

FRAGMENTATION AND REARRANGEMENT  
IN  
NITROGEN HETEROCYCLIC CHEMISTRY

By

EDWARD STANTON

A thesis submitted for the degree of  
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The work described in this thesis was carried out by the author at the Universities of Leicester and Liverpool under the supervision of Professor C.W. Rees and Dr. T.L. Gilchrist. No part of it is concurrently being submitted for any other degree.

The author wishes to express his sincere gratitude to Professor C.W. Rees and Dr. T.L. Gilchrist for their excellent supervision and constant encouragement and inspiration. The award of a Research Studentship by the Science Research Council is also acknowledged.

Signed

E. Stanton

E. STANTON

TO VAL

in recognition of her patience and  
invaluable help and encouragement  
throughout the work described in  
this thesis.

## ABSTRACT

The main methods of generating heterocyclic amino-nitrenes are summarised and the subsequent fate of the nitrenes is considered. The photochemistry of three-membered ring systems is reviewed.

Certain 1-phthalimido- and 1-(2-methylquinazol-4-on-3-yl)-aziridines, when irradiated in the presence of an olefin, undergo an exchange reaction which produces a new aziridine incorporating the added olefin. Evidence is presented for a mechanism involving amino-nitrene formation by concerted cleavage of the aziridine C-N bonds. The scope of this reaction is delineated.

Vapour phase flash pyrolysis of N-heterocyclic sulfoximides is used to generate amino-nitrenes under conditions such that nitrogen extrusion occurs. For example, phthalimido-nitrene gives benzocyclobutenedione and indazolyl-nitrene gives 1-cyanohepta-1,3-dien-5-yne. Sulfoximides containing active protons  $\alpha$  to the sulphur atom and involving amide or imide heterocycles undergo a competing fragmentation to the parent amide or imide.

Isoindolinyl-aziridines, prepared by reduction of the corresponding phthalimido-aziridines, are fragmented readily, possibly via isoindolinyl-nitrene.

The possibility of intramolecular insertion of phthalimido-nitrene to give phthalaz-1,4-dione is upheld since the generation of the latter species by vapour phase flash pyrolysis of its Diels Alder adducts with dienes or its [2+2] adduct with indene is found to give

benzocyclobutenedione. The retro Diels Alder reaction is also used to generate other reactive  $\alpha$ -carbonyl azo compounds in the vapour phase such that unimolecular decomposition then occurs.

Thermolysis of 1-(quinazol-4-on-3-yl)-2-vinylaziridines gives the corresponding 3-(trans-but-2-en-1-ylideneamino)quinazol-4-ones in a novel rearrangement which is in competition with formation of 3-pyrrolines. At higher temperatures a fragmentation involving cleavage of the N-N bond also competes and this occurs to the exclusion of rearrangement in substituted vinylaziridines. An analogous fragmentation of trans-2,3-diphenyl-1-phthalimidoaziridine gives 2,3-diphenyl-2H-azirine, which in turn rearranges to 2-phenylindole. Reaction mechanisms are discussed.

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1.

## I N T R O D U C T I O N

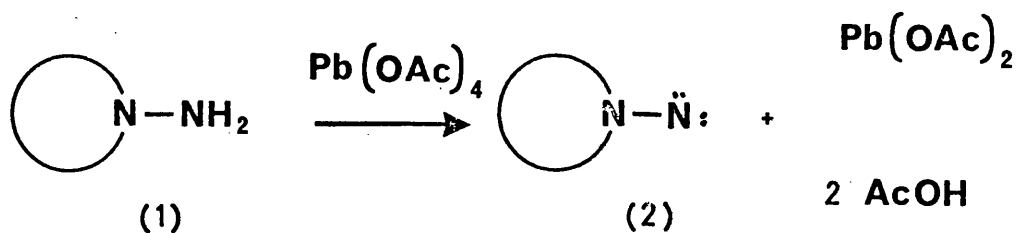
## THE GENERATION AND REACTIONS OF HETEROCYCLIC AMINO-NITRENES

Nitrenes have been the subject of a recent and comprehensive book<sup>1</sup> which, with other reviews<sup>2-5</sup> on nitrene chemistry, renders unnecessary a detailed introduction to the subject.

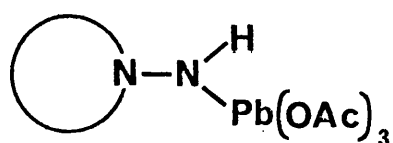
The following is a brief survey of the main methods that have been used for the generation of heterocyclic amino-nitrenes; the subsequent fate of the nitrenes is also considered and a classification of the possible modes of reaction is presented.

### 1. Generation

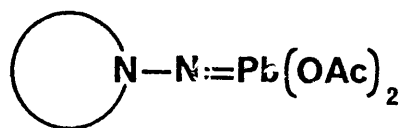
Amino-nitrenes of general structure (2) have most often been generated by lead tetra-acetate oxidation of the corresponding N-amino heterocyclic compound (1).



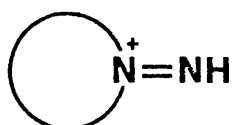
There is no conclusive evidence that the free nitrene (2) is involved but it is arguable that the alternatives, the lead complexes (3) and (4) or the nitrenium ion<sup>6-8</sup> (5), are less likely as the reactive species.



(3)

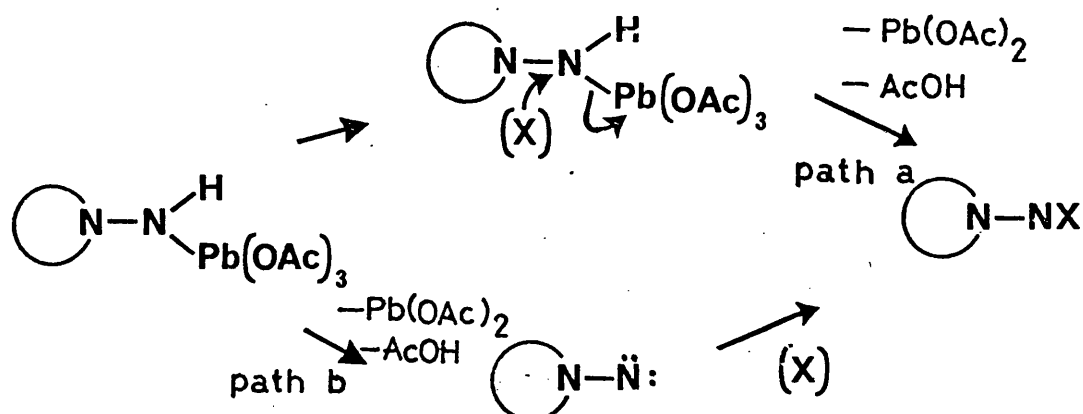


(4)



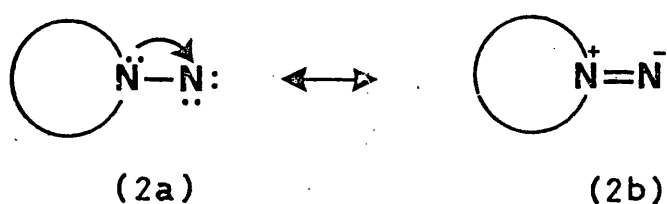
(5)

The complex (3) is probably involved initially and then loses lead diacetate and acetic acid, either in concert<sup>9</sup> with product formation (Scheme 1, path a), or to give the free nitrene (Scheme 1, path b), possibly via complex (4). There are, of course, an infinite number of intermediate situations and the precise mechanism and timing involved in any particular case must depend to a large extent on the nature of the species (X) with which the nitrene (2), or the nitrenoid (3), combines.



(Scheme 1)

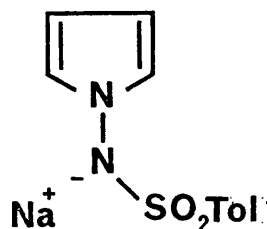
The discrete amino-nitrene (2) could be favoured, since the singlet state can be stabilised by delocalisation of the lone pair of electrons on the internal nitrogen into the vacant p-orbital of the terminal nitrogen. This concept was first proposed by Stevens.<sup>10</sup>



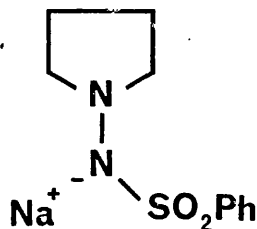
Discussion of the role of the nitrenium ion (5) is similarly complicated by the possibility of structures intermediate between the nitrene and the nitrenium ion. Anderson<sup>11</sup> has drawn an analogy with a similar situation in the acid catalysed decomposition of phenyldiazomethane in olefins to give cyclopropanes, where "partial" protonation of the diazo carbon atom has been invoked<sup>12</sup> and where the  $\text{pK}_a$  of the solvent is important.<sup>13</sup> He has also pointed out that, in the case of a nitrenium ion derived by protonation of an N-amido-nitrene, the carbonyl polarisation would destabilise the nitrenium ion. However, the same argument can be applied to the nitrene resonance form (2b).

A variety of oxidants other than lead tetra-acetate has been used for the oxidation of N-amino compounds. Diacetoxyiodobenzene appears to be comparable to lead tetra-acetate but other oxidants, which include





(6)



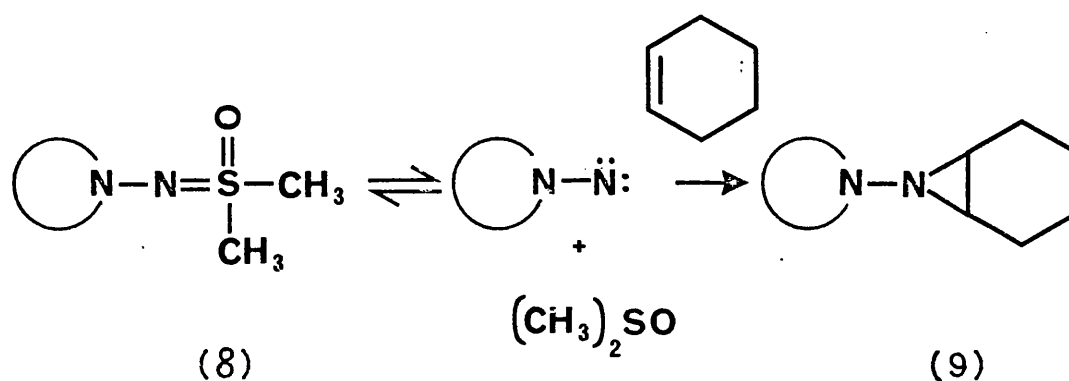
(7)

Nitrenes can also be obtained by the treatment of secondary amines either with sodium nitrohydroxylamate<sup>17</sup> ( $\text{Na}_2\text{N}_2\text{O}_3$ , Angeli's salt) and acid,<sup>18</sup> or with difluoramine,<sup>19-21</sup> and from the sodium dithionite reduction of N-nitroso compounds.<sup>19,22-24</sup> These methods have been less widely applied.

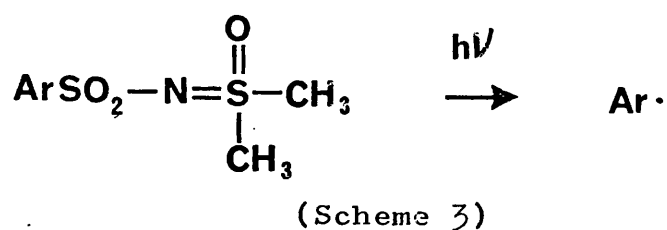
The photolysis and pyrolysis of azides are much utilised sources of C-nitrenes<sup>25</sup> but, because aminoazides are not readily available, these methods have found little application to the generation of heterocyclic amino-nitrenes.

The oxidation of certain N-amino heterocyclic compounds with lead tetra-acetate in the presence of dimethyl sulphoxide has been used to prepare sulfoximides (8).<sup>11,26</sup> Photolysis of these sulfoximides apparently regenerates the nitrene since, in the presence of cyclohexene, the azabicycloheptane (9) is formed.<sup>11,26-28</sup>

In the absence of an added olefin, the sulphoximides are unchanged.



This method of generating nitrenes is probably not a general reaction; sulphonylsulphoximides, for example, are reported<sup>29</sup> to give aryl radicals on photolysis (Scheme 3).



Fragmentation of the sulfoximides (8) to give the original nitrene and dimethyl sulphoxide has also been observed on thermolysis at temperatures around 250°, either in solution or in the melt.<sup>27,30</sup>

The above methods of amino-nitrene generation will be elaborated, with examples, in the following section.

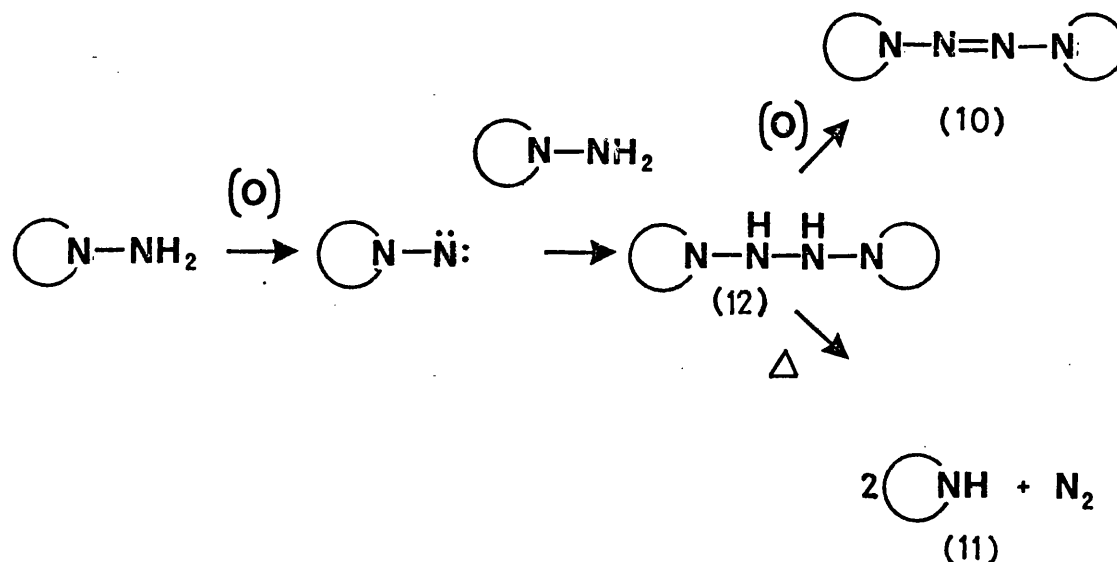


## 2. Reactions

The generation of heterocyclic amino-nitrenes by the methods outlined has led to a variety of subsequent reactions, which can conveniently be classed as either intermolecular or intramolecular.

### i) Intermolecular reactions

By far the majority of amino-nitrenes studied have been generated by oxidation of the corresponding N-amino compound, and frequent products are tetrazenes (10) and the parent lactam (11). Dreiding has proposed<sup>31</sup> that the origin of these is the intermolecular attack of the nitrene on unoxidised N-amino compound with formation of a tetrazane (12).

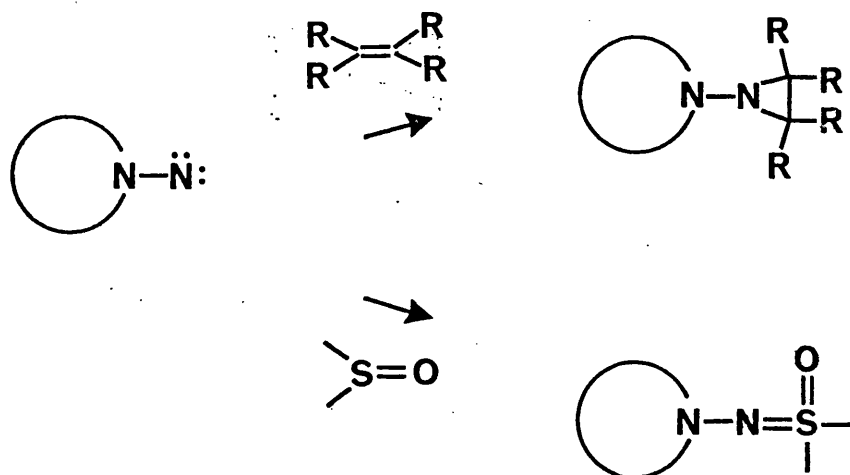


In some cases, e.g. phthalimido-nitrene, this tetrazane (12) has been isolated as an unstable solid, decomposing thermally to the parent lactam (11) and nitrogen.<sup>32</sup> Oxidation of the tetrazane has been observed to give tetrazene. The alternative origin of tetrazene is by dimerisation of two nitrenes,<sup>4, 31, 33</sup>

possibly less likely in view of their high energy content. Tetrazene (10) may be cis or trans; there is evidence that the former is favoured when heterogeneous oxidants are used, whereas homogeneous oxidants give mainly the more stable trans-tetrazene.<sup>11,34</sup>

Tetrazenes may also be obtained from arylsulphonylhydrazine decomposition<sup>15</sup> and again could arise from the attack of the amino-nitrene on unreacted arylsulphonylhydrazine followed by an elimination, or by nitrene dimerisation.

Other intermolecular reactions that have been observed are the formation of aziridines and sulfoximides by generation of certain amino-nitrenes in the presence of olefins and sulfoxides, respectively (Scheme 4).<sup>31,35-39</sup> The preferred source of the nitrene is again oxidation of the corresponding N-amino compound. Aziridine or sulfoximide formation generally competes favourably with the attack of the nitrene on the unoxidised N-amino compound.



(Scheme 4)

Azirine formation, by addition of a nitrene to an acetylene, has also been observed but only in the case of phthalimido-nitrene and even then phthalimide is the major product.<sup>40</sup>

Table 1 illustrates some systems which have been observed to react intermolecularly in the above manners; no intramolecular products have been observed from these systems.

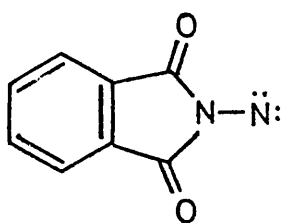
ii) Intramolecular reactions

Whereas Table 1 shows heterocyclic amino-nitrenes that have been observed only to react intermolecularly, certain nitrenes (Table 2) are known to react intramolecularly. In the latter case either intramolecular reaction only has been observed, or the two processes occur in competition.

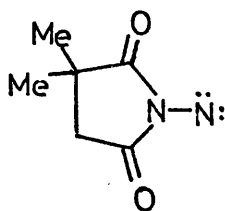
Intramolecular reaction involves either insertion of the nitrene to give a ring enlarged product, or fragmentation. The latter may be preceded by ring enlarging insertion in some cases.

TABLE 1. Heterocyclic amino-nitrenes known only to react intermolecularly

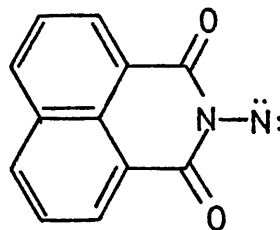
Below each structure is given the method of generation, according to the key below. References are given as superscripts. No intramolecular reactions have been observed for any of the systems shown.



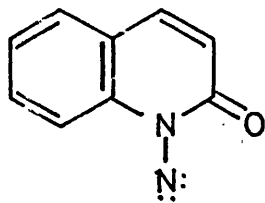
1,2,6.<sup>11,31,35</sup>



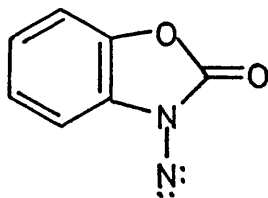
1.<sup>39</sup>



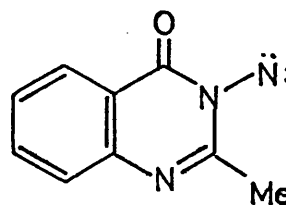
1.<sup>11</sup>



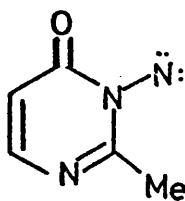
1.<sup>35,41</sup>



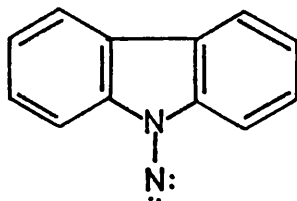
1,5.<sup>11,35,52</sup>



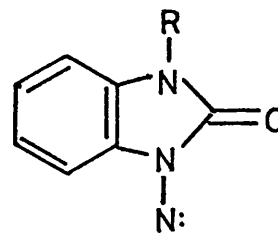
1.<sup>35,41</sup>



1.<sup>41</sup>

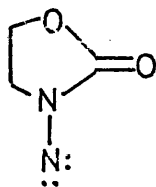


1.<sup>11,15</sup>

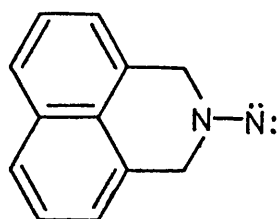


R = , , CH<sub>3</sub> .

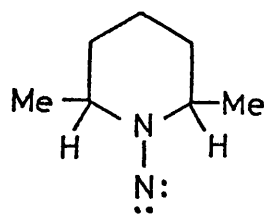
1.<sup>28</sup>



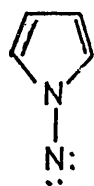
4.34



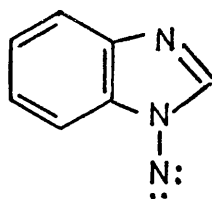
5.44



4.53



1,7.15



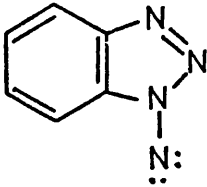
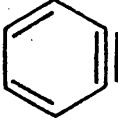
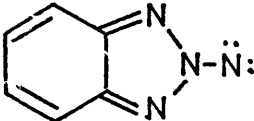
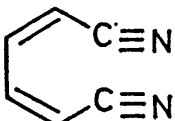
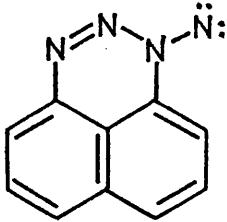
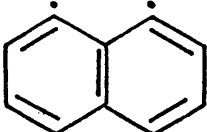
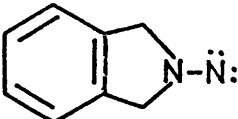
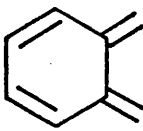
1,3.41,16

## Notes to Table 1.

1. Lead tetra-acetate oxidation of the N-amino compound.
2. Diacetoxyiodobenzene oxidation of the N-amino compound.
3. Potassium ferricyanide oxidation of the N-amino compound.
4. Mercuric oxide oxidation of the N-amino compound.
5. Manganese dioxide oxidation of the N-amino compound.
6. Photolysis of the appropriate sulphoximide.
7.  $\alpha$ -Elimination from the arylsulphonylhydrazine.

TABLE 2. Heterocyclic amino-nitrenes known to react, at least in part, intramolecularly.

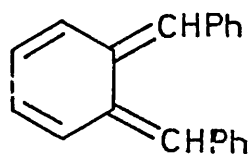
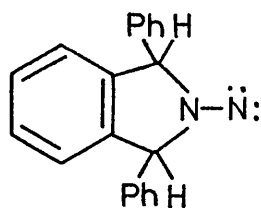
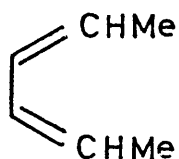
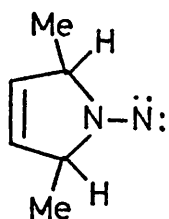
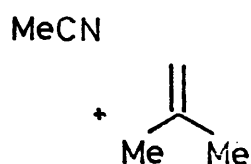
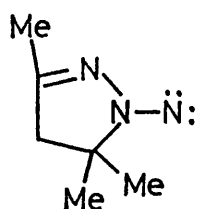
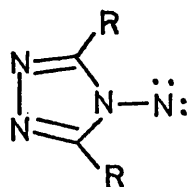
Fragmentation products enclosed in brackets are believed to arise via prior intramolecular insertion of the nitrene and are thus not primary products of the nitrenes. Where a nitrene is known to react intermolecularly, as well as giving the intramolecular products shown, then this is signified by an asterisk in the final column.

Nitrene	Fragmentation Product	Insertion Product	Method of Generation
			1-5, 8, 9, 16, 48
			1, 2, 48
			1, 2, 4, 5, 54
			3, 8, 14, 42

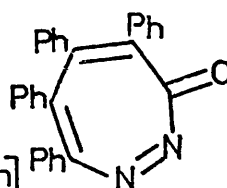
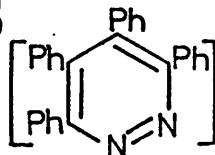
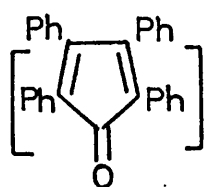
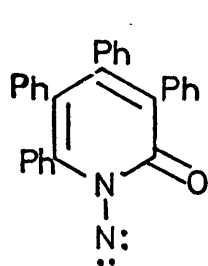
Nitrene	Fragmentation Product	Insertion Product	Method of Generation
			1, <sup>49</sup>
			1, <sup>41</sup>
			1, <sup>41</sup>
			1, <sup>41</sup> *
			1, 2, <sup>9, 28, 55, 58</sup>
			1, <sup>28</sup>



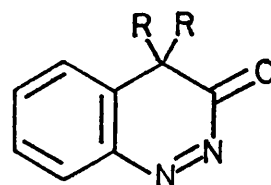
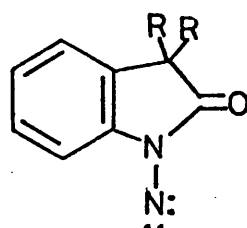
Nitrene

Fragmentation  
ProductInsertion  
ProductMethod of  
Generation3,4,8.<sup>14,42,43</sup>10.<sup>18</sup>11.<sup>19</sup>

2 RCN

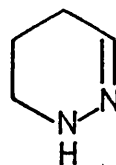
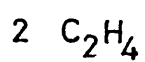
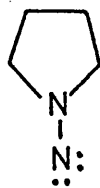
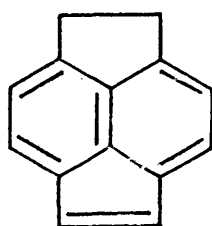
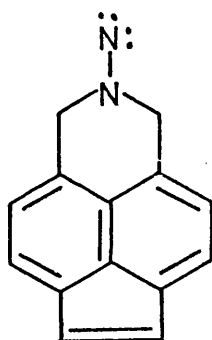
1.<sup>56</sup>1,7.<sup>57</sup>

\*

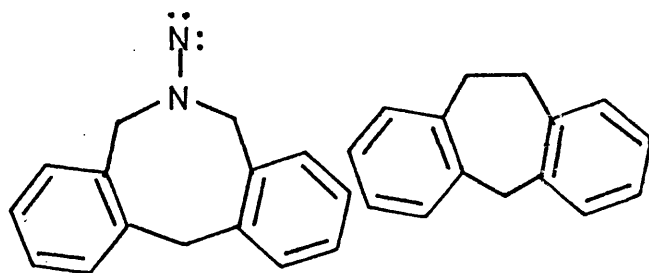
1,2,6.<sup>28</sup>

\*

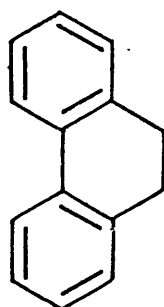
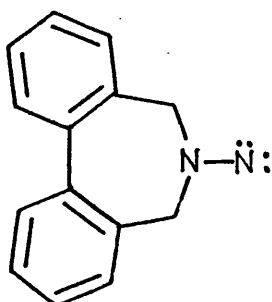
Nitrene

Fragmentation  
ProductInsertion  
ProductMethod of  
Generation3,8,10,15,24,51  
\*

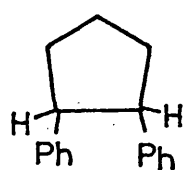
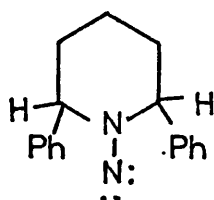
4.44



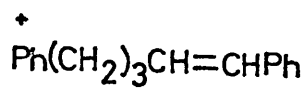
8.44



8.45,46



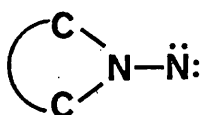
3,12,22,24



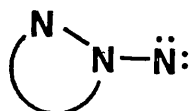
## Notes to Table 2.

1. Lead tetra-acetate oxidation of the N-amino compound.
2. Diacetoxyiodobenzene oxidation of the N-amino compound.
3. Mercuric oxide oxidation of the N-amino compound.
4. Manganese dioxide oxidation of the N-amino compound.
5. Nickel peroxide oxidation of the N-amino compound.
6. Photolysis of the sulphoximide.
7. Pyrolysis of the sulphoximide.
8.  $\alpha$ -Elimination of the arylsulphonylhydrazine.
9. Photolysis of the phosphineimine.
10. Secondary amine + Angeli's salt - hydrochloric acid.
11. Secondary amine + fluoramine.
12. Reduction of the nitrosamine.

The consideration of partial structures (a) and (b) is informative in attempting to rationalise the differing modes of reaction of the amino-nitrenes.



(a)

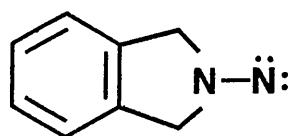


(b)

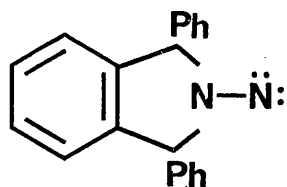
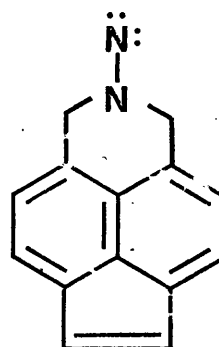
All nitrenes studied of general structure (b) are to be found in Table 2, whereas those containing structure (a) generally react only intermolecularly and appear in Table 1. Moreover, partial structure (b) seems conducive to fragmentation and this may be attributed to the difference in energy of a C-N bond ( $66 \text{ kcal mole}^{-1}$ ) compared to a N-N bond ( $37 \text{ kcal mole}^{-1}$ ).<sup>33</sup>

It is difficult, however, to categorise the nitrenes strictly. Partial structure (b) is sufficient for intramolecular reaction, yet not necessary. Partial structure (a) is neither sufficient nor necessary for intermolecular reaction.

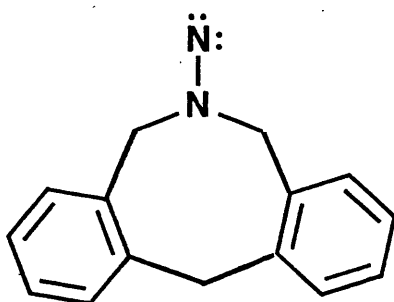
The systems (13) - (21) would appear superficially similar and all have partial structure (a), yet their known modes of reaction are different.



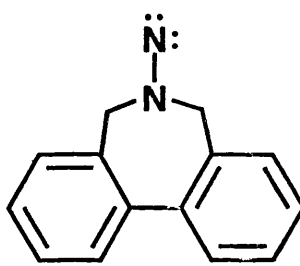
(13)

(14) a) trans  
b) cis

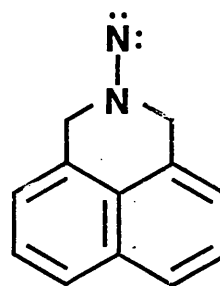
(15)



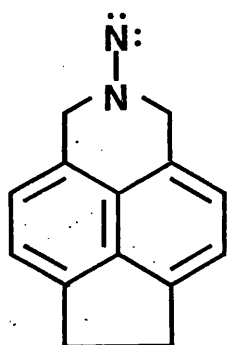
(16)



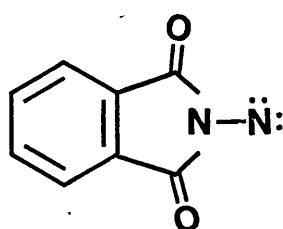
(17)



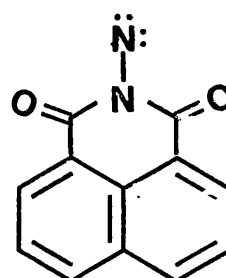
(18)



(19)



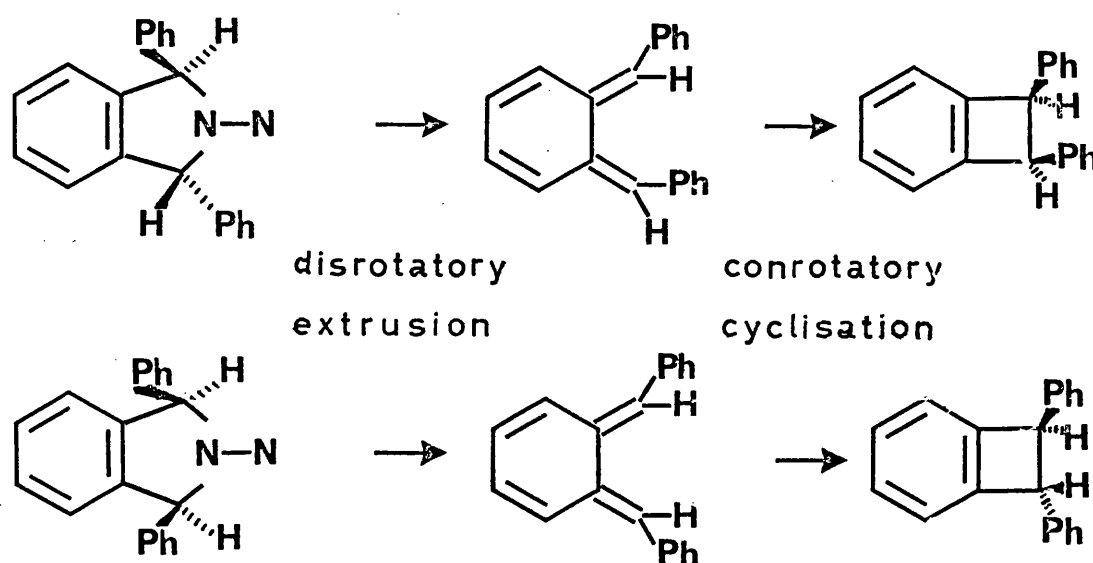
(20)



(21)

Isoindolinylnitrene (13) has been generated by oxidising N-aminoisoindole and also by treating the tosyl chloride derivative with base;<sup>14,42</sup> in both cases nitrogen extrusion occurs to give benzocyclobutene or its artefacts. Similarly, Carpino has found that the 1,3-diphenylisoindolinylnitrenes (14a, b) fragment

as shown in Scheme 5, the formation and cyclisation of the intermediate o-quinodimethanes providing a rationale for the observed stereochemistry.<sup>43</sup>



(Scheme 5)

The nitrenes (15) - (17) also fragment to the hydrocarbon product; the species (15) was formed by manganese dioxide oxidation and gave 1,2-dihydropyracylene.<sup>44</sup> Similarly, the hydrocarbon from (16) was obtained by the action of base on the tosylhydrazine,<sup>44</sup> and the fragmentation of the nitrene (17) gave 9,10-dihydrophenanthrene.<sup>45,46</sup>

On the other hand, Carpino has also studied the nitrenes (18) and (19) and no fragmentation has been observed.<sup>44,47</sup> In the case of (18), oxidation of the corresponding N-amino compound gave tetrazene, whilst

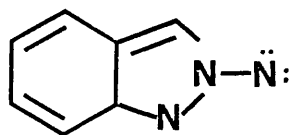
the tosyl derivative, an alkaline degradation, gave a different dimer of (18). In neither case was acenaphthene formed. Generation of (19), by manganese dioxide of the N-amino, similarly failed to afford any pyracene.<sup>44</sup>

Carpino has pointed out that the nitrenes (18) and (19) are incapable of fragmenting to form quino-dimethanes and that, although it is a similar molecule, (16) has a greater degree of flexibility.

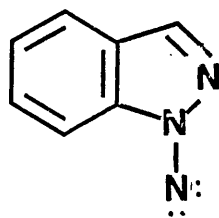
The nitrenes (20) and (21) have been generated by oxidation of N-aminophthalimide and N-aminonaphthalimide respectively.<sup>11,35</sup> Phthalimido-nitrene (20) has also been produced by photolysis of the corresponding sulphoximide.<sup>11,35</sup> In all cases the nitrene reacts intermolecularly and no fragmentation or insertion products have been observed.

Thus, although (13) and (18) are structurally comparable to (20) and (21), the similarity has not been observed to extend to the mode of reaction.

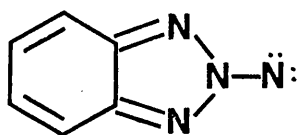
Again, the above argument concerning the relative energies of C-N and N-N bonds would indicate that the indazolyl-nitrenes (22) and (23) should extrude nitrogen, as do the species (24) - (26),<sup>48,49</sup> since all have the partial structure (b) referred to earlier.



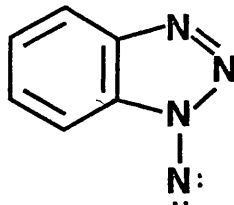
(22)



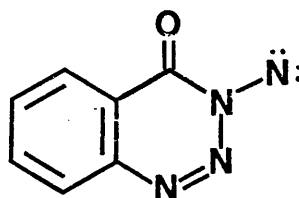
(23)



(24)

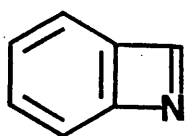


(25)

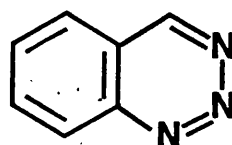


(26)

Indeed, the indazolylnitrenes (22) and (23), generated by lead tetra-acetate oxidation of the corresponding N-aminoindazole, were originally thought by Horwell<sup>41</sup> to fragment to give 1-azabenzocyclobutadiene (27). Recent work by Adams<sup>50</sup> has, however, proved the formation of benzo-1,2,3-triazine (28) by an insertion reaction.



(27)



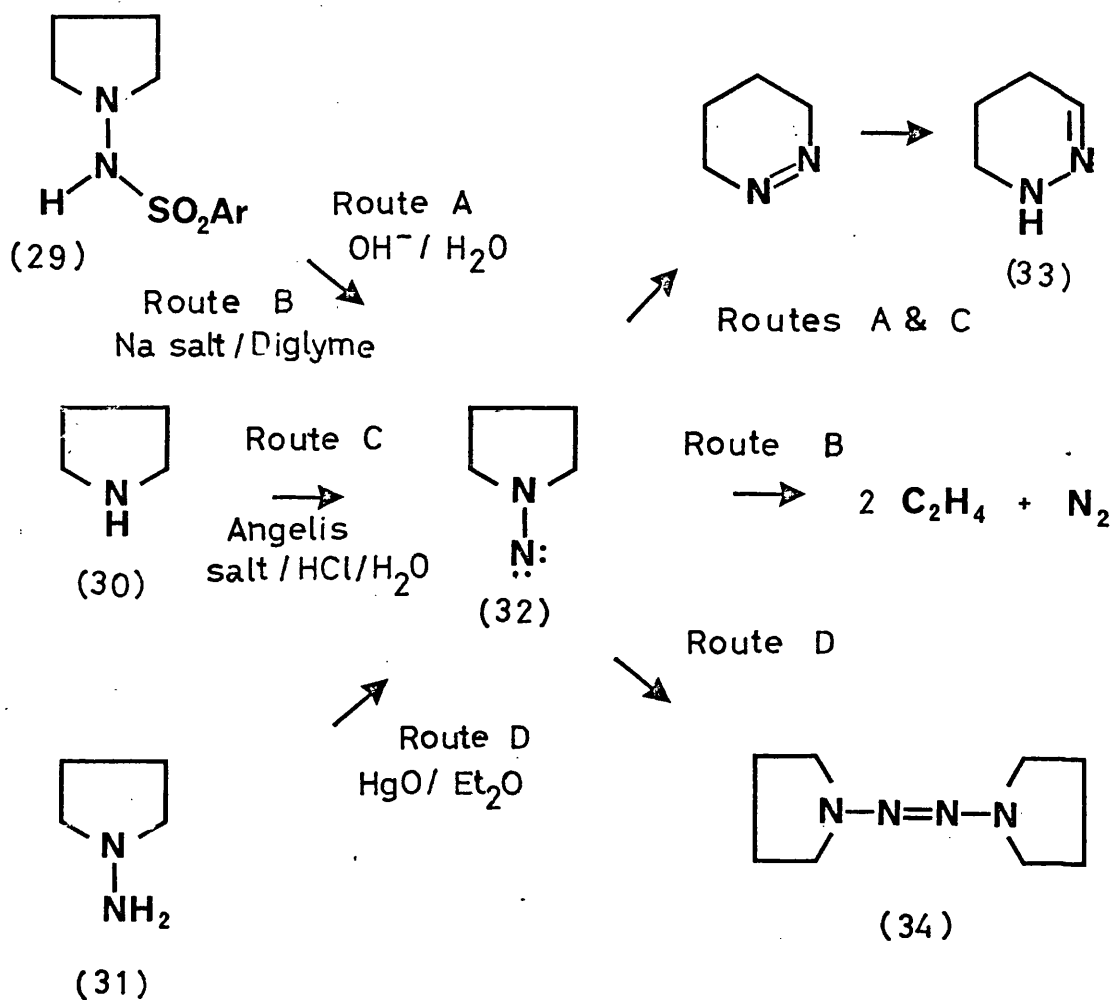
(28)



Very little is known of the effect of reaction conditions on the above processes and most of the nitrenes shown in Tables 1 and 2 have been generated under similar conditions at, or about, room temperature. Indeed, oxidation of the N-amino compound, generally by lead tetra-acetate, has been the method most used for generating the nitrenes.

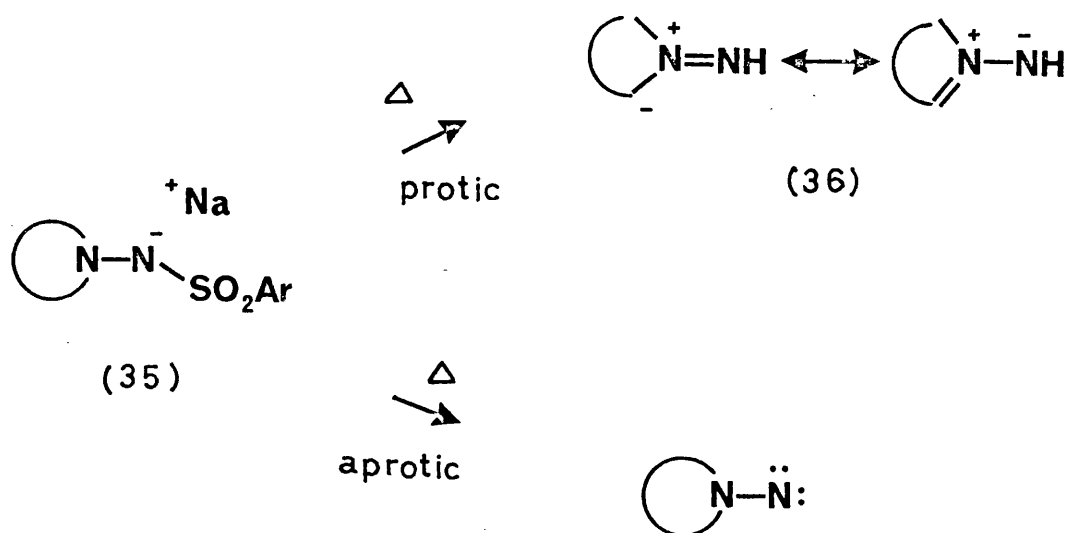
Oxidants other than lead tetra-acetate do sometimes give quite different products, but variation of the oxidant has not been observed to change the primary reaction of the nitrene. For example, 1-aminobenzotriazole may be oxidised by lead tetra-acetate, N-bromosuccinimide, nickel peroxide, diacetoxyiodobenzene, and manganese dioxide, but the different products observed are due to the differing rates at which the oxidations occur and no products from intermolecular reaction of benzotriazolyl-nitrene have ever been observed.<sup>15</sup>

Where nitrenes have been produced by both oxidative and non-oxidative routes, little difference has been noted in the mode of reaction. Possibly the one exception to this occurs in work by Lemal.

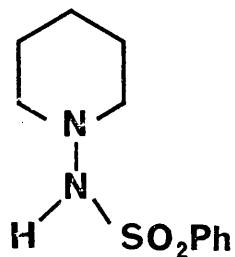


Decomposition of the tosylhydrazine (29) by base in a protic solvent (Route A) gave the insertion product (33) in 56% yield.<sup>51</sup> However, the sodium salt of the tosylhydrazine (29) in diglyme at  $160^\circ$  (Route B) fragmented to ethylene and nitrogen.<sup>15</sup> Treatment of pyrrolidine (30) with Angeli's salt in aqueous acid also gave the insertion product (33)<sup>51</sup> (Route C) but mercuric oxide oxidation of  $\text{N}$ -aminopyrrolidine (31) gave the tetrazene (34)<sup>15</sup> (Route D). The observed differences in reaction were attributed by Lemal to the protic and

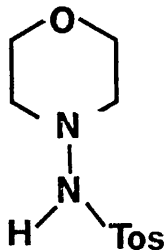
aprotic solvents used. In general, thermal decomposition of the salt (35) in a protic medium gives products derived from intermediates such as (36). These products are not obtained when the salts are decomposed in an aprotic medium and the nitrene intermediate is then involved.



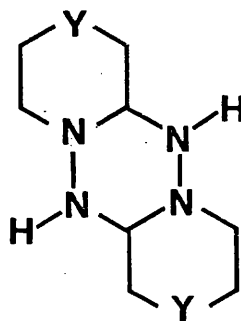
Lemal<sup>51</sup> has further demonstrated this difference in that the decomposition of the arylsulphonylhydrazines (37) and (38) in hydroxylic solvents gave the dimers (39) and (40) respectively. This was attributed to formation of the species (41). Thermal decomposition of the sodium salts of (37) and (38) in an aprotic solvent gave the corresponding tetrazenes (42) and (43).



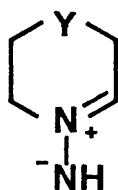
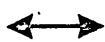
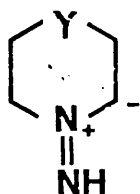
(37)



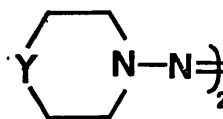
(38)

(39) Y = CH<sub>2</sub>

(40) Y = O



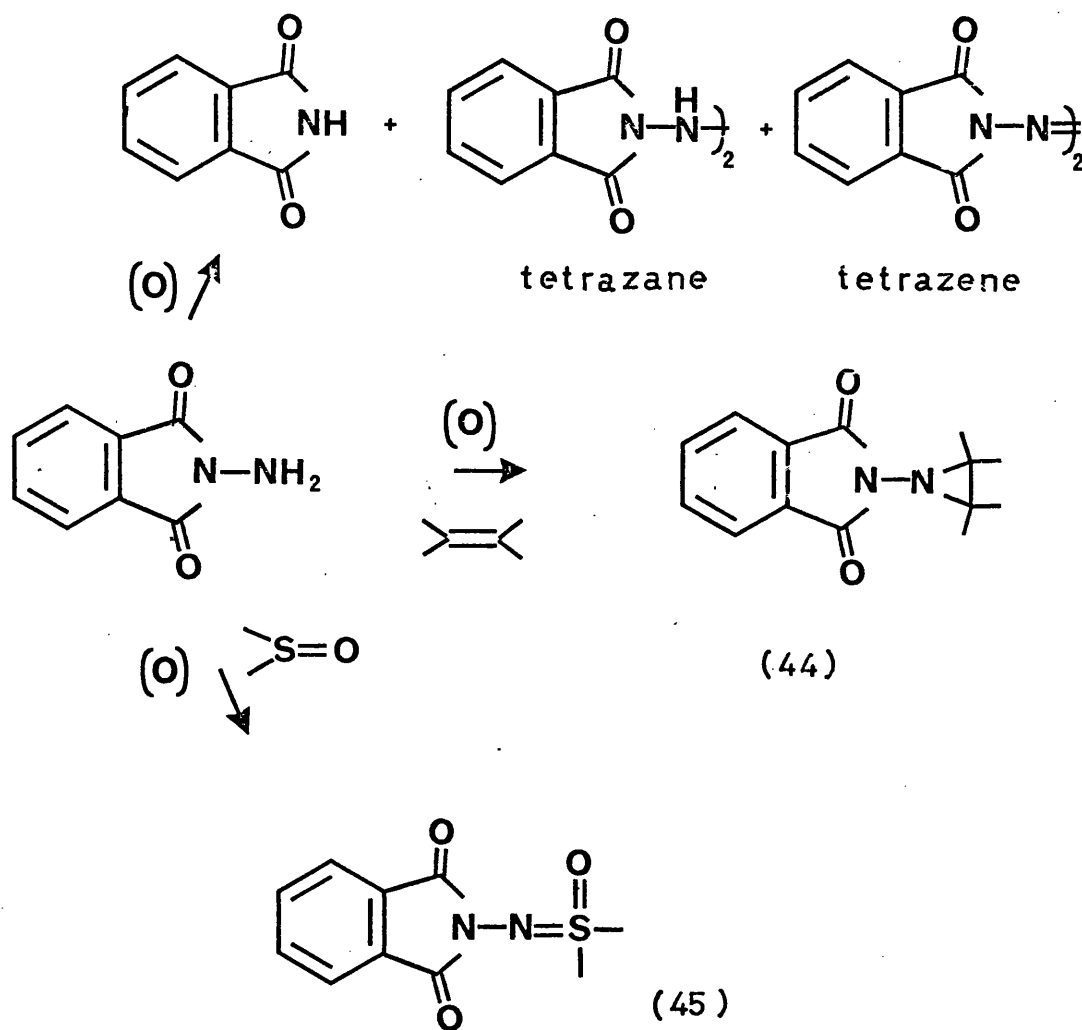
(41)

(42) Y = CH<sub>2</sub>

(43) Y = O

It was considered of interest to generate a heterocyclic amino-nitrene that was firmly classified in Table 1 as undergoing only intermolecular reactions, under differing conditions to investigate if the mode of decomposition could be varied. The generation of phthalimido-nitrene by oxidation of N-aminophthalimide has been extensively studied by Anderson<sup>11,35</sup> and, independently, by Dreiding.<sup>31</sup> Phthalimide, tetrazane, and tetrazene may be isolated in very high combined yield (Scheme 6). Oxidation of N-aminophthalimide in

the presence of a wide variety of olefins and sulphoxides gives aziridines and sulphoximides, respectively, with a corresponding decrease in phthalimide and tetrazene formation.



(Scheme 6)

No products from the intramolecular reaction of the nitrene have ever been obtained.

This work reports an investigation of the generation of phthalimido-nitrene by photolysis of the aziridines (44) and also by vapour phase flash pyrolysis of the sulphoximides (45). These methods were studied

in order to gain an understanding of the factors affecting the reactions undergone by phthalimido-nitrene; the photochemical reaction of the aziridines was also of interest when compared and contrasted to the known photochemistry of other three-membered ring systems.

## THE PHOTOCHEMISTRY OF SATURATED THREE-MEMBERED RING COMPOUNDS

The following section comprises a review of the main photochemical reactions exhibited by cyclopropanes, aziridines, oxiranes, thiiranes, and oxaziridines. The references quoted are not exhaustive; rather, a general picture is drawn of the known photochemistry of these systems. In general, emphasis has been placed on reactions inherently involving the three-membered ring and thus, for example, the Norrish Type I and II cleavage of appropriate cyclopropylketones is not included.

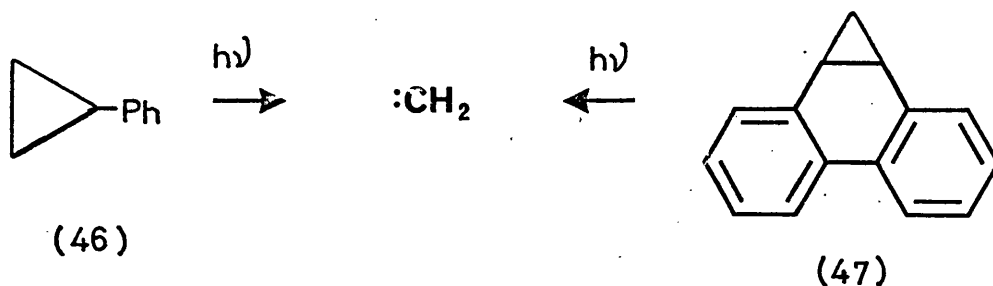
### 1. Cyclopropanes

The photochemistry of variously substituted cyclopropanes has been investigated both from synthetic and mechanistic aspects, and the following possibilities have been realised: i) scission of two of the strained cyclopropane bonds leading to carbene formation, ii) cleavage of only one cyclopropane bond to form a diradical intermediate. This latter process may result in a) bond rotation followed by radical closure with overall stereoisomerisation, b) when conjugated with an unsaturated unit, rearrangement to a five-membered ring, c) intramolecular rearrangement by atom or group transfer to form an acyclic olefin, and d) intermolecular proton abstraction by the diradical.

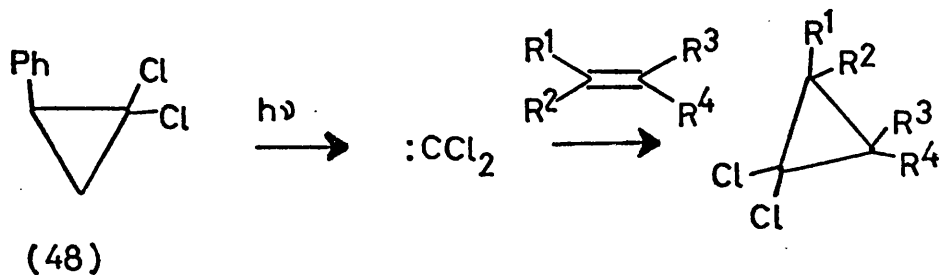
#### i) Generation of carbenes

Typically, arylcyclopropanes undergo photo-

cleavage of two cyclopropane bonds, so generating a carbene and an olefin. Methylene has been generated<sup>58</sup> by irradiation of both phenylcyclopropane (46) and 9,10-dihydro-9,10-methanophenanthrene (47); the methylene has been shown to undergo stereospecific addition to cis- and trans-4-methylpent-2-ene and indiscriminate insertion into alkane C-H bonds, comparable to that of methylene produced by photolysis of diazomethane.



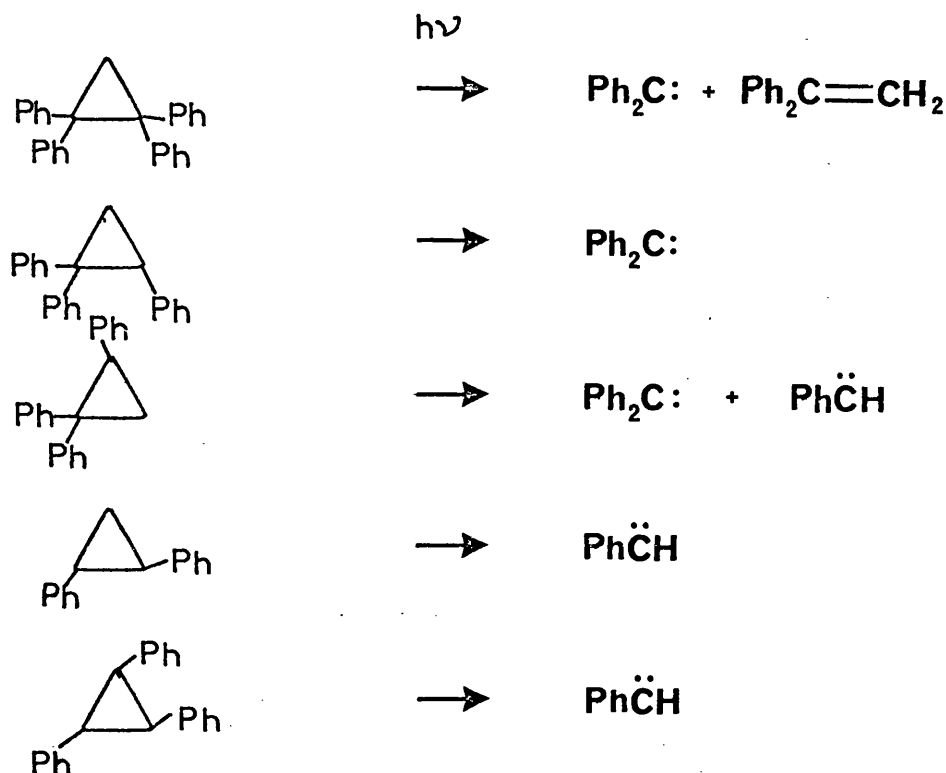
Jones<sup>59</sup> has similarly found that photolysis of 1,1-dichloro-2-phenylcyclopropane (48) leads to dichlorocarbene. Competition studies with olefin pairs showed that the dichlorocarbene added preferentially to the more substituted olefin, in common with dichlorocarbene generated by other methods.



Photofragmentation of arylcyclopropanes to arylcarbenes has been demonstrated by Kristinsson<sup>60</sup>



(Scheme 7).

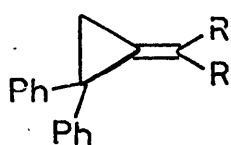


(Scheme 7)

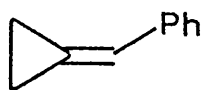
The carbenes were detected by the formation of adducts upon irradiation of the cyclopropanes in olefins and alcohols. Irradiation of trans-1,2-diphenylcyclopropane and 1,2,3-triphenylcyclopropane in n-pentane has also been studied<sup>61</sup> and the insertion selectivity of the phenylcarbene found to be very similar to that of phenylcarbene generated by irradiation of 2,3-diphenyloxirane, triphenyloxirane, and phenyldiazomethane. Arylcyclopropane fragmentations are often observed in competition with rearrangement reactions; for example, 1,2-diphenylcyclopropane also undergoes the isomerisations shown in Schemes 8, 13, and 15.

