

NITRENES IN HETEROCYCLIC SYNTHESIS.

by

S. BRADBURY

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STATEMENT.

The work described in this thesis was carried out by the author in the Department of Chemistry of the University of Leicester under the supervision of Professor C.W. Rees. No part of it is concurrently being submitted for any other degree.

November, 1970.

Signed

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## ABSTRACT.

### Section I.

Pyrolysis of 1-acyl and 1-arylamino-8-azidonaphthalenes gives 9-amino-2-substituted naphth[1,2,-d]oxazoles and 2-substituted perimidines. This new synthesis of oxazoles involves nucleophilic attack by the amide oxygen at the naphthalene 2-position accompanying intramolecular acid catalysed decomposition of the azide. An acid catalysed rearrangement is observed in the conversion of m-azido-benzanilide to 5-amino-2-phenylbenzoxazole. Replacement of the amide H in the thermolysis reactions generally leads to 1,2-dihydrobenz[cd]indazole derivatives. Although 1-azido-8-phthalimidonaphthalene only gave the corresponding perimidine. This formally involves nitrene insertion into a C=O bond and stoichiometric loss of oxygen. Mechanisms for the formation of the oxazoles, indazoles and perimidines are discussed.

Attempted synthesis of 1,2-dihydrobenz[cd]indazole from dimethyl 1,2-dihydrobenz[cd]indazole dicarboxylate and from 1-amino-naphthalene shows that it exists in the more stable tautomeric forms with the aromatic indazole rather than naphthalene nucleus. Decomposition of 1-amino-8-azidonaphthalene in the vapour phase results in direct insertion into an NH bond to give the indazoles. These indazoles can be reconverted into N,N-disubstituted dihydrobenz[cd]indazole derivatives but cannot be oxidised to benz[cd]indazole. Several other unsuccessful routes to this elusive heterocyclic system are discussed.

### Section II.

Benz[cd]indole could not be isolated on oxidation of 1,2-dihydrobenz[cd]indole but products were isolated that could be rationalised by nucleophilic attack on benz[cd]indole.

Photolysis of methyl 8-azido-1-naphthoate gave 2-methoxybenz [cd]indole but pyrolysis of this azide gave only the intermolecular dimer.

### Section III.

Oxidation of the hydrazones of o-aminoacetophenone and o-aminobenzophenone gave 4-methyl and 4-phenylbenzo-1,2,3-triazine, the simplest derivatives yet prepared of this heterocyclic system. Oxidation of 1- and 2-amino-3-substituted indazoles also gave the benzotriazines. Attempts to make the parent benzo-1,2,3-triazine and to generate 1-azabenzocyclobutadiene were unsuccessful. Mechanisms for the formation of the triazines are discussed.

### Section IV.

"5-Nitreno-1,4-diphenyl-1,2,3-triazole" in equilibrium with a ring opened cyanide had been reported in the literature. All attempts to intercept this nitrene with established nitrene traps failed and it seems to us that the nitrene plays no part in the proposed equilibrium.

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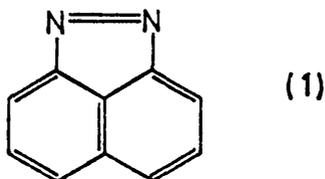
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I N T R O D U C T I O N .

## INTRODUCTION

No examples of the very simple benz[cd]indazole (1) heterocyclic system have been reported in the literature. Synthesis of (1) was therefore of interest to us particularly as it would also



be a potential precursor to 1,8-dehydronaphthalene. Irradiation of benz[cd]indazole under different conditions could lead to this dehydro species in different electronic states, and so shed considerable light on the nature of these dehydro intermediates, which have previously been generated by oxidation of 1-N-aminonaphthotriazine.<sup>1</sup> Although we were unable to synthesise (1) itself several examples of its hitherto unknown 1,2-dihydro derivatives were obtained.

Since aryl nitrenes have figured prominently in our efforts to form the peri N-N bond in the above systems, this introduction is devoted to a review of nitrenes.<sup>†</sup> A short section on azides is included since these were generally our nitrene precursors.

The chemistry of nitrenes has been reviewed by Horner and Christmann<sup>2</sup> in 1963, by Abramovitch and Davis<sup>3</sup> in 1969 and comprehensively in a very recent book edited by Lwowski<sup>4</sup> in 1969. A review by L'Abbé<sup>5</sup> in 1969 on decomposition and addition reactions of organic azides contains a useful section on nitrenes.

### 1. Structure of Nitrenes.

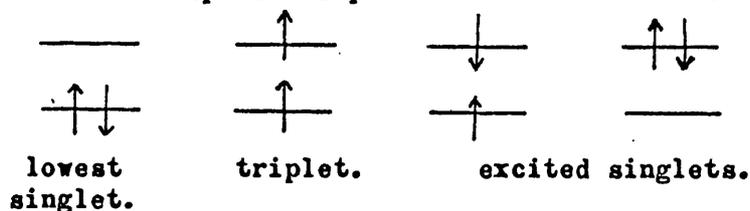
Nitrenes are uncharged, short lived univalent nitrogen species which have been postulated as reactive intermediates in

<sup>†</sup> These reactive intermediates have been variously termed "nitrenes", "azylens", "imenes", "imine radicals", and "imidogens". The "nitrene" nomenclature parallels that for carbenes and is now the most widely used. ( $:\ddot{\text{N}}\text{H}$  is nitrene,  $:\ddot{\text{N}}\text{Ph}$  is phenyl nitrene, etc.).

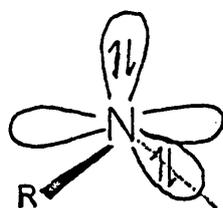
a large number of reactions. The nitrogen atom is electron deficient having a sextet of electrons in its outer shell. Two electrons are involved in bonding to a substituent and two occupy a lone pair orbital leaving two electrons distributed between the two remaining orbitals. Nitrenes are therefore the nitrogen analogues of carbenes.



If these two electron spins are anti-parallel, the nitrene is a singlet, and if the spins are parallel the nitrene is a triplet.

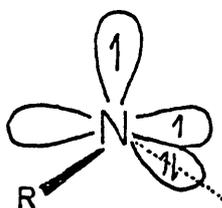


In principle nitrenes can be  $sp^2$  hybridised, (2a) and (2b)



(2a)

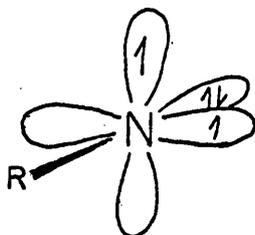
lowest singlet.



(2b)

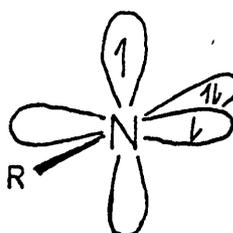
triplet.

or  $sp$  hybridised, (3a) and (3b). Structures intermediate between these two are also possible.



(3a)

triplet.



(3b)

excited singlet.

If the energy difference between the singlet and triplet states

is greater than the energy required to pair two electrons in one orbital in an  $sp^2$  hybridised nitrene the singlet state is more stable than the triplet. This therefore needs calculation and cannot be predicted simply. If the nitrogen is  $sp$  hybridised then from Hund's rule one electron occupies each of two degenerate p-orbitals and the triplet state is the more stable. From consideration of electron repulsion an  $sp^2$  hybridised singlet is of lower energy than an  $sp$  hybridised singlet. Prediction of the relative stabilities of a singlet  $sp^2$  hybridised nitrene and a triplet  $sp$  hybrid is much more difficult and again requires detailed molecular orbital calculations. Electron spin resonance (e.s.r.) studies for a few aryl nitrenes at very low temperature<sup>6</sup> have shown that these have triplet ground states, in agreement with molecular orbital calculations.<sup>7,8</sup> Energy considerations for an excited singlet nitrene (in which the electrons are in different orbitals but have opposite spins) are the same as for the triplet. Triplet nitrenes should act as diradicals, and singlet nitrenes as electrophiles. Since electron spin is conserved in thermal reactions nitrenes are usually generated in the singlet state. They may react in this singlet state but decay of singlet to triplet nitrene may compete with the reactions of the singlet so that products are formed from both the singlet and triplet.

## 2. Generation of Aryl Nitrenes.

Nitrenes have been suggested as intermediates in a variety of reactions. It is generally accepted that discrete nitrenes are involved, but in almost all cases it is possible to write alternative mechanisms that do not involve the nitrene.

### (a) Formation from azides.

The most widely used method of generating nitrenes is

elimination of nitrogen from azides. This can be effected by heating, by irradiation or by electric discharge.

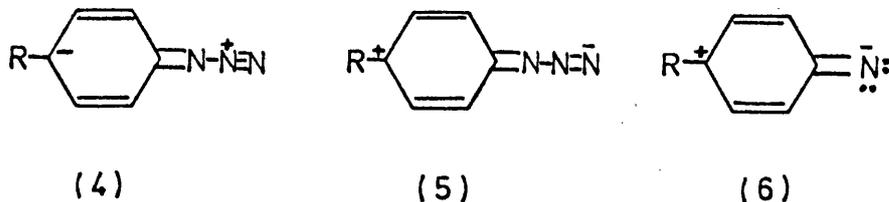
Photolysis can give a singlet or triplet nitrene depending on the conditions employed. Swenton<sup>9</sup> has used aromatic hydrocarbons as singlet sensitizers to give a singlet excited azide which decomposes to a singlet nitrene, and ketones as triplet sensitizers to give a triplet azide which decomposes to a triplet nitrene.<sup>†</sup>

Most aryl azides decompose smoothly in solution or vapour phase at fairly low temperatures (below 200°) and only in exceptional circumstances are temperatures higher than this needed. Aryl azides have usually been thermolysed in dilute solution in order to moderate the exothermic reaction and in some cases to minimise any bimolecular reactions of the nitrene. The rates of unimolecular decomposition of phenylazide in both nitrobenzene and tetralin solutions have been found to be the same, indicating that the solvent was not participating in the rate determining step and that phenyl nitrene was formed.<sup>10</sup> Smith and Hall<sup>11</sup> have studied the kinetics of the thermal decomposition of a series of phenyl azides and 2-azidobiphenyls bearing various substituents, and suggest that the rate determining step is the same with both, the initial common step being formation of the nitrene. The effect of para substitution indicated that changes in the degree of conjugation involving the azide group and the benzene ring were probably the determining factor. It was considered that such conjugation was better represented by

---

<sup>†</sup> However triplet nitrene<sup>12</sup> has been detected at 77° K and on warming singlet nitrene products were obtained. Partial or complete reaction from a singlet intermediate formed via the triplet cannot be excluded.

(4) than (5) and the presumed initial product, a singlet aryl nitrene, was described by the polar form (6).



(b) Formation from nitro and nitroso compounds.

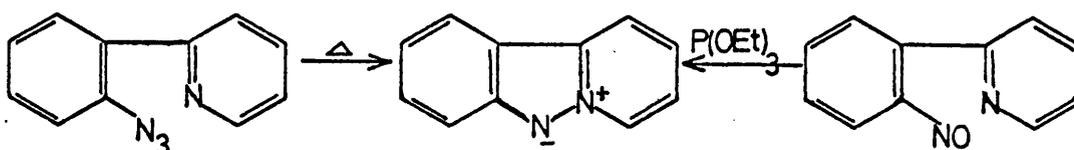
Products obtained when aromatic nitro and nitroso compounds are heated with certain reducing agents such as ferrous oxalate and particularly phosphines and phosphites may be explained by the intervention of nitrenes. Deoxygenation of nitro and nitroso compounds by tervalent phosphorus compounds has been reviewed by Cadogan<sup>13</sup> in 1968.

Simple aromatic nitro compounds have been shown to react with transition metal oxalates to give azo and azoxybenzenes and phenazines, and occasionally traces of aromatic amines.<sup>14,15</sup> More complicated nitro compounds on heating with ferrous oxalate give cyclization products and primary amines, and most of these results have been interpreted in the terms of formation of nitrene intermediates, although other mechanisms may be operative.

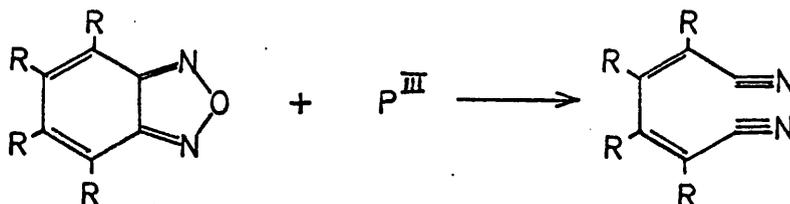
Following the initial observations of Hoffmann and Horner<sup>16</sup> who found that substituted nitroso benzenes reacted with triphenyl phosphine to give the corresponding azoxybenzene, Cadogan has developed this reaction further and has established deoxygenation of nitro and nitroso compounds with tertiary phosphines (such as  $P(OEt)_3$ ,  $(EtO)P(NEt)_2$ ,  $(Et_2N)_3P$ , and  $(EtO)_2PMe$ ) as a general method for generating nitrenes. Aromatic nitro compounds undergo the same reactions as C-nitroso compounds with tervalent phosphorus compounds

although much more vigorous conditions are required and the yields are lower.<sup>13</sup> Katritzky<sup>17</sup> has suggested that the nitro compound is first reduced to the corresponding nitroso compound which is deoxygenated further.

In general very similar products are obtained from deoxygenation of nitro and nitroso compounds and from decomposition of azides and this has usually been taken as evidence for the common involvement of a nitrene. Thus pyrido [1,2-b]indazole is formed not only from deoxygenation of the 2-o-nitrosophenylpyridine, but also from the pyrolysis of the 2-o-azidophenylpyridine.

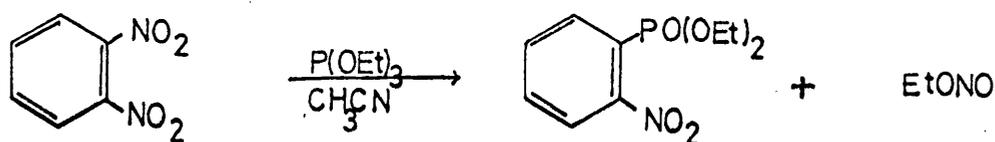


Irradiation of nitrobenzenes and olefins gave small amounts of azobenzene<sup>18</sup> and it has been suggested<sup>3</sup> that these could conceivably arise by nitrene formation. More recently photoinduced deoxygenation of nitro compounds has been studied.<sup>19,20</sup> Irradiation of aryl nitro compounds in the presence of triethyl phosphite at low temperature gave typical nitrene products and, very recently, irradiation of the furazan derivatives under similar conditions was shown to give 1,4-dinitrile derivatives in good yield.<sup>21</sup>



Whereas aromatic mono nitro compounds are deoxygenated to give nitrene-like intermediates which can then react in a variety

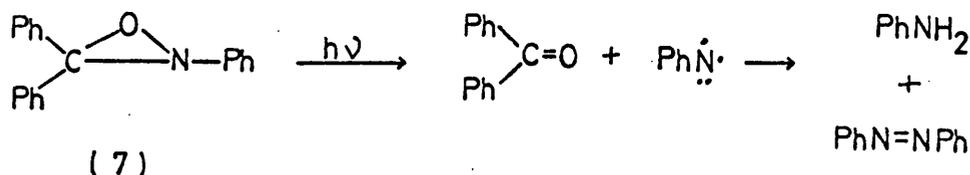
of ways, it has been found<sup>22</sup> that in contrast, reaction of o-dinitrobenzene and 1,2,4-trinitrobenzene with certain trivalent organophosphorus reagents leads to displacement of an o-nitro group.



(c) Formation by other routes.

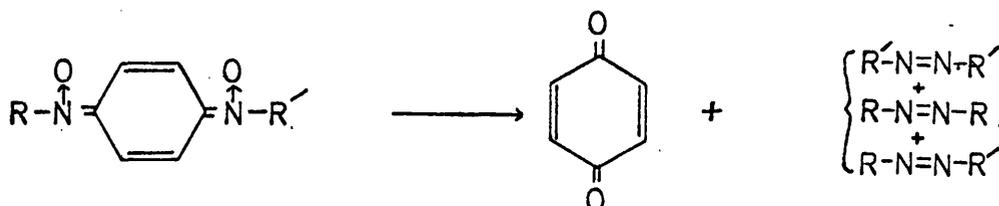
Aryl nitrenes have been suggested as reactive intermediates in a variety of other reactions. However there is often very little conclusive evidence that nitrenes are involved.

Phenyl nitrene has been generated by photolysis of oxaziranes,<sup>23</sup> a route which parallels the formation of carbenes from oxiranes. Irradiation of (7) gave aniline, azobenzene and benzophenone.



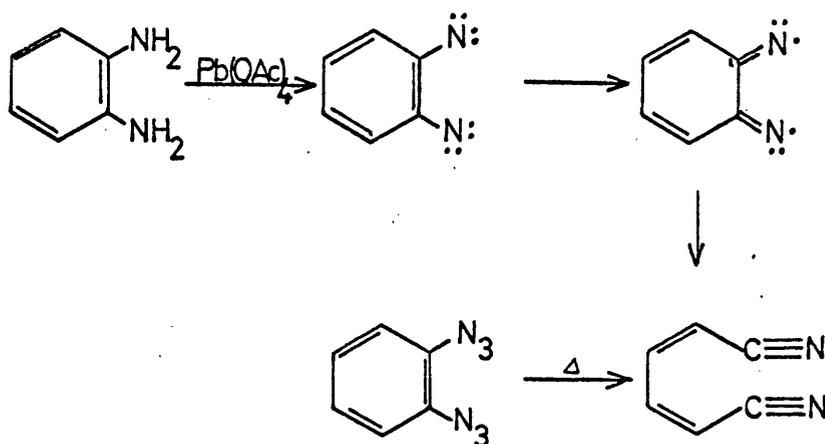
At 77°K e.s.r. spectroscopy indicated the presence of an intermediate identical in all respects to ground state triplet phenyl nitrene produced from phenyl azide under the same conditions.

