The photochemistry of highly fluorinated pyridazines

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A THESIS

entitled

THE PHOTOCHEMISTRY OF HIGHLY FLUORINATED PYRIDAZINES

Submitted by

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TO CAROLINE

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Thanks are also due to the University of Durham who supported this work through a Research Studentship.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1970 and January 1973. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of this work has been the subject of the following publications:

S.L. Bell, R.D. Chambers, M.Y. Gribble and J.R. Maslakiewicz, J. Chem. Soc., Perk. 1, 1973, 1716.

R.D. Chambers, M.Clark, J.R. Maslakiewicz and W.K.R. Musgrave, Tetrahedron Letters, 1973, 2405.

SUMMARY

Syntheses of perfluoro-4-isopropyl-, -4,5- and -3,5-di-isopropyl-pyridazines at atmospheric pressure have been developed.

The reaction between perfluoroisobutene and tetrafluoropyridazine, at atmospheric pressure and 40°C gave a mixture of perfluoro-mono-3,5- and -3,6-di-t-butylpyridazine and a trace of a trisubstituted product.

Flow thermolysis of perfluoro-4-isopropylpyridazine at 640°C gave a mixture of perfluoro-4- and -5-isopropyl and ethylpyrimidines as the principle products.

Flash vacuum thermolysis of perfluoro-4,5-bis-isopropylpyridazine at 750°C gave a mixture of four pyridazines all the result of fragmentation of the side chains.

A number of highly fluorinated substituted pyridazines have been photolysed. The perfluoro-4-alkylpyridazines were found to isomerise to the perfluoro-2-alkylpyrazines, the perfluoro-4,5-di-alkylpyridazines to the perfluoro-2,5-di-alkylpyrazines and the perfluoro-3,5-di-alkylpyridazines to the perfluoro-2,6-di-alkylpyrazines.

The isomerisation of pyridazines to pyrazines was found to occur most efficiently by excitation of the lowest $\pi \rightarrow \pi^*$ band.

No evidence has been found for the involvement of the triplet state in the photoisomerisation of pyridazines to pyrazines.

A secondary rearrangement, of pyrazine to pyrimidine, has been discovered, but this is much slower than the rearrangement of pyridazine to pyrazine. This is thought to occur as a result of the sensitisation of pyrazine by pyridazine.

A number of perfluoro-2,5-diazadewarbenzenes have been isolated by irradiation at 253·7 nm. In the cases of perfluoro-4-mono-isopropyl and sec.-butylpyridazine the perfluoro-2,5-diazadewarbenzenes could be isolated

in ca. 99% yield by irradiation at 300 nm. in Pyrex. Two perfluoro-1,2-diaza-dewarbenzenes have been isolated in high yield from perfluoro-4,5-bis-isopropyl and sec.-butylpyridazine by irradiation at 300 nm. These were found to rearrange to the perfluoro-2,5-diazadewarbenzenes both thermally and photochemically. The net result being a novel 1,3-shift of ring atoms.

The thermal stabilities of a number of diazadewarbenzenes have been investigated. The order of stabilities indicates that many factors influence the thermal stability of valence isomers, the relative importance of each being difficult to estimate.

Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene has been reacted with a variety of nucleophiles; $^{-}OCH(CH_3)_2$, ^{-}OMe, $^{-}C_3F_7$ and $^{-}C_6F_5$. Only the reaction with isopropoxide ion gave an isolatable product. The mono-isopropoxide derivative was isolated and converted to 2,5-bis-heptafluoroisopropyl-3-isopropoxy-6-fluoropyrazine upon heating. The di-isopropoxy derivative could not be isolated but after heating 2-(3'-isopropoxy-5'-heptafluoroisopropyl-6'-fluoropyrazin-2'-yl)-2-isopropoxyhexafluoropropane was isolated. A mechanism and reason for the replacement of the tertiary fluorine are given.

Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene has also been reacted with a variety of nucleophiles; ^{-}OMe, $^{-}C_3F_7$, ^{-}OPh and $^{-}C_6F_5$. However, no pure substituted derivatives of the latter 2,5-diazadewarbenzene could be isolated.

Attempted Diels-Alder reactions with diazadewarbenzenes were unsuccessful, as were attempts at preparing platinum(0) complexes.

The photolysis of perfluoro-3,5-bis-isopropylpyridazine whilst under slow transference, led to the isolation of two compounds, identified as perfluoro-bis-isopropyldiazacyclo-octatetraenes, and of a valence isomer of one of them. These latter compounds are thought to arise as a result of the dimerisation of perfluoroisopropyl-aza-cyclobutadienes.

CONTENTS

CHAPTER 1

Photochemical Isomerisation of 6-Membered Aromatic Rings

1.1. Introduction.

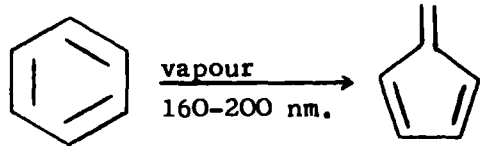
The discovery, by Bryce-Smith and co-workers,[1] that benzene (1) was not stable to ultraviolet irradiation and that fulvene was the major product led to much activity in the field of aromatic photochemistry. Many simultaneous explorations of the photochemistry of benzene and of its derivatives led to the isolation of many valence isomers. It was also found that substituted benzenes undergo isomerisations via valence bond isomers, rather than via inter- or intra-molecular movement of substituents.

1.2. Photolysis of Benzene: its Valence Bond Isomers.

The irradiation of liquid benzene (1) or its vapour, leads to electronic excitation and also to the formation of small quantities of dewar benzene (bicyclo[2,2,0]hexa-2,5-diene) (3), benzvalene (tricyclo[3,1,0]hexene) (4), and fulvene (2).[1,2,3,4,5]

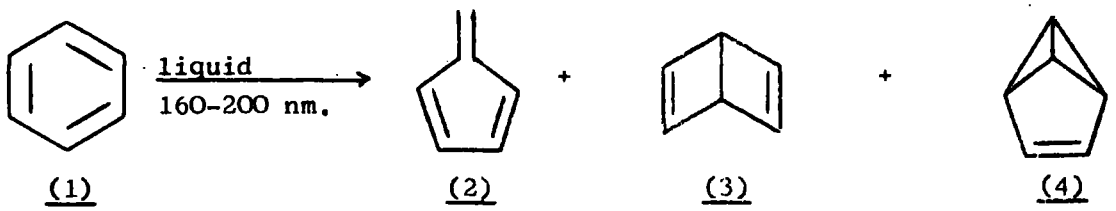
It has been shown that the irradiation of benzene (1) vapour at 253·7 nm. and at 237 nm. gives fulvene (2) and benzvalene (4), and that the latter upon irradiation gives fulvene (2) and benzene (1). The yield of benzvalene (4) was small, and this was shown to be due to efficient benzene (1) triplet sensitised destruction of benzvalene (4).[5]

The irradiation of benzene (1) at shorter wavelengths,[2] has been shown to give a number of products, and these vary whether the vapour or liquid is irradiated, i.e. irradiation of benzene vapour by light of between 160 and 200 nm. gives fulvene (2) and cis and trans hexa-1,3-dien-5-ynes.



(1) → (2) + CH_2=CH-CH=CH-C≡CH (cis and trans) + polymer + fragmentation products

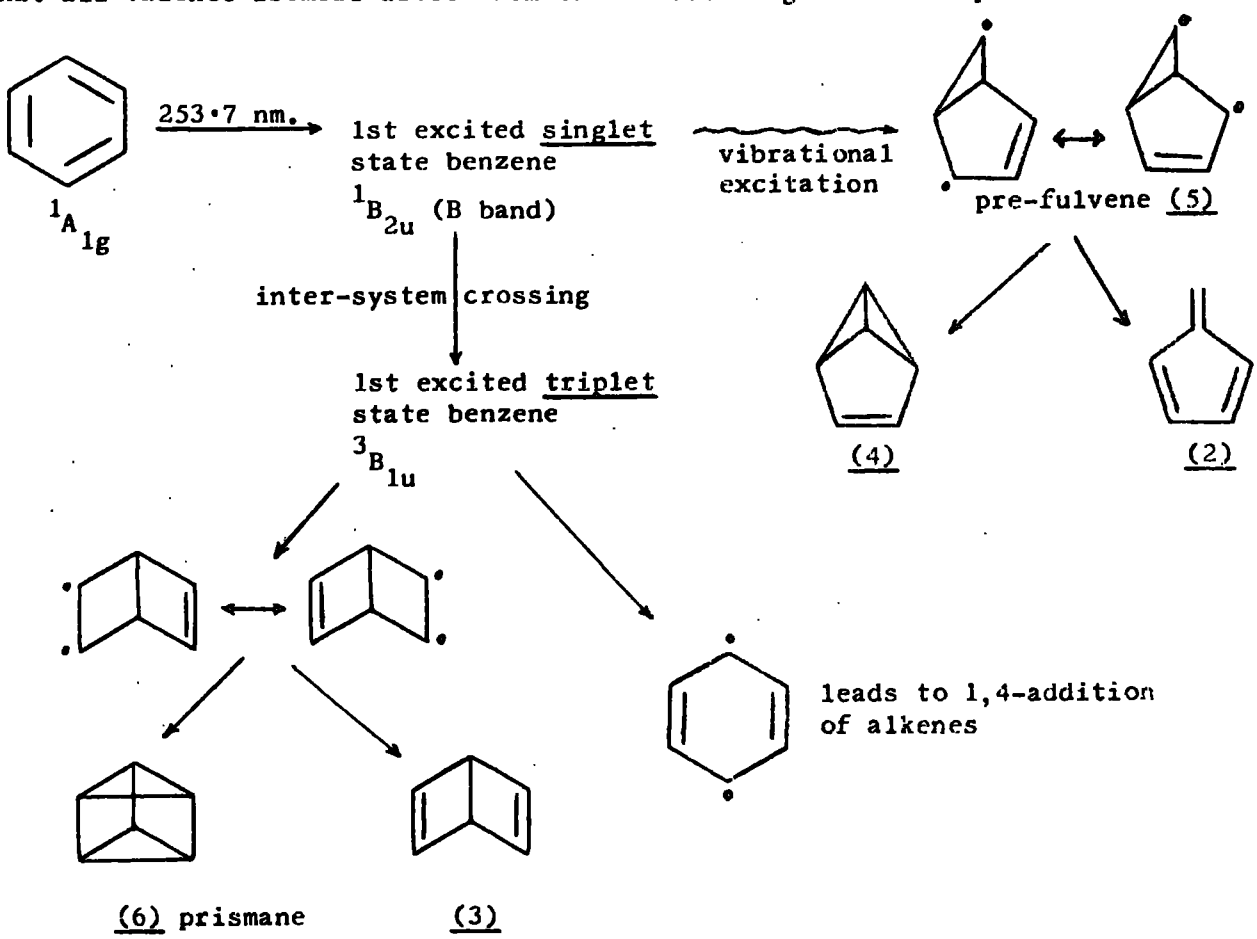
However irradiation of the liquid phase with the same light source gave (2), dewar benzene (3) and benzvalene (4).



(1) (2) (3) (4)

These two latter experiments show that at 160 - 200 nm. a great amount of energy is being supplied to the benzene molecule (formation of dienyne etc.). In the liquid phase, it is likely that excess vibrational energy can be lost much faster than in the vapour phase, and hence it is thought that the lower vibrational levels of these high excited states of benzene are responsible for the formation of (3) and (4).

It was, until recently, thought[6,7] that the scheme immediately below could account for the observed behaviour of benzene upon irradiation, i.e. that all valence isomers arose from the lowest singlet and triplet states.



However the above scheme does not take into consideration a number of experimental findings, the most important being:

1) No dewar benzene nor prismane have been found to be formed upon excitation of benzene to the $^1B_{2u}$ state.[1,2,3,4,5]

2) Dewar benzene is formed upon excitation of benzene to the $^1B_{1u}$ and $^1E_{1u}$ states.[2,5,8]

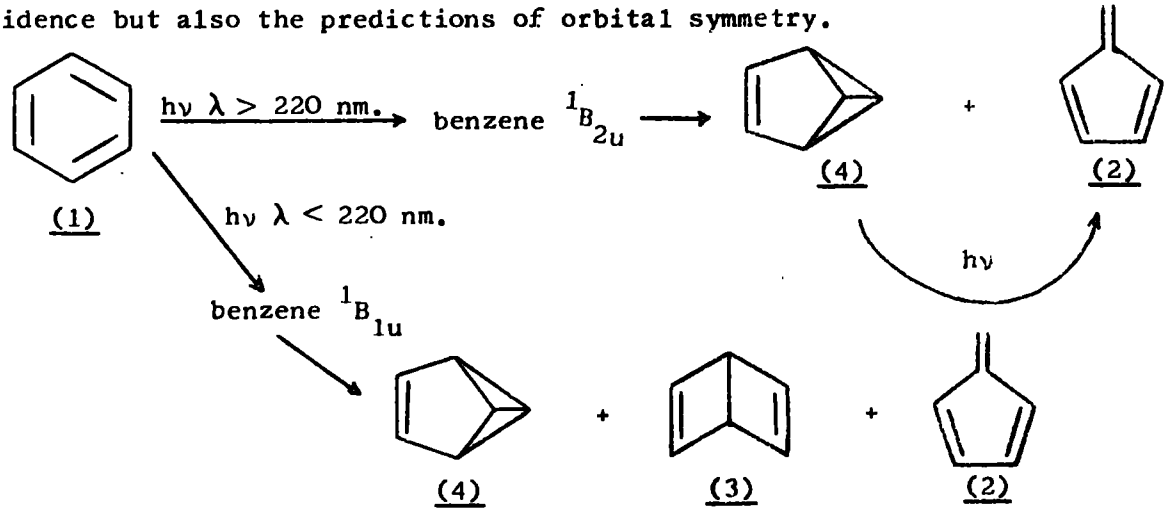
3) There is no evidence for a triplet state intermediate being involved in the formation of dewar benzene.[8]

The electronic states of benzene are shown on p. 4.

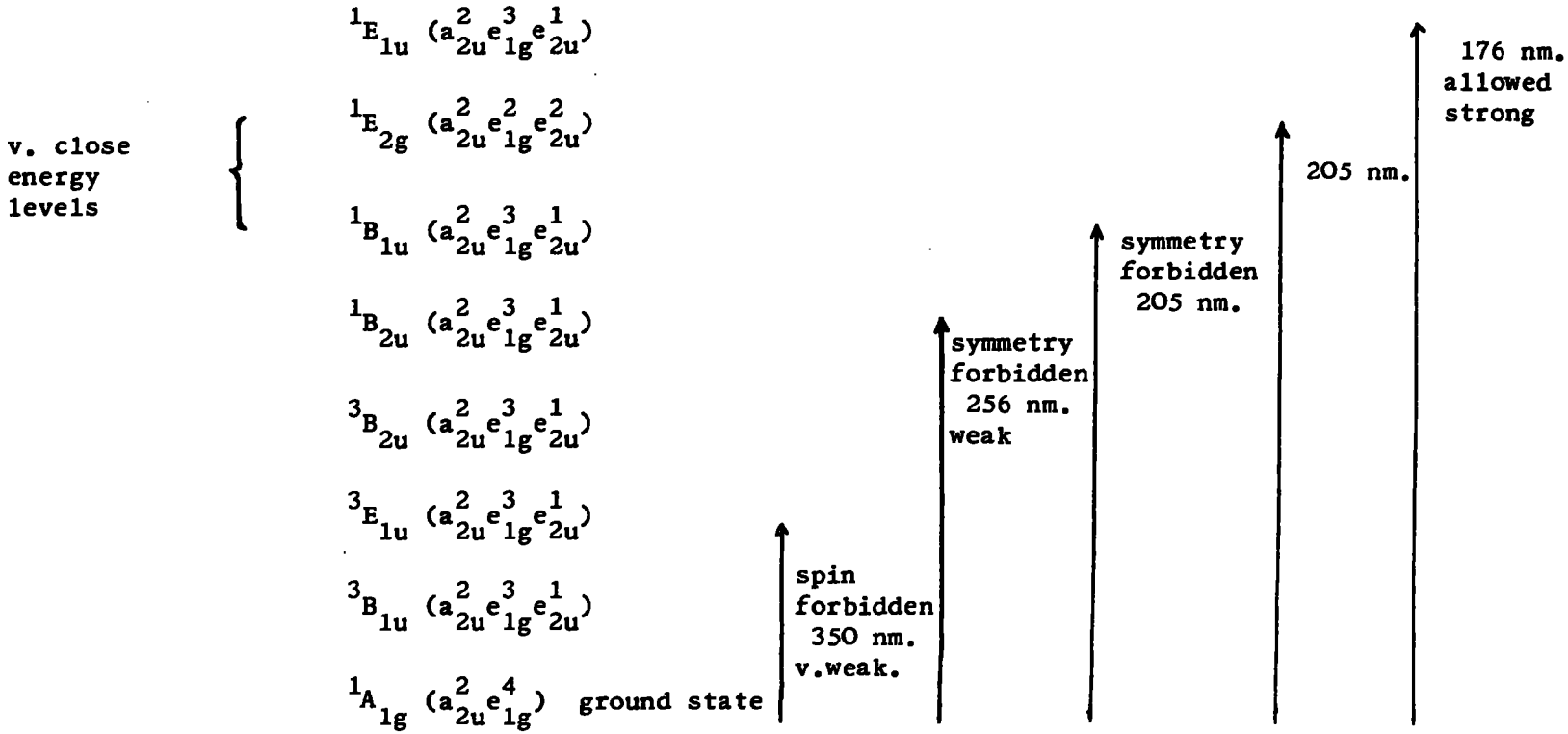
The absorption band centred at 256 nm., in the ultraviolet spectrum of benzene, which results in the population of the $^1B_{2u}$ state is generally referred to as the B band. The band at ca. 205 nm. resulting in the population of the $^1B_{1u}$ state is generally referred to as the K or E_2 band and the band at ca. 176 nm. which results in the population of the $^1E_{1u}$ state is generally referred to as the E_1 band.[9]

The experimental evidence above agrees well with the predictions of the Conservation of Orbital Symmetry,[10] which predicts that benzvalene formation from the $^1B_{2u}$ (B band) state should be symmetry allowed, whereas dewar benzene and prismane formation from this state should be disallowed. It also predicts that the formation of dewar benzene and prismane from the $^1B_{1u}$ (K band) and $^1E_{1u}$ (E_1 band) states should be allowed (see Section 1.9.).

Hence a new scheme can be proposed which not only fits the experimental evidence but also the predictions of orbital symmetry.



Electronic States of Benzene and Absorption Wavelengths



The fact that benzvalene (3) is more efficiently produced at 237 nm. than at 253·7 nm.[5] is again in agreement with the predictions of the conservation of orbital symmetry, for if one looks at the state correlation diagram for the benzene benzvalene transformation (see Section 1.9.B.) one sees that the benzvalene state which correlates with that of the $^1B_{2u}$ state of benzene is of slightly higher energy.

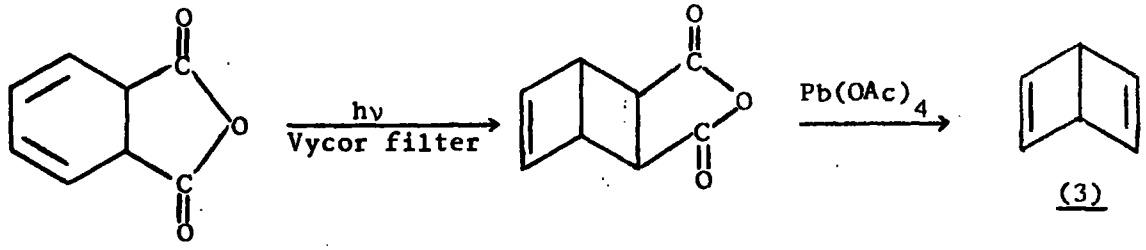
Although the above scheme fits the experimental findings for benzene itself, it will be seen later that it fails to explain the photochemical behaviour of many substituted benzenes, and that orbital symmetry rules fail to explain the observed products.

1.3. Synthesis of Dewar Benzene, Benzvalene and Prismane.

The photolysis of benzene only produces very small quantities of two of the three valence isomers. All three have been successfully synthesised now.

A. Dewar Benzene.

Dewar benzene was the first to be prepared by a synthetic route in 1962.[11,12]

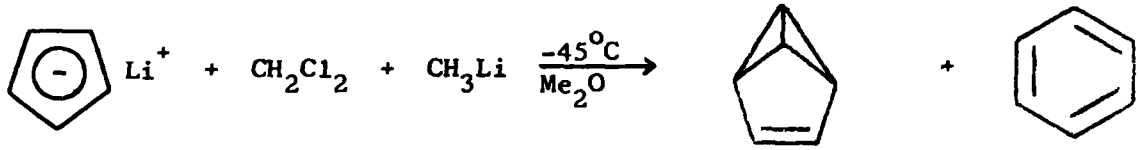


(3)

Irradiation of (3) resulted in benzene formation and not in the expected prismane.

B. Benzvalene.

Benzvalene was prepared more recently by Katz and co-workers.[13]

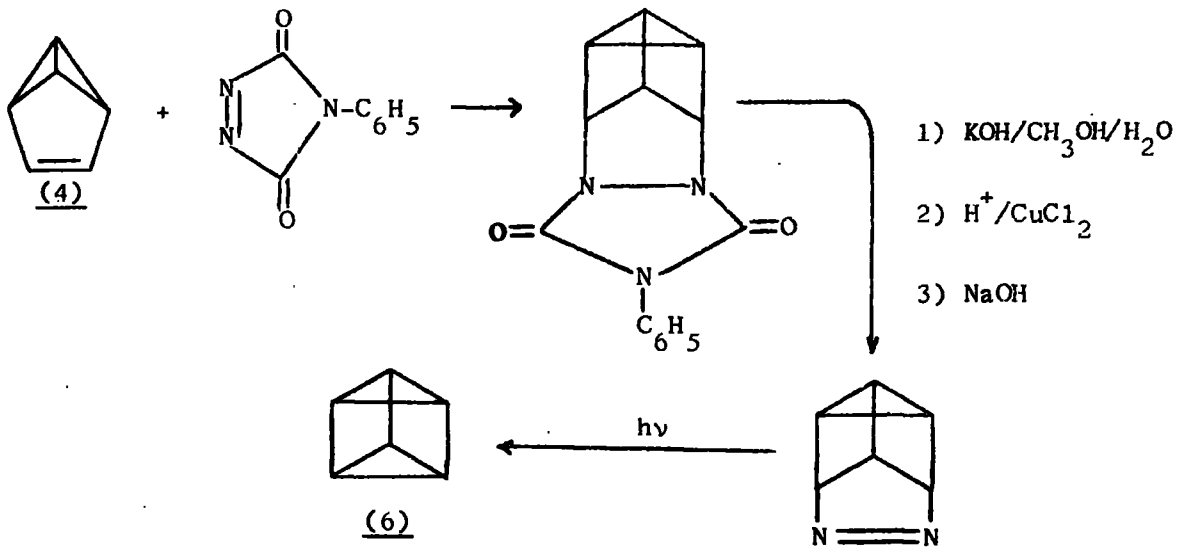


(4) 29%

(1) 6·4%

C. Prismane.

The same workers were also successful in preparing prismane[14] by an elegant route using (4) as a starting material.



1.4. Isomerisation of the Benzene Ring.

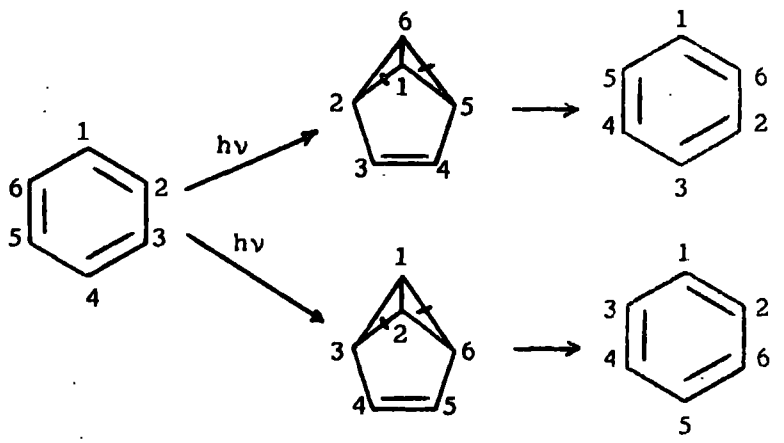
A. Introduction.

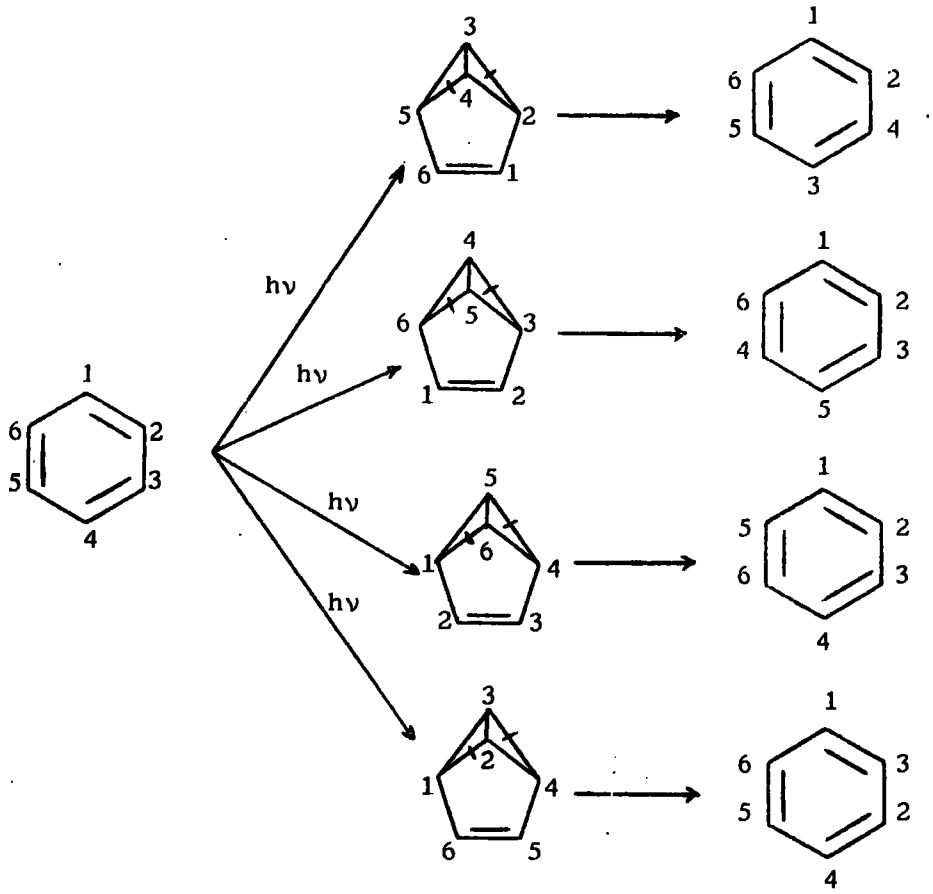
If all the carbon atoms of a benzene ring were labelled it can be seen that once formed, benzvalene and prismane intermediates could rearomatise to give different aromatic isomers.

B. Isomerisation Via Benzvalene Intermediates.

1. 1,2-Shifts.

With benzvalene as the intermediate, six different benzene isomers could be formed upon rearomatisation, all the result of 1,2-shifts, i.e.

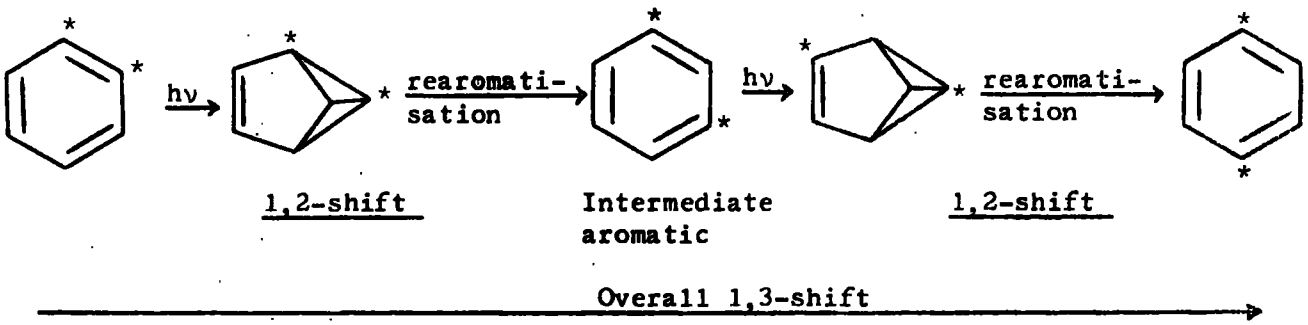




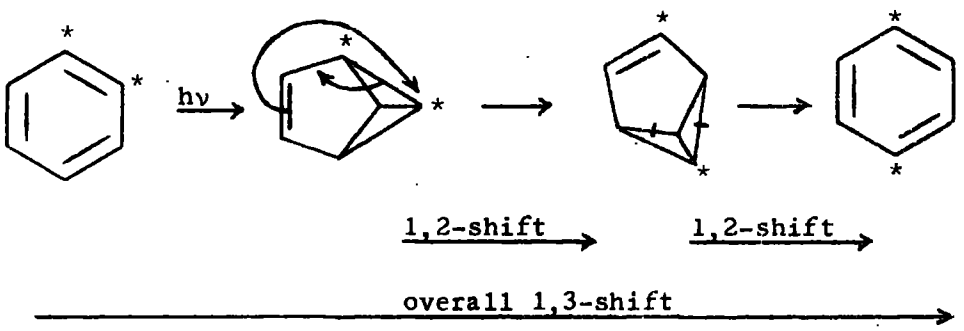
2. Pseudo-1,3-Shifts.

There is also the possibility of an overall 1,3-shift via benzvalene, but it is important that one notes that this occurs via two 1,2-shifts. There are two pathways for the overall 1,3-shift.

i) By formation of an intermediate aromatic followed by a further 1,2-shift, i.e.



ii) By a 'Cope type' rearrangement of the initially formed benzvalene to give a second benzvalene, i.e.



It would of course be difficult to differentiate between the two mechanisms if the aromatic intermediate alone underwent rearrangement very efficiently, hence preventing its detection.

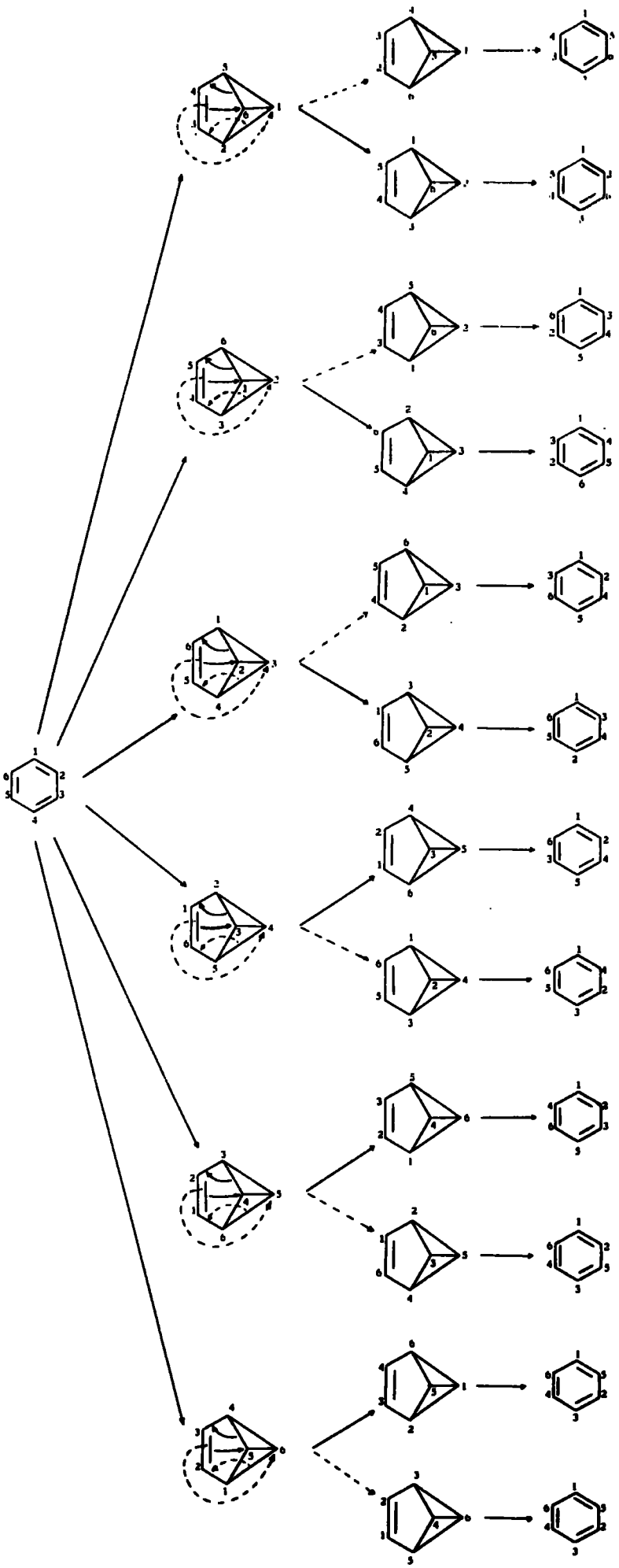
The possible products from an overall 1,3-shift via the latter mechanism are shown below. They are the same as would be obtained by the former.

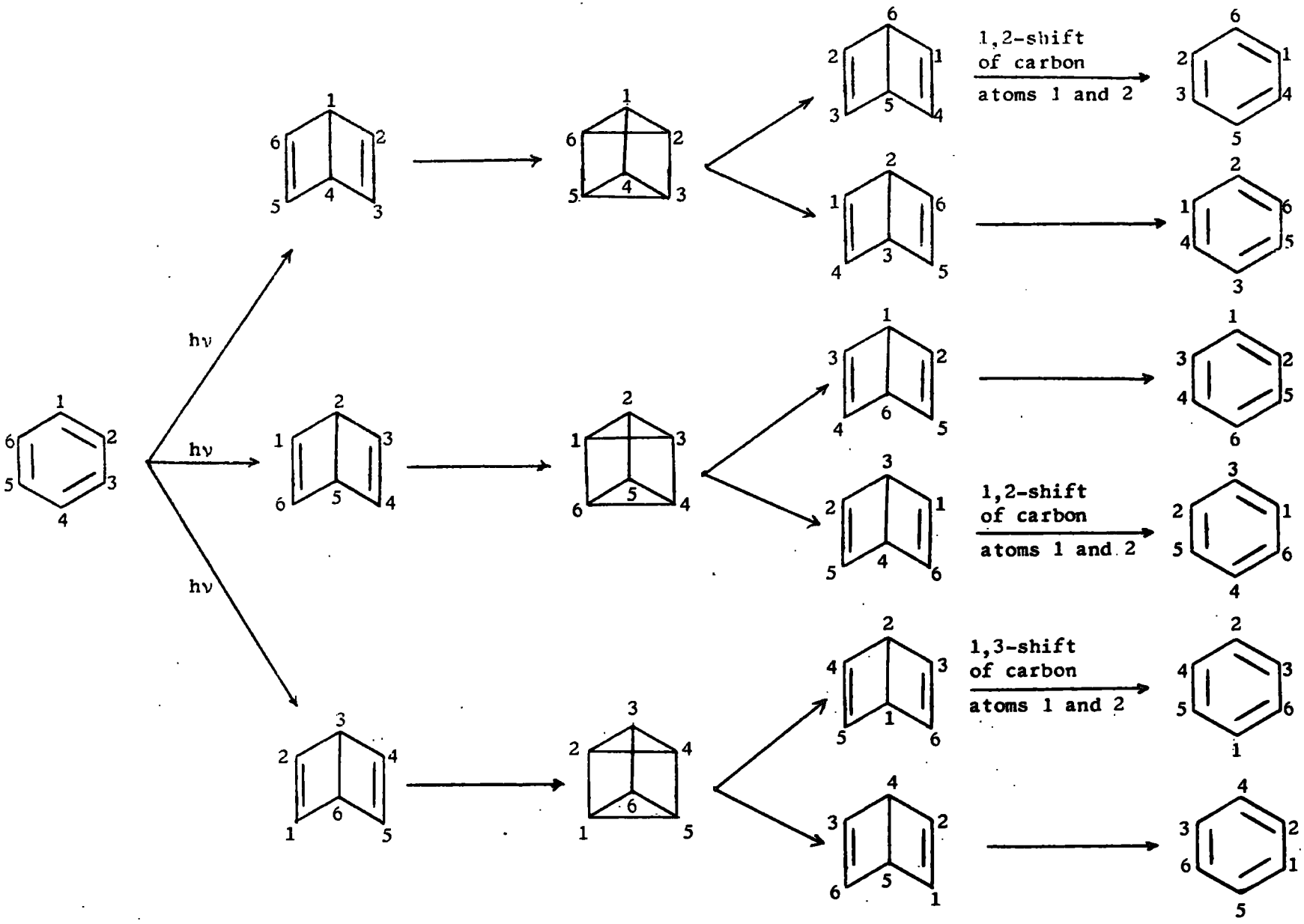
C. Isomerisation Via Dewar Benzene and Prismane Intermediates.

There is evidence that prismanes can only be formed via initially formed dewar benzenes. Whether or not this is always the case has not yet been shown, and orbital symmetry rules show its formation directly from benzene to be allowed. Dewar benzenes will be shown as intermediates in isomerisations involving prismane.

Both 1,2- and 1,3-shifts can occur directly with prismane as the intermediate (see below).

As can be seen, the products that arise from a prismane intermediate are not the same as those that arise from a benzvalene intermediate, and hence differentiation between the two intermediates is possible with substituted benzenes. If carbons 1 and 2 were substituted with different substituents to those on 3 and 6, there could be two benzenes produced as a result of 1,2-shifts of carbons 1 and 2 and one benzene produced as a result of a 1,3-shift of carbons 1 and 2. No actual 1,3-shift (i.e. that occurring via a prismane)

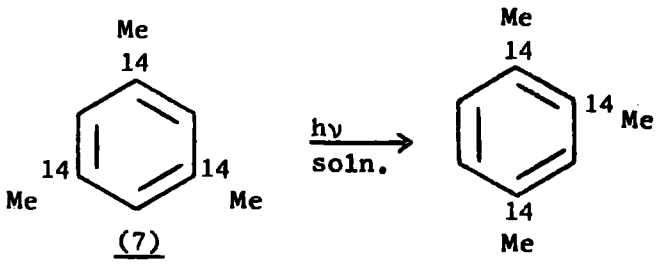



hν
hν
hν
1,2-shift
of carbon
atoms 1 and 2
1,2-shift
of carbon
atoms 1 and 2
1,3-shift
of carbon
atoms 1 and 2

has been observed in the photochemistry of substituted benzenes. In all cases where 1,3-shifts have been observed there has been very strong evidence for these to have been the result of two 1,2-shifts, e.g. xylenes. Whether or not these were via prismane or benzvalene intermediates is not clear.

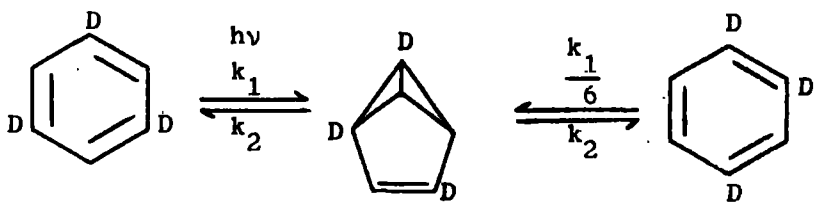
1.5. Photoisomerisation of Labelled Benzenes.

To demonstrate that rearrangement of the benzene skeleton can occur, Wilzbach and Kaplan[15] irradiated a ^{14}C labelled benzene (7) and showed that indeed, the skeleton rearranged and that an intra- or inter-molecular rearrangement of substituents was not the predominant process.



(7)

The irradiation of the vapour of 1,3,5-trideutero benzene (8) at 253·7 nm. yields 1,2,4-trideutero benzene (9).



(8) (8a) (9)

The rearrangement is found to occur with a higher quantum yield at 248 nm. than at 253·7 nm.

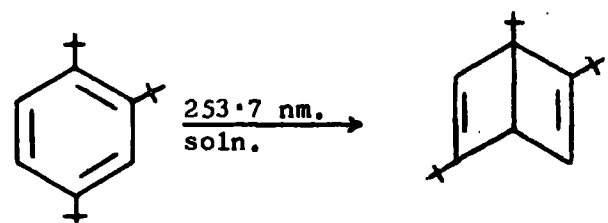
Since deuterium substitution in the benzene ring is unlikely to have any significant perturbing effect upon the benzene electronic orbitals, on valence isomers or on their formation relative to hydrogen it is probable that the benzvalene (8a) is the valence isomer responsible for the interconversion. This is because in benzene (H_6) no dewar benzene or prismane is formed upon

irradiation at 253·7 nm.[8] The fact that benzvalene (4) is produced in higher yield at 237 nm.[5] and that here there is a higher quantum yield at 248 nm. than at 253·7 nm. strengthens the argument that benzvalene is the intermediate responsible for the rearrangement.

1.6. Photoisomerisations of Alkyl Benzenes.

A. Introduction.

The introduction of alkyl groups into the benzene ring clearly has a perturbing effect upon the system. The isolation of the first valence bond isomer of the benzene system by van Tamelen and co-workers was the result of the irradiation of 1,2,4-tri-t-butyl benzene (10) with light of wavelength 253·7 nm. and gave the dewar benzene (11).[16]



(10) (11)

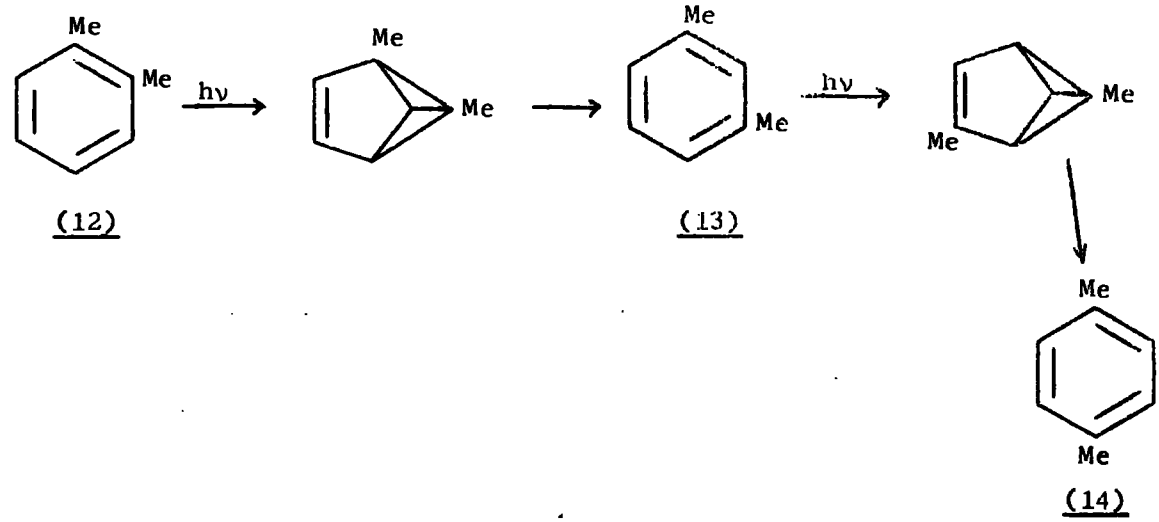
Clearly symmetry rules do not apply to this system, for they predict that the dewar isomer should not be formed upon the excitation of the benzene system to the $^1B_{2u}$ state.

B. Photoisomerisation of the Xylenes.

The rearrangement of the three xylenes upon irradiation ($\lambda > 230$ nm.) has been studied extensively by many workers.[17,18,19,20,21] The initial product formed upon irradiation of o-xylene (12) is m-xylene (13) which then upon further irradiation rearranges to p-xylene (14).[17,18] A closer study shows that although m- and p-xylenes are interconvertible and yield a photostationary mixture upon irradiation, neither can be photoisomerised to o-xylene.[17] To account for these 1,2-shifts a benzvalene intermediate was proposed but this

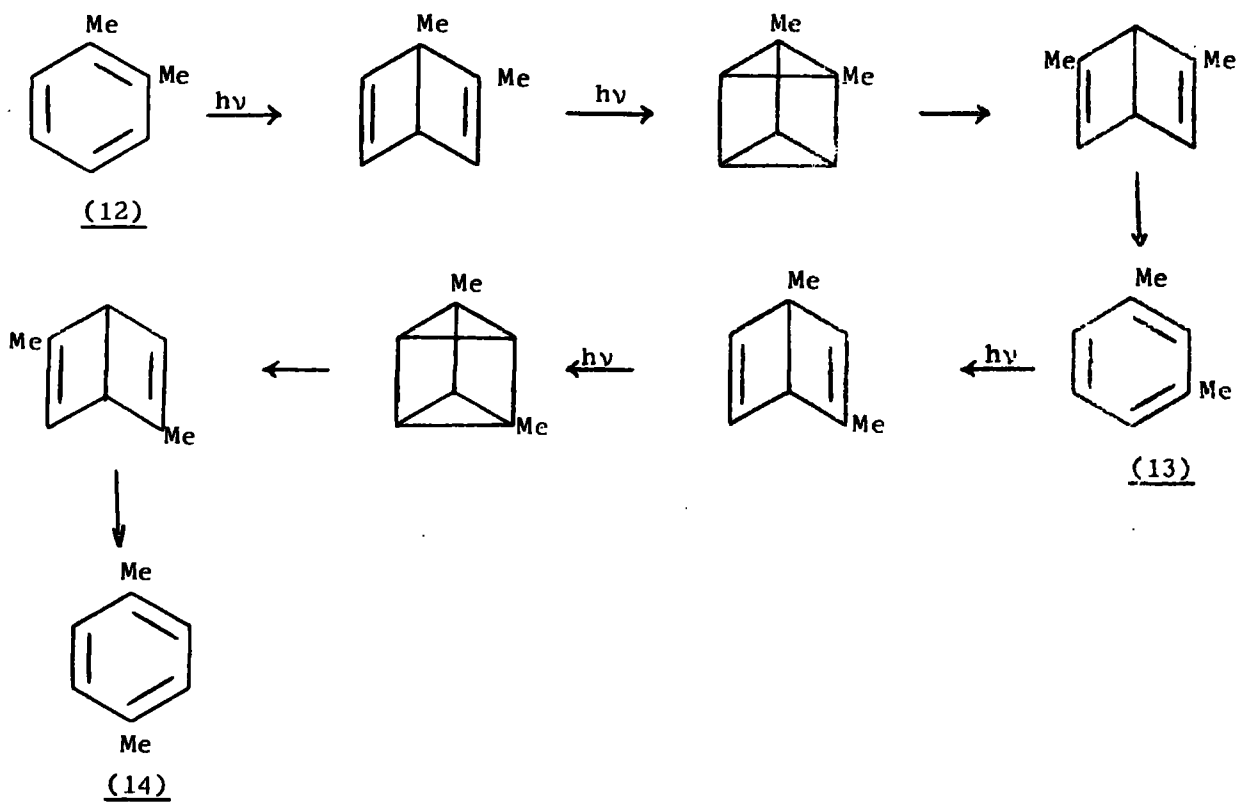
was because a triplet intermediate was found not to be involved.[20] Recent work by Bryce-Smith and workers[8] (above) has shown that dewar benzene can be produced from a singlet state and that indeed the triplet state is not involved at all. Hence a prismane intermediate could be involved.

1,2-Shifts Involving Benzvalene Via an Aromatic Intermediate.



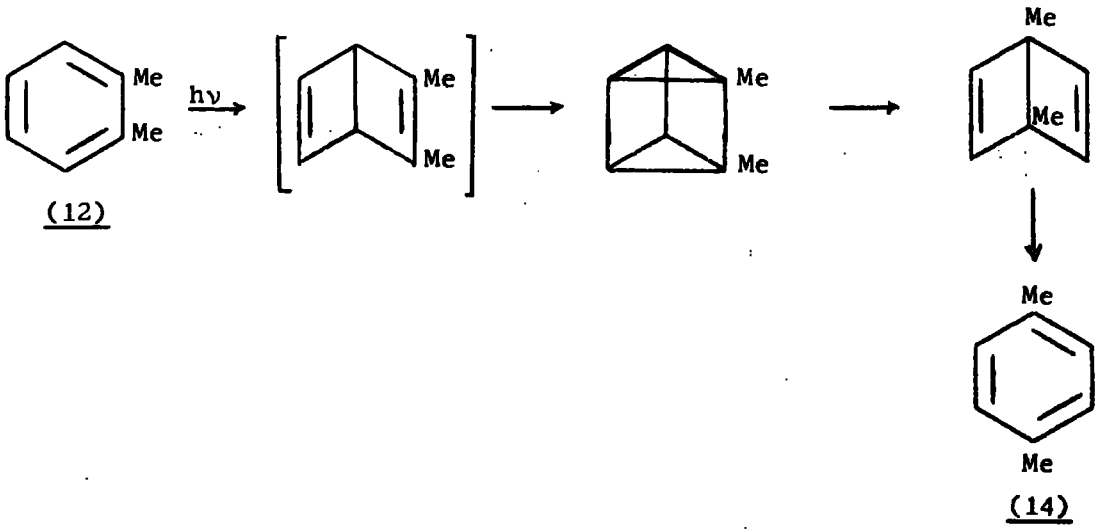
(12) (13) (14)

1,2-Shifts Involving Prismane Via an Aromatic Intermediate.



(12) (13) (14)

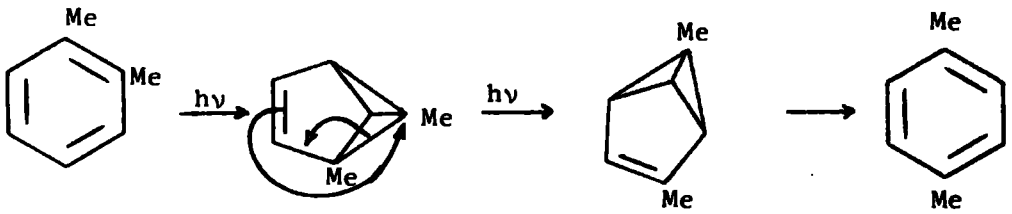
With prismane as the intermediate, p-xylene can be formed in a one stage process from o-xylene, i.e.



(12) (14)

without the intermediacy of (13). This does not occur.

Similarly p-xylene could be formed from o-xylene without the intermediacy of m-xylene, if the initially formed benzvalene rearranges to another benzvalene via a 'Cope-type' rearrangement (this has been observed, see later).



(12) (14)

Irradiation of o-xylene at 160 - 200 nm.[19] causes immediate formation of p-xylene. This would seem to indicate that a 1,3-shift had occurred at these shorter wavelengths and would be in accordance with prismane formation from the higher excited states of o-xylene. Hence the 1,2-shifts observed at longer wavelengths (above) $\lambda > 230$ nm. are likely to proceed via benzvalene intermediates.

The diethyl benzenes have been found to isomerise in an analogous manner, although quantum yields were higher.[17]

Work on the di-t-butyl benzenes[22] showed that o-di-t-butyl benzene gives m-di-t-butyl benzene as the only initial product and that this then undergoes

isomerisation to the para isomer. Prolonged irradiation of any of the three benzenes leads to a 1:4 mixture of meta to para isomers.

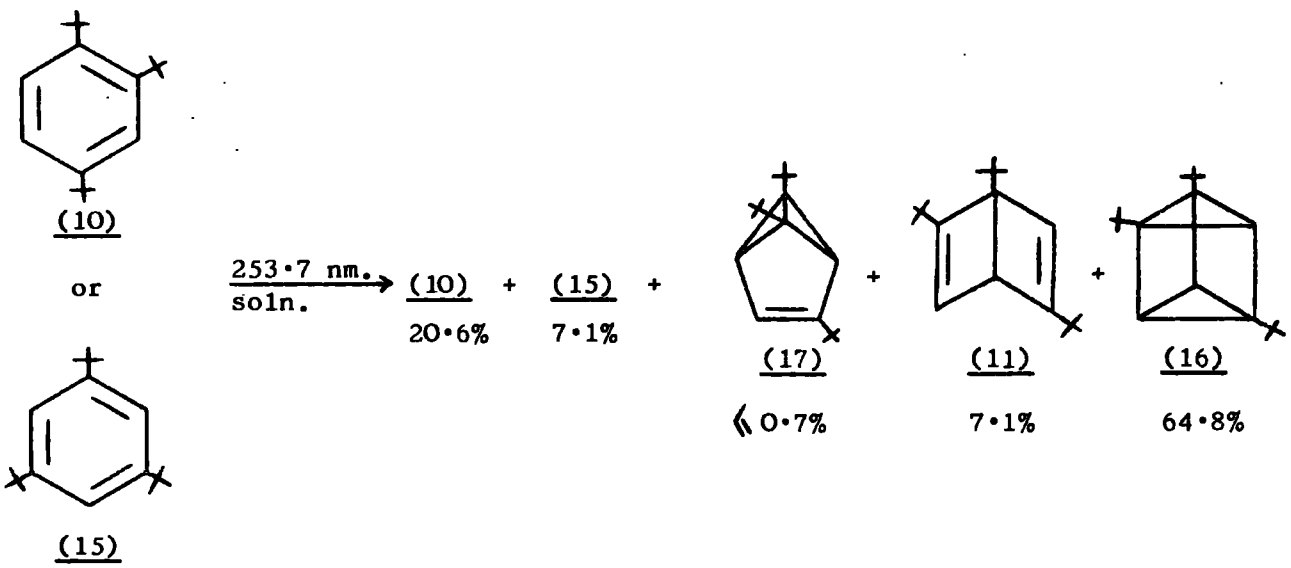
Hence, the three dialkyl benzenes studied all isomerise in the same manner. It is important to note that although there is an overall 1,3-shift in going from the ortho to para dialkyl benzenes, this is the result of two 1,2-shifts with isolatable aromatic intermediates (meta dialkyl benzene).

C. Photochemical Interconversion of Tri-t-butyl Benzenes.

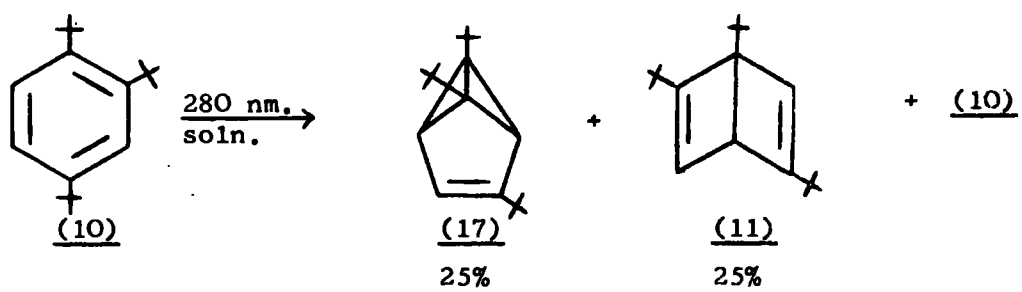
1. Photolysis of 1,2,4- and 1,3,5-tri-t-butyl Benzenes.

Careful work upon the photochemical interconversion of 1,3,5-tri-t-butyl benzene (15) and 1,2,4-tri-t-butyl benzene (10) produced some very interesting results.[23]

The irradiation of (15) or (10) for a prolonged period produces the following photostationary mixture in which prismane (16) is the major product.



The dewar (11) being the same valence isomer as that isolated by E.E. van Tamelen and co-workers upon irradiation of[16] (10).

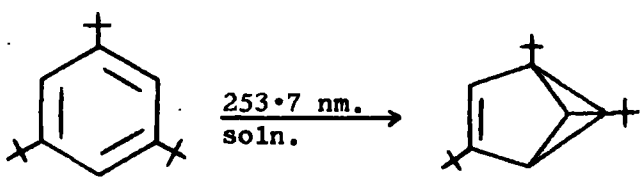


The quantity of benzvalene (17) can be increased from the ⟨0·7% in the 253·7 nm. irradiation to 25% by irradiation of (10) at 280 nm. However, the quantity of (11) also increases, although not by such a significant amount (7·1 to 25%). If it was possible to excite (10) to the B_{1u} state at 253·7 nm. it would certainly not be possible at 280 nm. and hence more efficient production of dewar (11) at the latter wavelength can only be accounted for by its production from the $^1B_{2u}$ state directly or indirectly. This being the case, means that the perturbing effect of the three t-butyl groups must be great enough to make orbital symmetry predictions, using the parent unsubstituted benzene as a model, meaningless.

2. Interconversion of Valence Bond Intermediates.

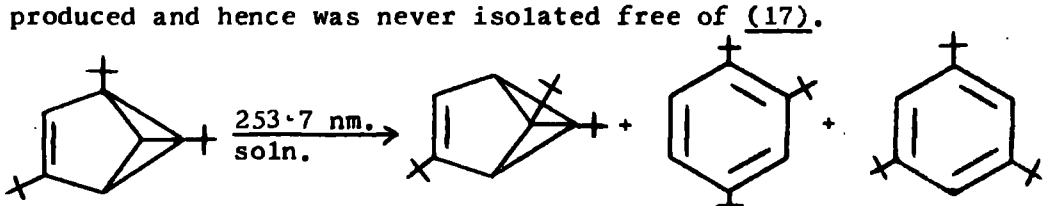
Further work on the system above by the same group of workers produced a very important result, namely that the photochemical interconversion of benzvalenes was possible, whereas thermal interconversion was not.[24]

1,2,4-Tri-t-butyl benzvalene (18) was shown to be produced as the only initial product in short irradiations of benzene (15) at 253·7 nm. with a quantum yield of 0·12.



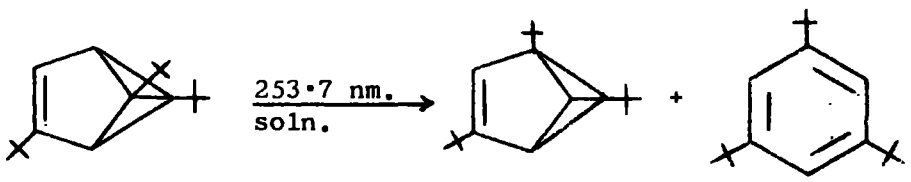
(15) (18)

It can be isomerised to benzvalene (17) more efficiently (ϕ=0·2) than it is produced and hence was never isolated free of (17).



(18) (17) (10) (15)

Benzvalene (18) can also be produced upon irradiation (253·7 nm.) of benzvalene (17) together with (15) although the quantum yield for this reaction

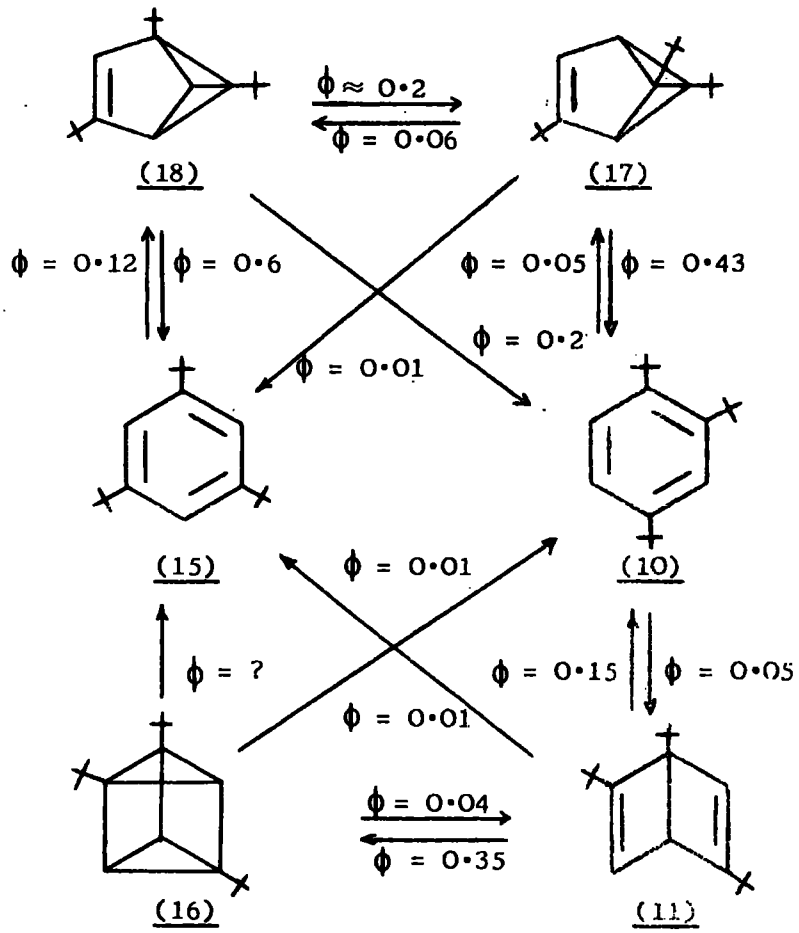


(17) (18) (15)

is much smaller (ϕ = 0·06) than for the reverse reaction.

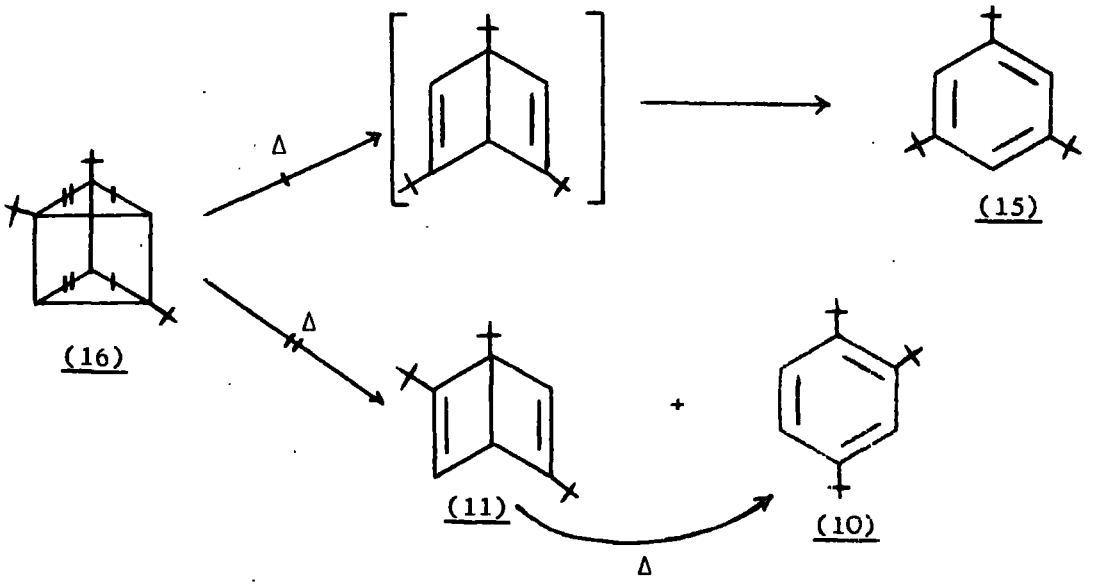
Prismane (16) and dewar (11) are also photochemically interconvertible but there is no evidence for interconversion of benzvalenes to dewars or prismanes.

A scheme can thus be drawn showing the possible photochemical transformations of this system together with quantum yields for each.



The irradiation of (11) gives (15) in a yield too large to have arisen from (10) initially formed, hence (11) must rearrange to (15) directly, or via a benzvalene or prismane intermediate. The latter seems most likely when one considers the quantum yield for the conversion of (11) to (16) is 0·35.

Thermally the benzvalenes (17) and (18) rearrange to the aromatics (10) and (15) respectively. The dewar (11) gives only (10) upon heating. In contrast prismane (16) gives a mixture of the two aromatics (10) and (15) and dewar (11). All three products can be readily explained, however, i.e.

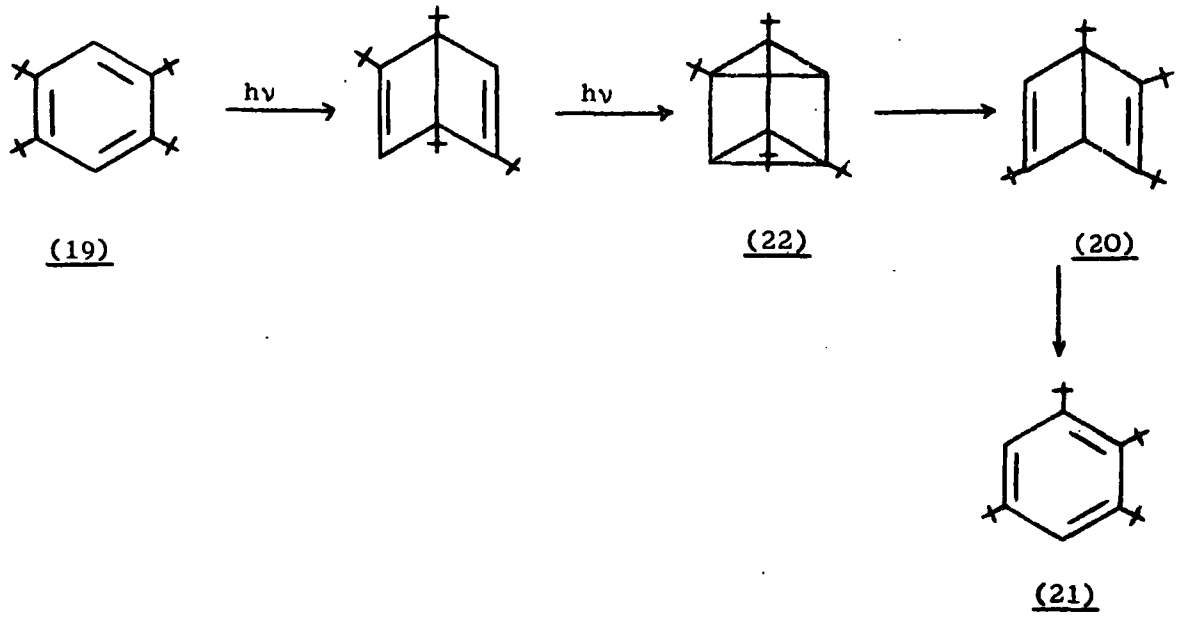


From the above results it can be concluded[21] that the isomerisation of (15) to (10) can only arise via benzvalene intermediates (18) and (17).

In the isomerisation of (10) to (15) the situation is by no means so clear. The production of dewar (11) is more efficient than that of benzvalene (17) (ϕ = 0·15 and ϕ = 0·05 respectively) and the production of prismane (16) is very much more efficient than the production of benzvalene (18) from (17). Since prismane (16) is the major product (64·8%) upon the irradiation of (10) (and (15)), and upon heating it converts to a mixture including (15), its intermediacy in the rearrangement and that of dewar (11) cannot be discounted.

D. Photoisomerisation of 1,2,4,5-Tetrakis-t-butyl Benzene (19).

The irradiation of (19)[25] in solution at 253·7 nm. gives a mixture of (20) and (21) and it is proposed, mainly upon the basis of (20) being isolated, that prismane (22) is responsible for the rearrangement of (19) to (21).



(19) (22) (20) (21)

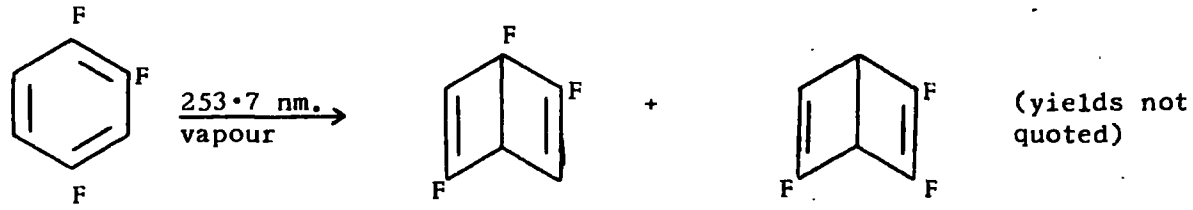
It was not established, however, whether the irradiation of (21) led to the production of (20), and hence one cannot rule out the possibility that a benzvalene intermediate could account for the rearrangement of (19) to (21), and that the (21) produced, then underwent rearrangement to the dewar benzene (20).