Methylenecarbenes have been generated<sup>62,63</sup> by photofragmentation of methylenecyclopropanes (49) - (51).

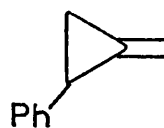
The reactions have been classed<sup>63</sup> as chelotropic fragmentations of the excited methylenecyclopropanes. A similar decomposition of unsubstituted methylenecyclopropane has been observed by Brinton.<sup>64</sup>



(49)



(50)

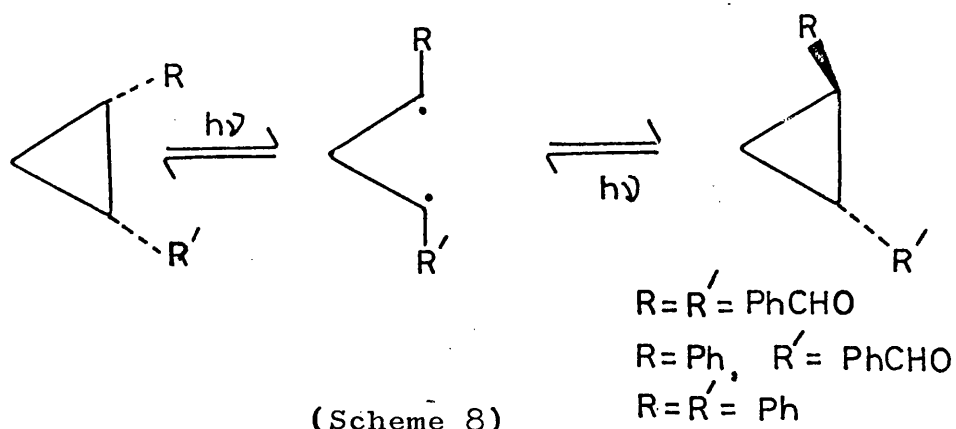


(51)

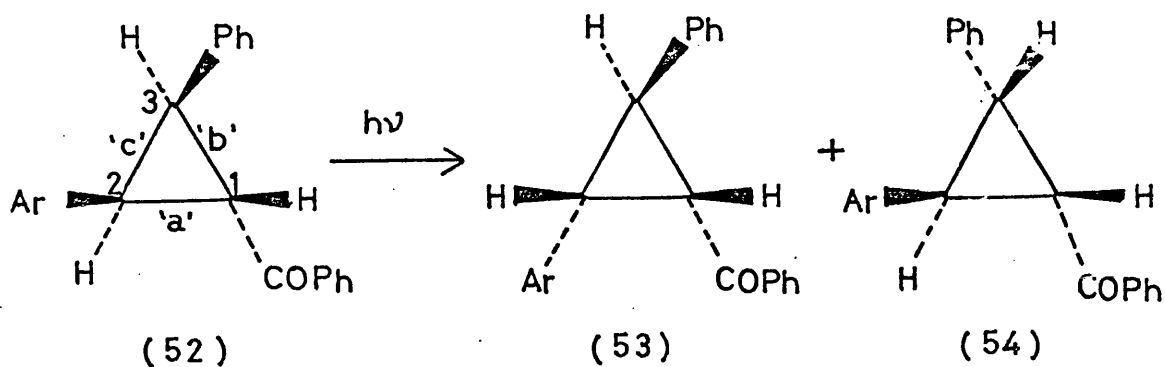
Other<sup>65-67</sup> cyclopropane irradiations in which fragmentation to a carbene and an olefin has been invoked include the gas phase photolysis of cyclopropylphenylmethane<sup>68</sup> and phenylcyclopropanes.<sup>69</sup> Both undergo extensive polymerisation and a plethora of products is found but in both cases ethylene is a primary photoproduct and its formation is attributed to a concerted cleavage of two cyclopropane bonds.

## ii) Diradical formation

a) The cis-trans photoconversion of 1,2-dibenzoyl-, 1-benzoyl-2-phenyl-, and 1,2-diphenylcyclopropanes has been observed by Griffin<sup>70,71</sup> and attributed to reversible bond scission (Scheme 8).



Hammond<sup>72</sup> has also observed the photoisomerisation of 1,2-diphenylcyclopropane and more detailed investigations by Zimmerman<sup>73-75</sup> have concerned photoisomerisation of (52 a,b,c) (Scheme 9).



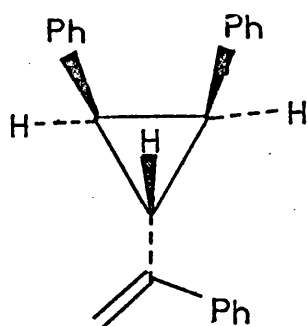
- a)  $\text{Ar} = \text{pCNPh}$   
 b)  $\text{pMeOPh}$   
 c)  $\text{Ph}$

(Scheme 9)

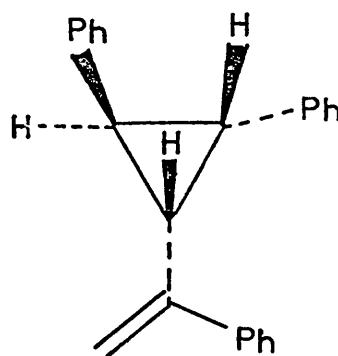
In the case of (52a), the reaction was shown<sup>73</sup> to proceed through the triplet excited state and lead to

formation of (53a) and (54a) in the ratio of 3.5 : 1. Using optically active [(+) 52a] it was found that [(-) 53a] was formed, involving inversion at C-2 and no loss of activity. The (54a) produced, however, was racemic. The conclusion drawn was that there existed an 8:1 preference for fission of bond 'a' compared to bond 'b', and that both scissions were followed by rotation about bond 'c' and ring closure. A similar process was shown to operate in the photoisomerisation of (52b) and (52c).

Zimmerman has also investigated<sup>76</sup> the photochemistry of (55) and (56), which as methylene analogues of the cyclopropylketones have no  $n \rightarrow \pi^*$  excited states available.



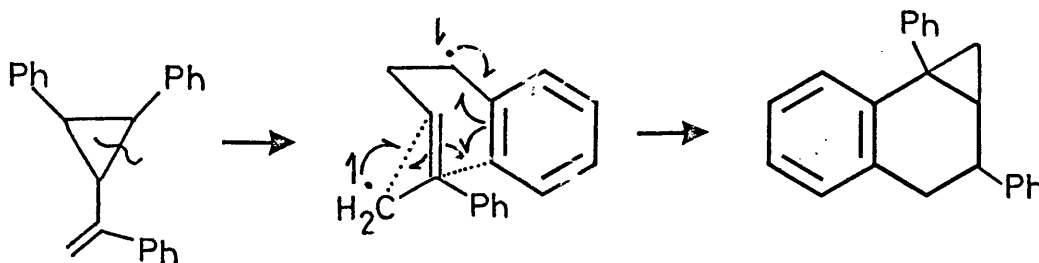
(55)



(56)

The stereoisomerisation involved cleavage of bond 1-2 and proceeded by both direct and triplet sensitised irradiation. The direct irradiation also led to a novel rearrangement (Scheme 10), presumably from the singlet excited state since triplet sensitisation

gave only stereoisomerisation.



(Scheme 10)

cis-trans Isomerisation of cyclopropane derivatives on photolysis has been observed<sup>77-83</sup> by other workers.

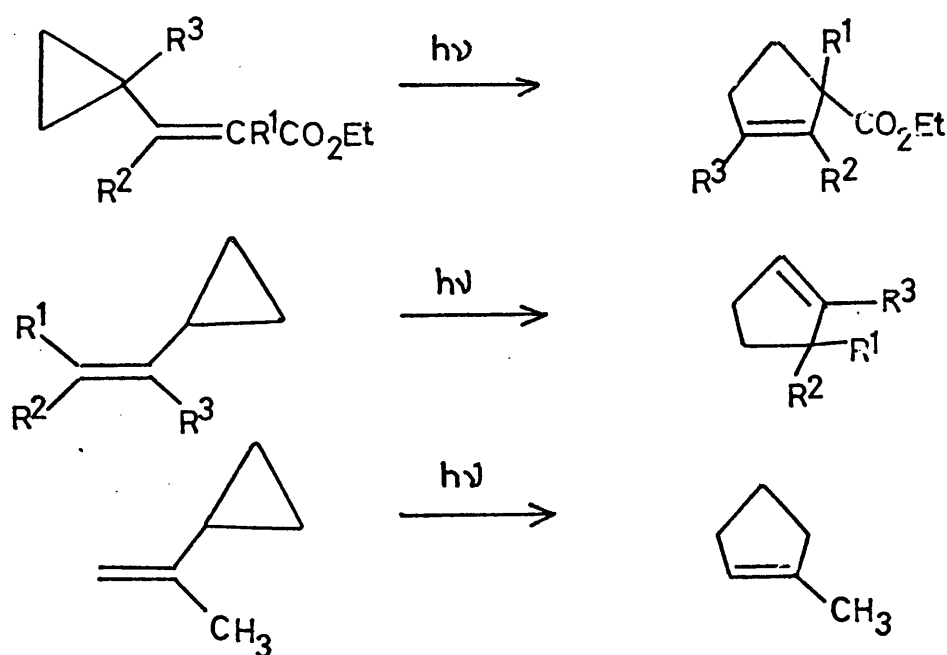
b) The cleavage of one cyclopropane bond in vinyl-cyclopropanes can lead to rearrangement to cyclopentenenes (Scheme 11).



(Scheme 11)

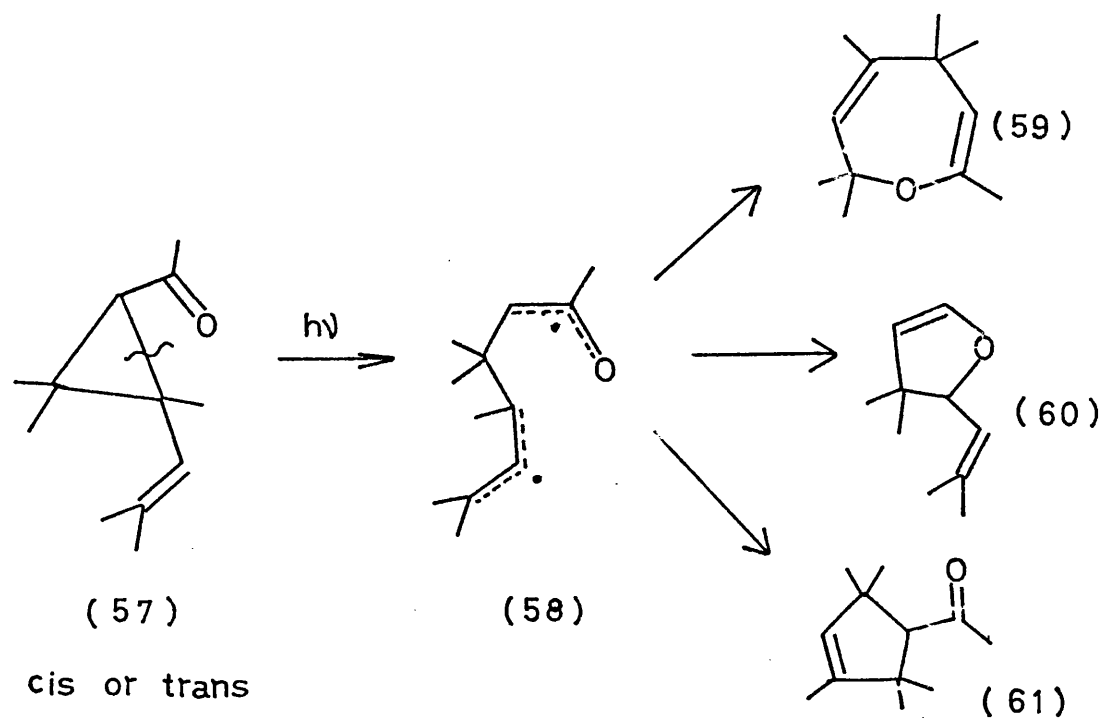
This reaction is well known thermally (see Part 2 of this thesis) but the photochemical counterpart is less well known and most compounds studied have contained the cyclopropane group constrained as part of

a bicyclic system.<sup>84-88</sup> However, several ring enlargements of monocyclic cyclopropanes have been studied<sup>65,89,90</sup> (Scheme 12). It is possible, but unlikely, that these reactions proceed by a concerted  $[1,3]$ -sigmatropic shift rather than via a diradical intermediate.

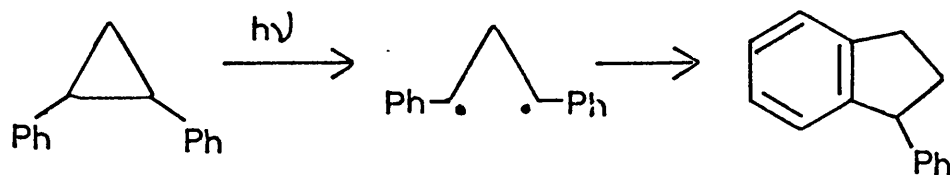


(Scheme 12)

Similar<sup>77,79</sup> ring enlargements are the formation of (59), (60), and (61) on irradiation of the vinylcyclopropane (57). The diradical (58) has been postulated as the intermediate.



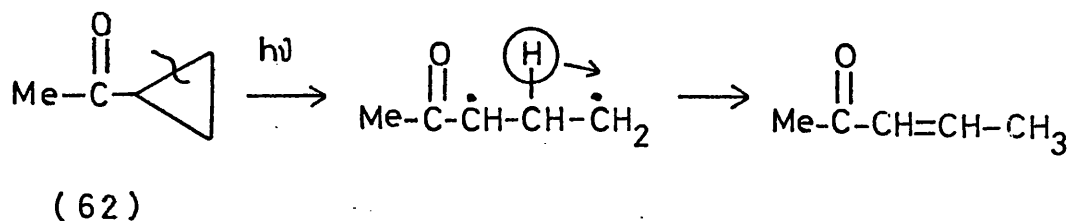
Griffin<sup>71</sup> has observed a related ring enlargement on irradiation of cis- and trans-1,2-diphenylcyclopropane (Scheme 13). This rearrangement is in competition with the fragmentation shown in Scheme 7.



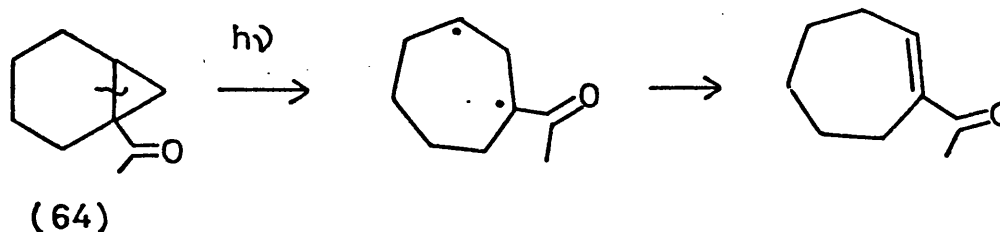
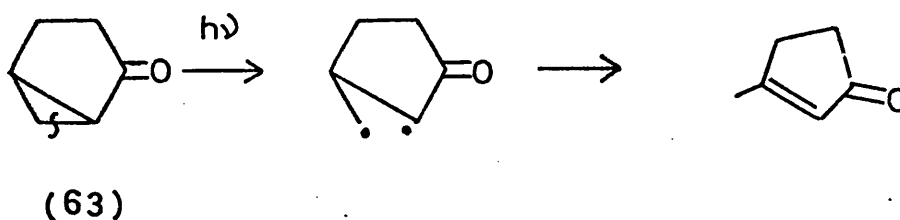
(Scheme 13)

c) Intramolecular <sup>hydrogen</sup> <sub>$\lambda$</sub>  transfer in the diradical intermediate is a well known process leading to olefin formation. Pitts and Norman<sup>91</sup> have found that methylcyclopropylketone (62), on irradiation, primarily under-

goes bond cleavage and hydrogen transfer, in competition with the Norrish Type I free radical process.



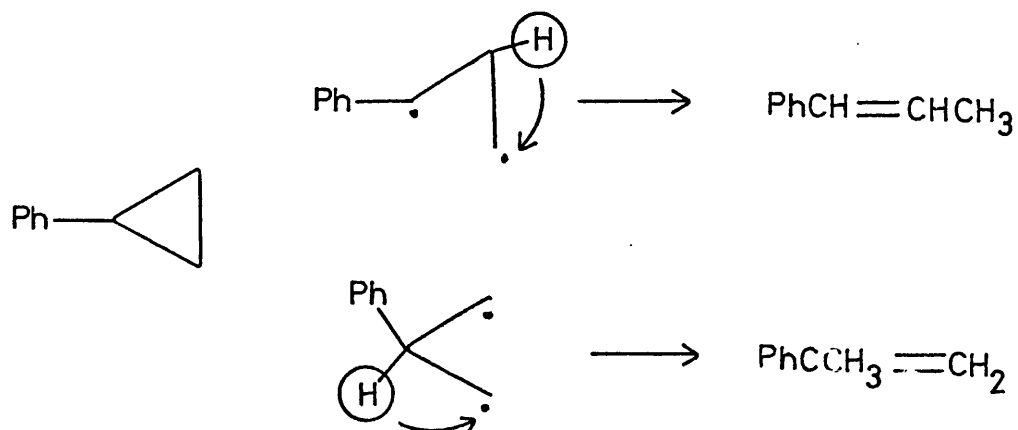
This process has also been extensively studied in bicyclic systems, for example,<sup>92,93</sup> (63) and (64). Winter<sup>93</sup> excluded the possible intervention of intermolecularly formed enolic intermediates in the rearrangement of (64) and concluded that intramolecular 1,2-hydrogen transfer was occurring, possibly concurrently with C<sub>1</sub>-C<sub>3</sub> bond cleavage.



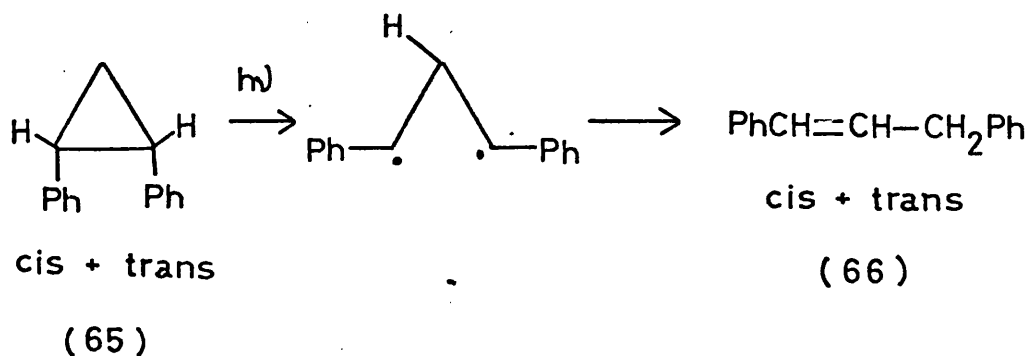
This rearrangement is not confined to cyclopropylketones; the detection of  $\alpha$ - and  $\beta$ -methylstyrenes



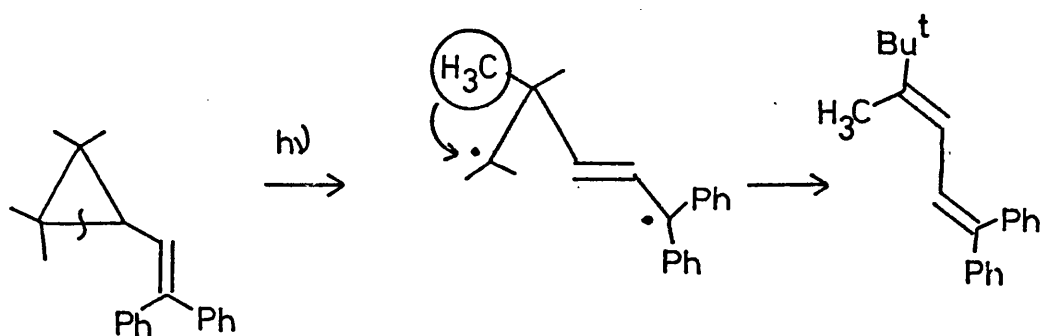
from the gas phase photolysis of phenylcyclopropane has been attributed to isomerisation of the intermediate diradicals<sup>69</sup> (Scheme 14).



Griffin<sup>71</sup> has proposed a similar mechanism for the photoisomerisation of 1,2-diarylcyclopropanes (65) to the diarylpropenes (66) (Scheme 15). This rearrangement competes with that shown in Scheme 13 and both are preceded by cis-trans isomerisation as shown in Scheme 8.

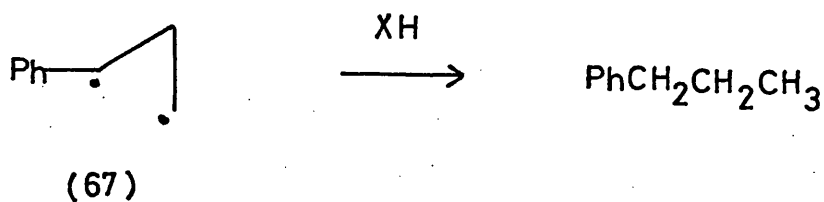


Many other examples<sup>79,81,94,95</sup> of bond cleavage and 1,2-hydrogen migration are known; Zimmerman<sup>66</sup> has observed a related methyl group migration (Scheme 16).



(Scheme 16)

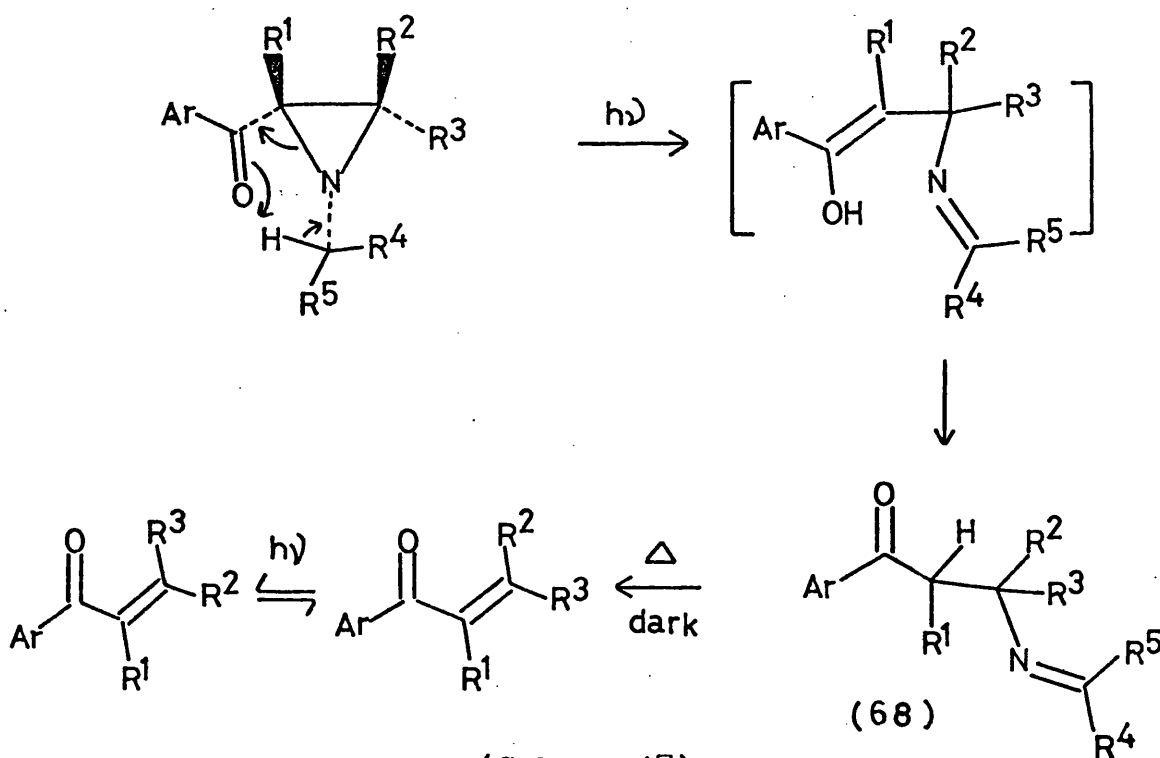
d) Intermolecular<sup>hydrogen</sup> abstraction by the diradical, formed by photocleavage of one of the cyclopropane bonds, has mainly been observed in vapour phase photolyses. Under these conditions there is little thermal deactivation with the result that less selective processes can occur. The diradical (67), as well as undergoing intramolecular proton abstraction (see Scheme 14), can undergo intermolecular reaction and form n-propylbenzene.<sup>69</sup>



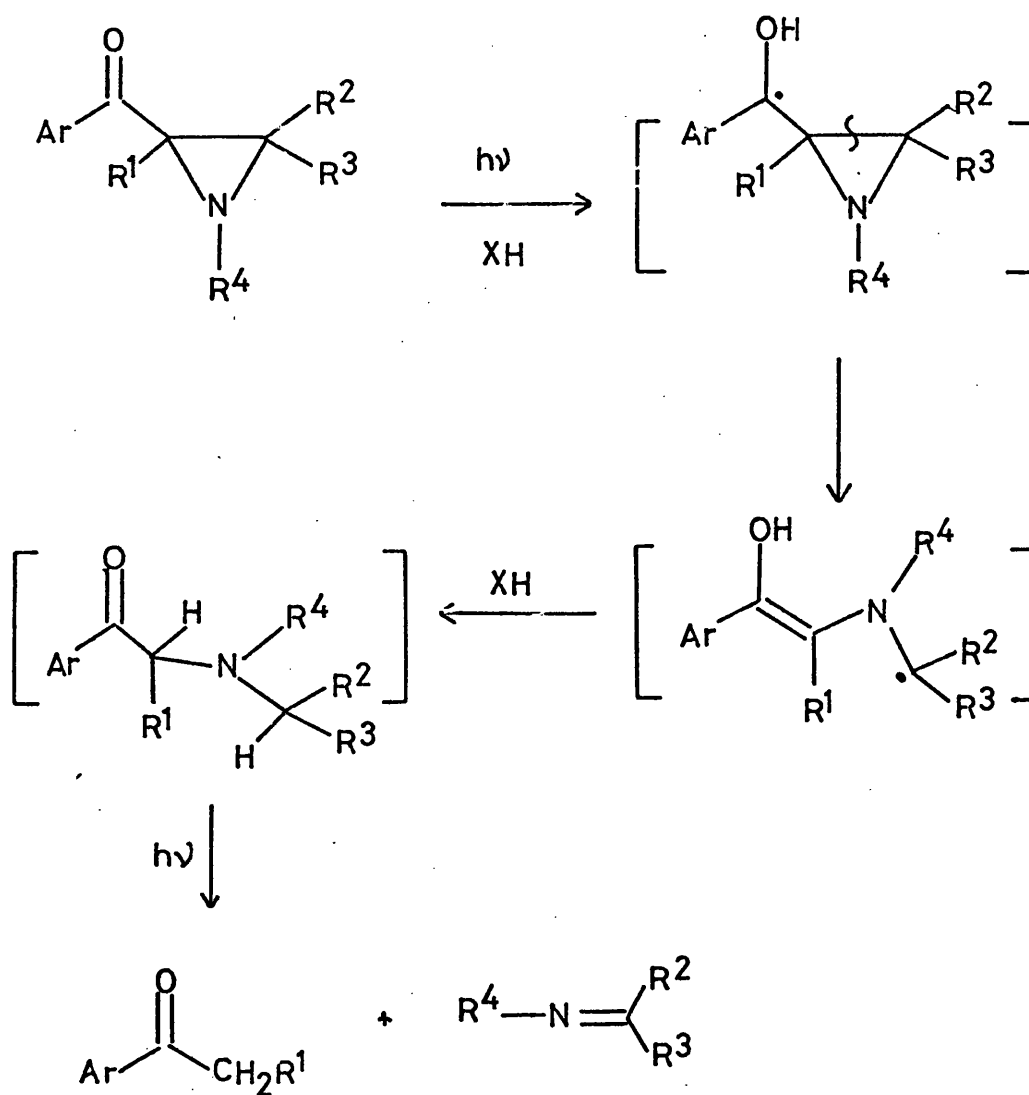
## 2. Aziridines

The photochemistry of several aroylaziridines has been investigated by Padwa<sup>96,98-100</sup> as part of a study<sup>101</sup> on the photochemical transformations of small ring carbonyl compounds. The mode of reaction was markedly dependent upon the solvent, the nature of the N-substituent, and upon the relative positions of the substituents on the three-membered ring. Padwa rationalised the products obtained by consideration of several basic mechanisms.

Mechanism A (Scheme 17) is a Norrish Type II cleavage and requires a cis arrangement of the N-substituent (which must bear an  $\alpha$ -proton). Intramolecular hydrogen transfer is involved to yield an enol, followed by rearrangement to the primary photoproduct (68).

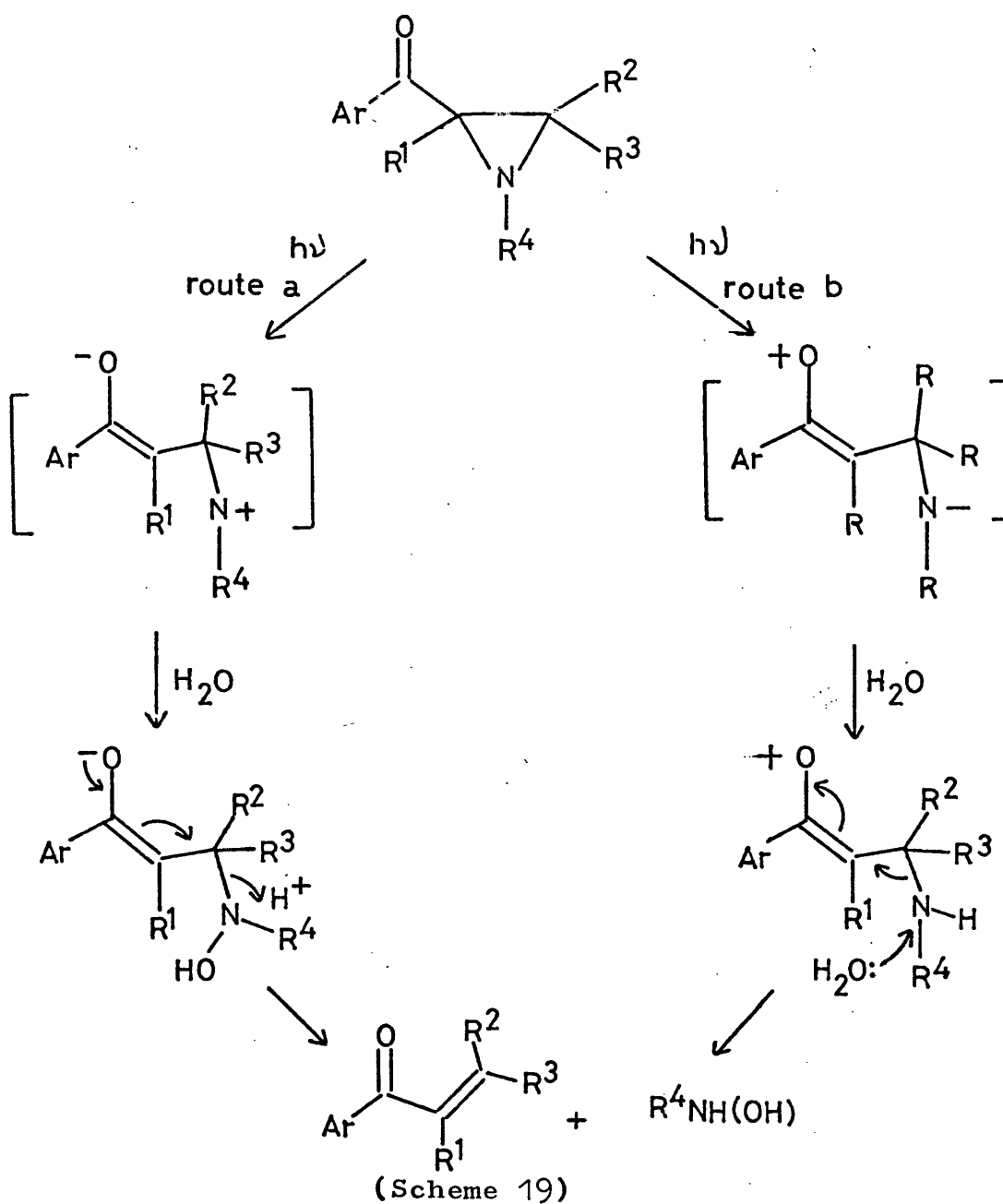


Mechanism B (Scheme 18) involves hydrogen abstraction from the solvent followed by cleavage of the C-C bond of the aziridine ring. Further proton abstraction from the solvent produces a labile  $\alpha$ -amino ketone, which photoeliminates to give the observed products. This reaction is formally similar to reaction ii.d of cyclopropanes but the detailed mechanisms are probably different because of the differing chromophores.

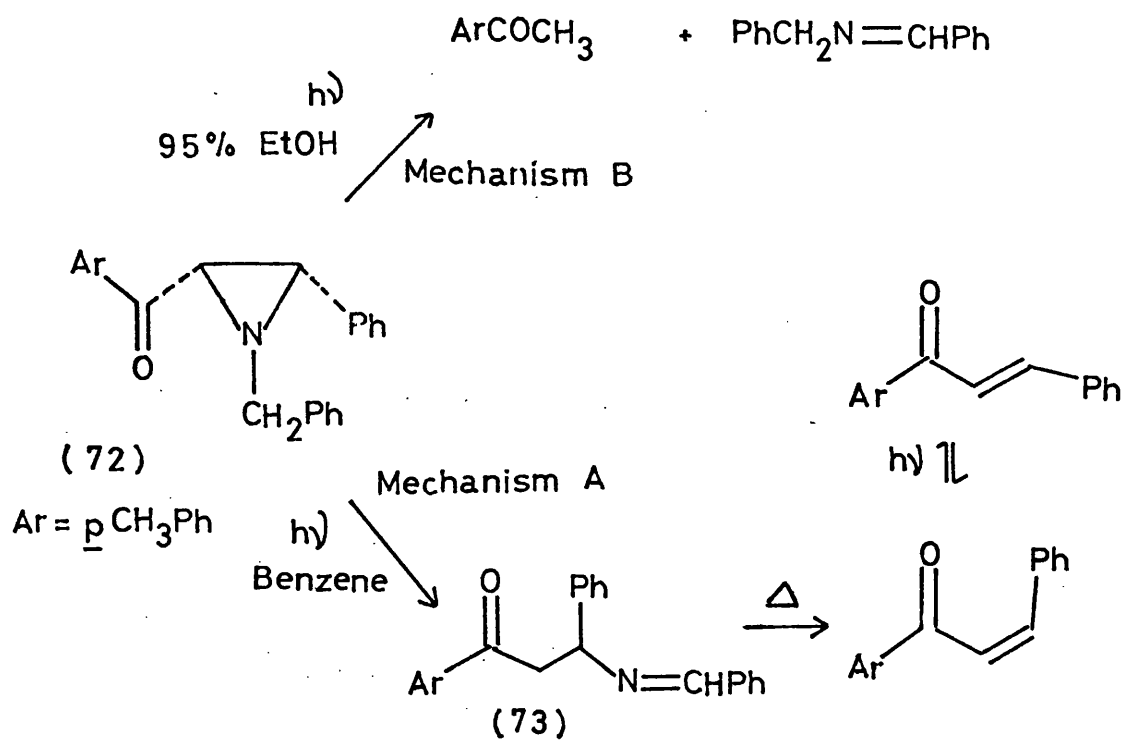
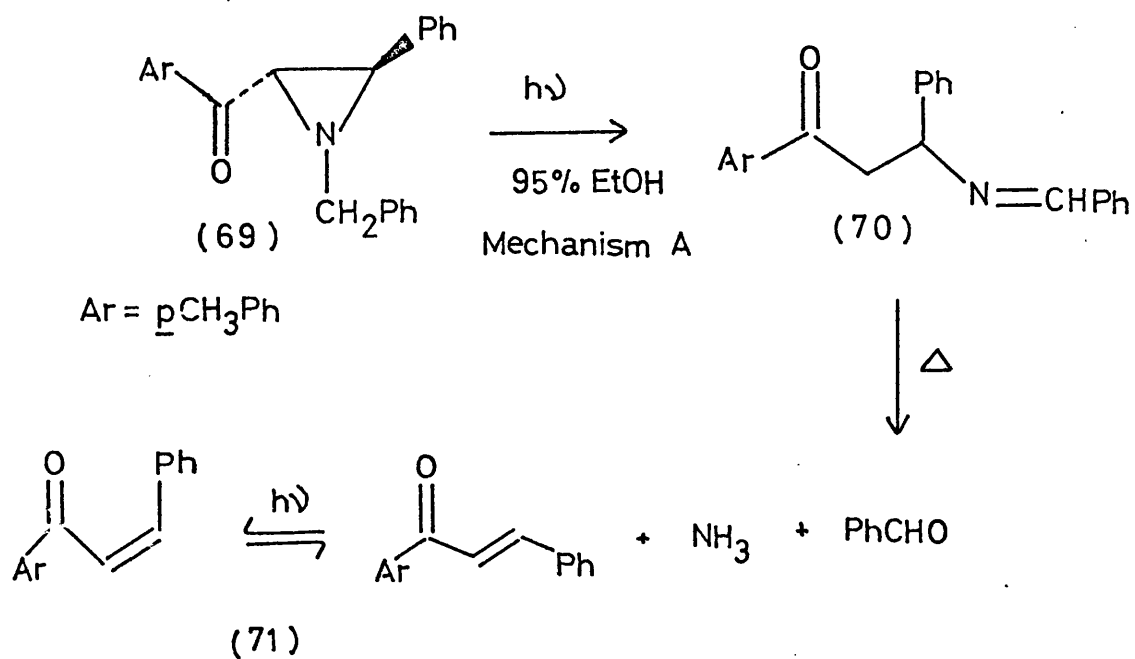


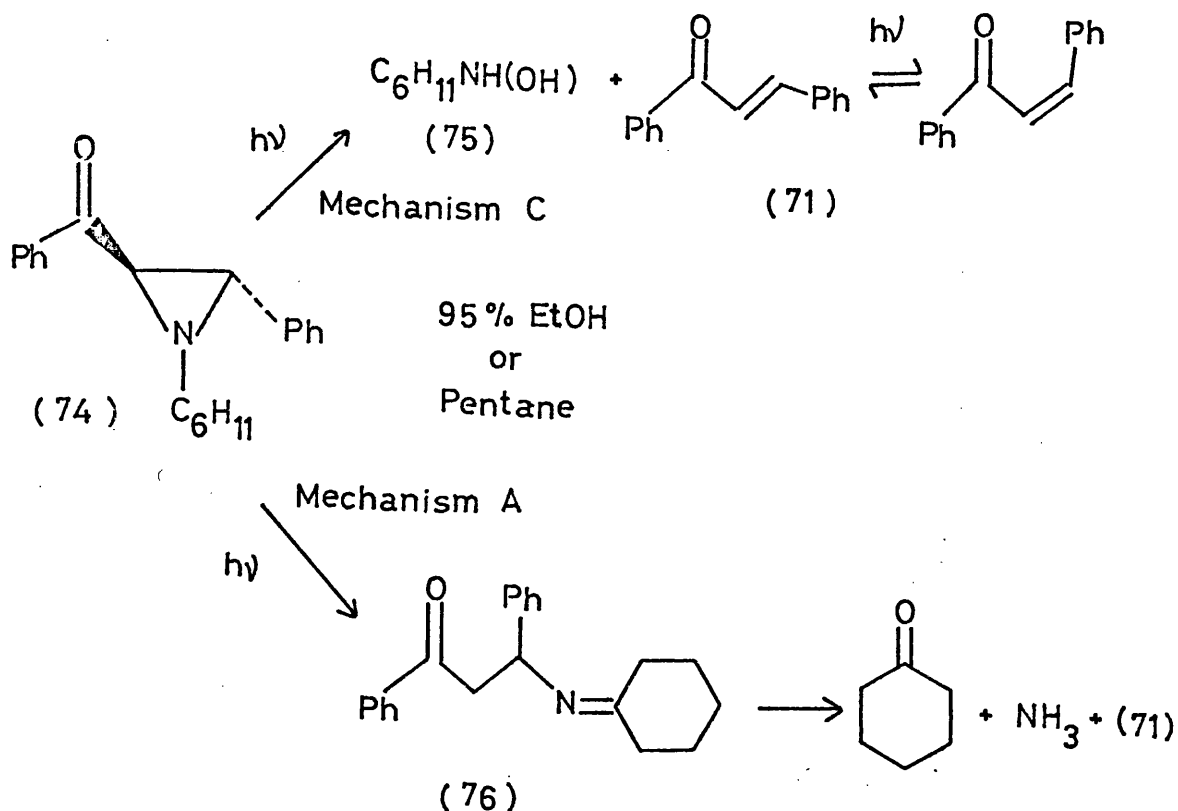
(Scheme 18)

In Mechanism C (Scheme 19), the aziridine C-N bond is cleaved photochemically to give either an electron deficient nitrogen (route a) or an electron rich nitrogen (route b). The intermediate then interacts with water to give the observed products.



The following examples serve to illustrate the mechanistic pathways:-

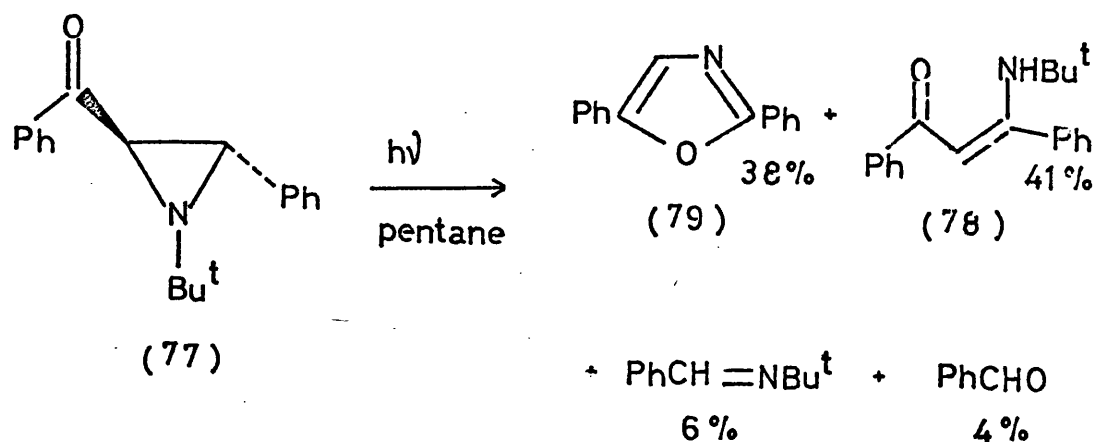




Mechanism A may be undergone by all three aziridines and involves transfer of a proton  $\alpha$  to the aziridine nitrogen onto the carbonyl oxygen. In the case of (72), the stereochemistry involved in this process demands that the bulky substituent on nitrogen be cis to the other large substituents and therefore the efficiency of this reaction is appreciably lower than that of (69). In ethanolic solution, (72) undergoes Mechanism B, involving proton abstraction from the solvent (a process not possible in benzene solution due to the high activation energy). Aziridine (74) undergoes Mechanism A to some extent but the removal of a

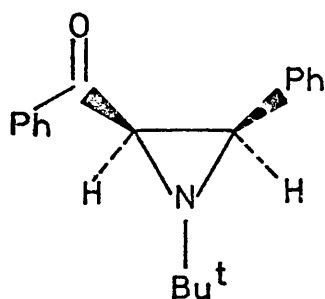
tertiary cyclohexyl proton is less favourable than removal of a benzylic proton from (69), thus allowing Mechanism C to compete. The possibility of epimerisation of the cis and trans aziridines studied by Padwa was discounted, the cis and trans olefins obtained being formed by photoisomerisation of the initially formed olefin.

Further work by Padwa<sup>98,99</sup> on the photolysis of a benzoylaziridine devoid of protons  $\alpha$  to the nitrogen atom has provided yet other decomposition routes. The major product of the irradiation of (77) is the enamine (78).

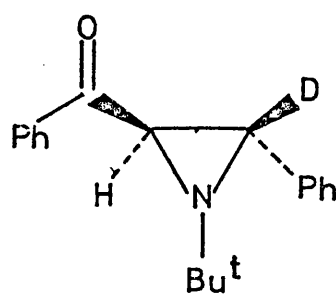


A deuterium isotope effect was observed on irradiating trans-1-*t*-butyl-2-phenyl-3-benzoylaziridine-2- $d_1$  (81) and the enamine (78) contained no deuterium. This shows that Mechanism D (Scheme 20) is operative, rather than the alternative C-N ring opening followed by a 1,2-hydrogen shift. Scheme 20 is also supported in that irradiation of cis-aziridine (80) produced oxazole (79) but no enamine (78).



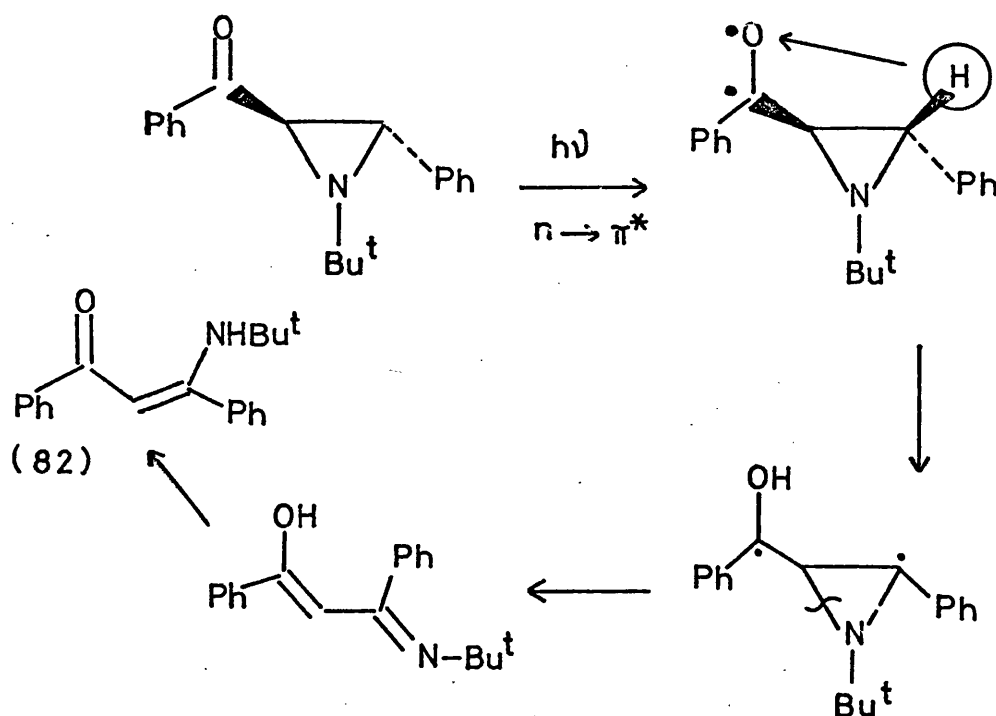


(80)



(81)

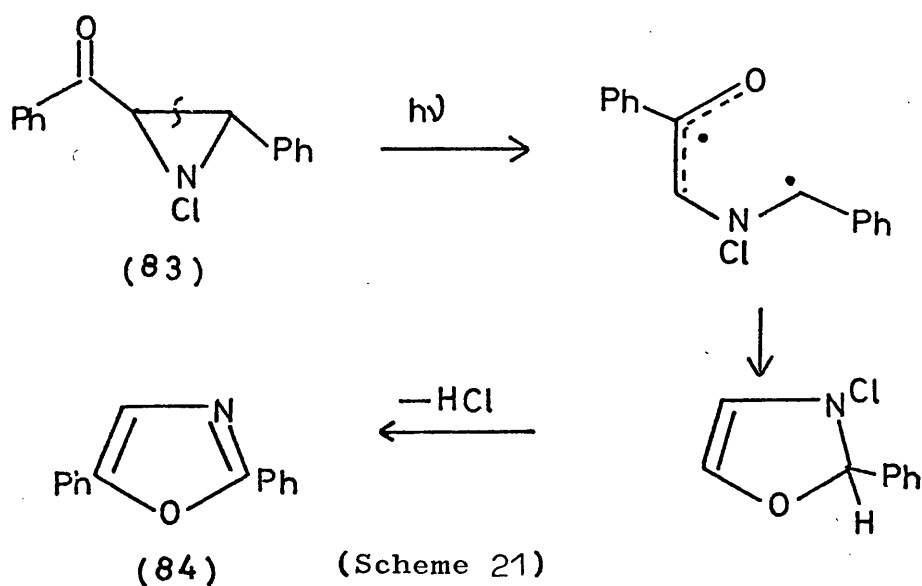
This mechanism is to be compared with the mechanisms of the formally similar reaction ii.c of cyclopropanes and the isomerisation of keto-oxiranes to  $\beta$ -diketones. Padwa has shown<sup>99</sup> that the latter occurs by ring cleavage prior to proton transfer.



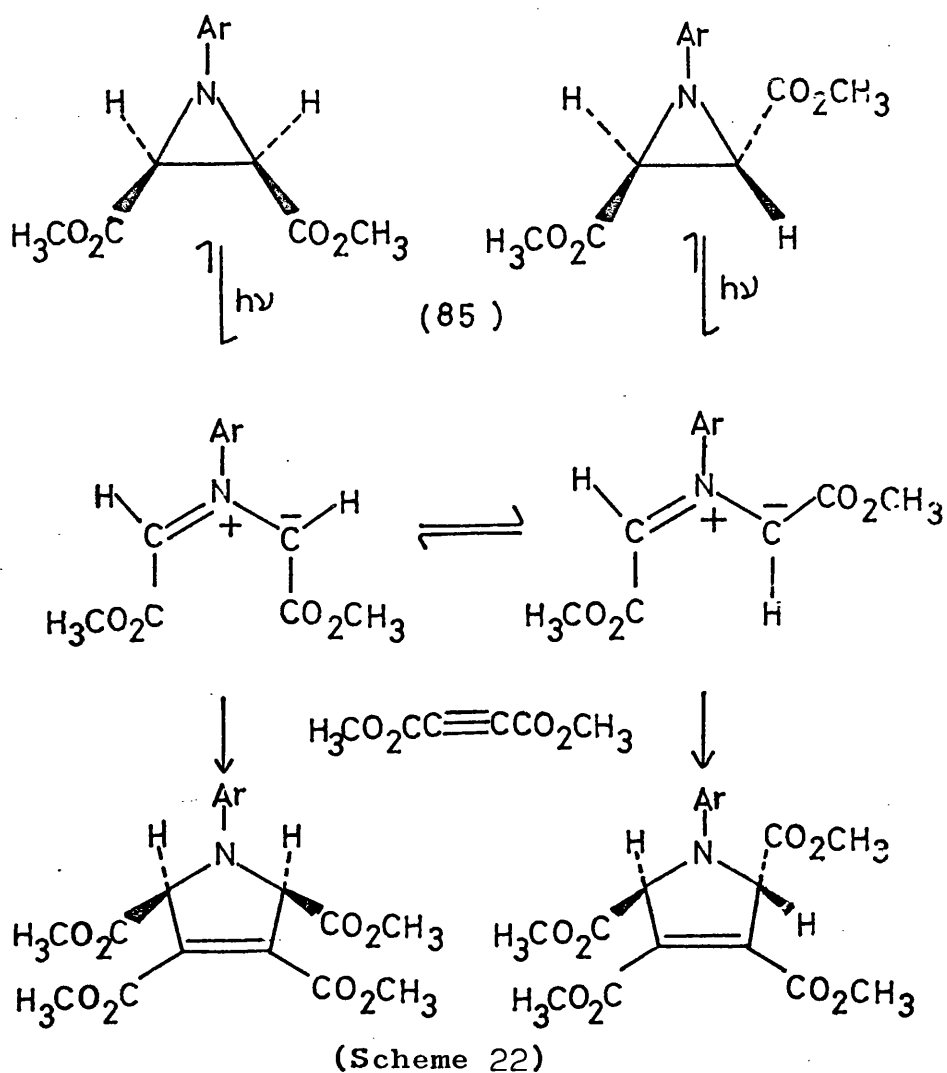
(Scheme 20)

The formation of 2,5-diphenyloxazole (79) is analogous to reaction ii.b of cyclopropanes and has

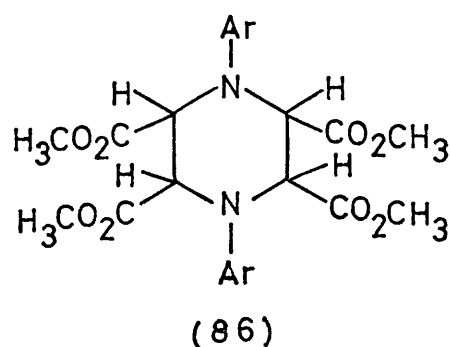
also been observed by Padwa<sup>100</sup> on irradiation of N-chlorobenzoylphenylaziridine (83). The complete absence of the iso-oxazole ring demonstrates that the aziridine ring opens exclusively by carbon-carbon fission (Scheme 21).



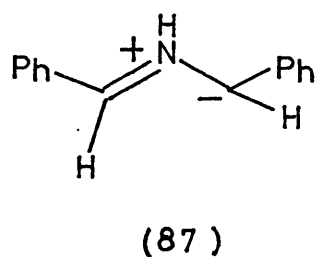
Huisgen has observed<sup>103,104</sup> C-C bond fission to lead to the formation of azomethine ylids. The photochemical ring cleavage was shown to be a disrotatory process, in agreement with the predictions<sup>105</sup> of Woodward and Hoffmann for the isoelectronic cyclopropyl anion to allyl anion rearrangement. The azomethine ylids were trapped by cycloaddition with dimethyl acetylene-dicarboxylate and the processes found to occur are shown in Scheme 22.



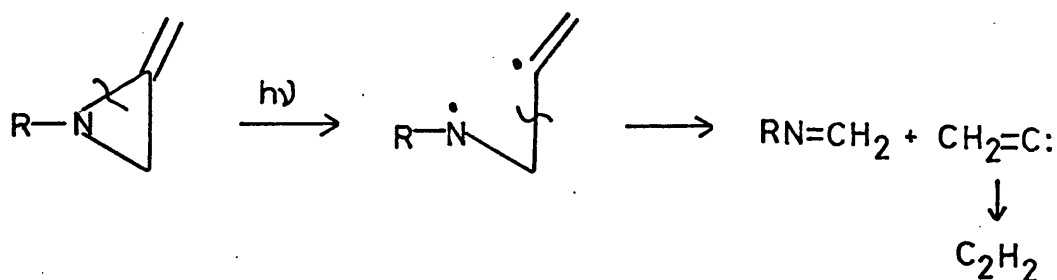
Irradiation in the absence of a dipolarophile led to isomerisation of cis - (85) to trans - (85). The reverse isomerisation did not occur and prolonged irradiation of trans - (85) produced<sup>103</sup> a mixture of diastereomeric dimers (86).



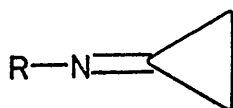
An azomethine ylid (87) has also been observed<sup>106</sup> as a yellow compound obtained on irradiation of cis-2,3-diphenylaziridine in a low temperature glass.



The gas phase photolysis of aliphatic alleneimines has been investigated<sup>107</sup> by Brinton. One of the major products was acetylene and this was rationalised as involving an initial C-N bond fission.



The other products ( $\text{RCN}$ ,  $\text{RNC}$ ,  $\text{C}_2\text{H}_4$ ) were attributed to rearrangement of the alleneimines to (88) and subsequent decomposition of this excited species.

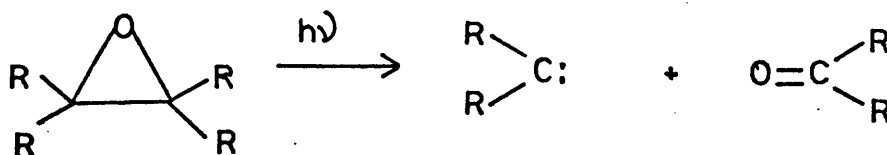


(88)

### 3. Oxiranes

Photofragmentation of oxiranes has been shown to involve both carbene formation and also alkene formation, the latter by intramolecular oxygen extrusion. At low temperatures, 1,3-dipolar species have been observed as precursors to carbene formation.

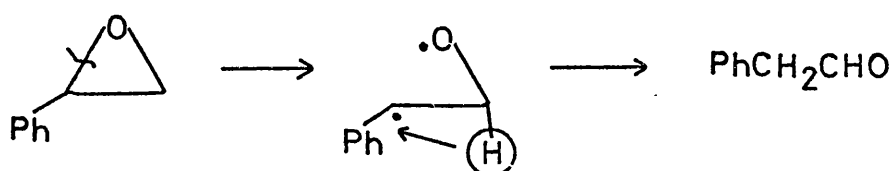
Griffin and co-workers have carried out extensive studies on carbene formation. Irradiation of a variety of phenyloxiranes has been shown<sup>61,108-110</sup> to generate arylcarbenes and aldehydes and/or ketones.



