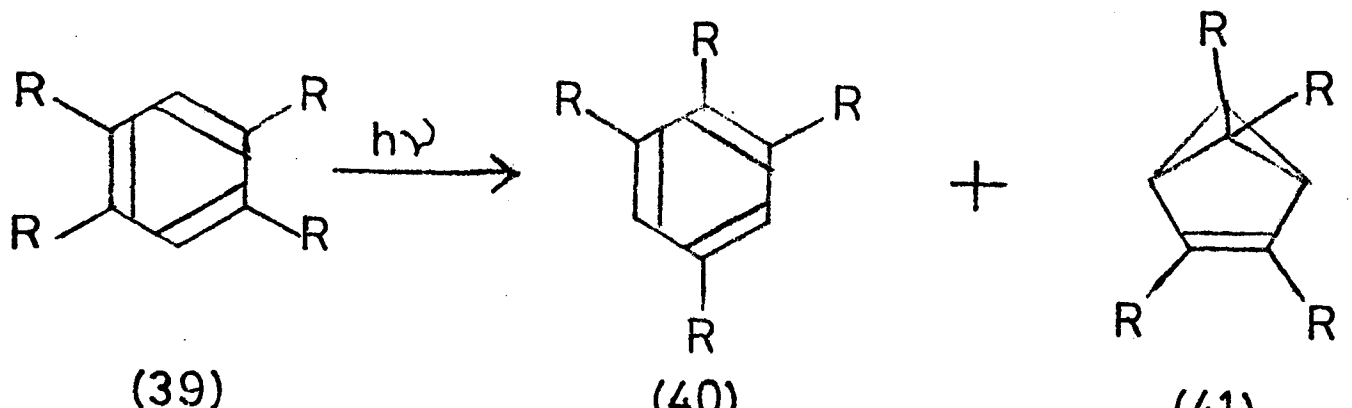
The tri-t-butylbenzene system is discussed more fully in Chapter 2 of this thesis.

A related photoreaction is that of 1, 2, 4, 5-tetra -t-butylbenzene (36), in which the benzene with three adjacent t-butyl groups, 1, 2, 3, 5-tetra-t-butylbenzene (37), is produced, together with another product identified as 1, 2, 3, 5-tetra-t-butyl Dewar benzene (38).[57] Although it is not proven that (38) is not produced from preformed (37), the authors propose the following mechanism:



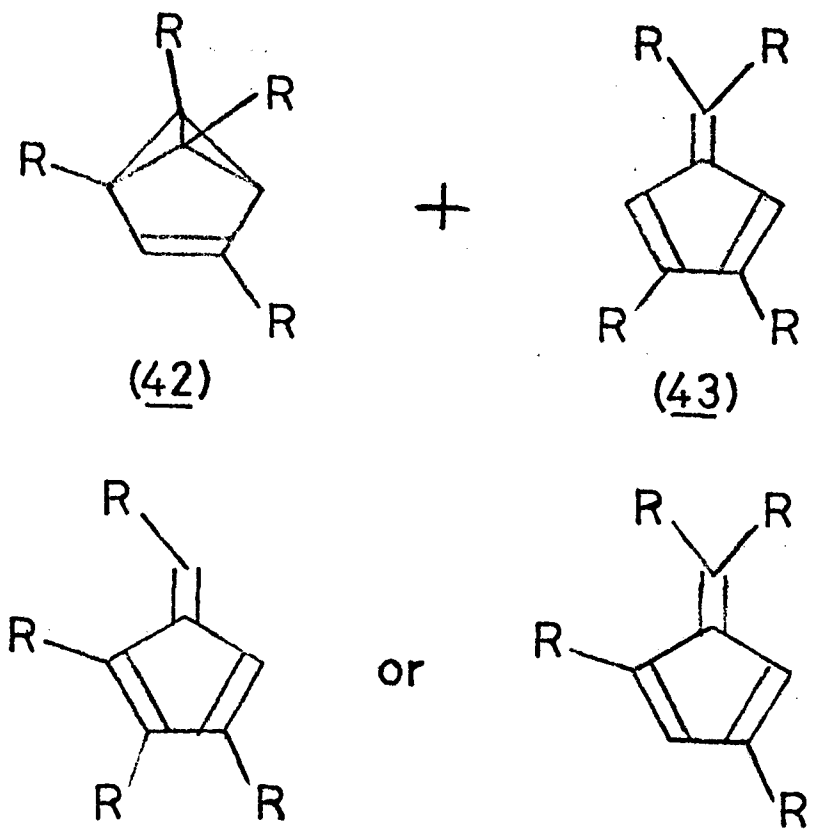
(36) (37) (38)

By contrast, 1, 2, 4, 5-tetrakis (trimethylsilyl) benzene (39), on photolysis, yields 1, 2, 3, 5-tetrakis (trimethylsilyl) benzene (40) together with two benzvalenes, (41) and (42) and two fulvenes (43) and (44) .[58]



(39) (40) (41)

R = $SiMe_3$

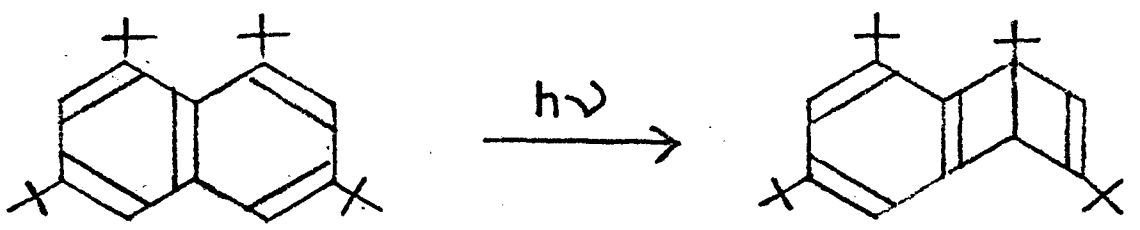


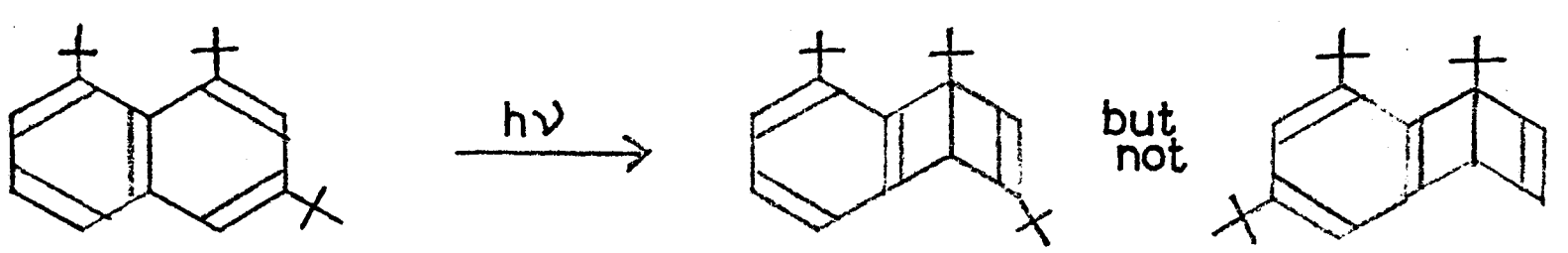
(42) (43)

(44)

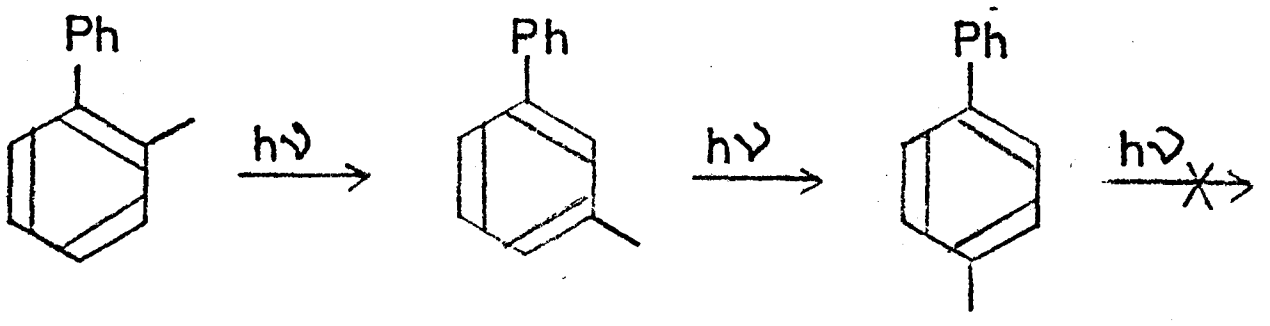
No Dewar benzene products were observed.

In the naphthalene series, it has recently been shown [59, 60] that poly-t-butyl substituted naphthalenes form Dewar analogues.

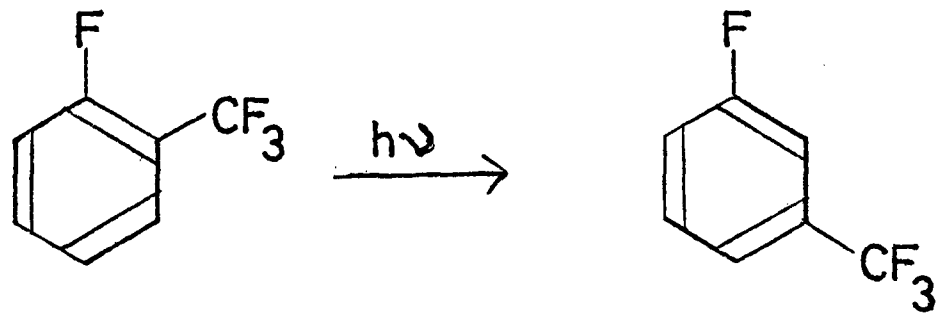


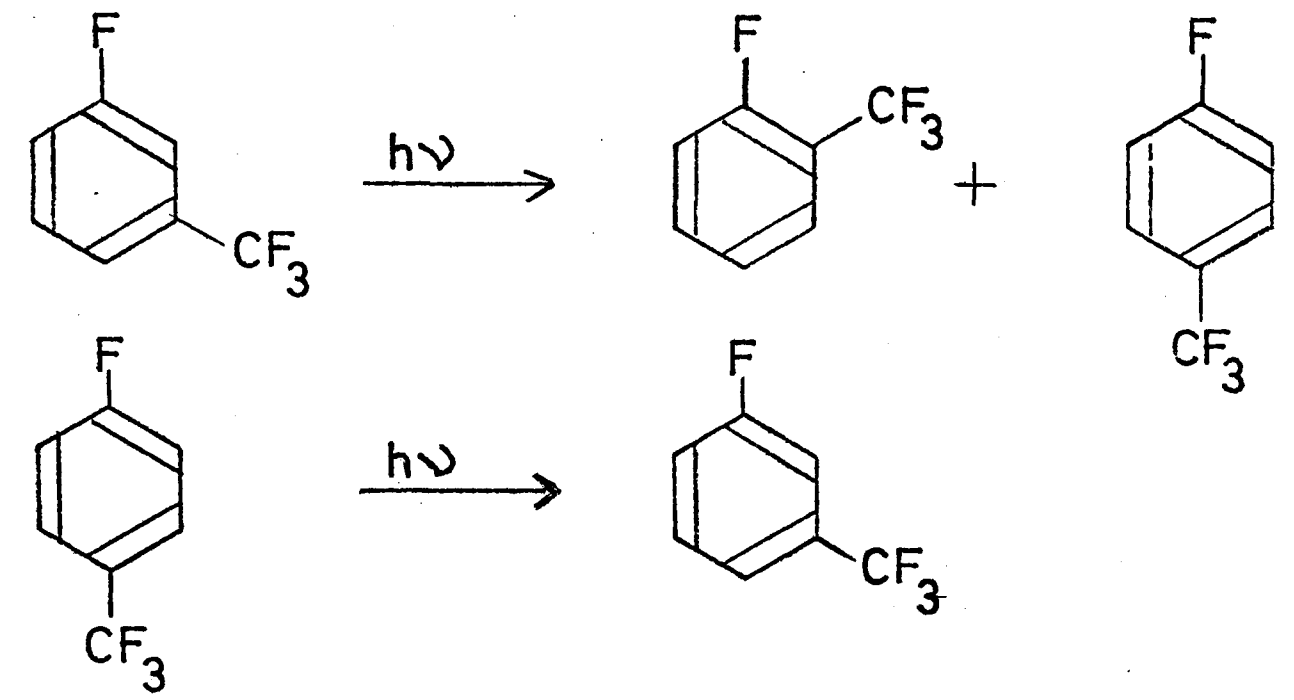


Another class of aromatic compounds found to undergo rearrangement are the biphenyls [61-66]. In all reported cases 1,2-shifts occur, any overall 1,3-shifts actually being comprised of two 1,2-shifts. [61, 62]

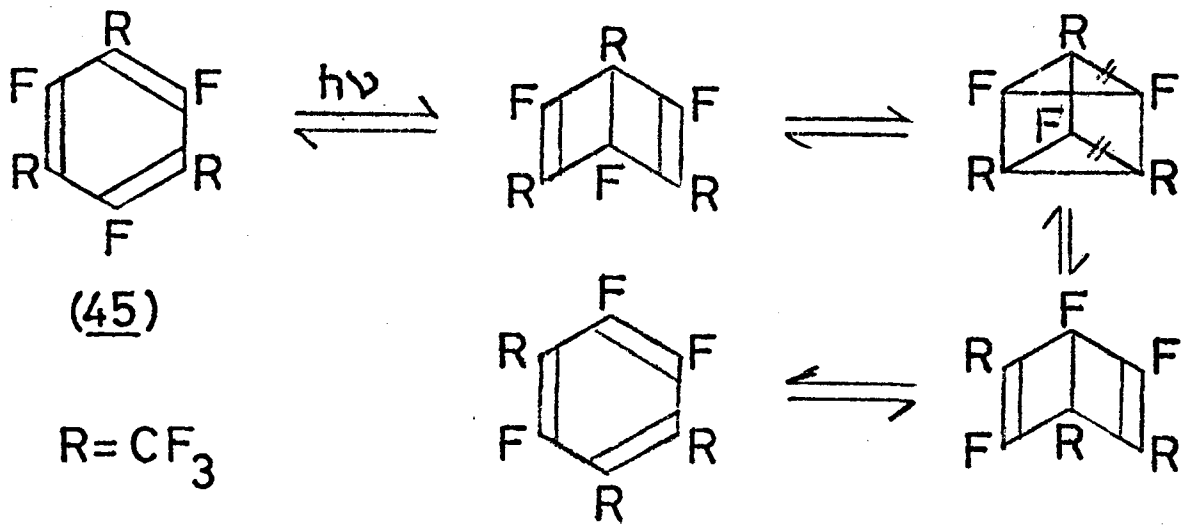


Since fluorinated benzenes readily form valence isomers, it is to be expected that phototranspositions might also take place. Thus, for the trifluoromethylfluoro-benzenes, the following low yield reactions have been reported and are assumed to involve benzvalenes. [67]





Phototransposition of perfluoro-1, 3, 5- and 1, 2, 4-trimethylbenzene, (45) and (46) occurs via a Dewar benzene and prismane mechanism.[68, 69]

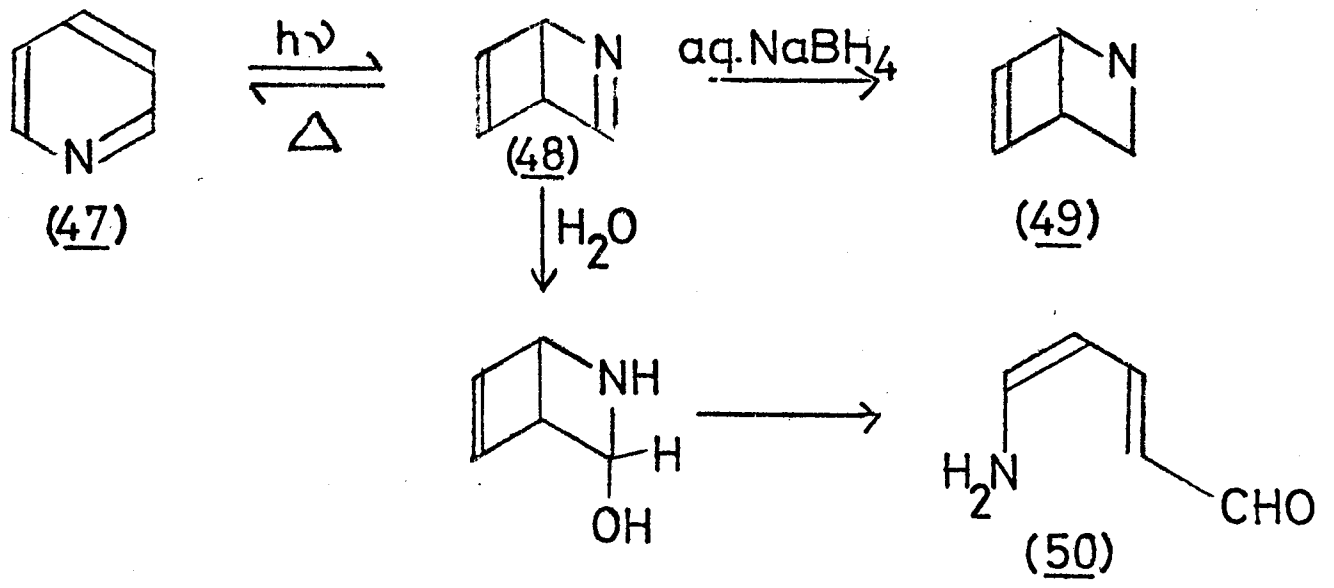


The 1, 2-shifts observed in the perfluoroxylenes [70] are assumed to involve a similar mechanism.

In general, therefore, it appears that the transposition reactions of benzene derivatives can be explained in terms of benzvalene or Dewar/prismane intermediates. However, as Barltrop and Day [71] stress, this is usually an assumption and the active participation of such entities has rarely been proven.

Phototransposition reactions are not confined to the benzenoid system. The pyridine system [72-96] is an example of a six-membered heterocycle which undergoes photochemical transposition. Most of the transpositions observed in this system have been rationalised in terms of the intermediacy of valenes or Dewars/prismanes similar to their benzenoid analogues. Since the photochemistry of pyridine is discussed fully in Chapter 3 of this thesis, only a brief review of the literature data is presented here.

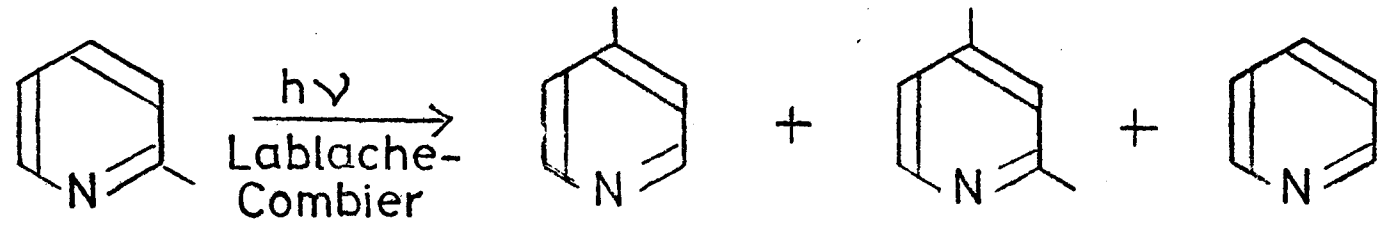
Wilzbach and Rausch studied the photochemistry of pyridine (47) itself and reported photoisomerisation to a Dewar pyridine, 2-azabicyclo [2.2.0] hexa-2,5-diene (48) in the liquid phase at 254nm.[72] The valence isomer, having a half-life of 2.5min at 25°, was reduced by aqueous sodium borohydride to 2-azabicyclo [2.2.0] hex-5-ene (49) and could be hydrated to yield, via the intermediate shown, 5-amino-2,4-pentadienal (50).[73,74]



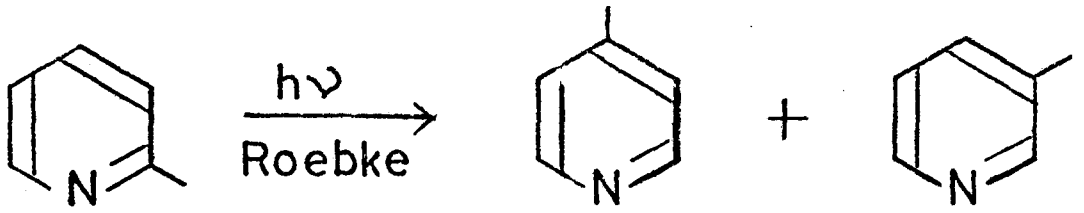
Mono- and di-methylpyridines react similarly.

Short wavelength (< 228 nm) photolysis of pyridine in the gas phase is reported to yield an isomer, which could not be identified.[75]

Phototransposition reactions of substituted pyridines occur in the gas phase [76,77]. Caplain and Lablache-Combier [76] reported that 2-methylpyridine (51) yielded 4-methylpyridine (52), 2,4-dimethylpyridine (53) and pyridine (47) on photolysis and suggested that possible mechanisms were (i) a de-methylation and re-methylation process or (ii) a rearrangement *via* the Dewar and azaprismane forms. Since they observed 1,3-transposition only and no 3-methylpyridine (54), an azabenzvalene-type mechanism was ruled out. However, in contrast, Roebke [77] reported that photolysis of (51) yielded both 3-methylpyridine (54) and 4-methylpyridine (52), with the former as major product, although no definite mechanism was proposed.



(51) (52) (53) (47)

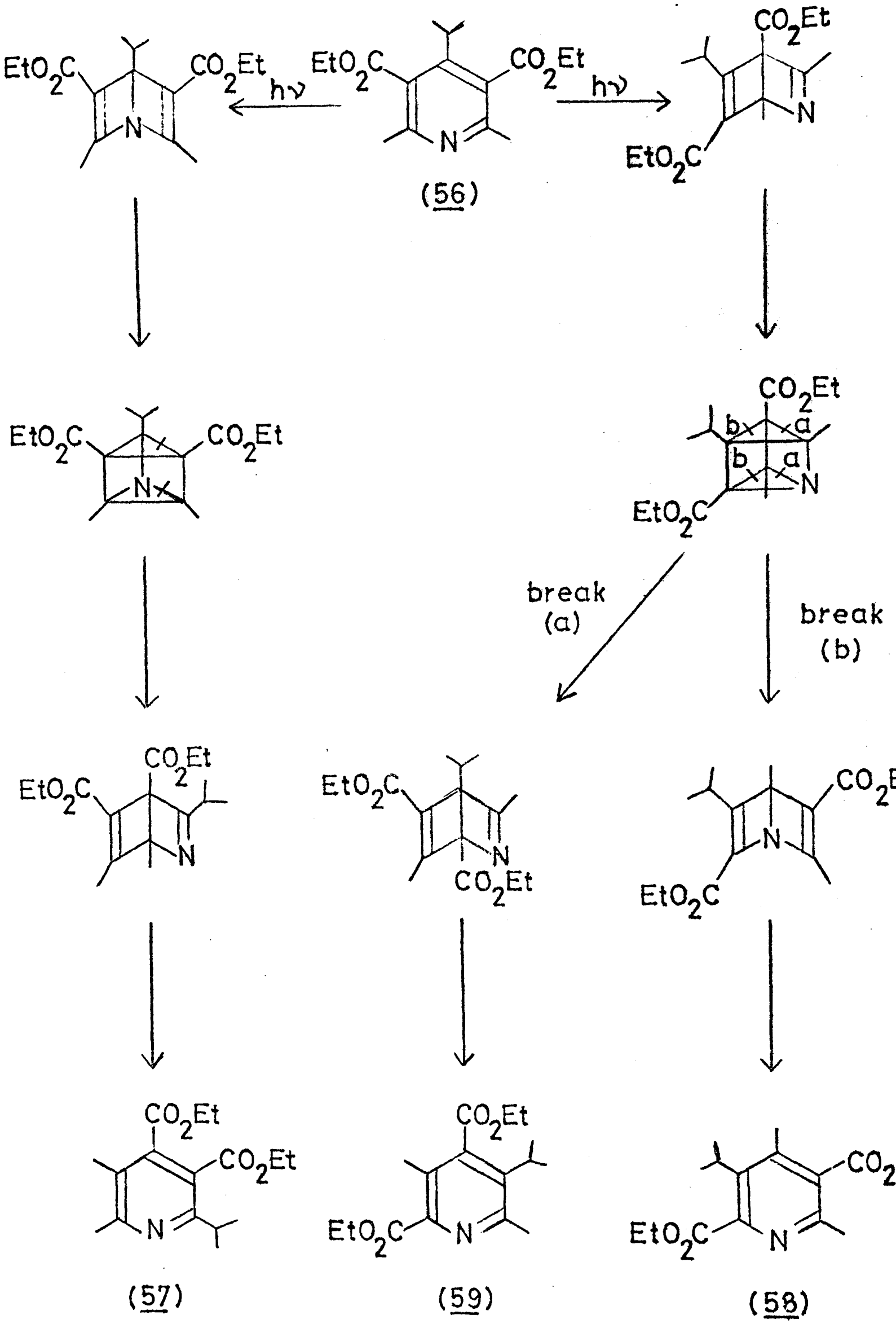


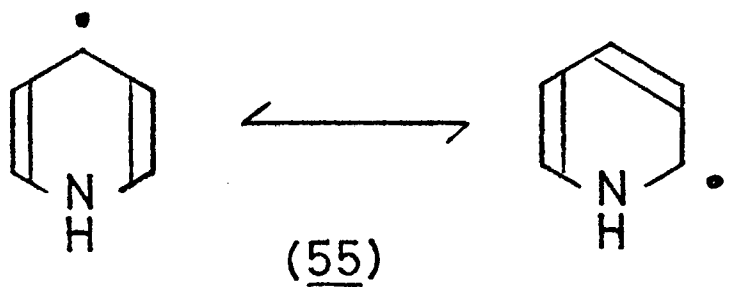
(51) (52) (54)

Dimethylpyridines also rearrange in the gas phase *via* a similar mechanism to that proposed for 2-methylpyridine.[76]

In cyclohexane solution, photointerconversion of 2- and 4-methylpyridine occurs as a very minor process together with radical substitution [78]; both 6-cyclohexyl-2-methylpyridine and 4-cyclohexyl-2-methylpyridine are formed from each isomer, indicating that a common intermediate is involved in both systems. In the case of pyridine the radical (55) has been characterised by e.s.r. [79,80] so an analogous species may be present in the methylpyridines. However, it is not clear how the radical formed from 4-methylpyridine rearranges to that from 2-methylpyridine, which presumably gives rise to the observed substitution products, unless prior interconversion of the methylpyridines has occurred.

Scheme 1



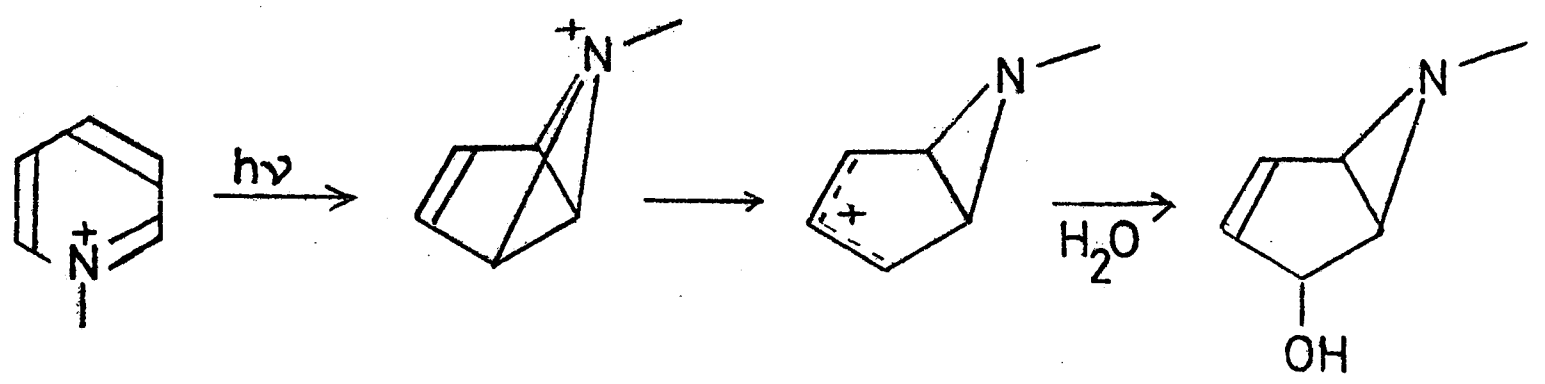


(55)

Van Bergen and Kellogg [81] irradiated 3, 5-di-carboethoxy-2, 6-dimethyl-4-isopropylpyridine (56) in cyclohexane with most interesting results. The products isolated, (57)-(59), are exactly those expected if production of both possible Dewar isomers is followed by formation and cleavage of the corresponding prismanes (Scheme 1).

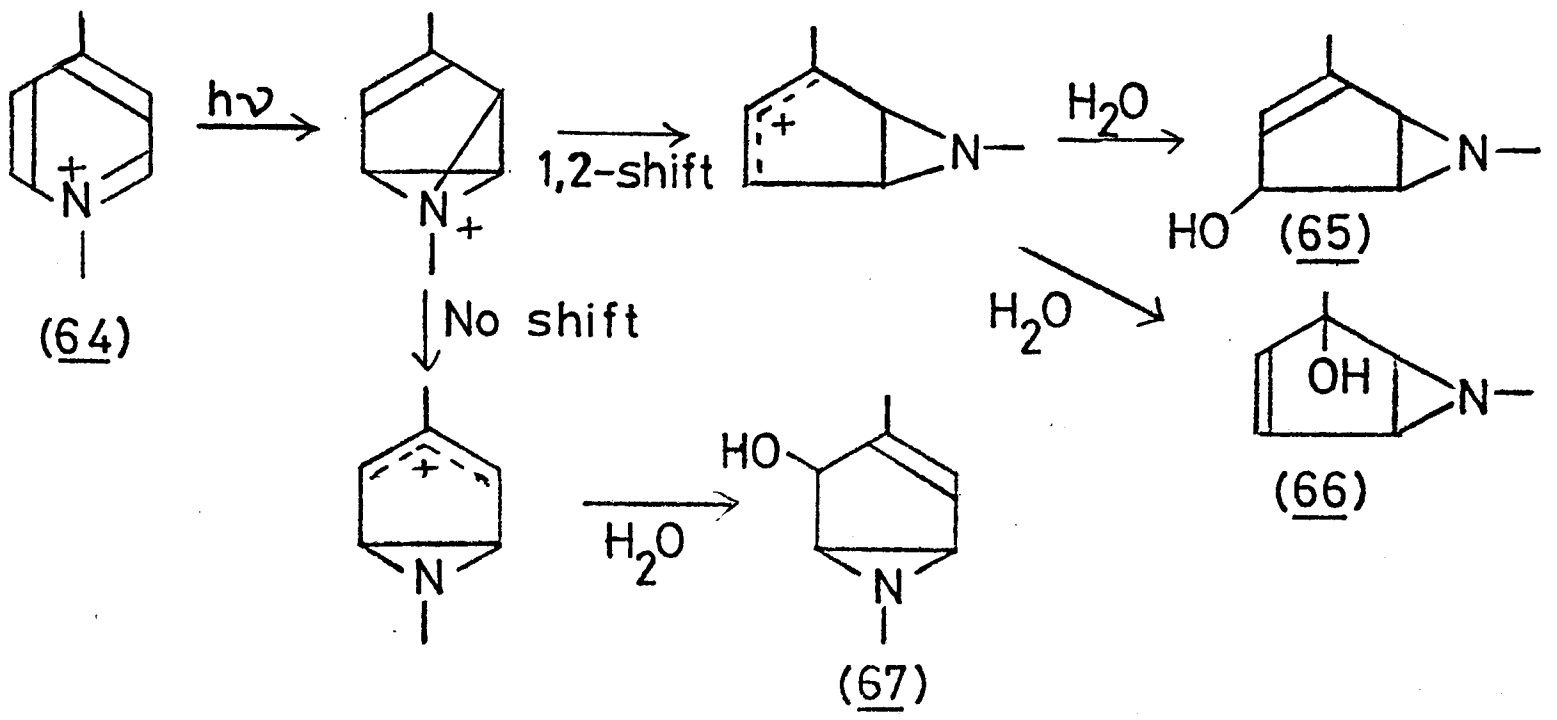
Unfortunately, there is no physical evidence for the participation of these Dewar intermediates.

It has been suggested [82] that the formation of Dewars and azaprismanes occurs preferentially from an $n\pi^*$ excited state of the pyridine since the photochemistry of quaternary pyridinium salts, perforce originating in $\pi\pi^*$ states, is totally different to that of neutral pyridines, being indicative of azabenzvalene intermediacy. Thus irradiation of 1-methylpyridinium chloride (60) in 0.05M aqueous potassium hydroxide at 254nm yields 6-methyl-azabicyclo [3.1.0]-hex-3-en-2-exo-ol (61) via an azabicyclo hexenyl cation (62), formed from the N-methyl-azoniabenzvalene (63).

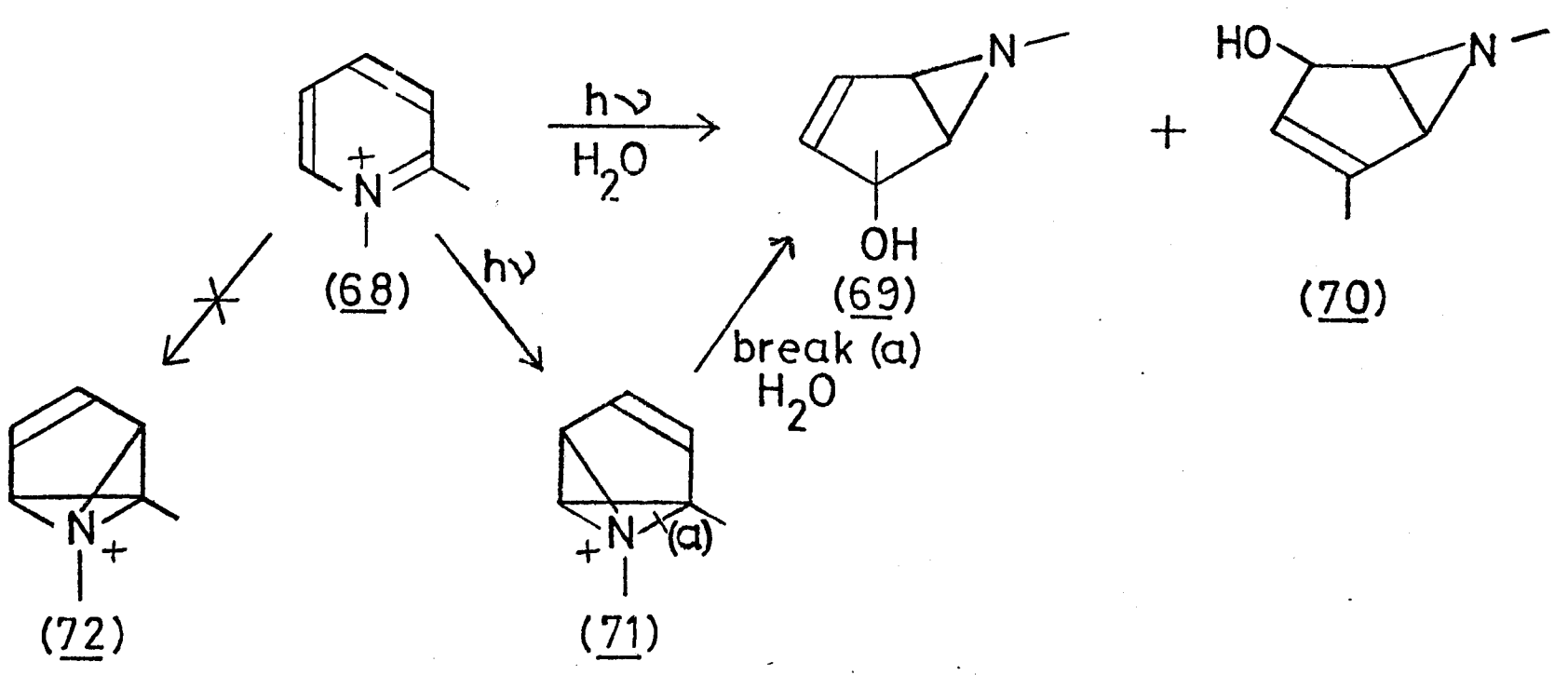


(60) (63) (62) (61)

Studies on quaternised 4-methylpyridine (64) indicate [82] that (62) can undergo 1,2-shifts of nitrogen prior to formation of (61). Thus, the three products observed from (64) are (65), (66) and (67) in a 1:1:2 ratio consistent with the 1,2-shift shown.

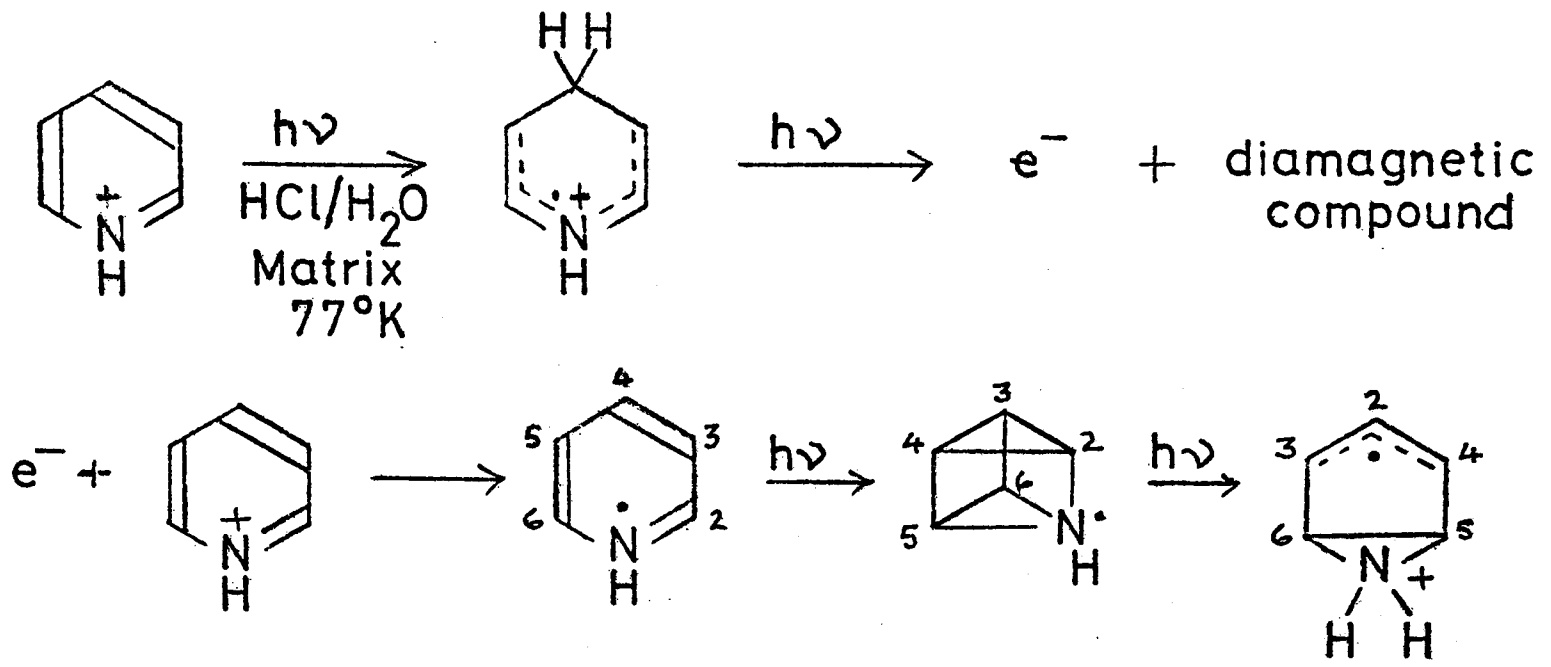


In the case of quaternised 2-methylpyridine (68), the exclusive formation of (69) and (70) indicates preferential formation of the azoniabenzvalene (71) over (72) and exclusive cleavage of bond (a).



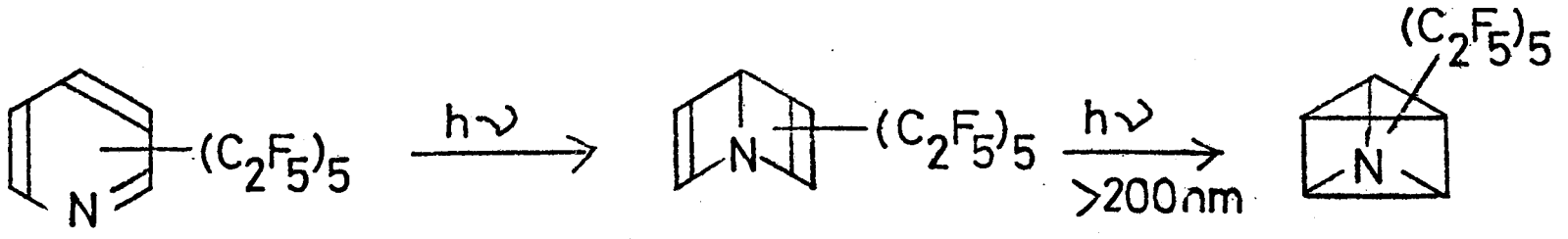
Similar results are observed in the dimethylpyridine methochloride series. [82]

An alternative mode of isomerisation occurs when pyridine is photolysed in an HCl-H_2O matrix at 77°K, an azaprismane radical being assumed an intermediate. [83, 84]



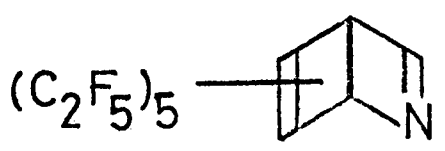
By analogy with benzene, it might be expected that fluorinated pyridines on photolysis should form more stable valence isomers and undergo more efficient transposition than the parent compound. The former is, indeed, borne out experimentally; however, no true transpositions have been observed (vide infra).

For example, irradiation of pentakis(pentafluoroethyl)pyridine (73) in solution produces the corresponding azaDewar and azaprismane, (74) and (75),



(73) (74) (75)

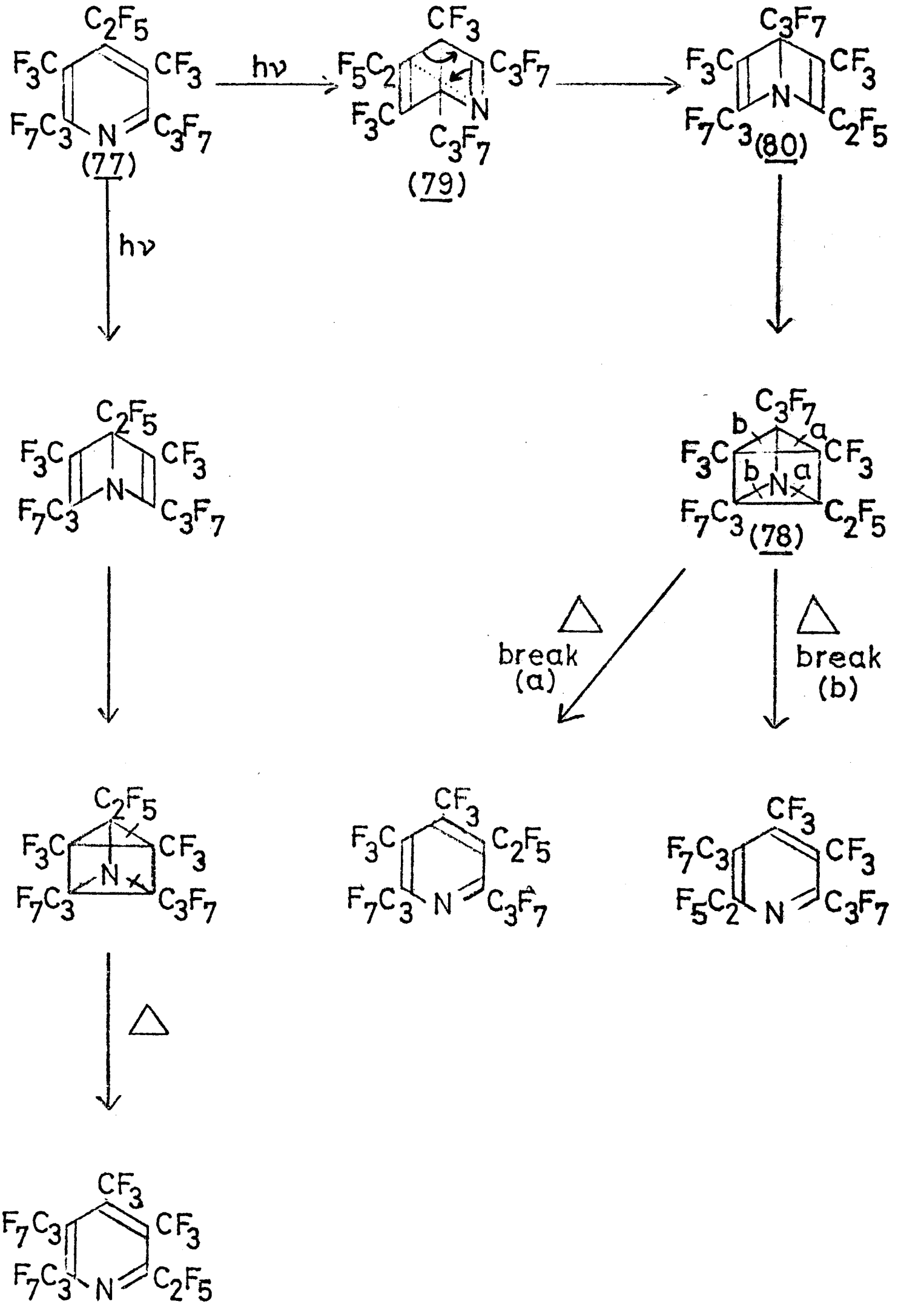
which are stable at 160° for several hours [85, 86] Heating (75) produces an additional unidentified compound which may be the alternative, less stable, Dewar (76).

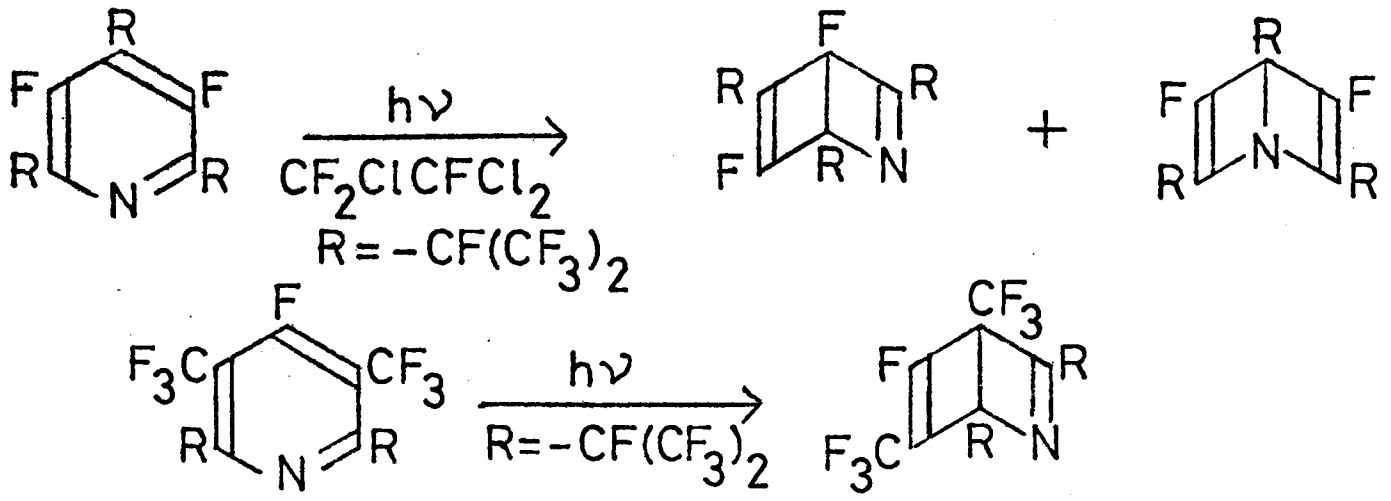


(76)

Similarly stable azaDewar products have been reported as photoproducts in the liquid phase photolyses of perfluorotri – and -tetra-alkyl pyridines [87] shown below:-

Scheme 2





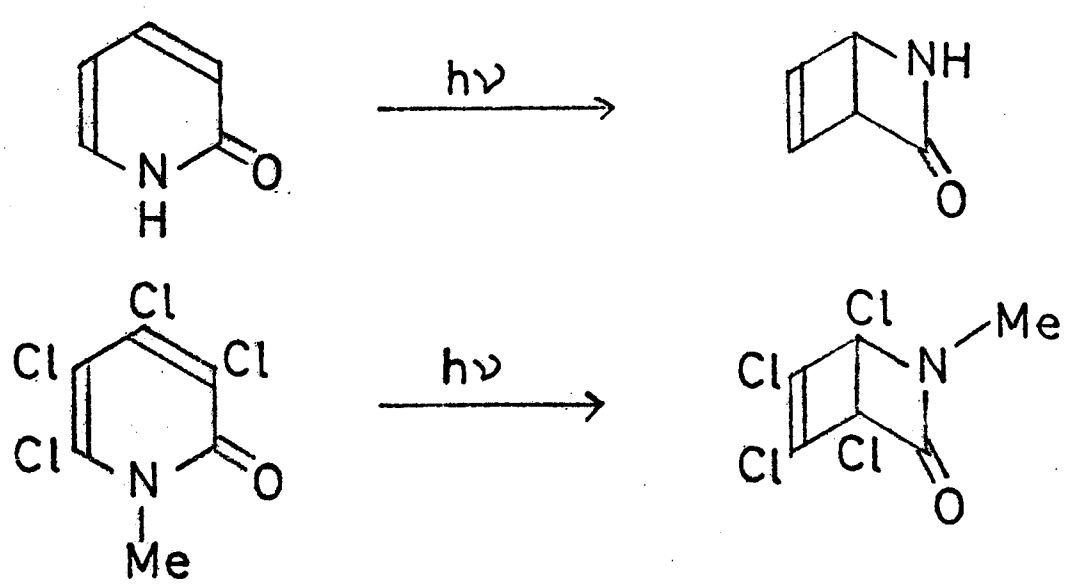
The polyfluorinated pyridine (77) has been observed to transpose as indicated in Scheme 2 [88].

Formation of the azaprismane (78) is assumed to occur via prior formation of the 2, 5-bonded Dewar (79) and its rearrangement to the Dewar (80), although there is no physical evidence that (79) or (80) are present in the photolysis mixture.

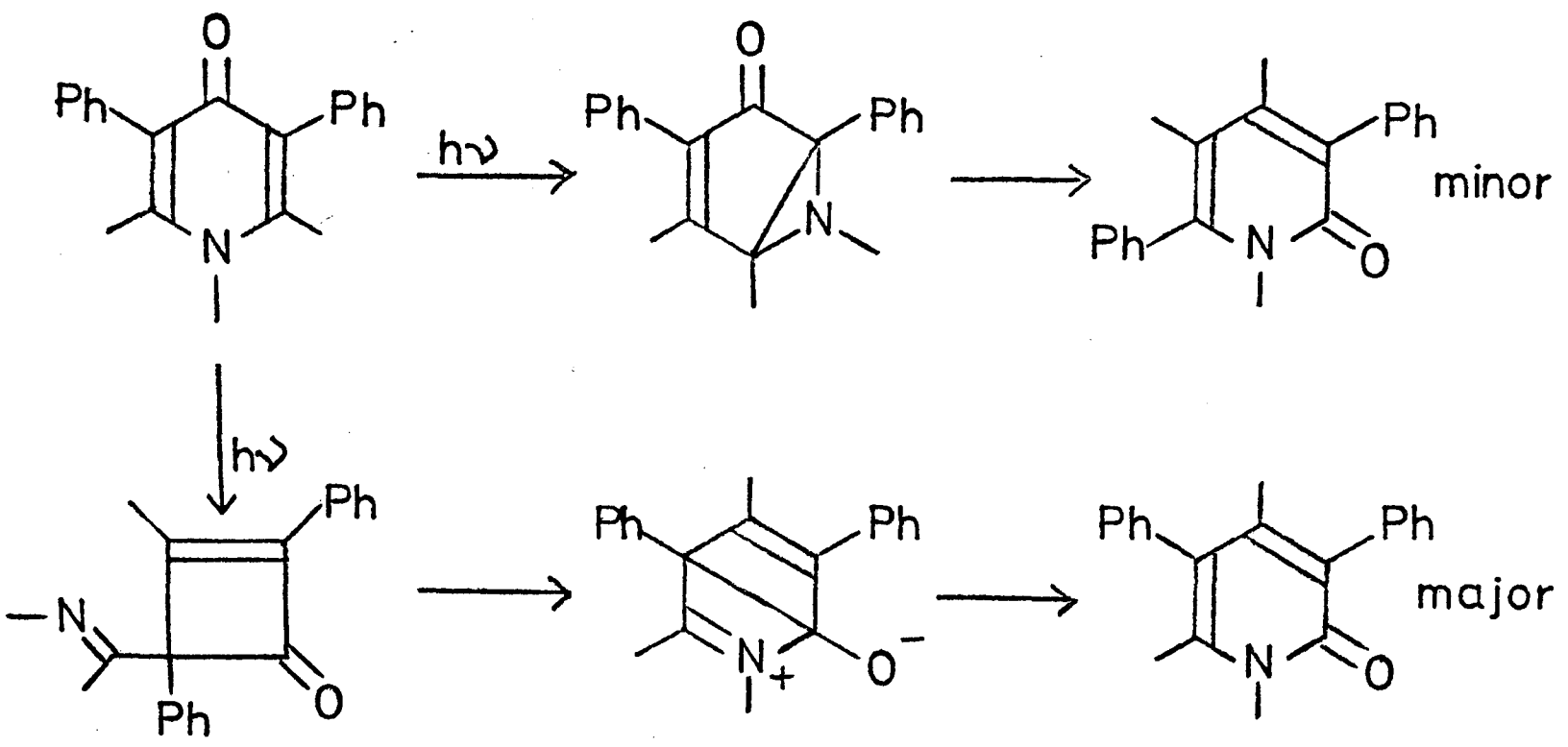
It is to be noted that the observation of overall transposition relies upon an independent thermal rearomatisation step, at 175°, of the azaprismanes to the pyridines.

Other systems of pyridine compounds have been investigated and shown to undergo isomerisation or transposition.

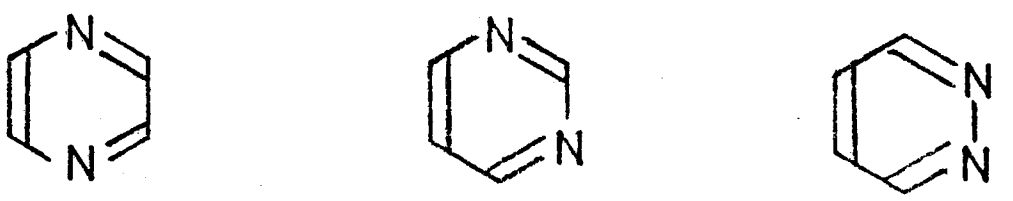
Dewar pyridones have been reported among the photolysis products of 2-pyridones, [89-93] although the principal reaction observed in these systems is photodimerisation. Some examples are shown below:- [91]



In contrast, hindered 4-pyridones undergo phototransposition to yield 2-pyridones, a necessary condition being the presence of phenyl groups at the 3- and 5- positions of the molecule [94, 95]. Compounds not bearing such phenyl groups are apparently photochemically inert. [96] The proposed mechanism of rearrangement is indicated.

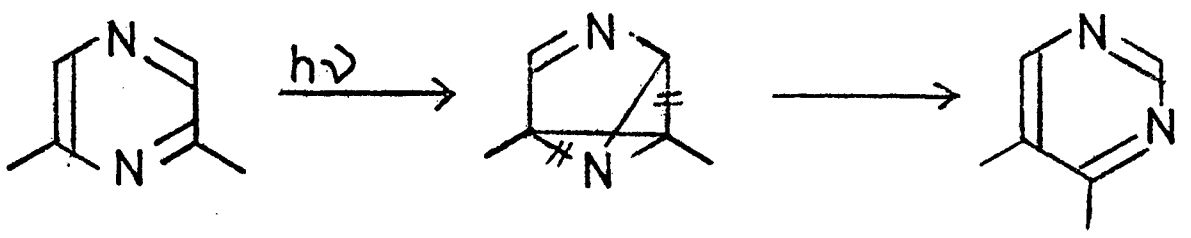


Closely related to pyridine are the three six-membered heterocycles containing two nitrogen atoms - pyrazine (81), pyrimidine (82) and pyridazine (83).

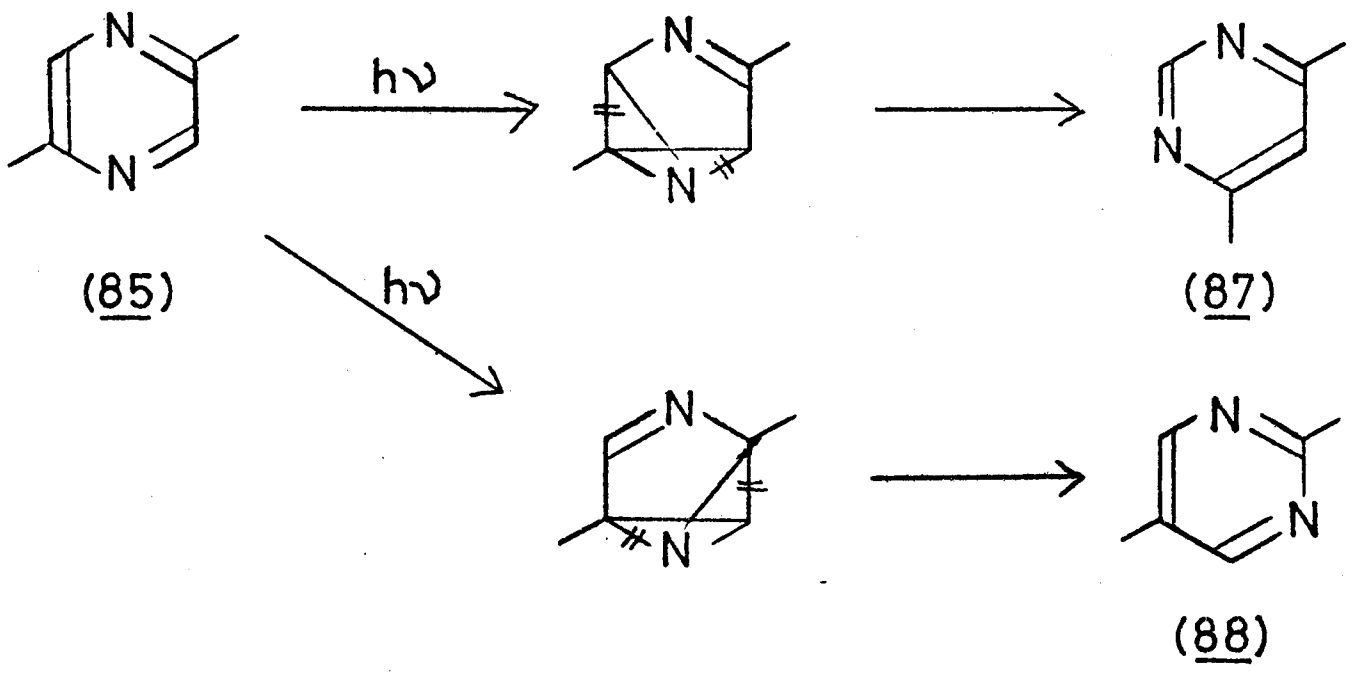


(81) (82) (83)

These compounds have been found to undergo similar types of photochemistry[97-103]. For example, vapour phase irradiation of pyrazine (81) results in an apparent 1, 2-shift of nitrogen to yield pyrimidine (82).[97, 98] Use of 2, 6 - and 2, 5 - dimethylpyrazine, (84) and (85), indicated that the products observed, 4, 5 - dimethylpyrimidine (86) and a mixture of 4, 6 - and 2, 5 - dimethylpyrimidine, (87) and (88), respectively, were consistent with a valene - type mechanism.

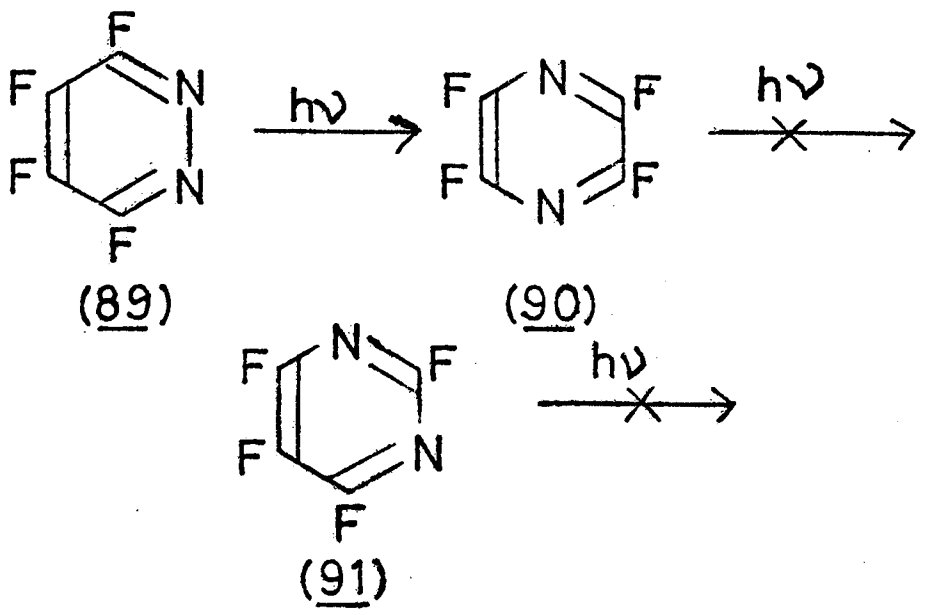


(84) (86)

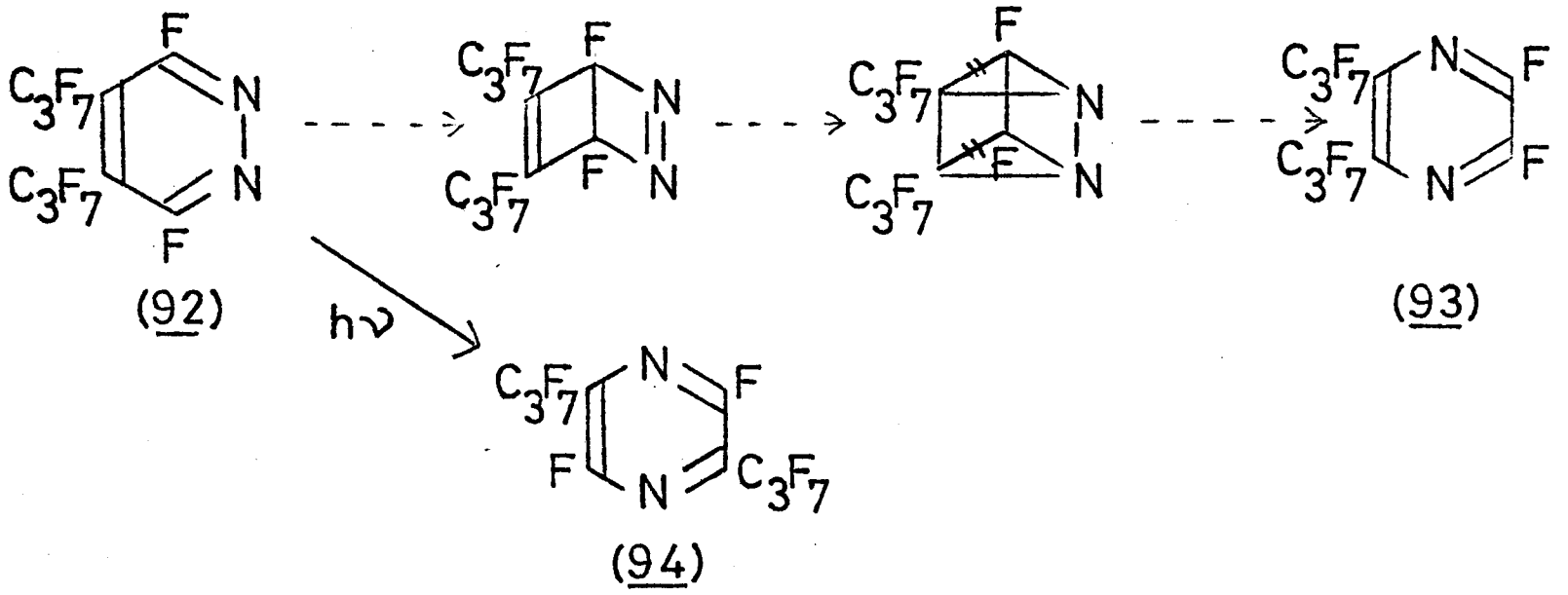


Since isomerisation occurs only upon irradiation at 254nm (and not at 313nm) the reaction is assumed to proceed via an $n\pi^*$ state of the pyrazine.[98]

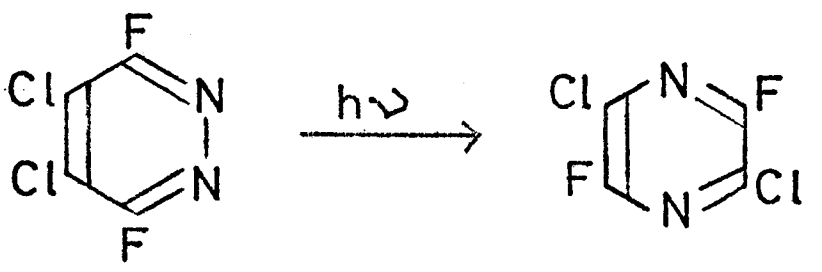
As in the pyridine series, polyfluorinated diazines have received a great deal of attention. Gas phase irradiation of tetrafluoropyridazine (89) yields tetrafluoropyrazine (90) whereas (90) itself, and tetrafluoropyrimidine (91) are unchanged.[99]



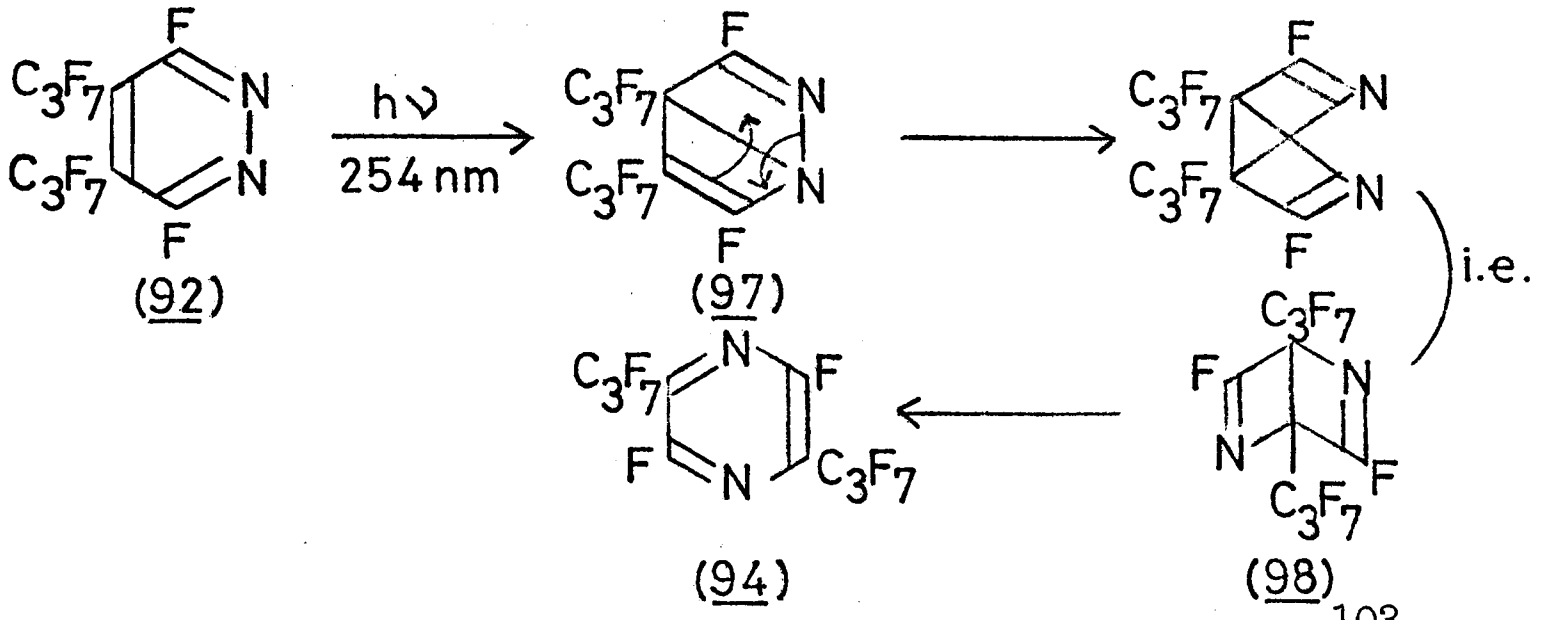
This overall 1,3-shift might, at first sight, be taken as evidence that an azaprismane mechanism is in operation. However, studies on the substituted pyridazine (92) show that, while (93) would be expected via a prismane route, the product obtained is actually (94).