1.7. Photoisomerisation of Fluorinated Benzenes.

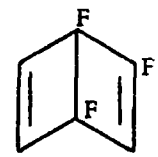
The effect of introducing fluorine or fluoroalkyl substituents into the benzene ring, in general, has the effect of making valence isomers more readily accessible than the hydrocarbon analogues. It will be seen that the reason for this is not simple and that a variety of factors come into play, and that their relative importance has not been established.

The irradiation of 1,2,4-trifluorobenzene (23) vapour at 253·7 nm. yields the dewars (24) and (25), but for some reason not (26), which has been

prepared from hexafluoro dewar benzene, and shown to be fairly stable.

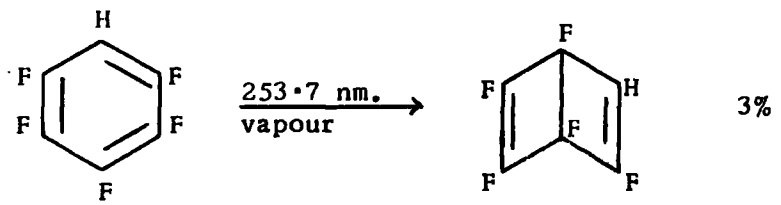


(23) (24) (25)

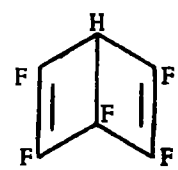


(26)

The irradiation of pentafluorobenzene (27)[27] vapour gives the dewar (28) in 3% yield but not the other possible dewar (29).

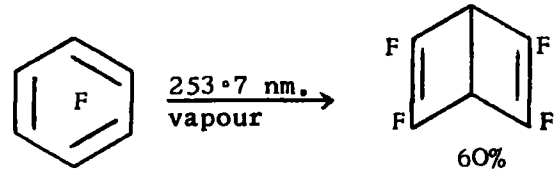


(27) (28)



(29)

With hexafluorobenzene (30) irradiation of its vapour[27,28,29] produces high yields of hexafluoro dewar benzene (31). Irradiation in the liquid phase and in solution leaves (30) unchanged.[28]

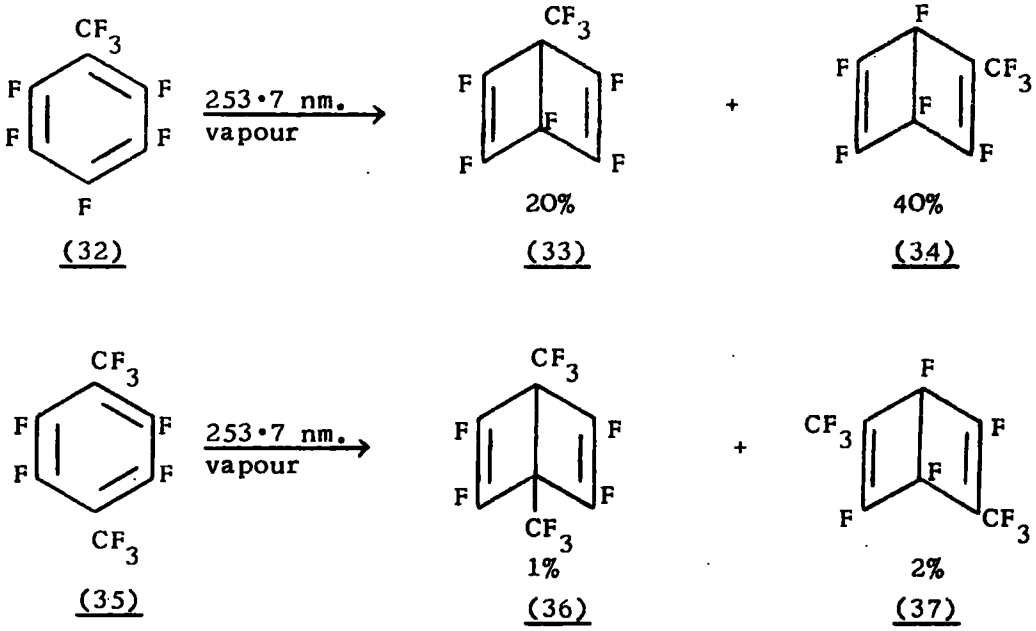


(30) (31)

In none of the three reactions above have any benzvalene or prismane valence isomers been detected. The absence of benzvalenes is in sharp contrast

with the parent hydrocarbon benzene in which it is the only isomer isolated upon irradiation of 253·7 nm.

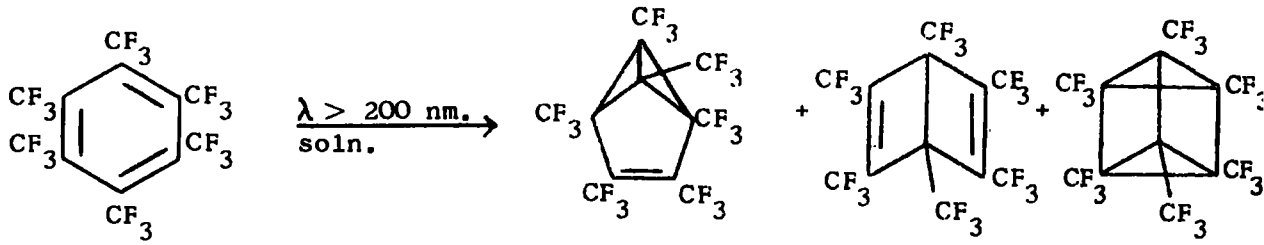
Perfluorotoluene (32) yields a product containing 20% (33) and 40% (34),[27] whereas perfluoro-1,4-dimethyl benzene (35) only yields a product containing 1% (36) and 2% (37)[27] upon irradiation.



It is indicated that the di(trifluoromethyl)dewars (36) and (37) are thermally more stable than the monotrifluoromethyl dewars (33) and (34), hence the stability of the valence isomer is not the dominant factor in these productions.

On comparison of the photochemistry of perfluoro-1,4-dimethyl benzene (35) with para-xylene (14) it is seen that there is a striking difference. In the latter case rearrangement occurs and m-xylene is formed but no valence isomers have been detected. In the perfluoro compound no rearranged aromatic product is observed but some valence isomers are formed and have been isolated.

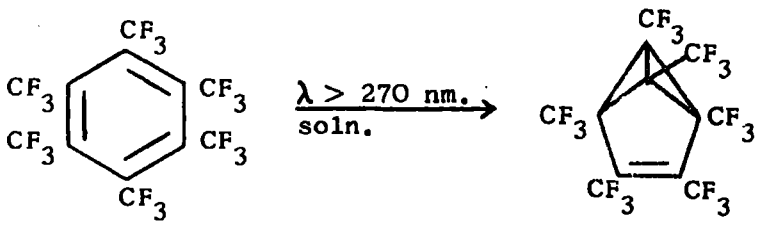
With hexakis(trifluoromethyl)benzene (38)[30,31,32] all three valence isomers mentioned so far are isolated, and (38) is seen to behave very similarly to the parent hydrocarbon (1) under irradiation.



(38) (39) (40) (41)

The proportions of the three valence isomers produced is highly dependent upon the time of irradiation. Initially, the benzvalene (39) and the dewar (40) are formed in a ratio of ca. 5:1 (after ca. 7 hrs.), and the optimum amount of dewar (40) (> 50%) is obtained after ca. 40 hrs. of irradiation. A photostationary state approaches 100% prismane (41).[32]

If, however, (38) is irradiated with light of wavelength greater than 270 nm. only benzvalene (39) is formed, and prolonged irradiation yields almost a quantitative conversion.



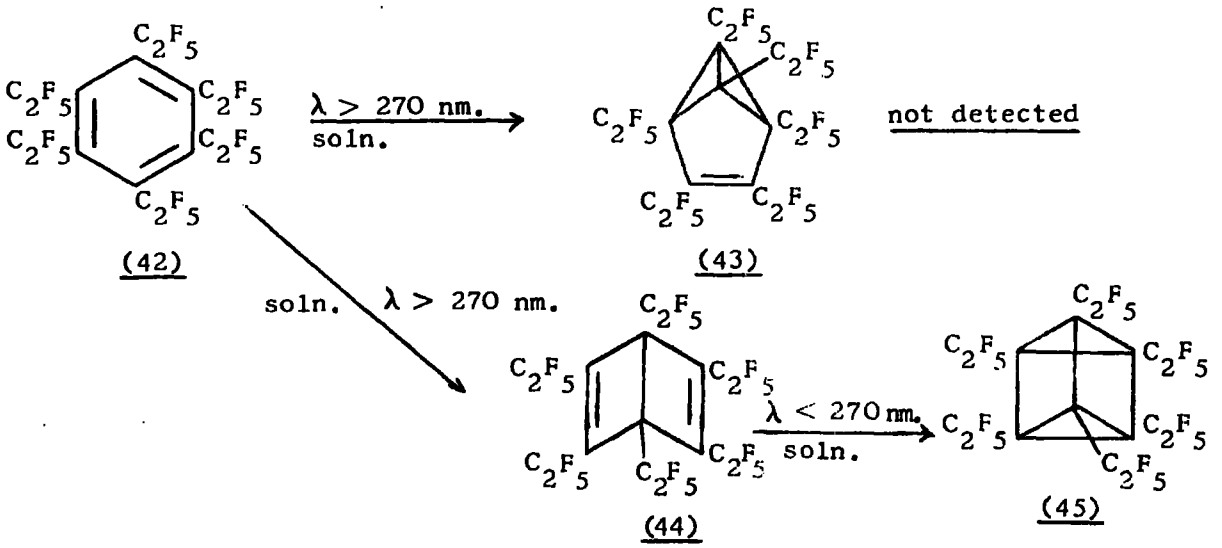
(38) (39)

Upon irradiation of the individual valence isomers at $\lambda > 200$ nm. it is found that benzvalene (39) is largely converted to benzene (38), the dewar (40) to benzene (38) and prismane (39) (in approximately equal amounts), and the prismane (39) is unaffected.

Hexakis(trifluoromethyl)benzene (38) absorbs in the u.v. at 212 (ϵ 10,150) and 283 (ϵ 140) and hence irradiation at $\lambda > 270$ nm. must cause population of the $^1B_{2u}$ state, just as irradiation of benzene (1) at 253·7 nm. does. The isolation of only benzvalene (39) by irradiation at $\lambda > 270$ nm. is analogous to the isolation of benzvalene (4) by irradiation of benzene (1) at 253·7 nm. Another similarity is that dewar (40) is formed when $\lambda < 270$ nm. when the $^1B_{1u}$ state is populated, just as in the irradiation of benzene (1) at wavelengths

$\lambda < 210$ nm. However prismane (6) has never been detected in the irradiation of (1) whereas here prismane (41) is the major product of irradiation at $\lambda > 200$ nm. Similar results to the above were obtained upon irradiation of the vapour of (38).[31]

Hexakis(pentafluoroethyl)benzene (42)[30,32] does not yield a benzvalene (43) intermediate when its $^1B_{2u}$ state is populated but instead the dewar (44) is produced exclusively.



(42) (43) (44) (45)

Irradiation of (42) or (44) at wavelengths greater than 200 nm. causes the prismane (45) to be produced in high yield (together with small amounts of (44)).

The valence isomers (39), (40), (41), (44), and (45) were all found to be thermally very stable and half lives at 170°C range from 135 hrs. for dewar (40) to 9 hrs. for benzvalene (39). The following order of stabilities has been determined (40) > (41) > (45) > (44) > (39).[32]

The increased stability of the above valence isomers as compared with hydrocarbon ones has been explained to be due to, at least in part, to the increased steric strain in the parent aromatic compounds. This does not, however, explain the order of stabilities, i.e. (40) is more stable than (44) and (41) is more stable than (45). This latter information would seem to suggest that the increased bulk of the pentafluoroethyl group as compared with the trifluoromethyl group results in a net destabilisation of the valence

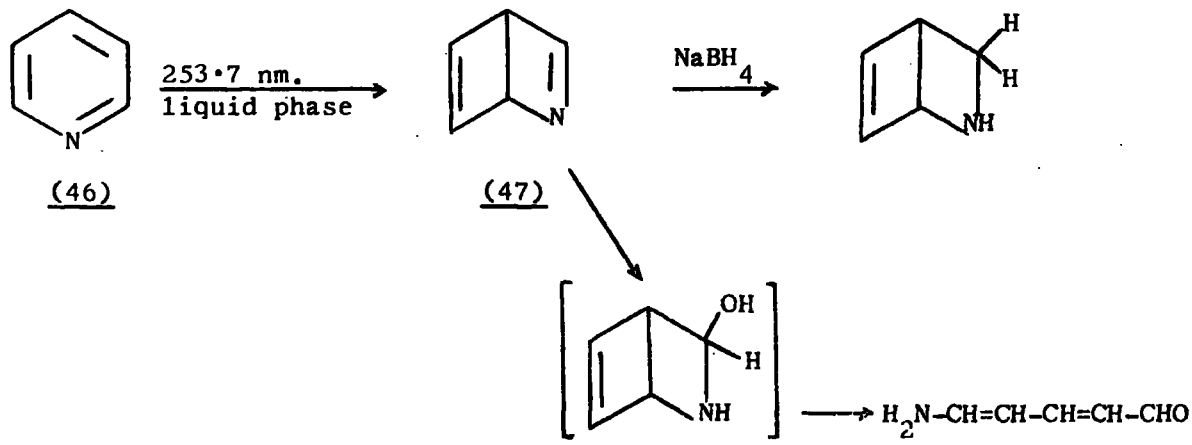
isomers; although there may be an optimum size for the substituents. The absence of (43) from the photo-product of (42) may be due to its limited stability, although this seems unlikely or due to its immediate destruction upon formation by reabsorption.

1.8. Photoisomerisations of Aza-aromatics.

The photochemistry of a number of aza-aromatic systems has been studied.

A. The Pyridine System.

Pyridine (46) itself has been photolysed in the liquid phase[33] and yields an unstable dewar (47) which has a half-life of 2 minutes at room temperature.



(46) (47)

The structure of (47) has been confirmed by reduction and hydrolysis as shown above.

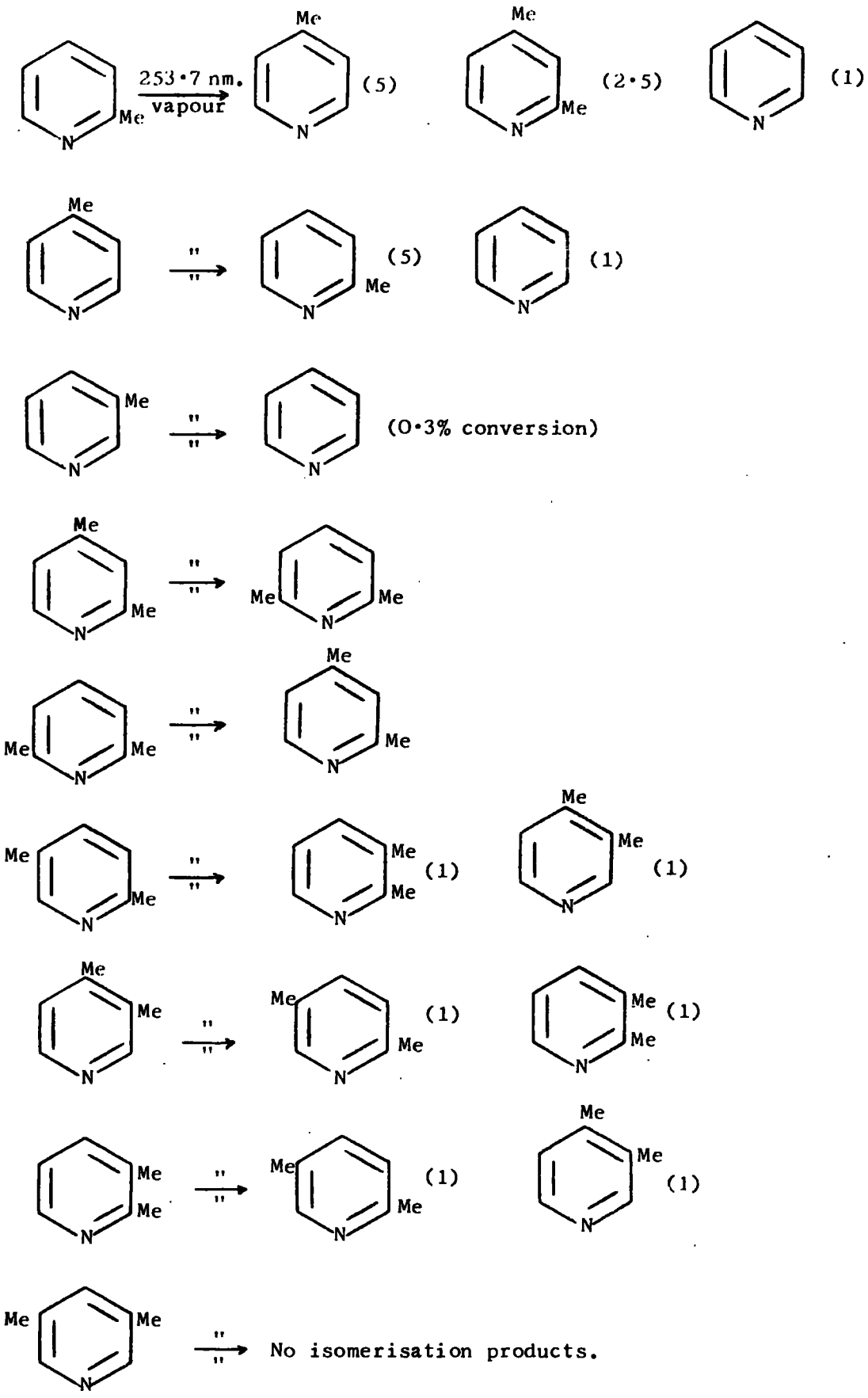
Picolines (methyl pyridines) and lutidines (dimethyl pyridines) have been isomerised by irradiation of their vapours at 253·7 nm.[34] No valence isomers were detected in these studies. Table 1 below summarises the results.

Only ca. 1-2% of the starting material was isomerised and the relative ratio of compounds formed is given in brackets.

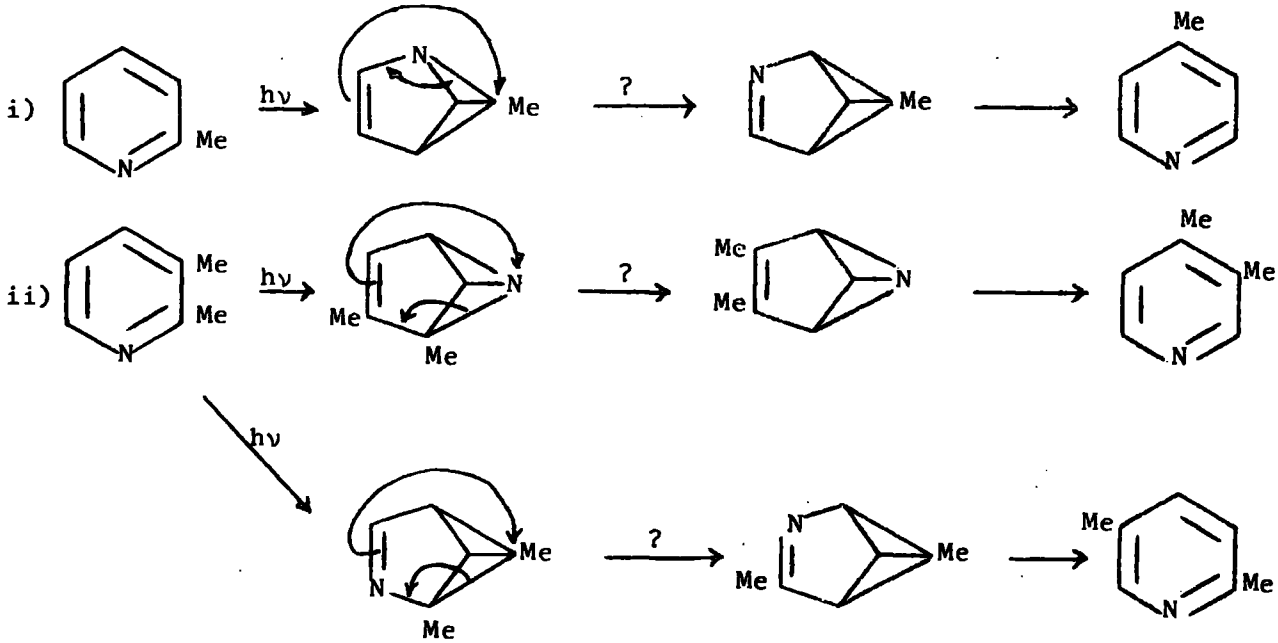
The formation of 2,4-lutidine from 2-picoline and of pyridine from all three picolines suggests that the photoisomerisation may proceed by a methylation-demethylation process, however, if this was the case one would expect the formation of lutidines from the 3- and 4-picolines. The rearrangement

TABLE 1

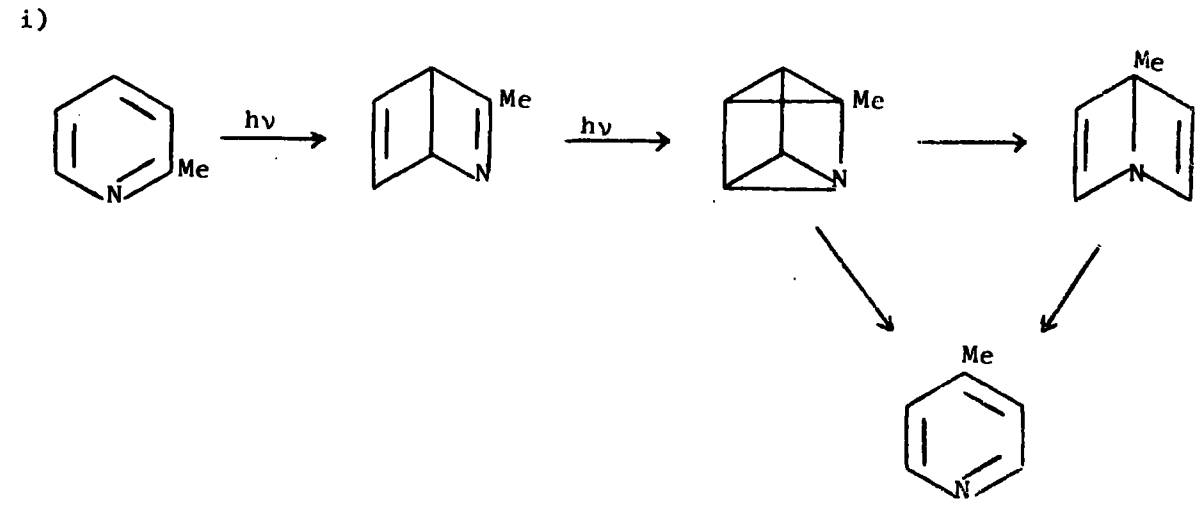
Photoisomerisation of Mono-methyl and Dimethyl Pyridines



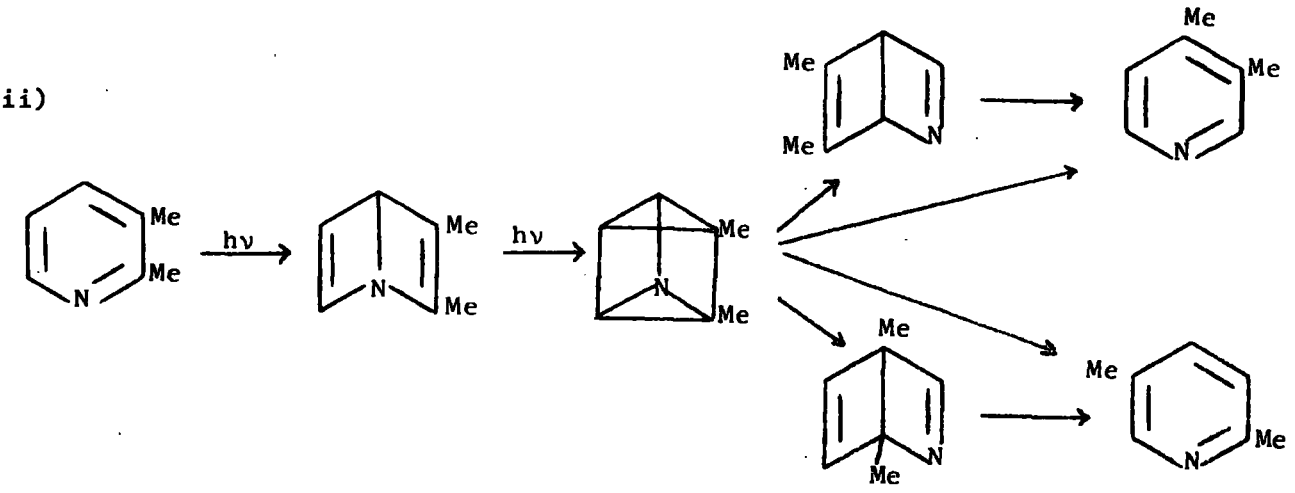
products can be better accounted for by the intermediacy of valence bond isomers. Either aza-benzvalene or aza-prismane intermediates can account for the observed products which arise as a result of 1,3-shifts, however, the former requires the rearrangement of initially formed aza-benzvalene before rearomatisation can occur to give the correct product, e.g.



With aza-prismanes as the valence isomers responsible for the isomerisations no rearrangement of the intermediate is necessary to obtain the correct isomeric product, i.e.

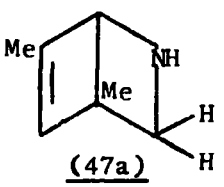


ii)

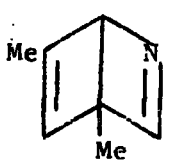


This however assumes that the aza-prismanes are formed directly without the intermediacy of aza-dewars, which is not wholly justifiable when one considers the evidence for the intermediacy of dewars in the formation of prismanes ((11) → (16), (40) → (41), and (44) → (45)). Therefore, even the latter process involves two intermediates if not three, i.e. the initially formed aza-dewar, the aza-prismane formed from it and the second aza-dewar formed from the aza-prismane.

The photolysis of 3,5-dimethyl pyridine[33] in aqueous sodium borohydride solution leads to the dihydro aza-dewar (47a) below, showing that the dewar (47b) is formed and indicating that the rearrangements may occur via the aza-prismane intermediate.

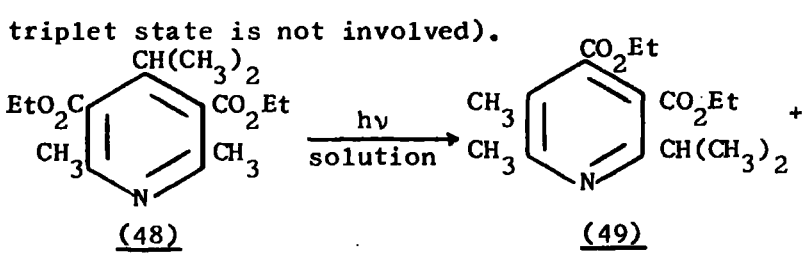


(47a)



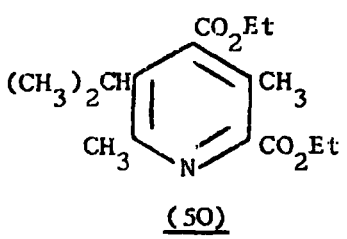
(47b)

The irradiation of the penta-substituted pyridine (48) yields three different isomeric penta-substituted pyridines (49), (50), and (51).[35] (A triplet state is not involved).

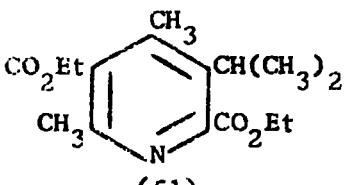


(48)

(49)



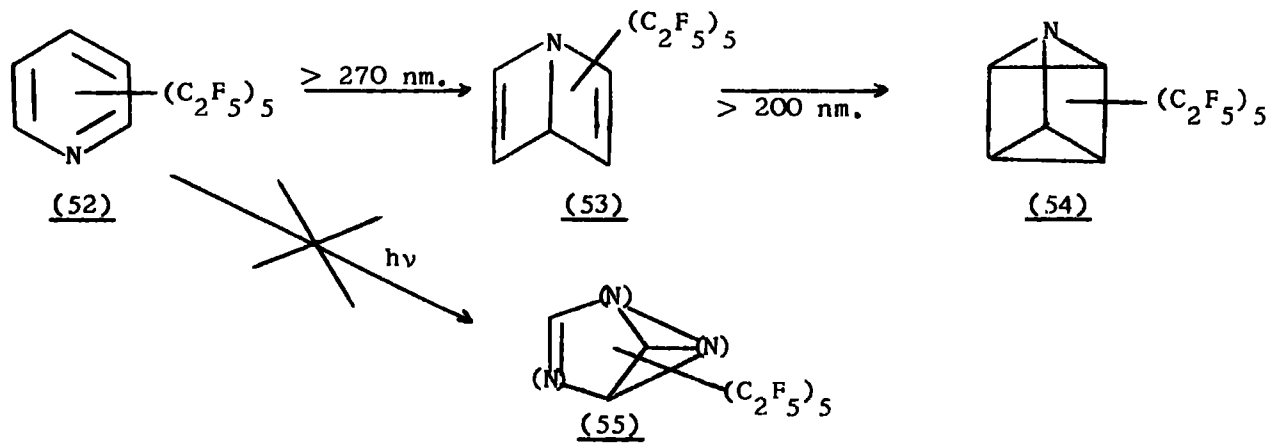
(50)



(51)

Aza-benzvalene intermediates cannot account for the observed products whereas aza-prismane intermediates can. This experiment has bearing upon the previous pyridine isomerisations, in that the aza-prismane intermediate seems more likely for them.

The irradiation of pentakis(pentafluoroethyl)pyridine[36] (52) gives the aza-dewar (53) and the aza-prismane (54). No aza-benzvalene (55) was detected and hence here there is a similarity to the photochemistry of hexakis(pentafluoroethyl)benzene (42) which also yielded a dewar and a prismane but no benzvalene.

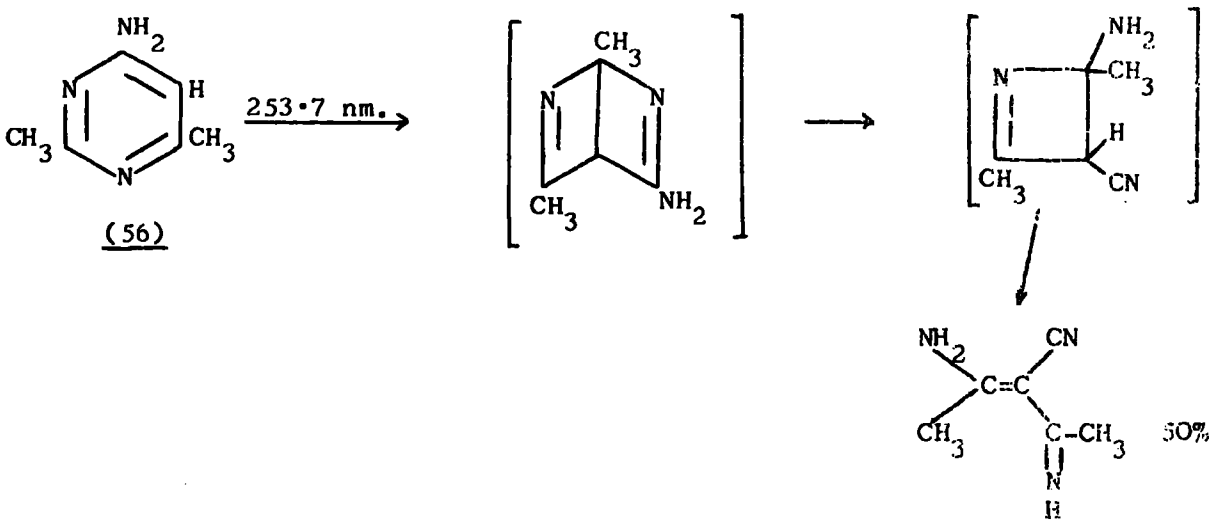


(52) (53) (54) (55)

B. Diaza-Aromatics.

1. Introduction.

The intermediacy of a valence bond isomer in a photochemical of a diaza-aromatic was first invoked[37] to explain the product upon the irradiation of the substituted pyrimidine (56).

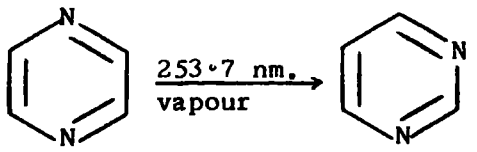


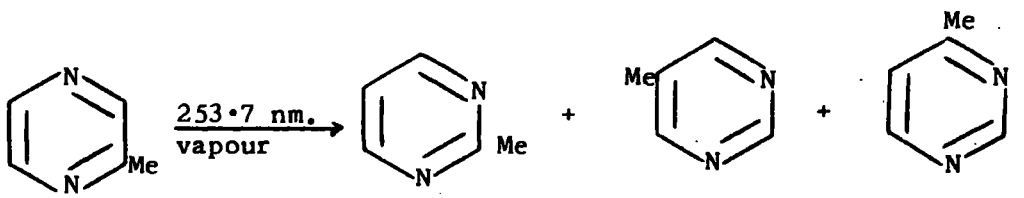
(56)

2. Photoisomerisation of Pyrazine.

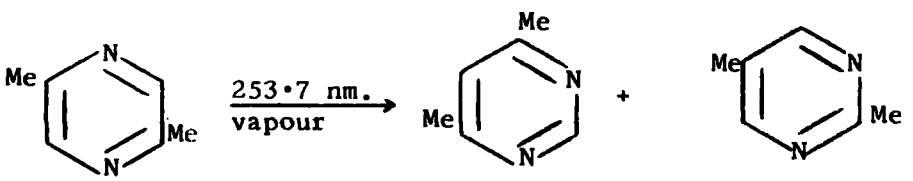
The study of the photoisomerisation of pyrazine to pyrimidine is the only such study in the field of diaza-aromatics.[38] Methyl substituted pyrazines were also photoisomerised and these led to specific substituted pyrimidines.

Although both pyrazine and its methyl derivatives have $n \rightarrow \pi^*$ bands at ca. 313 nm. isomerisation could not be achieved by irradiation at this wavelength. It could be achieved by irradiation of the lowest $\pi \rightarrow \pi^*$ band at ca. 253·7 nm.

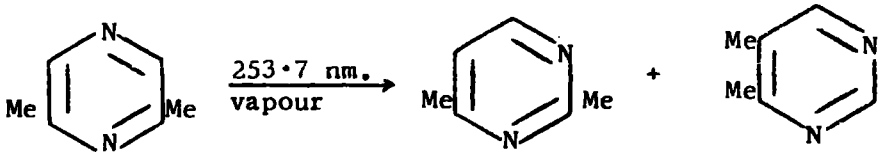




claimed, not isolated

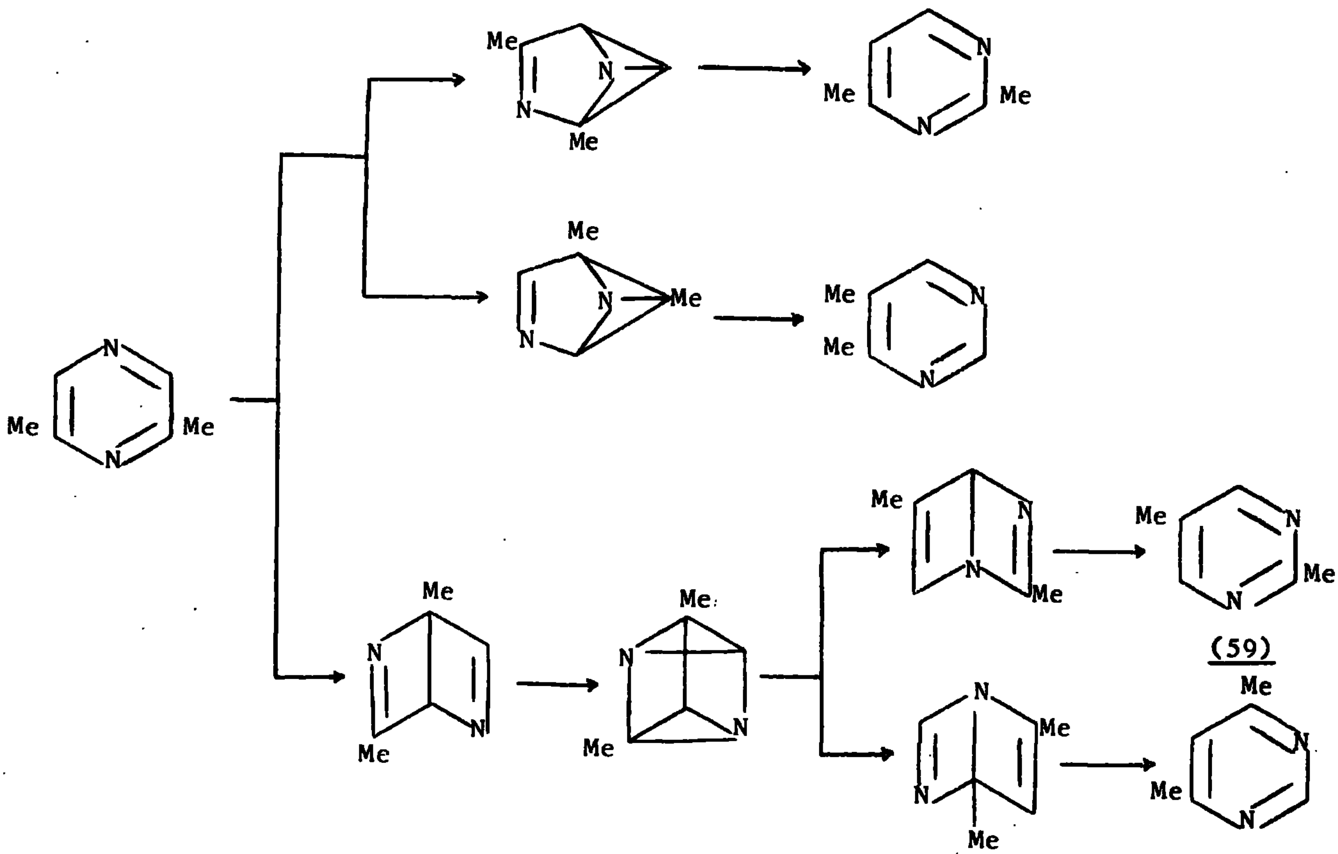


(57) (58) (59)



(60) (61) (62)

The result of the photoisomerisation of the doubly labelled pyrazines is unambiguous, because as can be seen below the correct products cannot be obtained as a result of a diaza-prismane intermediate, but can via a benzvalene, e.g. for the 2,6-dimethyl pyrazine.



(59)

The products that are obtained from the photolysis of <u>(60)</u> are <u>(61)</u> and <u>(62)</u> whereas the products via a diaza-prismane intermediate are the same as those that arise from the photolysis of <u>(57).</u>

1.9. Orbital and State Correlation Diagrams for the Transformation of Benzene to its Valence Isomers.[10]

A. Benzene-Dewar Benzene Transformation.

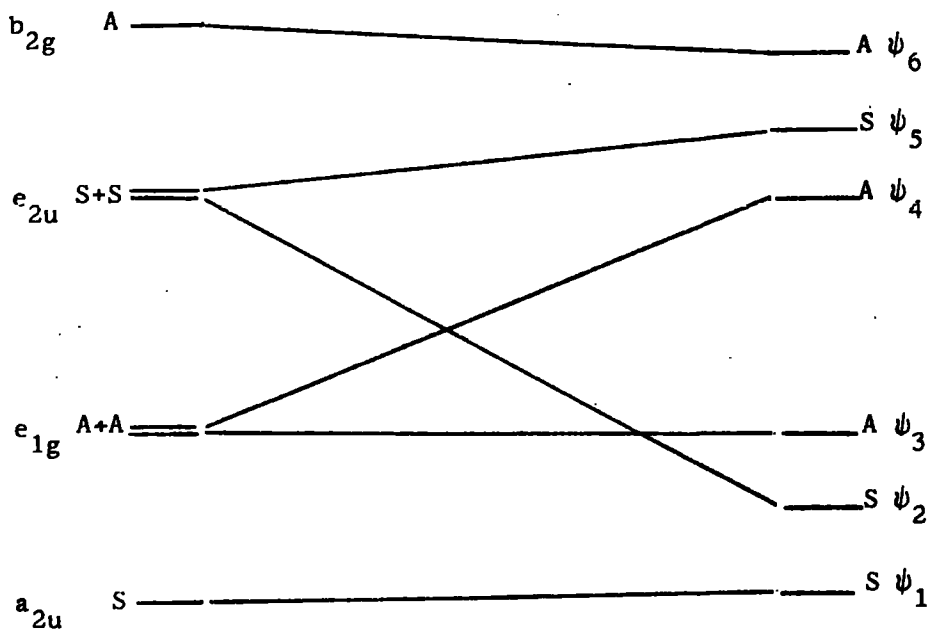
Since dewar benzene is not produced by population of the $^1B_{2u}$ state but is by the population of the $^1B_{1u}$ state, the state correlation diagram should show that production of dewar benzene from the $^1B_{2u}$ state is symmetry forbidden but allowed from the $^1B_{1u}$ state. The transition state for this transformation belongs to the C_s point group.

$\psi^*_6\sigma^*_{14}$	A
$\psi^*_5\pi^*_{23} + \pi^*_{56}$	S
$\psi^*_4\pi^*_{23} - \pi^*_{56}$	A
$\psi_3\pi_{23} - \pi_{56}$	A
$\psi_2\pi_{23} + \pi_{56}$	S
$\psi_1\sigma_{14}$	S

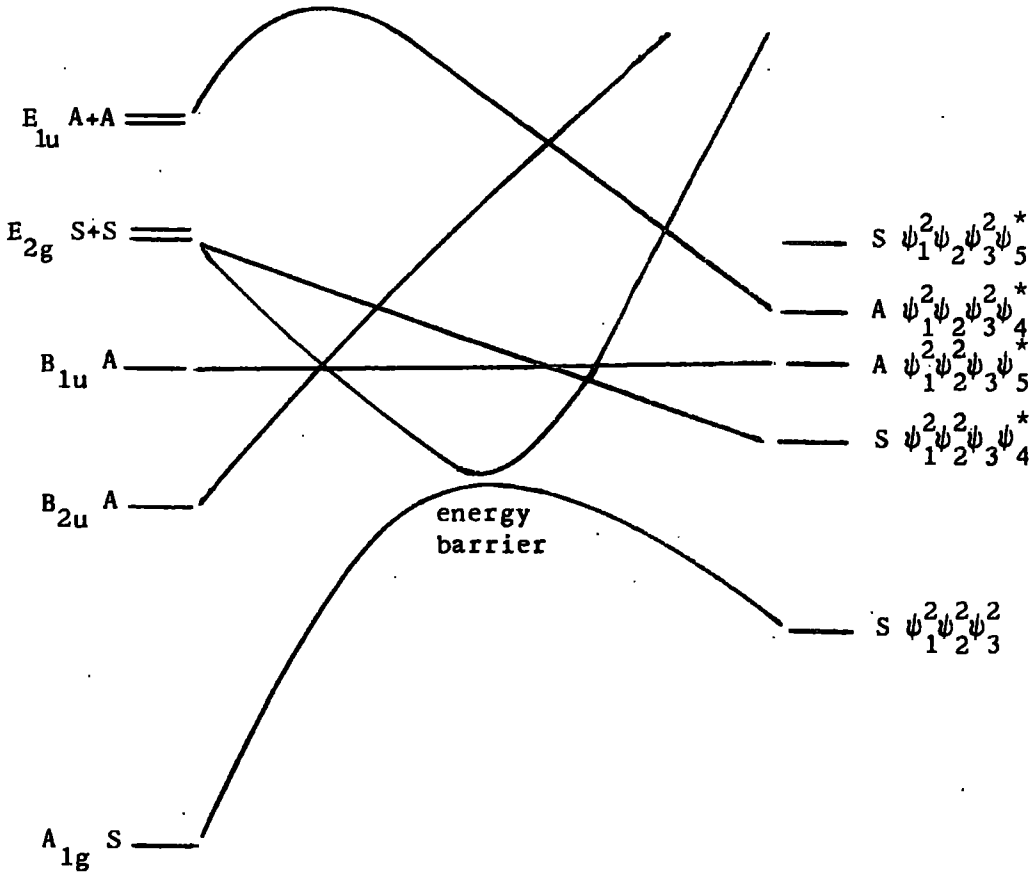
Symmetrised M.O.'s of Dewar Benzene

$\psi_1^2\psi_2\psi_3^2\psi^*_5$	S
$\psi_1^2\psi_2\psi_3^2\psi^*_4$	A
$\psi_1^2\psi_2^2\psi_3\psi^*_5$	A
$\psi_1^2\psi_2^2\psi_3\psi^*_4$	S
$\psi_1^2\psi_2^2\psi_3^2$	S

Electronic Configurations of Dewar Benzene



Orbital Correlation Diagram for the Transformation of Benzene to Dewar Benzene.



State Correlation Diagram for the Transformation of Benzene to Dewar Benzene.

Hence we see that indeed the formation of dewar benzene from the first excited state of benzene, the $^1B_{2u}$ state, is forbidden but that its formation from the $^1B_{1u}$ is allowed.

B. Benzene-Benzvalene Transformation.

The concerted rearrangement of benzene (1) to benzvalene (4) from the $^1B_{2u}$ state is symmetry forbidden. The treatment given in reference 89 being erroneous.

If, however, one first considers the $^1B_{2u}$ state of benzene (1) rearranging to prefulvene (5) (a symmetry allowed process[6,89,90]) then this can subsequently lead to benzvalene (4) by radical recombination.

The formation of benzvalene (4) from the $^1B_{2u}$ state could therefore, be considered to be formed via prefulvene (5) in an overall non-concerted process.

C. Benzene-Prismane Transformation.

Orbital and state correlation diagrams for the transformation of benzene to prismane can be similarly constructed and shows that prismane cannot be produced from the first excited state ($^1B_{2u}$) of benzene (see Ref. 10).

D. Stability of Valence Bond Isomers.

The valence bond isomers isolated so far, have in general to be heated in order to rearomatise, e.g. prismane (6) has a half-life of 11 hrs. at 90°C. Hence, there is quite a high activation energy for rearomatisation, in spite of there being in the order of 70 Kcals. of excess energy relative to the aromatic benzene. This activation energy can be explained by orbital symmetry rules, which predict a considerable energy barrier for the direct transformation.

CHAPTER 2

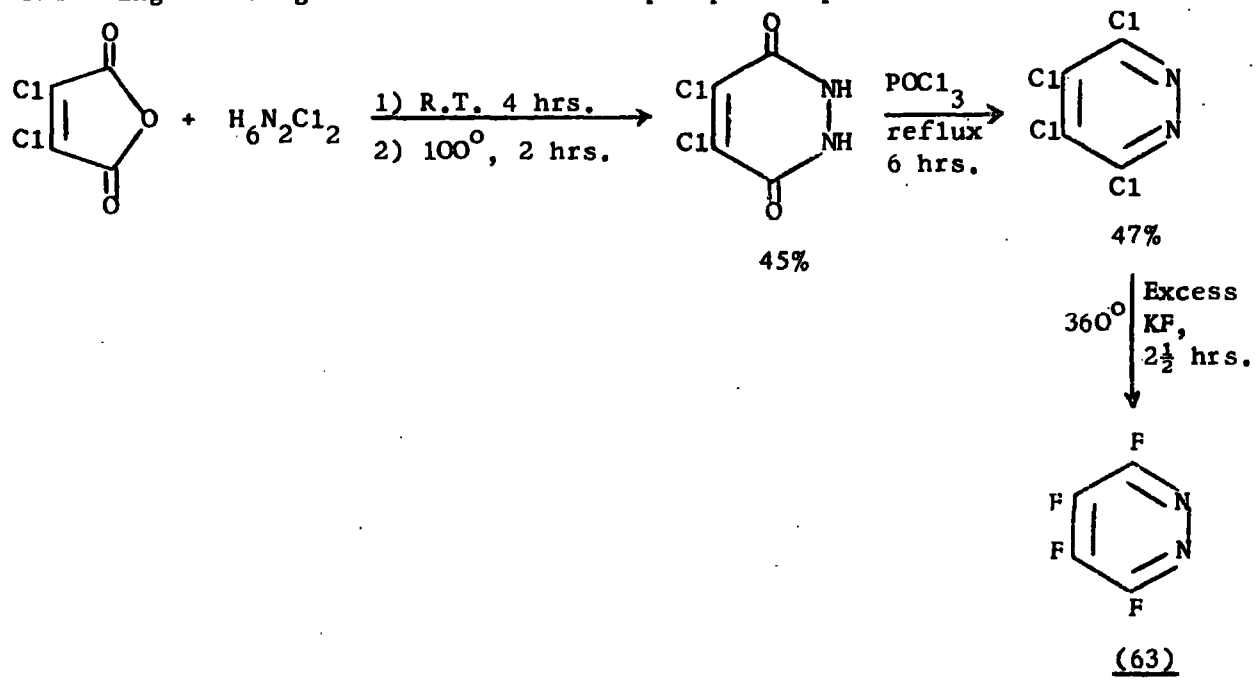
Synthesis of Polyfluoroalkylpyridazines

2.1. Introduction.

This chapter deals with the synthesis of highly fluorinated substituted pyridazines, for photolysis reactions described in Chapter 3, and also with thermolysis reactions.

2.2. Tetrafluoropyridazine.

Tetrafluoropyridazine (63)[39] can be prepared by the addition of a hydrazine salt, to dichloromaleic anhydride, chlorination of the resulting product by phosphorus oxychloride, followed by halogen exchange of tetrachloropyridazine with potassium fluoride without solvent, in an autoclave. This differs only slightly from the published[39] preparation, in that dichloromaleic anhydride is used instead of maleic anhydride itself, thus eliminating an autogenous reaction with phosphorus pentachloride.



The tetrafluoropyridazine (63) used in the original work to be described was prepared by technical staff, upon request, since it cannot be stored because autocatalytic hydrolysis occurs rapidly. Tetrafluoro-

pyridazine (63) was supplied in a crude state after vacuum transference from the halogen exchange autoclave. It generally contained impurities, ca. 5%, which were mainly chlorofluoropyridazines and some tetrafluoropyrimidine.[40] After addition of magnesium carbonate to remove any HF present, phosphorus pentoxide was added to remove moisture. Purification was by slow vacuum transference, hence leaving behind the vast majority of the chlorofluoropyridazines which are very much less volatile than tetrafluoropyridazine (63).

2.3. Preparation of Substituted Fluoropyridazines.

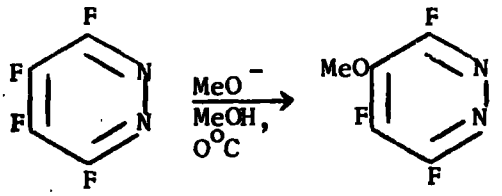
A. Introduction.

Tetrafluoropyridazine (63)[39] is highly susceptible to nucleophilic attack which occurs preferentially on the positions para to the nitrogens. This is so because the para nitrogen stabilises a negative charge much more effectively than a para carbon atom.

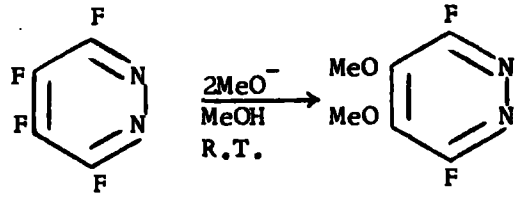
A variety of substituents can be introduced into the ring in the 4- and 5-positions,[39,41] although, as will be seen later, in general it is difficult to obtain the mono-perfluoroalkyl derivatives directly.[41] Under acidic conditions (63) is substituted preferentially in the 3- and 6-positions.[42]

B. Substitution by Methoxide and Chloride Ions.

With substitution by methoxide ion,[39] the reaction can be moderated to give good yields of 4-methoxy-3,5,6-trifluoropyridazine (64). This is presumably because the methoxyl group deactivates the ring to further attack.

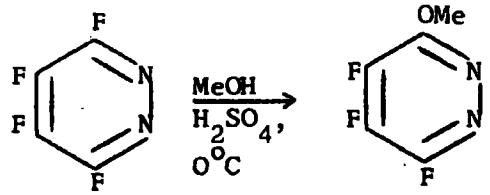


(63) (64)

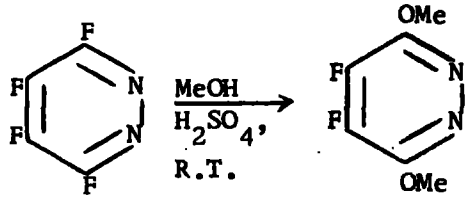


(63) (65)

At higher temperatures, however, the dimethoxy derivative (65) is produced.[39] By reacting tetrafluoropyridazine (63) with methanol in an acidic medium substitution occurs at the 3- and 6-positions.[42]



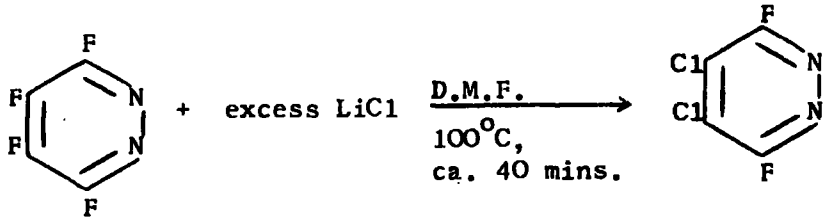
(63) (66)



(63) (67)

The methoxy pyridazines (64), (65), (66) and (67) were all prepared using the conditions described in literature.[39,42]

3,6-Difluoro-4,5-dichloropyridazine (68) was prepared in good yield by reacting (63) with lithium chloride for ca. 40 mins. in dimethyl-formamide (D.M.F.).[43]



(63) (68)

The 3-mono- and 3,6-di-chlorofluoropyridazines can be prepared by reaction of (63) with ethereal HCl, but only as components of mixtures,

containing many chlorofluoropyridazines, which proved to be very difficult to separate.[44]

C. Polyfluoroalkylation of Tetrafluoropyridazine.

1. Introduction.

Nucleophilic substitution in activated fluoroaromatic compounds with polyfluoroalkyl anions generated from fluoride ion and polyfluoroalkenes has been found to be very useful in the preparation of polyfluoroalkyl substituted aryl compounds. This type of reaction can be seen to be complementary to the Friedel-Crafts type of reaction in hydrocarbon chemistry.

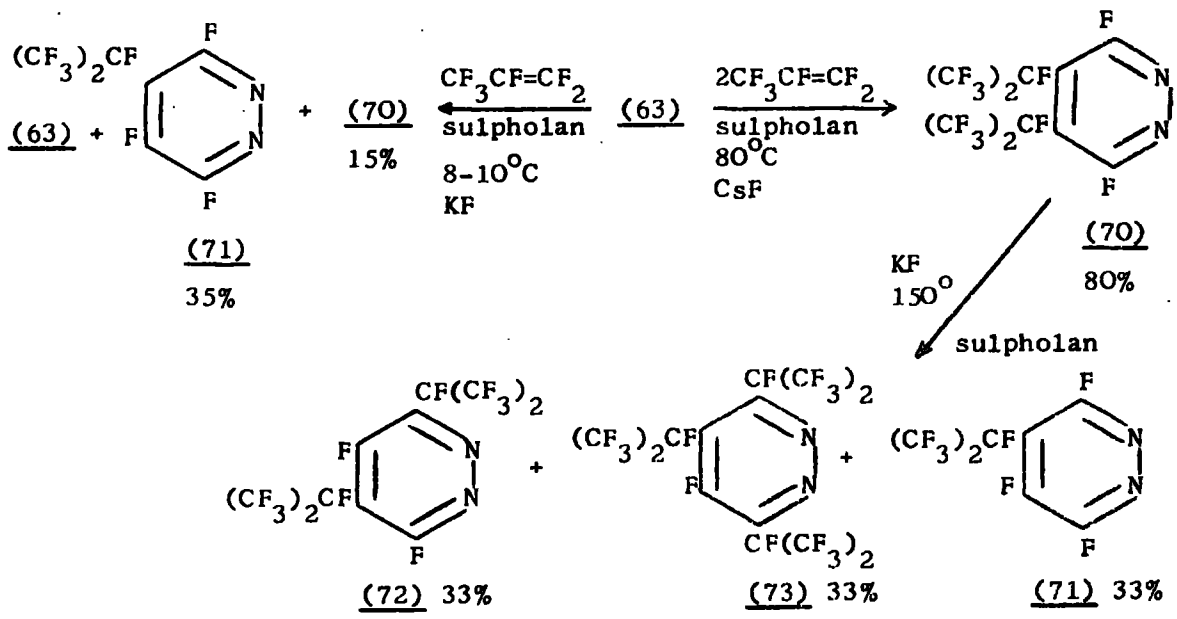
$$F^- + F_2C{=}C \longrightarrow CF_3\text{-}\bar{C}\text{-} \xrightarrow{ArF} CF_3\text{-}C\text{-}Ar + F^-$$

$$H^+ + H_2C{=}C \longrightarrow CH_3\text{-}\overset{+}{C}\text{-} \xrightarrow{ArH} CH_3\text{-}C\text{-}Ar + H^+$$

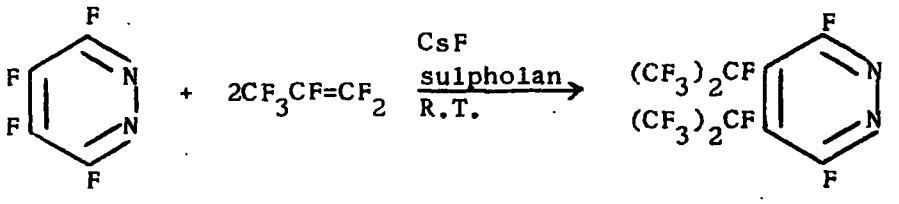
CsF has been shown to be the most effective initiating agent in promoting this type of reaction.[45] The choice of aprotic solvent is less clear cut, sulpholan, acetonitrile and the glymes have been used. Sulpholan was found by the author to give the highest yields of selected products, in the systems studied.

2. Substitution by Hexafluoropropene.

The reaction between the heptafluoroisopropyl anion generated from hexafluoropropene (69) and CsF, and tetrafluoropyridazine (63) has been studied under autogenous conditions.[41]

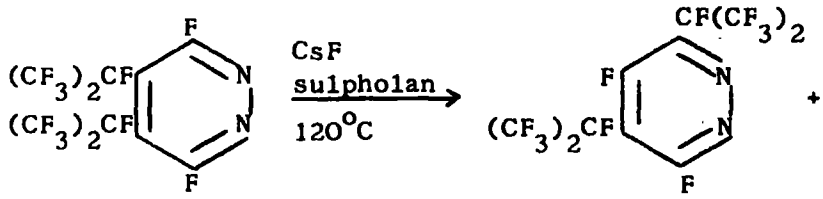


It has been found, however, that the results obtained under autogenous conditions are not reproducible, and that (70) can be better prepared in high yield, by reacting (63) with (69) in the presence of CsF at room temperature, and at ca. atmospheric pressure, in a system well described elsewhere.[46]

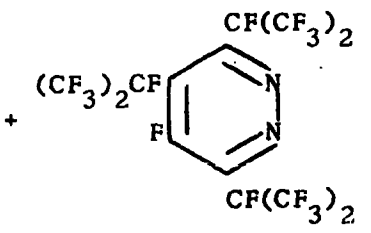


(63) (70)

Perfluoro-3,5-bis-isopropylpyridazine (72) has also been prepared in high yield, (ca. 76%) by rearrangement of (70) in the presence of fluoride ion at atmospheric pressure.

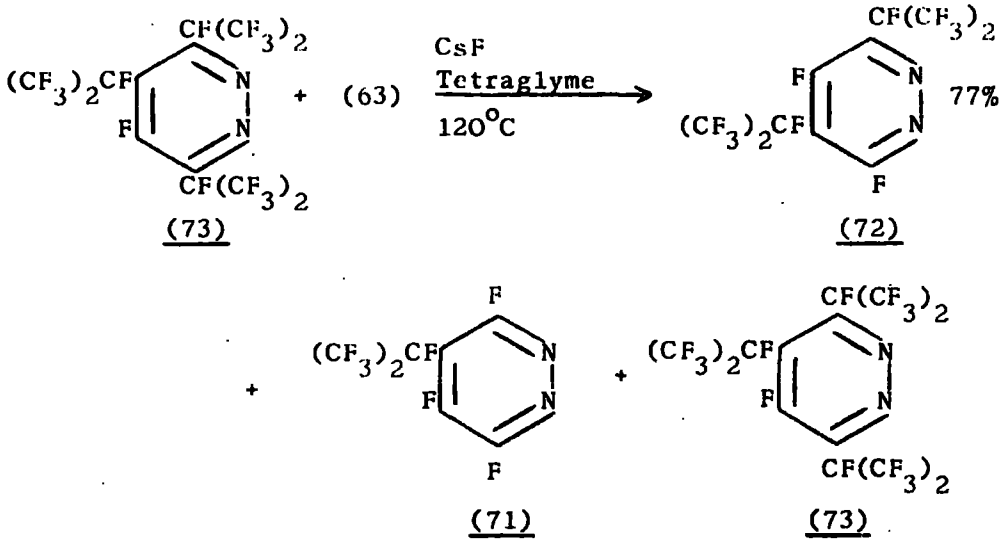


(70) (72) 81% (71) 4%



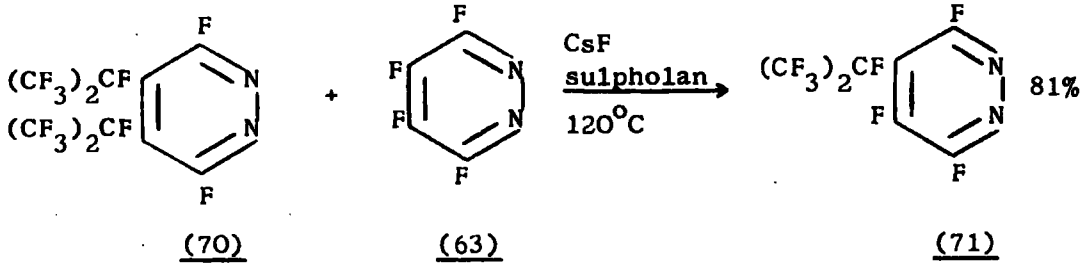
(73) 14%

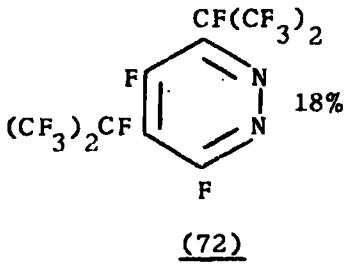
Perfluoro-3,5-bis-isopropylpyridazine (72) can also be prepared in good yield, by displacement of the 3-heptafluoroisopropyl group by fluoride ion from perfluoro-3,4,6-tris-isopropylpyridazine (73), in the presence of tetrafluoropyridazine (63).



It was thought, however, that the 4-heptafluoroisopropyl group would be displaced to give the 3,6-derivative.

A synthetic route to perfluoro-4-isopropylpyridazine (71) has also been developed. Upon heating (70), in the presence of (63) and fluoride ion at atmospheric pressure, (71) is produced in high yield (ca. 81% yield) free from (63) and (70) from which it is difficult to separate.

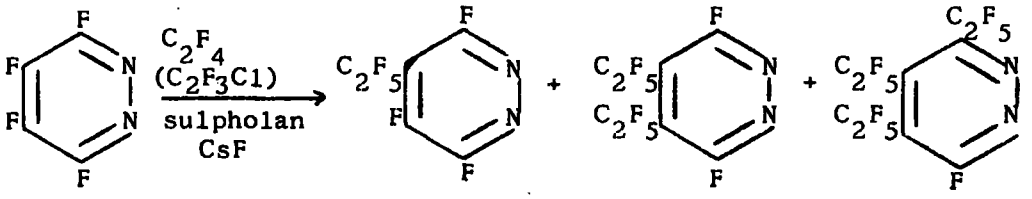




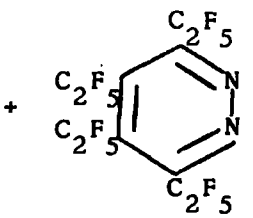
Hence (70), (71) and (72) can all be prepared in high yield at atmospheric pressure, and hence in fairly large quantities (up to 60 g. in one reaction).

3. Substitution by Tetrafluoroethylene and Trifluorochloroethylene.

The reaction between tetrafluoroethylene or trifluorochloroethylene and tetrafluoropyridazine was studied by Dr. M.Y. Gribble,[47,48] and shown to always give mixtures of 4-mono-, 4,5-di-, 3,4,5-tri- and tetraethyl-pyridazines in low yield, together with high molecular weight oils.



(63) (74) (75) (76)



(77) + (63)

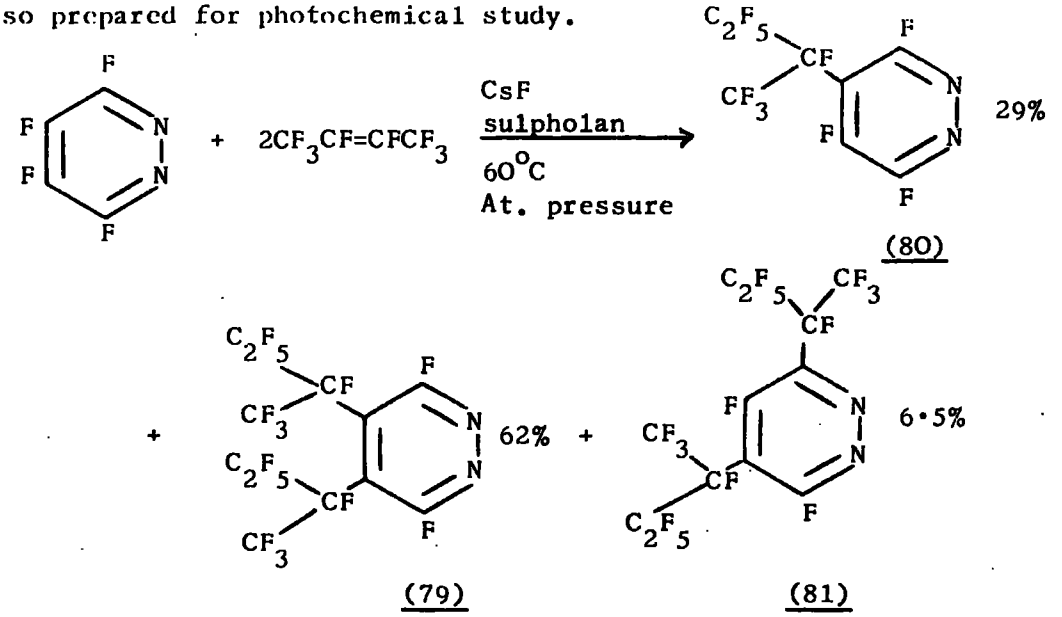
Separation of the products was found to be difficult, but could be achieved on a large scale, by distillation followed by preparative g.l.c. Small quantities of the individual isomers could be isolated by preparative g.l.c. alone but this involved a lot of work. Perfluoro-4,5-bis-ethyl-pyridazine (75) could not be rearranged to the 3,5-isomer upon heating with fluoride ion, and hence (74) cannot be produced by heating (75) in the presence of fluoride ion and (63).

Samples of (74), (75), and (76) used in photolysis experiments to be described in Chapter 3 were donated by Drs. M.Y. Gribble and M. Clark.

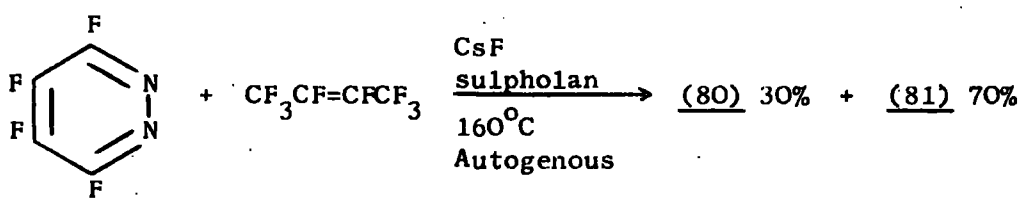
4. Substitution by Octafluoro-but-2-ene.