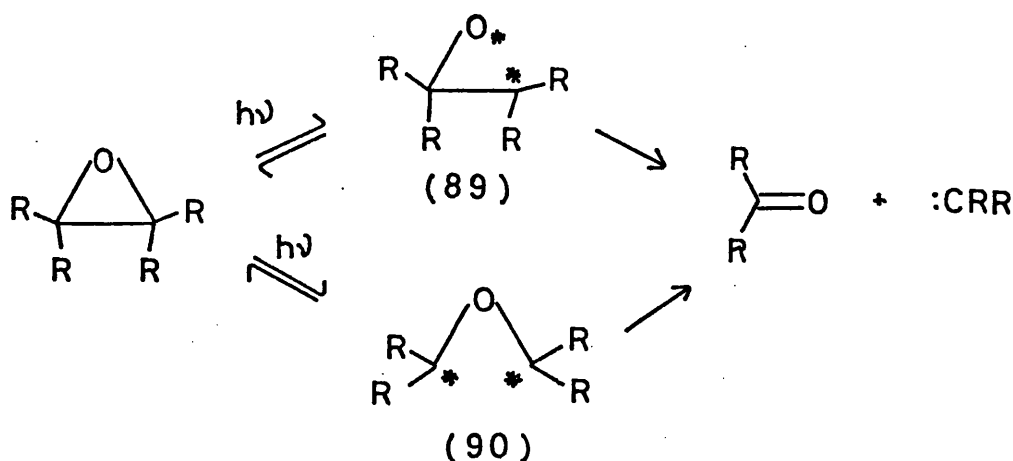
The arylcarbenes were found to react with alkanes<sup>61</sup>, alkenes<sup>109</sup>, and alcohols<sup>109</sup> both quantitatively and qualitatively in the same way as carbenes generated from diazo compounds. Oxiranes bearing cyano<sup>111</sup>,

methyl<sup>112</sup>, and carbomethoxy<sup>113</sup>, as well as phenyl substituents, photofragment similarly to give mainly the substituted arylcarbenes.

2-Phenyloxirane behaves anomalously<sup>109</sup> and gives no carbene products on irradiation. Instead, phenylacetaldehyde is formed, probably by a 1,2-hydrogen shift analogous to that observed in cyclopropane photoisomerisation (reaction ii.c of cyclopropanes).

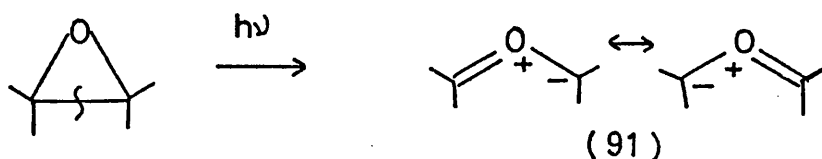


Becker and Griffin<sup>114,115</sup> have carried out rigid matrix studies at  $-196^{\circ}$  and have observed the formation of a coloured intermediate originally described as (89) or (90) (Scheme 23).

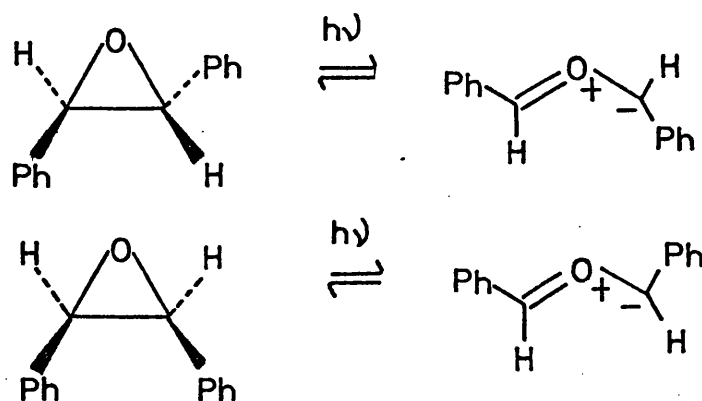


(Scheme 23)

Later work<sup>106</sup> has supported the carbonyl ylid structure (91) for the coloured intermediate. Such a structure is, of course, merely a different representation of the singlet state of the diradical (90).

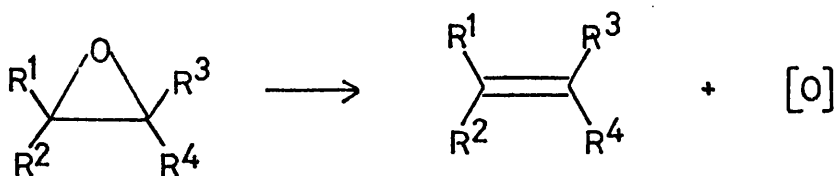


Evidence for the zwitterionic structures lies in the stereospecific ring opening and recycloisatation of cis- and trans-2,3-diphenyloxiranes with the formation of different intermediates in both cases. The intermediates are formed by a disrotatory electrocyclic reaction (Scheme 24) and were found either to regenerate the original oxirane on irradiation in the visible region, or to fragment to benzaldehyde and phenylcarbene on warming to 140°K.

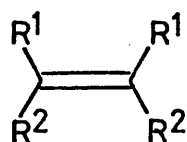


(Scheme 24)

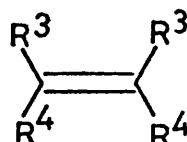
Griffin has also observed<sup>114,115</sup> oxygen extrusion and alkene formation (Scheme 25). The absence of crossover products (92) and (93) as primary photo-products excludes an intermolecular path for alkene formation.



(Scheme 25)

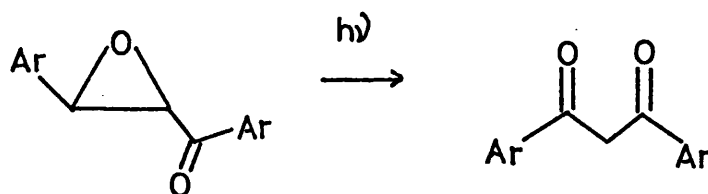


(92)



(93)

A further photochemical reaction of oxiranes is the isomerisation of keto-oxiranes to  $\beta$ -diketones.

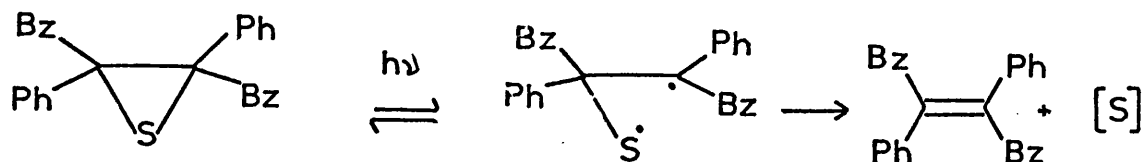




This well known reaction<sup>102,116,117</sup> is formally comparable to the photorearrangement of cyclopropylketones to keto-olefins (reaction ii.c of cyclopropanes) and has been shown<sup>99</sup> to involve ring bond cleavage before proton transfer, in contrast to the similar aziridine rearrangement (proton transfer before ring bond cleavage, see Scheme 20).

#### 4. Thiiranes

Photodesulphurisation of thiiranes has been observed<sup>114,115,118,119</sup> and the reaction has been postulated as proceeding by way of a diradical intermediate formed by C-S bond cleavage of the excited thiirane.

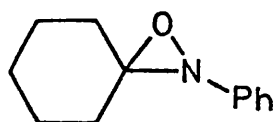


Thiiranes shown to undergo this reaction include cis- and trans-2,3-dibenzoyl-2,3-diphenylthiirane<sup>118</sup> (which were also observed to photoisomerise), trans-2,3-diphenylthiirane<sup>119</sup>, and tetraphenylthiirane.<sup>114,115</sup> The irradiation of the last, both in solution at 40° and at low temperature in a rigid matrix, gave no detectable thiobenzophenone or diphenylcarbene. The low temperature irradiation<sup>114,115</sup> was analogous to that observed for similar oxiranes and produced a coloured intermediate,

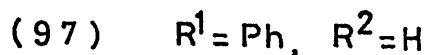
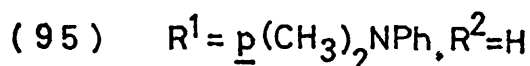
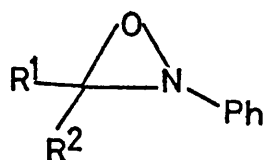
presumably of zwitterionic structure.

## 5. Oxaziridines

Oxaziridine photofragmentation has been found to be a convenient source of nitrenes. Phenyl-nitrene, for example, has been generated<sup>120,121</sup> by photolysis of the oxaziridines (94) - (97).

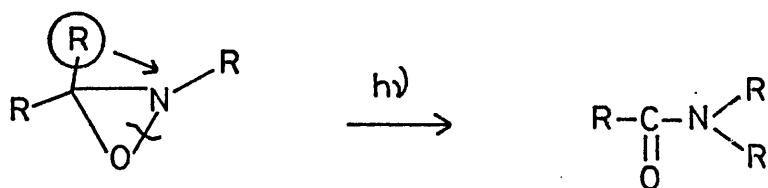


(94)

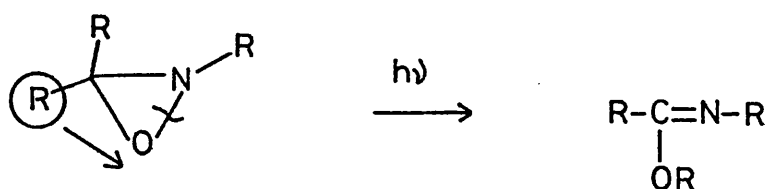


Quenching and photosensitisation experiments on (96) have shown<sup>121</sup> that the triplet state of the oxaziridine is involved in the fragmentation. No diphenylcarbene could be detected in the photolysis of (96).

Photorearrangement has also been observed<sup>121,122</sup>. Formally, N-O bond cleavage is followed by migration of a group (H, alkyl, or aryl), either from carbon to nitrogen (Scheme 26) or from carbon to oxygen (Scheme 27), in a process analogous to reaction ii.c of cyclopropanes.

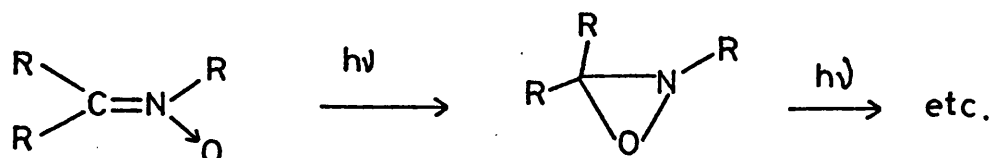


(Scheme 26)



(Scheme 27)

These rearrangements are often observed in the photolysis of nitrones, where oxaziridines are first formed<sup>122,123</sup> (Scheme 28).



(Scheme 28)

It is apparent that a variety of decomposition modes are available to an excited three-membered ring molecule and detailed mechanisms are often dominated by the electronic characteristics of the ring substituents. However, certain generalisations are possible.

Photocleavage of a single three-membered ring bond has been observed for cyclopropanes, aziridines, oxiranes, thiiranes, and oxaziridines. This may lead to cis-trans isomerisation (e.g. cyclopropanes, aziridines, and thiiranes) or ring enlargement (e.g. cyclopropanes, and aziridines) if suitable substituents are present. Formal migration of a hydrogen atom or group from the carbon atom situated between the two radicals has been observed in all systems (in some systems, however, the proton transfer may occur in concert with ring cleavage) and proton abstraction by the diradical has been observed in cyclopropanes and aziridines. In addition, zwitterions may be produced from aziridines at normal temperatures and from oxiranes and thiiranes at low temperatures. The carbonyl ylids have been suggested as intermediates in carbene formation by low temperature oxirane photolysis but need not be involved at normal temperatures. Indeed, there is evidence that cyclopropanes can undergo carbene formation by simultaneous cleavage of two bonds. The analogous fragmentation in aziridine photochemistry has not been observed although photochemically induced reaction of cis-2-phenyl-3-benzoyl-1-cyclohexylaziridine formally involves extrusion of the heteroatom.

EXPERIMENTAL

### Instrumentation and Experimental Techniques

1. Infra red (i.r.) spectra were recorded in the range 4000-625  $\text{cm}^{-1}$  using Perkin Elmer 237 and Pye Unicam SP200 spectrophotometers. Abbreviations used are strong (s), medium (m), weak (w), variable (v), broad (b), and sharp (sh). Spectra of solids were taken as Nujol mulls and liquids as thin films between sodium chloride plates.
2. Ultra violet and visible (u.v.) spectra were recorded in the range 200-700 nm. using a Pye Unicam SP800 recording spectrophotometer. Solvents used are indicated in the text.
3.  $^1\text{H}$  Nuclear magnetic resonance (n.m.r.) spectra were recorded on Varian T60, A60, DA60, HA100, and HR220 instruments; unless otherwise stated, one of the 60 MHz machines was used. Signals are quoted as singlets (s), doublets (d), triplets (t), quartets (q), or multiplets (m). Where a single  $\tau$  value is given for a multiplet, then that is the position of the centre of gravity of the signal, the signal being an envelope peak. Where a range of  $\tau$  values is given for a multiplet then there is more than one line and the values represent the positions of the extreme signals. Solvents used are indicated in the text and tetramethylsilane was used as an internal reference. For variable temperature spectra, the n.m.r. probe temperatures were determined by calibration with ethylene glycol.

4. Routine mass spectra were recorded at low resolution on A.E.I. mass spectrometers type MS9 and MS12. In the text, the mass peak is given first, followed by those of structural significance. Peak intensities are recorded as fractions of the intensity of the base peak. The structure of fragment ions, where given, is nominal. High resolution mass spectra were recorded using an A.E.I. MS902 machine linked to a Ferranti Argos 500 data processor. The purity of compounds submitted for high resolution mass spectrometry was carefully ascertained by thin layer chromatography on silica and alumina in several solvent systems. No peaks of significant intensity were observed at  $m/e$  greater than the mass peak. Unless otherwise stated all spectra were run at 70 eV and samples were introduced using a direct insertion probe with the ionisation temperature below the decomposition temperature of the sample.

5. Melting points (m.p.) were taken on a Kofler Micro Heating Stage using corrected thermometers.

6. Solvents:

Petroleum refers to petroleum spirit b.p. 40-60° unless otherwise stated. For mixed solvent recrystallisations with either ethyl acetate, benzene, or chloroform, petroleum spirit b.p. 60-80° was used.

Acetonitrile was purified and dried by reflux over phosphorus pentoxide and distillation from fresh phosphorus pentoxide

onto molecular sieves (4A).

Other solvents were dried by standard techniques.

7. Column chromatography was carried out using silica gel M.F.C. (B.D.H. or Hopkins and Williams) or basic alumina (Spence Type H). Unless otherwise stated, reagent grade solvents were used as eluants without preliminary drying.
8. Thin layer chromatography (t.l.c.) was used extensively as a qualitative guide during reactions and for assessing the purity of compounds. Samples were run in suitable solvent mixtures on glass plates coated with a 0.25 mm. layer of Silica Gel GF<sub>254</sub>, Aluminium oxide G(Type E), or Aluminium oxide GF<sub>254</sub> (Merck). The plates were observed under ultra violet light or developed with iodine vapour.
9. Preparative layer chromatography (p.l.c.) was performed using 20 x 20 or 100 x 20 cm. glass plates coated with a 1 mm. layer of Silica Gel PF<sub>254</sub> or Aluminium oxide PF<sub>254</sub> (Merck).
10. Gas chromatography (g.c.) was performed on Perkin Elmer F11 instruments using nitrogen carrier gas and a flame ionisation detector.
11. Lead tetra-acetate (B.D.H., Hopkins and Williams, or Koch-Light) was freed from acetic acid by filtration, washed with a little anhydrous ether, and stored over concentrated sulphuric acid.



12. Where possible, compounds were characterised by comparison of their m.p. and mixed melting points (m.m.p.), i.r., and n.m.r. spectra with those of authentic specimens. Literature m.p. values are given with references except for well authenticated compounds for which the values quoted are those given in the Heilbron Dictionary of Organic Compounds (4th Edition).

13. Photolysis procedures:

Method 1. The solution to be photolysed was contained in a vessel of capacity 100 ml. and was magnetically stirred. A water-cooled Hanovia 125 watt mercury arc medium pressure lamp was fitted internally. The lamp jackets were of quartz and the lamp output was mainly at the following lines:- 254, 265, 297, 313, and 366 nm..

Method 2. The solution was contained in a quartz tube of capacity 25 ml. and irradiated in an air-cooled Rayonet reactor fitted with 16 x 21 watt medium pressure mercury arc lamps, giving a broad emission spectrum between 250 and 360 nm. with a maximum at 300 nm.. When several solutions were irradiated concurrently then the tubes were mounted on a rotary stand at the centre of the Rayonet so that each solution would receive equal irradiation.

Method 3. The solution was irradiated as in Method 1 except that the lamp and apparatus were not of Hanovia make but were constructed in the workshops of the

University of Leicester, to a specification prepared by Dr. R.S. Davidson. The spectral characteristics were practically the same as those of Method 1.

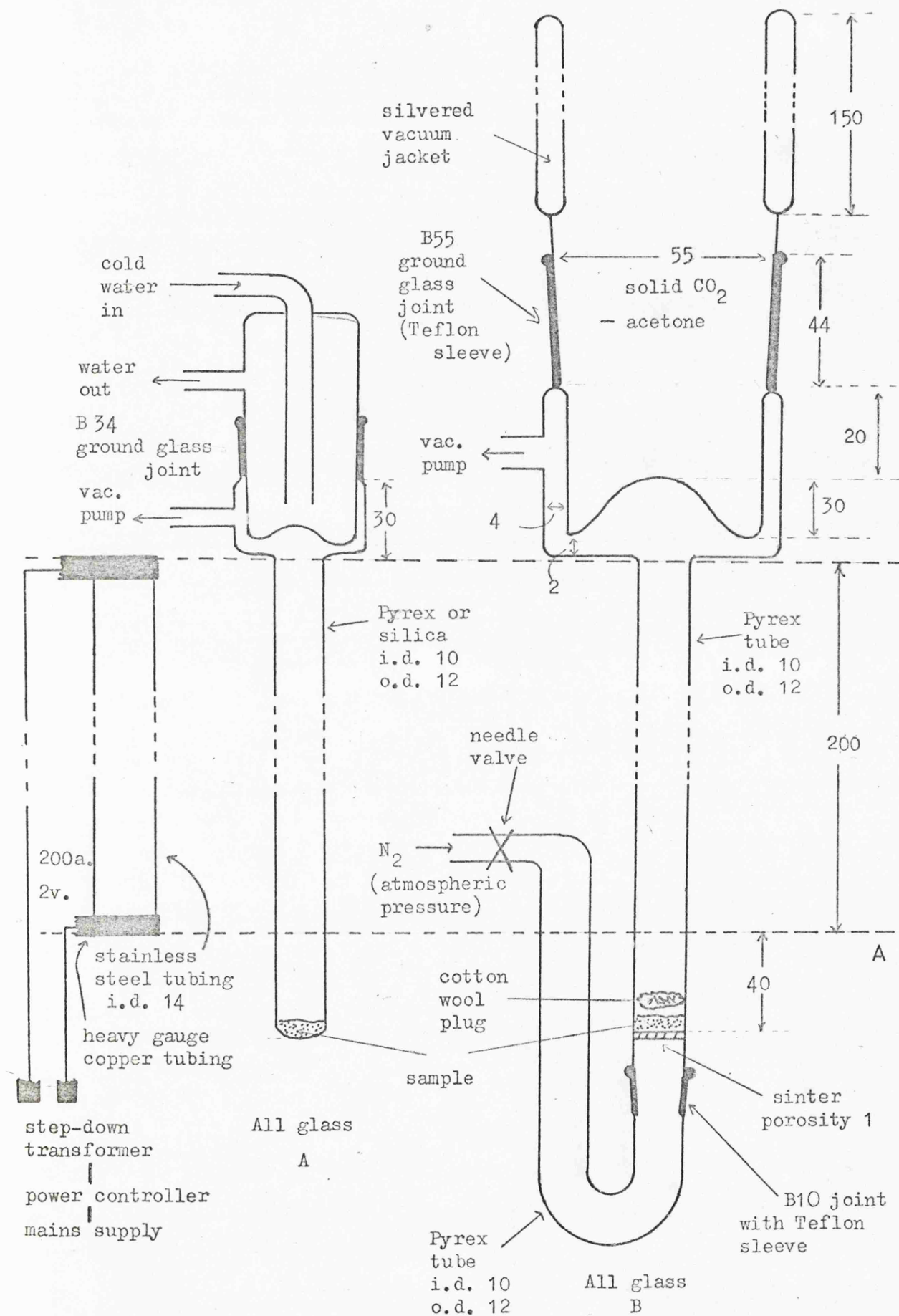
14. Vapour phase flash pyrolysis

The apparatus used for this high temperature-short contact time technique was constructed at the University of Liverpool by Mr. S.A. Minns, whose efforts are gratefully acknowledged, and evolved from a prototype constructed by Dr. D.L. Forster of the University of Leicester. Improvements, some of which are detailed below, were made in the course of this work and the final apparatus used is shown on page 67.

Controlled heating of the sample was obtained by immersion of the lower portion of the pyrolysis tube (the region below the dotted line A in the diagram) in an electrically heated oil bath. This procedure ensured uniform heating and enabled constant observation of the sample.

The pyrolysate was collected using either a water-cooled or a Drikold-acetone cooled trap. The latter was the more efficient and was also found preferable in that the pyrolysate was better protected from heat radiated by the furnace. Normally a closed pyrolysis system was used, either with a water-cooled or Drikold-acetone cooled trap, but several compounds decomposed before entering the vapour phase. The movement of a vapourised compound from the sample area at, say, 1000°, to the cold trap via the tube heated at, say, 5000°, is obviously energetically unfavourable. To overcome this the flow system was

designed so that the vapour of the compound would be diluted with inert gas and would only then exert a partial vapour pressure in opposition to passage of the compound through the tube. Although somewhat limited by the capacity of the vacuum pumps available, the system did enable some pyrolyses to be performed that had failed with the simpler closed apparatus. A pressure of 0.4 torr could be maintained with a nitrogen flow rate of 5 ml./min.; with a zero flow rate the pressure dropped to 0.05 torr. It should be noted that the pressures quoted for all pyrolyses were measured at a point just before the traps of the oil pump and are not intended to indicated pressures in the actual pyrolysis area.



Experimental : Part 1, Section 1Preparation of phthalimido-aziridines

N-Aminophthalimide was prepared by the method of Drew and Hatt,<sup>124</sup> from phthalimide and hydrazine hydrate, and had m.p. 200-202° (lit.,<sup>124</sup> 200-205°).

A suspension of N-aminophthalimide in a mixture of dichloromethane (ca. 15 ml./g. of N-amino) and the olefin (5 molecular equivalents) was stirred at room temperature while lead tetra-acetate (1.0 - 1.1 molecular equivalents) was added in portions over 5 min.. Stirring was continued for a further 10 min. and then the lead salts were filtered off and washed with a little dichloromethane. The combined filtrate and washings were extracted with 2% w/v aqueous sodium hydroxide (ca. 100 ml./g. of N-amino) and then water. The organic phase was dried and rotary evaporated to give the crude product as an oil which generally crystallised on scratching under petroleum. Recrystallisation gave the pure aziridine. The physical properties of the aziridines were as described<sup>35</sup> except for the following aziridines which are new compounds.

trans-3-Isopropyl-2-methyl-1-phthalimidoaziridine The oxidation of N-aminophthalimide in the presence of trans-4-methylpent-2-ene gave a crude product which could not be crystallised. P.l.c. on a 1 m. alumina plate eluted with ether gave an oil (12%) which crystallised on manipulation under petroleum. Recrystallisation from ether-petroleum, with cooling at -50°, gave trans-3-

isopropyl-2-methyl-1-phthalimidoaziridine as yellow

granules, m.p. 55-57° (Found: C, 68.7; H, 6.5; N, 11.6.

$C_{14}H_{16}N_2O_2$  requires C, 68.8; H, 6.6; N, 11.5%. M 244).

$\nu_{\max}$ . 1780, 1765, 1715 br. (C=O), 1470, 1380, 1141, 1055, 890, 717, and 710  $cm^{-1}$ .

$\tau$  (CDCl<sub>3</sub>, 220 MHz) 8.96 and 8.78 (two d, each 3H, J 6.8 Hz, Me groups of isopropyl), 8.71 (3H, d, J 5.8 Hz, aziridine ring Me), 8.46 (1H, m, isopropyl proton), 7.54 (1H, dq,  $J_{H-2,H-3}$  5.8 Hz,  $J_{H-2,2-Me}$  5.8 Hz, H on C-2), 7.34 (1H, dd,  $J_{H-3,H-2}$  5.8 Hz,  $J_{H-3}$ , isopropyl proton 8.4 Hz, H on C-3) and 2.28 (4H, m, aromatics).  
m/e 244 (0.33)  $M^+$ , 229 (0.17) (M-Me)<sup>+</sup>, 201 (0.11) (M-Pr<sup>i</sup>)<sup>+</sup>, 189 (0.22), 174 (0.08), 162 (0.08), 147 (0.25) (phthalimide)<sup>+</sup>, 130 (0.25), 104 (0.19), 98 (1.00), and 77 (0.25).

$\lambda_{\max}$ . (EtOH), nm. ( $\epsilon$ ) 240 (24,500), 285 shoulder (1060), 295 (1210), 305 shoulder (980), and 340 (500).

cis-3-Isopropyl-2-methyl-1-phthalimidoaziridine The oxidation of N-aminophthalimide in the presence of cis-4-methylpent-2-ene gave a crude product which could not be crystallised. P.l.c. on a 1 m. alumina plate eluted with ether gave an oil (17%) which solidified overnight. Recrystallisation from ether-petroleum gave cis-3-isopropyl-2-methyl-1-phthalimidoaziridine as yellow granules, m.p. 67-69° (Found: C, 68.7; H, 6.5; N, 11.4.  $C_{14}H_{16}N_2O_2$  requires C, 68.8; H, 6.6; N, 11.5%. M 244).

$\nu_{\text{max.}}$  1768, 1715 br. (C=O), 1470, 1380, 1295, 1190, 1180, 1150, 1089, 1040, 1025, 900, 890, 715, and 705  $\text{cm}^{-1}$ .

$\tau$  ( $\text{CDCl}_3$ , 220 MHz) 9.02 and 8.61 (two d, each 3H, J 6.8 Hz, Me groups of isopropyl), 8.57 (3H, d, J 6.0 Hz, aziridine ring Me), 8.43 (1H, m, isopropyl proton), 7.62 (1H, dd,  $J_{\text{H-3,H-2}}$  8.3 Hz,  $J_{\text{H-3,isopropyl proton}}$  9.5 Hz, H on C-3), 7.44 (1H, dq,  $J_{\text{H-2,H-3}}$  8.3 Hz,  $J_{\text{H-2,2-Me}}$  6.0 Hz, H on C-2), and 2.40 (4H, m, aromatics).

$m/e$  244 (0.75)  $\text{M}^+$ , 229 (0.42)  $(\text{M-Me})^+$ , 202 (0.44), 201 (0.38)  $(\text{M-Pr}^i)^+$ , 189 (0.69), 174 (0.17), 162 (0.19), 147 (0.96)  $(\text{phthalimide})^+$ , 130 (1.00), 104 (0.67), 98 (0.87), and 77 (0.67).

$\lambda_{\text{max.}}$  (EtOH), nm. ( $\epsilon$ ) 237 (25,000), 285 shoulder (790), 295 (950), 304 (810), and 340 shoulder (370).

All of the phthalimido-aziridines studied, with a conjugating substituent or not, gave very similar u.v. spectra as follows:

$\lambda_{\text{max.}}$  (EtOH), nm. ( $\epsilon$ ) 231-244 ( $\sim 25,000$ ), 285-288 shoulder ( $\sim 900$ ), 294-296 ( $\sim 1000$ ), 303-308 shoulder or weak maximum ( $\sim 950$ ) and 340-350 shoulder or weak maximum ( $\sim 400$ ).

#### Photolysis of phthalimido-aziridines in the presence of olefins

##### General Procedure:

The aziridine was dissolved in pure, dry acetonitrile and the appropriate olefin added. The solution was then irradiated by one of the Methods 1-3 detailed on page 64. After irradiation, the solution was examined

by t.l.c., and then rotary evaporated to remove acetonitrile and the added olefin. In some instances the residue was examined by n.m.r., in which case the occluded substances were removed by alternate addition of  $\text{CCl}_4$  and rotary evaporation. The residue was finally held under high vacuum for several hours to remove the last traces of volatile material before examination by n.m.r..

The photolyses were generally not taken to completion due to the prolonged irradiation periods required. Rl.c. was used to facilitate rapid separation of the aziridines, which have similar  $R_F$  values and are labile on chromatography. The residence time (the period between application to the plate and elution of the compound from the support) was kept to a minimum by running the plate only partly to completion where the aziridines were more easily separable. Even so, the recovery of the aziridines from the plates was often low. The separated aziridines were obtained as oils which crystallised spontaneously or on scratching. They were identified, and the purity established, by t.l.c. and n.m.r. comparison with authentic samples prepared by the oxidation of the N-amino compound in the presence of the appropriate olefin.

The results of the experiments are given in note form. In each case, the results are recorded in the following order: Experiment Number. Aziridine



photolysed (weight); olefin (volume); photolysis method (time); n.m.r. analysis of crude photolysate; method of p.l.c. work up; compounds isolated (yields); other remarks.

The solvent used was dry acetonitrile unless otherwise stated.

Expt. No. 1. 3-Acetyl-2,2-dimethyl-1-phthalimidoaziridine (500 mg.); cyclohexene (10 ml.); method 1 (48 hr.); no n.m.r. obtained; 1 m. silica/ether-petroleum (1:1); 7-phthalimido-7-azabicyclo[4,1,0]heptane (176 mg., 39%) and starting aziridine (133 mg., 27%).

Expt. No. 2. Methyl 2-methyl-1-phthalimidoaziridine-2-carboxylate (480 mg.); cyclohexene (10 ml.); method 1 (48 hr.); no n.m.r. obtained; 1 m. silica/ether-petroleum (1:1); 7-phthalimido-7-azabicyclo [4,1,0]heptane (342 mg., 81%). No starting aziridine was recovered but the authentic spot failed to run on the plate.

Expt. No. 3. 2-Phenyl-1-phthalimidoaziridine (500 mg.); cyclohexene (10 ml.); method 1 (60 hr.); no n.m.r. obtained; 1 m. silica/ether-petroleum (1:1); starting aziridine (45 mg., 9%) and 7-phthalimido-7-azabicyclo-[4,1,0]heptane (110 mg., 24%).

Expt. No. 4. Methyl trans-2-methyl-1-phthalimidoaziridine-3-carboxylate (500 mg.); cyclohexene (10 ml.); method 1 (68 hr.); no n.m.r. obtained; 1 m. alumina/ether-petroleum (7:3); 7-phthalimido-7-azabicyclo[4,1,0]heptane (70 mg., 15%), no starting aziridine recovered (authentic

failed to run on p.l.c.).

Expt. No. 5. Methyl 1-phthalimidoaziridine-2-carboxylate (500 mg.); cyclohexene (10 ml.); method 1 (48 hr.); no n.m.r. obtained; 1 m. alumina/ether-petroleum (1:1); 7-phthalimido-7-azabicyclo[4,1,0]heptane (54 mg., 11%), no starting aziridine recovered (authentic failed to run on p.l.c.). Residence time on p.l.c. plate : 2 hr..

Expt. No. 6. Methyl 1-phthalimidoaziridine-2-carboxylate (500 mg.); cyclohexene (10 ml.); method 1 (48 hr.); starting aziridine (50%) and exchange product (50%); 1 m. alumina/ether-petroleum (1:1); 7-phthalimido-7-azabicyclo[4,1,0]heptane (177 mg., 37%). Residence time on p.l.c. plate : 25 min..

Expt. No. 7. Methyl 1-phthalimidoaziridine-2-carboxylate (246 mg.); cyclohexene (10 ml.); method 2 (90 hr.); starting aziridine (50%) and 7-phthalimido-7-azabicyclo[4,1,0]heptane (50%); no work up.

Expt. No. 8. Methyl 1-phthalimidoaziridine-2-carboxylate (246 mg.); cyclohexene (5 ml.); method 2 (90 hr.); starting aziridine (58%) and 7-phthalimido-7-azabicyclo[4,1,0]heptane (42%); no work up.

Expt. No. 9. Methyl 1-phthalimidoaziridine-2-carboxylate (246 mg.); cyclohexene (2 ml.); method 2 (90 hr.); starting aziridine (62%) and 7-phthalimido-7-azabicyclo[4,1,0]heptane (38%); no work up.

Expt. No. 10. Methyl 1-phthalimidoaziridine-2-carboxylate (246 mg.); cyclohexene (0.4 ml.); method 2 (90 hr.); starting aziridine (57%) and 7-phthalimido-7-azabicyclo[4,1,0]heptane (43%); no work up.

(Experiments 7, 8, 9 and 10 were performed concurrently under identical conditions).

Expt. No. 11. Methyl 1-phthalimidoaziridine-2-carboxylate (123 mg.); cyclohexene (0.1 ml.); method 2 (60 hr.); starting aziridine (72%) and 7-phthalimido-7-azabicyclo[4,1,0]heptane (28%); no work up.

Expt. No. 12. Methyl 1-phthalimidoaziridine-2-carboxylate (123 mg.); cyclohexene (0.05 ml.); method 2 (60 hr.); starting aziridine (81%) and 7-phthalimido-7-azabicyclo[4,1,0]heptane (19%); no work up.

(Experiments 11 and 12 were performed concurrently under identical conditions).

Expt. No. 13. 3-t-Butyl-2,2-dimethyl-1-phthalimidoaziridine (544 mg.); cyclohexene (10 ml.); method 1 (48 hr.); starting aziridine (100%); 1 m. alumina/ether-petroleum (1:1); starting aziridine (542 mg., 99%); t.l.c. of photolysate showed no 7-phthalimido-7-azabicyclo[4,1,0]-heptane.

Expt. No. 14. trans-2,3-Dichloro-1-phthalimoaziridine (516 mg.); cyclohexene (10 ml.); method 1 (55 hr.); no n.m.r. obtained; no work up. T.l.c. showed starting aziridine and the absence of 7-phthalimido-7-azabicyclo[4,1,0]heptane and 2,2-dichloroethylideneaminophthalimide. Brown polymer formed on the walls of the photolysis vessel.

Expt. No. 15. 2-Acetoxy-1-phthalimidoaziridine (500 mg.); cyclohexene (5 ml.); method 3 (118 hr.); starting aziridine (100%); no work up. T.l.c. showed the absence of 7-phthalimido-7-azabicyclo[4,1,0]heptane.

Expt. No. 16. 3-Acetyl-2,2-dimethyl-1-phthalimido-aziridine (129 mg.); trans-1,2-dichloroethylene (2 ml.); method 2 (50 hr.); starting aziridine (25%), trans-2,3-dichloro-1-phthalimidoaziridine (50%) and unidentified signals; no work up. Brown polymer formed on walls of photolysis vessel.

Expt. No. 17. Methyl 2-methyl-1-phthalimidoaziridine-2-carboxylate (520 mg.); 2,4,4-trimethylpent-2-ene (10 ml.); method 1 (94 hr.); no n.m.r. obtained; 1 m. alumina/ether-petroleum (1:1); 3-t-butyl-2,2-dimethyl-1-phthalimido-aziridine (213 mg., 40%); no starting aziridine recovered (authentic failed to run on plate).

Expt. No. 18. Methyl 1-phthalimidoaziridine-2-carboxylate (123 mg.); 2,4,4-trimethylpent-2-ene (2 ml.); method 2 (50 hr.); starting aziridine (56%) and 3-t-butyl-2,2-dimethyl-1-phthalimidoaziridine (44%); no work up.

Expt. No. 19. Methyl 1-phthalimidoaziridine-2-carboxylate (123 mg.); trans-1,2-dichloroethylene (2 ml.); method 2 (14 hr.); starting aziridine (88%) and trans-2,3-dichloro-1-phthalimidoaziridine (12%); no work up.

Expt. No. 20. Methyl 1-phthalimidoaziridine-2-carboxylate (200 mg.); trans-4-methylpent-2-ene (2 ml.); method 2 (91 hr.); starting aziridine (25%) and trans-2-methyl-3-isopropyl-1-phthalimidoaziridine (75%); 1 m. alumina/ether-petroleum (1:1); trans-2-methyl-3-isopropyl-1-phthalimidoaziridine (40 mg., 20%). None of the cis-aziridine was detectable by t.l.c. and n.m.r. study of the photolysate and of the isolated aziridine.

Expt. No. 21. Methyl 1-phthalimidoaziridine-2-carboxylate (200 mg.); cis-4-methylpent-2-ene (2 ml.); method 2 (91 hr.); starting aziridine (50%) and cis-2-methyl-3-isopropyl-1-phthalimidoaziridine (50%); 1 m. alumina/ether-petroleum (1:1); cis-2-methyl-3-isopropyl-1-phthalimidoaziridine (30 mg., 15%). None of the trans-aziridine was detectable by t.l.c. and n.m.r. study of the photolysate and of the isolated aziridine.

Expt. No. 22. Methyl 1-phthalimidoaziridine-2-carboxylate (500 mg.); 2,4,4-trimethylpent-2-ene (10 ml.); method 3 (79 hr.); starting aziridine (60%), polymethylacrylate, and 3-t-butyl-2,2-dimethyl-1-phthalimidoaziridine (40%); 1 m. silica/ether; 3-t-butyl-2,2-dimethyl-1-phthalimidoaziridine (70 mg., 10%). This experiment was performed in absolute ethanol solution.

Expt. No. 23. Methyl 1-phthalimidoaziridine-2-carboxylate (496 mg.); mesityl oxide (0.2 ml.); method 3 (109 hr.); no n.m.r. obtained; 1 m. silica/ether; 3-acetyl-2,2-dimethyl-1-phthalimidoaziridine (28 mg., 5.4%).

Expt. No. 24. 2-Acetoxy-1-phthalimidoaziridine (500 mg.); 2,4,4-trimethylpent-2-ene (10 ml.); method 1 (144 hr.); starting aziridine (100%); no work up. T.l.c. showed no 3-t-butyl-2,2-dimethyl-1-phthalimidoaziridine.

Expt. No. 25. 3-Acetyl-2,2-dimethyl-1-phthalimidoaziridine (200 mg.); methyl acrylate (0.5 ml.); method 1 (94 hr.); starting aziridine, methyl 1-phthalimidoaziridine-2-carboxylate (~50%) and polymethylacrylate; no work up.

Expt. No. 26. 3-Acetyl-2,2-dimethyl-1-phthalimido-

aziridine (100 mg.); cyclohexene (2 ml.); method 2 using 350 nm. lamps and a Pyrex tube (48 hr.); starting aziridine (100%); no work up. T.l.c. showed the absence of the exchange product.

Expt. No. 27. 3-Acetyl-2,2-dimethyl-1-phthalimido-aziridine (516 mg.); cyclohexene (10 ml.); Hanovia low pressure mercury arc lamp (predominantly 254 nm. radiation) (23 hr.); no n.m.r. obtained; 1 m. alumina/ether-petroleum (1:1); 7-phthalimido-7-azabicyclo[4,1,0]-heptane (59 mg., 12%) and starting aziridine (127 mg., 25%).

Photolysis of phthalimido-aziridines alone

Expt. No. 28. 3-Acetyl-2,2-dimethyl-1-phthalimidoaziridine (500 mg.) was irradiated in acetonitrile by method 3 for 96 hr.. T.l.c. showed that no reaction had occurred and rotary evaporation gave starting aziridine, pure to n.m.r. analysis.

Expt. No. 29. 2-Phenyl-1-phthalimidoaziridine (500 mg.) was irradiated in acetonitrile by method 1. After 173 hr., t.l.c. showed total loss of the starting aziridine. Rotary evaporation gave an oil, the n.m.r. spectrum of which consisted of broad signals. The peaks of the starting aziridine and of polystyrene were absent.

Expt. No. 30. Methyl 1-phthalimidoaziridine-2-carboxylate (500 mg.) was irradiated in acetonitrile by method 3 for 173 hr.. T.l.c. showed starting aziridine to remain after

this period and the n.m.r. spectrum of the residue obtained by rotary evaporation of the photolysate contained the peaks of the starting aziridine and also three broad signals centred on 6.33, 7.80, and 8.35  $\tau$ . [Polymethylacrylate, prepared by irradiation of methyl acrylate (5 ml.) by method 1 for 48 hr., showed similar signals in its n.m.r. spectrum.] The photolysate was chromatographed on an alumina column. Petroleum-dichloromethane (5:1) eluted starting aziridine (84 mg., 17%). No other material was eluted from the column by solvent mixtures increasing in polarity to pure dichloromethane. The alumina was removed from the column and Soxhlet extracted with methanol for 3 days. The residue (mostly alumina) from evaporation of the methanol extract was treated with *o*-dichlorobenzene (in which polymethylacrylate is soluble) and studied by n.m.r.. The only signals were those of *o*-dichlorobenzene.

Photolysis of phthalimido-aziridines in the presence of acetylenes

Expt. No. 31. Methyl 1-phthalimidoaziridine-2-carboxylate (492 mg.), in acetonitrile containing dimethyl acetylenedicarboxylate (2 ml.), was irradiated by method 1 for 109 hr. Column chromatography on silica, eluting with petroleum-dichloromethane mixtures, gave only uncharacterisable oils derived from the acetylene.

Expt. No. 32. Methyl 1-phthalimidoaziridine-2-carboxylate (500 mg.) was irradiated (method 1, 74 hr.)

in acetonitrile containing hex-1-yne (2 ml.). The solution darkened and polymer formed on the lamp jacket. T.l.c. showed a plethora of products and the absence of any azirine. P.l.c. on a 1 m. silica plate eluted with ether-petroleum (1:1) failed to afford any homogeneous products.

Expt. No. 33. 3-Acetyl-2,2-dimethyl-1-phthalimido-aziridine (500 mg.) was irradiated (method 1, 92 hr.) in acetonitrile containing hex-3-yne (10 ml.). The initially pale yellow solution became deep yellow. T.l.c. showed that none of the expected azirine was formed. P.l.c. on a 1 m. silica plate eluted with ether gave starting aziridine (127 mg. 25%) and two oils ( $R_F$  0.6, 115 mg.;  $R_F$  0.4, 89 mg.). The former oil was rechromatographed [20 x 20 cm. silica (ether)] to give two viscous gums, neither of which could be identified. I.r. and mass spectral data were suggestive of polymers but the presence of a phthalimido group was inferred. The oil from  $R_F$  0.4 of the first plate was taken up in dichloromethane and petroleum was added to give yellow granules (26 mg.), m.p. 64-87°. The i.r. spectrum was suggestive of a polymer.  $m/e$  402 (0.20), 387 (0.80), 203 (0.60), 162 (0.40), 147 (0.50), 132 (0.50), 104 (1.00) and 76 (0.70).  $m^* 373 = 402 \rightarrow 387$ .

Preparation of 3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl-aziridines

3-Amino-3,4-dihydro-2-methyl-4-oxoquinazoline,



prepared<sup>35</sup> from methyl anthranilate, acetic anhydride, and hydrazine hydrate, was stirred in dichloromethane (ca. 15 ml./g.) and the appropriate olefin (5 molecular equivalents) added. Lead tetra-acetate (1.0-1.1 molecular equivalents) was added over 5 min. with cooling in ice. Filtration separated lead diacetate which was washed with dichloromethane. The combined filtrate and washings were chromatographed on a short column of alumina. Elution with petroleum-dichloromethane (4:1) gave the aziridine as an oil which generally crystallised on scratching. Recrystallisation from ethyl acetate-petroleum gave the pure aziridine. The physical properties of the aziridines were as described.<sup>35</sup> The following aziridines have not previously been described.

3-Acetyl-1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2,2-dimethylaziridine This was prepared by oxidation of 3-amino-3,4-dihydro-2-methyl-4-oxoquinazoline in the presence of mesityl oxide. A chromatographic work up followed by recrystallisation from ethyl acetate-petroleum gave the title compound (74%) as needles, m.p. 102-103° (Found: C, 66.2; H, 6.3; N, 15.2. C<sub>15</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub> requires C, 66.4; H, 6.3; N, 15.5%. M 271).

$\nu_{\text{max}}$ . 1722 (acetyl C=O), 1675 (oxoquinazolinyl C=O), 1600 (C=N), 1195, 770, and 690 cm.<sup>-1</sup>.

$\tau$ (CDCl<sub>3</sub>) 8.69 (3H, s, aziridine ring Me cis to heterocycle), 8.53 (3H, s, aziridine ring Me trans to heterocycle), 7.54 (3H, s, COMe), 7.32 (3H, s, quinazolinyl Me), 6.32 (1H, s, aziridine ring proton), 2.53-1.93 (3H, m)

and 1.72-1.52 (1H, m) (aromatics).

$\tau$  (o-dichlorobenzene) 8.96 (3H, s), 8.69 (3H, s), 7.60 (3H, s), 7.51 (3H, s) and 6.45 (1H, s). Elevated temperature spectra showed a slight decrease in the separation of the signals at 8.96 and 8.69 from 16.5 Hz at 39° to 15.0 Hz at 125°. No coalescence was observed up to the decomposition temperature of 160°.

m/e 271 M<sup>+</sup>, 228 (M-COMe)<sup>+</sup>, 186, 160.

$\lambda_{\text{max}}$ . (EtOH), nm. ( $\epsilon$ ) 225 (31,000), 255 shoulder (9700), 275 (6300), 284 (6200), 310 (3940) and 323 shoulder (2900).

1-(3,4-Dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-(prop-1-enyl)aziridine and 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-methyl-3-vinylaziridine See Section 2.

All of the 3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl-aziridines studied, with a conjugating substituent or not, gave very similar u.v. spectra as follows:

$\lambda_{\text{max}}$ . (EtOH), nm. ( $\epsilon$ ) 224-226 (30,000), 255 shoulder (1000), 272-275 (7000), 283-284 (7000), 308-310 (4000), and 317-323 shoulder (3000).

Photolysis of oxoquinazolinyl-aziridines in the presence of olefins

See page 70 for general procedure and page 71 for layout of results.

Expt. No. 34. 1-(3,4-Dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-phenylaziridine (100 mg.); cyclohexene (1 ml.); method 2 (70 hr.); no n.m.r. obtained; 20 cm. alumina/ether; the aziridines did not separate and were obtained

as a 1:2 molar mixture (47 mg.) of starting aziridine (16.5%) and 7-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-7-azabicyclo[4,1,0]heptane (33%).

Expt. No. 35. Ethyl 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-methylaziridine-2-carboxylate (60 mg.); cyclohexene (1 ml.); method 2 (70 hr.); no n.m.r. obtained; 20 cm. silica/ether; 7-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-7-azabicyclo[4,1,0]heptane (19.2 mg., 39%); no starting aziridine was isolated.

Expt. No. 36. 1-(3,4-Dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-vinylaziridine (300 mg.); cyclohexene (2 ml.); method 1 (83 hr.); starting aziridine (32%) and 7-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-7-azabicyclo[4,1,0]heptane (68%); 1 m. alumina/ether; 7-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-7-azabicyclo[4,1,0]heptane (77 mg., 20%) and starting aziridine (28 mg., 9.3%). The n.m.r. and t.l.c. of the photolysate showed the absence of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-3-pyrroline and 3,4-dihydro-2-methyl-4-oxoquinazoline.

Expt. No. 37. 2,3-Benzo-6-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-6-azabicyclo[3,1,0]hexane (300 mg.); cyclohexene (5 ml.); method 1 (91 hr.); no n.m.r. obtained; 1 m. silica/ether; the aziridines did not separate and a 9:1 molar mixture (150 mg.) of 7-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-7-azabicyclo[4,1,0]heptane (52%) and starting aziridine (6%) was obtained.

Expt. No. 38. 1-(3,4-Dihydro-2-methyl-4-oxoquinazolin-3-yl)-cis-2,3-dimethylaziridine (100 mg.); cyclohexene (2 ml.); method 3 (68 hr.); no n.m.r. obtained; 20 cm. silica/ether; starting aziridine (30%). T.l.c. of the photolysate showed the absence of 7-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-7-azabicyclo[4,1,0]heptane.

Expt. No. 39. 2,3-Benzo-6-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-6-azabicyclo[3,1,0]hexane (578 mg.); 2,4,4-trimethylpent-2-ene (10 ml.); method 1 (140 hr.); starting aziridine (14%) and 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2,2-dimethyl-3-t-butylaziridine (86%), 1 m. silica/ether, 3-t-butyl-1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2,2-dimethylaziridine (90 mg., 16%) and starting aziridine (25 mg., 4.3%).

Expt. No. 40. 3-Acetyl-1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2,2-dimethylaziridine (500 mg.); cyclooctene (10 ml.); method 3 (92 hr.); no n.m.r. obtained; 1 m. silica/ether; starting aziridine (91 mg., 18%) and 9-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-9-azabicyclo[6,1,0]nonane (40 mg., 7.7%).

Photolysis of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-(prop-1-enyl)aziridine. The title compound

(350 mg. of a 3:2 mixture of the cis and trans isomers about the propenyl double bond) in acetonitrile was irradiated by method 1. After 24 hr., t.l.c. showed the presence of the starting aziridines and also 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-methyl-3-vinyl-

aziridine. The n.m.r. spectrum of the residue obtained on evaporation of the photolysate confirmed the presence of the four isomeric aziridines.

Photolysis of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-2-yl)-3-pyrroline. The pyrroline (see Section 2) (52 mg.) was irradiated in acetonitrile for 21 hr. by method 2. Evaporation of the photolysate and trituration with carbon tetrachloride gave 3,4-dihydro-2-methyl-4-oxoquinazoline (33 mg., 90%) as needles, m.p. 240-242° after sublimation (lit., <sup>130</sup> 240-241°). When the experiment was repeated in the presence of cyclohexene, no 7-phthalimido-7-azabicyclo[4,1,0]heptane was formed (t.l.c.) and 3,4-dihydro-2-methyl-4-oxoquinazoline was again isolated.

#### Preparation of isoindolinyl-aziridines

1-(Isoindolin-2-yl)-2-phenylaziridine. 2-Phenyl-1-phthalimidoaziridine (2.65 g., 10 mmole) in anhydrous ether (100 ml.) was added dropwise during 30 min. to a stirred suspension of lithium aluminium hydride (1.5 g., ~40 mmole) in ether (100 ml.) at 35° under nitrogen. The mixture was heated under reflux for 6 hr., then cooled below 0°, and water was cautiously added to destroy the excess of lithium aluminium hydride. The mixture was filtered and the precipitated salts were washed with ether (100 ml.) under nitrogen. The combined ether solutions were dried under nitrogen and filtered to give a colourless ethereal solution of 1-(isoindolin-2-yl)-2-phenylaziridine (1.4 g., 58%, in ~200 ml. ether). The

compound invariably darkened on evaporation of the solvent and was found to be extremely susceptible to discolouration by atmospheric oxygen. The solution could be maintained as colourless for at least 1 week by the constant passage of nitrogen; prior to use the purity was established by rotary evaporating a sample and observing the n.m.r. spectrum. The analytical sample was obtained by short-path distillation at  $100^{\circ}/0.2$  mm. to give a pale red oil which solidified when cooled below room temperature and re-melted above  $20^{\circ}$ . (Found: C, 81.6; H, 7.0; N, 11.6  $C_{16}H_{16}N_2$  requires C, 81.3; H, 6.8; N, 11.9%. M 236).

$\nu_{\max}$ . 1608, 1500, 1480, 1460, 1260, 889, 740 and  $700\text{ cm}^{-1}$ .  
 $\tau$  ( $CDCl_3$ ) 7.98 (1H, d, J 5 Hz, 3-H cis to phenyl), 7.73 (1H, d, J 8 Hz, 3-H trans to phenyl), 7.06 (1H, dd,  $J_{H-2, \text{cis } H-3}$  8 Hz,  $J_{H-2, \text{trans } H-3}$  5 Hz, 2-H), 5.73 (4H, s, allylic protons), 2.71 (4H, s) and 2.66 (5H, m) (aromatics).

$\lambda_{\max}$ . (cyclohexane), nm. ( $\epsilon$ ) 230 (6800), 294 (1900), and 305 (1960).

m/e (direct insertion at  $\sim 110^{\circ}$ ) : 236 (0.04)  $M^+$ , 145 (0.16), 132 (0.14) (M-styrene) $^+$ , 117 (0.07), 104 (1.00) (M-styrene- $N_2$ ) $^+$ , 103 (0.90), 78 (0.80), and 77 (0.84).

$m^* 58.6 = 104 \rightarrow 78$ .

m/e (All-glass heated inlet system,  $170^{\circ}$ , approx 30 min. from insertion to spectrum scan) : No  $M^+$  at 236, 208 (0.30), 193 (0.28), 178 (0.15), 134 (0.27), 104 (1.00), and

77 (0.65).

An experiment carried out as above, except on half the scale and with reflux of the reagents for 3 hr. instead of 6 hr. gave a crude product containing unreduced phthalimidoaziridine. P.l.c. on a 1 metre silica plate eluted with ether-petroleum (1:1) gave the isoindolynylaziridine (9%) as a black oil which was nevertheless pure to i.r. and n.m.r..

7-(Isoindolin-2-yl)-7-azabicyclo[4,1,0]heptane. 7-Phthalimido-7-azabicyclo[4,1,0]heptane (2.42 g., 10 mmole) in anhydrous ether (100 ml.) was reduced in the same way with lithium aluminium hydride (1.5 g., ~40 mmole) over 6 hr. at reflux. Again a colourless ethereal solution of the product was obtained which was stored under nitrogen and remained colourless. A portion which was allowed contact with the atmosphere rapidly darkened in colour. The yield at this stage was 75%. Short-path distillation gave a colourless liquid which crystallised on scratching to give 7-(isoindolin-2-yl)-7-azabicyclo[4,1,0]heptane as needles, m.p. 30-35°. The needles became a black liquid on standing in the atmosphere overnight and also decomposed on storage in the dark, under nitrogen, for 1 month. (Found: C, 78.3; H, 8.4; N, 12.9.  $C_{14}H_{18}N_2$  requires C, 78.5; H, 8.5; N, 13.1%. M 214).

$\nu_{\text{max}}$  : 1460 and 740  $\text{cm}^{-1}$ .

$\tau$  ( $\text{CDCl}_3$ ) : 8.93-8.50 (4H, m), 8.25-8.10 (2H, m), 8.10-7.93 (2H, m), 6.00 (4H, s, allylic protons), and

2.92 (4H, s, aromatics).

m/e 214 (0.50)  $M^+$ , 171 (0.33), 132 (0.32) (M-cyclohexene)<sup>+</sup>, 118 (0.33) (isoindoliny radical)<sup>+</sup>, 104 (1.00), 96 (0.07), 78 (0.82), and 77 (0.63).

$\lambda_{\max}$ . (cyclohexane), nm. ( $\epsilon$ ) 230 (324), 258 (119), 265 (119), 273 (107), and 278 (55).

Photolysis of 1-(isoindolin-2-yl)-2-phenylaziridine

1) The title compound (0.5g.) was dissolved in de-oxygenated acetonitrile (100 ml.) and the dark-coloured solution irradiated, under nitrogen, by method 1. T.l.c. showed a decrease in the starting material but no new spots appeared except at  $R_F$  zero on silica/ether-petroleum (1:1). After 14 hr. the red solution was evaporated; the n.m.r. spectrum showed broad peaks suggestive of polymerisation. Rapid p.l.c. on a 1 m. silica plate eluted with ether gave only a band moving at the solvent front and a band at the base line. The former gave a red oil which was identified as un-changed starting aziridine (24%) by t.l.c. and n.m.r.. There was no sign of any hydrocarbon products.

2) The title compound was freshly prepared and the colourless ethereal solution obtained was irradiated by method 1. No gas was evolved and after 36 hr., t.l.c. of the pale yellow solution showed that all the starting aziridine had decomposed to a spot at  $R_F$  zero on silica/ether. Rotary evaporation gave a pale yellow oil which became deep red on exposure to the atmosphere and gave an n.m.r. spectrum showing broad polymeric-like signals. T.l.c. on silica and alumina with a range of elutes showed



no homogeneous material.

3) The photolysis was repeated in the presence of cyclohexene (10 ml.) with the same result. No 7-(isoindolin-2-yl)-7-azabicyclo[4,1,0]heptane was observed (t.l.c.).

A blank experiment showed the azabicycloheptane to be rather more photo-stable than the 2-phenylaziridine.

#### Preparation of sulphenyl-aziridines

1, 1a, 6, 6a-Tetrahydro-1-p-tolylsulphenylindeno[1,2-b]azirine. Indene was converted into 1, 1a, 6, 6a - tetrahydroindeno[1,2-b]azirine (90%) by addition of iodine azide followed by reduction with lithium aluminium hydride.<sup>126,127</sup> From the reduction, the aziridine was obtained in ethereal solution and could be stored at 0° overnight in this medium. A sample was rotary evaporated at room temperature to give the aziridine<sup>127,128</sup> as an initially colourless oil :  $\nu_{\text{max}}$  3260 br (NH), 3030, 2900, 1470, 1125, 955, 810, 755, and 720  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CDCl}_3$ ) 8.25 (1H, broad s, position dependent on concentration, NH), 7.48-7.10 (3H, m, methylene protons and adjacent aziridine ring proton), 6.95 (1H, d, J 3 Hz, other aziridine ring proton) and 3.05-2.72 (4H, m, aromatics), The oil decomposed in a few hours at 0°.

The ethereal indano-aziridine (75 ml., containing 1.81g., 13.6 mmole) and triethylamine (1.37g., 13.6 mmole) were added to a solution of p-tolylsulphenyl chloride (2.16g., 13.6 mmole), prepared<sup>129</sup> from p-tolythiol and chlorine, in ether (50 ml.) at 0°. After 2 hr. the

mixture was filtered, and the precipitate was washed thoroughly with ether. The oil which was obtained by evaporation of the ether solution was purified by p.l.c. on a 1 m. silica plate eluted with petroleum-ether (5:1) to give the title compound (Found: C, 75.6; H, 5.7; N, 5.2; S, 12.95,  $C_{16}H_{15}NS$  requires C, 75.9; H, 6.0; N, 5.5; S, 12.6%. M 253).

$\nu_{\max}$ . 1490, 803, 755, and 724  $\text{cm}^{-1}$ .