The photolytic decomposition of N,N'-disubstituted

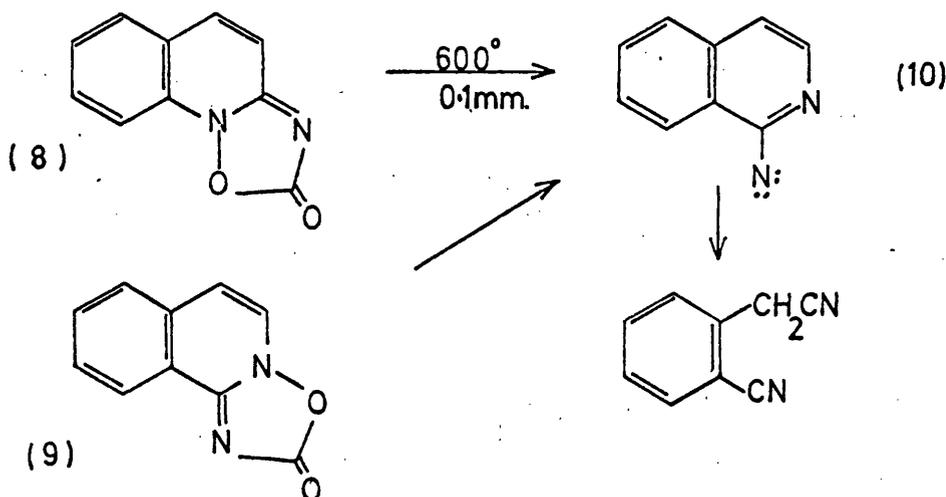


p-quinonediimine-N,N'-dioxides gives p-benzoquinone and azo compounds by an intermolecular process.<sup>24</sup> Nitrene formation via an oxazirane seems possible.

Although oxidation of hydrazines to give N-nitrenes is well established, there are very few examples of the corresponding oxidation of amines to give C-nitrenes. However, oxidation of various aryldiamines with lead tetra-acetate<sup>25</sup> and nickel peroxide<sup>26</sup> gave the same products as decomposition of *o*-diazido compounds. Thus *o*-phenylenediamine gives *cis*, *cis*-1,4-dicyanobutadiene.

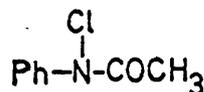
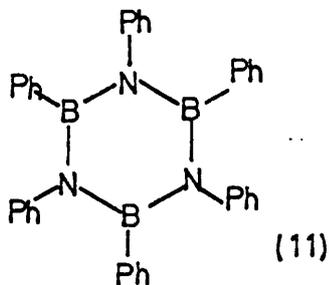


The isomeric oxadiazoles (8) and (9) on heating in the gas phase<sup>27</sup> give *o*-cyanobenzylcyanide, possibly via the nitrene (10);



(8) appears to undergo a profound rearrangement. (See section 3(d) on rearrangements).

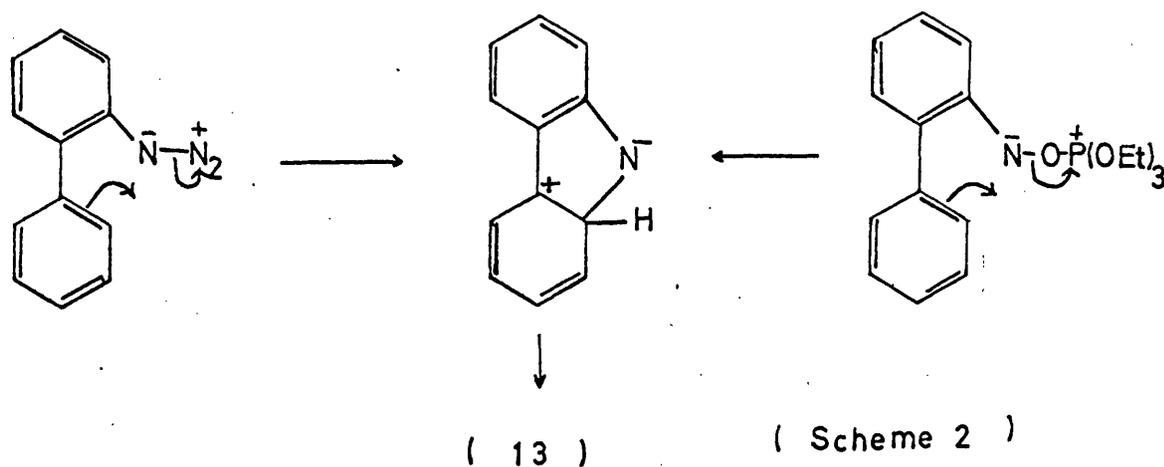
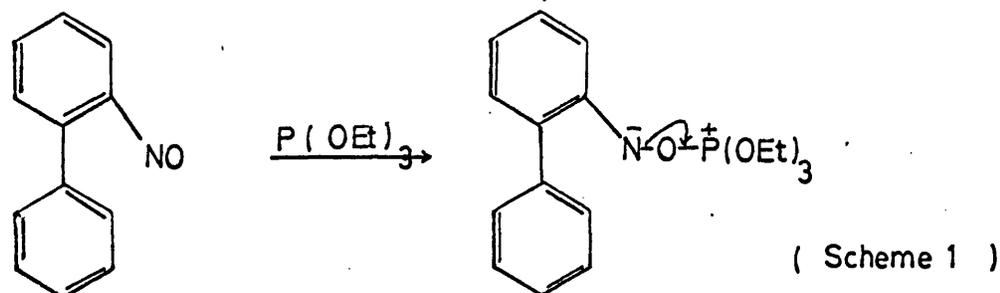
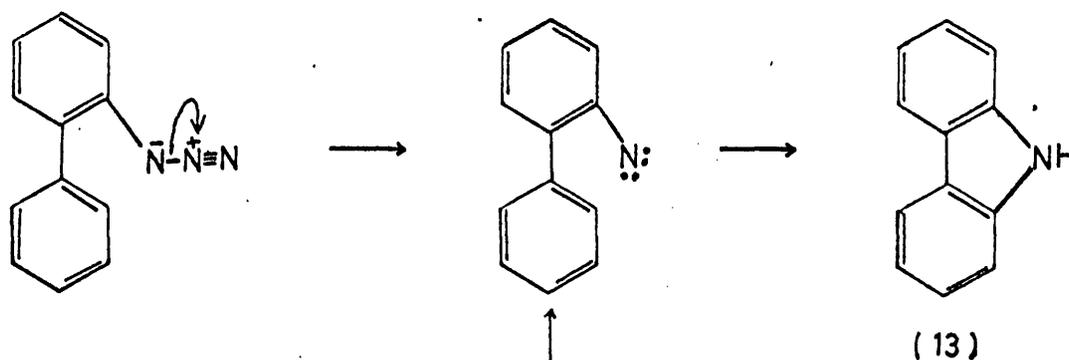
Formation of phenyl nitrene has been claimed in the ready decomposition of hexaphenylborazole<sup>28</sup> (11) and of N-chloroacetanilide<sup>29</sup> (12).



(12)

### 3. Reactions of Aryl Nitrenes.

Although nitrenes have been generally accepted as reactive intermediates, there is very little direct proof for their existence. There is, however, considerable circumstantial evidence mostly based on the reaction products isolated. The concept of "carbenoid" intermediates in carbene chemistry is well established and it would seem reasonable that "nitrenoid" intermediates could be involved in nitrene chemistry. Although it is convenient to discuss nitrene reactions in terms of free, discrete nitrenes it is possible that some or even all the reactions proceed through the precursor of the nitrene rather than through the actual high energy, free species. For example carbazole (13) is formed when 2-azidobiphenyl is pyrolysed and 2-nitrosobiphenyl (or 2-nitrobiphenyl) is deoxygenated. These can be explained by insertion of a common free nitrene intermediate into an aryl C-H bond (Scheme 1). However it is also possible to account for their formation as shown in Scheme (2). Experimental differentiation between these routes is a difficult problem.



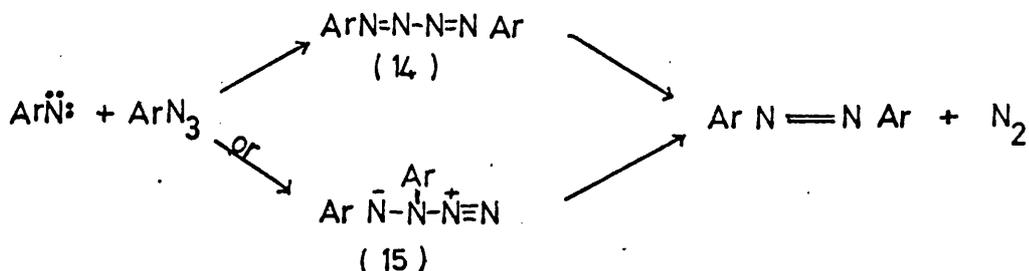
Nitrenes have a lifetime of only several microseconds and readily effect stabilization by many reactions including isomerization, dimerization, hydrogen abstraction, insertion and addition.

(a) Reaction with nucleophiles.

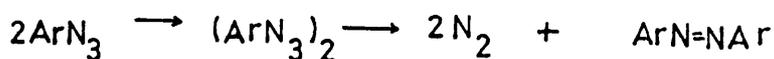
Singlet nitrenes are electrophilic and should be highly susceptible to nucleophilic attack. Nitrenes generated by deoxygenation of aromatic nitro and nitroso compounds with phosphines



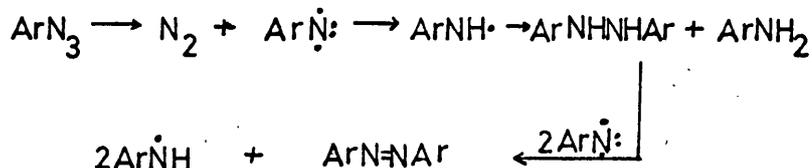
(ii) the nitrene may attack an undecomposed molecule of the azide to produce species such as (14) or (15) which then lose nitrogen to give the azo compound



(iii) the azide itself may dimerize and then lose two molecules of nitrogen



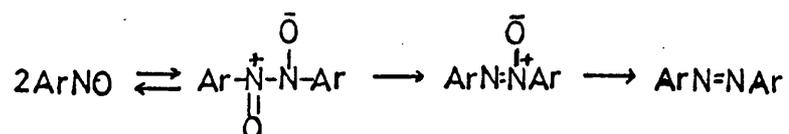
(iv) hydrogen abstraction may be involved to give amino radicals which dimerize to hydrazo compounds. These would themselves be dehydrogenated by more aryl nitrene to give a chain process.



The exact process for this formal dimerization of nitrenes is not known. No detailed study on this reaction has been carried out. However attack of a nitrene on its precursor (i.e. (ii)) seems most likely, although it is possible that all the above mechanisms may play some part depending on the conditions of the reaction. It seems unlikely that two azide molecules would dimerize, but it is possible that on irradiation a photoexcited azide may react with one in the ground state. The possibility of a route involving amino radicals is supported by the fact that nitrenes abstract hydrogen and amines are often isolated. In the thermolysis of phenyl azide to give azobenzene, hydrazobenzene and benzidine have been isolated. However

pyrolysis of azides in the vapour phase,<sup>30</sup> where H abstraction is unlikely, has given high yields of the azo compound. (These are conditions where actual dimerization of the nitrene itself <sup>is</sup> ~~are~~ most favoured).

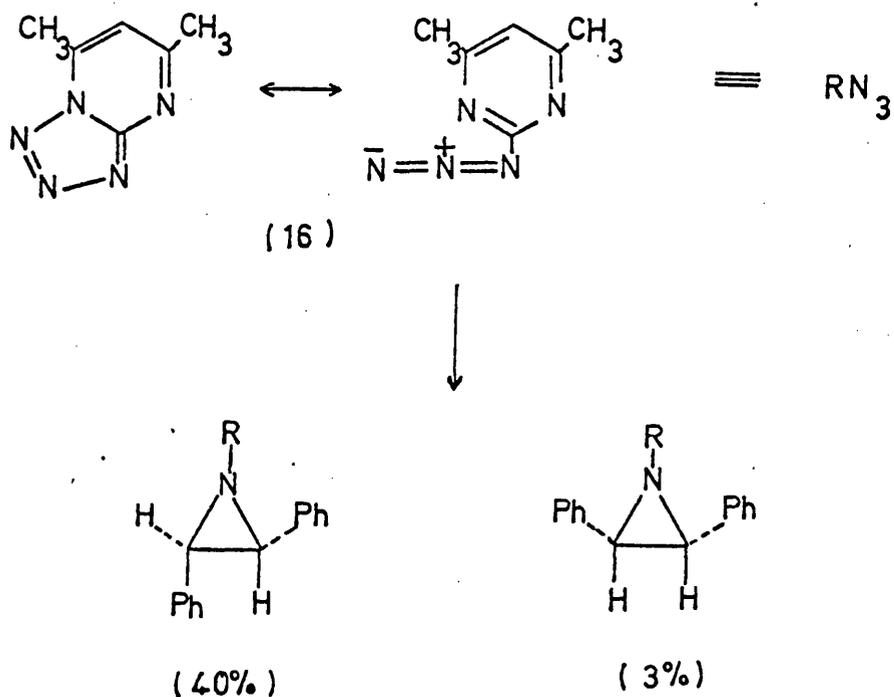
Azo compound formation is common in the decomposition of azides, but rare in the deoxygenation of nitro and nitroso compounds. Azo and azoxybenzenes and phenazines have been isolated<sup>14</sup> when nitroso and nitrobenzene derivatives were heated with transition metal oxalates. It was suggested that a nitrene intermediate, probably bound to the surface of the metal salt was involved. However stepwise deoxygenation of the nitroso dimer through the azoxy compound is perhaps a more likely route and does not involve a nitrene.



### (c) Cycloaddition reactions.

The review by Woodward and Hoffmann<sup>32</sup> on the conservation of orbital symmetry includes a section on cheletropic reactions, of which carbene and nitrene cycloadditions are examples.

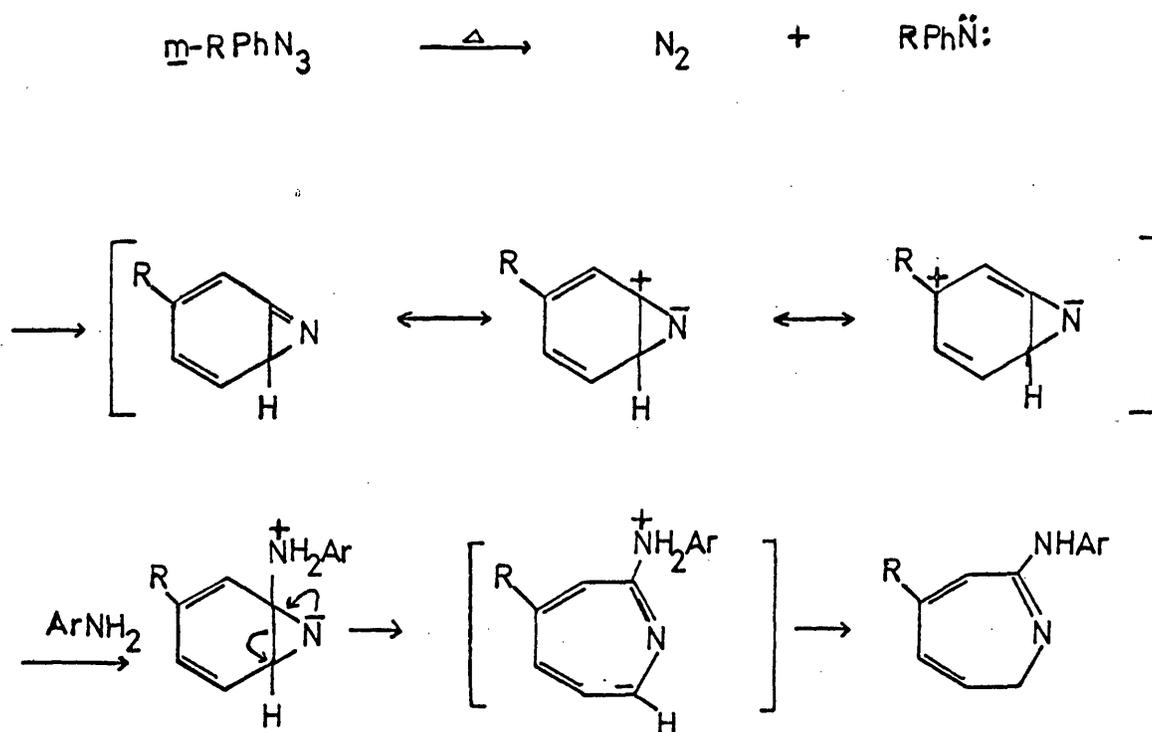
Although carbene and N-nitrene addition to olefins are well known only one example of an aryl nitrene adding to an olefin can be found in the literature. Huisgen and Fraunberg<sup>33,34</sup> thermolysed 4,6-dimethylpyrimidinylazide (16) with copper acetylacetonate as catalyst; the nitrene added stereoselectively to trans-stilbene, although 2-pyridylazide did not. The possibility of a nitrene copper complex was also considered.