The reaction between octafluoro-but-2-ene (78) and tetrafluoro-pyridazine (63) has also been studied at these laboratories.[49,50] The results show that this system is very similar to the hexafluoropropene (69), tetrafluoropyridazine (63) system, and this is to be expected since both

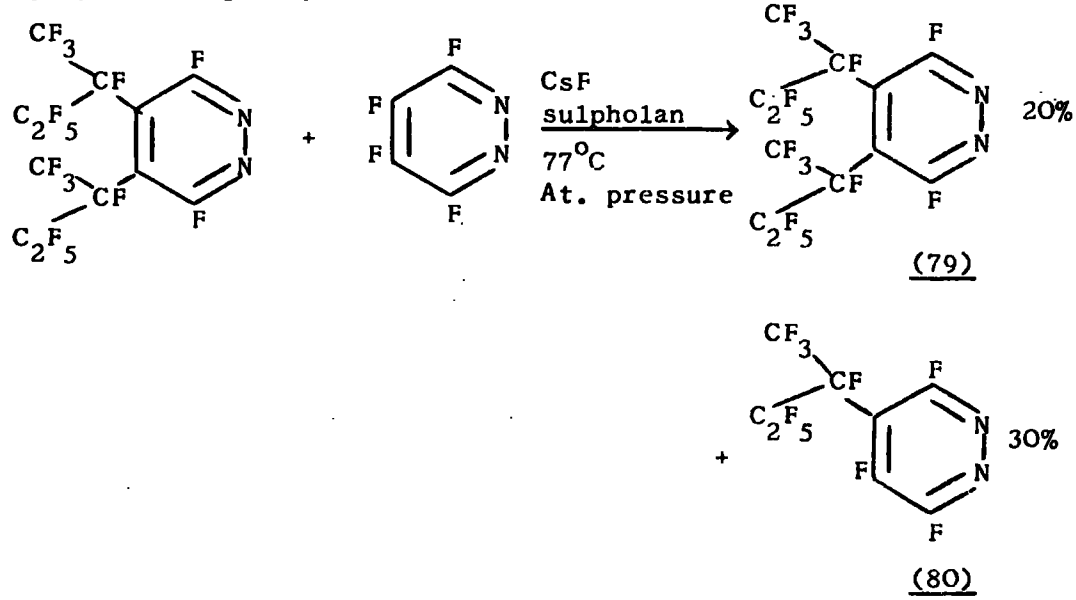
the alkenes (78) and (69) yield secondary anions with fluoride ion. The 4,5-di-substituted derivative (79) is formed in good yield at 60°C,[50] and was so prepared for photochemical study.



Perfluoro-4,5-bis-sec.butylpyridazine (79) suffers rearrangement at higher temperatures (ca. 150°C) to give the 3,5-di-substituted derivative (81).[50]



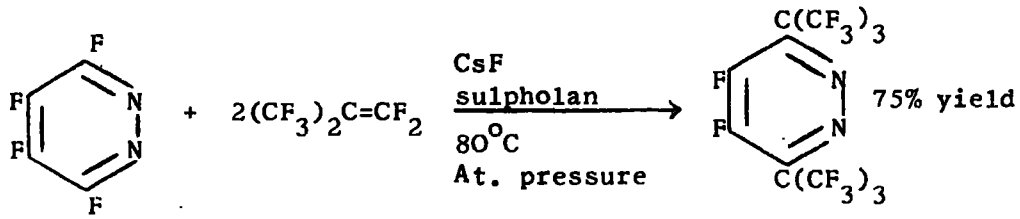
By use of the method developed above perfluoro-4-sec.butylpyridazine can be prepared in good yield.[50]



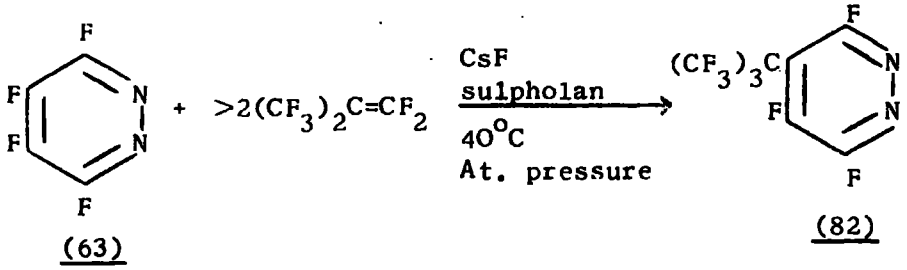
A tri-substituted derivative has been shown to exist by mass spectrometry.

5. Substitution by Octafluoroisobutene.

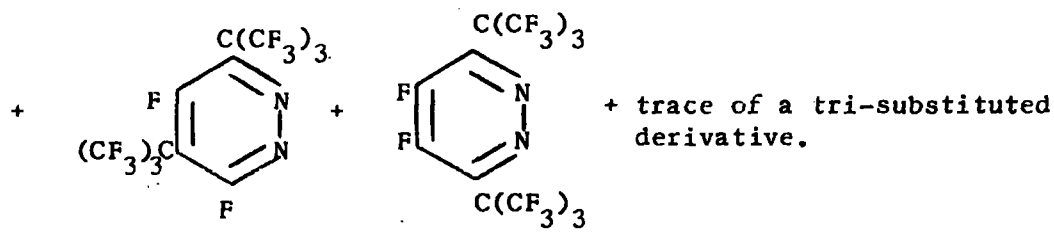
The reaction between octafluoroisobutene and tetrafluoropyridazine was studied in conjunction with Dr. M.Y. Gribble. The products derived from this system differ markedly from any of the systems described above. At 80°C the only observed product is perfluoro-3,6-di-tertiarybutylpyridazine.



At 40°C with a slight excess of the alkene a mixture of 4-mono-, 3,5- and 3,6-di- and a trace of a tri-substituted derivatives was isolated.

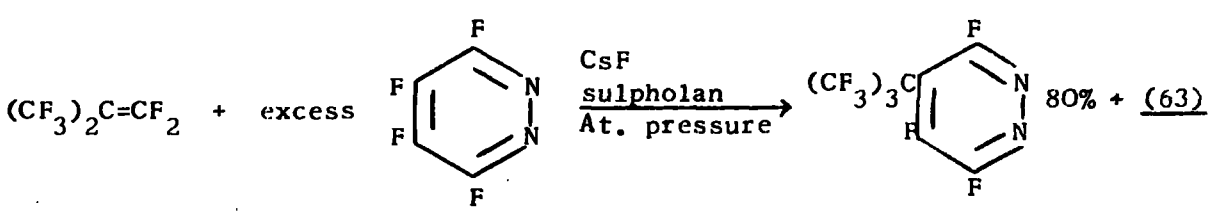


(63) (82)



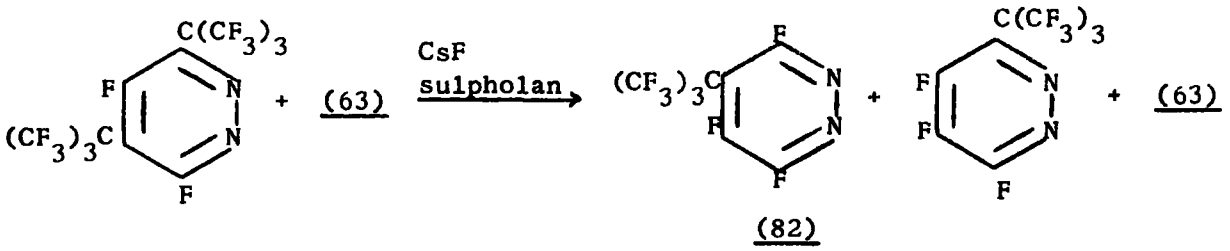
ca. 45% ca. 45%

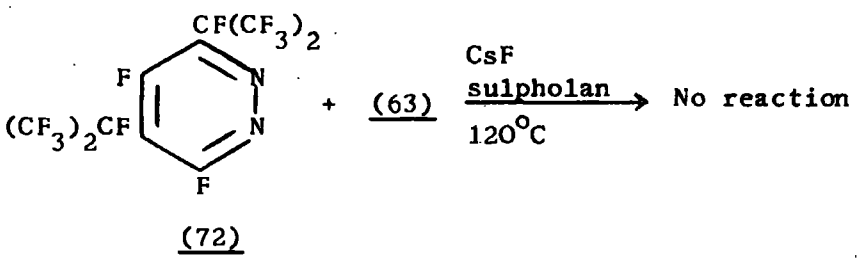
At room temperature and with an excess of tetrafluoropyridazine (82) was the major product.



(63) (82)

The 4,5-di-substituted derivative was not detected in any of the above reactions which is in sharp contrast with the results from reactions involving (63) and tetrafluoroethylene, hexafluoropropene, and octafluoro-but-2-ene. A further interesting point is that upon heating the 3,5-di-substituted isomer in the presence of tetrafluoropyridazine and fluoride ion, the 3- and 4-mono-substituted derivatives are isolated, whereas heating perfluoro-3,5-bis-isopropylpyridazine in the presence of (63) and fluoride ion no reaction was observed.

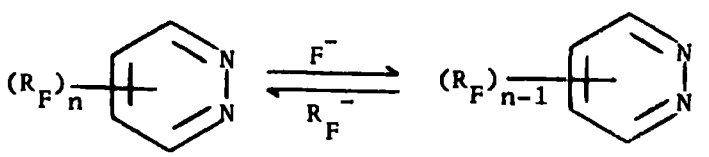




6. Mechanism of the Polyfluoroalkylation of Tetrafluoropyridazine.

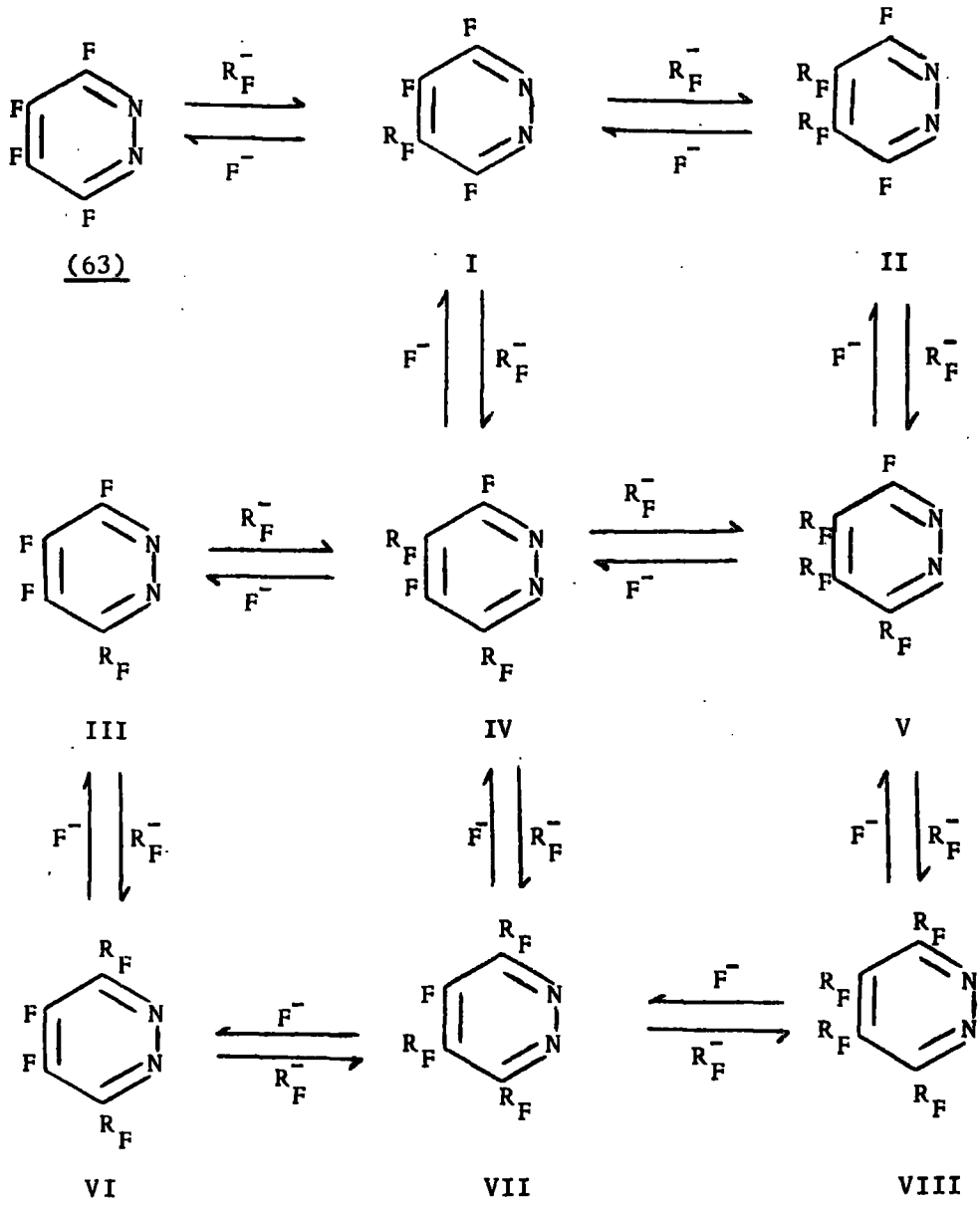
The results above have been summarised below in Scheme I and $R_F^- = C_2F_5^-$, $(CF_3)_2CF^-$, $(C_2F_5)CF_3\bar{C}F$, or $(CF_3)_3C^-$.

If each reaction step is considered an equilibrium the results obtained are not difficult to explain.



Eqn. 1.

The ease with which the equilibrium is set up, can be considered to be primarily dependent upon the stability of the perfluoro anion R_F^-. The



Scheme I

fluorines on the carbanionic carbon, i.e. $>\bar{C}-F$, destabilise a negative charge, due to unfavourable interaction between the lone pairs of the fluorine, and the full negatively charged P orbital upon the carbon, whilst the fluorines on the carbon adjacent to the carbanionic carbon, i.e. $CF-\bar{C}<$, stabilise the negative charge by induction. Hence the perfluoro anions have the following stability $C_2F_5^- < (CF_3)_2\bar{C}F \approx CF_3(C_2F_5)\bar{C}F < (CF_3)_3C^-$. Hence

the equilibrium should be most readily established with the perfluoro-t-butyl anion. A secondary effect is the steric interaction between adjacent perfluoroalkyl groups. If this occurs it will cause the equilibrium (1) to move to the right. The steric requirements of the perfluoroalkyl groups are in the following order $(CF_3)_3C^- > CF_3(C_2F_5)\bar{C}F > (CF_3)_2\bar{C}F > \bar{C}_2F_5$.

When $R_F^- = C_2F_5^-$, the reaction sequence is (63) → I → II → V → VIII and equilibrium (1) can be considered to be non-existent. Here then, is kinetic control.

When $R_F^- = (CF_3)_2\bar{C}F$, the reaction sequence is thought to be (63) → I → II → V → IV → VII, at room temperature, in the presence of an excess of R_F^- although V has not been isolated. In the absence of excess R_F^-, II is isolated, at room temperature, but can be rearranged to IV at higher temperatures in the presence of fluoride ion. This could not be achieved in the case of the pentafluoroethyl anion,[47] and is an indication of the increased stability and greater steric requirements of the heptafluoro-isopropyl group, in comparison with the former group.

When R_F^- is the perfluoro-t-butyl anion the equilibrium in equation (1) appears to be well over to the right, for II has not been isolated. The sequence is therefore thought to be (63) → I → IV → VII → VI, but here we have an ambiguity in that VI could also be formed via III, from IV since III and I are formed upon heating IV with (63) in the presence of fluoride ion. Also heating IV alone in the presence of fluoride ion causes formation of VI. It seems most likely, however, that the above sequence for $R_F^- = (CF_3)_3C^-$ is the one which operates at 40°C, whilst at higher temperatures VI may be formed via III.

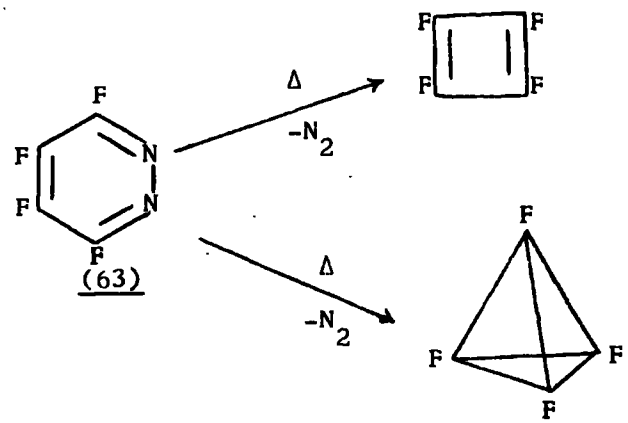
The reactions discussed above, illustrate well that it is the nature of the R_F^-, which determines whether kinetic or thermodynamic control occurs.

With R_F^- = $C_2F_5^-$ there is complete kinetic control but thermodynamic control occurs with R_F^- = $(CF_3)_3C^-$. With R_F^- = $(CF_3)_2\bar{C}F$ and $C_2F_5(CF_3)\bar{C}F$ there is kinetic control at lower temperatures, but a tendency to thermodynamic control is observed, which is accentuated by increased temperatures.

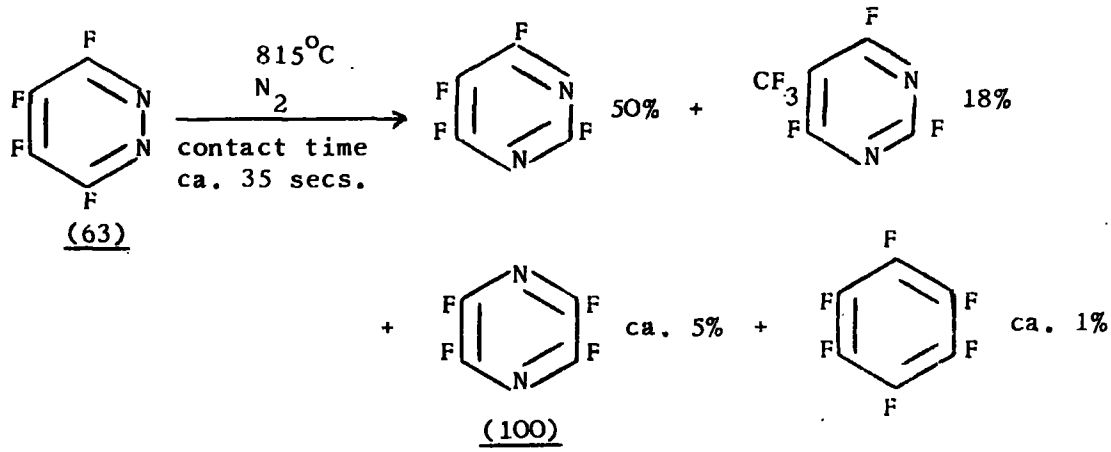
2.4. Thermolysis Reactions.

A. Introduction.

The mass spectrum of tetrafluoropyridazine (63) shows loss of nitrogen to occur, and hence it was thought that thermolysis might also cause elimination of nitrogen, and result in the formation of tetrafluorocyclobutadiene or tetrafluorotetrahedrane.

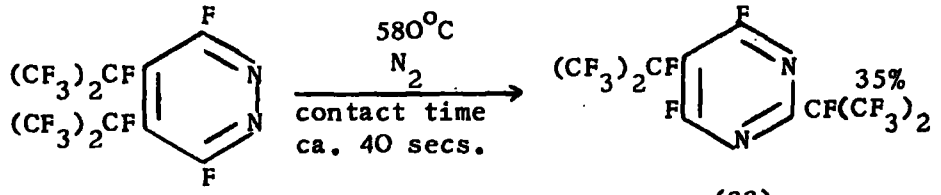


It was found, however, that the major product of the thermolysis of (63) was tetrafluoropyrimidine.[51]

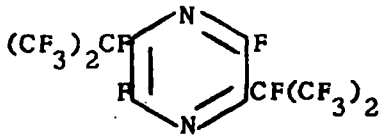


Perfluoro-5-methylpyrimidine was shown to be produced upon thermolysis of tetrafluoropyrimidine,[52] and at lower temperatures in the above reaction little of it was formed.

The thermolysis of perfluoro-4,5-bis-isopropylpyridazine (70) was claimed[51,53] to yield perfluoro-2,5-bis-isopropylpyrimidine (83) as the principle product, and perfluoro-2,5-bis-isopropylpyrazine (84) as the second most major product.



(70) (83)

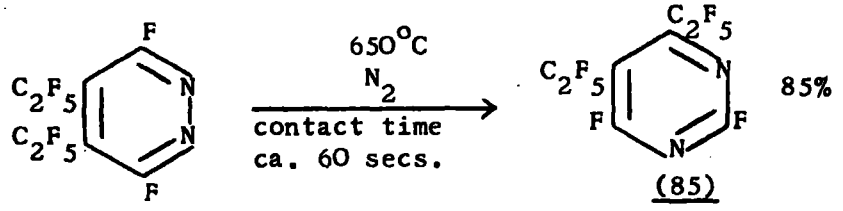


(84)

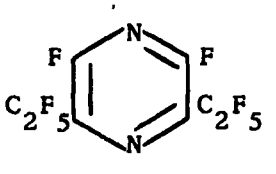
+ ca. 10% + ca. 10% fragmentation products

Percentages quoted are yields.

More recently the thermolysis of perfluoro-4,5-bis-ethylpyridazine (75) has been shown to yield perfluoro-4,5-bis-ethylpyrimidine (85)[54] as the major product, and perfluoro-2,6-bis-ethylpyrazine (86) as the second most major product.[55]



(75) (85)



(86)

The specificity of these rearrangements can best be accounted for by intermediacy of diazabenzvalenes. Although the formation of valence bond isomers from the ground electronic state is formally a disallowed process by symmetry rules, the quantitative conversion of perfluoro-hexa-kis-ethylbenzene (42) to the dewar form (44) upon flash vacuum thermolysis at 400°C,[55a] suggests that the symmetry imposed energy barriers in the conversion of highly fluorinated aromatics to their valence isomers, are very much lower than in their hydrocarbon counterparts.

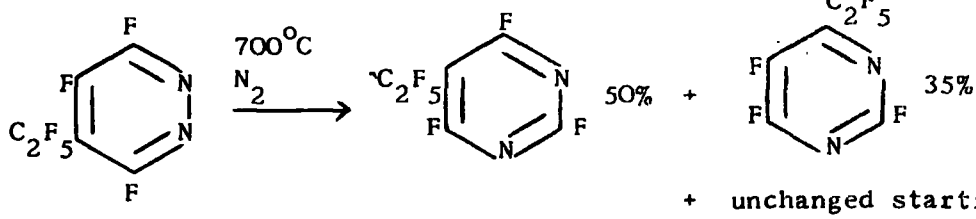
A diazaprismane intermediate cannot explain the formation of some of the products (83) and (86). It also predicts some products which are not formed.

B. Flow Thermolysis of Perfluoro-4-mono-isopropylpyridazine.

It was of interest to see which perfluoro-mono-isopropylpyrimidine was formed upon thermolysis of perfluoro-4-isopropylpyridazine (71).

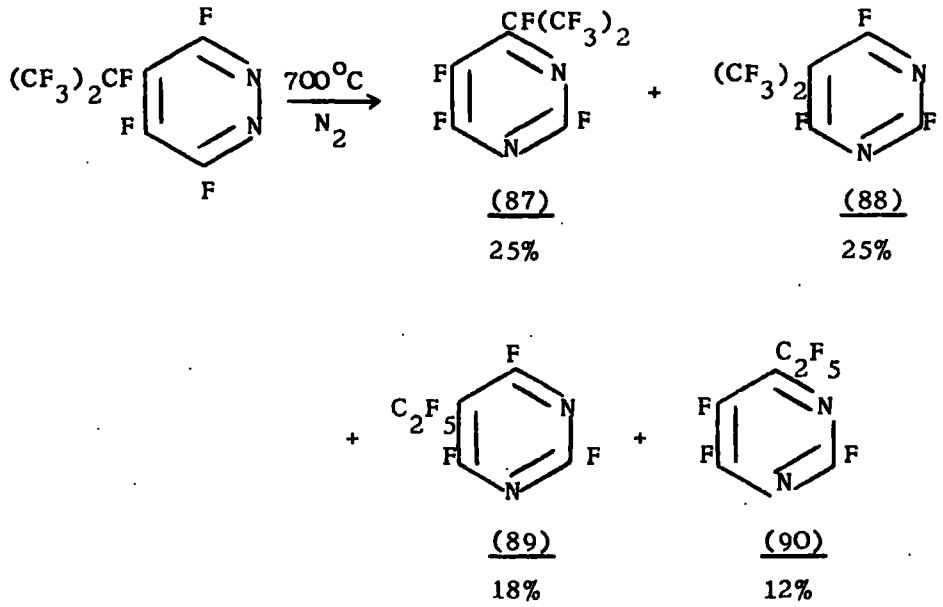
The product of the flow thermolysis of (71) at 640°C was shown to contain two major components, A (30%) and B (50%), which were isolated by preparative scale g.l.c.

Component A was shown by ^{19}F n.m.r. and mass spectrometry to be a mixture of perfluoro-4 and -5-mono-ethylpyrimidines in the ratio 2:3 respectively. These two latter compounds have subsequently been isolated[55] as the major products from the flow thermolysis of perfluoro-4-ethyl-pyridazine (74).



(74)

Component B was shown by ^{19}F and mass spectrometry to be a 1:1 mixture of perfluoro-4 and -5-mono-isopropylpyrimidines, the former of which has been prepared elsewhere.[56]



(87) 25%

(88) 25%

(89) 18%

(90) 12%

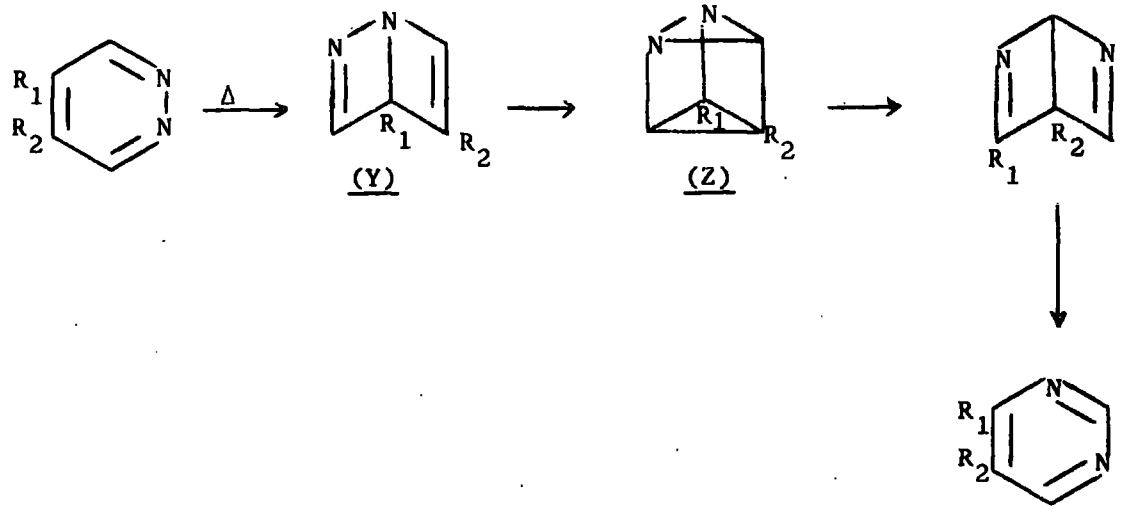
We see that only the 4- and 5-substituted pyrimidines are formed, which is in agreement with the results of the thermolysis of perfluoro-4,5-bis-ethyl- and 4-mono-ethyl-pyridazines but in conflict with the result of the earlier thermolysis of perfluoro-4,5-bis-isopropylpyridazine which was claimed to give the 2,5-di-substituted pyrimidine (83). Very recent work by Dr. P.G. Urben throws doubt upon the assigned structure of pyrimidine (83), and hence it will not be included in further discussion.

The formation of pyrimidines (87), (88), (89) and (90) upon thermolysis of perfluoro-4-mono-ethyl and isopropylpyridazine and of pyrimidine (85) from perfluoro-4,5-di-ethylpyridazine can be rationalised by the intermediacy of diazabicyclopropenyl, diazaprismanes or diaza-benzvalene intermediates.[54]

The intermediacy of diazabicyclopropenyl intermediates is least likely for they can lead to any isomer of pyrimidine or pyrazine without any stereospecificity.

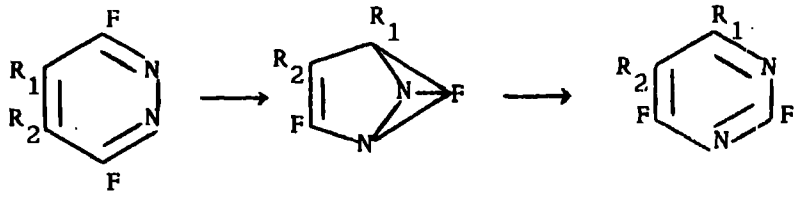
The diazaprismane intermediate, although it can lead to the correct products has also to be discounted. This is on the basis of the photo-

chemistry of pyridazines (see Chapter 3). The formation of prismane (Z) occurs via dewar Y which has been isolated in the photolyses of (70) and (79). No pyrimidines have been isolated in photolysis experiments prior to the formation of pyrazines, hence it is unlikely that the same intermediate (Y) should lead to different products.



(Y) (Z)

Hence the diazabenzvalene route seems most likely for it can also account for the observed products. The formation of pyrazines (100), (84),



(75) $R_1 = R_2 = C_2F_5$

(71) $R_1 = (CF_3)_2CF$, $R_2 = F$

(74) $R_1 = C_2F_5$, $R_2 = F$

(85) $R_1 = R_2 = C_2F_5$

(87) $R_1 = (CF_3)_2CF$, $R_2 = F$

(88) $R_1 = F$, $R_2 = (CF_3)_2CF$

(89) $R_1 = C_2F_5$, $R_2 = F$

(90) $R_1 = F$, $R_2 = C_2F_5$

and (85), however, complicates the picture and as yet it is not clear if these minor products arise as a result of a diazabenzvalene rearrangement, or as a result of some other process.

C. Flash Vacuum Thermolysis of Perfluoro-4,5-bis-isopropylpyridazine.

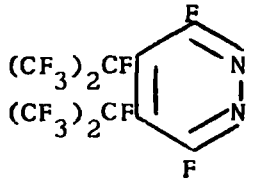
1. Introduction.

Three fragmentation components are produced as minor products in the flow thermolysis of perfluoro-4,5-bis-isopropylpyridazine (70) at 580°C.[53] These become the major products in the flash vacuum thermolysis of (70)[53] at higher temperatures.

It was of interest to characterise these components for it was thought they might arise as a result of valence bond isomer fragmentation (see Chapter 5).

2. Flash Vacuum Thermolysis at 740°C.

Initial attempts at reproducing the reaction mixture containing the three fragmentation components as principle products as obtained by Dr. J.A.H. MacBride were unsuccessful. (83) was obtained as the principle product upon flash thermolysis of (70) at 740°C under high vacuum. On re-packing the pyrolysis tube very loosely, with silica wool, the product mixture changed to that containing the three fragmentation components (g.l.c.) in the same proportions as had been found by Dr. J.A.H. MacBride, (83) now being a more minor product. The three major fragmentation components A, B and C in order of increasing g.l.c. retention time were separated by preparative scale g.l.c.

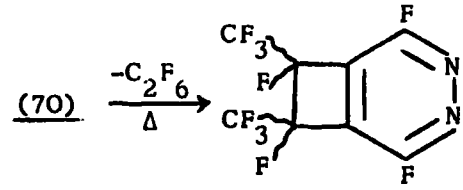


(70)

$\xrightarrow[\text{high vacuum}]{740^{\circ}C}$ A + B + C + (83) + (84)

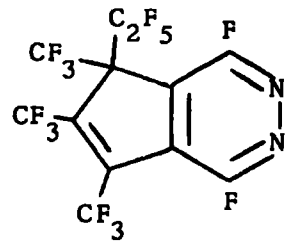
The relative amounts of components A, B, C, (83), and (84) varied under conditions essentially the same. Typical mixtures 24, 38, 15, 8 and 1% and 31, 11, 8, 15 and 4% of A, B, C, (83) and (84) respectively.

Component A was identified as a diazabenzocyclobutene (92) (parent peak at 314 in the mass spectrum) the result of loss of C_2F_6 from (70). The ^{19}F n.m.r. of (85) shows only three signals in the ratio 3:1:1 at 77·8 multiplet,



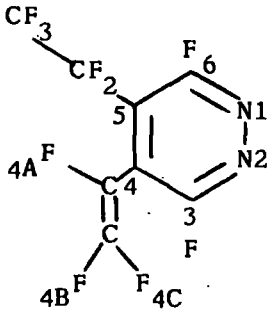
(92)

81·0 singlet and 162·5 multiplet p.p.m. and these have been associated with the trifluoromethyl group, the aromatic and tertiary fluorines respectively. The stereochemistry of the trifluoromethyl groups on the cyclobutene ring could not be determined, but the chemical shift of the aromatic fluorines compares well with that of the aromatic fluorines in perfluoro-(1,2,3-trimethyl)-1-ethyl-5,6-diazaindene (93) at 78·2 p.p.m.[49]

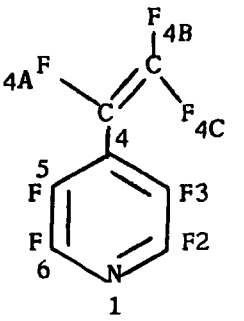


(93)

Component C was also found to be one compound, perfluoro-4-vinyl-5-ethylpyridazine (94). This compound (parent peak at 314 in the mass spectrum) is again the product of loss of C_2F_6 from (70). Its ^{19}F n.m.r. spectrum shows the characteristic signals for the pentafluoroethyl group at 85·2 p.p.m. (trifluoromethyl group cf. 87·0 p.p.m. in (74)), and at 115·2 p.p.m. (difluoromethylene group cf. 115·0 p.p.m. in (74)), for the aromatic fluorines at 80·5 (F-6) and 83·0 p.p.m. (F-3) (cf. 77·7 p.p.m. in (75)), and for the trifluorovinyl group at 95·5 (4B), 109·7 (4C) and 170·3 p.p.m. (4A), compared with 93·8 (4B), 124·1 (4C) and 175·6 p.p.m. (4A) in perfluoro-4-vinylpyridine (95).



(94)

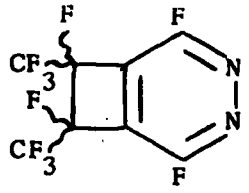


(95)

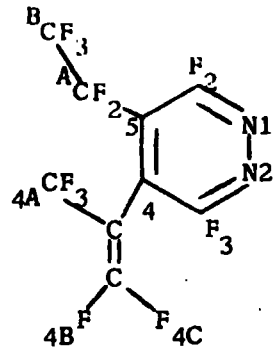
The coupling constants in (94) are also very similar to those observed between the equivalent fluorines in (95), i.e.

	(94)	(95)
J_{4A-4B}	34 Hz	36 Hz
J_{4A-4C}	117 Hz	116 Hz
J_{4B-4C}	56 Hz	52 Hz
J_{4C-3}	18 Hz	16 Hz
J_{3-6}	33 Hz	compared with 34 Hz in (74)

Component B, although pure according to a number of g.l.c. columns was shown by ^{19}F n.m.r. to be a mixture of two compounds in the ratio of ca. 1:1. By preparative g.l.c. the symmetrical peak was cut into two halves, and luckily the relative amounts of the two compounds within the two fractions differed (shown by ^{19}F n.m.r. and mass spectra) hence enabling assignment of signals in the n.m.r. to the relevant compounds. The original component B was thus shown to contain ca. 41% of a diaza-benzocyclobutene (96) (parent peak at 314 in mass spectra of first fraction g.l.c. retention time) an isomer of (92), and ca. 59% of perfluoro-4-(2'-propenyl)-5-ethylpyridazine (97) (parent peak at 364 in mass spectrum of second fraction g.l.c. retention time).



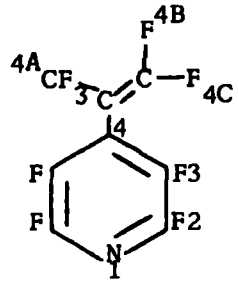
(96)



(97)

The ^{19}F n.m.r. spectrum of (96) is very similar to that of (92) (see above) showing absorptions at 77·1 (trifluoromethyl), 83·0 (aromatic fluorines) and 161·8 p.p.m. (tertiary fluorines) in the ratio 3:1:1. The aromatic signal is a singlet as in (92) and the trifluoromethyl and tertiary fluorine signals are complex multiplets similar in general shape to those of (92).

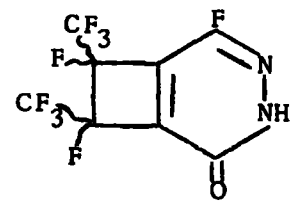
The ^{19}F n.m.r. spectrum of (97) contains seven signals in the ratio 3:1:1:1:1:3:2 in order of increasing chemical shift. Some of the signals are very complex. It shows two aromatic fluorines at 79·5 (6-F) and 82·1 p.p.m. (3-F) compared with 80·5 and 83·0 p.p.m. in (94) and the two characteristic pentafluoroethyl signals at 85·4 (trifluoromethyl) and 113·7 p.p.m. (difluoromethylene). The pentafluoroprop-2-enyl group shows signals at 60·5 (4A trifluoromethyl), 69·3 (4C) and 69·6 p.p.m. (4B) which compare well with those of the same group in perfluoro-4-(2'-propenyl)-pyridine (98) at 59·5 (trifluoromethyl), 68·0 (4B) and 68·9 p.p.m. (4C).



(98)

The coupling constant between the 3- and 6-aromatic fluorines of 32·5 Hz compares well with that in (94) 33Hz and with that in (74) 34 Hz. The two aromatic fluorines can be readily distinguished by the fact that the 6-F is a complex signal containing coupling constants, J_{6-5A} = 22 Hz, J_{6-5B} = 12 Hz and J_{6-3} = 32·5 Hz whereas the 3-F is a clear doublet J_{3-6} = 32·5 Hz with much fine splitting (J < 4 Hz). The trifluoromethyl group (4A) of the pentafluoroprop-2-enyl group shows a very complex signal coupling occurring with 5B J = 2 Hz, 5A J = 2·4 Hz, with 4B J = 13·8 Hz, with 4C J = 9 Hz, and with 3-F J 6·6 Hz resulting in 25 lines. The trifluoromethyl group (5B), apart from coupling with (4A) J = 2·0 Hz also couples with (4C) J = 8·8 Hz.

As can be seen the structures of the above four compounds are based upon ^{19}F n.m.r. and molecular weight (from mass spectra). All four hydrolyse readily in contrast to other perfluoro-4,5-bis-alkylpyridazines. Indeed (92) hydrolysed on standing to give (99) which showed four signals in its ^{19}F n.m.r. in the ratio 3:3:1:2 at 75·8 (CF_3), 76·5 (CF_3), 99·8 (vinylic F) and 165·4 p.p.m. (tertiary fluorine) respectively which is



(99)

consistent with what one would expect for this system.

3. Conclusion.

It is clear that the energy supplied to the aromatics upon thermolysis can be used in two ways: i) to isomerise the ring or ii) to fragment the side chain. It is also apparent that fragmentation occurs before isomerisation

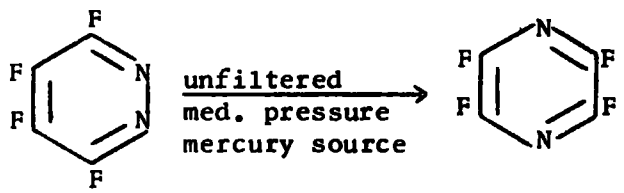
of the ring for no fragmentation products containing the pyrimidine ring were isolated upon thermolysis of (70). In the thermolysis of (71), however, 30% of the product arose as a result of fragmentation of the side chain, but this then underwent isomerisation to the pyrimidine ring system.

CHAPTER 3

Photoisomerisations of Highly Fluorinated Pyridazines

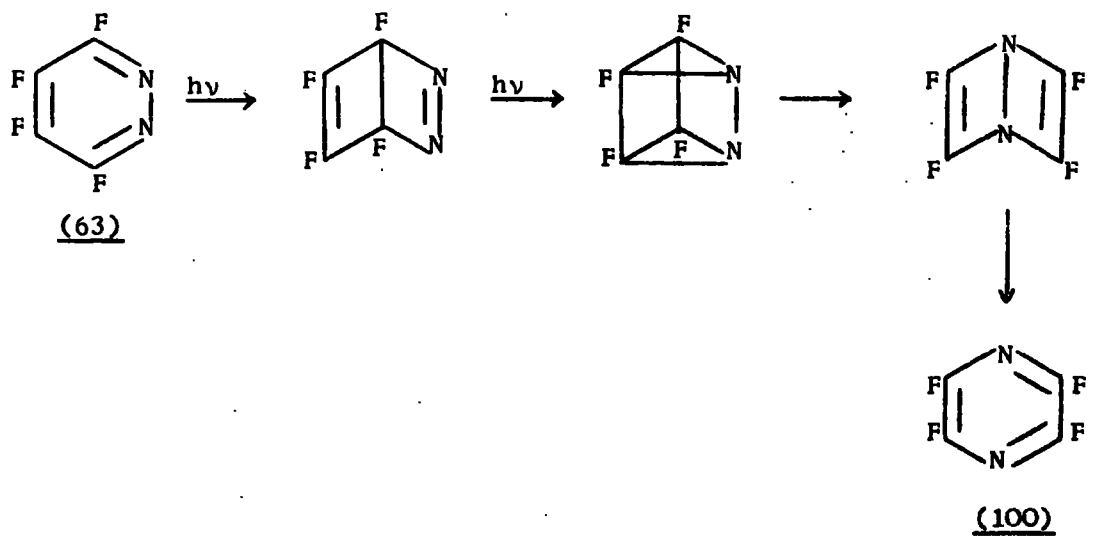
3.1. Introduction.

Original workers in this field were aiming at photochemically induced elimination of nitrogen from tetrafluoropyridazine, just as had been attempted in the pyrolysis reactions. These attempts were again based upon the finding that tetrafluoropyridazine shows loss of nitrogen in its mass spectrum. Although the elimination of nitrogen has now been observed with some pyridazines upon thermolysis,[58] the photolysis of tetrafluoropyridazine leads to almost quantitative rearrangement to tetrafluoropyrazine (100).[51]



(63) (100)

Hence we see that not only does thermolysis cause a 1,2-shift of nitrogens, photolysis is even more specific, and causes a 1,3-shift of the nitrogens. A diazaprismane intermediate can explain the 1,3-shift of the nitrogens, whereas a diazabenzvalene intermediate cannot, because



(63) (100)

tetrafluoropyrimidine can be formed and this has been found to be photostable.

3.2. Ultraviolet Light Sources.

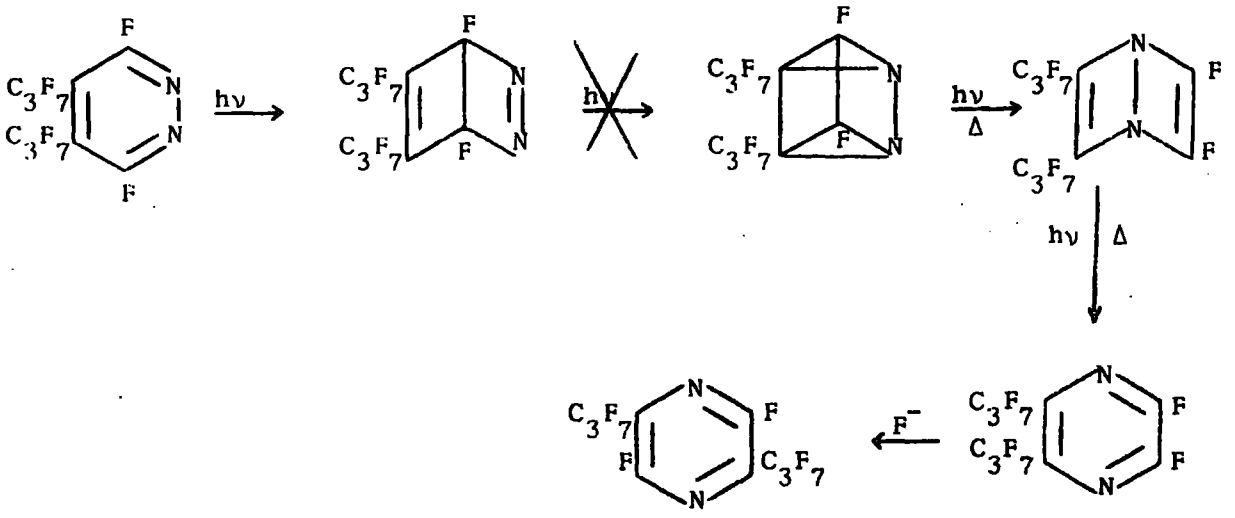
Preliminary irradiations were, in general carried out with light from medium pressure mercury arcs. These emit light at various wavelengths between λ = ca. 230 and ca. 600 nm. The major emissions are at 265, 302, 313 and 366 nm. (see Experimental Section for further details). These sources will be referred to as m.p. Hg sources. The light from low pressure mercury arcs is virtually monochromatic, having the wavelength 253·7 nm. It has been employed in some irradiations, which will be referred to as irradiations at 257·7 nm. Photoisomerisations have also been carried out using lamps which have an emission envelope, of wavelengths between 280 and 320 nm. These will be referred to as irradiations at 300 nm. A source which has an emission envelope of wavelengths between 325 and 387 nm. has also been employed in some irradiations. These will be referred to as irradiations at 376 nm.

Pyrex cuts out light of shorter wavelengths than 280 nm., and only transmits 50% of incident light at 310 nm. It has been employed as a filter in some reactions.

More details about light sources are given in the Experimental Section.

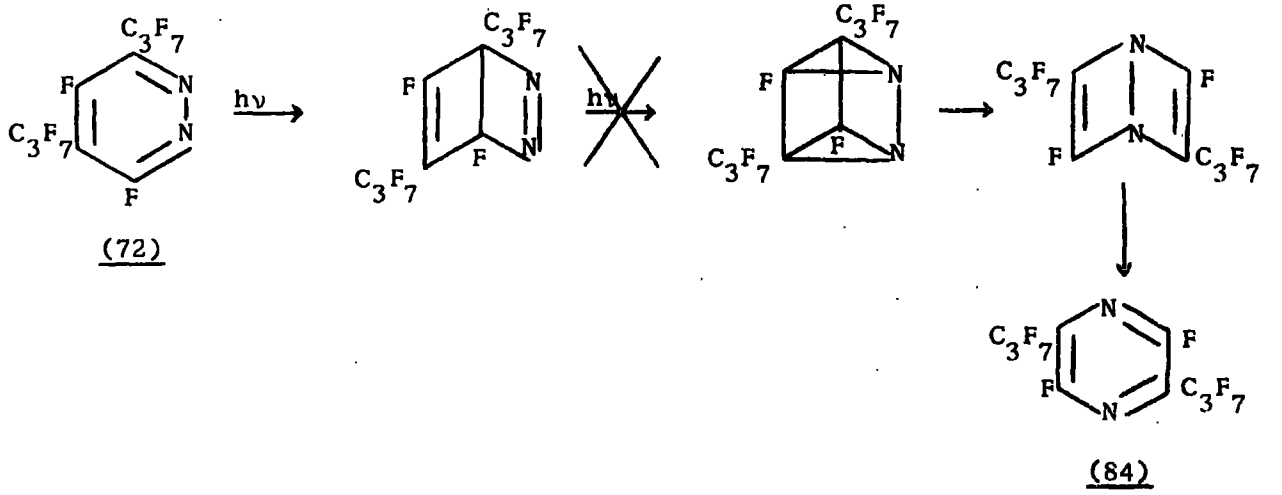
3.3. Labelling Experiments.

Early labelling experiments showed that perfluoro-4,5-bis-isopropylpyridazine (70) photoisomerised quantitatively to perfluoro-2,5-bis-isopropylpyrazine (84).[51] To account for the 1,3-shift of the nitrogen a diazaprismane intermediate was proposed and to account for the 1,3-shift of the perfluoroisopropyl groups fluoride ion initiated rearrangement was proposed. This was to relieve steric interaction between the groups.[41]



(84)

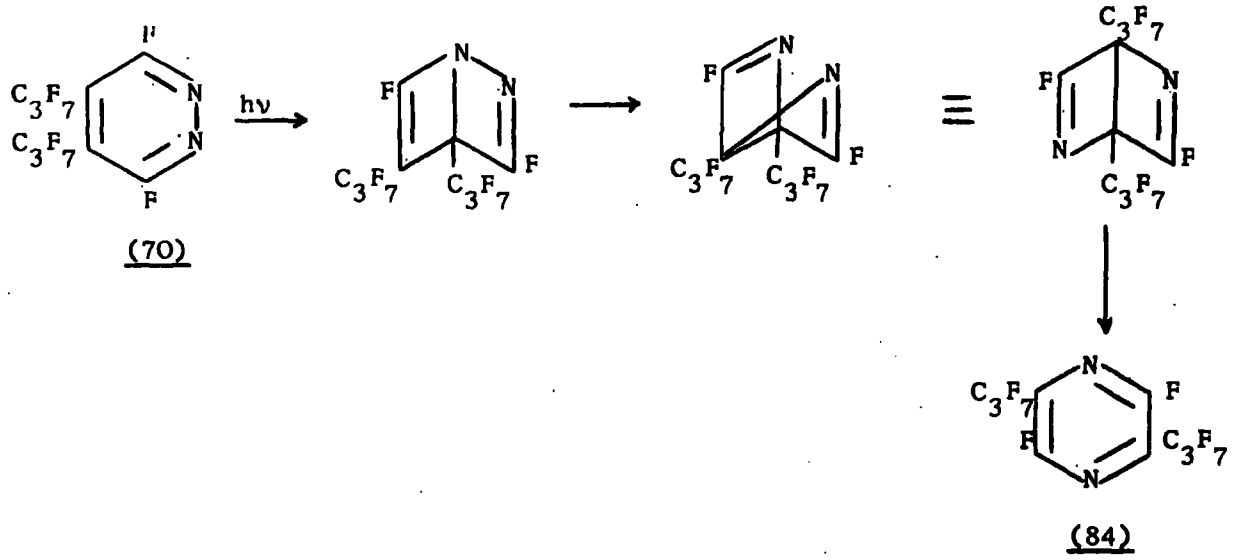
However, photoisomerisation of perfluoro-3,5-bis-isopropylpyridazine (72) yields only perfluoro-2,6-bis-isopropylpyrazine (101) whereas if the reaction proceeded via a diazaprismane intermediate the product would be the 2,5-isomer (84), i.e.



(72)

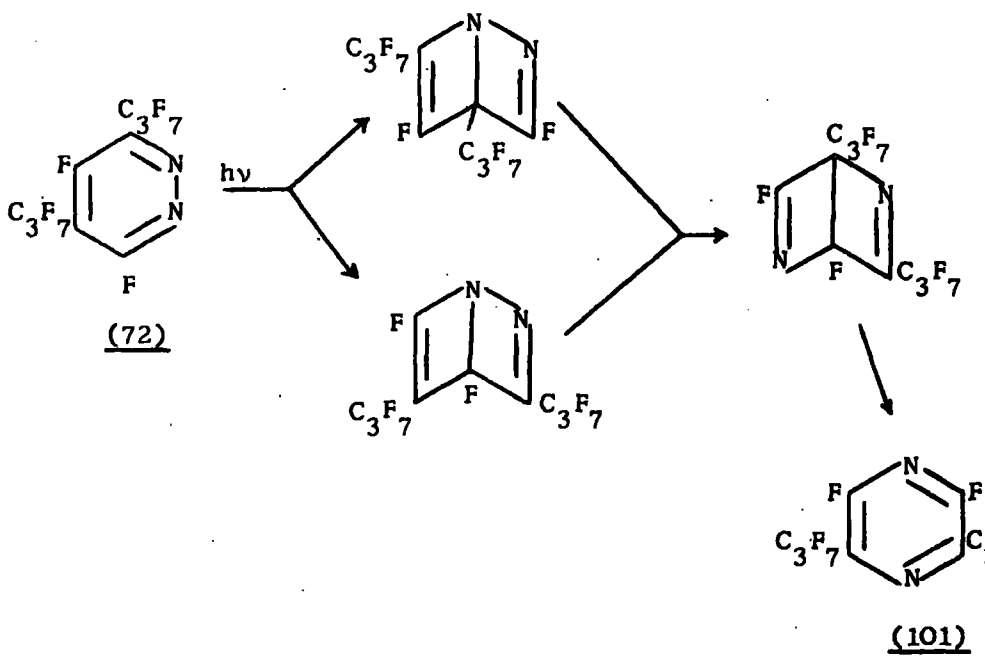
(84)

Fluoride ion initiated rearrangement of the 2,5-di-substituted pyrazine (84) is incompatible with what was observed above because the 2,6-isomer was not isolated in the photoisomerisation of (70). Hence a novel mechanism was proposed for the observed 1,3-shifts of the nitrogens and the groups which involves rearrangement of the initially formed diazadewarbenzene to another diazadewarbenzene followed by rearomatisation to the aromatic pyrazine, i.e.



(70)

(84)



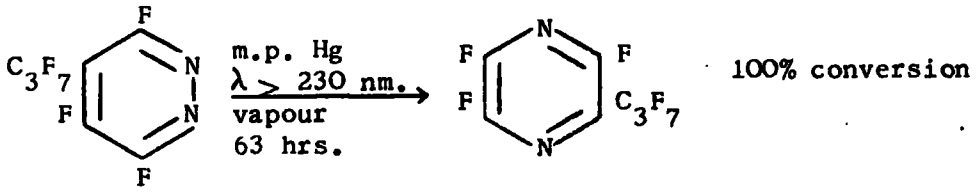
(72)

(101)

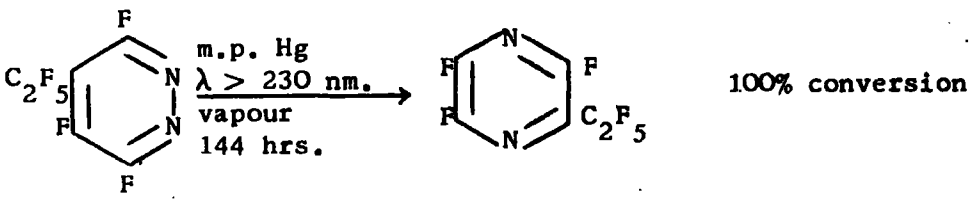
If this mechanism operates it would lead to a very specific 1,3-shift. No specific 1,3-shifts as such have been observed in benzene photochemistry, but the photoproducts of mono-methyl and di-methylpyridines can be explained by the above mechanism, and will be discussed later.

The photolysis experiments described above have been developed and other substituted pyridazines have also been photoisomerised. Perfluoro-4-mono-isopropyl-, -ethyl-sec.butyl-,[50] and -t-butyl-pyridazines have all been photoisomerised to give the respective mono-substituted perfluoropyrazines.

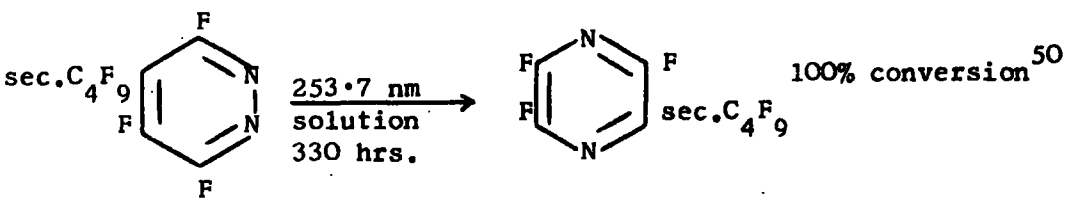
The structures of the pyrazines above were deduced from the ^{19}F n.m.r. spectra of the compounds (all contained three aromatic fluorines).



(71) (102)

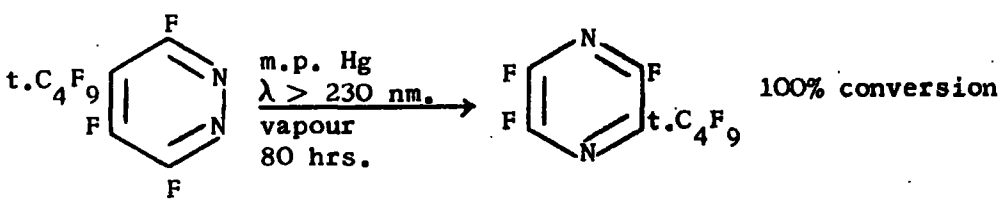


(74) (103)



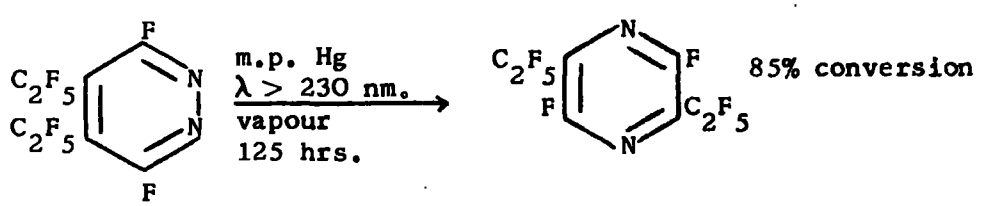
[50]

(80) (104)

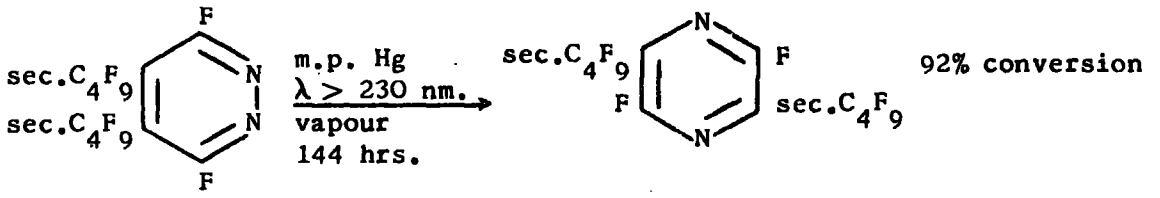


(82) (105)

Perfluoro-4,5-bis-ethyl- and -bis-sec.butyl-pyridazines have also been photoisomerised, and these yield the 2,5-di-substituted pyrazines as was observed in the case of (70).

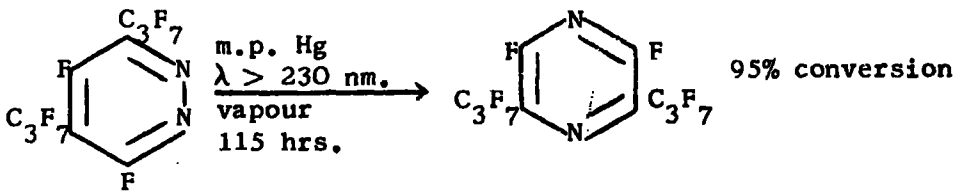


(75) (106)

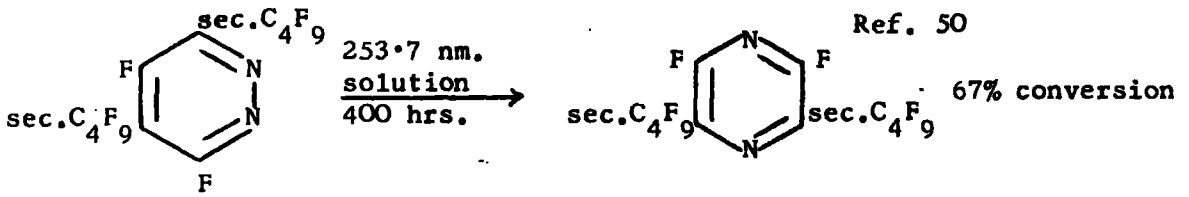


(79) (107)

Perfluoro-3,5-bis-secondary butylpyridazine[50] (81) gives the 2,6-di-substituted pyrazine (108) upon photolysis analogous to the isomer that was produced upon irradiation of perfluoro-3,5-bis-isopropylpyridazine (72).



(72) (101)



(81) (108)

3,6-Difluoro-4,5-dichloropyridazine (68) has been claimed[43] to have been photoisomerised to 2,5-difluoro-3,6-dichloropyrazine (109), in the solution phase, in high yield. This experiment has been repeated under the conditions reported.[43] Little isomerisation was found to occur, but a very considerable amount of decomposition did. The vapour phase irradiation of (68) has also been carried out. Little isomerisation was found to occur but again, very considerable decomposition did occur.

Tetrachloropyridazine (110), has also been claimed[43] to have been photoisomerised to tetrachloropyrazine (111), in the solution phase, in

high yield. This experiment has been repeated under the conditions reported[43] and also under other conditions: vapour phase and low temperature solution phase. Little isomerisation was found to occur but considerable decomposition was observed.

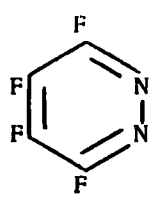
3.4. Substituent Effects Upon the Efficiency of the Photoisomerisation of Pyridazine.

Not all pyridazines isomerise to pyrazines. Indeed no hydrocarbon pyridazine has yet been photoisomerised to pyrazine. Perfluoropyridazine does photoisomerise as was pointed out above.

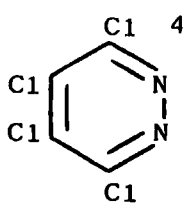
Table 2 contains those pyridazines which have been observed to photoisomerise, and Table 3 contains those which have not been observed to photoisomerise.

Table 2.

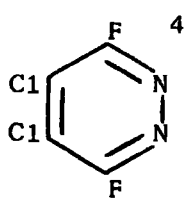
Pyridazines Observed to Photoisomerise to Pyrazines



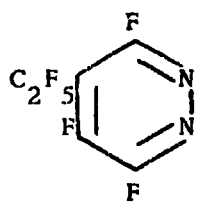
(63)



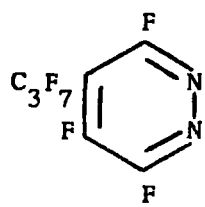
(110)



(68)



(74)



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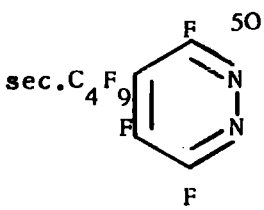

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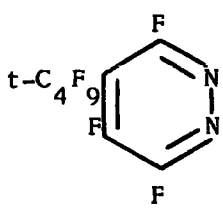

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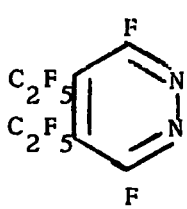

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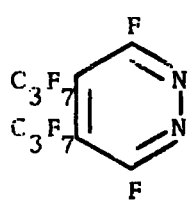

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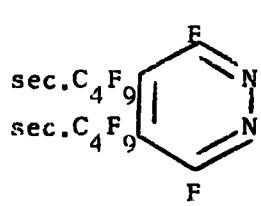
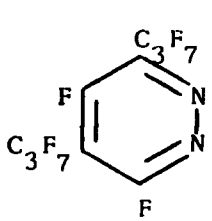


(79)



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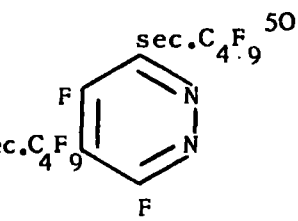
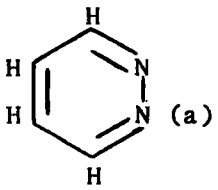
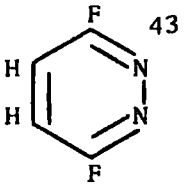


(81)

Table 3

Pyridazines NOT Observed to Photoisomerise to Pyrazines


(a)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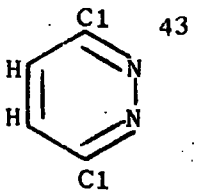
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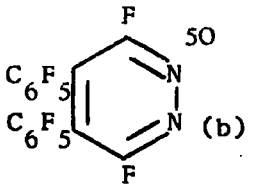
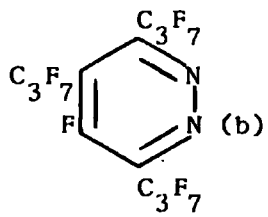
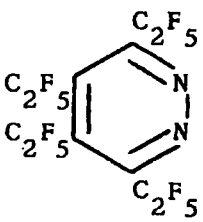
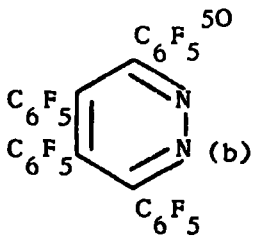

50 (b)

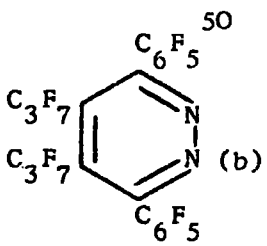

(b)

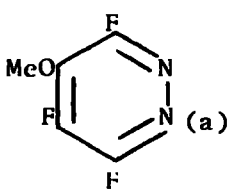
(73)



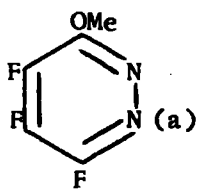
(77)


50 (b)

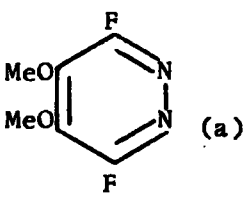

50 (b)


(a)

(64)


(a)

(66)


(a)

(65)

(a) Decompose.

(b) All starting material recovered.

The methoxyfluoropyridazines (64), (65), and (66) have all been irradiated by a medium pressure mercury arc, but did not photoisomerise to pyrazines. Some decomposition was observed, however.

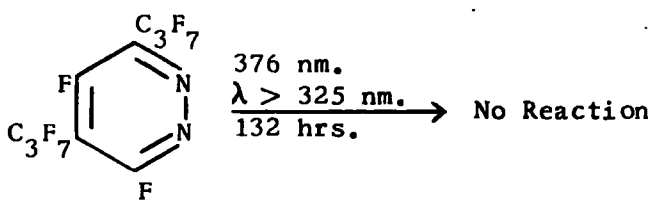
With the pyridazines claimed not to isomerise in ref. 43 it is not clear if decomposition occurred. It is not clear if groups other than fluorine, perfluoroalkyl, or perfluoroaryl destabilise the intermediate since decomposition has been observed upon irradiation of pyridazine and methoxyfluoropyridazines or if the ring-substituent bonds; C-H and C-O-Me, are less stable to irradiation.

Clearly perfluoroalkyl groups do not always enhance the photoisomerisation because perfluoro-3,4,6-tris-isopropyl- and perfluorotetrakis-ethyl-pyridazines[43] do not isomerise yet do not decompose. Perfluoroaryl groups prevent photoisomerisation. It is apparent, that perfluoroalkyl groups in the 3- and 6-positions retard photoisomerisation, because perfluoro-4,5-bis-isopropylpyridazine photoisomerises ca. 1-3 times as fast as perfluoro-3,5-bis-isopropylpyridazine. The tri-isopropyl derivative (73) with perfluoroalkyl groups in the 3- and 6-positions does not photoisomerise at all. Perfluoroalkyl groups in the 4- and 5-positions also hinder the photoisomerisation, because the quantum yield for tetrafluoropyridazine is $4{\cdot}7 \times 10^{-3}$, whereas for perfluoro-4,5-bis-isopropylpyridazine it is $2{\cdot}3 \times 10^{-5}$.[50]

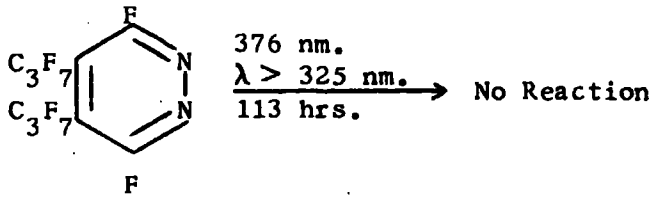
3.5. The Effect of Irradiation Wavelength Upon Photoisomerisation.

The ultraviolet spectra of pyridazines consist of two absorption bands, the lowest $\pi \rightarrow \pi^*$ and the $n \rightarrow \pi^*$ bands. The lowest $\pi \rightarrow \pi^*$ band always has its maxima at wavelengths shorter than 300 nm., whereas, the $n \rightarrow \pi^*$ band in general has its maxima at wavelengths longer than 300 nm. What has been attempted, is to isomerise various pyridazines by excitation of these bands at selected wavelengths.