$\tau$  ( $\text{CDCl}_3$ ) 7.68 (3H, s, Me), 7.20-6.70 (3H, m, 2H on C-4 and 1H on C-5), 6.43 (1H, d, J 4 Hz, 1H on C-1), and 3.05-2.45 (8H, m, aromatics).

$m/e$  253 (0.43)  $M^+$ , 246 (0.55), 238 (0.01)  $(M-\text{Me})^+$ , 139 (0.25), 130 (1.00) (indano-aziridiny radical) $^+$ , 123 (0.67) (p-tolylsulphenyl radical) $^+$  and 116 (0.90),  $m^* 66.9 = 253 \rightarrow 130$ .

$\lambda$  (EtOH), nm. ( $\epsilon$ ) 250 (9500) tailing to 380 (246), no maximum. The aziridine decomposed when distillation was attempted.

1-(2,4-Dinitrophenylsulphenyl)-1,1a,6,6a-tetrahydroindeno [1,2-b] azirine. This was prepared similarly from the indano-aziridine (1.44g., 10.8 mmole), triethylamine (1.7g., 10.8 mmole), and 2,4-dinitrobenzenesulphenyl chloride (2.53g., 10.8 mmole). The reaction mixture was partitioned between chloroform and water, and the organic layer separated, dried, and evaporated. Recrystallisation of the residue from petroleum-chloroform gave the aziridine (2.3g., 65%) as yellow needles, m.p. 161-163 $^{\circ}$  (Found: C, 54.9; H, 3.2; N, 12.5; S, 9.4.  $C_{15}H_{11}N_3O_4S$  requires

C, 54.7; H, 3.4; N, 12.8; S, 9.7%. M 329).

$\nu_{\text{max.}}$  1590, 1510, 1460, 1330, 1300, 915, and 735  $\text{cm.}^{-1}$ .

$\tau$  ( $\text{CDCl}_3$ ) 6.69-6.59 (2H, m, 2H on C-4), 6.55-6.45 (1H, m, 1H on C-5), 6.30 (1H, d, J 5 Hz, 1H on C-1), 3.05-2.95 (4H, m), and 2.04-1.96 (2H, m) and 1.17 (1H, s) (aromatics).

$m/e$  329 (0.02)  $\text{M}^+$ , 191 (0.06), 149 (0.05), 130 (0.44)

(indano-aziridiny radical) $^+$ , 116 (1.00) indene $^+$ .

$\lambda_{\text{max.}}$  (EtOH), nm. ( $\epsilon$ ) 250 shoulder (9650), 350 (8570) tailing to 500 nm..

7-(p-Tolylsulphenyl)-7-azabicyclo[4,1,0]heptane. Iodine

azide was reacted with cyclohexene to give trans-1-azido-2-iodocyclohexane<sup>126</sup> as a colourless unstable liquid,

$\nu_{\text{max.}}$  2930, 2090, 1450, and 1260  $\text{cm.}^{-1}$ . The iodo-azide

(24.9 g., 0.1 mole) in anhydrous ether (30 ml.) was

slowly added dropwise to a stirred slurry of lithium

aluminium hydride (7.6 g., 0.2 mole) in ether (100 ml.)

with cooling in an ice bath. There was an apparent

induction period in this reaction since on two occasions

gas evolution was initially slow. Continued addition of

the iodo-azide was terminated after 2 hr. by a vigorous

gas evolution, with discharge of the reagents from the

reaction vessel. The reaction was successfully conducted

by addition of 5 ml. of the ethereal iodo-azide and

stirring for 2 hr. The remainder of the iodo-azide

solution was then added dropwise and the reaction proceeded

normally to give 7-azabicyclo[4,1,0]heptane<sup>127</sup> (56%) :

$\nu_{\text{max.}}$  3240 br (NH), 2930, 1440, and 770  $\text{cm.}^{-1}$  (identical

to the published spectrum);  $\tau$  ( $\text{CDCl}_3$ ) 8.80-8.40 (m) and 8.54 (s, NH, intensity decreased on addition of  $\text{D}_2\text{O}$ ) (together 5H), 8.40-7.94 (4H, m), and 7.94-7.73 (2H, m).

The azabicycloheptane (4.8 g., 0.05 mole) and triethylamine (5.1 g., 0.05 mole) in ether (50 ml.) were added dropwise to p-tolylsulphenyl chloride (7.95 g., 0.05 mole) in ether (50 ml.) at  $0^\circ$ . After 2 hr., the mixture was filtered and the solids washed with ether. The combined filtrates were evaporated and the residue distilled to give 7-p-tolylsulphenyl-7-azabicyclo[4,1,0]-heptane (6.55 g., 60%) as a pale yellow liquid, b.p.  $165-168^\circ / 0.2$  torr (Found: C, 71.6; H, 7.6; N, 5.9; S, 14.4.  $\text{C}_{13}\text{H}_{17}\text{NS}$  requires C, 71.2; H, 7.8; N, 6.4; S, 14.6%. M 219).

$\nu_{\text{max}}$ . 1490 and 800  $\text{cm}^{-1}$ .

$\tau$  ( $\text{CDCl}_3$ ) 8.93-8.50 (4H, m), 8.40-8.02 (4H, m), 7.95-7.80 (2H, m), 7.73 (3H, s, Me), and 3.10-2.60 (4H, m, aromatics).  $m/e$  219 (1.00)  $\text{M}^+$ , 204 (0.04)  $(\text{M}-\text{Me})^+$ , 178 (0.39), 139 (0.20), 123 (1.00) (p-tolylsulphenyl radical) $^+$ , 96 (0.39) (7-azabicycloheptyl radical) $^+$ , and 91 (0.51).

$\lambda_{\text{max}}$ . (EtOH), nm. ( $\epsilon$ ) 248 (8880), 282 (2280) and 310 shoulder (1520).

7-(2,4-Dinitrophenylsulphenyl)-7-azabicyclo[4,1,0]heptane.

This was prepared<sup>130</sup> from 7-azabicyclo[4,1,0]heptane and 2,4-dinitrophenylsulphenyl chloride, and obtained as yellow needles, m.p.  $159-160^\circ$  (lit.,<sup>130</sup>  $160-161^\circ$ ),

$\nu_{\text{max}}$ . 1590, 1510, 1050, and 735  $\text{cm}^{-1}$ .  $\tau$  ( $\text{CDCl}_3$ )

8.74-8.24 (4H, m), 8.24-7.70 (4H, m), 7.63-7.45 (2H, m), and 1.50 (2H, m) and 0.85 (1H, s) (aromatics).

$\lambda_{\text{max}}$ . (EtOH) 255 shoulder (6000), 350 (6000) tailing to 500 nm..

Photolysis of 1,1a,6,6a-tetrahydro-1-p-tolylsulphenyl-indeno [1,2-b]azirine

1) The title compound (500 mg.) in acetonitrile (90 ml.) containing cyclohexene (10 ml.) was irradiated by method 1 for 30 hr.. T.l.c. and n.m.r. study of the residue obtained by evaporation of the photolysate showed that little change had occurred and that the aza-bicycloheptane was absent. P.l.c. on a 1 m. silica plate eluted with petroleum-ether (2:1) gave only unchanged aziridine (300 mg., 60%).

2) The experiment was repeated and irradiation was continued for 185 hr.. The solution darkened and the lamp jacket had to be cleaned several times to remove a polymeric coating. Evaporation of the photolysate gave a black tar, the n.m.r. spectrum of which showed only broad, unresolved signals. P.l.c. on a 1 m. silica plate eluted with petroleum-ether (3:1) gave no homogeneous material.

Photolysis of 1-(2,4-dinitrophenylsulphenyl)-1,1a,6,6a-tetrahydroindeno [1,2-b]azirine

The title compound (500 mg.) was dissolved in acetonitrile (90 ml.) and cyclohexene (10 ml.) added. The solution was irradiated by method 1 and periodically studied by t.l.c.. No formation of the azabicycloheptane

was observed. After 185 hr., the dark coloured solution was evaporated and the residue applied to a 1 m. silica p.l.c. plate which was eluted with ether. The only material obtained was unchanged aziridine (280 mg., 56%) and none of the exchange product was found.

Experimental : Part 1, Section 2

Preparation of heterocyclic N-sulphoximides

SS-Dimethyl-N-phthalimido-sulphoximide. Lead tetra-acetate (9.74 g., 22mmole) was added in portions to a solution of N-aminophthalimide (3.24 g., 20mmole) in anhydrous dimethyl sulphoxide (20 ml.). After stirring for 10 min., the solution was poured into ether (600 ml.) and the precipitated solids collected and extracted with boiling chloroform (300 ml.). Evaporation of the chloroform extract to a small volume and cooling in ice gave the sulphoximide (3.5 g., 74%), m.p. 208-210° (lit.,<sup>26</sup> 208°).

SS-Diphenyl-N-phthalimido-sulphoximide. N-Aminophthalimide (5.0 g., 0.31 mole) and diphenyl sulphoxide (25 g., 1.24 mole) were stirred in dichloromethane (80 ml.). Lead tetra-acetate (15.0 g., 0.34 mole) was added over 10 min., and after a further 10 min. the mixture was filtered and the solids washed with dichloromethane. The combined filtrate and washings were chromatographed on an alumina column. Ether-petroleum (3:1) and ether eluted a mixture of phthalimide and diphenyl sulphoxide. Ether-methanol (1:1) eluted the sulphoximide (3.0 g., 27%), m.p. 220-221° (lit.,<sup>11</sup> 220°) from ethanol.

SS-Dibenzyl-N-phthalimido-sulphoximide. Powdered N-aminophthalimide (1.62 g., 10mmole) was added in portions to a stirred mixture of dibenzyl sulphoxide (2.3 g., 10mmole) and lead tetra-acetate (4.9 g., 11 mmole) in

dichloromethane (100 ml.). The addition was performed over 1 hr., and after stirring for a further 15 min. the mixture was filtered and the solids washed with dichloromethane. Evaporation of the combined filtrate and washings gave a yellow oil. Trituration with ether and a few drops of ethanol gave an amorphous solid which was collected and crystallised from ethanol to give

SS-dibenzyl-N-phthalimido-sulphoximide (3.0 g., 77%), m.p. 147-150° (Found: C, 67.3; H, 4.7; N, 7.4; S, 8.4).

$C_{22}H_{18}N_2O_3S$  requires C, 67.7; H, 4.65; N, 7.2; S, 8.2%.

M 390).

$\nu_{\max}$ . 1720 br (C=O), 1220, 1025 (S=O), 890, 720, and 700  $cm^{-1}$ .

$\tau$  (CDCl<sub>3</sub>) 5.54 (4H, s, benzylic protons), 2.72 (10H, m, benzyl aromatics), and 2.41 (4H, m, phthalimido aromatics).

SS-Dimethyl-N-naphthalimido-sulphoximide. Lead tetraacetate (2.45 g., 5.5 mmole) was added in portions to a solution of N-aminonaphthalimide (1.06 g., 5 mmole) in anhydrous dimethyl sulphoxide (10 ml.). After 10 min. the mixture was poured into water (150 ml.), and the precipitate collected and recrystallised from ethanol to give the sulphoximide (1.0 g., 69%), m.p. 205° (lit.,<sup>11</sup> 205°).

SS-Dimethyl-N-(phenanthrid-6-on-5-yl)sulphoximide. This compound was available from the work of Yelland<sup>30</sup> and had m.p. 211-212° (decomp.) (lit.,<sup>30</sup> 211-212°).

SS-Dimethyl-N-(indazol-2-yl)sulphoximide. 2-Amino-indazole



(3.99 g., 30 mmole) in dry dimethyl sulphoxide (10 ml.) was added dropwise to a solution of lead tetra-acetate (14.65 g., 33 mmole) in dry dimethyl sulphoxide (20 ml.), with cooling in an ice bath. The dark coloured solution was stirred for 30 min. at 10° and then poured into water (150 ml.) and extracted with ethyl acetate (3 x 150 ml.). The extract was washed with saturated aqueous sodium metabisulphite (2 x 75 ml.) and then water (2 x 75 ml.), dried, and chromatographed on an alumina column. Oils were eluted by petroleum-dichloromethane mixtures; elution with pure dichloromethane gave the sulphoximide (620 mg., 9.9%), m.p. 139-140° (lit.,<sup>41</sup> 138-140°).  $\nu_{\text{max}}$  1195, 1035, and 745  $\text{cm}^{-1}$ , the absorptions previously assigned<sup>41</sup> to this compound at 3120 and 3020  $\text{cm}^{-1}$  were not observed. m/e 209 (0.75)  $\text{M}^+$ , 135 (0.05), 131 (0.05), 118 (0.10), 103 (0.80), and 76 (1.00).

#### Pyrolysis of heterocyclic N-sulphoximides

SS-Dimethyl-N-phthalimido-sulphoximide. The title compound (238 mg.) was sublimed at 205°/0.4 torr (nitrogen flow rate 5 ml./min.) and pyrolysed at 450°. A pale yellow solid (135 mg.) appeared on the Drikold-acetone trap. P.l.c. on a 20 x 20 cm. silica plate eluted with ether gave (i) bicyclo[4,2,0]octa-1,3,5-triene-7,8-dione (hereafter referred to as benzocyclobutenedione) (46 mg., 35%), m.p. 130-132° (from cyclohexane) (lit.,<sup>131</sup> 131-132, 130-131°, 132-135°, 128-130°),  $\nu_{\text{max}}$  1795, 1780, 1735, 1590, 1280, 1170, 1140, 940, 855, and 780  $\text{cm}^{-1}$ , identical to the published spectrum,<sup>131</sup> and (ii) phthalimide (70 mg.,

48%), m.p., m.m.p., i.r., and t.l.c. identical to authentic.

SS-Diphenyl-N-phthalimido-sulphoximide. The sulphoximide (162 mg.) was pyrolysed at 420° by sublimation at 220°/0.01 torr. The pyrolysate, which was trapped on a Drikold-acetone cold finger, was a pale yellow solid (140 mg.). T.l.c. and i.r. analysis showed the presence of diphenyl sulphoxide, benzocyclobutenedione, and a little starting material. No phthalimide could be detected. P.l.c. on a 1 m. silica plate eluted with ether-petroleum (1:1) gave (i) benzocyclobutenedione (40 mg., 68%), (ii) diphenyl sulphoxide (70 mg., 77%), identical i.r. and t.l.c. to authentic, and (iii) unchanged sulphoximide, (5.0 mg., 3%), identified by t.l.c. and i.r..

SS-Dibenzyl-N-phthalimido-sulphoximide. Volatilisation of the title compound (256 mg.) occurred at 150-170°/0.5 torr (nitrogen flow rate 5 ml./min.) and the vapour was pyrolysed at 450°. The Drikold-acetone cold finger trapped 211 mg. of pyrolysate, which was initially a yellow solid. A liquid nitrogen cooled trap, placed between the pyrolysis apparatus and the vacuum pump, failed to afford any material. The pyrolysate appeared to partly decompose on warming to room temperature and also appeared to be hygroscopic. T.l.c. showed several spots but benzocyclobutenedione and dibenzyl sulphoxide were not observed. P.l.c. on a 1 m. silica plate eluted with ether-petroleum (1:1) gave only phthalimide (77 mg., 80%).

The experiment was repeated and the pyrolysate

rapidly chromatographed on a 1 m. alumina plate eluted with ether-petroleum (1:1). Again, phthalimide was the only compound isolated.

SS-Dimethyl-N-naphthalimido-sulphoximide. The sulphoximide (138 mg.) was pyrolysed at 450° by volatilisation at 220°/0.005 torr. The pyrolysate was trapped on a Drikold-acetone cooled surface and chromatographed on a 20 x 20 cm. silica plate eluted by ether-ethanol (4:1) to give (i) acenaphthenequinone (35 mg., 40%), identical i.r., t.l.c., m.p., and m.m.p. to authentic (Koch Light, recrystallised from acetic acid), (ii) naphthalimide (28 mg., 30%), identified by comparison of i.r., t.l.c., and m.p. to authentic, and (iii) unchanged sulphoximide (38 mg., 28%). The yields based on unrecovered sulphoximide are acenaphthenequinone 55%, naphthalimide 41%.

SS-Dimethyl-N-(phenanthrid-6-on-5-yl)sulphoximide. The product from pyrolysis of this sulphoximide (50 mg.) at 400° (sublimed at 180-210° / 0.1 torr) was shown by i.r. and t.l.c. to be predominantly phenanthridone. T.l.c. showed a little fluorenone but benzo[*c*]cinnoline and biphenylene were absent. Extraction of the pyrolysate with dichloromethane left pure phenanthridone (27 mg., 80%), identical i.r., t.l.c., and m.m.p. to authentic. The dichloromethane extract was analysed by g.c. (1% OV 17, G.C.Q., 60-80 mesh, 5 ft. column at 170°); the only peak was that of fluorenone.

SS-Dimethyl-N-(indazol-2-yl)sulphoximide. The sulphoximide

(95 mg.) was pyrolysed at 450° by volatilisation at 140-170°/0.01 torr. The pyrolysate was trapped at Drikold-acetone temperature as a yellow solid which melted to a red liquid on attaining room temperature. The i.r. spectrum (thin film) showed the peaks of dimethyl sulphoxide and also sharp absorptions at 2200 and 2080 cm.<sup>-1</sup>. T.l.c. showed the absence of indazole. P.l.c. on a 20 x 20 cm. silica plate eluted with petroleum-ether (2:1) gave an oil which crystallised spontaneously to give 1-cyano-hexa-1,3-dien-5-yne as yellow needles, m.p. 55-65° (decomp.) (m.p. varies with rate of heating). No analysis was obtained,

$\nu_{\text{max}}$ . 3200 (alkyne C-H stretch), 3050 (cis or trans-disub alkene), 2200 (C $\equiv$ N stretch of an  $\alpha\beta$ -unsaturated alkyl nitrile), 2080 (C $\equiv$ C stretch of a mono-substituted alkyne), 1600 (C=C stretch of a diene), 1350, 1235, 1195, 945, 750 and 720 (cis-disubstituted alkene), and 680 (alkyne C-H bond) cm.<sup>-1</sup>.

$\tau$  (CCl<sub>4</sub>) 6.60 (1H, d, J 2.5 Hz, acetylenic proton), 4.80 - 4.03 (2H, m) and 3.25 - 2.40 (2H, m). This spectrum was obtained by M.K. Keating.

The compound decomposed to a black oil on standing overnight. The use of a Drikold-acetone cooled trap in the above pyrolysis was found to be essential; if a water-cooled trap was used then none of the acetylenic nitrile could be isolated.

Pyrolysis of 1-(isoindolin-2-yl)-2-phenylaziridine. The title compound (188 mg.) was flash pyrolysed at 400° by

vapourisation at  $80^{\circ}/0.2$  torr. A white crystalline material condensed on the walls of the Drikold-acetone trap. On attaining room temperature the crystals melted to a colourless liquid which was analysed by t.l.c. (silica, petroleum) and g.c. (SE30 and Epikote 1001, chromosorb P, column temperature  $120^{\circ}$ , internal standard: decalin) as pure styrene (76%). A pale yellow liquid condensed at the end of the pyrolysis tube, before reaching the Drikold-acetone trap, but this rapidly darkened and became a purple oil. Sublimation of the oil at  $125^{\circ}/0.01$  torr gave a pale yellow liquid (30 mg.) which was chromatographed on a 20 x 20 cm. silica plate eluted with petrol. o-Quinodimethane (12 mg., 16%) was obtained as a colourless liquid:  $\nu_{\max}$ . 3030, 2915, 1492, 1450, 1431, 1342, 1154, 1110, 1092, 877, and 745  $\text{cm}^{-1}$ , identical to the published spectrum;<sup>133</sup>  $\lambda_{\max}$ . (hexane) 3040 nm., spectrum identical to the published spectrum.<sup>133</sup> The liquid polymerised on standing for 1 day at room temperature and gave poly-o-xylylene, m.p.  $72-86^{\circ}$  (literature<sup>133</sup> quotes softening temperature of  $80^{\circ}$ ),  $\nu_{\max}$ . 1600, 1160, 1100, 1040, 970, and 760  $\text{cm}^{-1}$ , consistent with literature spectrum.<sup>133</sup> The mass spectrum showed the general characteristics of a polymer; base peak at 104, next most intense peak 208 (0.50), and low intensity peak at 312 (0.02).

Flash pyrolysis of this aziridine at  $200^{\circ}$  gave only about 10% yield of styrene (g.c.), the aziridine being largely unchanged (t.l.c.).

Attempted preparation of 2,3-diphenyl-1-(isoindolin-2-yl)-aziridine. N-aminophthalimide (3.24 g., 20 mmole) was stirred in a solution of trans-stilbene (18.0 g., 100 mmole) in dichloromethane (100 ml.). Lead tetra-acetate (8.86 g., 20 mmole) was then added portionwise. After stirring for 15 min., the mixture was filtered and the solids washed with dichloromethane. The combined filtrate and washings were then chromatographed on an alumina column. Petroleum-ether (20:1) eluted trans-stilbene, and petroleum-ether (1:1) eluted trans-2,3-diphenyl-1-phthalimidoaziridine (4.0 g., 59%), m.p. 171-173° (lit.,<sup>38,134</sup> 165°, 177-179°) from ethanol.

trans-2,3-Diphenyl-1-phthalimidoaziridine (1.0 g., 2.9 mmole) was added in portions, as a suspension in anhydrous ether (100 ml.), to a stirred suspension of lithium aluminium hydride (0.45 g., 12 mmole) in refluxing ether (100 ml.) under nitrogen. After 5 hr. reflux, the mixture was cooled below 0° and the excess of reducing agent destroyed by careful addition of water. The mixture was then filtered and the precipitated salts extracted with ether (100 ml.). On standing overnight, the combined filtrates deposited an unidentified compound (78 mg.) as needles, m.p. 120-121° (with vigorous gas evolution) (Found: C, 74.55; H, 5.7; N, 8.0%).  $\nu_{\text{max}}$  3250, 3160, 1625, 1595, 1309, 1005, 760, and 700  $\text{cm}^{-1}$ . The compound was poorly soluble in chloroform, acetone, and acetonitrile but readily soluble in dimethyl sulphoxide, with which it reacted (addition of water to the solution in dimethyl sulphoxide gave a white solid, m.p. 340°,  $\nu_{\text{max}}$  3230,

1630, 1040, 745, and  $700\text{ cm.}^{-1}$ ). The compound could not be recrystallised or sublimed (stilbene was formed ?) but t.l.c. showed a single spot at  $R_F$  0.2 on alumina/ether. A mass spectrum could only be obtained with the inlet at  $> 120^\circ$  and was complex, with a base peak at 180 (stilbene ?).

The ethereal filtrate, after removal of the above solid, was evaporated to give impure trans-stilbene (402 mg.). Chromatography on an alumina column gave only trans-stilbene (360 mg., 68%), eluted by petroleum-ether (20:1) and identified by t.l.c., i.r., and n.m.r..

Preparation and pyrolysis of 1-(carbazol-1-yl)-2-phenylaziridine. N-amino $\beta$ -carbazole (450 mg., 2.44 mmole) in dichloromethane (20 ml.) containing styrene (1.29 g., 12.4 mmole) was stirred and cooled in ice whilst a solution of diacetoxyiodobenzene (1.26 g., 2.44 mmole) in dichloromethane (20 ml.) was added dropwise over 10 min.. After 1 hr., the mixture was filtered to remove bisbiphenyltetrazene (143 mg., 32%), m.p.  $220^\circ$  (decomp.) (lit.,<sup>15</sup>  $216^\circ$ ), and the filtrate chromatographed on an alumina column. Elution with petroleum-ether (9:1) gave iodobenzene, followed by 1-(carbazol-1-yl)-2-phenylaziridine (194 mg., 28%), m.p.  $127-129^\circ$  (lit.,<sup>11</sup>  $127-129^\circ$ ) from ether-petroleum, i.r. identical to a sample prepared (3%) by lead tetra-acetate oxidation.

Pyrolysis was carried out at  $560^\circ$  and  $800^\circ$  by vapourisation at  $160^\circ/0.01$  torr. In both cases, the pyrolysate was trapped on a water-cooled cold finger as

an oil. T.l.c. showed the absence of biphenylene and styrene, and only carbazole and unchanged aziridine could be identified.

Preparation of Diels Alder adducts of  $\alpha$ -carbonyl azo compounds

1,4-Dihydro-1,4-methanopyridazino [1,2-b] phthalazin-6,11-dione. Lead tetra-acetate (12.2 g., 27.5 mmole) was added in portions to a stirred suspension of powdered phthalazin-1,4-dione (4.05 g., 25 mmole) in dichloromethane (200 ml.) and cyclopentadiene (10 g.) at  $-20^{\circ}$ . After 2 hr., the mixture was filtered and the filtrate washed with water (2 x 50 ml.) and dried. Evaporation to 10 ml. and addition of petroleum (100 ml.) gave the adduct (2.0 g., 35%), m.p.  $225-230^{\circ}$  (softens and darkens from  $200^{\circ}$ ). The analytical sample was recrystallised from aqueous acetic acid, then chloroform-petroleum, and had m.p.  $230^{\circ}$  (decomp. variable with rate of heating) (Found: C, 68.8; H, 4.4; N, 12.6.  $C_{13}H_{10}N_2O_2$  requires C, 69.0; H, 4.5; N, 12.4%. M 226).

$\nu_{\max}$ . 1635, 1615, 1310, 1120, 965, 775, and 695  $\text{cm}^{-1}$ .  
 $\tau$  ( $\text{CDCl}_3$ ) 7.82-7.91 (2H, m, methanoprotons), 4.15-4.03 (2H, m, allylic protons), 3.33-3.26 (2H, m, olefinic protons), and 2.34-1.66 (4H,  $A_2B_2$  m, aromatics).

m/e 226 (1.00)  $M^+$ , 199 (0.08), 148 (0.24), 130 (0.20), 104 (0.80), 79 (0.32), 76 (0.40), and 66 (0.08);  
 $m^*$  97.0 = 226  $\rightarrow$  148, 114.2 = 148  $\rightarrow$  130 and 55.5 = 104  $\rightarrow$  76.



6,9-Dihydro-6,9-methanopyridazino[1,2-a]indazol-11-one.

3-Aminobenzotriazin-4-one (1.7 g., 10.5 mmole) in dichloromethane (50 ml.) containing cyclopentadiene (5 ml.) was cooled to  $-20^{\circ}$ . Lead tetra-acetate (4.7 g., 10.6 mmole) was then added in portions to the stirred mixture. After stirring for 30 min., the reaction mixture was filtered and the filtrate chromatographed on a 1 m. silica plate eluted with ether. The title compound was obtained as a yellow oil (570 mg., 28%) which crystallised on prolonged scratching, m.p.  $90-93^{\circ}$  (lit.,<sup>135</sup>  $93-94^{\circ}$ ).

6,9-Dihydropyridazino[1,2-a]indazol-11-one was available from the work of Forster,<sup>136</sup> m.p.  $111-112^{\circ}$  (lit.,<sup>135</sup>  $114-115^{\circ}$ ).

1,4-Dihydro-7,8-diphenylpyrazolo[1,2-a]pyridazin-6-one was available from the work of Yelland,<sup>27</sup> m.p.  $186-187^{\circ}$  (lit.,<sup>137</sup>  $186-187^{\circ}$ ).

Pyrolysis of Diels Alder adducts of  $\alpha$ -carbonyl azo compounds

1,4-Dihydro-1,4-methanopyridazino[1,2-b]phthalazin-6,11-dione. The adduct (107 mg.) was pyrolysed at  $500^{\circ}$  by sublimation at  $200^{\circ}/0.01$  torr. It sublimed easily and clearly and the pyrolysate was trapped (Drikold-acetone) as a pale yellow solid. I.r. and t.l.c. analysis of this solid showed it to be pure benzocyclobutenedione (55 mg., 88%), m.p.  $130-132^{\circ}$  (from cyclohexane). Pyrolysis of the title compound at  $450^{\circ}$  gave benzocyclobutenedione containing about 10% of starting material.

6,9-Dihydro-6,9-methanopyridazino [1,2-a]indazol-11-one.

The title compound (75 mg.) was volatilised at 100°/0.4 torr (nitrogen flow rate 5 ml./min.) and pyrolysed at 400°. Yellow needles formed on the Drikold-acetone trap and were identified as pure biphenylene (18 mg., 63%) [t.l.c., i.r., and g.c. (5% OV17, G.C.Q., 60-80 mesh, 5 ft. column at 200°)] .

6,9-Dihydropyridazino [1,2-a]indazol-11-one. Pyrolysis of the adduct (106 mg.) was carried out at 750-800° by volatilisation at 140-160°/0.01 torr. Extensive charring occurred in the pyrolysis tube. The pyrolysate was trapped on a water cooled surface and chromatographed on a 20 x 20 cm. silica plate eluted with petroleum to give biphenylene (9 mg., 21%), identified by t.l.c., i.r., and g.c..

1,4-Dihydro-7,8-diphenylpyrazolo [1,2-a]pyridazin-6-one.

The adduct (100 mg.) was sublimed at 170°/0.4 torr (nitrogen flow rate 3 ml./min.) and pyrolysed at 500°. The pyrolysate was trapped on a Drikold-acetone cooled surface and chromatographed on a 20 x 20 cm. silica plate. Petroleum eluted diphenylacetylene (29 mg., 40%), identified by i.r., t.l.c., and m.m.p. comparison to authentic. Ether eluted starting material (30 mg., 30%). No diphenylcyclopropanone could be detected by t.l.c. study of the crude pyrolysate. A similar pyrolysis at 320° gave starting material containing about 5% of diphenylacetylene and, again, diphenylcyclopropanone

was not formed (t.l.c.). When pyrolysed at 250°, the adduct was very largely unchanged but t.l.c. analysis of the pyrolysate showed some diphenylacetylene had been formed. Diphenylcyclopropenone could not be detected.

Preparation and pyrolysis of phthalaz-1,4-dione — indene

adduct. Indene (1.16 g., 10 mmole) and powdered phthalazin-1,4-dione<sup>124</sup> (1.62 g., 10 mmole) were stirred in dichloromethane (50 ml.) at 0°. Lead tetra-acetate (4.87 g., 11 mmole) was added in portions over 5 min. After allowing it to come to room temperature and stirring for 3 hr., the mixture was filtered and the solids washed with dichloromethane. The combined filtrate and washings were then extracted with water (2 x 25 ml.), dried, and evaporated. The residue was recrystallised from chloroform-petroleum to give the adduct (1.4 g., 51%), m.p. 256° (decomp.) (lit.,<sup>138</sup> 256-258°).

Pyrolysis of the adduct (72 mg.) was carried out at 500°, by sublimation at 210°/0.02 torr. The pyrolysate was trapped on a Drikold-acetone cooled surface as a yellow solid but this melted on warming to room temperature. The presence of indene (f.p. -9°) was suggested by smell and confirmed by g.c. (5% OV17, Celite 560, 60-80 mesh, 15 ft. column at 170°). P.l.c. on a 20 x 20 cm. silica plate eluted with ether-petroleum (1:1) gave benzocyclobutenedione (20 mg., 64%).

Experimental.    Part 2Preparation of vinylaziridines

1-(3,4-Dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-vinyl-  
aziridine. This was prepared (72%) as described on  
page 79 and had m.p. 93-95° (lit.,<sup>35</sup> 93-95°).

1-(3,4-Dihydro-2-phenyl-4-oxoquinazolin-3-yl)-2-vinyl-  
aziridine. 3-Amino-3,4-dihydro-2-phenyl-4-oxoquinazoline<sup>139,140</sup>  
(2.37 g., 10 mmole) in dichloromethane (40 ml.) containing  
buta-1,3-diene (ca. 2.7 g., 50 mmole) was stirred at  
-20° and treated with lead tetra-acetate (4.9 g., 11 mmole)  
over 10 min.. The mixture was filtered and the filtrate  
chromatographed on a short alumina column. Elution with  
petroleum-dichloromethane (1:1) gave a colourless oil  
which solidified on scratching under petroleum.

Crystallisation from dichloromethane-petroleum gave  
1-(3,4-dihydro-2-phenyl-4-oxoquinazolin-3-yl)vinylaziridine  
(2.0 g., 69%), m.p. 91-92° (Found: C, 74.8; H, 5.1;  
N, 14.4. C<sub>18</sub>H<sub>15</sub>N<sub>3</sub>O requires C, 74.7; H, 5.2; N, 14.5%.  
M 289).

$\nu_{\text{max.}}$  1665 (C=O), 1605, 1590, 1563 (C=N), 1465, 1378,  
1345, 1291, 990, 920, 763, and 690 cm.<sup>-1</sup>.

$\tau$  (CDCl<sub>3</sub>) 7.73-7.04 (3H, m, aziridine ring protons), 5.10-  
4.30 (3H, m, vinylic protons), and 2.68-1.90 (8H, m)  
and 1.71-1.53 (1H, m) (aromatic protons).

m/e 289 (0.31) M<sup>+</sup>, 248 (0.48) (M-C<sub>2</sub>H<sub>5</sub>)<sup>+</sup>, 222 (0.96)  
(3,4-dihydro-2-phenyl-4-oxoquinazoline)<sup>+</sup>, 205 (0.18),  
179 (1.00), and 119 (0.88).

1-(3,4-Dihydro-4-oxoquinazolin-3-yl)-2-vinylaziridine.

3-Amino-3,4-dihydro-4-oxoquinazoline<sup>141,142a</sup> (4.8 g., 30 mmole) in dichloromethane (100 ml.) and buta-1,3-diene (ca. 8.1 g., 150 mmole) was stirred at -20° and lead tetra-acetate (14.6 g., 33 mmole) added over 5 min.. Filtration and chromatography of the filtrate on an alumina column eluted with petroleum-dichloromethane (4:1) gave an oil which crystallised on scratching to give 1-(3,4-dihydro-4-oxoquinazolin-3-yl)vinylaziridine (900 mg., 14%), needles m.p. 93-95° from ether-petroleum (Found: C, 67.7; H, 5.2; N, 19.7. C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>O requires C, 67.6; H, 5.2; N, 19.7%. M 213).

$\nu_{\text{max}}$ . 1670 (C=O), 1600 (C=N), 1460, 1375, 1323, 1300, 1245, 1168, 928, 775, and 695 cm.<sup>-1</sup>.

$\tau$  (CDCl<sub>3</sub>) 7.37-6.60 (3H, m, aziridine ring protons), 4.70-4.10 (3H, m, vinylic protons), 2.64-2.22 (3H, m, aromatic protons), and 1.81-1.61 (m, aromatic proton) and 1.78 (azomethine proton) (together 2H).

m/e 213 (0.40) M<sup>+</sup>, 172 (0.40) (M-C<sub>3</sub>H<sub>5</sub>)<sup>+</sup>, 146 (1.00) (3,4-dihydro-4-oxoquinazoline)<sup>+</sup>, and 118 (0.27).

1-(3,4-Dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-methyl-cis-3-vinylaziridine and 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-(prop-cis-1-enyl)aziridine. (1) Penta-

1-cis-3-diene (1.7 g., 2.5 ml., 25 mmole) and 3-amino-3,4-dihydro-2-methyl-4-oxoquinazoline (0.88 g., 5 mmole) in dry dichloromethane (10 ml.) were cooled in ice, and lead tetra-acetate (2.44 g., 5.5 mmole) added to the stirred mixture over 5 min.. Lead diacetate was filtered

off and washed with ether. The combined filtrate and washings showed the parent lactam and two other spots on t.l.c. [alumina/ether or ether-petroleum (1:1)] and were chromatographed on a short alumina column.

Petroleum-dichloromethane (4:1) eluted a colourless oil (682 mg.). Elution with pure dichloromethane gave a second oil (248 mg.) followed by 3,4-dihydro-2-methyl-4-oxoquinazoline.

The second oil to be eluted solidified on scratching and was recrystallised from chloroform-petroleum to give 3,4-dihydro-2-methyl-3(pent-trans-2-ene-4-hydroxy-1-ylamino)-4-oxoquinazoline (222 mg., 17%), yellow granules m.p. 99-101° (Found: C, 64.8; H, 6.5; N, 16.3.  $C_{14}H_{17}N_3O_2$  requires C, 64.8; H, 6.6; N, 16.2%. M 259).

$\nu_{\max}$ . 3280 sh (NH), 3220 br (OH), 1675 (C=O), 1595 (C=N), 1460, 1375, 1255, 1060, 770, and 695  $\text{cm}^{-1}$ .

$\tau(\text{CDCl}_3)$  8.29 (3H, d, J 5.0 Hz, pentene  $\text{CH}_3$ ), 7.28 (3H, s, quinazoline  $\text{CH}_3$ ), 6.95 (2H, dd, J 6 and 6 Hz, 2H on C-1), 6.40 (1H, broad s, OH), 5.50-5.10 (1H, m, H on C-4), 4.63-4.20 (2H, m, olefinic protons), 3.93 (1H, t, J 6 Hz, NH), and 2.70-2.20 (3H, m) and 1.80-1.70 (1H, m) (aromatic protons). On addition of  $\text{D}_2\text{O}$  the dd at 6.95  $\tau$  became a d, J 6 Hz, and the signals at 6.40  $\tau$  (OH) and 3.93  $\tau$  (NH) disappeared.

m/e 259 (0.004)  $\text{M}^+$ , 241 (0.008)  $(\text{M}-\text{CH}_3)^+$ , 188 (1.00)

$\text{C}_1-\text{C}_2$  cleavage, 160 (0.91), 145 (0.15).  $m^* 136.6 =$

259 → 188.

The first oil to be eluted from the column also solidified on scratching and the solid was recrystallised from chloroform - petroleum to give granules, m.p. 92-94°, of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-(prop-cis-1-enyl)aziridine (366 mg., 30%) (Found: C, 69.3; H, 6.0; N, 17.5.  $C_{14}H_{15}N_3O$  requires, C, 69.7; H, 6.3; N, 17.4%. M 241).

$\nu_{\max}$ . 1675 (C=O), 1590 (C=N), 1460, 1375, 1325, 1230, 1140, 937, 760, and 690  $\text{cm}^{-1}$ .

$\tau(\text{CDCl}_3)$  8.17 (3H, dd, J 1.5 and 7.0 Hz, propenyl  $\text{CH}_3$ ), 7.30 (3H, s, quinazoline  $\text{CH}_3$ ), 7.30-6.50 (3H, m, aziridine ring protons), 4.77 (1H, dd, J 8 and 11 Hz, 1-H of propenyl), 4.40-3.90 (1H, m, 2-H of propenyl), and 2.80-2.20 (3H, m) and 1.90-1.75 (1H, m) (aromatic protons).

m/e 241 (0.24)  $\text{M}^+$ , 226 (0.08)  $(\text{M}-\text{CH}_3)^+$ , 212 (0.04), 200 (0.04)  $(\text{M}-\text{C}_3\text{H}_5)^+$ , 186 (0.40)  $(\text{M}-\text{C}_4\text{H}_7)^+$ , 160 (1.00)  $(3,4\text{-dihydro-2-methyl-4-oxoquinazoline})^+$ , 143 (0.20), 117 (0.54).  $m^* \quad 212.0 = 241 \rightarrow 226$  and  $106.1 = 241 \rightarrow 160$

However, the n.m.r. of this recrystallised solid was much simpler than that of the crude solid before recrystallisation. T.l.c. of the crude solid showed only 1 spot on alumina with ether or ether-petroleum (1:1) but ether-petroleum (2:1) gave separation into 2 spots. Accordingly, the mother liquor from the recrystallisation (300 mg. of pale yellow oil) was carefully applied to a 1 m. alumina p.l.c. plate which was eluted with ether-petroleum (2:1). Separation of the 2 bands was just obtained.

The lower band furnished more 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-(prop-cis-1-enyl)aziridine (45 mg., 4%, total 34%), m.p. 92-94° after recrystallisation from chloroform-petroleum.

The upper band gave 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-methyl-cis-3-vinylaziridine (77 mg., 6%) as an oil which resisted all attempts at crystallisation. The purity of this oil was established by t.l.c. (alumina/ether-petroleum mixtures).

$\nu_{\text{max}}$ . 1670 (C=O), 1590 (C=N), 1460, 1375, 1320, 1295, 1230, 765, and 690  $\text{cm}^{-1}$ .

$\tau(\text{CDCl}_3)$  8.49 (3H, d, J 5.5 Hz, aziridine  $\text{CH}_3$ ), 7.32 (3H, s, quinazolinyl  $\text{CH}_3$ ), 7.12-6.65 (2H, m, aziridine ring protons), 4.70-4.14 (3H, m, vinylic protons), and 2.74-2.16 (3H, m) and 1.91-1.71 (1H, m) (aromatic protons).

The spectrum is consistent with one locked invertomer having the heterocycle trans to the other substituents and showed no signals due to the isomeric aziridine obtained as a solid.

m/e 241 (0.66)  $\text{M}^+$ , 226 (0.53)  $(\text{M}-\text{CH}_3)^+$ , 200 (0.47)  $(\text{M}-\text{C}_3\text{H}_5)^+$ , 186 (0.60)  $(\text{M}-\text{C}_4\text{H}_7)^+$ , 160 (1.00) (3,4-dihydro-2-methyl-4-oxoquinazoline) $^+$ , 143 (0.53), and 117 (0.93).

High resolution gave the mass peak at 241.1225

[ = 241.1215 ( $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}$ ) + 4 p.p.m.] .

(2) Penta-1, cis-3-diene (1.7 g., 2.5 ml., 25 mmole) and 3-amino-3,4-dihydro-2-methyl-4-oxoquinazoline (0.88 g., 5 mmole) in dry benzene (30 ml.) were heated to reflux under an efficient condenser. Lead tetra-acetate (2.44 g.,



5.5 mmole) was added over 3 min. to the stirred mixture under reflux. After a further 2 min. at reflux the mixture was cooled, filtered, and the solid washed with ether. The combined filtrate and washings were evaporated to small volume and carefully applied to a 1 m. alumina p.l.c. plate, which was eluted with ether-petroleum (2:1). No distinct separation of the isomeric aziridines was obtained so the broad band consisting of the aziridines was removed in two halves. The upper portion gave a colourless oil (332 mg.), found by n.m.r. to be slightly richer in the aziridine bearing a ring Me (ratio 7:6). The lower portion gave a colourless oil (289 mg.), found by n.m.r. to be mainly the product of addition to the less substituted double bond (ratio 1:6). This latter oil was crystallised from chloroform-petroleum, by seeding with a crystal of the solid aziridine, and yielded pure 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-(prop-cis-1-enyl)aziridine (195 mg.). The mother liquor from this crystallisation was combined with the oil from the upper portion of the p.l.c. band and the whole carefully applied to a 1 m. alumina p.l.c. plate which was then eluted with ether-petroleum (2:1). With this reduced quantity of applied material, separation was achieved and the 2 bands furnished 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-methyl-cis-3-vinylaziridine (155 mg., 13%), again as an oil, and 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-(prop-cis-1-enyl)aziridine (further 130 mg., total 325 mg., 27%), m.p. 92-94°.

1-(3,4-Dihydro-2-methyl-4-oxoquinazolinyl)-2-(prop-trans-1-enyl)aziridine and 1-(3,4-dihydro-2-methyl-4-oxoquinazolinyl)-2-methyl-trans-3-vinylaziridine. 3-Amino-3,4-dihydro-2-methyl-4-oxoquinazoline (0.88 g., 5 mmole) and a mixture of cis and trans penta-1,3-diene (5 ml., 25 mmole) in dichloromethane (20 ml.) were treated with lead tetra-acetate (2.44 g., 5.5 mmole) with stirring and cooling in ice-water. The addition was performed over 5 min. and the entire reaction mixture was then applied to the head of an alumina column packed in petroleum-dichloromethane (4:1). When the reaction mixture had been drawn down into the alumina, more petroleum - dichloromethane (4:1) was applied to the head of the column. Eight fractions of ca. 300 ml. were collected. The first fraction gave a pure colourless oil (93 mg.) which crystallised spontaneously. The other fractions, which were mixtures on t.l.c. [alumina/ether-petroleum (1:1)], were then combined to give colourless oils as follows : 2+3 gave 402 mg., 4+5 gave 360 mg., and 6+7+8 gave 275 mg..

The oil from fractions 2+3 was carefully applied to a 1 m. alumina p.l.c. plate which was eluted with ether - petroleum (4:1). Separation of the two bands was just achieved, the upper band furnished a pure colourless oil (123 mg.) which crystallised spontaneously and was identical (n.m.r. and t.l.c.) to the solid from column fraction 1. The lower band gave 1-(3,4-dihydro-2-methyl-4-oxoquinazolinyl)-2-(prop-trans-1-enyl)aziridine (128 mg., 10%) as an oil. All

attempts at crystallisation failed but purity was established by t.l.c. on alumina in several solvent systems.

$\nu_{\text{max}}$ . 1670 (C=O), 1590 (C=N), 1470, 1375, 1325, 1300, 1230, 960, 915, 768, and 691  $\text{cm}^{-1}$ .

$\tau$  ( $\text{CDCl}_3$ ) 8.20 (3H, d, J 6.5 Hz showing further splitting of J 0.5 Hz, propene  $\text{CH}_2$ ), 7.40 - 6.64 (3H, m, aziridine ring protons), 7.30 (3H, s, quinazolinyl  $\text{CH}_2$ ), 4.79 - 3.70 (2H, m, olefinic protons), and 2.78-2.20 (3H, m) and 1.92 - 1.70 (1H, m) (aromatic protons).

m/e 241 (0.30), 226 (0.06), 212 (0.05), 199 (0.02), 186 (0.45), 160 (1.00), 143 (0.20), and 117 (0.50).

High resolution gave the mass peak at 241.1207 [= 241.1215 ( $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}$ ) - 3.4 p.p.m.].

The oil from column fractions 4+5 was similarly rechromatographed to give an upper band of an oil (50 mg.) which crystallised spontaneously and was identical to the solid from column fraction 1. The lower band gave a colourless oil (205 mg.) found by n.m.r. to be a mixture of 1-(3,4-dihydro-2-methyl-4-oxoquinazolinyl)-2-(prop-cis and trans-1-enyl)aziridine (cis:trans ratio 2:1).

The oil from column fractions 6+7+8 was also rechromatographed on a 1 m. alumina plate eluting with ether-petroleum (4:1). The upper band furnished an oil (15 mg.) which solidified and was identical to the solid from column fraction 1. The lower band produced a colourless oil (152 mg.) found by n.m.r. to be a mixture of 1-(3,4-dihydro-2-methyl-4-oxoquinazolinyl)-

2-(prop-cis and trans-1-enyl)aziridine (cis:trans ratio 1:1).

The solids from column fraction 1 and the upper bands of the three plates were combined (total 281 mg., 23%) and recrystallised from dichloromethane - petroleum to give 1-(3,4-dihydro-2-methyl-4-oxoquinazolinyl)-2-methyl-trans-3-vinylaziridine, m.p. 97-100° (Found : C, 69.1; H, 6.1; N, 17.3.  $C_{14}H_{15}N_3O$  requires C, 69.7; H, 6.3; N, 17.4%. M 241).

$\nu_{\text{max}}$ . 1665 (C=O), 1600 (C=N), 1460, 1370, 1320, 1300, 1240, 1140, 1014, 955, 942, 770, and 692  $\text{cm}^{-1}$ .

$\tau$  ( $\text{CDCl}_3$ ) 8.77 and 8.43 (together 3H, each d, J 6.0 Hz, aziridine ring  $\text{CH}_2$  in minor and major invertomers respectively, ratio of the two signal areas 1:4.75, vinyl group cis to heterocycle preferred), 7.33 (3H, s, quinazolinyl  $\text{CH}_3$ ), 7.20-6.87 (1H, m, 3-H in major invertomer and 2-H in minor invertomer), 6.87-6.20 (1H, m, 2-H in major invertomer and 3-H in minor invertomer), 4.97-4.05 (3H, m, olefinic protons in both invertomers), and 2.87-2.03 (3H, m) and 1.88-1.68 (1H, m) (aromatic protons).

m/e 241 (0.45)  $\text{M}^+$ , 226 (0.35)  $(\text{M}-\text{CH}_3)^+$ , 200 (0.30)  $(\text{M}-\text{C}_3\text{H}_5)^+$ , 186 (0.20)  $(\text{M}-\text{C}_3\text{H}_7)^+$ , 171 (0.05), 160 (0.50)  $(3,4\text{-dihydro-2-methyl-4-oxoquinazoline})^+$ , 143 (0.30), 117 (1.00), and 90 (0.30).  $m^* 212.0 = 241 \rightarrow 226$  and  $106.1 = 241 \rightarrow 160$ .

1-(3,4-Dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-methyl-trans-3-(prop-cis-1-enyl)aziridine. 3-Amino-3,4-dihydro-2-methyl-4-oxoquinazoline (0.88 g., 5 mmole) in dry dichloromethane (15 ml.) containing hexa-cis,2-trans,4-diene (2.05 g., 3 ml., 25 mmole) was treated with lead tetra-acetate (2.44 g., 5.5 mmole) in one portion, with vigorous stirring and cooling in ice-water. After 3 min. the entire reaction mixture was poured into 60 ml. of petroleum in a column at the head of an alumina column packed in petrol. Suction was applied and the elute collected. When the reaction solution had been drawn into the alumina column, petroleum-dichloromethane (5:1) was applied to the head of the column and 300 ml. fractions collected, again under suction. Fractions 2-7 produced, on evaporation, colourless oils of identical i.r., n.m.r., and t.l.c. in several solvent systems. The n.m.r. spectra were consistent with exclusive addition to the trans double bond of the hexadiene and the product was assigned as 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-methyl-trans-3-(prop-cis-1-enyl)aziridine. (1.18 g., 93%). Crystallisation could not be induced. (Found : C, 70.5; H, 6.9; N, 16.2.  $C_{15}H_{17}N_3O$  requires C, 70.6; H, 6.7; N, 16.5%. M 255).

$\nu_{\max}$ . 1675 (C=O), 1595 (C=N), 1470, 1373, 1325, 1228, 1138, 1015, 945, 768, 692, and 650  $\text{cm}^{-1}$ .

$\tau$  ( $\text{CDCl}_3$ ) 8.80 and 8.36 (together 3H, each d, J 5.5 Hz, aziridine ring  $\text{CH}_2$  in minor and major invertomers respectively, invertomer ratio 7:1, vinyl group cis to

heterocycle preferred), 8.16 and 7.80 (together 3H, 8.16  $\tau$  signal comprised of dd, J 1.5 and 7.0 Hz, propenyl CH<sub>3</sub> in major and minor invertomers respectively), 7.34 (s, quinazolinyl CH<sub>3</sub>) and 7.70-6.32 (m, aziridine ring protons in both invertomers) (together 5H), 5.40-4.06 (2H, m, olefinic protons in both invertomers), and 3.00-2.23 (3H, m) and 1.83-1.62 (1H, m) (aromatic protons).

m/e 255 (0.19) M<sup>+</sup>, 240 (0.18) (M-CH<sub>3</sub>)<sup>+</sup>, 200 (0.61) (M-C<sub>4</sub>H<sub>7</sub>)<sup>+</sup>, 186 (0.26), 175 (0.11), 160 (1.00) (3,4-dihydro-2-methyl-4-oxoquinazoline)<sup>+</sup>, 143 (0.34), 131 (0.12), 117 (0.61), and 96 (0.84).

1-(3,4-Dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-isopropenyl-2-methylaziridine. 3-Amino-3,4-dihydro-2-methyl-4-oxoquinazoline (1.75 g., 10 mmole) was stirred at 0° in a mixture of dichloromethane (20 ml.) and 2,3-dimethylbuta-1,3-diene (4.10 g., 50 mmole). Lead tetra-acetate (4.87 g., 11 mmole) was added in portions during 10 min., and the mixture was then filtered. The filtrate was concentrated and applied to the head of an alumina column packed in petrol. Elution with petroleum-dichloromethane (10:1) gave a 2 component (t.l.c.) oil which was applied to two 1 m. alumina plates. Elution with ether-petroleum (1:1) gave separation into 2 bands.

The upper band gave an oil which crystallised on standing, and was recrystallised from chloroform-petroleum to give 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-

3-yl)-2-isopropenyl-2-methylaziridine (1.2 g., 47%),

m.p. 65-66° (Found : C, 70.4; H, 6.6; N, 16.3.

C<sub>15</sub>H<sub>17</sub>N<sub>3</sub>O requires C, 70.6; H, 6.7; N, 16.5%. M 255).

$\nu_{\text{max}}$ . 1675 (C=O), 1610 (C=N), 1330, 1225, 890, and 770 cm.<sup>-1</sup>.

$\tau$  (CDCl<sub>3</sub>) 8.70 (3H, s, aziridine ring Me), 8.20 (3H, d, J 1.0 Hz), 7.44 (3H, s, quinazolinyl Me), 7.07-6.89 (2H, m, aziridine ring protons), 4.91 (1H, q, J 1.2 Hz, olefinic proton trans to Me), 4.85 (1H, broadened s, olefinic proton cis to Me), and 2.83-2.36 (3H, m) and 2.00-1.80 (1H, m) (aromatics). In addition, signals were present at 8.49, 8.41, and 7.36  $\tau$ , presumably due to the minor invertomer with the isopropenyl group cis to the heterocycle.

m/e 255 (0.08) M<sup>+</sup>, 240 (0.03), 186 (0.35), 160 (1.00), 143 (0.09), and 117 (0.28).

The lower band from the plate gave an oil assigned as 3-(but-3-ene-2-hydroxy-2,3-dimethyl-1-ylamino)-3,4-dihydro-2-methyl-4-oxoquinazoline.

$\nu_{\text{max}}$ . 3450 br. (OH), 3320 (NH), 1680 (C=O), 1600 (C=N), 1250, 905, 780, and 700 cm.<sup>-1</sup>.

$\tau$  (CDCl<sub>3</sub>) 8.60 (3H, s, 2-Me), 8.15 (3H, d, J 1.0 Hz, 3-Me), 7.36 (3H, s, quinazolinyl Me), 7.20-6.64 (2H, m, non-equivalent protons on C-1), [collapses to 7.18 and 6.18 (2d, J 21 Hz) on treatment with D<sub>2</sub>O], 6.52 (1H, broad s, lost on addition of D<sub>2</sub>O), 5.16-4.79 (2H, m, olefinic protons), 4.35 (1H, dd, J 13 and 16 Hz, NH, lost on addition of D<sub>2</sub>O), and 2.86-2.37 (3H, m) and 2.04-1.87 (1H, m) (aromatics).

m/e 273 M<sup>+</sup>.

### Thermolysis of vinylaziridines

Thermolysis of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-vinylaziridine. (1) In decalin. The vinylaziridine (2.0 g.) in dry decalin (7.5 ml.) was stirred and heated under a nitrogen atmosphere for 3 hr. at 170-190°. The dark coloured solution was cooled and poured into petroleum (300 ml.) and the mixture stored at -50° overnight to complete precipitation. The gummy solids were filtered off and chromatographed on a deactivated alumina column.

Petroleum-dichloromethane (4:1) gave 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-3-pyrroline (80 mg., 4%), as colourless granules m.p. 108-110° from petroleum-ether (Found : C, 68.9; H, 5.7; N, 18.3. C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O requires C, 68.7; H, 5.8; N, 18.5% M 227).  $\nu_{\text{max}}$ . 1675 (C=O), 1600 (C=N), 1465, 1375, 1355, 1331, 1251, 1010, 773, and 704 cm.<sup>-1</sup>.

$\tau$ (CDCl<sub>3</sub>) 7.35 (3H, s, quinazolinyl CH<sub>3</sub>), 6.20-5.40 (4H, symmetrical m, 13 lines, assigned to the allylic protons of the pyrroline), 4.10 (2H, s, olefinic protons), and 2.73-2.10 (3H, m) and 1.84-1.68 (1H, m) (aromatic protons). For further details of this temperature dependent spectrum see page 132.

m/e (60 eV) 227 (0.0033) M<sup>+</sup>, 226 (0.01) (M-1)<sup>+</sup>, 225 (0.04) (M-2)<sup>+</sup>, 160 (1.00) (3,4-dihydro-2-methyl-4-oxoquinazoline)<sup>+</sup>, 145 (0.08), 143 (0.09), 118 (0.46),



102, (0.04), 90 (0.09), 75 (0.46), 67 (0.85) (pyrrole)<sup>+</sup>. At 10 eV, the molecular ion was still of low intensity but the intensity ratio of  $m/e$  227:225 was 9:1 while at 60 eV the ratio was 12:1. Dehydrogenation of 3-pyrrolines on electron impact has been noted previously<sup>142b</sup>.

$\lambda_{\text{max}}$ . (EtOH), nm ( $\epsilon$ ) : 225 (18,500), 265 (5900), 275 shoulder (4900), 305 (2580), and 317 shoulder (1950).

Further elution with petroleum-dichloromethane (4:1) gave 3-(but-trans-2-en-1-ylideneamino)-3,4-dihydro-2-methyl-4-oxoquinazoline (800 mg., 40%) as colourless needles, m.p. 141.5-142° from absolute ethanol (Found : C, 68.6; H, 5.8; N, 18.4.  $C_{13}H_{13}N_3O$  requires C, 68.7; H, 5.8; N, 18.5% M 227).

$\nu_{\text{max}}$ . 1675 (C=O), 1600 (C=N), 1460, 1380, 1325, 1238, 1161, 991, 960, 765, and 690  $\text{cm}^{-1}$ .

$\tau$  (CDCl<sub>3</sub>) 8.00 (3H, d, J 5.0 Hz, butenyl CH<sub>3</sub>), 7.46 (3H, s, quinazolinyl CH<sub>3</sub>), 3.64-3.44 (2H, m, olefinic protons), 2.27-2.25 (3H, m) and 1.82-1.65 (1H, m) (aromatic protons), and 1.60-1.40 (1H, m, azomethine proton).