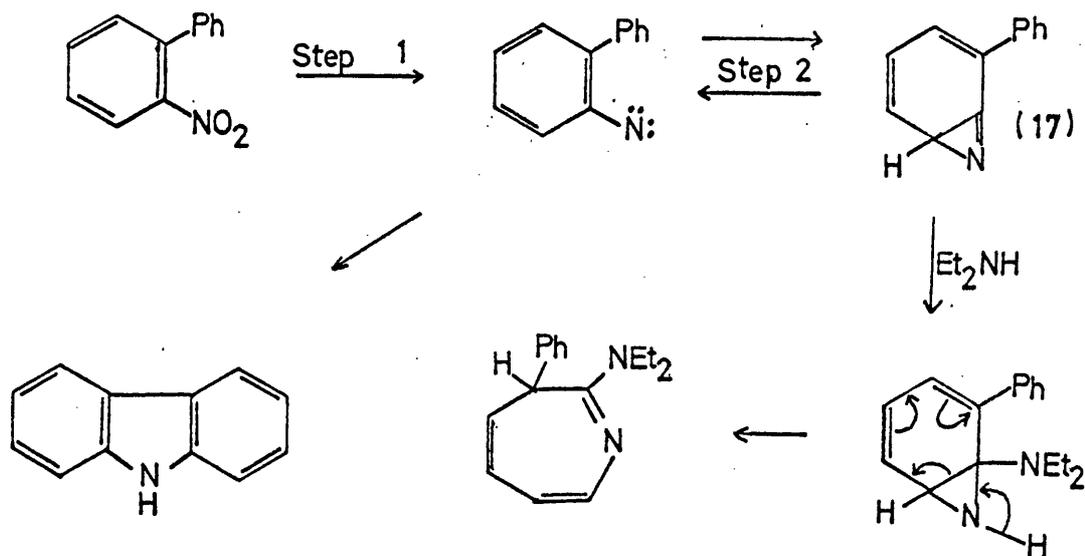
Intramolecular cycloaddition of aryl nitrenes to give ring expanded products has been investigated by many workers. (See following section on "rearrangements").

(d) Rearrangements.

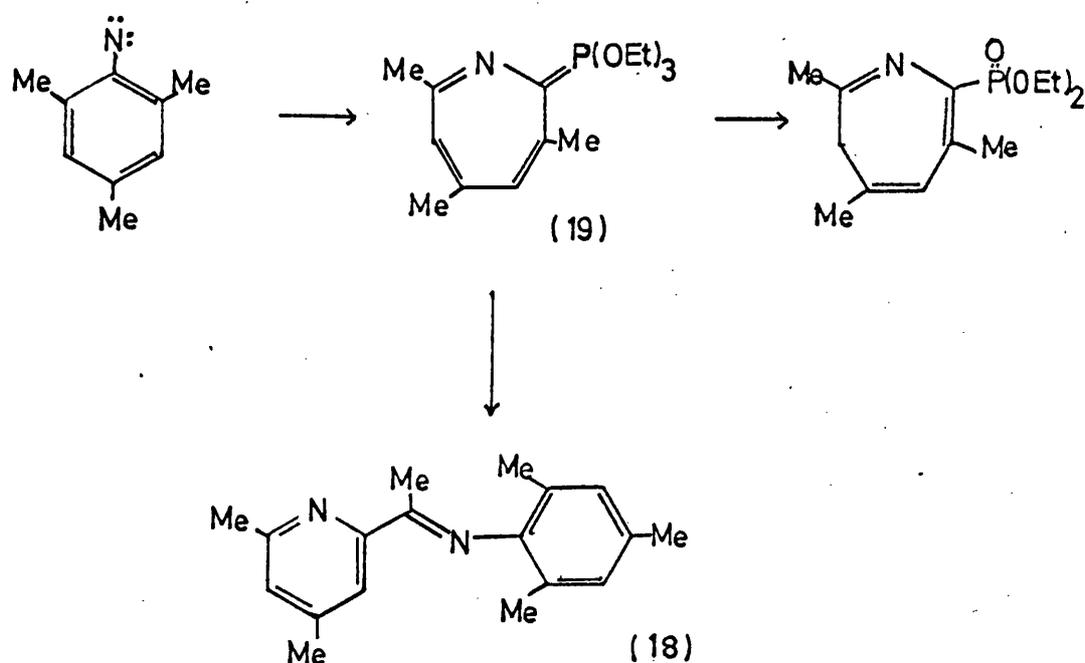
Studies of aryl nitrene chemistry have revealed a number of interesting rearrangements. One of the most general is an intramolecular cycloaddition which results in ring expansion, and is usually only detected in the presence of an amine. Thus decomposition of aryl azides in amines gave azepine derivatives,<sup>35</sup> and Huisgen<sup>36,37,38</sup> has suggested the following mechanism.



The participation of nitrenes has been suggested to account for the formation of azepines isolated from reactions of nitrosobenzene with triphenyl phosphine in the presence of dialkylamines.<sup>39</sup> Nitro compounds behave similarly with more powerful deoxygenating agents;<sup>40</sup> 2-nitrobiphenyl gave on deoxygenation in the presence of diethylamine 2-diethylamino-3H-phenylazepine and carbazole. Three possible mechanisms were considered; (a) that both products were formed from the nitrene with no intermediacy of (17), (b) that both products arose from (17), (c) that Step 2 is reversible and carbazole was formed from the nitrene and the azepine from (17). The last possibility seems most likely. In the decomposition of o-biphenylazide, Sundberg has shown that bond reorganization of o-biphenylnitrene is competitive with cyclization to carbazole and suggests such bond reorganization (Step 2) is reversible, as carbazole formation is not constant and is dependent on diethylamine concentration.<sup>200</sup>



Irradiation of aryl nitro compounds in the presence of triethyl phosphite and diethylamine<sup>19,20</sup> gave 2-diethylamino-3-H-azepines, whilst in the absence of diethylamine N-arylphosphorimidates were produced.

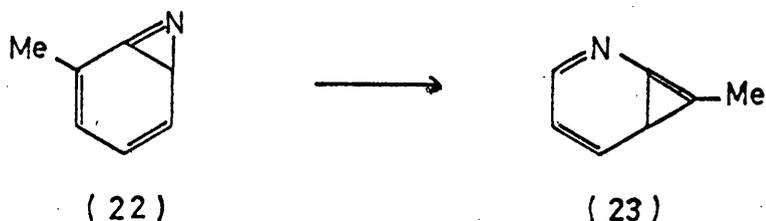
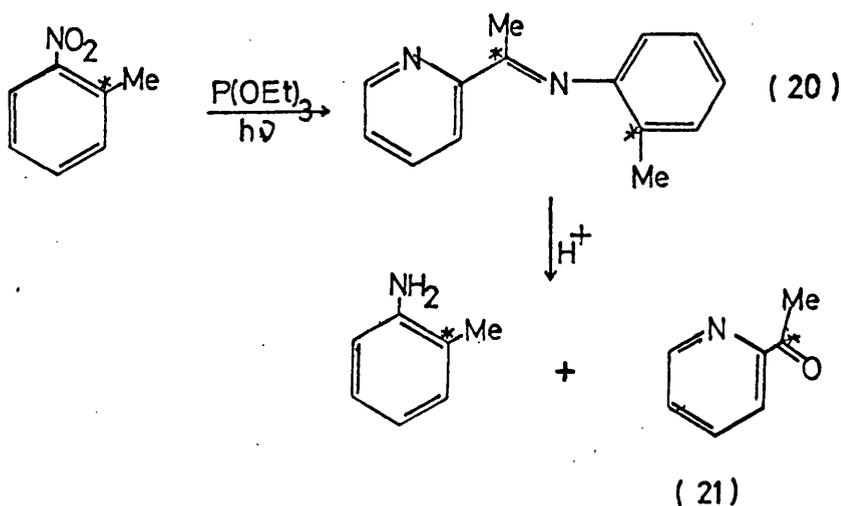


No products were found that were formed by C-H bond insertion or by hydrogen abstraction. On photoinduced deoxygenation with triethyl

phosphite, a pyridine (18) was formed in addition to a phosphorimidate and azepine and it was suggested that this pyridine arose from the azepine(19).

Ring substitution appears to effect significantly the efficiency of trapping of aryl nitrenes with triethyl phosphite.<sup>19</sup> Electron-releasing substituents may favour coupling by reducing the electron deficiency of the nitrogen atom and thereby slowing the rate of transformation of the nitrene to the azabicycloheptatriene intermediate.

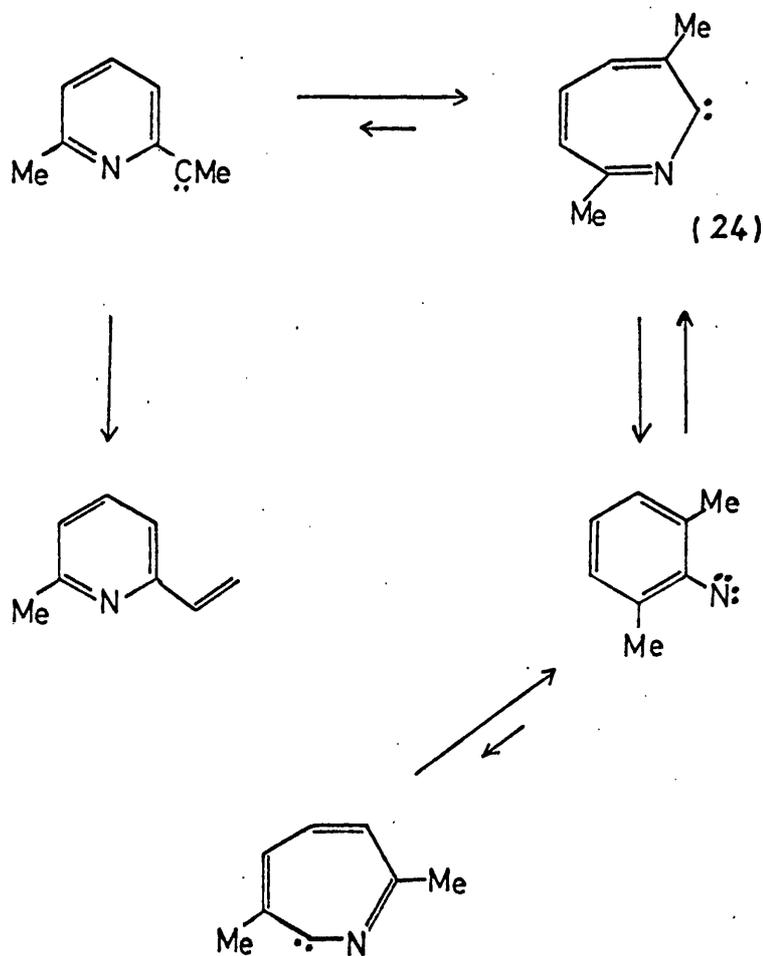
Photochemically induced deoxygenation of <sup>14</sup>C labelled



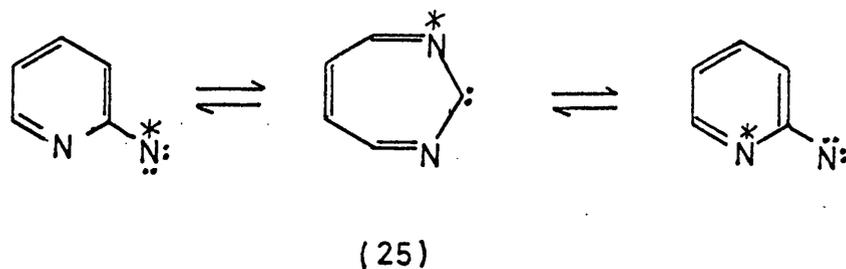
nitrotoluene with triethyl phosphite gave (20) which was hydrolysed to 2-aminotoluene (21). It was shown that C<sub>1</sub> in *o*-nitrotoluene became

the exocyclic carbon atom in (21), and it was proposed that the azirine (22) was formed as an intermediate which undergoes further skeletal arrangement to (23).

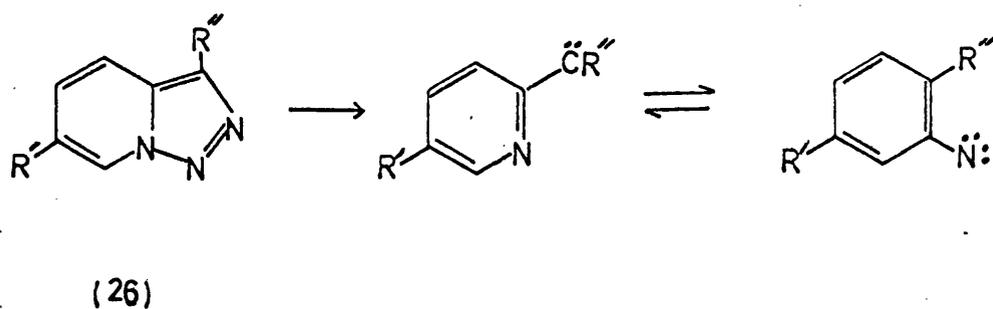
A seven membered ring intermediate was suggested to explain the reactions of nitrenes generated at very high temperatures in the gas phase. Thus 2,6-dimethylphenyl azide gave 2-vinyl-6-methylpyridine<sup>41</sup> suggesting the occurrence of a nitrene-carbene conversion via 2-azatropylidene (24).



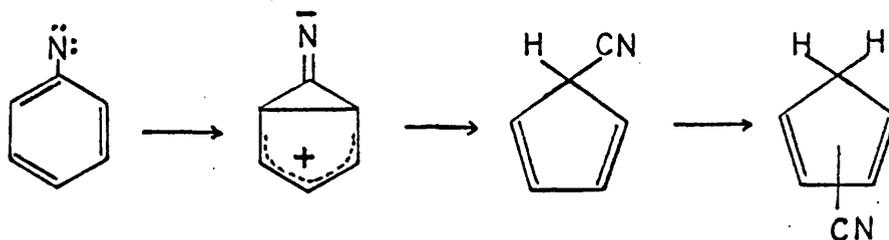
In the related case of 2-pyridylnitrene<sup>42</sup> it was shown that the two nitrogens became equivalent and a symmetrical carbene (25) intermediate was proposed.



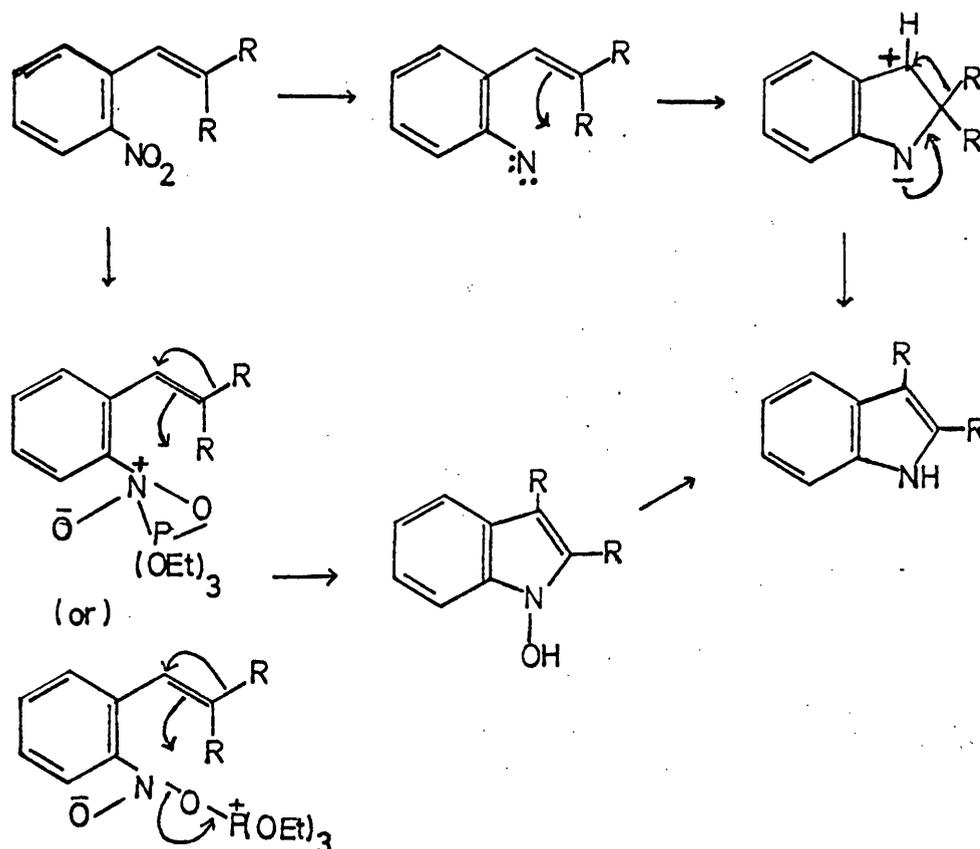
Gas phase thermolysis of triazolopyridine (26), ( $R' = R'' = H$ ), a precursor of 2-pyridylcarbene gave aniline and azobenzene, and the phenyl substituted triazolopyridine ( $R' = Ph$ ) gave 2-methylcarbazole.<sup>43</sup> It was suggested that again the phenylcarbene - phenylnitrene interconversion was involved.



Ring contraction to cyanocyclopentadienes<sup>44,45,46</sup> has also been observed at high temperatures in the gas phase pyrolysis of aryl azides.



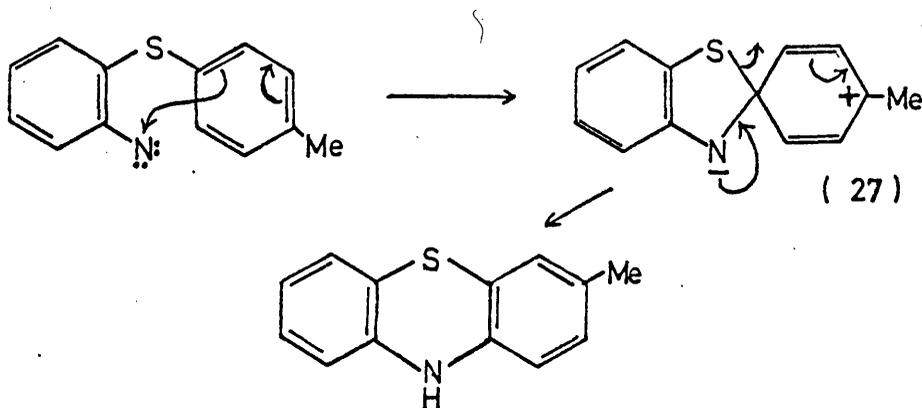
Deoxygenation of nitrostilbenes or nitrostyrenes with triethyl phosphite gives indoles. In some cases in interrupted reactions l-hydroxyindoles have been isolated;<sup>47</sup> these on heating with triethyl phosphite gave a product distribution similar to that obtained from the original nitrostilbene.