It has been found, that excitation of the $n \rightarrow \pi^*$ bands of perfluoro-4,5- ($\lambda_{max.}$ 340 nm.) and -3,5- ($\lambda_{max.}$ 325 nm.) bis-isopropylpyridazines, with ultraviolet light of $\lambda \gg 325$ nm., does not result in photoisomerisation to the respective pyrazines.

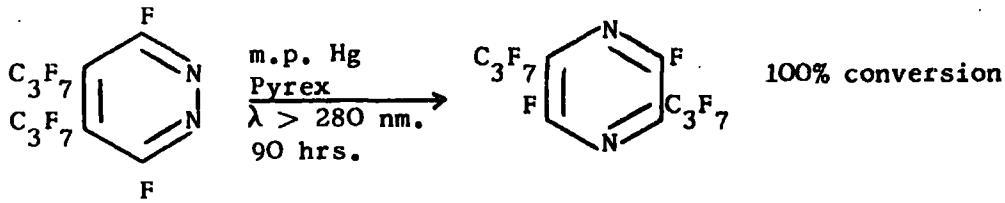


(72)

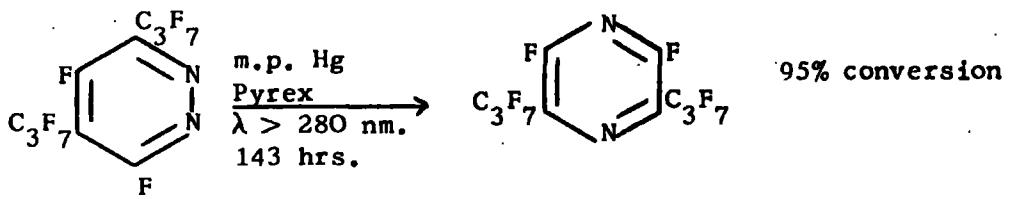


(70)

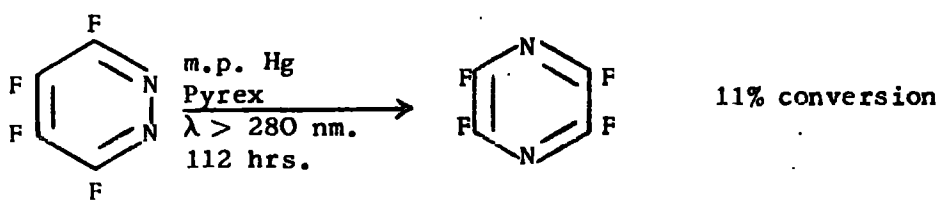
The photoisomerisations of (70), (72), and (63) have been effected, by irradiation, with the light from a medium pressure mercury arc, with a Pyrex filter (λ > 280 nm.), albeit at a slower rate.



(70) (84)



(72) (101)



(63) (100)

In the case of the di-substituted pyridazines (70) ($\lambda_{max.(\pi \rightarrow \pi^*)}$ 278 nm.) and (72) ($\lambda_{max.(\pi \rightarrow \pi^*)}$ 256·5 nm.), the result of irradiation at λ > 280 nm., is most probably to cause the major part of the photoisomerisation, to occur via excitation of the lowest π → π* band. With tetrafluoropyridazine (63) ($\lambda_{max.(\pi \rightarrow \pi^*)}$ 248 nm., $\lambda_{max.(n \rightarrow \pi^*)}$ 283·5 nm.) only excitation of the n → π*

band is possible, and hence, here, the reaction was observed to be much slower than for the di-substituted pyridazines (70) and (72). This is because, in general, it is thought, that the electronically excited pyridazine molecules, which arise as a result of the absorption of $n \rightarrow \pi^*$ bands, have insufficient energy to form the valence isomers responsible for isomerisation to pyrazine.

The 3,5-di-substituted pyridazine (72) is observed to isomerise at a slower rate than its 4,5-di-substituted isomer (70) at 253·7 nm. However, the extinction coefficient at 253·7 nm. is 1851 for (72), yet only 1033 for (70). It can thus be seen that the rate of photoisomerisation is not directly governed by the amount of energy supplied to the system. Since the systems absorb energy, the efficiency of the loss of energy of the excited species, be it an aromatic or a valence isomer, back to the pyridazine, has to be considered as a major factor in the efficiency of the photoisomerisation.

3.6. Triplet State Involvement.

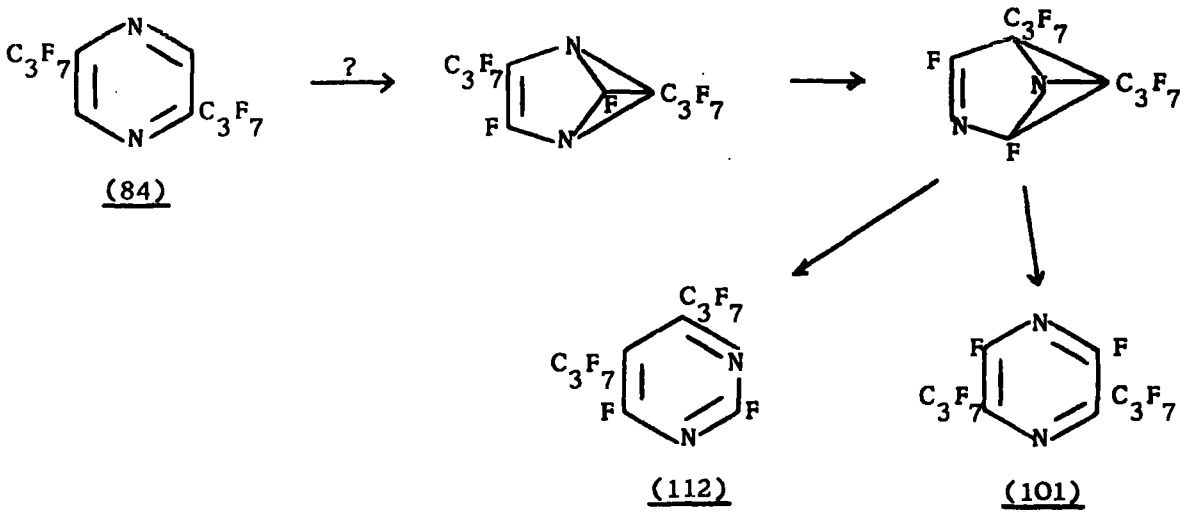
All of the photoisomerisations of pyridazines performed at these laboratories have been performed in the vapour phase, at low pressures ($P < 0{\cdot}5$ torr), and the evacuating system always contained mercury. Since mercury is a very efficient triplet sensitiser at 253·7 nm. it was thought that there might be triplet involvement in the photoisomerisations.

The irradiation of the vapour of perfluoro-4,5-bis-isopropylpyridazine (70) at 253·7 nm. has been carried out in the presence of added mercury and in the absence of mercury. A new silica tube with gold foil was used for the latter experiment and evacuation was by a new mercury free vacuum line. The irradiation of the two systems above for a prolonged period of time (ca. 800 hrs.), showed that the photoisomerisation of pyridazine (70)

to the pyrazine (84) occurs at about the same rate in the presence, and in the absence of mercury. This then, indicates that triplet intermediates play no significant role in this isomerisation.

In both these prolonged irradiations (800 hrs.), two other compounds were isolated, perfluoro-2,6-bis-isopropylpyridazine (101) and perfluoro-4,5-bis-isopropylpyrimidine (112). These latter compounds were not obtained in the other shorter irradiations, but were present in the ratio 1:1 as ca. 30% of the product in the absence of mercury and as ca. 20% of the product in the presence of mercury. It was also noted that much more decomposition occurred in the absence of mercury (ca. 48% recovery) than in the presence of mercury (ca. 80% recovery). This is to be expected because mercury can be expected to act as a filter absorbing much of the incident irradiation.

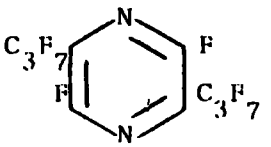
The two latter compounds (101) and (112) could be considered to arise from the rearrangement of the initially formed pyrazine (84) via a diaza-benzvalene intermediate, however irradiation of pure (84) at 253·7 nm. for an extended period (425 hrs.) in a much larger vessel did not result in the production of either (101) or (112).



(84)

(112)

(101)



$\xrightarrow[\text{vapour}]{253{\cdot}7\ \text{nm.}}$ No Reaction

Since a small amount of the starting material perfluoro-4,5-bis-isopropylpyridazine (70) was present in the final product, it could be that sensitisation of pyrazine (84) by pyridazine (70), leads to products (101) and (112). This is being investigated at the time of writing.

It is stressed, however, that these are extreme conditions (ca. 800 hrs.) and that relatively short irradiations (ca. 100 hrs.) of (70) give only pyrazine (84).

Many of the photoisomerisations above were performed without vigorous exclusion of oxygen. Hence, since oxygen is an efficient triplet quencher, the photoisomerisation of perfluoro-4-isopropylpyridazine (71) was carried out in the presence of oxygen and after rigorous degassing. The products of these reactions were found to be the same, indicating again that triplet intermediates play no part in the photoisomerisation of pyridazines to pyrazines.

The isomerisation of perfluoro-4,5-bis-isopropylpyridazine (70) has been attempted using fluorene (triplet energy 284 kJ $mole^{-1}$) as a triplet sensitiser. No isomerisation was observed. This could be because the triplet energy supplied to (70) was lower than the first triplet energy of (70) (first triplet energy of pyridazine is 297 kJ $mole^{-1}$ [60]) or because the isomerisation does not proceed via a triplet intermediate. The experiment needs repeating with a triplet sensitiser of higher energy than fluorene.

From the results obtained so far, there is a strong indication that the photoisomerisation of pyridazines to pyrazines, does not proceed via a

triplet intermediate.

Other workers have also found, that triplet intermediates are not involved, in the photoisomerisations of both benzenes[20] and azabenzenes.[35,43]

3.7. Substituent Effects on the Ultraviolet Spectrum of Pyridazine.

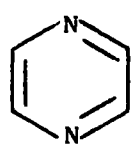
The electronic spectra of substituted pyridazines have been examined. What has been sought, is a simple relationship between ease of photo-isomerisation, and changes in absorption wavelength, due to substitution. It will become clear that no real relationship exists. Never-the-less it has been possible to establish a distinct substituent effect upon orbital energies, but at this stage it is not possible to say how relevant this is to the rearrangement process.

The absorption maxima of the lowest $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands of pyridazine change from 240 and 375 nm. to 248·5 and 283·5 nm. in tetra-fluoropyridazine. The bathochromic shift of the lowest $\pi \rightarrow \pi^*$ band upon the introduction of fluorine into pyridazine is probably due to the inter-action of the non-bonding electrons of fluorine and the highest occupied and lowest unoccupied orbitals of pyridazine. The highest occupied orbital is destabilised, and the lowest unoccupied orbital is stabilised, hence causing a net bathochromic shift. The $n \rightarrow \pi^*$ band is shifted to a much shorter wavelength, and this is as a result of the strongly electronegative fluorines causing the n bonding electrons of the nitrogens to be more tightly bound.

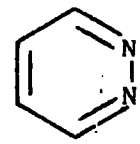
Before discussing the effects of substituents upon the ultraviolet spectra of tetrafluoropyridazine and pyridazine, it is useful to draw attention to the fact that in the aza-benzenes, the degenerate orbitals of benzene; the highest bonding e_{1g}, and lowest antibonding e_{2u} orbitals, become non-degenerate.[61] Hence the effects of substituents upon the ultra-

violet spectra can be considered as effects upon the highest bonding orbital ψ_3 and the lowest anti-bonding orbital ψ_4. Shown below are the effects of nitrogen upon the energy of the π orbitals of benzene.

Benzene

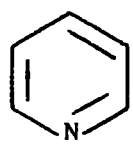


Pyrazine

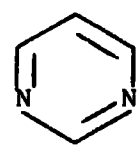


Pyridazine

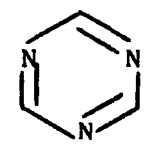
Sym-tetrazine



Pyridine



Pyrimidine



Sym-triazine

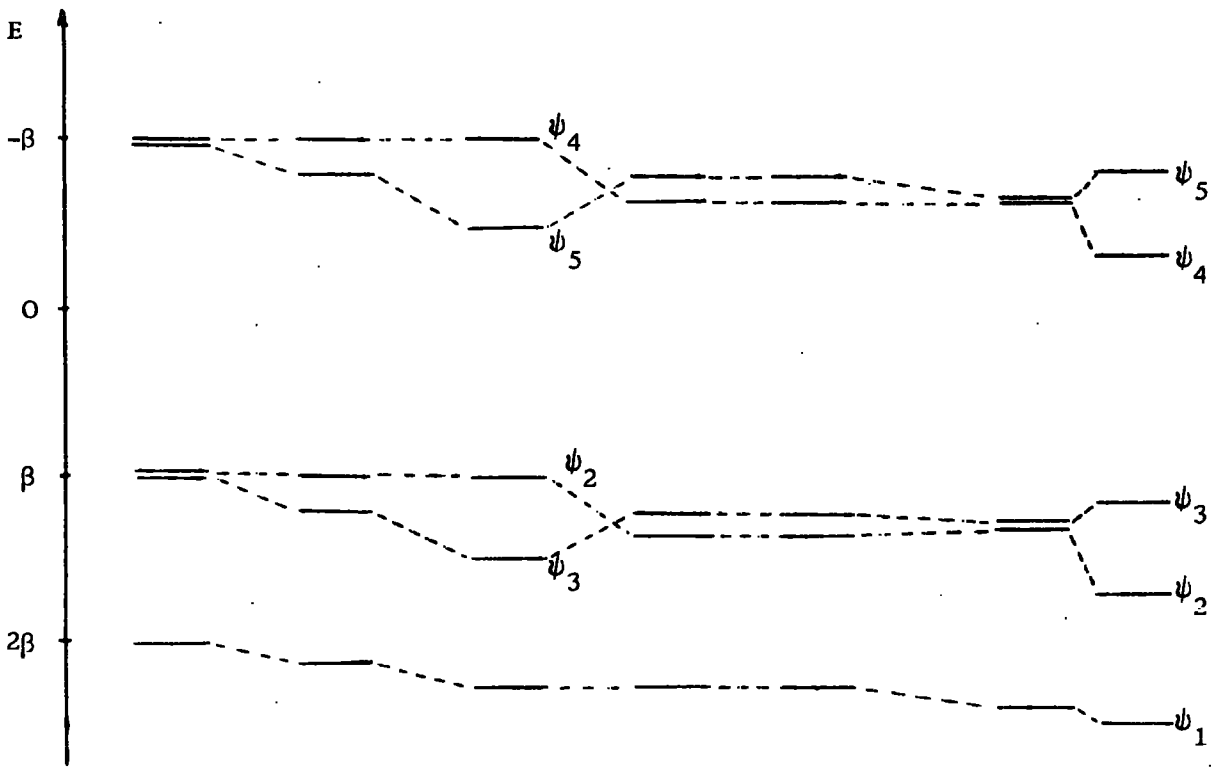
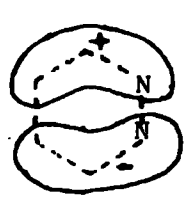
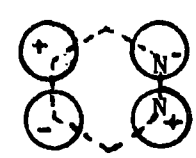


Fig. 3.1. Energy-level Diagram in Aza-benzenes.[61]



ψ_3



ψ_4

The absorption maxima for a number of pyridazines are shown below in Table 4.

Table 4.

Substituent Effects Upon the Ultraviolet Spectra of Pyridazine and Tetrafluoropyridazine.

Substituent	Tetrafluoropyridazine		Pyridazine	
	$\pi \rightarrow \pi^*$ $\lambda_{max.}$ nm.	$n \rightarrow \pi^*$ $\lambda_{max.}$ nm.	$\pi \rightarrow \pi^*$ $\lambda_{max.}$ nm.	$n \rightarrow \pi^*$ $\lambda_{max.}$ nm.
	248	283·5	240	375[61]
3MeO	263·5	285	272	327[61]
4MeO	251	275	259	307[61]
$3,6(MeO)_2$	272·5	-	292	325[61]
$4C_3F_7$	262	313·5		
$4,5(C_3F_7)_2$	278	340		
$3,5(C_3F_7)_2$	256·5	325		
$3,4,6(C_3F_7)_3$	255·5	326·5		
$4C_2F_5$	262·5	312		
$4,5(C_2F_5)_2$	278·5	349		
$3,4,5(C_2F_5)_3$	268	-		
$(C_2F_5)_4$	260	356		
$4\text{-sec.}C_4F_9$	261	306·5		
$4,5\text{-sec.}C_4F_9$	277·5	338		
$3,5\text{-sec.}C_4F_9$	257	325		

As can be seen from the table, the substitution of a methoxyl group for a proton or a fluorine in the pyridazine or tetrafluoropyridazine rings, causes a bathochromic shift in the $\pi \rightarrow \pi^*$ band. The situation is not as clear in the shift of the $n \rightarrow \pi^*$ band however.

The introduction of perfluoroalkyl groups into the 4- and 5-positions of tetrafluoropyridazine, causes bathochromic shifts in the lowest $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands, regardless of the particular perfluoroalkyl group.

Perfluoroalkyl groups in the 3- and 6-positions, however, cause a hypsochromic shift in the lowest $\pi \rightarrow \pi^*$ band, (compare $\lambda_{max.}$ of 4-mono- with 3,5-di- and 3,4,6-tri-heptafluoroisopropylpyridazines). This is not as great in magnitude, however, as the bathochromic shift due to perfluoroalkyl groups in the 4- and 5-positions. The $n \rightarrow \pi^*$ band suffers a very small bathochromic shift as a result of perfluoroalkyl groups in the 3- and 6-positions.

Clearly substituents in the 4- and 5-positions should affect the lowest anti-bonding orbital ψ_4, and to a lesser extent the highest bonding orbital ψ_3, whereas substituents in positions 3 and 6 should not affect ψ_4 at all but should affect ψ_3. Perfluoroalkyl groups in positions 4 and 5 are thought to stabilise ψ_4 more than fluorine, and have only a slight effect upon ψ_3, resulting in the bathochromic shift observed in the lowest $\pi \rightarrow \pi^*$ band. Perfluoroalkyl groups in the 3- and 6-positions cannot have any effect upon ψ_4, and are thought to have only a slight stabilising effect upon ψ_3, relative to fluorine. This is because the net hypsochromic effect observed in the lowest $\pi \rightarrow \pi^*$ band upon substitution of a perfluoroalkyl group in the 3-position is small (compare $\lambda_{max.}$ of 4-mono- with 3,5-bis-isopropyl-pyridazines).

Perfluoroalkyl groups in all positions on the pyridazine ring cause a bathochromic shift in the $n \rightarrow \pi^*$ band. The shift is greater for substituents in the 4- and 5-positions, than in the 3- and 6-positions (compare $\lambda_{max.}$ $n \rightarrow \pi^*$ of 4-mono- and -4,5-di- with -3,5-di- and -3,4,6-tri-heptafluoroisopropylpyridazines). This is thought to be because the stabilisation of the π orbital ψ_4, is far greater than the change in energy of the non-bonding orbitals of the nitrogens. Furthermore, if this was not the case perfluoroalkyl groups closest to the nitrogens (i.e. in positions 3 and 6) would be expected to have the greatest effect on the wavelength of the $n \rightarrow \pi^*$ band.

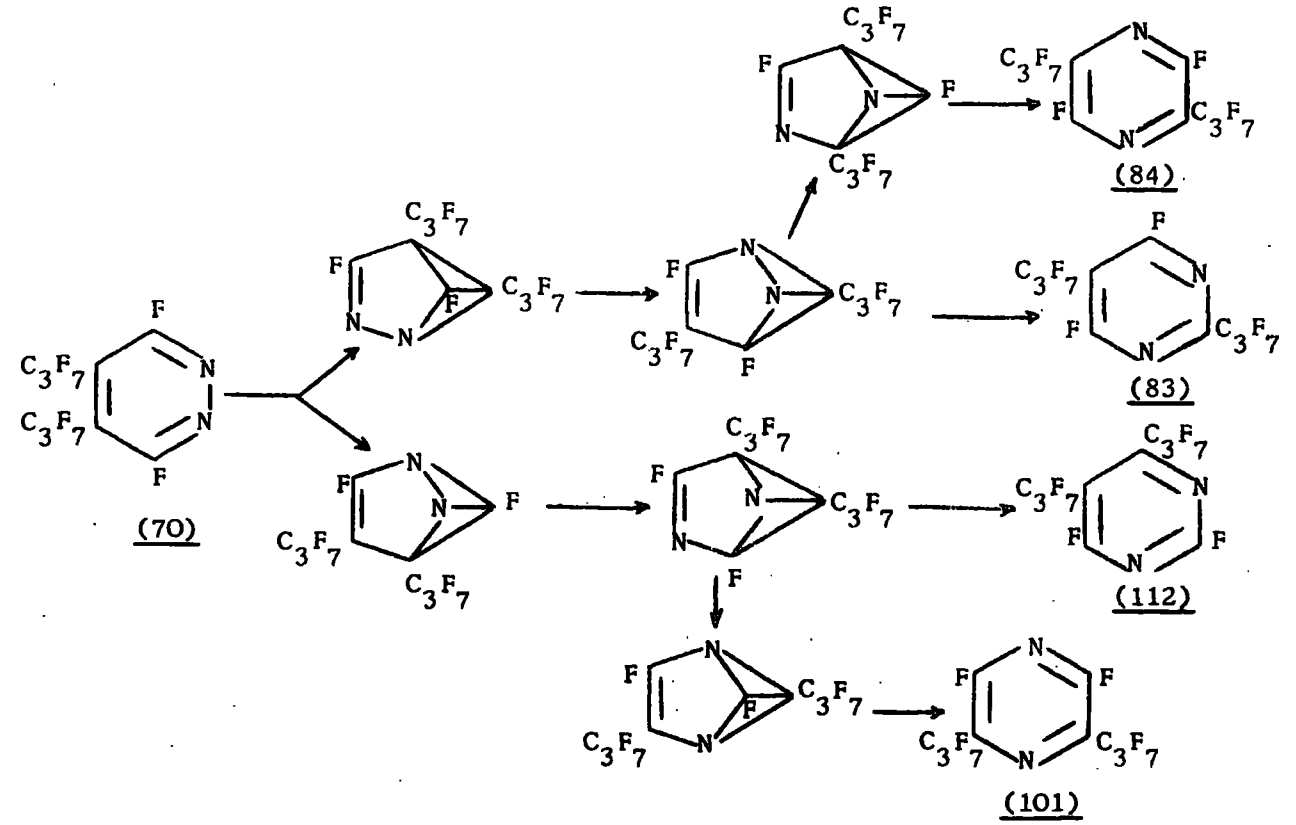
Perfluoroalkyl groups in positions 3 and 6 cannot affect ψ_4 yet a bathochromic shift is observed. This implies that perfluoroalkyl groups have a smaller inductive effect than fluorine.

It has been claimed, that if perfluoroalkyl groups are to promote the isomerisation of pyridazine to pyrazine, they should raise the energy of the ground state by distortion of the aromatic pyridazine, due to steric interaction between the perfluoroalkyl groups.[30,62] However, in order to explain the observed movement of the lowest $\pi \rightarrow \pi^*$ transitions, in the ultraviolet spectra upon substitution, one has to postulate that perfluoroalkyl groups lower the ground state energy relative to fluorine. Since perfluoroalkyl groups lower the energy of the highest occupied π-orbital ψ_3, in positions 3 and 6 more than in positions 4,5, it is logical that groups in the former positions should hinder the isomerisation more than when they are in the latter ones. Hence, there does appear to be an overt relationship between changes in the ultraviolet spectra and ease of isomerisation, however, how this effect arises cannot, at present, be explained.

3.8. Conclusion to Labelling Experiments.

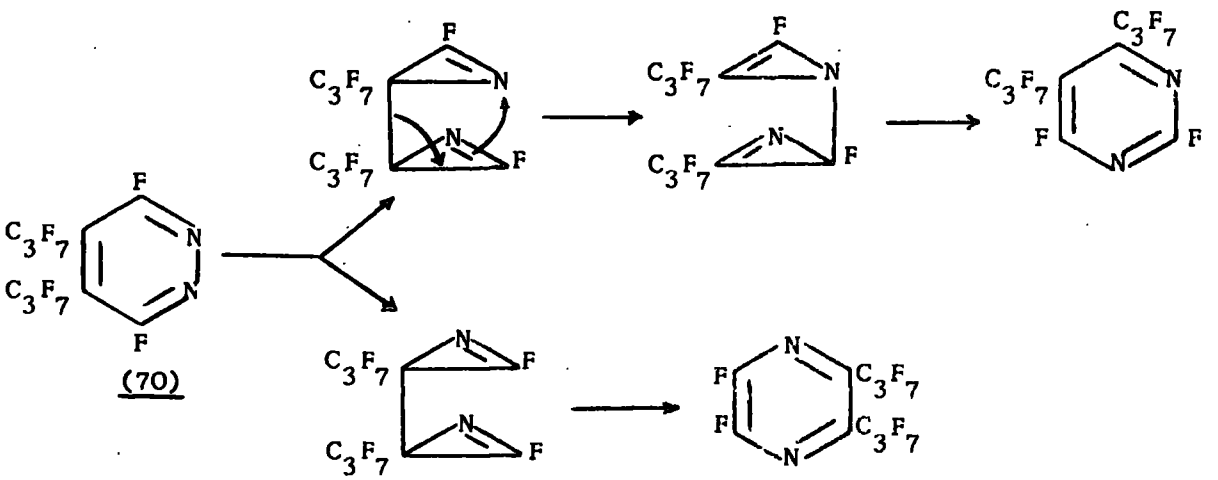
As was seen above a diazaprismane intermediate cannot explain the products formed upon photoisomerisation of various polyfluoroalkyl labelled pyridazines.

A diazabenzvalene intermediate cannot explain the observed specificity of the photoisomerisation. One would expect more than one isomer of pyrazine to be formed from the di-substituted pyridazines and also some pyrimidines and these have been shown to be photostable, e.g.



Since only the 2,5-di-substituted pyrazine (84) is isolated in relatively short irradiations of (70) the above mechanism would not be specific enough and hence cannot play a major role in the photo-isomerisation.

The 1,3-shift of groups and nitrogens can also be explained by rearrangement of diazabicyclopropenyl intermediates, however, it is by no means specific and hence also has to be considered an unlikely rearrangement.



Clearly it would be possible to produce any isomer of pyrimidine or pyrazine after the appropriate number of steps.

The only mechanism which explains the stereospecificity of the reaction is the one which involves a rearrangement of the initially formed diazadewarbenzene.

3.9. Isolation of Valence Isomers.

A. Introduction.

In order to establish conclusively which intermediates the photo-isomerisation of pyridazines to pyrazines occurs through the isolation of valence isomers was of high importance. The following deals with the attempts and success at trapping valence isomers and shows conclusively which intermediate valence isomers are responsible for photoisomerisations observed.

B. Apparatus.

Trapping experiments were performed in the apparatus shown below. The idea being that, since valence isomers are known to be more volatile[27,28,29,30,31] than their aromatic counterparts, they would as soon as they were formed condense in the cold trap, and hence be removed from the irradiation zone.

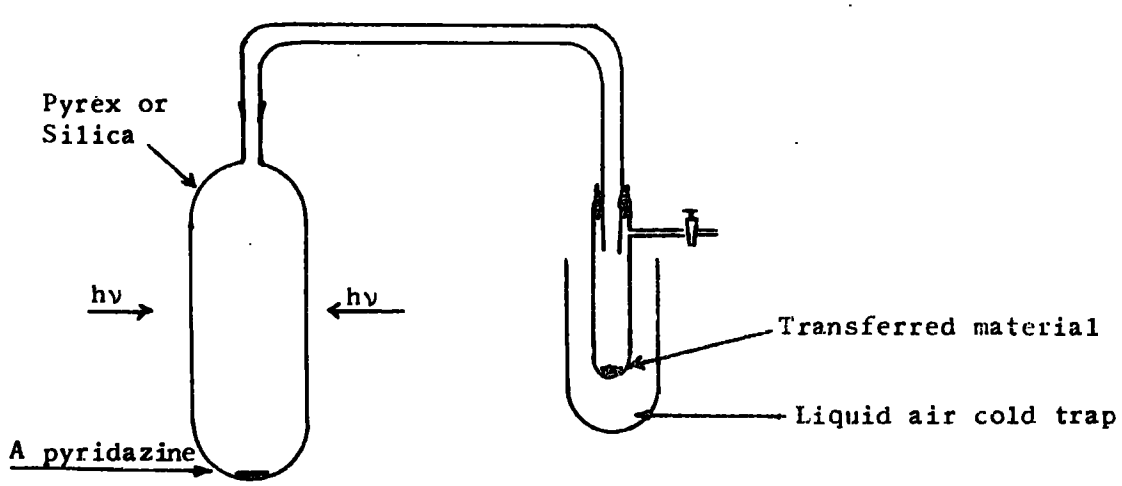


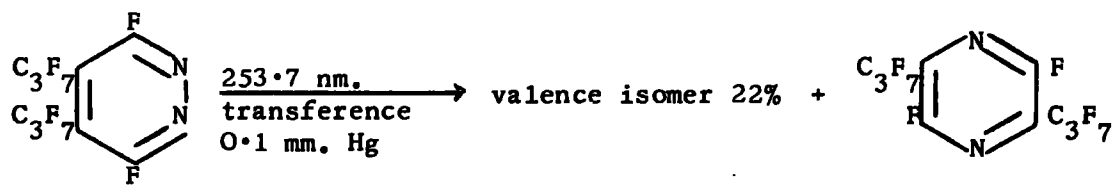
Fig. 2.

By variation in the pressure inside the transference apparatus, by addition of air, the pyridazines to be photolysed could be made to transfer at different rates, and by a hit and miss procedure, pyridazines of different volatilities could be made to transfer at ca. the same rate.

C. Attempted Isolation of Intermediates from Irradiations at 253·7 nm.

1. From Perfluoro-4,5-bis-isopropylpyridazine.

The first trapping experiments using the apparatus above were carried out on perfluoro-4,5-bis-isopropylpyridazine by K.C. Srivastava, and resulted in the isolation of the first diaza valence isomer, which converts to pyrazine (84) quantitatively upon heating and irradiation at 253·7 nm.

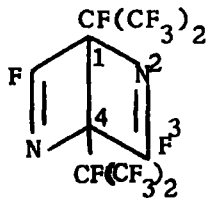


(70) (84)

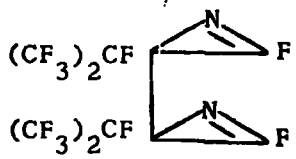
+ (70) 50%

This valence isomer showed only end absorption in its ultraviolet spectrum. A diazabenzvalene could be expected to absorb at ca. the wavelength as benzvalenes; ca. 230 nm.,[23,24,63] and hence can be ruled out. Since its infrared spectrum shows a strong absorption at 1680 $cm.^{-1}$ a diazaprismane can be ruled out. This leaves a diazadewarbenzene and a diazabicyclopropene as the only possible valence isomers since both have double bonds (C=N). The ^{19}F n.m.r. spectrum of the valence isomer shows four signals at 37·1, 74·2, 75·7, and 181·1 p.p.m. in the area ratio 1:3:3:1 respectively. The resonances at 74·2 and 75·7 p.p.m. are characteristic in chemical shift of the trifluoromethyl groups of perfluoroisopropyl groups, as is the resonance at 181·1 p.p.m. of the tertiary fluorine of the latter group. Both the diazadewarbenzene (113) and the

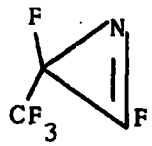
diazabicyclopropene (114) could give four resonances in ^{19}F n.m.r. spectrum (the trifluoromethyl groups are non-equivalent because the heptafluoro-isopropyl group is attached to an asymmetric centre).



(113)

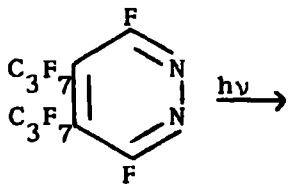


(114)

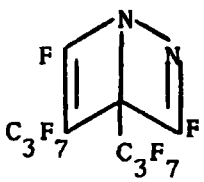


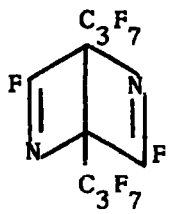
(115)

The chemical shift of the imine fluorines in (114) would be expected to be similar to that of imine fluorine in perfluoro-(2-methyl-2H-azirine) (115) which absorbs at 98·9 p.p.m. Since it is very different, occurring at a much lower field 37·1 p.p.m. the valence isomer is assigned the diazadewarbenzene structure (113). This is one of the diazadewarbenzenes proposed to take part in the photoisomerisation of (70), i.e.

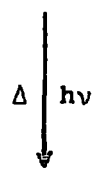


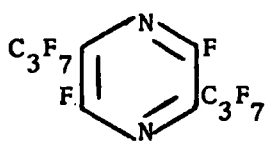
(70)





(113)



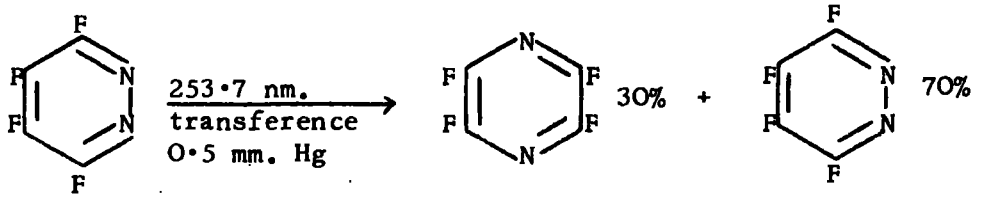


(84)

It was also shown that the pyrazine (84) did not yield the diazadewarbenzene (113) upon irradiation at 253·7 nm. whilst under transference.

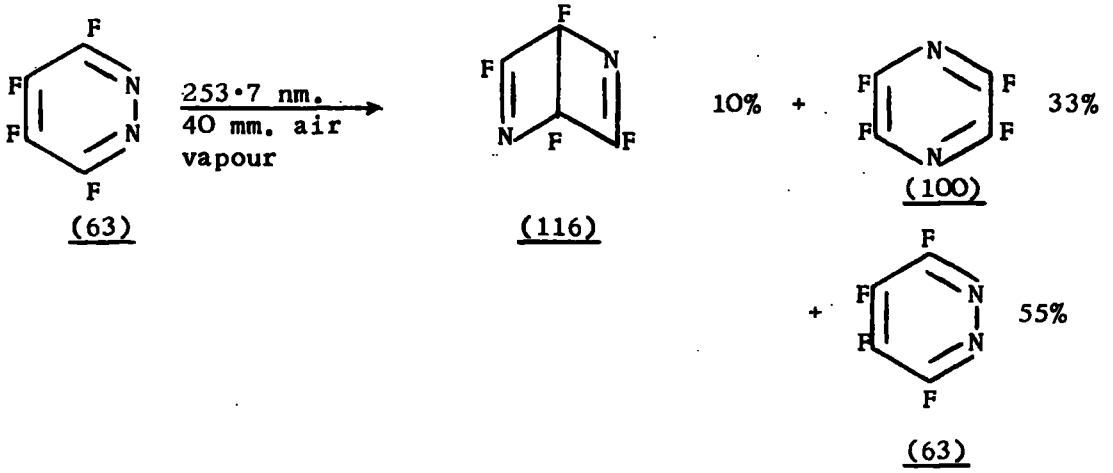
2. From Tetrafluoropyridazine.

The irradiation of tetrafluoropyridazine at 253·7 nm. whilst under transference was shown[50] to give only a mixture of starting material and tetrafluoropyrazine.



(63) (100) (63)

The irradiation of tetrafluoropyridazine vapour in a sealed tube yielded a mixture of diazadewarbenzene (116), tetrafluoropyrazine and tetrafluoropyridazine.



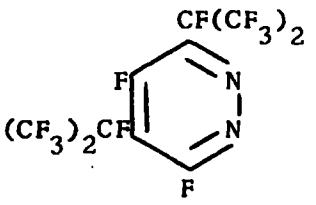
(63) (116) (100) (63)

The diazadewarbenzene (116) shows a strong absorption at 1656 $cm.^{-1}$ in its infrared spectrum and only end absorption in its ultraviolet spectrum. The ^{19}F n.m.r. spectrum shows only two resonances at 47·4 and 174·2 p.p.m. in the ratio 1:1 which are in the expected regions for the imine and tertiary fluorines respectively.

The diazadewarbenzene (116) isomerises to tetrafluoropyrazine upon heating and photolysis.

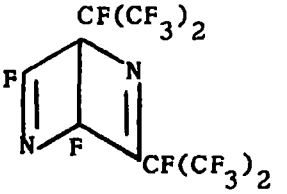
3. From Perfluoro-3,5-bis-isopropylpyridazine.

The original work aimed at the isolation of the diazadewarbenzene (117) from the irradiation of perfluoro-3,5-bis-isopropylpyridazine (72), and this proved difficult. Transference experiments with (72), at a variety of pressures with irradiation at 253·7 nm. gave (117) as less than 8% of the total product, and poorly separated from other products. In one experiment, however, a good yield of (117) was obtained. This latter experiment could not be repeated.

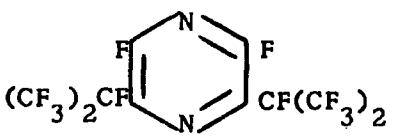


(72)

253·7 nm.
transference
0·01 mm. Hg



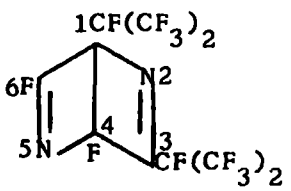
(117) 21%

+  13% + unidentified products 11%

+ (72) 55%

(101)

Perfluoro-1,3-bis-isopropyl-2,5-diazabicyclo[2,2,0]hexa-2,5-diene (117) shows a strong absorption in its infrared at 1688 cm. (cf. (113) at 1680 $cm.^{-1}$) and very weak absorptions at 218 and 268 nm. in its ultraviolet spectrum. The ^{19}F n.m.r. spectrum of (117) showed a low field fluorine at 42·2 p.p.m. and three tertiary fluorines at 162·1, 187·1 and 192·0 p.p.m. other than the resonances for the trifluoromethyl groups. The low field fluorine has a very similar shift to that of the imine fluorines in (113) and (116), which occur at 37·1 and 47·4 p.p.m. respectively, and is hence assigned to the 6-fluorine. The two tertiary fluorines at 187·1 and 192·0 p.p.m. can be assigned to the 1- and 3-heptafluoroisopropyl groups. The tertiary fluorine at 162·1 must be due to the bridgehead fluorine (cf. (116) at 174·2 p.p.m.). The structure of (117) was confirmed by its

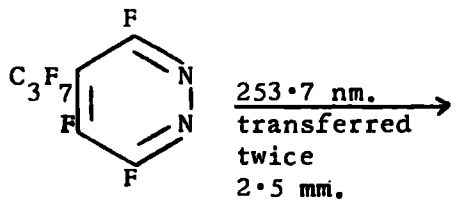


(117)

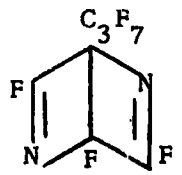
conversion to pyrazine (101) upon heating and photolysis at 253·7 nm. and at $\lambda > 280$ nm.

4. From Perfluoro-4-mono-isopropylpyridazine.

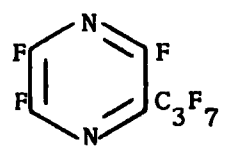
The irradiation of perfluoro-4-mono-isopropylpyridazine (71) at 253·7 nm. whilst under transference, gave the diazadewarbenzene (118) as 38% of the transferred product, in one experiment.



(71)



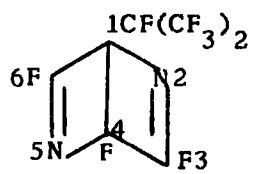
(118) 38%

+ 

(102) 52% + (71) 10%

The infrared spectrum of (118) showed a strong absorption at 1665 $cm.^{-1}$ (cf. 1656 $cm.^{-1}$ in (113)). The ultraviolet spectrum showed a weak absorption at 206 nm., a weaker one at 244 nm. and a very weak one at 325 nm.

The ^{19}F n.m.r. spectrum of (118) shows, apart from two trifluoromethyl resonances, two resonances at 42·4 and 45·0 p.p.m. which can be assigned to the 6- and 3-imine fluorines. It also shows two high field resonances



(118)

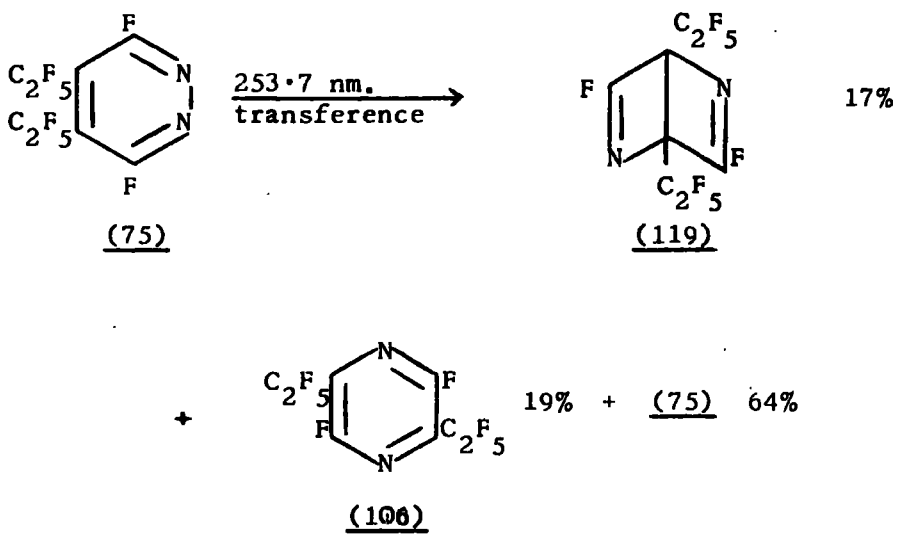
at 166·0 and 187·1 p.p.m., the latter of which is characteristic of the tertiary fluorines of the heptafluoroisopropyl group, and the former of the bridgehead fluorines of these 2,5-diazadewarbenzenes (e.g. 174·2 p.p.m. in (116)).

The high yield (38%) of the diazadewarbenzene (118) could not be reproduced although a variety of conditions were used. The irradiation of (71) at 253·7 nm. whilst under transference was carried out in the presence and absence of oxygen, acetone, and 40-60° petroleum ether, and at different pressures, but the yield of the diazadewarbenzene (118) never exceeded 22%.

The structure of the diazadewarbenzene (118) is confirmed by its conversion to the pyrazine (102) upon heating and photolysis at 300 nm.

5. From Perfluoro-4,5-bis-ethylpyridazine.

The irradiation of perfluoro-4,5-bis-ethylpyridazine (75) at 253·7 nm. whilst under transference gives the diazadewarbenzene (119) together with perfluoro-2,5-bis-ethylpyrazine (106).



(75) (119)

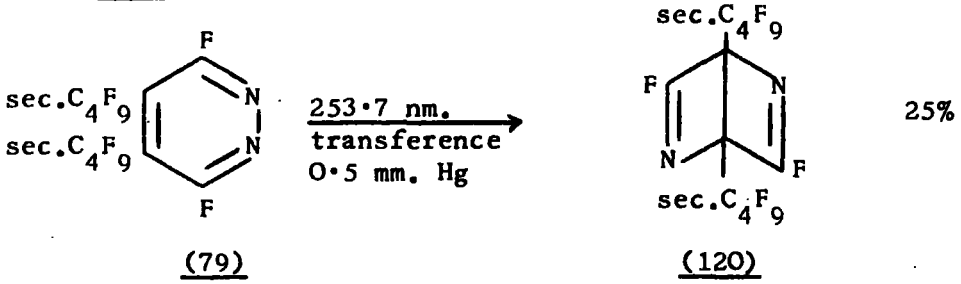
(106)

The relative amount of the diazadewarbenzene (119) can be increased, by re-irradiation of the transferred product to ca. 24% of the product mixture. The diazadewarbenzene (119), again shows a strong absorption in its infrared spectrum in the region expected for C=N at 1672 $cm.^{-1}$ (cf. 1680 $cm.^{-1}$ in (113)). The ultraviolet spectrum shows weak absorptions at 219 and 234 nm. with a tail absorbing down to ca. 330 nm. The ^{19}F n.m.r. spectrum shows four signals at 38·6, 84·9, 121·2, and 125·8 p.p.m. in the area ratio 1:3:1:1. The low field resonance at 38·6 p.p.m. can be

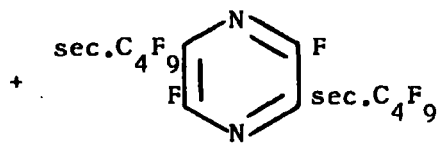
assigned to the 3- and 6-imine fluorines. The resonance at 84·9 is assigned to the trifluoromethyl groups of the pentafluoroethyl group. The most striking aspect of this spectrum is the non-equivalence of the difluoromethylene fluorines. This is presumably because the pentafluoroethyl groups are attached to asymmetric bridgehead carbons. The difluoromethylene fluorines couple with each other, J_{AB} being 286 Hz.

6. From Perfluoro-4,5-bis-sec.butylpyridazine.

The irradiation of perfluoro-4,5-bis-sec.butylpyridazine (79) at 253·7 nm. whilst under transference was shown[50] to yield perfluoro-1,4-bis-sec.butyl-2,5-diazabicyclo[2,2,0]hexa-2,5-diene (120) together with pyrazine (107).



(79) (120)



35% + (79) 30%

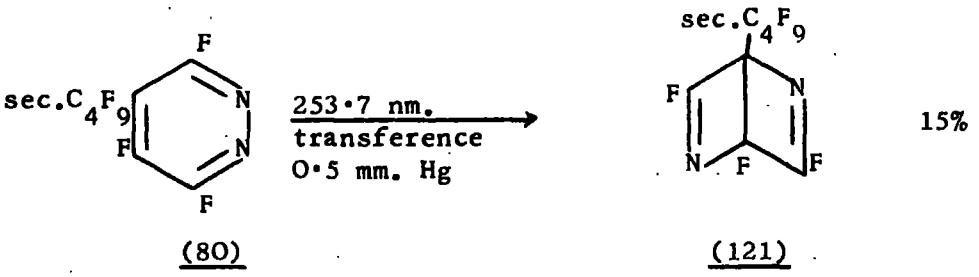
+ minor components 10%

(107)

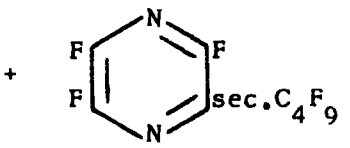
The diazadewarbenzene (120) showed a strong absorption at 1677 $cm.^{-1}$ in its infrared spectrum in the same region as other 2,5-diazadewarbenzenes above. The ^{19}F n.m.r. spectrum showed the perfluoro-sec.butyl resonances and a lowfield resonance at 36·6 p.p.m. which is assigned to the imine fluorines (cf. 37·1 in (113)).

7. From Perfluoro-4-mono-sec.butylpyridazine.

The irradiation of perfluoro-4-mono-sec.butylpyridazine (80) by a 253·7 nm. source whilst under transference has been shown[50] to yield the 2,5-diazadewarbenzene (121).



(80) (121)



(104)

The 2,5-diazadewarbenzene (121) showed the characteristic strong absorption in its infrared spectrum at 1661 $cm.^{-1}$ Its ^{19}F n.m.r. spectrum showed three resonances apart from those due to the perfluoro-sec.butyl group. Two of these were at low field, 42·1 and 45·5 p.p.m. and are assigned to the 6- and 3-imine fluorines (cf. 42·4 and 45·0 p.p.m. in (118)). The third resonance was at high field, 165·6 p.p.m. and is assigned to the bridgehead fluorine (cf. 166·0 p.p.m. in (118)).

8. From 3,6-Difluoro-4,5-dichloropyridazine.

The irradiation of 3,6-difluoro-4,5-dichloropyridazine at 253·7 nm. whilst under transference caused little reaction to occur. About 1 to 2% of a product more volatile than the starting material was formed together with much decomposition on the walls of the silica vessel.

9. From 3,5,6-Trifluoro-4-methoxylpyridazine.

The irradiation of 3,5,6-trifluoro-4-methoxylpyridazine at 253·7 nm. whilst under transference resulted in decomposition only, just as was observed in a sealed tube reaction (see above).

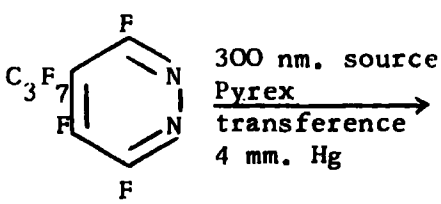
D. Attempted Isolation of Intermediates from Irradiations at 300 nm.

1. From Perfluoro-4-mono-isopropylpyridazine.

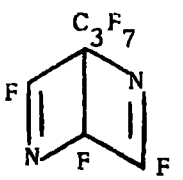
The high conversion of perfluoro-4-mono-isopropylpyridazine (71) to the 2,5-diazadewarbenzene (118) in transference experiments at 253·7 nm.

was found not to be reproducible. There are two possible reasons for this. Once formed the 2,3-diazadewarbenzene (118) can absorb energy at 253·7 nm. and hence be photochemically rearomatised to pyrazine (102), or, if it is formed with much excess vibrational energy it can immediately rearomatise to pyrazine (102).

Irradiation at a longer wavelength could eliminate both these factors. Hence perfluoro-4-mono-isopropylpyridazine (71) was irradiated by the source which has a maximum output of energy at 300 nm. Using a Pyrex filter and the latter source, only the excitation of the long wavelength tail of the lowest $\pi \rightarrow \pi^*$, and the high energy side of the $n \rightarrow \pi^*$ bands of (71) is possible (see Appendix 3). The 2,5-diazadewarbenzene (118) cannot absorb much energy either. Under these conditions, it was found that the transferred product contained less than 1% of the pyrazine (102). Re-irradiation several times caused almost quantitative conversion to the diazadewarbenzene (118).

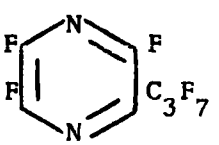


300 nm. source
Pyrex
transference
4 mm. Hg



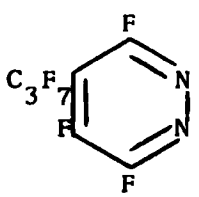
45%

(71) (118)

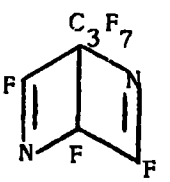
+ 

< ·5% + (71) 54·5%

(102)



300 nm. source
Pyrex
transferred
3 times
4 mm. Hg



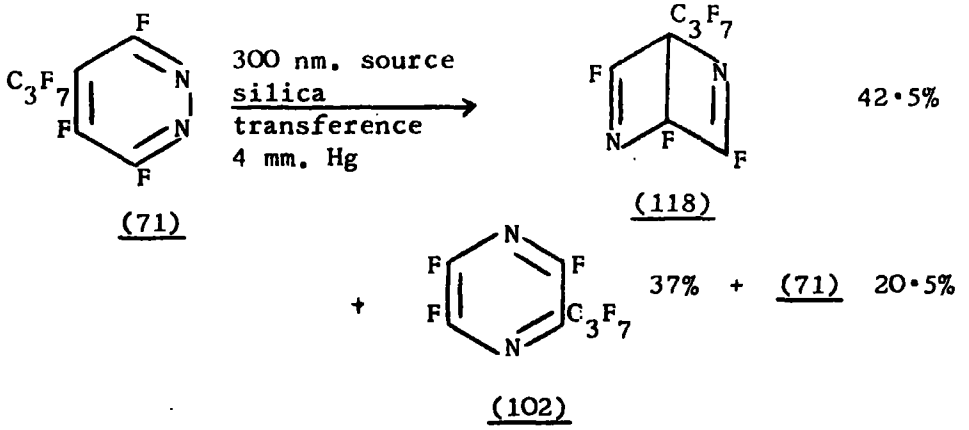
94%

(71) (118)

+ (102) < 1% + (71) ca. 5%

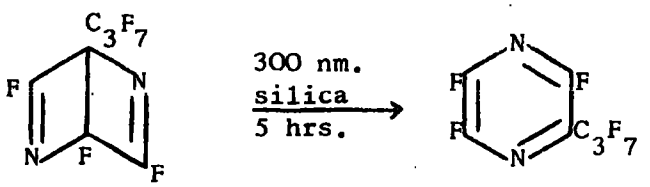
If more than ca. 8 g. of (71) is irradiated whilst under transference, decomposition products upon the walls of the Pyrex vessel, cause the conversion to (118) to go down. This is because the decomposition products prevent light from entering the vessel.

Irradiation of (71) at 300 nm. in silica whilst under transference causes more pyrazine to be formed.



(71) (118) (102)

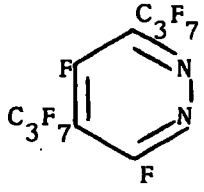
The higher yield of pyrazine (102) could be the result of the initially formed 2,5-diazadewarbenzene (118) containing enough excess vibrational energy to rearomatise, or the result of photochemical rearomatisation. A small amount of the 2,5-diazadewarbenzene was irradiated in a sealed silica tube at 300 nm., and found to convert quantitatively to the pyrazine (102), after only a short period of time.



This indicates that photochemical rearomatisation is extremely efficient, in comparison with the overall isomerisation. This is the likely cause of the formation of larger amounts of pyrazine (102) in irradiations in silica than in Pyrex, at 300 nm. Since the extinction coefficient of the diazadewarbenzene (118) is greater at 253·7 nm. than at ca. 300 nm., this can also explain the even larger amounts of pyrazine (102) formed in transference reactions at 253·7 nm.

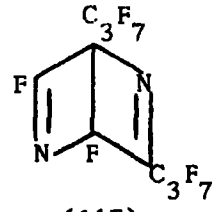
2. From Perfluoro-3,5-bis-isopropylpyridazine.

Because of the success with pyridazine (71), perfluoro-3,5-bis-isopropylpyridazine was also irradiated at 300 nm., both in Pyrex and in silica, whilst under transference. However, the amount of the 2,5-diazadewarbenzene (117) did not increase in comparison with irradiation at 253·7 nm. In Pyrex, however, fewer unknown compounds were formed.

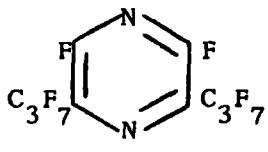


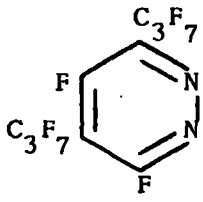
(72)

300 nm.
Pyrex
transference
4 mm. Hg



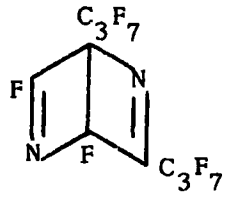
(117) 8%

+  3·5% + (72) 88% + unknowns 0·5%

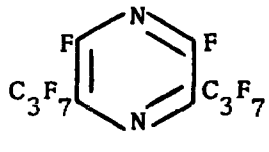


(72)

300 nm.
silica
transference
4 mm. Hg

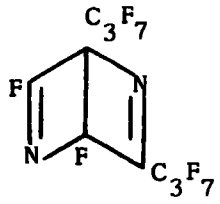


(117) 9%

+ 

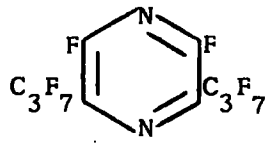
(101) 23% + (72) 58% + unknowns 10%

The irradiation of the diazadewarbenzene (117) by a medium pressure mercury arc in Pyrex causes quantitative conversion to the pyrazine (101). Hence it is likely, that the reason why a high yield of the diazadewarbenzene (117) cannot be obtained at 300 nm. is that the latter diazadewarbenzene absorbs (although weakly) at this wavelength causing rearomatisation.



(117)

m.p. Hg
Pyrex
105 mins.



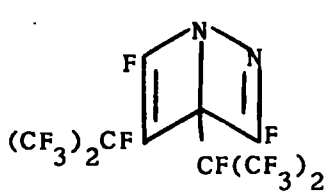
(101)

93% + (117) 6% + unknown 1%

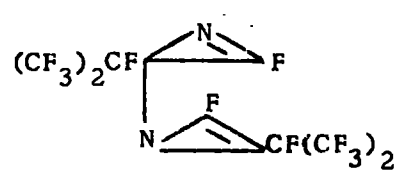
3. From Perfluoro-4,5-bis-isopropylpyridazine.

The irradiation of perfluoro-4,5-bis-isopropylpyridazine (70) at 300 nm. in Pyrex, whilst under transference results in no observable reaction. This is attributed to poor-overlap between the absorption bands of (70) and the irradiation envelope of the 300 nm. source in Pyrex.

The irradiation of (70) at 300 nm. in silica whilst under transference, however, gives ca. 19% of an intermediate which was at first thought to be the 2,5-diazadewarbenzene (113), because its g.l.c. retention time was identical to that of (113). Its infrared spectrum, however, shows two strong absorptions at 1735 and 1670 $cm.^{-1}$ indicating two types of double bonds, whereas the 2,5-diazadewarbenzene has only one type of double bond absorbing at 1680 $cm.^{-1}$. The infrared spectrum also eliminates diazabenzvalene and diazaprismane as possible intermediates. The ultraviolet spectrum shows only a weak absorption at 223 nm. (ϵ = 1745). The ^{19}F n.m.r. shows two low field resonances at 61·1 and 63·0 p.p.m. which each integrate to one fluorine, apart from the resonances due to the heptafluoroisopropyl groups, which are non-equivalent. There are two possible structures which could give the observed spectra, the 1,2-diazadewarbenzene (122) and the diazabicyclopropene (123).

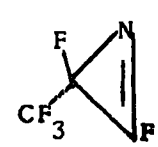


(122)



(123)

Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2,2,0]hexa-2,5-diene



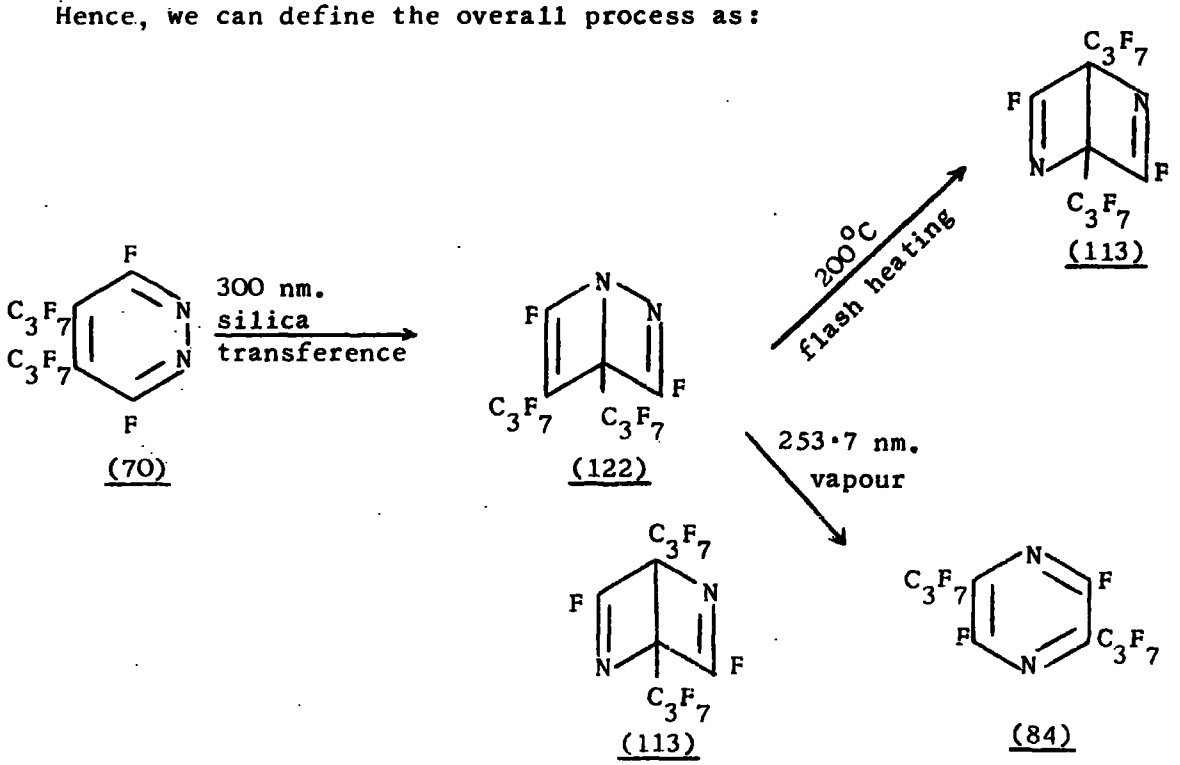
(115)

However, there are two difficulties with the diazabicyclopropene (123). One is that, one of the rings is antiaromatic, and hence we would expect, it to be very unstable, the product isolated is not unstable. The other is that the imine fluorine in the top ring should be similar to that of the imine fluorine in perfluoro-(2-methyl-2H-azirine) (115) which absorbs at 98·9 p.p.m.

Hence the valence isomer isolated is assigned the structure of the 1,2-diazadewarbenzene (122).

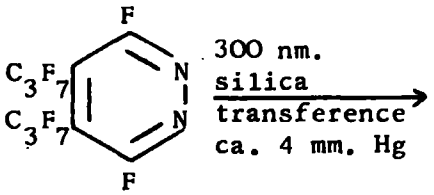
Upon flash heating at ca. 200°C (contact time < 1 sec.) the 1,2-diazadewarbenzene (122) is converted almost quantitatively to the 2,5-diazadewarbenzene (113), and on photolysis at 253·7 nm. it is converted to a 50/50 mixture of the 2,5-diazadewarbenzene (113) and pyrazine (84).

Hence, we can define the overall process as:



(70) (122) (113) (113) (84)

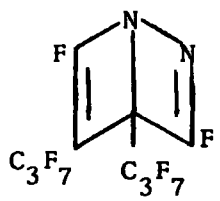
Re-irradiation of the product containing 19% of the 1,2-diazadewarbenzene (122) causes more of the starting material (70) to be converted to (122). A product mixture containing ca. 64% (122) was obtained upon re-irradiation 3 times.

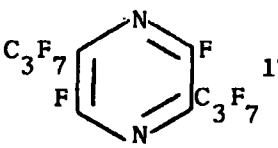


(70) → (122) 19% + (184) 6%

+ (70) 71% + unknowns 4%

300 nm. silica | transferred 3 times ca. 1 mm. Hg

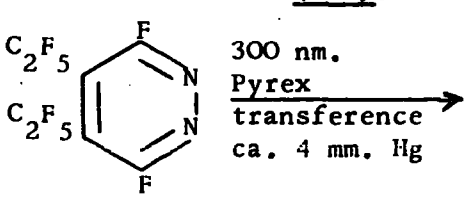


64% +  17% + (70) 11% + unknowns 8%

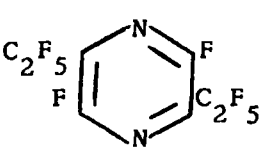
Decomposition upon the sides of the silica vessel used prevents more than ca. 5 gms. being transferred in any one reaction. Larger amounts of (70) cause the number of re-irradiations to be increased.

4. From Perfluoro-4,5-bis-ethylpyridazine.

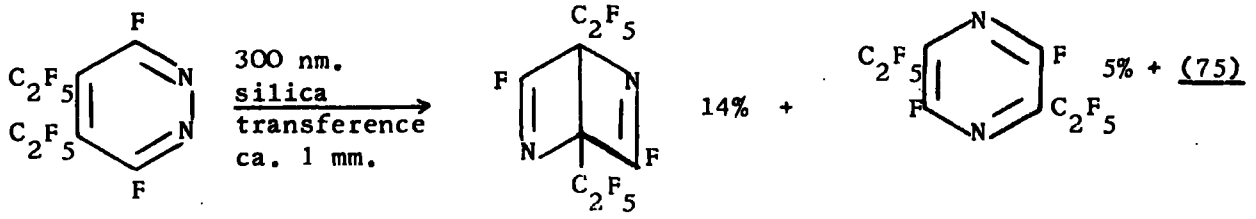
The irradiation of perfluoro-4,5-bis-ethylpyridazines (75) at 300 nm., in Pyrex and in silica, whilst under transference gave only the 2,5-diazadewarbenzene (119).



(75) → (119) 9%

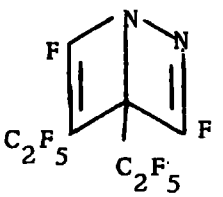
+  7% + (75)

(106)



(75) (119) (106) (75)

Re-irradiation in silica causes an increase in the amount of the 2,5-diazadewarbenzene (119) (17%) but also an increase in the amount of pyrazine (106) (16%). The reason why the 1,2-diazadewarbenzene (124) could not be isolated will be discussed in Chapter 4. However, the reasons



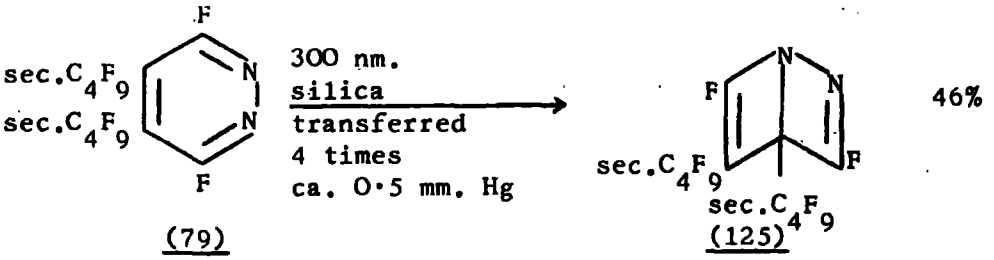
(124)

why the 2,5-diazadewarbenzene could not be isolated in high yield are not understood.

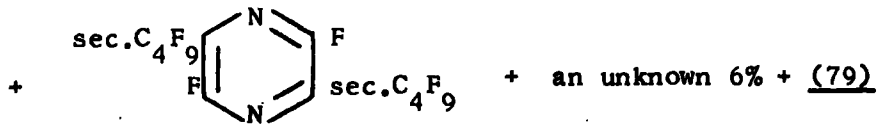
5. From Perfluoro-4,5-bis-sec.butylpyridazine.

The irradiation of perfluoro-4,5-bis-sec.butylpyridazine (79) at 300 nm., in silica, whilst under transference yields a different diaza-dewarbenzene to that which was isolated in the irradiation at 253·7 nm.[50] The infrared spectrum of this diazadewarbenzene shows two absorptions at 1735 and 1669 $cm.^{-1}$, indicating the isolation of a 1,2-diazadewarbenzene analogous to that which was isolated from perfluoro-4,5-bis-isopropylpyridazine. The ^{19}F n.m.r. shows two resonances at 62·2 and 62·6 p.p.m. integrating to one fluorine each, apart from the resonances due to the two non-equivalent perfluoro-sec.butyl groups. Hence this dewarbenzene is identified as the

1,2-diazadewarbenzene (125). The two resonances at ca. 62 p.p.m. are thus assigned to the 3- and 6-imine fluorines.



(79) (125)

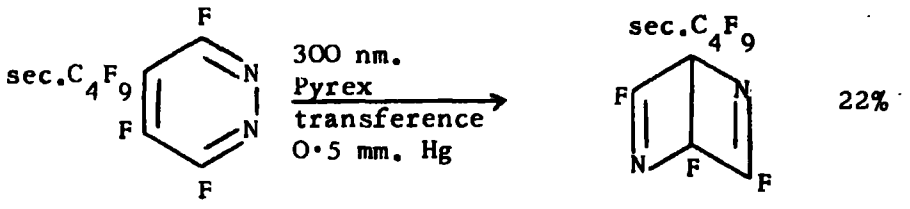


(107)

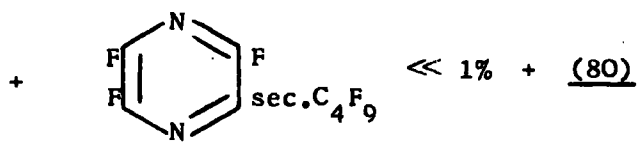
The 1,2-diazadewarbenzene (125) converts to pyrazine (107) via the 2,5-diazadewarbenzene (120) upon heating.