Similarly, pyridazine (95) yields pyrazine (96).[100]

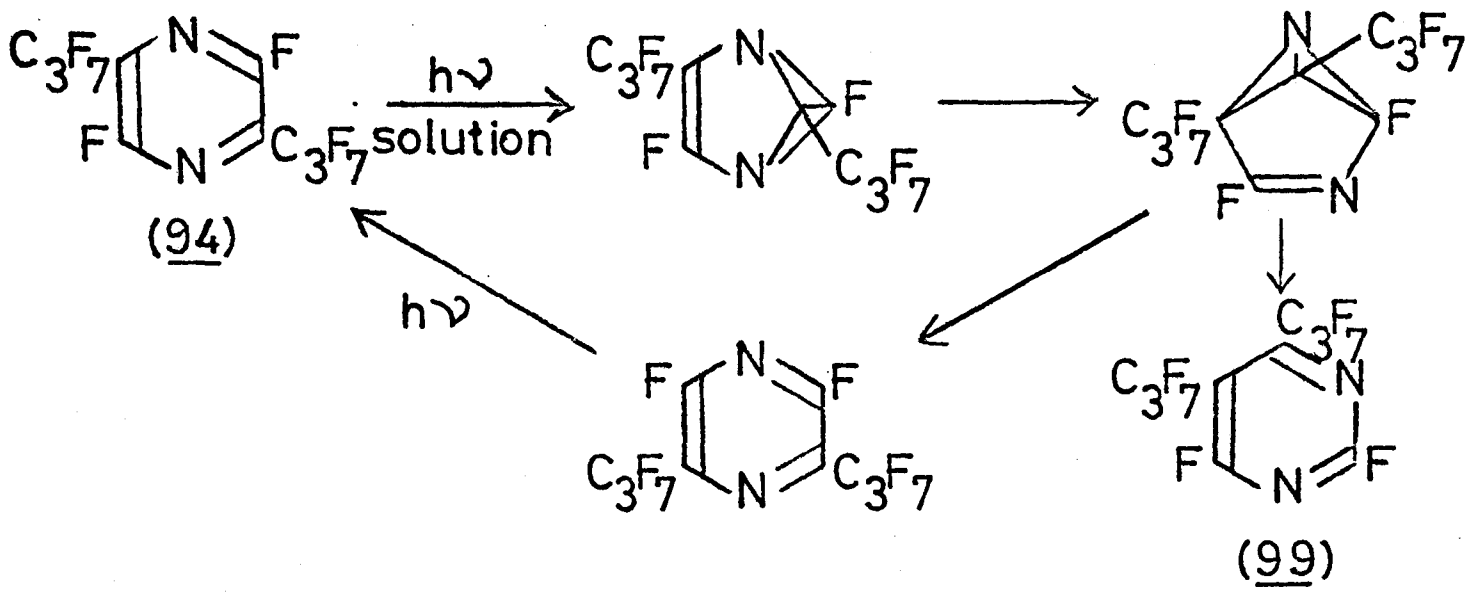


It is now proposed [101-103] that, in fact, the first formed product from, say (92), is the Dewar (97) which rearranges to Dewar (98), precursor to the final product (94) (c. f. pyridine (77) where Dewars (79) and (80) were invoked [88]).



In this case (97) and (98) have been isolated and identified.[103]

The liquid phase photochemistry of (94) has been studied [102] and is summarised below.



The overall conversion is very low compared to the gas phase; neither of the two azabenzvalenes proposed have been isolated and the formation of pyrimidine (99) is non-reproducible.

It is most important to realise that the assertion, made by Chambers,[88] that the pyridazine / pyrazine system constitutes an example in which the fate of all ring atoms is known, and hence, the absolute rearrangement mechanism, is erroneous. In the system employed, it is impossible to distinguish between carbon atoms which bear similar substituents and between the two nitrogen atoms; so that a single permutation, as defined by Barltrop and Day,[71] cannot be specified. Furthermore, although postulated intermediates, for example (97) and (98), have been isolated, it has not been demonstrated that these species do, in fact, give rise to the observed products.

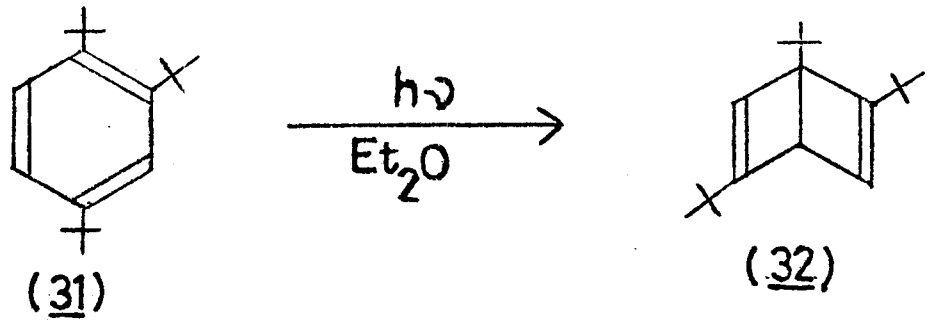
The aims of this present study were to investigate the phototransposition reactions of a variety of aromatic systems in order to gain further insight to the rearrangement processes taking place.

CHAPTER 2

PHOTOCHEMISTRY OF THE TRI-T-BUTYLBENZENES

INTRODUCTION

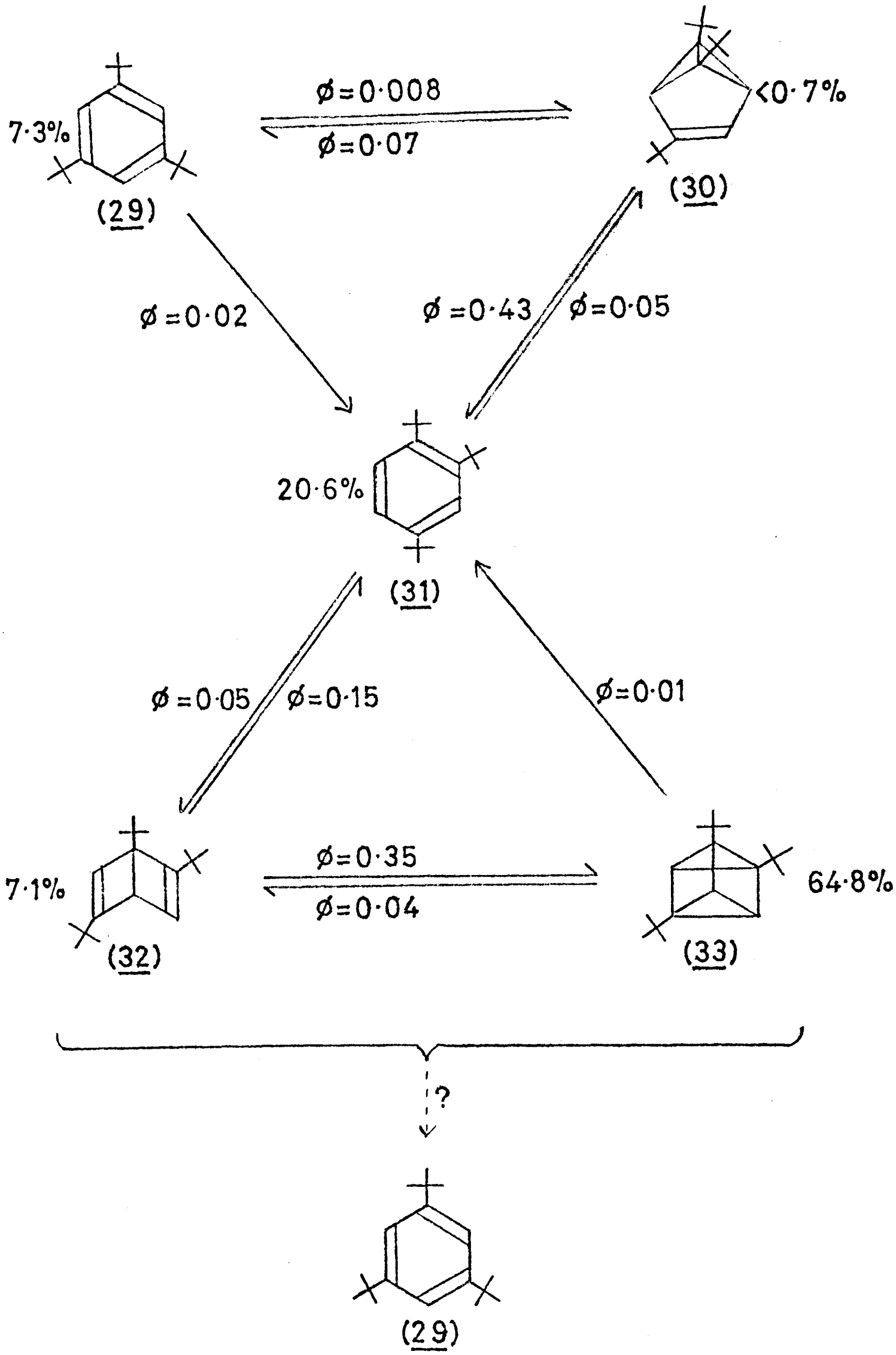
The tri-t-butylbenzene system has been used as a convenient experimental model for investigating benzenoid phototransposition reactions since the valence isomers formed in this system are comparatively stable.[26, 39, 52, 56] Van Tamelen et al showed that 1, 2, 4 - tri - t -butylbenzene (31), upon irradiation in ether, gave 1, 2, 5-tri-t-butylbicyclo [2. 2. 0] hexa-2,5-diene (1, 2, 5-tri-t-butylDewar-benzene) (32) as a stable product. The stability of this product relative to the parent compound was attributed to the decreased steric interaction between the adjacent t-butyl groups in the Dewar benzene isomer.[39]



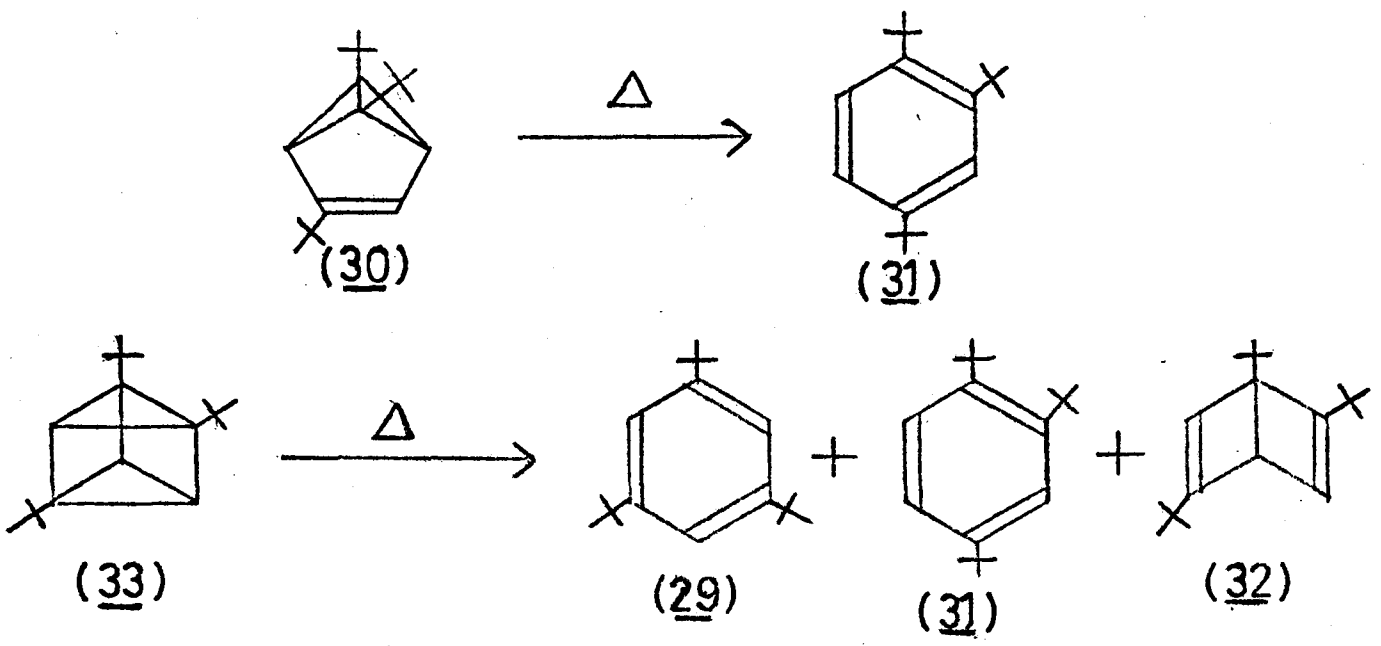
(31) (32)

Rather surprisingly, they did not report the formation of another valence isomer, 1, 3, 5-tri-t-butyltetracyclo [2. 2. 0. 0. ^{2,6} 0 ^{3,5}] hexane (1, 3, 5-tri-t-butylprismane) (33), which was subsequently observed by Wilzbach and Kaplan[56] who irradiated 1, 3, 5-tri-t-butylbenzene in hydrocarbon solvents. Formation of this prismane isomer (33), the major product of the photostationary mixture attained (See Scheme 3), was assumed to be derived by secondary photolysis of the Dewar isomer (32), itself produced by secondary photolysis of first formed 1, 2, 4-tri-t-butylbenzene (31). A third valence isomer, 1, 3, 6-tri-t-butyltricyclo [3. 1. 0. 0. ^{2,6}] hex-3-ene (1, 3, 6 -tri-t-butylbenzvalene) (30), formed from either 1, 3, 5 - or 1, 2, 4-tri-t-butylbenzene photolyses, was also identified

Scheme 3


7·3%
(29)
ø=0·008
ø=0·07
<0·7%
(30)
ø=0·02
ø=0·43
ø=0·05
20·6%
(31)
ø=0·05
ø=0·15
ø=0·01
7·1%
(32)
ø=0·35
ø=0·04
64·8%
(33)
?
(29)

in the photostationary mixture . Both the benzvalene (30) and the prismane (33) were stable at room temperature; the benzvalene (30) rearomatised at higher temperatures yielding 1, 2, 4-tri-t-butylbenzene (31) exclusively, while the prismane (33) gave a mixture of the two tri-t-butylbenzenes and the Dewar benzene (32).

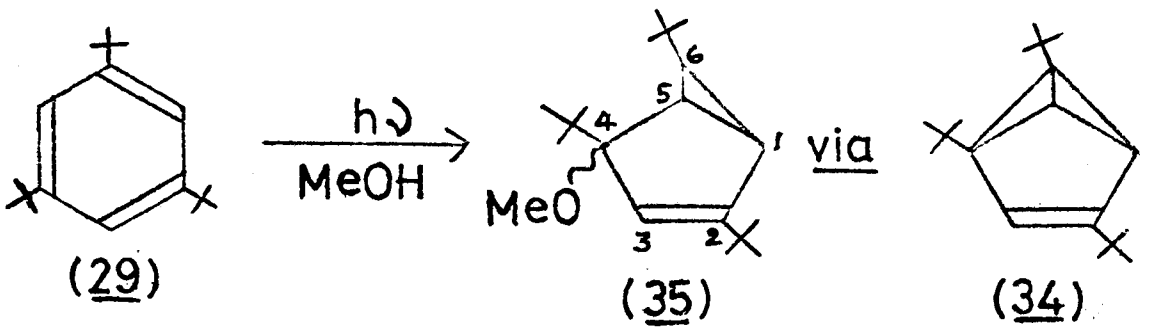


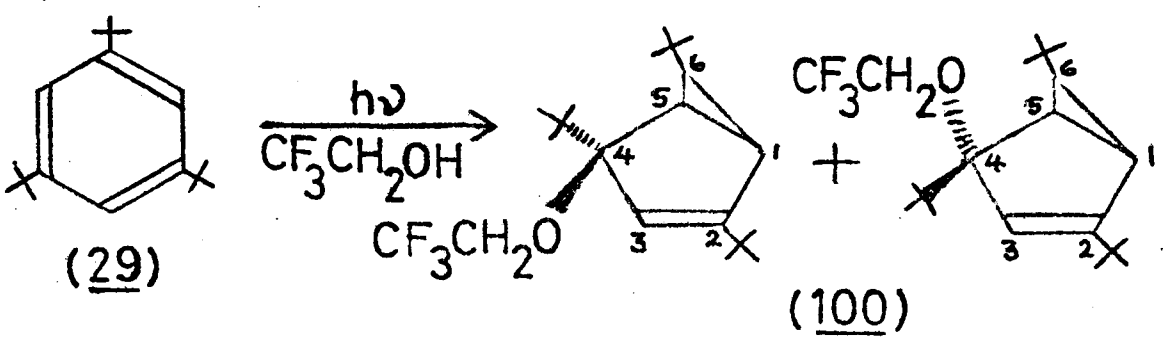
Scheme 3 shows that the major pathway for the rearrangement of 1, 2, 4 - to 1, 3, 5-tri-t-butylbenzene, (31) to (29), was apparently that involving the benzvalene (30). However, photolysis of the Dewar benzene isomer (32) also yielded some 1, 3, 5-tri-t-butylbenzene [56], but in too large a quantity to have been produced by secondary photolysis of the first formed 1, 2, 4-tri-t-butylbenzene alone. This was interpreted as evidence that the Dewar benzene (32) and/or the prismane (33) were also involved in the rearrangement.

For the reverse reaction, 1, 3, 5 - to 1, 2, 4-tri-t-butyl benzene, it was estimated that the benzvalene (30) pathway only accounted for ca one-third of the observed isomerisation, thereby indicating that an alternative mechanism was in operation.

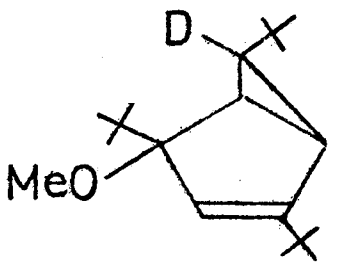
The product isolated after photolysis of 1, 3, 5-tri-t-butylbenzene in methanol [26], 4-methoxy-2, 4, 6- exo -tri-t-butylbicyclo [3. 1. 0]hex-2-ene (35), suggested that this alternative mechanism might involve 1, 2, 4-tri-t-butylbenzvalene (34) as an intermediate.

Similar adducts (100) stereoisomeric at C_4 were isolated on photolysis of 1, 3, 5-tri-t-butylbenzene in trifluoroethanol-saturated hydrocarbon solutions.





It was reported (i) that the quantum yield for ether formation was several times greater than that for isomerisation, (ii) that in methanol or trifluoroethanol, adduct formation occurred to the almost total exclusion of rearrangement, and (iii) that after photolysis in methanol-O-d, the proton resonance missing in the ether produced was that at C_6 - consistent with formation of the ether (101)



(101)

These observations were interpreted as follows: In methanol or trifluoroethanol, the benzvalene (34) underwent a rapid addition reaction thermally to yield the ethers (35) or (100). In hydrocarbon solvents it was rearranged, photochemically, to 1, 3, 5-tri-t-butylbenzene, 1, 2, 4-tri-t-butylbenzene and the benzvalene (30), the former as major product.

In contrast, it was shown that the benzvalene (30) was stable in methanol at room temperature; subsequent photolysis yielded 1, 2, 4-tri-t-butylbenzene.

Direct evidence for the involvement of the benzvalene (34) was provided by an elegant series of experiments by Wilzbach and Kaplan.[52] Firstly, they showed that the amount of 1, 3, 5-tri-t-butylbenzene reacted (ca 10%), after irradiation for 10 min. in trifluoroethanol-saturated isohexane, was equal to the total amount of trifluoroethanol adduct formed and, hence, they used this experiment as a quantitative diagnostic probe for the reactive intermediate. Secondly, solutions of 1, 3, 5-tri-t-butylbenzene in isooctane (3×10^{-4}M) were irradiated with 100 μsec flashes from a xenon lamp and the absorbance at 240nm was monitored. The absorbance, 2 min. after the flash, was 0.29 which decayed to a value of 0.11 with a half-life of 16 min. Addition of trifluoroethanol to a freshly flashed sample caused a decrease in absorbance to a value of 0.11 after 2 min. G.l.c. analysis of the resultant solution revealed the presence of the trifluoroethanol adducts (100). It was concluded from these results that an unstable, U.V. absorbing species which reacted with trifluoroethanol to form adducts had been formed.

In a third series of experiments, solutions of 1, 3, 5-tri-t-butylbenzene in isohexane (6×10^{-3}M) were irradiated at 254nm. Irradiation for 3 min produced a new absorbing band at 235 nm which decayed with a half-life of 17 min, at 24.5°. Addition of alcohols greatly shortened the half-life for decay (e.g. methanol, 1.4 min., trifluoroethanol, $<$ 10 sec). Aliquots from a solution which had been irradiated for 2 min., were removed after timed intervals, treated with trifluoroethanol and the total amount of adduct formed found by g.l.c.. The yield of adduct was shown to decrease with a half-life of 17 min. at 24.5° also.

Wilzbach and Kaplan next obtained the U.V. spectrum of the intermediate by comparing the U.V. spectrum of a freshly irradiated sample with that of an aged irradiated sample. The difference spectrum

Figure 1

Comparison of difference u.v. spectrum of freshly irradiated and aged solutions of 1,3,5-tri-t-butyl-benzene with those of benzvalene(2) and 1,3,6-tri-t-butylbenzvalene(30).

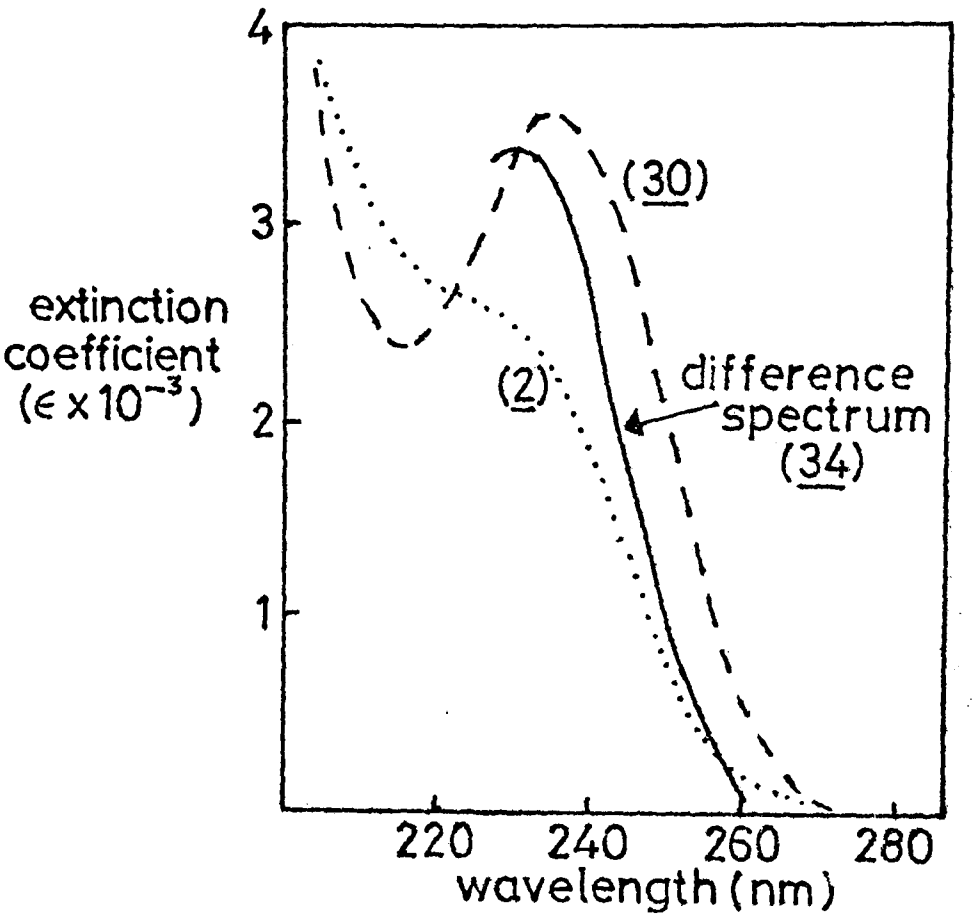
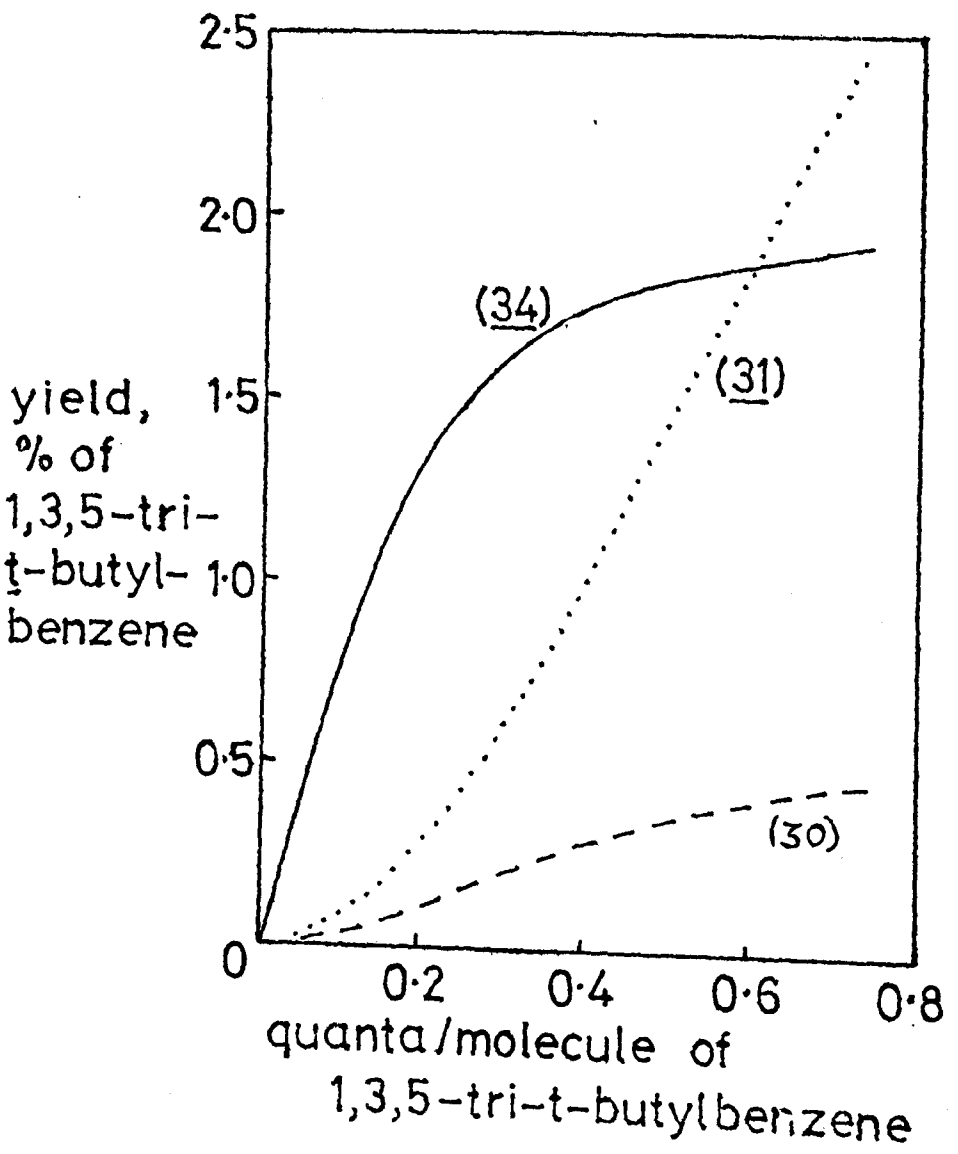


Figure 2

Dependence of photoproduct concentration upon extent of irradiation at 254nm.

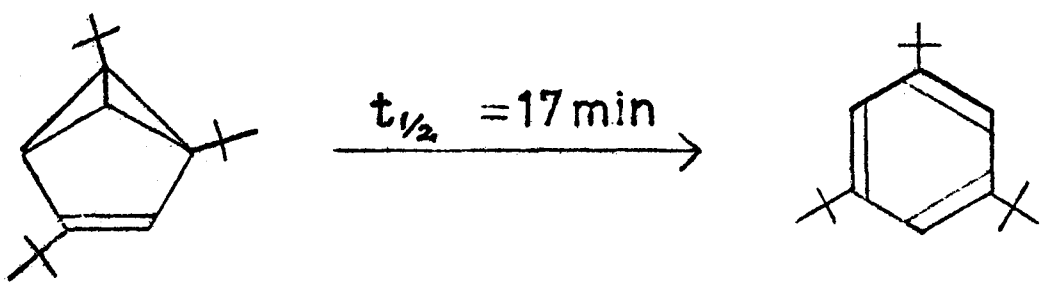


showed an absorption maximum at 230nm with an extinction coefficient, ϵ, of 3,400, calculated from the amount of adduct formed with trifluoroethanol. Comparison of this difference spectrum with the U. V. spectra of the stable benzvalene (30) and benzvalene (2) itself provided strong evidence that the intermediate was also a benzvalene (See Figure 1).

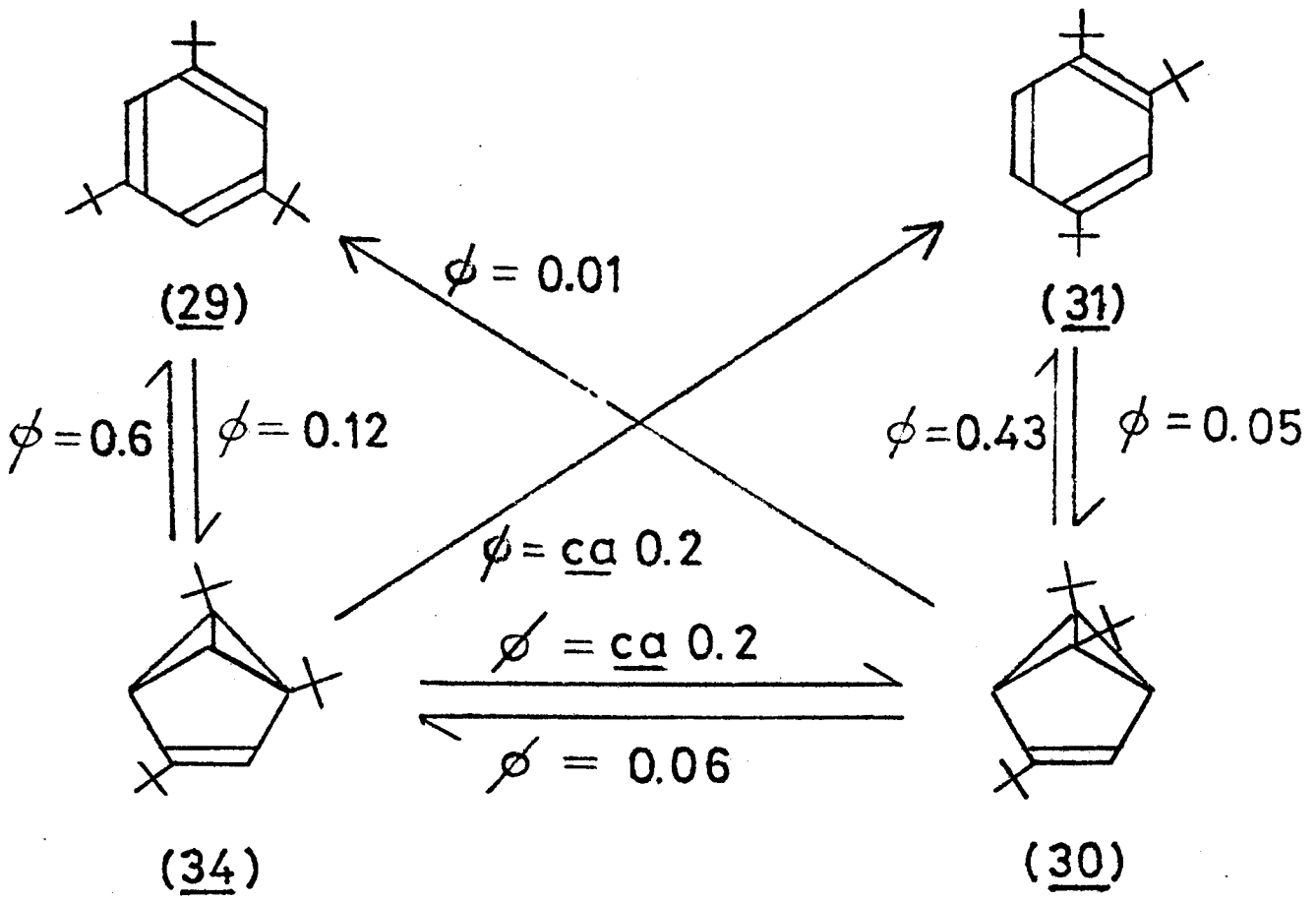
Finally, they carried out a kinetic experiment to show how the relative yields of photoproduct varied with irradiation times. Their results are shown in Figure 2.

The slow early rise in concentrations of the benzvalene (30) and 1,2,4-tri-t-butylbenzene indicated that they were not formed by direct photolysis of 1,3,5-tri-t-butylbenzene. The decrease in growth of the benzvalene (34) suggested that it was a precursor to the benzvalene (30) and 1,2,4 -tri-t-butylbenzene. These compounds must have been formed photochemically since the yield of benzvalene (30) and 1,2,4-tri-t-butylbenzene was the same in aged solutions and in solutions treated immediately with trifluoroethanol. The fall-off in the yield of the benzvalene (34), greater than its thermal loss, showed its photochemical lability. No photosensitisation had occurred since the percentage yield of products was the same at different concentrations of 1,3,5-tri-t-butylbenzene. Further it was shown that the unstable benzvalene (34), on photolysis, yielded the benzvalene (30), 1,2,4-, and 1,3,5-tri-t-butylbenzenes. All the benzvalene (30) and the 1,2,4-tri-t-butylbenzene observed could be accounted for by the photolysis of the unstable benzvalene (34).

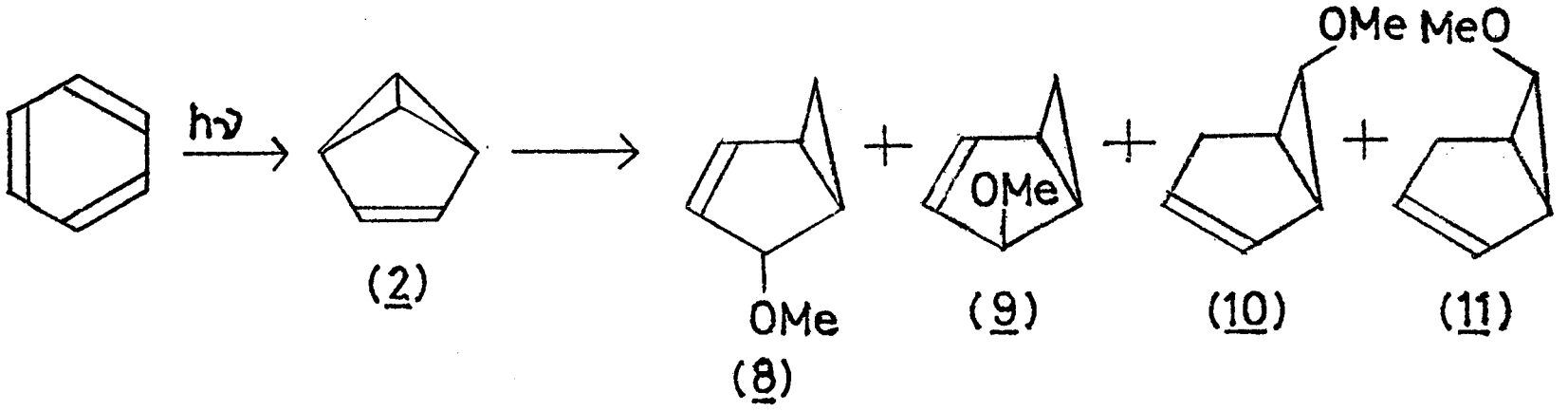
These findings of Wilzbach and Kaplan may be summarised thus:-



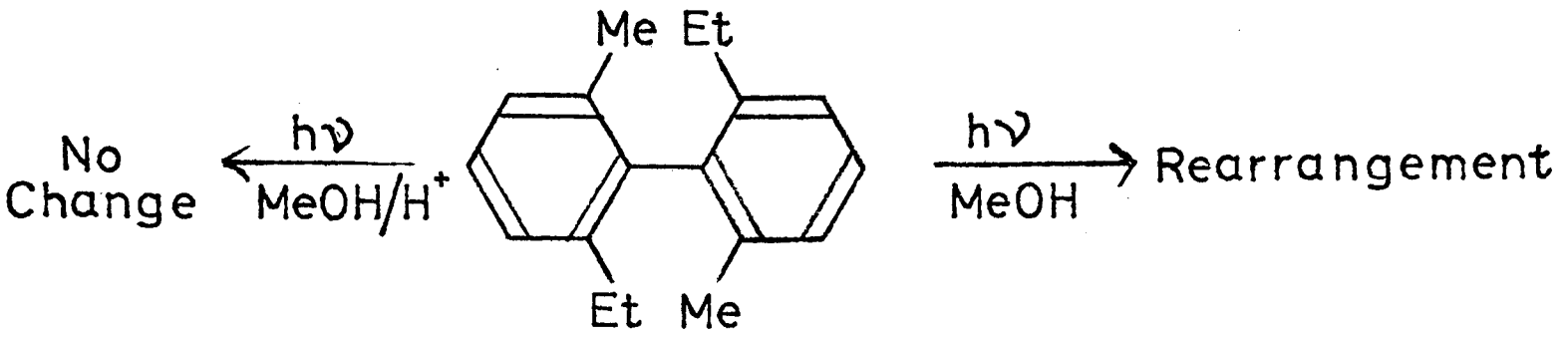
(34) (29)



Wilzbach and Kaplan [3, 25, 26, 52] also reported that, although benzene itself did not form any bicyclohexenyl ethers analogous to (35) in neutral methanol, similar species, (8) to (11), were formed when irradiation was carried out in weakly acidic methanol. These species were shown to form via solvation of benzvalene (2).[25]



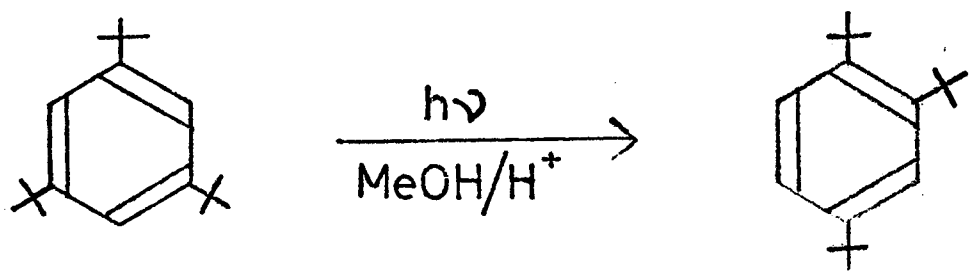
Since the rearrangement of benzenoid aromatics is assumed to require the intermediacy of a benzvalene, it might be expected that irradiations carried out in acidic solvents, where the benzvalene should be efficiently destroyed, will not show rearranged benzenoid isomers among the products. Indeed, 2,2'-dimethyl-6,6'-diethylbiphenyl (102), which rearranged photochemically in the absence of acid, showed no rearrangement upon photolysis in acidified methanol.[64]



(102)

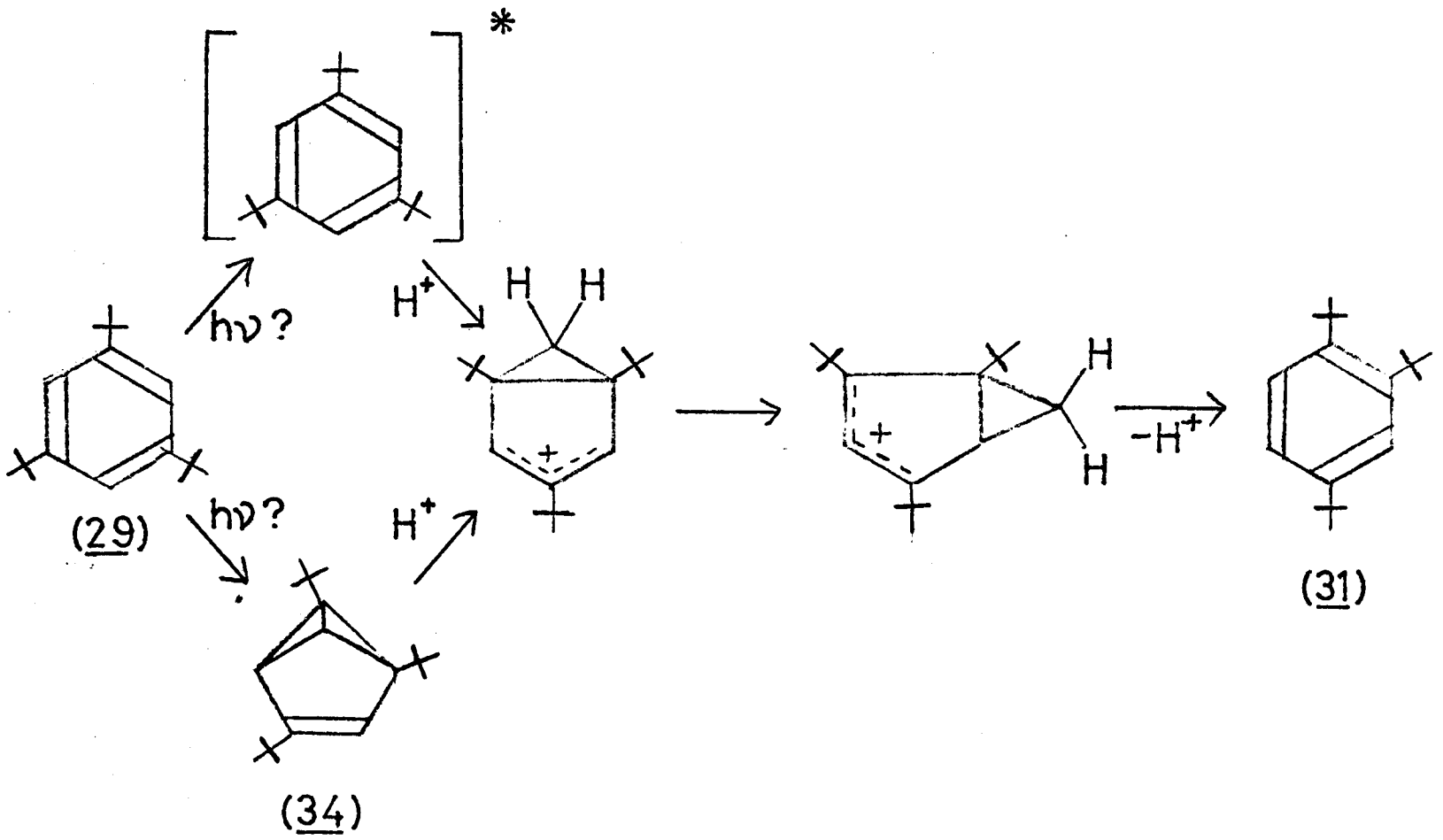
However, when Gem[104] irradiated o-xylene in acidified methanol, he found that isomerisation to m-xylene still occurred, the yield apparently increasing with acid concentration. In addition, he noted the formation of several species with molecular weights consistent with their being adducts of o-xylene with methanol, although none were isolated or identified.

Owing to the overall complexity of the xylene system, Tolliday[105] investigated the behaviour of the 1, 3, 5-tri-t-butylbenzene system. He found that irradiation of 1, 3, 5-tri-t-butylbenzene in weakly acidic methanol resulted in the formation of 1, 2, 4-tri-t-butylbenzene, together with the bicyclohexenyl ether (35) in close agreement with Gem's general observations. At higher acid concentrations the rearranged isomer was the exclusive product.



(29) (31)

Tolliday proposed that a novel mechanism for transposition was in operation, involving protonation of either the excited state or the unstable benzvalene (34), followed by a 1, 4- migration as indicated in the scheme below:-



The object of this study was to investigate further the nature of the rearrangement taking place in acidic methanol.

RESULTS AND DISCUSSION

Preliminary irradiations of 1, 3, 5-tri-t-butylbenzene (29) were employed as convenient synthetic routes to important reference compounds[3, 52,56]. Thus, 1, 2, 4-tri-t-butylbenzene (31) and 1, 2, 5-tri-t-butylDewarbenzene (32) were prepared by photolysis of 1, 3, 5-tri-t-butylbenzene in hexane and subsequent separation of the photoproducts. The Dewar isomer (32) isolated was slightly contaminated with hydrocarbon residues, presumably derived from the hexane and column chromatography eluent. The 1, 2, 4-tri-t-butylbenzene was separated by preparative g. l. c.. Wilzbach and Kaplan [52, 56] reported that, in addition to the Dewar benzene isomer (32) and 1, 2, 4-tri-t-butylbenzene, 1, 3, 5-tri-t-butylprismane (33) and 1, 3, 6-tri-t-butylbenzvalene (34) were present in the photolysis mixture; no attempt was made to isolate these compounds, however.

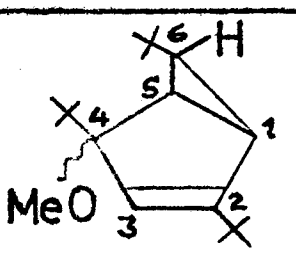
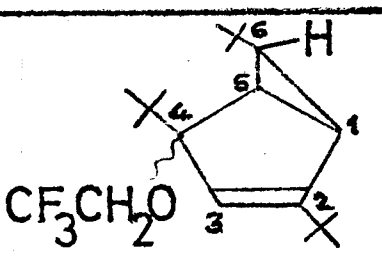
The methanol adduct, 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo-[3. 1. 0]hex-2-ene (35) [26, 52] was prepared by photolysis of 1, 3, 5-tri-t-butylbenzene in methanol. Interestingly, Wilzbach and Kaplan [26, 52], and Tolliday [105] reported that the adduct (35) was the only product visible in the n. m. r. spectrum of the photoproduct and the only product isolated. However, in this study, the n. m. r. spectrum of the crude photolysate showed two additional signals. The first, at 6. 75τ had intensity ca 10% that of the methoxy signal (7. 01τ) from the reported adduct (35). The second was at 8. 90τ and was ca 10% of the intensity of the t-butyl signal at 8. 87τ assigned to the adduct (35). Furthermore, the t-butyl signal at 9. 10τ , from the adduct (35), showed greater intensity than either of the other t-butyl signals at 8. 87 or 9. 04τ.

Closer analysis of Tolliday's spectra revealed that the signals at 6. 75 and 8. 90τ were, in fact, present in his photoproduct.

The n. m. r. spectrum of the mother liquor remaining after recrystallisation of the adduct (35) indicated that it contained ca 50% of an unreported product, X. Column chromatography yielded a fraction composed almost entirely of X. X was further purified by two successive p. l. c. s on neutralised alumina plates.

Microanalysis and the close correspondence of spectral data from X and adduct (35) suggested that X was also an adduct with methanol. The overlap of resonances in the 8.6 - 9.4 region did not allow unambiguous assignment of structure for X. However, comparison of Wilzbach and Kaplan's data [52] for the two 4-trifluoroethoxy-2,4,6-exo-tri-t-butyl-bicyclo [3.1.0] hex-2-enes (100), assumed to be stereoisomeric at C-4, with that for X and the adduct (35) showed that the spectral differences observed might be consistent with X and the adduct (35) also being stereoisomers (See Table 1).

TABLE 1

N.m.r. spectral assignment	X.	 (35)	 (100)	
	τ	τ	τ	τ
H at C-3	5.22	5.24	5.17	5.08
H at C-5	8.48	8.31	8.37	8.23
H at C-1	8.6 — 9.4	8.86	8.71	8.73
H at C-6		9.27	9.19	9.21
t-Bu	8.90	8.87	8.88	8.84
	9.10	9.04	9.06	8.97
		9.10	9.10	9.08
OR (R=CH_3 or CH_2 CF_3)	6.75	7.02	6.20	6.43
			6.22	6.46

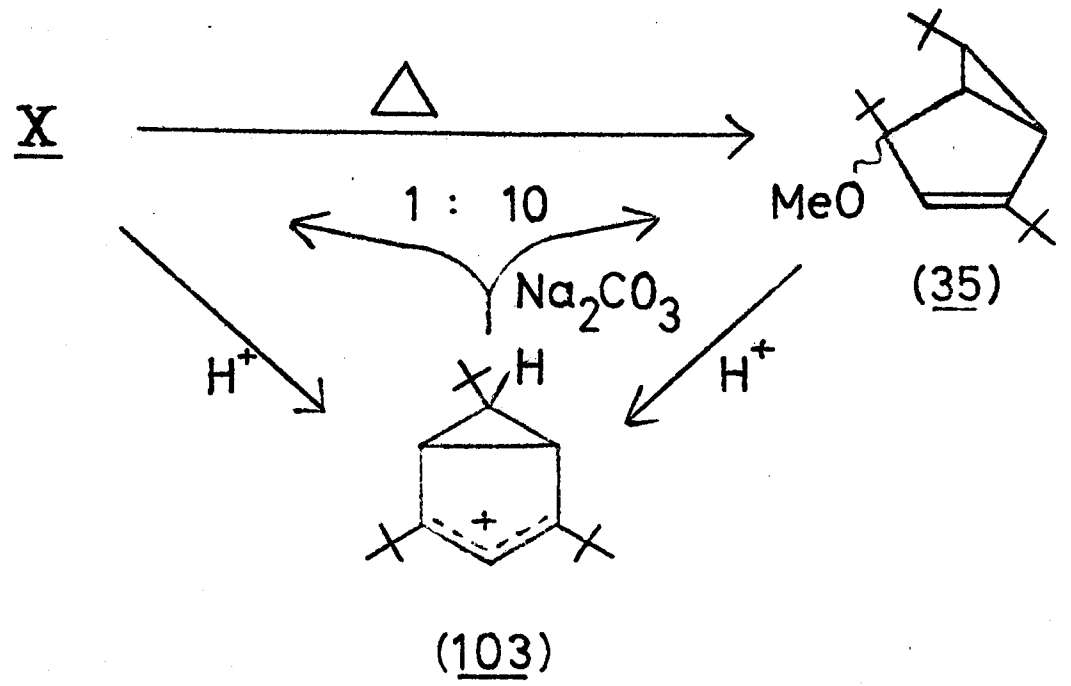
Wilzbach and Kaplan gave no i. r. data for the isomeric trifluoroethoxy adducts (100); however, the major differences in the i. r. spectra of X and the adduct (35) (in the 900-1000, 1070-1090 and 1620-1630 cm^{-1} regions) might result from the changed environment of the methoxy and olefinic groups in the two compounds.

On standing for several weeks at room temperature X rearranged to the adduct (35), as evidenced by n. m. r. and i. r. spectral changes.

The effects of acidification and subsequent neutralisation of both X and the adduct (35) were investigated by n. m. r. spectroscopy. Each was dissolved in methanol; for X the lowest field t-butyl signal was partially resolved into two singlets of equal intensity. Addition of acidified methanol to either sample produced the yellow bicyclohexenyl cation (103), identified by Tolliday, [105] implying that both X and the adduct (35) had the same basic skeletal structure. Subsequent neutralisation of either sample with sodium carbonate yielded a mixture of both the adduct (35) and X in a ratio ca 10:1.

It is possible that the observed transformation of X into adduct (35) over a period of several weeks reflects the presence of acid sites on the flask walls.

These experiments, taken in conjunction with the spectroscopic data, suggested most strongly that X was an adduct, stereoisomeric with the adduct (35) at C-4.



(103)

Since the photolyses of interest were to be carried out under acidic conditions, the effects of added acid on 1, 2, 5-tri-t-butylDewarbenzene (32), 1, 3, 5-tri-t-butylbenzene and 1, 2, 4-tri-t-butylbenzene were investigated.

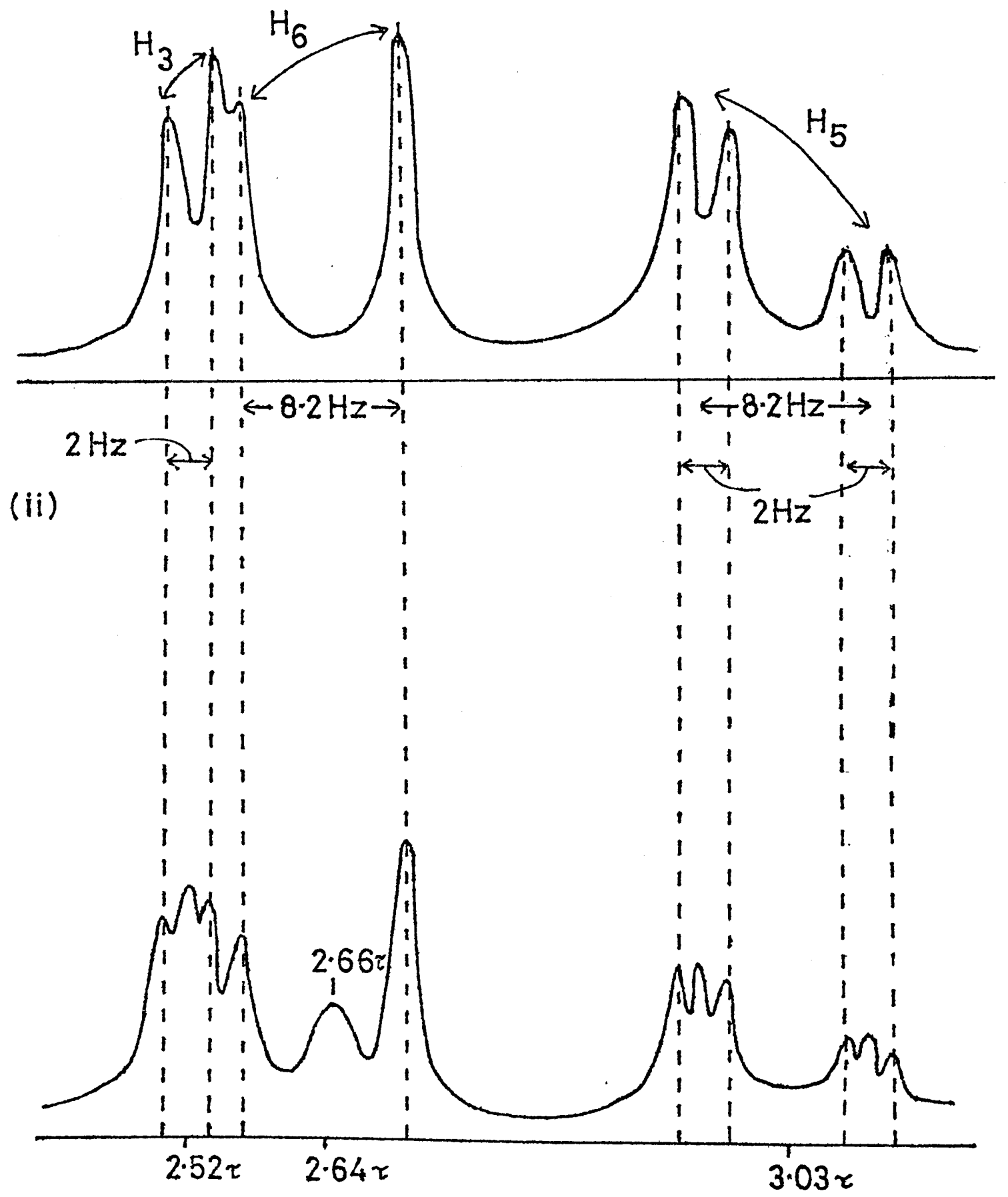
N. m. r, U. V., and g. l. c. analyses showed that 1, 2, 5-tri-t-butylDewarbenzene (32) remained unchanged and, hence, it was concluded that this isomer could only react photochemically(if at all) under acidic conditions.

The U. V. spectra of both 1, 3, 5- and 1, 2, 4-tri-t-butylbenzene showed no changes upon acidification. This indicated that the photochemistry of these compounds was initiated in neutral, ground-state molecules and not from protonated species. However, subsequent protonation of the excited state remained a possibility.

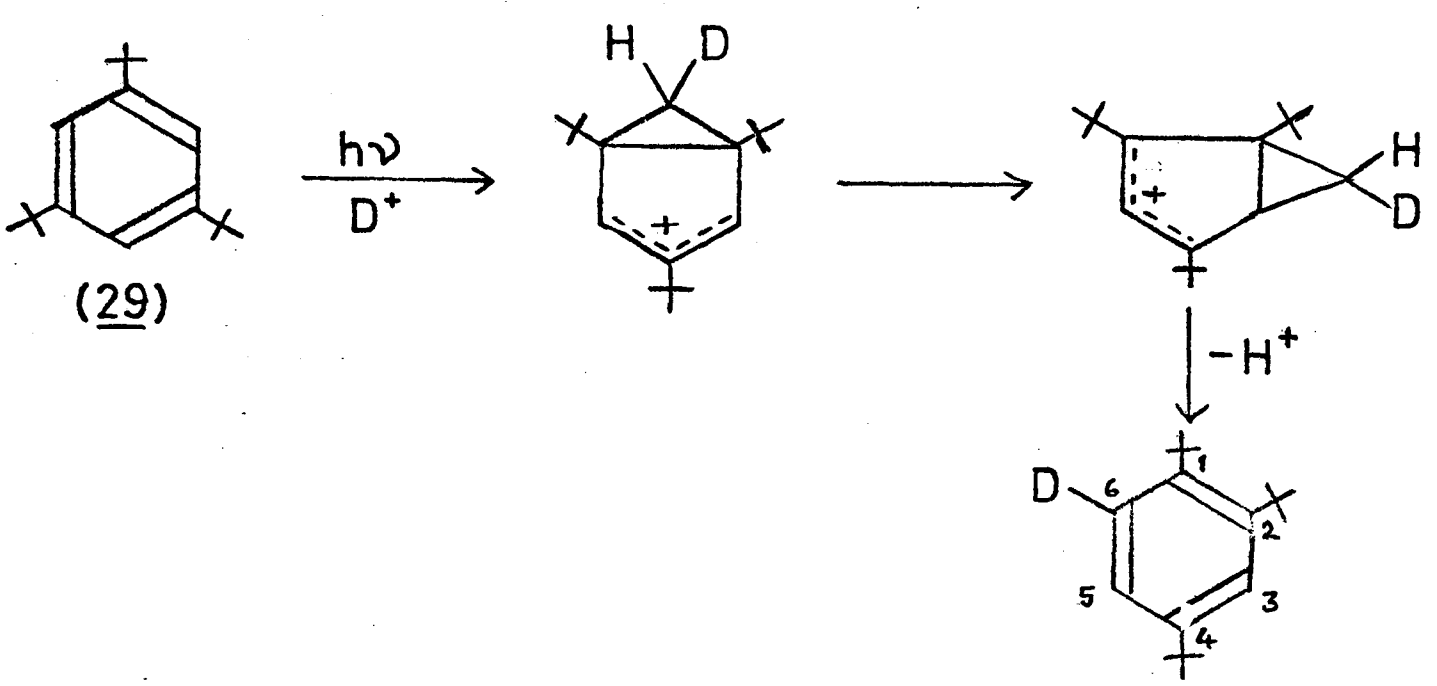
The first acidic photolysis carried out was a repeat of one of Tolliday's experiments.[105] 1, 3, 5-Tri-t-butylbenzene was irradiated in acidified methanol; g. l. c. analysis indicated that two new products were formed. The major product (ca 25%) had a retention time the same as that of 1, 2, 4-tri-t-butylbenzene, the product reported by Tolliday. The second product (ca 1%), not reported by Tolliday, had retention time ca 0. 5 that of 1, 3, 5-tri-t-butylbenzene, the same as 1, 2, 5-tri-t-butyl-Dewarbenzene (32). After neutralisation the n. m. r. spectrum of the photolysate confirmed that 1, 2, 4-tri-t-butylbenzene was the major photoproduct. Weak resonances at the same τ values as the t-butyl groups in 1, 2, 5-tri-t-butylDewarbenzene (32) could also be discerned.

Figure 3

N.M.R. Spectra : Aromatic Proton Regions of
(i) Authentic 1,2,4-tri-t-butylbenzene
(ii) 1,2,4-Tri-t-butylbenzene isolated from acidic methanol-O-d photolysis of 1,3,5-tri-t-butylbenzene



In order to obtain further information about the acidic photolyses, 1, 3, 5-tri-t-butylbenzene was irradiated in acidified methanol-O-d (> 95% d). If the mechanism proposed by Tolliday[105] (See page 31) had been in operation, the 1, 2, 4-tri-t-butylbenzene photoproduct would have shown deuterium incorporation at C-6 as shown below:-



(29)

The aromatic proton regions of the n. m. r. spectra of (i) authentic 1, 2, 4-tri-t-butylbenzene and (ii) the 1, 2, 4-tri-t-butylbenzene isolated from the acidic methanol-O-d irradiation are shown in Figure 3.

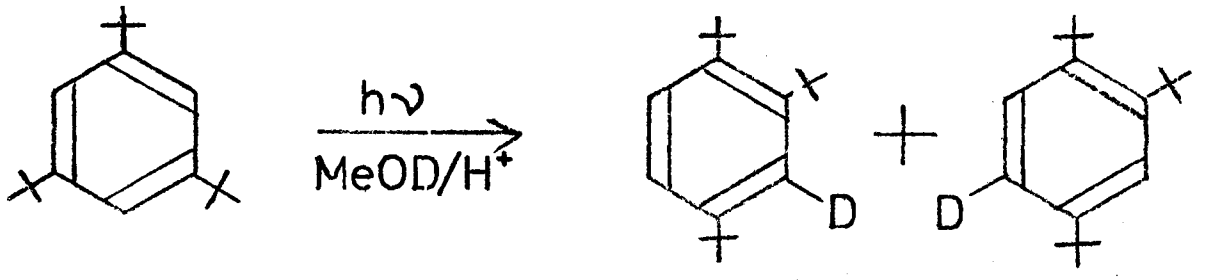
The origin of the signals in the aromatic proton region of the authentic 1, 2, 4-tri-t-butylbenzene are summarised below:-

2.52 τ	—	(d, $J_{3,5}$ = 2Hz)	- H_3
2.64 τ	—	(d, $J_{6,5}$ = 8.2Hz)	- H_6
3.03 τ	—	(d, d, $J_{5,3}$ =2 Hz, $J_{5,6}$ = 8.2Hz)	- H_5

N.B. No para-coupling of H_3 and H_6

It was clear that new resonances were present in each of the proton regions for the acidified methanol-O-d photoproduct. The observation that no new resonance was observed at ca 3.03 τ in the H_5 region indicated that no deuterium had been incorporated at C_6, since this would have resulted in an uncoupled H_5 resonance. In contrast, the new resonance at 2.66 τ , in the H_6 region, strongly suggested that deuterium incorporation at C_5 had occurred, resulting in an uncoupled H_6 resonance. Further, since the coupling observed in the H_3 region arose from H_3-H_5 coupling, the new signal at ca 2.52 τ must be due to H_3, no longer coupled to H_5, and thereby confirmed deuteriation at C_5.

Two new signals were also present in the H_5 region, coupled to H_6, but not to H_3. It was concluded therefore, that deuteration at C_3 must also have occurred.



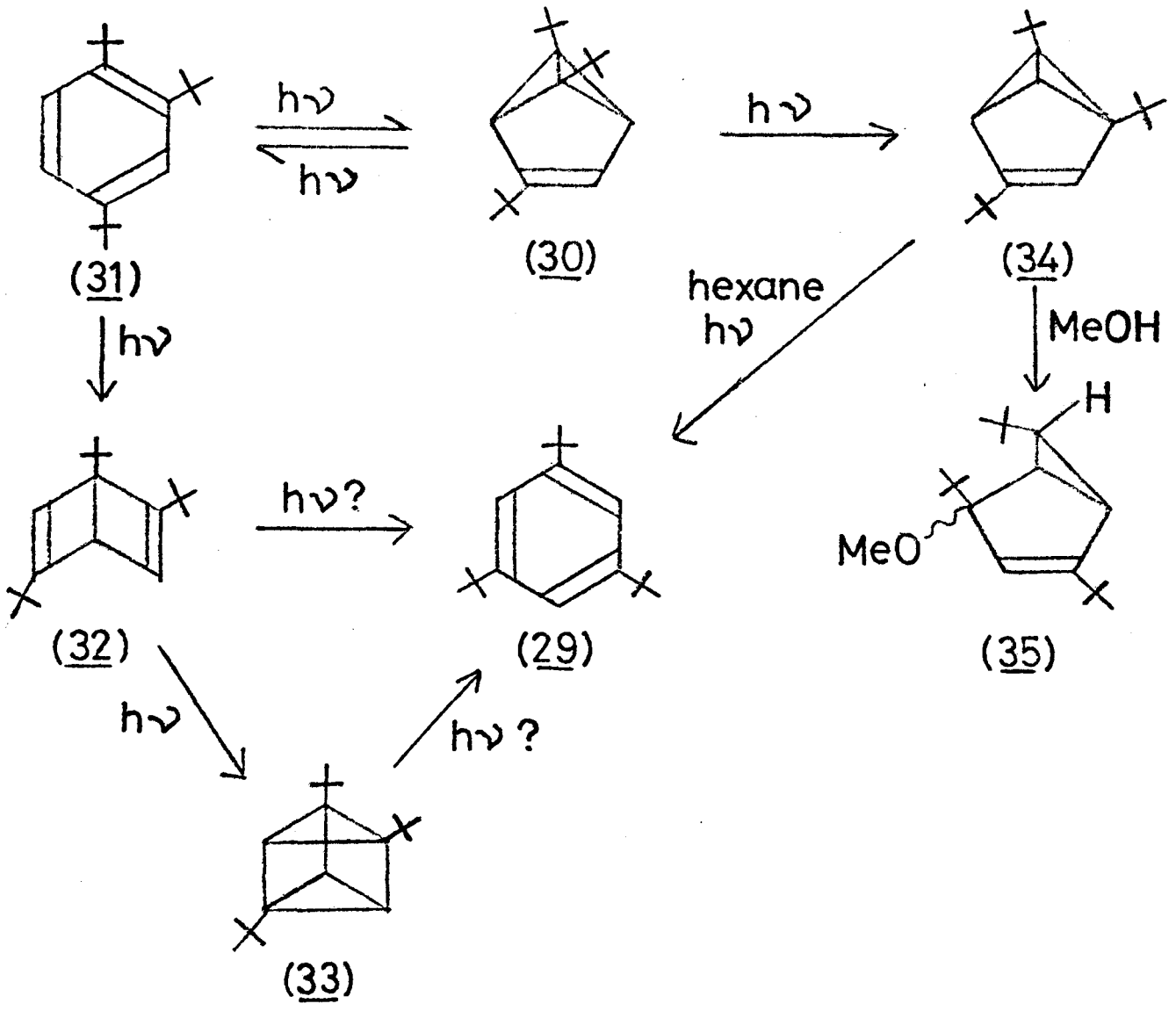
Mass spectroscopy confirmed that deuterium incorporation had occurred, but could not reveal the positions of deuteriation.

It was apparent from these observations that Tolliday's mechanism was not correct.

Since the degree of conversion to 1, 2, 4-tri-t-butylbenzene in the above experiment had to be high (ca 30%) in order to isolate sufficient product for analysis, it was very likely that the 1, 2, 4-tri-t-butylbenzene photoproduct itself underwent secondary photolysis. In order to evaluate any such effects the photochemistry of this isomer was studied in some detail.

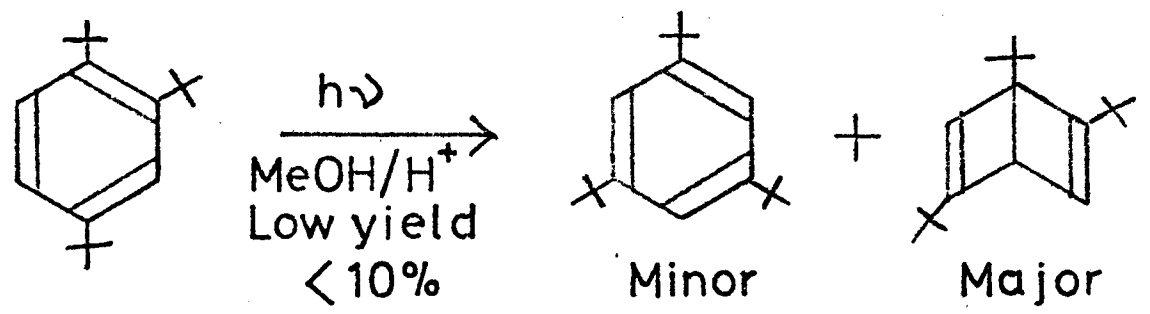
Comparative photolyses of 1, 2, 4-tri-t-butylbenzene in hexane, methanol and acidified methanol were carried out. As reported by Wilzbach and Kaplan [56], the principal products in hexane were 1, 3, 5-tri-t-butylprismane (33), 1, 2, 5-tri-t-butylDewarbenzene (32) and 1, 3, 5 -tri-t-butylbenzene. G. l. c. showed one signal only for both the Dewarbenzene (32) and the prismane (33), which, in fact, was the major product.

The n. m. r. spectrum of the methanol photoproduct revealed that again the prismane (33), the Dewarbenzene (32) and 1, 3, 5-tri-t-butylbenzene were present. However, the adduct (35) was also present . These two sets of results were rationalised using Wilzbach and Kaplan's data as indicated below:-



Photolysis of 1, 2, 4-tri-t-butylbenzene (31) in either methanol or hexane yielded the Dewarbenzene (32) and the prismane (33) as primary and secondary photoproducts respectively. As an alternative primary photochemical pathway, the 1, 2, 4-tri-t-butylbenzene also photolysed to the benzvalene (30), which was stable in methanol[26]. The benzvalene (30) then underwent secondary photolysis to the benzvalene (34) or back to 1, 2, 4-tri-t-butylbenzene. The final step in methanol was thermal and yielded the adduct (35), whereas, in hexane, it was photochemical and yielded 1, 3, 5-tri-t-butylbenzene. The formation of some 1, 3, 5-tri-t-butylbenzene in the methanol photolysis confirmed that the Dewarbenzene (32) and/or the prismane (33) can act as precursors to 1, 3, 5-tri-t-butylbenzene directly, as suggested by Wilzbach and Kaplan[56].