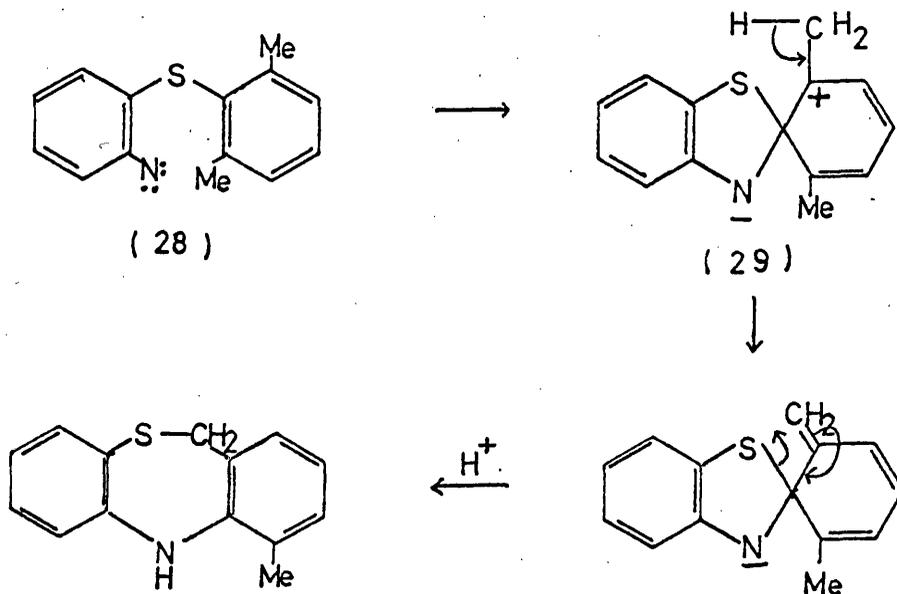
However in many cases the l-hydroxyindoles cannot be isolated and Cadogan<sup>13</sup> suggests that in these reactions a nitrene is involved,

perhaps competing with other possible mechanisms.

Thermal decomposition of 2-azidophenylarylsulphides and phosphite deoxygenation of 2-nitrophenylarylsulphides gave rearranged phenothiazines. It has been suggested<sup>13</sup> that intermediates of the type (27) derived from a nitrene are involved.

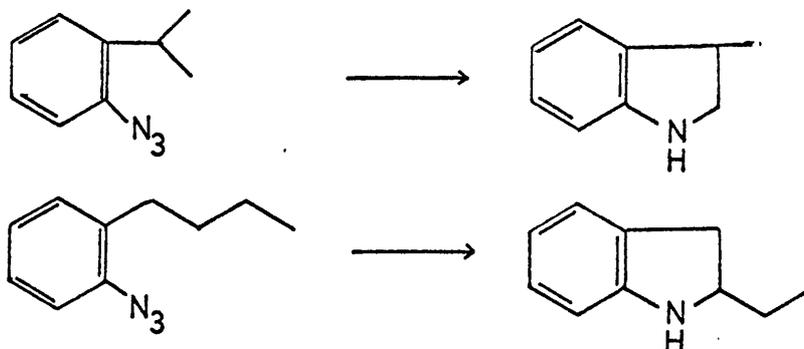


More recent work<sup>48</sup> in the related 2,6-dimethyl analogue has shown that the first formed nitrene (28) attacks the adjacent benzene ring at the nucleophilic 1' position to give the intermediate (29), analogous to (27), (rather than inserting into a methyl C-H bond) which then rearranges to give the observed product.

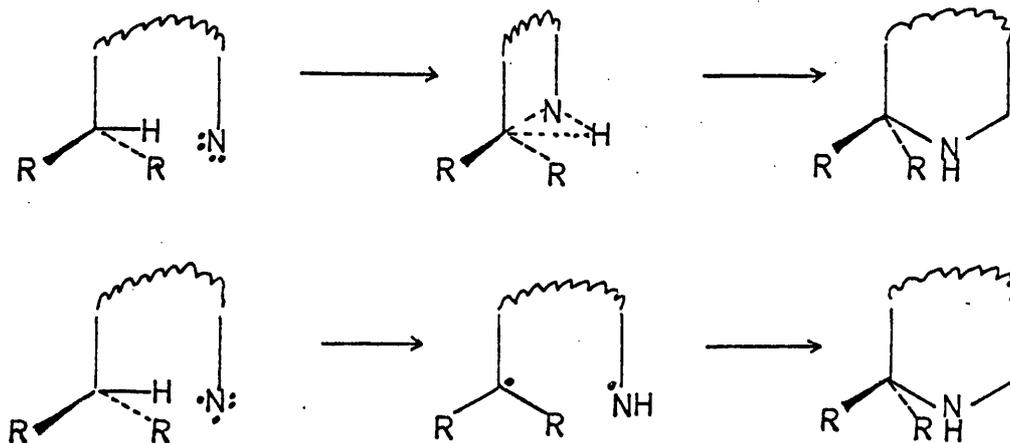


(e) Insertion reactions.

Intramolecular insertion of aryl nitrenes, formed by vapour phase pyrolysis, into alkyl CH has been observed.<sup>49</sup>

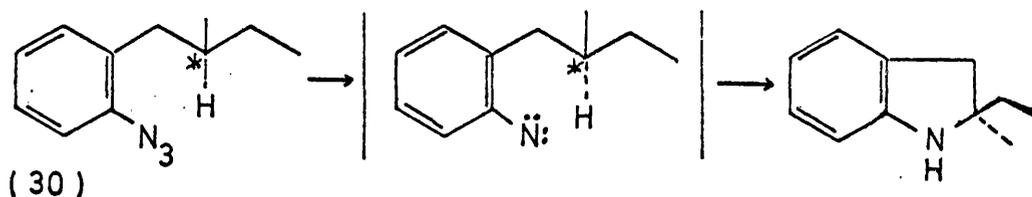


Both concerted and non-concerted mechanisms can be envisaged for the insertion reaction. Singlet nitrenes would be expected to insert in a concerted manner, and the stereochemistry of the substrate should be retained in the product. A triplet nitrene could also insert to give the same product, but a stepwise reaction involving hydrogen abstraction to give a radical pair and then recombination is more likely. If the carbon radical becomes planar before it combines with the nitrogen radical, the reaction will be non-stereospecific.



Pyrolysis of (+)-1-azido-2-(2-methylbutyl) benzene (30) in the vapour phase and in diphenyl ether solution was found to result

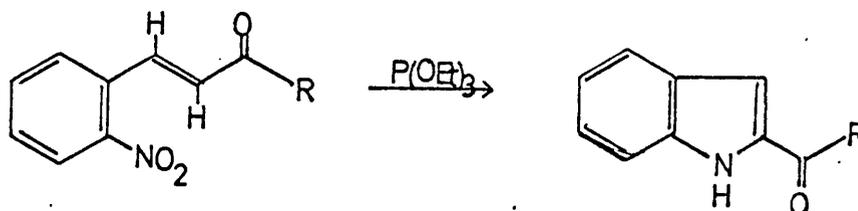
in the formation of optically active 2-ethyl-2-methylindole.<sup>3</sup>



Insertion of nitrenes into vinyl and aryl CH bonds

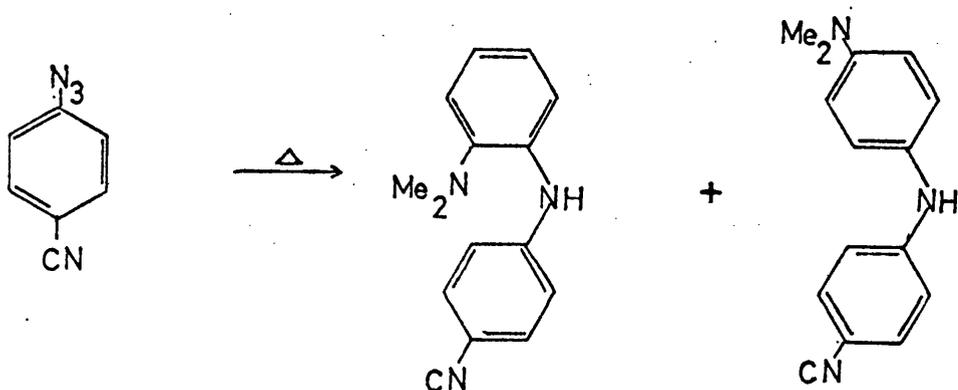
also occurs.

Generation of the aryl nitrene by deoxygenation of some *o*-nitrostyrenes and intramolecular insertion gave 2-acylindoles.<sup>50</sup>

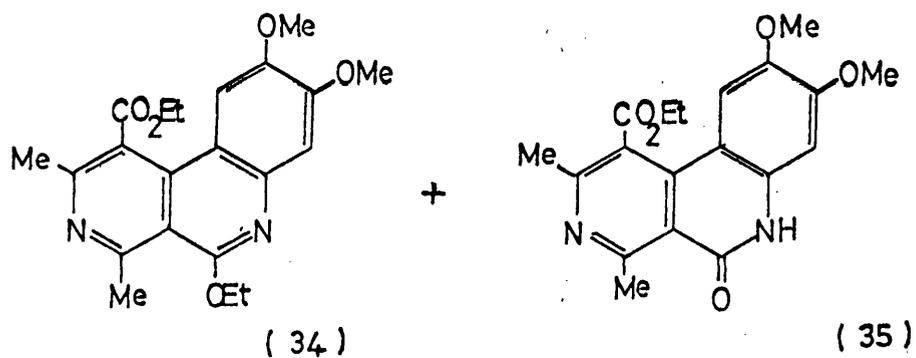
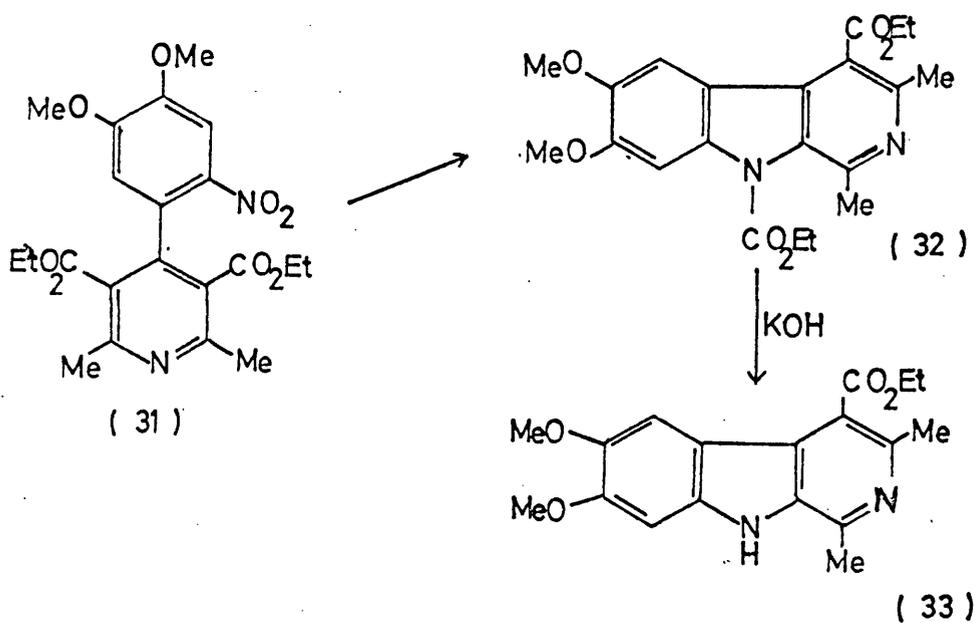


Carbazole is produced in good yield both by decomposition of 2-azidobiphenyl<sup>51</sup> and deoxygenation of 2-nitrosobiphenyl (or 2-nitrobiphenyl) with triethyl phosphite. A nitrene intermediate has been suggested in both cases, but other mechanisms are possible, (See section 2).

Although intramolecular insertions are common, intermolecular insertions are rare. We would expect to get intermolecular attack by introduction of electron-attracting substituents in the aryl nitrene, making it extremely electrophilic, and electron donating substituents in the aromatic solvent, making it highly nucleophilic. Such a process has now been observed experimentally,<sup>52</sup> and thermolysis of various cyano and nitro azides in *N,N*-dimethylaniline gave ortho and para substitution products as well as hydrogen abstraction.



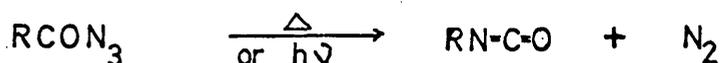
Kametani and his co-workers have utilised nitro compound deoxygenation by triethyl phosphite in the synthesis of natural products. Deoxygenation of (31) to give (32) provides the



only example of an apparent nitrene insertion into an aromatic C-C bond  $\alpha$  to a carbonyl group.<sup>53,54</sup> Kametani has also reported the formation of several products which can be formally rationalised by reaction of a nitrene with a C=O group followed by deoxygenation,<sup>55,56,57</sup> for example the formation of (34) and (35) from (31). (For a full discussion of this novel reaction see Discussion page 114).

#### 4. Acyl Nitrenes.

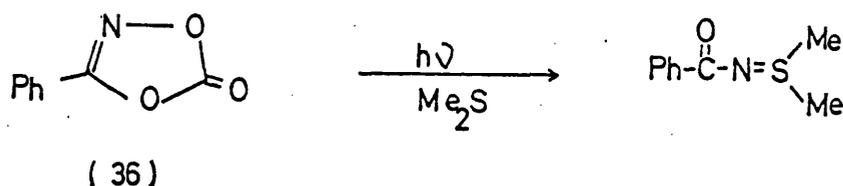
Acyl and aroyl nitrenes have in the past been proposed as intermediates in the Curtius rearrangement of acyl azides to isocyanates.



Nitrenes formed from acyl azides that undergo the Curtius rearrangement have however never been trapped, and the yield of isocyanate is independent of the presence of established nitrene traps.<sup>58</sup> Nitrenes are now thought not to be involved in the rearrangement and this has been confirmed by <sup>14</sup>C labelling, which shows that the bond to the migrating group is broken in the rate determining step.

Alkoxy carbonyl azides, e.g. EtOCON<sub>3</sub>, which do not undergo the Curtius rearrangement on thermolysis do give nitrenes which can be trapped.

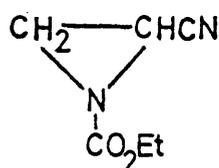
Acyl nitrenes have been generated by photolysis of acyl azides and fragmentation of heterocyclic rings.



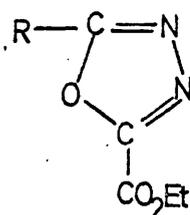
Photolysis of the compound (36) gives the nitrene which can be

trapped with dimethylsulphide.<sup>59</sup>

Carbonyl nitrenes are also 1,3-dipoles, and have been found to add to 1,3-dipolarophiles.<sup>60</sup> Ethoxycarbonylnitrene adds preferentially to the C=C bond in an unsaturated nitrile to give an aziridine (37), but with saturated nitriles 1,3-dipolar addition gives 1,3,4-oxadiazoles (38).

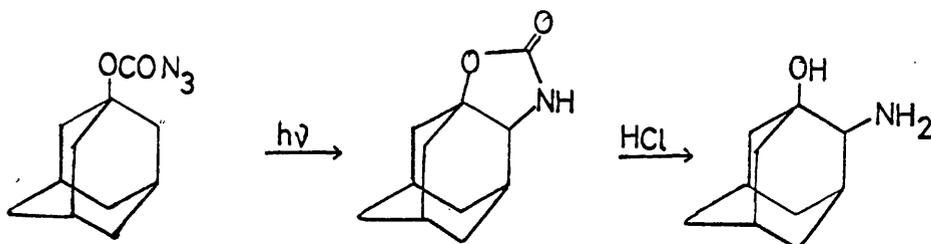


(37)

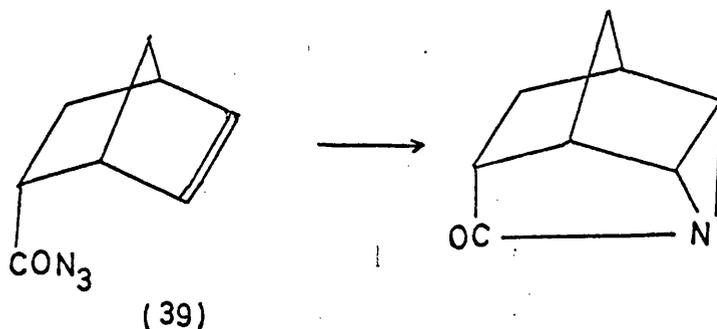


(38)

Acyl nitrenes undergo intramolecular insertion reactions<sup>61</sup> and cycloadditions. An intramolecular insertion has been used in the synthesis of 2-amino-1-adamantanol.<sup>62</sup> The azide (39) does not



undergo the Curtius rearrangement but an intramolecular cycloaddition of the nitrene is observed.<sup>63</sup>



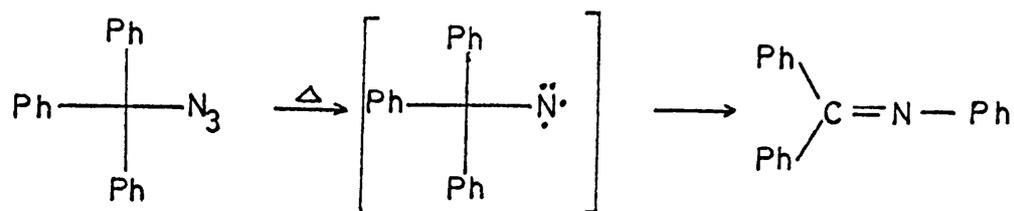
(39)

### 5. Alkyl Nitrenes.

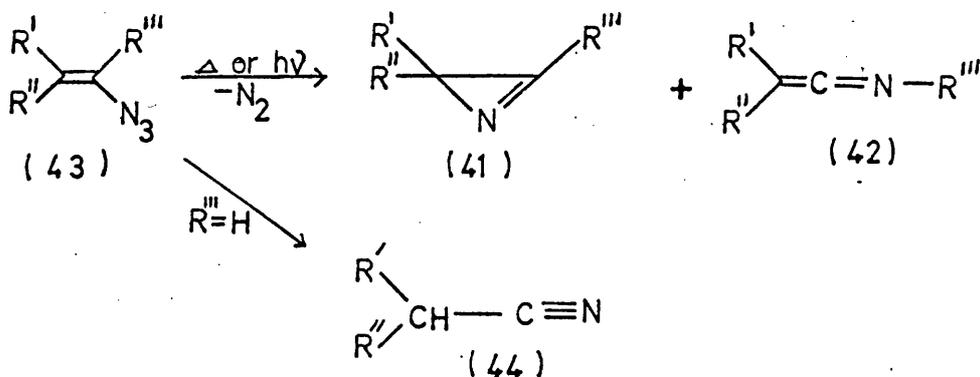
Alkyl nitrenes formed by thermolysis or photolysis of alkyl azides usually isomerise to an imine or hydrogen abstract to give an amine.