6. From Perfluoro-4-mono-sec.butylpyridazine.

The irradiation of perfluoro-4-mono-sec.butylpyridazine (80) at 253·7 nm. whilst under transference, has been shown[50] to give the 2,5-diazadewarbenzene (121) together with a large amount of the pyrazine (104) (see above). With the 300 nm. source and a Pyrex filter, however, less than 1% of the pyrazine (104) is formed. This would allow ca. quantitative conversion to the 2,5-diazadewarbenzene (121) upon re-irradiation.

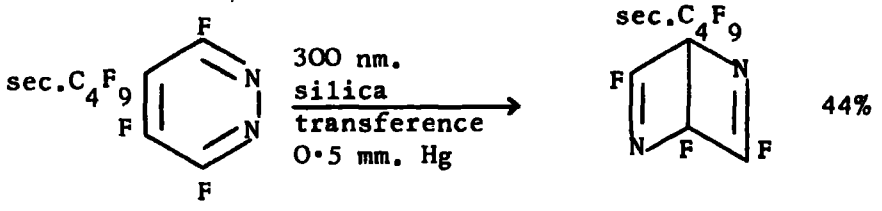


(80) (121)



(104)

The irradiation of (80) at 300 nm. on silica causes a larger amount of pyrazine (104) to be produced but also a larger amount of the 2,5-diaza-dewarbenzene (121).



(80) (121)

(104)

7. From 3,6-Difluoro-4,5-dichloropyridazine.

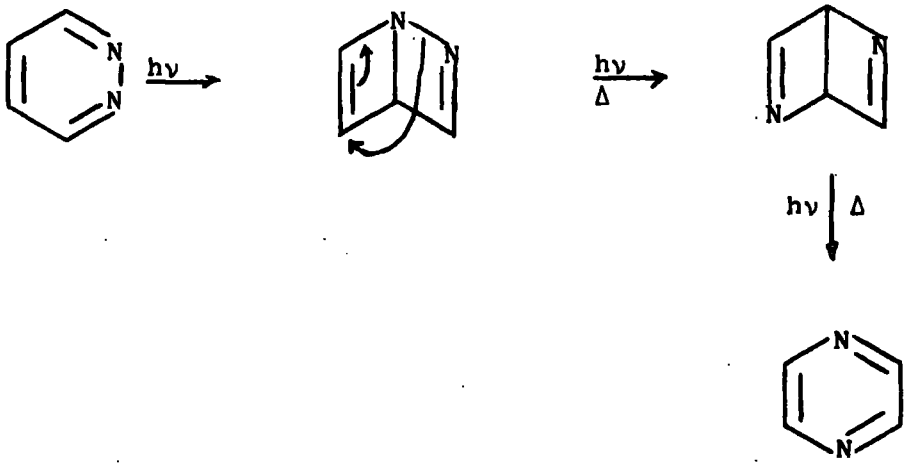
The irradiation of 3,6-difluoro-4,5-dichloropyridazine at 300 nm., in silica, whilst under transference has been carried out. The product after two transferences contained a small amount (4%) of a more volatile compound and ca. 7% of a much more involatile one than starting material. Neither were isolated. Some decomposition on the sides of the silica was observed also.

3.10. Conclusion.

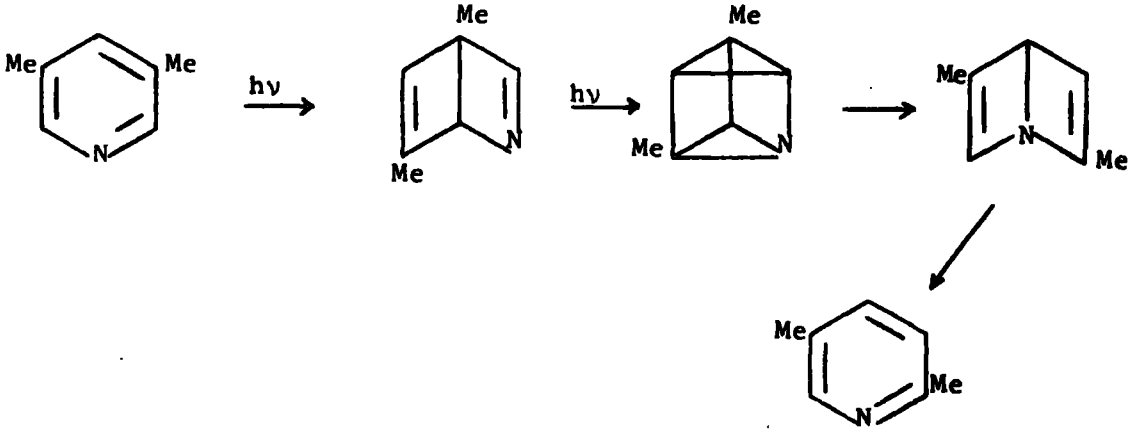
Described above is a new 1,3-shift of aromatic ring atoms. The labelling experiments show that there is no other reaction occurring simultaneously because reaction products are very specific. The 1,2-diazadewarbenzenes have been isolated in high yield in the perfluoro-4,5-bis-isopropyl and sec.butylpyridazines, and these were found to convert quantitatively to the respective 2,5-diazadewarbenzenes and pyrazines, upon heating and photolysis. These findings are a clear indication that a unique rearrangement has been discovered, where rearrangement of one dewar into another occurs

in preference to rearomatisation, both thermally and photochemically. The result is a 1,3-shift of the ring atoms.

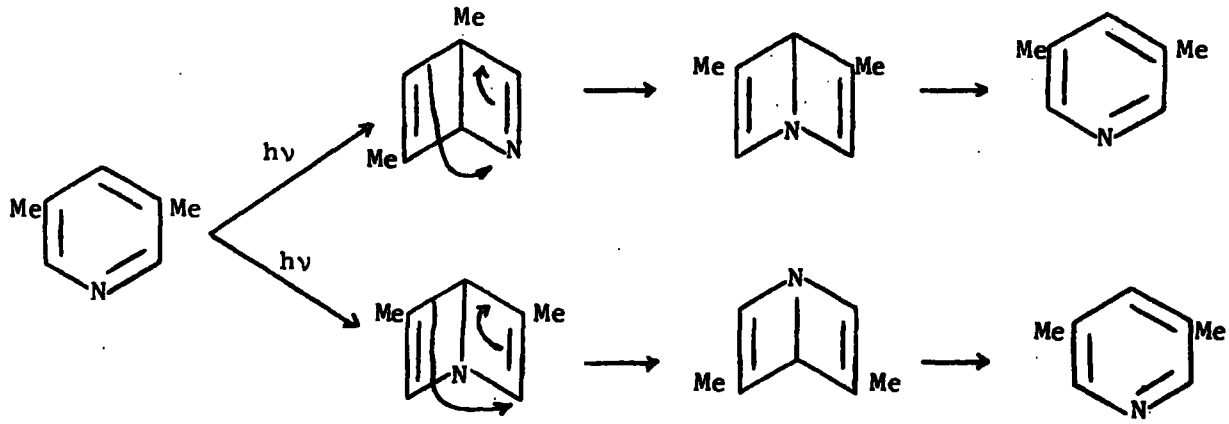
Furthermore, the almost quantitative conversion > 99% of perfluoro-4-mono-isopropyl- and sec.butyl-pyridazines, to the 2,5-diazadewarbenzenes and their quantitative rearomatisation to the respective pyrazines (102) and (104), leaves little doubt that the only photochemical pathway of a pyridazine to a pyrazine is, via rearrangement of the initially formed diazadewarbenzene i.e.



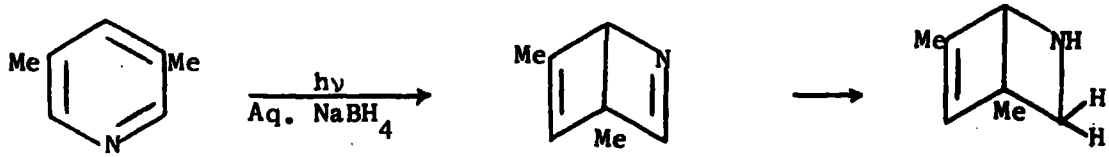
Only one other genuine 1,3-shift of ring atoms has been observed, and that was in the photoisomerisation of the mono-methyl- and di-methyl-pyridines (see Chapter 1). It was observed that the 3-mono-methyl- and 3,5-dimethyl-pyridines did not photoisomerise. This cannot be explained if the intermediacy of an azaprismane, is regarded as the only reaction pathway for isomerisation, i.e.



However, if the mechanism involving rearrangement of an initially formed diazadewarbenzene is considered, it is seen that the 3-mono- and 3,5-di-methylpyridines cannot rearrange.



The photolysis of 3,5-dimethylpyridine in aqueous sodium borohydride solution leads to the formation of the dihydroazadewarbenzene (47a) showing that azadewarbenzene (47b) is formed. This being the case it is possible that rearrangement of dewarbenzenes does occur in the isomerisation of mono-methyl- and di-methyl-pyridines.



(47b) (47a)

CHAPTER 4

Properties of Valence Bond Isomers

4.1. Introduction.

The following is a discussion of the thermal stability, reasons for isolation, and chemical reactivity of various valence isomers.

4.2. Thermal Stability of the Valence Bond Isomers of Benzene.

A. Introduction.

Valence bond isomers are very strained molecules, containing some 70 kcals of excess energy relative to their aromatic counterparts. Hence, one would expect them to have only a very short existence, if any at all. However, many valence bond isomers have been isolated, and some have been found to be remarkably stable w.r.t. thermal rearomatisation. Their stability has been explained, above, by orbital symmetry considerations, which show that there is an energy barrier to a thermal concerted rearomatisation. It has been shown that, both thermally and photochemically induced rearomatisations of valence isomers yield the aromatics in their TRIPLET states,[64,65] not in their singlet states. Hence the process, once it occurs, might not be a concerted process, indicating that for the concerted process to occur far more energy would have to be supplied.

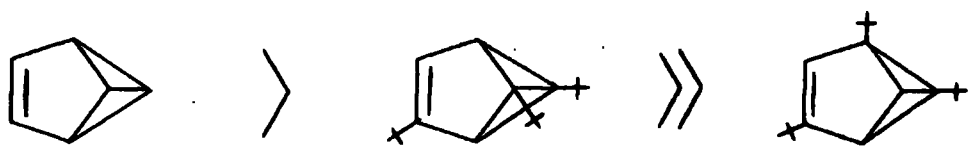
The rearomatisation step has also been reported to be catalysed by electrophiles[62,66,67] and freshly flamed glass,[5,62] in the case of some dewarbenzenes and benzvalenes. This latter finding has to be borne in mind in any discussion of the thermal stability of valence isomers. It could be, that the reason, why many hydrocarbon valence bond isomers are less stable than fluorocarbon ones, is that electrophilic catalised rearomatisation occurs much more efficiently in the hydrocarbon cases.

B. Valence Isomers of Benzene.

1. Hydrocarbon.

Although some alkyl substituted valence isomers are more stable than their unsubstituted counterparts this is not always the case. Benzvalene (4), which has a half life of 31 hrs. at 75°C, is more stable than either of the alkyl substituted benzvalenes (18) $t_{\frac{1}{2}}$ 17 mins. at 24·5°C, or (17) $t_{\frac{1}{2}}$ 7 hrs. at 90°C.

increasing stability ←



(4) (17) (18)

Prismane (6) is, however, marginally less stable than the t.-butyl substituted prismane (16) $t_{\frac{1}{2}}$ 11 hrs. at 90°C and 15 hrs. at 115°C respectively.

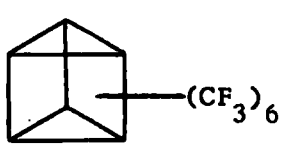
(6) (16)

As can be seen from the two illustrations above, alkyl groups do not necessarily stabilise valence isomers to rearomatisation.

2. Fluorocarbon.

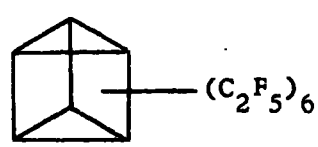
By far the most stable valence isomers are fluorinated ones, especially those with fluoroalkyl substituents e.g. $t_{\frac{1}{2}}$ = 135 hrs. at 170°C for hexakistrifluoromethyldewarbenzene (40).

Some workers have stressed[32,62] that perfluoroalkyl groups destabilise the ground state of aromatics, by distortion of planarity due to steric interaction between the perfluoroalkyl groups, and that there must be stabilisation of valence isomers due to a relief of this steric interaction. Lemal and co-workers have found that interaction between the trifluoromethyl groups in $(CCF_3)_6$, destabilises its ground state by ca. 30 kcals relative to $(CCH_3)_6$, and propose that perfluoroalkyl groups confer stabilising influences upon the strained carbon frameworks such as those of valence bond isomers. The larger the perfluoroalkyl group is, the larger the steric interaction in the ground state aromatic will be, and hence the larger the stabilisation of the valence isomer should be. That is, the stabilising effect of perfluoroalkyl groups should be in the order $CF_3 < C_2F_5 < C_3F_7$ etc. This is not found in the case of hexakistrifluoromethyl and pentafluoroethyl benzenes. The pentafluoroethyl valence isomers are less stable than the trifluoromethyl ones.



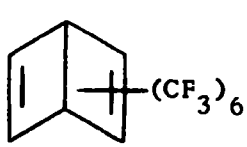
(41)

$t_{\frac{1}{2}}$ 29 hrs. at 170°C



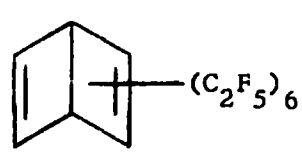
(45)

$t_{\frac{1}{2}}$ 14 hrs. at 170°C



(40)

$t_{\frac{1}{2}}$ 135 hrs. at 170°C



(44)

$t_{\frac{1}{2}}$ 7 hrs. at 170°C

Clearly, stabilisation of benzene valence bond isomers by perfluoroalkyl groups is a major effect, because hexafluorodewarbenzene (31) is much less stable (complete rearomatisation after four hours at 80°C) than either of the dewarbenzenes (40) or (44). The group -C-F appears to have the largest stabilising effect upon these valence isomers.

Both fluorine and perfluoroalkyl groups remove electrons relative to hydrogen and alkyl groups. This could prevent electrophilic catalysed rearomatisation, and hence result in stabilisation of valence isomers. With perfluoroalkyl groups there is additional stabilisation by the -C-F grouping.

C. Valence Isomers of Aza-Benzenes.

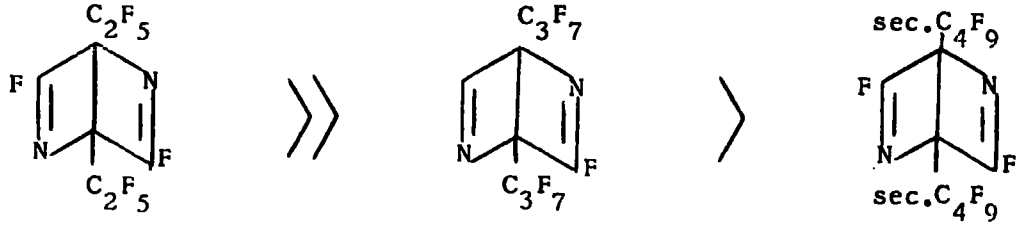
1. Pyridines.

The aza-dewarbenzene derived from pyridine has been reported[33] to have a half-life of 2 minutes at room temperature, whereas the aza-dewarbenzene derived from perfluoropentakisethylpyridine, have been shown[36] to be stable for several hours at 160°C. Hence here again, we see that perfluoroalkylated valence isomers are much more stable than hydrocarbon ones.

2. Pyridazines.

No valence isomers of pyridazine have been isolated. The diazadewarbenzenes of some perfluoropyridazines have been isolated, and the half lives of some of these have been measured. They are shown below (Table 5).

In the case of the 2,5-diazadewarbenzenes with perfluoroalkyl groups in both bridgehead positions, the thermal stability is decreased as the groups get larger.

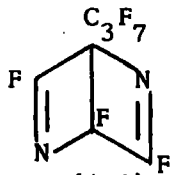
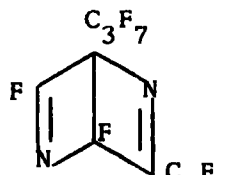
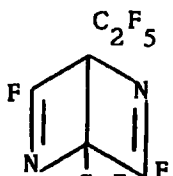
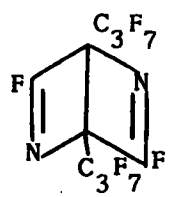
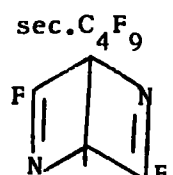
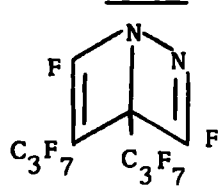
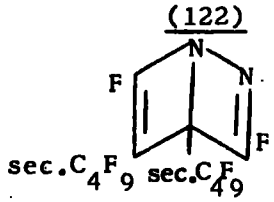


(119) (113) (120)

Although the 2,5-diazadewarbenzene (118) is more stable than the 2,5-diazadewarbenzene (113) it is less stable than (119). It would appear then, that perfluoroalkyl groups in the bridgehead positions stabilise the

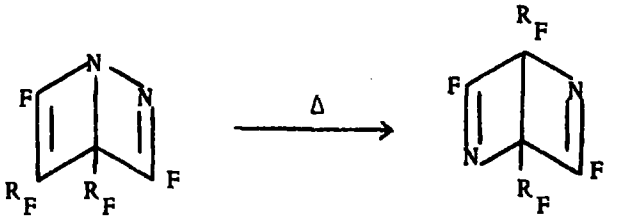
Table 5

The Half-lives of Some Diazadewarbenzenes

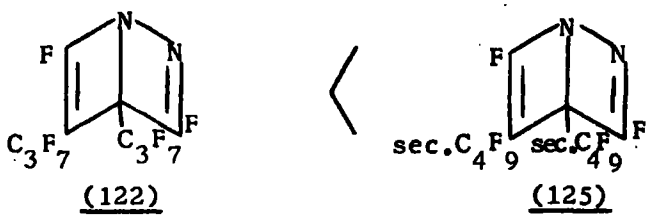
Diazadewarbenzene	$t_{\frac{1}{2}}$ at °C
 (118)	ca. 80 mins. at 105°C
 (117)	ca. 60 mins. at 60°C
 (119)	unchanged after 45 mins. at 100°C
 (113)	5 mins. at 100°C
 (120)	4 mins. at 100°C
 (122)	2·4 hrs. at 102°C
 (125)	unchanged after 44 mins. at 108°C

2,5-diazadewarbenzenes, but that steric interactions between the two groups in the bridgehead positions become important for groups larger than C_2F_5.

For the process,



there must be an activation energy. In the case where R_F = F = F (116); $R_F = C_3F_7$, R_F = F (118); R_F = sec.-C_4F_9, R_F = F (121); and $R_F = C_2F_5 = C_2F_5$ (119) this barrier must be small, because the corresponding 1,2-diazadewarbenzenes have not been isolated. As the groups become larger the energy of the 2,5-diazadewarbenzenes increases. The activation energy for the rearrangement, probably also increases, because the 1,2-diazadewarbenzene (122) is less stable than (125).



(122) (125)

$t_{\frac{1}{2}}$ 2·4 hrs. at 102°C — unchanged after 44 mins at 108°C

4.3. Factors Controlling the Isolation of Valence Isomers.

From the discussion above it is apparent that the thermal stability of valence isomers, in relation to rearomatisation, is not necessarily the major factor controlling the isolation of valence isomers. This is very apparent in the case of prismane (6) which has a half life of eleven hours at 90°C, yet cannot be isolated from the irradiation of benzene.

There must be other factors which are also important. The efficiency of distortion of the electronically excited molecule has to be considered. It has been claimed that bulky groups cause distortion of the aromatic

molecule, in its ground state, and that these would accentuate distortion in the excited state.[30,62] In the original work, perfluoroalkyl groups were found to hinder the photoisomerisation of pyridazine to pyrazine relative to fluorine. However, both fluorine and perfluoroalkyl groups were found to accelerate the isomerisation relative to hydrogen, methoxyl and chlorine.

Photochemical or sensitised destruction of valence isomers is an extremely important factor for the concentration and hence isolation of valence isomers. It is the only reason why benzvalene (4) can only be isolated as a very minor product in the irradiation of benzene (1).[5] Photoisomerisation of an aromatic can occur, however, even if the valence isomer has only a transient existence. It was found that photochemically induced rearomatisation of the diazadewarbenzenes (117), (118) and (122) occurs much more efficiently than the overall isomerisation of the respective pyridazines to pyrazines, at the same wavelength.

Another factor of importance is efficiency of loss of excess vibrational energy of the valence isomer once formed. If this was a major factor liquid phase irradiations could be the most efficient method of isolating valence bond isomers. Although some workers have found this the case with highly perfluoroalkylated benzenes[32] and pyridine,[36] it was not found to be the case with highly fluorinated and chlorinated pyridazines.

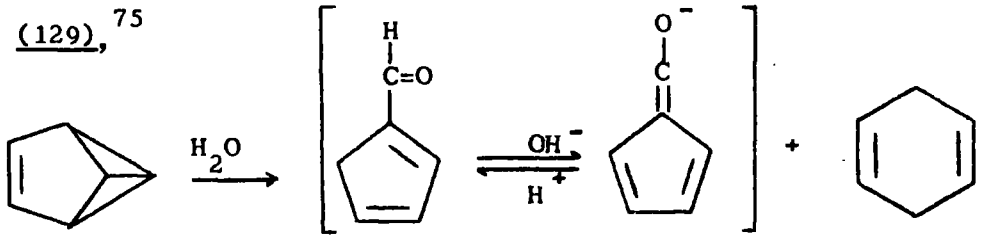
4.4. Chemical Reactions of Valence Bond Isomers.

A. Introduction.

The isolation of valence bond isomers, opens up a new area of research, because many are stable enough to undergo chemical reactions. Many photochemical reactions involving benzene have been reported.[4,24,27,66-78] However, in some of these reactions it is not clear if the valence bond isomers of benzene were actually involved. Reactions between valence bond

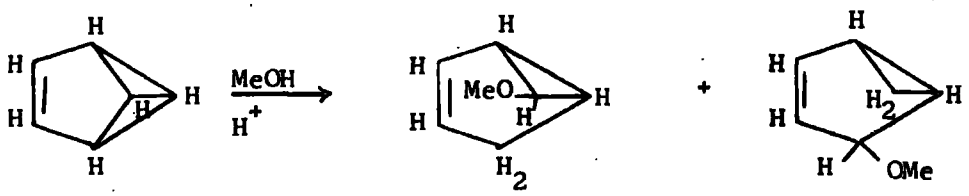
isomers in their ground state and various substrates have also[4,24,27,66,67,75,76,77,78] been performed.

Benzvalene (4) has been reacted with water to give compounds (128) and (129),[75]



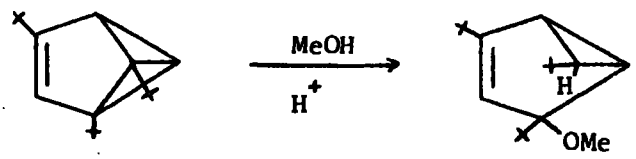
(4) (128) (129)

and with acidified methanol to give the methoxy compounds (130) and (131).[4]



(4) (130) (131)

The tri-t.-butylbenzvalene (18) has also been reacted with acidified methanol to give (132) as the major product.[24]



(18) (132)

Dewarbenzene (3) has been reacted[66] with bromine to yield di- and tetra-bromides, with osmium tetroxide to the tetrol, with hydrogen over Pd/C to cyclohexane and with other reagents. It is interesting to note that where the conjugate base of the electrophile is a weak nucleophile as in the case of sulphuric acid, benzene is formed.

Hexamethyldewarbenzene[67] has been reduced, oxidised, and found to yield hexamethylbenzene upon reaction with Lewis acids such as $AlCl_3$, $FeCl_3$ and $SbCl_5$. The irradiation of hexamethyldewarbenzene by a low pressure mercury arc yields hexamethyl prismane. It should be noted that, neither hexa-

methyldewarbenzene or prismane are produced upon irradiation of hexamethylbenzene.

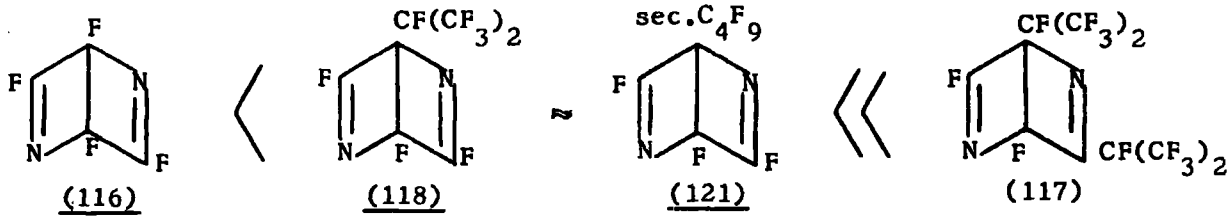
The chemistry of hexafluorodewarbenzene (31) has also been investigated.[27,76,77,78] It has been shown to undergo many nucleophilic substitution reactions, e.g. with methoxide ion, and phenyl-lithium, addition reactions, e.g. bromine and hydrogen, and diels-alder reactions e.g. with cyclopentadiene and furan.

Perfluoro-hexamethylbenzvalene (39) has also been reported to undergo a diels-alder reaction[76] with cyclopentadiene. This is, however, the only reaction of polyfluoroalkylated valence bond isomers reported.

B. Reactions of Diazadewarbenzenes.

1. Introduction.

The 2,5-diazadewarbenzenes with fluorine in the bridgehead positions (116), (117), (118) and (121) are chemically unstable, hydrolysing to give tars unless stored at liquid air temperature. The hydrolysis of the 2,5-



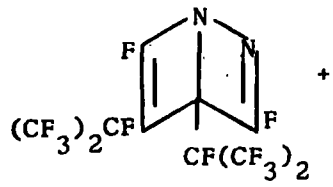
(116) (118) (121) (117)

diazadewarbenzene (118) has been attempted, however, no identifiable products were isolated. The latter diazadewarbenzene (118) reacted very violently with aqueous ammonia, again giving no identifiable products.

2. Nucleophilic Substitution Reactions.

a. With Isopropoxide Ion.

The reaction between the 1,2-diazadewarbenzene (122) and two molecular proportions of potassium isopropoxide has been carried out. Two major products were observed by g.l.c. (A) and (B).



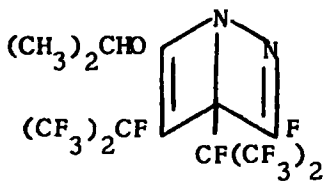
+ $2KOPr^i$ $\xrightarrow[\text{ca. } -20^oC]{^iPrOH}$ (A) ca. 55% + (B) ca. 35%

+ minor products ca. 10%

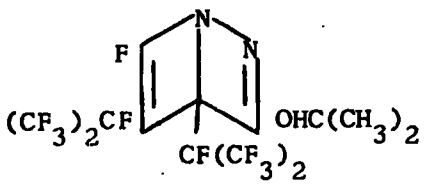
(122)

Fractional distillation at reduced pressure furnished component (A) in a pure state. This showed two strong absorptions in its infrared spectrum at 1700 and 1660 $cm.^{-1}$, and mass spectrometry showed a parent ion of molecular weight 492. This then indicates a mono-isopropoxy derivative of the 1,2-diazadewarbenzene (122). There are two possible structures for (A), (133) or (134).

A:-



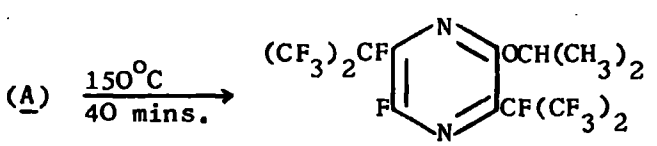
(133)



(134)

The ^{19}F n.m.r. spectrum shows a resonance at 61·5 p.p.m. (one fluorine), apart from the resonances due to the two heptafluoroisopropyl groups. This low field resonance is assigned to the imine fluorine because it has a very similar shift to those of the parent 1,2-diazadewarbenzene (122) (59·1 and 63·0 p.p.m.). The proton n.m.r. spectrum showed two signals in the ratio one to six, of shifts characteristic of tertiary and methyl hydrogens respectively.

Upon heating (A) for 40 minutes at 150°C, it rearomatised to the pyrazine (135) quantitatively.

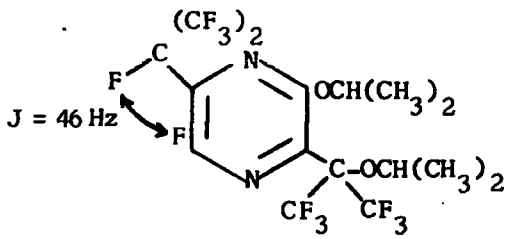


(135)

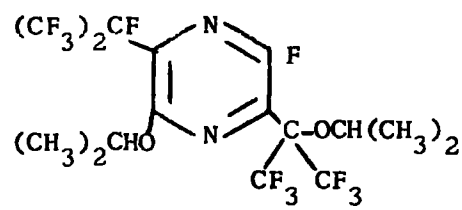
The pyrazine (135) was identified from its molecular weight (492) and its ^{19}F n.m.r. spectrum, which shows two types of heptafluoroisopropyl groups and an aromatic fluorine at 88·2 p.p.m., which is a doublet (J = 48 Hz).

From this data it is not possible to differentiate between the two possible structures of (A).

Compound (B) could not be isolated in a pure state, but showed a number of bands in the 1800 - 1600 $cm.^{-1}$ region of its infrared spectrum. Mass spectrometry showed it to have a molecular weight of 532. This indicates that compound (B) is a di-isopropoxy derivative of the 1,2-diazadewarbenzene (122). The small quantity of material prevented further purification. However, heating at 150°C for one hour gave the aromatic isomer of compound (B), which was purified by preparative scale g.l.c. at 200°C. Mass spectrometry established that this compound also has a molecular weight of 532. The ^{19}F n.m.r. spectrum of this compound shows resonances due to two different types of trifluoromethyl groups, only one tertiary fluorine and an aromatic fluorine at 88·0 p.p.m. (cf. aromatic fluorine in pyrazine (135) at 88·2 p.p.m.). This then, is not 2,5-bis-heptafluoroisopropyl-3,6-bis-isopropoxypyrazine for this would only show two resonances due to the heptafluoroisopropyl groups. Pyrazine (136a) fits the data above.



(136a)

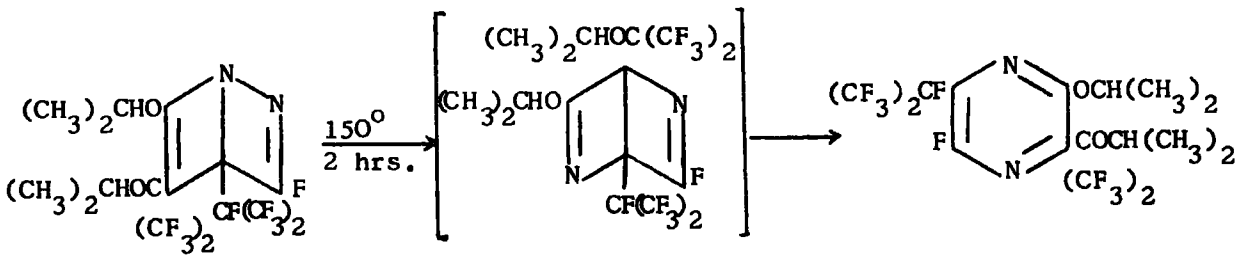


(136b)

The other possible isomer of (136a), (136b) can also be eliminated because the aromatic fluorine and the tertiary fluorine of the heptafluoroisopropyl group couple with each other (J = 46 Hz) just as was observed in

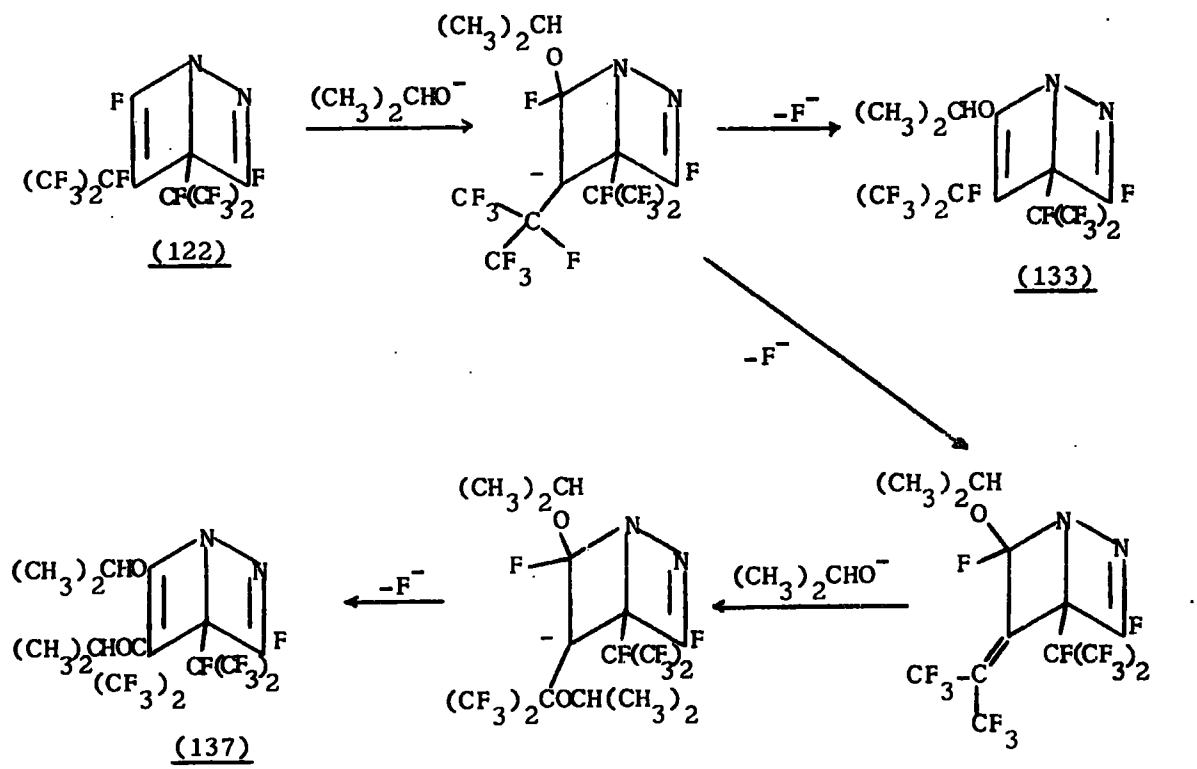
pyrazine (135) (J = 48 Hz).

This means that compound (B) from which pyrazine (136a) was derived upon heating, was the 1,2-diazadewarbenzene (137).



(137) (136)

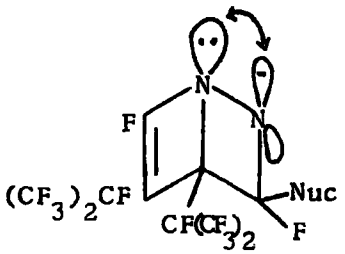
The diazadewarbenzene (137) is thought to arise in the following way:-



(122) (133) (137)

On the basis of this mechanism one would expect compound (A) to be the diazadewarbenzene (133) rather than (134).

It is surprising that the reaction proceeds to (137) when there is a carbon nitrogen double bond that could be attacked. This raises the question as to just how susceptible to nucleophilic attack the -N=C-F bond is in diazadewarbenzene systems. It has been observed that the tetrafluoro (116) and perfluoro-1-isopropyl-2,5-diazadewarbenzenes are chemically much less stable than the perfluoro-1,4-bis-isopropyl-2,5-diazadewarbenzene the former two giving tars if stored at room temperature. This suggests that the bridgehead fluorines are the cause of chemical instability. A possible reason is that fluorines in the 1- and 4-positions could be more electron-withdrawing than perfluoroalkyl groups hence causing the carbon of the -N=C-F bond to be more susceptible to nucleophilic attack. In the case of the 1,2-diazadewarbenzenes, the interaction between the lone pair on the bridgehead nitrogen and the full P orbital in the reaction intermediate (below), can be considered to cause preferential attack at the 6-position in the 1,2-diazadewarbenzene (122).



b. With Methoxide Ion.

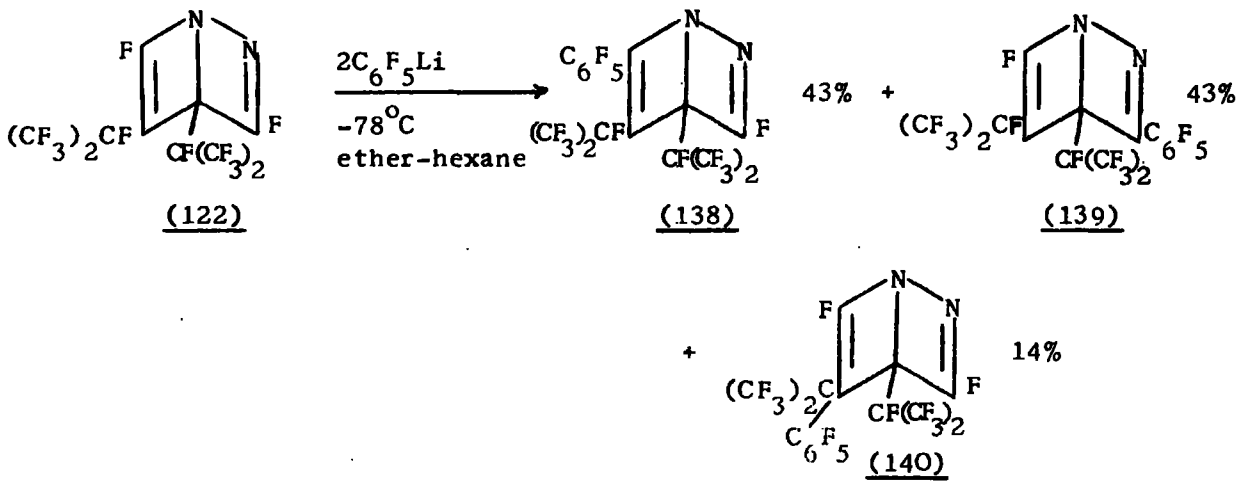
The reaction of the 1,2-diazadewarbenzene (122) with two molecular proportions of methoxide ion at ca. -20°C gave a mixture of two compounds, one of which was major, which were found to be chemically and/or thermally unstable. Mass spectrometry indicated that both the mono-methoxy (major) and dimethoxy derivatives of (122) were present in the product mixture.

The reaction of the 2,5-diazadewarbenzene (118) with one molecular proportion of methoxide ion at -78°C gave what appeared to be one very major product. However, the ^{19}F n.m.r. was found to be complex and the product

to be dangerously unstable. It is thought that the product hydrolysed very rapidly. This idea was strengthened when the 2,5-diazadewarbenzene (118) was reacted with sodium phenoxide. The product although free from phenol immediately after isolation contained free phenol after a few hours.

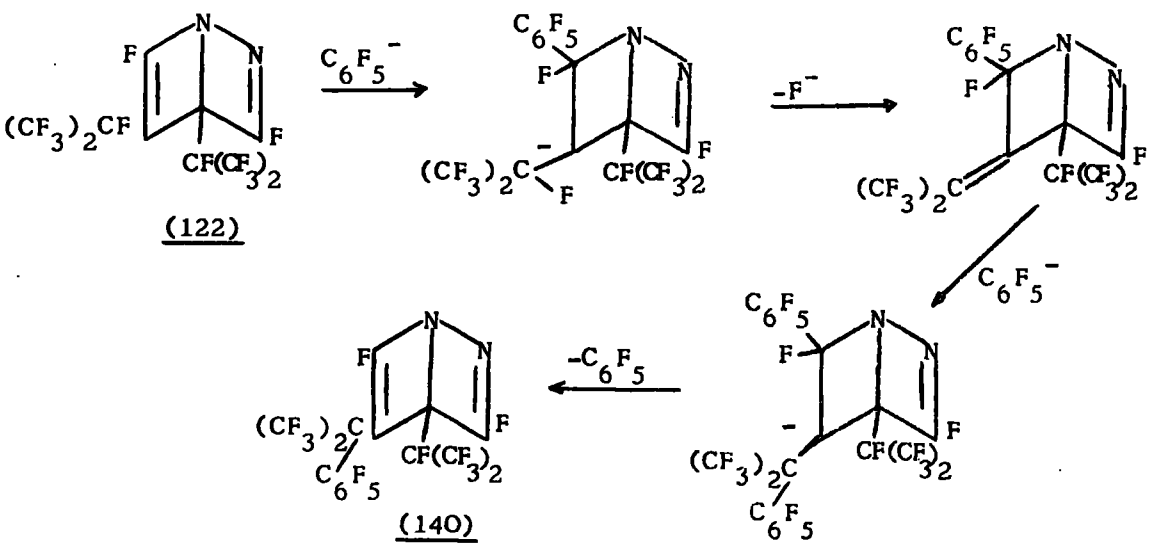
c. With Pentafluorophenyl-lithium.

The reaction of the 1,2-diazadewarbenzene (122) with two molecular proportions of pentafluorophenyl-lithium has been carried out. The product mixture could not be separated, however, its infrared spectrum showed a strong band at 1662 cm.$^{-1}$, and mass spectrometry showed a parent ion at 600, thus indicating that the product contained a mono-pentafluorophenyl derivative of the 1,2-diazadewarbenzene (122). ^{19}F n.m.r. spectrometry indicated that the product was a mixture of the 1,2-diazadewarbenzenes (138), (139) and (140) (relative amounts by integration).



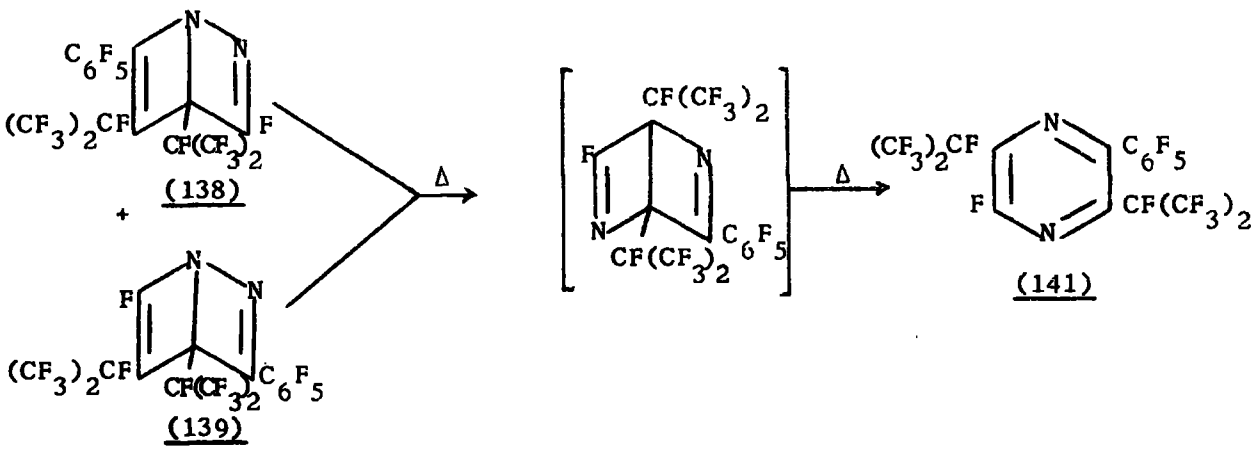
(122) (138) (139) (140)

The 1,2-diazadewarbenzene (140) could arise as follows:-



(122) (140)

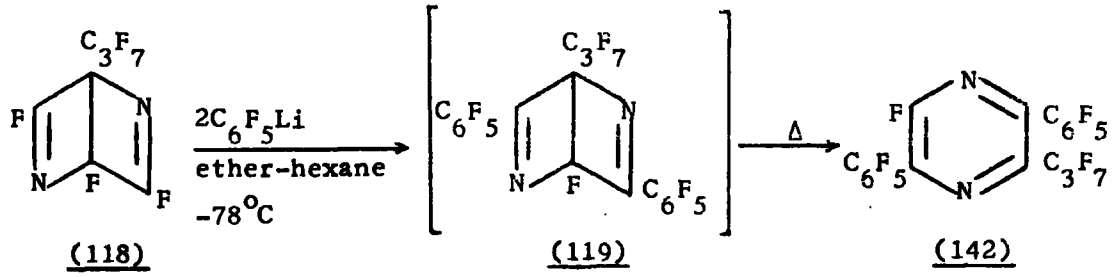
Heating the above reaction mixture at 220°C for 18 hrs., followed by sublimation, gave a pure product perfluoro-2,5-bis-isopropyl-3-pentafluorophenylpyrazine (141). The pyrazine from the minor substituted



(138) + (139) → [1,2-diazadewarbenzene (140)] → (141)

1,2-diazadewarbenzene (140) was not isolated.

Because the alkoxy derivatives of the 2,5-diazadewarbenzene (118) were found to be unstable, (118) was reacted with pentafluorophenyl-lithium, for here the derivative would have a carbon-carbon bond which would not be so likely to be hydrolysed. This reaction turned dark brown very early on, and the only product isolated was perfluoro-2-isopropyl-3,6-bis-phenyl-pyrazine (142).



(118) → (119) → (142)

d. With Hexafluoropropene.

The attempted polyfluoroalkylations of the 1,2-diazadewarbenzene (122) and the 2,5-diazadewarbenzene (117) with hexafluoropropene in the presence of fluoride ion at room temperature were unsuccessful. In the reaction of the

2,5-diazadewarbenzene (117), however, a small amount of perfluorotetra-kis-isopropylpyrazine was isolated. This has been separately prepared by reaction of hexafluoropropene with perfluoro-2,6-bis-isopropylpyrazine.

3. Attempted Addition Reactions.

One way of preventing the rearomatisation step from occurring is to add across a double bond of a dewarbenzene. This has been successfully carried out with hexafluorodewarbenzene.[27,78]

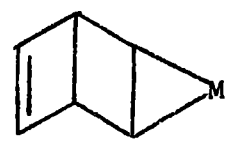
The addition of anhydrous hydrogen fluoride or of bromine to the 1,2-diazadewarbenzene (122) did not occur.

The attempted reduction of the 2,5-diazadewarbenzene (118) with hydrogen over Pd/C was unsuccessful.

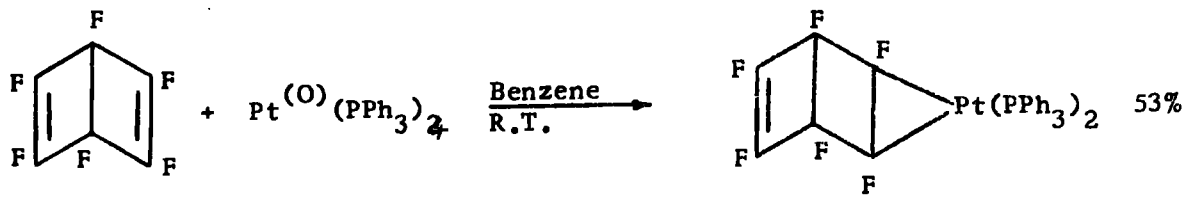
Diels-Alder reactions of the 2,5-diazadewarbenzene (118) with furan, cyclopentadiene and 2,5-dimethylfuran yielded no addition products. No addition product was isolated from the reaction between the 2,5-diazadewarbenzene (117) and furan.

4. Attempted Preparation of a Platinum Complex.

The formation of a transition complex of the type

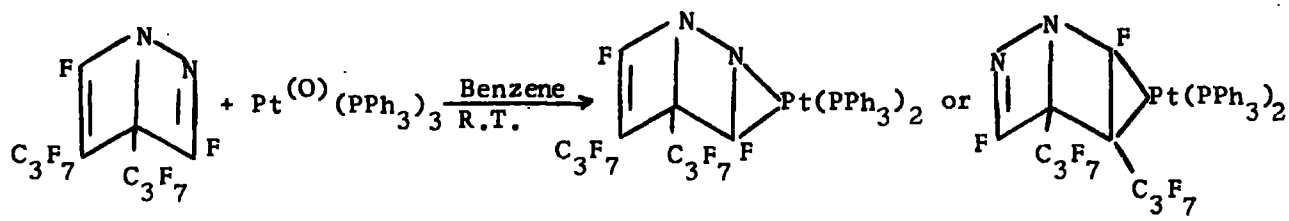


would inhibit the rearomatisation of dewarbenzenes. Such a complex has been isolated[79] upon the reaction of hexafluorodewarbenzene with tetrakis(triphenylphosphine)platinum (O) in benzene.

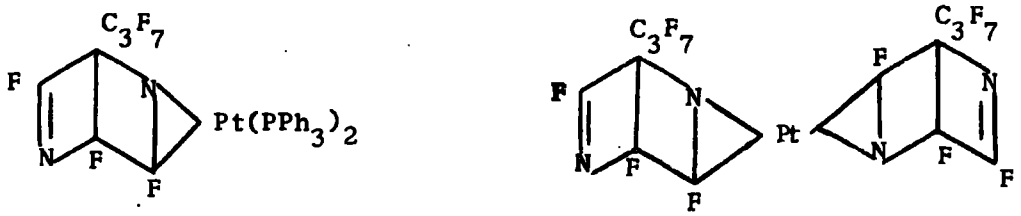


The reaction of the 1,2-diazadewarbenzene (122) with tris(triphenylphosphine)platinum (O) in dry benzene (O_2 free) at room temperature gave a dark red solution which when concentrated was found by ^{19}F n.m.r. spectrometry

to contain no fluorine.



The reaction of the 2,5-diazadewarbenzene (118) with tris(triphenylphosphine)platinum (O), gave an extremely small amount of a dark red product which contained fluorine, but not in the amount required for complexes of the type below.

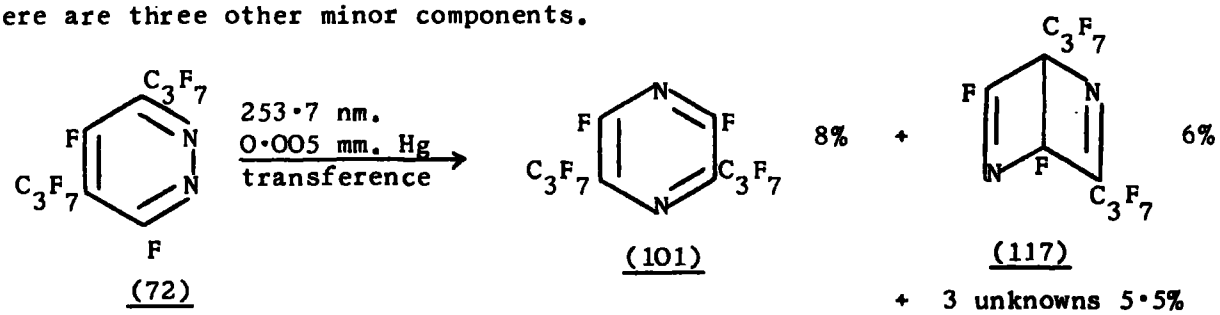


CHAPTER 5

Diazacyclo-octatetraenes

5.1. Introduction.

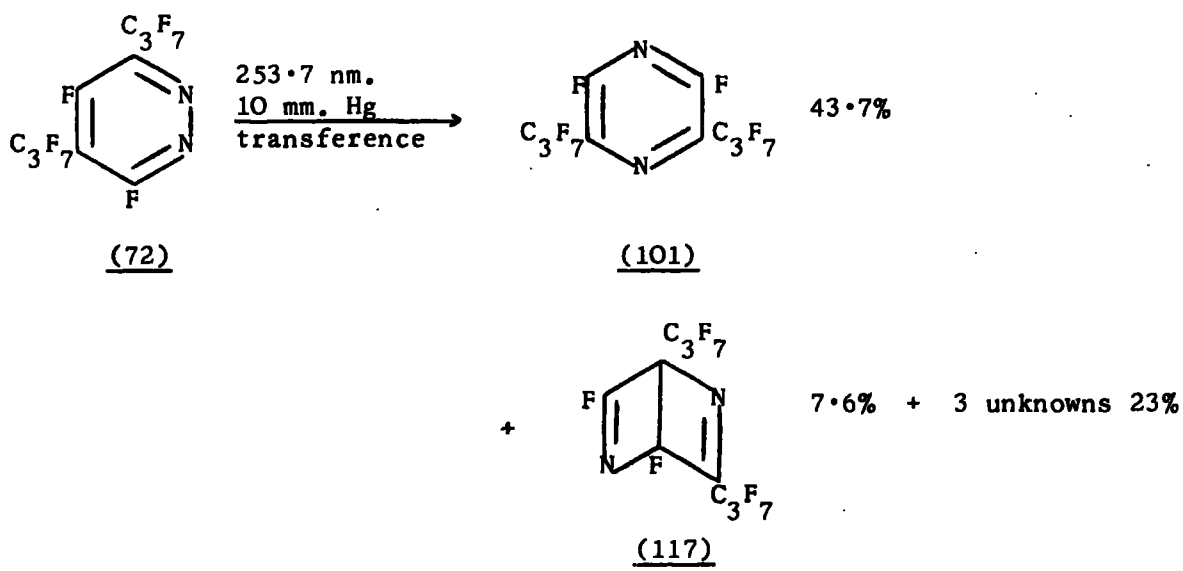
In the irradiation of perfluoro-3,5-bis-isopropylpyridazine (72) at 253·7 nm. and high vacuum, whilst under transference the major product is pyrazine (101). The diazadewarbenzene (117) is a more minor product and there are three other minor components.



(72) (101) (117)

+ 3 unknowns 5·5%

During attempts to increase the amount of the diazadewarbenzene (117) in transference experiments at 253·7 nm. it was found that increase in pressure (slower transference) resulted in the increase of the three unknown components.

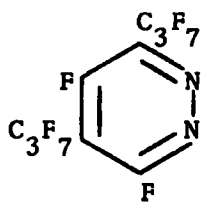


(72) (101) (117)

The present work set out to isolate and identify the three unknown components.

5.2. Preparation.

Perfluoro-3,5-bis-isopropylpyridazine (72) was irradiated at 253·7 nm. whilst under transference at a pressure of ca. 8 mm. Hg. A gas liquid chromatogram of the reaction mixture showed seven products A, B, C, D, E, F and G in increasing order of g.l.c. retention time. Compounds B, F and G were identified as the diazadewarbenzene (117), the pyrazine (101), and the starting material (72) respectively.



(72)

253·7 nm, 8 mm. Hg transference → A 6% + (117) 5% + C 13% + D 13% + E 11% + (101) 35% + (72) 17%

As can be seen the four unknowns now account for 37% of the product mixture. The relative amounts of compounds in the product mixture did not change upon irradiation in the presence or in the absence of oxygen. Hence irradiations were carried out in the presence of ca. 8 mm. of air.

Separation was achieved by distillation under reduced pressure followed by preparative g.l.c.

The most volatile component A was found to be a gas and was identified by ^{19}F n.m.r., i.r. and mass spectrometry as perfluoroisobutyrylnitrile.

All three unknowns C, D and E showed parent ions at 514 in their mass spectra, and hence are not isomers of the starting material (M^+ 452). Analysis showed them all to have the same chemical composition and thus they are thought to be isomers of the general formula $C_{12}N_2F_{18}$.

Compound C was found to convert to compound E upon heating. An impurity I in C before final purification also converted to E upon heating. It is not known, however, if I converts to E via C at the time of writing.

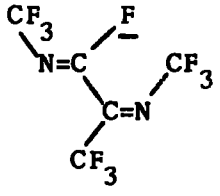
The ^{19}F n.m.r. spectra of compounds C, D, E and I are tabulated below.

Table 6

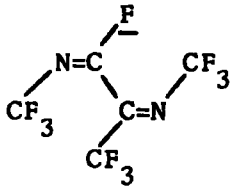
Chemical Shifts of Compounds I, C, D and E

I	C	D	E
2F 38·6 p.p.m.	1F 47·4 p.p.m.	1F 14·7 p.p.m.	2F 13·3 p.p.m.
12F 76-79 p.p.m.	1F 67·6 p.p.m.	1F 29·4 p.p.m.	2F 57·2 p.p.m.
2F 170·8 p.p.m.	3F 75·5 p.p.m.	2F 57·4 p.p.m.	12F 78·8 p.p.m.
2F 182·0 p.p.m.	3F 76·9 p.p.m.	12F 78·7 p.p.m.	2F 179·7 p.p.m.
	6F 79·2 p.p.m.	2F 179·0 p.p.m.	
	1F 122·7 p.p.m.		
	1F 161·8 p.p.m.		
	1F 179·8 p.p.m.		
	1F 181·1 p.p.m.		

All four compounds show resonances which can be attributed to two heptafluoroisopropyl groups (underlined). This leaves four fluorines in each compound. Compounds D and E show resonances at very low field. These could be vinylic fluorines adjacent to nitrogen, for such fluorines have been observed at such a low field,[80,81] e.g.



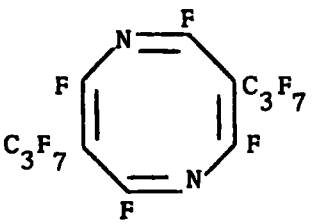
4·5 p.p.m.



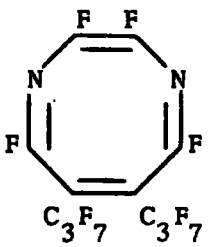
20·1 p.p.m.

$(C_3F_7)\underline{F}C{=}N{-}CF_3$ 24·0 p.p.m.

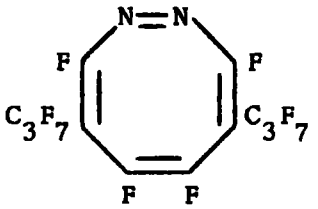
It is thought, that compounds D and E are perfluoro-bis-isopropyl-diazacyclo-octatetraenes, and that compounds C and I are valence bond isomers of the diazacyclo-octatetraene E. Compound E must have a fair degree of symmetry, for its heptafluoroisopropyl groups are equivalent and it only has two types of vinylic fluorine. There are three possible structures that could fit the simple ^{19}F n.m.r. spectrum observed for E.



(143)

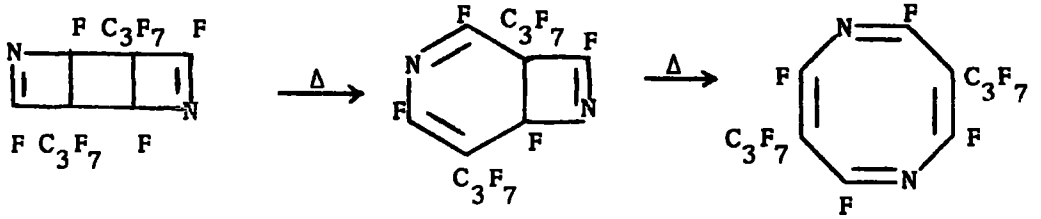


(144)



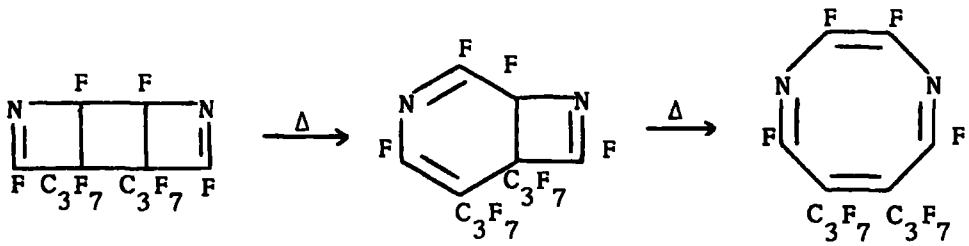
(145)

Although compound (145) would show the requisite number of resonances, it is unlikely that the 5 and 6 fluorines would occur at the low field observed i.e. 57·2 p.p.m. Hence, it is thought that the diazacyclo-octatetraene E is (143) or (144) but at the time of writing it is not possible to distinguish between the two structures. The diazacyclo-octatetraene system can have two possible valence bond isomers; the tricyclic and bicyclic systems. Compound I is thought to be the tricyclic system and compound C is thought to be the bicyclic system. Hence,



(146) (147) (143)

I C E



(148) (149) (144)

I C E

Both compounds (146) and (148) could give the ^{19}F n.m.r. spectra observed for I. They both have equivalent heptafluoroisopropyl groups, bridgehead fluorines (170·8 p.p.m.) and vinylic fluorines (38·6 p.p.m.). The latter occur in the same region as observed for the 2,5-diazadewars (37·1 p.p.m. in (113)) described in Chapter 3.

It is difficult to associate the observed ^{19}F n.m.r. spectrum of C with the structures (147) or (149). One would expect three different vinylic fluorines for the latter two compounds. One would also expect, however, two of these (the ones on the six membered ring) to have similar shifts. This is not observed.

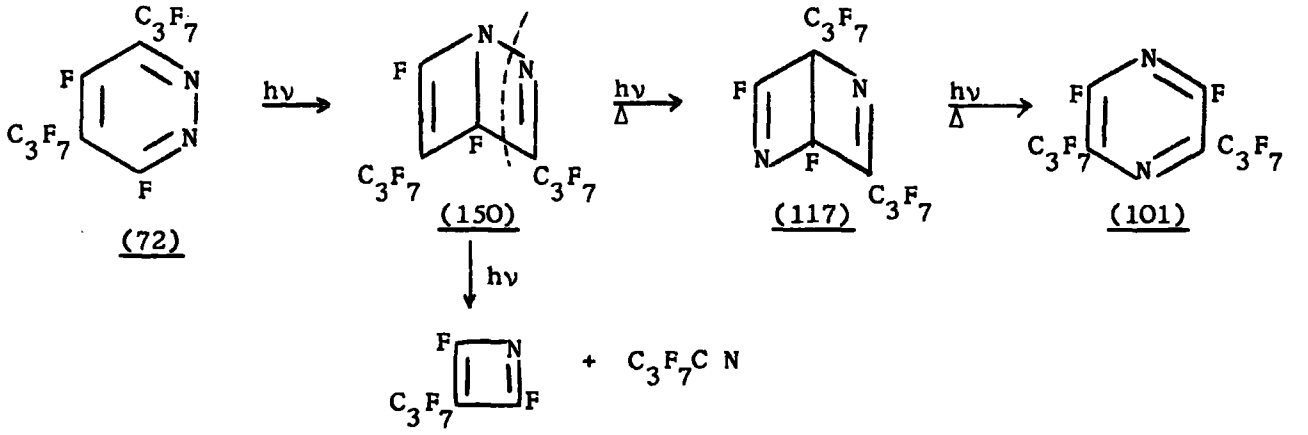
Compound D shows three different types of vinylic fluorines. These are two similar fluorines at very low field (14·7 and 29·4 p.p.m.) and a further two which are equivalent at a higher field (57·4 p.p.m.). This indicates that D is a perfluoro-bis-isopropyldiazacyclo-octatetraene like E. It is not possible at the time of writing to associate D with any particular structure as was possible with E.

5.3. Mechanism.

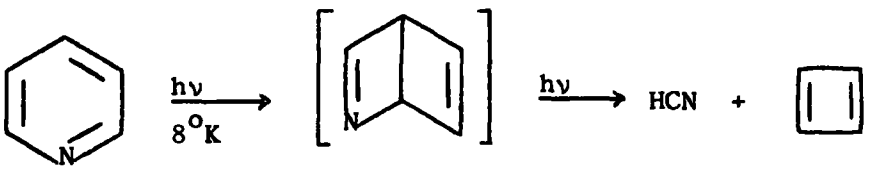
The diazacyclo-octatetraenes, and their valence bond isomers, isolated could arise as a result of the dimerisation of aza-cyclobutadienes.

Perfluoroisobutyryl nitrile was also isolated from the above reaction. Hence it is thought that the diazadewarbenzene (150), once formed from

perfluoro-3,5-bis-isopropylpyridazine (72), stays in the irradiation zone long enough to absorb more energy. As a result of this the diazadewarbenzene (150) dissociates to give perfluoroisobutyryl nitrile and a perfluoro-isopropyl-aza-cyclobutadiene, i.e.