$m/e$  227 (0.15) M<sup>+</sup>, 212 (0.03) C<sub>3</sub>-C<sub>4</sub> cleavage, 186 (0.05) C<sub>1</sub>-C<sub>2</sub> cleavage, 160 (1.00).

(2) In trichlorobenzene. The vinylaziridine (107 mg.) in dry 1,2,4-trichlorobenzene (0.5 ml.) was heated in an n.m.r. tube at 180°  $\pm$  2° and the reaction followed by n.m.r. Signals due to the vinylaziridine disappeared within 32-76 min., and the only products observable

by n.m.r. were the pyrroline and the hydrazone in the ratio 1:1.1-1.3. There was no change in the n.m.r. spectrum on further heating.

(3) In the melt. The vinylaziridine (2.0 g.) was heated as a stirred melt under nitrogen for 1.5 hr. at 220-240°. Chromatography as before gave the pyrroline in 7.5% yield, followed by the hydrazone (43%).

(4) In the vapour phase. The vinylaziridine was flash pyrolysed in the vapour phase at temperatures between 260° and 550° by sublimation at 130-140°/0.04 torr.

The pyrolysate was collected on a water-cooled cold finger and analysed by t.l.c. and n.m.r. spectroscopy.

(i) At 260°. The vinylaziridine (180 mg.) gave a white solid as pyrolysate (178 mg.), the n.m.r. spectrum of which showed it to be pure unchanged vinylaziridine.

(ii) At 320° ± 10°. The vinylaziridine (136 mg.) gave a pale yellow gum as pyrolysate (130 mg.). 3,4-Dihydro-2-methyl-4-oxoquinazoline (13 mg., 14%) was removed in the manner described below and the remaining material analysed by n.m.r. Unchanged vinylaziridine, hydrazone and pyrroline (ratio 0.4:1.0:1.5) were the only constituents. (iii) At 360° ± 10°. The vinylaziridine (135 mg.) gave a pale yellow gum as pyrolysate (130 mg.). 3,4-Dihydro-2-methyl-4-oxoquinazoline (18.5 mg., 20%) was removed as described below and the remaining material analysed by n.m.r.. Unchanged vinylaziridine, hydrazone, and pyrroline (ratio 0.3:1.0:1.9) were the only constituents. (iv) At 440° ± 10°. The vinyl-

aziridine (125 mg.) gave a pale yellow gum as pyrolysate (106 mg.). 3,4-Dihydro-2-methyl-4-oxoquinazoline (33 mg., 45.5%) was removed in the usual manner and the remaining material analysed by t.l.c. and n.m.r.. Hydrazone and pyrroline (ratio 1.3:3.5) were the only constituents. (v) At 550°. The vinylaziridine (122 mg.) gave a white solid as pyrolysate (81 mg.) shown to be 3,4-dihydro-2-methyl-4-oxoquinazoline (94%) by i.r. and t.l.c.. Vinylaziridine, hydrazone, and pyrroline were not observed on t.l.c. [alumina/ether-petroleum (1:1)].

The pyrolyses at 320°, 360°, and 440° (ii, iii and iv) were carried out consecutively under identical conditions of draught, method of temperature determination, and work up procedure. The gummy pyrolysate from each was washed from the cold finger with chloroform and the solution rotary evaporated to yield an oil which was triturated with 25 ml. of ether, refluxed, and allowed to cool. A yellow solid was so obtained with a supernatant yellow turbid solution. Chloroform (2 ml.) was added to clarify the solution and the solid removed by filtration and washed with 5 ml. of hot ether. The i.r. and t.l.c. of the solid showed it to be 3,4-dihydro-2-methyl-4-oxoquinazoline. Sublimation gave white crystals of m.p. and m.m.p. 240-242° (lit.,<sup>125</sup> 240-241°). The filtrate and washings were evaporated to a pale yellow oil. After removal of occluded solvent under high vacuum, the oil was treated with CDCl<sub>3</sub> (0.4 ml.) and the solution screened

through cotton wool into a pipette to remove a small amount (~1 mg.) of insoluble material. The solution was analysed by n.m.r.. The spectra were run consecutively under similar machine operating conditions. The above procedure was found to be a satisfactory method of separating 3,4-dihydro-2-methyl-4-oxoquinazoline from unchanged vinylaziridine, pyrroline and hydrazone.

Thermolysis of 1-(3,4-dihydro-2-phenyl-4-oxoquinazolin-3-yl)-2-vinylaziridine. (1) In the melt. The vinyl-

aziridine (1.0 g.) was heated as a stirred melt for 3 hr. at 160-190°. Chromatography on a basic alumina column eluting with petroleum-dichloromethane (3:2) gave 1-(3,4-dihydro-2-phenyl-4-oxoquinazolin-3-yl)-3-pyrroline as colourless needles, m.p. 134-135.5° from petroleum-ether (Found : C, 74.5; H, 5.1; N, 14.3.

C<sub>18</sub>H<sub>15</sub>N<sub>3</sub>O requires C, 74.7; H, 5.2; N, 14.5%. M 289).

$\nu_{\text{max}}$ . 1686 (C=O), 1600, 1585 (C=N), 1548, 1470, 1441, 1355, 1328, 1150, 773, 700, and 651 cm.<sup>-1</sup>.

$\tau$  (CDCl<sub>3</sub>) 6.60-5.20 (4H, broad, semi-resolved symmetrical doublet centred at 5.88  $\tau$ , separation of maxima 20 Hz, assigned to the allylic protons of the pyrroline ring), 4.20 (2H, s, olefinic protons), and 2.68-2.20 (8H, m) and 1.78-1.48 (1H, m) (aromatic protons). For further details of this temperature dependent n.m.r. spectrum see page 132.

m/e 289 (0.002) M<sup>+</sup>, 287 (0.01) (M-2)<sup>+</sup>, 248 (0.002), 242 (0.03), 222 (1.00), 205 (0.09), 179 (0.11), and 119 (0.73).

No other pure material was isolated on further elution of the column with solvent mixtures increasing in polarity to pure dichloromethane. The hydrazone was subsequently found to be labile on alumina chromatography.

(2) In decalin. The vinylaziridine (1.0 g.) in dry decalin (2 ml.) was stirred under a nitrogen atmosphere for 3 hr. at 180-200°. The black solution was poured into petroleum (80 ml.) and the mixture stored at -50° overnight. The precipitated gum (500 mg.) was taken up in dichloromethane and applied to a 1 m. silica p.l.c. plate which was eluted with ether-petroleum (1:1). The band of higher  $R_F$  yielded the pyrroline (60 mg., 10%), identified by t.l.c., i.r., and n.m.r.. The broader band just below the pyrroline furnished 3-(but-trans-2-en-1-ylideneamino)-3,4-dihydro-2-phenyl-4-oxoquinazoline (300 mg., 50%) as colourless needles, m.p. 98-100° from absolute ethanol (Found : C, 74.5; H, 5.2; N, 14.6.  $C_{18}H_{15}N_3O$  requires C, 74.7; H, 5.2; N, 14.5%. M 289).

$\nu_{\max}$ . 1680 (C=O), 1604, 1595 (C=N), 1460, 1375, 1325, 761, and 690  $\text{cm}^{-1}$ .

$\tau$  (CDCl<sub>3</sub>) 8.08 (3H, d, J 5.0 Hz, Me protons), 3.71 - 3.43 (2H, m, olefinic protons), 2.72-2.18 (3H, m, aromatic protons), and 1.75-1.43 (2H, m, remaining aromatic proton and azomethine proton). The doublet at 8.08  $\tau$  showed no evidence of further splitting. m/e 289 (0.17)  $M^+$ , 274 (0.13)  $C_3-C_4$  cleavage, 248 (0.08)

C<sub>1</sub>-C<sub>2</sub> cleavage, 222 (0.80), 179 (0.21), 146 (0.25), and 119 (1.00).

(3) In trichlorobenzene. The vinylaziridine (70 mg.) in dry 1,2,4-trichlorobenzene (0.3 ml.) was heated in an n.m.r. tube at  $180^{\circ} \pm 2^{\circ}$ . After 115 min., the n.m.r. showed only a little vinylaziridine to remain and within 175 min. the reaction was complete. The only products observable by n.m.r. were the pyrroline and the hydrazone in the ratio 1:1.4-1.6. There was no change on further heating.

Thermolysis of 1-(3,4-dihydro-4-oxoquinazolin-3-yl)-2-vinylaziridine. (1) In the melt. The vinylaziridine (700 mg.) was heated as a stirred melt under nitrogen for 2 hr. at  $175-185^{\circ}$ . Chromatography on a basic alumina column eluting with petroleum-dichloromethane (5:1) gave a mixture of the rearrangement products as an oil (300 mg., 43%). Fractional recrystallisation from ether-petroleum gave first the pyrroline, 1-(3,4-dihydro-4-oxoquinazolin-3-yl)-3-pyrroline (60 mg., 9%) as granules, m.p.  $150-152^{\circ}$  (Found : C, 67.7; H, 5.4; N, 19.3. C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>O requires C, 67.6; H, 5.2; N, 19.7%. M 213).

$\nu_{\text{max.}}$  1670 (C=O), 1600 (C=N), 1465, 1295, 1250, 775, and 695 cm.<sup>-1</sup>.

$\tau$  (CDCl<sub>3</sub>) 5.72 (4H, sharp singlet, methylene protons of pyrroline ring), 4.11 (2H, s, olefinic protons of pyrroline ring), 2.65-2.20 (3H, m, aromatic protons), and 1.90-1.60 (m, aromatic proton) and 1.79 (s,

azomethine proton) (together 2H). For further details of this temperature dependent n.m.r. spectrum see page 132.

m/e 213 (0.01)  $M^+$ , 211 (0.03)  $(M-2)^+$ , 184 (0.23), 172 (0.23), 146 (1.00), and 118 (0.35).

Further concentration and addition of petroleum gave two crops of solid, found by n.m.r. to be mixtures of the pyrroline and hydrazone, followed by a final crop of the hydrazone, 3-(but-trans-2-en-1-ylideneamino)-3,4-dihydro-4-oxoquinazoline (49 mg., 7%).

Further recrystallisation from absolute ethanol gave colourless needles m.p. 102-104° (Found : C, 67.5; H, 5.1; N, 19.6.  $C_{12}H_{11}N_3O$  requires C, 67.6; H, 5.2; N, 19.7%. M 213).

$\nu_{\max}$ . 1680 (C=O), 1610 (C=N), 1460, 1375, 1320, 1290, 1256, 985, 885, 770, and 690  $\text{cm}^{-1}$ .

$\tau$  ( $\text{CDCl}_3$ ) 8.08 (3H, d, J 5.0 Hz,  $\text{CH}_3$ ), 3.93-3.45 (2H, m, olefinic protons), 2.71-2.22 (3H, m, aromatic protons), 1.83-1.63 (m, aromatic proton) and 1.80 (s, azomethine proton of quinazoline) (together 2H), and 0.97-0.82 (1H, m, azomethine proton of butylidene-amino group). The doublet at 8.08  $\tau$  showed no further splitting.

m/e 213 (0.66)  $M^+$ , 198 (0.02)  $C_1-C_2$  cleavage, 172 (0.11)  $C_3-C_4$  cleavage, 146 (1.00), 130 (0.17), and 118 (0.49).

(2) In trichlorobenzene. The vinylaziridine (73 mg.) in 1,2,4-trichlorobenzene (0.3 ml.) in an n.m.r. tube was heated at  $180 \pm 2^\circ$ . The vinylaziridine signals disappeared within 39-99 min. and the only products

observable were the pyrroline and hydrazone in the ratio 1:0.5-0.7. There was no change in the n.m.r. spectrum on further heating.

Thermolysis of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-methyl-cis-3-vinylaziridine. The vinylaziridine (205 mg.) in dry decalin (2ml.) was stirred under nitrogen for 2 hr. at 180°. The solution darkened and a brown solid precipitated as the reaction proceeded. T.l.c. showed several very minor products, 3,4-dihydro-2-methyl-3-(pent-trans-3-en-2-ylideneamino)-4-oxoquinazoline not being one of them, and 3,4-dihydro-2-methyl-4-oxoquinazoline as the major product. The mixture was cooled, added to petroleum (75 ml.) and cooled at -50° overnight. The brown solid was filtered off and sublimed to give 3,4-dihydro-2-methyl-4-oxoquinazoline (88 mg., 65%), identified by i.r., m.p., and t.l.c.. A similar result was obtained when the vinylaziridine (170 mg.) was heated in the melt under nitrogen for 2 hr.. T.l.c. showed the absence of the hydrazone and the major product was again 3,4-dihydro-2-methyl-4-oxoquinazoline.

Thermolysis of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-methyl-trans-3-vinylaziridine. The vinylaziridine (136 mg.) in 1,2,4-trichlorobenzene (0.35 ml.) was heated at 180° for 170 min.. T.l.c. showed the major product to be 3,4-dihydro-2-methyl-4-oxoquinazoline and showed the absence of the expected hydrazone. Work



up as above gave 3,4-dihydro-2-methyl-4-oxoquinazoline (54 mg., 60%). A similar result was obtained when the vinylaziridine (80 mg.) was heated as a melt under nitrogen for 2 hr. at 180°.

Thermolysis of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-(prop-cis-1-enyl)aziridine. The vinylaziridine (285 mg.) in dry decalin (2 ml.) under nitrogen was stirred at 180° for 3 hr.. Addition to petroleum (100 ml.) and storage at -50° overnight gave a red-brown gum (250 mg.) which was chromatographed on a 1 m. silica plate eluted with ether. 3,4-Dihydro-2-methyl-4-oxoquinazoline (95 mg., 50%) was the only identifiable product.

Thermolysis of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-(prop-trans-1-enyl)aziridine. The vinylaziridine (50 mg.) was heated in dry decalin (1 ml.) at 180° for 3 hr.. T.l.c. of the dark solution showed that 3,4-dihydro-2-methyl-4-oxoquinazoline was the major product.

Thermolysis of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-methyl-trans-3-(prop-cis-1-enyl)aziridine. The vinylaziridine (600 mg.) in dry decalin (2 ml.) was stirred and heated at 180° for 3 hr. under nitrogen. The initially colourless solution became deep red and crystals sublimed onto the upper part of the flask. On cooling, these were removed and washed with petroleum to give 3,4-dihydro-2-methyl-4-oxoquinazoline

(109 mg., 30%) identified by i.r., and t.l.c.. The reaction solution and petroleum washings were combined and added to petroleum (75 ml.) and stored at  $-50^{\circ}$  overnight. Filtration separated a red gum (480 mg.) which was chromatographed on a basic alumina column. The first material from the column was a brown intractable oil eluted by petroleum-dichloromethane (4:3). Elution with dichloromethane gave 3,4-dihydro-2-methyl-4-oxoquinazoline (further 50 mg., 14%, total 44%), identified by i.r. and t.l.c..

Thermolysis of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-isopropenyl-2-methylaziridine. (1) In solution.

The aziridine (500 mg.) was heated in dry decalin (1 ml.) at  $160-185^{\circ}$  for 45 min.. On cooling, 3,4-dihydro-2-methyl-4-oxoquinazoline (23 mg., 7.5%) precipitated and was collected. The filtrate was applied to a 1 m. alumina plate which was then eluted with petroleum-ether (2:1). The decalin ran at the solvent front and two other bands were observed.

The middle band gave 4-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-3,4-dimethyl-3-pyrroline (300 mg., 60%), m.p.  $129-130^{\circ}$  (from chloroform-petroleum) (Found : C, 70.5; H, 6.7; N, 16.4.  $C_{15}H_{17}N_3O$  requires C, 70.6; H, 6.7; N, 16.5%. M 255).

$\nu_{\max}$ . 1680 (C=O), 1605 (C=N), 1250, 880, 780, and 700  $\text{cm}^{-1}$ .

$\tau$  ( $\text{CDCl}_3$ ) 8.32 (6H, s, pyrroline methyls), 7.38 (3H, s,

quinazolinyl  $\text{CH}_3$ ), 6.30-5.60 (4H, complex m, symmetrical about 5.95  $\tau$ ), and 2.75-2.30 (3H, m) and 2.00-1.80 (1H, m) (aromatics).

m/e 255 (0.001)  $\text{M}^+$ , 253 (0.02)  $(\text{M}-2)^+$ , 186 (0.01), 160 (0.50), 145 (0.04), 143 (0.09), 132 (0.03), 118 (0.08), and 96 (1.00).

From the lower band was obtained an unidentified substance (80 mg.) m.p. 103-106° (from chloroform-petroleum).

(2) In the vapour phase. The aziridine (84 mg.) was volatilised at 130-150°/0.005 torr and pyrolysed at 550°. The pyrolysate was trapped on the water-cooled cold finger as a white solid which was 3,4-dihydro-2-methyl-4-oxoquinazoline containing only a trace of the pyrroline (t.l.c.). Trituration with a little dichloromethane gave pure 3,4-dihydro-2-methyl-4-oxoquinazoline (34 mg., 64%), identified by m.p., i.r., and t.l.c..

Alternative preparation of hydrazones. 3-Amino-3,4-dihydro-2-methyl-4-oxoquinazoline (1.0 g.) was heated under reflux (104°) with crotonaldehyde (30 ml.) for 2 hr.. The excess of crotonaldehyde was removed by rotary evaporation and the residue crystallised from ethanol to give 3-(but-trans-2-en-1-ylideneamino)-3,4-dihydro-2-methyl-4-oxoquinazoline (1.2 g., 90%).

By a similar procedure were prepared 3-(but-trans-2-en-1-ylideneamino)-3,4-dihydro-2-phenyl-4-oxoquinazoline (60%) and 3-(but-trans-2-en-1-ylideneamino)-3,4-dihydro-4-oxoquinazoline (80%).

In all three cases the hydrazone was identical (t.l.c., m.p., m.m.p., i.r., and n.m.r.) to the corresponding hydrazone obtained by thermolysis of the appropriate vinylaziridine. In particular, the n.m.r. spectra of the hydrazones from the two methods of preparation showed identical splitting of the butenyl methyl group.

Preparation of 3,4-dihydro-2-methyl-3-(pent-trans-3-en-2-ylideneamino)-4-oxoquinazoline. 3-Amino-3,4-dihydro-2-methyl-4-oxoquinazoline (1.75 g., 10 mmole) and pent-3-en-2-one (0.84 g., 10 mmole) were heated under reflux in absolute ethanol (30 ml.) containing a drop of glacial acetic acid. Reaction was very slow and after 3 weeks t.l.c. showed that the reaction mixture contained starting material and several products in small amounts. Rotary evaporation and trituration with ether (10 ml.) gave unchanged 3-amino-3,4-dihydro-2-methyl-4-oxoquinazoline (0.6 g.). The ether soluble fraction was chromatographed on a 1 m. alumina plate eluted with ether-petroleum (2:1). The band at  $R_F$  0.3 gave an oil which crystallised on standing and was recrystallised from ether-petroleum to give 3,4-dihydro-2-methyl-3-(pent-trans-3-en-2-ylideneamino)-4-oxoquinazoline (8 mg., 0.33%), m.p. 135-139°.

$\nu_{\text{max}}$ . 1660 (C=O), 1584 (C=N), 1330, 970, and 765  $\text{cm}^{-1}$ .

$\tau$  (CDCl<sub>3</sub>, 100 MHz) 8.07 (3H, s, 1H on C-1), 8.02 (3H, d, J 5.0 Hz, 3H on C-5), 7.63 (3H, s, quinazoline Me), 3.52-3.34 (2H, m, olefinic protons), and 2.70-2.24

(3H, m) and 1.78-1.68 (1H, m) (aromatic protons). The doublet at 8.02  $\tau$  showed no sign of further splitting. m/e 241 (0.54)  $M^+$ , 226 (1.00)  $(M-CH_3)^+$ , 200 (0.23), 175 (0.08), 160 (0.16), 144 (0.42), and 117 (0.38).

High resolution gave the mass peak at 241.1223

[ = 241.1215 ( $C_{14}H_{15}N_3O$ ) + 3.2 p.p.m. ].

Variable temperature n.m.r. spectra of 3-pyrrolines. The

n.m.r. spectrum of 1-(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-3-pyrroline in *o*-dichlorobenzene solution (50 mg./0.4 ml.) was determined at temperatures between 25° and 150°. The signal assigned to the allylic protons of the pyrroline ring changed from a complex but symmetrical multiplet to a sharp singlet over this range (see Figure 1). The other signals were temperature invariant and the original spectrum was restored on cooling the sample.

The following pyrrolines showed very similar effects for the allylic protons, but over different temperature ranges.

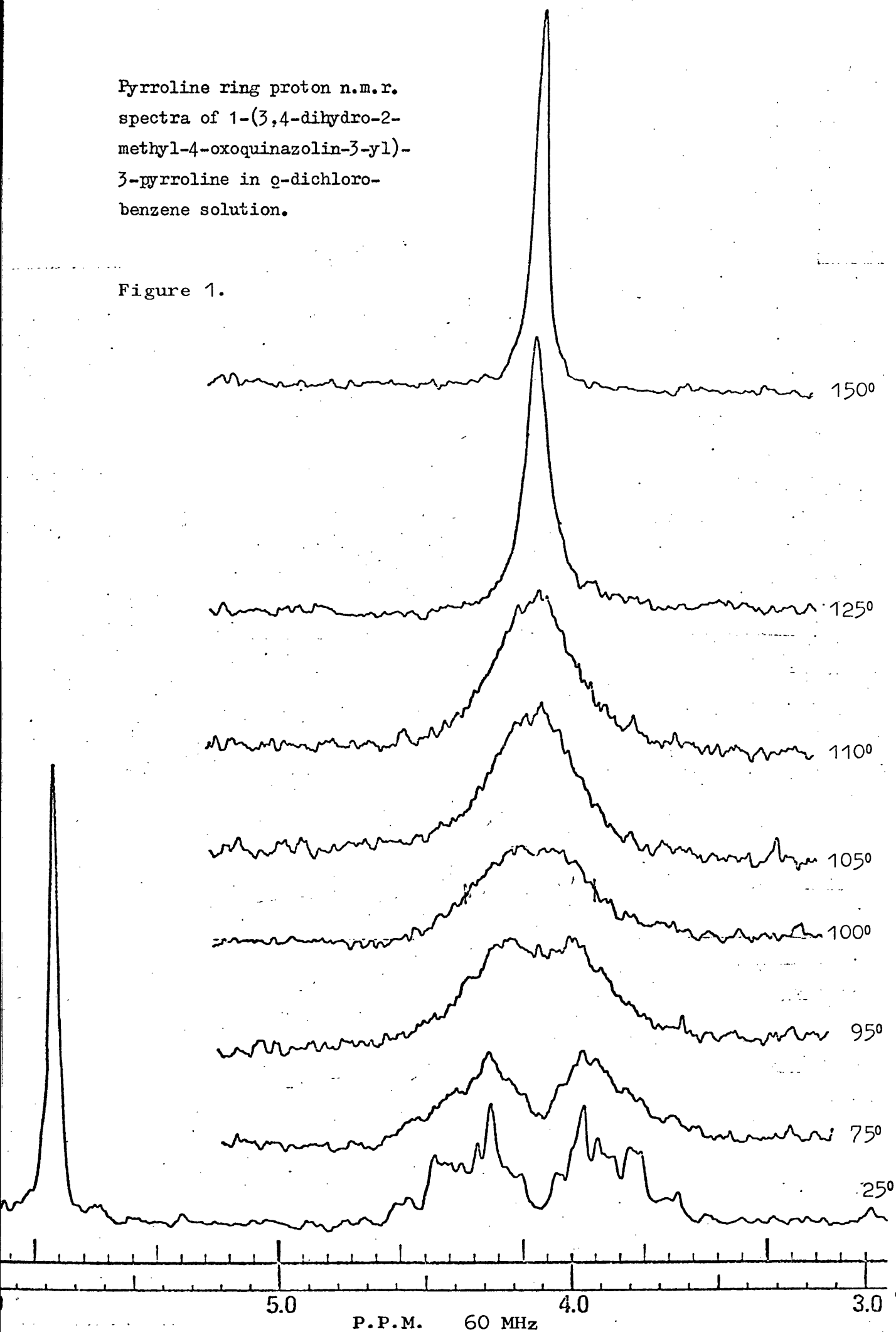
1-(3,4-Dihydro-2-phenyl-4-oxoquinazolin-3-yl)-3-pyrroline (in  $CDCl_3$  solution) : broad singlet at 55°; complex but symmetrical multiplet at -25°; coalescence temperature 45°.

1-(3,4-Dihydro-4-oxoquinazolin-3-yl)-3-pyrroline (in  $CDCl_3$  solution) : sharp singlet at 20°; broad singlet at -50°; coalescence temperature -60°.

1-(3,4-Dihydro-2-methyl-4-oxoquinazolin-3-yl)-3,4-

Pyrroline ring proton n.m.r.  
spectra of 1-(3,4-dihydro-2-  
methyl-4-oxoquinazolin-3-yl)-  
3-pyrroline in *o*-dichloro-  
benzene solution.

Figure 1.



dimethyl-3-pyrroline (in o-dichlorobenzene solution) :  
complex but symmetrical multiplet at 40°; sharp  
singlet at 170°; coalescence temperature 110°.

Preparation and thermolysis of 2-acetyl-1-(3,4-dihydro-2-methyl-4-oxoquinazolin-1-yl)aziridine. (1) Preparation.

3-Amino-3,4-dihydro-2-methyl-4-oxoquinazoline (5.25 g.,  
30 mmole) was stirred in dichloromethane (75 ml.)

containing freshly distilled methyl vinyl ketone  
(10.5 g., 150 mmole). Lead tetra-acetate (14.6 g.,  
33 mmole) was added portionwise with cooling in ice.

Filtration separated lead diacetate which was washed  
with dichloromethane. The combined filtrates were  
chromatographed on a short column of basic alumina.

Petroleum-dichloromethane (5:1) eluted 2-acetyl-1-  
(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)aziridine  
(2.5 g., 34%) as a colourless oil which crystallised  
on scratching under petroleum and was recrystallised  
from ether-petroleum to give plates, m.p. 76-78°

(Found : C, 64.4; H, 5.3; N, 17.3.  $C_{13}H_{13}N_3O_2$  requires  
C, 64.2; H, 5.4; N, 17.3%. M 243).

$\nu_{\text{max}}$ . 1690 (acetyl C=O), 1670 (quinazolone C=O),  
1605 (C=N), 1460, 1370, 1358, 1320, 1300, 1240, 1130,  
930, 770, and 695  $\text{cm}^{-1}$ .

$\tau$  ( $\text{CDCl}_3$ ) 7.71 (3H, s,  $\text{CH}_3\text{CO}$ ), 7.36 (3H, s, quinazolinyl  
 $\text{CH}_3$ ), 7.56-7.03 (2H, m, 3-H of aziridine ring), 6.65-  
6.28 (1H, m, 2-H of aziridine ring), 2.86-2.29 (3H, m)

and 2.08-1.86 (1H, m) (aromatics).

m/e 243 (0.73)  $M^+$ , 200 (0.04)  $(M-COMe)^+$ , 186 (0.18), 173 (0.14), 160 (1.00) (3,4-dihydro-2-methyl-4-oxoquinazoline) $^+$ , 143 (0.20), 117 (1.00), and 90 (0.32).  
 $m^* 105.3 = 243 \rightarrow 160$ .

(2) Pyrolysis. The title compound (900 mg.) was heated in dry decalin (3 ml.) under nitrogen for 4 hr. at 170-185°. A brown solid precipitated on cooling which was removed by filtration and washed with ether. Sublimation at 120-140° /0.2 torr gave 3,4-dihydro-2-methyl-4-oxoquinazoline (154 mg., 26%). Further sublimation at 220° /0.2 torr gave 3,4-dihydro-3-[(3,4-dihydro-2-methyl-4-oxoquinazolin-3-yl)-2-ketobutan-4-ylamino]-2-methyl-4-oxoquinazoline (447 mg., 60%), m.p. 250° (dec.) from ethanol (Found : C, 65.0; H, 5.0; N, 17.0.  $C_{22}H_{21}N_5O_3$  requires C, 65.5; H, 5.25; N, 17.4%. M 403).

$\nu_{max}$ . 3340 br (NH), 1660 (C=O), 1600 (C=N), 1460, 1375, 1215, 1000, 770, and 695  $cm^{-1}$ .

m/e No  $M^+$  at 403, 243 (0.06), 225 (1.00), 212 (0.10), 197 (0.24), and 160 (0.10).

#### Pyrolysis of trans-2,3-diphenyl-4-phthalimidoaziridine.

(1) In the vapour phase. (i) The title compound (50 mg.) (for preparation see Part 1, Section 2) was flash pyrolysed in the vapour phase at 350° by sublimation at 200° /0.04 torr. The pyrolysate (40 mg.) was trapped on a water-cooled cold finger. Analysis



by t.l.c. on silica and alumina with ether-petroleum mixtures showed largely unchanged aziridine but small amounts of 2,3-diphenyl-2H-azirine, phthalimide, and 2-phenylindole were positively identified by comparison to authentic samples. (ii) Pyrolysis of the aziridine (100 mg.) in a similar fashion but at 700° gave greater decomposition. T.l.c. showed the presence of unchanged aziridine, phthalimide, and 2-phenylindole in the pyrolysate. P.l.c. on a 20 x 20 cm. silica plate eluted with petroleum-ether (10:1) gave 2-phenylindole (15 mg., 38%), identified by comparison of i.r., m.p., m.m.p., and t.l.c. to authentic.

(2) In decalin. The aziridine (300 mg.) was heated at 180-190° for 3 hr. in dry decalin (5 ml.). On cooling, yellow crystals of unchanged aziridine (155 mg., 52%) were deposited. The filtrate was shown by t.l.c. to contain mainly unchanged aziridine but definite evidence was found for the presence of small amounts of 2,3-diphenyl-2H-azirine, 2-phenylindole, and phthalimide.

Pyrolysis of 2,3-diphenyl-2H-azirine. The azirine was prepared as follows. Iodine azide was prepared<sup>143</sup> from sodium azide (15.0 g.), iodine monochloride (18.3 g.) and acetonitrile (100 ml.) and reacted with trans-stilbene (18.0 g.) to give erythro-1-azido-2-iodo-1,2-diphenylethane<sup>143</sup> (32 g., 92%).  $\nu_{\text{max}}$  2200 ( $\text{N}_3$ ), 1240, 770, and 700  $\text{cm}^{-1}$ . This iodo-azide (17.45 g., 0.05 mole) was stirred at 0° for 18 hr. with potassium t-butoxide (6.75 g., 0.06 mole) in dry ether (150 ml.). The resulting mixture was washed with

water and dried over  $\text{MgSO}_4$ . Rotary evaporation at room temperature gave a mixture of the product and unreacted iodo-azide. This was treated with dry petroleum (b.p. 60-80°) and filtered to remove the relatively insoluble iodo-azide. The petroleum filtrate was passed down an alumina column (Merck activity 1, neutral) and the earlier fractions of pure unsaturated azide collected and made up to 500 ml. with dry petroleum (b.p. 60-80°). After reflux for 2.5 hr. the colourless solution was evaporated to give a colourless oil which crystallised overnight and was re-crystallised from hexane giving 2,3-diphenyl-2H-azirine (2.0 g., 20%) as needles, m.p. 68-69° (lit.,<sup>143</sup> 60-62°).  $\nu_{\text{max}}$  1740 (azirine C=N), 1330, 1000, 760, and 700  $\text{cm}^{-1}$ .  $\tau$  ( $\text{CDCl}_3$ ) 6.71 (1H, s, azirine proton), and 2.85 (5H, s) and 2.60-2.08 (5H, m) (together 10H, aromatics). m/e 193 (1.00)  $\text{M}^+$ , 103 (0.90)  $(\text{PhC}\equiv\text{N})^+$ , 90 (0.91)  $(\text{PhCH})^+$ , and 89 (0.91)  $(\text{PhC})^+$ .

(1) Pyrolysis in the vapour phase. The azirine (50 mg.) was flash pyrolysed in the vapour phase at 450° by sublimation at 60°/0.04 torr. The pyrolysate was trapped on a water-cooled cold finger as a yellow solid (40 mg.). T.l.c. showed this to be predominantly one product and no azirine remained. Purification on a 20 x 20 cm. silica plate eluted with petroleum-ether (10:1) gave 2-phenylindole (30 mg., 60%) as colourless plates, m.p. 187-190° from cyclohexane (lit., 186-188).  $\nu_{\text{max}}$  3400 (NH), 740, and 680  $\text{cm}^{-1}$ .

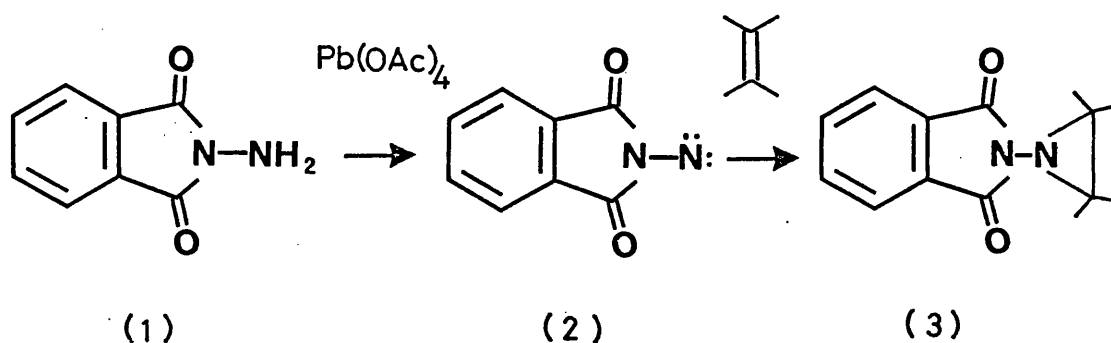
m/e 193 (1.00)  $M^+$ , 165 (0.18), 96.5 (0.13)  $M^{2+}$ , 90 (0.11), and 89 (0.11).  $m^* 141.5 = 193 \rightarrow 165$ . The i.r., m.p., and m.m.p. were identical to those of an authentic sample (Koch-Light, recrystallised from cyclohexane).

(2) Pyrolysis in decalin. The title compound (200 mg.) was heated at 180-190° for 3 hr. in dry decalin solution (4ml.). After this period t.l.c. [silica/petroleum-ether (10:1)] showed unchanged azirine, 2-phenylindole and other unidentified spots. The decalin solution was applied to a 1 m. silica p.l.c. plate and eluted with petroleum-ether (10:1). The major bands furnished unchanged azirine (90 mg., 45%) and 2-phenylindole (50 mg., 25%).

D I S C U S S I O N

Discussion : Part 1, Section 1

Aziridines can be prepared by the oxidation of N-aminophthalimide (1) and several other N-amino heterocyclic systems in the presence of olefins. The wide range of olefins that can be used enables the preparation of aziridines substituted with a variety of groups, both electrophilic and nucleophilic.<sup>35</sup> The probable mechanism for the reaction involves amino-nitrenes, e.g. (2), as intermediates (Scheme 1).

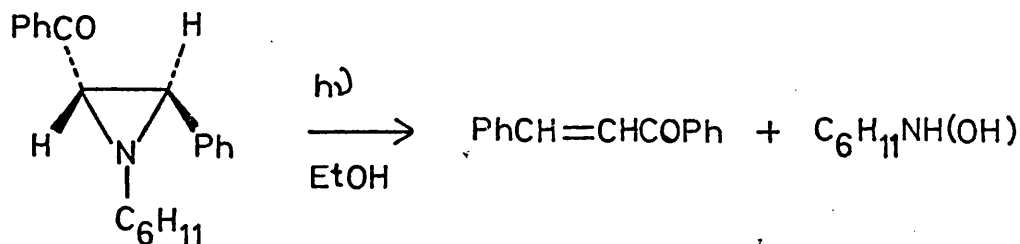


(Scheme 1)

It was considered a possibility that photolysis of the phthalimido-aziridines (3) might lead to fragmentation, regenerating the phthalimido-nitrene (2) and the olefin. This would provide a non-oxidative route to phthalimido-nitrene and would give information as to the reactions undergone by the nitrene, under differing conditions of generation.

The reported photolyses of aziridines implicate neither carbenes nor nitrenes and generally involve

cleavage of only one of the aziridine ring bonds. Huisgen's work<sup>103-104</sup> has shown a tendency for C-C cleavage to give azomethine ylids, and Padwa<sup>101</sup> has observed both C-C and C-N cleavage depending on the aziridine substituents. The one example of photochemical deamination of an aziridine lies in the photolysis of trans-1-cyclohexyl-2-phenyl-3-benzoyl-aziridine in ethanol; one of the reaction paths involves deamination, the products being cis- and trans-benzylideneacetophenone and N-cyclohexylhydroxylamine (Scheme 2). Cyclohexyl-nitrene, however, is not a likely intermediate.<sup>97</sup>



(Scheme 2)

Nevertheless, because of the resonance stabilisation available to the singlet states of amino-nitrenes and other nitrenes with a heteroatom substituent, it seemed possible that the appropriate aziridines would fragment to give the nitrenes.

#### Preparation of phthalimido-aziridines

The phthalimido-aziridines used in this investigation were prepared using the literature method.<sup>35</sup>  
N-Aminophthalimide, prepared from phthalimide and

hydrazine hydrate,<sup>124</sup> was stirred in a mixture of the olefin and dichloromethane; solid lead tetra-acetate was then added in portions. The technique of washing the filtrate from the reaction mixture with aqueous sodium hydroxide solution to remove phthalimide, as previously applied to the preparation of 7-phthalimido-7-azabicyclo[4,1,0]heptane,<sup>35</sup> was found to be applicable generally and enabled the preparation of pure aziridines without chromatography. However, the aziridines derived from trans- and cis-4-methylpent-2-ene were isolated using a chromatographic work-up, since the aziridine yield was lower than normal.

Photolysis of phthalimido-aziridines in the presence of olefins

To test the possibility of nitrene formation by aziridine ring cleavage, the phthalimido-aziridines were irradiated in acetonitrile and cyclohexene. The work of Anderson<sup>11,26</sup> on the photolysis of sulfoximides has shown that the azabicycloheptane (4) is photostable; thus it could be used as a means of detecting any phthalimido-nitrene (Scheme 3).

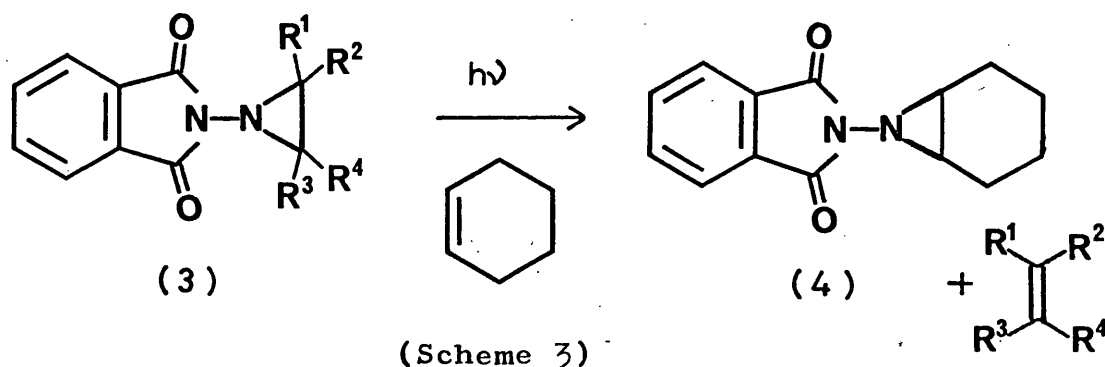


Table 1 shows the results of such experiments. Exchange according to the sequence shown was observed only when one of the substituents of the aziridine (3) had a conjugating group - a carbonyl group or an aromatic ring - adjacent to the aziridine ring, but not otherwise.

TABLE 1

Photolysis of phthalimido-aziridines (3) in the presence of cyclohexene according to Scheme 3.

Expt. no.	Aziridine (3)				Molar ratio aziridine: cyclohexene	Time (hr.)	Aziridine (4)	
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>			% n.m.r.	p.l.c.
1	Me	Me	H	COMe	1:50	48	-	39
2	H	H	Me	CO <sub>2</sub> Me	1:50	48	-	81
3	H	H	H	Ph	1:50	60	-	24
4	Me	H	H	CO <sub>2</sub> Me	1:50	68	-	15
5	H	H	H	CO <sub>2</sub> Me	1:50	48	-	11
6	H	H	H	CO <sub>2</sub> Me	1:50	48	50	37
7	H	H	H	CO <sub>2</sub> Me	1:100	90	50 <sup>±5</sup>	-
8	H	H	H	CO <sub>2</sub> Me	1:50	90	42 <sup>±5</sup>	-
9	H	H	H	CO <sub>2</sub> Me	1:20	90	38 <sup>±5</sup>	-
10	H	H	H	CO <sub>2</sub> Me	1:4	90	43 <sup>±5</sup>	-
11	H	H	H	CO <sub>2</sub> Me	1:2	60	28 <sup>±5</sup>	-
12	H	H	H	CO <sub>2</sub> Me	1:1	60	19 <sup>±5</sup>	-
13	Me	Me	H	Bu <sup>t</sup>	1:50	48	0	0
14	Cl	H	Cl	H	1:50	55	-	0
15	H	H	H	OCOMe	1:50	118	0	0

Notes : experiment 6 was performed similarly to experiment 5 but the p.l.c. work up was performed more rapidly; experiments 7, 8, 9, and 10 were performed concurrently under identical conditions; experiments 11 and 12 were performed concurrently under identical conditions. All photolyses were performed in acetonitrile solution.

Thus, aziridines bearing only alkyl substituents



were photostable (e.g. experiment 13), and the vinyl acetate derived aziridine (bearing an unsaturated unit  $\beta\gamma$  to the ring) similarly failed to undergo exchange (experiment 15). trans-2,3-Dichloro-1-phthalimidoaziridine did not undergo the exchange reaction but formed a polymer (experiment 14).

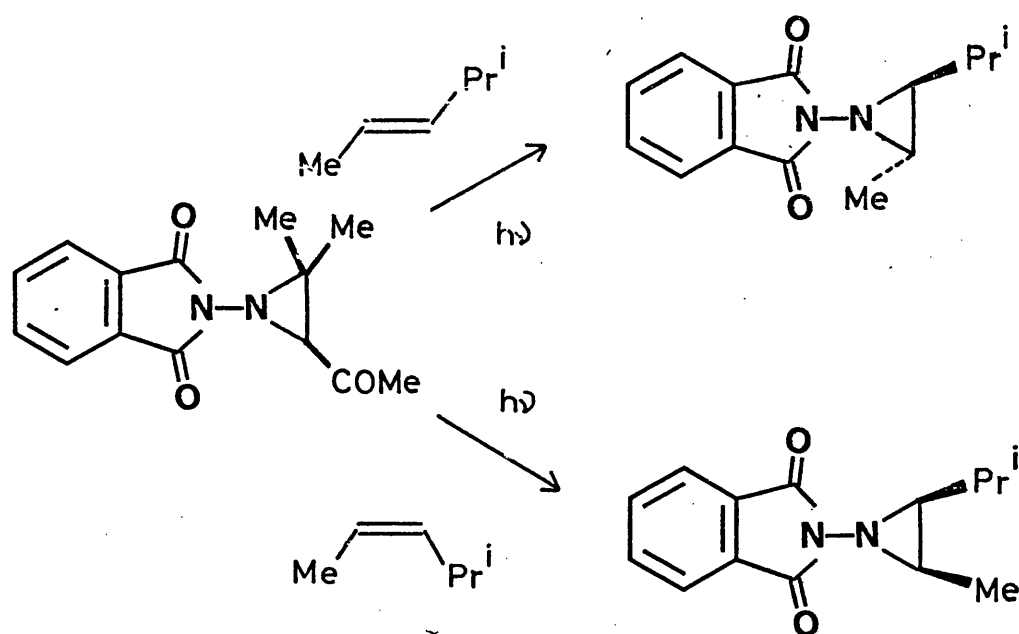
The photochemical exchange reaction was relatively slow and, to avoid prolonged periods of irradiation, the photolyses were generally terminated before all the starting aziridine (3) was consumed. The azabicycloheptane (4) could be separated from the remaining aziridine (3) by preparative layer chromatography (p.l.c.), but this entailed some loss of the aziridines due to decomposition on the plate (compare experiments 5 and 6) and it was found more convenient to determine the yield of aziridine (4) by  $^1\text{H}$  n.m.r. spectroscopy. Evaporation of the photolysate and study of the n.m.r. of the residue showed that side reactions were minimal; the aziridine (4) and sometimes polymer of the exchanged olefin were the only products.

Experiments 7-12 were carried out in order to investigate the effect of varying the amount of cyclohexene. It was found that the exchange reaction did not require a vast excess of cyclohexene and there was appreciable reaction even with 1 mol. of cyclohexene.

The use of olefins other than cyclohexene, and aziridines other than phthalimido-aziridines, was then considered in order to extend the exchange reaction.

As expected, it was found that other simple nucleophilic olefins could be used as traps instead of cyclohexene. Electrophilic olefins, such as mesityl oxide and methyl acrylate, were also used successfully.

The experiments with cis- and trans-4-methylpent-2-ene showed that the corresponding aziridines were formed stereospecifically (Scheme 4).



(Scheme 4)

The cis- and trans-aziridines had n.m.r. spectra which were readily distinguishable, and none of the 'opposite' isomer could be detected in the n.m.r. of the residue after evaporation of the photolysate, nor in the n.m.r. of the product aziridine as isolated by p.l.c.. In independent dilution experiments, the limits of detection of small amounts of the 'opposite' isomers were determined, and the stereospecificity was estimated as  $>97\%$  for the cis, and  $>94\%$  for the trans.

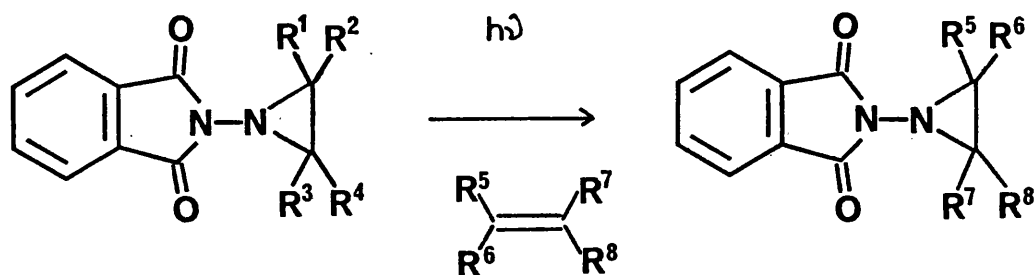
The results of these exchange reactions, according to Scheme 5, are summarised in Table 2.

TABLE 2

Photolysis of phthalimido-aziridines in the presence of olefins according to Scheme 5

Ex. no.	Starting Aziridine				Olefin	Exchange product				%	
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>		R <sup>5</sup>	R <sup>6</sup>	R <sup>7</sup>	R <sup>8</sup>	nmr	plc
16	Me	Me	H	COMe	<u>trans</u> -ClCH=CHCl	Cl	H	Cl	H	50	-
17	H	H	Me	CO <sub>2</sub> Me	Bu <sup>t</sup> CH=CMe <sub>2</sub>	Bu <sup>t</sup>	H	Me	Me	-	40
18	H	H	H	CO <sub>2</sub> Me	Bu <sup>t</sup> CH=CMe <sub>2</sub>	Bu <sup>t</sup>	H	Me	Me	44	-
19	H	H	H	CO <sub>2</sub> Me	<u>trans</u> -ClCH=CHCl	Cl	H	Cl	H	12	-
20	H	H	H	CO <sub>2</sub> Me	<u>trans</u> -Pr <sup>i</sup> CH=CHMe	Pr <sup>i</sup>	H	H	Me	75	20
21	H	H	H	CO <sub>2</sub> Me	<u>cis</u> -Pr <sup>i</sup> CH=CHMe	Pr <sup>i</sup>	H	Me	H	50	15
22	H	H	H	CO <sub>2</sub> Me	Bu <sup>t</sup> CH=CMe <sub>2</sub>	Bu <sup>t</sup>	H	Me	Me	40	10
23	H	H	H	CO <sub>2</sub> Me	Me <sub>2</sub> C=CHCOMe	Me	Me	H	COMe	-	5.4
24	H	H	H	OCOCH <sub>3</sub>	Bu <sup>t</sup> CH=CMe <sub>2</sub>	Bu <sup>t</sup>	H	Me	Me	0	0
25	Me	Me	H	COMe	H <sub>2</sub> C=CHCO <sub>2</sub> Me	H	H	H	CO <sub>2</sub> Me	50	-

All irradiations were performed in acetonitrile with the exception of experiment 22 which was performed in absolute ethanol.



Extension of the exchange reaction to the closely related 1-(2-methylquinazol-4-on-3-yl)aziridines (5) was then considered.

#### Preparation of 1-(2-methylquinazol-4-on-3-yl)aziridines (5)

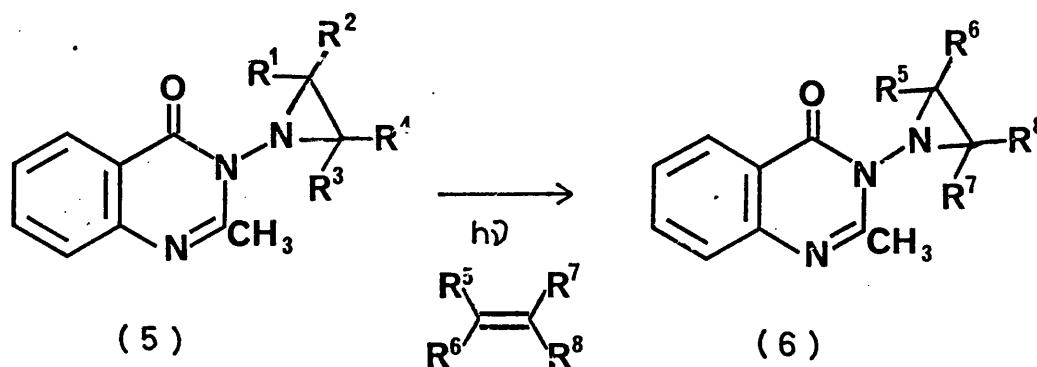
The aziridines were prepared using the published method.<sup>35</sup> 3-Amino-2-methylquinazol-4-one was prepared<sup>35</sup> from methyl anthranilate, acetic anhydride, and hydrazine hydrate. The aziridines were purified by chromatography on a short alumina column, followed by recrystallisation. 3-Acetyl-2,2-dimethyl-1-(2-methylquinazol-4-on-3-yl)aziridine,\* the aziridine derived from mesityl oxide, has not been described previously.

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\* The 60 MHz n.m.r. spectrum of this aziridine in CDCl<sub>3</sub> solution showed two distinct 3H singlets, separated by 9.5 Hz, for the aziridine ring methyl groups. This is in contrast to the analogous 3-acetyl-2,2-dimethyl-1-phthalimidoaziridine which gives one sharp 6H singlet in the 60 MHz n.m.r. spectrum in CDCl<sub>3</sub> solution. If this were due to the quinazolonyl- and phthalimidoaziridines undergoing, respectively, slow inversion and fast inversion (on the n.m.r. time scale), then temperature variation would be expected to cause spectral changes. However, the methyl signal of the phthalimidoaziridine in CH<sub>2</sub>Cl<sub>2</sub> was only partly resolved on cooling and at -80° the separation was only 4Hz. Moreover, the quinazolonyl-aziridine in o-dichlorobenzene solution gave two methyl signals separated by 16.5 Hz at 350

Photolysis of 1-(2-methylquinazol-4-on-3-yl)aziridines (5) in the presence of olefins

The exchange reaction (Scheme 6) of the aziridines (5) was found to occur cleanly; again, a substituent conjugated with the aziridine ring was necessary for reaction to take place.



(Scheme 6)

(c.f. 9.5 Hz at 35° in CDCl<sub>3</sub>) and this separation dropped only to 15 Hz at 125°. This prompted examination of the phthalimido-aziridine in *o*-dichlorobenzene solution and two singlets (4.2 Hz separation) were observed.

These facts are not in accord with a slow inversion-fast inversion phenomenon and the single peak observed for the gem-methyl groups of the phthalimido-aziridine in CDCl<sub>3</sub> solution must arise from a coincidental chemical shift of the methyl groups. In both aziridines, the chemical shift difference of the methyl groups is altered only slightly by temperature variation but is markedly changed by the use of *o*-dichlorobenzene as solvent. Benzene is known<sup>144</sup> to solvate aziridines on the side opposite to the nitrogen lone pair and presumably *o*-dichlorobenzene has the same effect and so enhances the magnetic non-equivalence of the gem-methyl groups.

The results of these photolyses are summarised in Table 3.

TABLE 3

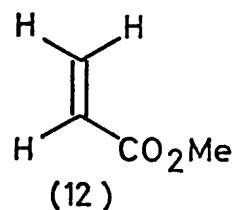
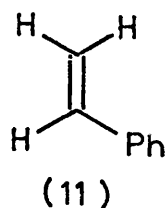
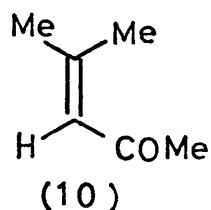
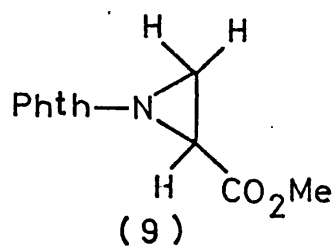
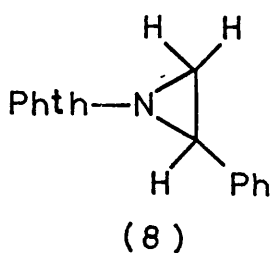
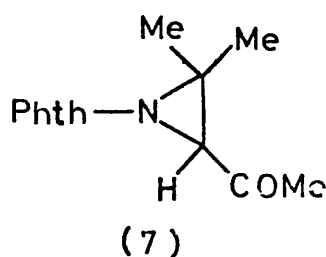
Photolysis of quinazolonyl-aziridines (5) in the presence of olefins according to Scheme 6.

Ex. no.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Olefin	Exchange product(6)				% nmr plc	
						R <sup>5</sup>	R <sup>6</sup>	R <sup>7</sup>	R <sup>8</sup>		
34	H	H	H	Ph	cyclo-hexene	R <sup>5</sup> R <sup>7</sup> = (CH <sub>2</sub> ) <sub>4</sub> R <sup>6</sup> = R <sup>8</sup> = H				-	33
35	H	H	Me	CO <sub>2</sub> Et	cyclo-hexene	R <sup>5</sup> R <sup>7</sup> = (CH <sub>2</sub> ) <sub>4</sub> R <sup>6</sup> = R <sup>8</sup> = H				-	39
36	H	H	H	CH=CH <sub>2</sub>	cyclo-hexene	R <sup>5</sup> R <sup>7</sup> = (CH <sub>2</sub> ) <sub>4</sub> R <sup>6</sup> = R <sup>8</sup> = H				68	20
37	R <sup>1</sup> R <sup>3</sup> = $\text{O}-\text{C}_6\text{H}_4 \cdot \text{CH}_2$ R <sup>2</sup> = R <sup>4</sup> = H				cyclo-hexene	R <sup>5</sup> R <sup>7</sup> = (CH <sub>2</sub> ) <sub>4</sub> R <sup>6</sup> = R <sup>8</sup> = H				-	52
38	H	Me	H	Me	cyclo-hexene	R <sup>5</sup> R <sup>7</sup> = (CH <sub>2</sub> ) <sub>4</sub> R <sup>6</sup> = R <sup>8</sup> = H				0	0
39	R <sup>1</sup> R <sup>3</sup> = $\text{O}-\text{C}_5\text{H}_4 \cdot \text{CH}_2$ R <sup>2</sup> = R <sup>4</sup> = H				Bu <sup>t</sup> CH=CMe <sub>2</sub>	Bu <sup>t</sup>	H	Me	Me	86	16
40	Me	Me	H	COMe	cyclo-octene	R <sup>5</sup> R <sup>7</sup> = (CH <sub>2</sub> ) <sub>6</sub> R <sup>6</sup> = R <sup>8</sup> = H				-	8

Other photolyses of phthalimido- and methylquinazolonyl-aziridines

The behaviour of the aziridines on irradiation in the absence of an olefin was investigated briefly. 3-Acetyl-2,2-dimethyl-1-phthalimidoaziridine (7) was photostable but 2-phenyl-1-phthalimidoaziridine (8) and methyl 1-phthalimidoaziridine-2-carboxylate (9) both underwent decomposition. It is interesting that

mesityl oxide (10) is reasonably photostable<sup>145</sup> whereas styrene (11) and methyl acrylate (12) are photolabile and polymerise readily.

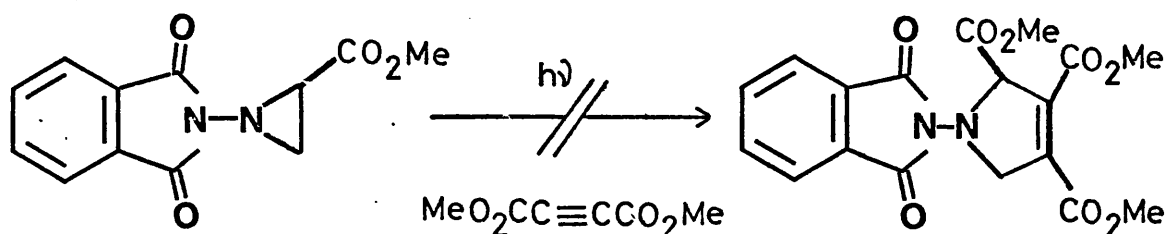


This could indicate that photocleavage to the nitrene and the olefin was occurring, followed by photopolymerisation of the olefin. N.m.r. evidence for polymethylacrylate formation on photolysis of (9) was obtained, but none could be isolated and the fate of the nitrene, if formed, is unknown; possibly the nitrene combines with the polymerised olefin. On the other hand, polymerisation of the aziridines themselves may have been occurring.