Aryl groups have also been found to migrate to the nitrene nitrogen atom. Thermolysis of triphenylmethlazide gives the anil of benzophenone. Although a nitrene intermediate is possible the migration of the phenyl group may be concerted with the loss of nitrogen from the azide.

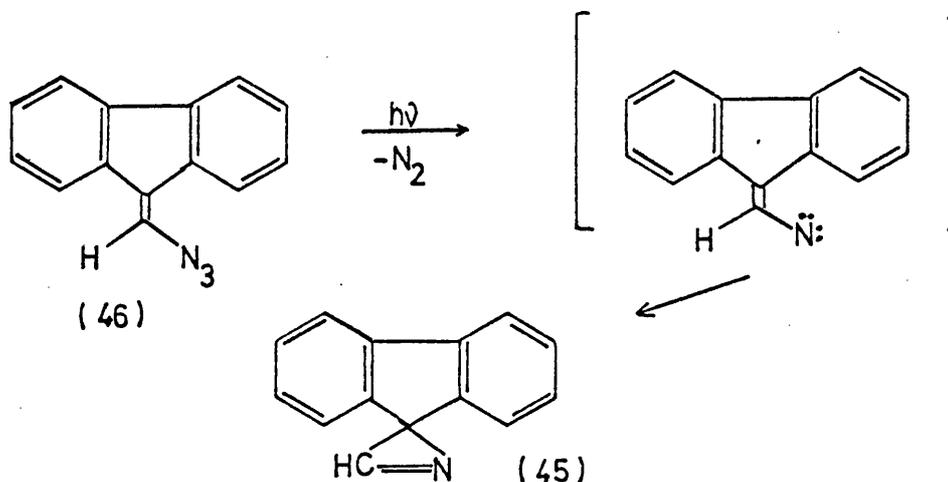


Pyrolysis<sup>64</sup> and photolysis<sup>65</sup> of 1-alkyl or 1-aryl vinyl azides<sup>66</sup> gives 2H-azirines (41) and ketenimines (42). However decomposition of terminal vinyl azides (43, R''' = H) gives only nitriles (44) and none of the 2H-azirine.



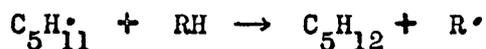
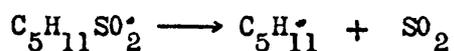
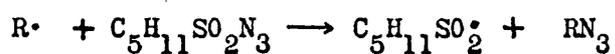
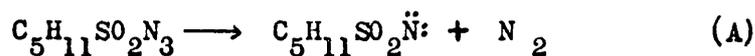
The formation of a 2H-azirine unsubstituted at C<sub>3</sub> has recently been reported.<sup>67</sup> The spirazine (45), which is only stable

at low temperature, is formed on irradiation of the azide (46) at  $-15^{\circ}$  presumably by initial formation of a nitrene followed by intramolecular cyclization.



#### 6. Sulphonyl and Sulphinyl Nitrenes.

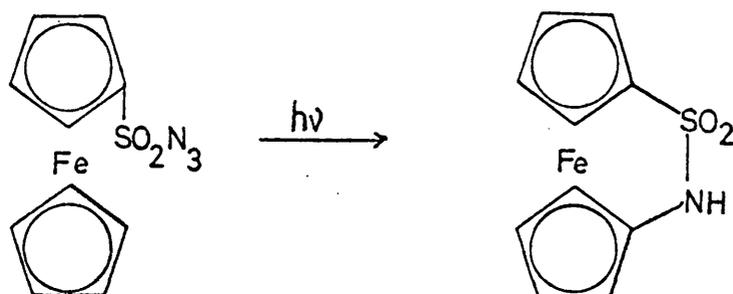
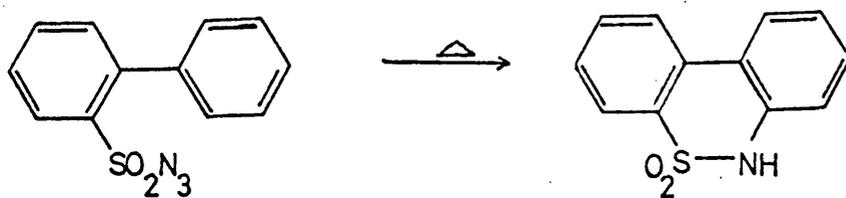
Nitrenes have been generated by photolysis and thermolysis of arylsulphonyl azides and alkylsulphonyl azides.<sup>68</sup> Aliphatic sulphonyl azides decompose in aliphatic solvents by the loss of nitrogen to give nitrenes (A) and by loss of sulphur dioxide in a radical chain decomposition (B) to alkyl azides which are stable under the reaction conditions.<sup>69,70</sup>



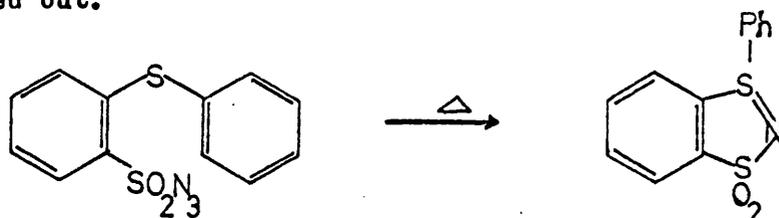
(B)

Sulphonyl nitrenes insert rather than abstract.

Sulphonyl azides decompose to give nitrenes that readily insert intramolecularly in <sup>to</sup> aromatic C-H bonds.<sup>71,72</sup>

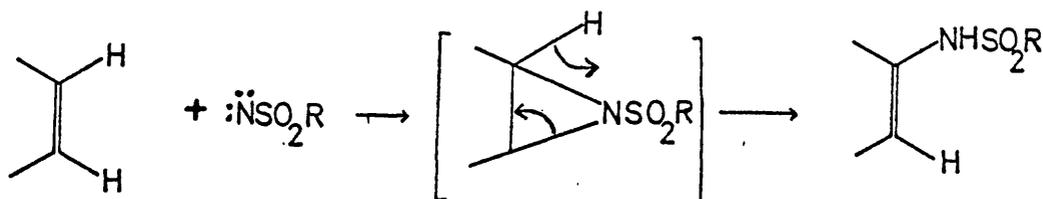


The novel intramolecular cyclization of the nitrene derived from the azide (47) is explained in terms of attack by electrophilic singlet nitrene at the electron rich sulphur atom resulting in expansion of its valence shell. Here again a concerted attack by sulphur on the azide and elimination of nitrogen cannot be ruled out.

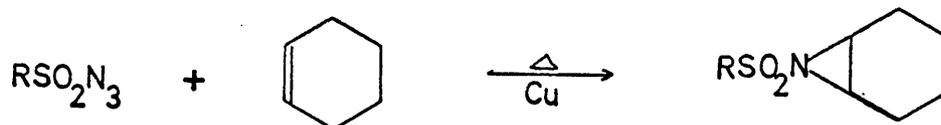


(47)

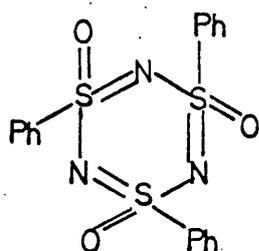
Addition reactions followed by rearrangement occur when sulphonyl azides are thermolysed in aromatic hydrocarbons.<sup>2,3</sup>



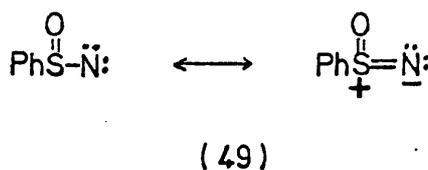
Aziridines have been formed, amongst other products, in copper catalysed decomposition of sulphonyl azides in cyclohexene;<sup>73a</sup> a copper nitrene intermediate was suggested.<sup>73b</sup>



There is only one suggestion of a sulphonyl nitrene, which appears to give some of the formal nitrene trimer (48).<sup>49</sup> The singlet state in benzenesulphonyl nitrene may be stabilized by delocalization of the lone pair of sulphur onto the vacant nitrogen orbital (49).



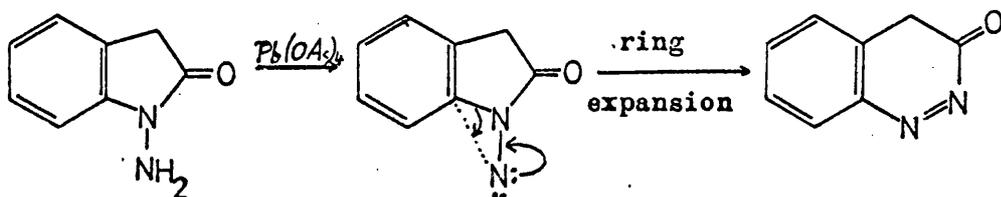
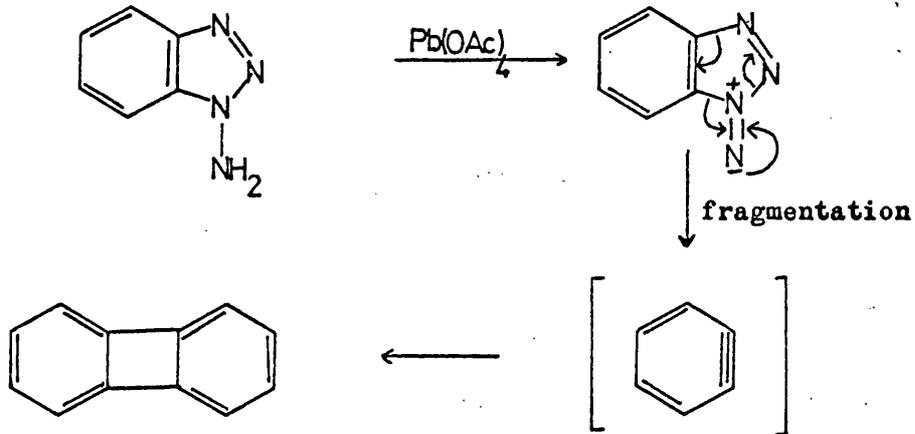
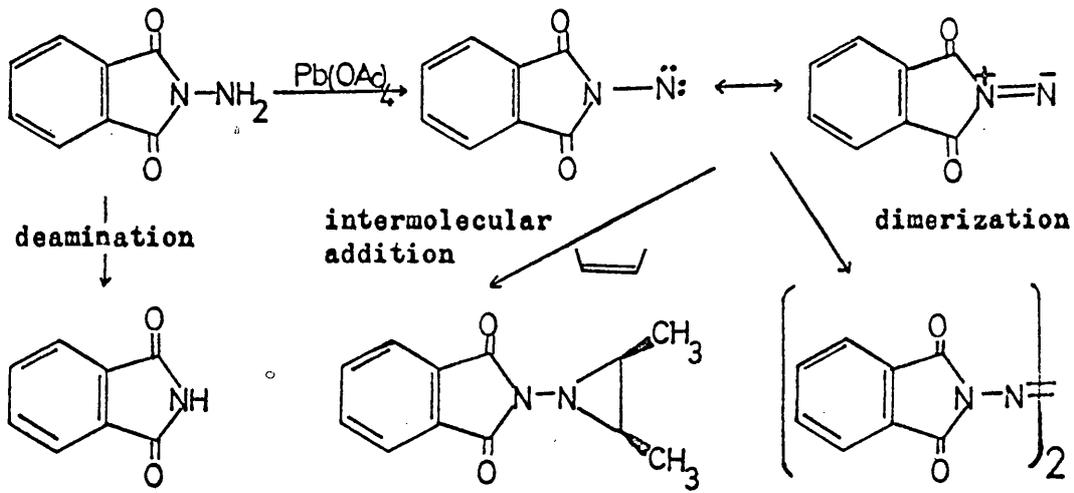
(48)



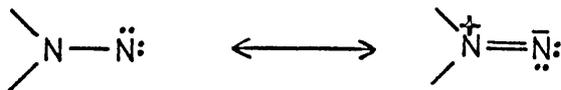
(49)

### 7. N-Nitrenes.

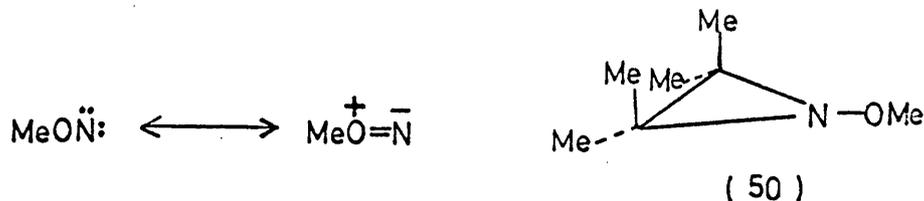
N-Nitrenes where N is part of a heterocyclic ring system are usually generated by oxidation of the N-amino compound. The reactions of N-nitrenes are influenced by solvent effects, temperature, and particularly the nature of the substituents. Oxidation of N-amino compounds results in deamination, formal nitrene dimerisation, intermolecular addition (Scheme 3<sup>74</sup>), fragmentation<sup>75</sup> and ring expansion.<sup>76</sup>



The N-nitrenes should have a "stable" singlet state.



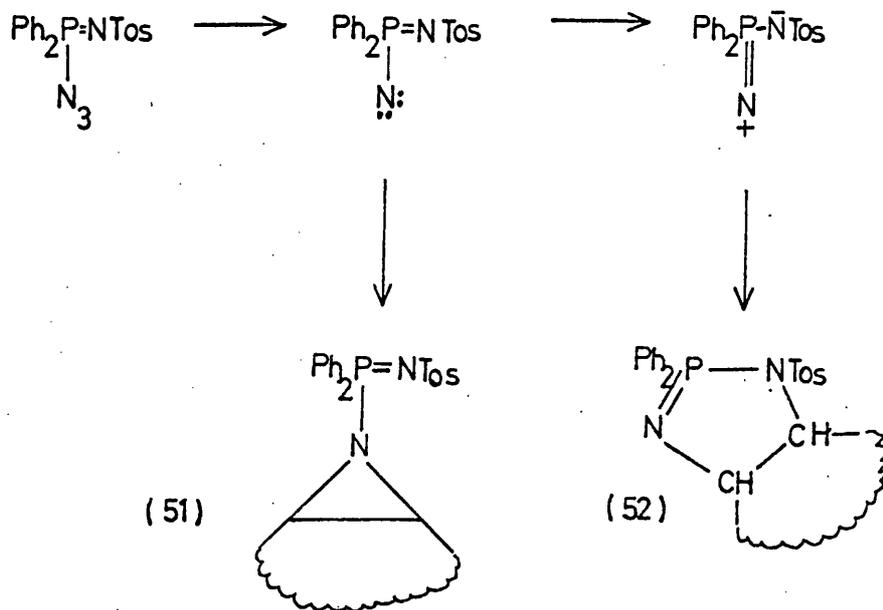
Similarly an O-nitrene would be expected to have a "stable" singlet state.



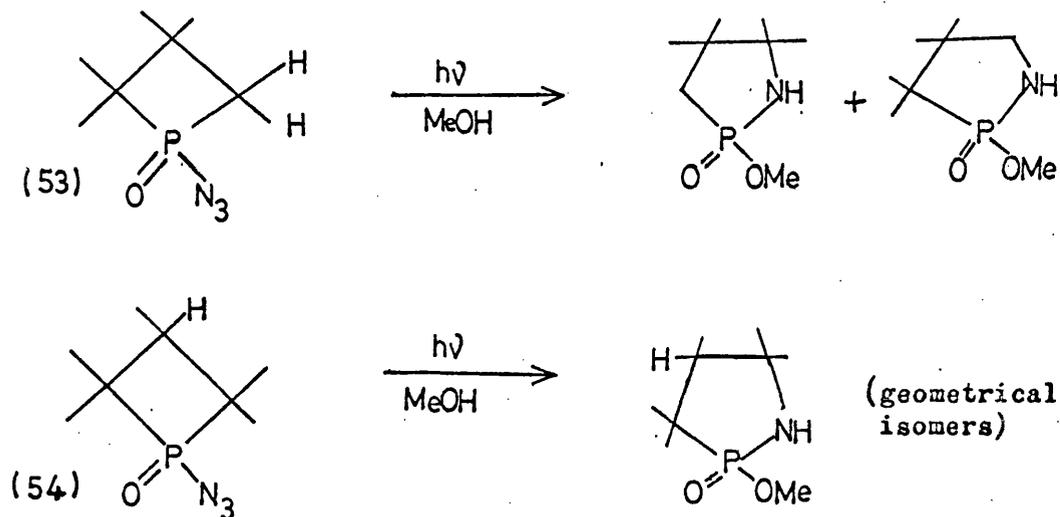
Brois<sup>77</sup> has oxidised methoxyamine with lead tetra-acetate in the presence of tetramethylethylene at  $-50^\circ$  and isolated the aziridine (50).