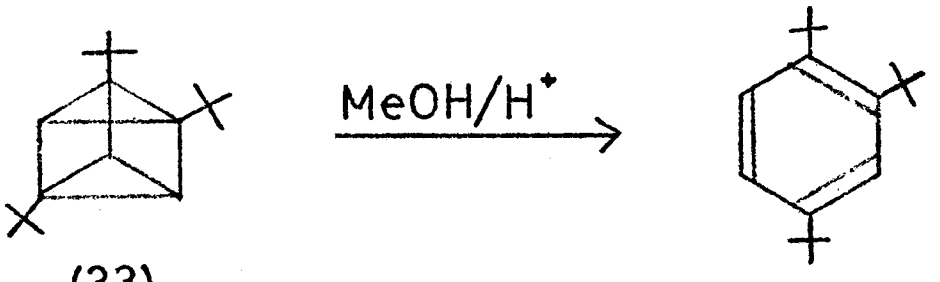
In contrast, 1, 2, 4-tri-t-butylbenzene in acidified methanol showed very little change after irradiation; > 90% of starting material remained. N. m. r. revealed that the Dewarbenzene (32) was the major photoproduct with a little 1, 3, 5-tri-t-butylbenzene also present.



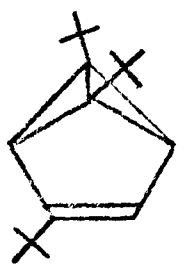
The fact that the prismane (33) was not observed among the photoproducts suggested that the prismane (33) might be labile in the presence of acid, tested by the experiment described below.

1, 2, 4-tri-t-butylbenzene was irradiated in hexane, as above, the photolysis products being analysed by g. l. c.. The hexane was removed and the residue dissolved in carbon tetrachloride for analysis by n. m. r. spectroscopy. This showed that the prismane (33), the Dewarbenzene (32) and 1, 3, 5-tri-t-butylbenzene had been formed.

G.l. c.revealed that no change had taken place during this procedure. The carbon tetrachloride was removed and the residue was dissolved in methanol. Yet again g.l. c. revealed that no change had occurred. The methanolic solution was then acidified to 0. 1M and again analysed by g.l. c., This now revealed that the signal assigned to both the Dewar (32) and the prismane (33) had decreased in intensity while that of the 1, 2, 4-tri-t-butylbenzene had increased. The residue was analysed by n. m. r. spectroscopy after neutralisation, removal of methanol and dissolution in carbon tetrachloride. Only the signals due to the prismane were no longer present and, therefore, it was clear that the acid had reacted with the prismane to yield 1, 2, 4-tri-t-butylbenzene. This observation was in agreement with the results of Kaiser et al [107] who had also noted that the stable benzvalene (30) was unchanged under acidic conditions.



(33) (31)



(30)

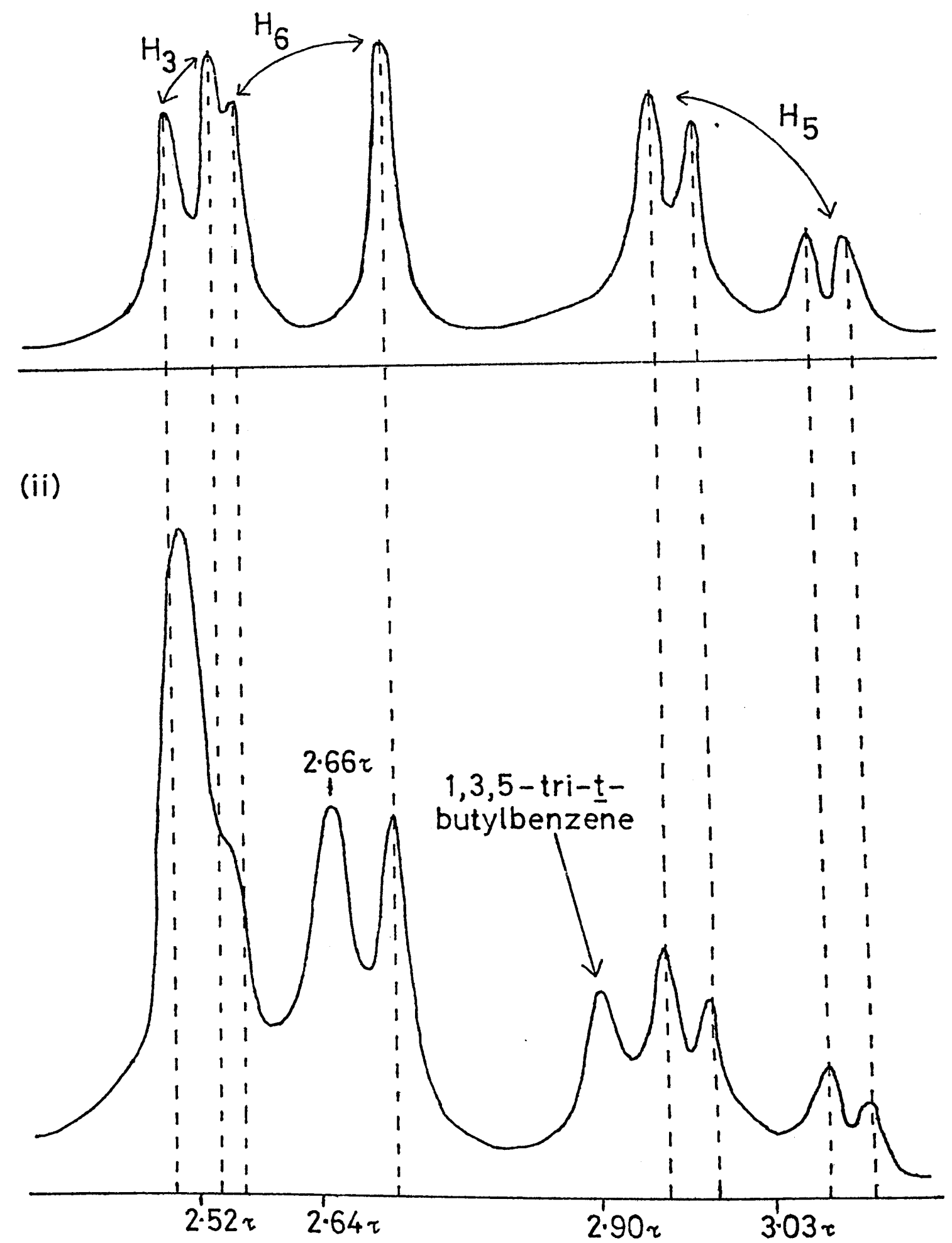
Thus a potential mechanism for the incorporation of deuterium into 1, 2, 4-tri-t-butylbenzene upon photolysis in acidic methanol-O-d existed. It was, therefore, necessary to find out if deuterium could be incorporated into the recovered 1, 2, 4-tri-t-butylbenzene and, if so, where. 1, 2, 4-Tri-t-butylbenzene was irradiated in 0. 1M acidified methanol-O-d for 40h. G. l. c. indicated that ca 80% starting material remained, the Dewarbenzene (32) and 1, 3, 5-tri-t-butylbenzene (29) being

Figure 4

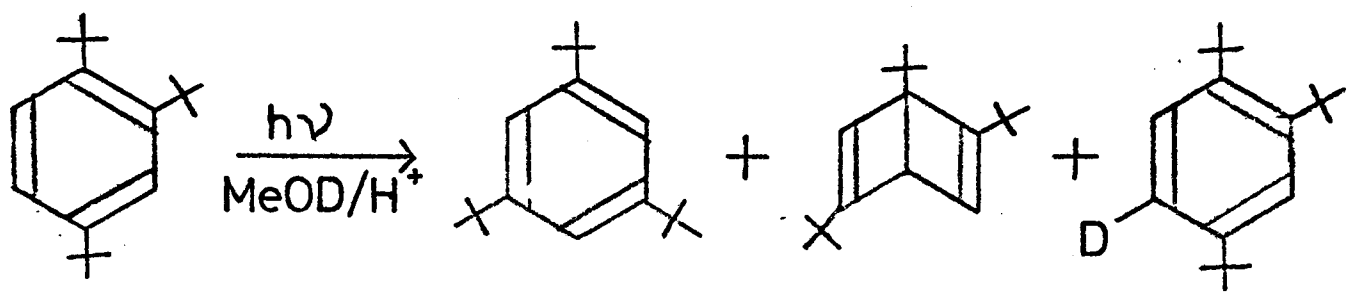
N.M.R. Spectra: Aromatic Proton Regions of

(i) Authentic 1,2,4-tri-t-butylbenzene

(ii) Product from 1,2,4-tri-t-butylbenzene photolysis in methanol-O-d

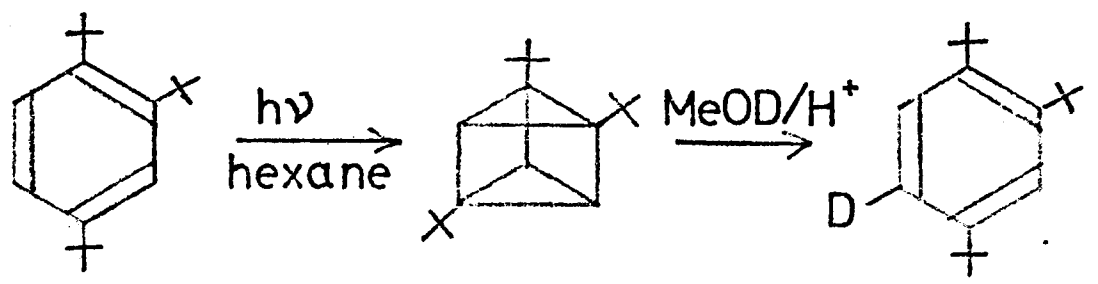


the products, as before. The n. m. r. spectrum of the photolysate in the aromatic proton region, is shown in Figure 4. It was clear that a new signal was present at 2.66 τ in the H_6 region (cf 1, 3, 5-tri-t-butylbenzene irradiation in acidic methanol-O-d) and that the H_3 doublet had been modified, presumably by a new signal formed between the two components of the H_3 doublet at 2.52 τ. There was no change in the H_5 region, consistent with deuteriation at C_5 having occurred. The mass spectrum confirmed that deuteriation had taken place.



(31) (29) (32)

This experiment showed that incorporation of deuterium at C_5 did take place upon photolysis of 1, 2, 4-tri-t-butylbenzene in acidic methanol-O-d but did not prove the intermediacy of the prismane (33). It was necessary to show that attack of acidified methanol-O-d on the prismane (33) did produce such incorporation. This was achieved by producing the prismane (33) as a photoproduct of 1, 2, 4-tri-t-butylbenzene in hexane, as in the experiment described earlier. The n. m. r. spectra taken after removal of the hexane and after addition of methanol-O-d were identical. This indicated that the prismane (33) was stable in neutral solution. Only after addition of acid did the signals due to the prismane (33) disappear. Analysis indicated that, as above, deuterium had been incorporated at H_5. The n. m. r spectra are shown in Figures 5 and 6.



(31) (33)

Figure 5

N.M.R. Spectra : t-Butyl Proton Regions of

(i) Product from photolysis of 1,2,4-tri-t-butylbenzene in hexane

(ii) Above photoproduct after addition of acidified methanol-O-d

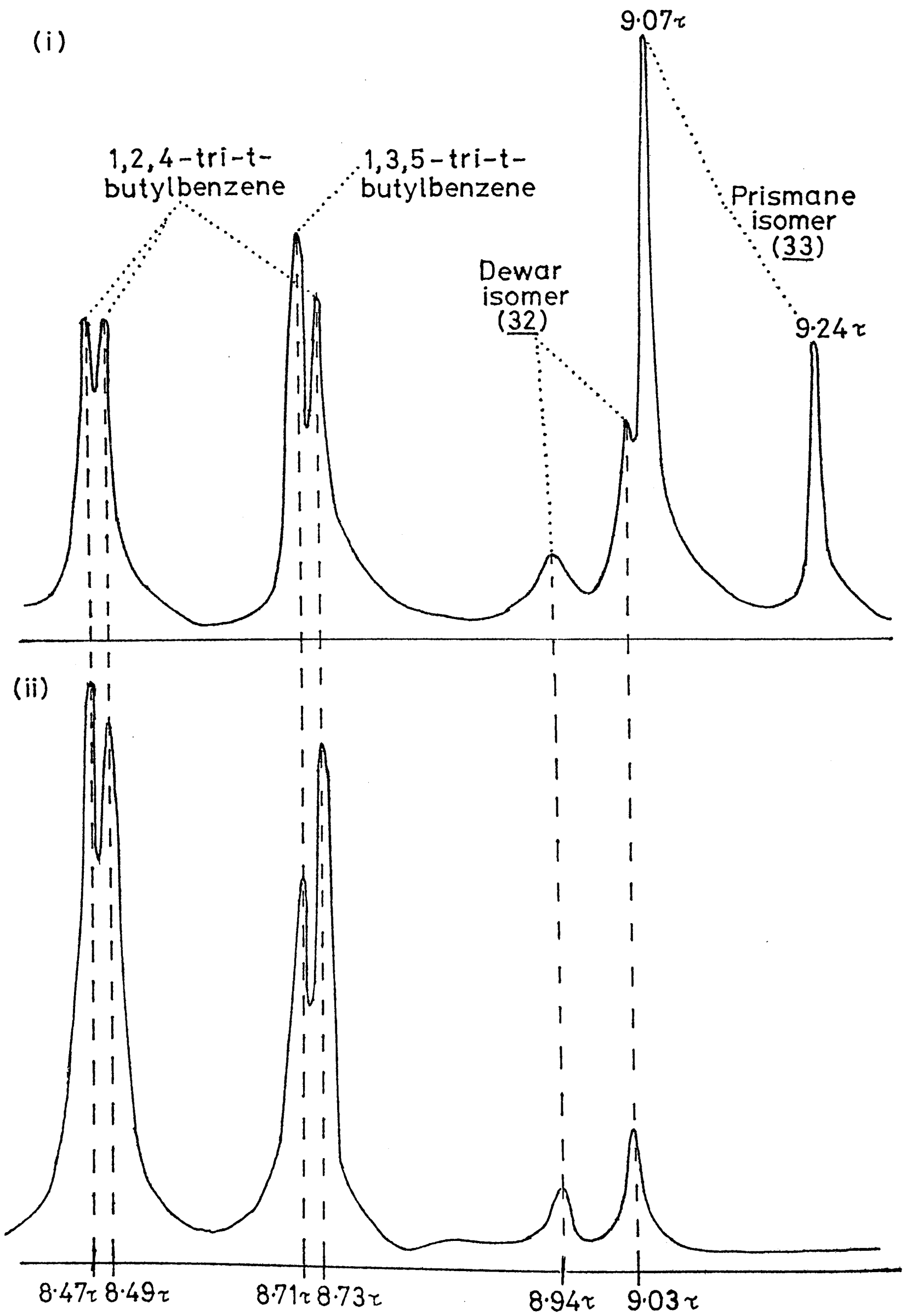
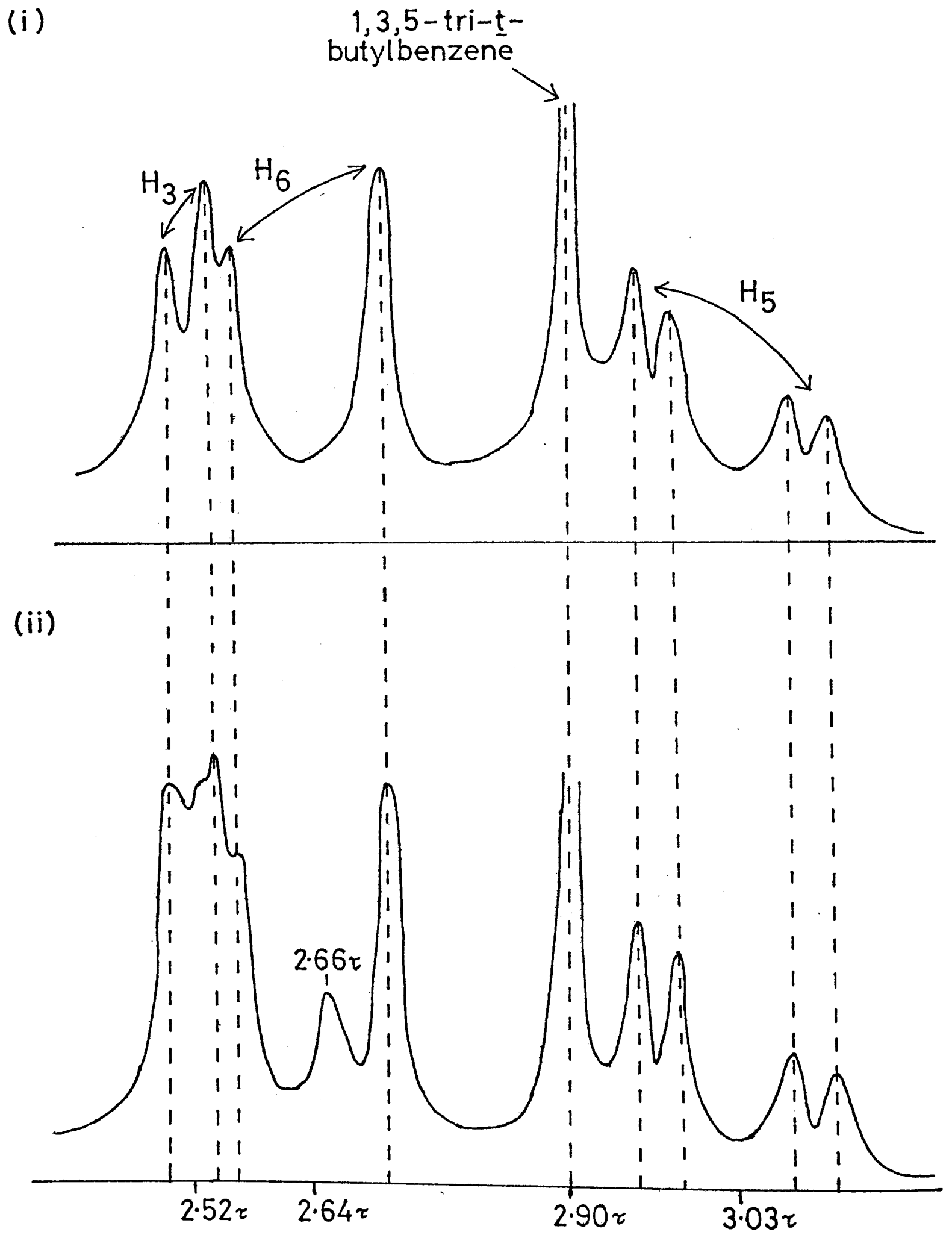
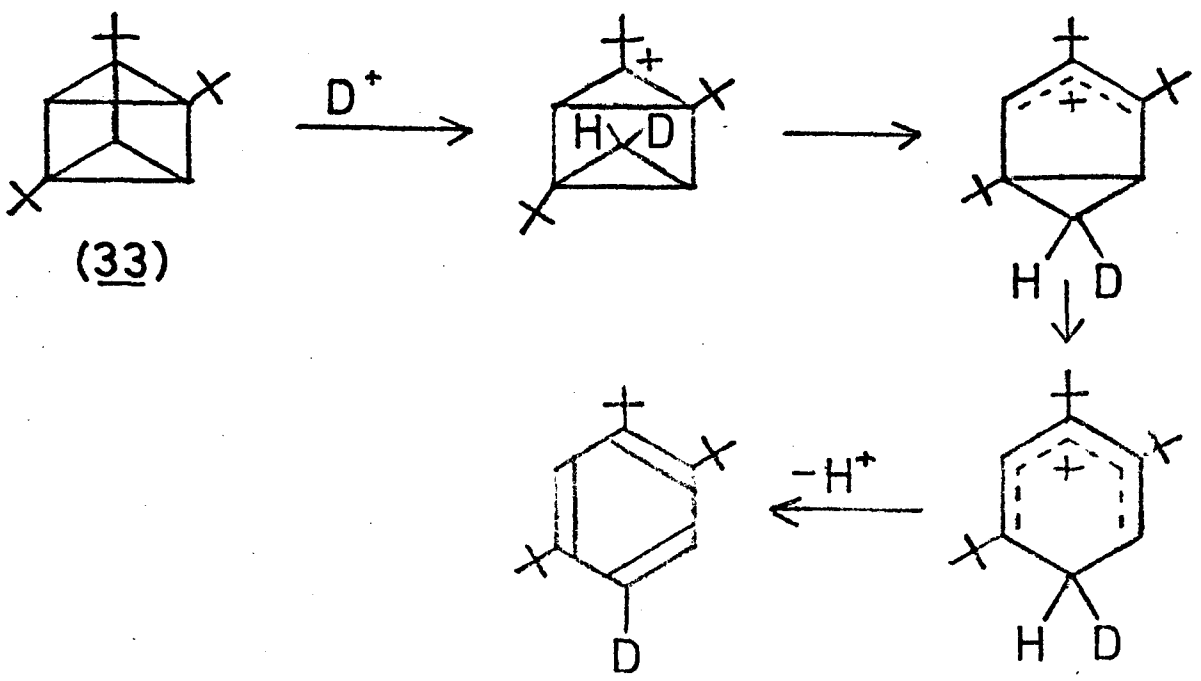


Figure 6

N.M.R. Spectra: Aromatic Proton Regions of
(i) Product from photolysis of 1,2,4-tri-t-butylbenzene in hexane
(ii) Above photoproduct after addition of acidified methanol-O-d

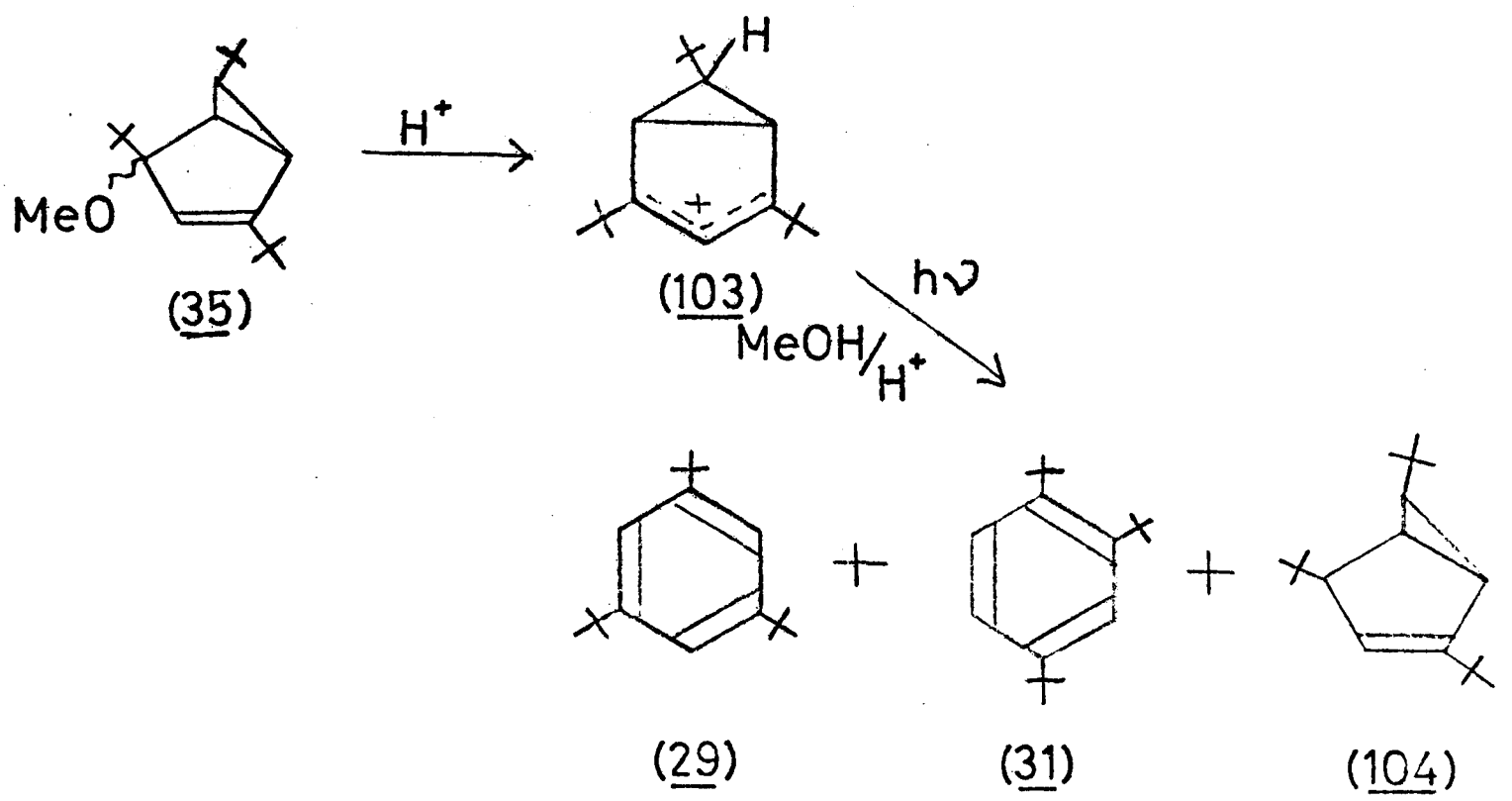


This series of experiments indicated that the deuterium incorporation observed at C_5 in the 1, 2, 4-tri-t-butylbenzene photoproduct, derived from photolysis of 1, 3, 5-tri-t-butylbenzene in acidic methanol-O-d, arose as a result of secondary photolysis of pre-formed 1, 2, 4-tri-t-butylbenzene, followed by attack of acid on the prismane (33) thereby produced. The mechanism of the reaction with acid is not known. A possible mechanism is shown below:-



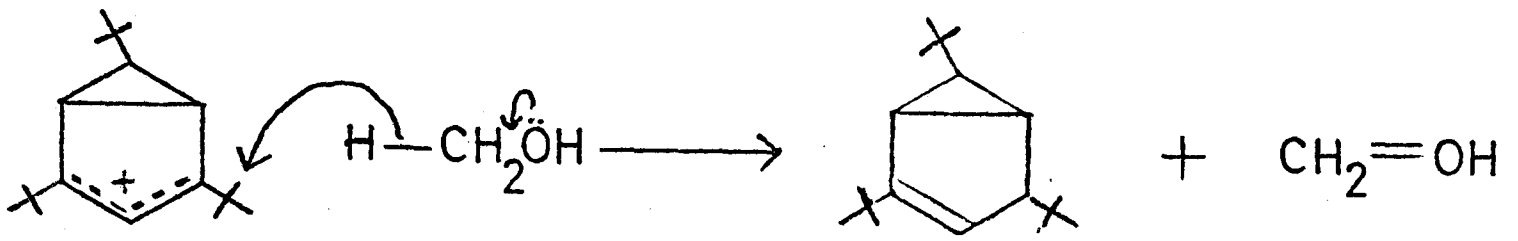
(33)

Tolliday [105] reported that irradiation of the 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3. 1. 0] hex-2-ene (35) in acidified methanol yielded 1, 3, 5-tri-t-butylbenzene, and 2, 4, 6-tri-t-butyl-bicyclo [3. 1. 0.] hex-2-ene(104) as major products, together with some 1, 2, 4-tri-t-butylbenzene.



(35) (103) (29) (31) (104)

The 2, 4, 6-tri-t-butylbicyclo [3. 1. 0]hex-2-ene (104) had been shown to be formed in a thermal reaction of the bicyclohexenyl cation with methanol, presumably via a hydride transfer reaction [105].



(103) (104)

The formation of 1, 2, 4-tri-t-butylbenzene among the photo-products of the adduct (35) in acidified methanol provided another possible route to the 1, 2, 4-tri-t-butylbenzene, seen in the acidic photolysis of 1, 3, 5-tri-t- butylbenzene, if the adduct (35) should be formed as a transient intermediate. This was thought unlikely since none of the bicyclo[3. 1. 0]hex-2-ene (104) was ever observed; nevertheless the photolysis of the adduct (35) was investigated further.

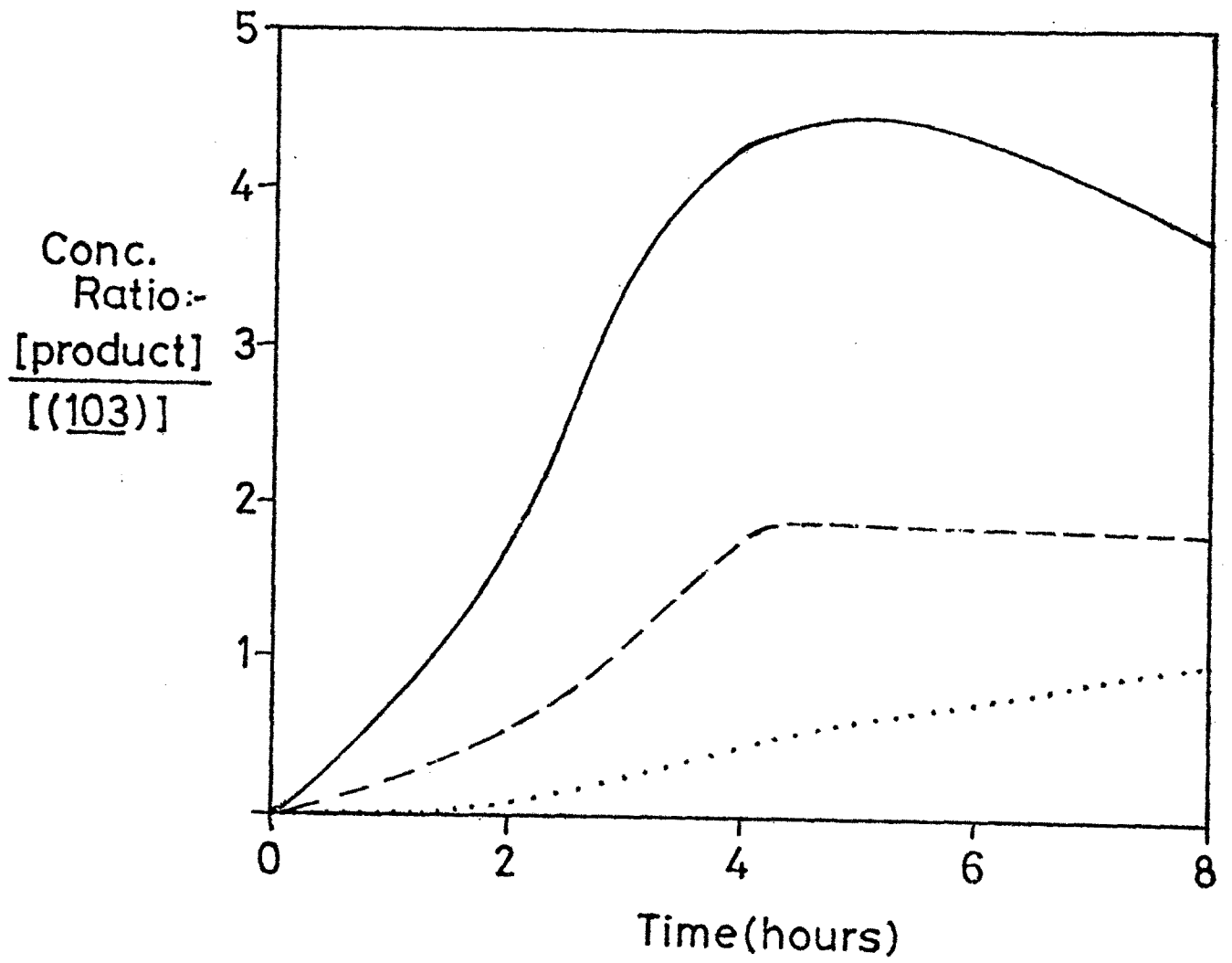
In a preliminary experiment the adduct (35) was irradiated both in methanol and in acidified methanol. N. m. r. revealed that only X (ca 10%) had been produced from photolysis of the adduct (35) in methanol. However, whether this was really a photochemical process or whether it was due to the presence of some acidic impurity in the methanol was not clear and the reaction was not investigated further. In acidic methanol there was immediate formation of the bicyclohexenyl cation (103) which was actually the species photolysed. Analysis of the photoproduct by n. m. r. spectroscopy confirmed that, as Tolliday reported, the major products were 1, 3, 5-tri-t-butylbenzene and 2, 4, 6-tri-t-butylbicyclo [3. 1. 0.] hex-2-ene together with a little 1, 2, 4-tri-t-butylbenzene.

It appeared that insufficient 1, 2, 4-tri-t-butylbenzene was produced to account for that observed in the acidic photolyses of 1, 3, 5-tri-t-butylbenzene; however, an n. m. r. tube scale photolysis was carried out and the yields of the various products monitored by their n. m. r. spectra. Although the results obtained were only qualitative it was apparent that the yield of 1, 3, 5-tri-t-butylbenzene reached a maximum value and then began to decrease at the same time

Figure 7

Irradiation of 4-methoxy-2,4,6-exo-tri-t-butylbicyclo-[3.1.0]hex-2-ene : Variation of photoproduct concentration with time

(———) 1,3,5-tri-t-butylbenzene (29)
(- - - -) 2,4,6-tri-t-butylbicyclo[3.1.0]hex-2-ene (104)
(·····) 1,2,4-tri-t-butylbenzene (31)



as the yield of 1, 2, 4-tri-t-butylbenzene started to increase i. e. the appearance of 1, 2, 4-tri-t-butylbenzene was due to secondary photolysis of 1, 3, 5-tri-t-butylbenzene (See Figure 7). This experiment confirmed that the intermediacy of adduct (35) was not an issue in the production of 1, 2, 4-tri-t-butylbenzene from 1, 3, 5-tri-t-butylbenzene in acidic methanol.

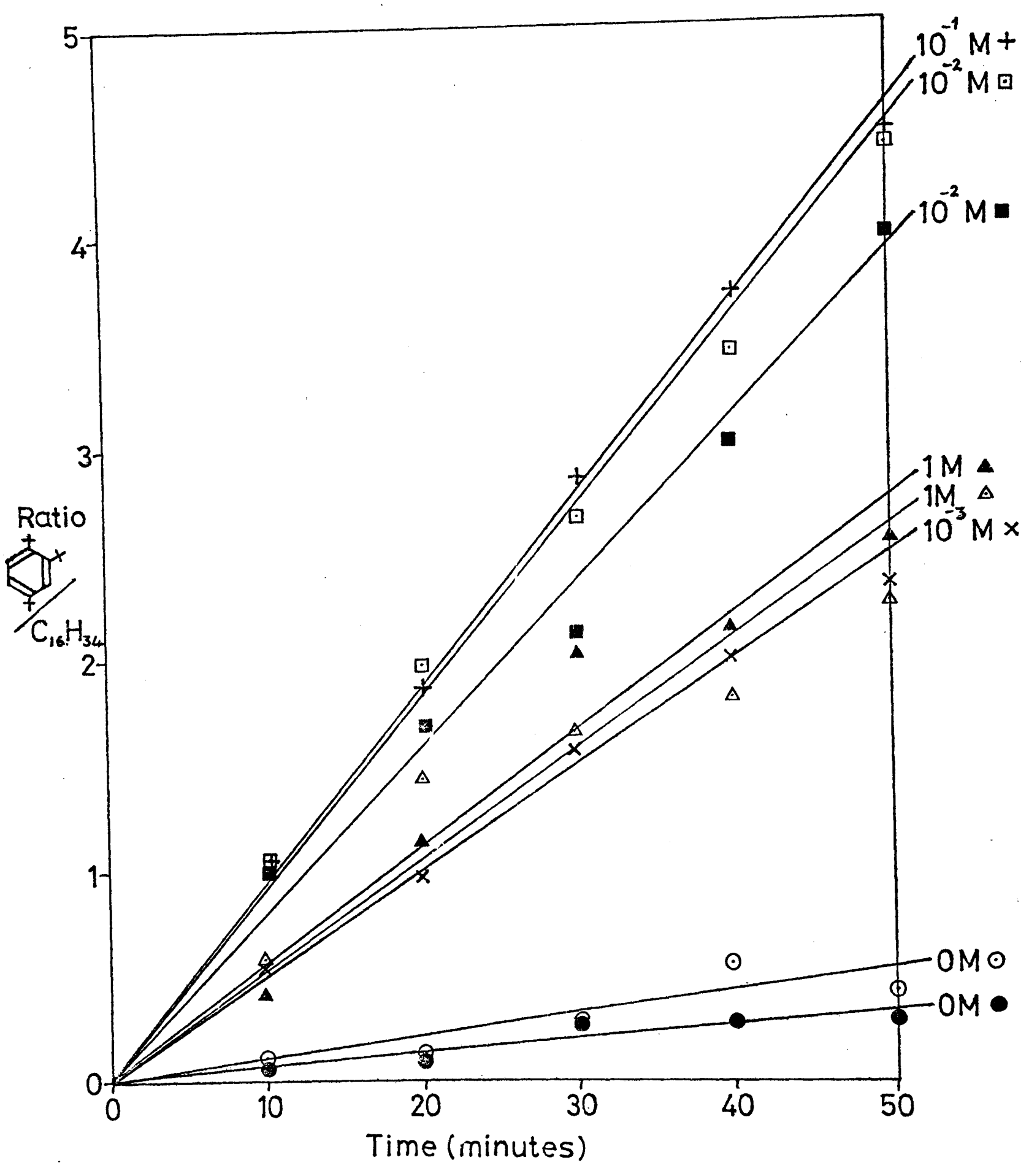
As yet, the equally improbable explanation that 'dark' deuterium incorporation reactions might be taking place had not been ruled out. Therefore, two independent series of four experiments were carried out. In each series, 1, 3, 5- or 1, 2, 4-tri-t-butylbenzene was dissolved in either neutral methanol-O-d (with excess sodium carbonate present) or acidified methanol-O-d. One set was kept in the dark; the other was irradiated to ensure that the photochemistry, previously observed, was taking place. Analysis of each of the 'dark' reactions by n. m. r. and mass spectroscopy showed that the starting materials were chemically unchanged and contained no deuterium. Spectroscopic evidence confirmed that the 'light' reactions had given the same products as those in earlier experiments. It is noteworthy that the irradiation of 1, 3, 5-tri-t-butylbenzene in neutral methanol-O-d, yielded the adduct (35) deuteriated at C_6, in agreement with Wilzbach and Kaplan's results [26].

The next parameter to be investigated was the change in yield of 1, 2, 4-tri-t-butylbenzene, from 1, 3, 5 -tri-t-butylbenzene, with change of acid concentration. Solutions of 1, 3, 5-tri-t-butylbenzene (ca 0. 04M) in methanol were acidified and irradiated for various times. The yield of the 1, 2, 4-tri-t-butylbenzene was found by cutting and weighing of g. l. c. peaks. In the first series of experiments the 1M acidic solution proved to be too polar and some of the hexadecane marker separated out. In order that the results from this solution might be compared with those from the remaining samples the measured weight of the hexadecane peak was scaled up by a factor, f, defined by the relation:

$$f = \frac{\text{Average hexadecane peak weight for all other samples}}{\text{Average hexadecane peak weight for the 1M sample.}}$$

Figure 8

Irradiation of 1,3,5-tri-t-butylbenzene in acidic methanol : Variation in yield of 1,2,4-tri-t-butylbenzene with acid concentration



This correction was quantitatively unsatisfactory, but did allow a qualitative comparison of the results.

In a second series of experiments, solutions of 1, 3, 5-tri-t-butylbenzene in OM, 10^{-2}M and 1M acidic methanol were studied. In the case of the 1M acid solution the weight of the hexadecane added was one-fifth of that added to the other solutions and, hence, an accurate scaling factor could be applied.

In all experiments the extent of conversion to 1, 2, 4-tri-t-butylbenzene was $< 5\%$.

The results obtained were analysed using a least mean squares computer programme. This programme provided a value for the correlation factor, which determined how 'good' the straight line actually was, in addition to the intercept and gradient of the line.

The experimental values may be found on page 78 of this thesis. The graphical representations of the results are shown in Figure 8.

'Good' straight lines (correlation factor > 0.99) were obtained for the two 10^{-2}, the 10^{-3} and the 10^{-1}M solutions. The gradients increased with increasing acid concentration and the intercepts on the y-axis were very close to the origin. The difference in gradient of the two 10^{-2}M samples may have resulted from slight variation in acid concentration, irradiation lamp output, g.l.c. detector response or some systematic error.

As expected, the first 1M acidic solution produced a 'poor' straight line plot (correlation factor 0.958) owing to the non-reproducability of sampling. However, the repeated 1M sample produced a straight line plot with correlation factor 0.980. Both lines passed close to the origin. The gradients of the straight lines were less than those of the

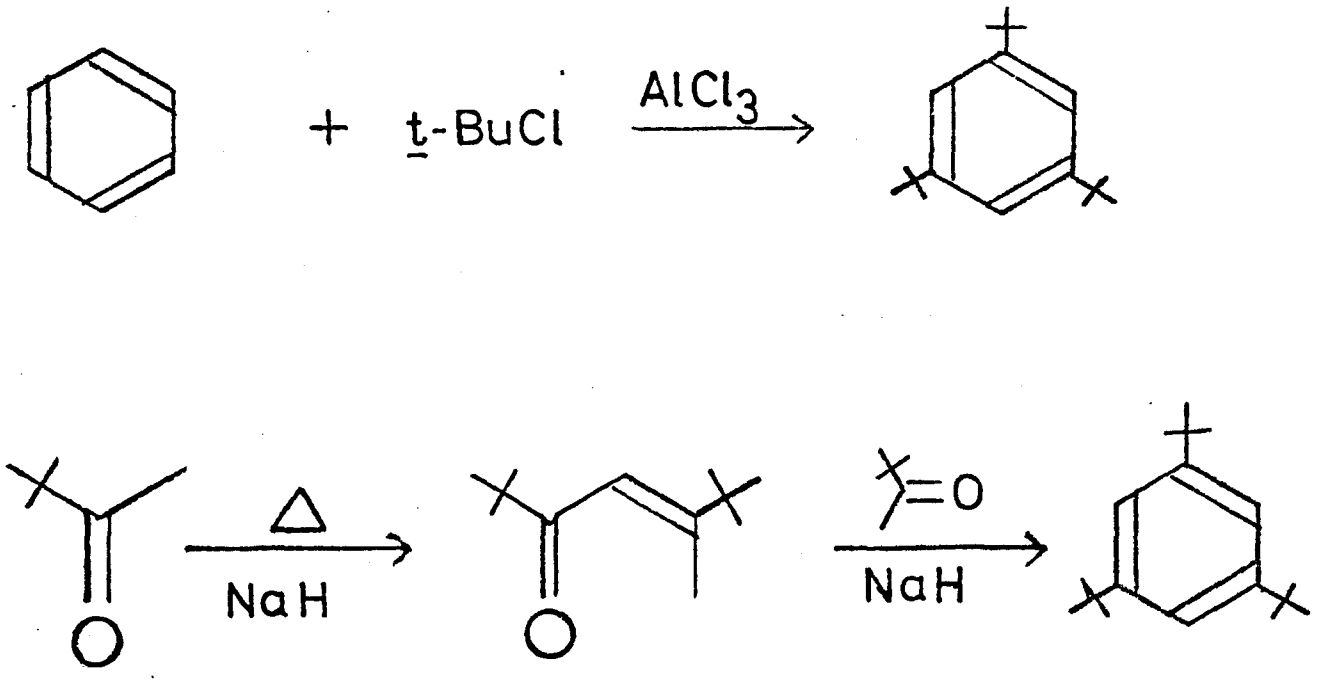
lower acid concentrations implying that the rate, at which 1, 2, 4-tri-t-butylbenzene was produced, initally increased with increasing acid concentration and then decreased.

In contrast, to the acidified solutions, the solutions which were not acidified showed very 'poor' straight line plots (correlation factor < 0.95). This was probably a reflection of the inaccuracy of measuring such small product peaks. It had been expected that no 1, 2, 4-tri-t-butylbenzene would be formed; in fact, the results indicated some conversion ($< 0.5\%$) to 1, 2, 4-tri-t-butylbenzene after 50 min. The small conversion observed might have been caused by a trace of acid present, either as an impurity in the methanol used or as a photo-oxidation product.

The reason for the cut-off in rate of 1, 2, 4-tri-t-butylbenzene formation at high acid concentrations was not clear. A possible explanation was that, at lower acid concentrations, the acid reacted with an intermediate, formed on photolysis of 1, 3, 5-tri-t-butylbenzene, to yield 1, 2, 4-tri-t-butylbenzene. At higher concentrations of acid, partial quenching of the excited state of 1, 3, 5-tri-t-butylbenzene may have occurred resulting in reversion to starting material and a reduction in the amount of 1, 2, 4-tri-t-butylbenzene produced. A recent paper reported that a similar effect had been observed in the photochemical addition reaction of a 4-pyrone with furan, as concentrations of furan were changed.[108]

It was hoped that by measuring the quenching of 1, 3, 5-tri-t-butylbenzene fluorescence in methanol with increasing acid concentration, the results of the above experiment might be rationalised more fully. Unfortunately, although it has been reported that 1, 3, 5-tri-t-butylbenzene does fluoresce[109], no fluorescence was observed in either hexane or methanol. Both solvents were fluorescer-free and the samples of 1, 3, 5-tri-t-butylbenzene were purified by recrystallisation and sublimation. Furthermore, two samples of 1, 3, 5-tri-t-butylbenzene were used in this study, each

prepared by a different synthetic route as outlined below:-



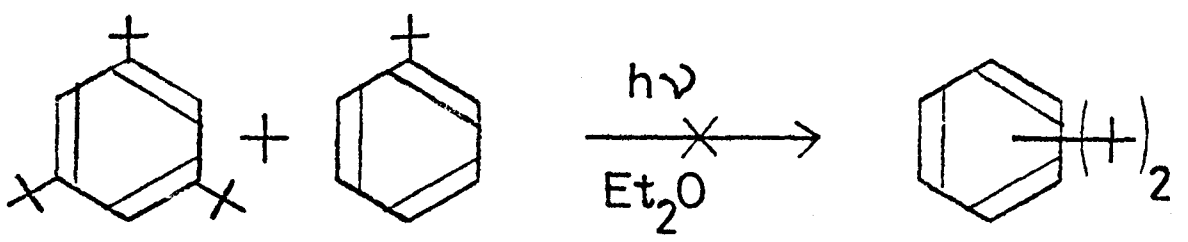
Since the fluorescence of 'Analar' toluene was readily observed in non-deoxygenated solution using the same apparatus, it was concluded that the reported observation of 1, 3, 5-tri-t-butyl-benzene fluorescence, supposedly 0.07 as intense as that for toluene, was erroneous. Such intensity should have been observed with the equipment used.

As fluorescence quenching could not be used as an indicator of the way in which acid affected the excited state, no further experiments to determine the effects of increasing acid concentration were attempted.

A number of alternative mechanisms were proposed to explain the incorporation of deuterium at C_3 in the 1, 2, 4-tri-t-butylbenzene after photolysis of 1, 3, 5-tri-t-butylbenzene in acidic methanol-O-d. Some of these included a t-butyl shift mechanism which could not be excluded a priori . The t-butyl substituted benzene was thought to be one of the alkyl substituted benzenes most susceptible to such a shift as a consequence of the stability of the t-butyl radical or cation.

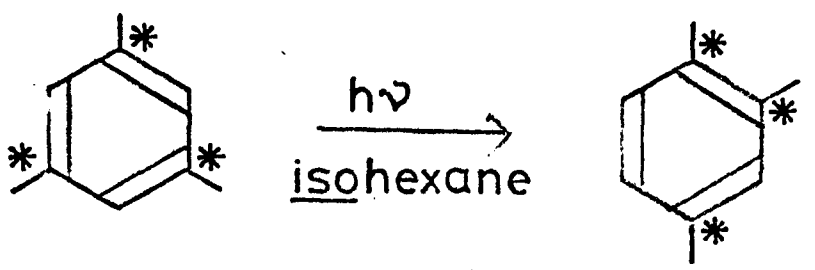
In general, rearrangements of polyalkylbenzenes are assumed to proceed via the participation of valence isomers by analogy with three experiments reported in the literature, summarised below:

(i)



Ref 54

(ii)



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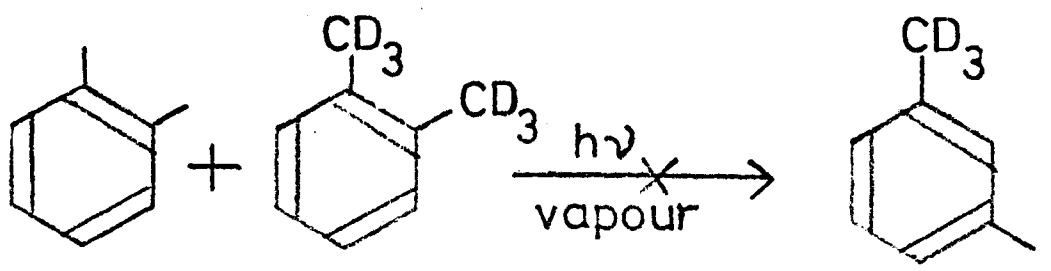
(iii)

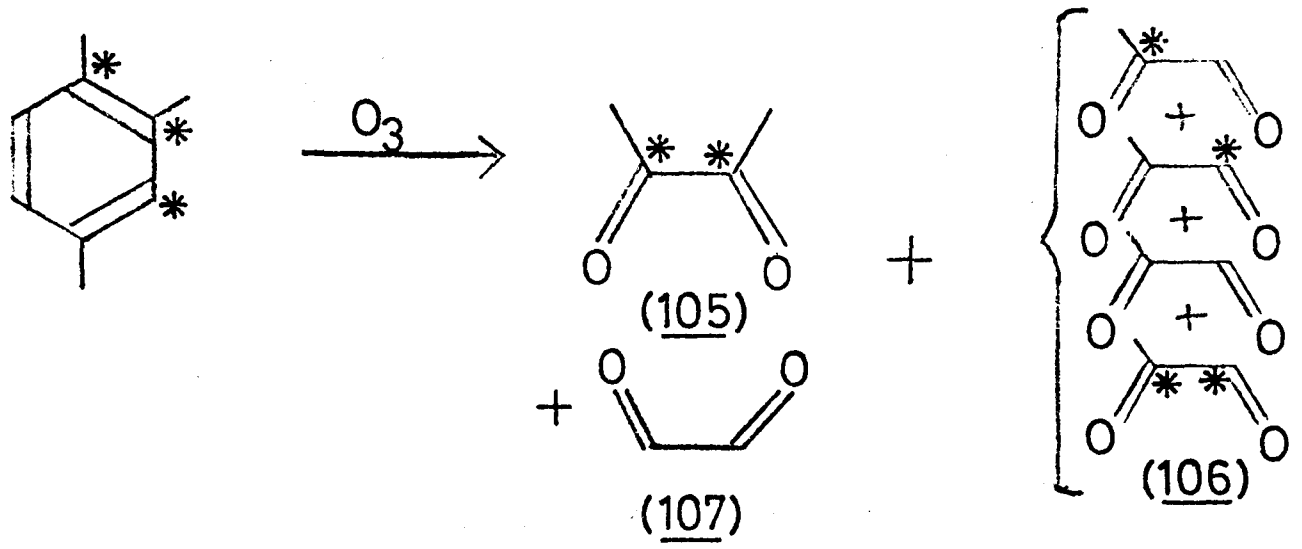


Ref 44

As none of these experiments were carried out under acidic conditions they were not necessarily good models for the irradiations carried out in this work. Furthermore, other objections to them may be raised. In experiment (i) [54], where no 'crossed' products were observed, it was concluded that no intermolecular radical processes were in operation. However, since no isomerisation of the 1, 3, 5-tri-t-butylbenzene was observed either, it need not follow that, if any isomerisation were to be seen, it would be intramolecular.

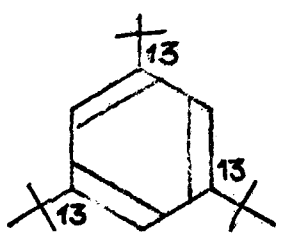
Experiment (ii) [41], the phototransposition of 1, 3, 5-$^{14}C_3$-mesitylene, does not prove that the rearrangement occurs via a skeletal rearrangement involving valence isomers. The positions of the labelled carbon atoms in the product, 1, 2, 4-tri-methylbenzene, were determined by analysis of the ozonolysis products (as oximes).

As predicted the dimethylglyoxal (105) was found to contain two ^{14}C atoms, the methylglyoxal (106) one and the glyoxal (107) none. However, the labelled 1, 2, 4-trimethylbenzene below would also lead to the same average distributions of radioactivity after ozonolysis.



Experiment (iii) [44] is rather more difficult to fault. The experiment certainly shows that the rearrangement is intramolecular, since no 'crossed' species are observed in the rearranged product, but does not show conclusively that an alkyl-shift reaction is not in operation. At a more fundamental level it is not certain that the processes occurring in the gas phase are the same as those in the condensed state,

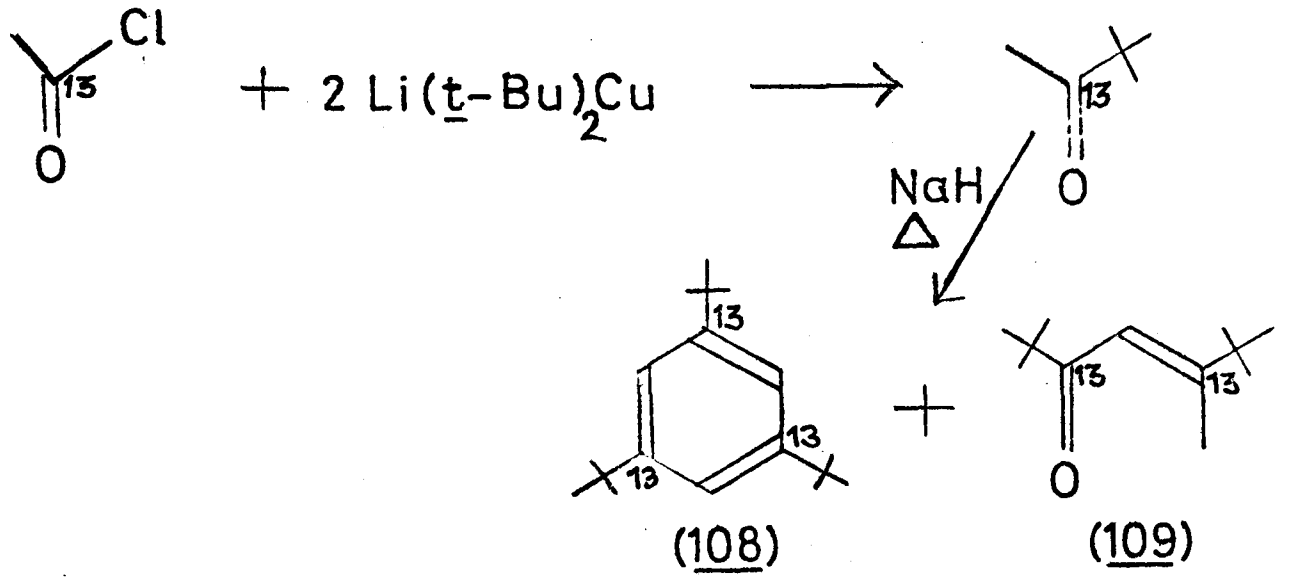
It was therefore deemed necessary to perform an experiment on a labelled compound to determine whether the rearrangement observed in acidic media was intra- or inter-molecular and whether a t-butyl shift mechanism was in operation. The compound of choice was 1, 3, 5-$^{13}C_3$-tri-t-butylbenzene (108).



(108)

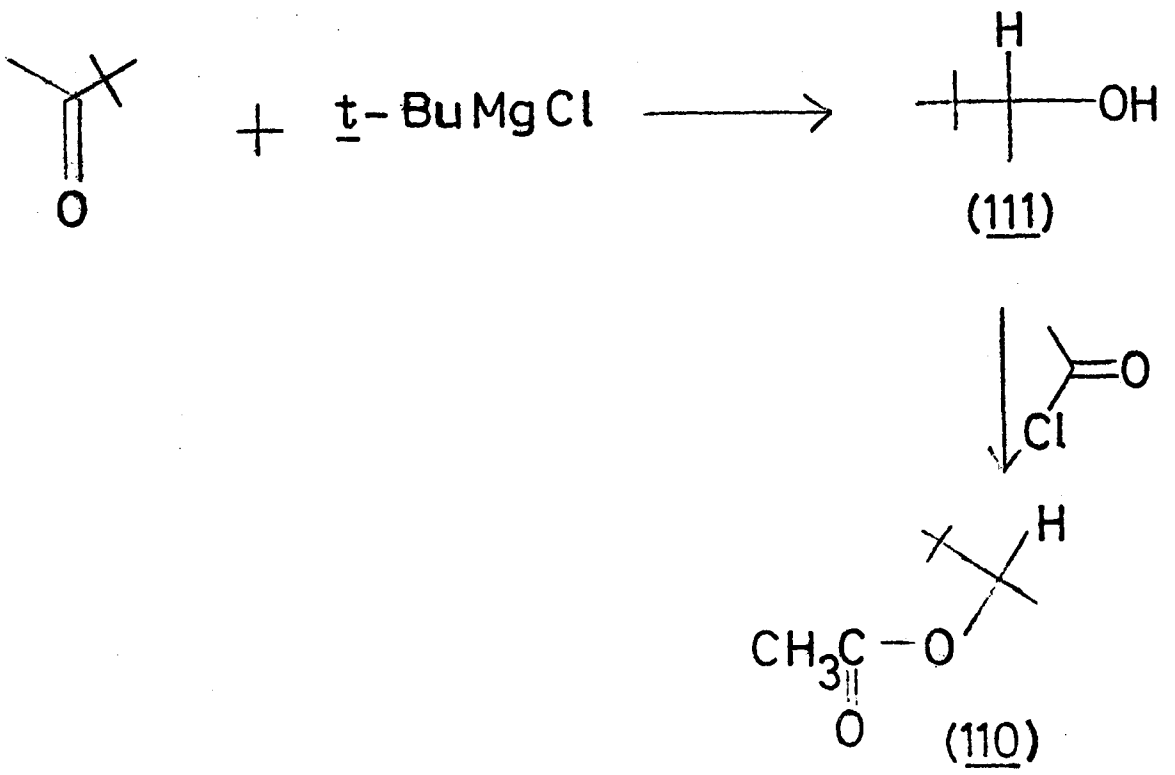
^{13}C labelling was chosen since analysis, by ^{13}C n. m. r. spectroscopy, could be carried out directly without the need for a degradation procedure. The 1, 3, 5-labelling pattern was preferred over 2, 4, 6-for reasons that will become clear (vide infra).

A number of potential synthetic routes to the labelled compound were investigated; that which was finally employed is indicated below:-

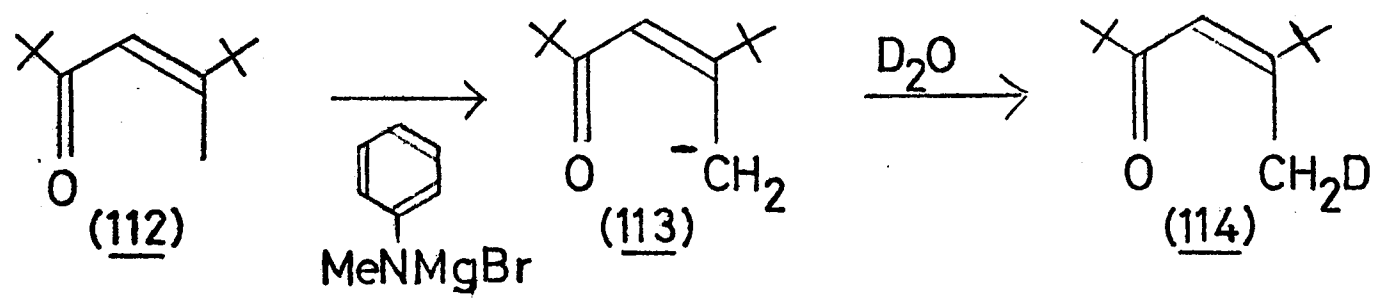


(108) (109)

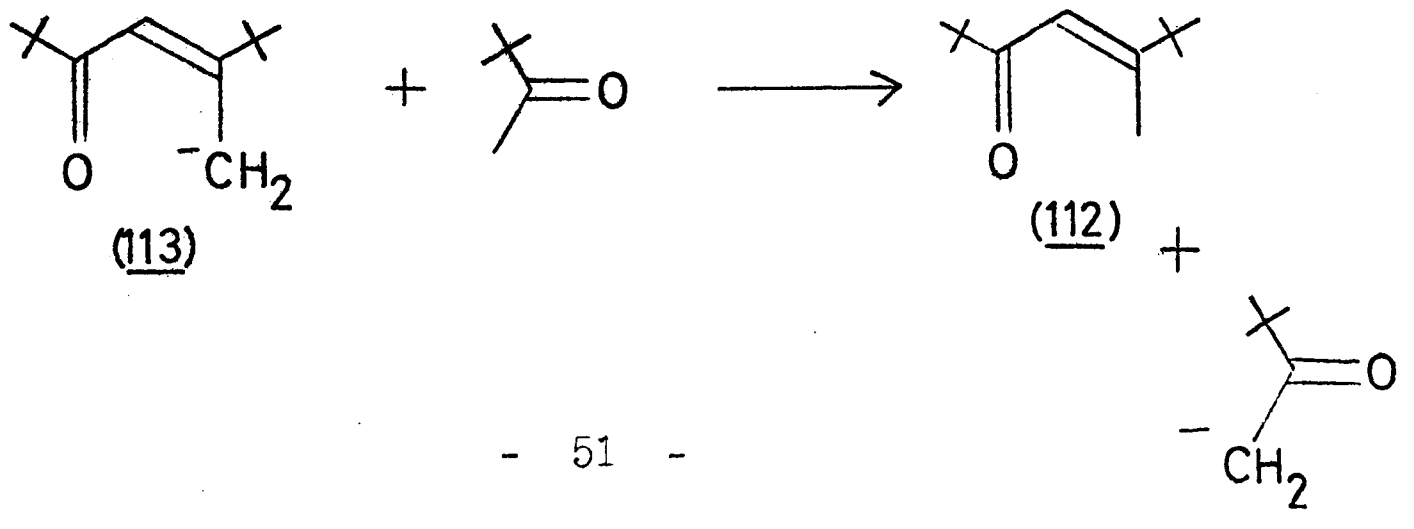
The first step, the reaction of acetylchloride with two equivalents of lithium di-butylcuprate [110], was found to be the most efficient of several methods employing organometallic reagents. In most other cases complex mixtures of unidentified products were obtained. These complex mixtures presumably resulted from secondary reaction of the pinacolone with the organometallic compound. For example, when t-butylmagnesium chloride was used, 3,3-dimethylbutan-2-yl acetate (110) was identified among the products. This compound was produced, perhaps, by the Grignard reagent reacting with the pinacolone as a reducing agent, thereby yielding the alcohol (111) which was readily attacked by acetyl chloride.

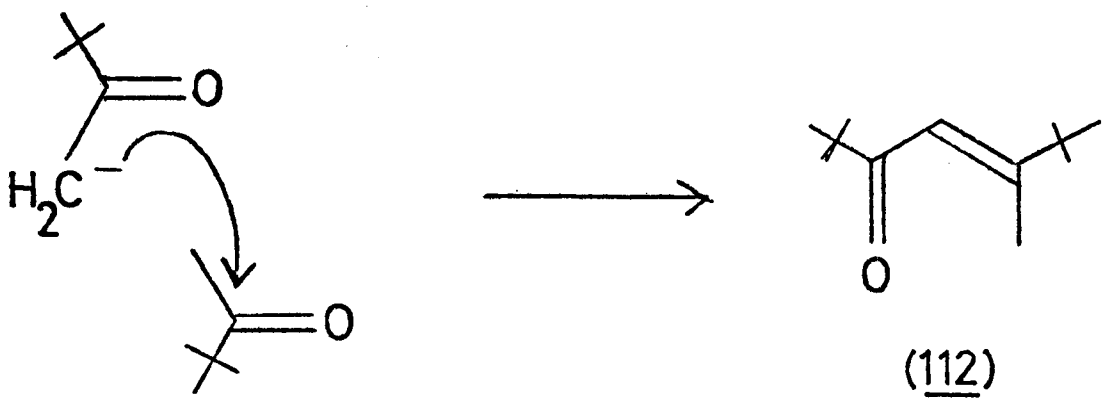


The second step, the pinacolone self-condensation, used sodium hydride as the carbanion producer[111]. Unfortunately this solid phase reaction was a low yield process, giving labelled 2, 2, 5, 6, 6-pentamethyl-4-heptene-3-one (109) as major product. Attempts to improve the yield of 1, 3, 5-tri-t-butylbenzene by doing the reaction in various liquid phases were unsuccessful. Since the exact course of the reaction was uncertain the 'half-reaction' of pinacolone with sodium hydride was studied. This revealed that prior to the addition of the second portion of pinacolone, only the ketone (112) was present. Formation of this ketone as major product would result in the loss of ^{13}C and therefore methods of recycling the ketone were investigated. Attempts to hydrolyse it back to pinacolone were unsuccessful. Similarly, attempts to couple it efficiently with more pinacolone using N-methylanilino-magnesium bromide as condensing agent[112] were unsuccessful. Quenching the 'half-reaction' with deuterium oxide demonstrated that the carbanion (113) had been formed. N. m. r. and mass spectroscopy of the product (114) revealed that deuterium had been incorporated in the 5-methyl group.



The failure of the condensation, and the isolation of ketone (112) as the sole product suggested that the carbanion (113) reacted with pinacolone as a base rather than as a nucleophile as shown below:-





(112)

If this process was general, the low yield of 1, 3, 5-tri-t-butylbenzene from pinacolone was readily explained.

In order that the results of the eventual ^{13}C n. m. r. analysis could be interpreted a number of compounds were studied by natural abundance ^{13}C n. m. r. spectroscopy. Spectra of 1, 3, 5- and 1, 2, 4-tri-t-butylbenzene were obtained. In the aromatic ^{13}C region of the decoupled spectrum the 1, 3, 5-tri-t-butylbenzene showed two singlets at 119. 5 and 150. 0 ppm. That at 119. 5ppm was ca 3 times as intense as that at 150. 0 ppm and showed up as a doublet in the non-decoupled spectrum, while the 150. 0ppm signal remained a singlet. This evidence allowed assignment of the signals. The signal at 150. 0 ppm was due to the carbon atoms carrying t-butyl groups; that at 119. 5 ppm, the carbon atoms carrying hydrogen. The difference in intensity of the signals reflected the greater efficiency of relaxation for the hydrogen-bearing carbon atoms.

In contrast, the ^{13}C spectrum from 1, 2, 4-tri-t-butylbenzene, obtained under identical conditions, showed three singlets of approximately equal intensity in the aromatic region of the decoupled spectrum, each of which became a doublet in the non-decoupled spectrum. Therefore, resonances must have been due to the

three aromatic carbon atoms bearing hydrogen. Only after 7300 scans (cf 1600 for 1, 3, 5-tri-t-butylbenzene) was it possible to discern three weak singlet resonances, above the baseline noise, assigned to the carbon atoms carrying t-butyl groups. The chemical shifts in the aromatic region are summarised in the table below:-

	C^{13} -t-butyl (ppm)	C^{13} - H (ppm)
1, 3, 5 -	150.0	119.5
1, 2, 4 -	148.2 147.4 145.6	122.3 126.8 129.1

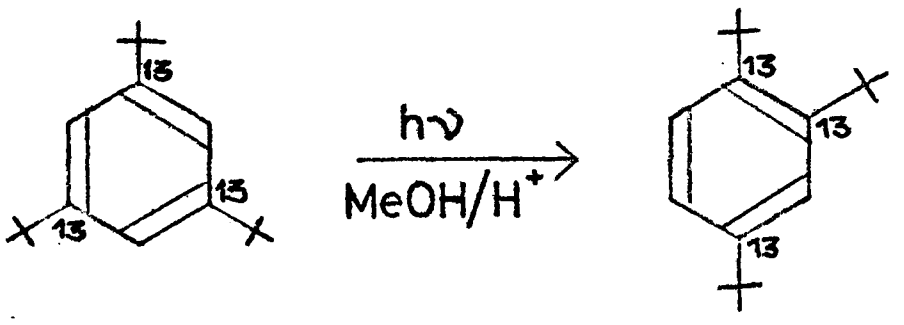
It should now be clear why the 1, 3, 5-tri-t-butylbenzene, in which the carbon atoms carrying t-butyl groups were enriched, was chosen. In the recovered 1, 2, 4-tri-t-butylbenzene photoproduct any t-butyl shift to a none-enriched aromatic carbon atom would result in the loss of a resonance in the C^{13}-t-butyl region together with an enormous increase of intensity of a resonance in the ^{13}C-H region. Even a minor component of such a shift would be observable.

As the products of the photochemical experiments previously carried out in acidified methanol-O-d were 1, 2, 4-tri-t butylbenzene, labelled with deuterium at C_5 or at C_3 and C_5, it was possible to assign each of the ^{13}C-H resonances to the carbon atoms in the ring. The ^{13}C n. m. r. spectrum of 1, 2, 4-tri-t-butyl-benzene-5-d showed the 129.1 ppm ^{13}C resonance as a multiplet, while the other resonances remained unchanged. Since partial deuteriation at C_5 would be expected to produce a multiplet signal (triplet plus residual singlet) it was concluded that the 129.1 ppm resonance corresponded to the carbon atom at C_5.

Similarly the ^{13}C n.m.r. spectrum of the 1, 2, 4-tri-t-butylbenzene partially deuteriated at C_3 or C_5 showed the 129.1 ppm resonance as multiplet. However, the 126.8 ppm signal was shown as a broad singlet, with the 122.2 ppm resonance again unchanged. Hence, the 126.8 ppm resonance must have corresponded to the carbon atom, C_3, whilst that at 122.2 ppm corresponded to C_6.