The photolyses summarised in Tables 1-3 were all carried out using quartz-filtered light from medium pressure mercury arc lamps; the wavelengths under these conditions lie between 200 nm. and 360 nm.. It was

found that light emitted from 350 nm. Rayonet lamps and filtered through Pyrex gave no exchange reaction between 3-acetyl-2,2-dimethyl-1-phthalimidoaziridine and cyclohexene. Exchange was observed using quartz-filtered light from a low pressure lamp (predominantly 254 nm. radiation). Thus, wavelengths effective in the exchange reaction lie below 300 nm..

The work of Huisgen<sup>103-104</sup> on the photochemistry of aziridinedicarboxylic esters has shown C-C cleavage to occur with formation of azomethine ylids, which can be trapped by dipolarophiles such as dimethyl acetylenedicarboxylate (see Scheme 22, page 50). No analogous cleavage (Scheme 7) of methyl 1-phthalimidoaziridine-2-carboxylate was observed on irradiation in the presence of dimethyl acetylenedicarboxylate. These aziridines also fail to give azomethine ylids on heating.<sup>146</sup>

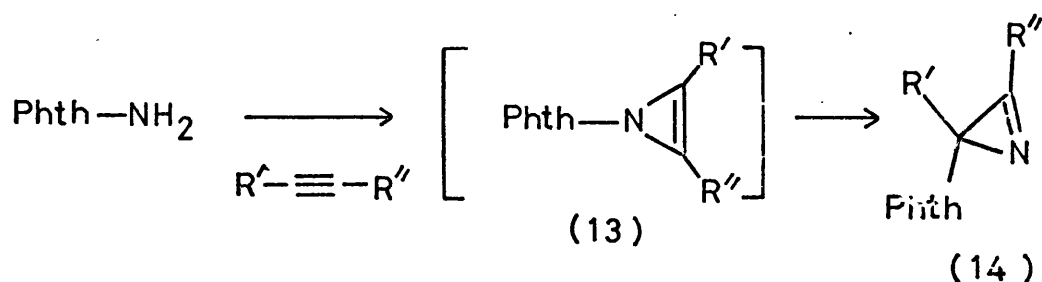


(Scheme 7)

Phthalimido-nitrene, as generated by lead tetraacetate oxidation of N-aminophthalimide, has been



observed to add to acetylenes in low yield with postulated formation of  $1\text{H}$ -azirines.<sup>40</sup> The anti-aromatic  $1\text{H}$ -azirines are thought to rearrange to the more stable  $2\text{H}$ -azirines, which are the products isolated (Scheme 8).

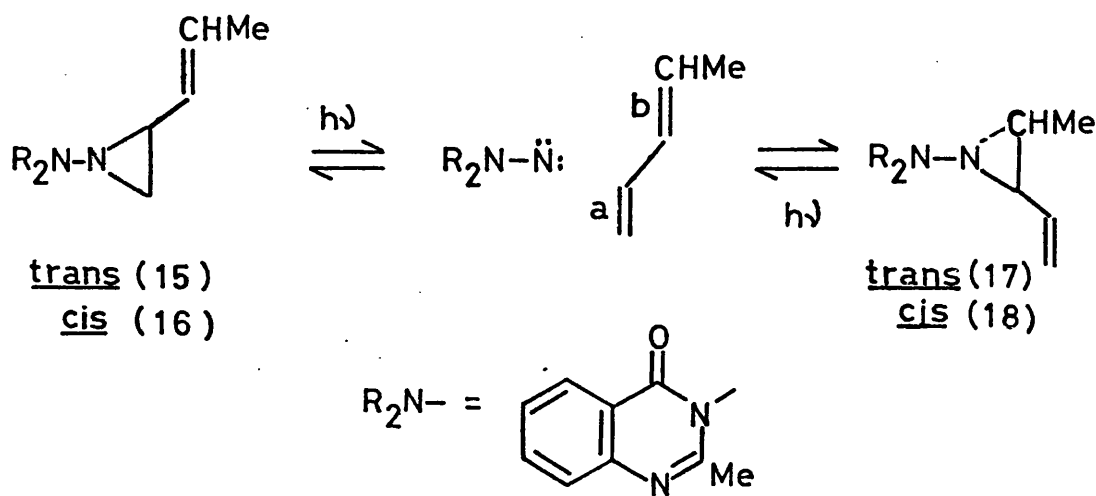


(Scheme 8)

Irradiation of methyl 1-phthalimidoaziridine-2-carboxylate in the presence of hex-1-yne did not lead to observable formation of the  $2\text{H}$ -azirine (14; R'=H, R''=Bu). A complex mixture was indicated on t.l.c. and nothing homogeneous could be isolated by p.l.c.. The irradiation of 3-acetyl-2,2-dimethyl-1-phthalimidoaziridine in the presence of hex-3-yne similarly failed to afford any  $2\text{H}$ -azirine (14; R'=R''=Et) although three substances (homogeneous on t.l.c.) were isolated from the reaction mixture by p.l.c.. The physical properties of these substances were suggestive of polymers. The substance obtained as a solid, m.p. 64-87°, gave a mass spectrum indicating the presence of the phthalimido group (m/e: 147, 132, 104, 76; supported by i.r.) and the loss of a methyl group from

$m/e$  402 to  $m/e$  387 was confirmed by a metastable transition at  $m/e$  373. Thus there must have been some interaction between the heterocycle and the acetylene. The polymers observed may be of the  $2H$ -azirines; they could also conceivably be of the  $1H$ -azirines. After this work was completed, it was reported<sup>147</sup> that azirines are themselves photolabile, and therefore are unlikely to be isolated as such.

The methylquinazolonyl-aziridines (15)-(18) were prepared in connection with work reported in Part 2 of this thesis. Irradiation of a 2:3 mixture of (15) and (16) was observed to lead to the formation of all four isomers (15)-(18) in the photolysate. The simplest explanation for this behaviour is shown in Scheme 9.

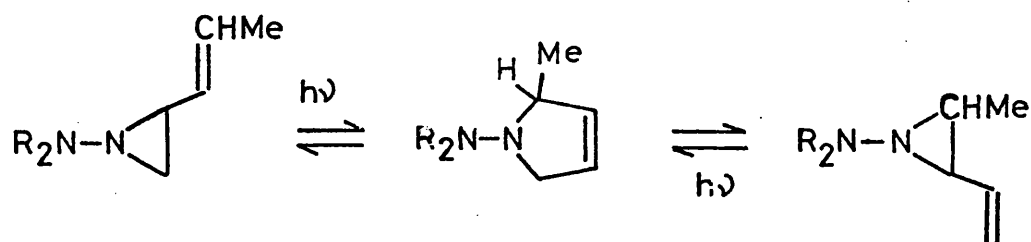


(Scheme 9)

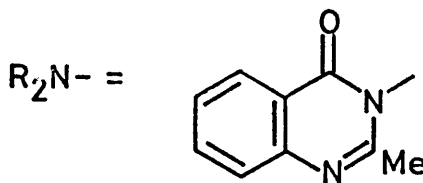
Photocleavage of the starting aziridines (15)

and (16) generates the nitrene and 1,3-pentadiene. The nitrene may then recombine with the double bond (a) just formed, so regenerating the starting aziridines, or add to the other double bond (b), so generating the isomeric aziridines (17) and (18).

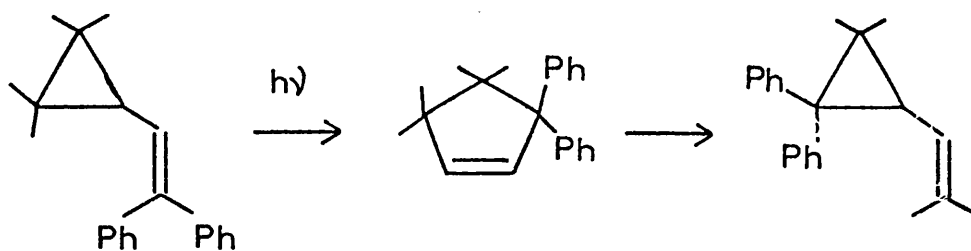
The possibility exists that the aziridines (15) and (16) may have undergone photochemical vinyl-aziridine  $\rightarrow$  pyrroline ring expansions followed by ring contractions, so forming the isomeric mixture (Scheme 10).



(Scheme 10)



Zimmerman<sup>66</sup> has considered a similar possibility (Scheme 11), although in fact the reaction was not observed.

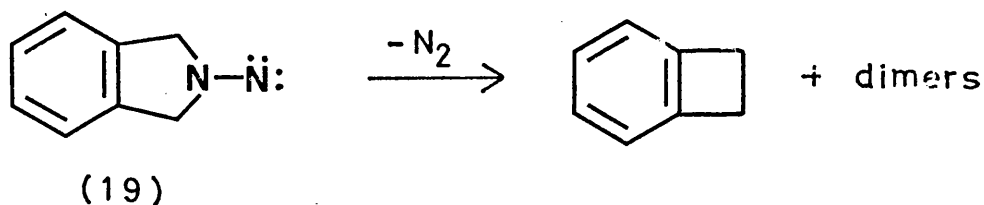


(Scheme 11)

Photochemical vinylcyclopropane  $\rightarrow$  cyclopentene rearrangements are known (see Introduction), yet the analogous photochemical vinylaziridine rearrangements are unknown. Indeed, work described later in this thesis demonstrates that 1-(2-methylquinazol-4-on-3-yl)-2-vinylaziridine does not form the pyrrole on irradiation. Thus Scheme 10 seems only a remote possibility and Scheme 9 is much more tenable.-

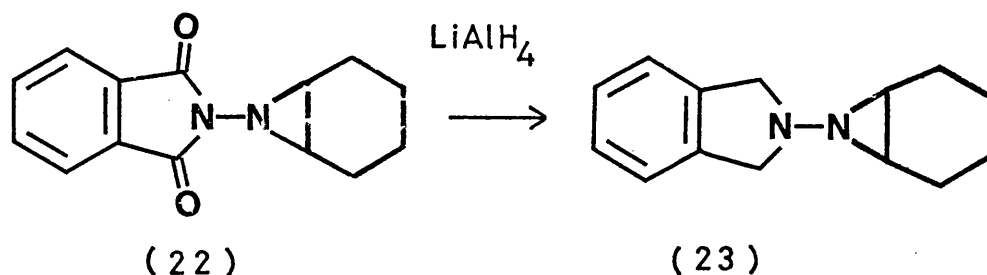
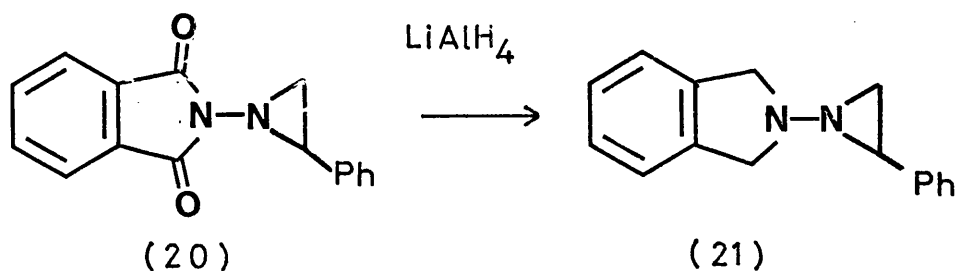
#### Preparation and photolysis of isoindoliny]-aziridines

The photochemistry of isoindoliny]-aziridines was considered since such systems are similar to phthalimido-aziridines but lack the carbonyl chromophore. Moreover, isoindoliny]-nitrene (19) has been shown to fragment<sup>14,42</sup> (see Introduction), so that, if it were an intermediate in the photolyses, the fragmentation products, benzocyclobutene and its dimers (Scheme 12), would be expected.



(Scheme 12)

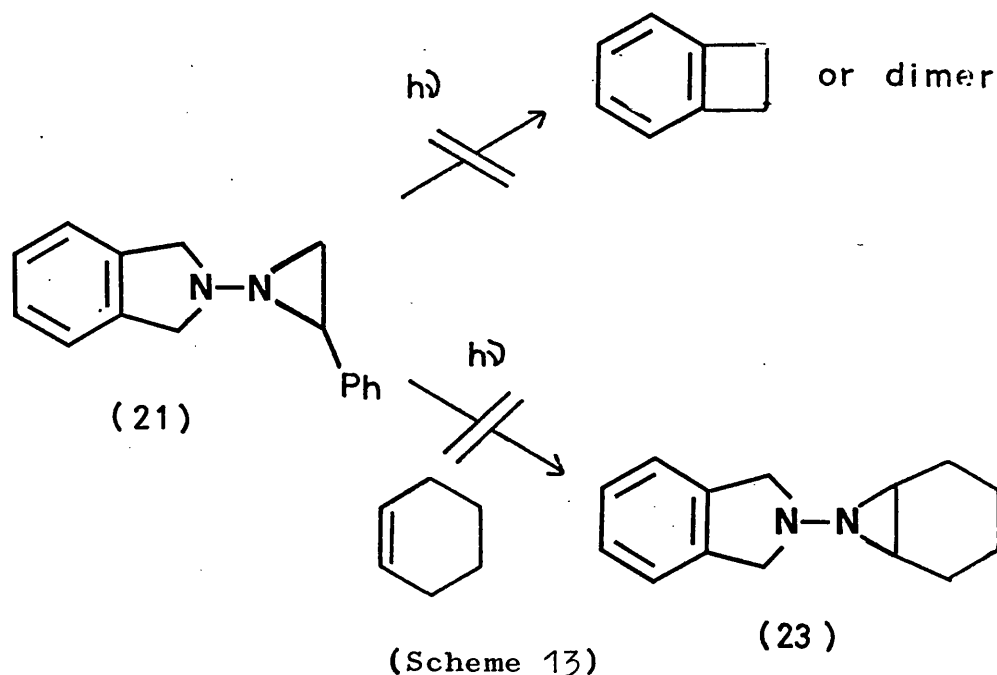
The aziridines chosen for study were the derivatives (21) and (23), only one of which has a conjugating substituent on the aziridine ring. The fragmentation of isoindolinyl-nitrene (19) precludes preparation of these aziridines by nitrene addition to olefins, and before the present study no isoindolinyl-aziridines were known. However, it was thought that reduction of phthalimido-aziridines could furnish the corresponding isoindolinyl-aziridines. A complication was expected in that the N-N bond of the phthalimido-aziridines might have been reductively cleaved. However, no cleavage was observed and the required aziridines (21) and (23) could be prepared in reasonable yield by treatment of the phthalimido-aziridines (20) and (22) with lithium aluminium hydride, in refluxing ether, for 3-6 hr..



The aziridines (21) and (23) were obtained as an oil and a low melting solid respectively; both were very susceptible to atmospheric oxidation but could be stored for several days in deoxygenated solvents. The structures of the compounds were fully supported by analytical data. The mass spectrum of (21) was particularly interesting and is further discussed in Section 2. The vapour phase flash pyrolysis of (21) and the attempted preparation of 1-(isoindolin-2-yl)-trans-2,3-diphenylaziridine are also discussed in the same Section.

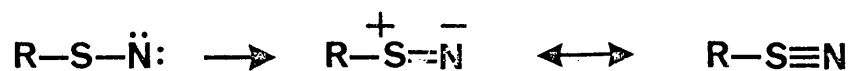
When the phenylaziridine (21) was irradiated, with careful exclusion of oxygen, no gas was evolved and no hydrocarbon products corresponding to benzocyclobutene or its dimers were detected. Rapid chromatography after a short period of irradiation gave

only the phenylaziridine (24% recovery). Irradiation to complete decomposition of the phenylaziridine similarly failed to afford any of the expected products (Scheme 13) and gave only a nitrogen-containing polymer. When the photolysis was carried out in the presence of cyclohexene, none of the exchange product (23) could be detected and polymerisation again occurred. A blank experiment showed that the aziridine (23) was rather more photostable than (21) and would have been detected if formed.



#### Preparation and photolysis of sulphenyl-aziridines

Photoreaction of sulphenyl-aziridines in an analogous manner to phthalimido-aziridines would involve a sulphenyl-nitrene. It is reasonable to suppose that such species are capable of stabilisation in the singlet state (Scheme 14) by analogy with amino-nitrenes.

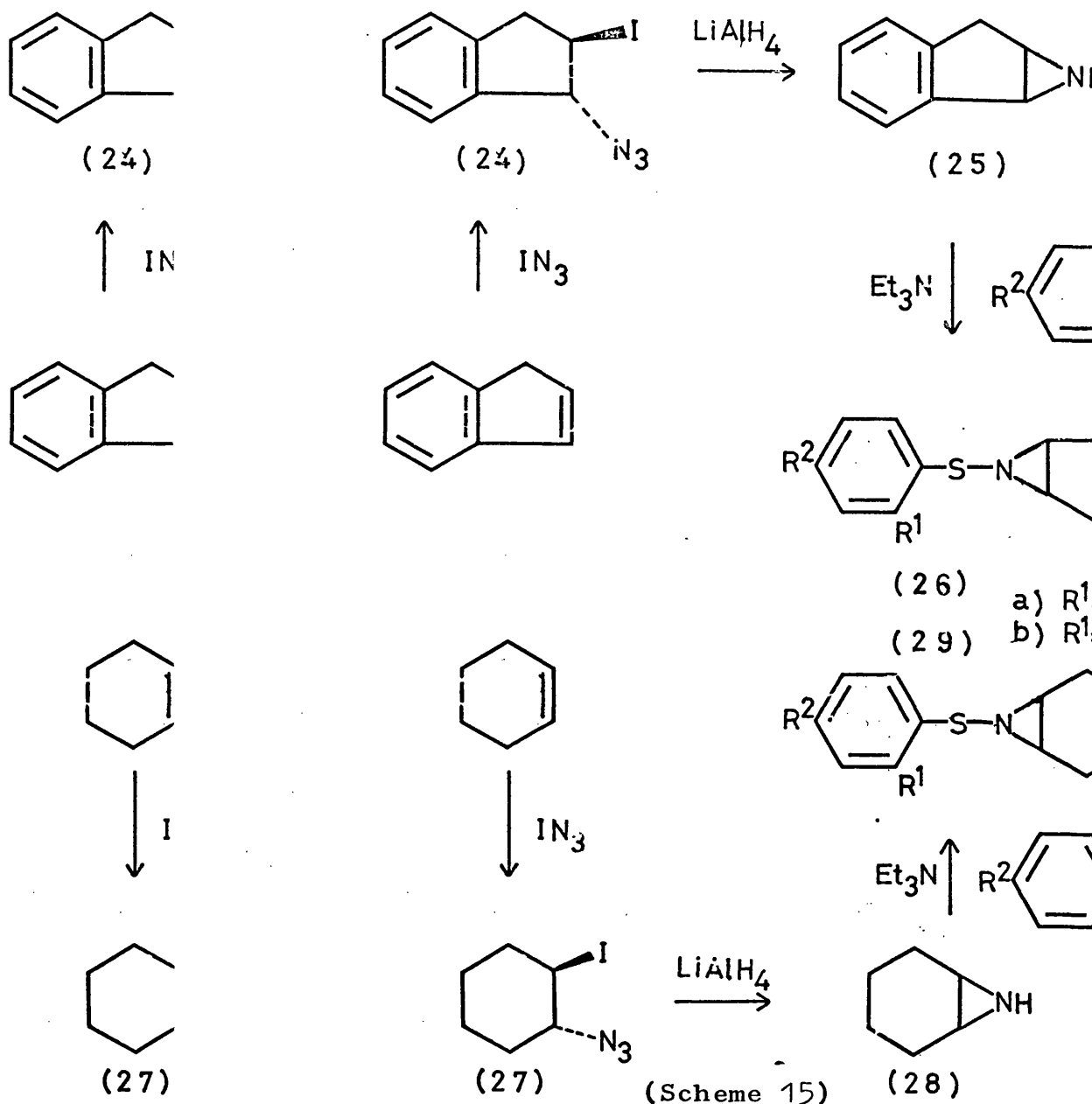


(Scheme 14)

However, little is known of sulphenyl-nitrenes and the one report in the literature to invoke such a species suggests that they undergo combination and loss of nitrogen, so forming disulphides.<sup>148</sup> Indeed, many unpublished reactions designed to generate and trap sulphenyl-nitrenes have led to the isolation of disulphides only.<sup>149</sup>

The aziridines (26a,b) and (29a,b) were prepared according to the procedure shown in Scheme 15.





The parent aziridines (25) and (28) were prepared by Hassner's aziridine synthesis.<sup>126</sup> Thus the olefin (indene or cyclohexene) was treated with iodine azide in acetonitrile to give the corresponding iodo-azides (24) and (27). Reduction with lithium aluminium hydride gave (25) and (28) in good yields although the reduction of trans-1-

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iodocyclohexane (27) was found to be somewhat erratic and potentially hazardous. Condensation of (25) and (28) with the appropriate sulphenylchloride was carried out using a modification of the method of Fanta for the preparation of (29b).<sup>130</sup>

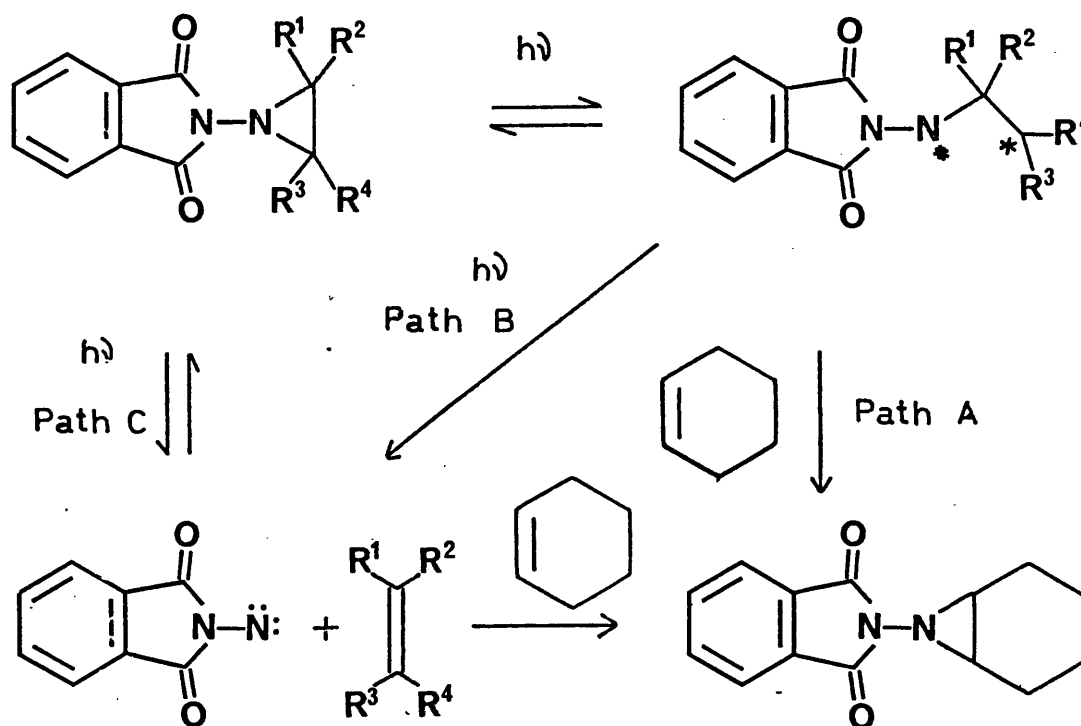
Both the *p*-tolylsulphenylaziridines (26a) and (29a) were unstable under the photolysis conditions used, although decomposition was slow. The only products were polymeric and none of the cyclohexene adduct (29a) could be detected when the aziridine (26a) was irradiated in the presence of cyclohexene. The dinitro compounds (26b) and (29b) were more stable and could be recovered in fair yields after irradiation for several days. Again, no exchange product (29b) could be obtained from irradiation of (26b) in the presence of cyclohexene. No disulphides were formed in any of the above photolyses.

#### Discussion of mechanism

The exchange reaction undergone by the phthalimido- and quinazolonyl-aziridines which bore conjugating substituents must involve cleavage of the aziridine C-N bonds and the following observations are thought to be relevant : (1) the exchange is stereospecific, as shown by experiments 20 and 21 of Table 2; (2) the reactions went cleanly to give only the exchanged aziridine and no evidence was found for the formation of side products; (3) 1-(2-methylquinazol-4-on-3-yl)-

2-vinylaziridine exchanged well with cyclohexene  
(experiment 3 of Table 3).

Possible mechanisms for the exchange reaction  
(that between a phthalimido-aziridine and cyclohexene  
is used as an example) are shown in Scheme 16.

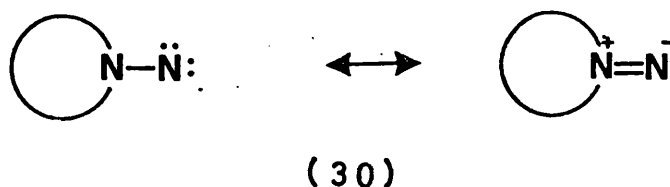


(Scheme 16)

Three possible routes to the product are shown. Paths A and B require the initial cleavage of one of the ring C-N bonds to give a 1,3-dipole or diradical. In Path A, the intermediate then reacts directly with cyclohexene, but in Path B, it is cleaved photochemically to give the nitrene, which is then trapped by cyclohexene.

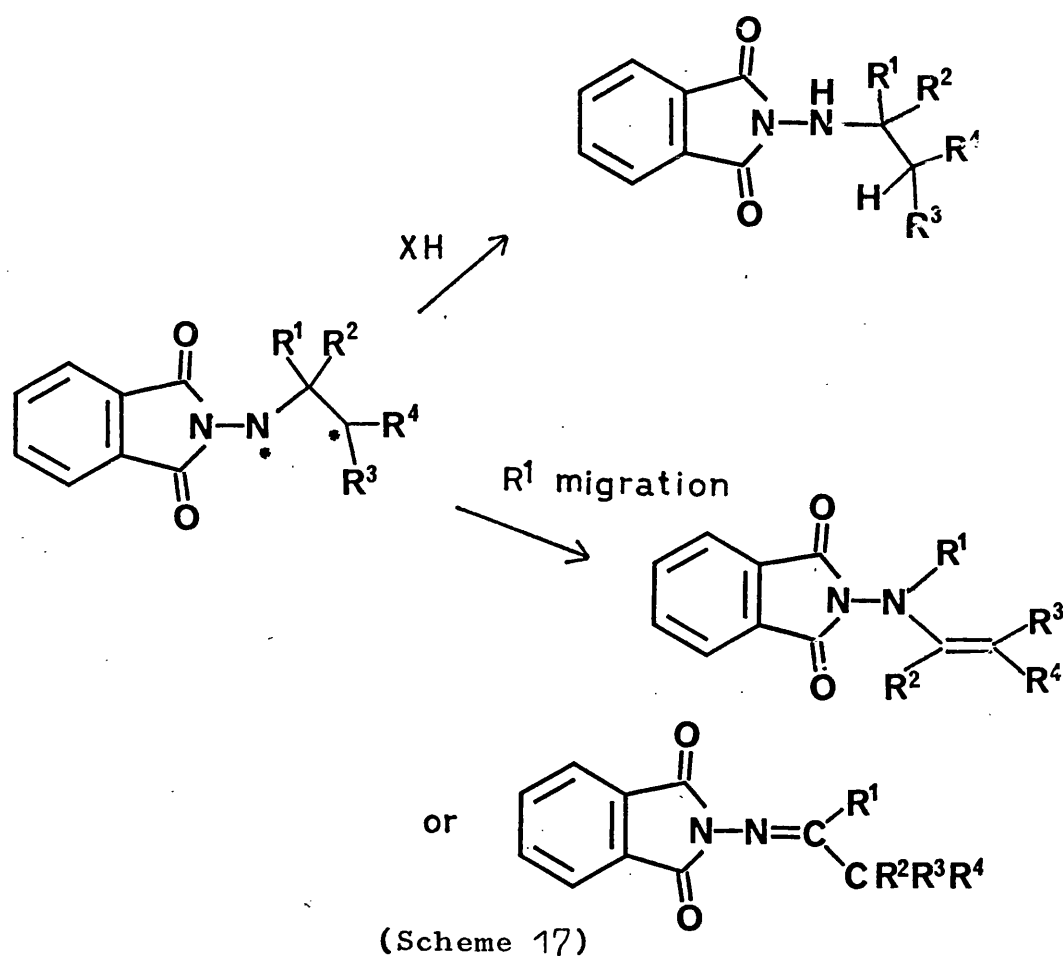
Path C is a concerted cleavage of both C-N bonds to give the nitrene directly.

Path A does not involve the intermediacy of phthalimido-nitrene. This path is rendered unlikely by the stereospecificity of the reaction, since any route involving stepwise formation of the bonds of the new aziridine is likely to lead to the loss of stereospecificity. On the other hand, phthalimido-nitrene is known<sup>35</sup> to add stereospecifically to olefins — a consequence of the probable singlet state in which it exists. Further support for the involvement of the nitrene lies in the interconversion of the 1,3-pentadiene adducts and in the ease of exchange with both nucleophilic and electrophilic olefins. The latter property is in accord with the reactivity of phthalimido-nitrene, which, having the stabilised singlet state (30) can show increased nucleophilic character and add to olefins bearing electron withdrawing groups as well as to olefins bearing electron releasing groups.<sup>35</sup>

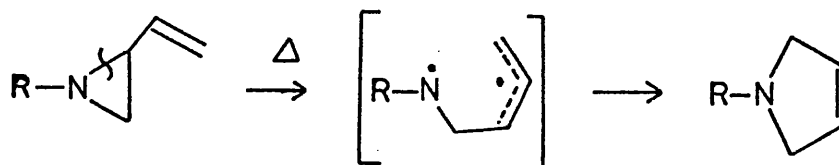


Path B involves stepwise cleavage of the aziridine C-N bonds and occurs via a diradical or dipolar intermediate. However, there is ample support

in the literature for the prediction that such an intermediate should lead to hydrogen abstraction from the solvent or to rearrangement (see Introduction) as shown in Scheme 17. No such products are in fact observed, neither in acetonitrile nor in ethanol as solvent.

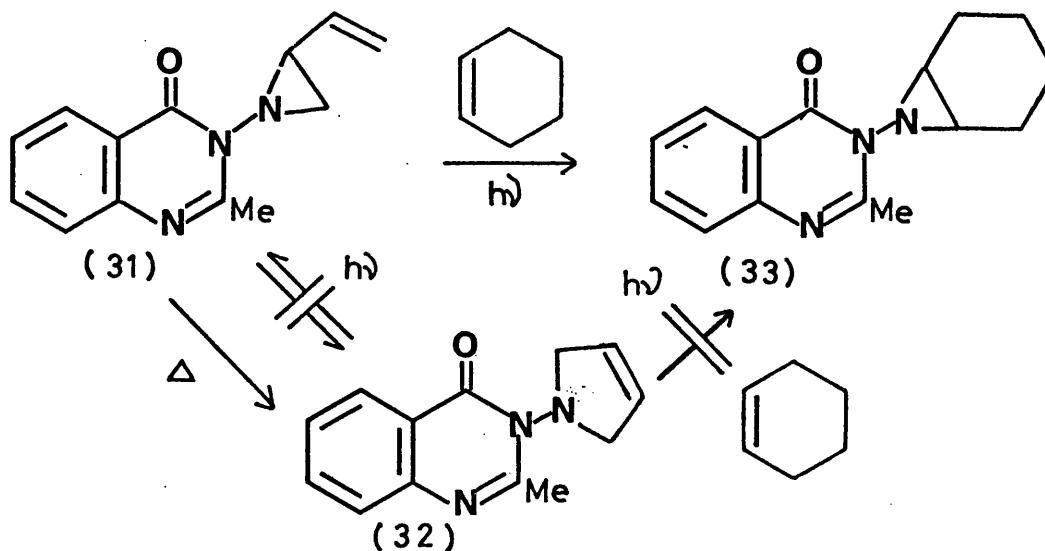


Moreover, vinylaziridines are known to rearrange thermally to 3-pyrrolines (see Part 2 ), and the mechanism (Scheme 18) is thought to involve an intermediate diradical.<sup>52</sup>



(Scheme 18)

If this diradical were intermediate in the photolytic exchange reaction of vinylaziridine (31), then it might similarly collapse to the 3-pyrroline (32). However, the pyrroline was not formed in the photolysis of (31), though it was synthesised by thermal rearrangement of the vinylaziridine (see Part 2 of this thesis). The possibility that the aziridine undergoes a fast photoisomerisation to the pyrroline, and that this then slowly exchanges with cyclohexene, was eliminated by irradiating the pyrroline in cyclohexene. No aziridine (33) was formed; the only product was 2-methylquinazol-4-one.



Path C, involving concerted cleavage of the aziridine C-N bonds to give the nitrene, is thus favoured. By this mechanism, the olefin must be liberated stereospecifically but experiments to test this were precluded by the extremely ready photoisomerisation of such conjugated olefins. The stereochemistry of the liberated olefin could only have been determined if it were a mono-ene and then the precursor aziridine would have lacked the conjugating substituent necessary for the exchange reaction to occur.

Although the formation of a nitrene by irradiation of an aziridine is new, there is ample analogy in the photochemistry of cyclopropanes, oxiranes, thiiranes, and oxaziridines (see Introduction).

In particular, several workers have shown that some of these analogous reactions probably proceed by similar concerted bond cleavages rather than via diradical or dipolar intermediates.<sup>63,68,69</sup> Leermakers and Ross, for example, in a study of the mechanism of the photocleavage of phenylcyclopropane, concluded that the major mechanism was a concerted fragmentation to phenylcarbene and ethylene.<sup>69</sup>

It is concluded then, that the exchange reaction occurs by a concerted fragmentation to the nitrene and an olefin (Path C in Scheme 16). It is notable that all of the aziridines which underwent the exchange reaction bore  $\alpha\beta$  unsaturated units on one of the aziridine ring

carbon atoms. The unsaturated unit could be a cyclic or an acyclic C=C (for example the aziridines derived from butadiene, styrene, and indene) or a C=O of a ketone or ester. The  $\beta\gamma$ -unsaturated aziridine derived from vinyl acetate was photostable. The energy of the light used ( $95\text{--}108 \text{ kcal mole}^{-1}$ ) is probably just sufficient to allow this concerted cleavage of the two C-N bonds,<sup>†</sup> especially if the transition state energy is lowered by a conjugating substituent on the ring, such that the liberated olefin is conjugated. It is not thought that the conjugating substituent provides the effective chromophore (the phthalimido- and quinazolonyl-

<sup>†</sup> The C-N bond energy of unsubstituted aziridine can be estimated by the method of Senbold.<sup>150</sup>

$$\text{Equation 1 : } \Delta H_f^{\circ}(\text{g}) (\text{aziridine}) = \Delta H_f^{\circ}(\text{g}) (\cdot\text{CH}_2\text{CH}_2\dot{\text{N}}\text{H}) + D(\text{C-N})$$

$$\text{Equation 2 : } \Delta H_f^{\circ}(\text{g}) (\cdot\text{CH}_2\text{CH}_2\dot{\text{N}}\text{H}) = \Delta H_f^{\circ}(\text{g}) (\text{CH}_3\text{CH}_2\text{NH}_2) + D(\text{C-H}) \\ + D(\text{N-H}) + \text{association energy of H}_2$$

Combination of equations 1 and 2, and substitution of the following values:<sup>151-152</sup>

$$\Delta H_f^{\circ}(\text{g}) (\text{aziridine}) = +26 \text{ kcal mole}^{-1};$$

$$\Delta H_f^{\circ}(\text{g}) (\text{CH}_3\text{CH}_2\text{NH}_2) = -11.6 \text{ kcal mole}^{-1}; D(\text{N-H}) = \\ +100 \text{ kcal mole}^{-1}; \text{association energy of H}_2 = -103.2 \\ \text{kcal mole}^{-1}, \text{ gives}$$

$$D(\text{C-N}) = 54 \text{ kcal mole}^{-1} \text{ for unsubstituted aziridine.}$$



aziridines possessed very similar ultraviolet spectra whether or not there was a conjugating substituent on the aziridine ring), since its presence is necessary but not sufficient for the cleavage reaction. Thus the isoindoliny- and sulphenyl-aziridines probably fail to react analogously because they lack an effective chromophore.

Therefore the striking contrast in the behaviour of the phthalimido-aziridines with that of other aziridines is probably due to a combination of the possession of a suitable chromophore and the unusual stability of singlet phthalimido-nitrene.

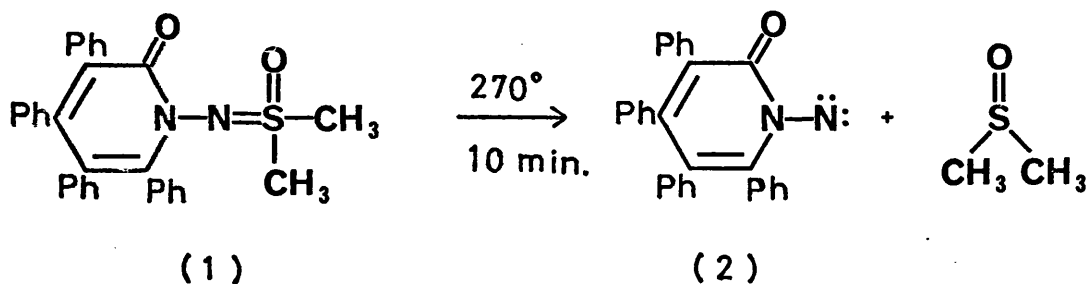
Discussion.    Part 1,    Section 2

1.    The Generation and Fragmentation of Heterocyclic N-nitrenes in the Vapour Phase.

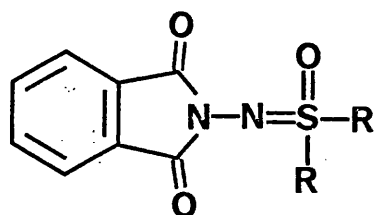
i)    Pyrolysis of heterocyclic N-sulphoximides

SS-Disubstituted-N-phthalimido-sulphoximides

In some preliminary experiments, Rees and Yelland<sup>30</sup> showed that the sulphoximide (1) can be thermally cleaved to give the nitrene (2) and dimethyl sulphoxide. The thermolysis was performed in the melt at 270° and gave the same products as were obtained by oxidative generation of the nitrene (2).



This cleavage reaction has now been extended by flash pyrolysis of N-phthalimido-sulphoximides (3a,b,c) in the vapour phase, in an attempt to promote the intramolecular fragmentation of phthalimido-nitrene (4).



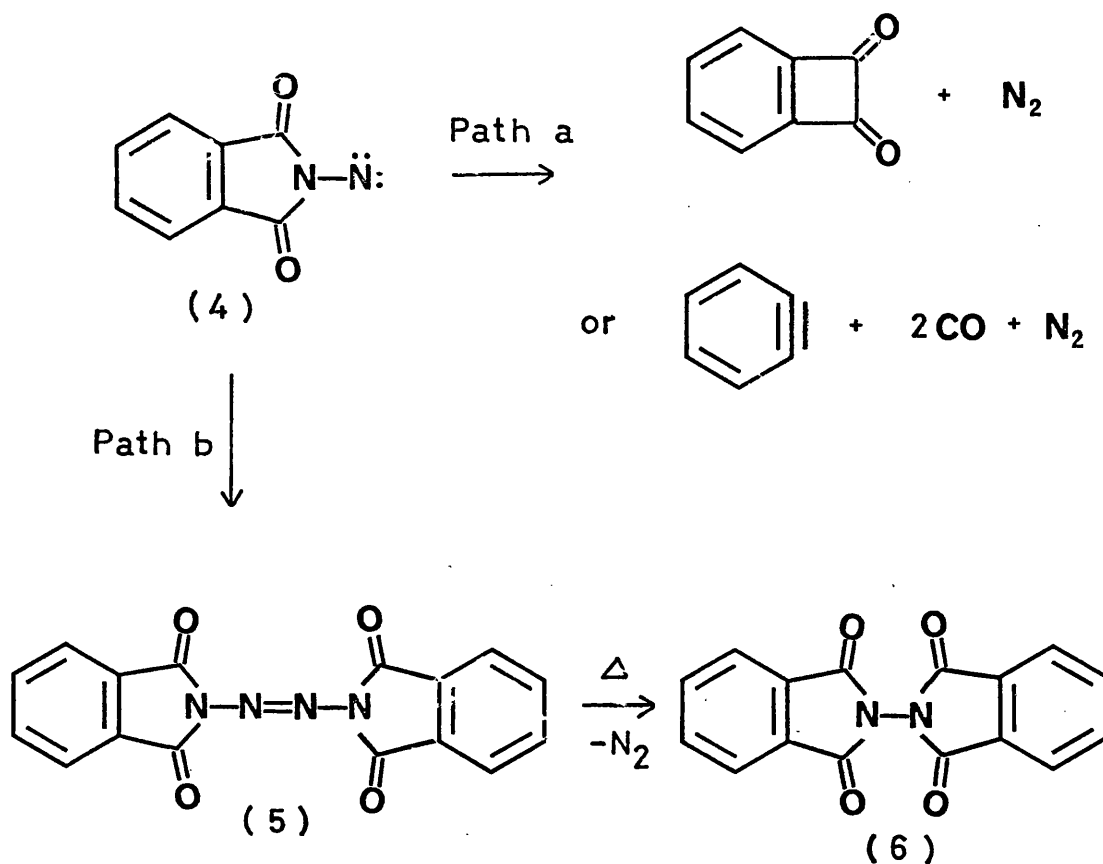
(3a) R = Ph

(3b) Me

(3c) CH<sub>2</sub>Ph

Cleavage of the sulfoximide (3b) has been achieved by solution photolysis in the presence of cyclohexene, but under these conditions the phthalimido-nitrene does not fragment and intermolecular reaction occurs to give the corresponding aziridine.<sup>26</sup>

Possible modes of intramolecular fragmentation are shown in Scheme 1, path a. The nitrene (4) has been generated oxidatively<sup>35</sup> and photochemically<sup>26</sup> (Part 1, Section 2) but loss of nitrogen (path a) has never been observed and, as explained in the Introduction, only intermolecular reactions of the nitrene are known. Intermolecular reaction under vapour phase pyrolysis conditions would presumably lead to the tetrazene (5) (Scheme 1, path b), which might then lose nitrogen and form biphthalimide (6).

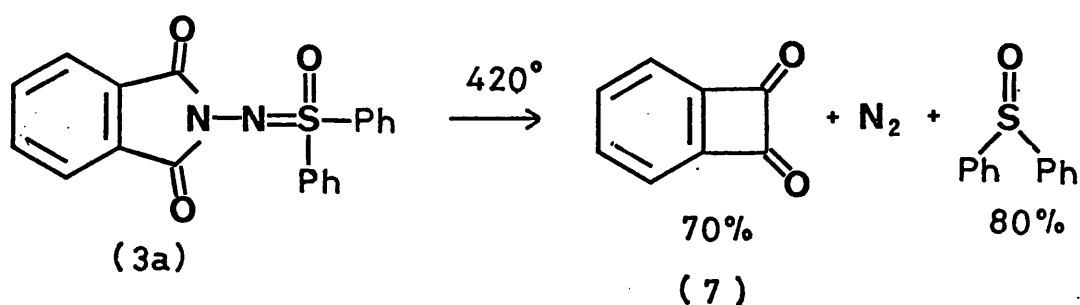


(Scheme 1)

The sulphoximides (3a) and (3b) were prepared, as described,<sup>11</sup> by the addition of lead tetra-acetate to a mixture of N-aminophthalimide and the sulfoxide. In the case of (3a), the diphenyl sulfoxide (5 equivalents) was dissolved in dichloromethane; for (3b), the sulfoxide was used as the solvent. Application of the former procedure to preparation of the previously-unknown dibenzyl sulphoximide (3c) gave only a low yield of the adduct (3c), and much phthalimide. Moreover, chromatographic separation of the adduct from the excess of dibenzyl sulfoxide was difficult, since the  $R_F$  values were very similar. However, when the oxidation was performed in the inverse manner, i.e. by

addition of N-aminophthalimide to a solution of lead tetra-acetate and dibenzyl sulphoxide, using only 1 equivalent of sulphoxide, the reaction occurred in much higher yield. Only a small amount of phthalimide was formed and very little dibenzyl sulphoxide remained. Both of these impurities could be removed from the crude product by recrystallisation.

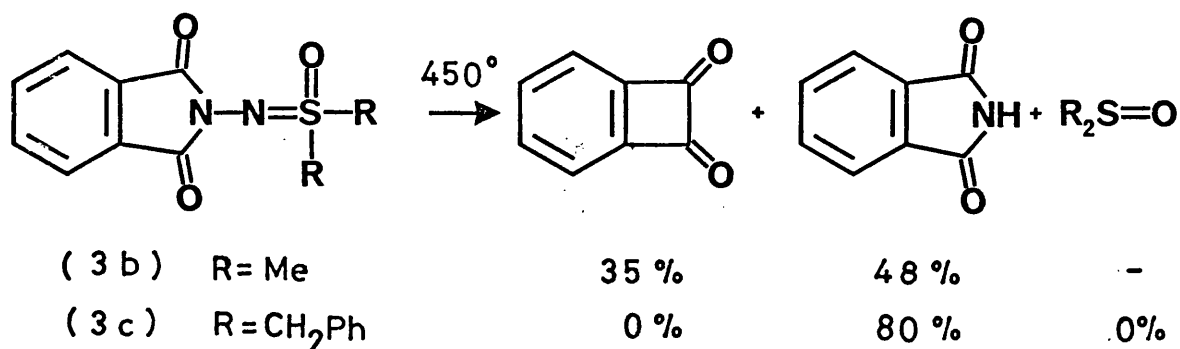
Pyrolysis of the diphenylsulphoximide (3a) at 420°/0.01 torr was very 'clean' and gave a pale yellow solid pyrolysate which was a two-component mixture (t.l.c.). Separation of the products by p.l.c. on a silica plate gave benzocyclobutenedione (7) in 70% yield and diphenyl sulphoxide in 80% yield (Scheme 2).



(Scheme 2)

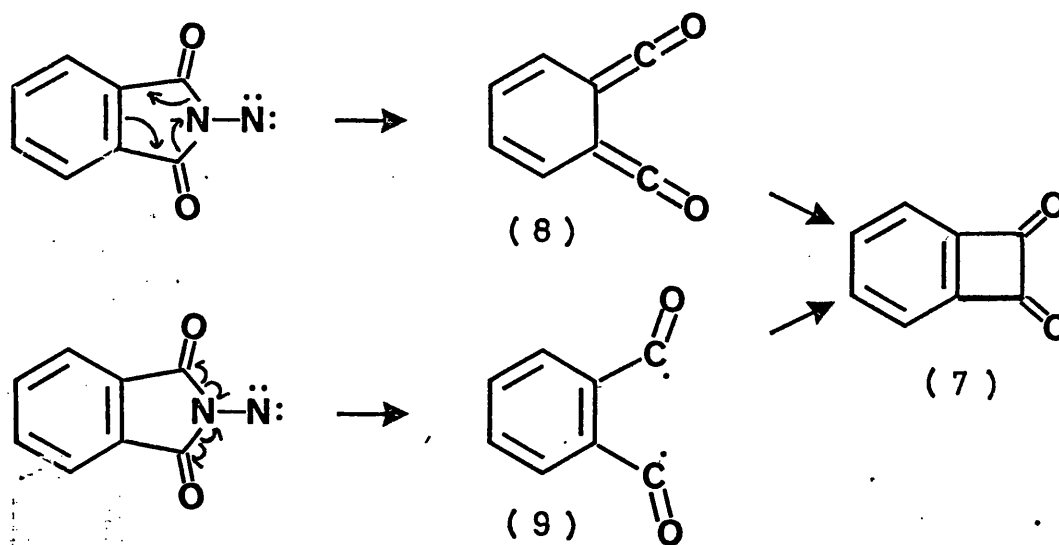
The dimethylsulphoximide (3b) also gave the dione (7) (35%) on pyrolysis at 450°; dimethyl sulphoxide was identified (i.r.), but not isolated. However, in this case there was a competitive reaction which gave phthalimide (48%) and the mass balance of the pyrolysis was lower than usual.

The fragmentation to phthalimide occurred to the complete exclusion of benzocyclobutenedione (7) formation on pyrolysis of the dibenzylsulphoxide (3c) at 450°, but in this case the mass balance was good. The pyrolysate was deposited on the cold surface of the trap as a yellow solid but, on warming to room temperature and opening to the atmosphere, it rapidly absorbed water and gave a dark coloured oil. T.l.c. showed several spots but only phthalimide (80%) could be isolated from p.l.c. on silica or alumina and it was evident that the other products were labile.



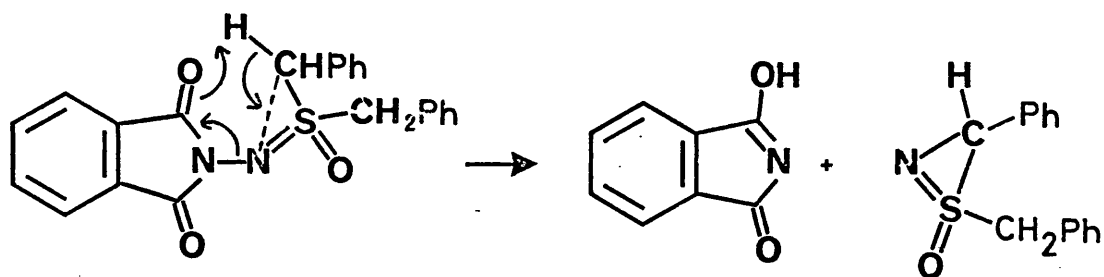
The isolation of benzocyclobutenedione (7) from pyrolysis of the sulfoximides (3a) and (3b) showed that intramolecular reaction of the phthalimido system had, indeed, been achieved. In particular, the fragmentation of (3a) to benzocyclobutenedione, nitrogen, and diphenyl sulphoxide occurred in high yield. It is reasonable, by analogy with the work of Rees and Yelland on the sulfoximide (1),<sup>30</sup> that pyrolysis of the

sulphoximide (3a) first causes cleavage to phthalimido-nitrene (4) and diphenyl sulphoxide. The nitrene may then either undergo a linear chelotropic reaction to form the bis-ketene (8) or lose nitrogen to give the diradical (9). The further possibility of a ring expansion is dealt with on page 191. Cyclisation of the bis-ketene (8), or radical combination in (9), then gives the dione (7). The species (8) and (9) have been invoked as possible intermediates in the formation of several dimers on photolysis of benzocyclobutenedione (7).<sup>153,154</sup>

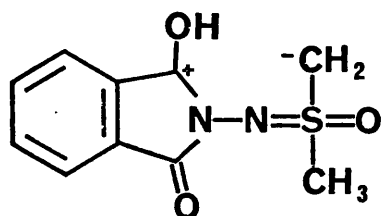


The formation of phthalimide on pyrolysis of the dimethyl- and dibenzyl-sulphoximides (3b) and (3c) presumably arises because of the active hydrogens in these molecules. The greater yield of phthalimide in (3c) is consistent with the increased activity of the benzylic protons compared to the methyl protons and,

indeed, (3c) was chosen for this reason. The diphenylsulphoximide (3a), with no active hydrogens, gave no phthalimide on pyrolysis. This indicates that hydrogen transfer, which would probably be intramolecular under these conditions, must be involved in the initial step of the cleavage. A possible concerted mechanism is shown in Scheme 3, although a stepwise process via a dipolar (10) or diradical intermediate cannot be ruled out.



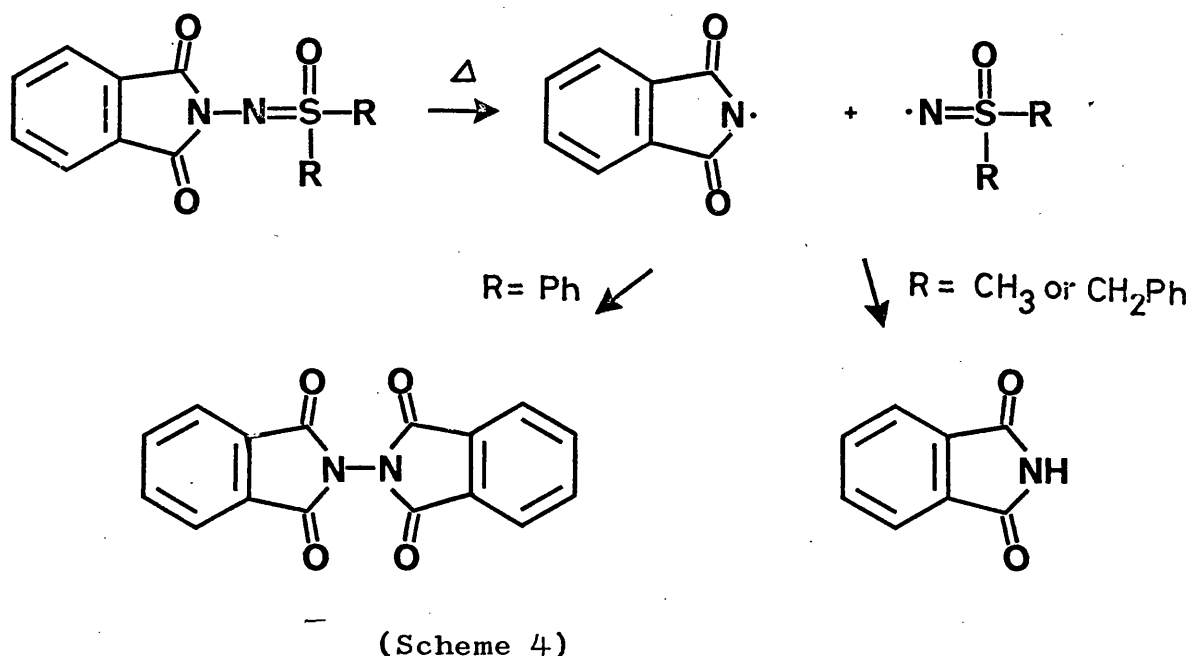
(Scheme 3)



(10)



The alternative stepwise mechanism for phthalimide formation from (3b) and (3c) would involve the phthalimido radical; however, this should have led to the formation of biphtalimide (Scheme 4) from the diphenylsulphoximide (3a), and none was observed.

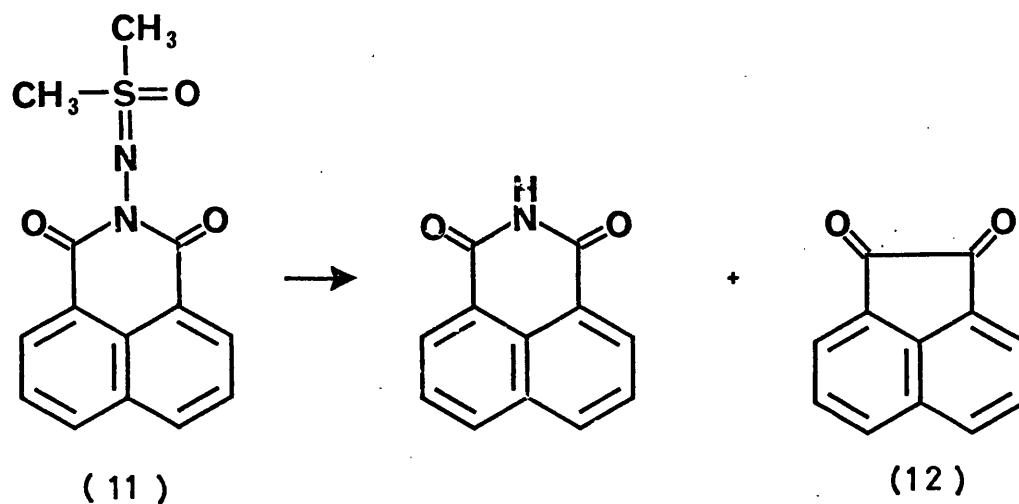


The fate of the sulphur containing moiety in Scheme 3 is unknown. It was hoped that pyrolysis of the dibenzylsulphoximide (3c) would enable characterisation of this species, or its decomposition products, but only phthalimide could be isolated from the pyrolysis and the other products were obviously very unstable.

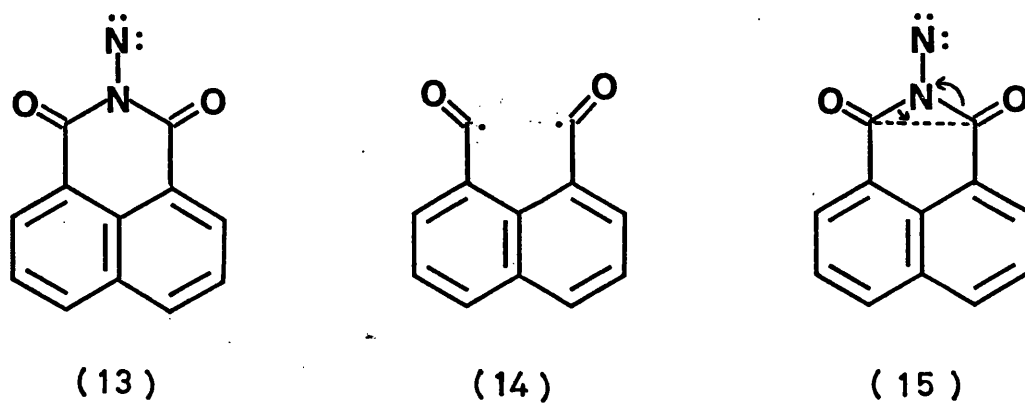
#### SS-Dimethyl-N-naphthalimido-sulphoximide (11)

The title compound (11) was prepared, as described,<sup>11</sup> and pyrolysed at 450°. The active S-methyl

protons caused some formation of naphthalimide (41%) but nevertheless acenaphthenequinone (12) was isolated in 55% yield (Scheme 5). In this case, no bis-ketene can be written and the extrusion of nitrogen from the naphthalimido-nitrene (13) must occur via the diradical (14) or by a non-linear  $[\sigma^{-2}_s + \sigma^{-2}_a]$  chelotropic reaction (15).