#### 8. Other Nitrenes.

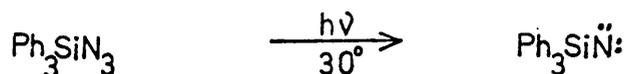
P,P-Diphenyl-N-tosylphosphazene azide decomposes on heating with elimination of one molecule of nitrogen, and it has been postulated that a nitrene which can also be formulated as a 1,3-dipole is involved. In the presence of dicyclopentadiene a 1:1 adduct was formed which could either be the aziridine (51) formed by the addition of the nitrene, or the phosphadiazoline (52) resulting from a 1,3-dipolar addition.<sup>78</sup>



Irradiation of the azides (53) and (54) in methanol gives products that could be explained by a nitrene intermediate.<sup>79</sup>



A silylnitrene has been claimed<sup>80</sup> as an intermediate in the photolysis of triphenylsilylazide.

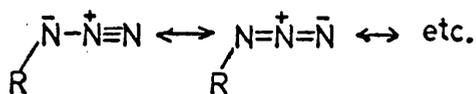


### 9. Some Chemistry of Aryl Azides.

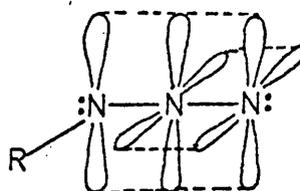
Extensive reviews of azide chemistry have appeared in 1953 by Boyer and Canter<sup>81</sup> and more recently in 1969 by L'Abbé<sup>5</sup> and only the more essential principles will be mentioned here.

#### (a) Structure of azides.

X-ray and electron diffraction patterns<sup>82,83,84</sup> indicated a linear structure with the substituents on the nitrogen lying at an angle of about  $120^\circ$ . In organic azides the two unsubstituted nitrogens are slightly closer together. The structural formula can be represented by resonance hybrids such as (55) or delocalized molecular orbital (56).



( 55 )



( 56 )

The infrared spectra of azides<sup>85,86</sup> show absorption in the range where stretching frequencies of the triple bonds and allenic systems are usually found (2140 - 2240 cm.<sup>-1</sup>, often a doublet). The azido group absorbs very weakly in the near U.V. but not in the visible range,<sup>87</sup> thus aryl azides are colourless.

The decomposition temperature<sup>5</sup> of organic azides decreases in the order alkyl and aryl azides > azidoformates and sulphonyl azides > acyl azides.

(b) Decomposition reactions.

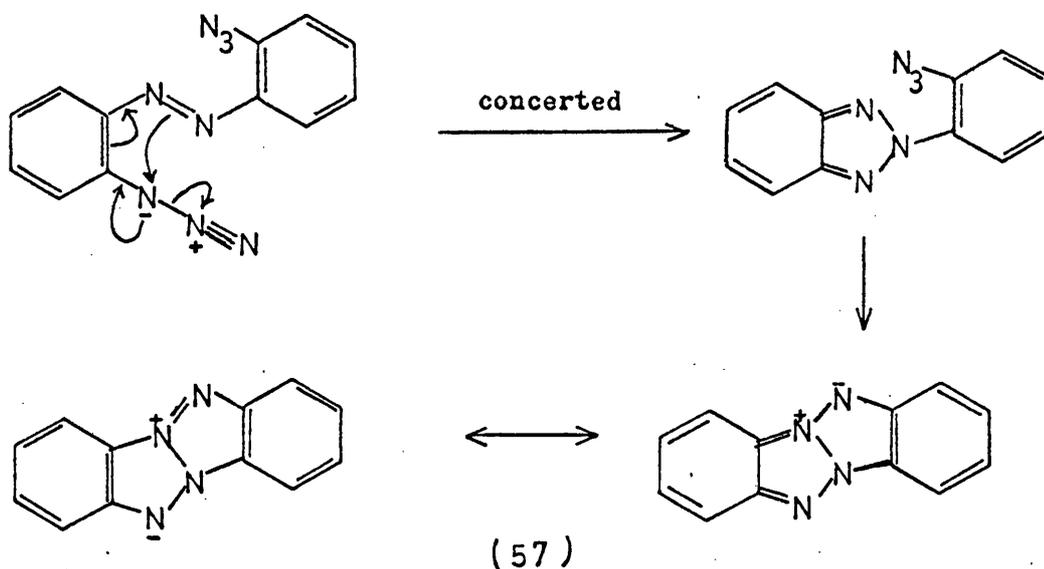
(i) By thermolysis and photolysis.

Thermolysis and photolysis of aryl azides leads to many products that can be best explained by involving a nitrene intermediate (see section 2(a)).

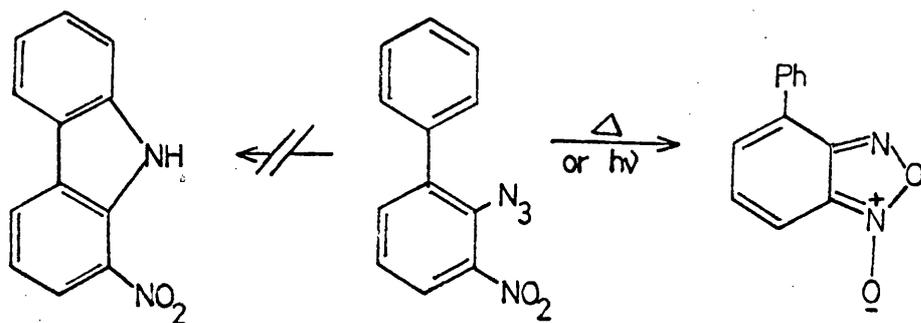
Products from o-substituted aryl azides can also be explained by a nitrene intermediate. However the lower decomposition temperature often observed suggests considerable neighbouring group participation and such reactions are more easily explained by assisted decomposition of the azide group. Kinetic studies<sup>88</sup> have shown that the azido group and the o-substituent must lie in the plane of the aromatic ring for ready cyclization, and it was suggested that the driving force for the reaction is not provided merely by a lone pair of electrons on the o-substituent, but by concerted  $\pi$  bond reorganisation leading to the new heterocyclic ring. The energy of activation of the cyclic transition state was

thought to reflect steric strains, changes in delocalisation energy of the initial  $\pi$  bond systems, and the extent to which the delocalisation energy of the new heterocyclic system has become available.

Nitrogen was found to be liberated in two distinct stages on thermolysis of 2,2'-diazidoazobenzene;<sup>89,90</sup> one mole below  $60^\circ$  to give 2-(o-azidophenyl)-2H-benzotriazole in a concerted process and the second at  $170^\circ$  to give compound (57) via a nitrene.



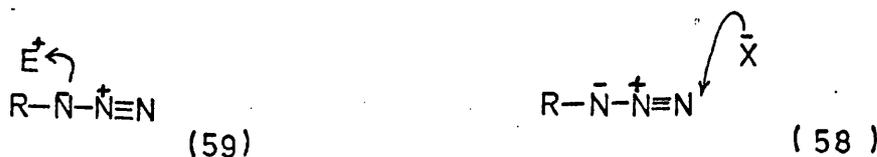
Carbazole formation is believed to arise from nitrene insertion into a C-H bond. If a nucleophilic centre is suitably situated within a molecule then on thermolysis or photolysis



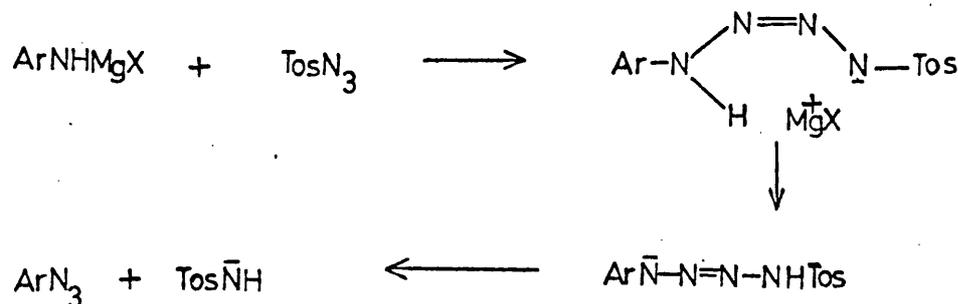
carbazole is not formed and the lower energy concerted cyclisation and loss of nitrogen is observed. Thus 2-azido - 3 - nitrophenyl gave 4 - phenylbenzofuroxan<sup>91</sup> and no carbazole.

(ii) By reaction with nucleophiles and electrophiles.

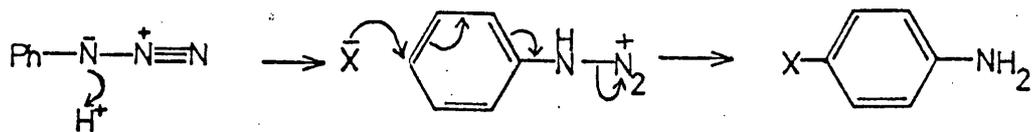
Azides are subject to attack by nucleophiles at the terminal nitrogen (58) and by electrophiles (usually  $H^+$ ) at the substituted nitrogen (59).



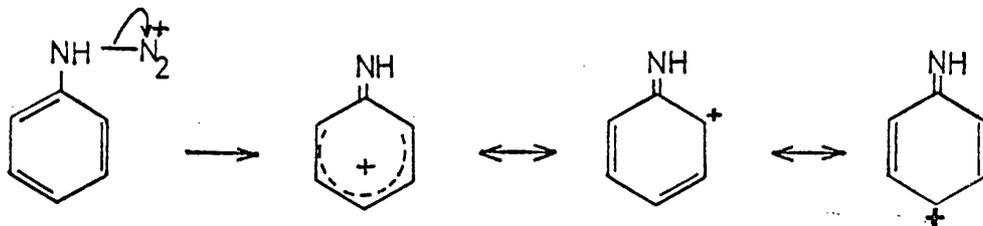
Reaction with nucleophiles.- Nucleophilic attack at the terminal nitrogen atom by tertiary phosphines<sup>92</sup> and Grignard reagents<sup>93,94</sup> has been observed. Anselme<sup>95</sup> has utilised the latter reaction in a new synthesis of aryl azides



Reaction with electrophiles (acid catalysed decomposition.) - Attack by an electrophile ( $H^+$ ) at the substituted nitrogen (59, R=Ph) leads to nucleophilic attack at the ortho and para position of the aryl ring. In principle this can occur either by protonation of the azide followed by concerted attack by a nucleophile and loss of nitrogen, (scheme 4), or by loss of nitrogen from the protonated azide to give a nitrenium ion<sup>96,97</sup> (scheme 5) which then undergoes nucleophilic attack.

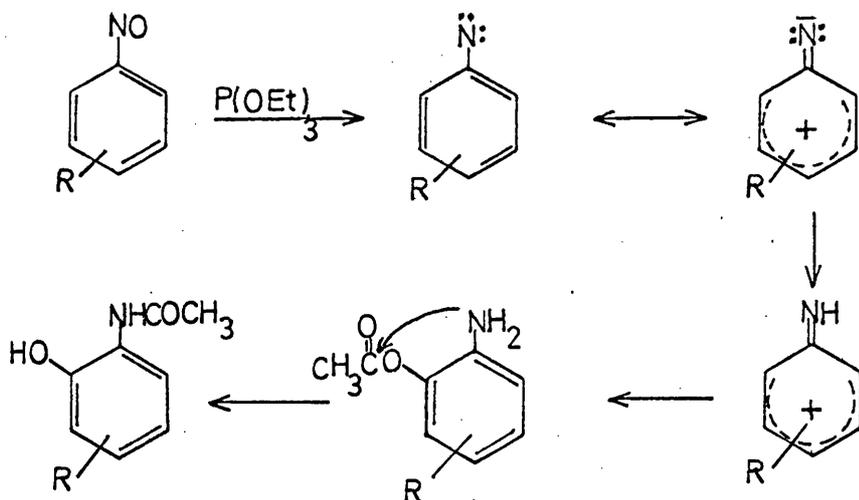


( Scheme 4 )



( Scheme 5 )

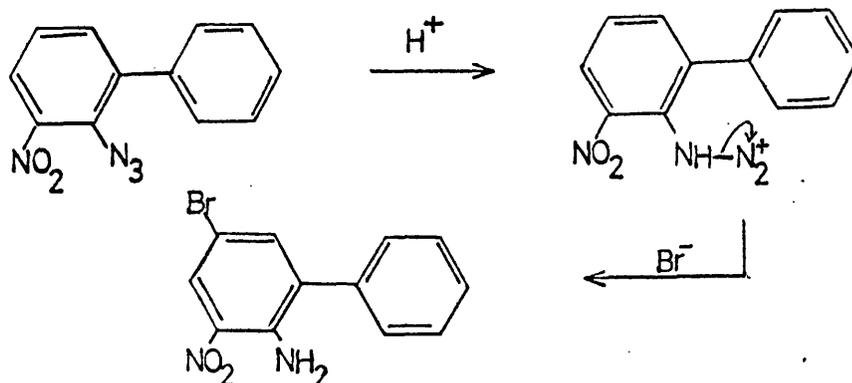
Generation of aryl nitrenes in the presence of acetic acid by deoxygenation of aromatic nitro and nitroso compounds gave significant amounts of *o*-hydroxyacetanilides. It was suggested that aryl nitrenes were formed, and as relatively basic intermediates, protonation occurred to give the nitrenium ion prior to product formation.



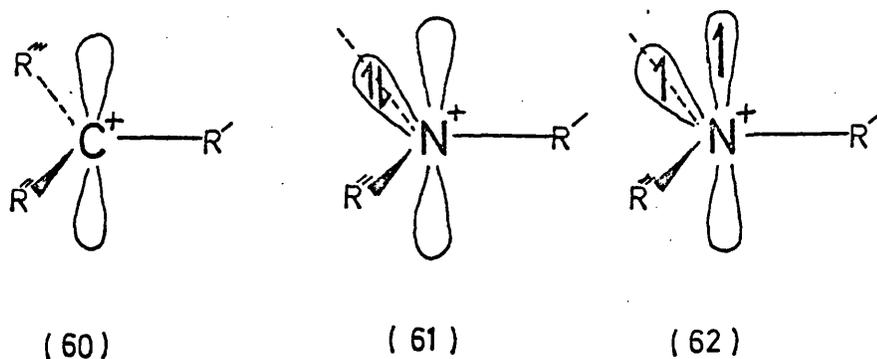
The aryl nitrenium ion in this system could be formed by protonation of the intermediate in the oxygen transfer reaction, prior to expulsion of triethyl phosphate.

An example of nucleophilic attack in the aryl ring

accompanying acid catalysed decomposition of an azide, is the ready decomposition at 50-60° of *o*-azidobiphenyls in a solution of hydrogen bromide in acetic acid.<sup>99</sup>

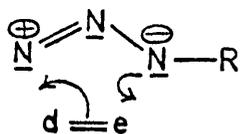


Nitrenium ion intermediates have been established in the solvolysis of N-chloro compounds and have recently been reviewed by Gassman.<sup>100</sup> Nitrenium ions are positively charged nitrogen analogues of carbonium ions (60). They resemble carbonium ions in their chemical behaviour, but are much more reactive. Gassman has considered the possibility of singlet (61) and triplet (62) nitrenium ions.



### (C) Addition reactions.

Azides are 1,3-dipoles which have 4  $\pi$ -electrons distributed over the three N-atoms so making concerted addition to  $\pi$  bonds allowed. Huisgen<sup>101,102</sup> has described fully the 1,3-dipolar cycloaddition mechanism of azides to a dipolarophile (de).



Since azides can add onto unsymmetrical dipolarophiles in two directions the product distribution is determined by steric effects and/or electronic effects occurring in the rate determining step.

EXPERIMENTAL .

INSTRUMENTATION AND EXPERIMENTAL TECHNIQUES.

1. Infrared spectra were recorded in the range 4000-625  $\text{cm.}^{-1}$  on a Perkin-Elmer 237 or 257 spectrometer. Solid samples were run either as nujol mulls or as potassium bromide discs and liquids as thin films, using polystyrene as reference.
2. Proton magnetic resonance (p.m.r.) spectra were recorded on a Varian A60 or a Varian T60 instrument. Carbon tetrachloride, deuteriochloroform, hexadeuteroacetone and hexadeuterodimethylsulphoxide were used as solvents with tetramethylsilane as internal reference.
3. Ultraviolet (u.v.) spectra were recorded in the range 200-450  $\text{m}\mu$ . on a Unicam SP800 spectrophotometer. Absolute ethanol was used as solvent in 1 cm. cells.
4. Mass spectra were recorded on an Associated Electrical Industries M.S. 9 spectrometer.
5. Melting point (m.p.) determinations were carried out on a Kofler Micro Heating Stage using corrected thermometers.
6. Thin layer chromatography (t.l.c.) was used extensively as a qualitative guide to the composition of reaction mixtures and as a means of assessing the purity of compounds. Samples were run in suitable solvent mixtures on glass plates coated with a 250  $\mu$  layer of Kieselgel G. (E. Merck), or aluminium oxide G (Type E, pH 7.5) (E. Merck). The plates were observed under ultraviolet light or developed by spraying with iodine.
7. Preparative thin layer chromatography (Preparative t.l.c.) was used to separate small amounts of reaction mixtures by a similar technique to that of t.l.c.; 20x20 and 100x20 cm. glass plates coated with a 1mm. layer of Kieselgel PF 254 with a fluorescent indicator were used.