It would now be possible to see from the ^{13}C n.m.r spectrum of the photoproduct whether the reaction did involve a t-butyl shift and, if it did, where the enriched carbon atoms ended up in the product.

In fact, the labelled 1, 2, 4-tri-t-butylbenzene, recovered after photolysis of the labelled 1, 3, 5-isomer in acidified methanol, showed two sets of three singlets in the aromatic region of the ^{13}C n.m.r. spectrum, due to ^{13}C-H and ^{13}C-t-butyl resonances. Within each set the three singlet resonances showed approximately equal intensities, proof that the photorearrangement was intramolecular and that the t-butyl groups remained bonded to the same carbon atoms throughout.



The only compound which had been reported by Wilzbach and Kaplan [52] as a photoproduct from 1, 3, 5-tri-t-butylbenzene, but which had not been investigated, was 1, 2, 4-tri-t-butylbenzvalene (34), which had a reported half-life of 17 min at 24.5°. Having considered the experimental problems involved in investigating this species (e.g. monitoring its presence and subsequent loss, isolating it, isolation and analysis of deuterium labelled product and reliability of results) it was decided that such a study was not possible with the equipment available.

Without this information the mechanism of the acid-catalysed rearrangement must remain unknown; however this study has provided information which lay certain constraints upon such a mechanism:-

(i) It must be intramolecular and involve no t-butyl shift.

(ii) It must explain how deuterium is incorporated at C_3 in the 1, 2, 4-tri-t-butylbenzene photoproduct when 1, 3, 5-tri-t-butylbenzene is irradiated in acidic methanol-O-d. (Deuterium incorporation at C_5 in the 1, 2, 4-tri-t-butylbenzene may be assumed to be derived *via* secondary photolysis to 1, 3, 5-tri-t-butylprismane (33) and subsequent acid attack on this species.)

(iii) It cannot invoke the acid lability of 1, 2, 5-tri-t-butylDewar-benzene (32), 1, 3, 6-tri-t-butylbenzvalene (34) [107], 4-methoxy-2, 4, 6-*exo*-tri-t-butylbicyclo [3. 1. 0]hex-2-ene (35) or the protonation of the ground state aromatic molecules.

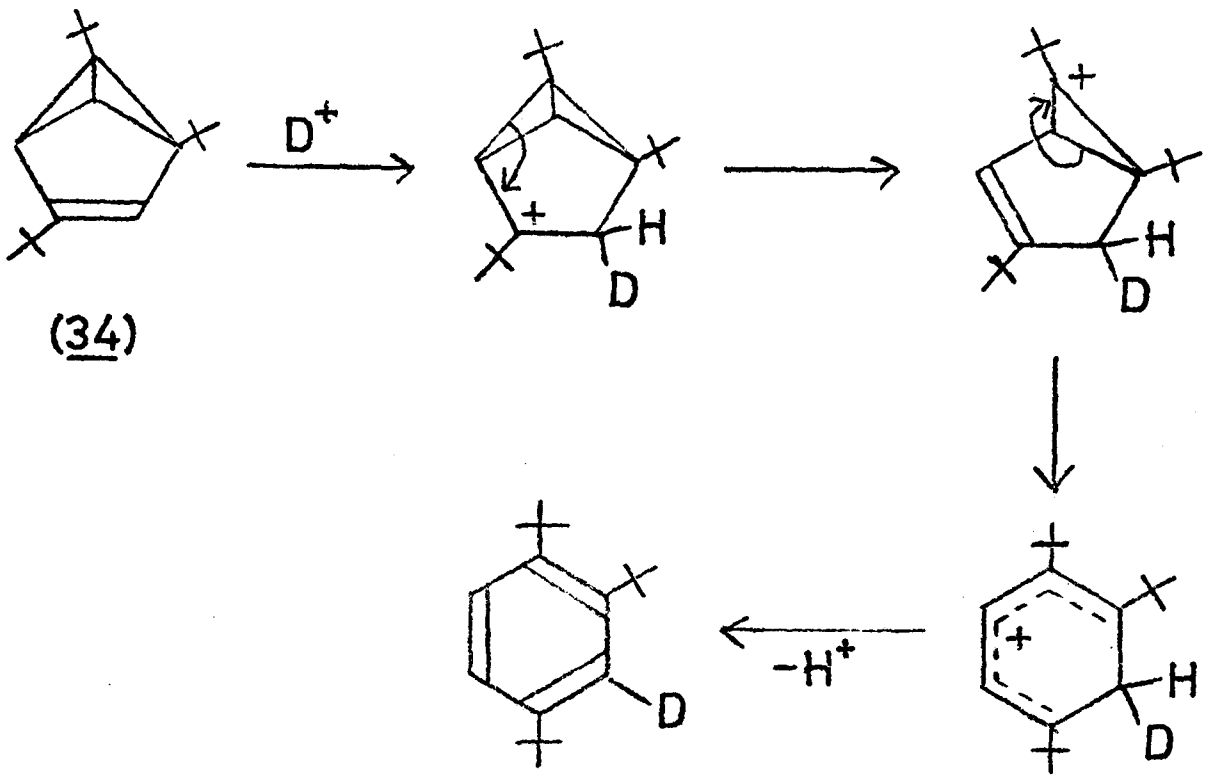
Given these constraints, the acid present must attack one of the following:-

a) the excited state of the aromatic molecule, about which nothing is known.

b) 1, 2, 4-tri-t-butylbenzvalene (34) or its precursor.

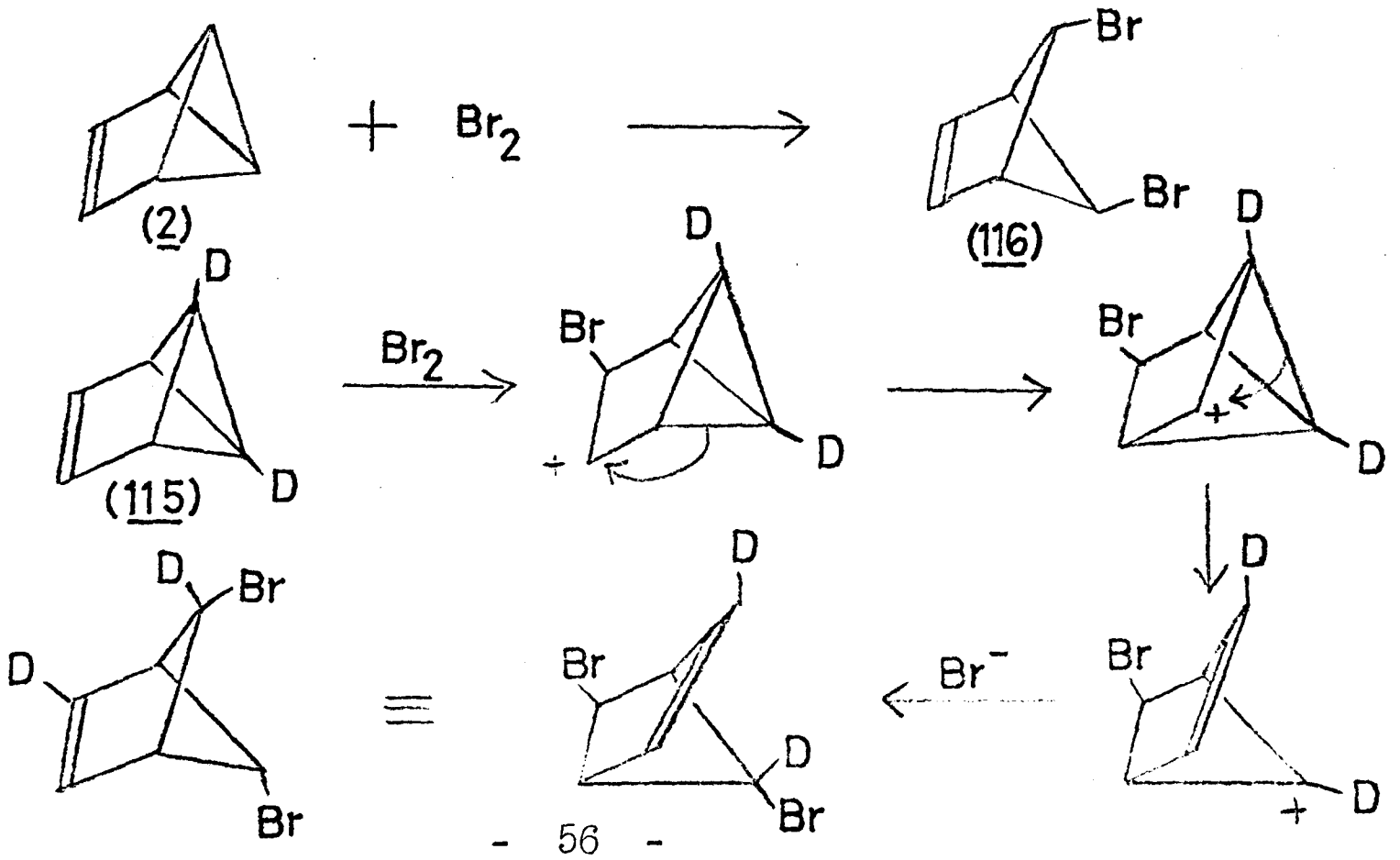
c) a hitherto-unknown intermediate.

Of these alternatives, attack by acid on 1, 2, 4-tri-t-butylbenzvalene (34) is most attractive especially as it has been shown to be a primary photoproduct from 1, 3, 5-tri-t-butylbenzene. It is possible to write a novel mechanism involving this entity such that deuterium is incorporated at C_3 in the photoproduct.



(34)

There is some precedence for considering that electrophilic attack might take place at the double bond rather than at the cyclopropyl bridge. Using the dideuteriated benzvalene (115), Katz[113] showed that, while bromination of benzvalene (2) gave the product (116), formally derived by direct addition across the bridge, it was actually formed in major part via initial electrophilic attack on the double bond.



(2)

(116)

(115)

This investigation was undertaken to gain further insight to the nature of the photochemical rearrangement process taking place in the tri-t-butylbenzene system in solution under acidic conditions. It has been shown that the rearrangement does not involve a de-alkylation /re-alkylation process and does not proceed via the participation of at least three of the four valence isomers reported for this system of compounds. Although the exact nature of the rearrangement has not been established, it is apparent that a novel rearrangement process is taking place in solution under acidic conditions.

EXPERIMENTAL SECTION

A) GENERAL TECHNIQUE

(1) Routine Procedures

All melting points (m.p.) were taken on a hot stage Kofler block and are uncorrected.

Infrared (i.r.) and ultraviolet (u.v.) spectra were recorded on Pye-Unicam S.P. 1000 and S.P. 800 spectrometers respectively. Spectral data are quoted as follows:- i.r. frequencies (ν) are given in cm^{-1}, with the intensities indicated as strong (s), medium (m), weak (w) or shoulder (sh) if on a stronger band. In addition, phase and path length are specified. Each U.V. band is defined by wavelength (λ) and molar decadic extinction coefficient (ϵ), where appropriate.

Proton nuclear magnetic resonance (n.m.r.) spectra were recorded on Perkin Elmer R32 (90MHz) and R24 (60MHz) spectrometers, using tetramethylsilane (TMS) as a reference standard. N.m.r. spectra are recorded in the form:(solvent), τ value (number of protons, multiplicity), multiplicity being indicated by s, d, t, q and m (singlet, doublet, triplet, quartet and multiplet, respectively).

^{13}C nuclear magnetic resonance spectra were recorded on a Bruker WH-90 Fourier-Transform (90 MHz) spectrometer, using deuterochloroform ($CDCl_3$) as solvent and T.M.S. as internal standard. All chemical shifts are reported in parts per million (ppm) downfield from T.M.S.

Mass spectra were recorded on A.E.I. MS. 9., Varian CH7 and V.G. Micromass 16F mass spectrometers, the latter having the facility for attachment to a Pye-Unicam Series 104 gas-liquid chromatograph for routine measurement of the mass spectra of eluted compounds.

Routine analytical gas-liquid chromatography (g. l. c.) was carried out on a Pye-Unicam Series 104 chromatograph, fitted with a flame ionisation detector using coiled glass columns (1. 5m x 4mm) and nitrogen as carrier gas. The following columns were used:-

1) 20% Carbowax 20M + 5% Polyethyleneimine on Embacel (Carbowax/P. E. I.)

2) 1% Q. F. 1. on Embacel (Q. F. 1.)

3) 20% Carbowax 1000 + 5% Potassium Hydroxide on Embacel (Carbowax/ KOH).

Preparative g. l. c. was achieved with a Pye-Unicam Series 105 chromatograph using a preparative OV1 column throughout.

Thin layer chromatography (t. l. c.) was carried out on analytical plates (200mm x 50mm x 0. 3mm), coated with alumina or Kieselgel MF 254/366, or on Polygram SIL-G-UV 254 precoated plastic sheets (80mm x 40mm x 0. 25mm). Preparative t. l. c. (p. l. c.) employed either analytical plates or preparative plates (200mm x 200mm x 1mm) coated with alumina or silica gel, after thorough elution with acetone to remove plasticiser.

Except where otherwise stated solvents were removed on a rotary evaporator.

Analyses were performed by the microanalysis service.

(2) Photochemical Techniques

All irradiations were carried out, using quartz apparatus, in a Srinivasan-Griffin photochemical reactor ('Rayonet'), fitted with air-cooled 254nm lamps.

U.V. cells, n.m.r. tubes and test-tubes were used for small scale photolyses; a 3-litre vessel was used for large scale work.

Where stated, solutions were deoxygenated with a slow stream of dry, oxygen-free nitrogen ('White Spot'), using hypodermic needles or thin glass tubes as gas inlets and outlets.

Fluorescence data were recorded on a Perkin Elmer MPF-2A fluorescence spectrophotometer.

(3) Materials

Acidified methanol was prepared by passing dry hydrogen chloride through 'Analar' methanol. Acid concentration was determined by titration against standard sodium hydroxide solution, using phenolphthalein as indicator.

Methanol-O-d was prepared as follows: Dimethyl carbonate (200ml), deuterium oxide (50ml) and dimethyl sulphate (8g) were heated together under reflux for ten days. After this time the i.r. spectrum of the mixture showed no carbonyl absorption indicating that all the dimethyl carbonate had reacted. The methanol-O-d (120ml) was isolated by distillation (64.5-65°) and shown by n.m.r. to contain no hydroxyl protons.

Acidified methanol-O-d was prepared by the same method as acidified methanol above.

'Petrol' refers to light petroleum, bp 40-60°.

(B) Synthesis and Photochemistry

(i) 1, 3, 5-Tri-t-butylbenzene (29) [114]

A mixture of benzene (15. 6g) and t-butyl chloride (194g) was cooled to -40° with stirring, such that the reactants just remained liquid. Aluminium trichloride (13. 2g) was added over 10 min and the mixture was stirred for a further 15 min; the temperature was then rapidly raised to -10°, whereupon evolution of hydrogen chloride was observed, and stirring continued for a further 2h. The resultant mixture was poured onto ice (800g) and water (800ml) and vigorously stirred. The organic layer was separated, washed with water and dried over anhydrous magnesium sulphate. Excess t-butyl chloride was removed on a rotary evaporator, the residue being heated at 60° for a further 30 min to ensure removal of all volatile components. On cooling a crystalline product formed which on recrystallisation from methanol yielded pure 1, 3, 5 -tri-t-butylbenzene (29) (34g, 64%)

Product: m. p. 74-74. 5° (lit [52] 75°)
N. m. r. (CCl_4), τ :8. 71 (27H, s) 2, 90 (3H, s)

(ii) Photolysis of 1, 3, 5-Tri-t-butylbenzene (29) in Hexane [39, 52, 56]

(a) 1, 3, 5-Tri-t-butylbenzene (5g) in 'aromatic free' hexane (2150ml), deoxygenated for 1h, was photolysed in the large quartz vessel. The reaction was monitored by g. l. c. (Carbowax/ PEI; 150°). After 94h, very little increase in the intensity of that signal assigned to 1, 2, 4-tri-t-butylbenzene (31) was apparent with further photolysis, and the irradiation was stopped. Removal of the hexane left an orange coloured liquid (6g). Column chromatography on silica gel (250g), with petrol as eluent, yielded 1, 2, 5-tri-t-butylbicyclo [2. 2. 0]hexa-2, 5-diene

('Dewar benzene') (32) (750mg), as a liquid slightly contaminated with hexane residues, and a mixture of isomeric tri-t-butylbenzenes. Separation of the isomers by preparative g.l.c. yielded crude 1, 2, 4-tri-t-butylbenzene (480mg).

(b) As for (a), except that the entire photoproduct was purified by preparative g.l.c. to give a higher yield of crude 1, 2, 4-tri-t-butylbenzene (800mg) which, after recrystallisation from aqueous ethanol, afforded pure (31) (500mg), m.p. 48-49° (lit [106] 49-50°).

1, 2, 5-Tri-t-butylDewarbenzene (32)

N.m.r. (CCl_4) τ : 9.02 (s), 8.94 (s), 6.80 (1H, d), 3.95 (1H, d), 3.87 (1H, s)

1, 2, 4-Tri-t-butylbenzene (31)

N.m.r. (CCl_4) τ :8.73 (9H, s), 8.49 (9H, s), 8.47 (9H, s) 3.03(1H, d. d), 2.64(1H, d) , 2.52 (1H, d)

(iii) Photolysis of 1, 3, 5-Tri-t-butylbenzene (29) in Methanol.

The method employed was a modification of that described by Wilzbach and Kaplan [26, 52].

1, 3, 5-Tri-t-butylbenzene (5g) in methanol (1500ml) was deoxygenated for 1h. and then photolysed for 23h. After this time, aliquots (500ml) were diluted with water (1000 ml) and extracted with hexane (4 x 100ml). The hexane extracts were combined, dried over

anhydrous magnesium sulphate and evaporated to yield crude photoproduct (5.88g). This was recrystallised twice from methanol to yield pure 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3.1.0.]hex-2-ene (35) (3.6g), m.p. 34.5-35° (lit [52] 35°).

N.m.r. (CCl_4) τ : 9.27 (1H, m), 9.10 (9H, s), 9.04 (9H, s), 8.87 (9+1H, s*), 8.30 (1H, m), 7.01 (3H, s), 5.24 (1H, m).

* See Ref. 26.

I.r. ($CHCl_3$, 0.1.mm) ν_{max}: 865 (w), 873 (w), 910 (w), 943 (w), 970 (w), 1015 (w), 1038 (w), 1060 (sh), 1072 (s), 1093 (m), 1105 (m), 1152 (w), 1257 (m) 1275 (sh), 1365 (s), 1392 (m) 1467 (sh), 1477 (s), 1620 (m), 2820 (sh), 2870 (sh), 2910 (sh), 2960 (v.s), 3010 (sh), 3065 (sh)

Mass spectrum m/e : 278 (9), 247(9), 221(32), 151(17), 149(16), 121(9), 91 (10), 57 (100).

U.v. : End absorption only above 200 nm.

The residue (1.8g) obtained from the first recrystallisation was a yellow oil. Purification by column chromatography on alumina (250g), with petrol as eluent, yielded five fractions, identified by their n.m.r. spectra.

Fraction (a) (480mg) - exclusively 1, 3, 5 - Tri-t-butylbenzene (29)

Fraction (b) (190mg) - ca 1:1 mixture of 1, 3, 5-Tri-t-butylbenzene (29) and 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3.1.0]hex-2-ene) (35)

Fraction (c) (350mg) - Almost wholly 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3.1.0]hex-2-ene) (35)

Fraction (d) (120mg) - ca 1:1 mixture of 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3. 1. 0]hex-2-ene (35) and new unreported compound, X.

Fraction (e) (490mg) - almost wholly compound X.

Attempts to purify fraction (e) by crystallisation from methanol or aqueous methanol were unsuccessful, although cooling these solutions to -78° did yield a white solid, which could not be isolated.

A pure sample of X was eventually obtained after two successive p. l. c. s on alumina (pretreated in an ammoniacal atmosphere to neutralise any acid sites) with redistilled 'Analar' light petroleum, b. p. 30-40°, as eluent. The product, X, was a colourless liquid.

N. m. r. (CCl_4) τ : 8. 6-9. 4 (ca 2H, m,), 9. 1 (ca 18H, s), 8. 9 (ca 9H, s), 8. 48 (1H, m), 6. 75 (3H, s), 5. 22 (1H, m),

I. r. ($CHCl_3$, 0. 1mm) ν_{max} : 873 (w), 958 (m), 1010 (w), 1068(sh), 1090 (s), 1110 (m), 1152 (w), 1252 (w), 1260 (sh), 1366 (s), 1392 (m), 1455 (sh), 1466 (s), 1478 (s), 1633 (m), 2825 (sh), 2880 (sh), 2910 (sh), 2965 (vs), 3010 (sh), 3060 (sh).

Mass spectrum m/e: 278(7), 247(14), 235(27), 222(16), 221 (90), 207 (27), 191 (10), 189 (18), 175 (20), 165 (15), 151 (42), 149 (15), 137 (19), 121 (16), 91 (16), 57 (100).

U. V. : End absorption above 200 nm.

Microanalysis: found C81. 65, H 12. 11; $C_{19}H_{34}O$ requires C81. 95, H 12. 31

(iv) Thermal Reaction of X

A solution of X in carbon tetrachloride was allowed to stand for a few weeks at room temperature in a stoppered flask. It was found, on recording the i.r. and n.m.r. spectra, that almost complete (ca 90%) chemical change had taken place, the product formed having the spectral data indicated below, consistent with formation of 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3.1.0]hex-2-ene (35)

N.m.r. (CCl_4) τ : 9.27 (m), 9.10 (s), 9.04 (s), 8.87 (s), 8.30 (m), 7.01 (s), 5.24 (m).

I.r. ($CHCl_3$, 0.1.mm) ν_{max} : 865 (w), 873 (w), 910 (w), 943 (w), 970 (w), 1038 (w), 1072 (s), 1093 (m), 1105 (m), 1257 (m), 1365 (s), 1392 (m), 1467 (sh), 1477 (s), 1620 (m) 2820 (sh), 2870 (sh), 2910 (sh), 2960 (v.s) 3010 (sh).

(v) Effect of Acidification and Subsequent Neutralisation on 4 methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3.1.0]hex-2-ene (35) and on X

The two compounds (15mg) were dissolved in methanol (0.5 ml) in separate n.m.r.tubes. To each was added acidic methanol (ca 3.5M in acid; 15μl) and the resultant change in the t-butyl region of the n.m.r. spectrum noted in each case.

(35), N.m.r.(MeOH) τ : 9.11 (9H, s), 9.02 (9H, s), 8.87 (9H, s)

X, N.m.r.(MeOH τ : 9.14 (9H, s), 9.12 (9H, s), 8.95 (9H, s)

(35) + H^+ , N.m.r.(MeOH/H^+) τ : 9.10 (9H, s), 8.94 (18H, s)

X + H^+ , N.m.r. (MeOH/H^+) τ : 9.10 (9H, s), 8.94 (18H, s)

Each sample was then neutralised with anhydrous sodium carbonate and the n. m. r. spectra re-run.

(35) + H^+ + base N. m. r. (MeOH) τ : 9.11 (9H, s), 9.02 (9H, s), 8.87 (9H, s) (major)

9.14, 9.12, 8.95 (minor)

X + H^+ + base N. m. r. (MeOH) τ : 9.11 (9H, s), 9.02 (9H, s), 8.87 (9H, s) (major)

9.14, 9.12, 8.95. (minor)

(vi) Effect of Adding Acid to 1, 2, 5-Tri-t-butylDewarbenzene (32)

The U. V and n. m. r. spectra of 1, 2, 5-tri-t-butylDewarbenzene (32) in methanol were recorded, together with a g. l. c. trace (Carbowax/PEI; 150°). Acidic methanol was added tc the sample and the U. V, n. m. r, and g. l. c. analyses repeated, immediately and after standing at room temperature for several hours. No change was apparent by any method. .

(vii) Effect of Adding Acid to 1, 3, 5-Tri-t-butylbenzene (29) and 1, 2, 4-Tri-t-butylbenzene (31)

U. V. spectra of each of the isomers in methanol (4.0×10^{-3} M; 2ml) were recorded. Each sample was then acidified with acidic methanol (5M; 0. 5ml) and the spectra re-taken immediately and after aging at room temperature for several hours.

1, 3, 5 -Tri-t-butylbenzene (29) U. V. (MeOH) λmax 263 (ϵ=186) } unchanged on aging.
U. V. (MeOH/H^+) λmax 263 (ϵ=186) }

1, 2, 4-Tri-t-butylbenzene (31) U. V. (MeOH) λmax 266 (ϵ=226) } unchanged on aging
U. V. (MeOH/H^+) λmax 266 (ϵ=226) }

(viii) Irradiation of 1, 3, 5-Tri-t-butylbenzene in Acidified Methanol

1, 3, 5-Tri-t-butylbenzene (50mg) was dissolved in acidified methanol (0. 1;2ml) in a quartz U. V. cell and irradiated. The reaction was monitored by g. l. c.(Carbowax/PEI;150°) and photolysis continued for 16h. G. l. c. indicated that two products were present; one had retention time equal to that of 1, 2, 5-tri-t-butyl-Dewar benzene (32), formed in low yield (ca 1%) and the other that of 1, 2, 4-tri-t-butylbenzene, formed as major product (ca 25%).

The n. m. r. spectrum of the photolysate after neutralisation and removal of methanol showed new signals indicated below:-

N. m. r. (CCl_4) τ : 9. 02, 8. 94, cf 1, 2, 5-Tri-t-butylDewarbenzene (32)
8. 73, 8. 49, 8. 47, 3. 03, 2. 64, 2. 52 cf 1, 2, 4-Tri-t-butylbenzene (31)

This was consistent with the conclusion from g. l. c.

(ix) Irradiation of 1, 3, 5-Tri-t-butylbenzene in Acidified Methanol-O-d

A deoxygenated solution of 1, 3, 5- tri-t-butylbenzene (738mg) in acidified methanol-O-d (0. 1M;30ml) was irradiated, the photolysis being monitored by g. l. c. (Carbowax/PEI;150°) to follow build-up of g. l. c. signal corresponding to 1, 2, 4-tri-t-butylbenzene (31). After 41h the irradiation was stopped; the solution was neutralised with sodium carbonate and the partially deuterated 1, 2, 4-tri-t-butyl-benzene (115mg) isolated by preparative g. l. c, together with some starting material. The former was investigated by n. m. r. and mass spectroscopy.

Partially deuterated 1, 2, 4-isomer—

N. m. r. (CCl_4) τ: 8.73 (9H, s), 8.49 (9H, s), 8.47 (9H, s),
3.07 (m), 2.98 (m)
2.69 (s), 2.66 (s)
2.59 (s), 2.52 (m)
} 2.3 - 3.3 (ca 2H, m)

Mass spectrum m/e: 247 (28), 246 (21), 233 (38), 232 (100), 231 (74), 190 (20), 189 (16), 176 (33), 175 (28) 57 (71)

[c. f. 1, 2, 4-Tri-t-butylbenzene - Mass spectrum m/e 247 (5), 246 (29), 233 (2), 232 (18), 231 (100), 190 (2), 189 (18), 176 (4), 175 (31), 57 (42)]

(x) Comparative Photolyses of 1, 2, 4-Tri-t-butylbenzene (31) in (a) Hexane , (b) Methanol and (c) Acidified Methanol (0. 1M)

Samples of 1, 2, 4-tri-t-butylbenzene (50mg) in solvent (2ml) were irradiated in similar 10 mm u. v. cells for a total of 40h. In each case the photolysis was followed by g. l. c. (Carbowax /PEI;150°) and the final photolysate analysed by its n. m. r. spectrum.

(a) Hexane : - G. l. c showed steady build-up of signals at retention times consistent with formation of 1, 3, 5-tri-t-butylbenzene (29) and 1, 3, 5-tri-t-butylDewarbenzene (32), the latter being the major product, ratio ca 4:1 after 40h. The n. m. r. spectrum showed the following new signals.

N. m. r. (CCl_4) τ: 8.71, 2.90 c. f. 1, 3, 5 -tri-t-butylbenzene (29)

9.02, 8.94, 6.80, 3.95, 3.87 c.f. 1, 2, 5-tri-t-butyl-Dewarbenzene (32)

9.24, 9.07, 7.94 cf. 1, 2, 5- Tri-t-butylprismane (33)[56]

1, 2, 5-Tri-t-butylprismane (33)[56]:-

N.m.r. (CCl_4) τ: 9.24 (9H, s), 9.07 (18 H, s), 7.94 (3H, m)

b) Methanol - G.l.c showed that, as in (a), signals appeared at retention times the same as 1, 3, 5-tri-t-butylbenzene (29) and 1, 2, 5-tri-t-butylDewarbenzene (32) the latter being major product, ratio ca 3:1 after 40h. In addition very small amounts (< 10% 1, 3, 5-tri-t-butylbenzene (29)) of other products were visible. The n.m.r. spectrum had new signals:

N.m.r. (CCl_4) τ: 8.71, 2.90 c.f. 1, 3, 5-tri-t-butylbenzene (29)
9.02, 8.94, 6.80, 3.96, 3.88 c.f 1, 2, 5-tri-t-butyl-Dewarbenzene (32)
9.23, 9.07, 7.93 c.f. 1, 2, 5-tri-t-butylprismane (33)
9.11, 9,04, 8.87, 7.00, 5.23 c.f. 4-methoxy-2, 4-6-exo-tri-t-butylbicyclo [3.1.0] hex-2-ene (35)

(c) Acidified Methanol: G.l.c. showed that very little overall photochemistry occurred (>90% starting material remained). Yet again, the two major products had retention times the same as 1, 3, 5-tri-t-butylbenzene (29) and 1, 2, 5-tri-t-butylDewarbenzene (32). The n.m.r. spectrum showed new resonances below

N.m.r. (CCl_4) τ: 8.71, 2.90 c.f. 1, 3, 5-tri-t-butylbenzene (29)
9.03, 8.95, 6.80, 3.98, 3.90 c.f. 1, 2, 5-tri-t-butylDewarbenzene (32).

(xi) Effect of Acidifying the Photolysate of 1, 2, 4-Tri-t-butylbenzene (31) in Hexane.

The photolysis conditions were those of experiment (xa). The hexane was removed and the residue dissolved in carbon tetrachloride. Analysis by g.l.c. (Carbowax/PEI;150°) revealed that no change was brought about by these processes. The n.m.r. spectrum of the product was exactly that observed in experiment (xa). After removal of the carbon tetrachloride the residue was dissolved in methanol (2ml)

and, again, no change was apparent by g.l.c, even after standing for several hours at room temperature. The methanolic solution was then acidified to 0.1M with acidic methanol; analysis by g.l.c. showed decreased intensity of the signal with retention time the same as 1,2,5-tri-t-butylDewarbenzene and build-up of the signal due to starting material. Subsequently the solution was neutralised with sodium carbonate, the methanol removed and the n.m.r. of the residue obtained and compared with that of initial photolysate. Addition of the acid had caused loss of photoproduct signals at 9.24, 9.07 and 7.94 τ with exclusive build-up in the resonances due to 1,2,4-tri-t-butylbenzene (31).

(xii) Irradiation of 1,2,4-Tri-t-butylbenzene (31) in Acidified Methanol-O-d

1,2,4-Tri-t-butylbenzene (31) (50mg) in acidified methanol-O-d (0.1M;2.0 ml) was photolysed for 40h. Analysis by g.l.c. (Carbowax/PEI;150°) revealed the presence of products with retention times those of 1,3,5,-tri-t-butylbenzene (29) and 1,2,5-tri-t-butylDewarbenzene in a ratio ca 1:3, with ca 80% starting material remaining. After neutralisation with sodium carbonate the methanol was removed and the residue extracted into carbon tetrachloride for analysis by n.m.r.

N.m.r. (CCl_4) τ: 8.71 (s), 2.88(s) c.f. 1,3,5-tri-t-butylbenzene (29)
9.03 (s), 8.94(s), 6.80(s), 3.95(m),
3.87 (m), c.f. 1,2,5-tri-t-butylDewarbenzene(32)
8.73 (s), 8.49 (s), 8.47 (s), 3.03 (dd)
2.66 (s), 2.64 (d), 2.53 (m)
c.f. 1,2,4-tri-t-butylbenzene (31)

The carbon tetrachloride was removed and the mass spectrum of the residue compared with that of undeuterated starting material (31).

Product m/e: 247 (11), 246 (18), 232 (36), 231 (60), 189 (11), 176 (10), 175 (18), 57 (100).

1, 2, 4-tri-t-butylbenzene (31)
m/e: 247 (5), 246 (25), 232 (13), 231 (72), 189 (10), 176 (5) 175 (16), 57 (100)

(xiii) Irradiation of 1, 2, 4-Tri-t-butylbenzene (31) in Hexane and Addition of Acidified Methanol-O-d to the Product

The experiment was identical to experiment (xi) except that acidification was by acidic methanol-O-d. G. l. c revealed that the signal with retention time that of 1, 2, 5-tri-t-butylDewarbenzene had reduced intensity, although it was still present after standing for 2h at room temperature. The signal due to starting material had increased intensity. Neutralisation, removal of methanol-O-d and dissolution in carbon tetrachloride was followed by n. m. r. analysis. The n. m. r. again showed loss of signals at 9.24, 9.07, and 7.94 τ with build-up of the resonances due to 1, 2, 4-tri-t-butylbenzene and new singlets at 2.66 and 2.52 τ.

(xiv) Irradiation of 4-Methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3. 1. 0] hex-2-ene (35) in (a) Methanol and (b) Acidified Methanol

4-Methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3. 1. 0] hex-2-ene (35) (50mg) in (a) methanol (2ml) and (b) acidified methanol (0. 1M;2ml) was irradiated in identical U. V. cells for a total of 16h, the photolyses being monitored by g. l. c. (QF1;100°) and the final products being analysed by n. m. r. spectra after removal of solvent.

(a) Methanol : G. l. c indicated that the ether was stable to photolysis in methanol. The n. m. r. of the photoproduct showed additional

resonances at 6.75τ and 8.90τ and an increased intensity (ca 20%) in the 9.10τ t-butyl signal of the starting material. The ratio of intensities of the 6.75τ signal to that of the starting material methoxy-signal (7.01τ) was ca 10:1.

(b) Acidified Methanol: The addition of acidic methanol to the ether caused immediate formation of a pale yellow solution, although g.l.c. suggested that no change had taken place. Upon photolysis, the signal due to starting material steadily decreased and had disappeared after 4h, replaced by two signals, one with retention time the same as 1,3,5-tri-t-butylbenzene (29). The product was analysed by n.m.r. after neutralisation and removal of solvent.

N.m.r. (CCl_4) τ : 8.71 (s), 2.90 (s) c.f. 1,3,5-tri-t-butylbenzene
9.50 (m), 9.12 (s), 9.07 (s), 8.93 (s),
7.18 (m), 5.14 (m) 8.49 (s), 8.47 (s)

These latter were v. minor signals (< 5% 8.71τ signal)

P.l.c. (alumina, pre-treated with ammonia vapour) with petrol as eluent, yielded two fractions.

Product (1) N.m.r (CCl_4)τ: 8.71 (27 H, s), 2.90 (9H, s)
c.f. 1,3,5-tri-t-butylbenzene (29)

Product (2) N.m.r. (CCl_4)τ: 9.50 (1H, m) , 9.12 (9H, s), 9.07 (9H, s)
8.93 (9H, s) 8.75 (1H, m), 8.44 (1H, m),
7.18 (1H, m), 5.14 (1H, m)

cf 2, 4, 6-Tri-t-butylbicyclo [3. 1. 0] hex-2-ene [105] :-

N. m. r. (CCl_4) 9. 48 (1H,m), 9. 12 (9H,s,) 9. 07 (9H, s) 8. 93 (9H, s)
8. 75 (1H,m), 8. 42 (1H, m), 7. 18 (1H,m.), 5. 14 (1H, m).

(xv) Irradiation of 4-Methoxy-2, 4, 6-exo-tri-t-butylbicyclo-[3. 1. 0] hex-2-ene (35) in Acidic Methanol

4-Methoxy-2, 4, 6-exo-tri-t- butylbicyclo [3. 1. 0] - hex-2-ene (35) (25mg) was dissolved in methanol (1ml) in a quartz n. m. r. tube and the n. m. r. spectrum was recorded in the 8. 3.- 9. 5 τ region.

N. m. r (MeOH) τ: 9. 10, 9. 01, 8. 86 Relative intensities 1:1:1.

The sample was then made acidic (0. 1M) by addition of acidified methanol and the n. m. r. spectrum was re-taken.

N. m. r. (MeOH/H^+) τ: 8. 92, 9. 10 Relative intensities 2:1

The sample was irradiated and the n. m. r spectrum was recorded after differing irradiation times. The results are tabulated below:-

TIME (h)	N. m. r. τ Value (approximate relative intensities)							
	8. 92	9. 10*	8. 71	8. 93	9. 05	9. 12	8. 47	8. 49
0	(2. 0)	(1. 0)	(0)	(0)	(0)	(0)	(0)	(0)
1	(2. 0)	(1. 0)	(2. 3)	(0. 25)	(0. 25)	(0. 25)	(0)	(0)
2	(2. 0)	(1. 0)	(4. 6)	(0. 50)	(0. 50)	(0. 50)	(0)	(0)
4	(2. 0)	(1. 0)	(13. 0)	(1. 8)	(1. 8)	(1. 8)	(0. 5)	(0. 5)
8	(2. 0)	(1. 0)	(11. 0)	(1. 8)	(1. 8)	(1. 8)	(1. 0)	(1. 0)

* After 8h the 9. 10 τ signal had reduced to ca 10% of its initial intensity.

(xvi) 'Dark' and 'Light' Reactions of 1, 3, 5- and 1, 2, 4-Tri-t-butylbenzene in Neutral and Acidic Methanol-O-d.

Eight experiments were carried out, in identical 10mm U. V. cells, summaried below:-

(a) 1, 3, 5-tri-t-butylbenzene(29) /MeOD/Dark
(b) 1, 3, 5-tri-t-butylbenzene(29) /MeOD/Light
(c) 1, 2, 4-tri-t-butylbenzene(31) /MeOD/Dark
(d) 1, 2, 4-tri-t-butylbenzene(31) /MeOD/Light
(e) 1, 3, 5-tri-t-butylbenzene(29) /MeOD/H^+/Dark
(f) 1, 3, 5-tri-t-butylbenzene(29) /MeOD/H^+/Light
(g) 1, 2, 4-tri-t-butylbenzene(31) /MeOD/H^+/Dark
(h) 1, 2, 4-tri-t-butylbenzene(31) /MeOD/H^+/Light

Each experiment comprised sample (50mg) in solvent (2ml); the neutral methanol-O-d contained a small amount of solid sodium carbonate. All samples were deoxygenated for 5 min, and irradiated for 16h, the 'dark' u. v. cells being completely enclosed in aluminium foil. The samples were worked up in the usual manner and analysed by n. m. r. and mass spectra:-

'Dark' Reactions

(a) N. m. r. (CCl_4) τ: 8. 71 (27H, s), 2. 90 (9H, s)

Mass spectrum m/e: 247(3), 246 (18), 232 (22), 231 (100), 57 (42).

(c) N. m. r. (CCl_4) τ: 8. 73 (9H, s), 8. 49 (9H, s), 8. 47 (9H, s)
3. 03 (1H, dd), 2. 64 (1H, d) 2. 52 (1H, d)

Mass spectrum m/e: 247(7), 246 (33), 232 (23), 231 (100), 189 (18), 175 (29), 57 (79)

(e) N.m.r. (CCl_4) τ: 8.71 (27H, s) 2.90 (9H, s)

Mass Spectrum m/e : 247 (3), 246 (15), 232 (22), 231 (100), 57 (53)

(g) N.m.r. (CCl_4) τ: 8.73 (9H. s), 8.49 (9H, s), 8.47 (9H, s) 3.03 (1H, dd), 2.64 (1H, d), 2.52 (1H, d)

Mass Spectrum m/e : 247 (7), 246 (35), 232 (19), 231 (100), 189 (14) 175 (24), 57 (44).

'Light'Reactions

(b) N.m.r. (CCl_4) τ :

8.71 (s), 2.90 (s)
9.10 (s), 9.04 (s), 8.87 (s)
8.30 (m), 7.01 (s), 5.24(m)
No signal at 9.27

} 1,3,5 -tri-t-butylbenzene (29) (ca 30%)
4-methoxy-2,4,6-exo-tri-t-butylbicyclo[3.1.0]hex-2-ene(35) (ca 70%)

Mass Spectrum m/e: 279 (11), 248 (12), 247 (5), 246 (15), 232 (27), 231 (100), 222 (48), 209 (12), 208 (48), 176 (14), 151 (27), 137 (15), 136 (13), 57 (72).

(d) N.m.r. (CCl_4) τ :

8.73 (s), 8.49 (s), 8.47 (s)
3.03 (dd), 2.64 (d), 2.52(d)
} 1,2,4-tri-t-butylbenzene (31) (ca 65%)

8.94, 9.02, 6.80, 3.95, 3.87 – 1,2,5-tri-t-butylDewarbenzene (32) (ca 15%)

9.23, 9.07, 7.93 – 1,2,5-tri-t-butylprismane (33) (ca 8%)

8.71, 2.90 – 1,2,4-tri-t-butylbenzene (29) (ca 5%)

9.10, 9.04, 8.87, 8.30, 7.01, 5.24 – 4-methoxy-2,4,6-exo-tri-t-butylbicyclo[3.1.0]hex-2-ene (ca 8%)

Mass Spectrum m/e: 247(5), 246 (25), 232 (13), 231 (72), 189 (10), 175 (16), 57 (100).

(f) N.m.r. (CCl_4) τ:

8.71 (s), 2.90 (s)	– 1,3,5-tri-t-butylbenzene (29) (ca 75%)
8.73, 8.49, 8.47 3.03, 2.64, 2.52	} 1,2,4-tri-t-butylbenzene (31) (ca 20%)
8.94, 9.02	– 1,2,5-tri-t-butylDewarbenzene (32) (ca 5%)

Mass spectrum m/e: 247(4), 246 (13), 232 (28), 231 (100), 57 (66)

(h) N.m.r. (CCl_4) τ:

8.73 (s), 8.49 (s), 8.47 (s) 3.03 (dd), 2.64 (d), 2.52 (d) +2.66(s) + 2.53 (s)	} 1,2,4-tri-t-butylbenzene (31) (ca 80%)
9.03, 8.94, 6.80, 3.95, 3.87	(ca 20%)
8.71, 2.90	Very little.

Mass spectrum m/e: 247(11), 246 (18), 233 (8), 232 (36), 231 (60), 189 (11), 176 (10), 175 (18), 57 (100.)

(xvii) Effect of Acid Concentration Upon the Photochemical Rearrangement of 1,3,5-Tri-t-butylbenzene (29) in Methanol.

1,3,5-Tri-t-butylbenzene (1g) and hexadecane (1g), as internal standard, were dissolved in methanol (80ml); five aliquots (15ml) were taken and made up to a constant volume (20.8 ml, 0.037M) with varying proportions of methanol and acidic methanol (3.58M) such that the five solutions were 0, 0.001, 0.01, 0.1 and 1M with respect to acid. Unfortunately, the 1M solution proved too polar and the hexadecane separated out, so that a correction had to be applied to results obtained from this sample. The five solutions were irradiated in identical quartz test-tubes. At timed intervals aliquots (0.5ml) were removed, neutralised with sodium carbonate

and sampled by g.l.c.(Carbowax/PEI, 150°). The peaks due to starting material, hexadecane and photoproduct were xeroxed, cut out and weighed.

Calibration using a standard solution of hexadecane and 1, 2, 4-tri-t-butylbenzene showed that the detector response for both benzenoid isomers was the same.

The OM, O.O1M and 1M acid irradiations were repeated, the 1M solution containing one fifth the amount of hexadecane as the OM and O.O1M samples.

The results were analysed using a least mean squares programme on a Hewlett-Packard 9100 calculator.

Equation to line has form $y = m x + c$

where $y = \frac{\text{mass 1, 2, 4-tri-t-butylbenzene g.l.c. peak.}}{\text{mass hexadecane g.l.c. peak.}}$

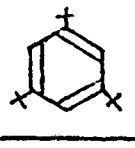
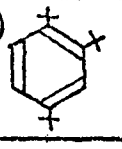
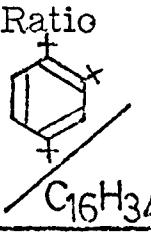
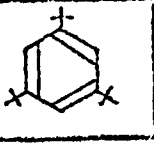
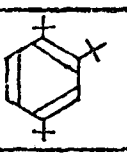
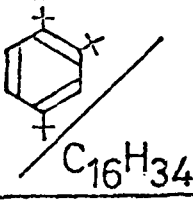
$x =$ time (min)

$m =$ gradient

$c =$ intercept on y-axis.

	Acid Concentration							
	OM	OM	10^{-3}M	10^{-2}M	10^{-2}M	10^{-1}M	1M	1M
m	0.012	0.006	0.050	0.085	0.072	0.094	0.047	0.058
C	-0.034	-0.016	-0.002	0.118	0.116	0.030	0.143	-0.036
Correlation factor.	0.935	0.945	0.999	0.997	0.993	0.999	0.958	0.980

The detailed results are tabulated on page 78 and are shown in Figure 8 (page 45) of this thesis.

Acid Conc. Irradn Time (min)	Weight (mg) of g.l.c. peak after photolysis			Ratio	Weight (mg) of g.l.c.peak after photolysis.			Ratio
		$C_{16}H_{34}$	(1) 			$C_{16}H_{34}$	(1) 	
OM 0	45.3	40.8	-	0	40.5	35.8	-	0
10	45.3	38.9	4.3	0.11	43.5	38.8	1.6	0.041
20	43.8	40.8	6.1	0.15	40.9	41.5	2.9	0.070
30	40.6	40.9	9.8	0.24	36.9	37.7	8.8	0.23
40	40.5	40.9	22.1	0.54	37.4	40.0	9.2	0.23
50	34.9	39.8	16.1	0.41	38.6	39.2	10.4	0.27
10^{-3}M								
0	49.1	40.7	-	0				
10	48.5	39.9	20.5	0.51				
20	40.8	39.2	37.1	0.95				
30	41.4	41.1	63.8	1.55				
40	41.1	40.5	80.0	1.98				
50	39.0	41.2	95.2	2.31				
10^{-2}M								
0	44.9	37.7	-	0	41.1	35.8	-	0
10	48.3	45.0	46.9	1.04	42.0	35.8	34.2	0.96
20	43.0	39.6	77.9	1.97	42.0	37.6	62.9	1.67
30	43.5	42.3	112.4	2.66	41.3	38.5	81.4	2.11
40	42.3	43.1	149.2	3.46	39.0	37.6	113.3	3.01
50	40.7	38.8	170.7	4.40	39.1	38.0	151.1	3.98
10^{-1}M								
0	47.4	39.3	-	0				
10	45.5	41.4	42.7	1.03				
20	44.1	38.2	70.9	1.86				
30	44.1	38.4	111.1	2.89				
40	42.5	40.0	150.8	3.77				
50	40.2	41.8	186.9	4.47				
1M								
0	-	-	-	-	46.1	39.5 (3)	-	0
10	31.7	12.7 (2)	20.0	0.55	47.5	41.4	17.1	0.41
20	37.0	13.3	55.1	1.44	44.5	35.6	39.6	1.11
30	36.8	14.3	67.9	1.65	40.3	36.0	72.2	2.01
40	35.3	14.2	74.3	1.82	39.8	39.5	83.3	2.11
50	36.4	15.5	101.1	2.27	39.9	35.6	89.8	2.52

Experiment Not Repeated.

Experiment Not Repeated.

(1) Measured at sensitivity x 100 that for 1, 3, 5-isomer and $C_{16}H_{34}$

(2) Corrected for hexadecane which separated out.

(3) Actual mass multiplied by 5.

(xviii) Fluorescence Studies

The fluorescence of 1, 3, 5-tri-t-butylbenzene (29) at room temperature in hexane (ca 1:3 x 10^{-3}M) has been reported, by Froehlich and Morrison [109], as being ca. 0.07 as intense as that of toluene, with quantum yield of fluorescence ca 0.01.

All attempts to reproduce this experiment and observe the fluorescence spectrum of 1, 3, 5-tri-t-butylbenzene were unsuccessful.

Methanol and hexane were used as solvents. The methanol was dried and purified by fractional distillation from magnesium; the 'Spectrosol' hexane (500ml) was washed with a 1:1 mixture of fuming and concentrated sulphuric acid (4 x 25 ml), with water until neutral and then fractionally distilled. Fluorescence studies, at maximum sensitivity, showed that both were free of fluorescent impurities.

The 1, 3, 5-tri-t-butylbenzene (29) was derived by two different synthetic routes. (See experiment (i), Sections B and D) Each sample was recrystallised four times and sublimed (60°, 15mm) twice. Recrystallisations were from fluorescer-free aqueous methanol.

Solutions (ca 4 x 10^{-3}M; optical density 0.7) were investigated, with and without deoxygenation with nitrogen for 10 min, in quartz 10mm fluorescence cells. A number of cells were used to ensure that contamination did not arise from this source.

In all cases exitation at 265nm produced very weak fluorescence with λ_{max} ca. 290nm; however, the excitation spectrum recorded did not show a 'mirror-image' relationship to the emission spectrum, and showed λ_{max} 280nm (cf absorption spectrum λ_{max} 263 nm). Rayleigh and Raman scattering also obscured much of the spectrum.

In contrast, excitation at 265nm of a non-deoxygenated 'Analar' toluene solution in hexane (4 x 10^{-3} M) produced a fluorescence

emission spectrum (λ_{max} 285nm), similar to that published[117] and showing a 'mirror-image' relationship with the excitation spectrum, which also corresponded closely to the toluene absorption spectrum.

Assuming that Froehlich and Morrison's value of 0.07 is correct for the ratio of fluorescence intensities of toluene and 1,3,5-tri-t-butylbenzene (29), that expected from 1,3,5-tri-t-butylbenzene (29) ought to have been readily observable with the equipment used.

C) Synthesis of 3,3-Dimethyl-2-butanone (Pinacolone) from Acetyl Chloride - Attempts to Maximise the Yield.

(i) t-Butylmagnesium Chloride and Acetyl Chloride [115]

(a) Magnesium turnings (98g) and a few crystals of iodine were placed in a flask fitted with stirrer, reflux condenser and dropping funnel. A portion (3ml) of a solution of t-butyl chloride (37.0g) in ether (50ml) was added. After the initial reaction had subsided, dry ether (20ml) was added. A further portion (47.5ml) of the halide/ether mixture was added dropwise with rapid stirring. The remaining mixture was further diluted with dry ether (30ml) and added dropwise after completion of the first addition. No external heating or cooling was applied. The flask was allowed to stand overnight to allow settling; the solution was standardised approximately by adding an aliquot (0.1ml) to hydrochloric acid (0.1M, 10ml) and titrating the resultant solution with standard sodium hydroxide solution (0.1N).

A sample of this Grignard reagent (2.4M; 50ml) was added very slowly, over 3h, to acetyl chloride (10g) in dry ether (20ml) at -70^{o}. The mixture was stirred for a further 2 h and then allowed to reach room temperature. The solution colour changed from

pale yellow to brown and then underwent a very rapid and vigorous reaction which yielded a yellow semi-solid product. The mixture was stirred for 15h and then added to a concentrated solution of ammonium chloride in water. The aqueous layer was extracted with ether; the ethereal extracts were combined, dried over anhydrous magnesium sulphate and the ether removed at room temperature on a rotary evaporator to yield a brown liquid (5g).

The n. m. r. spectrum indicated that pinacolone was present as a minor product only (ca 25%), the remaining signals being consistent with 3, 3-dimethylbutan-2-yl acetate formation.

N. m. r.($CDCl_3$) τ: 9. 11 (9H, s) 8. 90 (3H, d), 7. 97 (3H, s), 5. 30 (1H, q)
8. 87 (9H, s), 7. 87 (3H, s)

Pinacolone N. m. r.($CDCl_3$) τ: 8. 87 (9H, s), 7. 87 (3H, s)

An attempt to separate the mixture by fractional distillation was unsuccessful.

(b) Repeating the experiment at -10° also gave a mixture of these products with pinacolone in poor yield. Similarly repeating the experiment at -70° using tetrahydrofuran (freshly distilled from lithium aluminium hydride) as solvent gave pinacolone in low yield only.

(ii) t-Butyl-lithium and Acetyl Chloride

t-Butyl-lithium in pentane (ca 0. 8M;20ml) was added over 1. 5h to acetyl chloride (1. 0g) in dry ether (20ml) with vigorous stirring under nitrogen at room temperature, so that the solvent was maintained at gentle reflux. The mixture was stirred for a further 1h

and then allowed to stand for 15h. The resulting mixture was poured onto ice and hydrochloric acid (2M) and the organic products extracted with ether. After drying over anhydrous magnesium sulphate, removal of the ether and pentane by fractional distillation yielded a red-brown liquid (3.66g) which showed n.m.r. resonances at 8.87 and 7.87 τ in an approximate ratio of 3:1. Analysis by g.l.c. (Carbowax/KOH, 105°) indicated that pinacolone was present in low yield only (< 10%).

(iii) t-Butyl-lithium and Acetic Acid

(a) Acetic acid (1g), freshly distilled from acetic anhydride, in dry ether (20ml) was vigorously stirred under nitrogen at room temperature; to the solution was added t-butyllithium in pentane (0.75M;45ml) over 2h, at such a rate to keep the ether under gentle reflux. The solution was stirred for a further 15h. The product was poured onto ice and hydrochloric acid (2M) and extracted with ether. After drying with anhydrous magnesium sulphate, fractional distillation yielded a yellow oil as residue (1.13g) shown by g.l.c. (Carbowax/KOH, 105°) to contain ca 15% pinacolone.

(b) Repeating the reaction at -72° yielded a yellow liquid (1.3g) shown by g.l.c to contain ca 20% pinacolone.

(iv) Lithium Di-t-butylcuprate[110] and Acetyl Chloride

(a) To a suspension of cuprous iodide (2.5g) in dry ether (26ml) at -78° was added dropwise t-butyllithium in pentane (26mmole) under nitrogen. The initial suspension turned black, but at the end point a red-brown colouration was discernible. After 5 min, a cold (-78°) solution of acetyl chloride (1g) in ether (13ml) was added rapidly. After 1.25h, when the black solution had gone a lighter colour, the reaction was quenched with dry methanol (6.5ml). The

product was added to saturated ammonium chloride solution (300ml) and extracted with ether (3 x 100 ml). The extracts were combined, washed with a 1% sodium thiosulphate solution and dried over anhydrous magnesium sulphate. Fractional distillation of the ether yielded a green oil (0.8g), ca 40% being pinacolone, estimated by g.l.c.(Carbowax/KOH;105°).

(b) Repeating the experiment with a 2:1 molar ratio of organocopper compound to acetyl chloride yielded a green oil (1.64g) containing ca 50% pinacolone by g.l.c.

(v) Lithium t-Butoxy(t-Butyl)cuprate [116] and Acetyl Chloride.

To a stirred suspension of cuprous iodide (5g) in dry ether (40ml) under nitrogen at room temperature was added an ethereal solution of lithium t-butoxide (26 mmol), prepared by adding t-butyllithium (26mmol) to dry t-butanol (2g, 26mmol) in ether at 0° under nitrogen. After 15 min. all the grey cuprous iodide had been replaced by a green suspension. The mixture was cooled to -78° and t-butyllithium (26mmol) in pentane added dropwise. Precooled (-78°) acetyl chloride (1g) in ether (12ml) was rapidly added and the reaction quenched after 30 min with dry methanol (10ml).

Work-up by the procedure used in experiment (iv) yielded a green liquid (1.44g) containing ca 10% pinacolone by g.l.c. (Carbowax/KOH;105°).

D) Synthesis of 1, 3, 5-Tri-t-butylbenzene (29) from Pinacolone - Attempts to Maximise Yield

(i) Pinacolone and Sodium Hydride [111]

(a) Sodium hydride, as an 80% dispersion in oil (1.5g), was placed in a flask equipped with magnetic stirrer, reflux condenser and pressure-equalising dropping funnel, under nitrogen.

Pinacolone (5g) was added with stirring; hydrogen was evolved and the reaction allowed to subside at room temperature. The mixture was then heated to 65-70° when a more vigorous reaction took place. After completion of this reaction the orange solid was cooled to room temperature. Pinacolone (2.5g) was added and the temperature raised to 190° for 20h. After cooling, water was slowly added and the mixture neutralised with dilute sulphuric acid. The organic products were extracted into ether, washed with aqueous sodium carbonate and water, dried over magnesium sulphate and the ether evaporated to leave a yellow oily liquid (5.0g). Column chromatography on silica gel (150g) using petrol as eluent yielded a colourless liquid (1.94g) which when crystallised from aqueous methanol yielded 1,3,5-tri-t-butylbenzene (29) (1.25g);

m.p. 74 -74.5° (lit 75°)

N.m.r.(CCl_4) τ: 8.71 (27H, s) 2.90(3H, s)

Further column chromatography using 10% ether/90% petrol as eluent yielded a second product (2.7g), a yellow oily liquid with n.m.r. consistent with that expected from 2,2,5,6,6,-pentamethyl-4-heptene-3-one, reported as a by-product of the reaction.[111]

N.m.r. (CCl_4) τ : 8.91 (18H, s), 8.00 (3H, d, J = 1 Hz)
3.75 (1H, q, J = 1 Hz)

(b) Repeating the reaction in dry diglyme, freshly distilled off sodium, yielded the ketone product above, with no 1,3,5-tri-t-butylbenzene (29) present.

(ii) Attempted Hydrolysis of 2, 2, 5, 6, 6 -pentamethyl-4-heptene-3-one.

2, 2, 5, 6, 6-Pentamethyl-4-heptene-3-one (182mg) and sodium hydroxide solution (0. 1N, 5ml) were heated under reflux for 24h. The organic products were extracted into ether. After drying over anhydrous magnesium sulphate and fractional distillation, analysis of the residue by n. m. r. revealed that it was exclusively unreacted starting material. Extraction with ether of the neutralised aqueous solution yielded no further organic products.

(iii) 'Half' Reaction of Pinacolone with Sodium Hydride.

This experiment was a repeat of experiment (i) except that the reaction was quenched with alcohol when the reaction at 65° of the first pinacolone portion was completed. Routine work-up of the resultant mixture and analysis by n. m. r. revealed that the sole product was 2, 2, 5, 6, 6-pentamethyl-4-heptene-3-one.

(iv) Pinacolone and Aqueous Sodium Hydroxide.

(a) Pinacolone (1g) and aqueous sodium hydroxide (2N;50ml) were heated together for 170h under reflux. Removal of aliquots (1ml) at timed intervals, followed by ether extraction and analysis by g. l. c.(Carbowax/KOH, 90°) revealed that no 1, 3, 5-tri-t-butyl-benzene (29) had been produced.

(b) Repeating the experiment in ethylene glycol at 173° for 170h also failed to produce any 1, 3, 5-tri-t-butylbenzene (29) although g. l. c.did indicate that a little 2, 2, 5, 6, 6-pentamethyl-4-heptene-3-one might be present.

(v) Attempted Coupling of 2, 2, 5, 6, 6 - Pentamethyl-4-heptene-3-one and Pinacolone

This experiment used a method analogous to that described by Nielson et al [112] using N-methylanilinomagnesium bromide as condensing agent.

(a) Bromoethane (400mg) in dry ether(1 ml) was added to magnesium turnings (80mg) in a pear shaped flask fitted with air stirrer, condenser and dropping funnel, under nitrogen. Freshly distilled N-methylaniline (320mg) in dry benzene (1ml) was added with cooling. 2, 2, 5, 6, 6 - Pentamethyl-4-heptene-3-one (640mg) in dry benzene (0. 5ml) was added over 15 min, keeping the temperature at ca 15°. After addition was complete the mixture was stirred for 30min and then pinacolone (240mg) in dry benzene (0. 25ml), added over 30 min at -12°. The mixture was further stirred at -10° to -5° for 1h and then at room temperature for 1h. Hydrochloric acid (3M;3ml) was added and the organic layer separated. It was washed with hydrochloric acid (6N) and with water. After drying over anhydrous sodium sulphate, the volatile components were removed. The n. m. r. spectrum of the residue (712mg) revealed that it was predominantly starting ketone with no 1, 3, 5-tri-t-butylbenzene (29) present.

(b) Repeating the experiment at room temperature and allowing the mixture to stand overnight after addition of pinacolone again yielded starting ketone (725mg) only.

(vi) 'Half' Reaction of 2, 2, 5, 6, 6-Pentamethyl-4-heptene-3-one and N-Methylanilinomagnesium Bromide

The reaction was repeated exactly as for (v), except that deuterium oxide (2ml) was added instead of pinacolone. After a similar work-up procedure a yellow oil (480mg) was isolated.

After p.l. c.of this product on silica gel, with 5% ether/ 95% petrol as eluent, analysis by n. m. r.and mass spectra showed that deuterium had been incorporated in the recovered 2, 2, 5, 6, 6-pentamethyl-4-heptene-3-one.

N. m. r. (CCl_4) τ: 8. 91 (18H, s), 8. 00 (2. 5H, m), 3. 75 (1H, m)

Product mass spectrum m/e 183 (3), 127 (13), 126 (100), 125 (36), 57 (65)

Authentic ketone mass spectrum m/e 182 (2), 127 (3), 126 (11), 125 (100), 57 (20).

E) Carbon-13 N. M. R. Studies on Tri-t-butylbenzenes - Assignment of Hydrogen - Carrying Aromatic Carbon Atom Signals.

(i) Spectrum of 1, 3, 5-Tri-t-butylbenzene (29)

^{13}C N. m. r. ($CDCl_3$) 50mg/1600 scans.

Assignment	Decoupled p. p. m.	Non-decoupled form	Intensity
t- butyl $^{13}CH_3$	31. 6	q	169
- ^{13}C $(Me)_3$	35. 0	s	14
Aromatic ^{13}C - H	119. 5	d	57
Aromatic ^{13}C-t-Bu	150. 0	s	18

(ii) Spectrum of 1, 2, 4-Tri-t-butylbenzene (31)

^{13}C N.m.r. ($CDCl_3$) 50mg/1300 Scans.

Assignment	Decoupled ppm	Non-decoupled form	Intensity
t-butyl $^{13}CH_3$	31.3	q	67
	34.8	q	136
- $^{13}C(Me)_3$	37.2	s	11
	38.0	d	12
Aromatic ^{13}C-H	122.3	d	27
	126.8	d	22
	129.1	d	26
Aromatic ^{13}C-t-Bu	148.2	s	very weak visible only above baseline after 7,300 scans.
	147.4	s	
	145.6	s	

(iii) Preparation and Spectrum of 5-d-1, 2, 4-Tri-t-butylbenzene

1, 2, 4-Tri-t-butylbenzene (31) (500mg) was irradiated for 40h (See experiment (xiii), Section B). Preparative g.l.c. yielded 5-d-1, 2, 4-tri-t-butylbenzene mixed with starting material (130mg, ca 25% D incorporation), sufficient for ^{13}C n.m.r. analysis.

^{13} N.m.r. ($CDCl_3$) 130mg/2850 scans.

Assignment	Decoupled ppm	Decoupled Multiplicity	Intensity
t-butyl-$^{13}CH_3$	31.3	s	182
	34.8	s	368
-$^{13}C(Me)_3$	37.2	s	25
	38.0	s	39
Aromatic ^{13}C-H	122.2		34
	126.8		59
	128.9	m	14
	129.0		38
	129.1		41
Aromatic ^{13}C-t-Butyl	145.5	s	16
	147.3	s	17
	148.1	s	25

(iv) Spectrum of a mixture of 3-d-and 5-d-1,2,4-Tri-t-butylbenzene

(a) For preparative details see experiment (ix), Section B, which produced a mixture of the deuterated isomers. A sample (90mg) was analysed by ^{13}C n.m.r. The signal at 129.1 ppm was again a multiplet (see above); the ^{13}C-H resonance at 126.8 ppm appeared to have been broadened, but had not become a multiplet. The signal at 122.2 ppm remained unchanged.

(b) The preparation was repeated on a larger scale: 1,3,5-isomer (1.5g) in acidic methanol (0.1M;60ml) was photolysed. Preparative g.l.c. yielded a greater quantity of 1,2,4-isomer (250mg). The ^{13}C n.m.r. spectrum of this product showed the 129.1 ppm resonance as a broad multiplet and the 126.8 ppm signal as a much broadened singlet. Again the 122.2 ppm resonance was unaltered.

F) Preparation and Photolysis of 1, 3, 5-$^{13}C_3$ Enriched 1, 3, 5-Tri-t-butylbenzene

(i) 2-^{13}C -Enriched 3, 3-Dimethyl-2-butanone (2-^{13}C-Pinacolone)

The same experimental procedure was employed as that described in experiment (ivb) Section C, using 1-^{13}C acetyl chloride (90%;1g). The labelled pinacolone was collected in a diluted state by fractional distillation of the reaction product, to which had been added unlabelled pinacolone (6g). Addition of a further portion of unlabelled pinacolone (1g) and a second fractional distillation yielded sufficient pinacolone (7. 67g) for the next stage of the synthesis. The approximate level of ^{13}C incorporation was, by mass spectrometry, determined to be ca 4. 6% after consideration of the absolute count numbers of the m/e 43 and 44 signals (loss of 57 from 100 and 101) in both enriched and unlabelled compounds.

Non-enriched

Mass spectrum m/e 43 (345), 44 (9), 57 (489)

Average of 8 runs

Enriched

Mass spectrum m/e 43 (344), 44(25), 57(489)

Average of 5 runs

(ii) 1, 3, 5-$^{13}C_3$ Enriched 1, 3, 5-Tri-t-butylbenzene

This compound was synthesised using the partially labelled pinacolone (7. 5g) and sodium hydride, by the method of experiment (i), Section D . Column chromatography yielded crude, partially labelled 1, 3, 5-tri-t-butylbenzene. Crystallisation from aqueous methanol gave 1, 3, 5-tri-t-butylbenzene (275mg) partially labelled with ^{13}C in the 1, 3 and 5 positions. The approximate extent of ^{13}C incorporation was estimated from the ^{13}C n. m. r spectrum as ca 5% by comparing signal intensities of enriched and non-enriched samples run under identical conditions.

Assignment	Decoupled ppm	Intensity	
		Enriched	Unlabelled.
Aromatic ^{13}C-H	119.5	104	104
Aromatic ^{13}C-t-Butyl	150.0	100	17

(iii) Photolysis of 1, 3, 5-^{13}C Enriched 1, 3, 5-Tri-t-butylbenzene in Acidic Methanol

^{13}C-Enriched 1, 3, 5-tri-t-butylbenzene (275mg) in acidic methanol (0.1M; 11.5ml) was deoxygenated for 10 min and then irradiated for 41h. The solution was neutralised with sodium carbonate and the methanol removed. The yellow liquid remaining (270mg) was investigated by ^{13}C n.m.r.

^{13}C n.m.r. ($CDCl_3$)

Assignment	Decoupled p.p.m.	Intensity
1, 3, 5 Aromatic ^{13}C - t-Butyl	150.0	161
1, 3, 5 Aromatic ^{13}C-H	119.5	76
1, 2, 4 Aromatic ^{13}C-t-Butyl	148.2	16
	147.4	14
	145.6	15
1, 2, 4 Aromatic ^{13}C-H C_5	129.1	12
C_3	126.8	13
C_6	122.3	12

The photolysis mixture was subsequently separated by preparative g.l.c, yielding partially labelled 1,3,5-tri-t-butylbenzene (54.8mg) and 1,2,4-tri-t-butylbenzene (30.5mg). The ^{13}C n.m.r. spectra of both enriched isomers were obtained, that of the 1,3,5-isomer being compared with a spectrum of non-enriched isomer run under exactly the same conditions. Comparison of signal intensities gave the extent of ^{13}C incorporation in recovered 1,3,5-isomer as ca 5%.

Assignment	Decoupled p.p.m.	Intensity	
		Enriched	Unlabelled
1,3,5 Aromatic ^{13}C-t-butyl	150.0	254	42
1,3,5 Aromatic ^{13}C-H	119.5	131	124
1,2,4 Aromatic ^{13}C-t-butyl	148.2	63	
	147.4	51	
	145.6	73	
1,2,4 Aromatic ^{13}C-H C_5	129.2	45	
C_3	126.9	47	
C_6	122.3	40	

CHAPTER 3

PHOTOCHEMISTRY OF THE DIMETHYLPYRIDINES

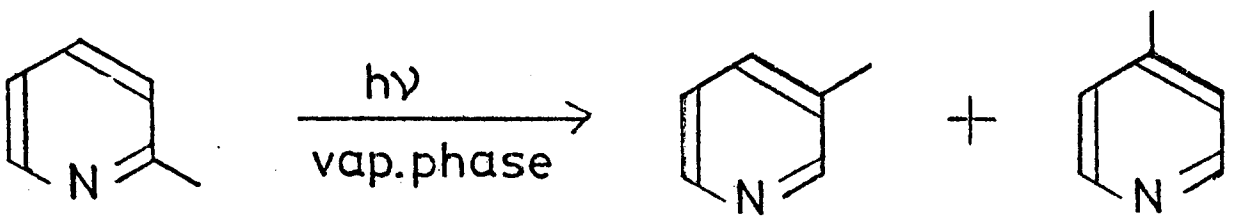
INTRODUCTION.

The gas-phase photochemistry of 2-methylpyridine (51) has been investigated by two groups of workers, (i) Roebke[77] and (ii) Caplain and Lablache-Combier[76]. These two groups reported rather different results.