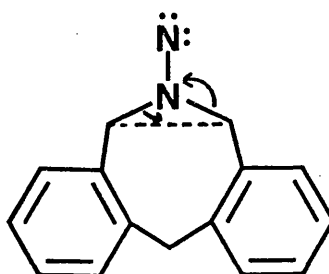
(Scheme 5)



A similar chelotropic reaction has been suggested<sup>155</sup> for the stereospecific extrusion of nitrogen from aziridinylnitrenes (16) and could also occur in the loss of nitrogen from the nitrene (17).<sup>44</sup>



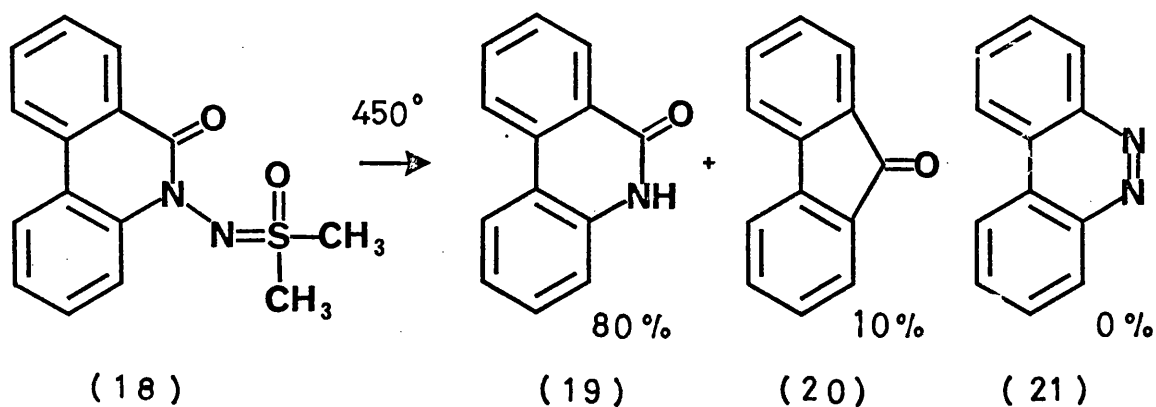
(16)



(17)

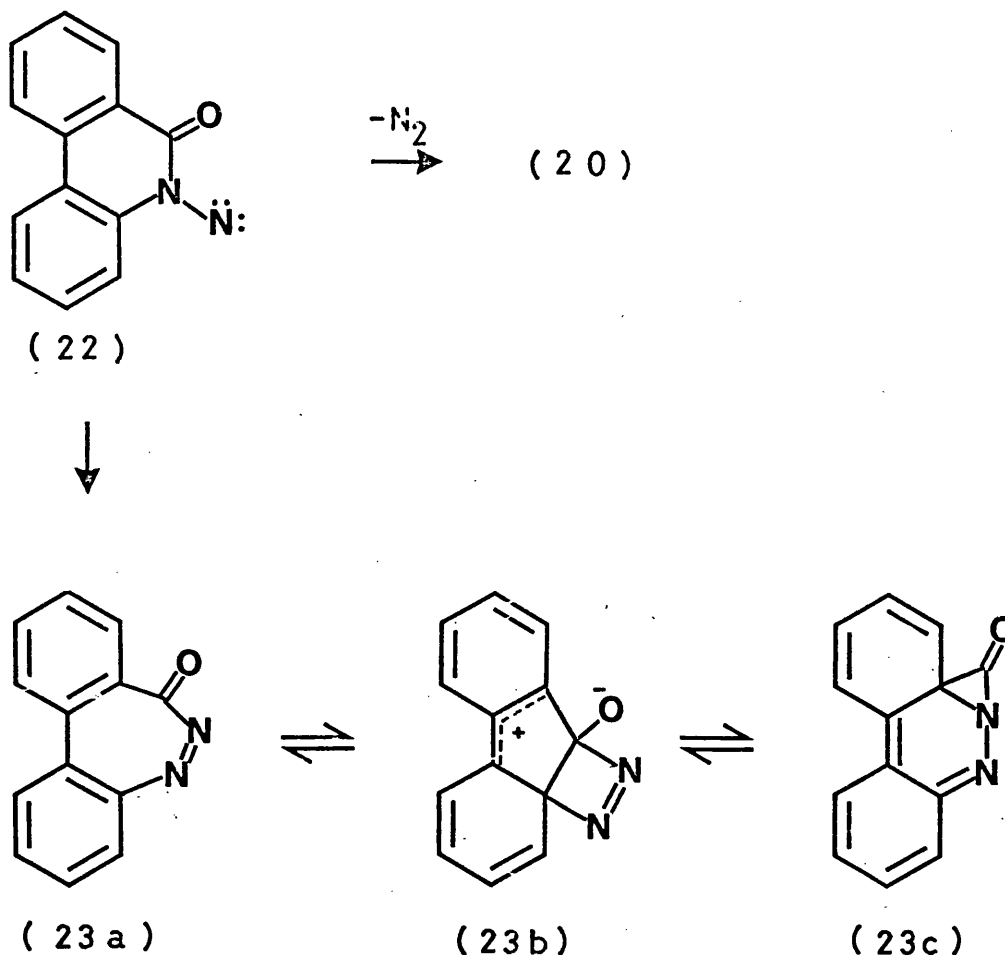
SS-Dimethyl-N-(phenanthrid-6-on-5-yl)sulphoximide (18)

Yelland pyrolysed the sulphoximide (18) in the melt at 200° but obtained only phenanthridone (19) (50%). The other products were described as a "black polymeric coke".<sup>27</sup> The vapour phase flash pyrolysis, however, was very much cleaner. The active S-methyl groups led to the formation of phenanthridone (19) as the major product but fluorenone (20) (10%) was detected (Scheme 6) by t.l.c. and g.c.. The t.l.c. analysis showed that benzo[c]cinnoline (21) and biphenylene were absent.



(Scheme 6)

The fluorenone (20) may have arisen by direct extrusion of nitrogen from the nitrene (22), or may have been formed via the diazepinone (23). The analogous insertion of 3,4,5,6-tetraphenylpyridonyl-nitrene to give a tetraphenyldiazepinone, and the tautomeric forms of the diazepinone, have been discussed by Rees and Yelland.<sup>30</sup> Fluorenone and benzo[c]cinnoline are the expected products from concerted decomposition of the diazepinone valence tautomers (23b) and (23c), respectively, but in this case the loss of aromaticity in these forms renders their contribution unlikely and fluorenone is probably formed by loss of nitrogen from (23a) and radical closure. The failure to observe benzo[c]cinnoline certainly indicates that (23c) is not an important tautomer of (23).

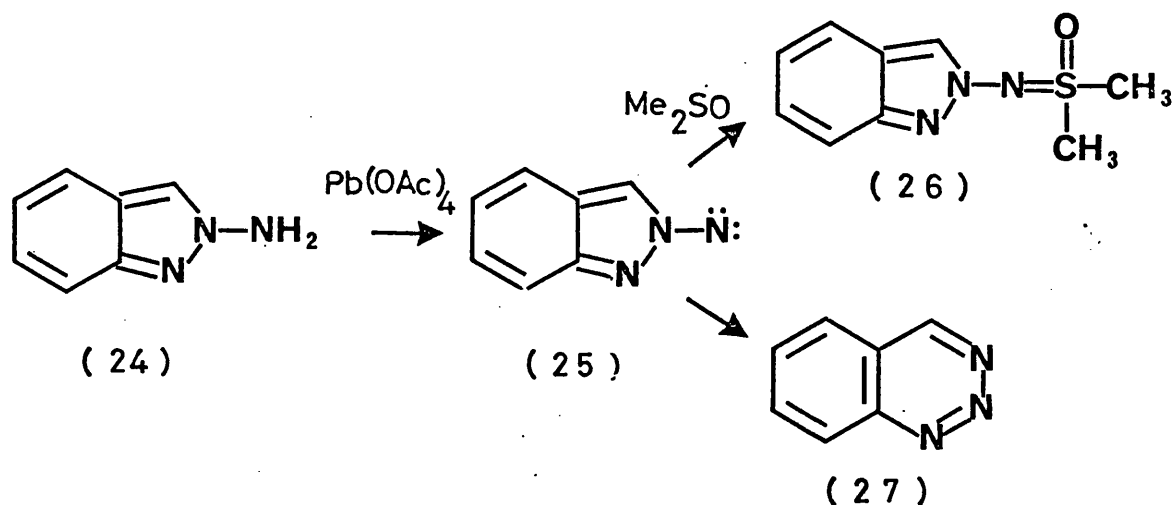


SS-Dimethyl-N-(indazol-2-yl)sulphoximide (26)

The pyrolyses of the dimethylsulphoximides (3b), (11), and (18) all gave some of the respective parent lactam. The mechanism suggested involves transfer of a hydrogen to the oxygen of the heterocyclic carbonyl group. The dimethylsulphoximide (26), however, has no such carbonyl group and thus no indazole would be expected in its pyrolysis; it should give the 2-indazolyl-nitrene (25) in good yield. The nitrene (25) has been formed by oxidation of 2-aminoindazole (24)

and shown to insert in good yield to give 1,2,3-benzotriazine (27).<sup>50</sup> Only by using dimethyl sulphoxide, a highly efficient nitrene trap, can the nitrene (25) be trapped intermolecularly and even then insertion still predominates and the nitrene adduct (26) is obtained in only 9% yield.<sup>41</sup>

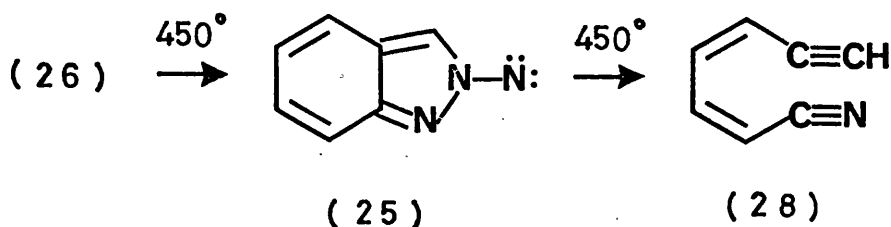
A further stimulus to investigate the pyrolysis of the sulfoximide (26) was the possibility of observing fragmentation of the nitrene (25), a process which is not observed when it is generated oxidatively.



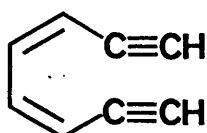
Accordingly, the dimethylsulphoximide (26) was prepared by oxidation of 2-aminoindazole in dimethyl sulphoxide and obtained in a reproducible yield of 9%. Although this yield could not be improved, the work up procedure was simplified by inverse addition of the 2-aminoindazole to lead tetra-acetate in neat dimethyl sulphoxide as solvent.

Vapour phase flash pyrolysis of the sulfoximide

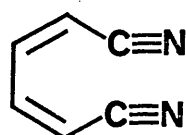
(26) was carried out at  $450^{\circ}/0.01$  torr and the crude pyrolysate was examined by t.l.c. and i.r.. The prediction that indazole would not be formed was upheld by the t.l.c. examination and subsequent work up, and supports the proposed mechanism of parent lactam formation in the pyrolyses of sulfoximides (3b), (11), and (18). Moreover, the i.r. of the pyrolysate showed the characteristic peaks of dimethyl sulphoxide and also signals at 2200 and 2080  $\text{cm}^{-1}$ . Careful p.l.c. enabled the isolation of an oil which crystallised spontaneously to give yellow needles, m.p.  $55^{\circ}$  decomp.. The i.r. of this solid showed that it was 1-cyanohepta-cis,cis-1,3-diene-5-yne (28), the product of nitrogen extrusion from the nitrene (25). No insertion of the nitrene was observed under these conditions; the 1,2,3-triazine (27) was absent, and no biphenylene, the product of thermal decomposition of the triazine (27),<sup>50</sup> was found.



The nitrogen extrusion product (28) may be compared to the analogous diacetylene (29) and dicyanide (30)

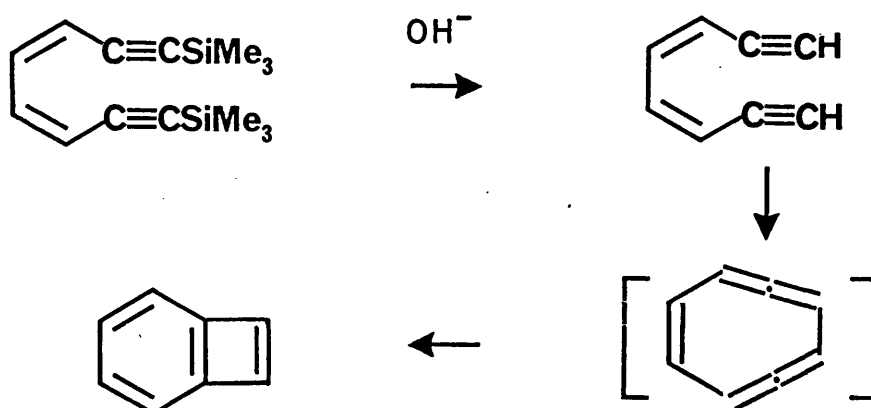


( 29 )



( 30 )

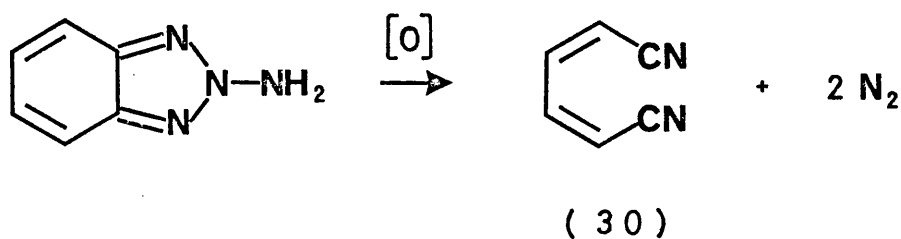
The diacetylene (29) has been generated by Sondheimer<sup>156</sup> and found to be of transient existence, rapidly forming benzocyclobutadiene possibly as shown in Scheme 7.



(Scheme 7).

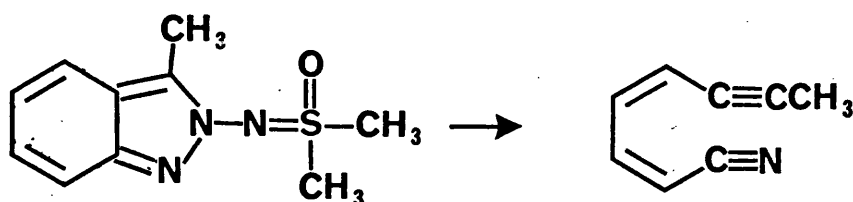
The dicyanide (30), however, is a stable solid; it can be prepared in high yield by the oxidation of 2-aminobenzotriazole (Scheme 8).<sup>48</sup>





(Scheme 8)

The stability of the cyano-acetylene (28) appears to be intermediate between that of (29) and (30). Thus it is isolable, but decomposes in the dark at room temperature during some 24 hrs. The study of the reactions of the cyano-acetylene (28), and the application of this pyrolysis method to the preparation of non-terminal acetyleneic analogues, e.g. Scheme 9, is currently under investigation in these laboratories.



(Scheme 9)

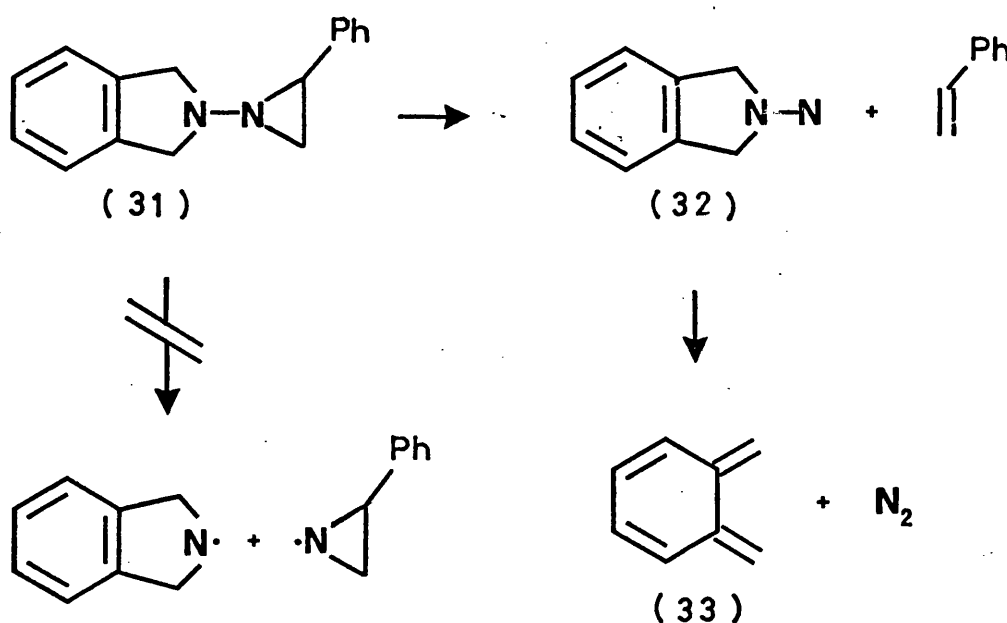
These results suggest that the difference between the nitrenes which are known to react only intermolecularly (Table 1, Introduction) and those which can react intramolecularly (Table 2, Introduction) is simply due to a relatively small difference in activation energy for the intramolecular reactions. Thus, even phthalimido-nitrene and naphthalimido-nitrene can be induced to fragment in the vapour phase. Moreover, the difference between the two possible intramolecular reactions (insertion and fragmentation) is also due to a relatively small difference of activation energies. Thus, 2-indazolyl-nitrene will insert at room temperature in solution, but fragment at 450° in the vapour phase. It has also been shown that these processes are quite distinct, in that the fragmentation which occurs at 450° (to give nitrogen and the cyano-acetylene) is not preceded by insertion to give the 1,2,3-triazine, since this is known to fragment in the same conditions to different products (biphenylene, nitrogen, and HCN).

ii) Pyrolysis of isoindolinyl-aziridines and related systems

1-(Isoindolin-2-yl)-2-phenylaziridine (31)

The title compound (31) was prepared in connection with the photochemical work described in Part 1, Section 1 of this thesis. In the course of characterisation of this new aziridine, it was noted that the mass spectral breakdown pattern was unusual. The primary breakdown pattern of the phthalimido- and quinazolonyl-

aziridines studied in this work involves N-N cleavage and hydrogen transfer. Similarly, Brois<sup>157</sup> has synthesised an N-methoxyaziridine and reports very ready O-N cleavage on electron impact. Moreover, the sulphenyl-aziridines studied in Part 1, Section 1 of this thesis similarly showed S-N cleavage in the mass spectrometer and the same is observed in sulphonyl-aziridines.<sup>146</sup> However, the mass spectrum of the isoindoliny-aziridine (31) showed no N-N cleavage but indicated formation of o-quinodimethane (Scheme 10).

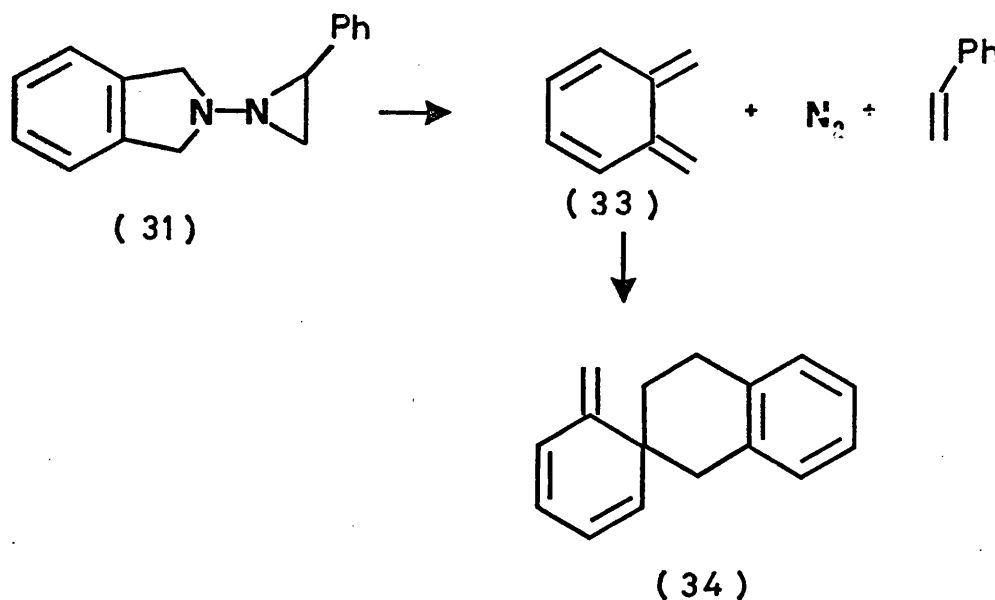


(Scheme 10)

When the mass spectrum was obtained using an all glass heated inlet system at 170<sup>o</sup>, instead of direct insertion at 110<sup>o</sup>, then no parent ion was observed and the mass peak corresponded to a dimer of o-quino-

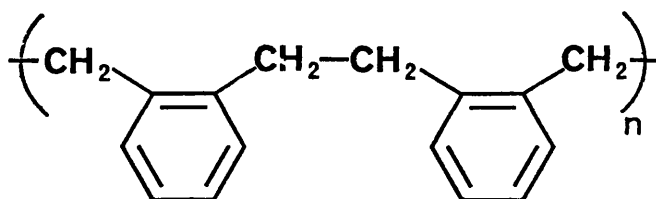
dimethane (33).

These observations prompted a study of the vapour phase flash pyrolysis of the aziridine (31). Pyrolysis at 400°/0.2 torr gave styrene (76%) and the spiro compound (34), a known<sup>133</sup> dimer of o-quino-  
dimethane (33) (Scheme 11).



(Scheme 11)

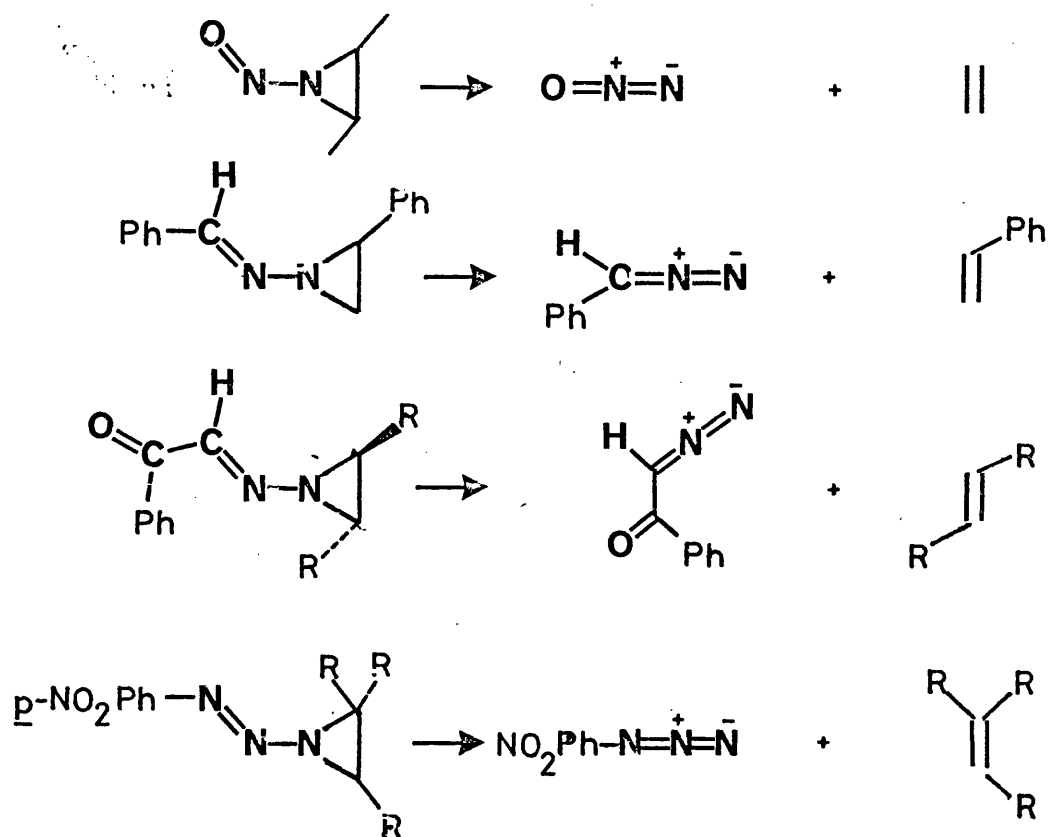
The low yield of the dimer (34) is attributable to its known instability.<sup>133</sup> The pure sample obtained by p.l.c. gave the polymer (35) within 1 day at room temperature.



(35)

Styrene, benzocyclobutene, and o-quinodimethane are isomeric but the possibility of substantial inter-conversion of the latter two to the former in the above pyrolysis can be excluded by the work of Cava and Deana.<sup>158</sup> They found that generation of o-quinodimethane by vapour phase flash pyrolysis of 1,3-dihydroisothianaphthene-2,2-dioxide at 770° gave only 2% of styrene.

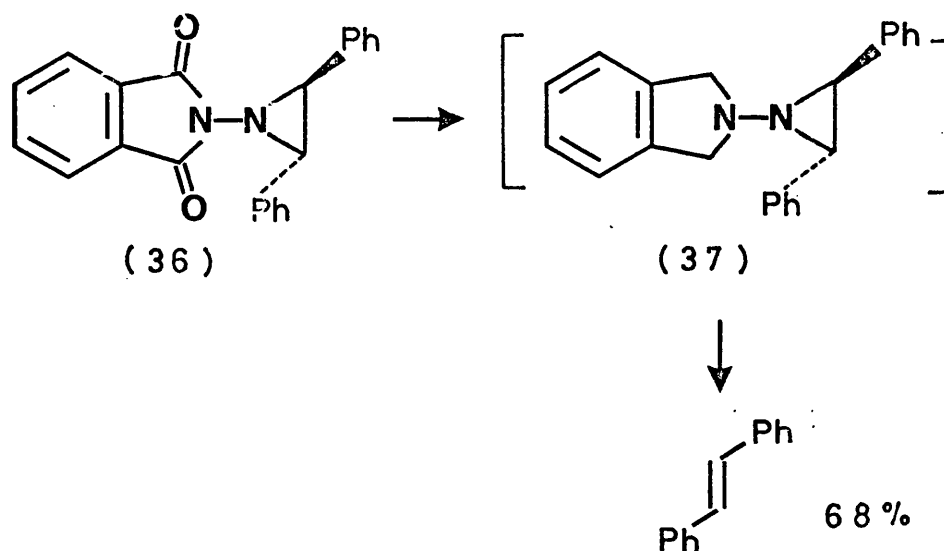
Related thermal cycloeliminations have been observed in N-nitroso-, N-imino-, and N-arylazo-aziridines (Scheme 12).<sup>134, 159-164</sup> In the last case an electron withdrawing substituent is necessary for the cyclo-elimination to occur and, in the absence of such a substituent, then homolytic expulsion of nitrogen gives aziridiny1 and aryl radicals.



(Scheme 12)

### Reduction of trans-2,3-diphenyl-1-phthalimidoaziridine (36)

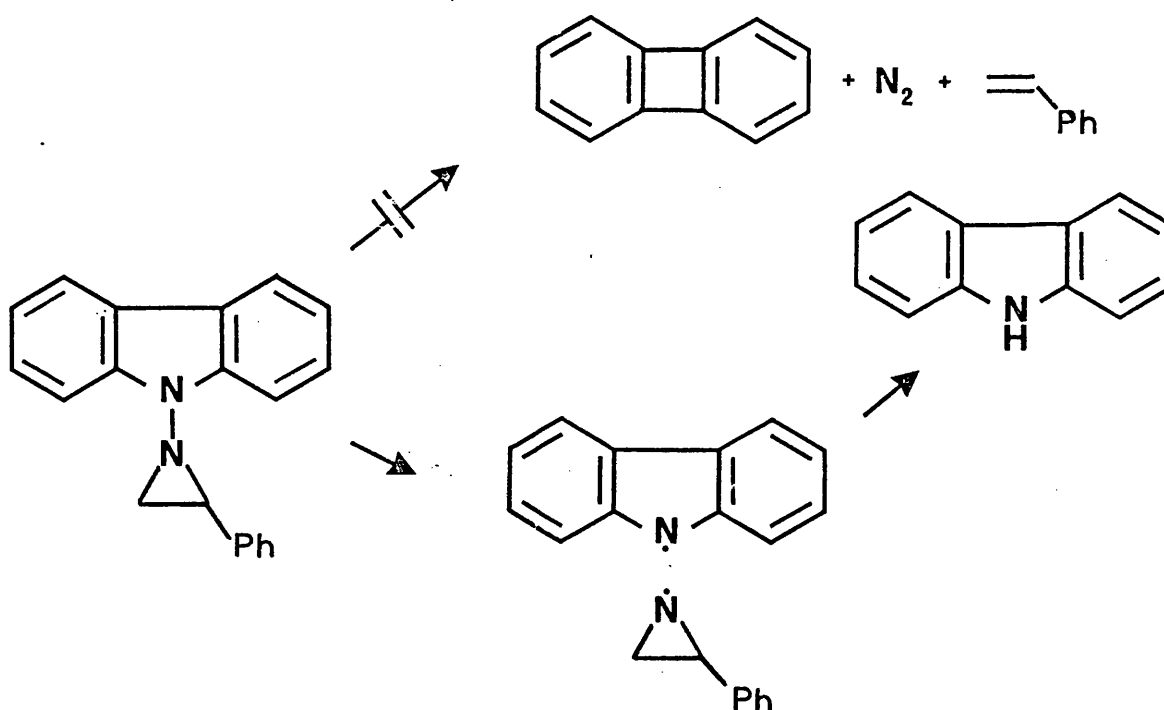
Treatment of the title compound (36), prepared<sup>38,134</sup> by oxidation of N-aminophthalimide in trans-stilbene, with lithium aluminium hydride was expected to give the isoindolinyln-aziridine (37). However, no aziridine was found and the only product identified was trans-stilbene (68%). An unidentified compound was also isolated in very low yield.



It is tempting to suggest that the aziridine (37) was formed transiently and underwent a very ready fragmentation, analogous to that of the aziridine (31), to give stable trans-stilbene.

#### 1-(N-Carbazolyl)-2-phenylaziridine (38)

Vapour phase flash pyrolysis of the aziridine (38) was briefly investigated. The aziridine was prepared by lead tetra-acetate oxidation of N-amino-carbazole in styrene but, as described,<sup>11</sup> was obtained in less than 4% yield. It was found possible however to increase the yield to 28% by the use of diacetoxy-iodobenzene as oxidant. Pyrolysis of the aziridine (38) was carried out at 560° and 800° but gave no biphenylene nor styrene. The formation of carbazole showed that N-N cleavage was occurring. (Scheme 13).

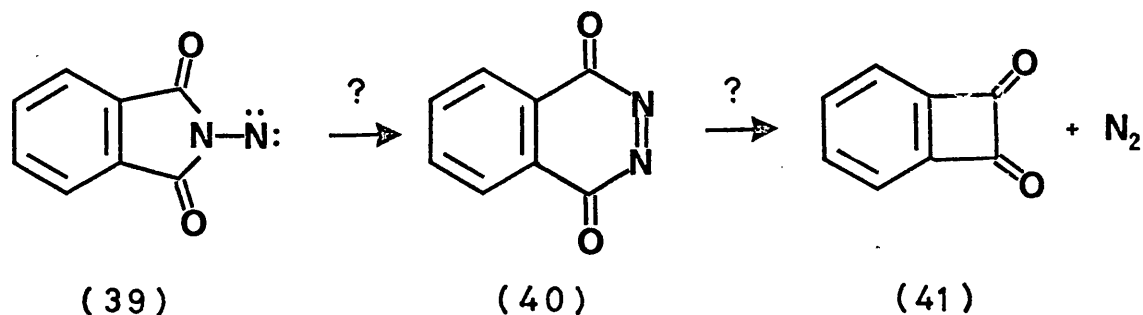


(Scheme 13)

2. The Generation and Fragmentation of Phthalaz-1,4-dione, and other  $\alpha$ -Carbonyl-Azo Compounds, in the Vapour Phase

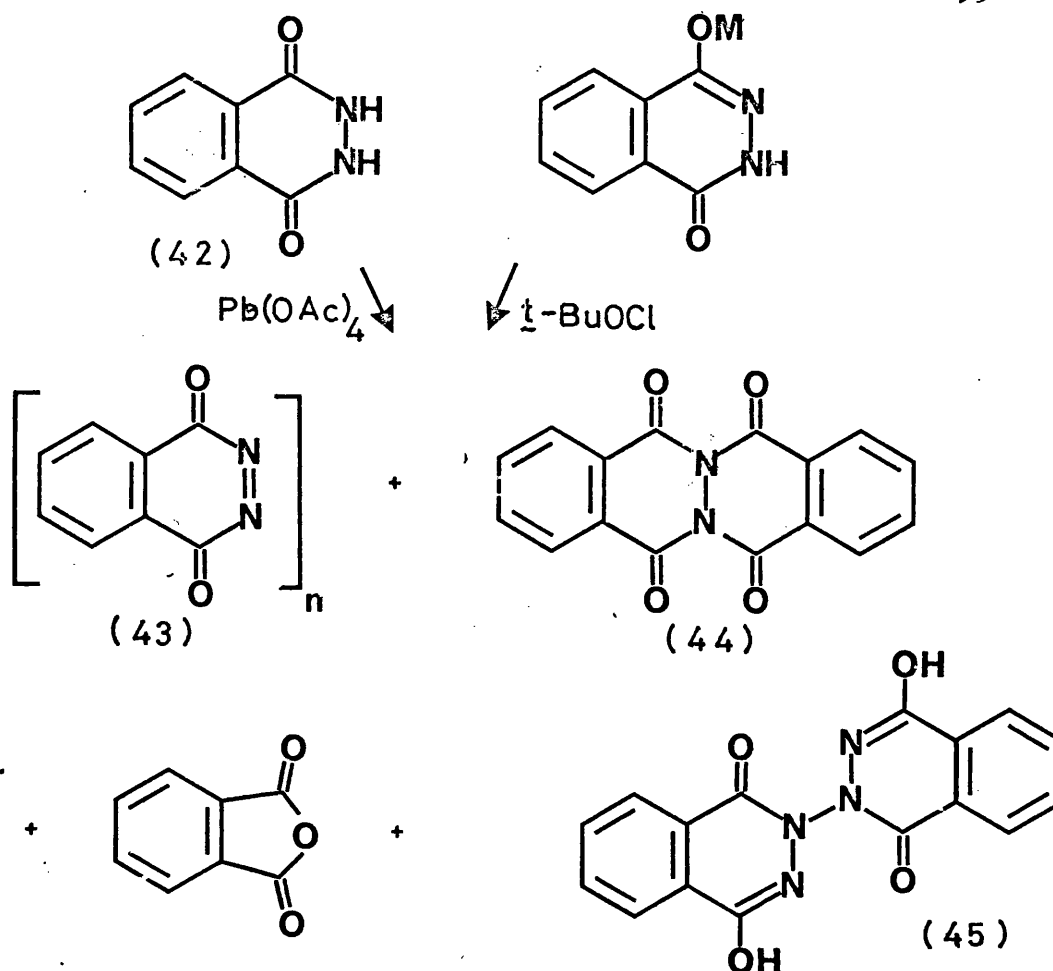
In the previous section it has been shown that phthalimido-nitrene (39), when generated in the vapour phase at elevated temperature, extrudes nitrogen to form benzocyclobutenedione (41). The possibility exists that the extrusion is preceded by insertion of the nitrene (Scheme 14) and it was thought desirable to ascertain if phthalaz-1,4-dione (40) could fragment in this manner.





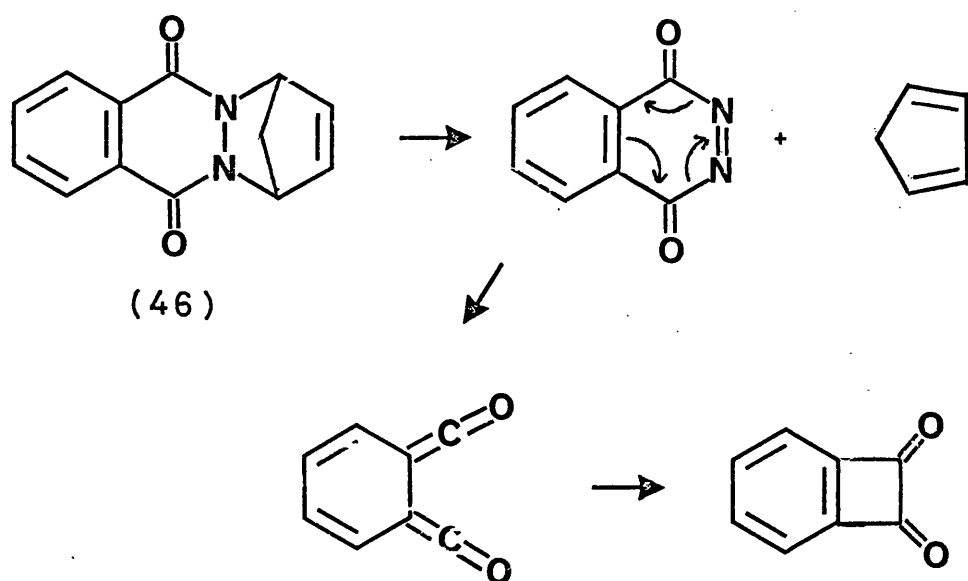
(Scheme 14)

The species (40) has been generated in solution by lead tetra-acetate oxidation of phthalazin-1,4-dione (42) and by treatment of an alkali metal salt of (42) with t-butyl hypochlorite.<sup>165-167</sup> It is stable at -78° in acetone solution but rapidly decomposes on warming to room temperature. The polymer (43) and the phthalazino-phthalazine (44) are formed, along with small amounts of phthalic anhydride and the bis-hydrazide (45). No evidence has been found for fragmentation to benzo-cyclobutenedione (41) or benzyne.



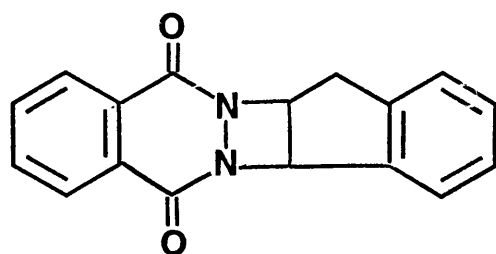
However, preliminary work in these laboratories<sup>136</sup> showed that oxidation of the hydrazide (42), in the presence of cyclopentadiene, gave the Diels Alder adduct (46); pyrolysis of this adduct in the vapour phase then gave benzocyclobutenedione (41), albeit in low yield.

Closer examination of this reaction now reveals that the fragmentation of the adduct (46), which has now been characterised, is essentially quantitative. The likely mechanism involves the formation of phthalaz-1,4-dione by a retro Diels Alder reaction, followed by a pericyclic  $[\sigma^2_s + \sigma^2_s + \pi^2_s]$  fragmentation. Closure of the bis-ketene so formed then gives benzocyclobutenedione.

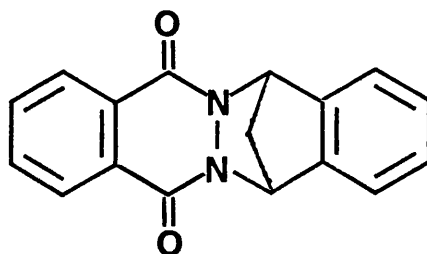


The high yield, and the volatility of the other products ( $N_2$ ,  $CO$ , and cyclopentadiene), makes this reaction a very useful synthetic route to benzocyclobutenedione (41). Moreover, since the phthalaz-1,4-dione (40) is generated under very comparable conditions to those used for the generation of phthalimido-nitrene, it is quite possible that insertion of phthalimido-nitrene could be occurring in the vapour phase pyrolyses studied earlier.

Phthalaz-1,4-dione is a potent dienophile but enophilic character is less well known.<sup>165</sup> However, addition to indene is reported to give the  $[2+2]$  adduct (47) rather than the  $[2+4]$  adduct (48).<sup>138</sup> The addition presumably occurs by a stepwise mechanism since concerted thermal formation of adduct (47) is a disallowed process.<sup>155</sup>



( 4 7 )



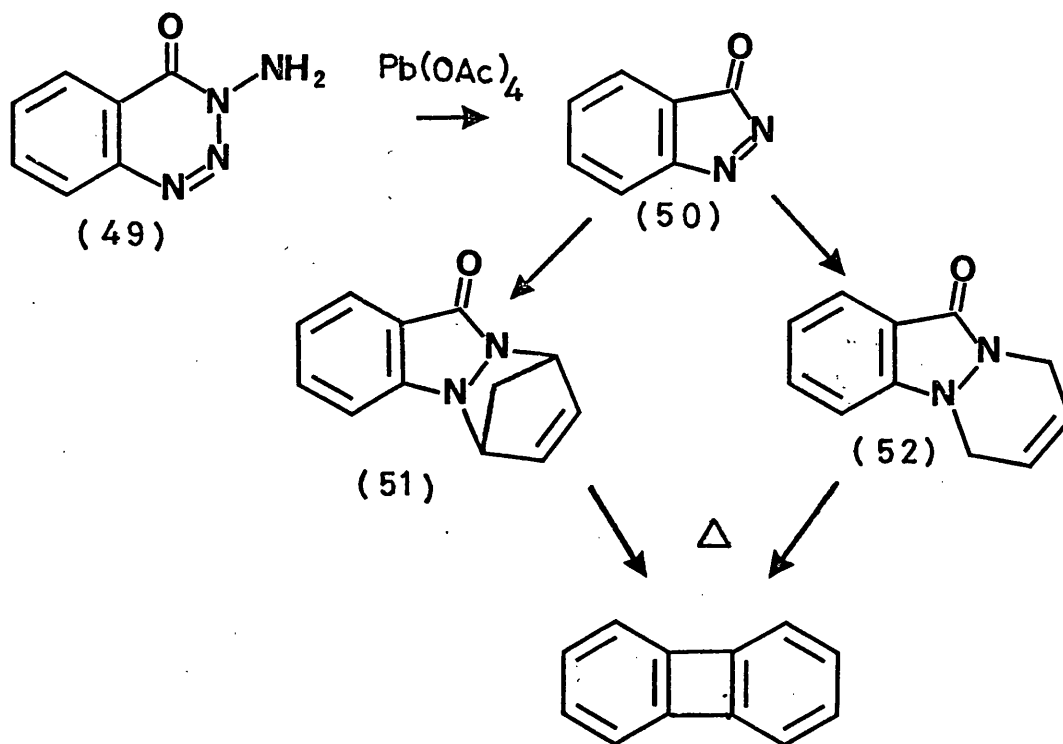
( 4 8 )

The adduct (47) was prepared by the literature procedure<sup>138</sup> and vapour phase flash pyrolysis showed that it too can undergo retro-addition to give indene and phthalaz-1,4-dione; the latter again gave benzocyclobutenedione (64%). Thus this method of generating reactive species, such as phthalaz-1,4-dione, is not confined to diene adducts.

The possibility of generating other  $\alpha$ -carbonyl azo compounds was also briefly investigated by Forster.<sup>136</sup> The adducts (51) and (52) of indazol-3-one (50) were prepared by oxidation of 3-aminobenzo-1,2,3-triazin-4-one (49) in the presence of the appropriate diene. Forster pyrolysed the adducts at 380° and 610°, respectively, and obtained biphenylene in yields of 13% and 19%.

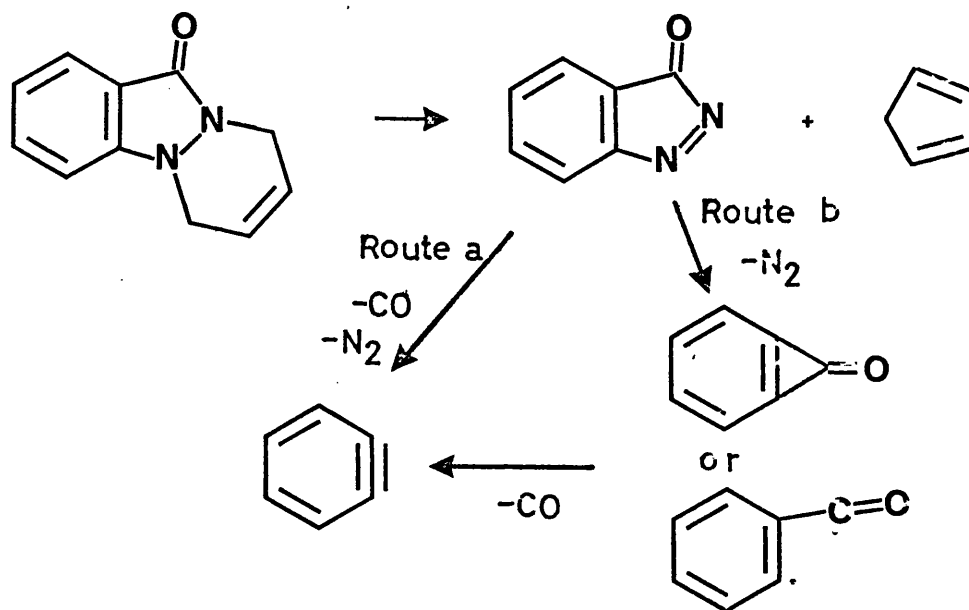
Further investigation of these pyrolyses now shows that the yield of biphenylene can be improved. The adduct (51) is rather involatile and in a closed pyrolysis system tends to decompose before volatilisation.

However, the use of a nitrogen flow system partly overcame this problem and passage of the vapour through a tube at  $400^{\circ}$  gave a pyrolysate of pure biphenylene (63%). The adduct (52) is rather more stable and complete loss of starting material was only obtained by pyrolysis at  $750-800^{\circ}$ . At this temperature charring was extensive and biphenylene was obtained in only 21% yield.



The fragmentations observed presumably arise by an initial retro Diels Alder reaction forming indazol-3-one and the diene (Scheme 15). Decomposition of the indazol-3-one may then occur either by a concerted pathway (route a) or by a stepwise process possibly via benzocyclopropenone (route b). However,

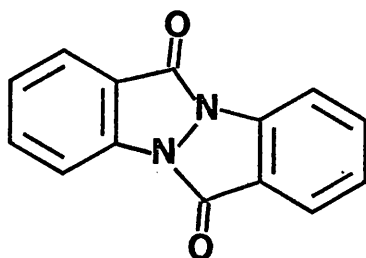
extended Hückel calculations have shown<sup>49</sup> that benzo-cyclopropenone would not be expected from the indazolone.



(Scheme 15)

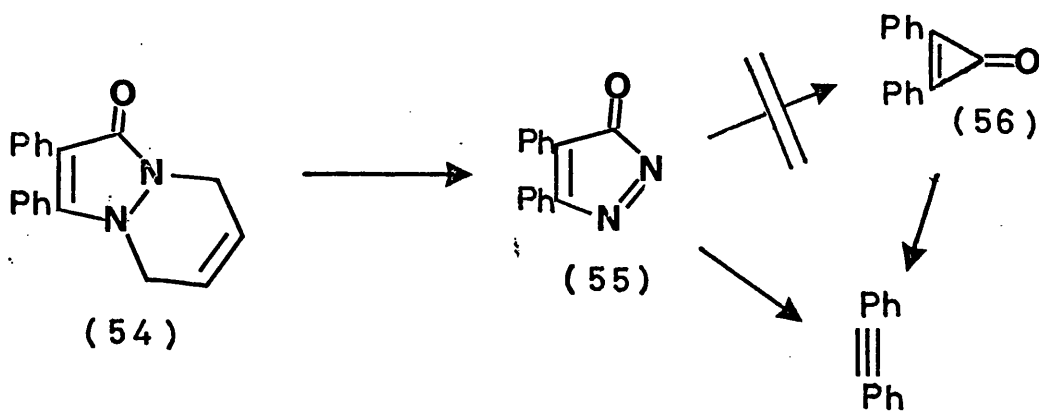
Our failure to observe cycloaddition between benzyne and the liberated diene (cyclopentadiene or butadiene) is probably reasonable in that in order to compete efficiently with dimerisation, the trapping agent must be present in high concentration.<sup>168,169</sup>

In spite of the known thermal instability of indazol-3-one (50), it has never before been observed to yield benzyne by fragmentation. When generated at room temperature in solution, indazol-3-one either polymerises or forms the indazolino-indazolone (53).<sup>135</sup>



(53)

Pyrolysis of the system (54) was then investigated, since in this case the intermediate cyclopropenone would be an isolable compound.



Pyrolysis of the adduct (54) at 500° gave diphenylacetylene (40%) and starting material (30%). A blank experiment showed that diphenylcyclopropenone (56) was completely decarbonylated to diphenylacetylene under these conditions. Other blank experiments showed that diphenylcyclopropenone was completely destroyed even on pyrolysis at 320° but that about 50% survived on flash pyrolysis at 250°. Pyrolysis of the adduct (54)

under the latter conditions gave only a few percent decomposition but the product was easily identified as diphenylacetylene and no diphenylcyclopropenone was found. Thus, the loss of CO and N<sub>2</sub> from the  $\alpha$ -carbonyl azo compound (55) cannot occur via the cyclopropenone (56). This parallels the behaviour of indazol-3-one when generated in solution by oxidation of 3-aminobenzo-1,2,3-triazin-4-one; it has been shown<sup>49</sup> that benzocyclopropenone is not formed from the indazolone but arises by concerted loss of nitrogen from the nitrene.

The technique of vapour phase flash pyrolysis of these types of compounds is thus seen to be a very useful tool for the generation of reactive species at high temperature and low dilution, under which conditions unimolecular decomposition is highly favoured.

Many nitrenes other than those studied in this work are known to react intermolecularly when generated at room temperature in solution and good yields of sulphoximides can generally be isolated by generation of these nitrenes in the presence of sulphoxides. The vapour phase flash pyrolysis of these adducts promises to enable the study of further nitrene fragmentations and the preparation of novel systems. Where the sulphoximides are prepared from N-amido- or N-imido-nitrenes then the diphenyl sulphoxide adducts are preferable for study but for other N-amino systems, where hydrogen abstraction does not compete, then the dimethyl sulphoxide adducts are more satisfactory.

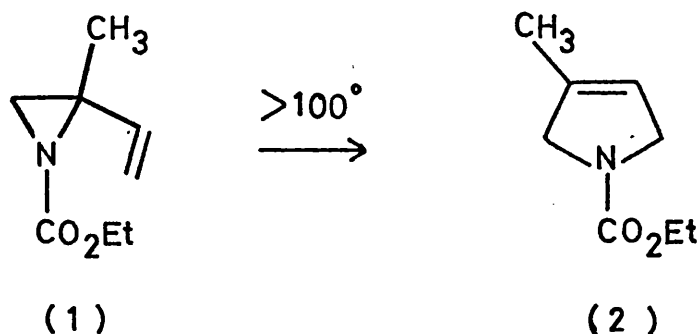


Similarly, several other  $\alpha$ -carbonyl and  $\alpha,\alpha'$ -dicarbonyl azo compounds form Diels Alder adducts with cyclopentadiene, and pyrolysis of these adducts should lead to the observation of novel fragmentations and enable the preparation of interesting molecules.

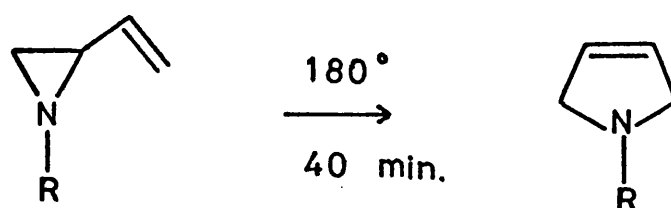
The pyrolysis technique has the advantage that the reaction products are rapidly trapped at low temperature and thus even thermally labile molecules can be isolated. However, the involatility of certain systems may be a problem and may necessitate the use of large capacity vacuum pumps and fast nitrogen flow rates.

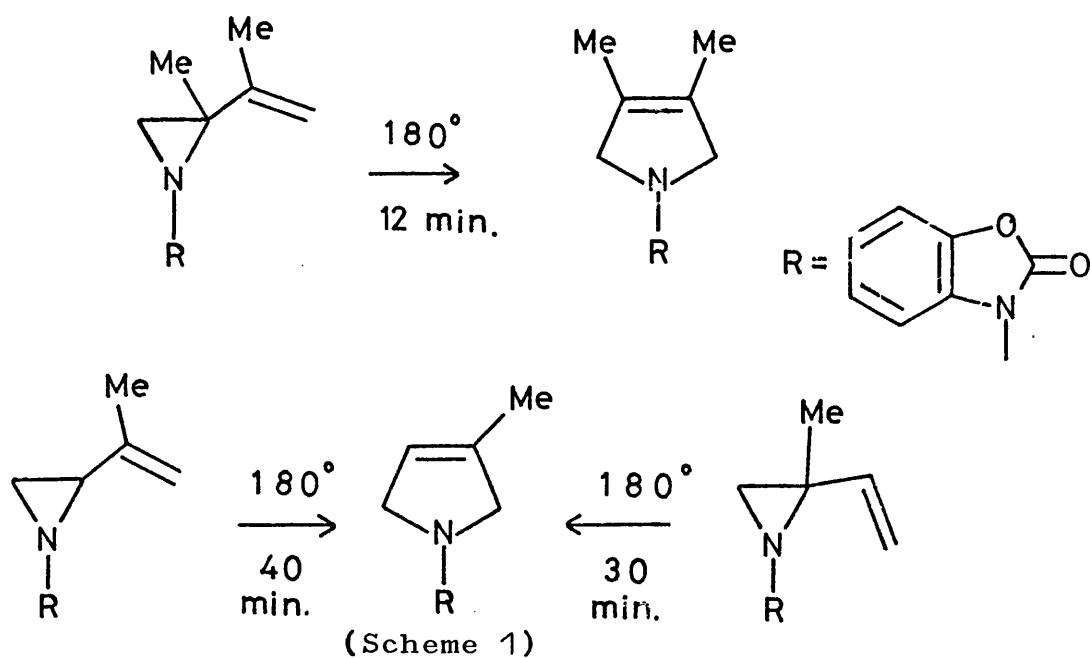
Discussion.    Part 2.

Vinylaziridines are known to rearrange thermally to 3-pyrrolines, in a reaction analogous to the well known vinylcyclopropane to cyclopentene rearrangement. Thus, N-ethoxycarbonyl-2-methyl-2-vinylaziridine (1) isomerises<sup>170</sup> when subjected to gas chromatography at column temperatures above 100°, giving N-ethoxycarbonyl-3-methyl-3-pyrroline (2).

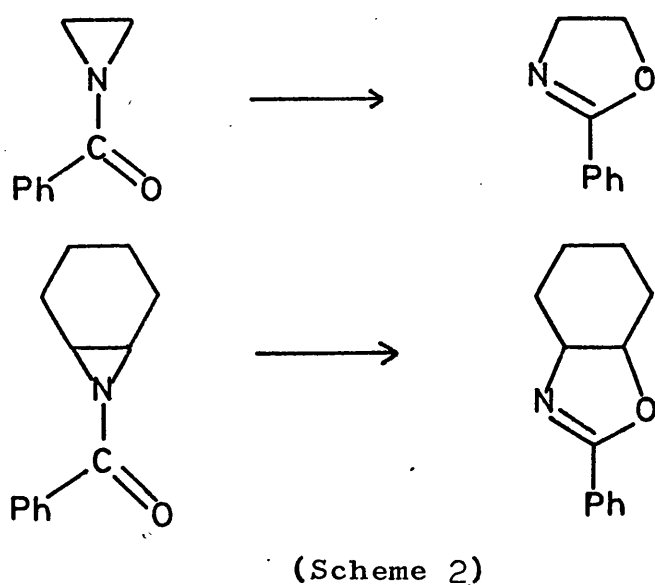


Similarly, the N-benzoxazolonyl-aziridines shown in Scheme 1 are rearranged on heating at 180° in decalin to give the corresponding 3-pyrrolines.<sup>52</sup>



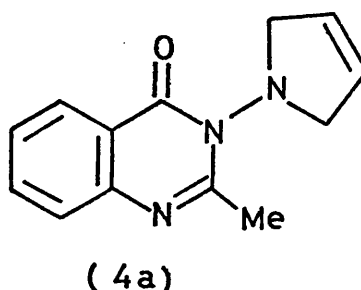
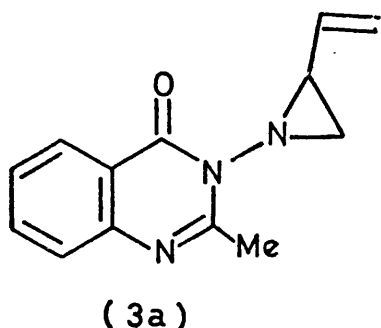


Aziridines having unsaturated N-substituents undergo somewhat analogous thermal rearrangements (Scheme 2).<sup>171</sup>



Similar isomerisations by nucleophilic and acidic reagents are also well known;<sup>171</sup> for example, N-acylaziridines are converted into oxazolines by sodium iodide in acetone solution.<sup>172</sup>

In connection with the photochemical work described in Part 1, Section 1 of this thesis, the N-methylquinazolonyl-3-pyrroline (4a) was required. By analogy with the rearrangements mentioned above, it was expected that this would be obtained in high yield by the thermal rearrangement of the vinylaziridine (3a).