8. Column chromatography was carried out using silica gel MFC (B.D.H.), basic alumina (Spence type H), and deactivated alumina (prepared by deactivation of basic alumina with 6% by weight of water in a ball-mill for 12hr.). The mixture to be chromatographed was adsorbed onto the support, from a suitable solvent, by evaporation using a rotary evaporator. Alumina columns were packed under petrol and silica columns were either packed by this method or packed dry, and then eluted with solvent mixtures of increasing polarity.

9. Solvents were purified as follows:

Benzene and other aromatic solvents, methylene chloride, methanol, ethanol, acetonitrile, and ether were purified by refluxing over and distilling from calcium hydride. Aromatic solvents, methylene chloride, methanol, ethanol and acetonitrile were stored over molecular sieves (type 4A) and ether over sodium wire.

Dimethyl sulphoxide and dimethyl formamide were dried by storage over molecular sieves (type 4A).

10. Petroleum used for chromatography and for recrystallisations with ether was light petroleum, b.p. 40-60°. Petrol used for recrystallisations with benzene, chloroform or ethyl acetate was petroleum b.p. 60-80°, unless stated otherwise.

11. Lead tetra-acetate (B.D.H. or Hopkin and Williams) was freed from acetic acid by filtration and stored over concentrated sulphuric acid.

12. Where possible, compounds were characterised by comparison of their melting points (m.p.) and mixed melting points (m.m.p.) and i.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).

PREPARATION OF DIHYDROBENZ[cd]INDAZOLE AND ITS DERIVATIVES AND  
ATTEMPTED PREPARATION OF BENZ[cd]INDAZOLE.

1. Preparation of Azides.

1-Amino-8-azidonaphthalene -- 1-Amino-8-azidonaphthalene was prepared by a modification of the method of Storr and Rees,<sup>139</sup> Naphtho[1,8-de]triazine was prepared from 1,8-diaminonaphthalene and N-nitrosodiphenylamine by the method of Sieper.<sup>103</sup>

Naphtho[1,8-de]triazine (10g., 60mmole) suspended in aqueous potassium hydroxide (14g., 240mmole in 200ml. of water) was stirred at 70-80° while solid hydroxylamine-O-sulphonic acid<sup>104</sup> (7g., 60mmole) was added in small portions. More potassium hydroxide (14g.) was added followed by more hydroxylamine-O-sulphonic acid (14g.) over a period of 1½hr. After stirring at 60-70° for a further 1hr. the mixture was cooled and filtered, and the residue was thoroughly washed with aqueous potassium hydroxide and then water. The residue was extracted with alcohol (3 x 125ml.) and the ethanolic solution was heated under reflux while concentrated hydrochloric acid (50ml) was added over 5 min. Activated charcoal (5g.) was added and the mixture was refluxed for a further 5min. and then filtered and poured into water (400ml.) The solution was neutralized with sodium carbonate and extracted with ether (2 x 200ml.) to give 1-amino-8-azidonaphthalene. (6.15g., 56% m.p. 78-79° lit.,<sup>139</sup> m.p.79-80°).

1-Amido-8-azidonaphthalenes. -- All 1-amido-8-azidonaphthalenes were prepared in high yield by treatment of 1-amino-8-azidonaphthalene in pyridine with a small excess of the appropriate acid chloride or anhydride. The crude amides were recrystallised from ethanol to give 1-acetamido-8-azidonaphthalene as needles, m.p. 147-148°;

(lit.,<sup>105</sup> 147-148°); 1-azido-8-benzamidonaphthalene as crystals, m.p. 123-124° (Found: C, 71.4; H, 4.15; N, 19.35.  $C_{17}H_{12}N_4O$  requires: C, 70.8; H, 4.2; N, 19.45%)  $\nu_{\max}$ . 3355 (NH), 2140 ( $N_3$ ), and 1668  $cm^{-1}$

(C=O); 1-azido-8-p-nitrobenzamidonaphthalene as yellow crystals, m.p. 160-161° (Found: C, 62.0; H, 3.25; N, 20.95.  $C_{17}H_{11}N_5O_3$  requires: C, 61.25; H, 3.35; N, 21.0%);  $\nu_{\max}$ . 3345, 2140, and 1678  $cm^{-1}$ ;

1-azido-8-p-methoxybenzamidonaphthalene as crystals, m.p. 133.5-134.5° (Found: C, 67.35; H, 4.75; N, 18.1.  $C_{18}H_{14}N_4O_2$  requires: C, 67.9; H, 4.45; N, 17.6%);  $\nu_{\max}$ . 3340, 2135, and 1680  $cm^{-1}$ ; 1-azido-8-propionamidonaphthalene as crystals, m.p. 115-116° (Found: C, 65.4; H, 5.1; N, 23.15.  $C_{13}H_{12}N_4O$  requires: C, 65.0; H, 5.05; N, 23.3%)  $\nu_{\max}$ . 3320, 2120 and 1643  $cm^{-1}$ .

1-Acetamido-3-azidonaphthalene. — Sodium nitrite (1 g.) was added to a stirred suspension of 1-acetamido-3-aminonaphthalene (3 g.) in 2N hydrochloric acid (30 ml.) at 0°. Sodium azide (2 g.) was added to the filtered solution and the resulting precipitate was collected and recrystallised from ether-petroleum to give 1-acetamido-3-azidonaphthalene (0.8 g., 24%), m.p. 199-200° (Found C, 63.4; H, 5.2.  $C_{12}H_{10}N_4O$  requires C, 63.7; H, 4.5%);  $\nu_{\max}$ . 3272, 2122 and 1663  $cm^{-1}$ .

6-Azido-1-benzamidonaphthalene - 1-Amino-6-nitronaphthalene was converted into 1-benzamido-6-nitronaphthalene by treatment with benzoyl chloride in pyridine. The nitro amide was dissolved in ethanol and hydrogenated over Pd/C catalyst. After removal of ethanol the resulting amine (0.8 g.) was suspended in 2N hydrochloric acid (15 ml.) and diazotised at 0° with sodium nitrite (0.5 g.) Addition of sodium azide (1 g.) to the filtered diazonium solution

gave a precipitate of 6-azido-1-benzamidonaphthalene (0.25 g., 15.5%), needles from ethanol, m.p. 177-178° (decomp.) (Found: C, 69.9; H, 4.4; N, 19.2.  $C_{17}H_{12}N_4O$  requires: C, 70.8; H, 4.2; N, 19.45%)  $\nu_{\max}$ . 3218, 2115 and 1635  $cm^{-1}$ .

1-Azido-8-N-methylaminonaphthalene.-- Dimethyl sulphate (5 ml.) was added to 1-amino-8-azidonaphthalene (1.84 g., 10mmole) in acetone (30ml.) and dilute sodium hydroxide (20ml.) After refluxing for 1hr. the mixture was cooled and poured into water (150ml.) Extraction with chloroform (2x50ml.) gave 1-azido-8-N-methylamino-naphthalene (600 mg. 30%) which crystallised as colourless cubes from ether, m.p. 103-4°.  $\nu_{\max}$ . 3435, 2125  $cm^{-1}$ ;  $\tau$  2.35-3.65 (m, 7H, aromatic H and NH), 7.15 (s, 3H,  $CH_3$ ); m/e 198, 170. (m/e required 198).

1-N,N-Diacetyl-amino-8-azidonaphthalene.-- 1-Amino-8-azidonaphthalene was heated to reflux in acetic anhydride for 1 hr., and after cooling, the resulting mixture was poured into water. The aqueous suspension was extracted with ether and after washing with dilute sodium carbonate solution and water the ether extracts were dried and evaporated to give 1-N,N-diacetyl-amino-8-azidonaphthalene (27%) m.p. 114-115° (from ether) (Found: C, 62.75; H, 4.6; N, 20.3.  $C_{14}H_{12}N_4O_2$  requires: C, 62.7; H, 4.5; N, 20.9%),  $\nu_{\max}$ . 2120, 1720, 1700  $cm^{-1}$ ;  $\tau$  2.05-2.90. (m, 6H, aromatic H), 7.7 (s, 6H, MeCO).

1-(N-Acetyl-N-methylamino)-8-azidonaphthalene. -- Sodium hydride (46 mg., 50% dispersion in oil) was added to 1-acetamido-8-azidonaphthalene (200 mg.) in dry dimethylformamide. Dimethyl sulphate (124 mg.) was added and the mixture was left to stand for 30 min. and then poured in to water. Extraction with ether gave 1-(N-acetyl-N-methylamino)-8-azidonaphthalene (36%) m.p. 97-98°

(from ether) (Found: C, 65.0; H, 5.2; N, 23.1.  $C_{13}H_{12}N_4O$  requires: C, 65.0; H, 5.05; N, 23.3%);  $\nu_{\max}$ . 2120, 1647  $cm^{-1}$ .

1-(N-Benzoyl-N-methylamino)-8-azidonaphthalene.— Similar treatment of 1-benzoylamino-8-azidonaphthalene with dimethyl sulphate gave 1-(N-benzoyl-N-methylamino)-8-azidonaphthalene (42%) m.p. 109–110° (from ether), (Found: C, 70.8; H, 4.6; N, 18.1.  $C_{18}H_{14}N_4O$  requires: C, 71.5; H, 4.7; N, 18.55%);  $\nu_{\max}$ . 2120, 1690  $cm^{-1}$ .

1-Azido-8-methoxycarbonylaminonaphthalene.— Methyl chloroformate (274 mg., 3mmole) in methylene chloride (2.5ml.) was added at 0° to a stirred solution of 1-amino-8-azidonaphthalene (184 mg., 1mmole) and triethylamine (212 mg., 2mmole) in methylene chloride (5ml.) After 30min. at 0° the mixture was stirred for a further 4hr. at 20°. A little insoluble material was filtered off and washed with methylene chloride. The solution was evaporated onto silica gel and the products separated by preparative t.l.c. to give 1-azido-8-methoxycarbonylaminonaphthalene (50%) which crystallised as colourless needles from ether-petroleum m.p. 103–104°, (Found: C, 58.6; H, 4.0; N, 22.95  $C_{12}H_{10}N_4O_2$  requires: C, 59.5; H, 4.15; N, 23.15%);  $\nu_{\max}$ . 2120, 1728  $cm^{-1}$ ;  $\tau$  0.55 (broad s, 1H, NH), 1.75 (t, 1H, J=4.5 c.p.s.,  $C_7H$ ), 2.4 – 3.1 (m, 5H, aromatic H), 6.3 (s, 3H,  $CO_2CH_3$ ).

1-Azido-8-di(methoxycarbonyl)aminonaphthalene — Sodium hydride (25 mg.) was added to 1-azido-8-methoxycarbonylaminonaphthalene (124 mg., 0.5mmole) in dry dimethylformamide. Methyl chloroformate (137 mg., 1.5mmole) was added and the mixture was stirred for 30min. and then poured in to water. Extraction with ether gave 1-azido-8-di(methoxycarbonyl)aminonaphthalene (88%), m.p. 180–182° (decomp.) (colourless needles from ether – petroleum); (Found: C, 55.95;

H,4.00; N,18.9.  $C_{14}H_{12}N_4O_4$  requires: C,56.0; H,4.05; N,18.65%);  
 $\nu_{\max}$ . 2110, 1800  $cm^{-1}$ ;  $\tau$  2.05-2.85 (m,6H, aromatic H), 6.3  
 (s,6H, $CO_2CH_3$ ).

1-Azido-8-phthalimidonaphthalene (30)<sup>†</sup>.— A solution of  
 1-amino-8-azidonaphthalene (1.84g., 10mmole) and phthalic anhydride  
 (1.48g., 10mmole) in glacial acetic acid (15 ml.) and pyridine  
 (0.1 ml.) was heated under reflux for 1hr. After cooling the  
 suspension was poured into water (100ml.) Extraction with ether  
 gave 1-azido-8-phthalimidonaphthalene (75%), m.p. 184-185°  
 (colourless needles from glacial acetic acid); (Found: C,69.0;  
 H,2.9; N,17.65.  $C_{18}H_{10}N_4O_2$  requires: C,68.8; H,3.2; N,17.85%);  
 $\nu_{\max}$ . 2120, 1725  $cm^{-1}$  Similar treatment of 1-amino-8-azido-  
 naphthalene with maleic anhydride gave 1-azido-8-maleimidonaphthalene  
 (40%), m.p. 220° (decomp.) (colourless needles from glacial acetic  
 acid) (Found: C,62.9; H,3.9; N,21.5.  $C_{14}H_8N_4O_2$  requires: C,63.6;  
 H,3.05; N,21.2%);  $\nu_{\max}$ . 2120, 1670  $cm^{-1}$ . Succinic anhydride  
 gave N-(8-azido-1-naphthyl)-succinamic acid (33, n=2)(45%), m.p.  
 140° resolidifies and melts again at 165-167° (decomp.), (colourless  
 needles from ether-petroleum); (Found: C,59.2; H,3.7; N,19.8.  
 $C_{14}H_{12}N_4O_3$  requires: C,59.15; H,4.25; N,19.7%);  $\nu_{\max}$ . 3340, 2108,  
 1710, 1678  $cm^{-1}$ ; m/e 266 (m/e required 284 (-H<sub>2</sub>O gives 266) ).  
 Glutaric anhydride gave N-(8-azido-1-naphthyl)glutaramic acid (33, n=3)  
 (25%), m.p. 146-148° (decomp.), (colourless needles from ether-  
 petroleum); (Found: C,60.75; H,5.05; N,18.15.  $C_{15}H_{14}N_4O_3$  requires:  
 C,60.4; H,4.75; N,18.75%);  $\nu_{\max}$ . 3320, 2125, 1710, 1670  $cm^{-1}$ ;  
 m/e 298 (m/e required 298).

Cyclisation of N-(8-azido-1-naphthyl)succinamic acid. —  
 Thionyl chloride (1ml.) was added to N-(8-azido-1-naphthyl)  
succinamic acid (568mg., 2mmole) and the mixture slowly heated

<sup>†</sup>Diagram number in appropriate section of Discussion.

to 150° allowing the excess thionyl chloride to distil off.

Crystallisation of the residue from ether-petroleum gave colourless

needles of 1-azido-8-succinimidonaphthalene (50%), m.p. 180-182°;

(Found: C, 62.7; H, 4.05; N, 20.85.  $C_{14}H_{10}N_4O_2$  requires: C, 63.15;

H, 3.8; N, 21.05%);  $\nu_{\max}$  2110, 1785  $\text{cm.}^{-1}$ ; m/e 266. (m/e required 266).

o-Azidophenol — o-Azidophenol was prepared by the method of Forster and Fierz.<sup>106</sup> Treatment of o-azidophenol in dilute sodium hydroxide solution with benzoyl chloride gave o-azidophenyl benzoate m.p. 42-3° (lit.,<sup>106</sup> 45°).

m-Azidoaniline — m-Azidoaniline was prepared from m-nitroaniline by a modification to the method of Hall and Smith.<sup>107</sup>

m-Nitroaniline (69g., 0.5M) and phthalic anhydride (74g., 0.5M) in glacial acetic acid (1 l.) were heated under reflux for 1 hr. and the mixture was then allowed to cool to 20°. The precipitate was filtered off and washed with a little cold glacial acetic acid. The m-phthalimidonitrobenzene was added to acetone (1.5 l.) and the mixture was heated under reflux while glacial acetic acid (250ml.) and water (190ml.) were added. Fine iron powder (210g.) was added over 1 hr. and the mixture was stirred vigorously and heated under reflux for a further 4 hr. The reaction slurry was filtered while hot and the residue was washed with hot acetone (2x50ml.). The filtrate was neutralized with aqueous saturated sodium carbonate solution and the acetone layer was removed. This was concentrated to one quarter of its original volume by distillation under reduced pressure and then diluted with water (2 l.). The precipitate (m-phthalimidoaniline) was filtered off and suspended in an ice cold mixture of water (500ml.) and concentrated hydrochloric acid (100ml.). Sodium nitrite (14g.) in water (50ml.) was then added dropwise over 10 min. with ice when

required to keep the temperature down to  $0^{\circ}$ . The solution was stirred at this temperature for 1hr. and a little insoluble material was removed by filtration. Sodium azide (13g.) in water (30ml.) was added to the filtrate and the precipitate was collected, washed well with water and dried under reduced pressure in a desiccator to give m-azidophthalimidobenzene (29g., 22%). Hydrazine hydrate (3.5ml.) was added dropwise to a suspension of m-azidophthalimidobenzene (10g., 38mmole) in methanol (45ml.) and the mixture was stirred for 30min. The resulting solution was poured into water (300ml.) and 2N sodium hydroxide solution (30ml.) was then added. Extraction with ether (2x50ml.) gave m-azidoaniline (4g., 80%) as a straw-coloured oil.

m-Azidoanilides — The crude oily m-azidoaniline was treated with benzoyl chloride in pyridine to give m-azidobenzanilide, needles, m.p.  $128-129^{\circ}$  (from ethanol) (Found: C, 64.85; H, 4.75; N, 23.2.  $C_{13}H_{10}N_4O$  requires: C, 65.55; H, 4.25; N, 23.5%)  $\nu_{\max}$ . 3264, 2112 and 1663  $cm^{-1}$ ; with p-methoxybenzoyl chloride in pyridine to give m-azido-p-methoxybenzanilide, needles, m.p.  $116-117^{\circ}$  (from ethanol) (Found: C, 62.7; H, 4.8; N, 20.8.  $C_{14}H_{12}N_4O_2$  requires: C, 62.7; H, 4.5; N, 20.9%);  $\nu_{\max}$ . 3320, 2118 and 1645  $cm^{-1}$ ; and with acetic anhydride in pyridine to give m-azidoacetanilide, needles, m.p.  $123-124^{\circ}$  (from ethanol) (lit.,<sup>105</sup>  $123-124^{\circ}$ ).