In his experiments, Roebke analysed the products formed after photolysis of 2-methylpyridine at various wavelengths. To ensure that the amount of light absorbed at each wavelength was the same, differing pressures of 2-methylpyridine vapour were used. These pressures lay in the range 1-7 torr. Roebke found that irradiation within the $\pi\pi^*$ band (0-0 band at 265. 7nm) gave 3- and 4- methylpyridines, (54) and (52) as products, identified by g. l. c.on two columns. In contrast, irradiation within the $n\pi^*$ band (0-0 band at 277. 6nm) yielded no detectable products. At shorter wavelengths ($<$ 265. 7nm) increased yields of isomers were produced, the ratio of 3- to 4- methylpyridine being 10 to 1 at all wavelengths. This observation suggested that vibrationally excited molecules were required for transposition to take place. To support this conclusion, it was found that the presence of an inert gas quenched the formation of isomers, presumably by aiding vibrational relaxation. The presence of cis-but-2-ene and, especially, oxygen caused enhanced quenching, possibly implying that the triplet excited state was of importance in the transposition process. Roebke drew no specific conclusion about the mechanism of the rearrangement, beyond stating that a prismane-type or a sequential 1, 2 -shift-type mechanism would be consistent with the products observed.

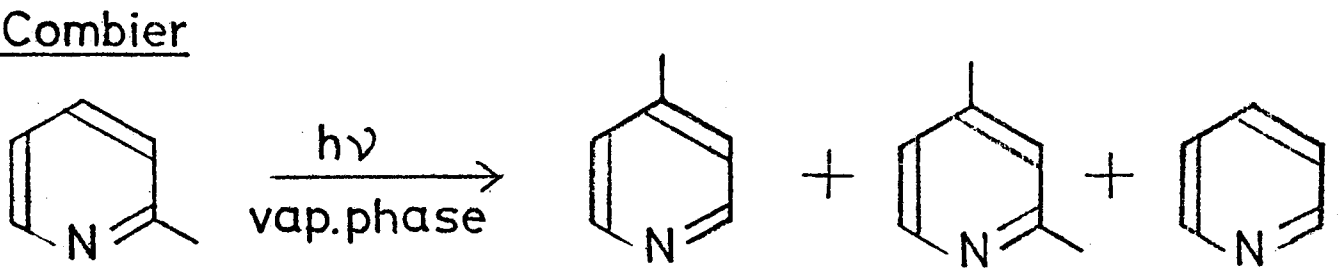
Lablache-Combier performed his irradiation of 2-methylpyridine in a Rayonet reactor at 254nm with a pressure of 10 torr of starting material vapour. He reported that 4-methylpyridine was produced as the major product together with 2,4-dimethylpyridine (53) and pyridine (47); all of these compounds were characterised by g.l.c.on a capillary column. The presence of 4-methylpyridine was also established by n.m.r.spectroscopy, even though it was only present in a 1-2% yield. No 3-methylpyridine was observed as a product, in sharp contrast to Roebke's observations where it was the major photoproduct.

Roebke



(51) (54) (52)

Lablache-Combier

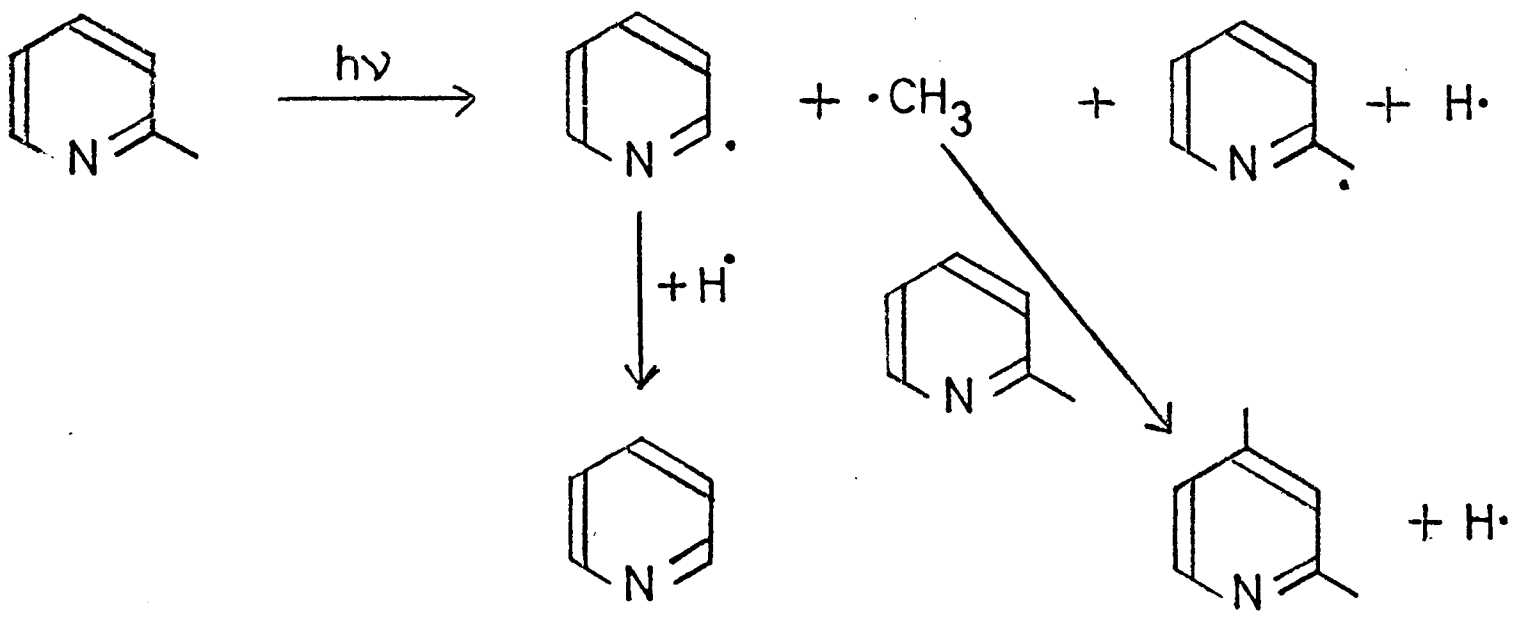


(51) (52) (53) (47)

Lablache-Combier also irradiated 3- and 4-methylpyridines, (54) and (52), and the six dimethylpyridine isomers in the vapour phase. From the results of these nine experiments he proposed a mechanism for the rearrangements. His results for the nine compounds are tabulated below:-

Starting Material	Products
2-Me-pyridine	4-Mepyridine + 2, 4 Me_2pyridine + pyridine
3-Me-pyridine	pyridine
4-Me-pyridine	2-Mepyridine + pyridine
2, 3-Me_2pyridine	2, 5Me_2pyridine + 3, 4-Me_2pyridine
2, 4-Me_2pyridine	2, 6-Me_2pyridine
2, 5-Me_2pyridine	2, 3-Me_2pyridine + 3, 4-Me_2pyridine
2, 6-Me_2pyridine	2, 4-Me_2pyridine
3, 5-Me_2pyridine	No isomeric products
3, 4-Me_2pyridine	2, 3-Me_2pyridine + 2, 5-Me_2pyridine.

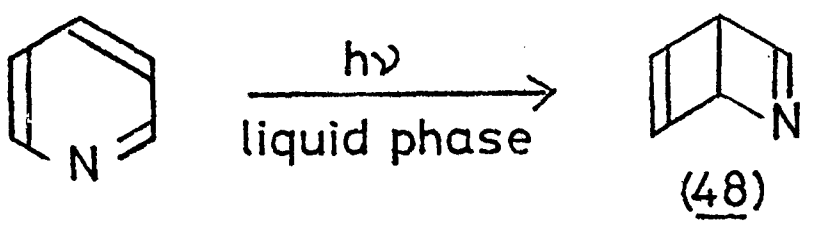
The results for the three methylpyridine isomers are rather puzzling. The formation of 2, 4-dimethylpyridine and pyridine from 2-methylpyridine were readily explained in terms of a demethylation/ remethylation process:-



However, it is not at all clear why both 3- and 4-methyl-pyridines should both yield pyridine, presumably by an analogous process, but no dimethylpyridine products. Similarly,it is surprising that none of the dimethylpyridines yield monomethyl- or trimethyl-pyridine products. All that may be concluded is that, in part at least, a radical mechanism

is in operation.

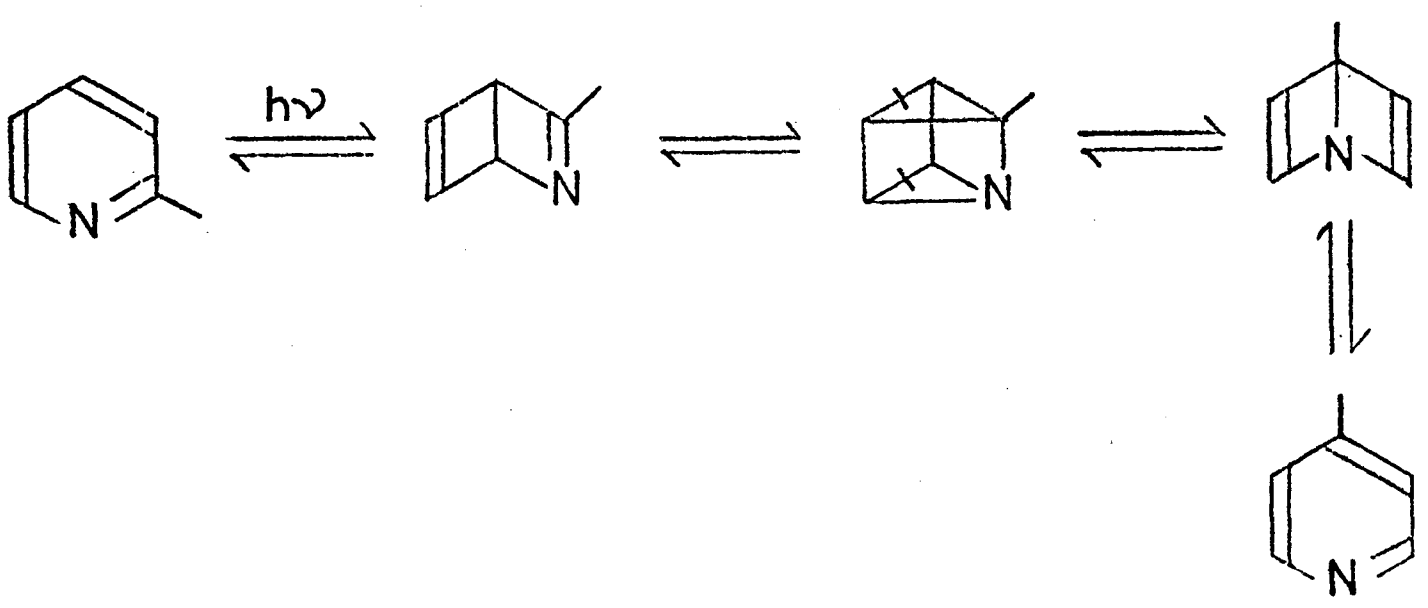
Analysis of all of the results indicated (i) that the carbon atoms at C_2 or C_6 were exchanging with that at C_4 and (ii) that the atoms at C_3 and C_5 or C_2 and C_6 were exchanging with one another. All of these exchanges were 1,3-transpositions and, therefore, according to Lablache-Combier, were most readily explained in terms of the intermediacy of azaDewarbenzene and/or azaprismane isomers. His rationale was that the azaDewarbenzene (48) had been isolated by Wilzbach and Rausch after photolysis of pyridine in the liquid phase [72].



(48)

Hence, the following mechanistic schemes were proposed:-

(i)



(ii)

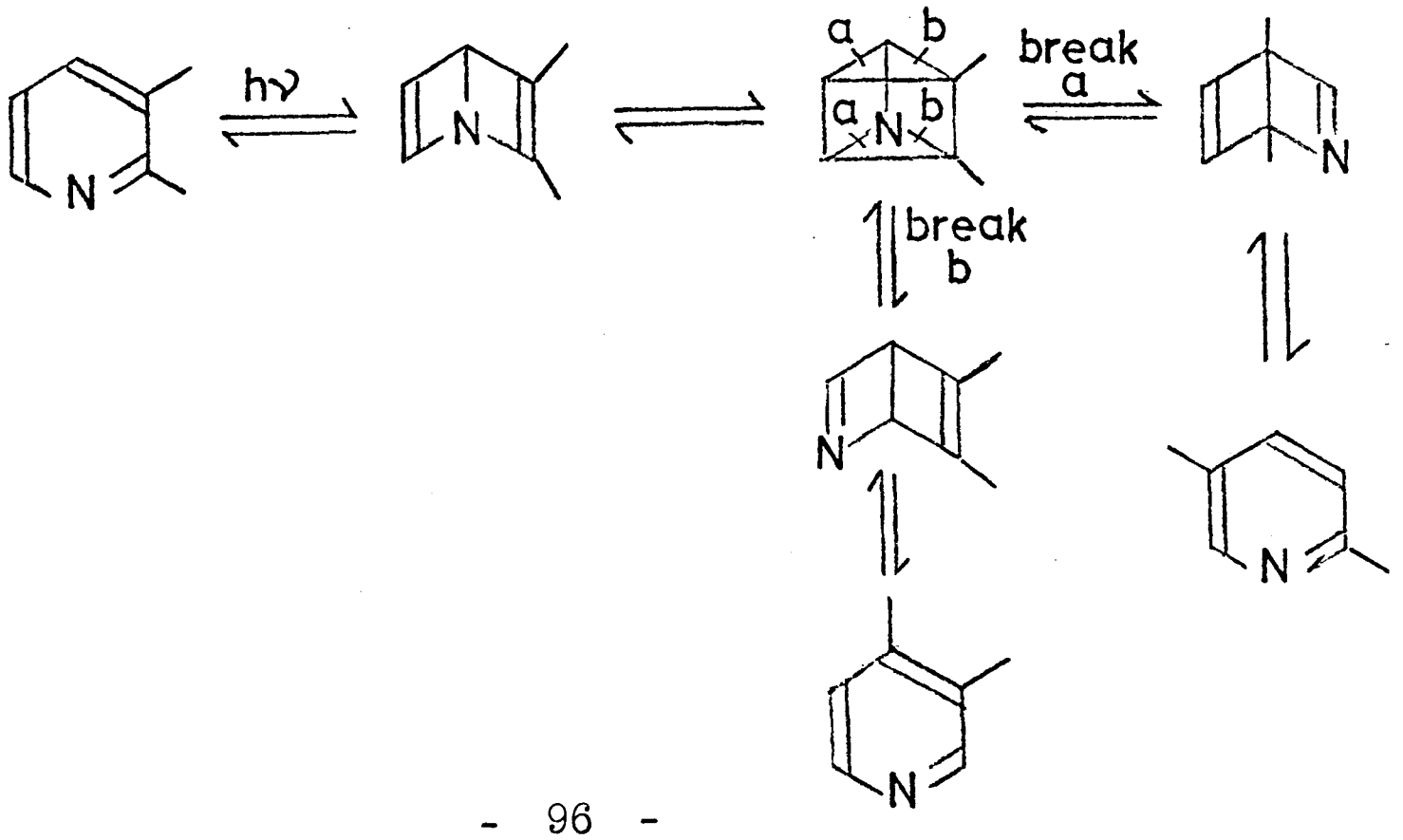
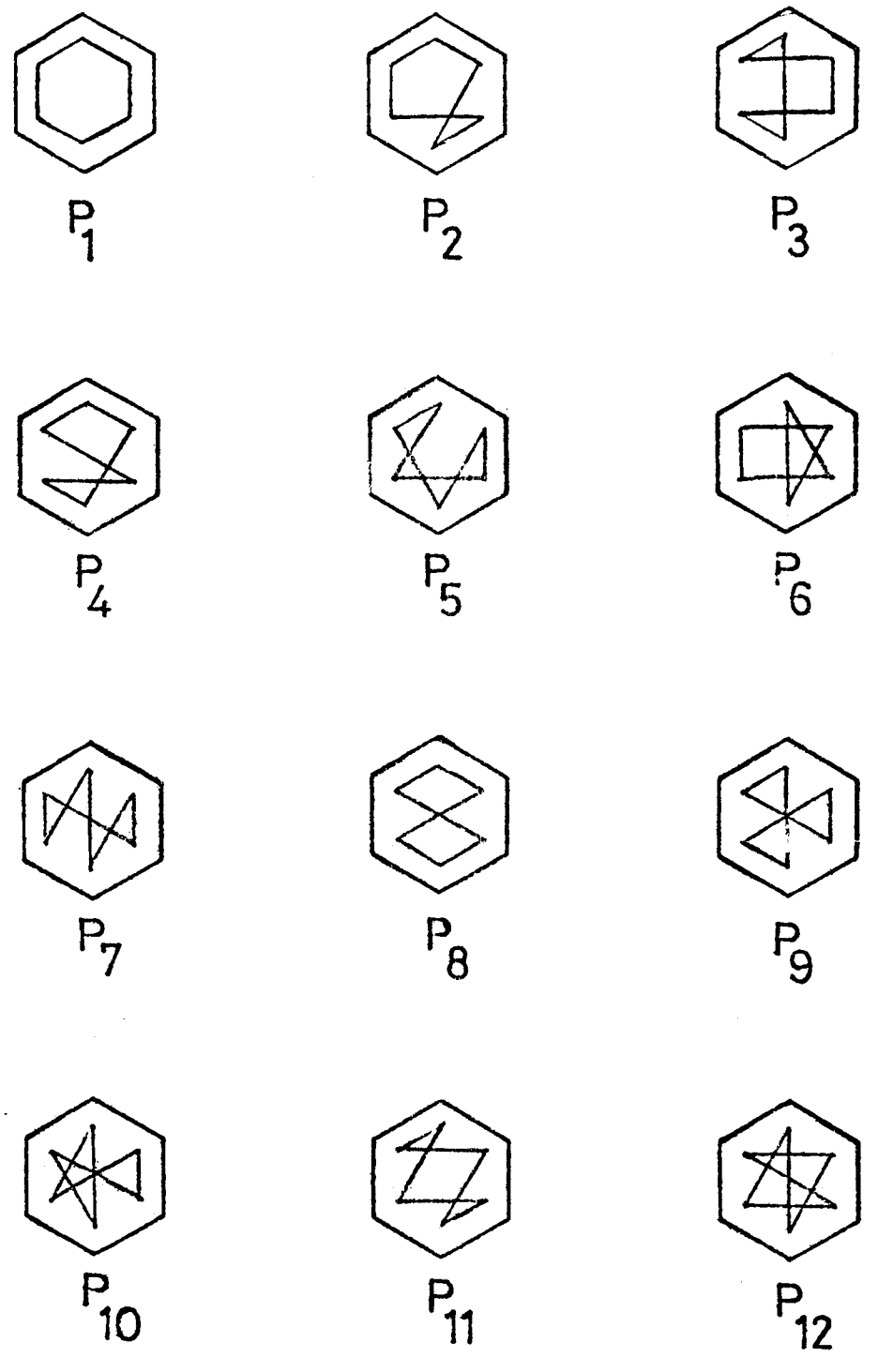
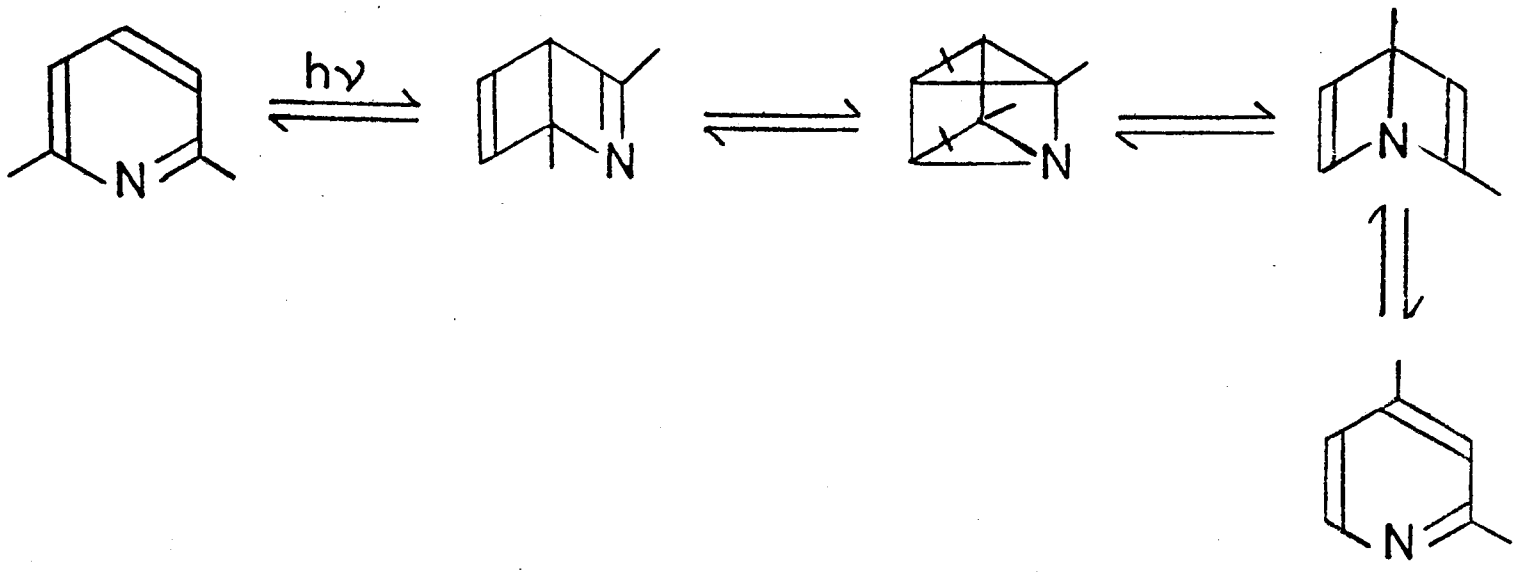


Figure 9

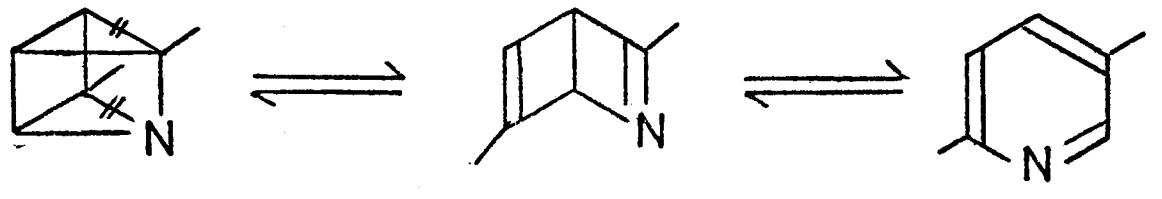
Permutation patterns for six-membered rings [71]



(iii)



However, for example (iii) there is a third mode of cleaving the prismane which would yield 2, 5-dimethylpyridine:



This compound was, apparently, not observed. Since all possible cleavage products were observed in example (ii), a doubt must arise as to whether the intermediate in example (iii) really was the azaprismane shown.

This point introduces a general objection to the mechanisms proposed by Lablache-Combier; namely, that while a particular prismane and subsequent cleavage can lead to the observed photoproducts, it is often necessary to discount the formation of other prismanes and alternative cleavage modes. Evidently such an objection could be overcome if there was a general rule to predict which of the possible azaprismanes would be formed (i.e. whether the azaDewar precursor undergoes C_2-C_5, C_6-C_3 or C_4-N bonding) and how it would cleave. However, this is not possible since no such pattern emerges from these results.

It might be, therefore, that an alternative mechanism is in operation. To ascertain whether this is likely, it is convenient to make use of Barltrop and Day's permutation pattern approach [71] to determine whether a common permutation can account for all the products that were observed. The permutation approach is very simple to apply to Lablache-

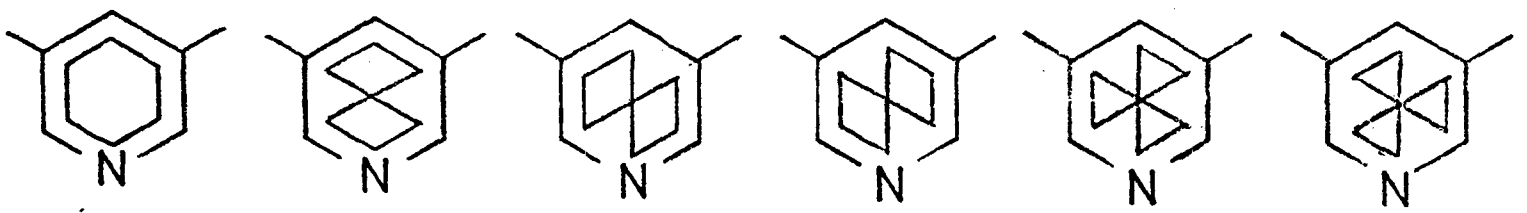
TABLE 2

Permutation Analysis of Lablache-Combier's Results for Dimethylpyridine Photolyses

Starting Material	Product After Permutation				
	$P_8(1)$	$P_8(2)$	$P_8(3)$	$P_9(1)$	$P_9(2)$
2, 6-Me_2Py	2, 6-Me_2Py	2, 6-Me_2Py	2, 4-Me_2Py	2, 4-Me_2Py	2, 4-Me_2Py
2, 5-Me_2Py	2, 3-Me_2Py	2, 5-Me_2Py	3, 4-Me_2Py	2, 3-Me_2Py	3, 4-Me_2Py
2, 4-Me_2Py	2, 4-Me_2Py	2, 6-Me_2Py	2, 4-Me_2Py	2, 6-Me_2Py	2, 4-Me_2Py
2, 3-Me_2Py	2, 5-Me_2Py	2, 3-Me_2Py	3, 4-Me_2Py	2, 5-Me_2Py	3, 4-Me_2Py
3, 5-Me_2Py	3, 5-Me_2Py	3, 5-Me_2Py	3, 5-Me_2Py	3, 5-Me_2Py	3, 5-Me_2Py
3, 4-Me_2Py	3, 4-Me_2Py	2, 5-Me_2Py	2, 3-Me_2Py	2, 3-Me_2Py	2, 5-Me_2Py

Combier's results.

Consider the case of 3, 5-dimethylpyridine which was unchanged photochemically. Using Barltrop and Day's notation (See Figure 9) only the following permutation patterns result in no overall rearrangement:-



$P_1(1)$ $P_8(1)$ $P_8(2)$ $P_8(3)$ $P_9(1)$ $P_9(2)$

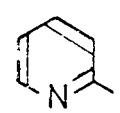
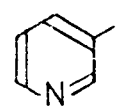
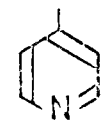
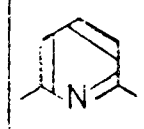
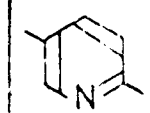
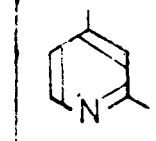
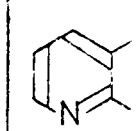
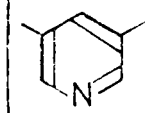
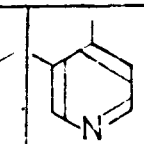
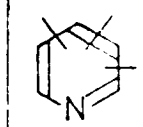
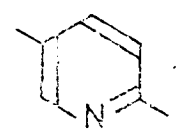
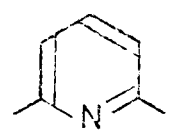
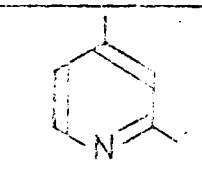
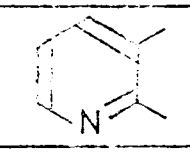
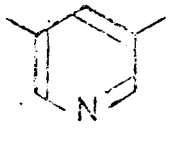
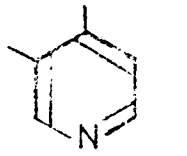
Neglecting the trivial permutation, P_1, and assuming that a common set of permutation patterns must be preserved for each dimethylpyridine, it may readily be shown that P_8, in the orientations (1), (2) and (3), or P_9, in the two orientations (1) and (2), give specifically those dimethylpyridine photoproducts observed and no others (See Table 2).

This analysis provides strong evidence that alternative reaction mechanisms could account accurately for the products observed. However, this approach does require that the results reported by Lablache-Combier are correct. In view of the disagreement between his result and that of Roebke for the photolysis of 2-methylpyridine, it appeared necessary to repeat Lablache-Combier's work.

The purpose of the present study was to repeat those irradiations and to attempt to rationalise the results obtained.

TABLE 3

RESULTS OF DIMETHYLPYRIDINE PHOTOLYSES

Starting Material	Test Method: Irradiation Condition	Irradiation Source	Irradiation Time (h)	G.l.c. Column	Pyridine Products (%)[3]										Conclusion Major Products
															
	(a)[1]	MP[2]	48	Carb/KOH	Minor	Minor	-	Minor	95	?	v. minor	major	v. minor	major	3,5-Me$_2$Py
	(b)	MP	17	Carb/TEA	4.0	4.0	-	1.0	76	?	0.3	11.0	0.3	3.0	3,5-Me$_2$Py
	(b)	MP	17	Capill	-	-	-	-	98	2	-	-	-	-	2,4-Me$_2$Py
	(b)	R	17	Carb/TEA	0.3	0.3	-	0.05	98	?	-	1.0	-	0.3	3,5-Me$_2$Py
	(b)	R.	17	Capill.	-	-	-	-	98	2.0	-	-	-	-	2,4-Me$_2$Py
	(a)	MP	48	Carb/KOH	Major	-	-	84	-	-	major	-	major	major	2,3- +3,4-Me$_2$Py
	(b)	MP	17	PPE/TEA	Major	-	-	90	-	-	major	-	?	major	2,3-Me$_2$Py
	(b)	MP	17	Carb/TEA	10	-	-	68	0.2[4]	0.2[4]	12	-	3.5	6	2,3- +3,4-Me$_2$Py
	(b)	R	17	Carb/TEA	5	-	-	80	0.1	0.1	9.0	-	3.0	5.0	2,3- +3,4-Me$_2$Py
	(b)	R	1	Carb/TEA	0.6	-	-	96	-	-	1.9	-	0.6	0.6	2,3- +3,4-Me$_2$Py
	(b)	MP	17	Carb/TEA	3.0	-	3.0	1.5	?	87	-	3.3	0.2	1.5	3,5-Me$_2$Py
	(b)	MP	17	Capill.	-	-	-	-	8.3	91	-[5]	-	-	-	2,5-Me$_2$Py
	(b)	R	17	Carb/TEA	0.9	-	1.0	0.8	?	94	?[5]	1.8	0.09[4]	1.8	3,5-Me$_2$Py
	(b)	R	17	Capill.	-	-	-	-	8.0	92	-	-	-	-	2,5-Me$_2$Py
	(b)	MP	17	Carb/TEA	2.9	3.2	-	12	0.1[4]	0.1[4]	77	?[5]	2.3	2.8	2,6- +3,4-Me$_2$Py
	(b)	R	17	Carb/TEA	1.3	1.4	-	6.7	0.1[4]	0.1[4]	87	0.1[4]	3.7	0.1	2,6- +3,4-Me$_2$Py
	(a)	MP	48	Carb/KOH	0.3[4]	1.8	-	-[4]	1.6	1.1	-	95	-	-	2,5- + 2,4-Me$_2$Py
	(b)	MP	17	Carb/TEA	0.4[4]	2.3	-	0.3[4]	7.4	5.8	-	80	-	3.4	2,5- +2,4-Me$_2$Py
	(b)	R	17	Carb/TEA	0.05[4]	0.5	-	0.05[4]	4.2	3.1	0.02[4]	92	0.02[4]	0.1	2,5- +2,4-Me$_2$Py
	(b)	R	17	Capill.	-	-	-	-	5.9	4.5	-	90	-	-	2,5- +2,4-Me$_2$Py
	(a)	MP	48	Carb/KOH	OVER PHOTOLYSED NO PRODUCTS DETECTED.										
	(a)	MP	8	Carb/KOH	-	Major[4]	Major[4]	Minor[4]	-	-	Minor[4]	-	97	Minor	2,6-+2,3-Me$_2$Py
	(b)	MP	24	Carb/KOH	-	Major[4]	Major[4]	Minor[4]	-	-	Minor[4]	-	95	Minor	2,6-+2,3-Me$_2$Py
	(b)	MP	17	Carb/TEA	1.0	13.1		3.1	0.2	0.2	4.1	0.3	77	0.3	2,6-+2,3-Me$_2$Py
	(b)	R	17	Carb/TEA	2.1	22.9		4.7	?[5]	?[5]	5.1	?[5]	64	-	2,6-+2,3-Me$_2$Py

1 (a) Liquid present in photolysis vessel
(b) No Liquid present

2. MP = Medium pressure lamp
R = Rayonet reactor.

3. Expressed as % of recovered material.
4. Indentified by g. l. c. retention time only.
5. Some evidence by g. c. m. s. No discrete g. l. c. signal.

PHOTOCHEMISTRY OF THE DIMETHYLPYRIDINES

RESULTS AND DISCUSSION

Photoproduct identities were established by the following criteria: (i) g.l.c. retention time (ii) single signal formation on co-injection of the photoproduct with authentic compound and (iii) mass spectroscopy of the eluted g.l.c.peaks, where possible. The g.c.m.s. system did not always allow detection of signals caused by minor products. In all cases, signals assigned to dimethylpyridines showed either a parent ion or a strong signal at m/e 107; stronger signals showed the characteristic splitting pattern of a dimethylpyridine, i.e. m/e 107, 106, 92, 79, 77, 66, 65, 63, 53, 52, 51, 50, 39, 38. Peaks with parent ions at m/e 93 or m/e 121 were assigned to methylpyridines or trimethylpyridines respectively.

2, 4- And 2, 5-dimethylpyridines could only be completely separated from each other by using a capillary g.l.c.column and the presence of one of these isomers as a photoproduct of the other isomer was established by g.l.c.retention time and co-injection with authentic compound on this column.

Since photoisomerisation to minor products was a very low-yield process, (typically $< 0.5\%$), each of the dimethylpyridines, except 2,3-dimethylpyridine, were purified by re crystallisation of the corresponding picrates. Subsequent g.l.c.analysis showed that each isomer was free of the other isomers.

The results of photolysing the six isomeric dimethylpyridines, under a variety of conditions, are presented in Table 3. The percentages of isomers found in the products under different photolysis conditions should not be quantitatively compared. In all cases the percentages merely serve to differentiate those compounds which were formed as major products and those which were formed as minor products.

The following general observations may be made:-

(i) Each of the six dimethylpyridines was irradiated for 17h with the medium pressure lamp or the Rayonet (at 254nm) as irradiation source, under conditions where only the vapour was present in the photolysis vessel. Although the degree of conversion was greater in the Rayonet, the identities of the major photoproducts or the minor photoproducts (where identifiable) were identical.

(ii) Four of the isomeric dimethylpyridines were irradiated with the medium pressure lamp under conditions where a little liquid remained at the bottom of the photolysis vessel. In each case the major photoproducts were identical with those obtained after photolysis where no liquid was present. The yields of products were apparently very low as a result of having excess non-photolysed starting material present, so that some minor photoproducts were not observable.

(iii) Each dimethylpyridine produced both monomethyl and trimethyl-pyridines among the photoproducts, often in comparable yields to the dimethylpyridine isomers.

On account of the similarity of results, obtained under various irradiation conditions, and to avoid needless repetition, only the experimental results for the irradiations carried out in the Rayonet reactor are presented in detail below for the individual compounds.

0 min →

Assignment

Figure 10

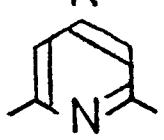
2,5-Dimethylpyridine photolysis
G.l.c. trace and mass spectra of products

solvents

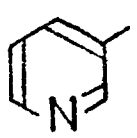
Carbowax / TEA , 92°

?

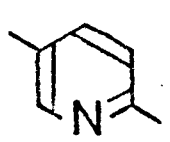
m/e 93(100),92(25),66(45),65(25),51(35),50(25)



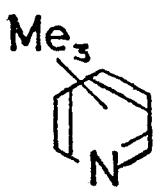
m/e 107(100)



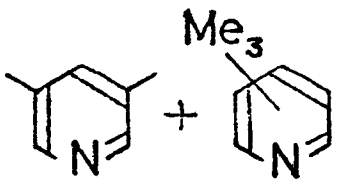
m/e 93(100),92(31),66(31),65(42),63(26),50(26)



m/e 107(100),106(63),92(16),79(40),77(25),66(12),65(16),63(12),
53(16),52(20),51(32),50(20),39(58),38(14)



m/e 121



m/e 121(23),107(76),106(100),92(19),79(53),77(19),63(19),
53(19),52(19),51(19),50(19),39(38)

45 min →

(i) 2, 5-Dimethylpyridine

The g. c. m. s.trace of the 2, 5-dimethylpyridine Rayonet photoproduct is shown in Figure 10 together with product assignments.

The approximate composition of the product was:-

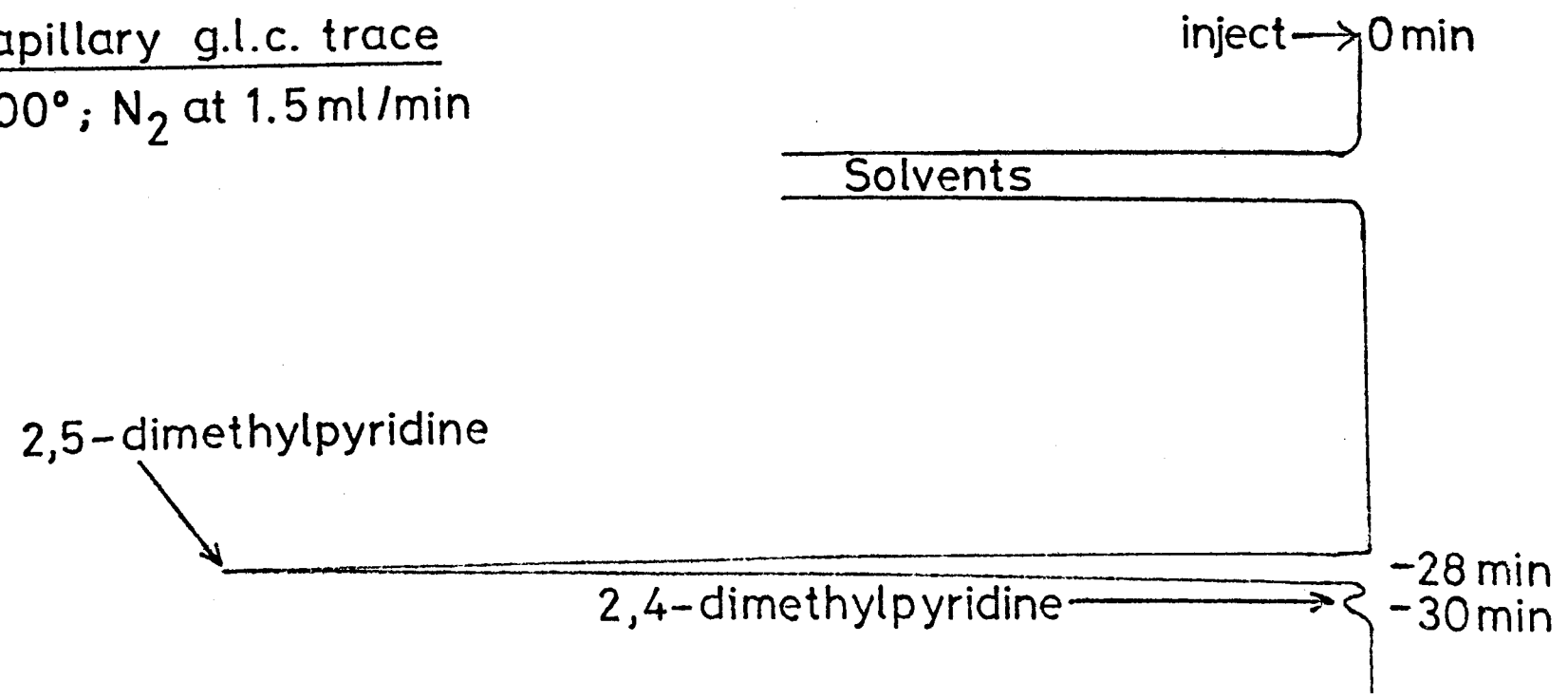
2 - methylpyridine	< 0.3%
3 - methylpyridine	< 0.3%
2, 5-dimethylpyridine (+2, 4-dimethylpyridine)	> 98%
3, 5-dimethylpyridine	< 1%
2, 6-dimethylpyridine	< 0.05%
trimethylpyridines	< 0.3%

The overall conversion to other isomers for this compound was much lower than for any of the other isomeric dimethylpyridines. There was no evidence to suggest that 3, 4-dimethylpyridine was present; however, if it was present at low conversions, signal broadening for this isomer might render it non-observable above the baseline. (c. f. medium pressure lamp irradiation where 3, 4-dimethylpyridine was observed in very low yield). The signal assigned to 3, 5-dimethylpyridine contained some trimethylpyridine (m/e 121), but the high intensity of the m/e 107 clearly showed that 3, 5-dimethylpyridine was the major constituent.

Analysis using the capillary column revealed that 2, 4-dimethylpyridine was also present as a photoproduct (ca 2%):

Capillary g.l.c. trace

100°; N_2 at 1.5 ml/min



0 min →

Assignment

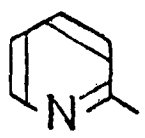
solvents

Figure 11

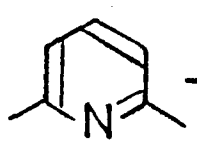
2,6-Dimethylpyridine photolysis
G.l.c. trace and mass spectra of products

Carbowax/TEA, 92°

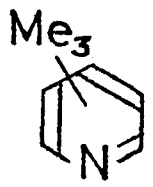
?



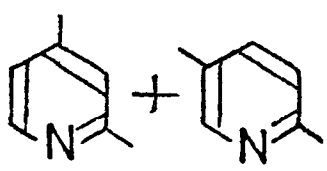
m/e 93(100),92(16),66(39),65(12),63(14),52(24),51(25),50(16)



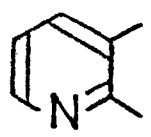
m/e 107(100),106(22),92(14),79(9),77(7),66(24),65(24),
63(22),53(18),52(11),51(16),39(83),38(24)



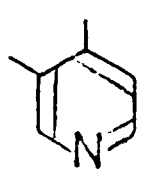
m/e 121(44),120(57),93(78),92(26),66(34),65(47),45(39),
43(34),39(100)



m/e 107(80),106(25),79(40)



m/e 107(100),106(52),92(23),79(20),77(11),66(25),
65(20),63(19),53(9),52(19),51(28),39(79),38(15)



m/e 107(100),106(37),92(31),79(50),63(21),53(21),52(34),51(40),39(68)

45 min →

(ii) 2, 6 -Dimethylpyridine

The g. c. m. s. data shown in Figure 11 indicates most clearly that 2, 3-dimethylpyridine and 3, 4-dimethylpyridine were the major isomeric photoproducts, together with a little 2, 5- and 2, 4-dimethylpyridines. The overall composition of the photoproduct was:-

2, 6-dimethylpyridine	80%
2, 3-dimethylpyridine	9%
3, 4-dimethylpyridine	3%
2-methylpyridine	4%
trimethylpyridine	4%
2, 4 and 2, 5-dimethylpyridines	$<$0.2%

There was no evidence, at all, for 3, 5-dimethylpyridine formation.

In an attempt to emulate Lablache-Combier's data 2, 6-dimethylpyridine was also photolysed for 1h in the Rayonet reactor. Of the recovered products $<$97% was starting material. Visible above the baseline,or as a shoulder, were signals assigned, by their retention times, to 3, 4- and 2, 3-dimethylpyridines. The ratio of 2, 3-:3, 4-isomer was ca 3:1. It is interesting to note that this is also the ratio obtained after irradiation for 17h in the Rayonet reactor. This observation might suggest that both products are primary; however the non-reproducibility of the experimental techniques employed does not allow a definite conclusion to be drawn.

0 min

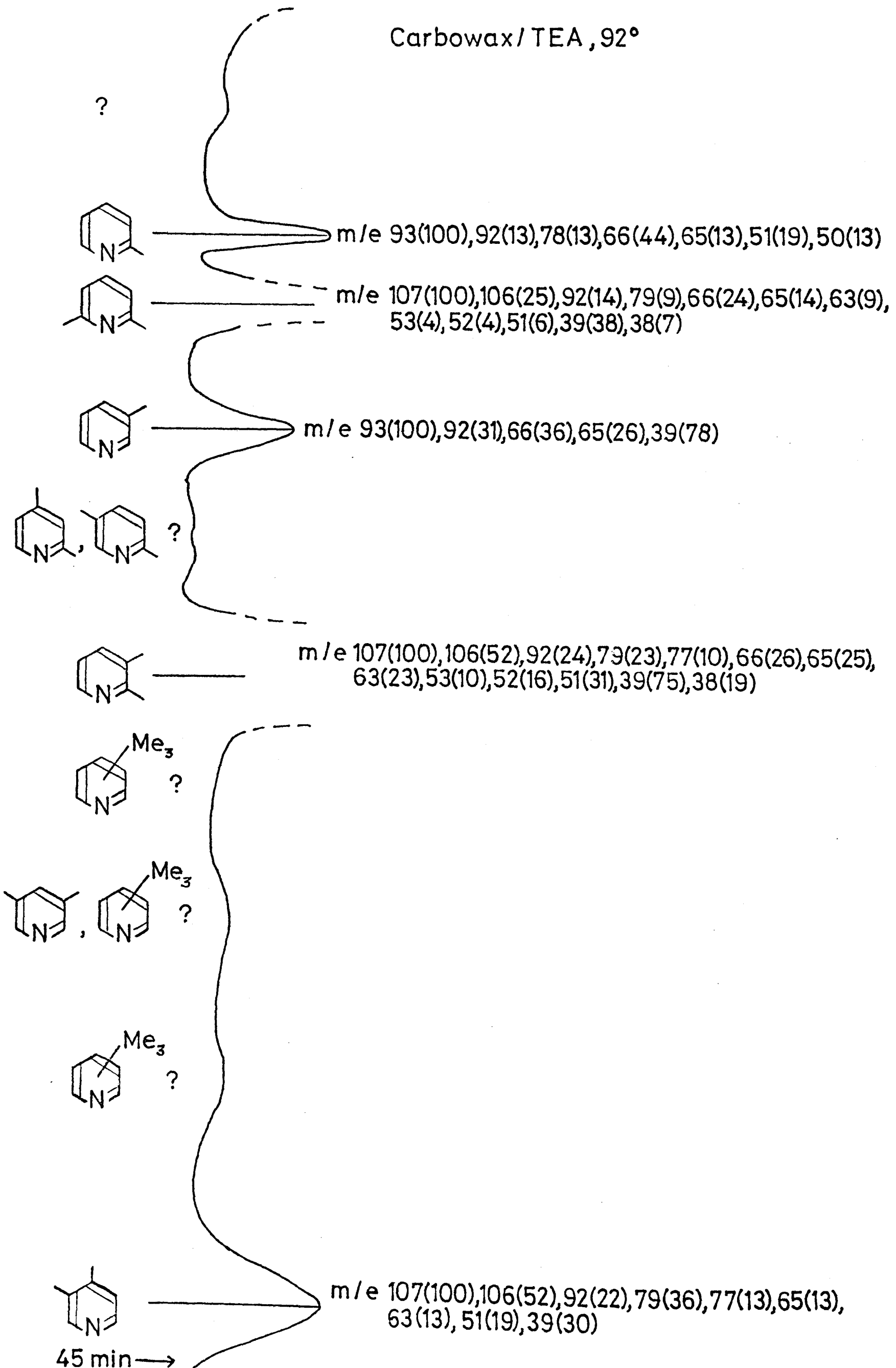
Assignment

Figure 12

2,3-Dimethylpyridine photolysis

solvents

G.l.c. trace and mass spectra of products



(iii) 2, 3-Dimethylpyridine

The g. c. m. s. data in Figure 12 shows that both 2, 6- and 3, 4-dimethylpyridines were produced as photoproducts in addition to 2- and 3-methylpyridines. Although no mass spectroscopic evidence was available for the minor products in this irradiation, the close correspondence of this g. l. c. trace with that obtained from the medium pressure lamp irradiation (for which some mass spectral evidence was available) indicated that 2, 4-and 2, 5-dimethylpyridines, together with a little 3, 5-dimethylpyridine and some trimethylpyridines, were present, as indicated.

The relevant mass spectra for the medium pressure lamp irradiation were as follows:-

Peak R_t = ca 22min; m/e = 107(100), 106(55), 92(14), 79(27), 66(7), 65(12), 39(29)

Peak R_t = ca 29min; m/e = 121(55), 120(34)

Peak R_t = ca 33min; m/e = 121(64), 120(100), 107(22), 106(19)

Peak R_t = ca 38min; m/e = 121(68), 120(33), 107(12), 106(100)

Thus the overall composition of the photoproduct was approximately:-

2, 3-dimethylpyridine	87%
2, 6-dimethylpyridine	6.7%
3, 4-dimethylpyridine	3.7%
2 - methylpyridine	1%
3 - methylpyridine	1.4%
2, 5-, 2, 4-, 3, 5 - dimethylpyridines trimethylpyridines	0.4%

0 min

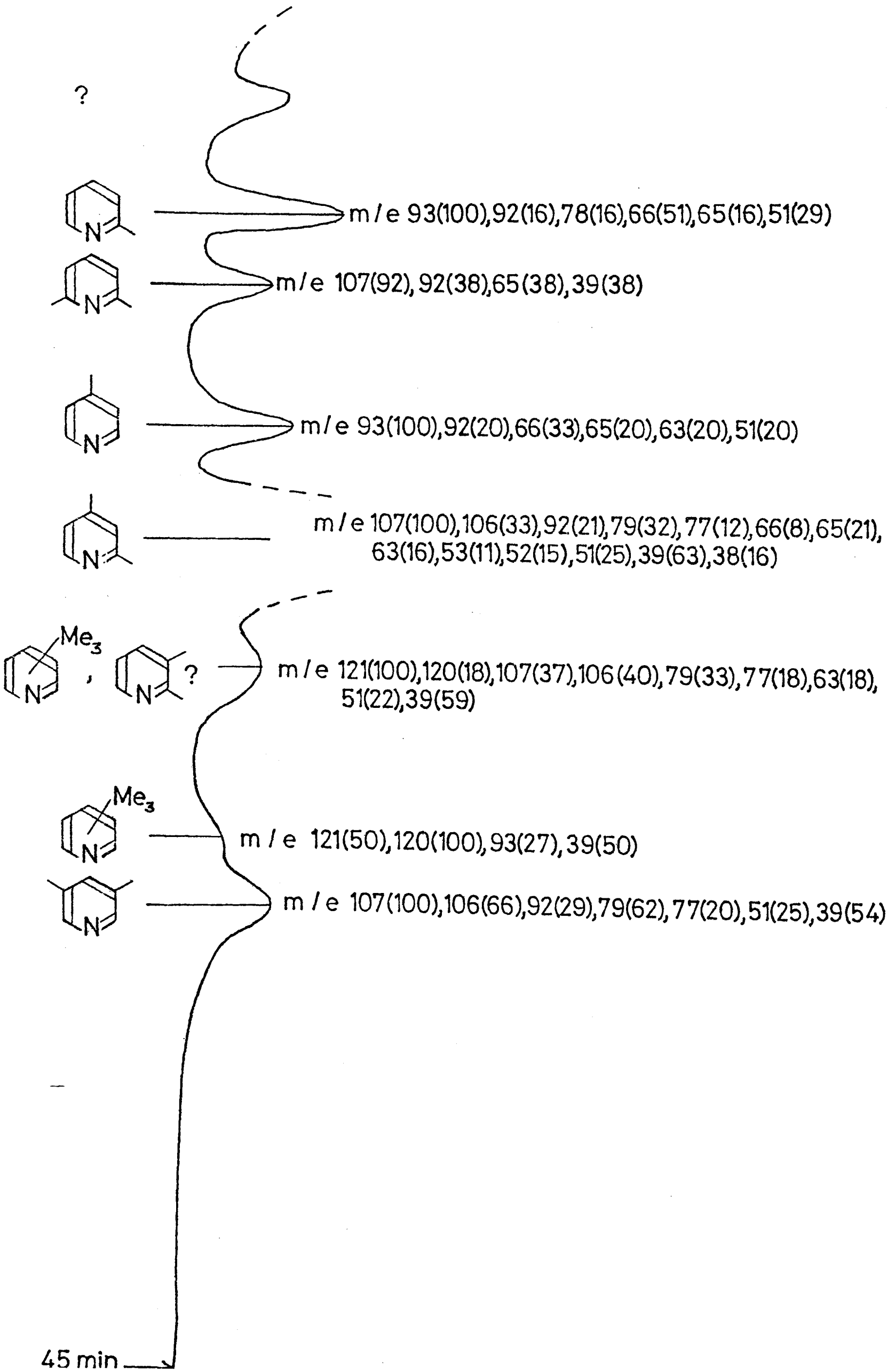
Assignment

Figure 13

2,4-Dimethylpyridine photolysis
G.l.c. trace and mass spectra of products

solvents

Carbowax / TEA, 92°



45 min

(iv) 2, 4-Dimethylpyridine

Analysis of the g. c. m. s. data in Figure 13 reveals that 3, 5-dimethylpyridine was the major isomeric photoproduct with some 2, 6-dimethylpyridine also present. In addition 2- and 4- methylpyridines were present together with some trimethylpyridines. The intensity of the m/e= 107 signal for the R_t = ca 25min peak indicated that a little 2, 3-dimethylpyridine might also be present. Similarly, a small signal at R_t = ca 42min might be assigned, on its retention time only, to a little 3, 4-dimethylpyridine.

The photoproduct composition was approximately:-

2, 4-dimethylpyridine	94%
3, 5-dimethylpyridine	1.8%
2, 6-dimethylpyridine	0. 8%
2-methylpyridine	0. 9%
4-methylpyridine	1. 0%
trimethylpyridines, 2, 3 dimethylpyridine	1. 8%
3, 4-dimethylpyridine	0. 09%

Analysis of the photoproduct using a capillary column showed that the signal assigned to 2, 4-dimethylpyridine contained ca 10% of 2, 5-dimethylpyridine:

Capillary g.l.c. trace

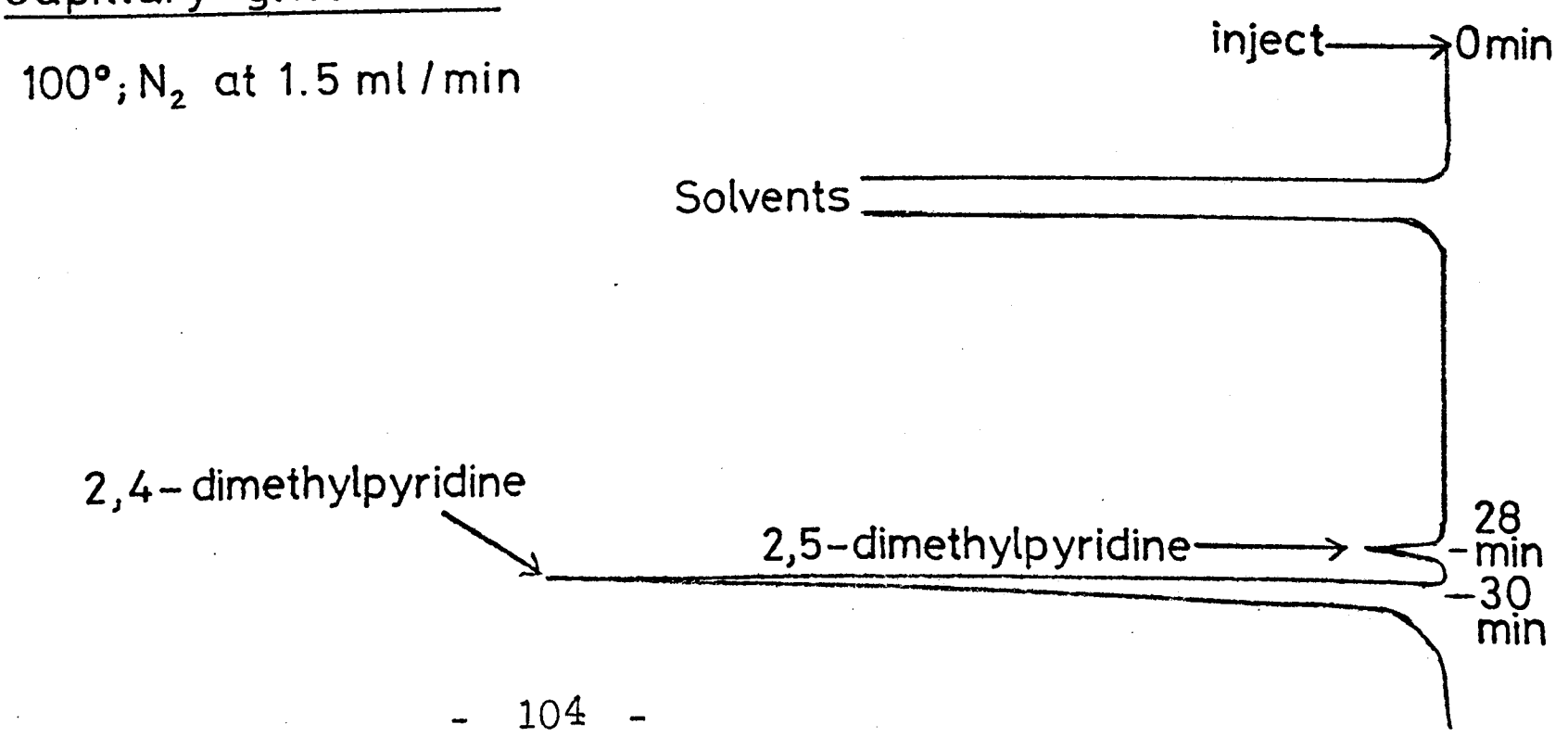
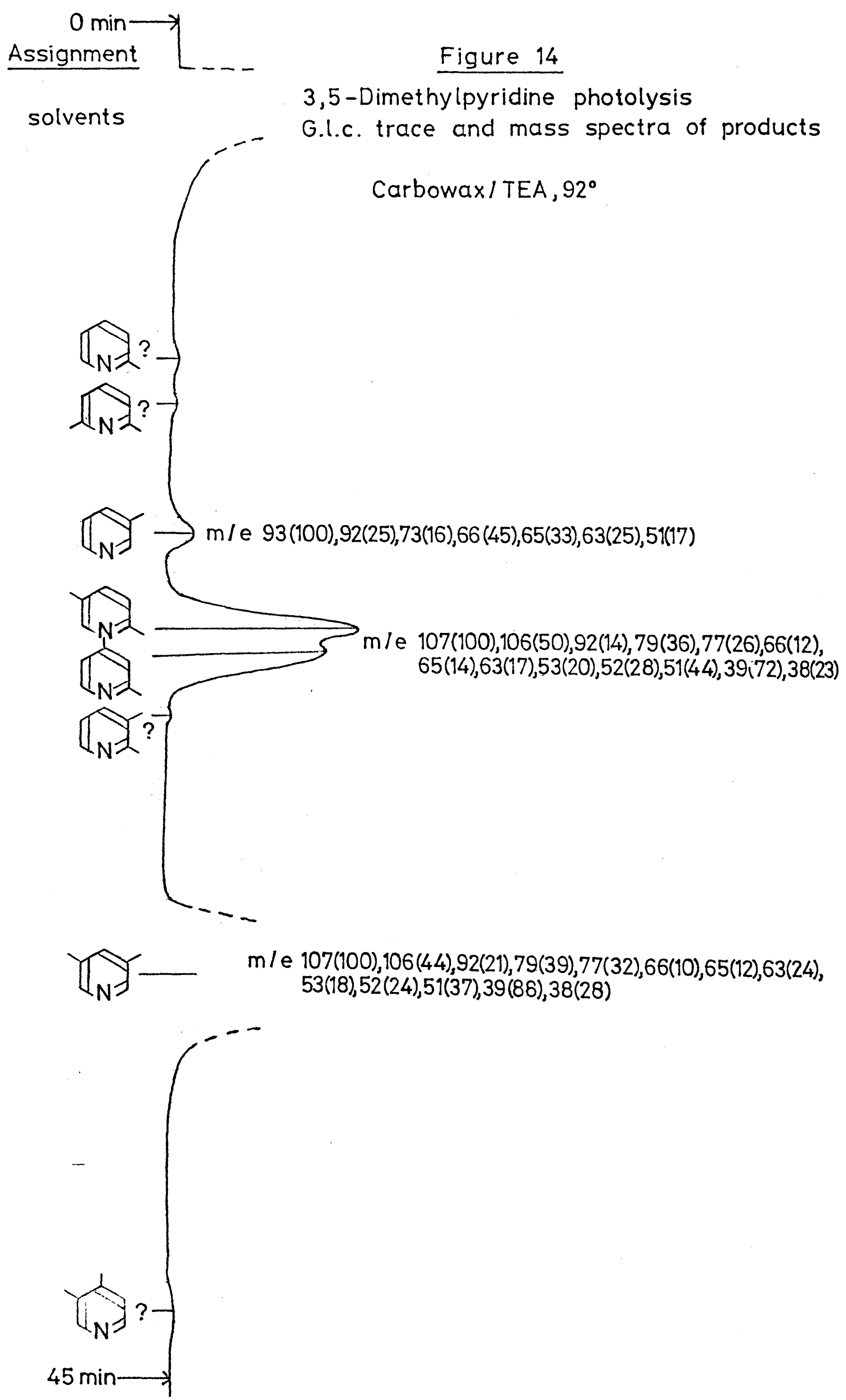


Figure 14

3,5-Dimethylpyridine photolysis
G.l.c. trace and mass spectra of products



(v) 3, 5 -Dimethylpyridine

Figure 14 shows that the photoproducts derived from 3, 5-dimethylpyridine were 2, 4- and 2, 5 dimethylpyridines and 3-methylpyridine. G.l.c. retention times of very minor products were consistent with their being 2-methylpyridine and 2, 3-, 2, 6- and 3, 4-dimethylpyridines.

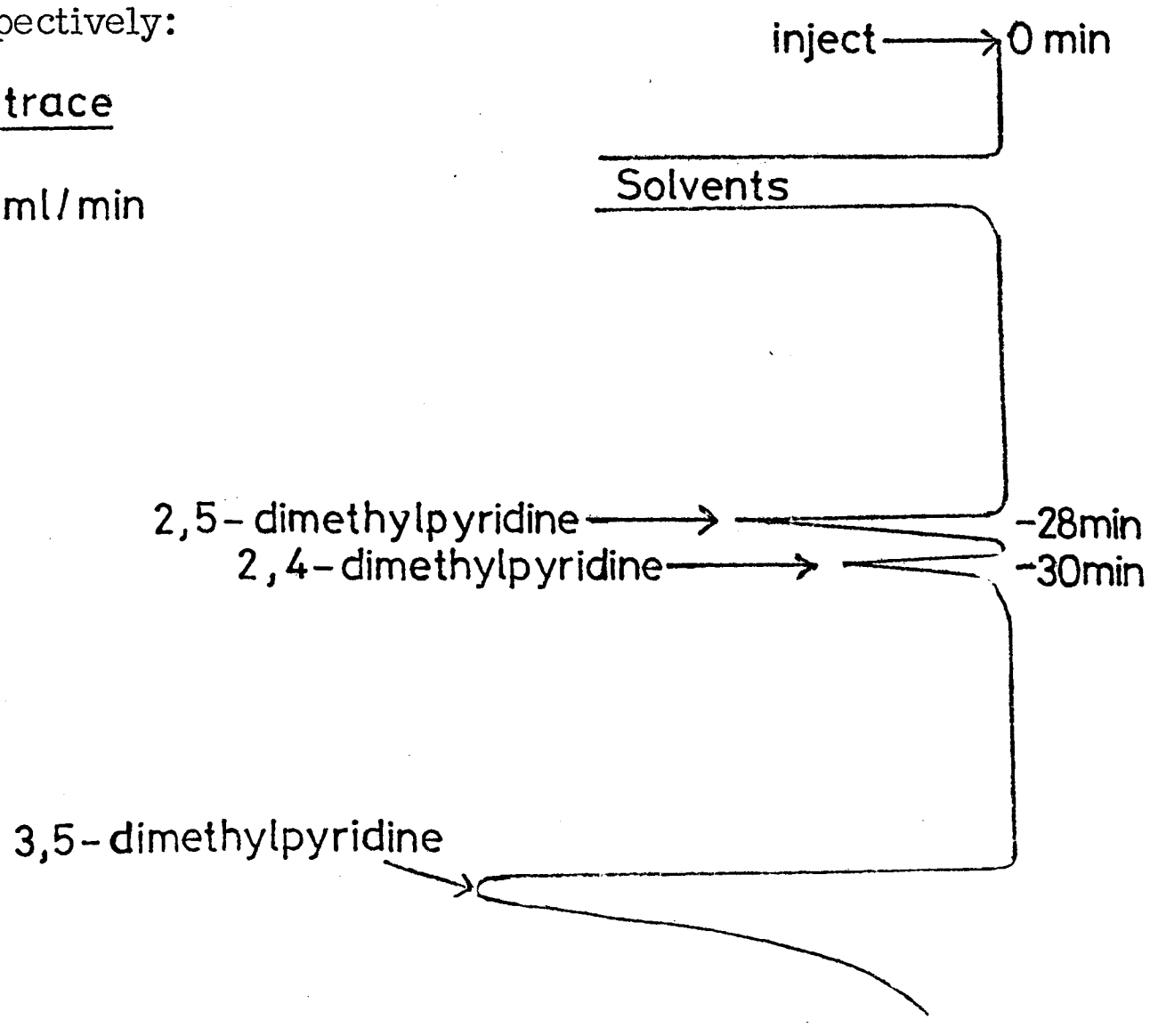
The approximate composition of the photoproduct was:-

3, 5-dimethylpyridine	92%
2, 5-dimethylpyridine	4.2%
2, 4-dimethylpyridine	3.1%
3 methylpyridine	0.5%
2 -methylpyridine 2, 6-dimethylpyridine 2, 3-dimethylpyridine 3, 4-dimethylpyridine	0.2%

Analysis of the photoproduct using the capillary column confirmed that 2, 5-and 2, 4-dimethylpyridines were present at ca 4% and 3% respectively:

Capillary g.l.c. trace

100° ; N_2 at 1.5ml/min



0 min →

Assignment

Figure 15

3,4-Dimethylpyridine photolysis
G.l.c. trace and mass spectra of products

solvents

Carbowax / TEA , 92°

(vi) 3, 4-Dimethylpyridine

It is apparent from the g. c. ms.data in Figure 15 that the major products from photolysing 3, 4-dimethylpyridine were 2-, 3-, and 4-methylpyridines and 2, 3- and 2, 6- dimethylpyridines. The presence of 2, 4-, 2, 5- and 3, 5-dimethylpyridines was tentatively suggested by the observation of signals in the g. c. m. s.with m/e = 107; however, in these spectra other signals (at m/e = 73 and 45) comprised the base signals, indicating that the g. l. c.peaks were not entirely due to dimethylpyridine isomers. Furthermore, inspection of the 3, 5-dimethylpyridine signal mass spectrum shows a non-dimethylpyridine break-down pattern, indicative of the presence of another compound.

The approximate composition of the photoproduct mixture was:-

3, 4-dimethylpyridine	64%
3/4-methylpyridines	22. 9%
2, 6-dimethylpyridine	4. 7%
2, 3-dimethylpyridine	5. 1%
2-methylpyridine	2. 1%

+ some 2, 5-, 2, 4-, and 3, 5- dimethylpyridines.

It is interesting to note that the degree of conversion for this isomer was the highest and that photolysis for 48h with the medium pressure lamp destroyed the starting material completely. These observations probably reflect the lower volatility of the 3, 4-dimethylpyridine relative to the other isomers.

The prime purpose of this work was to investigate the photorearrangement reactions of the dimethylpyridines, and, therefore, little attention was paid to the methyl- and trimethylpyridine photoproducts. These were assumed to be derived by demethylation and methylation mechanisms respectively. Where methylpyridines were formed, which could not be formally derived from starting material (e. g. 2-methylpyridine from 3, 4-dimethylpyridine), it was assumed that either secondary photolysis of products or demethylation of a rearranged intermediate was taking place.

It is clear from Table 3 and the detailed results presented above that photolysis of each dimethylpyridine isomer yielded two dimethylpyridines as major products, together with other dimethylpyridines as minor products. Each minor product always accounted for less than 5% of the smaller major product component, with the exception of the 2, 6-dimethylpyridine produced on photolysis of 2, 4-dimethylpyridine.

Only the major photoproducts will be considered at present. These are tabulated below together with Lablache-Combier's results.

Starting Material	Products	Lablache-Combier Products
2, 6-Me_2pyridine	2, 3 + 3, 4-Me_2pyridines	2, 4-
2, 3-Me_2pyridine	2, 6 + 3, 4- "	2, 5 + 3, 4-
3, 4-Me_2pyridine	2, 6 + 2, 3- "	2, 3 + 2, 5-
2, 4-Me_2pyridine	2, 5 + 3, 5- "	2, 6-
2, 5-Me_2pyridine	2, 4 + 3, 5- "	2, 3 + 3, 4-
3, 5-Me_2pyridine	2, 5 + 2, 4- "	None

The most important point to note is that these results are totally at variance with those of Lablache-Combier, with the exception that both sets of results show interconversion of 2, 3- and 3, 4- dimethylpyridines. In the light of the other results it is likely that this agreement is fortuitous. As with Roebke's data, it is difficult to explain why the two sets of results should be so different, since Lablache-Combier carried out his irradiations at 254nm in a Rayonet reactor also. The irradiation time variation (17h vs 1h) cannot be a factor since irradiation of 2, 6-dimethylpyridine, in this study, for 1h gave only 2, 3- and 3, 4-dimethylpyridine as photoproducts, consistent with the results of the longer irradiation time. An alternative explanation might be that the two sets of experiments were carried out at different pressures of starting material. This was certainly very likely. It was not possible to measure the pressure of dimethypyridine used in this study, due to lack of appropriate equipment. However, an approximate value can be calculated by the Antoine modification (Equation 2) of the Clapeyron equation (Equation 1).