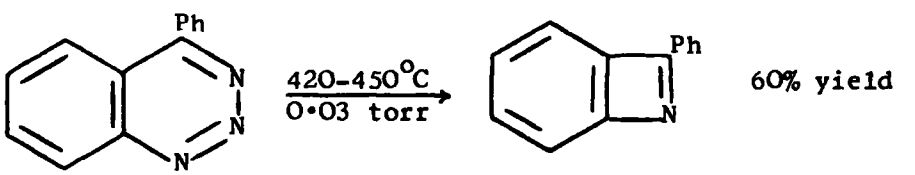


This can be compared with the observation that the pyridine dewar upon irradiation at low temperature in a matrix dissociates to give hydrogen cyanide and cyclobutadiene.[82]



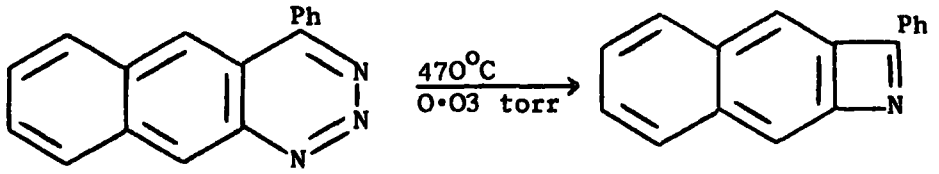
Argon Matrix

Aza-cyclobutadienes have been isolated in high yield in the vapour phase pyrolysis of triazines.[83]



2-Phenylbenzazete (151)

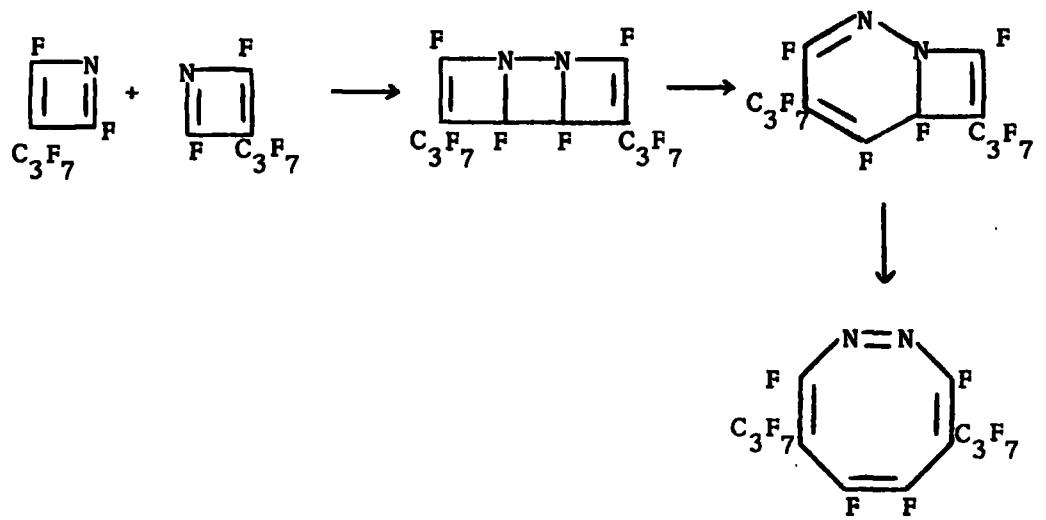
Also

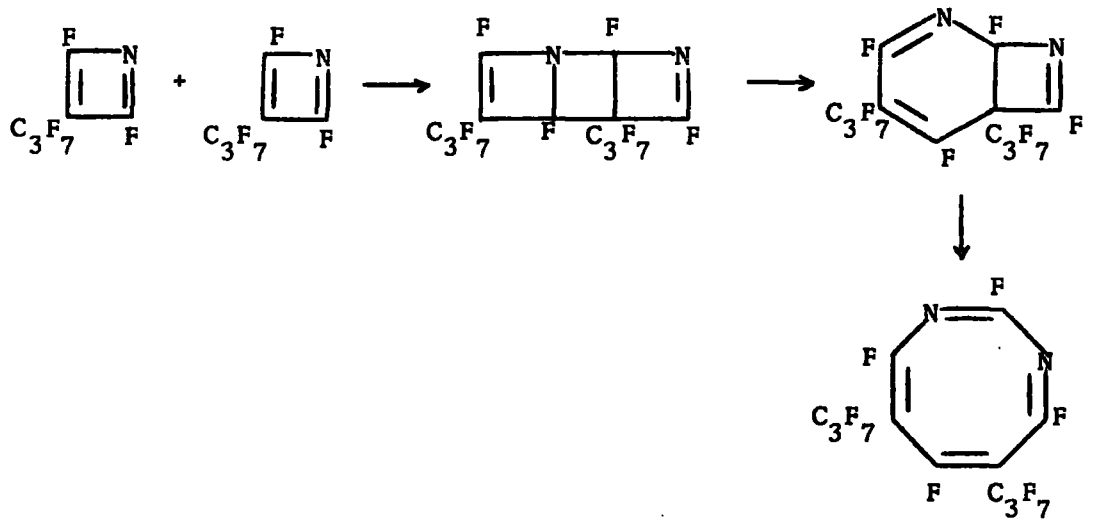


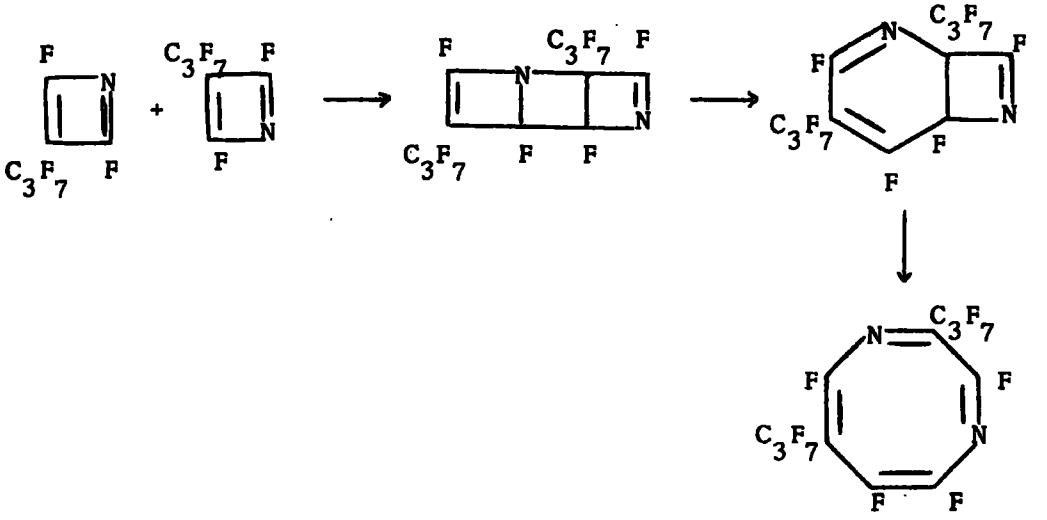
2-Phenylnaphth[2,5-b]azete (152)

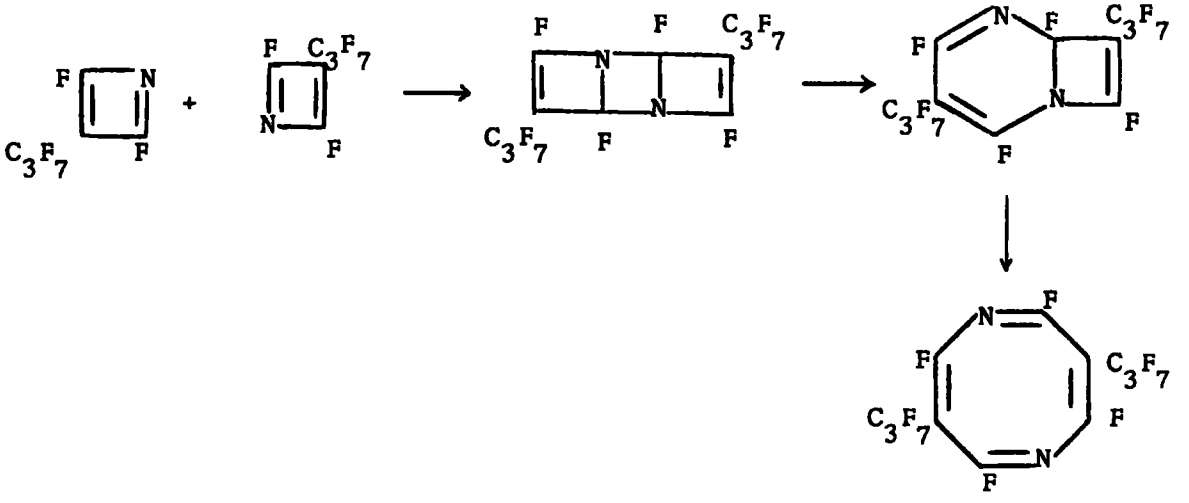
The latter aza-cyclobutadiene (152) is thermally more stable than (151) indicating that the aromatic rings stabilise the aza-cyclobutadiene.

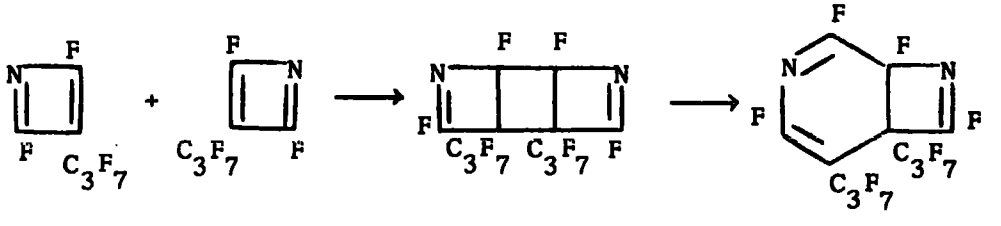
Once formed perfluoroisopropyl-aza-cyclobutadiene can dimerise to form tricyclic diazaoctadienes. These may then open to give the bicyclic isomers and finally diazacyclo-octatetraenes, i.e.





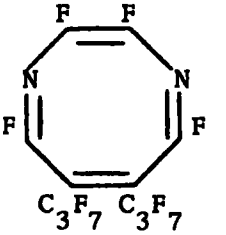






(148)

(149)



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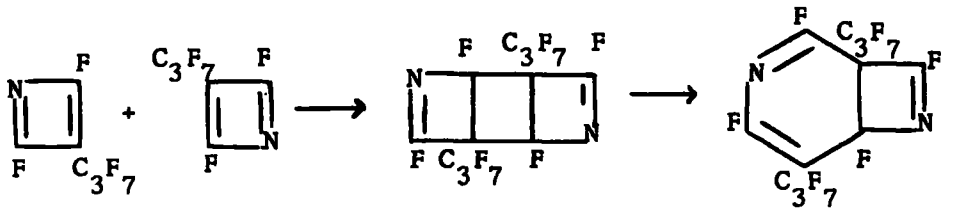
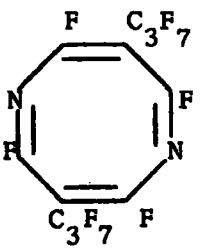


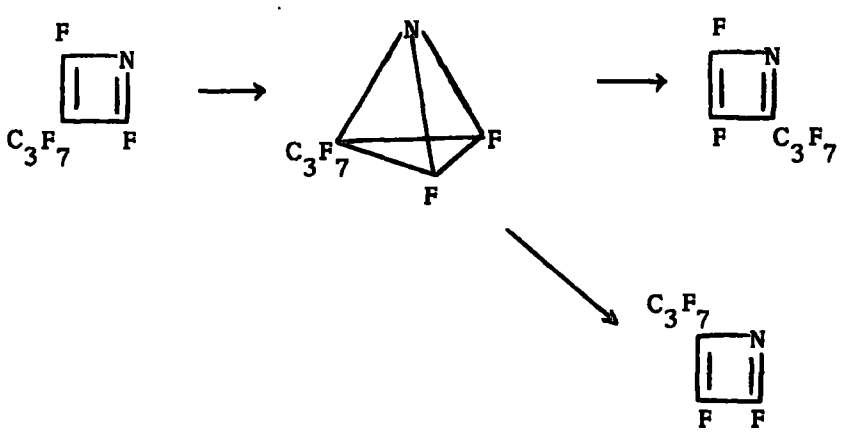
(146) (147)



(143)

As can be seen both the possible alternatives for I, C and E can be formed. There are a number of possible structures for compound D, however, none overtly fit the ^{19}F n.m.r. spectrum.

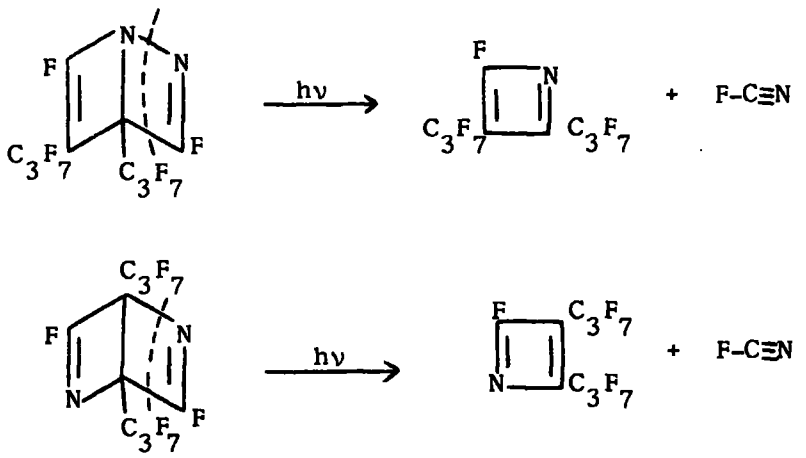
It is possible that the perfluoroisopropyl-aza-cyclobutadiene rearranges via an aza-tetrahedrane, i.e.



in which case a variety of other perfluoro-bis-isopropyl-aza-cyclo-octa-tetraenes can be formed.

The irradiation at 253·7 nm. of perfluoro-4,5-bis-isopropylpyridazine whilst under transference has also been carried out at ca. 1 cm. pressures.[50]

No products other than isomers of the molecular weight of the starting material were observed to be formed, however. A possible reason for this is that fluoro-nitrile would have to be formed, and this could be expected to be very unfavourable.

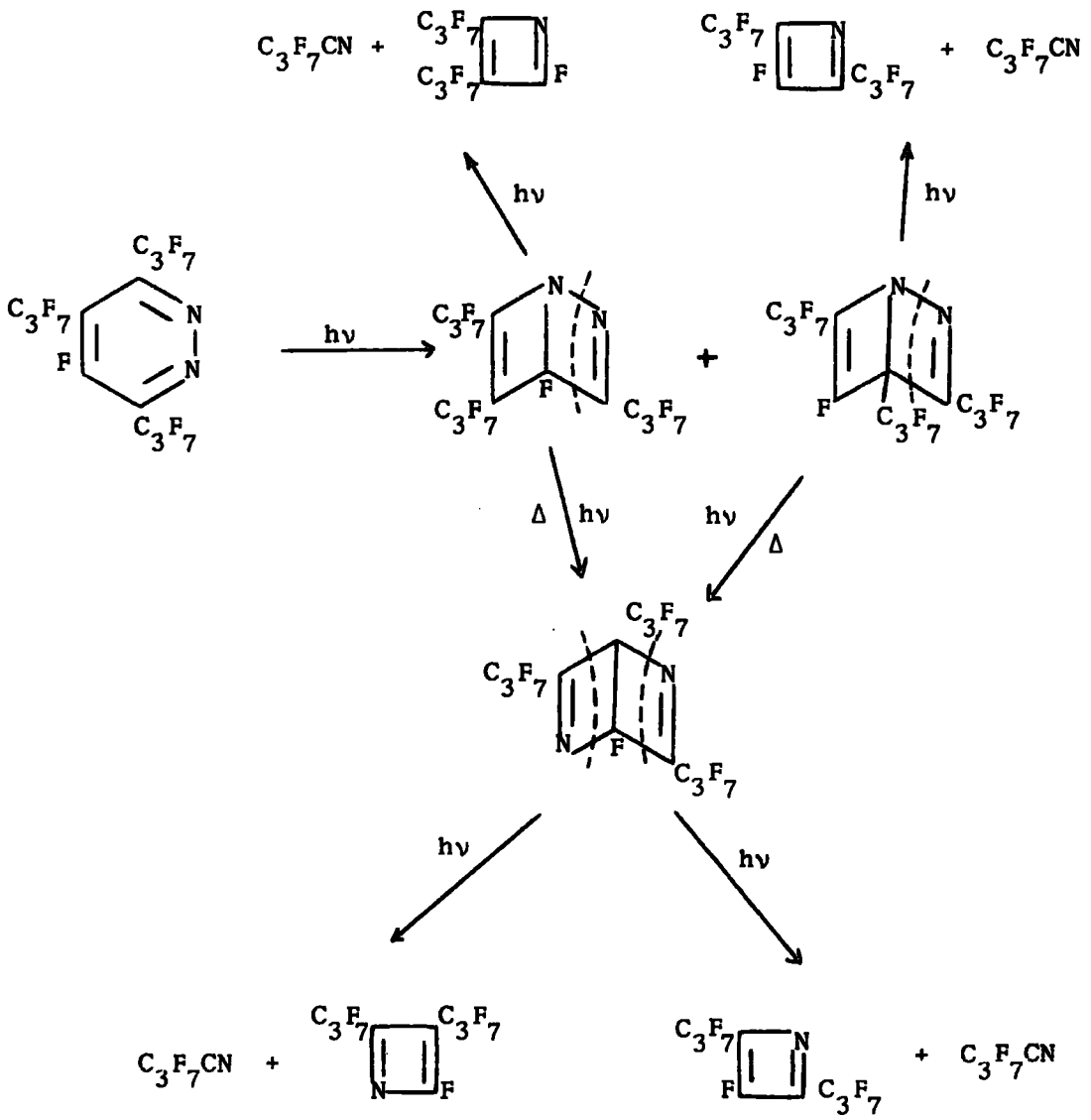


5.4. Conclusion.

At the time of writing, it is not possible, to assign definite structures to the compounds isolated from the reaction described above. It is possible, however, to identify the compounds as perfluoro-bis-isopropyl diazacyclo-octatetraenes or valence isomers thereof.

Much more work needs to be carried out in this area, so that more data can be accumulated, thus enabling full identification of the isomers of perfluorodiazacyclo-octatetraenes.

Another compound which may undergo the same type of reaction is perfluoro-3,4,6-tris-isopropylpyridazine (73). This may also eliminate perfluoroiso-butyrylnitrile from its diazadewarbenzenes.


C3F7CN +
C3F7
C3F7
F
C3F7
F
C3F7
+ C3F7CN
hν
hν
C3F7
C3F7
F
C3F7
hν
N
N
N
F
C3F7
C3F7
C3F7
C3F7
F
C3F7
C3F7
+
Δ
hν
hν
Δ
C3F7
C3F7
N
N
F
C3F7
hν
hν
C3F7CN +
C3F7
C3F7
N
F
C3F7
F
C3F7
+ C3F7CN

EXPERIMENTAL

Instrumentation.

Infrared spectra were recorded on a Grubb-Parsons 'Spectromaster' spectrometer and a Perkin-Elmer Model 457 'Grating Infrared Spectrophotometer'. Gaseous samples were introduced into an evacuated cylindrical cell with potassium bromide end windows; liquid and low melting point solid samples were in the form of thin contact films between potassium bromide plates; solid samples were pressed into homogeneous thin discs with potassium bromide.

Mass spectra were recorded using an A.E.I. M.S.9. spectrometer, and all molecular weights were determined using this instrument.

Ultraviolet spectra, in cyclohexane (Spectrosol grade) as solvent, were recorded on a Unicam S.P. 800 spectrophotometer and a Unicam S.P. 8000 spectrophotometer.

Proton (^{1}H) and fluorine (^{19}F) nuclear magnetic resonance spectra were recorded on a Varian A56/60D spectrometer, operating at 60 and 56·4 Mc./s. respectively. Chemical shifts are quoted in p.p.m. relative to T.M.S. and $CFCl_3$ respectively. Variable temperature facilities permitted spectra to be recorded at temperatures different from 40°C, the standard temperature.

Carbon, nitrogen and hydrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Analysis for halogens was as described in literature.[84]

Quantitative gas liquid chromatographic analysis (g.l.c.) was carried out on a Griffin and George, D6, Gas Density Balance (G.D.B.), using columns packed with silicone gum rubber SE-30 on chromosorb P, di-isodecylphthalate on chromosorb P, and trixylenylphosphate on chromosorb P. For this instrument, when correctly standardised, the number of moles of any compound in a mixture is directly proportional to its peak area. Calibration of the instrument with standard mixtures indicated that, within experimental error, this relationship was valid. Preparative scale gas liquid chromatography was performed on either a Varian 'Aerograph' instrument or a Perkin-Elmer 'F-21' instrument using the columns above in both instruments.

CHAPTER 6

Experimental for Chapter 2.

Reagents.

Tetrafluoropyridazine was prepared as was described earlier by technical staff and supplied upon request. It was stored for short periods of time over phosphorus pentoxide and magnesium carbonate, and vacuum distilled just before use.

Perfluoroisobutene was prepared[85] at these laboratories by atmospheric pressure pyrolysis of hexafluoropropene.[86] Other perfluoroalkenes used in polyfluoroalkylation reactions were purchased from Peninsular Chemical Research Inc.

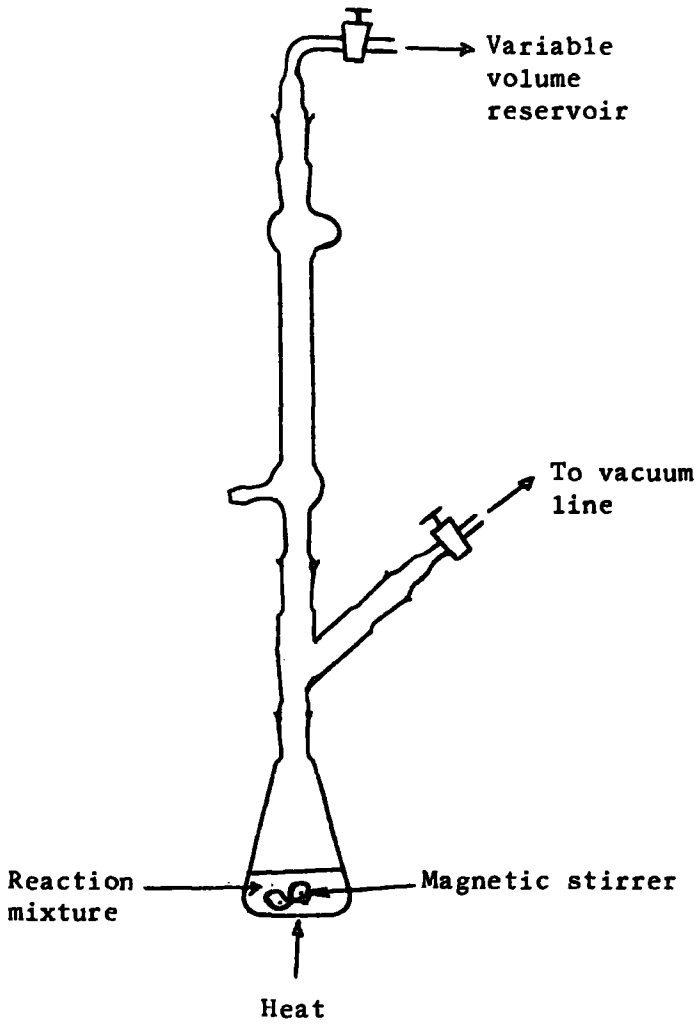
Caesium fluoride was reagent grade, dried by heating under high vacuum for several days, powdered in a glove bag under dry nitrogen, heated under high vacuum again, and stored under dry nitrogen. Tetrahydrothiophen dioxide (sulpholan) and 2,5,8,11,14-pentaoxapentadecane (tetraglyme), were purified by fractional vacuum distillation. The middle fraction, collected over dried molecular sieves (Type IVA), was stored under dry nitrogen at room temperature.

Experimental Procedure for Polyfluoroalkylation and Related Reactions.

A static atmospheric pressure system was employed, for fluoride initiated reactions of perfluoroalkenes with tetrafluoropyridazine. This had been developed by previous workers at these laboratories.

The required quantities of dry caesium fluoride and dry aprotic solvent were rapidly introduced into the baked, purged reaction apparatus (Fig. 3), against a flow of dry nitrogen. Evacuation of the apparatus was accompanied by degassing of the solvent. The requisite amount of gaseous perfluoroalkene was introduced into the system to equilibriate it to atmospheric pressure.

Fig. 3.



Tetrafluoropyridazine was then rapidly added to the reaction mixture which was then vigorously stirred.

Collapse of the perfluoroalkene reservoir and colouration of the reaction mixture was always observed during the reaction.

In fluoride ion induced rearrangement and disproportionation reactions the same reaction apparatus was used. In these reactions the pyridazines were added immediately after the introduction of caesium fluoride and aprotic solvent.

On completion, products were vacuum transferred from the reaction vessel into a cold trap (liquid air), at temperature up to 100°C. Gas liquid chromatography (Gas Density Balance) permitted analysis of the product, and yield estimation.

6.1. Reactions of Tetrafluoropyridazine with Methoxide Ion.

A. Preparation of 4-Methoxy-3,5,6-trifluoropyridazine.

A solution of tetrafluoropyridazine (4·0 g., 26·7 m.moles) in dry methanol (20 mls.), was treated dropwise with 10·1 mls. of 2·62M methanolic sodium methoxide (26·4 m.moles) over a period of one hour, with vigorous stirring, at -10°C. The mixture was then stirred for a further 10 minutes at -10°C, allowed to attain room temperature, evaporated to ca. 10 mls., and extracted with ether. The extract was washed with water, dried ($MgSO_4$), evaporated, and the residue was distilled in vacuo, to give 4-methoxy-3,5,6-trifluoropyridazine (64) (2·0 g., 46%) b.p. 68-70°/2·5 mm., identified by comparison of its i.r. and ^{19}F n.m.r. spectra with those of an authentic sample.[40]

B. Preparation of 3,6-Difluoro-4,5-dimethoxypyridazine.

A solution of tetrafluoropyridazine (1·95 g., 12·8 m.moles) in dry methanol (10 mls.), was treated dropwise with 9·5 mls. of 2·71M methanolic sodium methoxide (25·7 m.moles) over a period of one hour, with vigorous stirring at 0°C. The mixture was then stirred for a further 10 minutes at 0°C, allowed to attain room temperature, evaporated to ca. 5 mls., and extracted with ether. The extract was washed with water, dried ($MgSO_4$), evaporated, and the residue was distilled in vacuo, to give 3,6-difluoro-4,5-dimethoxypyridazine (65) (1·69 g., 73%) b.p. 65-70°C/0·005 mm., identified by comparison of its i.r. and ^{19}F n.m.r. spectra with those of an authentic sample.[40]

6.2. Reaction of Tetrafluoropyridazine with Acidified Methanol.

Tetrafluoropyridazine (2 g., 13·2 m.moles) in conc. sulphuric acid (16 mls.) was treated dropwise with a mixture of methanol (8 mls.) and conc. sulphuric acid (8 mls.) during 45 mins. with stirring at 0°C. After 5 mins., methanol (16 mls.) was added dropwise during 60 mins.; the mixture was stirred for a further 40 mins. at 0°C, diluted with ether, and poured into ice water. The organic layer was washed with water, dried ($MgSO_4$), and the ether evaporated off. Sublimation at 30°C/ca. 20 mm., gave a solid (1·0 g., 47%) pure by g.l.c. (silicone elastomer, 100°C), which was identified as 3,4,5-trifluoro-6-methoxypyridazine (66) by comparison of its i.r. and ^{19}F n.m.r. spectra with those of an authentic sample.[42]

6.3. Reaction of Tetrafluoropyridazine with Chloride Ion.

Tetrafluoropyridazine (13·0 g., 85·5 m.moles), lithium chloride (13 g., 307 m.moles), and dimethylformamide (40 mls.) were introduced into dry apparatus (Fig. 3), against a flow of dry nitrogen. The mixture was then stirred at 100°C for 40 mins., poured into ice water and filtered. The cream solid was dried in a desiccator (P_2O_5), and sublimed at 20°C/ 0·001 mm., to give 3,6-difluoro-4,5-dichloropyridazine (68)[43] (10·9 g., 69%), m.pt. 50°C [Found: C, 26·2; M, 184. $C_4F_2Cl_2N_2$ requires C, 25·94; M, 184.

I.R. spectrum No. 1, u.v. spectrum No. 9, ^{19}F n.m.r. spectrum No. 1 showed a singlet at 82·3 p.p.m.

6.4. Preparation of Perfluoro-4,5-bis-isopropylpyridazine.

Perfluoro-4,5-bis-isopropylpyridazine (70), was prepared on many occasions. A typical experiment is described below.

The standard experimental procedure for polyfluoroalkylation was adopted (see p.125). Caesium fluoride (0·9 g., 5·9 m.moles), tetrahydrothiophen dioxide (40 mls.), hexafluoropropene (19·0 g., 127 m.moles), and tetra-

fluoropyridazine (8·5 g., 56 m.moles), were stirred at room temperature for one day, by which time a partial vacuum had formed in the apparatus. Chromatographic analysis (G.D.B., di-isodecylphthalate, 78°C) of the vacuum transferred product showed it to be mainly one component (> 95%), which was identified as perfluoro-4,5-bis-isopropylpyridazine (70) (23·5 g., 82%), by comparison of its i.r. and ^{19}F n.m.r. spectra with those of an authentic sample,[41] and also by mixed injection. U.v. spectrum No. 2.

Final purification could be achieved by recrystallisation from ether or hexane.

6.5. Reaction of Perfluoro-4,5-bis-isopropylpyridazine (70) with Fluoride Ion.

The standard experimental procedure for fluoride ion induced rearrangement was adopted (see p.125).

A mixture of caesium fluoride (3·3 g., 21 m.moles) and perfluoro-4,5-bis-isopropylpyridazine (70) (8·0 g., 17·7 m.moles), in tetrahydrothiophen dioxide (45 mls.), was stirred vigorously for 17 hrs. at 120°C. A volatile product (7·6 g.) was isolated by vacuum transference and shown by g.l.c. to contain perfluoro-3,4,6-tris-isopropylpyridazine (73) (14%), perfluoro-3,5-bis-isopropylpyridazine (72) (81%) u.v. spectrum No. 3, and perfluoro-4-mono-isopropylpyridazine (71) (4%). These components were separated by preparative g.l.c. (Aerograph, di-isodecylphthalate, 125°C), and the i.r.'s and ^{19}F n.m.r.'s compared with those of authentic samples.[41] Separation of the three components could also be achieved by fractional distillation on a Büchi spinning band fractionation column.

6.6. Reaction of a Mixture of Perfluoro-3,4,6-tris-isopropylpyridazine (73) and Tetrafluoropyridazine (63) with Fluoride Ion.

The same experimental procedure was adopted as in the previous experiments (6.4.).

A mixture of perfluoro-3,4,6-tris-isopropylpyridazine (73) (3·1 g., 5·15 m.moles), tetrafluoropyridazine (63) (1·15 g., 7·57 m.moles), and caesium fluoride (3·0 g., 19·8 m.moles), in 2,3,8,11,14-pentaoxapentadecane (20 mls.), was stirred vigorously for two days at 120°C. A volatile product (2·5 g.) was isolated by vacuum transference and shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to contain perfluoro-3,4,6-tris-isopropyl-pyridazine (73) (5·8%), perfluoro-3,5-bis-isopropylpyridazine (72) (77·4%), and perfluoro-4-isopropylpyridazine (71) (16·8%), u.v. spectrum No. 4. These components were separated by preparative g.l.c. (Aerograph, di-isodecyl-phthalate, 125°C) and identified by comparison of their i.r.'s and ^{19}F n.m.r.'s with those of authentic samples.[41]

6.7. Reaction of a Mixture of Perfluoro-4,5-bis-isopropylpyridazine (70) and Tetrafluoropyridazine (63) with Fluoride Ion.

The preparation of perfluoro-4-isopropylpyridazine (71), was carried out on many occasions. Described below is a typical experiment.

A mixture of perfluoro-4,5-bis-isopropylpyridazine (70) (15·8 g., 34·9 m.moles), tetrafluoropyridazine (6·4 g., 42·1 m.moles), and caesium fluoride (5 g., 33 m.moles), in tetrahydrothiophen dioxide (95 mls.), was stirred for 18 hrs. at 120°C. The volatile product (16·9 g.) was shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to contain perfluoro-4-isopropylpyridazine (71) (81%) and perfluoro-3,5-bis-isopropylpyridazine (72) (19%). A portion was separated by preparative g.l.c. (Aerograph, di-isodecylphthalate, 135°C) and the two components identified by comparison of their i.r.'s and ^{19}F n.m.r.'s with those of authentic samples.[41] Separation of the two components could also be achieved by fractional distillation, on a Büchi Spinning Band Fractional Distillation Column, at atmospheric pressure.

6.8. Reaction of Tetrafluoropyridazine with Perfluorobut-2-ene.

This reaction was carried out several times. A typical experiment is described below.

The standard experimental procedure for polyfluoroalkylation was adopted (see p.125). Caesium fluoride (5 g., 33 m.moles), tetrahydrothiophen dioxide (100 mls.), perfluorobut-2-ene (35 g., 175 m.moles) and tetrafluoropyridazine (63) (11·0 g., 72·4 m.moles), were stirred at 60°C for days. Not all the perfluorobut-2-ene was absorbed. The volatile product (34·0 g.) was isolated by transfer under vacuum and shown by g.l.c. (G.D.B. trixylenyl phosphate, 100°C), to contain perfluoro-3,5-bis-sec.-butylpyridazine (81) (6·5%), perfluoro-4,5-bis-sec.-butylpyridazine (79) (62%), and perfluoro-4-sec.-butylpyridazine (80) 29%. The products of three such reactions were partially separated by fractional distillation on a Büchi Spinning Band Fractional Distillation Column. Final purification was by preparative g.l.c. (Aerograph, trixylenyl phosphate, 140°C), and the three components were identified by comparison of their i.r.'s and ^{19}F n.m.r.'s with those of authentic samples.[49,50]

6.9. Reaction of Tetrafluoropyridazine (63) with Perfluoroisobutene.

It is important to stress that perfluoroisobutene is an extremely hazardous compound[86] because of its acute toxicity. During the manipulation of this compound and in the work-up stringent safety precautions were employed, which included the wearing of breathing apparatus. The reaction performed was at ca. atmospheric pressure in a simple apparatus which has been described above (Fig. 3).

Caesium fluoride (2 g., 13 m.moles), tetrahydrothiophen dioxide (20 mls.), and tetrafluoropyridazine (4·0 g., 26·3 m.moles) were introduced into the dry apparatus (Fig. 3) above, the flask was then cooled in liquid air, and the system evacuated. The apparatus was then heated to 40°C and

perfluoroisobutene (11 g., 55 m.moles) was admitted. The mixture was then vigorously stirred, and a partial vacuum formed within one hour. The mixture was allowed to stir for a total of ca. 18 hrs. Transfer of products under vacuum gave a mixture (8·1 g.) of perfluoro-t-butylpyridazines, shown by g.l.c. (G.D.B., silicone elastomer, 78°C), and mass spectrometry to contain perfluoro-mono, -3,5-di, -3,6-di, and -tri-t-butylpyridazines. Crystallisation from ether gave a solid (3·0 g.), which was shown to be perfluoro-3,5-bis-t-butylpyridazine, m.pt. 50°C (Found: C, 26·1; F, 68·5%; M^+, 552. $C_{12}F_{20}N_2$ requires C, 26·1; F, 68·85%; M, 552); ^{19}F n.m.r. spectrum No. 2, i.r. spectrum No. 2. Removal of volatile material from the residue, from the crystallisation, gave perfluoro-3,6-bis-t-butyl-pyridazine (3·1 g.) which was identified by comparison of its i.r. spectrum with that of an authentic sample.[46]

6.10. Reaction of a Mixture of Perfluoro-3,5-bis-isopropylpyridazine (72) and Tetrafluoropyridazine (63) with Fluoride Ion.

A mixture of caesium fluoride (4 g., 26 m.moles), perfluoro-3,5-bis-isopropylpyridazine (72) (4·0 g., 8·85 m.moles), and tetrafluoro-pyridazine (2·5 g., 16·45 m.moles), in 2,5,8,11,14-pentaoxapentadecane (30 mls.), was vigorously stirred for 20 hrs. at 125°C. A volatile product (3·6 g.) was isolated by transfer under vacuum and shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to be pure perfluoro-3,5-bis-iso-propylpyridazine (72). This was confirmed by comparison of the i.r. of the product with that of an authentic sample of (72).[41]

6.11. Flow Thermolysis of Perfluoro-4-isopropylpyridazine.

Perfluoro-4-isopropylpyridazine (2·5 g.) was passed in a stream of dry nitrogen through a silica tube loosely packed with silica wool at 640°C (contact time ca. 100 secs.). The gas chromatogram of the product (1·6 g.) (G.D.B., silicone elastomer, 78°C) showed two major components

A (30%) and B (50%) in order of increasing retention time. Preparative scale g.l.c. (F.21, silicone elastomer 85°C) provided pure samples of A and B. Component A (0·12 g.) showed a parent peak at $^{m}/e$ 252 in its mass spectrum and ^{19}F n.m.r. showed it to be a mixture of perfluoro-4- and -5-ethylpyrimidines. These were not separated but have been subsequently prepared[55] and shown to have ^{19}F n.m.r. spectra identical to those observed for component A. Component B (0·30 g.) showed a parent peak at $^{m}/e$ 302 in its mass spectrum. ^{19}F n.m.r. indicated a mixture (1:1) of perfluoro-4-isopropylpyrimidine, ^{19}F n.m.r. (acetone) δ 47·8 (F-2), 69·2 (F-6), 75·8 [$(\underline{CF_3})_2CF$], 152·8 (F-5) and 187·1 p.p.m. [$(CF_3)_2\underline{CF}$] in agreement with published data,[56] and perfluoro-5-isopropylpyrimidine, ^{19}F n.m.r. (acetone) δ 39·6 (F-2), 47·6 (F-4 and 6), 77·1 [$(\underline{CF_3})_2CF$] and 182·3 p.p.m. [$(CF_3)_2\underline{CF}$]. ^{19}F N.M.R. spectrum No. 3.

6.12. Flash Vacuum Thermolysis of Perfluoro-4,5-bis-isopropylpyridazine (70).

Perfluoro-4,5-bis-isopropylpyridazine (5·30 g.) was sublimed through a silica tube very loosely packed with silica wool and heated to 750°C over 27 cm. (backing pressure ca. 0·04 mm.). Chromatographic analysis (G.D.B. di-isodecylphthalate, 78°C) of the product (2·93 g.) showed it to contain perfluoro-2,5-bis-isopropylpyrazine (84) (ca. 4%), perfluoro-2,5-bis-isopropylpyrimidine (83) (ca. 15%) and three other major components in order of retention time: A, 31%; B, 11%; and C, 8%. Preparative g.l.c. (F.21, di-isodecylphthalate, 125°C) gave pure samples of these three latter compounds. A was identified as the diazabenzocyclobutene (92) (1·85 g.) (Found: C, 31·0; $^{m}/e$ 314. $C_8F_{10}N_2$ requires C, 30·6%; M, 314). ^{19}F n.m.r. spectrum No. 4, I.R. spectrum No. 3, λ_{max} 263 and 329 nm. Component B (0·90 g.) was shown by mass spectrometry and ^{19}F n.m.r. to be an inseparable mixture of the diazabenzocyclobutene (96), M, 314, ^{19}F n.m.r.

spectrum No. 5 (an isomer of 92) and perfluoro-4-(2'-propenyl)-5-ethyl-pyridazine (97), $^{m}/e$ 364, ^{19}F n.m.r. spectrum No. 6. Component C was identified as perfluoro-4-vinyl-5-ethylpyridazine (94) (0·3 g.). Analysis gave inconsistent results, $^{m}/e$ 314, ^{19}F n.m.r. spectrum No. 7, I.R. spectrum No. 4. λ_{max} 273·25, 284·8, 298·0 and 337·0 nm.

Hydrolysis of Diazabenzocyclobutane (92).

Upon standing for a few weeks, the diazabenzocyclobutene (92) hydrolysed. Sublimation at R.T./0·001 mm. Hg gave the perfluoropyridazinone (99) (Found: F, 55·1; $^{m}/e$ 312, $C_8HF_9N_2O$ requires F, 54·8; $^{m}/e$ 312). ^{19}F n.m.r. spectrum No. 8. I.R. spectrum No. 5.

CHAPTER 7

Experimental for Chapter 3

Reagents.

All the pyridazines used in photolysis experiments were of purity greater than 99·5%, and were either prepared as in the previous chapter or prepared at these laboratories.

Experimental Procedure.

Some experiments were carried out in sealed silica or Pyrex tubes, under high vacuum. In general degassing was not performed, and it will be stated if it was. Photolysis experiments in solution, were again carried out in sealed tubes and here degassing was carried out in each case.

In transference experiments the apparatus was as in Fig. 2 (see p. 76). The pyridazine to be irradiated was introduced into the large silica (or Pyrex) vessel and then the system was evacuated to the requisite pressure, air being the residual gas unless otherwise stated.

Ultraviolet Light Sources and Filters.

A number of ultraviolet light sources were employed. These were briefly mentioned in Chapter 3 (p. 58).

Medium Pressure Mercury Arcs.

An Hanovia U.V.S. 1000 lamp was used for many of the sealed tube reactions. The light intensity of this lamp is ca. 250 watts. The absolute output of light in watts, at different wavelengths for each 100 watts of loading on the tube, for a typical medium pressure mercury arc tube in quartz operating at ca. 800 mm. internal pressure is shown below in Table 7.

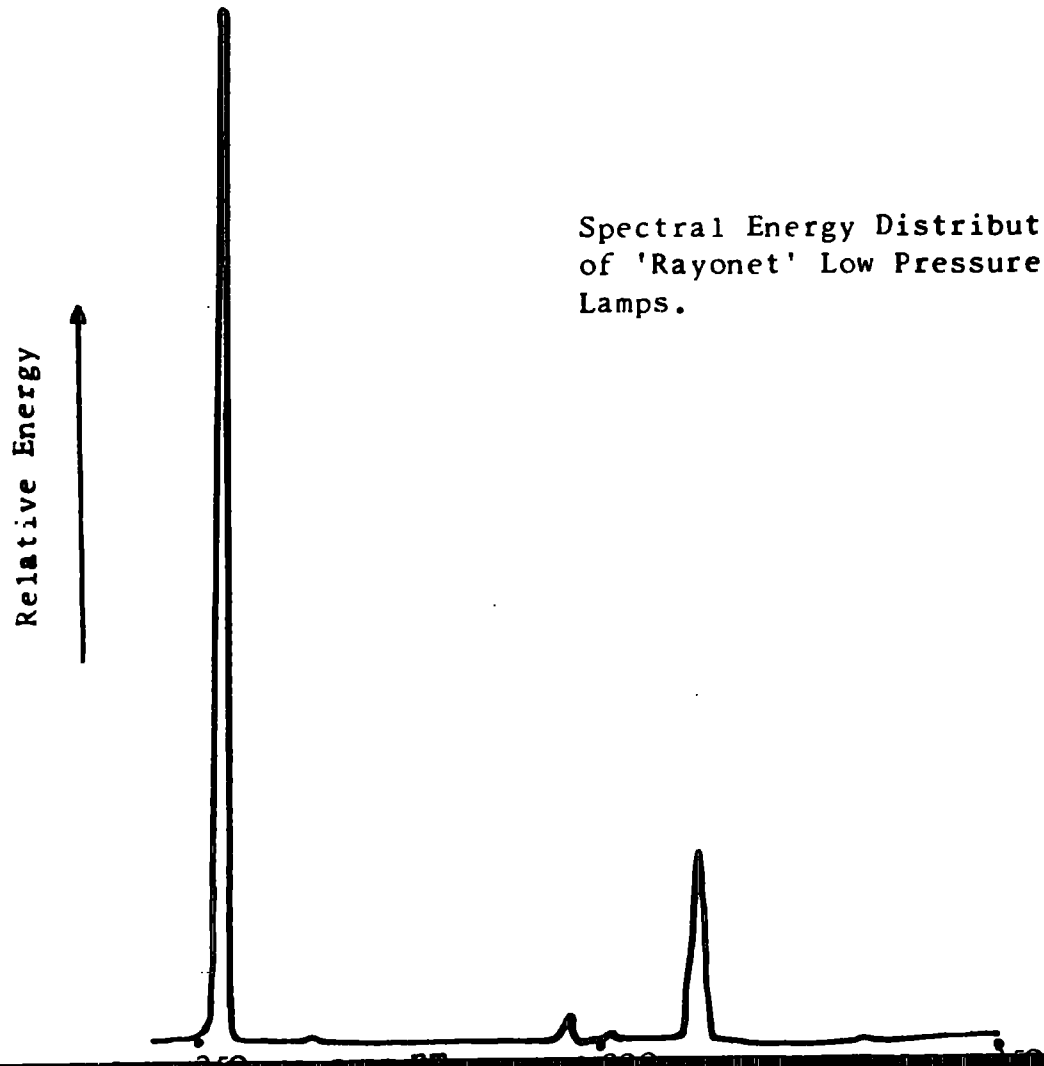
The light from two Hanovia U.V.S. 500 watt medium pressure mercury lamps has also been employed. These lamps were mounted in a 'Reading' photochemical reactor, and have the same light output characteristics as the previous source.

Table 7.

Wavelengths in mu	Intensity in watts
235	0·12
238	0·23
240	0·21
246	0·09
248	0·53
254	0·68
258	0·08
260	0·11
264	0·14
265	0·98
270	0·23
275	0·17
280	0·55
289	0·26
292	0·11
297	0·74
302	1·42
313	2·72
334	0·37
366	4·30
391	0·06
405	1·14
406	0·24
436	2·10
492	0·06
546	2·76
477/9	3·42
691	0·08
1014	1·18
Total =	25.08

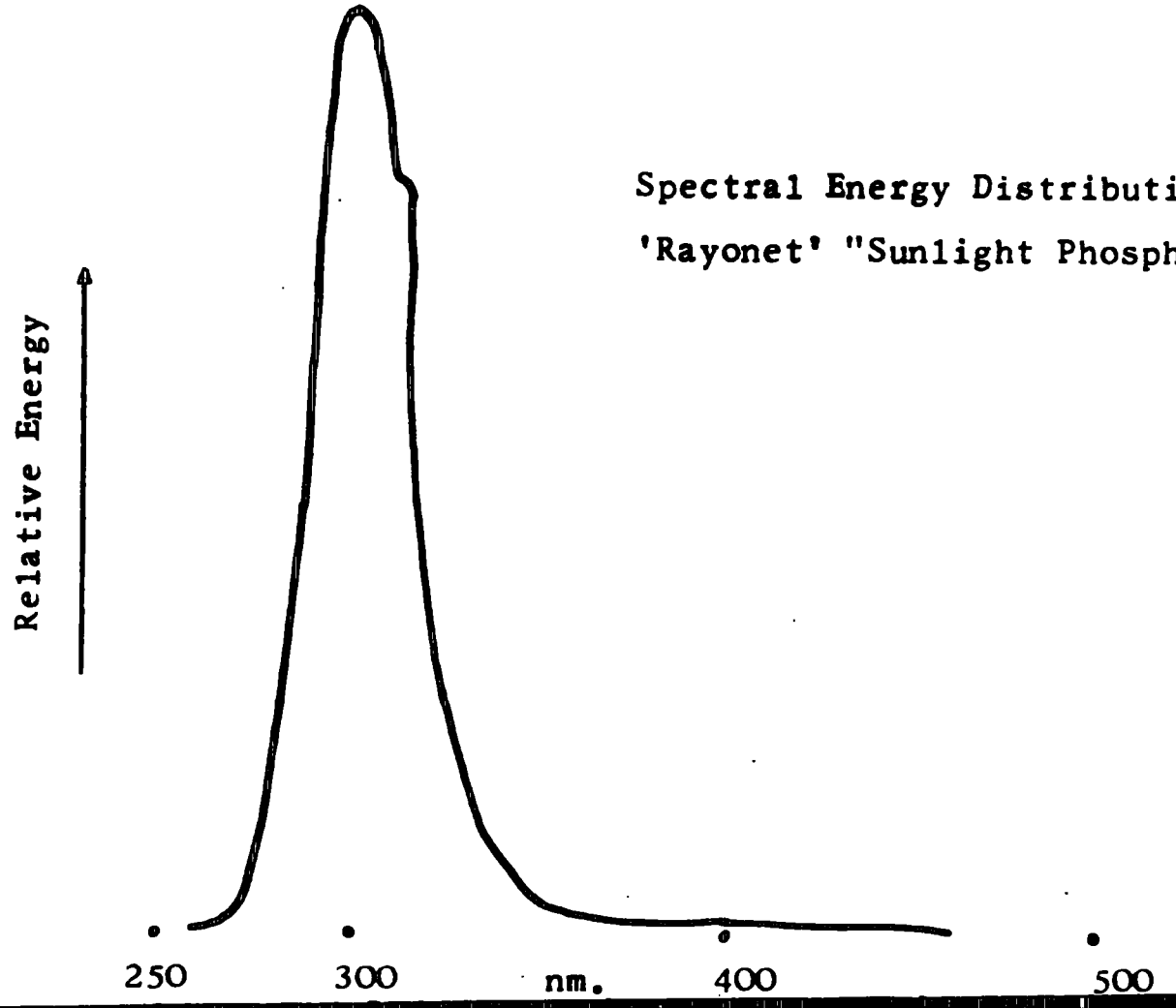
The 'Rayonet' preparative photochemical reactors 'R.P.R.-208' and 'R.P.R.-204' have also been employed in many reactions. The former is twice as powerful as the latter, and was used in all transference reactions. The 'R.P.R.-208' reactor contains eight lamps. Three types of lamps are available with these reactors: low pressure mercury lamps, 8 of which provide 120 watts of 253·7 nm. light (see Fig. 4.); 'Sunlight phosphor' conversion lamps, 8 of which provide ca. 85 watts of ultraviolet light with maximum output

FIG. 4.



Spectral Energy Distribution of 'Rayonet' Low Pressure Mercury Lamps.

FIG. 5.



Spectral Energy Distribution of
'Rayonet' "Sunlight Phosphor" Lamps.

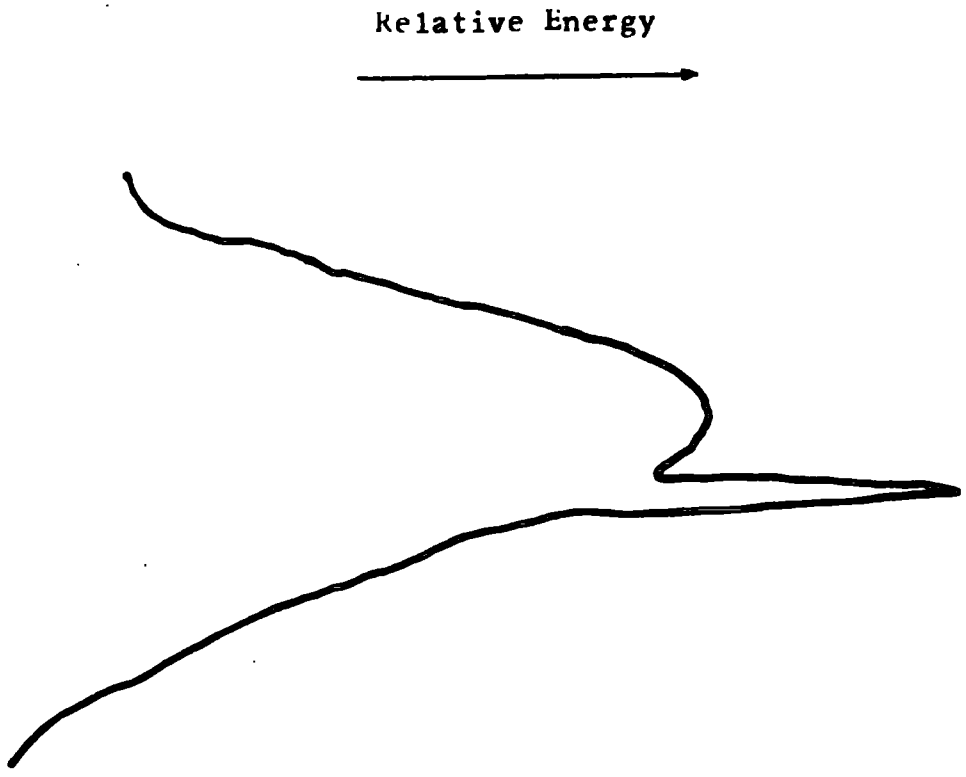
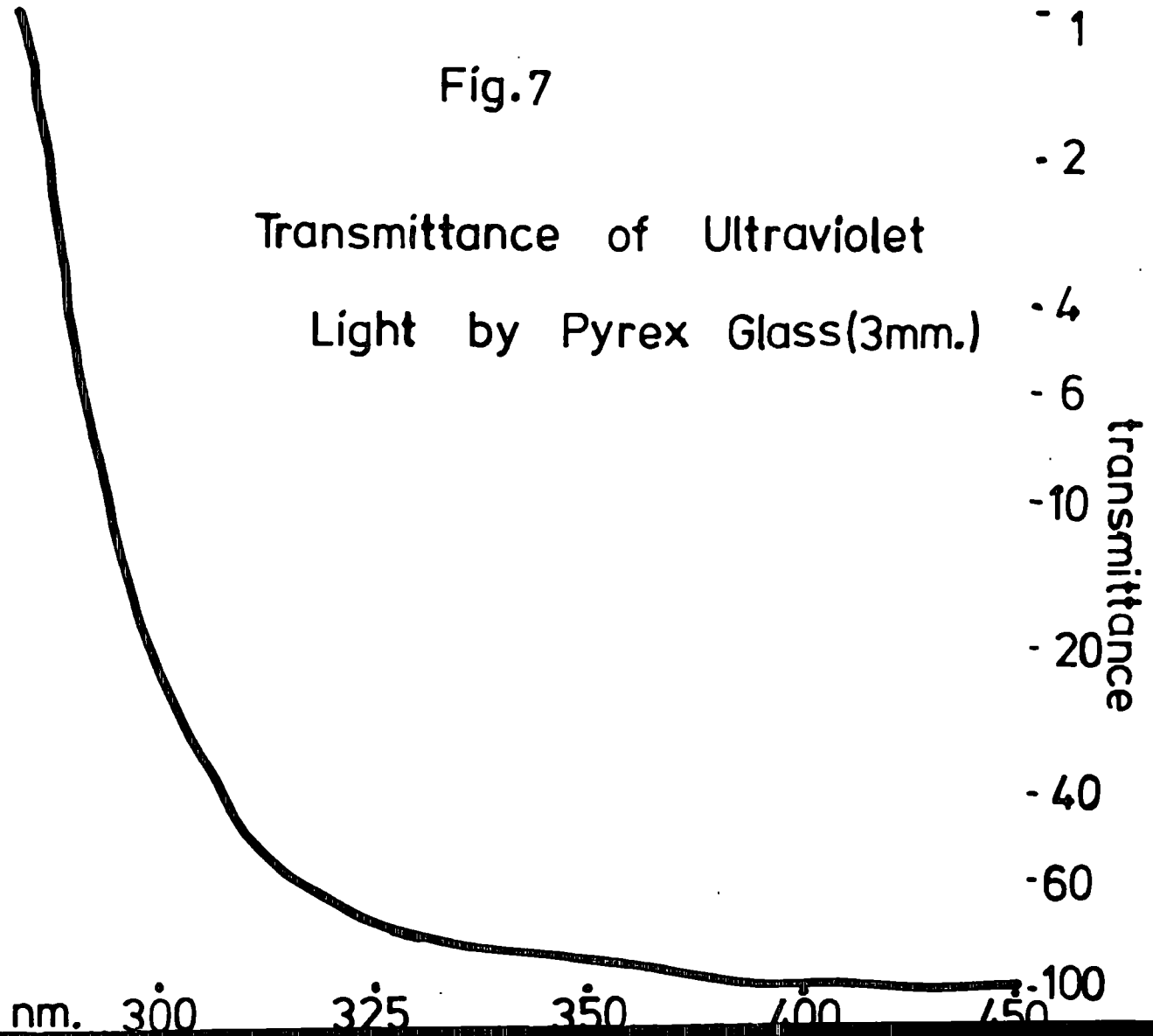


FIG. 6.

Spectral Energy Distribution of 'Rayonet' "Black Light Phosphor" Lamps.

Fig.7

Transmittance of Ultraviolet Light by Pyrex Glass(3mm.)



at 300 nm. (see Fig. 5.); 'Black light phosphor' conversion lamps, 8 of which provide ca. 100 watts of ultraviolet light with a miximum output at ca. 376 nm. (see Fig. 6.).*

Pyrex was the only filter employed in this work and its ultraviolet spectrum is shown in Fig. 7.

7.1. Irradiation of Static Systems.

(i) Irradiation of Perfluoro-4,5-bis-isopropylpyridazine by a Medium Pressure Mercury Arc.

Perfluoro-4,5-bis-isopropylpyridazine (70) (1·5 g., 3·32 m.moles), was sealed in a dry silica tube (29 x 320 mm.) under high vacuum, (0·001 mm.) and irradiated for 96 hrs. by two Hanovia U.V.S. 500 lamps within a 'Reading' reactor. The vacuum transferred product (1·15 g.) was shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to be a single component, identified as perfluoro-2,5-bis-isopropylpyrazine (84) by comparison of its ^{19}F n.m.r. (No. 9) and i.r. (No. 6) spectra with those of an authentic sample. Perfluoro-2,5-bis-isopropylpyrazine (84) had been previously prepared by direct polyfluoroalkylation of tetrafluoropyrazine with hexafluoropropene[53] and also by a route analogous to that described above.[51]

(ii) Irradiation of Perfluoro-4-isopropylpyridazine (71) by a Medium Pressure Mercury Arc.

Perfluoro-4-isopropylpyridazine (71) (0·6 g., 1·99 m.moles), was sealed in a dry silica tube (29 x 320 mm.) under high vacuum, (0·001 mm.) and irradiated for 66·5 hrs. by an Hanovia U.V.S. 1000 lamp; at a distance of ca. 10 cm. from the lamp. The vacuum transferred product was shown by g.l.c. (G.D.B. di-isodecylphthalate, 78°C) to be one component, which was identified as perfluoro-2-isopropylpyrazine (102) (0·55 g., 91·6%), (Found: C, 27·6; N, 9·4; F, 63·3; M, 302; $C_7F_{10}N_2$ requires C, 27·78; N, 9·28; F, 52·91;

*Operating temperatures.- Rayonet 'R.P.R.-208' reactor 40 ± 2°C.
Hanovia 'Reading' reactor (m.p. Hg lamps) 70 ± 5°C.
Hanovia U.V.S. 1000 lamp at ca. 10 cm. 65 ± 5°C.

M, 302), i.r. spectrum No. 7, ^{19}F n.m.r. spectrum No. 10, λ_{max} 274 nm.

(iii) Irradiation of Perfluoro-4-ethylpyridazine (74) by a Medium Pressure Mercury Arc.

Perfluoro-4-ethylpyridazine (74) (0·5 g., 1·99 m.moles), was sealed in a dry silica tube (29 x 320 mm.) under high vacuum (0·001 mm.), and irradiated for 144 hrs. by an Hanovia U.V.S. 1000 lamp; at a distance of ca. 15 cm. from the lamp. The vacuum transferred was shown by g.l.c. (G.D.B., di-iso-decylphthalate, 85°C) to be one component, which was identified as perfluoro-2-ethylpyrazine (103) (0·4 g., 80%), (Found: C, 28·2; F, 60·8; M, 252; $C_6F_8N_2$ requires, C, 28·57; F, 60·32; M, 252), i.r. spectrum No. 8, ^{19}F n.m.r. spectrum No. 11; λ_{max} 275 nm.

(iv) Irradiation of Perfluoro-4-t-butylpyridazine (82) by a Medium Pressure Mercury Arc.

Perfluoro-4-t-butylpyridazine (82) (1·2 g., 3·41 m.moles), was sealed in a dry silica tube (35 x 300 mm.) under high vacuum (0·005 mm.), and irradiated for ca. 75 hrs. by two Hanovia U.V.S. 500 lamps within the 'Reading' reactor. Nitrogen was bubbled through the vacuum transferred product, in case any perfluoroisobutene had been formed, and then into alkaline acetone for ca. 20 mins. Chromatographic analysis (G.D.B. silicone elastomer, 78°C) of the product (0·75 g.) showed it to be mainly one component (ca. 92%). Purification by preparative g.l.c. (F.21 silicone elastomer, 100°C) gave perfluoro-2-t-butylpyrazine (105) (0·6 g., 50%), (Found: C, 27·6; N, 7·9; F, 64·4; M, 352; $C_8F_{12}N_2$ requires, C, 27·30; N, 7·95; F, 64·75; M, 352), i.r. spectrum No. 9, ^{19}F n.m.r. spectrum No. 12.

(v) Irradiation of Perfluoro-4,5-bis-ethylpyridazine (75) by a Medium Pressure Mercury Arc.

Perfluoro-4,5-bis-ethylpyridazine (75) (0·45 g., 1·28 m.moles), was sealed in a dry silica tube (29 x 320 mm.) under high vacuum (0·001 mm.),

and irradiated by an Hanovia U.V.S. 1000 lamp for 125 hrs. at a distance of ca. 16 cm. from the lamp. The vacuum transferred product (0·33 g.) was shown by g.l.c. (G.D.B. di-isodecylphthalate, 90°C) to contain one major component (85%) and starting material (15%). Preparative g.l.c. (F.21, di-isodecylphthalate, 100°C) gave perfluoro-2,5-bis-ethylpyrazine (0·2 g., 44%) (Found: C, 27·3; F, 64·5; M, 352; $C_8F_{12}N_2$ requires C, 27·27; F, 64·48; M, 352), i.r. spectrum No. 10, ^{19}F n.m.r. spectrum No. 13.

(vi) Irradiation of Perfluoro-4,5-bis-sec.-butylpyridazine (79) by a Medium Pressure Mercury Arc.

Perfluoro-4,5-bis-sec.-butylpyridazine (79) (1·28 g., 2·32 m.moles) was sealed in a silica tube (40 x 430 mm.) and irradiated for 144 hrs., by two Hanovia U.V.S. 500 lamps within the 'Reading' reactor. The vacuum transferred product (0·75 g.) was shown by g.l.c. (G.D.B. silicone elastomer, 78°C), to contain two major components, starting material (8%) and perfluoro-2,5-bis-sec.-butylpyrazine (107) (83%). The latter was identified by comparison of the ^{19}F n.m.r. and i.r. spectra of the product with those of an authentic sample. This pyrazine (107) had been previously prepared by direct polyfluoroalkylation of tetrafluoropyrazine with perfluorobut-2-ene (ref. 49, p.149).

(vii) Irradiation of Perfluoro-3,5-bis-isopropylpyridazine (72) by a Medium Pressure Mercury Arc.

Perfluoro-3,5-bis-isopropylpyridazine (72) (2·1 g., 4·65 m.moles), was sealed in a dry silica tube (29 x 320 mm.) under high vacuum (0·001 mm.), and irradiated by an Hanovia U.V.S. 1000 lamp for 115 hrs., at a distance of ca. 6 cm. from the lamp. The vacuum transferred product (1·8 g.) was shown by g.l.c. (G.D.B. silicone elastomer, 78°C) to contain perfluoro-3,5-bis-isopropylpyridazine (72) (4%) and perfluoro-2,6-bis-isopropylpyrazine (101) (96%). The latter was identified by comparison of the i.r. and ^{19}F n.m.r.

spectra of the product with those of an authentic sample of (101) which was prepared in a similar experiment.[59] The i.r. (spectrum No.11) and ^{19}F n.m.r. (spectrum No. 4) spectra of a pure sample of (101) are included in this work for comparison.

(viii) Irradiation of 3,6-Difluoro-4,5-dichloropyridazine (68) by a Medium Pressure Mercury Arc.

3,6-Difluoro-4,5-dichloropyridazine (0·6 g., 3·24 m.moles), was sealed in a dry silica tube (29 x 320 mm.) under high vacuo (0·001 mm.), and irradiated for 98 hrs. by an Hanovia U.V.S. 1000 lamp at a distance of ca. 15 cm. from the lamp. Much decomposition occurred. The vacuum transferred product (0·11 g.) was shown by g.l.c. (G.D.B., di-isodecylphthalate, 150°C) to consist of two major components, the one of longer retention time being shown to be starting material (40%). The component of shorter retention time was not isolated because of the small amount of product isolated.

(ix) Irradiation of 3,6-Difluoro-4,5-dichloropyridazine (68) in Solution by a 253·7 nm. Source.

3,6-Difluoro-4,5-dichloropyridazine (68) (0·85 g., 4·6 m.moles), was introduced into dry silica tube, then Freon 114 (ca. 30 mls.) was condensed into the tube and then the tube was sealed under vacuo. The system was then irradiated for 168 hrs. by 120 watts of 253·7 nm. light. Considerable decomposition was observed upon the walls of the silica tube. After evaporation of the solvent, the contents of the tube were dissolved in ether, the ether evaporated and the solid (brown) sublimed (20% ·001 mm.) to give a white solid (0·16 g.) which was shown by g.l.c. (G.D.B., di-isodecylphthalate, 150°C) to be mainly starting material (96%) together with compound of shorter retention time (same as in previous expt.) (4%).

(x) Irradiation of Tetrachloropyridazine (110) in Solution at 253·7 nm.

Tetrachloropyridazine (110) (0·25 g., 1·15 m.moles), was introduced into a dry silica tube, and then Freon 114 (106 mls.) was condensed in. The system was then irradiated at 253·7 nm. (120 watts) for 100·5 hrs., the solvent evaporated, the contents of the tube (dark brown) dissolved in ether, and the ether evaporated. Sublimation 60°C/0·001 mm. gave a white crystalline product (0·05 g.) which was shown by g.l.c. (G.D.B. silicone elastomer, 135°C), to contain starting material (32·5%) and a component (67·5%) of identical retention time to tetrachloropyrazine (111).

(xi) Irradiation of Tetrachloropyridazine (110) by a Medium Pressure Mercury Arc.

Tetrachloropyridazine (110) (1·80 g., 8·26 m.moles) was sealed in a dry Pyrex tube (34 x ca. 260 mm.) under high vacuum and irradiated by an Hanovia U.V.S. 1000 lamp for 161 hrs. at a distance of ca. 15 cm. from the lamp. Considerable decomposition occurred. The contents were dissolved in acetone, the solvent evaporated and the product sublimed 50°C/0·001 mm. to give a white crystalline product (0·5 g.) which was shown by g.l.c. (G.D.B., silicone elastomer, 220°C) and i.r. to be unchanged starting material.

(xii) Irradiation of Tetrachloropyridazine (110) by a Medium Pressure Mercury Arc in Silica.

Tetrachloropyridazine (110) (1·85 g., 8·48 m.moles) was sealed in a dry silica tube (34 x ca. 260 mm.) under high vacuum and irradiated by an Hanovia U.V.S. 1000 lamp for 161 hrs. at a distance of ca. 15 cm. from the lamp. Considerable decomposition occurred. The contents of the tube were treated as in the previous experiment. The product (0·4 g.) was similarly shown to be unchanged starting material.

(xiii) Irradiation of Tetrachloropyridazine (110) in Solution at -78°C by a 253·7 nm. Source.

The Hanovia 1L photochemical reactor with 2-watt low pressure mercury arc was employed.

Tetrachloropyridazine (110) (2·0 g., 9·17 m.moles) in Freon 114 (ca. 1 litre) was irradiated for 64 hrs., whilst at -78°C. Evaporation of the solvent gave a light brown solid (1·9 g.) which was shown by g.l.c. (G.D.B. silicone elastomer, 180°C) to be unchanged starting material. No tetrachloropyrazine was formed.

(xiv) Irradiation of Pyridazine by a Medium Pressure Mercury Arc.

Pyridazine (0·5 g., 6·25 m.moles), was sealed in a dry silica tube (36 x 250 mm.) under high vacuum (0·001 mm.), and irradiated for 96 hrs. by two Hanovia U.V.S. 500 lamps within the 'Reading' photochemical reactor. The vacuum transferred product (0·33 g.) was shown by g.l.c. (G.D.B., silicone elastomer, 120°C) to be starting material. This was confirmed by comparison of the i.r. of the product with that of an authentic sample.[40] This confirms the result obtained from similar experiment.[51]

(xv) Irradiation of 3,5,6-Trifluoro-4-methoxypyridazine (64) by a Medium Pressure Mercury Arc.

3,5,6-Trifluoro-4-methoxypyridazine (64) (0·45 g., 2·74 m.moles), was sealed in a dry silica tube (27 x ca. 320 mm.), under high vacuum (0·001 mm.), and irradiated for 137 hrs., by an Hanovia U.V.S. 1000 lamp, at a distance of ca. 10 cm. from the lamp. The vacuum transferred product (0·15 g.) was shown by g.l.c. (G.D.B. silicone elastomer, 150°C) to be unchanged starting material.

(xvi) Irradiation of 3,6-Difluoro-4,5-bis-methoxypyridazine (65) by a Medium Pressure Mercury Arc.

3,6-Difluoro-4,5-bis-methoxypyridazine (65) (0·65 g., 3·7 m.moles), was sealed in a dry silica tube (27 x ca. 320 mm.), under high vacuum (0·001 mm.), and irradiated for 137 hrs., by an Hanovia U.V.S. 1000 lamp, at a distance of ca. 10 cm. from the lamp. The vacuum transferred product (0·22 g.) was shown by g.l.c. (G.D.B. silicone elastomer, 150°C) to be unchanged starting material.

(xvii) Irradiation of 3,4,5-Trifluoro-6-methoxypyridazine (66) by a Medium Pressure Mercury Arc.

3,4,5-Trifluoro-6-methoxypyridazine (66) (0·42 g., 2·56 m.moles), was sealed in a dry silica tube (29 x ca. 300 mm.), under high vacuum (0·001 mm.), and irradiated for 112 hrs. by an Hanovia U.V.S. 1000 lamp, at a distance of ca. 15 cm. from the lamp. The vacuum transferred product (0·10 g.) was shown by g.l.c. (G.D.B. silicone elastomer, 100°C) to contain two major components, the one of shorter retention time being starting material (74·5%). The component (24·5%) of longer retention was not identified, but was found to have the following ^{19}F n.m.r. spectrum; δ (acetone) 106·2 (1F), 140·0 (1F), and 150·9 p.p.m. (1F). The compound could not be a methoxy trifluoro-pyrazine or -pyrimidine.

(xviii) Irradiation of Perfluoro-3,4,6-tris-isopropylpyridazine (73) by a Medium Pressure Mercury Arc.

Perfluoro-3,4,6-tris-isopropylpyridazine (73) (1·0 g., 1·66 m.moles) was sealed in a dry silica tube (29 x 320 mm.) under high vacuum (0·001 mm.), and irradiated for 67 hrs. by an Hanovia U.V.S. 1000 lamp, at a distance of ca. 20 cm. from the lamp. The dark red liquid (0·95 g.) was shown by g.l.c. (G.D.B., di-isodecylphthalate, 40°C) to be mainly starting material (ca. 95%) contaminated with a large number of more volatile components.

(xix) Irradiation of Perfluoro-3,5-bis-isopropylpyridazine (72) at 376 nm.

Perfluoro-3,5-bis-isopropylpyridazine (72) (1·35 g., 2·98 m.moles), was sealed in a Pyrex tube (58 x 340 mm.), under high vacuum (ca. 0·001 mm.), and irradiated for 132 hrs. at ca. 376 nm. (ca. 50 watts). The liquid was discoloured, but shown by g.l.c. (G.D.B. di-isodecylphthalate, 60°C) to be unchanged starting material.

(xx) Irradiation of Perfluoro-4,5-bis-isopropylpyridazine (70) at ca. 376 nm.

Perfluoro-4,5-bis-isopropylpyridazine (70) (0·9 g., 1·99 m.moles), was sealed in a Pyrex tube (58 x 340 mm.) under high vacuum (ca. 0·001 mm.) and irradiated for 113 hrs. at ca. 376 nm. (ca. 50 watts). The solid was slightly discoloured, but shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to be unchanged starting material.