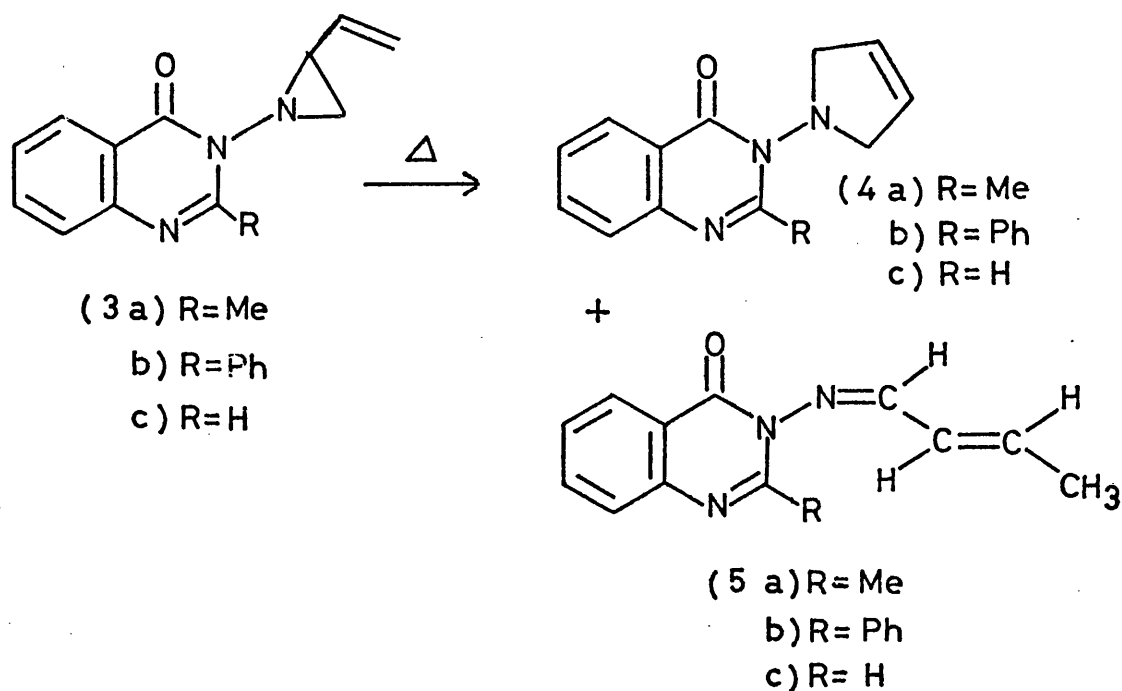


The 3-pyrroline (4a) was obtained, but only as the minor product. This observation prompted a more detailed study of the thermolysis of (3a) and related systems.

Preparation and thermolysis of 1-(2-methylquinazol-4-on-3-yl)-2-vinylaziridine (3a).

The title compound was prepared as described<sup>35</sup> by oxidation of 3-amino-2-methylquinazol-4-one with lead tetra-acetate in the presence of buta-1,3-diene.

Thermolysis of the vinylaziridine (3a) in dry decalin at 170-190° was complete within 3 hrs. Chromatographic work-up gave the 3-pyrroline (4a) in 4% yield and a major product (40%) identified as the hydrazone (5a) (Scheme 3).



(Scheme 3)

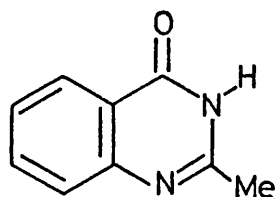
The trans stereochemistry about the double bond of hydrazone (5a) was inferred from the lack of further splitting of the doublet (J 5.0 Hz) of the terminal methyl group in the n.m.r. spectrum. This was confirmed by an independent synthesis of (5a) by condensation of 3-amino-2-methylquinazol-4-one with trans-crotonaldehyde. The product from the condensation reaction was identical in all respects with the major product from thermal rearrangement of the vinylaziridine (3a).

Rearrangement of the vinylaziridine (3a) could also be effected by heating in the melt at 220-240° for 1.5 hr. As before, the pyrroline (4a) and the hydrazone (5a) were obtained, the latter again as the major product.

The reaction could be conveniently followed by

carrying out the thermolysis in 1,2,4-trichlorobenzene solution in an n.m.r. tube. The tube was heated and periodically cooled for measurement of the spectrum. Signals due to the vinylaziridine (3a) disappeared within 76 min. and were replaced by those of the pyrroline (4a) and hydrazone (5a). No other signals were observed in the spectrum and there was no change on further heating. In particular, the ratio of the two products remained constant, so indicating that no inter-conversion was occurring. Indeed, a blank experiment showed that both the pyrroline (4a) and the hydrazone (5a) were stable under the thermolysis conditions. The signals of the pyrroline (4a) and hydrazone (5a) were well separated in the n.m.r. spectrum of the mixture and the ratio of the two products could be calculated as 1:1.2 (see Table 2, page 215).

To investigate the effect of temperature on the relative yields of the products, the rearrangement was carried out by the vapour phase flash pyrolysis technique. The aziridine (3a) sublimed easily and cleanly and the vapour was pyrolysed at oven temperatures between 260° and 550°. In these reactions, a third product was also obtained and was identified as 2-methylquinazol-4-one (6). Control experiments showed that none of the products were interconverted under the reaction conditions. None of this parent lactam (6) was detected by t.l.c. examination of the solution pyrolyses above.



(6)

The results of the vapour phase pyrolyses are summarised in Table 1.

TABLE 1

Vapour phase flash pyrolysis of 1-(2-methylquinazol-4-on-3-yl)-2-vinylaziridine (3a)

Temp.	% Vinylaziridine (3a) unchanged	Ratio		% 2-methyl- quinazol-4-one (6)
		Pyrroline: (4a)	Hydrazone (5a)	
260	100			0
320	12	1.5	: 1	14
360	7	1.9	: 1	20
440	0	3.5	: 1	46
550	0			96

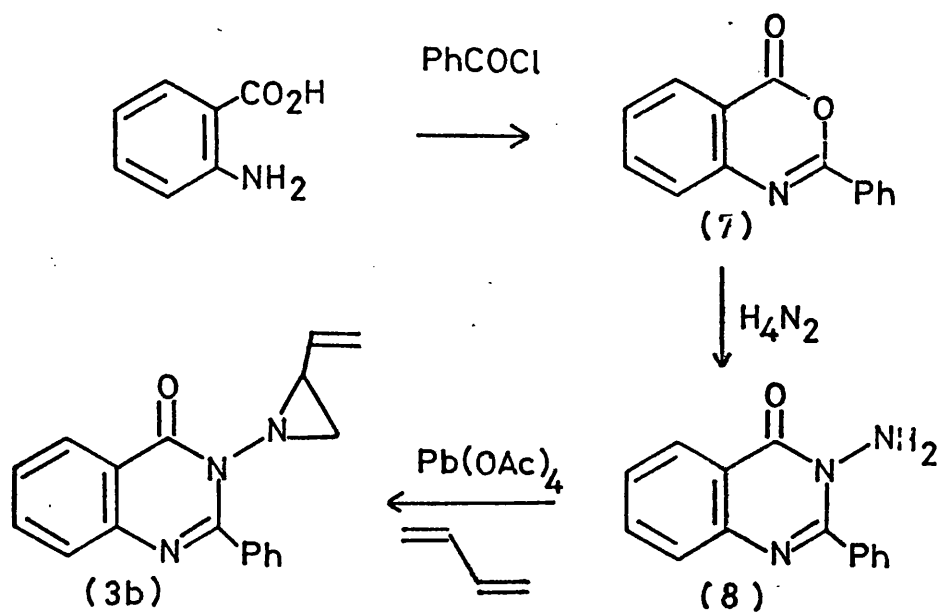
It can be seen that, as the temperature is increased, the pyrroline becomes more favoured over the hydrazone, but that the combined yield of these rearrangement products falls, because of the increasing tendency of the vinylaziridine to fragment and so form 2-methylquinazol-4-one.

The higher temperature thermolyses gave imperfect mass balance and this is probably due to the formation of volatile fragments that were not trapped

by the water-cooled cold surface used. Negligible charring was observed on the walls of the pyrolysis tube.

Preparation and thermolysis of 1-(2-phenylquinazol-4-on-3-yl)-2-vinylaziridine (3b)

Anthranilic acid and benzoyl chloride were reacted together to form 2-phenyl-4H-3,1-benzoxazin-4-one (7).<sup>139</sup> The benzoxazinone (7), with hydrazine hydrate, gave 3-amino-2-phenylquinazol-4-one (8),<sup>140</sup> which was oxidised in the presence of buta-1,3-diene to give the title compound (3b).



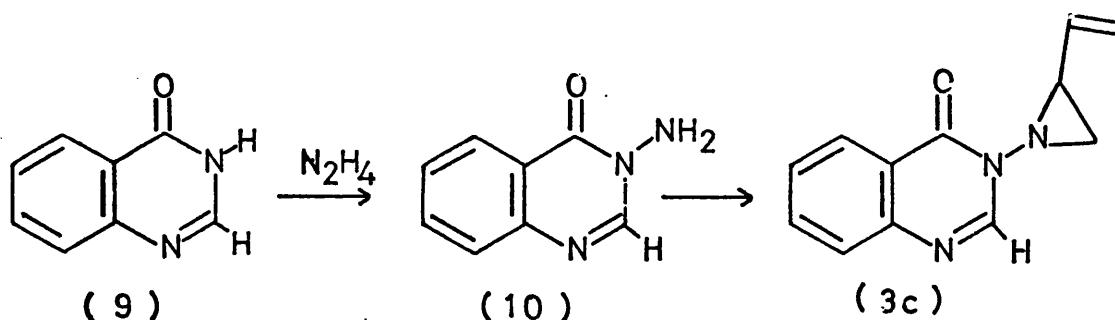
Thermolysis of the vinylaziridine (3b) was performed both in the melt at 160-190° and in decalin solution at 180-200°. As before, two rearrangement products (4b) and (5b) were formed (Scheme 3, p.204). The hydrazone (5b) was synthesised independently by condensation of the N-amino compound (8) with crotonaldehyde and again is assigned the trans configuration.



A pyrroline (4b) to hydrazone (5b) ratio of 1:1.5 was obtained (see Table 2, page 215) by thermolysing the vinylaziridine (3b) in 1,2,4-trichlorobenzene at  $180^{\circ} \pm 2^{\circ}$  and following the reaction by n.m.r.. The reaction gave no products other than (4b) and (5b) and the ratio found was unaffected by further heating.

Preparation and thermolysis of 1-(quinazol-4-on-3-yl)-2-vinylaziridine (3c)

3-Aminoquinazol-4-one (10) was prepared from quinazol-4-one (9) and hydrazine hydrate.<sup>142</sup> The quinazol-4-one (9) was obtained by a Niementowski synthesis from anthranilic acid and formamide.<sup>141</sup> Oxidation of the N-amino (10) in the presence of buta-1,3-diene gave the required vinylaziridine (3c), although in rather poor yield.



The vinylaziridine (3c), on thermolysis in the melt, gave the pyrroline (4c) and the hydrazone (5c) (Scheme 3, p.204). The latter was synthesised

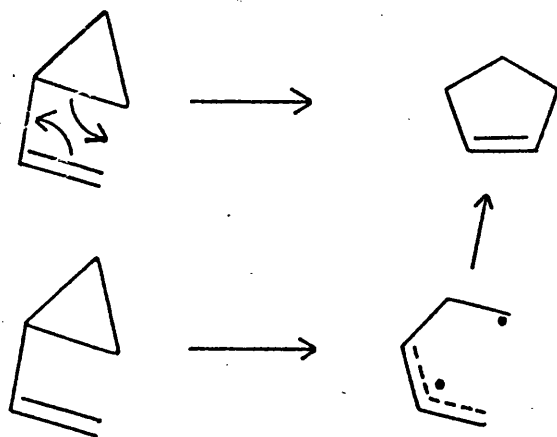
independently from the N-amino compound (10) and crotonaldehyde.

Rearrangement of the vinylaziridine (3c) at  $180^{\circ} \pm 2^{\circ}$ , and study of the reaction by n.m.r., showed that reaction was complete within 99 min. and gave a ratio of 1:0.6 (see Table 2, p.215 ) for the yield of pyrroline (4c) compared to hydrazone (5c).

#### Mechanisms of the rearrangement of vinylaziridines (3a,b,c)

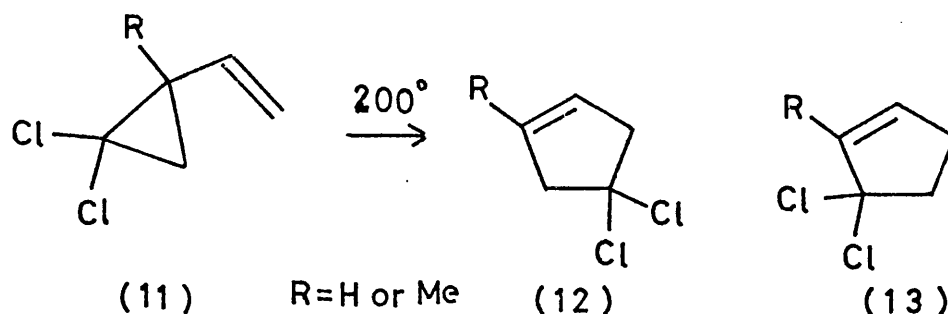
The formation of the hydrazones (5a,b,c) has no parallel in the reported rearrangements of other vinylaziridines. Indeed, there is no report of analogous products from thermolysis of vinylcyclopropanes.

The thermal isomerisation of vinylcyclopropanes to cyclopentenenes has received considerable attention since 1959 and yields have been reported as generally high and approaching quantitative.<sup>173</sup> An exception is when the vinyl group bears a cis-methyl substituent at its terminus; the reaction then gives only a small amount of the cyclopentene and the major product is a polymer.<sup>174</sup> The mechanism of the ring expansion is still a matter for discussion. Two extremes are possible (Scheme 4):- the reaction may occur by a [1,3]-sigmatropic mechanism, or through an alkyl-allyl diradical which collapses with allylic rearrangement.

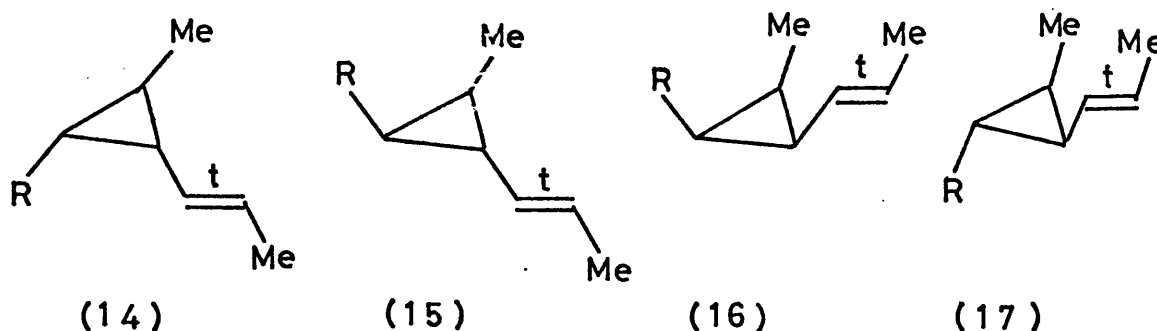


(Scheme 4)

The subject was reviewed in 1968<sup>173</sup> and the conclusion drawn that the reaction is completely synchronous for most systems but that certain vinylcyclopropanes, substituted by particular groups at particular positions, may involve discrete biradical intermediates on rearrangement. For example, the rearrangement of the vinylcyclopropane (11) occurs at the comparatively low temperature of 200° and gives specifically the cyclopentene (12). None of the isomeric cyclopentene (13) is formed.<sup>175</sup> This indicates at least a measure of diradical character in a discrete intermediate. The diradical can, of course, be stabilised by the  $\alpha$ -chlorine atoms.



Mazzocchi, however, has presented evidence<sup>176</sup> against a concerted process for the ring expansion of the vinylcyclopropanes (14) - (17), and supports the ideas of Sarel and co-workers.<sup>177</sup>



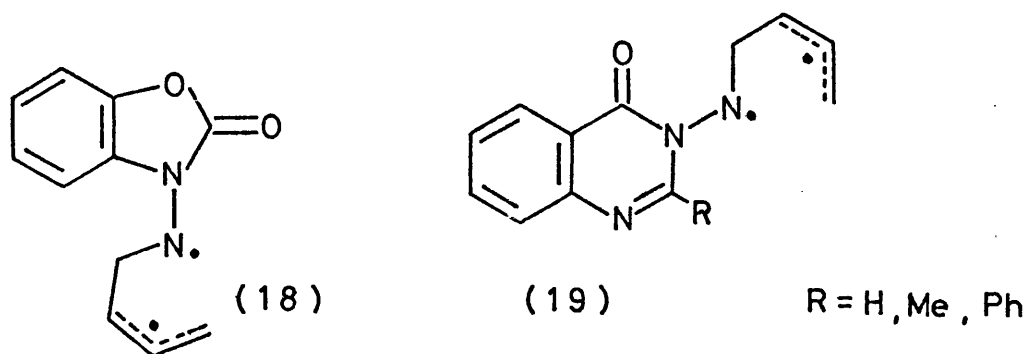
Three possibilities were considered by Mazzocchi :

(1) the reaction is a concerted [1,3]-sigmatropic reaction and takes place either antarafacially with retention of stereochemistry at the migrating carbon or suprafacially with inversion of stereochemistry at the migrating carbon; (2) the reaction is not concerted and takes place via a diradical intermediate; (3) a mixture

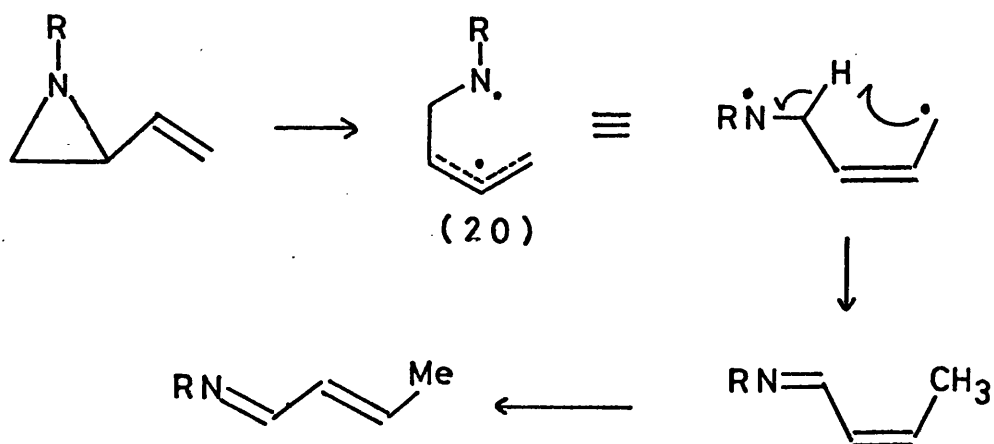
of the mechanistic pathways occurs. A detailed analysis of the products, and their yields, from thermolysis of the cyclopropanes (14) - (17) enabled the first possibility to be excluded, but no comment could be made on the last.

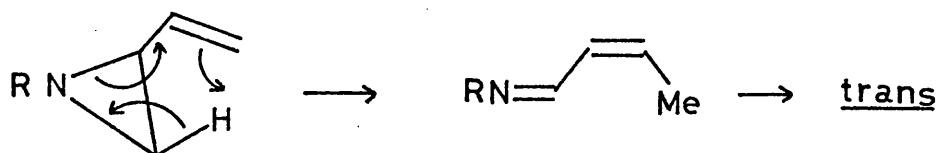
Thus, the mechanism of alkyl substituted vinyl-cyclopropane ring expansion is disputed, but it seems generally agreed that the diradical mechanism is operative in systems which can stabilise the non-allylic radical.

The mechanism of ring expansion of vinyl-aziridines to 3-pyrrolines has not been studied closely. However, it has been proposed<sup>52</sup> that allylic-hydrazino diradicals, of the type (18), are involved in the formation of the pyrrolines shown in Scheme 1, page 202. This was based on the known stability of the isoelectronic nitroxide radicals and was supported by the relative rates of rearrangement of the vinylaziridines. Since the diradical (19) can be stabilised in exactly the same way, it is considered to be a very reasonable intermediate in the formation of the pyrrolines (4a,b,c) from the vinylaziridines (3a,b,c).



Two mechanisms may be considered for formation of the hydrazones (5a,b,c) on thermolysis of the vinylaziridines (3a,b,c) : a stepwise hydrogen transfer involving the same diradical intermediate (20) as leads to pyrroline formation (Scheme 5) and a thermally allowed, concerted, 1,5-hydrogen shift through a rather strained, but accessible, cyclic transition state (Scheme 6).





(Scheme 6)

Both mechanisms require that the hydrazone be formed with cis substituents of the carbon-carbon double bond; however, isomerisation to the trans isomer would be extremely rapid under the reaction conditions. All of the hydrazones isolated possessed trans stereochemistry.

The concerted process shown in Scheme 6 represents a new type of 1,5-hydrogen shift, in which all annular positions of the three-membered ring are involved in the transition state.

The product compositions shown in Table 2 were obtained by n.m.r. analysis of the thermolyses carried out at  $180^{\circ} \pm 2^{\circ}$  in 1,2,4-trichlorobenzene solution.

TABLE 2

Product composition from complete rearrangement of vinyl-aziridines (3a,b,c) at 180°±2°.

3c, R=H	4c : 5c = 1 : 0.6	(±0.1)
3a, R=Me	4a : 5a = 1 : 1.2	"
3b, R=Ph	4b : 5b = 1 : 1.5	"

The product compositions show a tendency for hydrazone formation to increase as the aziridine N-substituent increases in size. This appears reasonable in view of the greater steric requirements of the pyrroline ring compared with the linear hydrazone. The absence of hydrazone formation with the benzoxazolonyl-vinylaziridines shown in Scheme 1 can be similarly explained by the smaller bulk of the N-benzoxazolonyl compared to the N-quinazolonyl group. A difference between the two heterocyclic groups is also reflected in the n.m.r. spectra of their pyrrolines. Whilst the N-benzoxazolonyl-pyrrolines shown in Scheme 1, in common with most other 3-pyrrolines, show a singlet for the pyrroline methylene protons and a singlet for the pyrroline olefinic protons, the pyrroline methylene protons of the 2-methylquinazolonyl-pyrroline (3a) appear as a complex multiplet at normal temperature. This becomes a singlet at 150° with a coalescence temperature of about 100° in o-dichlorobenzene solution (see Fig. 1, page 133). This appears to be the first example of a 3-pyrroline showing a temperature dependent n.m.r. spectrum above room temperature, although 1-chloro-



3-pyrroline in  $\text{CFCl}_3$  solution shows a similar effect below room temperature (coalescence temperature  $-98^\circ$ ).<sup>178</sup> The quinazolonyl-pyrrolines (3b), (3c), and 1-(2-methylquinazol-4-on-3-yl)-3,4-dimethyl-3-pyrroline (35) (page 230) also exhibit temperature dependent spectra and the coalescence temperatures were determined as  $45^\circ$ ,  $-60^\circ$ , and  $110^\circ$ , respectively, in  $\text{CDCl}_3$ ,  $\text{CDCl}_3$ , and  $\text{o}$ -dichlorobenzene solutions respectively. Temperature dependence in the n.m.r. spectra of other hydrazines is well known<sup>179</sup> and has been attributed to hindered nitrogen inversion, restricted N-N bond rotation, or a combination of the two. The factors controlling these phenomena are complex and involve steric, inductive, conjugative and electrostatic effects.<sup>180,181</sup>

The results of Table 1 (page 206) on the flash pyrolysis of 1-(2-methylquinazol-4-on-3-yl)-2-vinylaziridine (3a) show that as the temperature is increased, so the ratio of pyrroline to hydrazone increases. This suggests that the rearrangement to the hydrazone has a lower activation energy than that which leads to formation of the pyrroline. This is not inconsistent with stepwise formation of pyrroline and concerted formation of the hydrazone. Fragmentation to 2-methylquinazol-4-one appears to be a process of higher activation energy than both pyrroline and hydrazone formation.

The observation of chemically induced dynamic nuclear polarisation (CIDNP) is evolving into a powerful

tool for the detection of radical precursors to reaction products.<sup>182,183</sup> Basically, a long lived radical intermediate should be revealed by enhanced absorption or stimulated emission in the n.m.r. signals from the product. In simplified terms this arises because the free electron of the radical intermediate becomes polarised by the applied magnetic field and interacts with nearby protons, so causing an anomolous population of the proton nuclear spin energy levels. This anomolous population is retained as the product is formed. If the upper energy level, when compared to the lower energy level, possesses a higher population than the normal Boltzmann distribution, then a comparatively intense emission occurs, and vice versa.

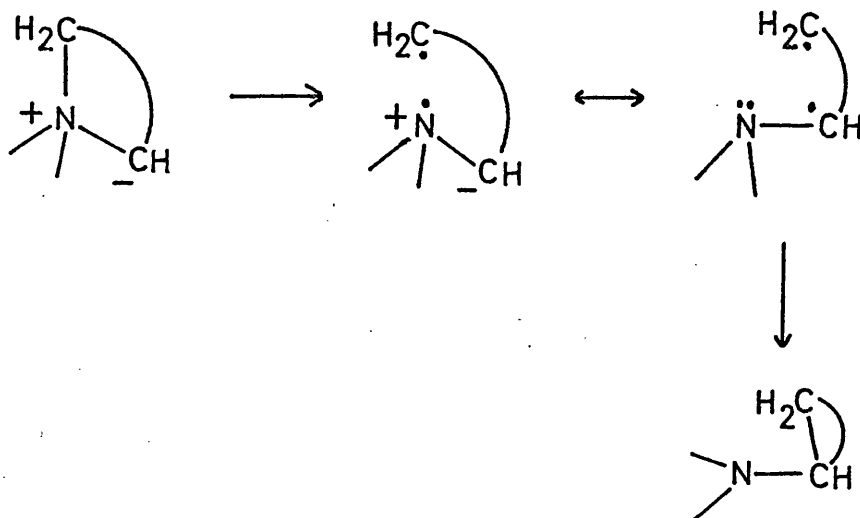
Application of this technique to vinylaziridine rearrangement promised to give information as to the mechanisms involved.

The first system chosen for study was 1-(benzoxazol-2-on-3-yl)-2-methyl-2-isopropenylaziridine (Scheme 1; page 202). Atkinson has shown<sup>52</sup> that this aziridine rearranges very cleanly to the corresponding pyrroline and has proposed a diradical intermediate. A 10% solution of the vinylaziridine in 1,2,4-trichlorobenzene was placed in the probe, preheated to 170°, of a Varian A-60 n.m.r. spectrometer and the spectrum repeatedly scanned. However, the only effect observed was a diminishing in intensity of the vinylaziridine signals and the appearance of signals due to the allylic

and olefinic protons of the pyrroline. The rearrangement was complete in about 450 sec. and no enhanced absorption or stimulated emission was observed at any time.

1-(2-Methylquinazol-4-on-3-yl)-2-vinylaziridine (3a) was also studied. A 20% solution was repeatedly scanned in the n.m.r. probe heated to 170° but, as before, no CIDNP effect was observed. Signals due to the vinylaziridine disappeared and there was a simultaneous build up of pyrroline and hydrazone signals. This reaction was still incomplete after 20 min. at 170°.

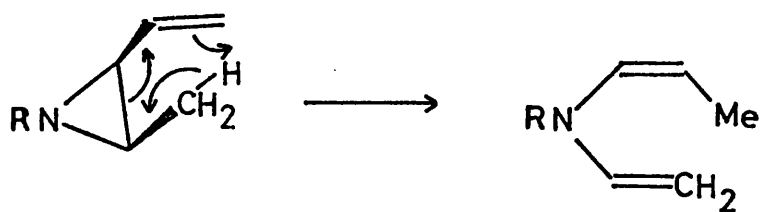
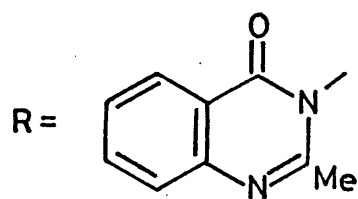
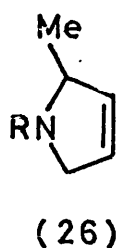
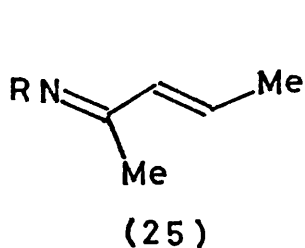
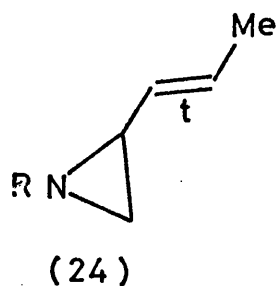
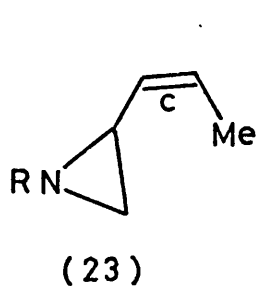
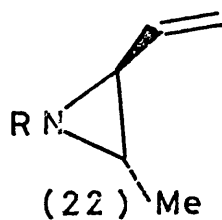
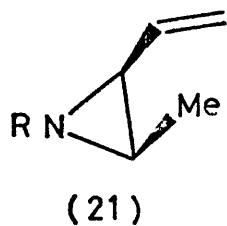
The intermediacy of diradical species is not, however, ruled out by the above results. Although the observation of CIDNP is extremely good evidence for the formation of radical species, the reverse does not necessarily hold and several factors may operate which prevent the observation of CIDNP from systems involving radical intermediates. It is possibly very relevant that the Stevens rearrangement of a system in which the migrating group and the residue are joined (Scheme 8) has failed to afford CIDNP signals<sup>183</sup> whereas CIDNP has often been observed in acyclic Stevens and related rearrangements.<sup>183</sup>



(Scheme 8)

Preparation and thermolysis of the aziridines derived from 3-aminoquinazol-4-one and 1,3-pentadiene

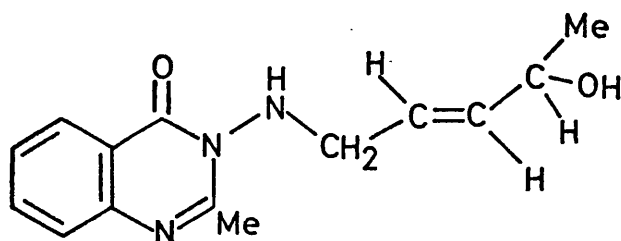
In a further attempt to distinguish between the concerted and stepwise mechanisms for hydrazone formation (Schemes 5 and 6), the cis and trans-3-methyl-2-vinylaziridines (21) and (22) were synthesised. The concerted rearrangement to the hydrazone (25) should be impossible in the cis isomer (21), but not in the trans isomer (22); if a diradical intermediate were involved, however, both should be equally likely to give the hydrazone. Pyrroline (26) formation should be possible in both cases. A homodienyl 1,5-hydrogen shift (Scheme 9) was also considered a possibility in the case of aziridine (21) since the analogous rearrangement of cis-1-alkyl-2-vinylcyclopropanes is well known.<sup>185</sup>



(Scheme 9)

The required aziridines (21) and (22) were prepared by the oxidation of 3-amino-2-methylquinazol-4-one in the presence of cis- and of a mixture of cis and trans-penta-1,3-diene. The addition to cis-penta-1,3-diene took place preferentially at the monosubstituted double bond, so that the major product was the aziridine (23). A further complication was the ready ring opening

of the aziridines and separation of the aziridines (21) and (23) by column chromatography also yielded the alcohol (27) arising from hydrolysis of aziridine (23).



(27)

However, the mixtures were eventually separated by very careful p.l.c. and specimens of all four isomeric aziridines (21) - (24) were obtained. The structures of the isomers were assigned from the n.m.r. spectra and from their method of synthesis.

In an attempt to decrease the selectivity of addition, 3-amino-2-methylquinazolin-2-one was oxidised, in the presence of cis-1,3-pentadiene, in benzene solvent at reflux. This experiment gave a 13% yield of the aziridine (21), whereas the oxidation performed in dichloromethane at 0° gave only a 6% yield of that aziridine. From the products isolated, the ratio of addition to the two double bonds was 1:8.5 at 0° but 1:2 at 80°. It is recognised, however, that some of the observed difference may have originated from variation in work up procedure.

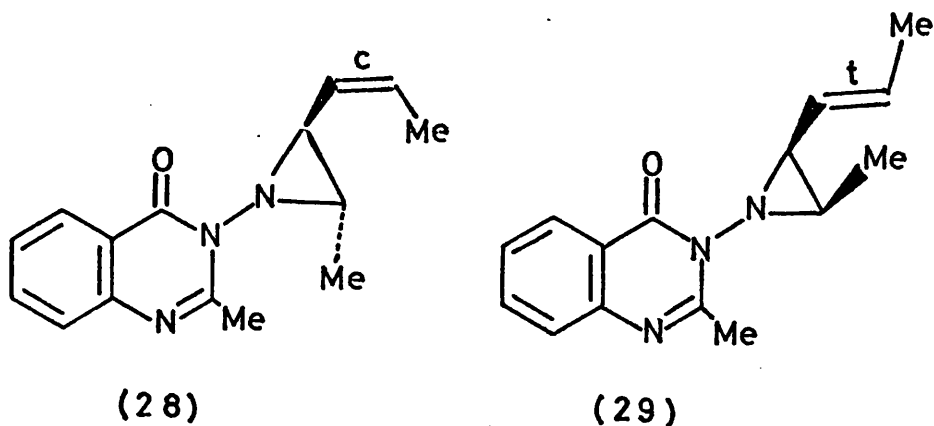
When the aziridines (21) - (24) were subjected to thermolysis, either neat or in a solvent, the only

product that could be isolated, in each case, was 2-methylquinazol-4-one (6). In particular, none of the hydrazone (25) could be detected on thermolysis of aziridines (21) or (22). An authentic specimen of the hydrazone (25) was prepared by condensation of 3-amino-2-methylquinazol-4-one with penten-2-one and this was used as a reference material; it was stable under the reaction conditions.

Thus, the experiment failed in its main objective, which was to distinguish between the stepwise and concerted mechanisms for the formation of the hydrazones, though it did emphasize the sensitivity of these systems to the presence of substituents.

Preparation and thermolysis of 1-(2-methylquinazol-4-on-3-yl)-2-methyl-trans-3-(prop-cis-1-enyl)aziridine (28)

Oxidation of 3-amino-2-methylquinazol-4-one in 2-cis,4-trans-hexadiene yielded the aziridine (28). The structure (28) was assigned on the basis of the n.m.r. spectrum.



It is interesting that a very high yield of this aziridine was obtained but none of the aziridine (29), the product of addition to the cis-double bond, was observed. A similar effect was found in the addition of the nitrene to cis-penta-1,3-diene but in that case the important factor could be the extent of substitution of the two double bonds. In this case, both double bonds are equally substituted but addition occurred exclusively to the trans-disubstituted double bond. This phenomenon, which does not appear to have a simple explanation, has been observed previously. For example, phthalimido-nitrene adds well to trans-1,2-dichloroethylene and to 1,2,3-trichloroethylene, but not at all to cis-1,2-dichloroethylene.<sup>35</sup> The present example is the most definitive however, since both cis and trans bonds are equally substituted and occur in the same molecule.

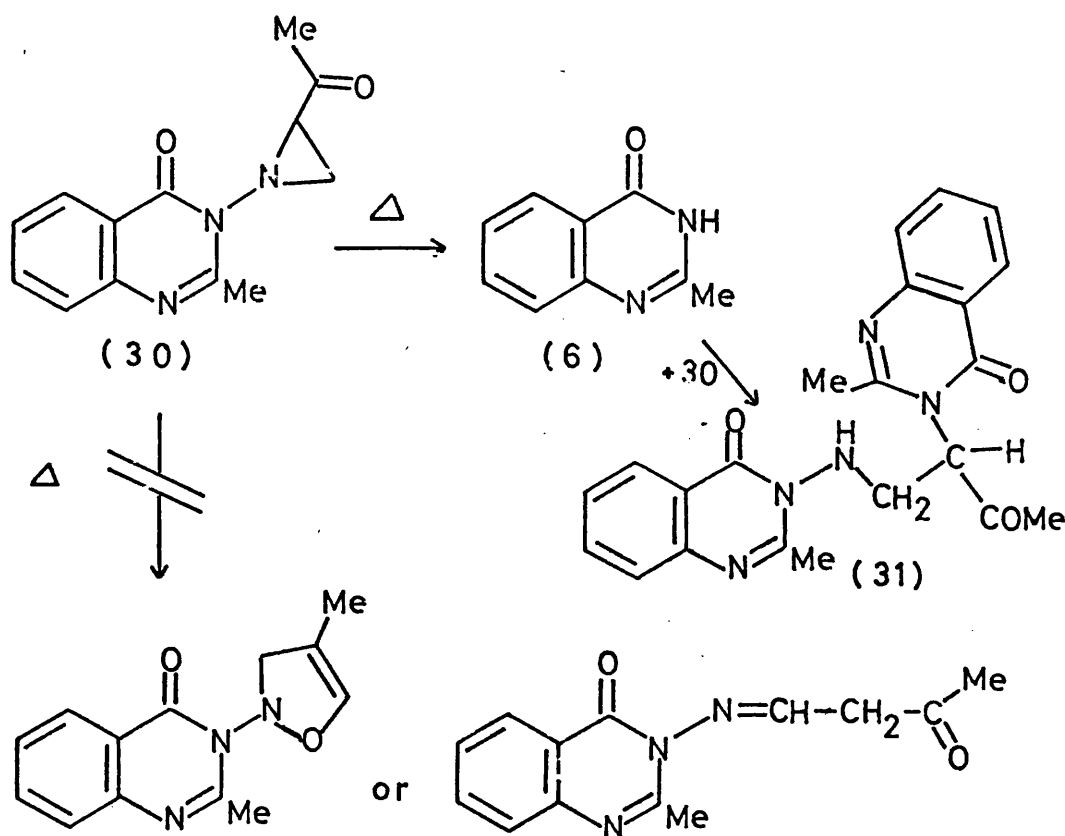
Thermolysis of the aziridine (28) gave only 2-methylquinazol-4-one (6) showing again that alkyl substitution causes fragmentation to be preferred over rearrangement.

Preparation and thermolysis of 1-(2-methylquinazol-4-on-3-yl)-2-acetylaziridine

The aziridine (30) was prepared and thermolysed to investigate if rearrangement or fragmentation occurred. Oxidation of 3-amino-2-methylquinazol-4-one in methyl vinyl ketone gave the aziridine (30) in fair yield. Thermolysis at 170°-185° in dry decalin gave 2-methyl-



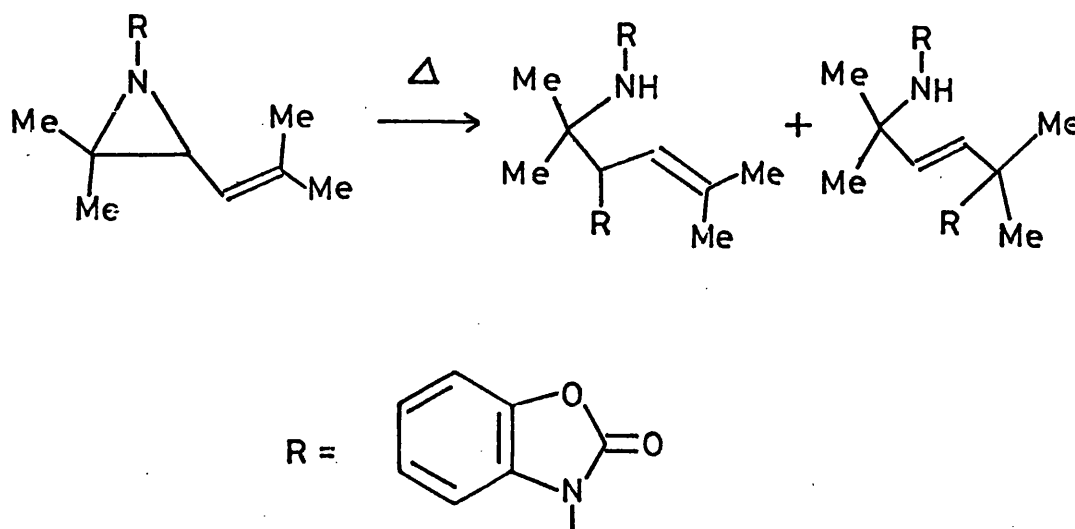
quinazol-4-one (6) (26%) and (31) in 60% yield. The latter presumably arises from the attack of 2-methylquinazol-4-one (6) on unreacted aziridine (30). No rearrangement products were observed.



#### Mechanism of fragmentation

The aziridines (21) - (24), (28), and (30) all fragmented to 2-methylquinazol-4-one (6) under conditions which gave rearrangement of the unsubstituted vinylaziridines (3a,b,c). The unsubstituted vinylaziridine (3a) did not fragment at all on heating in solution at 180°, but flash pyrolysis at temperatures up to 550° showed an increasing tendency for fragmentation to be favoured over rearrangement.

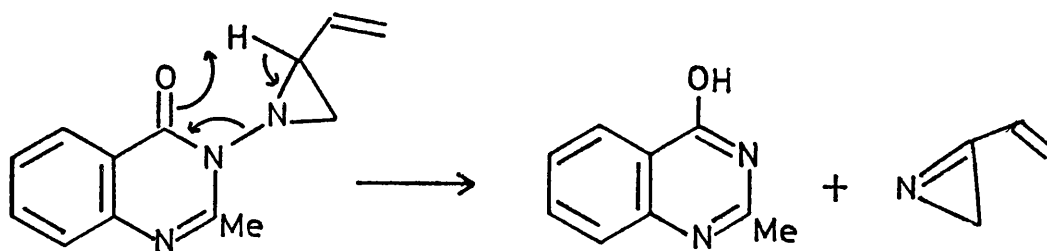
It is not clear why the presence of an alkyl substituent causes fragmentation to occur in preference to rearrangement. Models show no extra steric compression in the transition state for the rearrangement of (22) compared to (3a), for example. It may be that it is the activation energy of the fragmentation to 2-methyl-quinazol-4-one which is lowered in these systems; Atkinson and Rees<sup>52</sup> have previously noted that tetra-alkyl substitution at the aziridine 3-position and the vinyl terminus leads to fragmentation rather than rearrangement (Scheme 10).



(Scheme 10)

A likely mechanism for the fragmentation is a retro-ene reaction giving an azirine as the other fragment (Scheme 11). The azirine is presumed to

polymerise when formed by thermolysis in solution at 180° and it, or its decomposition products, must have been too volatile to be trapped in the vapour phase flash pyrolyses performed.



(Scheme 11)

A similar rearrangement has been invoked by Atkinson and Rees<sup>52</sup> to explain the formation of the products shown in Scheme 10. In their case, the lactam could not be isolated and its formation could only be inferred.

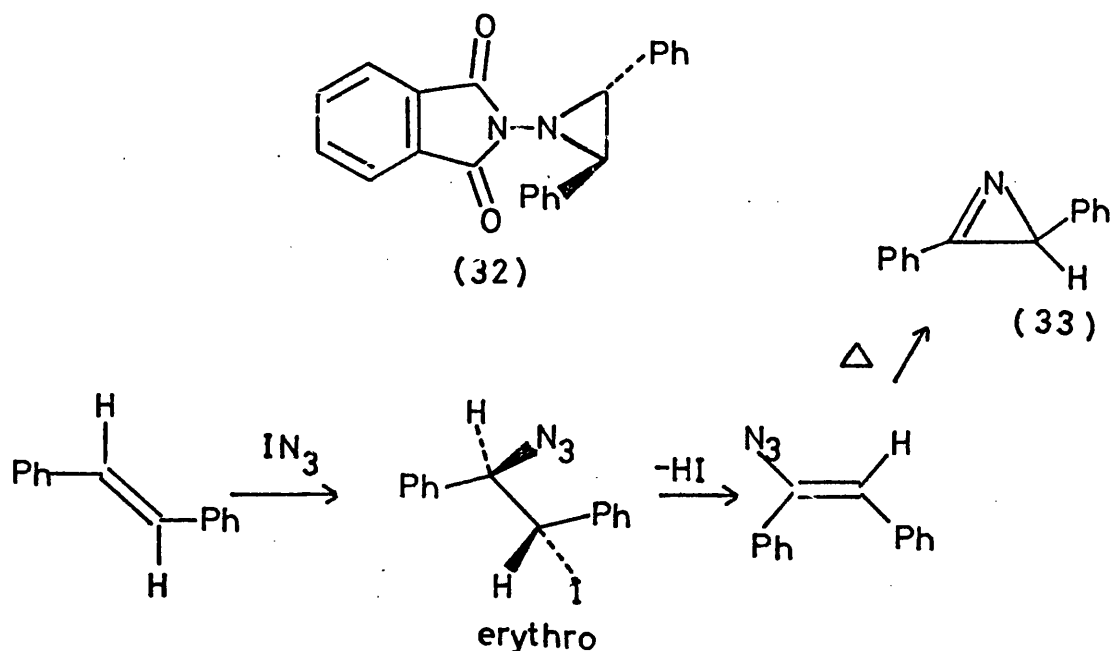
The thermal fragmentation shown in Scheme 11 is probably paralleled in the mass spectrometer. The phthalimido- and quinazolonyl-aziridines studied in this thesis show a typical mass spectral breakdown pattern involving a base peak corresponding to the mass of the parent lactam. Often the concerted nature of this decomposition is supported by the observation of the appropriate metastable transition.

Preparation and thermolysis of 2,3-diphenyl-1-phthalimido-aziridine and 2,3-diphenyl-2H-azirine

It was thought possible to test the mechanism

shown in Scheme 11 by investigating the fragmentation of a system where the azirine fragment is known; the diphenylaziridine (32) was chosen.

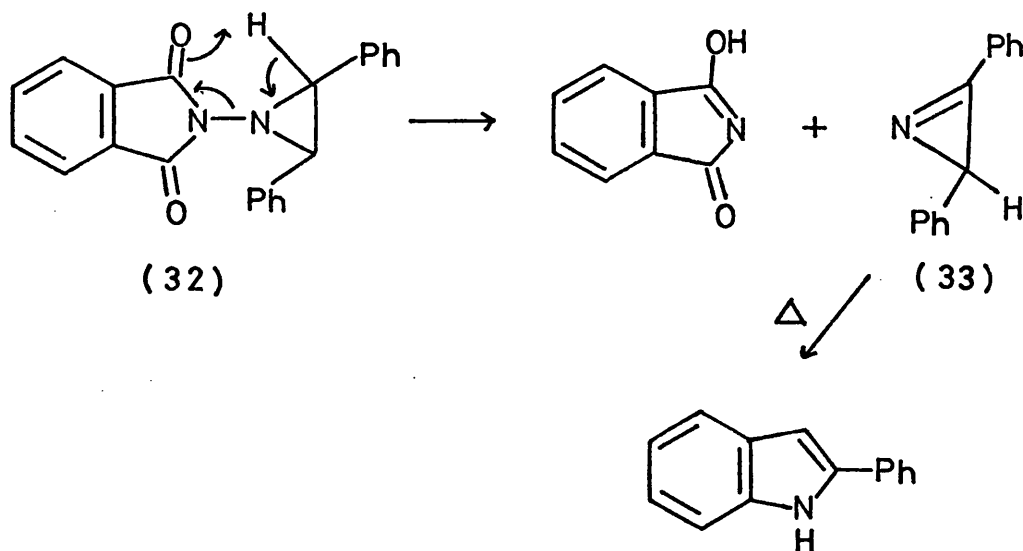
The aziridine (32) was prepared using the literature method<sup>38</sup> which involves oxidation of N-amino-phthalimide in the presence of trans-stilbene. Authentic azirine (33) was synthesised by the method of Hassner<sup>126</sup> (Scheme 12). Iodine azide was prepared in acetonitrile solution and added to trans-stilbene. The iodo-azide adduct was then treated with potassium t-butoxide to give the unsaturated azide which was decomposed in petroleum at 80° to give the azirine (33).



(Scheme 12)

Flash pyrolysis of trans-2,3-diphenyl-1-phthalimidoaziridine (32) at 350° gave little decomposition but t.l.c. evidence was gained for the formation of

2,3-diphenyl-2H-azirine (33) and phthalimide in small amounts. At temperatures above 350°, the aziridine (32) did decompose but no azirine could be isolated and another compound was formed. This was identified as 2-phenylindole by its spectral properties and by comparison with an authentic sample. The intermediacy of the azirine (33) was confirmed in that pyrolysis of the authentic azirine (33) under similar conditions showed it to be converted in high yield to 2-phenylindole (Scheme 13).



(Scheme 13)

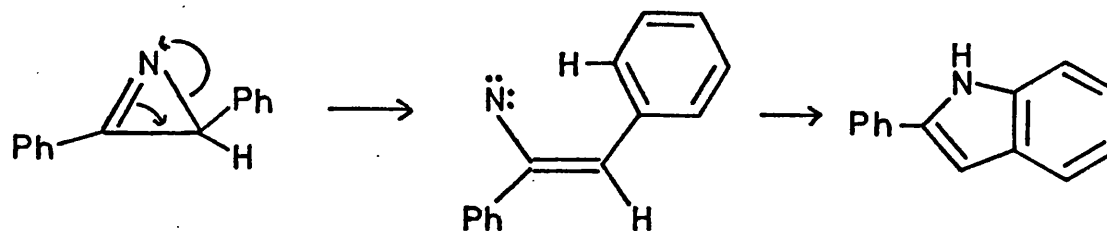
Thermolysis of the aziridine (32) was also performed in decalin solution at 180-190°. After 3 hr, the aziridine was largely unchanged but t.l.c. showed some formation of 2,3-diphenyl-2H-azirine, 2-phenylindole, and phthalimide. Thermolysis of the authentic azirine

(33), under the same conditions, also gave partial conversion into 2-phenylindole and other unidentified products.

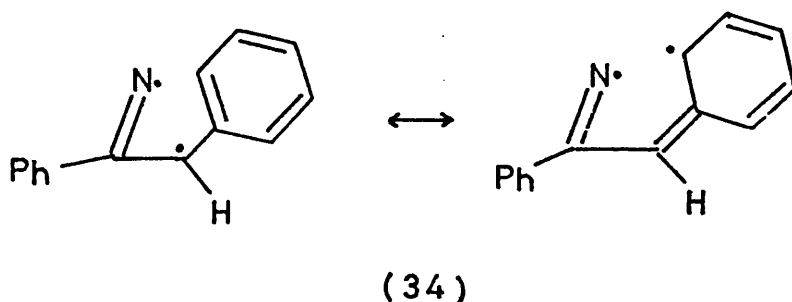
The rearrangement of 2,3-diphenyl-2H-azirine to 2-phenylindole has subsequently been reported by Bowie and Nussey.<sup>185</sup> They effected the reaction by g.c. of the azirine (33) on a column at 220°, and, amongst the products, obtained 2-phenylindole in 60% yield. Thermolysis in a sealed tube at 250° gave the indole in lower yield and eight other products were characterised by these workers.

The much cleaner conversion to 2-phenylindole observed in the present vapour phase flash pyrolysis is attributable to the inhibition of intermolecular reactions.

Several analogous reactions are known<sup>187,188</sup> and the mechanism has been generally assumed as a nitrene insertion reaction (Scheme 14) though this could also be viewed as a diradical coupling (34).



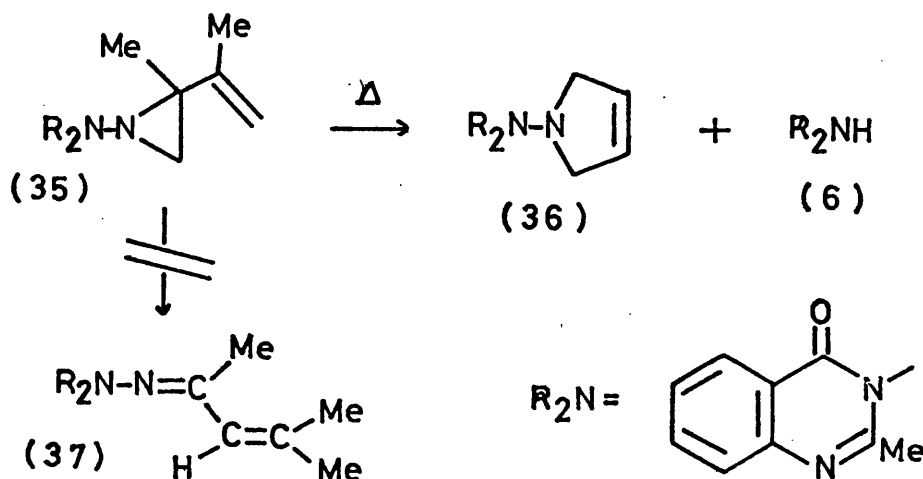
(Scheme 14)



Preparation and thermolysis of 1-(2-methylquinazol-4-on-3-yl)-2-methyl-2-isopropenylaziridine (35)

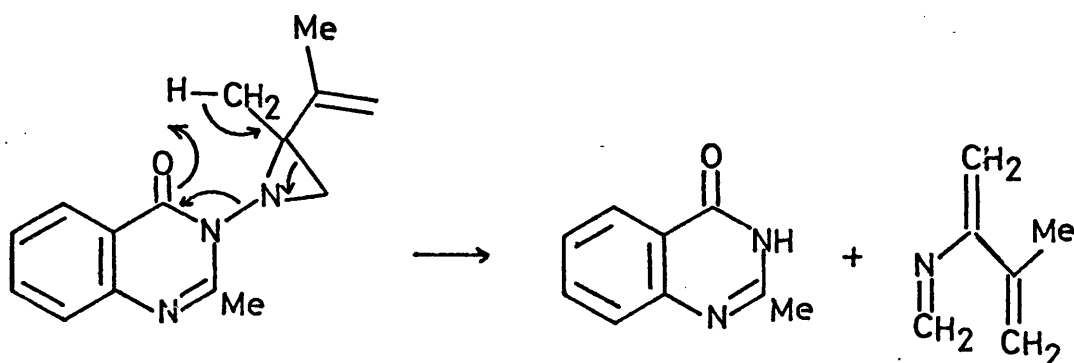
The aziridine (35) was prepared, by the oxidation of 3-amino-2-methylquinazol-4-one in the presence of 2,3-dimethyl-1,3-butadiene, in order to investigate if the methyl group at aziridine C-2 would preclude formation of 2-methylquinazol-4-one.

Thermolysis in solution at 180° gave the corresponding pyrroline (36) in 60% yield. An unknown substance was also formed in low yield and appeared to be an isomer of the aziridine (35). The n.m.r. was not, however, consistent with the hydrazone structure (37). The solution thermolysis also furnished 2-methylquinazol-4-one (6) (7.5%).



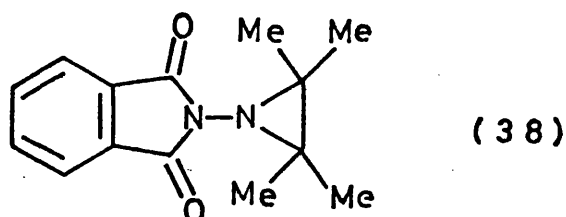
Vapour phase flash pyrolysis of (35) at 550° led almost entirely to fragmentation to 2-methylquinazol-4-one (6) and only a trace of the pyrroline (36) was formed.

Possibly this fragmentation occurred by transfer of a proton from C-3 of the aziridine ring, so forming a non-conjugated azirine as the other fragment; alternatively the fragmentation could proceed as shown in Scheme 14.



(Scheme 14)

Just as the thermal fragmentation shown in Scheme 11 can be paralleled in the mass spectrometer, so too can Scheme 14. Thus, the mass spectral breakdown of the aziridine (38) shows a base peak at the mass of phthalimide and its formation in a concerted process is supported by relevant metastable transition.





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Ph.D. Thesis

ABSTRACT

The main methods of generating heterocyclic amino-nitrenes are summarised and the subsequent fate of the nitrenes is considered. The photochemistry of three-membered ring systems is reviewed.

Certain 1-phthalimido- and 1-(2-methylquinazol-4-on-3-yl)-aziridines, when irradiated in the presence of an olefin, undergo an exchange reaction which produces a new aziridine incorporating the added olefin. Evidence is presented for a mechanism involving amino-nitrene formation by concerted cleavage of the aziridine C-N bonds. The scope of this reaction is delineated.

Vapour phase flash pyrolysis of N-heterocyclic sulfoximides is used to generate amino-nitrenes under conditions such that nitrogen extrusion occurs. For example, phthalimido-nitrene gives benzocyclobutenedione and indazolyl-nitrene gives 1-cyanohepta-1,3-dien-5-yne. Sulfoximides containing active protons  $\alpha$  to the sulphur atom and involving amide or imide heterocycles undergo a competing fragmentation to the parent amide or imide.

Isoindolinyl-aziridines, prepared by reduction of the corresponding phthalimido-aziridines, are fragmented readily, possibly via isoindolinyl-nitrene.

The possibility of intramolecular insertion of phthalimido-nitrene to give phthalaz-1,4-dione is upheld since the generation of the latter species by vapour phase flash pyrolysis of its Diels Alder adducts with dienes or its [2+2] adduct with indene is found to give

benzocyclobutenedione. The retro Diels Alder reaction is also used to generate other reactive  $\alpha$ -carbonyl azo compounds in the vapour phase such that unimolecular decomposition then occurs.

Thermolysis of 1-(quinazol-4-on-3-yl)-2-vinyl-aziridines gives the corresponding 3-(trans-but-2-en-1-ylideneamino)quinazol-4-ones in a novel rearrangement which is in competition with formation of 3-pyrrolines. At higher temperatures a fragmentation involving cleavage of the N-N bond also competes and this occurs to the exclusion of rearrangement in substituted vinyl-aziridines. An analogous fragmentation of trans-2,3-diphenyl-1-phthalimidoaziridine gives 2,3-diphenyl-2H-azirine, which in turn rearranges to 2-phenylindole. Reaction mechanisms are discussed.