Equation 1 $$\frac{d\ln P}{d(T^{-1})} = \frac{\Delta H}{R}$$

where P = vapour pressure (mm)
T = Temperature (^{o}K)
R = gas constant
ΔH = Latent heat of vapourisation.

Integrating $$\log_{10} P = -\frac{\Delta H}{RT} + \text{constant}$$

OR the Antoine modification

Equation 2 $$\log_{10} P = A - \frac{B}{(t + C)}$$

where A, B and C are constants
and t is the temperature in ^{o}C

The constants A, B and C which have been determined for each of the dimethylpyridines by Coulson and co-workers[118] are tabulated below:-

Dimethylpyridine	A	B	C
2, 6-Me_2pyridine	7.05246	1467.362	207.701
2, 5-Me_2pyridine	7.05816	1527.016	207.820
2, 4-Me_2pyridine	7.11647	1564.800	211.032
2, 3-Me_2pyridine	7.05075	1528.935	205.499
3, 5-Me_2pyridine	7.08598	1593.028	206.916
3, 4-Me_2pyridine	7.06898	1607.874	204.776

The calculated values of the vapour pressures at 30° and 40° are as follows:-

	$P_{30°}$ (mm)	$P_{40°}$ (mm)
2, 6-Me_2pyridine	7.57	13.44
2, 5-Me_2pyridine	4.47	8.10
2, 4-Me_2pyridine	4.21	7.64
2, 3-Me_2pyridine	3.62	6.65
3, 5-Me_2pyridine	2.30	4.31
3, 4-Me_2pyridine	1.66	3.16

The calculated values for the vapour pressures at 30° and 40° give values for the saturated vapour pressures of the compounds and, therefore, provide an upper limit to the pressures actually used in this study. The pressures are of the same order as those reported by Lablache-Combier (10mm). However, it is not obvious from his experimental description whether the figure of 10mm, which he reported, was exclusively due to starting material vapour or whether the pressure was made up to 10mm by addition of an inert gas. It is interesting to note that, while a saturated vapour pressure of 10mm for 3, 4-dimethylpyridine corresponds to a temperature of 60° by the Antoine equation, no mention is made, by Lablache- Combier, of the necessity to heat his reactor vessel nor, indeed, of the temperature he actually used.

Since the exact experimental conditions employed by Lablache-Combier are not known for certain, it is not possible to comment further on the validity of his results.

Examination of the results from this study reveals that the major products form two non-interconverting triad systems: 2, 3-, 2, 6- and 3, 4- dimethylpyridines and 2, 5-, 2, 4- and 3, 5-dimethyl-pyridines. Within each triad each member is photolysed, in major part, to the other two members.

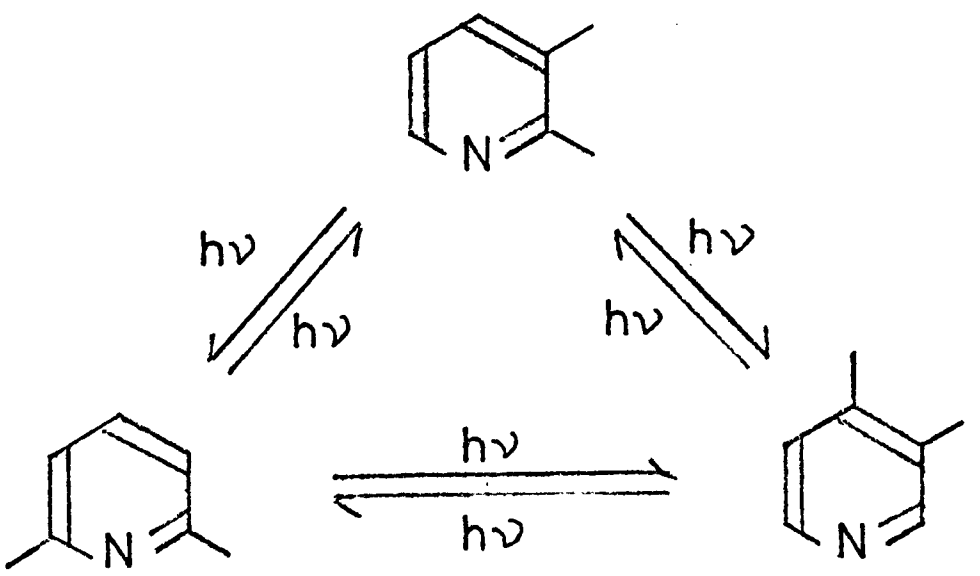
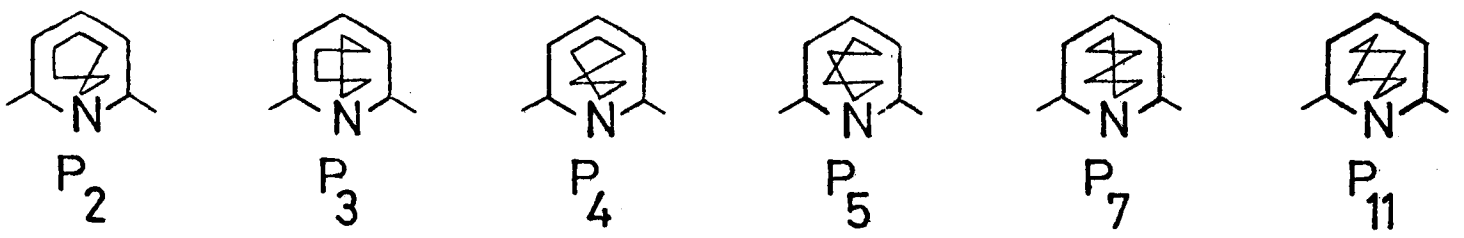


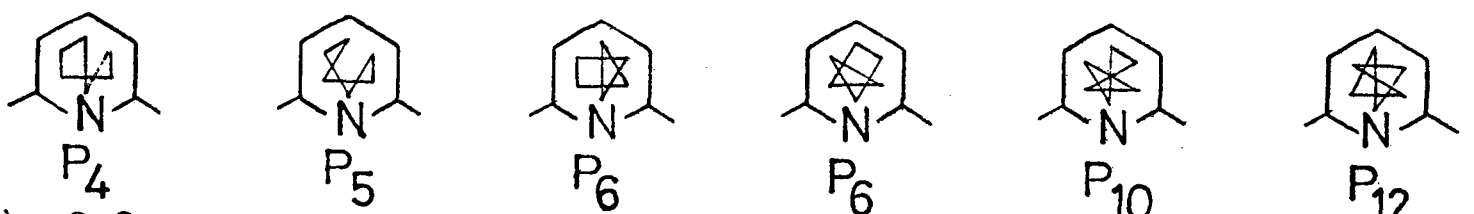
TABLE 4

Permutation Analysis of 2, 6-, 2, 3- and 3, 4-Dimethylpyridine Interconversions

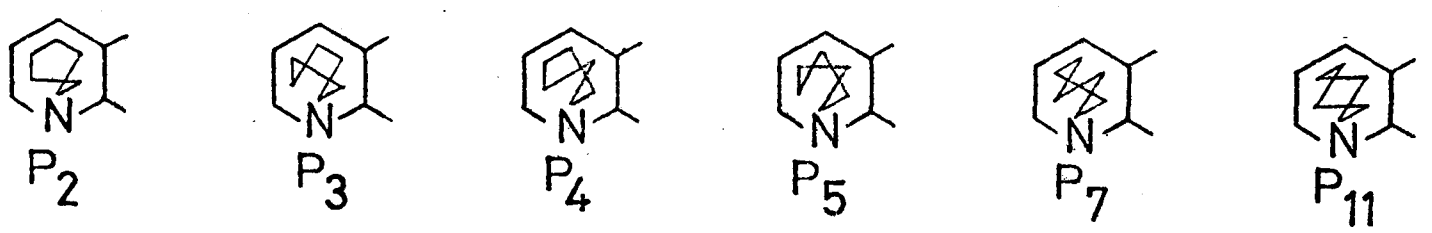
(i) 2, 6-Dimethylpyridine to 2, 3-Dimethylpyridine



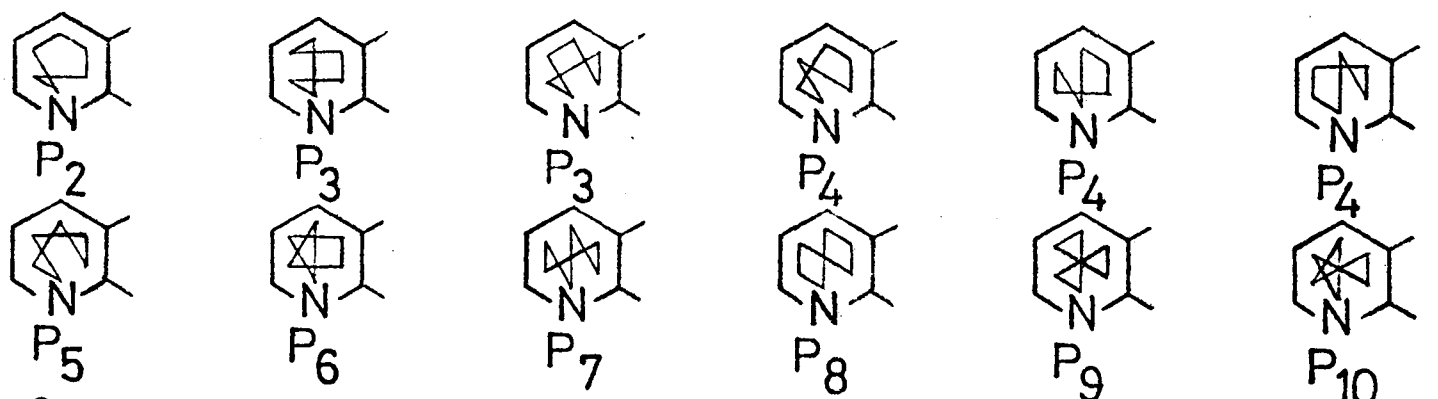
(ii) 2, 6-Dimethylpyridine to 3, 4-Dimethylpyridine



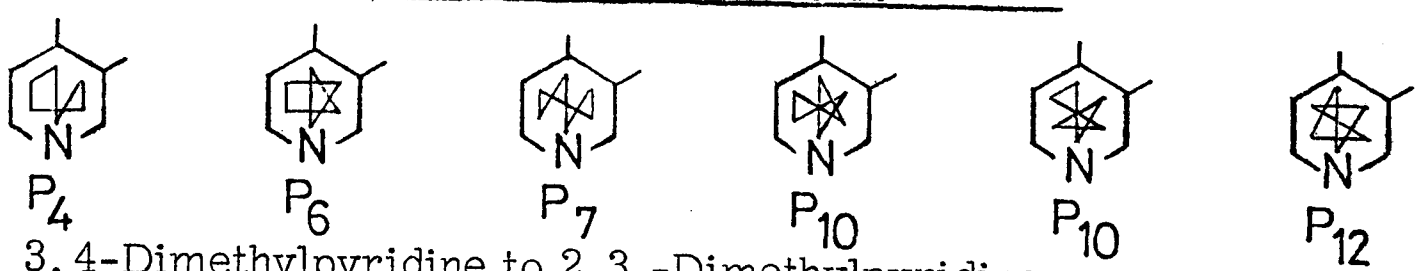
(iii) 2, 3-Dimethylpyridine to 2, 6-Dimethylpyridine



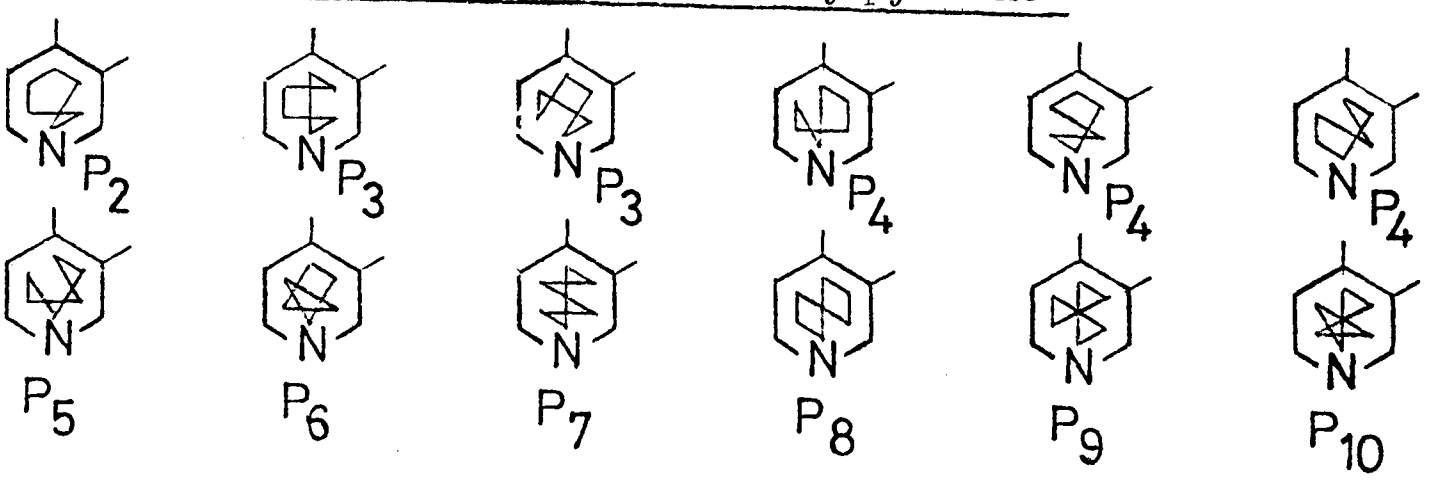
(iv) 2, 3-Dimethylpyridine to 3, 4-Dimethylpyridine

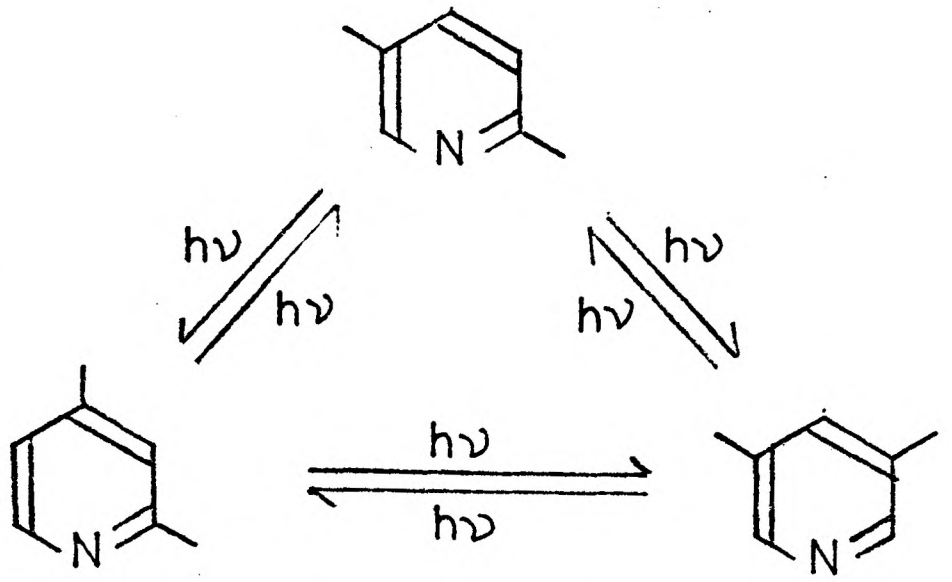


(v) 3, 4-Dimethylpyridine to 2, 6-Dimethylpyridine



(vi) 3, 4-Dimethylpyridine to 2, 3 -Dimethylpyridine





As with Lablache-Combier's results, these results are amenable to analysis in terms of Barltop and Day's permutation pattern approach. The results of applying their approach to these systems are presented in Tables 4 and 5.

Analysis of these tables reveals that no permutation is common to all the observed transformations. Therefore, it might be concluded that one of the products was formed by one permutation pattern, while the second was formed by another. An alternative explanation might be that one product was primary, the other secondary. However, after consideration of the relative amounts of products formed (always $<$ 10%) and the low efficiency of individual rearrangement processes it is evident that this is not possible. Further analysis of the tables shows that the only pair of common permutations, for each compound, which can account accurately for the observed products are P_2 and P_4 oriented as shown and their symmetry-related (about N-C4 axis) counterparts.

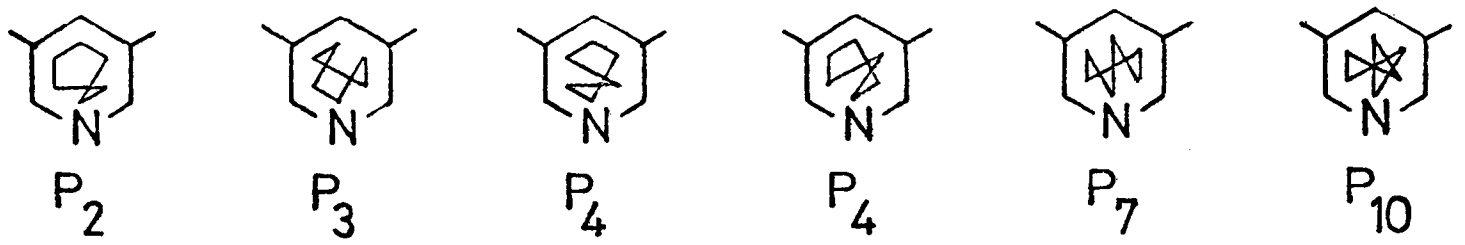
$P_2(1)$ $P_2(2)$ $P_4(1)$ $P_4(2)$

It can be shown that when P_2 or P_4, in either orientation, are applied to each dimethypyridine isomer, only the observed major photolysis products or starting material are formed and no other products.

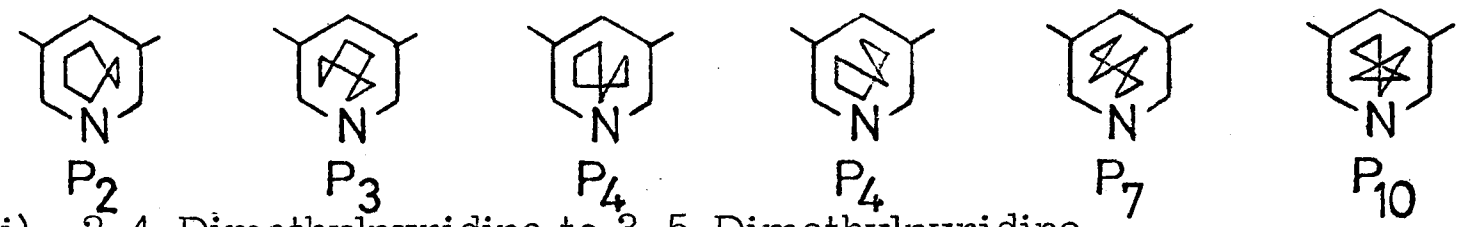
TABLE 5

Permutation Analysis of 2, 5-, 2, 4- and 3, 5 - Dimethylpyridine Interconversions

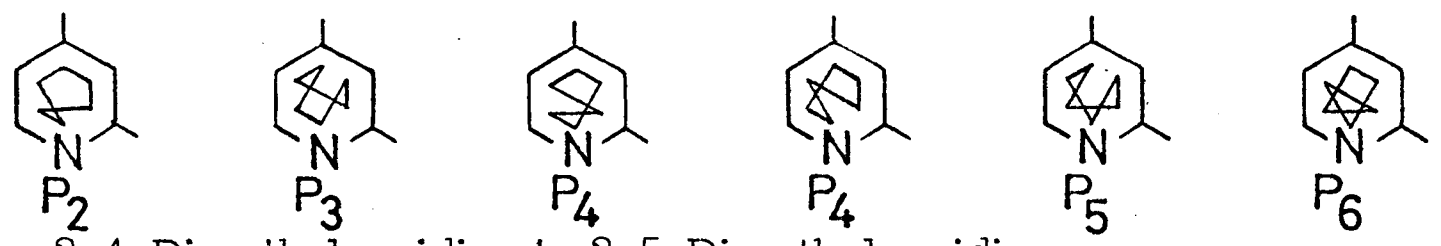
(i) 3, 5-Dimethylpyridine to 2, 4-Dimethylpyridine



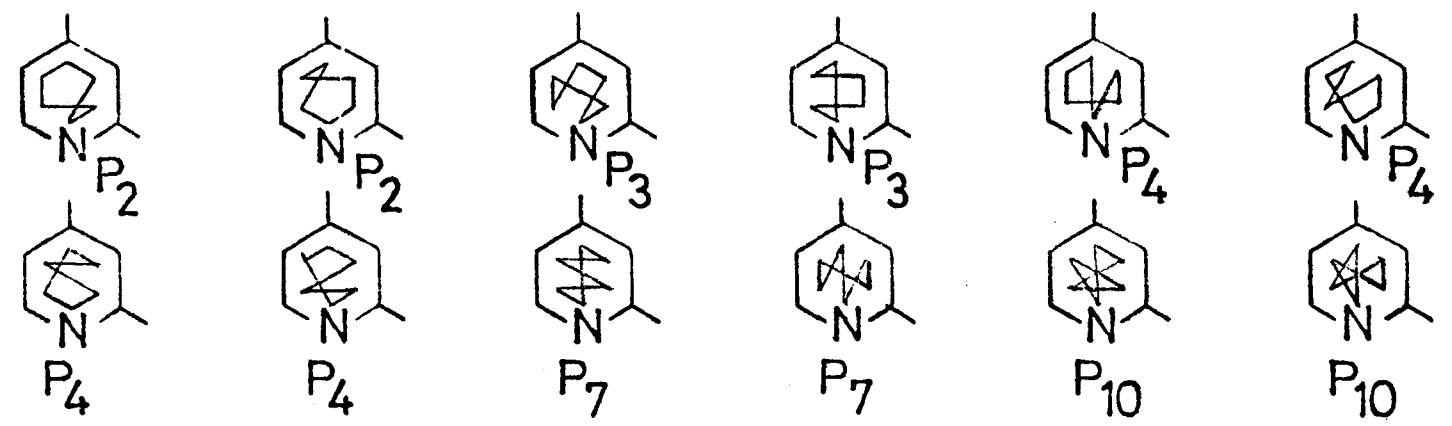
(ii) 3, 5-Dimethylpyridine to 2, 5-Dimethylpyridine



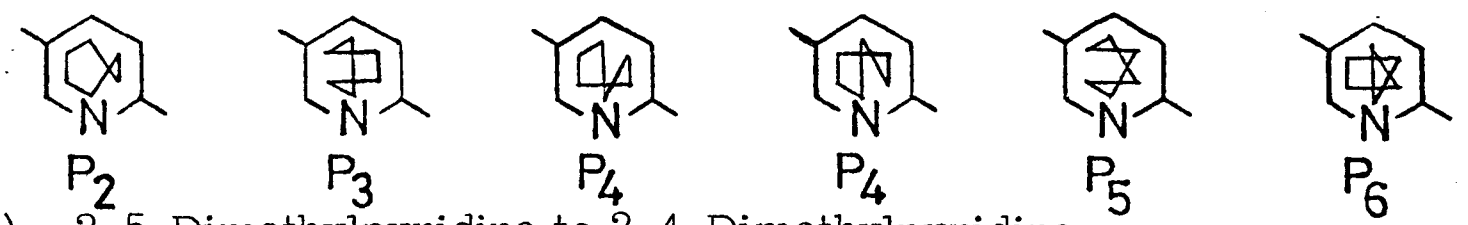
(iii) 2, 4-Dimethylpyridine to 3, 5-Dimethylpyridine



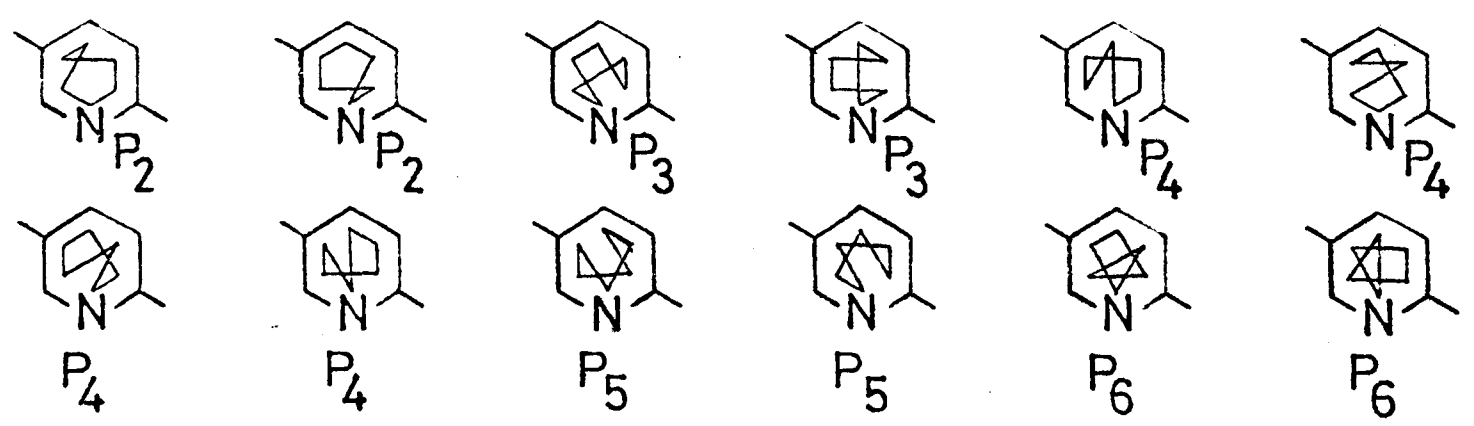
(iv) 2, 4-Dimethylpyridine to 2, 5-Dimethylpyridine



(v) 2, 5-Dimethylpyridine to 3, 5-Dimethylpyridine



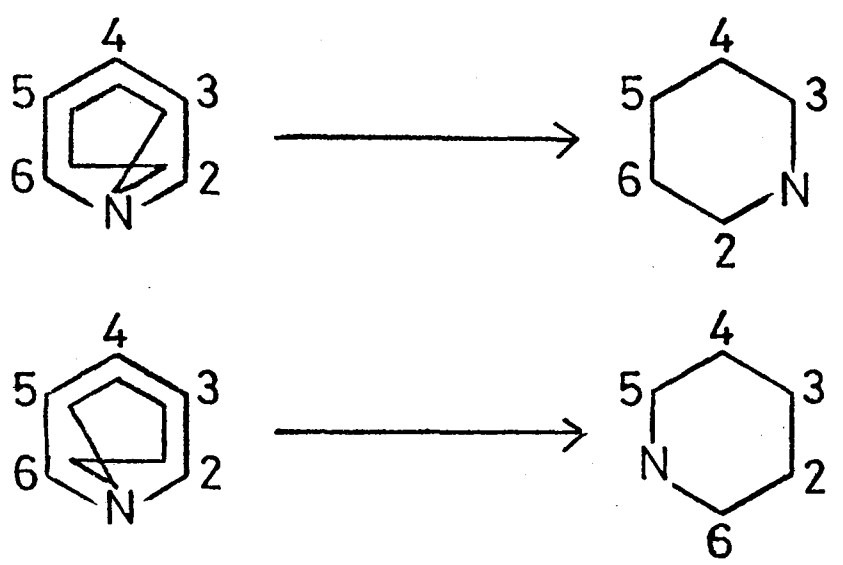
(vi) 2, 5-Dimethylpyridine to 2, 4-Dimethylpyridine



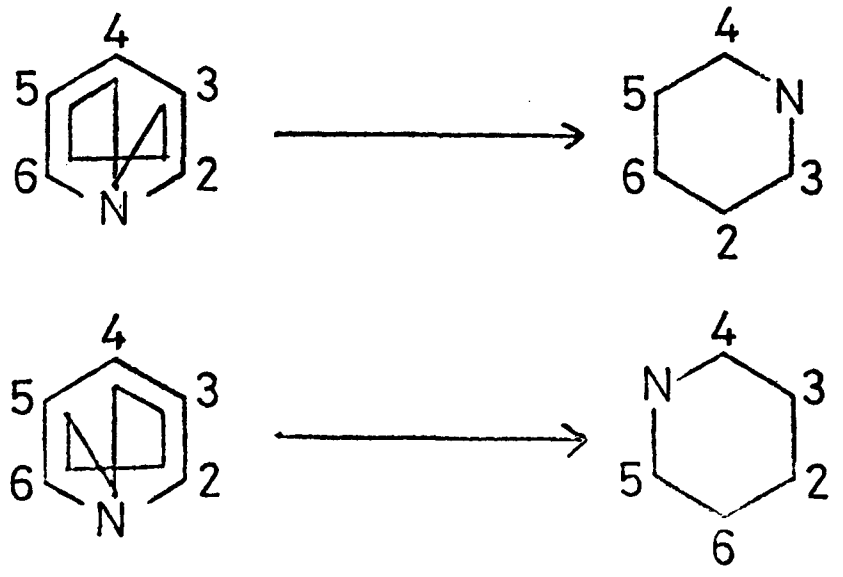
i.e.

	$P_2(1)$	$P_2(2)$	$P_4(1)$	$P_4(2)$
2, 6	2, 3	2, 3	3, 4	3, 4
2, 3	2, 6	3, 4	2, 3	3, 4
3, 4	2, 3	3, 4	2, 6	2, 3
2, 4	2, 5	3, 5	2, 5	2, 4
2, 5	2, 4	2, 4	3, 5	2, 5
3, 5	2, 4	2, 4	2, 5	2, 5

Following Barltrop and Day's usual procedure, it is next possible to consider the mechanism of the rearrangement processes. The two P_2 permutation patterns pictorially represent the insertion of the nitrogen atom between carbon atoms C_2 and C_3 or C_5 and C_6.

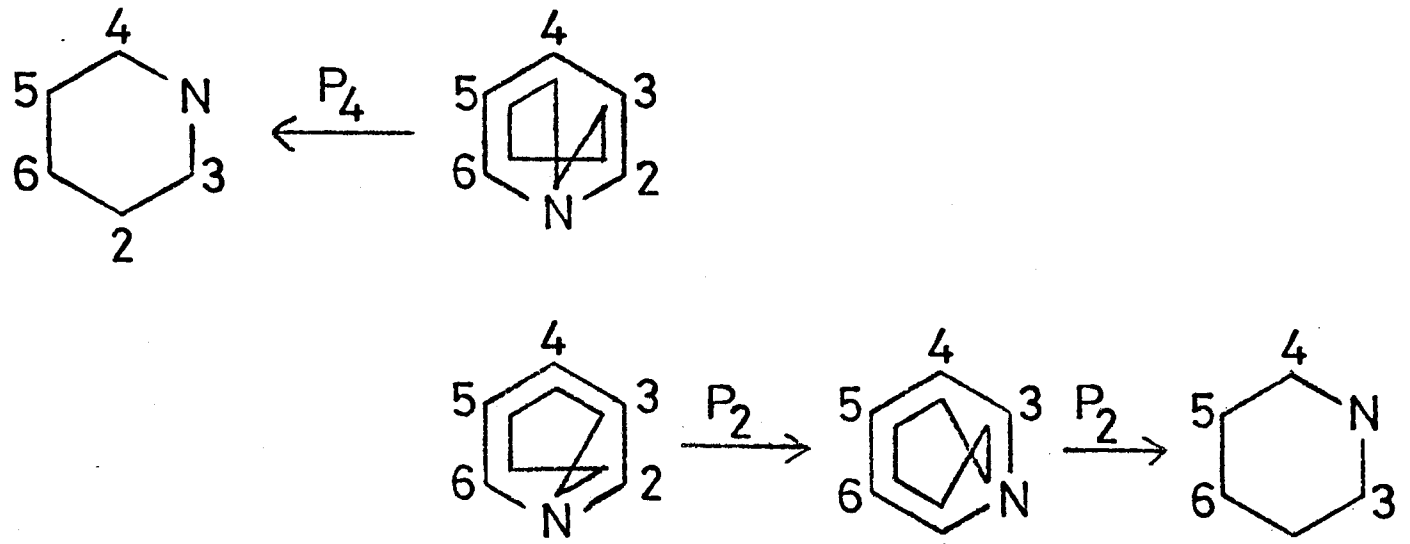


The P_4 permutation patterns correspond to insertion between the atoms C_3 and C_4 or C_4 and C_5 :-



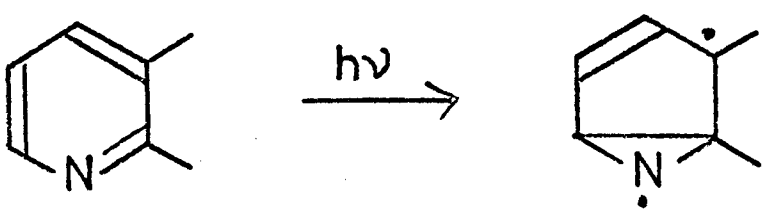
Hence, the permutation patterns taken together correspond to the nitrogen interposing itself between any two adjacent carbon atoms of the ring.

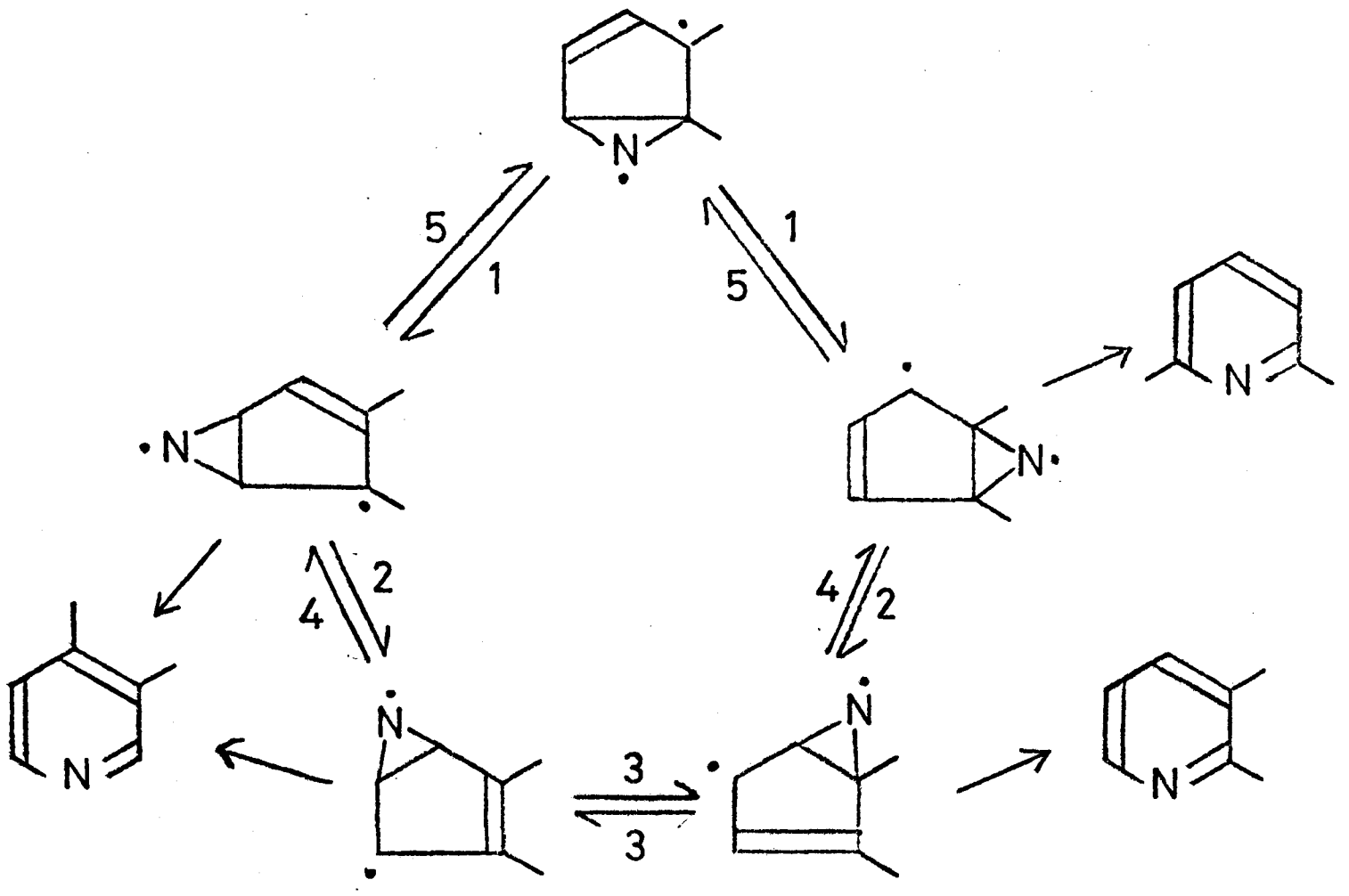
It is to be noted that the permutation pattern P_4, in fact, is equivalent to two sequential P_2 processes.



In terms of an actual mechanism the permutations P_2 and P_4 can be considered to correspond to a system in which the nitrogen atom is 'walking' around a five-membered ring of carbon atoms and interposing itself between any two carbon atoms.

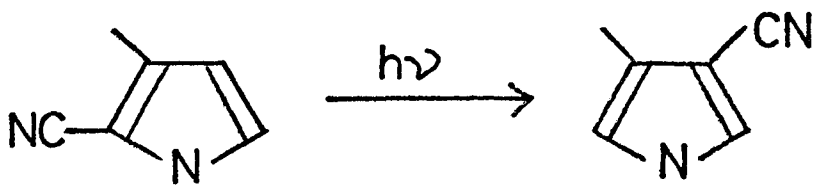
e. g. for 2, 3-dimethylpyridine:-

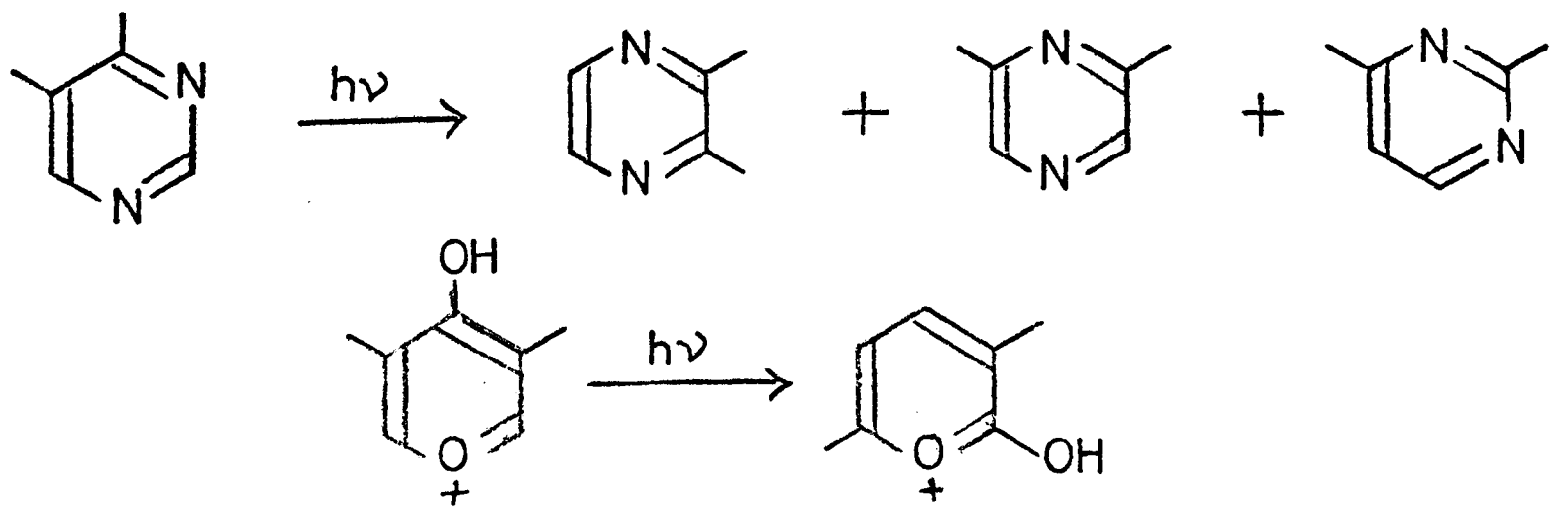




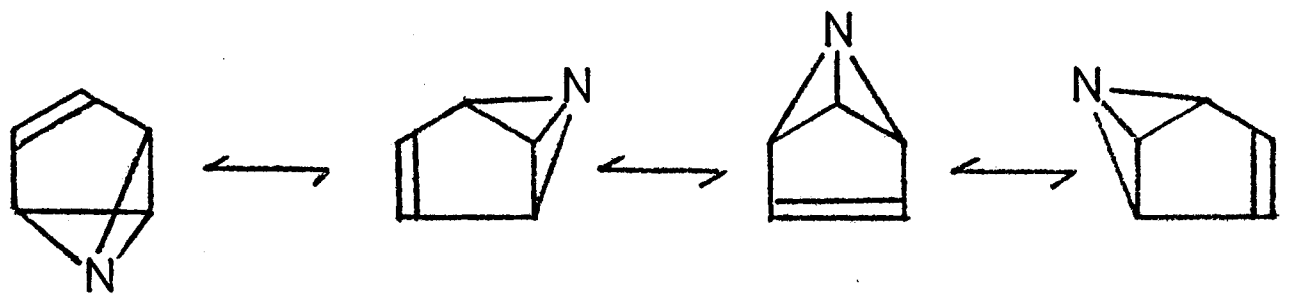
Whether the nitrogen actually 'walks' all the way around the carbon atom ring is not known; obviously the 4 'walk' and 5 'walk" intermediates could be formed by the nitrogen 'walking' once or twice round the carbon ring in the opposite direction.

This reaction scheme has close similarities to those proposed for the rearrangements observed in the cyanopyrroles [119], diazines[120] and hydroxypyrylium salts [121].

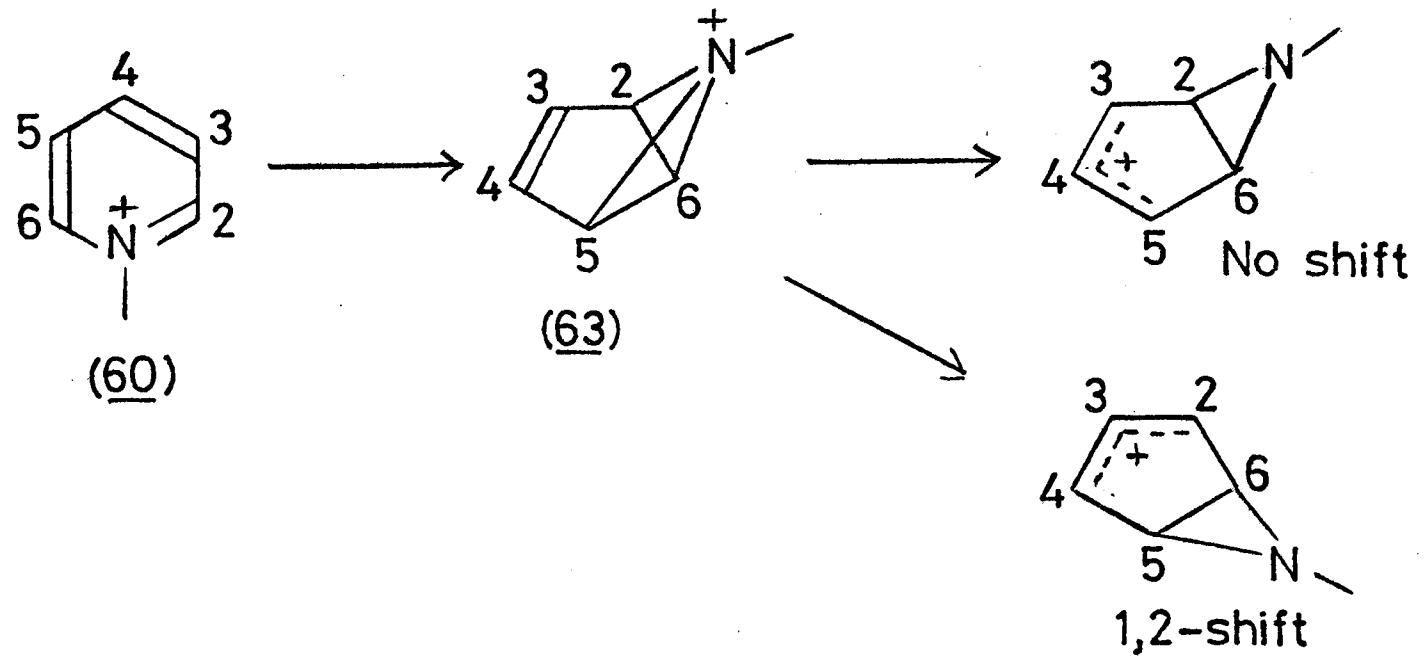




The intermediate in the scheme for the rearrangement of the dimethylpyridines is shown as a biradical. However, whether the intermediate is a biradical or a charged species is not known. The form of the radical is analogous to the prevalene biradical (6) which was proposed by Bryce-Smith [24] to account for the formation of benzvalene after photolysis of benzene; hence, the set of intermediates might correspond to a set of interconverting azabenzvalenes.

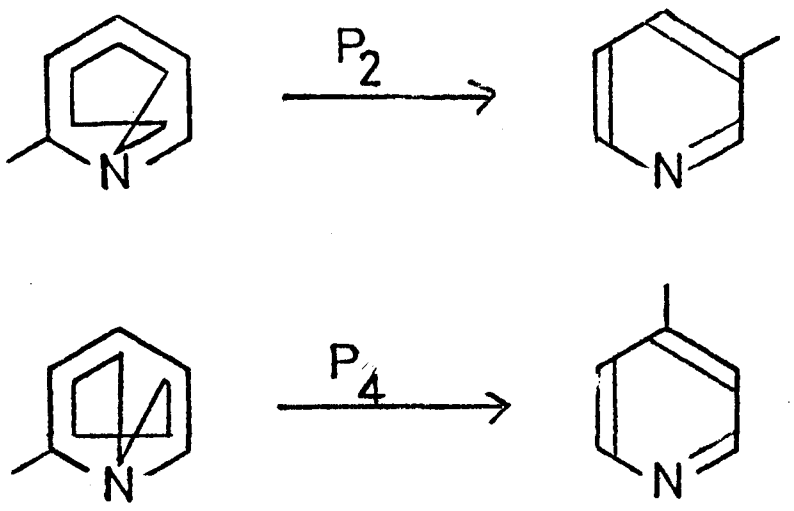


It has already been proposed by Kaplan and co-workers [82] that 1,2-shifts of nitrogen (formally a P_2 permutation pattern) occur during the photohydration of pyridinium ions. These workers suggested that a 1-methylazoniabenzvalene(63)was involved as an intermediate, produced as a result of $\pi\pi^*$ excitation of the N-methylpyridinium cation (60).



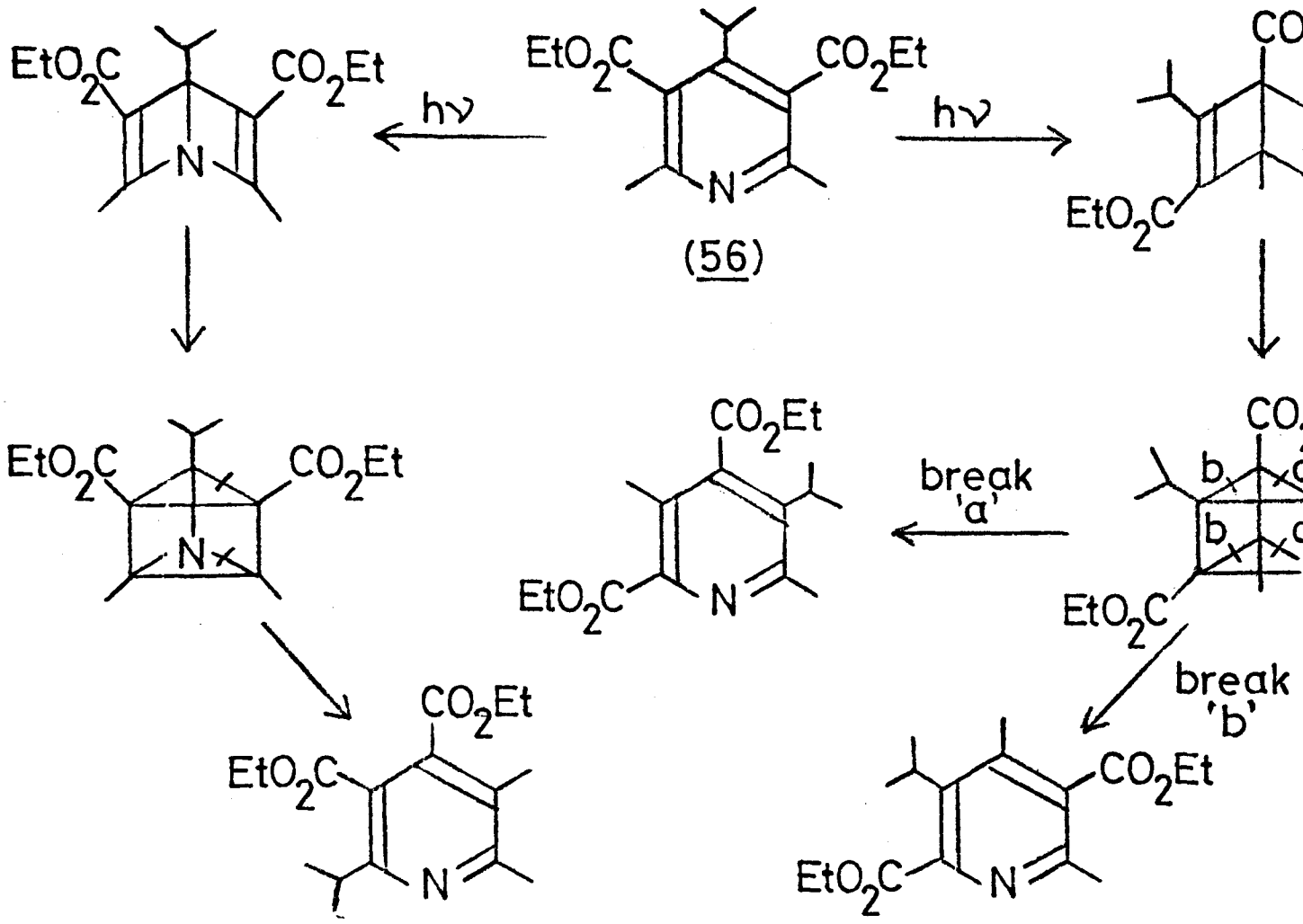
Obviously where a quaternised nitrogen is present in the molecule, the excitation must be $\pi\pi^*$; however, it will be recalled that Roebke concluded that, for 2-methylpyridine, only $\pi\pi^*$ excitation led to transposition in the gas phase. In this study, the 254nm irradiation used lies in the $\pi\pi^*$ region of all the dimethylpyridines and so it is likely that $\pi\pi^*$ excitation is again occurring here. It is

interesting to note that the 'walking' nitrogen mechanism applied to 2-methylpyridine predicts the formation of both 3- and 4-methyl-pyridines in agreement with Roebke's results. Therefore, the major photoproducts observed in this series of compounds are entirely consistent with those of Roebke.

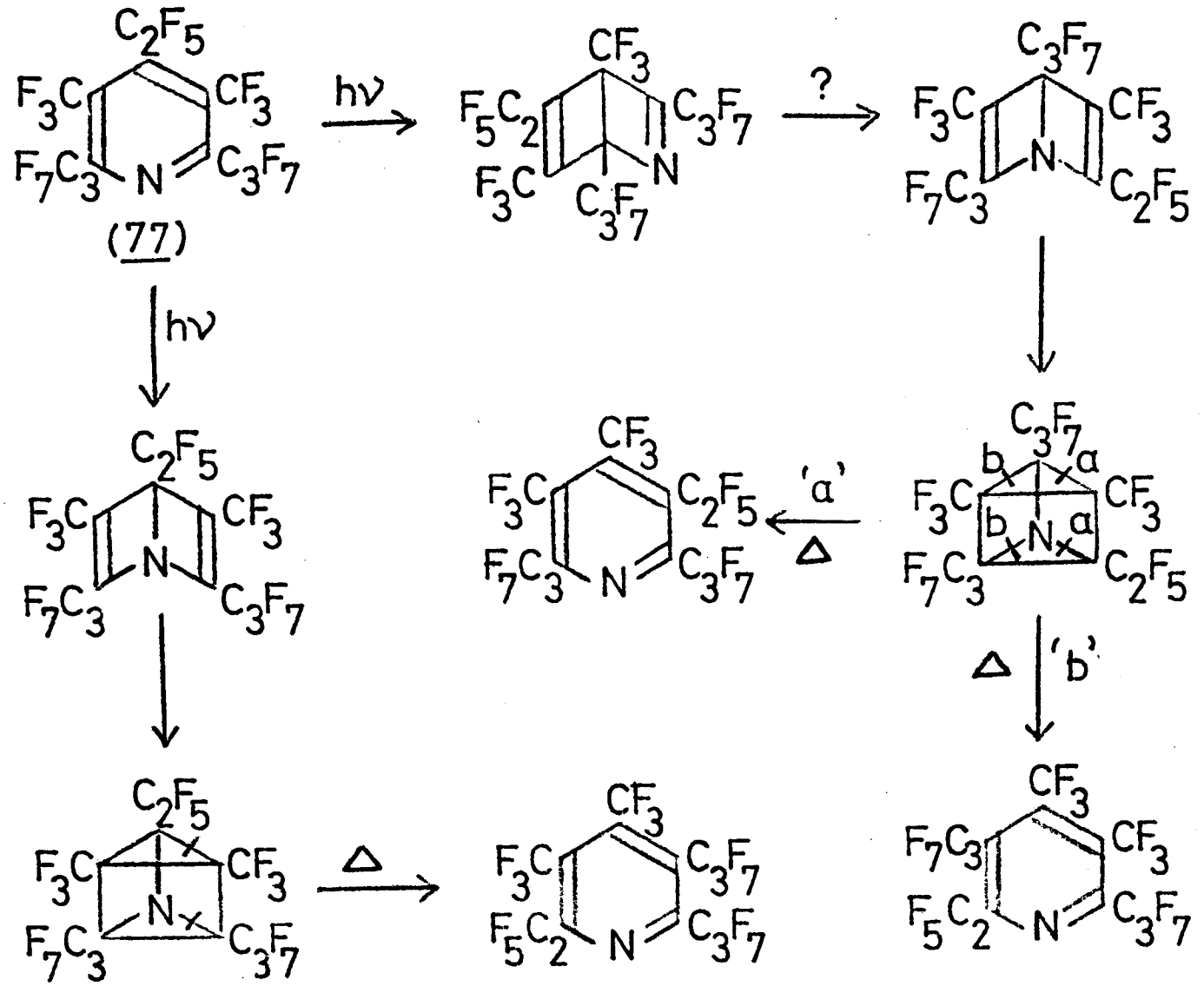


If $\pi\pi^*$ excitation really does lead to the major transposed products, it is necessary to explain why the Dewar isomer, only, is observed after photolysis of neutral pyridines at 254nm in solution.[72] In fact, it has not been established conclusively that an azabenzvalene is not formed - it merely has not been observed.. Unfortunately nothing is known, for certain, about the photophysics involved in the rearrangement process and so it is not possible to give a definitive answer to this problem. However, a rationale might be that, in solution, the 254nm irradiation does, indeed, cause $\pi\pi^*$ excitation and, thereby, populates an upper singlet state. In the vapour phase, the rearrangement occurs from this state or another upper state (maybe triplet) derived from it. In solution, rapid collisional quenching may increase internal conversion to a lower singlet state which subsequently either returns to the ground state or produces the azaDewarbenzene isomer. Some support for this view is provided by Roebke's observation that the presence of an inert gas, in the vapour phase photolyses, quenched the rearrangement reaction. It must therefore be provisionally concluded that any rearrangement of a neutral pyridine occurring in solution should require the intermediacy of an azaDewarbenzene and should not be explicable via a 'walk' mechanism.

Unfortunately, it is not clear whether rearrangement of methylpyridines does occur in solution since Roebke reported that irradiation of 2-methylpyridine in solution yielded no rearranged products,[77] while Lablache-Combier reported that rearrangement to 4-methylpyridine occurred.[78] However, some rearrangements of substituted pyridines in solution are known. Van Bergen and Kellogg[81] irradiated the pyridine (56), and reported that the rearranged products formed were exactly those expected if each of the two possible prismane isomers were produced and then cleaved by all possible modes.



The products formed cannot be derived by a 'walking' nitrogen mechanism. Similarly, Chambers[88] has irradiated the perfluorinated substituted pyridine (77) in solution and isolated azaDewar and azaprismane isomers which subsequently may react thermally to yield rearranged products.



Again, a 'walking' nitrogen mechanism cannot explain the product.

It should be borne in mind that, in the above examples, substitution in the pyridine of -COOEt or especially -F groups may alter the energy levels of the neutral molecule and, hence, the photophysics involved in the rearrangements may be altered. However, such evidence as is available does indicate that azaDewar isomers are required to explain the rearrangements in solution.

It has been shown that the major photolysis products formed in the dimethylpyridine series of compounds are readily explained by a coherent mechanistic scheme involving 'walking' of nitrogen. However, this cannot be the whole story since other dimethylpyridines are observed as minor photoproducts. Their appearance, which cannot be explained by 'walk' mechanisms, indicates that an alternative mechanism is in operation.

A possible candidate, to explain these 'leakage' products, was a demethylation/remethylation reaction. The analysis of the results for the major products has assumed they were derived

Figure 16

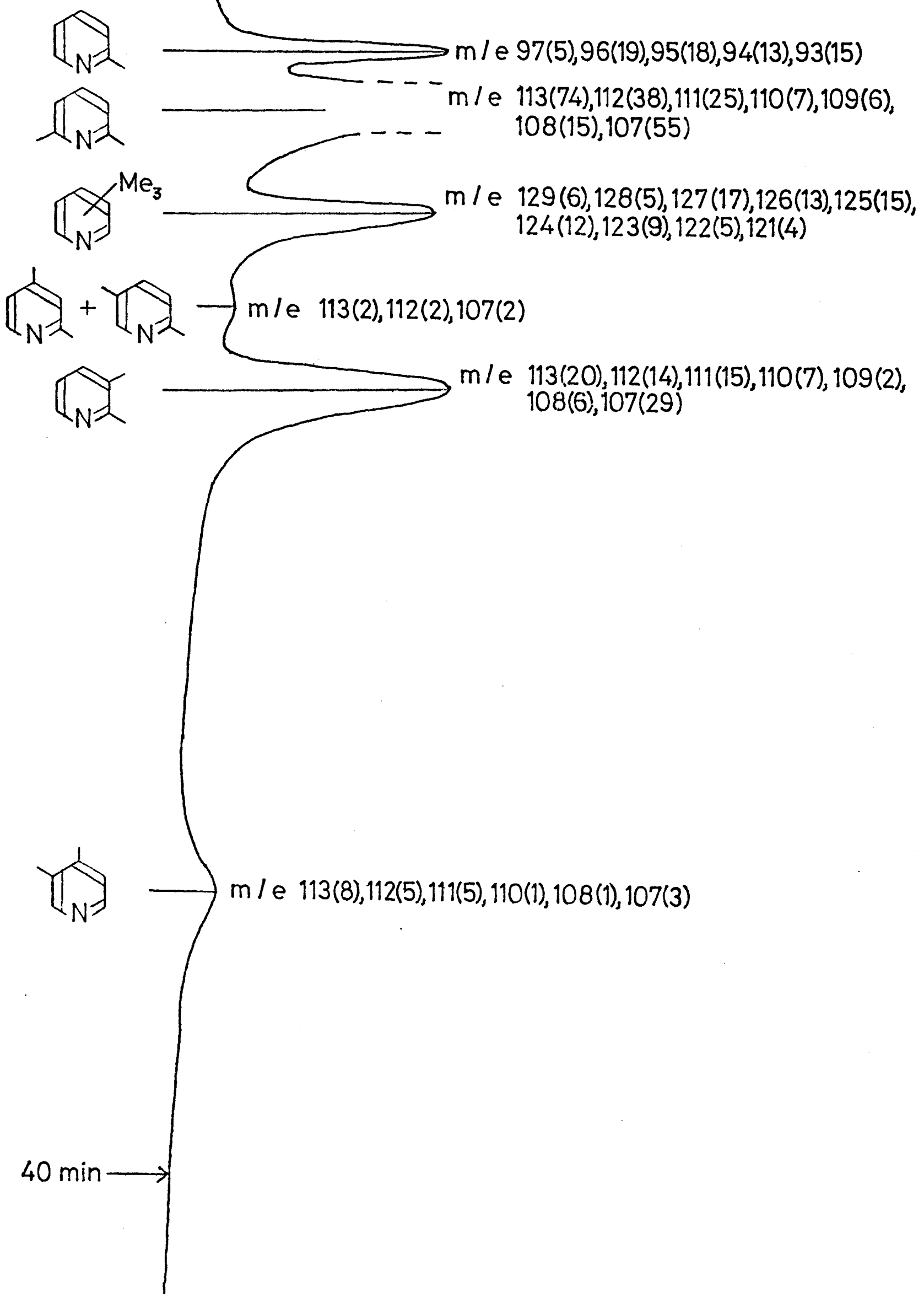
2,6-d_0/d_6-Dimethylpyridine photolysis
G.l.c. trace and mass spectra of products

Assignment

solvents

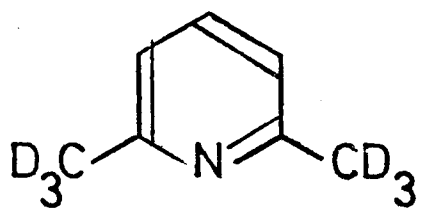
Carbowax / TEA, 100°

0 min →

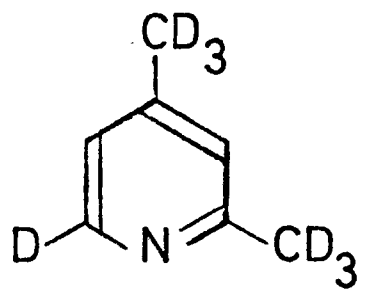


40 min →

intramolecularly; no evidence has been presented to support this assumption. In order to investigate this aspect of the rearrangement and to gain some insight to the nature of the minor photoproducts $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$, -$d_6$ - 2, 6-dimethylpyridine (105) and $\alpha,\alpha,\alpha,\gamma,\gamma,\gamma$-6-$d_7$- 2, 4-dimethylpyridine (106) were prepared



(105)



(106)

Photolyses, were carried out, in which a 1:1 mixture of the deuteriated compound and the corresponding non-deuteriated compound were irradiated for 17h in the Rayonet reactor at 254nm. The g. c. m. s. of the photoproducts were investigated. A dimethylpyridine photoproduct derived from an intramolecular process would be expected to retain the 1:1 isotopic composition and should, therefore, show major m/e signals at 107 and 113 (for the 2, 6-isomer irradiation) or 107 and 114 (for the 2, 4-isomer irradiation.) Any dimethylpyridines derived from an intermolecular process should show major m/e signals at 110 (for the 2, 6-isomer) or 110 and 111 (for the 2, 4-isomer).

The results of the two photolyses are presented below:

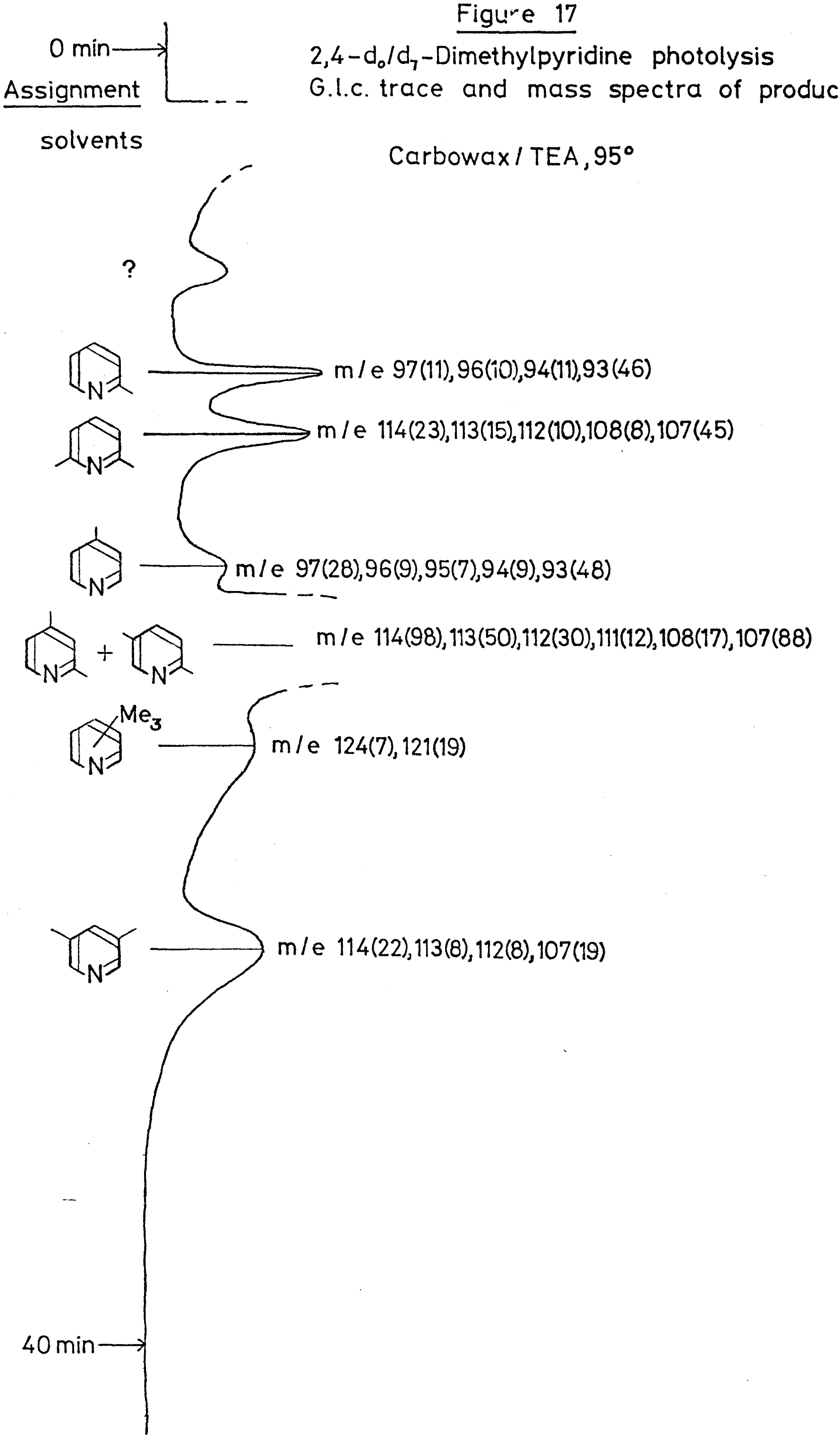
(i) 1:1 Mixture of 2, 6-d_6- and 2, 6-d_o- dimethylpyridines.

The g. l. c. trace of the photolysis mixture is shown in Figure 16 together with the recorded mass spectrum for each signal. It is clear that the mixture produced in this irradiation is the same as that produced in the non-deuteriated experiment.

The mass spectra of the peaks assigned to 2, 6-, 2, 3- and 3, 4 - dimethylpyridine indicate very clearly that the process which leads to their formation must be intramolecular, as evidenced by the increased intensities of the signals at m/e = 113 and 107 over those at 110.

Figure 17

2,4-d_0/d_7-Dimethylpyridine photolysis
G.l.c. trace and mass spectra of products



Hence, it has been shown that the major phototransposition reactions of 2, 6-dimethylpyridine are intramolecular. Unfortunately, the mass spectra of the minor products, 2, 4- and 2, 5-dimethylpyridines, were very weak. However, the appearance of signals at m/e 113 and 107 and the absence of a signal at m/e 110 is evidence that these minor products were formed intramolecularly as well.

(ii) 1:1 Mixture of 2, 4-d_0 - and 2, 4-d_7 -dimethylpyridines

The g. l. c. trace of the photoproduct is shown in Figure 17. It is identical with that obtained after photolysis of the non-deuteriated compound.

The most important result from this experiment is the observation that formation of both 3, 5-dimethylpyridine (the major product) and 2, 6-dimethylpyridine (the minor product) is intramolecular as shown by the presence of signals at m/e 114 and 107 and the absence of signals at 111 or 110.

It was not possible to take the mass spectrum of the 2, 5-dimethylpyridine photoproduct, which could only be separated from the 2, 4-isomer using a capillary column.

Thus, it has been shown that both major and minor transposed photoproducts for 2, 6- and 2, 4-dimethylpyridines are derived intramolecularly and it is, perhaps, not unreasonable to suggest that all such rearrangements in this series of compounds are intramolecular by analogy.

It is not possible to draw any firm conclusions about the processes leading to the formation of the minor photoproducts for a number of reasons. In some cases, the identity of the photoproduct was established by g. l. c. retention time only, without mass spectroscopic data. Even when mass spectroscopic data was available the m/e = 107 signal was often present either as a low percentage signal or together with signals clearly due to another species (often a trimethylpyridine). It is possible that the minor

m/e 107 signals were derived, in part, from some other dimethylpyridine or a decomposing product 'bleeding' off the column. Certainly, a measurement of the mass spectrum of the background from the column, in a region where no signal was evident, did sometimes contain a signal at m/e 107. Furthermore, signal broadening may have made observation of isomers impossible, if present as minor quantities. This might have been a particularly important factor where small quantities of 3, 5- or 3, 4-dimethylpyridine were present.

However, it is quite clear that 2, 6-dimethylpyridine is a product of the irradiation of 2, 4-dimethylpyridine and that other minor products are present for some isomers. It is noteworthy that 2, 6-dimethylpyridine is the product reported by Lablache-Combier[76] to be derived from 2, 4-dimethylpyridine. Could it be, after all, that some rearrangement *via* a prismane is occurring? This question will remain unanswered until further knowledge is gained about the minor products.