(xxi) Irradiation of Perfluoro-4,5-bis-isopropylpyridazine (70) by a Medium Pressure Mercury Arc in Pyrex.

Perfluoro-4,5-bis-isopropylpyridazine (70) (0·6 g., 1·33 m.moles), was sealed in a Pyrex tube (34 x 320 mm.), under high vacuum (ca. 0·001 mm.), and irradiated for 90 hrs. by an Hanovia U.V.S. 1000 lamp at a distance of ca. 15 cm. from the lamp. The vacuum transferred product (0·55 g.) was shown to be one component by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) which was identified as perfluoro-2,5-bis-isopropylpyrazine (84) by comparison of its ^{19}F n.m.r. spectrum with that of an authentic sample.[51]

(xxii) Irradiation of Perfluoro-3,5-bis-isopropylpyridazine (72) by a Medium Pressure Mercury Arc in Pyrex.

Perfluoro-3,5-bis-isopropylpyridazine (72) (1·0 g., 2·21 m.moles), was sealed in a dry Pyrex tube (34 x 320 mm.), under high vacuum (ca. 0·001 mm.), and irradiated for 143 hrs. by an Hanovia U.V.S. 1000 lamp at a distance of ca. 15 cm. from the lamp. The vacuum transferred product (0·85 g.) was shown by g.l.c. to consist of two components; starting material (5%) and

perfluoro-2,6-bis-isopropylpyrazine (95%) which was identified by comparison of the i.r. of the product with that of an authentic sample,[59] prepared by a similar experiment.

(xxiii) Irradiation of Tetrafluoropyridazine (63) by a Medium Pressure Mercury Arc in Pyrex.

Tetrafluoropyridazine (63) (1·1 g., 7·24 m.moles), was sealed in a dry Pyrex tube (34 x 320 mm.), under high vacuum (ca. 0·001 mm.), and irradiated for 112 hrs. by an Hanovia U.V.S. 1000 lamp at a distance of ca. 15 cm. from the lamp. Much decomposition occurred. The vacuum transferred product (0·52 g.) was shown by g.l.c. (G.D.B. di-isodecylphthalate, 78°C), to be mainly starting material (89%), with tetrafluoropyrazine (11%) as a minor product.[51]

(xxiv) Irradiation of Perfluoro-4,5-bis-isopropylpyridazine (70) at 253·7 nm. in the ABSENCE of Mercury.

Perfluoro-4,5-bis-isopropylpyridazine (70) (0·95 g., 2·1 m.moles), was sealed in a new, dry, silica tube (41 x 300 mm.) under high vacuum (0·075 mm., mercury free new vacuum line used), together with gold foil (10 x 100 mm.), and irradiated for 800 hrs. at 253·7 nm. (120 watts). The vacuum transferred product (0·45 g.) was shown by g.l.c. (G.D.B. di-isodecylphthalate, 60°C) to contain a major component (64%), a minor component (30%) and starting material (6%). Preparative scale g.l.c. ('F.21', di-isodecylphthalate, 125°C) furnished pure samples of the major component, perfluoro-2,5-bis-isopropylpyrazine (84)[51] (by comparison of its ^{19}F n.m.r. and i.r. spectra with those of an authentic sample), and the minor component which was found by g.l.c. (G.D.B. silicone elastomer, 60°C) and ^{19}F n.m.r. to be a 1:1 mixture of perfluoro-2,6-bis-isopropylpyrazine (101)[59] and perfluoro-4,5-bis-isopropylpyrimidine[88] (112). These were separated by preparative g.l.c. ('Aerograph', silicone elastomer 80°C) and identified by comparison of their i.r. spectra with those of authentic samples of (101) and (112).[88]

(xxv) Irradiation of Perfluoro-4,5-bis-isopropylpyridazine (70) at 253·7 nm. in the PRESENCE of Mercury.

Perfluoro-4,5-bis-isopropylpyridazine (70) (1·0 g., 2·2 m.moles), was sealed in a dry silica tube (41 x 300 mm.) under high vacuum (0·075 mm.), together with mercury (0·5 g.), and irradiated for 800 hrs. at 253·7 nm. (120 watts). The vacuum transferred product (0·80 g.), was shown by g.l.c. (G.D.B. di-isodecylphthalate, 60°C) to contain a major product (75%), a minor component (20%) and starting material (5%). By the same procedure as in the previous experiment the major component was shown to be perfluoro-2,5-bis-isopropylpyrazine (84)[51] and the minor component to be a 1:1 mixture of perfluoro-2,6-bis-isopropylpyrazine (101)[59] and perfluoro-4,5-bis-isopropylpyrimidine[88] (112), by comparison of their ^{19}F n.m.r. and i.r. spectra with those of authentic samples.

(xxvi) Irradiation of Perfluoro-4-isopropylpyridazine (71) at 253·7 nm. in the Absence of Oxygen Whilst Under Transference.

Perfluoro-4-isopropylpyridazine (71) (1·25 g., 4·14 m.moles) was introduced into the apparatus shown in Fig. 2. (silica vessel used, 81 x 340 mm.). The pyridazine (71) was then frozen (liquid air) the system evacuated, allowed to warm up and then let down to atmospheric pressure with pure dry nitrogen. This procedure was carried out five times and then the system was evacuated to 2·5 mm. (residual pressure being due to nitrogen. The system was then irradiated at 253·7 nm. (120 watts), whilst pyridazine (71) transferred into the cold trap (liquid air). The transferred material (1·15 g.) was shown by g.l.c. (G.D.B. silicone elastomer, 78°C) to be a mixture of the 2,5-diazadewarbenzene (118) (23%), (see 7.2.(iii)), perfluoro-2-isopropylpyrazine (102) (67%), and starting material (10%).

(xxvii) Irradiation of Perfluoro-4-isopropylpyridazine (71) at 253·7 nm. in the Presence of Oxygen Whilst Under Transference.

Perfluoro-4-isopropylpyridazine (71) (1·20 g., 3·97 m.moles), was introduced into the apparatus used in the previous experiment. The

pyridazine (71) was then frozen down (liquid air), the system evacuated and 3·0 mm. of oxygen admitted. The system was then irradiated at 253·7 nm. (120 watts), whilst pyridazine (71) transferred into the cold trap (liquid air). The transferred material (1·1 g.) was shown by g.l.c. (G.D.B. silicone elastomer, 78°C) to be a mixture of the 2,5-diazadewar-benzene (118) (21%) (see 7.2.(iii)), perfluoro-2-isopropylpyrazine (102) (70%) and starting material (9%).

(xxviii) Irradiation of Perfluoro-4,5-bis-isopropylpyridazine (70) in the Presence of Fluorene at ca. 300 nm.

Perfluoro-4,5-bis-isopropylpyridazine (70) (1·1 g., 2·43 m.moles) and fluorene (0·43 g., 2·65 m.moles) in CF_2Cl-CF_2Cl (74 mls.), were sealed in a Pyrex tube under high vacuum and irradiated for 64·4 hrs. at ca. 300 nm. (85 watts). Evaporation of the solvent left a solid which upon adding hexane followed by filtration (to dissolve fluorene) gave pure starting material (0·88 g.).

(xxix) Irradiation of Perfluoro-4,5-bis-isopropylpyridazine (70) at ca. 300 nm.

Perfluoro-4,5-bis-isopropylpyridazine (70) (1·1 g., 2·43 m.moles) in CF_2Cl-CF_2Cl (74 mls.) was sealed in a Pyrex tube under high vacuum and irradiated for 64·4 hrs. at ca. 300 nm. (85 watts). Evaporation of solvent gave pure starting material (1·05 g.).

7.2. Irradiation Whilst Under Transference.

The irradiations whilst under transference were allowed to proceed for approximately one day. The pressure was varied such that all the material transferred into the cold trap within a day (see Fig. 2).

(i) Irradiation of Perfluoro-3,5-bis-isopropylpyridazine (72) at 253·7 nm.

Perfluoro-3,5-bis-isopropylpyridazine (72) (8·2 g., 18·15 m.moles), was introduced into the apparatus shown in Fig. 2. (silica vessel 84 x

340 mm.). The pyridazine (72) was then frozen (liquid air) and the system evacuated to 0·001 mm. The system was then irradiated at 253·7 nm. (120 watts). Because a joint streaked the vacuum decreased to 9·0 mm. after 18 hrs. and not all the starting material transferred to the cold trap (liquid air). G.l.c. (G.D.B. di-isodecylphthalate, 60°C) of the transferred material (7·5 g.) showed three major components, in order of retention time, perfluoro-1,3-bis-isopropyl-2,5-diazabicyclo[2.2.0.]hexa-2,5-diene (117) (21%), perfluoro-2,6-bis-isopropylpyrazine (101) (13%), and starting material (55%). Preparative g.l.c. ('F21' di-isodecylphthalate, 55°C) provided pure samples of the 2,5-diazadewarbenzene (117) (Found: C, 26·8; F, 67·0; M, 452; $C_{10}F_{16}N_2$ requires C, 26·55; F, 67·26; M, 452), i.r. spectrum No. 12. ^{19}F n.m.r. spectrum No. 14, u.v. spectrum No. 12; perfluoro-2,6-bis-isopropylpyrazine (101)[59] and starting material.[41] The identity of the latter two compounds was confirmed by comparison of their i.r. and ^{19}F n.m.r. spectra with those of authentic samples.

(ii) Irradiation of the 2,5-Diazadewarbenzene (117) at 257·7 nm. in a Static System.

The 2,5-diazadewarbenzene (117) (75 mg.) was sealed in a dry silica tube (8·5 x 240 mm.), under high vacuum (ca. 0·001 mm.) and irradiated at 253·7 nm. (120 watts) for two hours. The product was shown by (75 mg.) g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to be perfluoro-2,6-bis-isopropylpyrazine (101).

(iii) Irradiation of Perfluoro-4-isopropylpyridazine (71) at 253·7 nm.

Perfluoro-4-isopropylpyridazine (71) (5·0 g., 16·58 m.moles), was introduced into the apparatus shown in Fig. 2 (silica vessel, 36 x 490 mm.), frozen and the system evacuated to 2 mm. The system was then irradiated at 253·7 nm. (120 watts) whilst the pyridazine (71) transferred. The transferred material was then transferred again at 3 mm. in the same system.

G.l.c. (G.D.B., silicone elastomer, 40°C) of the transferred material (4·9 g.) showed three major components, in order of retention time, perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (118) (38%), perfluoro-2-isopropylpyrazine (102) (52%) and starting material (10%). Preparative scale g.l.c. ('F-21' silicone elastomer, 50°C) provided pure samples of the 2,5-diazadewarbenzene (118) (1·84 g.), (this compound did not give consistent analysis results); M, 302; i.r. spectrum No. 13, ^{19}F n.m.r. spectrum No. 15, u.v. spectrum No. 13; perfluoro-2-isopropylpyrazine (102), and starting material (71). The identity of the two latter compounds was confirmed by comparison of their i.r. and ^{19}F n.m.r. spectra with those of authentic samples.

A more typical yield of the 2,5-diazadewarbenzene (118) in transference experiments (ca. 3 mm.) at 253·7 nm. (120 watts) is ca. 20% together with ca. 70% pyrazine (102) and ca. 10% starting material. Oxygen, acetone and 40-60° petroleum ether were found to have no effect upon the relative amounts of the 2,5-diazadewarbenzene (118) and pyrazine (102) produced in transference experiments. If the pressure is lowered the relative amount of the 2,5-diazadewarbenzene (118) and pyrazine (102) to starting material decreases e.g. at 0·3 mm. the transferred product mixture consisted of the 2,5-diazadewarbenzene (118) ca. 0·3%, pyrazine (102) ca. 10% and starting material (71) ca. 89·7%. This is consistent with the transferring molecules spending less time in the irradiation zone.

The structure of the 2,5-diazadewarbenzene (118) was confirmed by its conversion to pyrazine (102) upon heating and photolysis at 300 nm. (see Sections 8.1.A. and 7.2.(ix) respectively).

(iv) Irradiation of Perfluoro-4,5-bis-ethylpyridazine (75) at 253·7 nm.

Perfluoro-4,5-bis-ethylpyridazine (75) (1·65 g., 4·68 m.moles), was introduced into the apparatus shown in Fig. 2. (silica vessel, 81 x 340 nm.),

the pyridazine (75) (frozen (liquid air), and the system evacuated to 0·001 mm. The system was then irradiated at 253·7 nm., (120 watts) whilst the pyridazine (75) transferred into the cold trap (liquid air). The transferred material was shown by g.l.c. (G.D.B. Di-isodecylphthalate, 60°C) to contain perfluoro-1,4-bis-ethyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (119) (17%), perfluoro-2,5-bis-ethylpyrazine (106) (19%), and starting material (75) (64%). Re-irradiation at 253·7 nm. (120 watts) whilst under transference (0·03 mm.) gave a mixture (1·58 g.) shown by g.l.c. to contain the 2,5-diaza-dewarbenzene (119) (24%), the pyrazine (106) (31%) and starting material (75) (45%). Separation by preparative scale g.l.c. ('F-21', Di-isodecyl-phthalate, 60°C) gave the 2,5-diazadewarbenzene (119) (0·33 g.) [Found: F, 65·3; M, 352; $C_8F_{12}N_2$ requires F, 64·77; M, 352], i.r. spectrum No. 14, ^{19}F n.m.r. spectrum No. 16, u.v. spectrum No. 14; the pyrazine (106) and starting material (75). The latter two compounds were identified by comparison of their i.r. spectra with those of authentic samples of (106) and (75).[46]

(v) Irradiation of 3,6-Difluoro-4,5-dichloropyridazine (68) at 253·7 nm.

3,6-Difluoro-4,5-dichloropyridazine (68) (1·94 g., 10·5 m.moles), was introduced into the apparatus shown in Fig. 2 (silica vessel 81 x 340 mm.), frozen (liquid air), and the system evacuated to 0·001 mm. The system was then irradiated whilst the pyridazine (68) transferred to the cold trap (liquid air). Decomposition products were observed upon the walls of the silica vessel. The transferred product (1·62 g.), was shown by g.l.c. (G.D.B. di-isodecylphthalate, 150°C) to be mainly starting material ($\geq$99%) with a small amount of a more volatile component ($\ll$1%).

(vi) Irradiation of 3,5,6-Trifluoro-4-methoxypyridazine (64) at 253·7 nm.

3,5,6-Trifluoro-4-methoxypyridazine (64) (1·5 g., 9·15 m.moles), was introduced into the apparatus in Fig. 2 (silica vessel 84 x 340 mm.), the system evacuated to 0·5 mm., and irradiated at 253·7 nm. (120 watts) whilst the pyridazine (64) transferred into the cold trap (liquid air). After 40½ hrs.

a small amount of material (0·15 g.) had transferred. G.l.c. (G.D.B. silicone elastomer, 100°C) and i.r. showed the transferred material to be starting material. Much decomposition was observed upon the walls of the silica vessel.

(vii) Irradiation of Perfluoro-4-isopropylpyridazine (71) at 300 nm. in Pyrex.

Perfluoro-4-isopropylpyridazine (71) (1·5 g., 4·97 m.moles) was introduced into the apparatus shown in Fig. 2 (Pyrex vessel 87 x 420 mm.), frozen (liquid air), and the system evacuated to 2·5 mm. The system was then irradiated at ca. 300 nm. (85 watts) whilst the pyridazine (71) transferred into a cold trap (liquid air). The transferred product (1·45 g.) was shown by g.l.c. (G.D.B. silicone elastomer, 78°C) to consist of perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (118) (45%), perfluoro-2-isopropylpyrazine (102) (⩽0·5%) and starting material (71) (54·5%).

Using the same apparatus and procedure as above perfluoro-4-isopropyl-pyridazine (71) (8·45 g., 28·0 m.moles) was irradiated whilst under transference (8·0 mm.), then re-irradiated (5·5 mm.), and re-irradiated again (4·5 mm.). The final product (7·5 g.) was shown by g.l.c. (as above) to consist of the 2,5-diazadewarbenzene (118) (94%), the pyrazine (102) (1%) and starting material (71) (5%). Separation by preparative scale g.l.c. ('F-21', silicone elastomer, 60°C) gave the pure 2,5-diazadewarbenzene (118) (4·6 g.) which was identified by comparison of its i.r. and ^{19}F n.m.r. spectra with those of an authentic sample.

(viii) Irradiation of Perfluoro-4-isopropylpyridazine (71) at ca. 300 nm. in Silica.

Using the same procedure as in the previous experiment and a silica vessel (81 x 340 mm.), perfluoro-4-isopropylpyridazine (71) was irradiated, whilst under transference (4 mm.), at ca. 300 nm. (85 watts). G.l.c. (G.D.B., silicone elastomer, 78°C) of the transferred product (0·55 g.), showed it to contain the 2,5-diazadewarbenzene (118) (42·5%), the pyrazine (102) (37%) and starting material (71) (20·5%).

(ix) Irradiation of the 2,5-Diazadewarbenzene (118) at ca. 300 nm. in Silica in a Static System.

The 2,5-diazadewarbenzene (118) (10 µl.) was sealed in a dry silica tube (8·5 x 240 mm.) under high vacuum (ca. 0·001 mm.) and irradiated at ca. 300 nm. (85 watts) for 5 hrs. G.l.c. (G.D.B., di-isodecylphthalate, 78°C) of the resulting product (10 µl.) was shown to be pure perfluoro-2,6-bis-isopropyl-pyrazine (102).

(x) Irradiation of Perfluoro-3,5-bis-isopropylpyridazine (72) at ca. 300 nm. in Pyrex.

Using the procedure in 7.2.(vii) and a Pyrex vessel (87 x 420 mm.), perfluoro-3,5-bis-isopropylpyridazine (72) (0·7 g., 1·55 m.moles) was irradiated at ca. 300 nm. (85 watts), whilst under transference (4 mm.). G.l.c. (G.D.B., di-isodecylphthalate, 78°C) of the product showed (0·65 g.) it to contain perfluoro-1,3-bis-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (117) 8%, an unknown (see Chapter 5) (0·5%), perfluoro-2,6-bis-isopropylpyrazine (101) (3·5%), and starting material (72) (88%). Re-irradiation of the mixture obtained above, in the same apparatus, with the same light source gave a mixture (0·60 g.), shown by g.l.c. (as above) to contain the 2,5-diazadewar-benzene (117) (9%), an unknown 0·6%, the pyrazine (101) (10%) and starting material (72) (80·4%).

(xi) Irradiation of Perfluoro-3,5-bis-isopropylpyridazine (72) at ca. 300 nm. in Silica.

Using the procedure in 7.2.(vii) (silica vessel 81 x 340 mm.), perfluoro-3,5-bis-isopropylpyridazine (72) (0·8 g., 1·77 m.moles), was irradiated at ca. 300 nm. (85 watts), whilst under transference (4 mm.). The product (0·74 g.) was shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to contain the 2,5-diazadewarbenzene (117) (9%), some unknowns (10%), perfluoro-2,6-bis-isopropylpyrazine (23%), and starting material (58%).

(xii) Irradiation of the 2,5-Diazadewarbenzene (117) by a Medium Pressure Mercury Arc in Pyrex in a Static System.

The 2,5-diazadewarbenzene (117) (75 mg.) was sealed in a dry Pyrex tube (8 x 250 mm.), and irradiated by an Hanovia U.V.S. 1000 lamp for ca. 100 mins. at a distance of ca. 30 cm. from the lamp. The product (0·075 g.) was shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to be a mixture of perfluoro-2,6-bis-isopropylpyrazine (101) (93%) and the starting material (117) (6%).

(xiii) Irradiation of Perfluoro-4,5-bis-isopropylpyridazine (70) at ca. 300 nm. in Pyrex.

The same procedure was adopted as in 7.2.(ii). Perfluoro-4,5-bis-isopropylpyridazine (70) (1·5 g., 3·32 m.moles), was irradiated at ca. 300 nm. (85 watts), whilst under transference (1·3 mm.), in the apparatus in Fig. 2 (Pyrex vessel 87 x 420 mm.). The transferred product, in ether, was shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to be unchanged starting material (70).

(xiv) Irradiation of Perfluoro-4,5-bis-isopropylpyridazine (70) at ca. 300 nm. in Silica.

The procedure in 7.2.(ii) was adopted. Perfluoro-4,5-bis-isopropyl-pyridazine (70) (5·2 g., 11·5 m.moles), was irradiated at ca. 300 nm. (85 watts), whilst under transference, (2 mm.) in the apparatus shown in Fig. 2 (silica vessel, 81 x 340 mm.), for 17·2 hrs. Only 2·2 g. of the material transferred and this was shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to contain perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (122) (44·7%), unknowns (ca. 8%), perfluoro-2,5-bis-isopropylpyrazine (84) (14·3%), and starting material (70) (33·0%). As percentages of the total amount of material present in the experiment: 1,2-diazadewarbenzene (122) (19%), pyrazine (84) (ca. 6%), unknowns (4%), and starting material (70) (71%). All the material (5·0 g.) was irradiated (ca. 300 nm.) whilst under transference at 2 mm. then

at 0·04 mm. and again at 0·01 mm. The resulting mixture (4·7 g.) was shown by g.l.c. (as above) to contain the 1,2-diazadewarbenzene (122) (64%), pyrazine (84) (7%), unknowns (ca. 8%), and starting material (70) (11%). Preparative scale g.l.c. ['F-21', di-isodecylphthalate, 60°C (all parts at 60°C)] of 4·35 g. of the mixture gave the 1,2-diazadewarbenzene (122) (2·25 g.), [Found: F, 67·3; M, 4·52; $F_{10}F_{16}N_2$ requires F, 67·26; M, 452], i.r. spectrum No. 15, ^{19}F n.m.r. spectrum No. 17, u.v. spectrum No. 15, pyrazine (84) and starting material (70). The latter two components were identified by comparison of their i.r. spectra with those of an authentic samples.[90,51,41]

A small portion of the reaction mixture (250 µl., 0·35 g.) was separated on the 'F-21', using the same conditions except that, an exit tube (stainless steel, 2 x 15 mm.) was at 200°C. The flow of dry nitrogen was 120 mls./min. and hence the contact time was ca. 0·24 secs. Under these conditions perfluoro-1,4-bis-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (113) (0·2 g.) was isolated and was identified by comparison of its ^{19}F n.m.r. and i.r. spectra with those of an authentic sample.

The 1,2-diazadewarbenzene (122) can also be isolated by distillation at reduced pressure (1·0 mm.) in a Büchi Fischer Concentric Tube Fractionation Column.

(xv) Irradiation of Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (122) at 253·7 nm. in a Static System.

The 1,2-diazadewarbenzene (122) (100 mg., 0·22 m.moles) was sealed in a dry silica tube (4 x 190 mm.) under high vacuum (0·001 mm.), and irradiated at 253·7 nm. (120 watts) for 19 hrs. ^{19}F n.m.r. spectrometry showed the product to be a mixture of starting material (122) (ca. 33·3%), perfluoro-1,4-bis-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (113) (ca. 33·3%) and perfluoro-2,5-bis-isopropylpyrazine (84)[90,51] (ca. 33·3%).

(xvi) Irradiation of Perfluoro-4,5-bis-ethylpyridazine (75) at ca. 300 nm. in Pyrex.

The procedure in 7.2.(vii) was adopted. Perfluoro-4,5-bis-ethylpyridazine (75) (1·0 g., 2·84 m.moles), was irradiated at ca. 300 nm. (85 watts), whilst under transference (4 mm.) in the apparatus shown in Fig. 2 (Pyrex vessel, 87 x 420 mm.). The product (1·0 g.) was shown by g.l.c. (G.D.B., silicone elastomer, 60°C) to be a mixture of perfluoro-1,4-bis-ethyl-2,5-diazabicyclo-[2.2.0]hexa-2,5-diene (119) (9%), perfluoro-2,5-bis-ethylpyrazine (106) (7%), and starting material (75).

(xvii) Irradiation of Perfluoro-4,5-bis-ethylpyridazine (75) at ca. 300 nm. in Silica.

The procedure in 7.2.(vii) was adopted. Perfluoro-4,5-bis-ethylpyridazine (75) (1·0 g., 2·84 m.moles), was irradiated at ca. 300 nm. (85 watts), whilst under transference (1 mm.), in the apparatus shown in Fig. 2. (silica vessel, 81 x 340 mm.). The product (1·0 g.) was shown by g.l.c. (G.D.B., silicone elastomer, 60°C) to consist of the 2,5-diazadewarbenzene (119) (14%), the pyrazine (106) (5%) and starting material (75).

Re-irradiation of a mixture (0·95 g.) of the 2,5-diazadewarbenzene (119) (9%), pyrazine (106) (7%) and pyridazine (75) at ca. 300 nm. in silica (81 x 340 mm.) whilst under transference (4 mm.) gave a product (0·95 g.) shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C), to consist of the 2,5-diaza-dewarbenzene (119) (17%), the pyrazine (106) 16% and pyridazine (75). An infrared spectrum of the latter mixture showed a single weak band at 1672 $cm.^{-1}$ confirming that the diazadewarbenzene formed was (119).

(xviii) Irradiation of Perfluoro-4,5-bis-sec.butylpyridazine (79) at ca. 300 nm. in Silica.

The procedure in 7.2.(vii) was adopted. Perfluoro-4,5-bis-sec.butylpyridazine (79) (1·1 g., 2·0 m.moles), was irradiated at ca. 300 nm. (85 watts), whilst

under transference (0·4 mm.) in the apparatus shown in Fig. 2. (silica vessel, 81 x 340 mm.). The product was shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to be a mixture of perfluoro-4,5-bis-sec.butyl-1,2-diazabicyclo[2.2.0]-hexa-2,5-diene (125) (ca. 26%), perfluoro-2,5-bis-sec.butylpyrazine (107) (ca. 8%), an unknown (ca. 2%) and starting material (79). Re-irradiation of the latter mixture at ca. 300 nm. (in silica), whilst under transference at 0·7 mm., then again at 1·0 mm. and lastly at 1 mm. gave a product shown by g.l.c. (G.D.B. di-isodecylphthalate, 78°C) to contain the 1,2-diazadewarbenzene (125) (46%), the pyrazine (107) (22%), an unknown ca. 6%, and starting material (79). Preparative scale g.l.c. using the columns available was impractical because of the poor separation, between the (125) and (107). Perfluoro-4,5-bis-sec.butylpyridazine (12·4 g., 22·5 m.moles) was irradiated in ca. 3 g. aliquots at ca. 300 nm. in silica (vessel 81 x 340 mm.) whilst under transference (0·01 - 0·1 mm.). The samples were each re-irradiated 8 times to give a product (10·9 g.) containing ca. 45% of the 1,2-diazadewarbenzene (125). The mixture was then distilled (Büchi Fischer Concentric Tube Fractionation Column), at reduced pressure to give the 1,2-diazadewarbenzene (125) (3·6 g.), b.p. 44-45°C/4·5 ± 0·2 mm. [Found: C, 26·4; F, 68·5; M, 552; $C_{12}F_{20}N_2$ requires C, 26·09; F, 68·84; M, 552], i.r. spectrum No. 16, ^{19}F n.m.r. spectrum No. 18, u.v. spectrum No. 16; and pyrazine (107) (0·8 g.) b.p. ca. 50°C/3·0 - 3·5 mm. which was identified by comparison of its i.r. spectrum with that of an authentic sample.

Heating the 1,2-diazadewarbenzene (125) at 180°C for one hour converts it quantitatively to the pyrazine (107).

(xix) Irradiation of Perfluoro-4-sec.butylpyridazine (80) at ca. 300 nm. in Pyrex.

The procedure in 7.2.(vii) was adopted. Perfluoro-4-sec.butylpyridazine (80) (1·5 g., 4·26 m.moles), was irradiated at ca. 300 nm. (85 watts), whilst under

transference (0·5 mm.) in the apparatus shown in Fig. 2. (Pyrex vessel, 87 x 420 mm.). The product was shown by g.l.c. (G.D.B., silicone elastomer, 78°C), to be a mixture of perfluoro-1-sec.butyl-2,5-diazabicyclo[2.2.0]-hexa-2,5-diene (121)[50] (22%), perfluoro-2-sec.butylpyrazine (104)[50] (trace), and starting material (80). Re-irradiation with the same source in the same apparatus whilst under transference (1·55 mm.) gave a mixture shown by g.l.c. (as above) to contain the 2,5-diazadewarbenzene (121)[50] (40%), the pyrazine (104) (trace) and starting material (80). Re-irradiation, again, with the same source, in the same apparatus, whilst under transference (1·50 mm.) gave a mixture shown by g.l.c. (as above) to contain the 2,5-diazadewarbenzene (121) (57%), the pyrazine (104) (trace), and starting material (80). An infrared spectrum of the latter mixture, showed a band at 1661 $cm.^{-1}$, confirming that the diazadewarbenzene produced was (121).

(xx) Irradiation of Perfluoro-4-sec.butylpyridazine (80) at ca. 300 nm. in Silica.

The procedure in 7.2.(vii) was adopted. Perfluoro-4-sec.butylpyridazine (80) (1·5 g., 4·26 m.moles), was irradiated at ca. 300 nm. (85 watts), whilst under transference (0·5 mm.) in the apparatus shown in Fig. 2. (silica vessel, 81 x 340 mm.). The product was shown by g.l.c. (G.D.B. silicone elastomer, 78°C), to be a mixture of the 2,5-diazadewarbenzene (121) (44%), the pyrazine (104) (11%) and starting material (80). An infrared spectrum of the mixture, showed a band at 1661 $cm.^{-1}$, confirming that the diazadewarbenzene was (121).

(xxi) Irradiation of 3,6-Difluoro-4,5-dichloropyridazine (68) at ca. 300 nm. in Silica.

The procedure in 7.2.(vii) was adopted. 3,6-Difluoro-4,5-dichloropyridazine (68) (0·5 g., 2·78 m.moles), was irradiated at ca. 300 nm. (85 watts), whilst under transference (0·5 mm.) in the apparatus shown in Fig. 2. (silica vessel, 81 x 340 mm.). The resulting solid was re-irradiated, using the same apparatus

and source, whilst under transference (0·5 mm.). The product (0·3 g.) in ether, was shown by g.l.c. (G.D.B., di-isodecylphthalate, 150°C) to contain a small amount (4%) of a component more volatile than starting material (70) and also a more involatile component (ca. 7%). Decomposition was also observed upon the sides of the silica vessel.

CHAPTER 8

Experimental for Chapter 4

8.1. Half-Life Studies.

A. Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (118).

The 2,5-diazadewarbenzene (118) (ca. 100 mg.) was sealed in a Pyrex tube (8 x 70 mm.) and heated at 105°C for exactly one hour. Chromatographic analysis (G.D.B., silicone elastomer, 78°C) showed the product to consist of (118) (60%) and perfluoro-2-isopropylpyrazine (102) (40%). Hence the half life of (118) at 105°C is calculated to be 81 mins.

$$\ln \frac{[A]_o}{[A]_{t_{\frac{1}{2}}}} = kt_{\frac{1}{2}} \qquad \ln \frac{[A]_o}{[A]_t} = kt$$

$$1{\cdot}303 \log \frac{100}{60} = k.60$$

$$k = 2{\cdot}303 \times 0{\cdot}2219/60$$

$$t_{\frac{1}{2}} = \frac{\log 2 \times 2{\cdot}303 \times 60}{k}$$

$$t_{\frac{1}{2}} \quad 81 \text{ mins.}$$

B. Perfluoro-1,3-bis-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (117).

The 2,5-diazadewarbenzene (117) was heated in an n.m.r. tube at 60°C for 20 minutes. Chromatographic analysis (G.D.B., di-isodecylphthalate, 78°C) showed the product to consist of (117) (78%) and perfluoro-2,6-bis-isopropyl-pyrazine (101) (22%). The half life of (117) is calculated to be ca. 56 mins. at 60°C.

C. Perfluoro-1,4-bis-ethyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (119).

The 2,5-diazadewarbenzene (119) was heated in an n.m.r. tube at 100°C for 45 minutes. Chromatographic analysis (G.D.B., silicone elastomer, 60°C)

showed no rearomatisation had occurred. A sample of (119) was stored at room temperature for 22 months and found by g.l.c. (as above) to be unchanged.

D. Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (122).

The 1,2-diazadewarbenzene (122) (0·4 g., 0·885 m.moles), was sealed in a dry silica n.m.r. tube and heated at 82·4°C for 142 mins., at 96·0°C for 104 mins., and at 102·3°C for 53 mins., in the probe of a Varian A56/60 n.m.r. spectrometer. The conversion of (122) to perfluoro-2,5-bis-isopropylpyrazine (84) was monitored, by recording or electronic integrations of the resonances due to the trifluoromethyl groups of (122) and (84), at intervals of between 2 and 10 minutes. The relative peak areas of the recorded spectra were obtained using a DuPont 310 Curve Resolver. The half-life of (122) at the temperatures above were obtained by graphical means.

$t_{\frac{1}{2}}$ at 82·4°C = 15 hrs.

$t_{\frac{1}{2}}$ at 96·0°C = 5·4 hrs.

$t_{\frac{1}{2}}$ at 102·3°C = 2·4 hrs.

E. Perfluoro-4,5-bis-sec.-butyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (125).

The 1,2-diazadewarbenzene (125) together with a small amount of hexafluorobenzene was sealed in a silica n.m.r. tube. The tube was then heated at 108·5°C for 44 minutes. The expected conversion of (125) to perfluoro-2,5-bis-sec.-butylpyrazine (107) was monitored by electronic integration of the imine fluorines of (125) and C_6F_6. No rearomatisation occurred in the time for which (125) was heated.

Heating (125) at 180°C for two hours, caused quantitative conversion to pyrazine (107), which was identified by comparison of its ^{19}F n.m.r. spectrum with that of an authentic sample.[49]

8.2. Reactions of Diazadewarbenzenes.

A. Base Hydrolysis of Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (118).

The 2,5-diazadewarbenzene (118) (0·5 g., 1·66 m.moles), was added to an aqueous solution of sodium hydroxide (2M, 10 mls.), with stirring. The solution turned dark brown immediately. After stirring for two days, the reaction mixture was acidified, extracted with ether, and the ether extract dried ($MgSO_4$). Evaporation of ether gave a black involatile tar.

B. Acid Hydrolysis of Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (118).

The 2,5-diazadewarbenzene (118) (0·35 g., 1·16 m.moles), was added to dilute sulphuric acid (conc. H_2SO_4, 2 mls., water 10 mls.) with vigorous stirring. A yellow waxy material was formed on the surface of the solution. Ether extraction gave insufficient material for further investigation.

C. Reaction of Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (118) with Dilute Aqueous Ammonia.

The 2,5-diazadewarbenzene (118) (0·5 g., 1·66 m.moles), was added to a dilute solution of aqueous ammonia (2 drops 880 ammonia in water, 15 mls.), with stirring. The solution went a yellowish-brown colour immediately and white fumes were liberated. After stirring for one hour the solution was acidified, extracted with ether, the ether extract dried ($MgSO_4$) and ether evaporated. Crystallisation from acetone gave a white semi-solid (ca. 50 mg.). An infrared spectrum of the latter showed very broad absorptions centred at 3335, 3035 $cm.^{-1}$ and a series of overlapping absorptions between 1853 and 445 $cm.^{-1}$.

D. Reaction of Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (122) with Isopropoxide Ion.

The 1,2-diazadewarbenzene (122) (0·95 g., 2·11 m.moles), was condensed into a dry Pyrex tube containing 4·37 m.moles of isopropanolic potassium isopropoxide (0·84M, 5·2 mls.) and dry isopropanol (10 mls.). The tube was

sealed under vacuum (0·001 mm.) and then allowed to reach -20°C at which temperature the mixture became miscible. The contents were maintained at -20°C for ca. one hour and then allowed to obtain room temperature (ca. two hours). The contents of the tube were then added to wet ether, washed with water, the ether layer dried (Na_2SO_4) and ether and isopropanol evaporated off. The product (0·90 g.), was shown by g.l.c. (G.D.B., silicone elastomer, 150°C) to be a mixture of two components, the one with shorter retention being major (55%) and the one with longer retention time being minor (35%).

The reaction above was carried out on exactly twice the scale and after work-up, gave a product (1·85 g.) shown by g.l.c. (as above) to be exactly the same as above.

Distillation under reduced pressure gave 3-fluoro-4,5-bis-heptafluoroisopropyl-6-isopropoxy-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (133) (0·72 g.), stillpot 80°C/1 mm. [Found: C, 31·5; H, 1·2; F, 57·4; M, 492; $C_{13}F_{12}N_2H_7O$ requires C, 31·71; H, 1·42; F, 57·93; M, 492], i.r. spectrum No. 17, ^{19}C n.m.r. spectrum No. 19, u.v. spectrum No. 17.

Heating (133) at 150°C for 40 mins gave 2,5-bis-isopropyl-3-isopropoxy-6-fluoropyrazine (135) [Found: C, 32·0; N, 5·7; M, 1·3; M, 492; $C_{13}F_{12}N_2H_7O$ requires C, 31·71; H, 1·42; F, 57·93; M, 492], i.r. spectrum No. 18, ^{19}F n.m.r. spectrum 20, u.v. spectrum No. 18.

The residual material in the stillpot was shown by g.l.c. (as above) to consist mainly of the minor component (ca. 90%). An infrared spectrum of the latter impure compound showed some medium strength absorptions at 2930, 1816, 1750, 1700, 1660 and 1628 $cm.^{-1}$ and mass spectrometry showed a parent ion at 532. This data indicates a di-isopropoxy derivative of (122). An infrared spectrum of the latter mixture after heating at 150°C for one hour showed the

disappearance of the band at 1816, 1750, 1700 and 1660 cm.$^{-1}$ G.l.c. (as above) showed no change upon heating, indicating that at the temperature of study rearomatisation was occurring anyway. Purification by preparative scale g.l.c. (F.21, silicone elastomer, 200°C) gave 2-(3'-isopropoxy-5'-heptafluoro-isopropyl-6'-fluoropyrazin-2'-yl)-2-isopropoxyhexafluoropropene (136) (0·13 g.) [Found: C, 36·3; N, 4·9; H, 2·6; M, 532; $C_{16}F_{14}N_2H_{14}O_2$ requires C, 36·09; N, 5·26; H, 2·63], i.r. spectrum No. 19, ^{19}F n.m.r. spectrum No. 21, u.v. spectrum No. 19.

E. Reaction of Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (122) with Methoxide Ion.

The 1,2-diazadewarbenzene (122) (0·6 g., 1·33 m.moles), was condensed into a dry Pyrex tube, containing 2·86 m.moles of methanolic sodium methoxide (2·6M, 1·1 mls.) and dry methanol (10 mls.). The tube was sealed under vacuo and allowed to warm up to -20°C when the mixture became homogeneous. The tube was then maintained at -20°C, with shaking at ca. 5 min. intervals, for ca. 30 mins., and then slowly allowed to attain room temperature (ca. 14 hrs.). The contents of the tube were added to ether (100 mls.), the mixture washed with water, dried ($MgSO_4$), and ether evaporated. Vacuum distillation at 40°C/ 0·001 mm. gave a colourless mobile liquid (0·23 g.) shown by g.l.c. (G.D.B. di-isodecylphthalate, 150°C) to be one major component (ca. 85%). Mass spectrometry showed a weak parent ion at 476 and a strong one at 464, whilst infrared spectrometry showed weak absorptions at 2985 and 2879 cm.$^{-1}$ (C-H), and strong ones at 1718 and 1650 cm.$^{-1}$ This data indicates the product to be a mixture of methoxy substituted derivatives of (122). ^{19}F n.m.r. spectrometry, however, showed two apparently unrelated resonances at 73·2 and 75·7 p.p.m. (CF_3 region), and one at 169 p.p.m. which integrated to the ratio 5:12:1 respectively. The contents of the tube suddenly erupted with the evolution of

much heat. The material left in the tube was a dark yellow waxy solid which was not investigated further.

F. Reaction of Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (118) with Methoxide Ion.

The 2,5-diazadewarbenzene (118) (0·75 g., 2·49 m.moles) was condensed into a dry Pyrex tube containing 2·6 m.moles of methanolic sodium methoxide (2·6M, 1·0 ml.) and dry methanol (15 mls.), and the tube sealed under vacuo. The contents of the tube were then allowed to warm up to -18°C at which temperature the mixture became homogeneous. The tube was then maintained at -18°C, and shaken at intervals, for ca. 10 hrs., after which time it was allowed to attain room temperature. G.l.c. (G.D.B., di-isodecylphthalate, 130°C) of the reaction mixture showed only one major component (ca. 95%). The methanol was then evaporated, the residue dissolved in ether, washed with water and dried ($MgSO_4$). Evaporation of ether gave a yellow oil (0·3 g.) which was shown by g.l.c. (as above) to be one component (ca. 98%). An infrared spectrum of the yellow oil showed weak absorptions at 3076 and 2858 $cm.^{-1}$ (C-H) and a strong absorption at 1643 $cm.^{-1}$ indicating a methoxy derivative of (118). Mass spectrometry showed a weak peak at 326 and a strong one at 314 indicating the major component to be a mono-methoxy derivative of (118). The ^{19}F n.m.r. spectra of the product was complex, showing 10 resonances. The spectrum changed with time and after ca. one hour the contents of the tube erupted and gave out much heat.

G. Reaction of Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (122) with Pentafluorophenyl-lithium.

In a dry 250 ml. three necked flask containing a magnetic stirrer, and filtered with a pressure equilising dropping funnel, was placed pentafluorobenzene (0·75 g., 4·47 m.moles) and a dry ether-hexane (in ratio 4:1, 75 mls.) mixture. The apparatus was flushed with dry nitrogen gas, the mixture cooled

to -78°C and 5·63 m.moles of n.butyl-lithium in hexane (2·5M, 2·25 mls. in 15 mls. of hexane) added dropwise over a period of 10 mins., with stirring. Stirring at -78°C was continued for 2 hrs. to allow formation of C_6F_5Li. The 1,2-diazadewarbenzene (122) (1·0 g., 2·21 m.moles) in dry hexane (15 mls.) was added dropwise over a period of 20 mins., the reaction stirred for a further 2 hrs. at -78°C and then allowed to warm up to room temperature slowly. The mixture was then acidified with dil. hydrochloric acid (30 mls.), the organic layer separated, the aqueous layer ether extracted and the combined organic fractions dried ($MgSO_4$). Evaporation of ether gave a yellow slurry, which was distilled under high vacuum (60°C/0·001 mm.) to give a yellow oil (1·1 g.). G.l.c. (G.D.B., di-isodecylphthalate, 125°C showed the product to contain a major component (ca. 85%) and a minor one (ca. 15%). Its infrared spectra showed strong absorptions at 1662, 1522 and 1506 $cm.^{-1}$ (spectrum No. 20), and mass spectrometry showed a parent ion at 600. ^{19}F n.m.r. showed resonances at 58·0, 60·4, 74·8, 77·2, 138·9, 149·4, 162·9, 176·6 and 180·8 p.p.m. in the ratio 1:1:6:6:1:2:0·86:1 respectively. It is apparent from the simplicity of the spectrum and the integration that fluorines in similar environments have overlapped e.g. all the trifluoromethyl fluorines are at 74·8 and 77·8 p.p.m. The ^{19}F n.m.r. data is consistent with the spectrum expected for a mixture of the diazadewarbenzenes (138) (43%), (139) (43%) and (140) (14%) (see p. 109 for structures). The resonance at 176·6 p.p.m. is assigned to the tertiary fluorines of the 5-heptafluoroisopropyl groups of (138) and (139), because it only integrates to 0·86 fluorines. This is consistent with the fact that 14% of the product, i.e. (140) contains no fluorine in this position.

Heating the above mixture at 220°C for 18 hrs. in a sealed Pyrex tube, followed by sublimation (60°C/0·001 mm.) gave a pure product by g.l.c. (G.D.B. as above) identified as perfluoro-2,5-bis-isopropyl-3-phenylpyrazine

(141) (0·33 g.) [Analysis results inconsistent; M, 600]; i.r. spectrum No. 21, ^{19}F n.m.r. spectrum No. 22.

H. Reaction of Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (118) with Pentafluorophenyl-lithium.

In a dry 250 ml. three-necked flask containing a magnetic stirrer, fitted with a pressure equalising dropping funnel was placed pentafluorobenzene (1·2 g., 6·8 m.moles) and a dry ether-hexane mixture (ratio 4:1, 40 mls.) against a counter current of dry nitrogen. The mixture was cooled to -75°C and 6·8 m.moles of n-butyl-lithium in hexane (2·0M, 3·4 mls. in 10 mls. of dry hexane) were added dropwise over a period of 10 mins., with stirring. The mixture was then stirred at -78°C for two hours to allow formation of C_6F_5Li, the 2,5-diazadewarbenzene (118) (1·0 g., 3·32 m.moles) in dry hexane (15 mls.) was then added dropwise over a period of 20 mins. The reaction mixture turned dark brown upon addition of the 2,5-diazadewarbenzene (118). The reaction temperature was maintained at -78°C for a further two hours after which time it was allowed to slowly attain room temperature. The mixture was then acidified with dil. hydrochloric acid (30 mls.), the organic layer separated, the aqueous layer ether extracted and the combined organic fractions dried ($MgSO_4$). Evaporation of ether gave a viscous brown liquid, which upon crystallisation from methanol yielded a white crystalline compound perfluoro-2-isopropyl-3,6-bis-phenylpyrazine (142) (0·30 g.) [Found: C, 38·0; N, 4·5; M, 598, $C_{19}F_{18}N_2$ requires C, 38·10; N, 4·51; M, 598], i.r. spectrum 22, ^{19}F n.m.r. spectrum 23.

I. Reaction of Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (122) with Hexafluoropropene.

The standard experimental procedure for polyfluoroalkylation described earlier (see p.125) was adopted. Caesium fluoride (1·0 g., 6·58 m.moles), tetrahydrothiophen dioxide (15 mls.), hexafluoropropene (7·0 g., 46·6 m.moles),

and the diazadewarbenzene (122) (2·0 g., 2·43 m.moles) were stirred for one day at room temperature, after which time a partial vacuum had formed in the apparatus. The vacuum transferred product (6·7 g.) was shown by g.l.c. (G.D.B. silicone elastomer, 60°C) to consist of the dimers and trimers of hexafluoropropene, plus at least ten other minor components. This was confirmed by infrared spectrometry.

A similar experiment was carried out with perfluoro-1,3-bis-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (117), however, the only identifiable products were dimers and trimers of hexafluoropropene, and perfluorotetrakis-isopropylpyrazine which was identified by comparison of its infrared spectrum with that of an authentic sample (see below).

J. Reaction of Perfluoro-2,6-bis-isopropylpyrazine (101) with Hexafluoropropene.

Experimental procedure as in previous experiment. Caesium fluoride (3·0 g., 19·75 m.moles), 2,5,8,11,14-pentaoxapentadecane (20 mls.), hexafluoropropene (10·0 g., 66·7 m.moles) and perfluoro-2,6-bis-isopropylpyrazine (101) (1·5 g., 9·87 m.moles) were stirred at room temperature for one hour after which time a partial vacuum had formed in the system. All volatile products were isolated by vacuum transference with heating. The dimers and trimers of hexafluoropropene were distilled from the rest of the product under vacuo at room temperature. This left a slurry containing 2,5,8,11,14-pentaoxapentadecane, which was removed by washing with water. The product was dried in a desiccator (P_2O_5) to give a white powder, insoluble in all common solvents, identified as perfluoro-tetrakis-isopropylpyrazine (2·25 g., 90%) m.pt. 105°C [Found: C, 27·8; N, 3·8; F, 70·3; M, 752, $C_{16}F_{28}N_2$ requires C, 27·56; N, 3·73; F, 70·71; M, 752] i.r. spectrum No. 22, ^{19}F n.m.r. spectrum No. 23.

K. Reaction of Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (122) with Anhydrous Hydrogen Fluoride.

To the 1,2-diazadewarbenzene (122) (0·6 g., 1·33 m.moles), in a dry teflon

bottle, anhydrous hydrogen fluoride (ca. 3 mls.) was added and the mixture stirred whilst a slow stream of dry nitrogen was blown into the bottle. When the gas coming out of the bottle was neutral to damp litmus paper water (10 mls.) and then dil. sodium hydroxide solution (2M, 5 mls.) were added. Filtration gave a white solid (ca. 0·05 g.). The infrared spectrum of the solid showed very broad absorptions centred at 3493, 1138, 752 and 476 $cm.^{-1}$ Ether extraction of the aqueous filtrate yielded no other product.

L. Reaction of Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (122) with Bromine

To the 1,2-diazadewarbenzene (122) (0·2 g., 0·44 m.moles) in a dry Pyrex tube was added bromine (0·7 g., 43·8 m.moles). The tube was stoppered, shaken, and left for one hour at room temperature. G.l.c. (G.D.B., silicone elastomer, 78°C) of the resulting mixture indicated no reaction had occurred. Carbon tetrachloride (1 ml.) was added to the reaction mixture and a bright light shone on the mixture for one hour. G.l.c. (as above) again showed no reaction had taken place.

M. Attempted Hydrogenation of Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]-hexa-2,5-diene (118).

Palladium (10%) on charcoal (catalyst grade, 200 mg.), in a 200 ml. florentine flask was thoroughly degassed by evacuation and then let down to atmospheric pressure with pure dry nitrogen. Dry, oxygen free methanol (10 mls.) and the 2,5-diazadewarbenzene (118) (1·0 g., 3·31 m.moles) were rapidly introduced into the flask (heat evolved at this stage), the mixture frozen (liquid air), and the flask evacuated. The flask was then shaken and dry hydrogen admitted. Absorption of hydrogen was slow. A total of 215 mls. of hydrogen (8·95 m.moles) were absorbed at 20°C, over a period of 48 hrs. Evaporation of methanol followed by sublimation (60°C/0·001 mm.) gave a very small amount of a sticky material which was shown by g.l.c. (G.D.B., silicone

elastomer, 250°C) to contain ca. six components. Infrared spectrometry showed N-N and C-H absorptions and also a strong absorption at 1725 $cm.^{-1}$

N. Attempted Diels-Alder Reaction Between Perfluoro-1-isopropyl-2,5-diaza-bicyclo[2.2.0]hexa-2,5-diene (118) and Furan.

Into a dry 25 ml. flask full of dry nitrogen gas and a magnetic stirrer, were injected the 2,5-diazadewarbenzene (118) (0·5 g., 1·66 m.moles) and furan (0·11 g., 1·66 m.moles). The contents of the flask were shielded from light and stirred. G.l.c.,(di-isodecylphthalate, 50°C) of the reaction mixture showed no reaction had occurred after 15, 30 mins. and after one day. The mixture set into a black solid after a week. Sublimation 80°C/0·001 mm. yielded no product.

Similar experiments were carried out between the 2,5-diazadewarbenzene (118) and freshly distilled cyclopentadiene and 2,5-dimethylfuran, and between the 2,5-diazadewarbenzene (117) and furan, however no products were isolated from these experiments either.

O. Attempted Preparation of a Platinum (O) Complex with Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (122).

Into a dry three-necked 100 ml. flask under dry nitrogen gas was added, $Pt^{(O)}(PPh_3)_3$ (0·3 g., 0·3 m.moles) [prepared as described in ref. 89], the 1,2-diazadewarbenzene (122) (0·15 g., 0·32 m.moles) and oxygen free benzene (15 mls.) against a counter current of nitrogen, and the mixture stirred at R.T. A red solution was formed, which was concentrated, after stirring for two days by the vacuum transference of most of the benzene. The vacuum transferred benzene was shown by g.l.c. (G.D.B., di-isodecylphthalate 78°C) to contain the 1,2-diazadewarbenzene (122). ^{19}F n.m.r. spectrometry of the concentrate showed no resonances.

P. Attempted Preparation of a Platinum (O) Complex with Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (118).

Into a dry, three-necked 100 ml. flask under dry pure nitrogen gas, was added, $Pt^{(O)}(PPh_3)_3$ (0·40 g., 0·4 m.moles) [prepared as described in ref. 87],

the 2,5-diazadewarbenzene (0·124 g., 0·41 m.moles) and dry, oxygen free benzene (30 mls.) against a couter current of nitrogen. The resulting red solution was stirred for 14 hrs. at R.T. About half of the benzene was evaporated and this was found to contain no (118). Some precipitation occurred as a result of the evaporation of the benzene, so dry, oxygen free hexane was added dropwise until precipitation stopped. Filtration gave a beige powder 0·25 g. the infrared spectrum of which showed similarity to $Pt^{(0)}(PPh_3)_3$. The beige powder was found to contain 22·6% fluorine. Recrystallisation from a benzene-hexane mixture (O_2 free) gave a reddish brown material (33 mg.). Found: F, 22·4; Pt, 16·5; $Pt(PPh_3)_2$ (118) requires F, 18·63; Pt, 19·1; $Pt(PPh_3)_2$ (118) requires F, 33·8; Pt, 18·38.

CHAPTER 9

Experimental for Chapter 5

9.1. Irradiation of Perfluoro-3,5-bis-isopropylpyridazine (72) at 253·7 nm. Whilst Under Transference (0·005 mm.)

Perfluoro-3,5-bis-isopropylpyridazine (72) (5·0 g., 11·08 m.moles), was introduced into the apparatus shown in Fig. 2 (see page 76) (silica vessel, 81 x 340 mm.), frozen (liquid air) and the system evacuated to 0·005 mm. The system was then irradiated at 253·7 nm. (120 watts) whilst the pyridazine (72) transferred into a cold trap (liquid air). The transferred product was shown by g.l.c. (G.D.B., di-iso-decylphthalate, 60°C) to contain perfluoro-1,3-bis-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (117) (6%), perfluoro-2,6-bis-isopropylpyrazine (101) 8%, three unknown components (5·5%) and starting material.

9.2. Irradiation of Perfluoro-3,5-bis-isopropylpyridazine (72) at 253·7 nm. Whilst Under Transference (10 mm.)

Procedure and apparatus as in Section 9.1. Perfluoro-3,5-bis-isopropylpyridazine (72) (1·6 g., 3·54 m.moles) was irradiated at 253·7 nm. (120 watts) whilst under transference (10 mm.). The transferred product was shown by g.l.c. (G.D.B., di-iso-decylphthalate, 78°C) to be a mixture of the 2,5-diazadewarbenzene (117) (7·6%), pyrazine (101) (43·7%) and three unknowns (23%).

9.3. Irradiation of Perfluoro-3,5-bis-isopropylpyridazine (72) at 253·7 nm. Whilst Under Transference (8 mm.).

Procedure and apparatus as in Section 9.1. Perfluoro-3,5-bis-isopropylpyridazine (72) (1·75 g., 3·87 m.moles) was irradiated at 253·7 nm. (120 watts) whilst under transference (8 mm., 2 days). The transferred

material (1·1 g., 63%) was shown by g.l.c. (G.D.B., di-isodecylphthalate, 78°C) to consist of seven major components A (6%), B (5%), C (13%), D (13%), E (11%), F (35%) and G (17%). This reaction was repeated, using the same apparatus, ca. the same pressure, and between 1·30 and 1·80 gms. of (72) a total of 16 times to give 16·31 g. of product having essentially the same composition as above. Vacuum distillation at 5 mm. gave component A in a pure state, perfluoro-isobutyryl nitrile (0·35 g.) i.r. spectrum No. 24, ^{19}F n.m.r. spectrum No. 25. Mass spectrum shows no parent ion as expected but shows a peak at ($P-F^+$) 176 (4%). The rest of the material was fractionally distilled in a 'Fischer Spaltrohr-Column FB-MMS200' microdistillation apparatus at reduced pressure (5 mm.) to give partial separation of the mixture. Final separation was achieved by preparative scale g.l.c. (F.21, di-isodecylphthalate, 70°C) to give: B, identified as perfluoro-1,3-bis-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (117) (0·3 g.) by comparison of its i.r., ^{19}F n.m.r. and mass spectra with those of an authentic sample; (C) (0·15 g.) [Found: F, 66·1; M, 514; $C_{12}F_{18}N_2$ requires F, 66·54; M, 514] i.r. spectrum No. 25, ^{19}F n.m.r. spectrum No. 26, u.v. spectrum No. 20; (D) (0·6 g.) [Found: C, 28·0; N, 5·2; F, 66·3; M, 514, $C_{12}F_{18}N_2$ requires C, 28·01; N, 5·45; F, 66·54; M, 514] i.r. spectrum No. 26, ^{19}F n.m.r. spectrum No. 27, u.v. spectrum No. 21; (E) (0·4 g.), [Found: F, 66·3; M, 514; $C_{12}F_{18}N_2$ requires F, 66·54; M, 514] i.r. spectrum No. 27, ^{19}F n.m.r. spectrum No. 28, u.v. spectrum No. 22; F and G are identified as perfluoro-2,6-bis-isopropyl-pyrazine (101) and perfluoro-3,5-bis-isopropylpyridazine (72) by comparison of their i.r. spectra with those of authentic samples.

Prior to the isolation of (C) an impure sample was obtained which was shown by ^{19}F n.m.r. (neat) spectrometry to contain ca. 33% of an impurity I which showed resonances at 38·6, 76·79, 170·8 and 182·0 p.p.m. in the ratio 1:6:1:1.

APPENDIX 1

^{19}F and ^{1}H n.m.r. Spectra

APPENDIX 1

^{19}F and ^{1}H n.m.r. spectra

Index to n.m.r. spectra.

25. Perfluorotetra-kis-isopropylpyrazine.

26. Perfluoroisobutyryl nitrile.

27. Perfluoro-bis-isopropyldiazabicyclo[4.2.0]octa-2,4,7-triene (C).

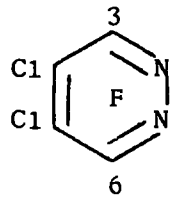
28. Perfluoro-bis-isopropyldiazacyclo-octatetraene (D).

29. Perfluoro-bis-isopropyldiazacyclo-octatetraene (E).

The following abbreviations have been used in presenting data concerning the fine structure of absorptions:- S = singlet; D = doublet; T = triplet; Q = quartet; H = heptet; M = multiplet.

1. 3,6-Difluoro-4,5-dichloropyridazine (68).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
82·3	S		3,6

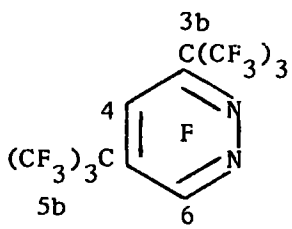


(68)

Recorded in acetone solution with an internal $CFCl_3$ reference.

2. Perfluoro-3,5-bis-t.-butylpyridazine.

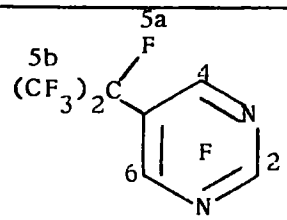
Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
62·9	M	19	3b,5b,6
87·8	M	1	4



Recorded in acetone solution with an external $CFCl_3$ reference.

3. Perfluoro-5-isopropylpyrimidine (88).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
39·6	Broad S	1	2
47·6	D($J_{4,5a}$ = 37·0) of H($J_{4,5b}$ = 12·1 Hz)	2	4,6
77·1	D($J_{5a,5b}$ = 6·0) of T($J_{5b,4}$ = 12·1 Hz)	6	5b
182·3	T($J_{5a,4}$ = 37·0) of H($J_{5a,5b}$ = 6·0)	1	5a

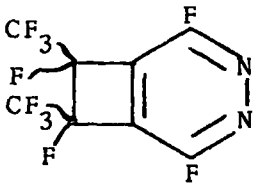


(88)

Recorded in acetone solution with an external $CFCl_3$ reference.

4. Perfluorodiazabenzocyclobutene (92).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
77·8	Complex M	3	CF_3
81·0	S	1	ArF
162·5	Complex M	1	T.F.



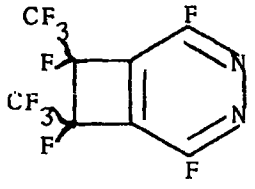
(92)

Recorded in acetone solution with external $CFCl_3$ reference.

Stereochemistry unknown.

5. Perfluorodiazabenzocyclobutene (96)

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
77·1	Complex M	3	CF_3
83·0	S	1	ArF
161·8	Complex M	1	T.F.



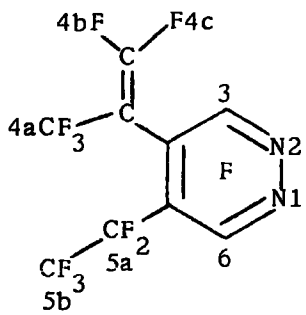
(96)

Recorded in acetone solution with external $CFCl_3$ reference.

Stereochemical isomer of (92).

6. Perfluoro-4-(2'-propenyl)-5-ethylpyridazine (97).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
60·5	Complex M. D($J_{4a,3}$ = 6·6) of D($J_{4a,4c}$ = 8·8) of D($J_{4a,4b}$ = 13·8) of T($J_{4a,5a}$ = 2·4) of Q($J_{4a,5b}$ = 2·0)	3	4a
69·3	Broad M	1	4c
69·6	Q($J_{4b,4a}$ = 14 Hz) of M	1	4b
79·5	D($J_{6,3}$ = 32·5) of T($J_{6,5a}$ = 23·5) of Q($J_{6,5b}$ = 14·6)	1	6
82·1	D($J_{3,6}$ = 32·5) of M	1	3
85·4	D($J_{5b,6}$ = 14·6) of D($J_{5b,4c}$ = 8·8) of Q($J_{5b,4a}$ = 2·0)	3	5b
113·7	D($J_{5a,6}$ = 23·5) of M(including $J_{5a,4a}$ = 2·4)	2	5a

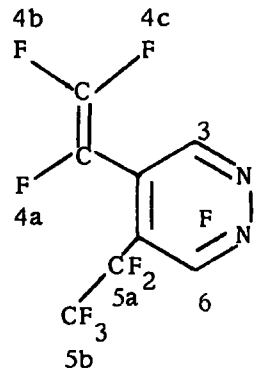


(97)

Recorded in acetone solution with an external $CFCl_3$ reference.

7. Perfluoro-4-vinyl-5-ethylpyridazine (94).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
80·5	Broad M	1	6
83·0	$D(J_{3,6} = 33)$ of $D(J_{3,4c} = 19)$	1	3
85·2	M	3	5b
95·5	$D(J_{4b,4a} = 34)$ of $D(J_{4b,4c} = 56)$	1	4b
109·7	$D(J_{4c,3} = 18)$ of $D(J_{4c,4b} = 56)$ of $D(J_{4c,4a} = 117)$	1	4c
115·2	$D(J_{5a,4a} = 18)$ of $D(J_{5a,6} = 22)$	2	5a
170·3	$D(J_{4a,4c} = 117)$ of M	1	4a

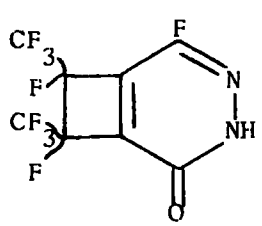


(94)

Recorded in acetone solution with an external $CFCl_3$ reference.

8. Perfluoropyridazinone (99)

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
75·8	M	3	CF_3
76·5	M	3	CF_3
99·8	S	1	vinylic F
165·4	Broad M	2	T.F.

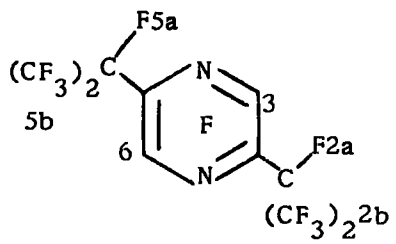


(99)

Recorded in acetone solution with external $CFCl_3$ reference.

9. Perfluoro-2,5-bis-isopropylpyrazine (84).

Shift (p.p.m.)	Fine Structure Coupling constants in Hz	Relative intensity	Assignment
73·6	Broad $D(J_{3,2a} = 46·2)$	1	3,6
76·7	M	6	2b,5b
184·8	$D(J_{2a,3} = 46·2)$ of $H(J_{2a,2b} = 6·7)$	1	2a,5a

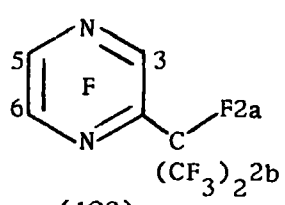


(84)

Recorded in acetone solution with internal $CFCl_3$ reference.

10. Perfluoro-2-isopropylpyrazine (102).

Shift (p.p.m.)	Fine Structure Coupling constants in Hz	Relative intensity	Assignment
76·7	$D(J_{2b,2a} = 6·5)$ of M	6	2b
78·0	$D(J_{3,2b} = 46·0)$ of $D(J_{3,6} = 43·5)$ of $D(J_{3,5} = 5)$	1	3
83·7	$D(J_{5,3} = 5)$ of $D(J_{5,6} = 19·25)$	1	5
93·4	$D(J_{6,5} = 19·25)$ of $D(J_{6,3} = 43·5)$	1	6
186·7	$D(J_{2a,3} = 46·0)$ of $H(J_{2a,2b} = 6·5)$ of M	1	2a

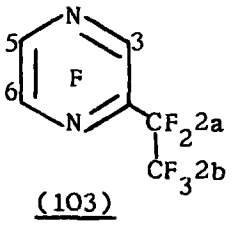


(102)

Recorded neat with external $CFCl_3$ reference.

11. Perfluoro-2-ethylpyrazine (103).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
79·3	Broad M	1	3
82·5	Broad D($J_{5,6}$ = 19)	1	5
86·0	D($J_{2b,3}$ = 5)	3	2b
93·5	D($J_{6,5}$ = 19) of D($J_{6,3}$ = 42)	1	6
118·4	D($J_{2a,3}$ = 21)	2	2a

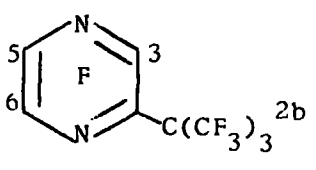


(103)

Recorded neat with external $CFCl_3$ reference.

12. Perfluoro-2-t.-butylpyrazine (105).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
64·0	D($J_{2b,3}$ = 18·1)	9	2b
69·7	D($J_{3,5}$ = 3·25) of D($J_{3,6}$ = 44·5) of M	1	3
84·7	D($J_{5,3}$ = 3·25) of D($J_{5,6}$ = 19·25)	1	5
93·0	D($J_{6,5}$ = 19·25) of D($J_{6,3}$ = 44·5)	1	6

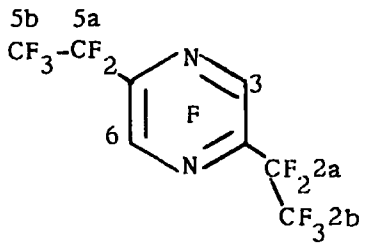


(105)

Recorded neat with an external $CFCl_3$ reference.

13. Perfluoro-2,5-bis-ethylpyrazine (106).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
78·3	Broad S	1	3,6
85·4	S	3	2b,5b
119·0	M	2	2a,5a

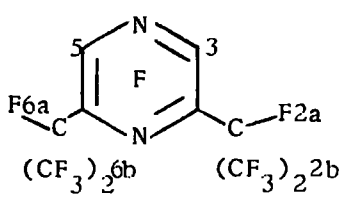


(106)

Recorded neat with an external $CFCl_3$ reference.

14. Perfluoro-2,6-bis-isopropylpyrazine (101).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
66·2	Broad $D(J_{3,2a} = 46)$	1	3,5
77·0	$D(J_{2b,2a} = 6·0)$ of $D(J_{2b,3} = 4·5)$	6	2b,6b
187·0	$D(J_{2a,3} = 46)$ of $H(J_{2a,2b} = 6·0)$	1	2a,6a

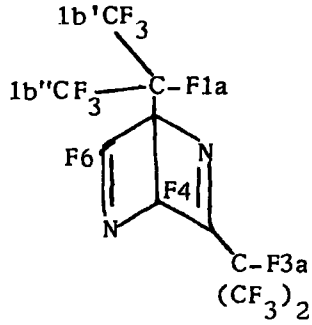


(101)

Recorded neat with external $CFCl_3$ reference.

15. Perfluoro-1,3-bis-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (117).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
42·2	S	1	6
75·0	M	3	1b'
76·2	M	9	1b", 3b
162·1	M	1	4
187·1	M	1	1a
192·0	M	1	3a

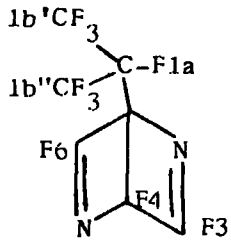


(117)

Recorded neat with external $CFCl_3$ reference. The resonance due to one of the trifluoromethyl groups (1b) lies under the resonance due to the two trifluoromethyl groups (3b).

16. Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (118).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
42·4	Broad S	1	6
45·0	M	1	3
75·9	M	3	1b'
77·1	M	3	1b"
166·6	Broad M	1	4
187·7	Broad M	1	1a



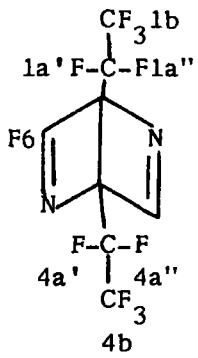
(118)

Recorded neat with an external $CFCl_3$ reference.

Trifluoromethyl groups 1b' and 1b" non-equivalent because the heptafluoroisopropyl group is attached to an asymmetric centre.

17. Perfluoro-1,4-bis-ethyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (119).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
38·6	S	1	3,6
84·9	S	3	1b,4b
121·2	D($J_{1a',1a''}$ = 286)	1	1a',4a'
125·8	D($J_{4a',4a''}$ = 286)	1	1a'',4a''

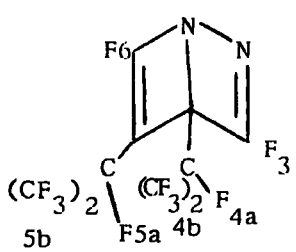


(119)

Recorded neat with external $CFCl_3$ reference.

18. Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (122).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
61·1	Broad S	1	3
63·0	Broad S	1	6
76·4	Broad M	6	4b
80·1	Broad M	6	5b
181·1	Broad S	1	4a
186·8	Broad S	1	5a

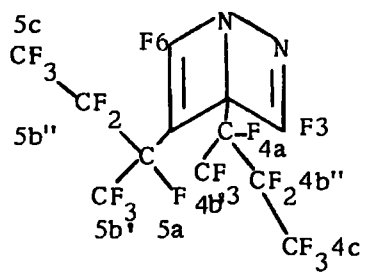


(122)

Recorded neat with external $CFCl_3$ reference.

19. Perfluoro-4,5-bis-sec.-butyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (125).

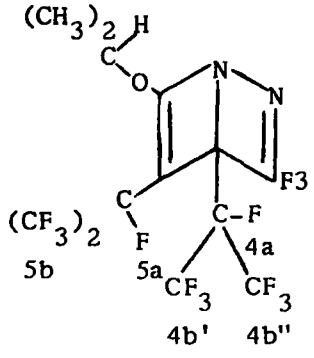
Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
62·2	Unsymmetrical D(J = 154)	1	3
62·6	S	1	6
74·5	Broad D(J = 50)	3	4b'
77·8	S	3	5b'
82·8	M	6	4c,5c
117·7	Complex asymmetric M	2	4b''
123·4	Complex asymmetric M	2	5b''
176·4	Broad S	1	4a
186·6	Broad S	1	5a



(125)

20. 3-Fluoro-4,5-bis-heptafluoroisopropyl-6-isopropoxy-1,2-diazabicyclo-[2.2.0]hexa-2,5-diene (133).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
61·5	S	1	3
75·2	Broad S	6	5b
77·9	M	3	4b'
79·2	M	3	4b"
178·4	unsymmetrical M	1	4a
180·0	Broad S	1	5a



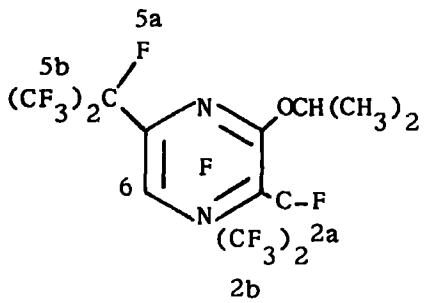
(133)

Recorded neat with an external $CFCl_3$ reference.

^1H n.m.r. spectrum showed two resonances 1·32 and 5·15 p.p.m. downfield from T.M.S. in the ratio 6:1. These are assigned to the methyl and tertiary hydrogens of the 6-isopropoxy group.

21. 2,5-Bis-heptafluoroisopropyl-3-isopropoxyfluoropyrazine (135).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
76·3	Broad D(J = 4)	6	2b or 5b
77·2	Broad S	6	2b or 5b
88·2	D($J_{6,5a}$ = 48)	1	6
184·6	Broad M	1	2a
187·8	Broad D($J_{5a,6}$ = 48)	1	5a



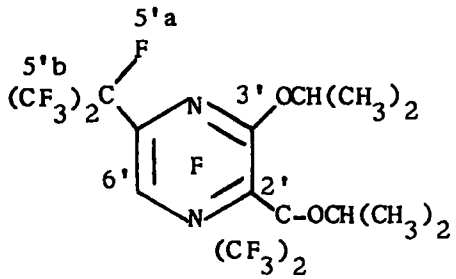
(135)

Recorded neat with external $CFCl_3$ reference.

^1H n.m.r. spectrum showed two resonances 0·83 and 4·70 p.p.m. downfield from T.M.S. in the ratio 6 to 1. These have been assigned to the methyl and tertiary hydrogens of the 3-isopropoxy group.

22. 2-(3'-Isopropoxy-5-heptafluoroisopropyl-6'-fluoropyrazin-2'-yl)-2-isopropoxyhexafluoropropane (136).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
69·8	S	6	
76·1	Broad S	6	5'b
88·0	$D(J_{6',5'a} = 46)$	1	6'
186·6	$D(J_{5'a,b'} = 46)$	1	5'a



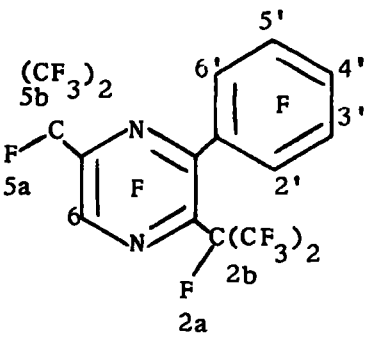
(136)

Recorded in $CDCl_3$ solution with an external $CFCl_3$ reference.

^1H n.m.r. spectrum showed three resonances, 1·2, 4·0 and 5·1 p.p.m. downfield from T.M.S. which integrated in the ratio 12·1·1. These have been assigned to the methyl and tertiary hydrogens of the two isopropoxy groups.

23. Perfluoro-2,5-bis-isopropyl-3-phenylpyrazine (141).

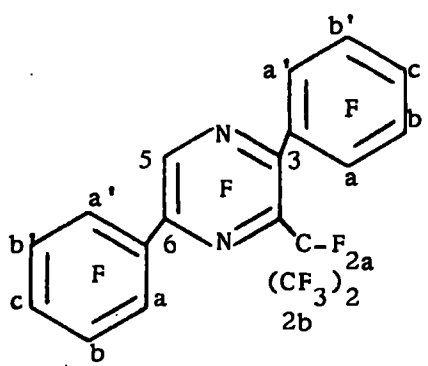
Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
71·0	$D(J_{6,5a} = 42)$ of M	1	6
75·9	Complex M	12	2b,5b
143·7	Broad complex M	2	2',6'
153·7	$T(J_{4',3'} = 20)$	1	4'
164·8	M	2	3',5'
185·3	M	1	2a
186·4	$D(J_{5a,6} = 42)$ of $H(J_{5a,5b} = 7)$	1	5a



(141)

24. Perfluoro-2-isopropyl-3,6-bis-phenylpyrazine (142).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
70·9	T($J_{5,6a}$ = 18·0 Hz)	1	5
75·5	M	6	2b
140·8	M	2	3a,3a' 6a,6a'
141·5	M	2	
151·6	T(J = 4·0) of T(J_{cb} = 19·5)	1	3c,6c
153·2	T(J_{cb} = 19·5) of M	1	
163·9	Complex M	4	3b,3b',6b, 6b'
184·1	H($J_{2a,2b}$ = 6·0)	1	2a

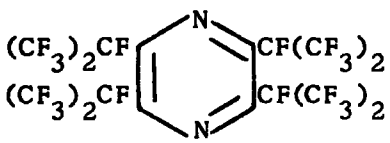


(142)

Recorded in acetone solution with an external $CFCl_3$ reference.

25. Perfluorotetra-kis-isopropylpyrazine.

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
74·6	Broad M	6	CF_3
181·4	M	1	Tertiary F



Recorded in perfluoromethylcyclohexane solution with internal $CFCl_3$ reference.

26. Perfluoroisobutyryl nitrile.

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
79·7	$D(J_{b,a} = 10·0)$	6	CF_3
178·5	$H(J_{a,b} = 10·0)$	1	Tertiary F

$(CF_3)_2C\text{-}C\equiv N$
b Fa

Recorded neat at -26°C with an external $CFCl_3$ reference.

27. Perfluoro-bis-isopropyldiazabicyclo[4.2.0]octa-2,4,7-triene (C).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
47·4	Broad S	1	
67·6	Broad S	1	
75·5	Broad S	3	$\underline{CF_3}(CF_3)CF$
76·9	Broad S	3	$\underline{CF_3}(CF_3)CF$
79·2	Broad S	6	$(\underline{CF_3})_2CF$
122·7	Broad M	1	
161·8	Broad S	1	
179·8	Broad S	1	$(CF_3)_2\underline{C}F$
181·1	Broad D (J = 25)	1	$(CF_3)_2\underline{C}F$

Recorded neat with an external $CFCl_3$ reference.

28. Perfluoro-bis-isopropyldiazacyclo-octatetraene (D).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
14·7	Broad S	1	
29·4	Broad S	1	
57·4	Broad M	2	
78·7	Broad M	12	$2(\underline{CF_3})_2CF$
179·0	M	2	$2(CF_3)_2\underline{C}F$

Recorded neat with an external $CFCl_3$ reference.

29. Perfluoro-bis-isopropyldiazacyclo-octatetraene (E).

Shift (p.p.m.)	Fine structure Coupling constants in Hz	Relative intensity	Assignment
13·3	Broad M	1	
57·2	M	1	
78·8	unsymmetrical M	6	$(\underline{CF}_3)_2CF$
179·7	Broad S	1	$(CF_3)_2C\underline{F}$

Recorded neat with an external $CFCl_3$ reference.

APPENDIX 2

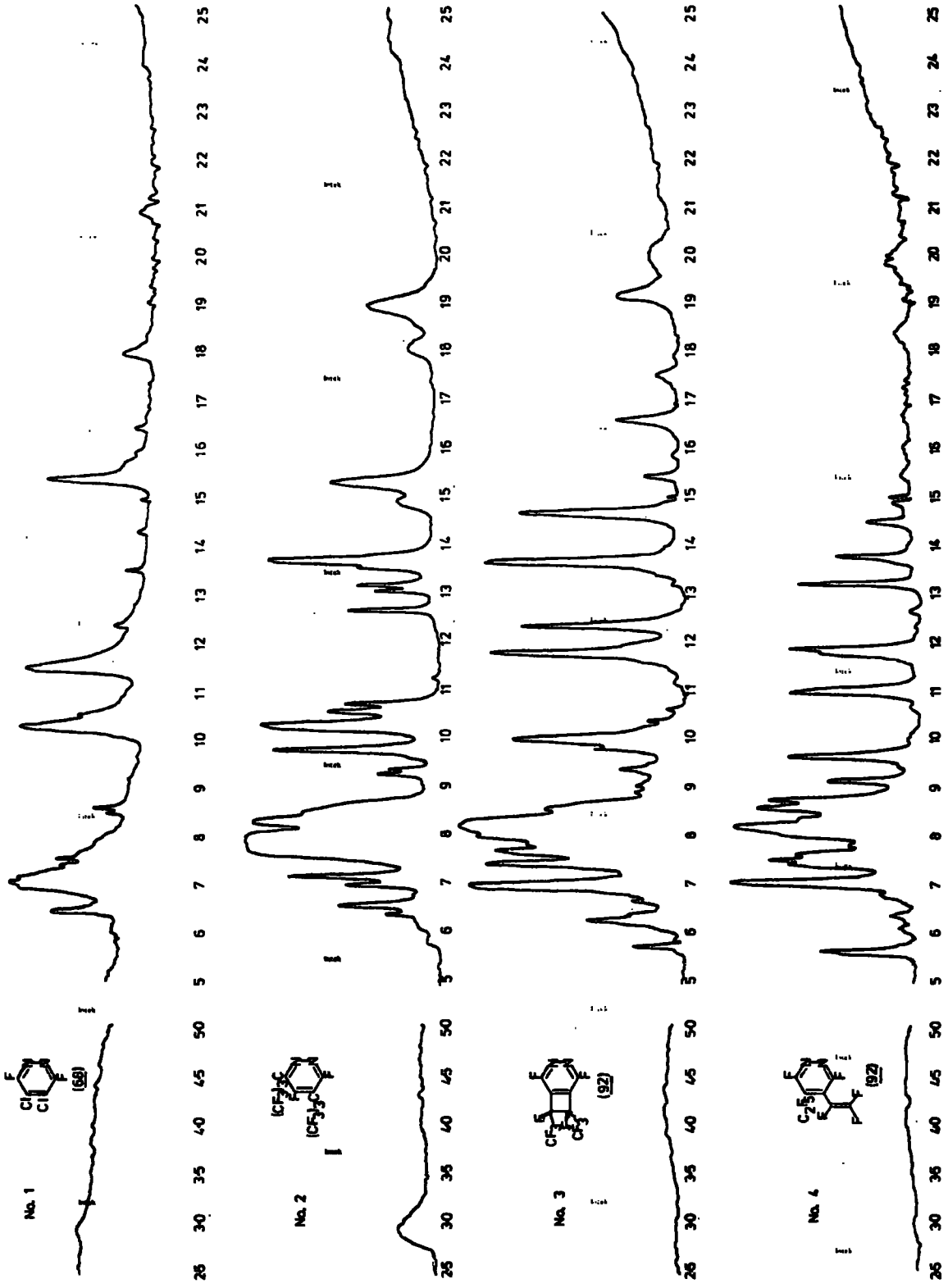
Infrared Spectra

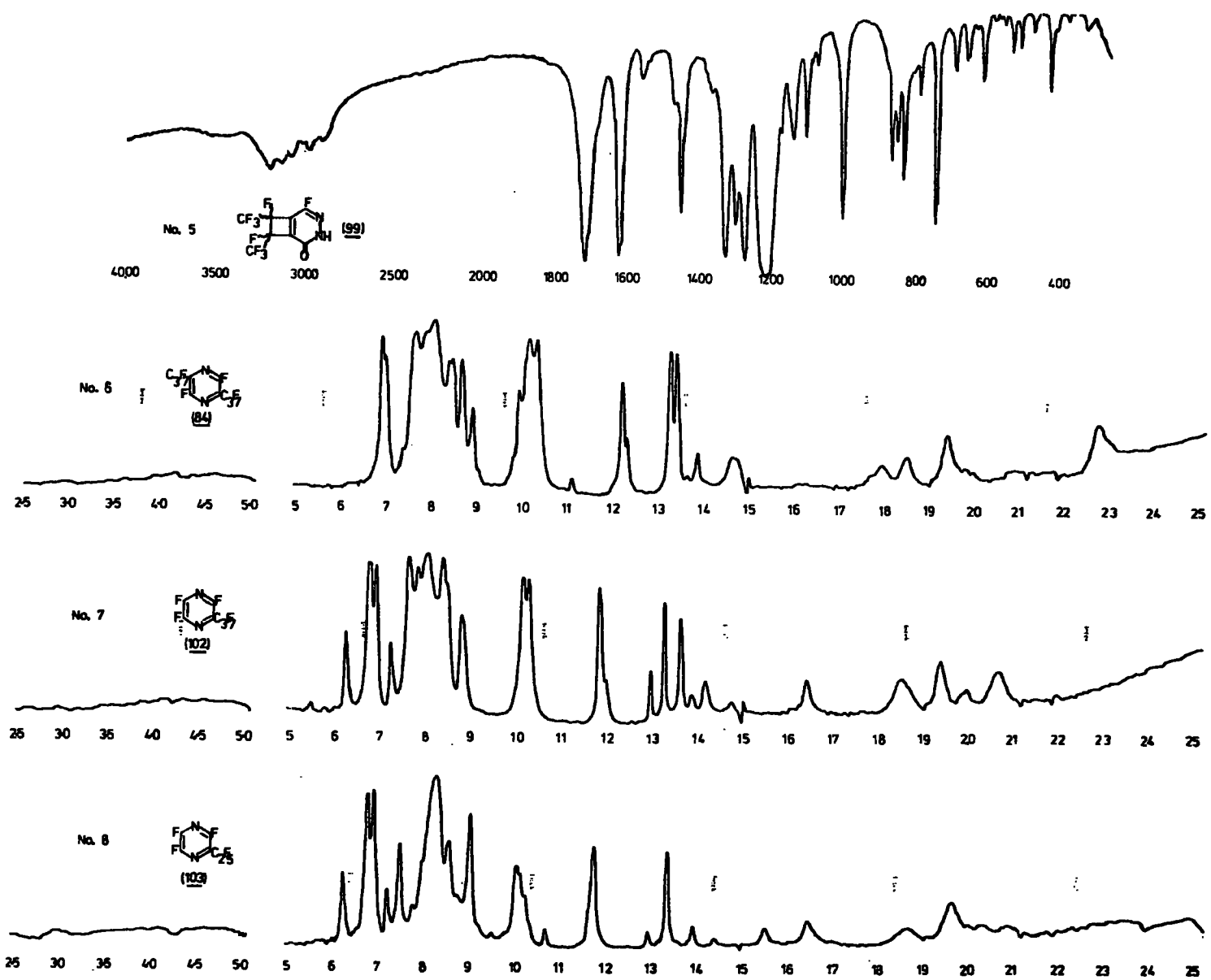
Gaseous samples were admitted into an evacuated cylindrical cell with potassium bromide end windows.

Solid samples were recorded as KBr discs and liquid or low melting solid samples as contact films between KBr plates.

Spectrum No.	Compound	
1	3,6-Difluoro-4,5-dichloropyridazine (68)	(s)
2	Perfluoro-3,5-bis-t.-butylpyridazine	(1)
3	Perfluorodiazabenzocyclobutene (92)	(1)
4	Perfluoro-4-vinyl-5-ethylpyridazine (94)	(1)
5	Perfluoropyridazinone (99)	(s)
6	Perfluoro-2,5-bis-isopropylpyrazine (84)	(1)
7	Perfluoro-2-isopropylpyrazine (102)	(1)
8	Perfluoro-2-ethylpyrazine (103)	(1)
9	Perfluoro-2-t.-butylpyrazine (105)	(1)
10	Perfluoro-2,5-bis-ethylpyrazine (106)	(1)
11	Perfluoro-2,6-bis-isopropylpyrazine (101)	(1)
12	Perfluoro-1,3-bis-isopropyl-2,5-diazabicyclo[2.2.0]-hexa-2,5-diene (117)	(1)
13	Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]-hexa-2,5-diene (118)	(1)
14	Perfluoro-1,4-bis-ethyl-2,5-diazabicyclo[2.2.0]-hexa-2,5-diene (119)	(1)
15	Perfluoro-4,5-bis-isopropyl-1,2-diazabicyclo[2.2.0]-hexa-2,5-diene (122)	(1)
16	Perfluoro-4,5-bis-sec.-butyl-1,2-diazabicyclo-[2.2.0]hexa-2,5-diene (125)	(1)
17	3-Fluoro-4,5-bis-heptafluoroisopropyl-6-isopropoxy-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (133)	(1)
18	2,5-Bis-heptafluoroisopropyl-3-isopropoxy-fluoropyrazine (135)	(1)

Spectrum No.	Compound	
19	2-(3'-Isopropoxy-5'-heptafluoroisopropyl-6'-fluoropyrazin-2'-yl)-2-isopropoxyhexafluoropropane (136)	(l)
20	A mixture of mono-pentafluorophenyl substituted derivatives of perfluoro-4,5-bis-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene	(l)
21	Perfluoro-2,5-bis-isopropyl-3-phenylpyrazine (141)	(s)
22	Perfluoro-2-isopropyl-3,6-bis-phenylpyrazine (142)	(s)
23	Perfluorotetrakisisopropylpyrazine	(s)
24	Perfluoroisobutyryl nitrile	(g)
25	Perfluoro-bis-isopropyldiazabicyclo[4.2.0]-octa-2,4,7-triene (C)	(l)
26	Perfluoro-bis-isopropyldiazacyclo-octa-tetraene (D)	(l)
27	Perfluoro-bis-isopropyldiazacyclo-octatetraene (E)	(l)


No. 1
(68)
No. 2
No. 3
(92)
No. 4
(92)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(99)
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No. 6
(84)
25 30 35 40 45 50
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
No. 7
(102)
25 30 35 40 45 50
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
No. 8
(103)
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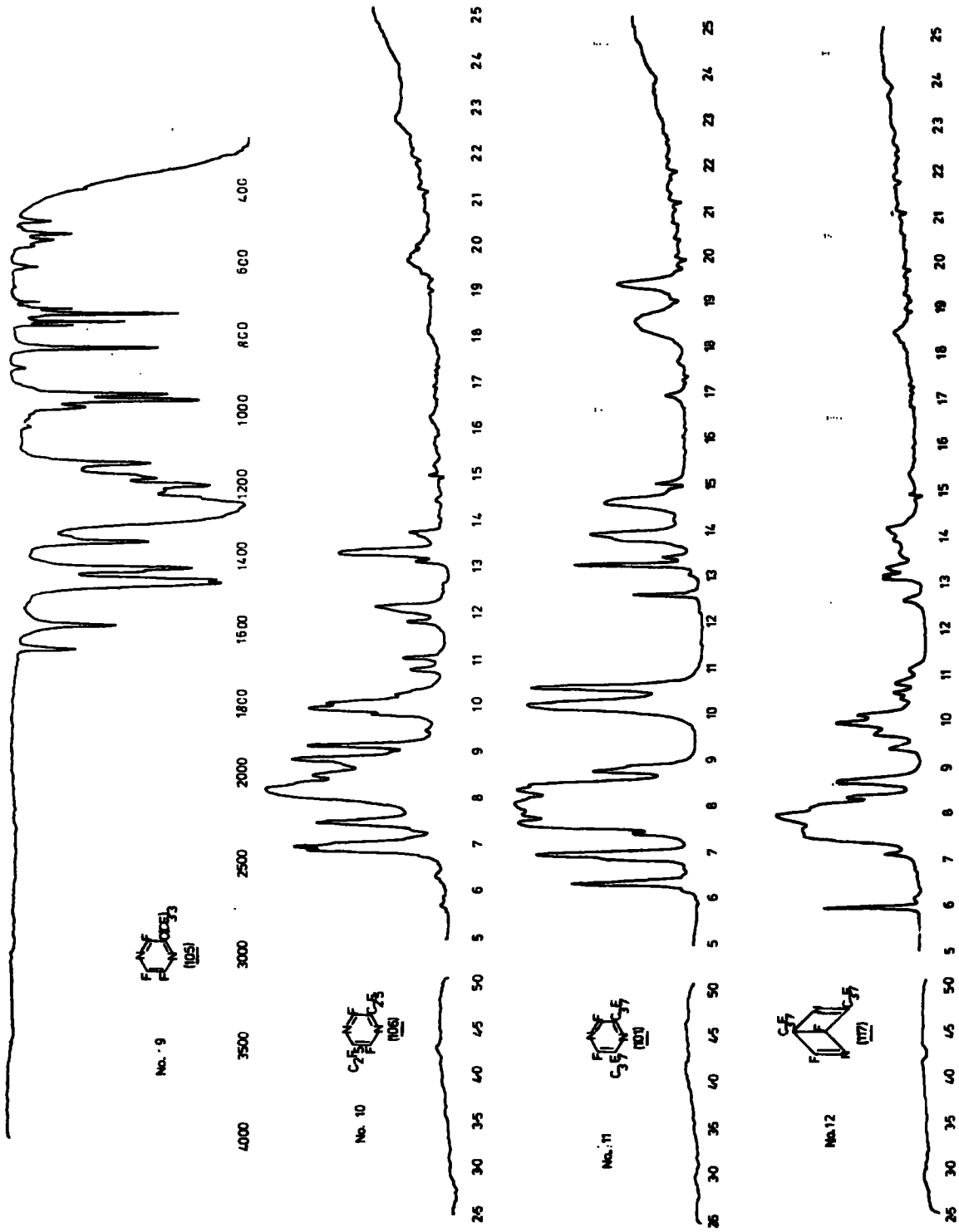
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(105)
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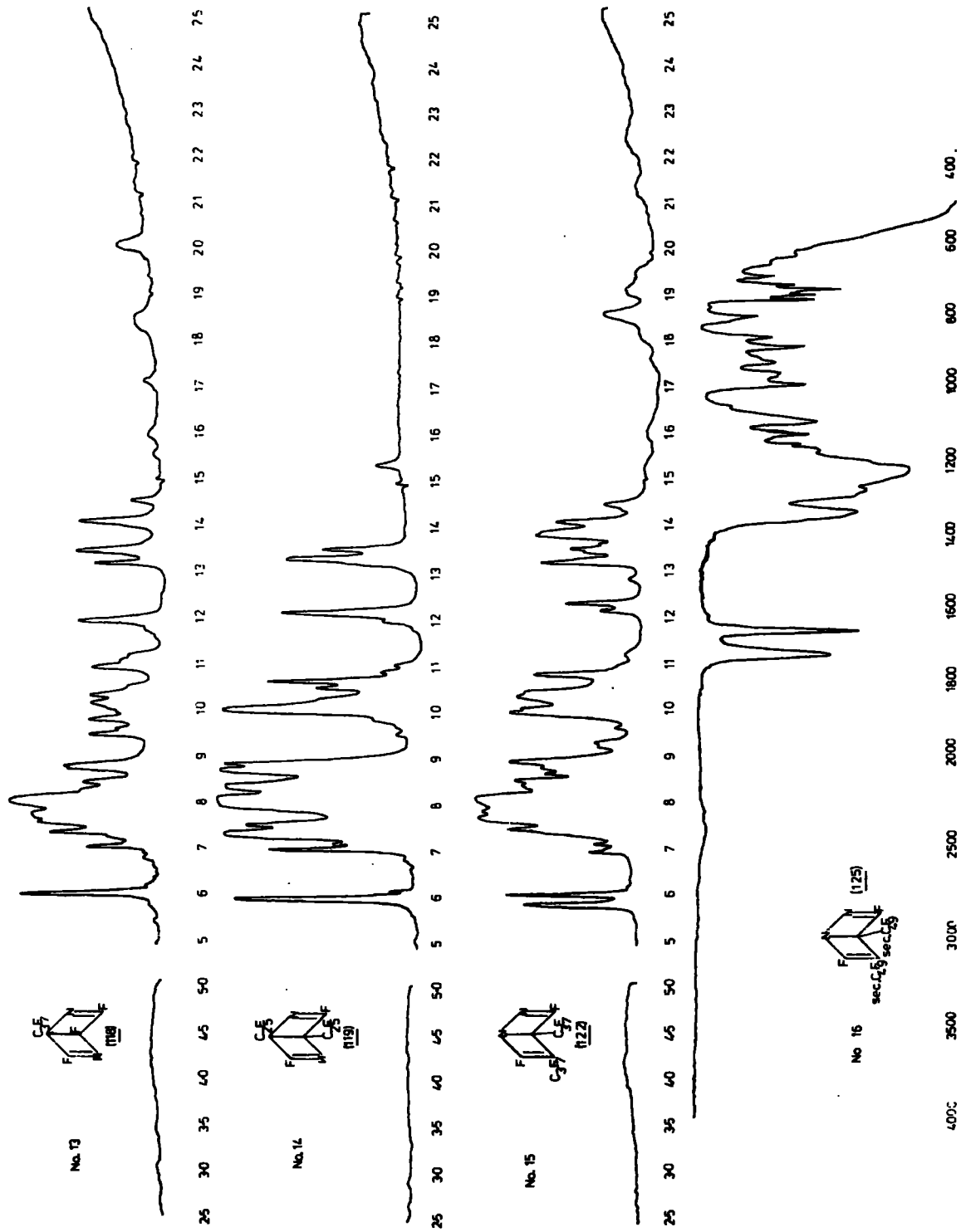
(101)
No.12
(117)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No. 14
(119)
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(122)
No. 16
(125)
sec.C6
sec.C5
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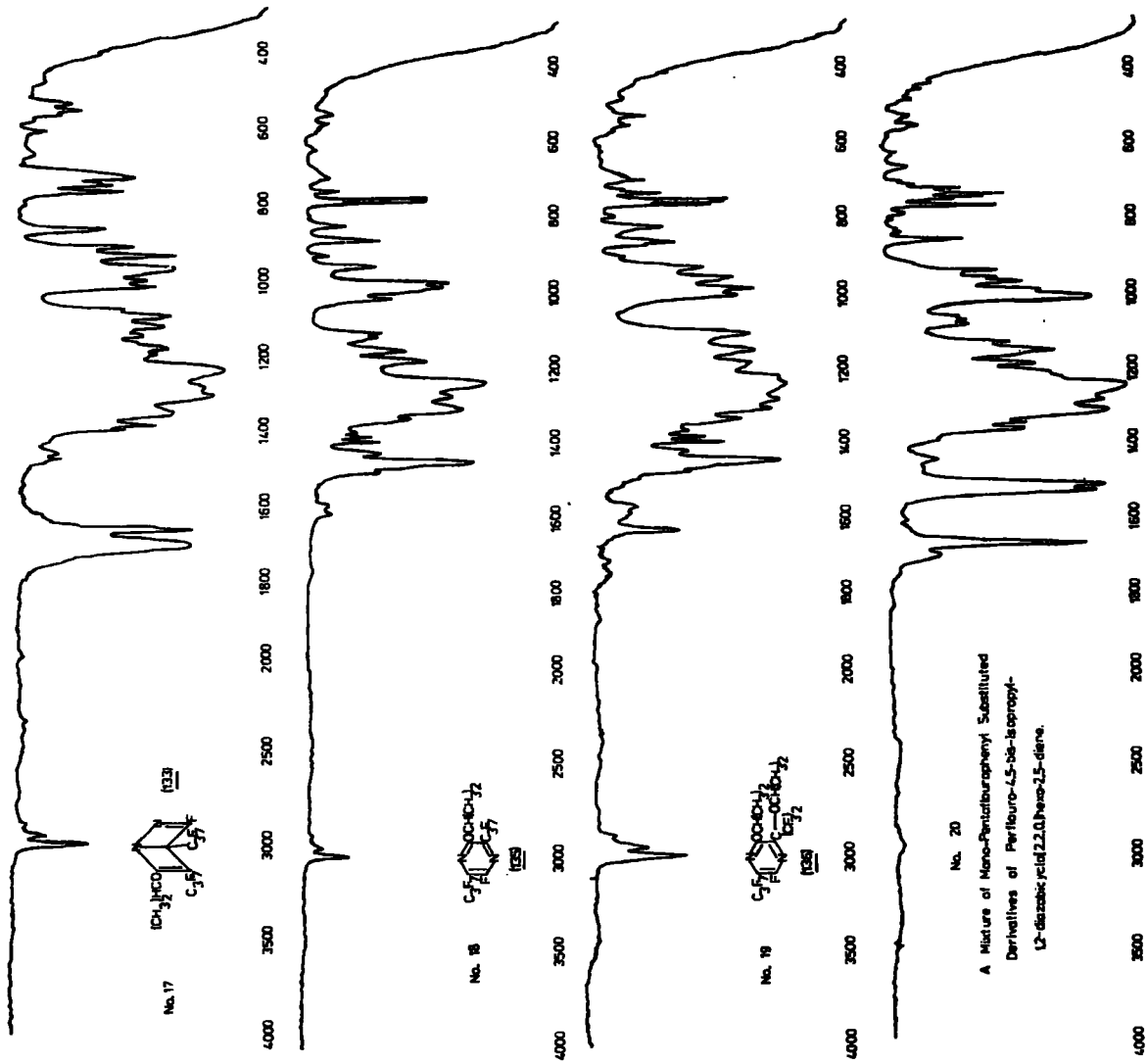
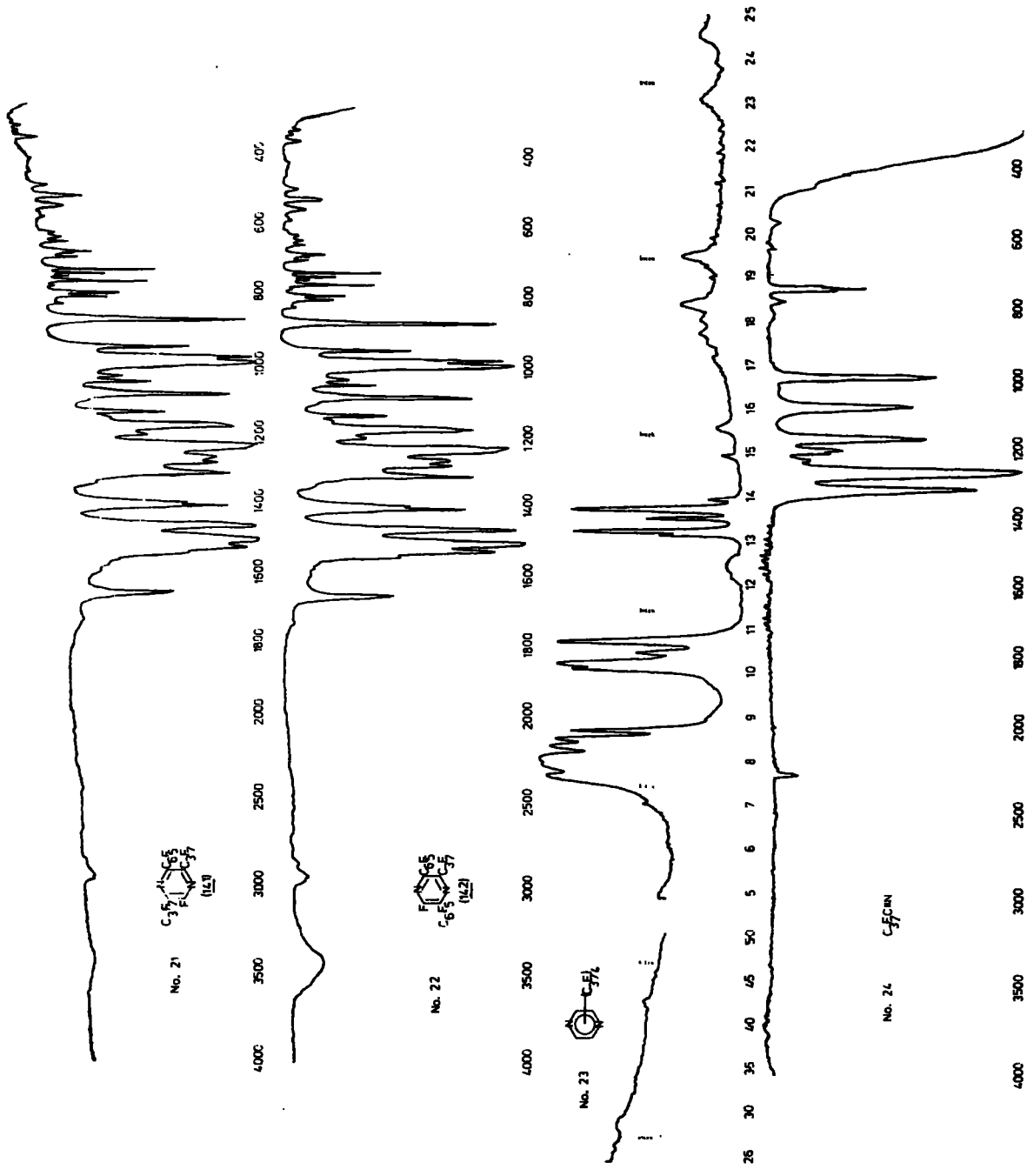

No. 17
No. 18
No. 19
No. 20
A Mixture of Mono-Pentafluorophenyl Substituted
Derivatives of Perfluoro-4,5-bis-isopropyl-
1,2-diazabicyclo[2.2.0]hexa-2,5-diene.
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400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(1.4)
No. 22
(1.42)
No. 23
No. 24
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3500
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2500
2000
1800
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1000
800
600
400
25
30
35
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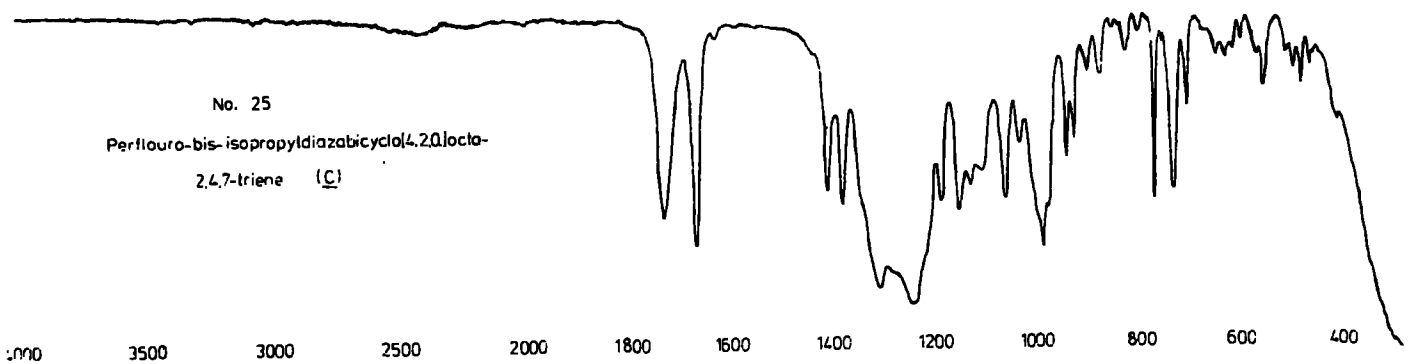
No. 25
Perflouro-bis-isopropyldiazabicyclo[4.2.0]octa-
2,4,7-triene (C)
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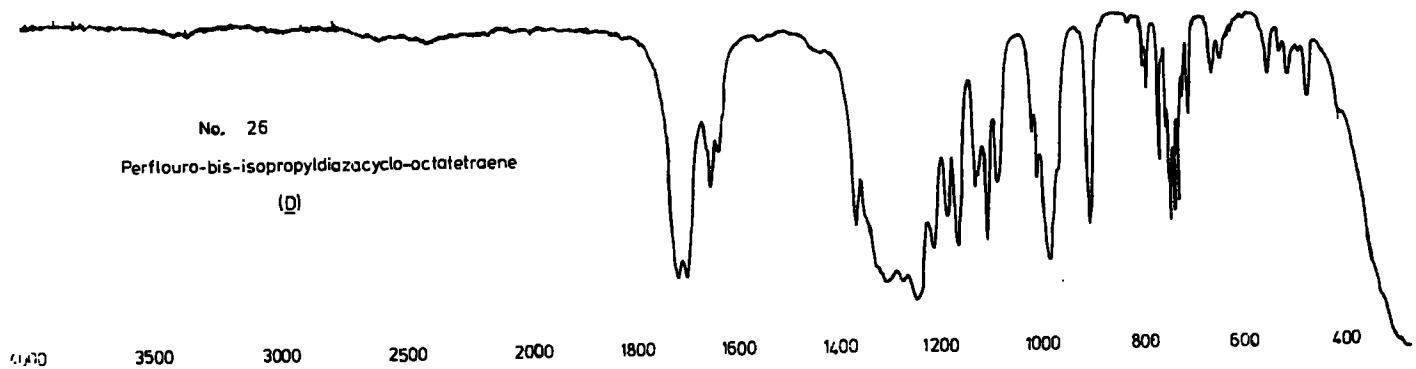
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Perflouro-bis-isopropyldiazacyclo-octatetraene
(D)
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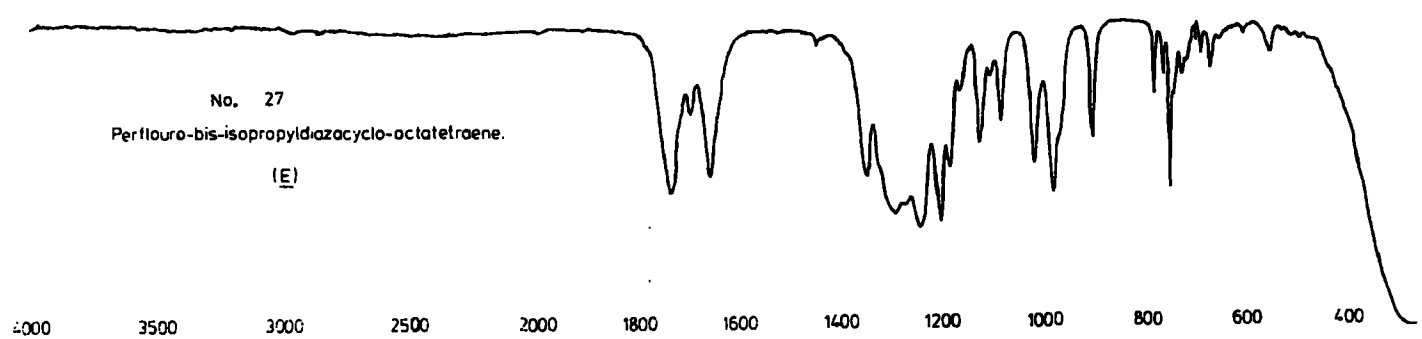
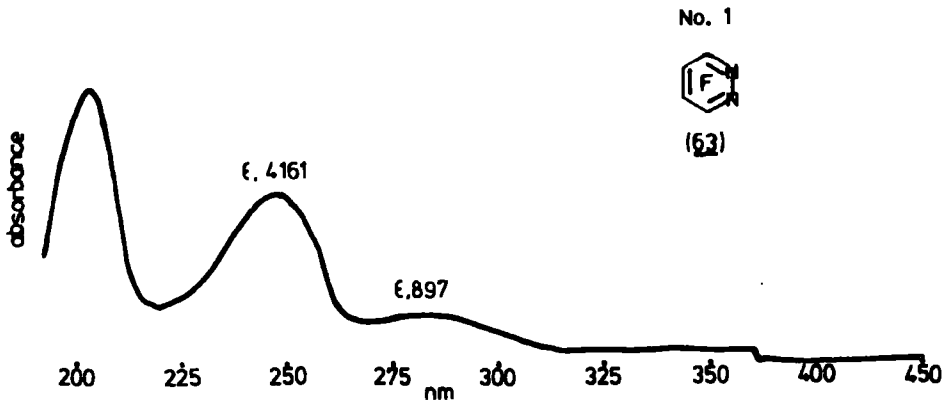
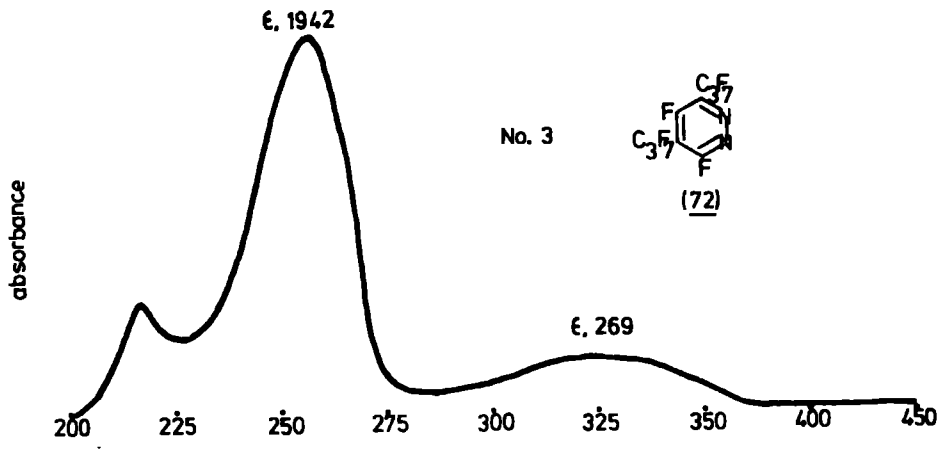

No. 27
Perflouro-bis-isopropyldiazacyclo-octatetraene.
(E)
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400

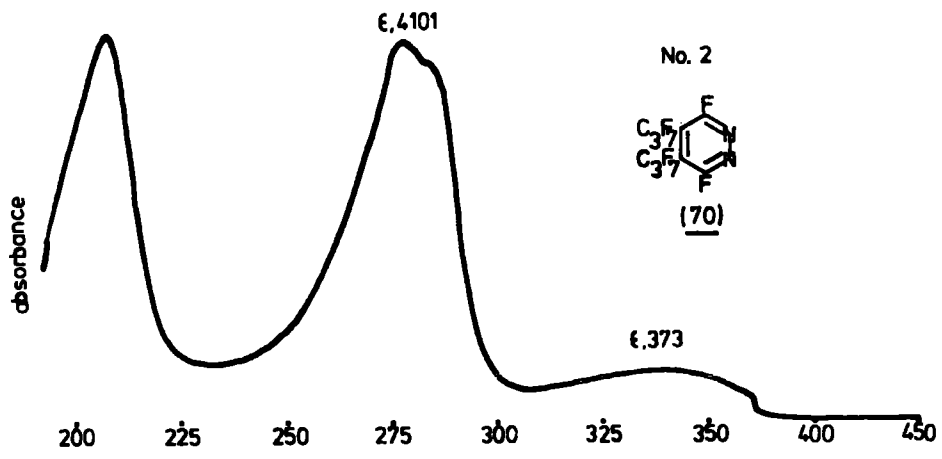
APPENDIX 3

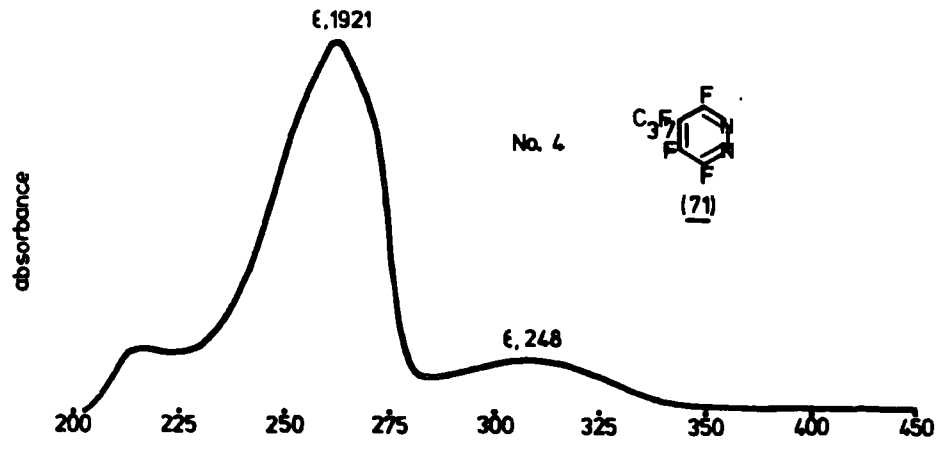
Ultraviolet Spectra

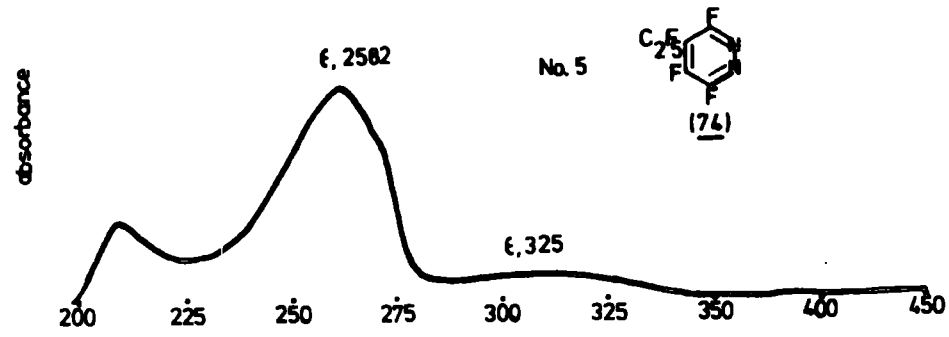
Spectrum No.	Compound
1	Tetrafluoropyridazine (63) (cyclohexane)
2	Perfluoro-4,5-bis-isopropylpyridazine (70) (cyclohexane)
3	Perfluoro-3,5-bis-isopropylpyridazine (72) (cyclohexane)
4	Perfluoro-4-isopropylpyridazine (71) (cyclohexane)
5	Perfluoro-4-ethylpyridazine (74) (cyclohexane)[46]
6	Perfluoro-4-t.-butylpyridazine (82) (acetonitrile)
7	Perfluoro-4,5-bis-ethylpyridazine (75) (cyclohexane)[46]
8	Perfluoro-4,5-bis-sec.-butylpyridazine (79) (cyclohexane)[50]
9	3,6-Difluoro-4,5-dichloropyridazine (68) (cyclohexane)
10	Tetrachloropyridazine (110) (cyclohexane)
11	Perfluoro-3,4,6-tris-isopropylpyridazine (73) (cyclohexane)
12	Perfluoro-1,3-bis-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (117) (cyclohexane)
13	Perfluoro-1-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (118) (cyclohexane)
14	Perfluoro-1,4-diethyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (119) (cyclohexane)
15	Perfluoro-1,4-bis-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (122) (cyclohexane)
16	Perfluoro-1,4-bis-sec.-butyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (125) (cyclohexane)
17	3-Fluoro-4,5-bis-heptafluoroisopropyl-6-isopropoxy-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (133) (cyclohexane)
18	2,5-Bis-heptafluoroisopropyl-3-isopropoxyfluoropyrazine (135) (cyclohexane)
19	2-(3'-isopropoxy-5'-heptafluoroisopropyl-6'-fluoropyrazin-2'-yl)-2-isopropoxyhexafluoropropane (136) (cyclohexane)
20	Perfluoro-bis-isopropyldiazabicyclo[4.2.0]oct-2,4,7-triene (C) (cyclohexane)
21	Perfluoro-bis-isopropyldiazacyclo-octatetraene (D) (cyclohexane)
22	Perfluoro-bis-isopropyldiazacyclo-octatetraene (E) (cyclohexane)


No. 1
(63)
absorbance
ε, 4161
ε,897
200 225 250 275 nm 300 325 350 400 450


ε, 1942
No. 3
(72)
absorbance
ε, 269
200 225 250 275 300 325 350 400 450

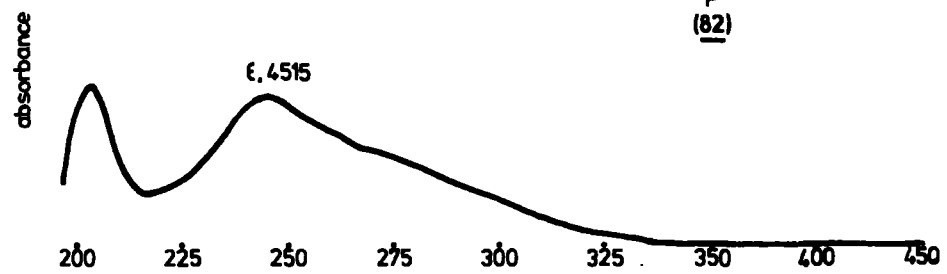

ε,4101
No. 2
(70)
absorbance
ε,373
200 225 250 275 300 325 350 400 450


ε,1921
No. 4
(71)
absorbance
ε, 248
200 225 250 275 300 325 350 400 450



No. 5

(74)



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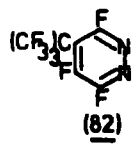
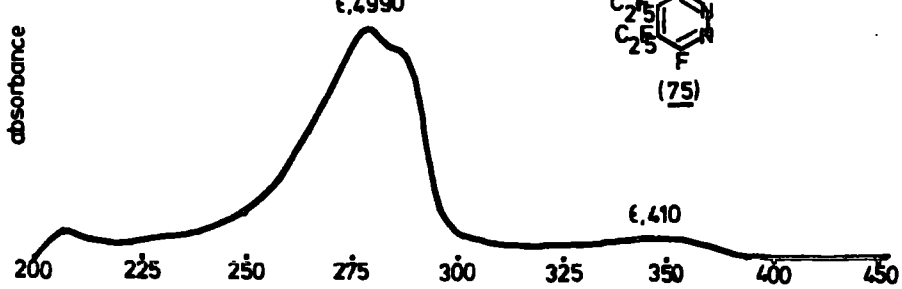


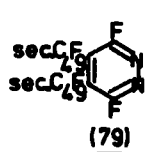
(82)

No. 7



(75)

No. 8



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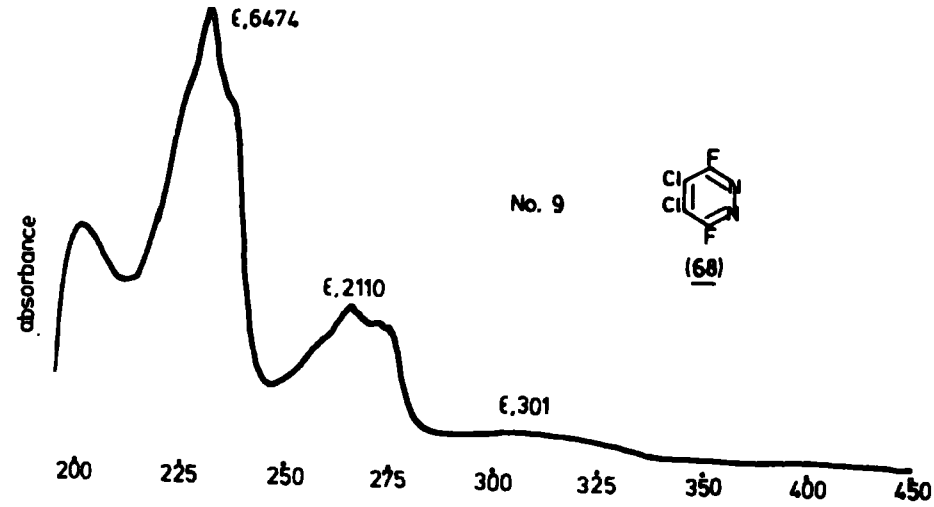

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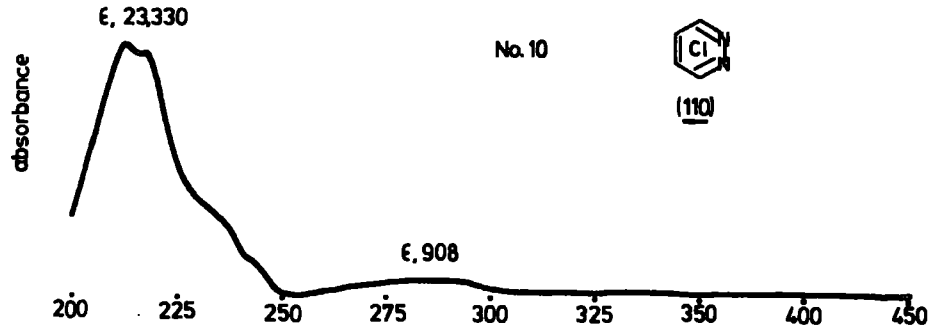
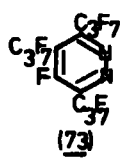
(68)



No. 10

(110)

No. 11



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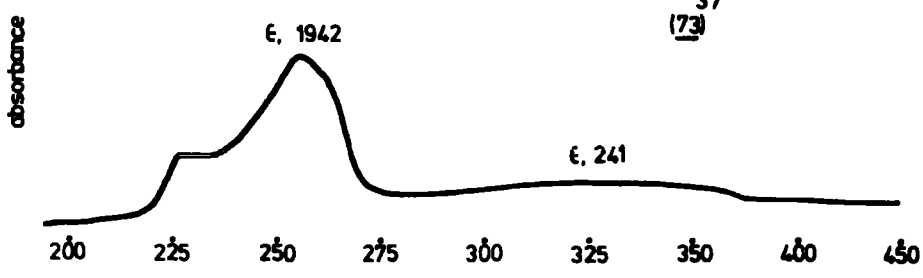

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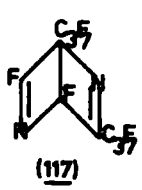

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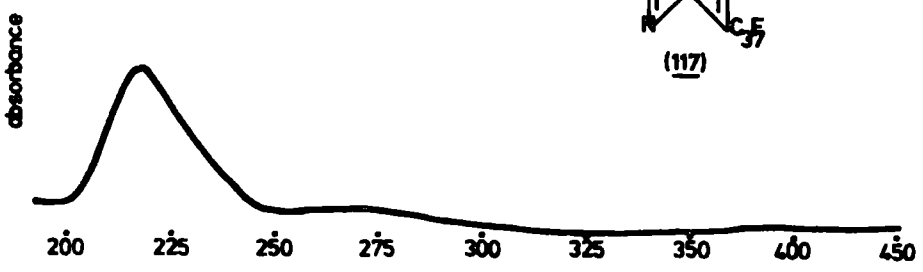

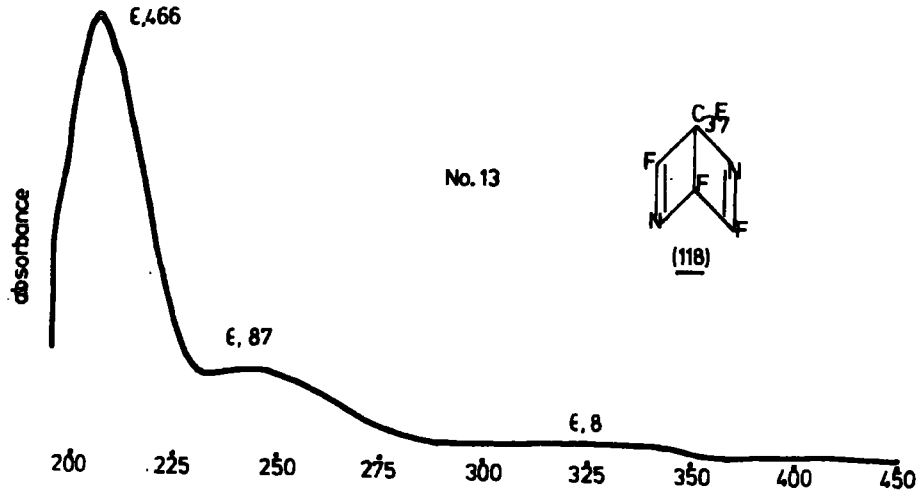

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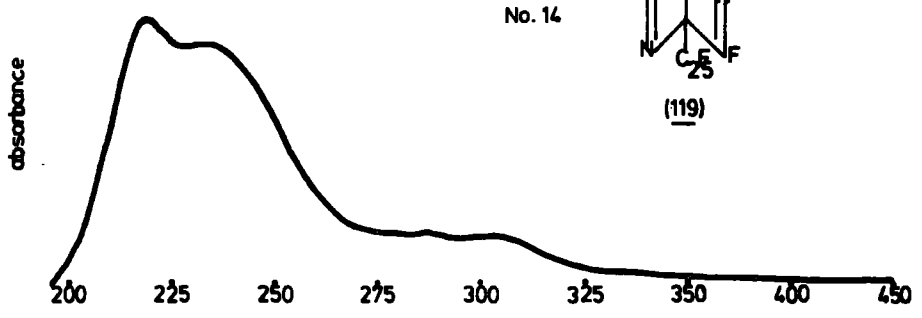

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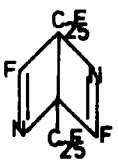

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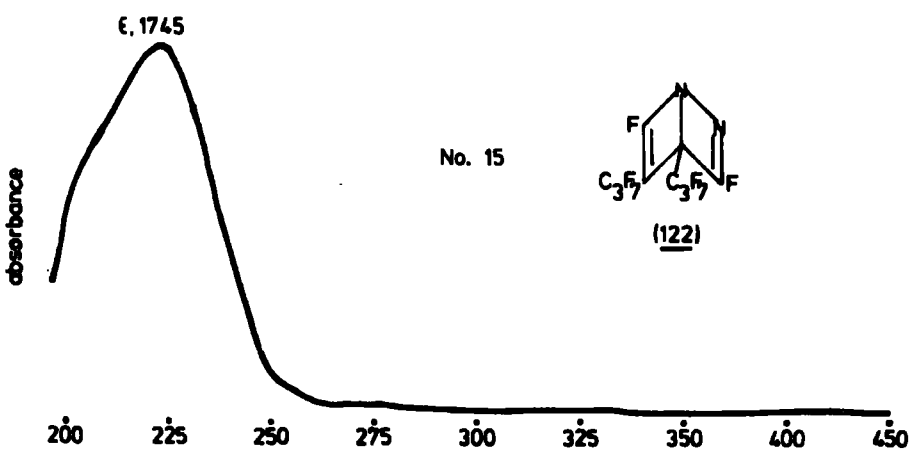

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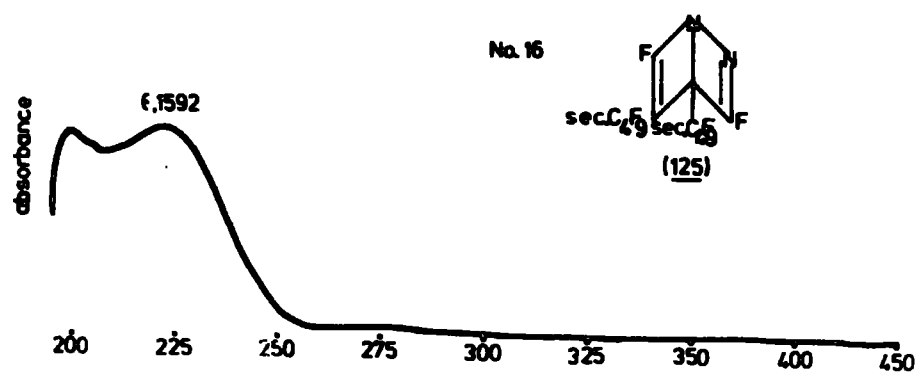

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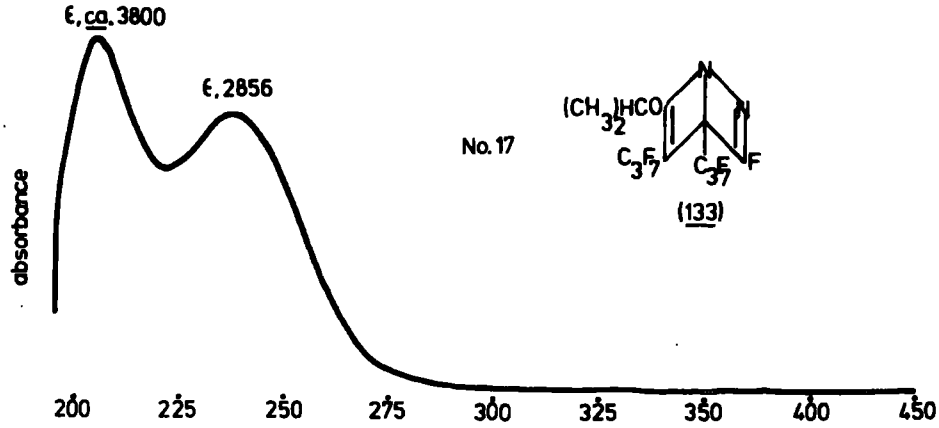

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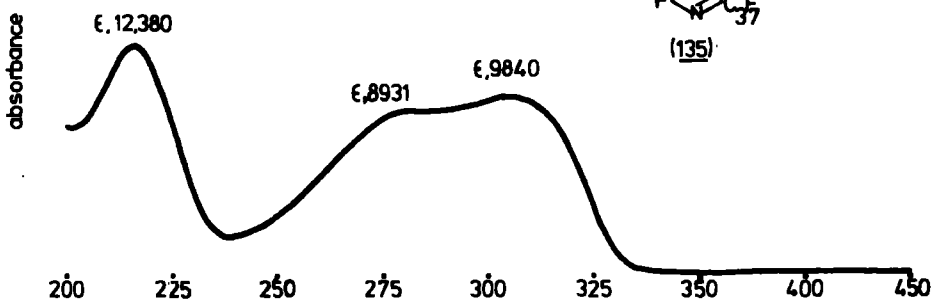

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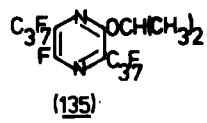

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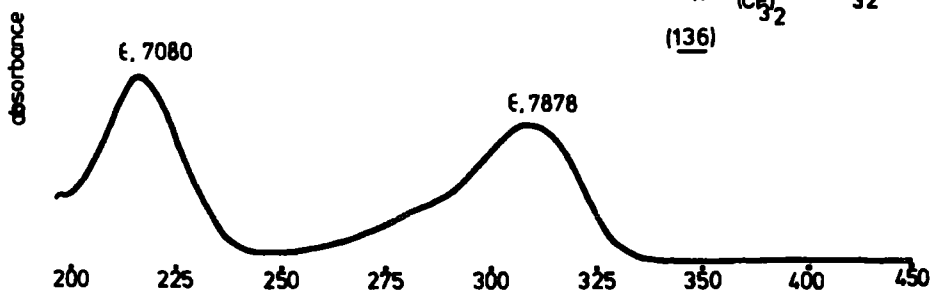

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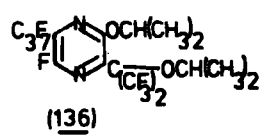

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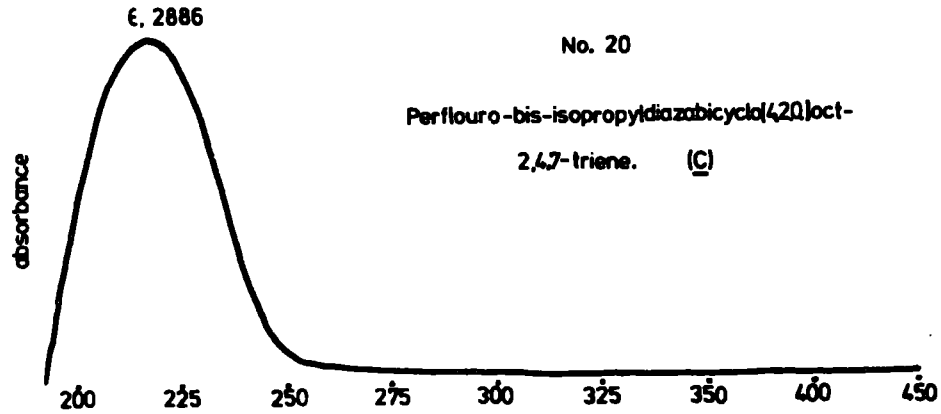


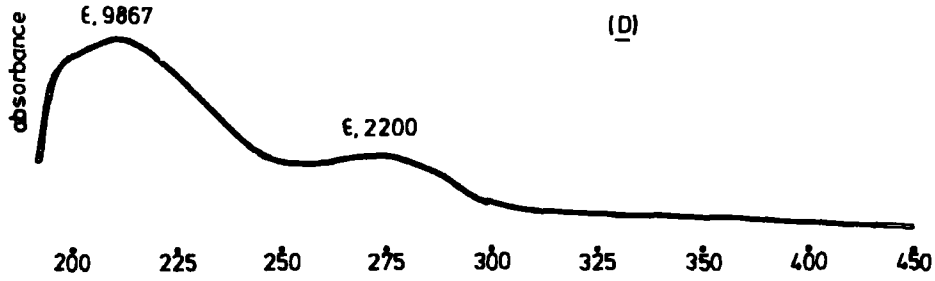
No. 20

Perflouro-bis-isopropyldiazabicyclo(4.2.0)oct-2,4,7-triene. (C)

No. 21

Perflouro-bis-isopropyldiazacyclo-octatetraene.

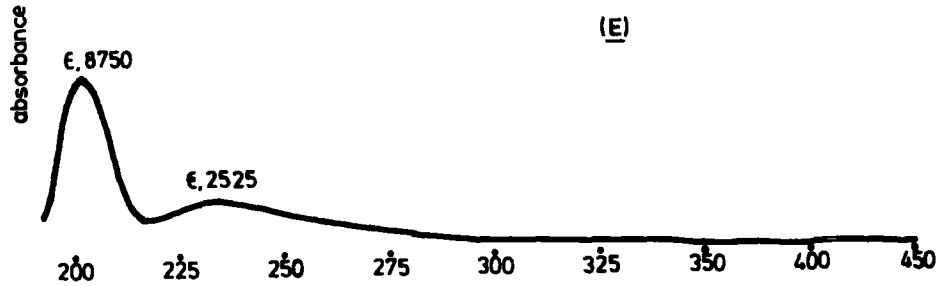
(D)



No. 22

Perflouro-bis-isopropyldiazacyclo-octatetraene.

(E)



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