A possible approach to this problem would be the photolysis of a radioactive dimethylpyridine. Isotopic dilution techniques applied to the photolysate, followed by isomer separation (by preparative g. l. c) and purification (*via* the picrate, recrystallised to constant activity) should give information about the minor products. If an isomer is a minor product, residual radioactivity should remain in the purified compound.

Additional experimentation might consider ways of trapping intermediates and determining the detailed photophysics of the system.

This study has shown that dimethylpyridine photo-transposition reactions are intramolecular in the gas phase and that the major photoproducts, at least, can be accommodated by a 'walk' mechanism, novel to the neutral pyridine system. In addition, some minor photoproducts are also formed intramolecularly and seem to be derived by an alternative mechanism as yet unspecified.

It is hoped that this study will arouse new interest in the phototransposition reactions of alkylated pyridines, both in the vapour and liquid phases.

PHOTOCHEMISTRY OF THE DIMETHYLPYRIDINES

EXPERIMENTAL SECTION.

A) General Technique.

Routine procedures were carried out with the same equipment described for the tri-t-butylbenzenes (see Chapter 2.).

The following columns (coiled glass 1.5m x 4mm) were used for routine g.l.c.analysis.

(i) 20% Carbowax 20M + 5% Potassium Hydroxide on Embacel (Carbowax/KOH)

(ii) 20% Carbowax 20M + 5% Triethanolamine on Embacel (Carbowax/TEA)

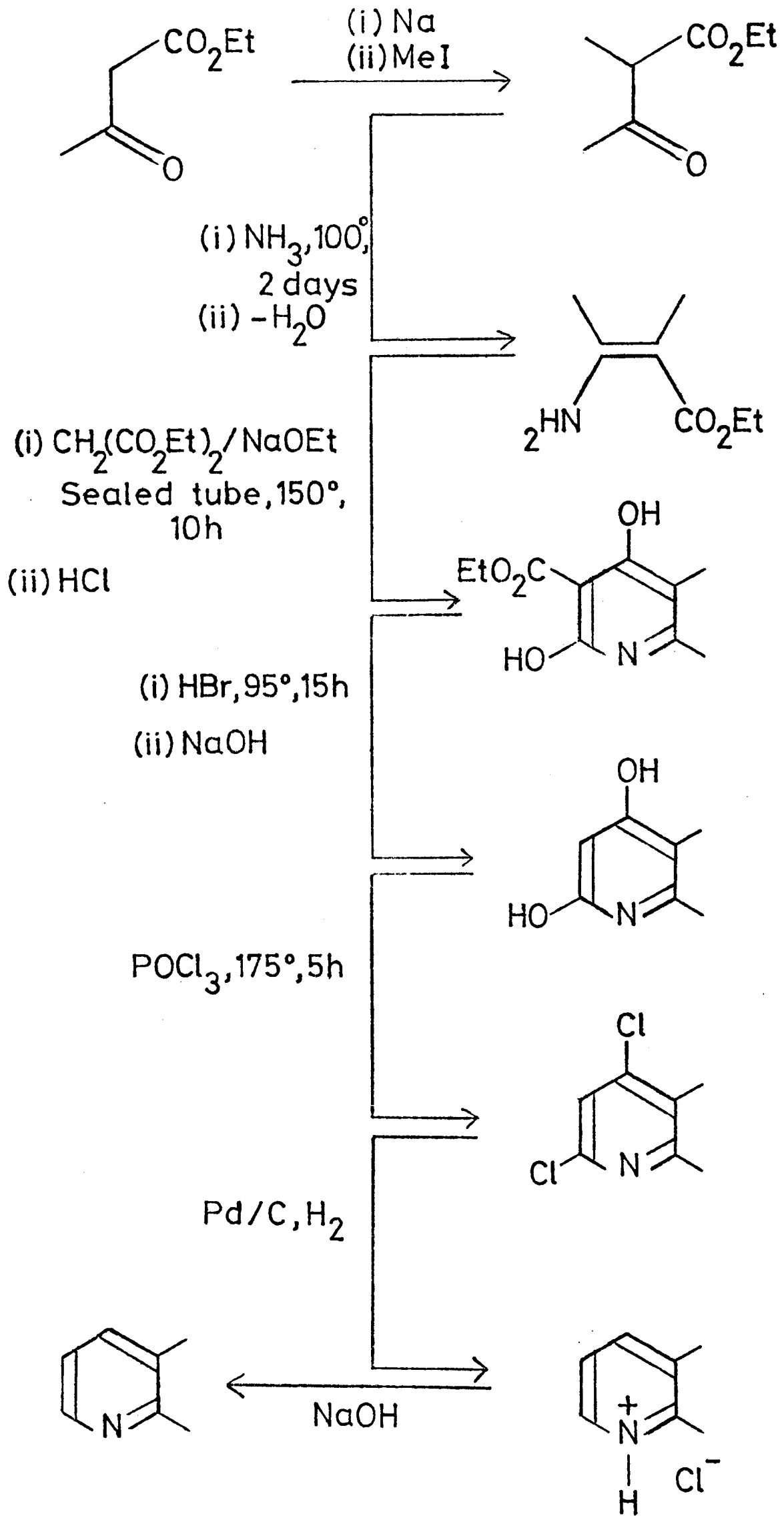
(iii) 20% Polymetaphenylether + 5% Triethanolamine on Embacel (PPE/TEA)

For analytical separation of 2, 4- and 2, 5- dimethylpyridines a Hewlett-Packard 5700A g.l.c, fitted with a Perkin-Elmer W.C.O.T. Carbowax 1540 + Potassium Hydroxide capillary column (50mx 0.2mm) was used. The g.l.c.was fitted with a splitting device (ca 60:1) and a flame ionisation detector and used nitrogen as the carrier gas.

B) Irradiation Technique.

In this section, all irradiations were performed in the vapour phase. Samples of compound were placed in a 3 litre quartz reactor, which was cooled to -78°, evacuated ($<$ 0.3 torr) and then sealed. The sample was allowed to reach room temperature prior to photolysis. After irradiation was completed, the quartz reactor was cooled to -78°

Scheme 4


CO2Et
(i) Na
(ii) MeI
CO2Et
O
O
(i) NH3, 100°,
2 days
(ii) -H2O
2HN
CO2Et
(i) CH2(CO2Et)2/NaOEt
Sealed tube, 150°,
10h
(ii) HCl
OH
EtO2C
HO
N
(i) HBr, 95°, 15h
(ii) NaOH
OH
HO
N
POCl3, 175°, 5h
Cl
Cl
N
Pd/C, H2
N
NaOH
+
N
H
Cl−

for ca- 1. 5h, opened to the atmosphere and the product, which had condensed out, was dissolved in ether (10ml). Subsequently most of the solvent was removed and the residue (ca 1 ml) analysed by g. l. c. and gas liquid chromatography linked to mass spectroscopy (g. c. m. s.)

Two light sources were employed:-

(i) A 450W medium pressure mercury arc lamp

(ii) A Rayonet reactor fitted with 254nm lamps.

The medium pressure lamp was enclosed in a reflective ellipse, such that the lamp was positioned at one focus and the quartz reactor at the other. In this way, the maximum amount of light was focussed on the sample.

The quantitative analyses were performed by cutting and weighing of g. l. c. peaks.

C) Materials

Each of the dimethylpyridine isomers, with the exception of 2, 3 -dimethylpyridine, was supplied commercially. 2, 3-dimethyl-pyridine was prepared by an unambiguous route and was shown to be free of the other isomers ($>$ 99. 9%) by g. l. c. Each of the other isomers except 2, 4-dimethylpyridine was purified via the picrate which was recrystallised twice (Methanol). 2, 4-dimethylpyridine was also purified via the picrate, but this was recrystallised four times (Methanol). The isomers, purified by these techniques, were each shown to be free of the other isomers ($>$ 99. 9%) by g. l. c..

D) Synthesis

(i) 2, 3-Dimethylpyridine

This compound was prepared by a slightly modified method of E. A. Coulson and co-workers,[118] and has previously been reported[122] (Scheme 4).

(ii) $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ - d_6 -2, 6-Dimethylpyridine.

Purified 2, 6-dimethylpyridine (10g), deuterium oxide (30ml) and sodium carbonate (300mg) were heated in a sealed tube at ca 175° for 48h. The acidic solution produced was neutralised with sodium carbonate and extracted with ether. After drying the combined extracts over anhydrous magnesium sulphate, the ether was fractionally distilled to leave a yellow liquid. After decolourisation with activated charcoal, a colourless liquid (280mg) remained.

N. m. r. (CCl_4) τ : 7.60 (0.1H, m), 3.13 (2H, d), 2.60 (1H, dd)

Analysis of the n. m. r. spectral integration indicated that $<2\%$ of hydrogen remained in the two methyl groups.

(iii) $\alpha,\alpha,\alpha,\gamma,\gamma,\gamma$ -6-d_7 - 2, 4-Dimethylpyridine.

Purified 2, 4-dimethylpyridine (1g), deuterium oxide (30ml) and sodium carbonate (300mg) were heated at 175° for 48h in a sealed tube. In this case the aqueous product was strongly basic and was readily extracted with ether. Fractional distillation of the ether, after drying over magnesium sulphate and decolourising with activated charcoal, yielded a colourless liquid product (600mg).

N. m. r. (CCl_4) τ : 7.79 (0.06, m), 7.59 (0.06, m),
3.15 (2H, m), 1.70 (0.14H, d).

Analysis of the n. m. r. spectral integration revealed that $<4\%$ of hydrogen remained in the two methyl groups and that 85% deuteriation had occurred at the C-6 position.

E) Photolyses

(i) Preliminary Irradiations with Medium Pressure Lamp as source.

In this series of experiments, samples (ca 150mg) were irradiated for 48h. In each case some of the sample did not go into the vapour phase and remained at the bottom of the reactor, below the level of the mercury arc lamp. In all experiments the major photoproduct was polymer which was formed on the walls of the photolysis vessel. Only the irradiation products which were soluble in ether were investigated.

Compounds irradiated under these conditions were:-

(a) 2, 5-dimethylpyridine
(b) 2, 6-dimethylpyridine
(c) 3, 5-dimethylpyridine
(d) 3, 4-dimethylpyridine

(ii) Other Irradiations with Medium Pressure Lamp as Source.

In this set of experiments, all of the sample (30mg) vapourised prior to irradiation, which lasted for 17h. Again much polymer formed on the walls of the photolysis vessel.

Compounds investigated by this method were:

(a) 2, 6-dimethylpyridine
(b) 2, 5-dimethylpyridine
(c) 2, 4-dimethylpyridine
(d) 2, 3-dimethylpyridine
(e) 3, 5-dimethylpyridine
(f) 3, 4-dimethylpyridine

(iii) Irradiations Carried Out in the 'Rayonet' Reactor.

In these experiments, samples (60mg) in the vapour phase were irradiated for 17h. Yet again, much polymeric material formed on the walls of the reactor.

Compounds investigated using this technique were:-

(a) 2, 6-dimethylpyridine
(b) 2, 5-dimethylpyridine
(c) 2, 4-dimethylpyridine
(d) 2, 3-dimethylpyridine
(e) 3, 5-dimethylpyridine
(f) 3, 4-dimethylpyridine
(g) 1:1 mixture of $\alpha, \alpha, \alpha, \alpha', \alpha', \alpha'$ -$\underline{d}_6$-2, 6-dimethylpyridine and 2, 6-dimethylpyridine.
(h) 1:1 mixture of $\alpha, \alpha, \alpha, \gamma, \gamma, \gamma$ -6-$\underline{d}_7$- 2, 4-dimethylpyridine and 2, 4-dimethylpyridine.

The results of photolysing each compound are reported in the Results and Discussion Section of the Dimethylpyridines (Page 99) and are summarised in Table 3.

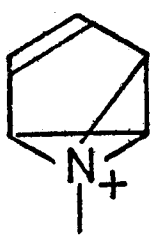
CHAPTER 4.

PHOTOCHEMISTRY OF THE N-METHYL-DIMETHYLPYRIDINIUM CHLORIDES

INTRODUCTION

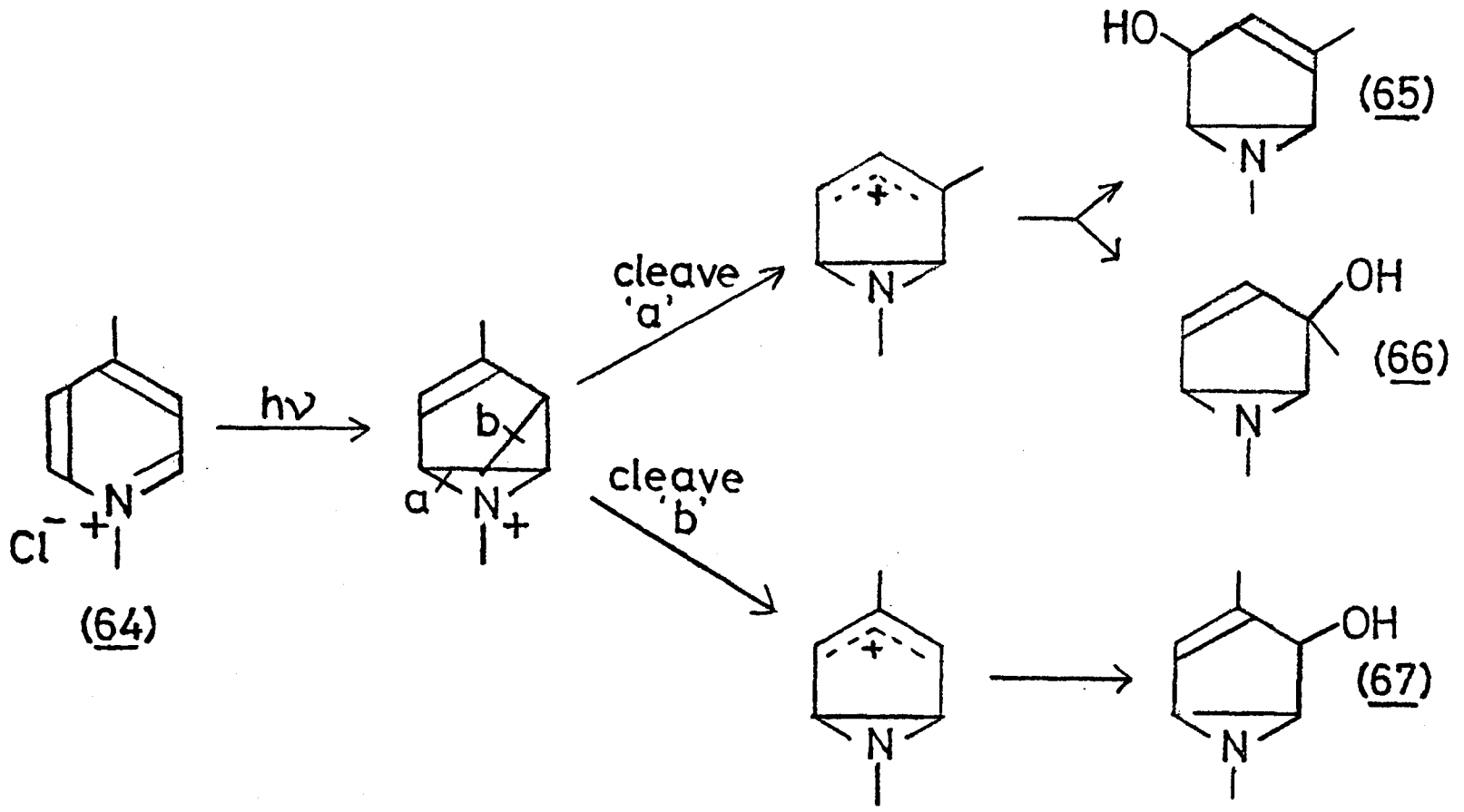
The proceeding chapter of this thesis was concerned with the detailed gas-phase photochemistry of the dimethylpyridines. In that section it was concluded that phototransposition probably occurred from an excited $\pi\pi^*$ state of the molecule. This section reports a brief study of the photochemistry in solution of the related N-methyl-dimethyl-pyridinium chlorides. These compounds possess no n - electrons and, hence, are presumably constrained to undergo $\pi\pi^*$ excitation. Therefore, the origin of any transposed photoproducts observed should be known. It was anticipated that this data would eventually enable a general mechanism to be postulated for the photochemical rearrangement of alkyl pyridines.

The photorearrangement of quaternary pyridine compounds has not been directly observed in neutral solutions; however, a photorearrangement step has been proposed by Kaplan[82] to explain the nature of some of the products observed during a study of the photosolvation of quaternary pyridine compounds. It was reported that an intermediate, considered to be an N-methylazoniabenzvalene (63), was involved and underwent 1,2-shifts of nitrogen prior to the formation of the photosolvated species.



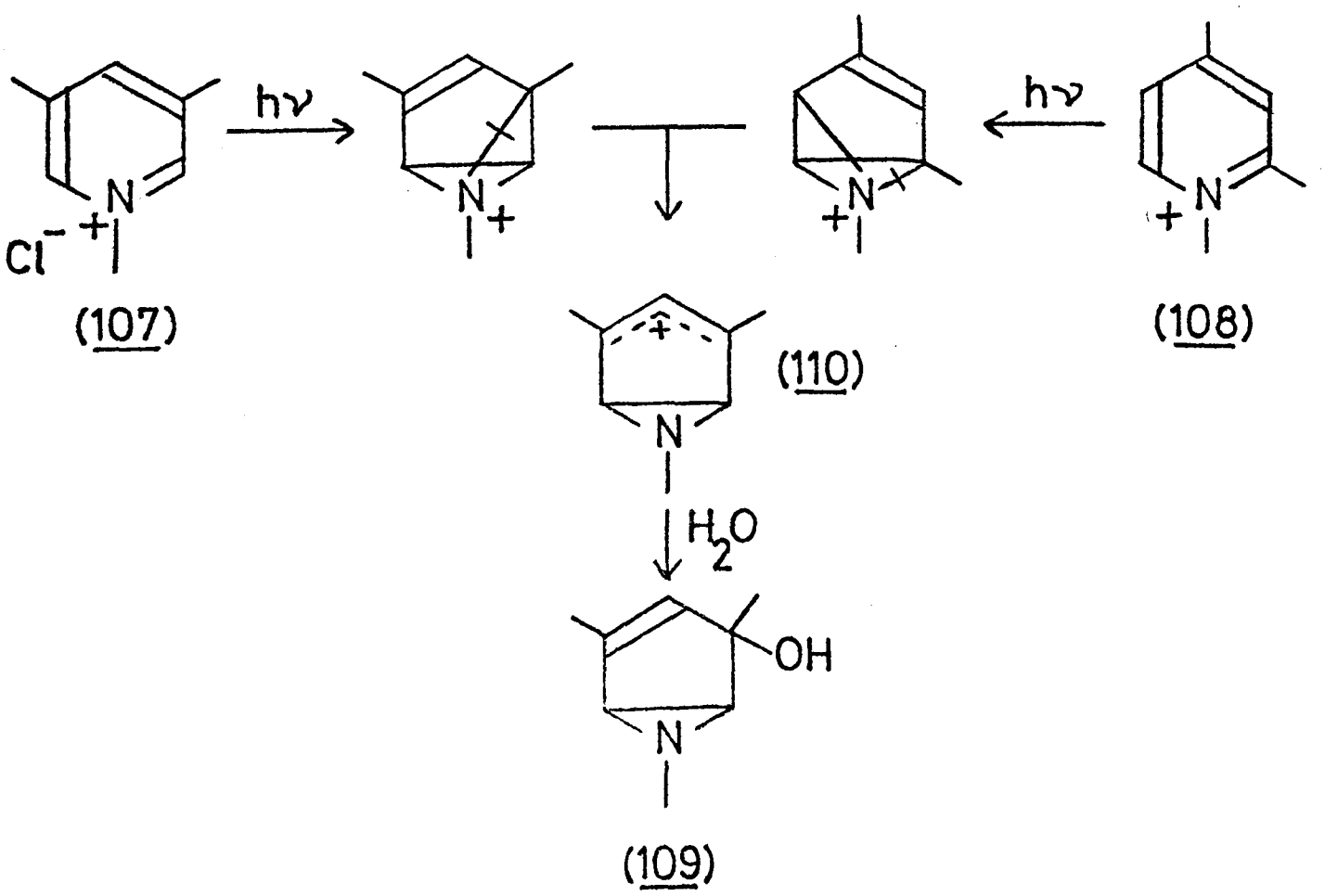
(63)

The case of N-methyl-4-methylpyridinium chloride (64) may be used as an illustrative example of the transposition step (cleavage of bond (a)).

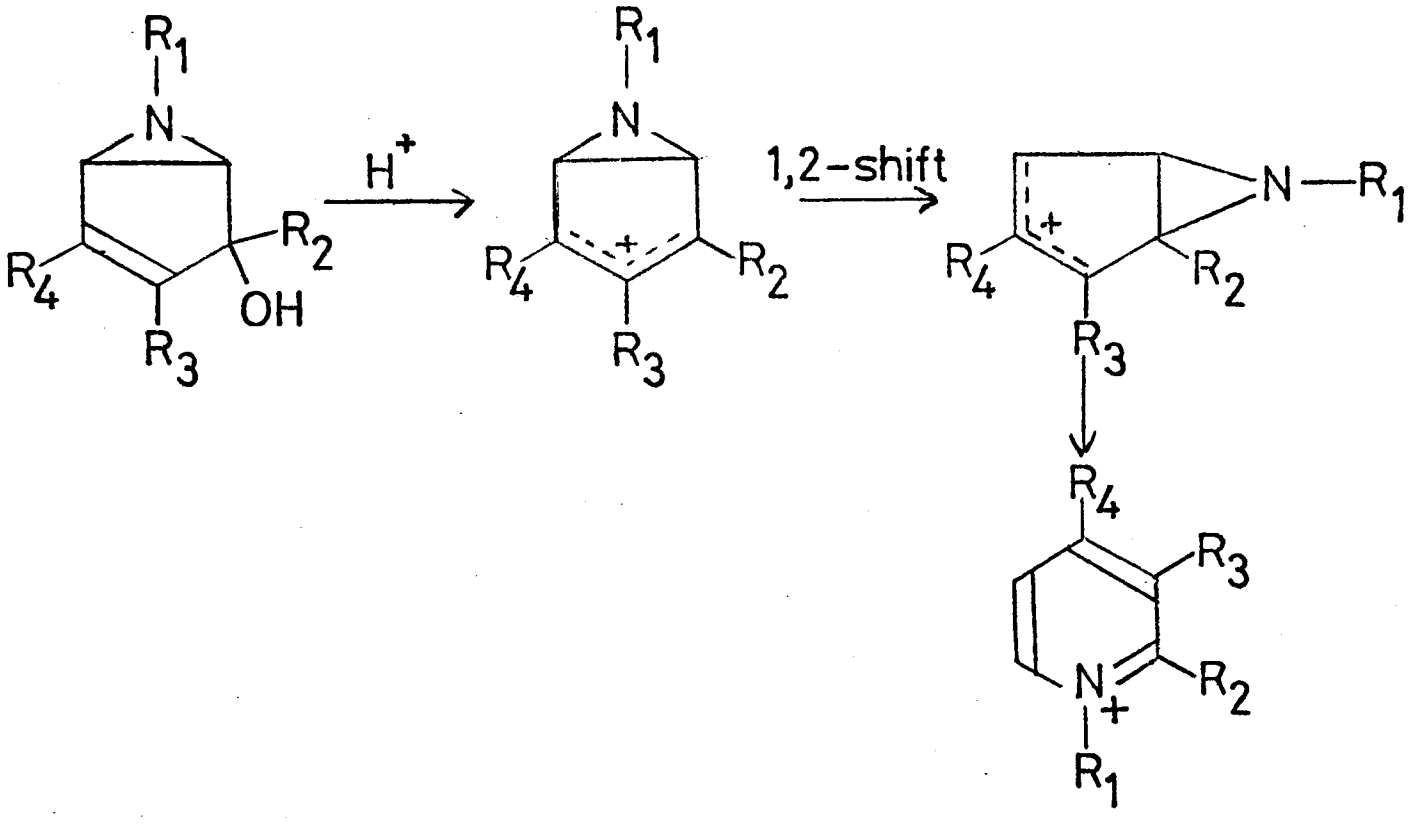


The formation of the three species (65), (66) and (67) in a 1:1:2 ratio is strong evidence that a 1, 2-shift of nitrogen is effectively taking place.

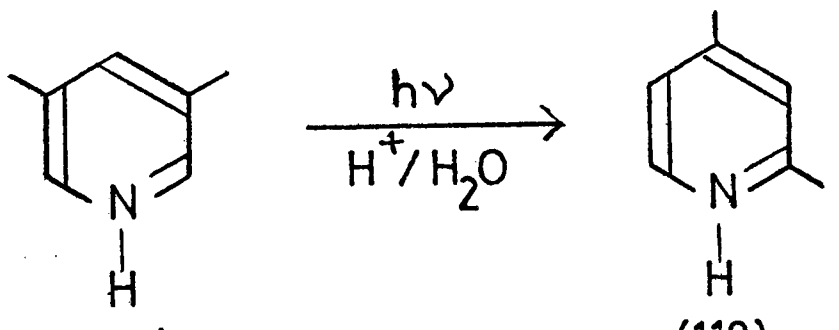
Similar 1, 2-shifts of nitrogen are proposed in the photosolvation of N-methyl-3, 5-dimethylpyridinium chloride (107) and N-methyl-2, 4-dimethylpyridinium chloride (108).



The formation of the same azabicyclohexenol (109) from both 2, 4- and 3, 5- dimethyl isomers is indicative of the common intermediacy of the azabicyclohexenyl cation (110), which could be produced from the 3, 5-dimethyl isomer with no shift and from the 2, 4-dimethyl isomer after an effective 1, 2-shift of nitrogen. In the presence of acid the azabicyclohexenols are unstable and reform the quaternary pyridinium compounds, again with 1, 2-shifts of nitrogen taking place. Hence, in the general bicyclohexenol below the effect of acid is to yield a pyridinium salt in which R_2, R_3 and R_4 become situated at α, β and γ positions respectively, consistent with a 1, 2-shift of nitrogen.



In the case of protonated 3, 5-dimethylpyridine (111), photorearrangement to protonated 2, 4-dimethylpyridine (112) was observed in acidic water, suggesting that a similar mechanism was operating.



(111) (112)

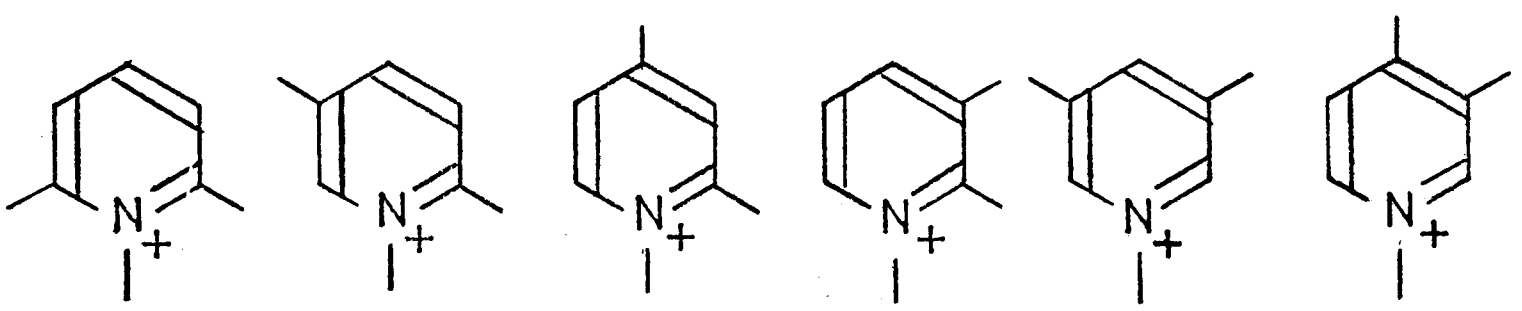
In an effort to add to Kaplan's data, Thompson [122] irradiated N-methyl-2, 5-dimethylpyridinium chloride (113) in a variety of solvents (acetonitrile, concentrated sulphuric acid, hydrochloric acid, trifluoroacetic acid) under different conditions. Unfortunately, the results

he obtained were very complex and could not readily be interpreted in terms of transposition reactions.

The present study extends some of that earlier work and broadens the investigation to include the remainder of the N-methyl-dimethylpyridinium chlorides.

RESULTS AND DISCUSSION.

The six N-methyl-dimethylpyridinium chlorides were irradiated at 254nm in the Rayonet reactor as 2% solutions contained in either quartz nmr tubes or quartz test tubes. In the case of the n. m. r. tube scale photolyses the course of reaction was followed by recording the n. m. r. spectrum of the photolysate at timed intervals. For the test tube scale photolyses various analytical techniques were employed to determine the course of reaction and the nature of the photoproducts. In some experiments the residue which remained after removal of the photolysis solvent was de-quaternised by heating in a bulb-to-bulb distillation apparatus at reduced pressure. The distillate was subsequently analysed for the presence of dimethylpyridine products.



(114) (113) (108) (115) (107) (116)

The detailed experimental and spectroscopic observations and the conclusions drawn from each of the photolyses are presented in tabular form (Tables 6 to 8) at the end of the experimental section of this chapter.

The photolyses that were performed and the overall results are summarised in the following table:-

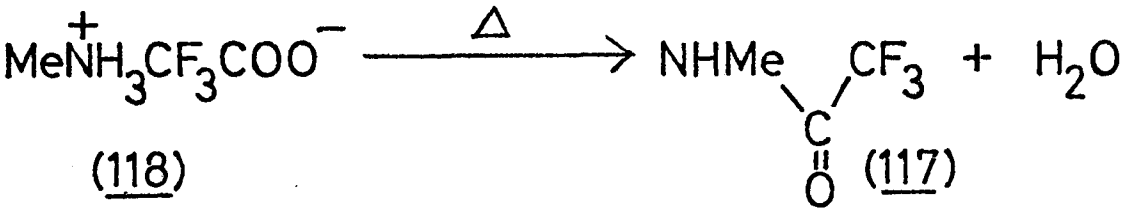
Photolysis Vessel	Compound	Solvent	Conclusion
N. m. r. tube	N-Me-2, 6-Me_2Py Cl (114)	T F A	No rearrangement
N. m. r.tube	N-Me-2, 5-Me_2Py Cl (113)	T F A	No rearrangement
N. m. r.tube	N-Me-2, 4-Me_2Py Cl (108)	T F A	Rearrangement to N-Me-2, 5-Me_2Py Cl (113)
N. m. r. tube	N-Me-2, 3-Me_2Py Cl (115)	T F A	No rearrangement
N. m. r.tube	N-Me-3, 5-Me_2Py Cl (107)	T F A	No rearrangement
N. m. r.tube	N-Me-3, 4-Me_2Py Cl (116)	T F A	No rearrangement
N.m.r.tube	N-Me-2, 4-Me_2Py Cl (108)	CD_3OD	No rearrangement
N. m. r. tube	N-Me-3, 4-Me_2Py Cl (116)	CD_3OD	No rearrangement

Photolysis Vessel	Compound	Solvent	Conclusion
Test Tube	N-Me-2,3-Me_2Py Cl (115)	T. F. A	Rearrangement to N-Me-2,6-Me_2Py Cl (114) plus N-Me-3,4-Me_2Py Cl (116)
Test Tube	N-Me-3,4-Me_2Py Cl (116)	T. F. A	No rearrangement
Test Tube	N-Me-3,4-Me_2Py Cl (116)	MeOH	No rearrangement
Test Tube	N-Me-3,5-Me_2Py Cl (107)	MeOH	Rearrangement to N-Me-2,4-Me_2Py Cl (108)
Test Tube	N-Me-2,4-Me_2Py Cl (108)	MeOH	Rearrangement to N-Me-3,5-Me_2Py Cl (107)
Test Tube	N-Me-2,5-Me_2Py Cl (113)	CH_3CN	No rearrangement
Test Tube	N-Me-2,4-Me_2Py Cl (108)	CH_3CN	No rearrangement

Photolysis Vessel	Compound	Solvent	Conclusion
Test Tube	N-Me-2, 5-Me_2Py Cl (113)	T F A	Formation of CF_3·C(=O)·NHMe on bulb-to-bulb distillation of photolysis residue. No rearrangement.
Test Tube	N-Me-2, 4-Me_2Py Cl (108)	T F A	Rearrangement to N-Me-2, 5-Me_2Py Cl (113), plus formation of $CF_3C(=O)HNMe$ N-Me-3, 5-Me_2Py Cl (107) also formed (?)

The data included in the tables indicate that in the majority of cases photorearrangement had not occurred and, in fact, in all cases the major photochemical process was polymerisation as evidenced by the formation of broad, low-intensity signals in the n. m. r. spectrum of the photolysate . In some cases, there was n. m. r. evidence for the presence of N-methyl-trifluoroacetamide (117) in the bulb-to-bulb distillation products. It is reasonable to assume that this product was derived by thermal decomposition of N-methylammonium trifluoroacetate (118) during the bulb-to-bulb distillation process.

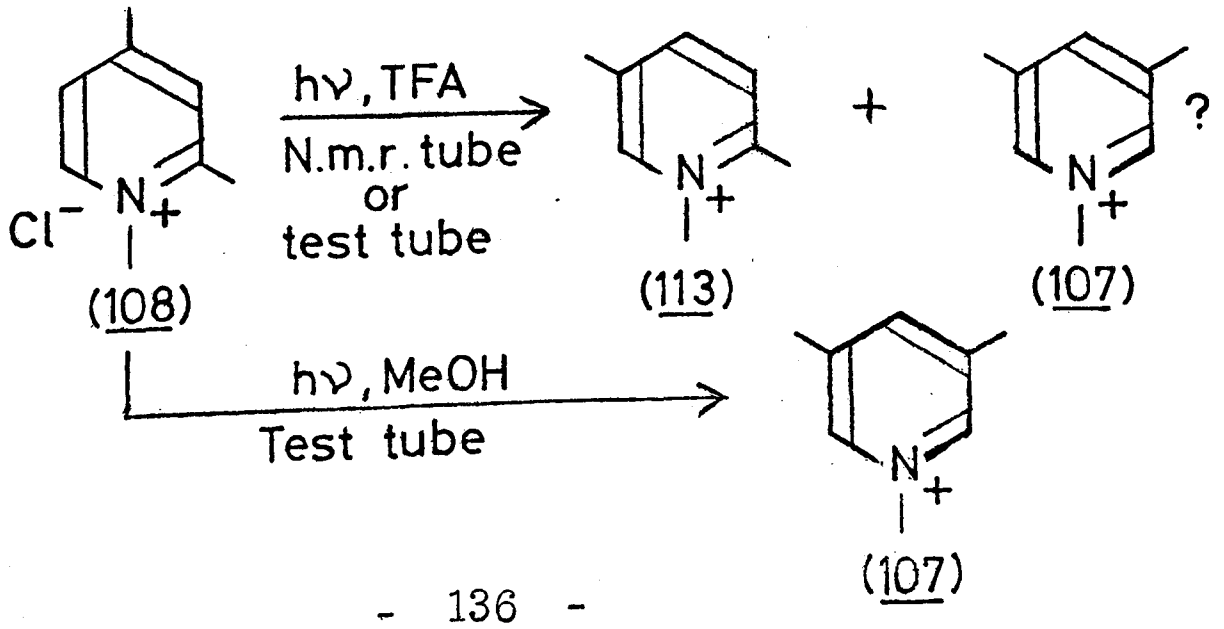
It was shown independently that this compound (118) did indeed, under the bulb-to-bulb distillation conditions, decompose to yield N-methyl-trifluoroacetamide (117).



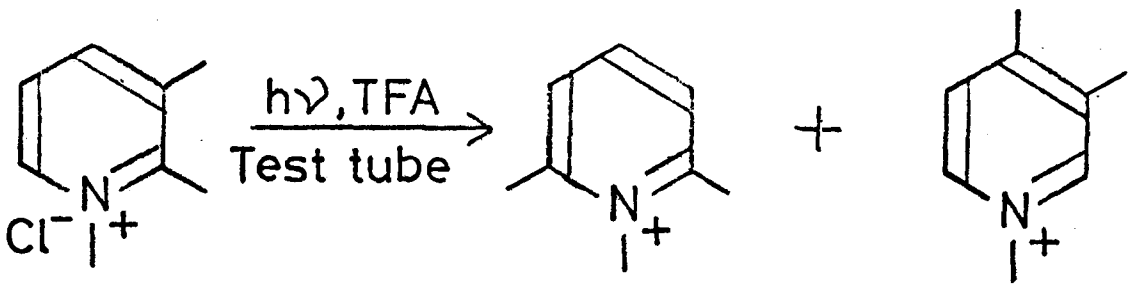
(118) (117)

The N-methylammonium trifluoroacetate must be formed as a result of cleavage of the pyridine nucleus. Whether this is a wholly photochemical process or involves both photochemical and thermal processes is not known.

Only in the four cases detailed below was there any evidence at all for rearrangement having occurred.

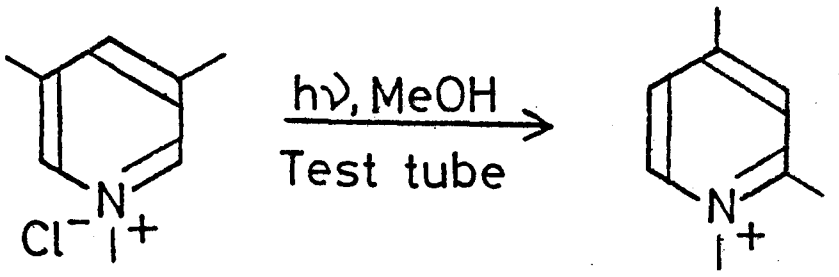


(iii)



(115) (114) (116)

(iv)



(107) (108)

The evidence for any of these rearrangements is tenuous, being inferred from g. l. c. retention times (with no co-injection or conclusive mass spectroscopic data) and/or the formation of weak n. m. r. signals in the appropriate spectral regions of the photolysate mixtures. In no case were any products isolated.

Under most circumstances it would seem reasonable to dismiss this evidence for rearrangement as being too unreliable. However, it should be noted that this series of compounds presented considerable experimental problems, so that any evidence for rearrangement might be significant and worthy of further consideration. The major problem encountered with these compounds was their general photochemical stability and consequent low degree of conversion to isomeric compounds. Furthermore, it was rarely possible to satisfactorily monitor the course of reaction due to (i) the spectroscopic similarity of the isomers

(ii) the difficulty of de-quaternising the isomers on g. l. c.

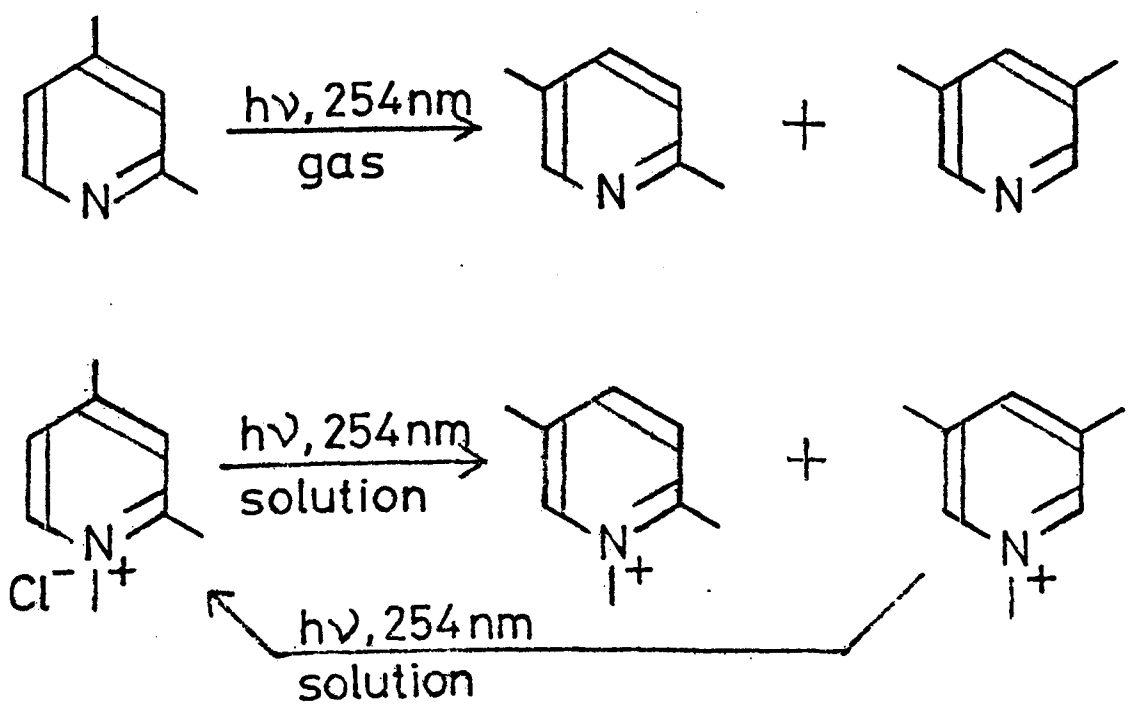
(iii) the incompatibility of trifluoroacetic acid with the g. l. c. column materials.

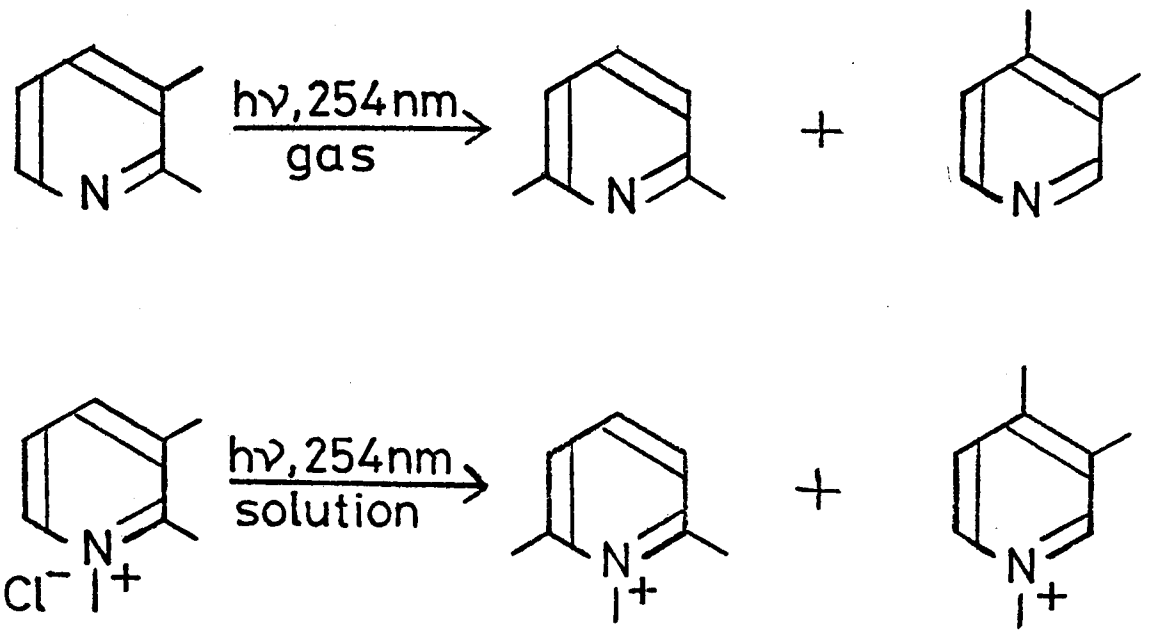
(iv) the formation of polymer during the course of reaction.

Finally, it should be noted that the identification of individual isomeric products, by g.l. c.analysis for parent dimethylpyridines in the bulb-to-bulb distillates, was also hampered by the combination of low overall photochemical conversion to isomer and low efficiency of the thermal dequaternisation process.

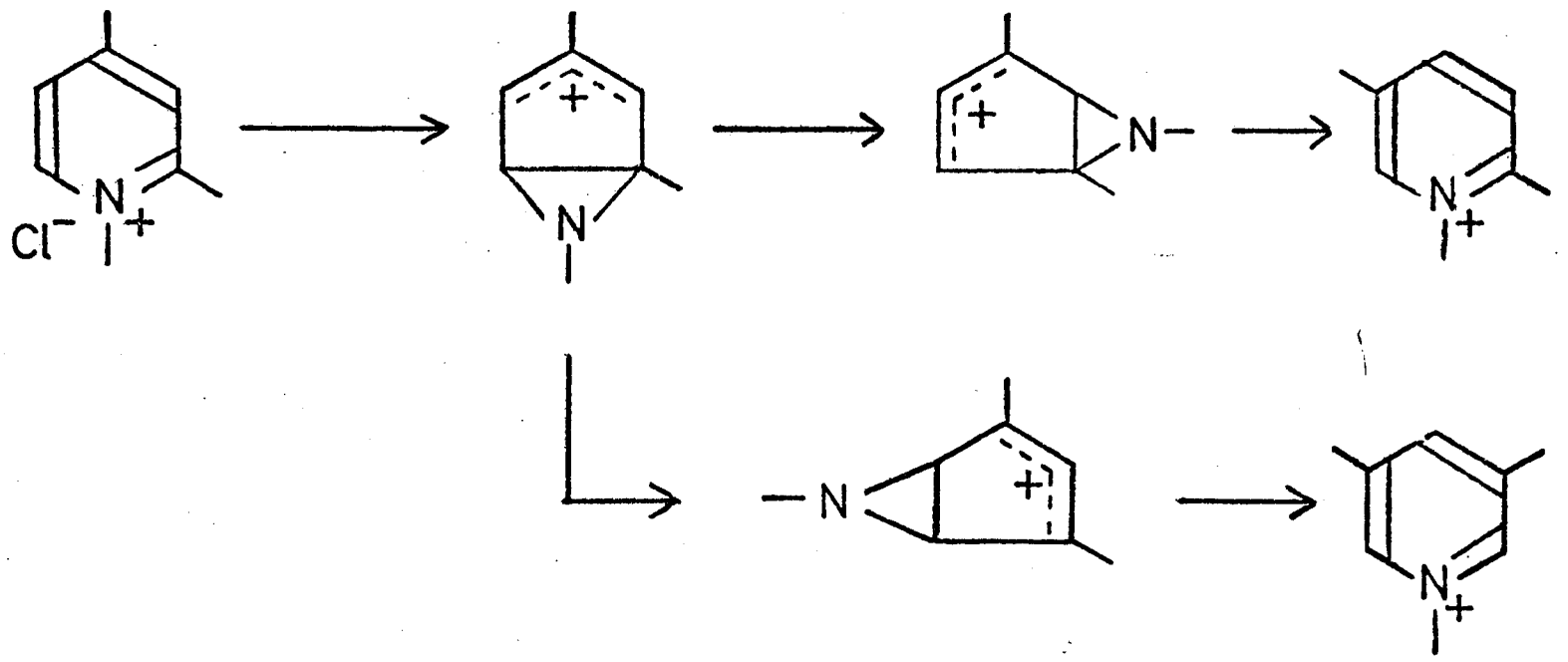
Taking account of these factors, it is, perhaps, not surprising that the evidence is not conclusive and that rearrangement was only indicated for some of the isomers and appeared to yield slightly modified products as experimental scale and solvent were varied.

Leaving this aside, it is of very great interest to note that every isomeric photolysis product corresponds precisely with at least one of the gas phase photolysis products of the corresponding dimethyl-pyridine compound. Thus, it will be recalled that 2, 4-, 2, 5- and 3, 5-dimethylpyridine were interconverted photochemically in the gas phase. In this series of compounds the N-methyl - 2, 5 -, and 3, 5-dimethyl-pyridinium chlorides were apparently formed photochemically from N-methyl-2, 4-dimethylpyridinium chloride and N-methyl-2, 4-dimethylpyridinium chloride from N-methyl-3, 5-dimethylpyridinium chloride. Similarly, 2, 3-, 3, 4- and 2, 6- dimethylpyridine formed a set of photochemically interconverting compounds; in this series N-methyl-2, 3- dimethylpyridinium chloride appeared to yield N-methyl-2, 6- and 3, 4-dimethylpyridinium chlorides.





By analogy with the neutral pyridine compounds it is obvious that the photolysis products from the N-methyl quaternary compounds might similarly be derived via 1, 2-shifts of the nitrogen atom around a skeletal ring of five carbon atoms, as in the scheme below:-



This type of mechanism is entirely consistent with that proposed by Kaplan [82] for the photosolvation of N-methylpyridinium salts, although in this present study no photosolvated products, analogous to those described by Kaplan, were observed.

Further, since the photochemical excitation induced in these quaternary pyridine systems is necessarily $\pi\pi^*$ and the irradiation products correspond with those of the neutral compounds, these preliminary results might provide some confirmation that the products from the neutral compounds are also derived from a $\pi\pi^*$ state, as was suggested previously.

Before any final conclusion can be reached it is essential that further studies be carried out on this series of compounds. However, prior to carrying out a photochemical investigation it will be necessary to develop better experimental techniques to either separate the quaternary pyridine isomers or dequaternise these compounds.

It is hoped that this study will provide the impetus for such investigations.

EXPERIMENTAL SECTION

A) General Technique

Routine procedures were carried out with the same equipment described in an earlier experimental section of this thesis (Chapter 2).

The following column (coiled glass 1.5m x 4mm) was used for routine g.l.c.analysis.

20% Carbowax 20M + 5% Potassium Hydroxide on Embacel
(Carbowax/KOH)

B) Experimental Technique.

Each photolysis in this section was performed on solutions contained in quartz test tubes or quartz n.m.r.tubes. The Rayonet reactor (fitted with 254nm lamps) was used as irradiation source.

Where stated, solutions were deoxygenated by passage of dry, oxygen-free ('white spot') nitrogen as described previously.

All solvents were of spectroscopic grade. In the case of trifluoroacetic acid (TFA) a trace of trifluoroacetic anhydride was added to remove any water that might be present.

The quaternary pyridine compounds were decomposed by heating (at ca 150^{o} using an air bath), in a bulb-to-bulb distillation apparatus under reduced pressure (ca 20 torr). The collecting bulb was cooled in an acetone/dry ice bath.

C) Synthesis

(i) N-Methyl-dimethylpyridinium Methosulphates.

Dimethylpyridine (5.3g) and redistilled dimethyl sulphate (6.3g) were dissolved separately in ether (50ml) and the two solutions mixed together. The reactants were allowed to stand at room temperature for 12h, and then the solid product, which had formed, was filtered off and dried. In all cases, the solids were extremely deliquescent.

(ii) N-Methyl-dimethylpyridinium Chlorides.

An aqueous solution of N-methyl-dimethylpyridinium methosulphate (2.33g) was added to an aqueous solution of barium chloride (1.04g), whereupon a fine white precipitate was formed. The precipitate was removed by filtration through a celite filter and the solvent evaporated. In all cases an off-white deliquescent solid remained.

N.m.r. (TFA)

N-Me-2, 6-Me_2 Py^+ Cl^- τ: 7.11 (6H, s) 5.80 (3H, s), 2.25 (2H, m), 1.76 (1H, m),

N-Me-2, 5-Me_2 Py^+ Cl^- τ: 7.45 (3H, s), 7.17 (3H, s), 5.71 (3H, s) 2.21 (1H, d), 1.78 (1H, d), 1.56 (1H, s),

N-Me-2, 4-Me_2 Py^+ Cl^- τ: 7.34 (3H, s), 7.18 (3H, s), 5.75 (3H, s) 2.33 (2H, m), 1.56 (1H, s)

N-Me-2, 3-Me_2 Py^+ Cl^- τ: 7.37 (3H, s) 7.15 (3H, s), 5.60 (3H, s), 2.23 (1H, t), 1.71 (1H, d), 1.42 (1H, d)

N-Me-3, 4-Me_2 Py^+ Cl^- τ: 7.38 (3H, s), 7.28 (3H, s) , 5.66 (3H, s) 2.24 (1H, m) 1.64 (2H, m).

N-Me-3,5-Me_2Py$^+$ Cl^- τ: 7.41 (6H, s), 5.60 (3H, s), 1.82 (1H, s)
1.63 (2H, s),

(iii) N-Methylammonium Trifluoroacetate.

Sodium hydroxide (1.2g) in water (5ml) was added dropwise to N-methylammonium chloride (2.0g), The N-methylammonia thereby produced was carried with nitrogen into trifluoroacetic acid (5ml). After several hours the unreacted trifluoroacetic acid was removed under vacuum and the crystalline solid (1.86g) which remained was dried over phosphorous pentoxide.

N.m.r. (TFA) τ: 7.05 (3H, q), 3.27 (3H, m)

^{19}F N.m.r. (Acetone) : Singlet 75.8 ppm upfield from CCl_3F.

(iv) N-Methyl-trifluoroacetamide.

N-Methylammonium trifluroacetate (0.3g) was heated in the bulb-to-bulb distillation apparatus, using an air bath, under reduced pressure (20 torr). The solid initially melted and showed signs of decomposing at ca 135°. On further heating (ca 160°) a liquid could be seen to be refluxing in the bulb. With a little further heating, a white solid began to collect in the collection bulb which was cooled in an acetone/dry ice bath. After heating for 1.5h no starting material remained in the reaction bulb. The white solid in the collection bulb was isolated by washing out with a little carbon tetrachloride.

N.m.r. (CCl_4) τ: 7.11 (3H, d), 2.3 (ca 1H, br)

^{19}F N.m.r. ($CDCl_3$) : Singlet 77 ppm upfield from CCl_3F.

Ir ($CHCl_3$) ν_{max} : 3470 (m), 3350 (m), 3050 (w), 2960 (w)
1732 (s), 1715 (sh), 1562 (s), 1423 (m),
1340 (m), 1220 (sh), 1180 (s), 1019 (m)
845 (m).

Mass spectrum m/e 127 (12), 126 (4), 78 (8), 69 (37), 58 (100), 50 (3)

D) Photochemistry.

The detailed results from this series of experiments are presented in Tables 6, 7 and 8 at the end of this experimental section.

(i) Irradiation of the N-Methyl-dimethylpyridinium Chlorides in Trifluoroacetic Acid in Quartz N. M. R. Tubes.

Solutions (2%) of the quarternary salts in trifluoroacetic acid were irradiated in a quartz n.m.r. tube at 254nm in the Rayonet reactor. The resultant photochemistry was followed by recording the n.m.r. spectra of the samples at timed intervals.

(ii) Other Photolyses of the N-Methyl-dimethylpyridinium Chlorides in Quartz N. M. R. Tubes.

The following solutions (2%) were also irradiated in quartz n. m. r. tubes at 254 nm in the Rayonet reactor:-

(iia) N-Methyl-2, 4-dimethylpyridinium chloride in methanol-$\underline{d}_4$

(iib) N-Methyl-3, 4-dimethylpyridinium chloride in methanol-$\underline{d}_4$

The photochemistry which occurred was monitored by recording the n.m.r. spectrum of the sample at timed intervals.

(iii) Irradiations of the N-Methyl-dimethylpyridinium Chlorides Carried Out in Quartz Test Tubes.

(iiia) N-Methyl-2, 5-dimethylpyridinium Chloride in Trifluoroacetic Acid

N-Methyl-2, 5-dimethylpyridinium chloride (0. 4g) in deoxygenated trifluoroacetic acid (20ml), was irradiated at 254nm in the Rayonet reactor. After 46h the trifluoroacetic acid was evaporated and the brown oily residue that remained was bulb-to-bulb distilled (ca 160°/20 torr) after n. m. r. analysis. The distillate was analysed by g. l. c. and g. c. m. s.

(Carbowax/KOH 110°) and by n.m.r. spectroscopy.

(iii b) N-Methyl-2, 5-dimethylpyridinium Chloride in Acetonitrile.

Experimentally as in (iiia); the bulb-to-bulb distillate was analysed by g.l.c. and n.m.r. spectroscopy.

(iii c) N-Methyl-2, 4-dimethylpyridinium Chloride in Trifluoroacetic Acid.

Experimentally as for (iiia); the distillate was analysed by g.l.c., g.c.m.s.(Carbowax/KOH, 110°) and by n.m.r. spectroscopy.

The experiment was repeated using four samples of the quaternary compound in trifluoroacetic acid. The product (ca 300 mg) isolated from the bulb-to-bulb distillation was purified by preparative g.l.c.. A white, needle-shaped crystalline solid (74 mg) was collected. This fraction had the following spectroscopic properties.

N.m.r. (CCl_4) τ : 7.11 (3H, d) 2.3 (ca 1H, br)

I.r. ($CHCl_3$) ν_{max}: 3470(m), 3350 (m), 3050 (w), 2960 (w), 1732 (s), 1715 (sh), 1562 (s), 1423 (m) 1340 (m), 1220 (sh), 1180 (s), 1019 (m) 845 (m)

Mass spectrum m/e 127 (14), 126 (5), 78 (10), 69 (36), 59 (3), 58 (100), 50 (6).

^{19}F N.m.r. ($CDCl_3$) : Singlet 77 ppm upfield from CCl_3F

(iii d) N-Methyl-2, 4-dimethylpyridinium Chloride in Acetonitrile.

N-Methyl-2, 4-dimethylpyridinium chloride (0. 1g) in acetonitrile (5ml) was irradiated at 254nm in the Rayonet reactor. The course of the photolysis was monitored by g. l. c. (Carbowax/KOH, 110°).

(iii e) N-Methyl-2, 4-dimethylpyridinium Chloride in Methanol.

N-Methyl-2, 4-dimethylpyridinium chloride (0. 4g) in methanol (20ml) was irradiated at 254nm in the Rayonet reactor. The course of the reaction was monitored by g. l. c.(Carbowax/KOH, 110°). After 7h the photolysis was ceased and the methanol removed to leave a brown oil which was investigated by n. m. r. spectroscopy.

(iii f) N-Methyl-2, 3-dimethylpyridinium Chloride in Trifluoroacetic Acid.

Experimentally as for (iiia), except that photolysis was continued for 27h. The bulb-to-bulb distillate was analysed by g. l. c.(Carbowax/KOH, 110°).

(iii g) N-Methyl-3, 4-dimethylpyridinium Chloride in Trifluoroacetic Acid.

N-Methyl-3, 4-dimethylpyridinium chloride (0. 4g) in trifluoroacetic acid (20ml) was irradiated at 254nm in the Rayonet reactor; the course of the photolysis was followed by n.m.r. spectroscopy on the photolysate at timed intervals.

(iii h) N-Methyl-3, 4-dimethylpyridinium Chloride in Methanol

Experimentally as for (iii a) except that after 6 h the irradiation was ceased and the methanol evaporated. The brown oil remaining was analysed by n.m.r. spectroscopy.

(iii i) N-Methyl-3, 5-dimethylpyridinium Chloride in Methanol.

Experimentally as for (iii e). After 5. 5h the photolysis was stopped and the photolysate was analysed by g. l. c. (Carbowax/KOH, 110°). The methanol was then removed to leave a brown oily residue which was analysed by n. m. r spectroscopy.

TABLE 6

PHOTOLYSIS OF THE N-METHYL-DIMETHYLPYRIDINIUM CHLORIDES IN TRIFLUOROACETIC ACID : QUARTZ N.M.R.TUBE PHOTOLYSES.

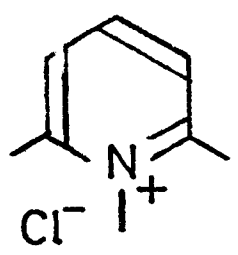
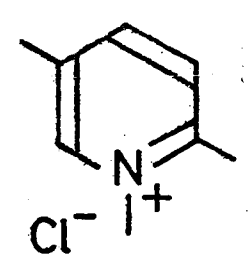
Compound	Time	Experimental Observations (N.m.r.spectra)
	0h	N.m.r. spectrum (TFA)of starting material:- τ: 1.76 (1H, m), 2.25 (2H, m) 5.80 (3H, s), 7.11 (6 H, s)
	2h, 4h	No visible change in n.m.r.spectrum.
	20h	Reduced intensity of starting material signals. New broad signal at ca 8τ.
	24h	As for 20h; new singlet at 1.8τ.
	28h, 33h	Further reduced intensity of starting material signals. Further build-up of 8τ and 1.8τ signals.
	52h	Starting material almost depleted. Further increase in 8τ and 1.8τ signals. Broad signal at ca 6.8τ has developed.
Conclusion	Nature of signals at 1.8τ, 8τ and 6.8τ unknown- possibly polymer formation. No evidence for rearrangement.	
	0h	N.m.r.spectrum (TFA) of starting material:- τ: 1.56 (1H, s), 1.78 (1H, d), 2.21 (1H, d), 5.71 (3H, s), 7.17 (3H, s), 7.45 (3H, s)
	21h	The 1.82 τ component of 1.78τ doublet has split. New broad signals at 8.0 τ, 8.3τ, and 7.75 τ.
	44h	Singlet now apparent at 1.81 τ. Further increase in 8.0, 8.3 and 7.75 τ signals. New broad base-line signals developing.
	68h	Starting material still major component N.m.r.spectrum typical of polymer-low intensity, broad signals developing throughout spectrum.
Conclusion	Nature of photoproducts unknown-probably polymeric. No evidence for rearrangement.	

TABLE 6 (continued.....)

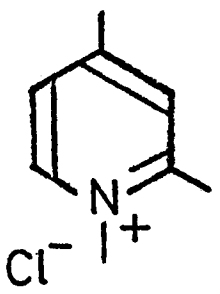
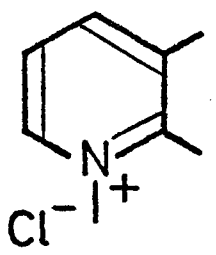
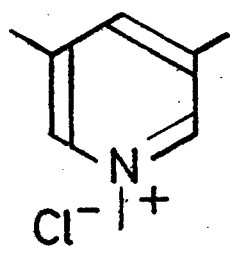
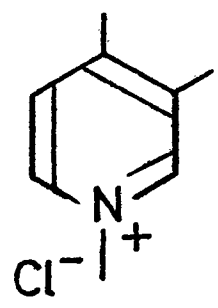
Compound	Time	Experimental Observations (N. m. r. spectra)
	0h	N. m. r. spectrum (TFA) of starting material: τ: 1. 56 (1H, d), 2. 33 (2H, m), 5. 75 (3H, s), 7. 18 (3H, s). 7. 34 (3H, s).
	1. 5h	New sharp signals at ca 1. 7τ , 1. 8τ, 5. 71τ , 7. 44τ . Broad signal at ca 8. 0τ.
	3h	All new signals have increased intensity.
	18h	Signals at 1. 7τ and 1. 8τ appear to be multiplets centred at ca 1. 78τ. 2. 33τ signal of starting material is apparently shifting to a lower τ value. 5. 71τ and 7. 44τ signals show increased intensity. 7. 18τ signal of starting material has increased intensity compared to 7. 34τ signal. Other baseline signals, typical of polymer are developing.
	40h	Very unstable baseline. 7. 34τ and 5. 75τ signals of starting material have reduced intensity, although the 1. 56τ has remained relatively larger than expected. 2. 33τ signal now at ca 2. 2τ and of equal intensity to 1. 56 and 1. 78τ signals.
Conclusion	Polymer formation has taken place. Formation of signals at 7. 44 τ , 1. 78 τ and 5. 71τ with enhancement of 1. 56τ and 7. 18τ signals, plus shift of 2. 33τ signal to 2. 2τ is fully consistent with the formation of N-Methyl-2, 5-dimethylpyridinium chloride. (c. f N. m. r spectrum τ: 1. 56 (1H, s), 1. 78 (1H, d), 2. 21 (1H, d), 5. 71 (3H, s), 7. 17 (3H, s), 7. 45 (3H, s))	

TABLE 6 (Continued.....)

Compound	Time	Experimental Observations (N. m. r. spectra)
	0h	N. m. r. spectrum (TFA) of starting material τ: 1.42 (1H, d), 1.71 (1H, d), 2.23 (1H, t), 5.60 (3H, s), 7.15 (3H, s), 7.37 (3H, s)
	1h	New broad signals at ca 8.0τ, 6.1τ, 7.6τ
	2h, 3h	Broad signals show increased intensity.
	4h	Starting material signals decreasing. Formation of additional, broad, baseline signals.
	5h	Increased formation of broad, weak signals.
Conclusion	Nature of photoproducts unknown-probably polymeric. No evidence for rearrangement.	
	0h	N. m. r. spectrum (TFA) of starting material τ: 1.63 (2H, s), 1.82 (1H, s), 5.60 (3H, s), 7.41 (6H, s)
	1.5h	Formation of broad signals at 7.91τ, 6.25τ
	4.25h	Increased intensity of 7.91τ and 6.25τ signals. Additional formation of broad baseline signals.
	5.5h, 7h 9h	As for 4.25h; baseline becoming increasingly noisy, especially in 3.5 - 5.0τ and 6.5-7.0τ regions.
	27h	Starting material almost depleted. Noisy baseline throughout.
Conclusion	Nature of photoproducts unknown-probably polymeric No evidence for rearrangement.	
	0h	N. m. r. spectrum (TFA) of starting material τ: 1.64 (2H, m), 2.24 (1H, m), 5.66 (3H, s), 7.28 (3H, s), 7.38 (3H, s)
	3h	Starting material shows much reduced intensity. Formation of broad signals at ca 6.7 and 8τ
	4.5h	Starting material almost gone. Increased intensity of 6.7 and 8τ signals. New broad signals at 2.5τ, 3.6τ, 5.8τ, 8.2τ, 8.4τ.
	7h	No starting material remaining.

Compound	Time	Experimental Observations (N. m. r. spectra)
		Signals present are all very broad.
Conclusion	Nature of photoproducts unknown - probably polymeric. No evidence for rearrangement.	

TABLE 7

QUATERNARY SALT PHOTOLYSES IN METHANOL - d_4

QUARTZ N.M.R.TUBE PHOTOLYSES

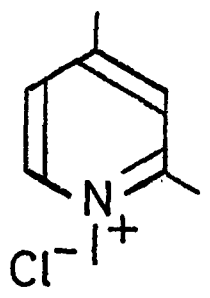
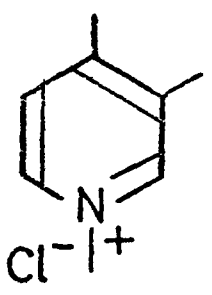
Compound	Time	Experimental Observations (N. m. r. spectra)
	0h	N. m. r. spectrum (CD_3OD) of starting material τ: 1.35 (1H, d), 2.25 (2H, m), 5.80 (3H, s), 7.23 (3H, s), 7.40 (3H, s)
	1h, 2h	Very little change. Formation of broad signals at ca 8.1 τ and 8.6 τ.
	4h, 6h	Very little further change. Starting material shows reducing intensity. Continued build up of 8.1τ and 8.6τ signals. New broad, baseline signals developing. New sharp signal at 1.92 τ.
	10.5h	Starting material almost completely gone. Continued build up of broad signal systems.
Conclusion	Nature of photoproducts unknown-probably polymeric. No evidence of rearrangement or formation of Kaplan-type photosolvated species.	
	0h	N. m. r. spectrum (CD_3OD) of starting material τ: 1.36 (2H, m), 2.17 (1H, m), 5.69 (3H, s), 7.42 (3H, s), 7.54 (3H, s)
	6h	Major component starting material. Appearance of broad signals at 3.6 τ, 7.15 τ, 8.2 τ and 8.7 τ Baseline very noisy
Conclusion	Nature of photoproducts unknown - probably polymeric. No evidence of rearrangement or formation of Kaplan-type photosolvated species.	

TABLE 8.

PHOTOLYSES OF THE N-METHYL-DIMETHYLPYRIDINIUM CHLORIDES

TEST TUBE SCALE PHOTOLYSES.

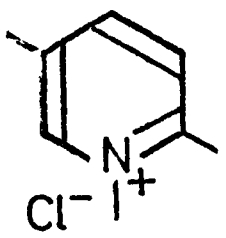
Compound	Time	Experimental Observations.
(iii a)  in TFA	46h	(i) Crude photoproduct n.m.r. spectrum (D_2O) is almost wholly that of starting material. Additional signals at 4.10, 6.85, 7.05, 7.20, 8.10 and 8.55 τ. (ii) Bulb-to-bulb distillate: n m r spectrum (CCl_4) was mainly that due to 2, 5-dimethyl-pyridine, (τ: 1.70 (s), 2.10 (d), 2.59 (d), 7.45 (s), 7.6 (s). In addition a doublet was visible at 7.11τ with a broad signal centrered at ca 2.2 τ. (iii) G.l.c. of distillate also indicated that the major product was 2, 5-dimethylpyridine. A second signal which gave a single signal on co-injection with authentic 2, 3-dimethyl pyridine was also present. (iv) Gcms confirmed that 2, 5-dimethylpyridine was the major component showing mass spectrum: m/e 107(100), 106(62), 92(12), 79(33), 77(15), 66(14), 65(13), 51(12). The peak with retention time that of 2, 3-dimethylpyridine had mass spectrum: m/e 96(100), 95(10), 69(12), 68(30), 67(69), 58(27), 53(41, 41(23). i.e. is not due to 2, 3-dimethylpyridine.
Conclusion	(1) 7.05τ signal in crude photoproduct n.m.r. may be due to $H_3MeN^{+}\,\dot{O}OCCF_3$ (ii) Signals at 7.11τ and 2.2τ may be due to $HMeNCOCF_3$ (iii) Nature of additional photoproducts is not known. (iv) No evidence at all for rearrangement.	

TABLE 8 (Continued.....)

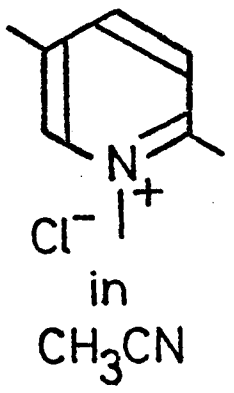
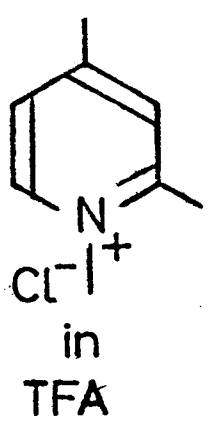
Compound	Time	Experimental Observations
(iii b) 	46hr	(i) The n.m.r.spectrum (D_2O) of the crude photoproduct was exclusively that of starting material, τ: 1.48 (s), 1.80(d), 2.25(d), 5.84(s) 7.28(s), 7.55(s). (ii) Similarly the n.m.r.spectrum (D_2O) of the bulb-to-bulb distillate was exclusively due to 2,5-dimethylpyridine, τ: 1.73 (s), 2.22(s), 2.65(d), 7.50(s). 7.70(s). (iii) G.l.c.of the distillate produced a single peak coincident with that of authentic 2,5-dimethylpyridine.
Conclusion	No evidence at all for rearrangement.	
(iii c) 	46hr	(i) Crude photoproduct showed signals in n.m.r. spectrum (TFA) due to starting material. τ: 1.56(d), 2.33(m), 5.75(s), 7.18(s), 7.34(s). Additional signals were present at 1.78τ, 5.71τ, and 7.45τ. The 7.18τ signal in the starting material had increased intensity compared to the 7.34τ signal and the 2.33τ signal had a modified form. (ii) The bulb-to-bulb distillate showed the following weak signals in the n.m.r.spectrum (CCl_4)τ:1.81, 2.77, 3.05, 7.10, 7.53, 7.71, 8.00, 8.85. In CCl_4 solution authentic 2,4- and 2,5-dimethylpyridines show the following n.m.r. signals: 2,4 τ:1.79, 3.22, 7.58, 7.76. 2,5 τ: 1.81, 2.77, 3.12, 7.57, 7.76. (iii) G.l.c. of the distillate revealed the presence of signals at retention times identical to 2,4-, 2,5-, and 3,5- dimethylpyridines, although no co-injections with authentic compounds were performed.

TABLE 8 (Continued.....)

Compound	Time	Experimental Observations.
		(iv) Gcms of the distillate was inconclusive owing to poor resolution of the weak product signals in the gcms apparatus. The signals did all, however, show signals at m/e 107. (v) In a repeated experiment (on 4x the scale) preparative g.l.c.of the distillate yielded a crystalline solid, spectroscopically identical to $HMeNCOCF_3$ (see parts C(iv) and D(iiic) of experimental section)
Conclusion	(i) Nmr signals at 1.78, 5.71 and 7.45τ in crude photo-product may be due to , N-Methyl-2, 5-dimethylpyridinium chloride. Similarly, the enhanced intensity of the 7.18 τ signal and modified 2.33 τ signal may also be due to the presence of this compound. (ii) The weak n.m.r. spectrum of the distillate may contain contributions from 2, 4- and 2, 5-dimethylpyridine. The signal at 2.77 τ is strongly indicative of the presence of a γ-proton in a pyridine nucleus. The signal at 7.1 τ may be caused by $CF_3CONHMe$. The 8.0 and 8.85 τ signals arise from unknown species. (iii) The g.l.c(and gcms) evidence provides some confirmation that 2, 5-dimethylpyridine is present; in addition 3, 5-dimethylpyridine is possibly present. (iv) Presumably the dimethylpyridine products are too volatile to be collected by preparative g.l.c. The presence of $CF_3CONHMe$ suggested above is confirmed. (v) Overall, there is supporting evidence from several sources that N-Methyl-2, 4-dimethylpyridinium chloride yields N-methyl-2, 5-dimethylpyridinium chloride on photolysis in TFA. An additional product may be N-methyl-3, 5-dimethylpyridinium chloride.	

TABLE 8 (Continued.....)

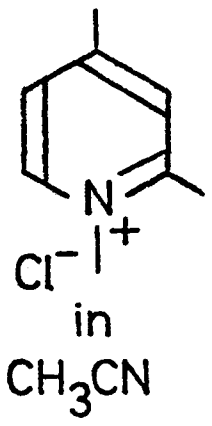
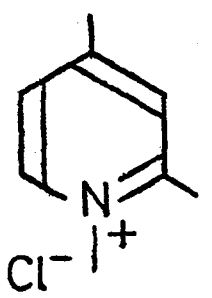
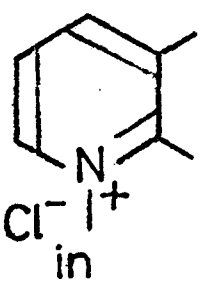
Compound	Time	Experimental Observations.
(iii d)  Cl^- I^+ in CH_3CN	8h	(i) The reaction was monitored by periodic sampling and analysis by g.l.c. No signals, except that of 2, 4-dimethylpyridine produced from starting material, were observed.
Conclusion	(i) No evidence for rearrangement.	
(iii e)  Cl^- I^+ in MeOH	7h	(i) The reaction was monitored by periodic g.l.c. analysis. There was build-up of a signal with retention time equivalent to that of authentic 3, 5-dimethylpyridine. However, co-injection with authentic sample was not carried out. After 7h, the signal was ca 10% that of the 2, 4-dimethylpyridine produced from the starting material. (ii) The n.m.r. spectrum (CD_3OD) of the crude photolysate showed the following signals. τ: 1.33(m), 2.27(m), 5.78(s), 7.12(s), 7.40(s) due to 2, 4-dimethylpyridine and additional signals at τ : 5.70(s), and 7.50(s), possibly due to N-methyl- 3, 5 -dimethyl - pyridine chloride.
Conclusion	There is evidence from two analytical techniques that rearrangement to N-methyl-3, 5-dimethylpyridinium chloride may occur on photolysis in methanol.	
(iii f)  Cl^- I^+ in TFA	27h	(i) The bulb-to-bulb distillate was analysed by g.l.c. Two products, in addition to the 2, 3-dimethylpyridine derived from starting material, were present. They were in ratio of ca 1:1 and had retention

TABLE 8 (Continued.....)

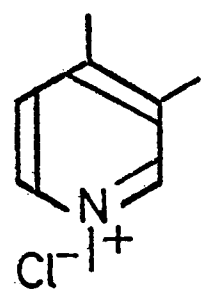
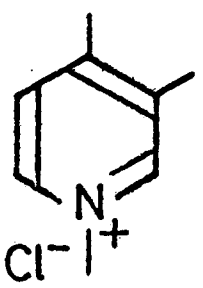
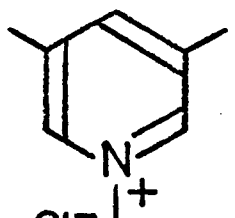
Compound	Time	Experimental Observations
		times identical to 2, 6- and 3, 4-dimethyl-pyridines, although no co-injection with authentic compound was performed. The extend of conversion was < 1%
Conclusion	The evidence suggests that phototransposition to N-Methyl-2, 6-and 3, 4-dimethylpyridinium chlorides may occur in TFA.	
(iii g)  in TFA	0h	Reaction monitored by n. m. r. spectroscopy Starting material (TFA):- τ : 1.64(2H, m) 2.24(1H, m), 5.66 (3H, s), 7.28 (3H, s), 7.38(3H, s).
	2h	New broad signals formed at ca 6.8τ , 8.1τ and 8.4 τ.
	4h	Starting material signal decreased intensity Broad signals show increased intensity. A new broad signal is present in the 3-4 τ region.
	6h	Starting material almost depleted. Further build-up in broad signal intensity. Unstable baseline.
Conclusion	(i) Nature of photoproducts unknown (probably polymeric) (Note similarity of process to nmr tube photolysis) (ii) No evidence at all for rearrangement.	
(iii h)  in MeOH	6h	(i) Nmr spectrum (D_2O) of the crude photo-product revealed that it was mainly unreacted starting material. No new aromatic proton signals, $\overset{+}{N}$-Me signals or aromatic Me signals were present. Weak, broad signals were formed at 6.2-6.7τ , 6.8-7.1τ , 7.9-8.2 τ and 8.2 - 8.6τ.
Conclusion	(i) Nature of photoproducts is unkhown (probably polymeric) (ii) No evidence at all for rearrangement.	

TABLE 8 (Continued.....)

Compound	Time	Experimental Observations
(iii i)  in MeOH	5.5h	(i) The crude photolysis solution was analysed by g.l.c. In addition to 3,5-dimethylpyridine, a product (ca 25% of 3,5-dimethylpyridine) with retention time that of 2,4-dimethylpyridine was present. (ii) N.m.r.analysis (CD_3OD) of the crude photoproduct showed that the major component was starting material (τ: 1.39, 1.78, 5.67 and 7.49). In addition weak signals at τ: 2.3, 5.78 and 7.4 were present. These signals correspond to three of the signals in the spectrum of N-methyl-2,4-dimethylpyridinium chloride. The 7.23τ signal from this compound would have been obscured by solvent signals. Some broad, baseline signals were also present.
Conclusion	(i) There is evidence from two analytical techniques that rearrangement to N-methyl-2,4-dimethylpyridinium chloride may occur on photolysis in methanol.	

REFERENCES

1. D. Bryce-Smith, J. Chem. Soc., 1956, 1603.
2. H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, J. Chem. Soc., 1960, 2003.
3. K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, J. Amer. Chem. Soc., 1967, 89, 1031.
4. H. Lutz and G. Stein, J. Phys. Chem., 1974, 78, 1909.
5. D. Bryce-Smith and A. Gilbert, Tetrahedron, 1976, 32, 1309.
6. L. Kaplan and K. E. Wilzbach, J. Amer. Chem. Soc., 1968, 90, 3291.
7. H. R. Ward and J. S. Wishnok, J. Amer. Chem. Soc., 1968, 90, 1085.
8. H. R. Ward, J. S. Wishnok, and P. D. Sherman, J. Amer. Chem. Soc., 1967, 89, 162.
9. K. E. Wilzbach and L. Kaplan, J. Amer. Chem. Soc., 1967, 89, 1030.
10. H. R. Ward and J. S. Wishnok, J. Amer. Chem. Soc., 1968, 90, 5353.
11. D. Bryce-Smith, A. Gilbert, and D. A. Robinson, Angew. Chem. Internat. Edn., 1971, 10, 745.
12. Y. Ilan and G. Stein, Chem. Phys. Letters, 1975, 31, 441.
13. T. J. Katz and N. Acton, J. Amer. Chem. Soc., 1973, 95, 2738.
14. T. J. Katz, E. J. Wong, and N. Acton, J. Amer. Chem. Soc., 1971, 93, 3782.
15. E. E. Van Tamelen and S. P. Pappas, J. Amer. Chem. Soc., 1963, 85, 3297.
16. E. E. Van Tamelen, S. P. Pappas, and K. L. Kirk, J. Amer. Chem. Soc., 1971, 93, 6092.
17. R. Srinivasan and K. A. Hill, J. Amer. Chem. Soc., 1965, 81, 4653.
18. D. Bryce-Smith, A. Gilbert and B. H. Orger, Chem. Comm., 1966, 512.
19. K. E. Wilzbach and L. Kaplan, J. Amer. Chem. Soc., 1971, 93, 2073.
20. A. Mori Kawa, S. Brownstein and R. J. Cvetanovic, J. Amer. Chem. Soc., 1970, 92, 1471.
21. K. E. Wilzbach and L. Kaplan, J. Amer. Chem. Soc., 1966, 88, 2066.
22. G. Koltenberg and K. Kraft, Tetrahedron Letters, 1966, 389.
23. J. C. Berridge, D. Bryce-Smith, and A. Gilbert, Tetrahedron Letters, 1975, 2325.
24. D. Bryce-Smith and H. C. Longuet-Higgins, Chem. Comm., 1966, 593.
25. L. Kaplan, D. J. Rausch, and K. E. Wilzbach, J. Amer. Chem. Soc., 1972, 94, 8638.
26. L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, J. Amer. Chem. Soc., 1966, 88, 2881.

27. E. Farenhorst and A. F. Bickel, Tetrahedron Letters, 1966, 5911.

28. J. A. Berson and N. M. Hasty, J. Amer. Chem. Soc. , 1971, 93, 1549.

29. K. E. Wilzbach, A. L. Harkness and L. Kaplan, J. Amer. Chem. Soc., 1968, 90, 1116.

30. I. Haller, J. Amer. Chem. Soc., 1966, 88, 2070.

31. G. Camaggi, F. Gozzo, and G. Cevidalli, Chem. Comm., 1966, 313.

32. M. G. Barlow, R. N. Haszeldine, and R. Hubbard, Chem. Comm., 1969, 202.

33. D. M. Lemal, J. V. Staros, and V. Austel, J. Amer. Chem. Soc., 1969, 91, 3373.

34. M. G. Barlow, R. N. Haszeldine, and R. Hubbard, J. Chem. Soc. (C), 1970, 1232.

35. E. D. Clifton, W. T. Flowers, and R. N. Haszeldine, Chem. Comm., 1969, 1216.

36. A. M. Dabbagh, W. T. Flowers, R. N. Haszeldine, and P. J. Robinson, Chem. Comm., 1975, 323.

37. G. P. Semeluk and R. D. S. Stevens, Chem. Comm., 1970, 1720.

38. E. Ratajezak, Proc. Nauk. Chem. Technol. Nafty. Wegla. Politech. Wroclaw, 1974, 17, 3 (Chem. Abst., 1975, 83, 130901).

39. E. E. Van Tamelen and S. P. Pappas, J. Amer. Chem. Soc., 1962, 84, 3789.

40. E. M. Anderson and G. B. Kistiakowsky, J. Chem. Phys., 1969, 51, 182.

41. L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, J. Amer. Chem. Soc., 1965, 87, 675.

42. K. E. Wilzbach and L. Kaplan, J. Amer. Chem. Soc., 1964, 86, 2307.

43. H. R. Ward, J. Amer. Chem. Soc., 1967, 89, 2367.

44. H. R. Ward and C. I. Barta, J. Amer. Chem. Soc., 1968, 90, 5347.

45. C. I. Barta, Diss. Abs. Int. B, 1970, 31, 142.

46. R. B. Cundall and A. J. R. Voss, Chem. Comm., 1969, 116.

47. R. B. Cundall and A. J. R. Voss, Chem. Comm., 1969, 902.

48. R. B. Cundall, D. A. Robinson, and A. J. R. Voss, J. Photochem., 1974, 2, 221.

49. D. Anderson, J. Phys. Chem., 1970, 74, 1686.

50. I. Jano, Chem. Phys. Letters, 1968, 2, 205.

51. W. A. Noyes and D. A. Harter, J. Phys. Chem., 1971, 75, 2741.

52. I. E. Den Besten, L. Kaplan, and K. E. Wilzbach, J. Amer. Chem. Soc., 1968, 90, 5868.

53. C. A. Renner, T. J. Katz, J. Pouliquen, N. J. Turro, and W. H. Waddell, J. Amer. Chem. Soc., 1975, 97, 2568.

54. A. W. Burgstahler and P. L. Chien, J. Amer. Chem. Soc., 1964, 86, 2940.

55. A. W. Burgstahler, P. L. Chien, and M. O. Abdel-Rahman, J. Amer. Chem. Soc., 1964, 86, 5281.

56. L. Kaplan and K. E. Wilzbach, J. Amer. Chem. Soc., 1965, 87, 4004.

57. E. M. Arnett and J. M. Bollinger, Tetrahedron Letters, 1964, 3803.

58. R. West, M. Furue, and V. N. M. Rao, Tetrahedron Letters, 1973, 911.

59. W. L. Mandella and R. W. Frank, J. Amer. Chem. Soc., 1973, 95, 971.

60. R. W. Frank, W. L. Mandella, and K. J. Faki, J. Org. Chem., 1975, 40, 327.

61. R. A. Abramovitch and T. Takaya, Chem. Comm., 1969, 1369.

62. R. A. Abramovitch and T. Takaya, J. Chem. Soc. Perkin I, 1975, 1806.

63. U. Mende, J. L. Laseter, and G. W. Griffin, Tetrahedron Letters, 1970, 3747.

64. H. E. Zimmerman and D. S. Crumrine, J. Amer. Chem. Soc., 1972, 94, 498.

65. R. A. Finnegan and D. Knutson, Tetrahedron Letters, 1968, 3429.

66. W. C. Schumann, D. B. Vaschi, J. A. Ross, and R. W. Binkley, J. Org. Chem., 1972, 37, 21.

67. K. E. Al-Ani, J. Chem. Phys., 1973, 58, 5073.

68. M. G. Barlow, R. N. Haszeldine, and M. J. Kershaw, J. Chem. Soc. Perkin I, 1974, 1736.

69. M. G. Barlow, R. N. Haszeldine, and M. J. Kershaw, Tetrahedron, 1975, 31, 1649.

70. M. G. Barlow, R. N. Haszeldine, and M. J. Kershaw, J. Chem. Soc. Perkin I, 1975, 2005.

71. J. A. Barltrop and A. C. Day, Chem. Comm., 1975, 117.

72. K. E. Wilzbach and D. J. Rausch, J. Amer. Chem. Soc., 1970, 92, 2178.

73. J. Joussot-Dubien and J. Houdard, Tetrahedron Letters, 1967, 4389.

74. J. Joussot-Dubien and J. Houdard, Bull. Soc. chim. France, 1969, 2619.

75. E. Mathias and J. Heicklen, Mol. Photochem., 1972, 4, 483.

76. S. Caplain and A. Lablache-Combier, Chem. Comm., 1970, 1247.

77. W. Roebke, J. Phys. Chem., 1970, 74, 4198.

78. S. Caplain, J. P. Catteau, and A. Lablache-Combier, Chem. Comm., 1970, 1475.

79. S. Caplain, A. Castellano, J. P. Catteau, and A. Lablache-Combier, Tetrahedron, 1971, 27, 3541.

80. A. Castellano, J. P. Catteau, and A. Lablache-Combier, Tetrahedron, 1975, 31, 2255.

81. T. J. Van Bergen and R. M. Kellogg, J. Amer. Chem. Soc., 1972, 94, 8451.

82. L. Kaplan, J. W. Pavlik, and K. E. Wilzbach, J. Amer. Chem. Soc., 1972, 94, 3283.

83. C. Chachaty, J. C. Ronfard-Haret, A. Lablache-Combier, J. P. Quagebeur, and H. Offenberg, Chem. Comm., 1974, 579.

84. C. Chachaty, J. C. Ronfard-Haret, A. Lablache-Combier, J. P. Quagebeur, and H. Offenberg, J. Chem.Soc. Faraday Transactions I, 1976, 72, 143.

85. M. G. Barlow, J. G. Dingwall, and R. N. Haszeldine, Chem. Comm., 1970, 1580.

86. M. G. Barlow, R. N. Haszeldine and J. G. Dingwall, J. Chem. Soc. Perkin I, 1973, 1542.

87. R. D. Chambers and R. Middleton, Chem Comm., 1977, 154.

88. R. D. Chambers, R. Middleton,and R. P. Corbally, Chem. Comm., 1975, 731.

89. E. C. Taylor and R. O. Kan, J. Amer. Chem. Soc., 1963, 85, 776.

90. E. J. Corey and J. Streith, J. Amer. Chem. Soc., 1964, 86, 950.

91. R. C. De Selms and W. R. Schleigh, Tetrahedron Letters, 1972, 34, 3563.

92. E. Ager, G. E. Chivers, and H. Suschitzky, J. Chem. Soc. PerkinI, 1973, 1125.

93. W. L. Dilling, N. B. Tefertilter, and A. B. Mitchell, Mol. Photochem., 1973, 5, 371.

94. N. Ishibe and J. Masui, J. Amer. Chem. Soc., 1973, 95, 3396.

95. N. Ishibe and J. Masui, J. Amer. Chem. Soc., 1974, 96, 1152.

96. N. Sugiyama, Y. Sato, and C. Kashina, Bull. Chem. Soc. Japan, 1970, 43, 3205.

97. F. Lahmani, N. Ivanoff, and M. Magat, Compt. rend., 1966, 263C, 1005.

98. F. Lahmani and N. Ivanoff, Tetrahedron Letters, 1967, 3913.

99. C. G. Allison, R. D. Chambers, Y. A. Cheburkov, J. A. H MacBride, and W. K. R. Musgrave, Chem. Comm., 1969, 1200.

100. D. W. Johnson, V. Austel, R. S. Feld, and D. M. Lemal, J. Amer. Chem. Soc., 1970, 92, 7505.

101. R. D. Chambers, W. K. R. Musgrave, and K. C. Srivasta, Chem. Comm., 1971, 264.

102. R. D. Chambers, J. A. H. MacBride, J. R. Maslakiewicz, and K. C. Srivasta, J. Chem. Soc. Perkin I, 1975, 396.

103. R. D. Chambers, J. R. Maslakiewicz,and K. C. Srivasta, J. Chem. Soc. Perkin I, 1975, 1130.

104. M. G. de M. Gem, Part II Thesis, University of Oxford, 1974.

105. P. D. Tolliday, Part II Thesis, University of Oxford, 1975.

106. C. Hoozgand and W. Hubel, Tetrahedron Letters, 1961, 637.

107. K. L. Kaiser, R. F. Childs, and P. M. Maitlis, J. Amer. Chem. Soc., 1971, 93, 1270.

108. J. A. Barltrop, A. C. Day, and C. J. Samuel, Chem. Comm., 1976, 822.

109. P. M. Froehlich and H. A. Morrison, J. Phys. Chem., 1972, 76, 3566.

110. C. R. Johnson and G. A. Dutra, J. Amer. Chem. Soc., 1973, 95, 7777.

111. P. Martinson and J. Marton, Acta. Chem. Scand., 1968, 22, 2382.

112. A. T. Nielson, C. Gibbons, and C. A. Zimmerman, J. Amer. Chem. Soc., 1951, 73, 4696.

113. R. J. Roth, and T. J. Katz, J. Amer. Chem. Soc., 1972, 94, 4770.

114. J. M. A. Baas, H. Van Bekkum, M. A. Hoefnagel, and B. M. Wepster, Rec. Trav. Chim., 1969, 88, 1110.

115. F. C. Whitmore and D. E. Badertscher, J. Amer. Chem. Soc., 1933, 55, 1559; M. S. Newman and W. T. Booth, ibid., 1945, 67, 154.

116. G. A. Posner, C. E. Witten, and J. J. Sterling, J. Amer. Chem. Soc., 1973, 95, 7788.

117. I. D. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Hydrocarbons,' 2nd Edition, Academic Press, New York, 1971.

118. E. A. Coulson, J. D. Cox, E. F. G. Herington, and J. F. Martin, J. Chem. Soc., 1959, 2, 1936.

119. R. W. Ward, J. A. Barltrop, A. C. Day, and P. D. Moxon, Chem. Comm., 1975, 786.

120. G. P. Wood, D. Phil, Thesis, University of Oxford, 1977.

121. J. Barltrop, R. Carder, A. C. Day, J. R. Harding, and C. Samuel, Chem. Comm., 1975, 729.

122. M. Thompson, Part II Thesis, University of Oxford, 1974.

SUMMARY

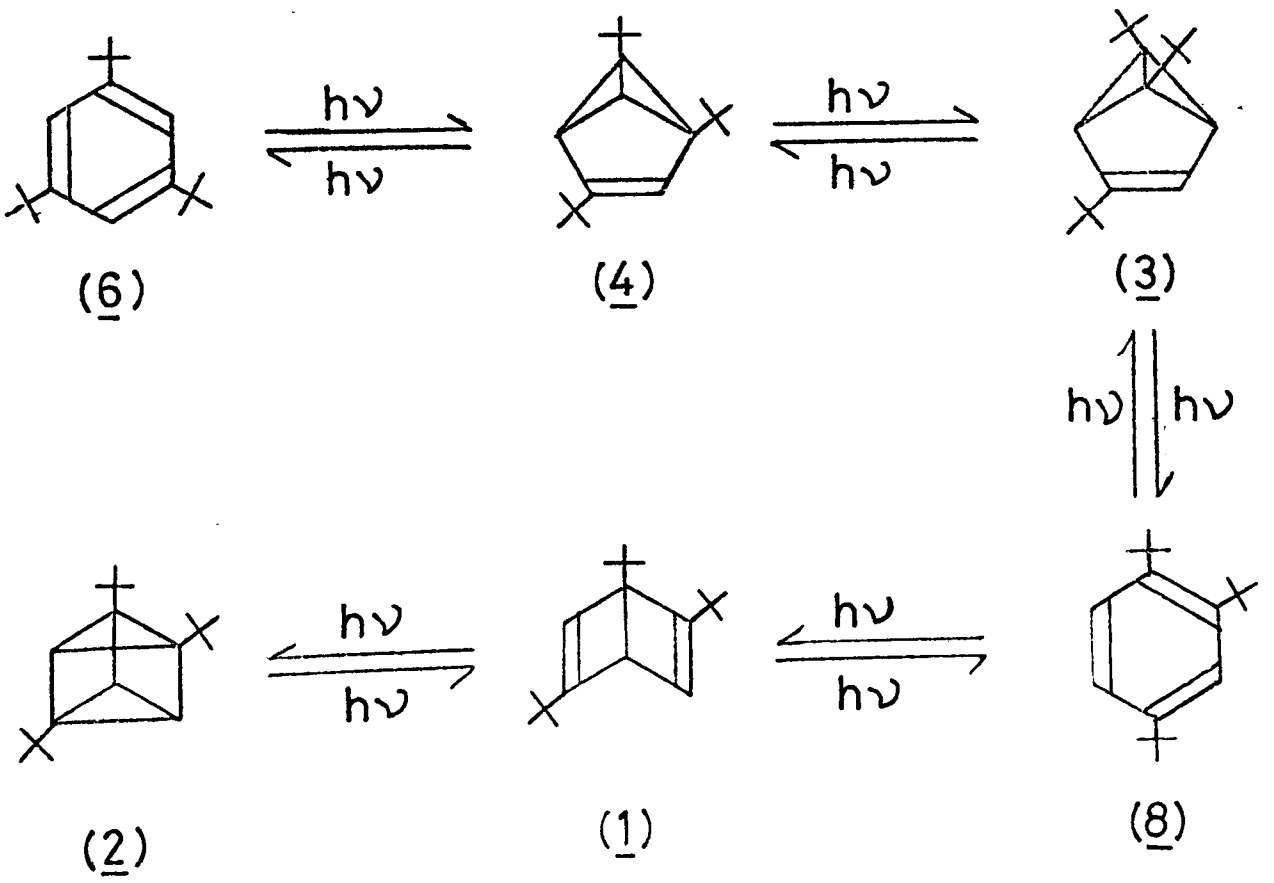
This thesis describes the photo-rearrangement reactions which were observed upon photolysis of three different types of alkylated aromatic compounds:-

1) Tri-t-butylbenzenes
2) Dimethylpyridines
3) N-Methyl-dimethylpyridinium chlorides .

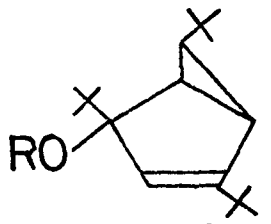
Other workers have published results on each of these classes of compound and the object of this study was to extend our knowledge of these photorearrangements.

1) Tri-t-butylbenzenes.

The tri-t-butylbenzene system has been examined in detail by Wilzbach and Kaplan [1], who have rationalised the photochemistry in terms of benzvalene, Dewar benzene and prismane intermediates as indicated in the following scheme:

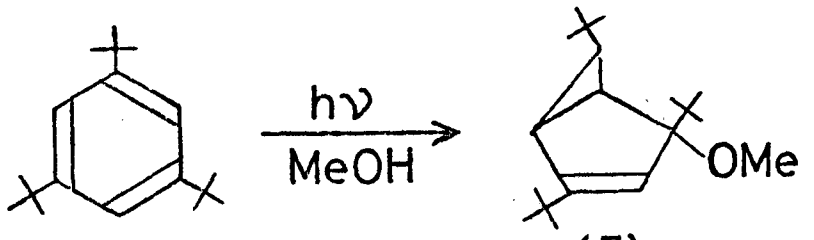


Dewar benzene (1), prismane (2) and benzvalene (3) have all been isolated and the presence of the unstable benzvalene (4) has been established by a series of kinetic experiments [1(b)] and by the formation of bicyclohexenyl ethers, of the form (5), upon photolysis of 1, 3, 5-tri-t-butylbenzene (6) in alcoholic media.



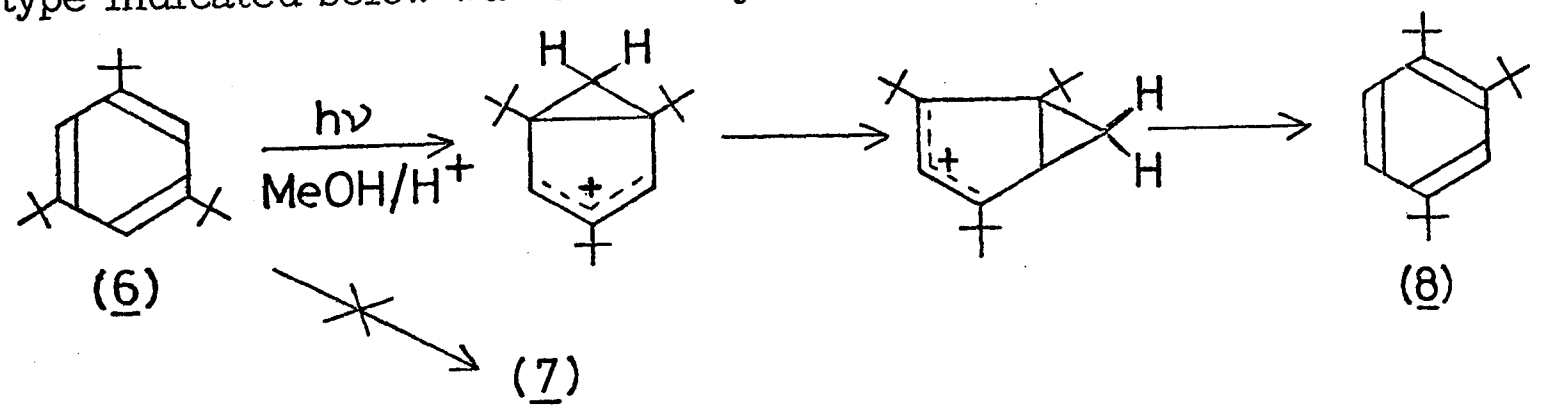
(5)

Thus, for example, 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo-[3. 1. 0] hex-2-ene (7) was the only product isolated by Wilzbach and Kaplan when 1, 3, 5-tri-t-butylbenzene (6) was irradiated in neutral methanol.[1a]



(6) (7)

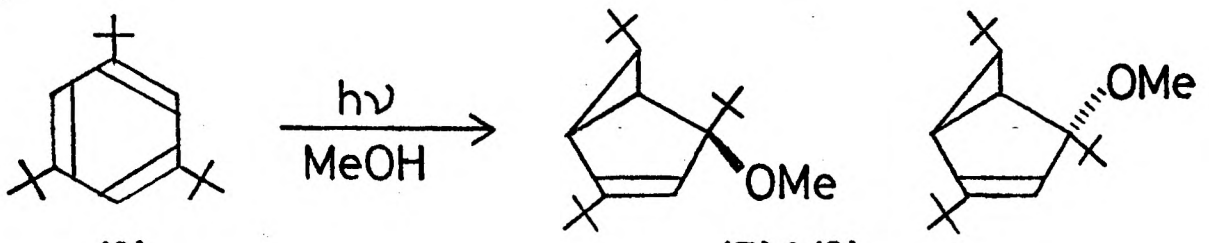
Tolliday [2] extended the studies on the 1, 3, 5-tri-t-butyl-benzene system and found that photolysis in acidic methanol yielded 1, 2, 4-tri-t-butylbenzene (8) and none of the 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo-[3. 1. 0] hex-2-ene (7). He proposed that a rearrangement process of the type indicated below was occurring:-



(6) (8) (7)

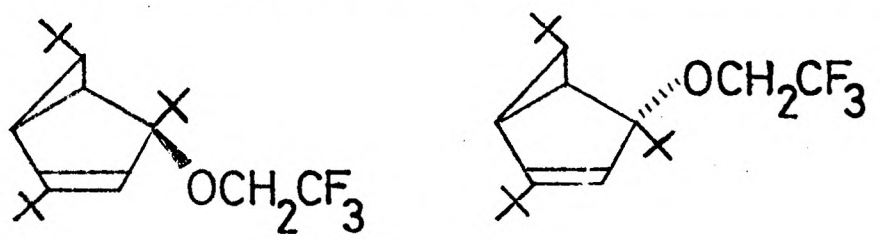
In this study, photolysis of 1, 3, 5-tri-t-butylbenzene (6) in neutral methanol, followed by preparative thin layer chromatography of the photoproducts, yielded two compounds, one of which was spectroscopically identical to 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3. 1. 0] hex-2-ene (7).

The other product, (9), had very similar spectroscopic properties to 4-methoxy-2, 4, 6-exo -tri-t-butylbicyclo [3.1.0] hex-2-ene (7) and, in fact, was converted into this compound on standing at room temperature for several weeks. Similarly, addition of acid to (9) and subsequent neutralisation also yielded 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3.1.0] hex-2-ene (7). For this reason it is believed that the new compound (9) and 4-methoxy-2, 4, 6-exo -tri-t-butylbicyclo [3.1.0] hex-2-ene (7) were isomers, stereoisomeric at the C-4 position.i. e.



(6) (7)&(9)

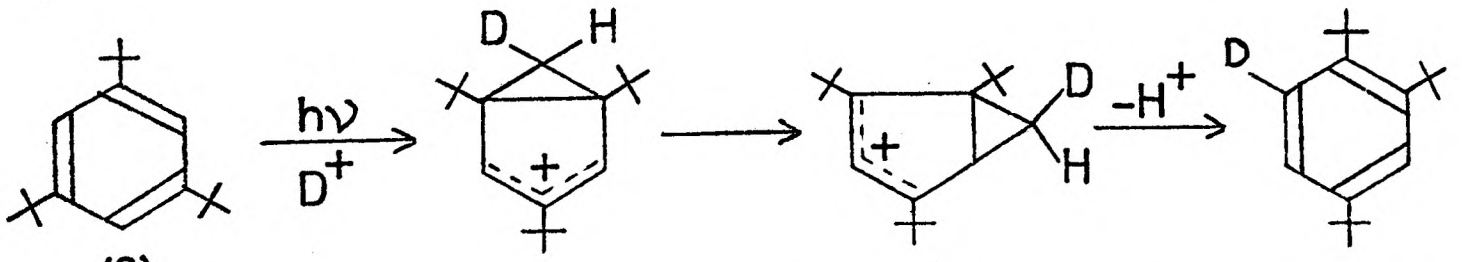
These two compounds are analogous to the stereoisomeric products, (10) formed upon photolysis of 1, 3, 5-tri-t-butylbenzene in trifluoroethanol [1(b)]



(10)

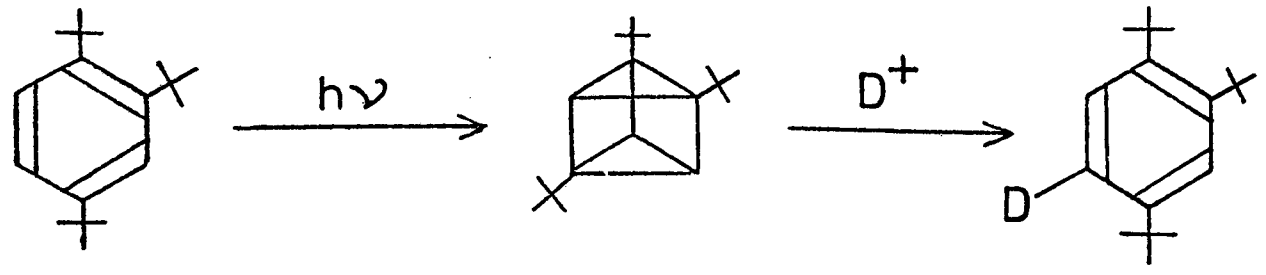
It is probable that Wilzbach and Kaplan's work-up procedure involved (9) coming into contact with acid and, hence, forming 4-methoxy-2, 4, 6-exo-tri-t-butylbicyclo [3.1.0] hex-2-ene (7), the product isolated.

If Tolliday's mechanism [2] for the rearrangement of 1, 3, 5, -tri-t-butylbenzene (6) in acidic methanol was correct, irradiation of 1, 3, 5-tri-t-butylbenzene (6) in acidic methanol-O-d should have yielded 1, 2, 4-tri-t-butylbenzene containing deuterium in the 6- position:

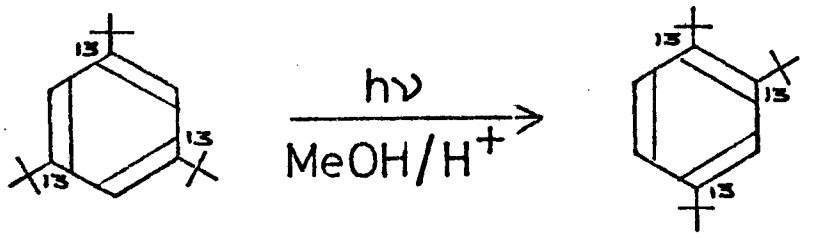


(6)

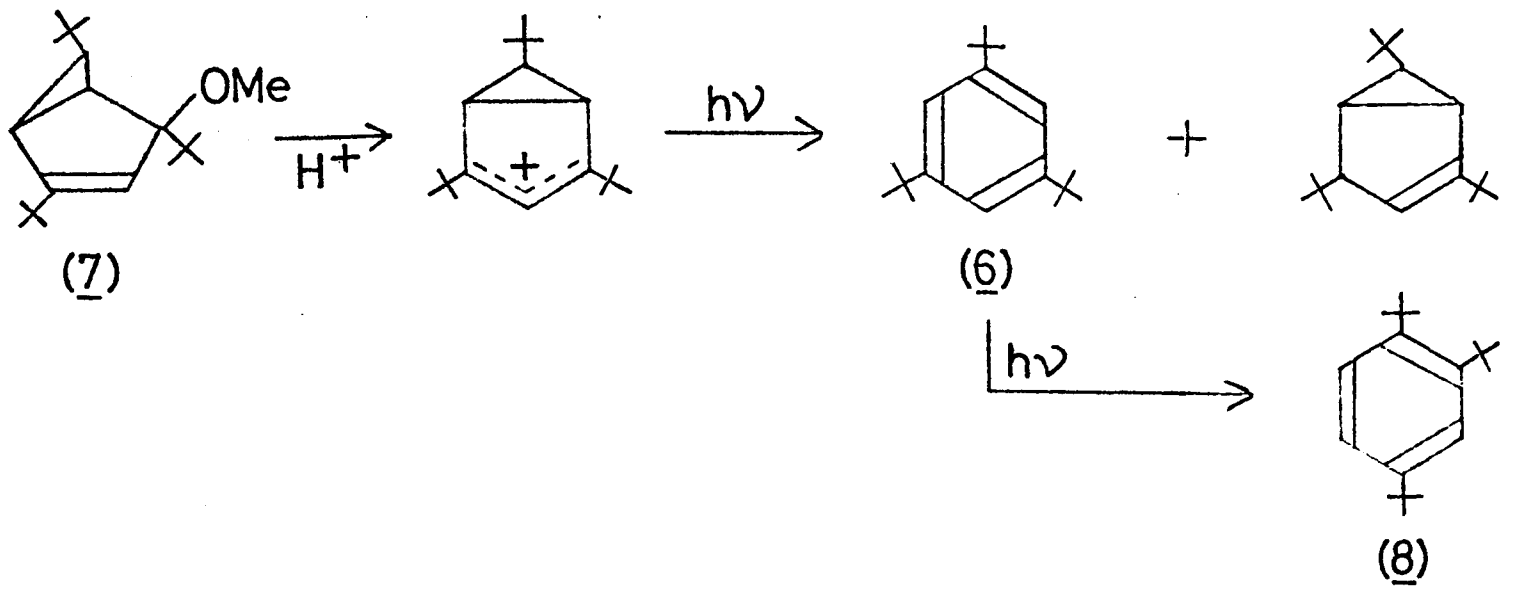
In fact, it was established that deuteriation actually occurred at positions 3 or 5, by two independent processes. The incorporation of deuterium at position 5 was shown by g. l. c. and detailed 'H n. m. r. spectroscopy, to result from attack by acid on the prismane (2), formed by secondary photolysis of the 1, 2, 4-tri-t-butylbenzene photoproduct.



The incorporation at position 3 was a consequence of attack by acid on another species and was considered in further detail. First, it was established that the photorearrangement reaction in methanol was an intramolecular process. The intramolecular nature of the rearrangement process was shown by photolysing 1, 3, 5-tri-t-butylbenzene, labelled in the 1, 3 and 5 positions with C^{13}, in acidified methanol. Analysis of the recovered 1, 2, 4-tri-t-butylbenzene by C^{13} n. m. r. spectroscopy indicated conclusively that the t-butyl groups in the photoproducts had remained attached to carbon atoms labelled with C^{13}, and, hence, that a skeletal rearrangement of the aromatic ring had taken place.



Having established that the reaction was intramolecular, the mechanism of the photorearrangement in acidic methanol was considered further. It was shown that 1, 3, 5-tri-t-butylbenzene (6), 1, 2, 4-tri-t-butylbenzene (8) and Dewar benzene (1) were unchanged in acidic methanol-O-d and that no deuterium incorporation took place in this media. Tolliday also reported that photolysis of 4-methoxy-2, 4, 6-exo-tri-t- butylbicyclo [3. 1. 0]-hex-2-ene (7) in acidic methanol yielded some 1, 2, 4-tri-t-butylbenzene (8). This study considered this reaction in some further detail and showed that the formation of 1, 2, 4-tri-t-butylbenzene (8) was actually a result of secondary photolysis of first-formed 1, 3, 5-tri-t-butylbenzene (6) and therefore was not a factor in the formation of 1, 2, 4-tri-t-butylbenzene from 1, 3, 5-tri-t-butylbenzene in acidified methanol.



(7) (6) (8)

Furthermore, since the work of Kaiser et al had showed that the stable benzvalene (3) was also unchanged in acid, it was also assumed that attack by acid on benzvalene (3) was not an issue in this system.

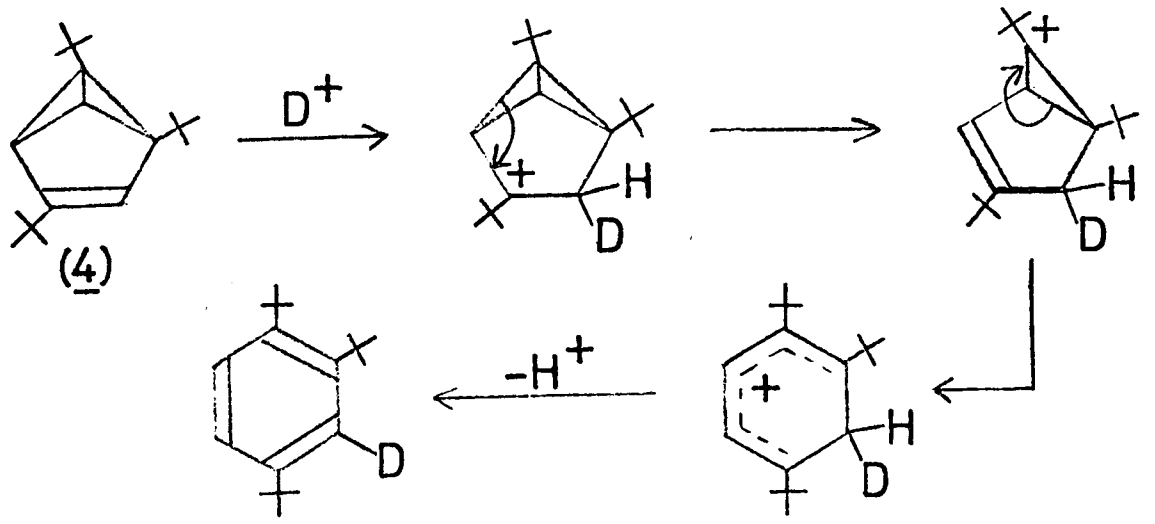
It is, therefore, concluded that the incorporation of deuterium in the 3-position was the result of attack by acid on either:

a) unstable benzvalene (4)

b) an excited state

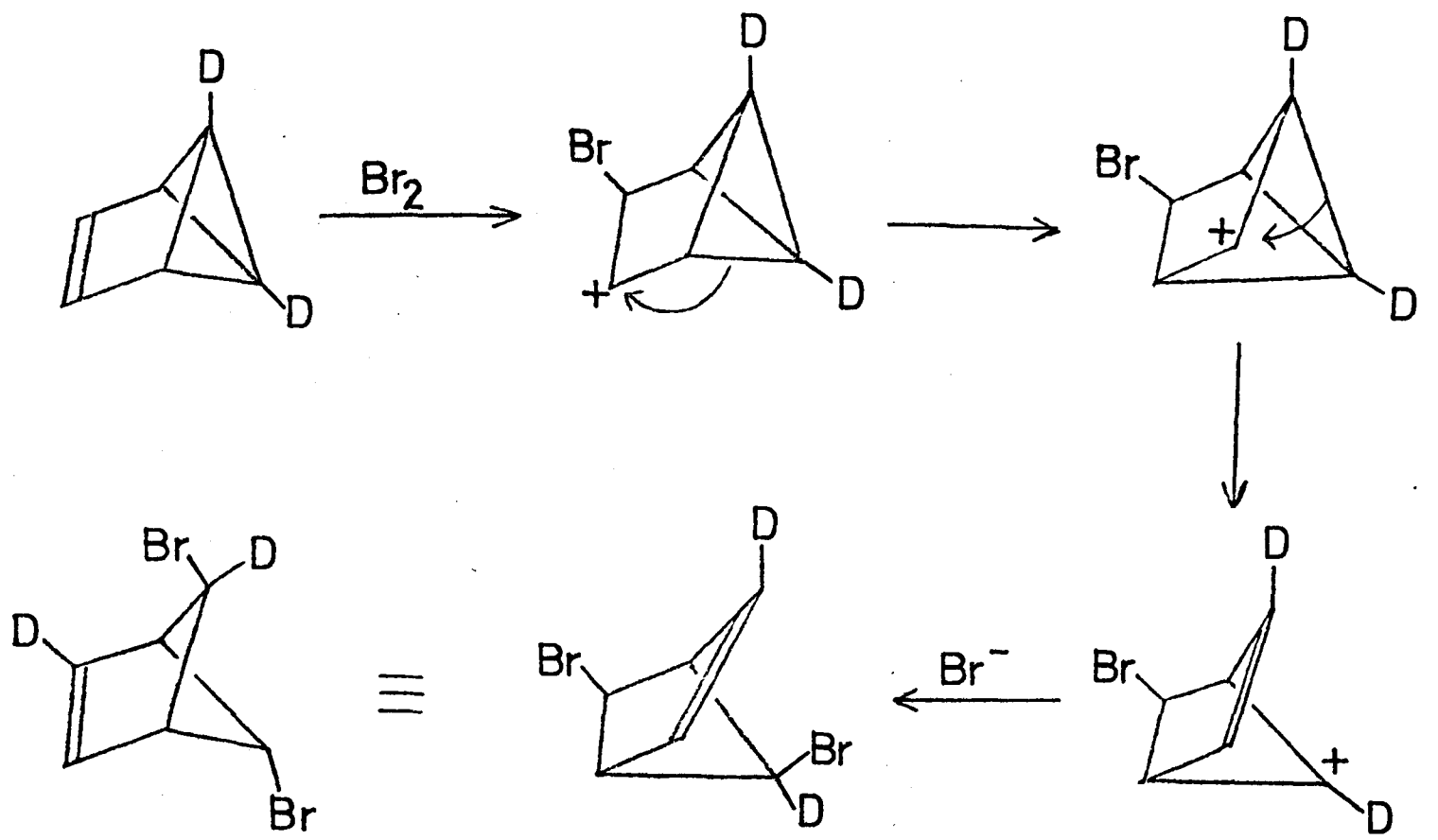
c) an, as yet,unidentified intermediate.

In view of the fact that the unstable benzvalene (4) has been identified as a primary product from the photolysis of 1, 3, 5-tri-t-butyl-benzene (6) it was considered most likely that this species was also formed in acidic methanol. The following novel rearrangement mechanism is proposed in which protonation at the olefinic bond in the benzvalene (4) occurred.



(4)

The precise course of reaction is not known but a similar type of process has previously been postulated by Katz[4] for the bromination reaction of the deuterated benzvalene indicated below:



The present study has established that:

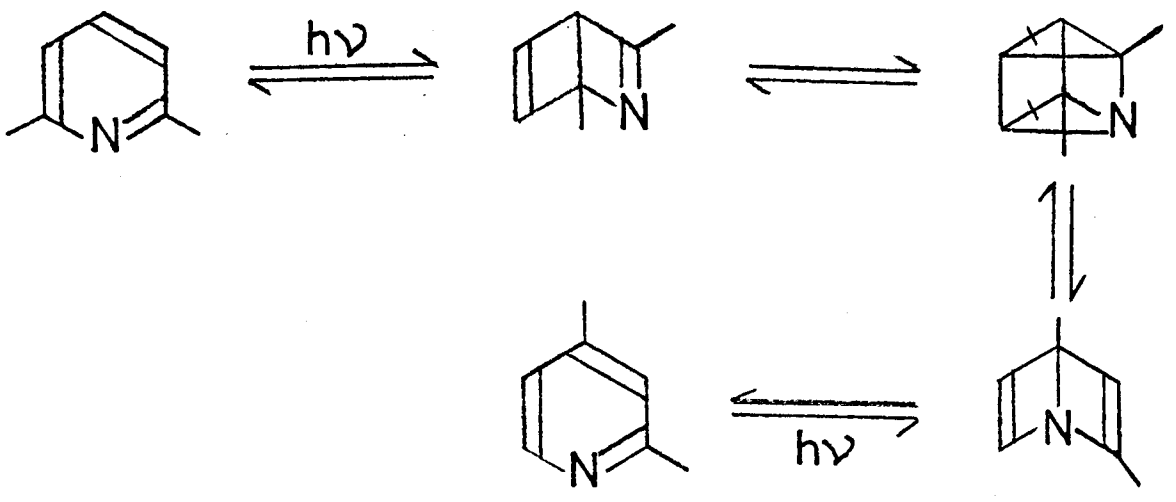
(i) The bicyclohexenyl ether (7) is not the only product formed in the photolysis of 1, 3, 5-tri-t-butylbenzene (6) in methanol

(ii) The mechanism proposed by Tolliday is incorrect

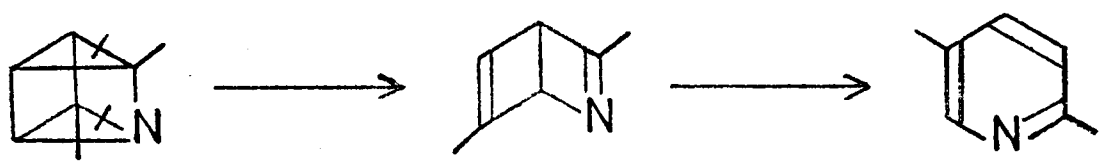
(iii) A novel, intramolecular rearrangement process is taking upon photolysis in acidic methanol. A tentative mechanism is proposed for the rearrangement.

2) Dimethylpyridines

The gas phase photorearrangement of the dimethylpyridines has already been reported by Lablache-Combier [5], who rationalised the phototransposition reactions in terms of the intermediacy of azaprismanes e. g.

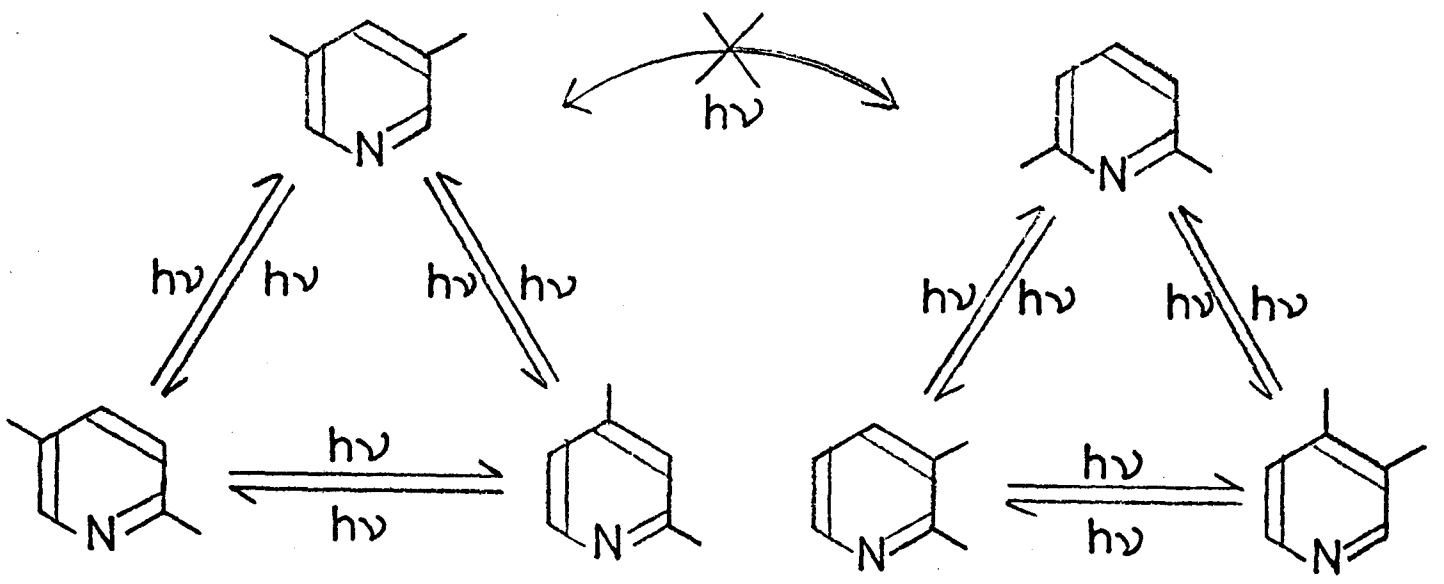


However, it might be predicted that additional products should also be observed by alternative modes of cleavage of the azaprismane. Thus, for the above example, the following additional product may be expected:

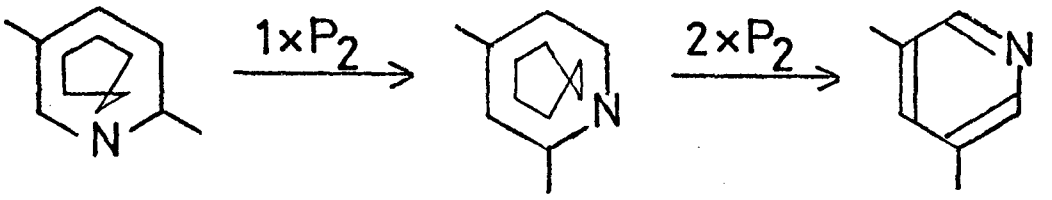


Therefore, the photochemistry of the six dimethylpyridines was studied in order to determine whether any products, other than those reported by Lablache-Combier, were formed.

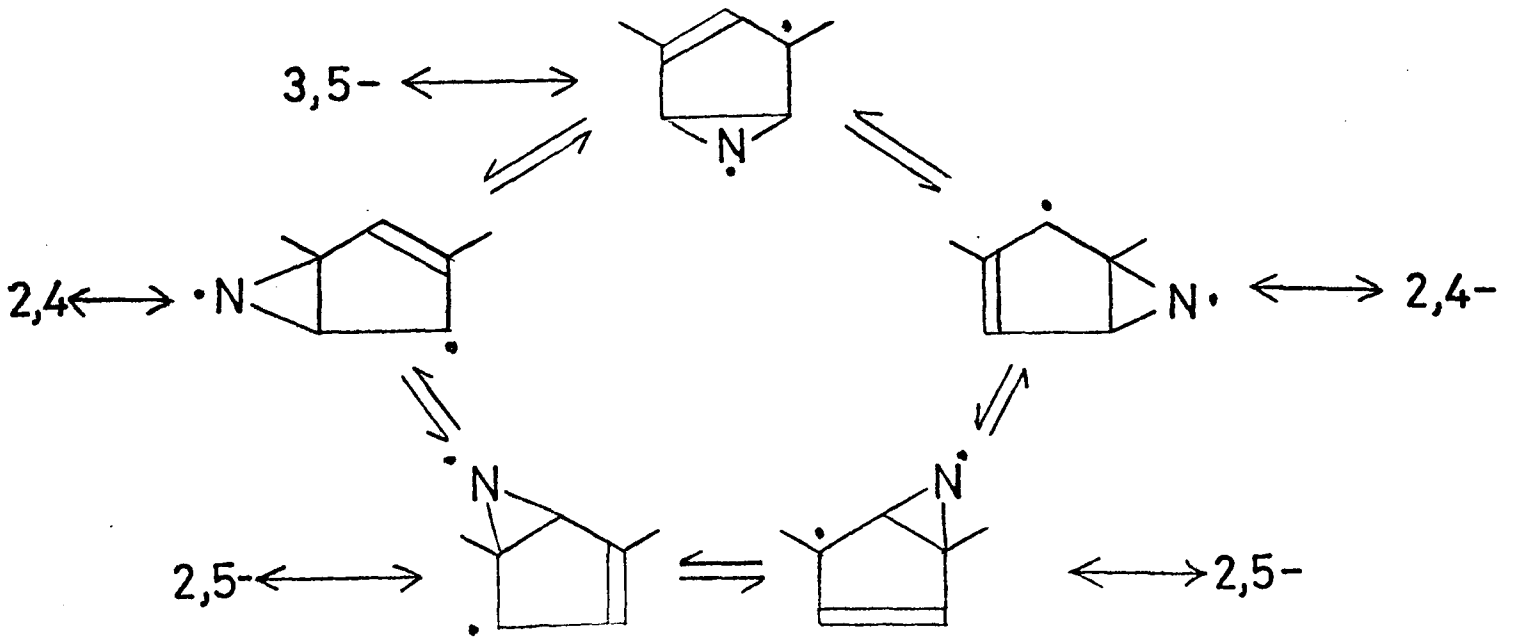
The results from this study were totally at variance with those of Lablache-Combier. For each compound, it was possible to identify (by gcms) two major dimethylpyridine products. In addition some minor dimethylpyridine products and some mono- and tri-methylpyridine products were also observed. In all cases, but one, the concentration of minor products was less than 5% of the smaller major product concentration. For this reason, the major products were considered primarily. Analysis of the major products revealed that the six dimethylpyridines could be divided into two groups of three compounds. Within each group, all members were photochemically interconverted:



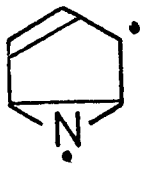
Analysis in terms of Barltrop and Day's permutation pattern [6] approach revealed that each product within the group of three could be obtained by either one or two P_2 permutations applied to the other members: e. g.



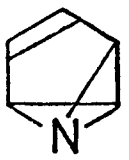
This may be rationalised in terms of a reaction mechanism in which the nitrogen atom effectively migrates around a five-membered ring of carbon atoms:



The form of the actual intermediate is not known; possible intermediates may be biradical species (11) (as shown above) or azabenzvalenes (12)



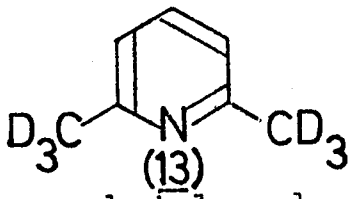
(11)



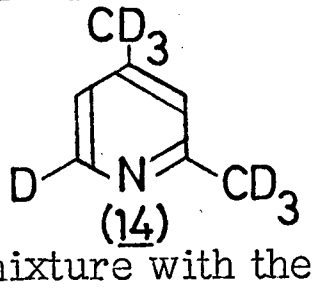
(12)

The latter have been proposed as intermediates in the photochemistry of quaternary pyridine compounds (vide infra).

The formation of the minor products is not so readily explained. They did not appear to be produced by a single mechanism. A demethylation/remethylation process could not be excluded and, therefore, the intramolecular nature of the rearrangement to both major and minor products was confirmed by experiment. Two partially deuteriated dimethylpyridines, (13) and (14), were prepared.



(13)



(14)

Each was photolysed as a 50% mixture with the non-deuteriated compound and the gcms of the various products was measured. For the 2,6-isomer (13), major signals were observed at m/e 113 and 107 for the products assigned to dimethylpyridines; for the 2,4-isomer (14), major signals were seen at m/e 114 and 107. This confirmed the intramolecular nature of the reaction, since a demethylation/remethylation process would lead to dominant m/e 110 and m/e 110 and 111 signals in the mass spectra of the products from the 2,6-and 2,4-isomers, respectively.

The nature of the process leading to the minor products is still not known, but could possibly involve the intermediacy of other valence isomers.

The results from this part of the study may be summarised thus:

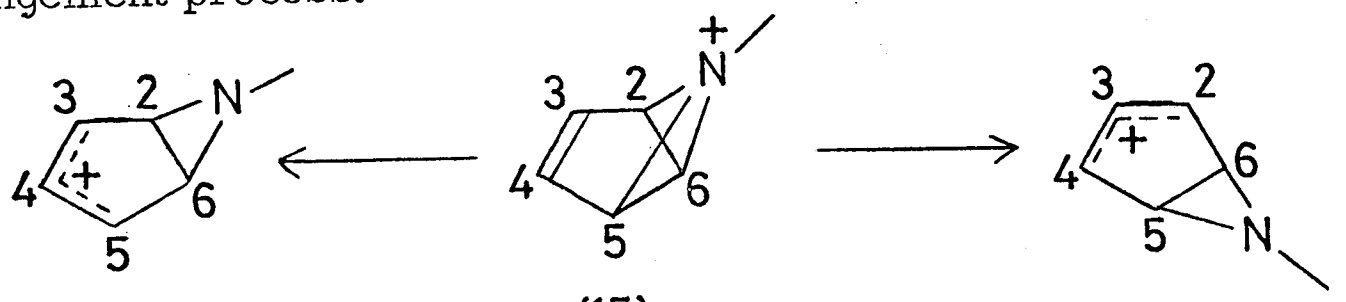
(i) Photolysis of each dimethylpyridine yielded two major isomeric products, and a number of minor isomeric products, by intramolecular processes.

(ii) The six dimethylpyridines could be divided into two groups of three; within each group, photolysis of each member gave the other two members as major products.

(iii) The mechanism for rearrangement to the major products is one in which the nitrogen atom effectively inserts itself between the five carbons of the aromatic nucleus.

3) N-Methylpyridinium Chlorides.

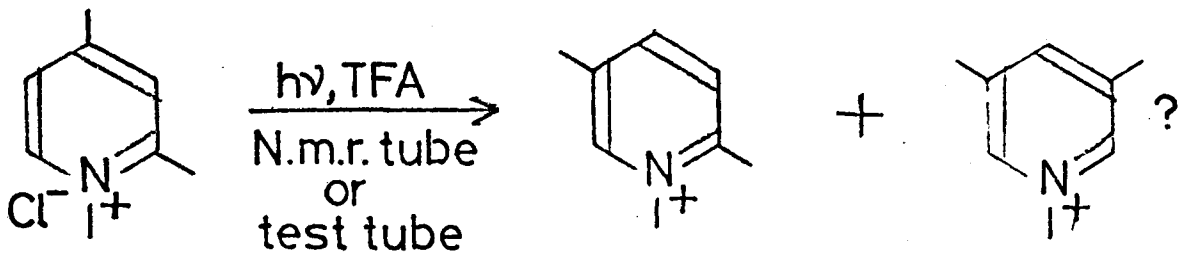
Photorearrangement for this system of compounds has not been observed directly; however, a rearrangement step has been postulated to accommodate the products formed during the photosolvation of quaternary pyridine compounds.[7] It is believed that an N-methyl-azoniabenzvalene (15) which can undergo 1,2-shifts of nitrogen, may be an intermediate in the rearrangement process.

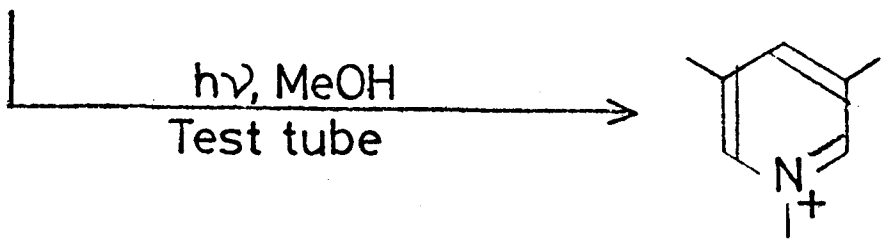


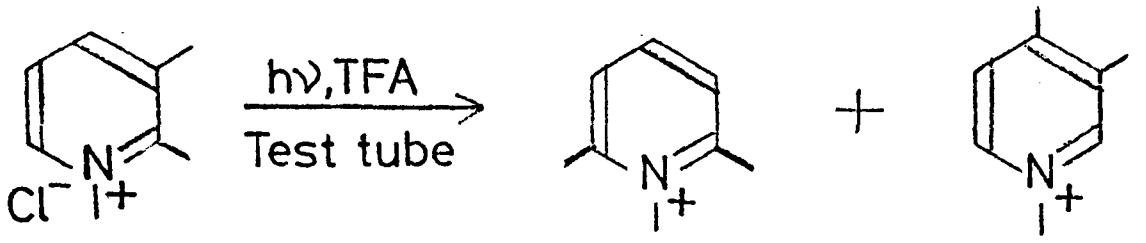
(15)

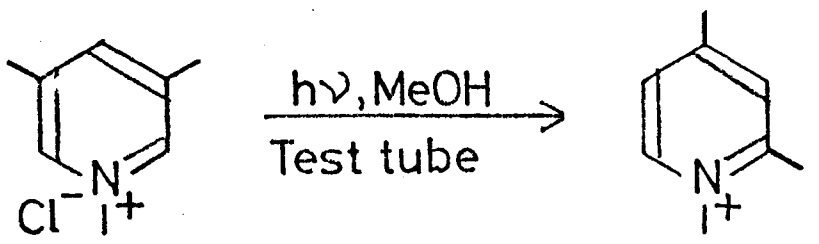
In this study, the six isomeric N-methyl-dimethylpyridinium chlorides were irradiated at 254 nm in a variety of solvents (trifluoroacetic acid, methanol, acetonitrile) in an attempt to observe the rearrangement process directly.

Only in four of the experiments was there the slightest evidence for rearrangement;

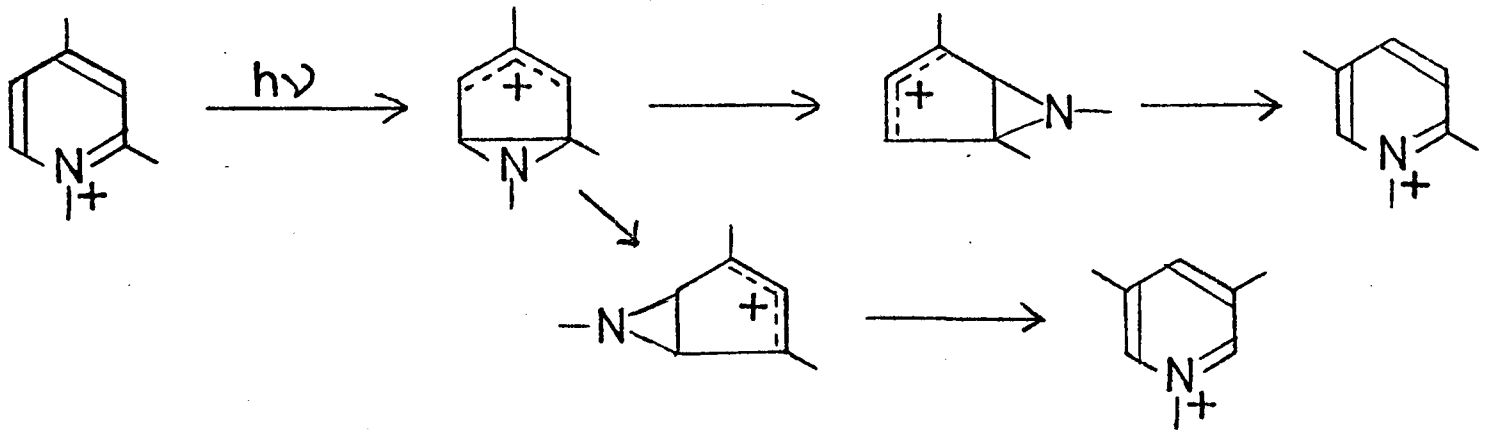
(i) 

(ii) 

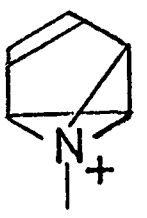
(iii) 

(iv) 

In each case, the products could be derived from the starting material via 1,2-shifts of nitrogen, in the same way as for the neutral dimethylpyridines.



The exact nature of the intermediates is again not known but could involve a benzvalene of the type proposed by Kaplan i.e.



Thus, the results of this study are entirely consistent with and, therefore, to some extent substantiate, the mechanism proposed by Kaplan for the photosolvation of quaternary pyridinium compounds.

SUMMARY REFERENCES.

1. (a) L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, J. Amer. Chem. Soc., 1966, 88, 2881; (b) I. E. Den Besten, L. Kaplan, and K. E. Wilzbach, ibid., 1968, 90, 5868; (c) L. Kaplan and K. E. Wilzbach, ibid., 1965, 87, 4004.

2. P. D. Tolliday, Part II Thesis, University of Oxford, 1975.

3. K. L. Kaiser, R. F. Childs, and P. M. Maitlis, J. Amer. Chem. Soc., 1971, 93, 1270.

4. R. J. Roth and T. J. Katz, J. Amer. Chem. Soc., 1972, 94, 4770.

5. S. Caplain and A. Lablache-Combier, Chem. Comm., 1970, 1247.

6. J. A. Barltrop and A. C. Day, Chem. Comm., 1975, 117.

7. L. Kaplan, J. W. Pavlik, and K. E. Wilzbach, J. Amer. Chem. Soc., 1972, 94, 3283.