## 2. Decomposition of Azides.

(a) Pyrolysis of Azides in Solution.— Pyrolyses were carried out by dropwise addition of suspensions of the azides in small volumes of 1,2,4-trichlorobenzene to refluxing 1,2,4-trichlorobenzene. After 5min. the mixtures were cooled and trichlorobenzene was removed by distillation under reduced pressure. The residues were thoroughly extracted with hot chloroform and the extracts were

evaporated on to silica gel for chromatography. 9-Amino-2-alkyl- or aryl-naphth [1,2-d] oxazoles were eluted with 10% ether-petroleum and were further purified by sublimation or by distillation through a short horizontal tube. 2-Alkyl or aryl perimidines were eluted with ether and directly compared with authentic samples prepared by treatment of 1,8-diaminonaphthalene with the appropriate acid chloride.<sup>108,109</sup>

1-Azido-8-benzamidonaphthalene gave 9-amino-2-phenyl-naphth [1,2-d] oxazole (29%), crystals, m.p. 126-127° (Found: C, 78.4; H, 4.9; N, 10.9.  $C_{17}H_{12}N_2O$  requires: C, 78.5; H, 4.7; N, 10.8%),  $\nu_{\max}$ . 3440, 3350 ( $NH_2$ )  $cm^{-1}$ ; and 2-phenylperimidine<sup>109</sup> (10.3%).

1-Azido-8-p-nitrobenzamidonaphthalene gave 9-amino-2-p-nitrophenyl-naphth [1,2-d] oxazole (12%), yellow crystals, m.p. 217-218° (Found: C, 66.7; H, 3.8; N, 14.1.  $C_{17}H_{11}N_3O_3$  requires: C, 66.9; H, 3.6; N, 13.8%),  $\nu_{\max}$ . 3480, 3370,  $cm^{-1}$ ; and 2-p-nitrophenylperimidine<sup>108</sup> (3.5%).

1-Azido-8-p-methoxybenzamidonaphthalene gave 9-amino-2-p-methoxyphenyl-naphth [1,2-d] oxazole (27.5%), colourless crystals, m.p. 161-162° (Found: C, 74.8; H, 5.0; N, 9.9.  $C_{18}H_{14}N_2O_2$  requires: C, 74.5; H, 4.9; N, 9.7%),  $\nu_{\max}$ . 3470, 3358  $cm^{-1}$ . and 2-p-methoxyphenylperimidine<sup>108</sup> (10.5%).

1-Acetamido-8-azidonaphthalene gave 9-amino-2-methylnaphth [1,2-d] oxazole (13.5%), colourless solid, m.p. 78° (lit.<sup>105</sup> 78°) and 2-methylperimidine<sup>109</sup> (37%).

1-Azido-8-propionamidonaphthalene gave 9-amino-2-ethylnaphth [1,2-d] oxazole (7%), as a colourless oil,  $\nu_{\max}$ . 3470, 3365  $cm^{-1}$  (satisfactory analysis was not obtained); and 2-ethylperimidine (18%).

1-Azido-8-benzamidonaphthalene pyrolysed at a low temperature (110°) gave only 9-amino-2-phenyl-naphth [1,2-d] oxazole (20%).

Pyrolysis of m-azidoacetanilide, m-azidobenzanilide, 6-azido-1-benzamidonaphthalene and 1-acetamido-3-azidonaphthalene gave substantial amounts of recovered azide. Prolonged heating gave no trace of amino oxazoles, giving instead some amido amines (t.l.c.) together with much polymeric material.

1-(NN-Diacetylamino)-8-azidonaphthalene gave, on elution with 30% ether-petroleum, 1,2-diacetyl-1,2-dihydrobenz[cd]indazole (7%), needles, m.p. 110-111° after sublimation, (Found: C, 69.6; H, 5.15; N, 12.2.  $C_{14}H_{12}N_2O_2$  requires: C, 70.0; H, 5.1; N, 11.7%);  $\nu_{\max}$  1700  $cm^{-1}$  (C=O);  $\tau$  2.3-2.8 (m, 6H, aromatic), 7.6 (s, 6H, Me); m/e 240, 225, 198, 197.

1-(N-Acetyl-N-methylamino)-8-azidonaphthalene gave, on elution with 30% ether-petroleum, 1-acetyl-2-methyl-1,2-dihydrobenz[cd]indazole (17.5%), prisms, m.p. 84-85° after sublimation, (Found: C, 73.8; H, 6.0; N, 13.45.  $C_{13}H_{12}N_2O$  requires: C, 73.55; H, 5.7; N, 13.2%);  $\nu_{\max}$  1660  $cm^{-1}$  (C=O);  $\tau$  2.4-3.5 (m, 6H, aromatic), 6.8 (s, 3H, N.Me), 7.6 (s, 3H, MeCO); m/e 212, 170, 169, 155, 140, 127, 126.

1-Azido-8-phthalimidonaphthalene gave 12H-isoindolino[2,1-a]perimid-12-one (32) (32%), orange crystals, m.p. and mixed m.p. 229-230°. Similar pyrolysis in triglyme gave the perimidine (60%).

1-Azido-8-succinimidonaphthalene gave 10H-pyrrolino[2,1-a]perimid-10-one (34) (10%).

1-Azido-8-maleimidonaphthalene gave 10H-pyrrolidino[2,1-a]perimid-10-one (2%).

1-Amino-8-azidonaphthalene (500 mg.) in dry 1,2,4-trichlorobenzene was added to refluxing 1,2,4-trichlorobenzene. After 5 min. the mixture was cooled and a dark polymeric solid (230 mg.) separated and was filtered off. The filtrate was extracted with dilute

hydrochloric acid and the acid layer was basified and re-extracted with ether to give 1,8-diaminonaphthalene (150 mg., 35%) as a colourless oil. Distillation, followed by crystallisation from petroleum gave needles, m.p. and mixed m.p. 62-63°. No other tractable products were isolated from the trichlorobenzene layer after evaporation under reduced pressure.

1,8-Diazidonaphthalene in trichlorobenzene gave 1,8-diaminonaphthalene (13%).

1,8-Diazidonaphthalene pyrolysed in refluxing mesitylene gave 1,8-diaminonaphthalene (14%). (No 1-(2,4,6-trimethylphenyl)naphthalene could be detected by t.l.c.).

o-Azidophenyl benzoate gave o-benzamidophenol (18%) which crystallised from ethanol as colourless needles m.p. 169° (lit.,<sup>120</sup> 169-171°).  $\nu_{\max}$  3405 (NH), 3000 (broad, OH) and 1640  $\text{cm}^{-1}$  (C=O);  $\tau$  0.55 (s, 1H), 0.75 (s, 1H), 2.0-3.5 (m, 9H, aromatic H),  $m/e$  213 ( $m/e$  required 213).

Pyrolysis in N-sulphinylaniline. — Pyrolyses were carried out by addition of the azides to refluxing N-sulphinylaniline. After 5 min. the mixtures were cooled and excess N-sulphinylaniline was removed by distillation under reduced pressure. The residues were extracted with chloroform and the products separated by chromatography on silica gel.

Phenylazide gave, on elution with 20% ether-petroleum, azobenzene (33.5%), m.p. 67-68°, mixed m.p. 67-68°, (lit., 68° for trans, 71° for cis).

p-Chlorophenyl azide gave, on elution with 1% ether-petroleum, p-chloroazobenzene (14.5%), vacuum sublimation gave orange prisms m.p. 85-86° (lit.,<sup>121</sup> m.p. 88-89°). (Found: C, 66.5; H, 4.1; N, 12.95. Calculated for  $\text{C}_{12}\text{H}_9\text{N}_2\text{Cl}$  C, 66.65; H, 4.15; N, 12.9%);  $\nu_{\max}$  1482,

1375, 1149, 1086, 1005, 840, 762, 710, 681  $\text{cm.}^{-1}$ ;  $m/e$  216, 139, 111.

p-Methoxyphenyl azide gave, on elution with 1% ether-petroleum p-methoxyazobenzene (17.5%), vacuum sublimation gave orange prisms  $m.p.$  55-56°; (Found: C, 73.4; H, 5.5; N, 13.4.  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$  requires: C, 73.55; H, 5.7; N, 13.2%);  $\nu_{\text{max}}$ . 1600, 1500, 1250, 1140, 1030, 838, 762, 720, 686  $\text{cm.}^{-1}$ ;  $\tau$  1.95-3.2 (m, 9H, aromatic H), 6.25 (s, 3H,  $\text{OCH}_3$ );  $m/e$  212, 135, 107. Elution with 5% ether-petroleum gave p-dimethoxyazobenzene (24.5%)  $m.p.$  161-2°, (lit.,<sup>122</sup>  $m.p.$  158°), (Found: C, 69.05; H, 5.9; N, 11.75; Calculated for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$  C, 69.4; H, 5.85; N, 11.55%);  $\nu_{\text{max}}$ . 1590, 1495, 1250, 1142, 1022, 842, 740  $\text{cm.}^{-1}$ ;  $\tau$  2.1 (d, 4H,  $J=5\text{c.p.s.}$ , aromatic H) 2.95 (d, 4H,  $J=5\text{c.p.s.}$ , aromatic H), 6.15 (s, 6H,  $\text{OCH}_3$ );  $m/e$  242, 135, 107.

(b) Pyrolysis of azides on silica — Pyrolyses were carried out by adsorption of the azide on to dry, pure precipitated silica and heating to 215° with constant agitation for 10min. Continuous extraction of the cooled silica with ether gave the products which were purified and separated by chromatography on silica gel.

1-Azido-8-phthalimidonaphthalene gave 12H-isoindolino[2,1-a]-perimid-12-one (99%).

1-Azido-8-succinimidonaphthalene gave 10H-pyrrolino[2,1-a]-perimid-10-one (56%).

1-Azido-8-benzamidonaphthalene gave 9-amino-2-phenylnaphth-[1,2-d]oxazole (<1%) and 2-phenylperimidine (65%).

1-(N-Acetyl-N-methylamino)-8-azidonaphthalene gave 1-acetyl-2-methyl-1,2-dihydrobenz[cd]indazole (<1%).

1-Amino-8-azidonaphthalene gave 1,8-diaminonaphthalene (7%).

(c) Vapour phase pyrolyses.—These were carried out by vacuum sublimation (0.2–0.4 mm.) of the azides through a 10" pyrex tube maintained at 350°. Products condensed on the cold part of the sublimation tube and on a cold trap.

1-Amino-8-azidonaphthalene gave a mixture of dihydrobenz-[cd]indazole (70%), identical to that obtained by hydrolysis of dimethyl 1,2-dihydrobenz[cd]indazole-1,2-dicarboxylate.

1-Azido-8-benzamidonaphthalene gave 9-amino-2-phenylnaphth[1,2-d]-oxazole (28%) and 2-phenylperimidine (13%).

1-Azido-8-phthalimidonaphthalene gave 12H-isoindolino[2,1-a]-perimid-12-one in variable yield (ca. 20%) together with several other unidentified minor products.

(d) Pyrolyses on fusion— The azides were heated to 10° above their melting point for 10 min. The residue was extracted with chloroform and the products separated by chromatography on silica gel.

1-Azido-8-benzamidonaphthalene gave 9-amino-2-phenylnaphth-[1,2-d]oxazole (11%) and 2-phenylperimidine (22%).

1-Azido-8-p-methoxybenzamidonaphthalene gave 9-amino-2-p-methoxyphenylnaphth[1,2-d]oxazole (17%) and 2-p-methoxyphenylperimidine (23%).

6-Azido-1-benzamidonaphthalene gave 6-amino-1-benzamidonaphthalene (9%).

(e) Decomposition by acid catalysis.— m-Azidobenzanilide (200 mg.) in chloroform (5 ml.) was added to conc. sulphuric acid (5 ml.) and the mixture was stirred until gas evolution ceased (ca. 10 min.). The reaction mixture was then poured into an excess of ice-water, neutralised with 2N ammonium hydroxide solution and extracted with chloroform. The extracts were dried and evaporated on to silica

gel for chromatography. Elution with 95% ether-petroleum gave 5-amino-2-phenylbenzoxazole (85 mg., 49%), identical with an authentic specimen.

1-Azido-3-methoxyphenylbenzanilide gave on elution with 90% ether-petroleum 5-amino-2-*p*-methoxyphenylbenzoxazole (35%).

Similar treatment of 1-azido-8-benzamidonaphthalene gave only a trace of 9-amino-2-phenylnaphthoxazole (t.l.c.), and *m*-azidoacetanilide, 1-acetamido-3- and 1-benzamido-6-azidonaphthalenes gave no trace of amino oxazoles.

*m*-Azidoacetanilide (400 mg.) in ethanol (4 ml.) and concentrated hydrochloric acid (1 ml.) was heated under reflux for 1 hr. The reaction mixture was worked up as above to give *m*-azidoaniline (75%).

Similar treatment of 1-azido-8-benzamidonaphthalene gave 1-amino-8-azidonaphthalene (20%).

(f) Photolysis of azides.—1-Azido-8-phthalimidonaphthalene (0.5 mmole) in benzene (100 ml.) was irradiated at 16° for 20 hr. with a Hanovia 100 W medium pressure lamp surrounded by a pyrex jacket. The resulting solution was concentrated and poured into petroleum to give a precipitate probably containing 12H-isoindolino-[2,1-a]perimid-12-one-7-oxide which decomposed on heating to give the perimidine and other unidentified products. A satisfactory analysis was not obtained for this N-oxide,  $\bar{\nu}_{\max}$  1720, 1580, 1375, 1262, 1105, 760, 715  $\text{cm}^{-1}$ .  $m/e$  286, 270 ( $\text{C}_{18}\text{H}_{10}\text{N}_2\text{O}_2$ ,  $m/e$  286).

Similar photolysis of 1-azido-8-benzamidonaphthalene gave, after chromatography on silica gel, 9-amino-2-phenylnaphth[1,2-*d*]oxazole (2%) and 2-phenylperimidine (16.5%). Control experiments showed that 9-amino-2-phenylnaphth[1,2-*d*]oxazole and 2-phenylperimidine were recovered after photolysis for 20 hr. in benzene in (90%) and (85%) yield, respectively.

Similar photolysis of phenyl azide and N-sulphinylaniline in hexane gave azobenzene (1%). p-Chlorophenyl azide and p-methoxyphenyl azide gave p-chloroazobenzene (1%) and p-methoxyazobenzene (1%) respectively.

### 3. Preparation of Nitro Compounds.

Monoreduction of 1,3-dinitronaphthalene. — 1,3-Dinitronaphthalene was reduced with sodium sulphide and the mixed nitro amines were separated as their acetyl derivatives by the method of Hodgson and Turner<sup>111</sup> to give 1-acetamido-3-nitronaphthalene (36%) m.p. 259-260° (lit.,<sup>111</sup> 259°);  $\tau$  0.4 (s, 1H, NH), 2.0-3.4 (m, 6H, aromatic H), 4.7 (s, 2H, NH<sub>2</sub>), 7.85 (s, 3H, COCH<sub>3</sub>); and 1,3-diacetamidonaphthalene (12%) m.p. 259-260° (lit.,<sup>123</sup> 263-265°);  $\tau$  0.15 (broad s, 2H, NH), 1.9-3.4 (m, 6H, aromatic H), 7.75 (s, 6H, COCH<sub>3</sub>). Treatment of 1-acetamido-3-nitronaphthalene with 50% sulphuric acid and ethanol (1:1) gave 1-amino-3-nitronaphthalene (78%) m.p. 133-135° (lit.,<sup>111</sup> 135°).

Monoreduction of 1,6-dinitronaphthalene. — 1-Amino-6-nitronaphthalene was prepared by monoreduction of 1,6-dinitronaphthalene using the method of Hodgson and Turner.<sup>111</sup> The reducing agent was prepared by passing hydrogen chloride into a hot solution of stannous chloride in glacial acetic acid.

1-Benzamido-8-nitronaphthalene. — Treatment of 1-amino-8-nitronaphthalene in pyridine with a small excess of benzoyl chloride gave 1-benzamido-8-nitronaphthalene (68%) m.p. 181-182° (lit.,<sup>112</sup> 181°) (pale yellow needles from ethanol).

Similar treatment of 1-amino-3-nitronaphthalene and 1-amino-6-nitronaphthalene gave respectively 1-benzamido-3-nitronaphthalene (72%) m.p. 218-219° (lit.,<sup>113</sup> 220°) (pale yellow prisms from ethanol) and 1-benzamido-6-nitronaphthalene (60%) m.p. 218-22° (pale yellow needles from ethanol); (Found C, 69.4; H, 4.05; N, 9.7

$C_{17}H_{12}N_2O_3$  requires: C, 69.85; H, 4.15; N, 9.6%);  $\nu_{\max}$ . 3220 and 1638  $\text{cm}^{-1}$

1-Benzamido-8-nitrosonaphthalene.— Zinc dust (1.2g.) was added over 5min. to a vigorously stirred solution of 1-benzamido-6-nitronaphthalene (750 mg., 25mmole) and ammonium chloride (500 mg.) in water (10 ml.) and ethanol (10 ml.) at 20°. The mixture was heated to 55° for 30min. After cooling to 0° the insoluble material was filtered off and the residue was washed with hot water (10ml.). The filtrate and washings were combined and cooled to 0° by the addition of ice. Sulphuric acid (2.2ml.) was added carefully followed by ice to cool the reaction mixture to -5°. An ice-cold solution of sodium dichromate (600 mg.) in water (2.5ml.) was added to the reaction mixture which was stirred for 15min. The precipitate was filtered off and washed with brine (20% w/w) and dried in a desiccator in the dark to give 1-benzamido-8-nitrosonaphthalene as fawn prisms m.p. 146-148° (decomp.)  $\nu_{\max}$ . 3300, 1665, 1550, 1537, 1310, 1268, 815, 753, 705  $\text{cm}^{-1}$ . The rapid decomposition of 1-benzamido-8-nitrosonaphthalene to polymeric material in air and light made satisfactory analysis impossible.

1-Phthalimido-8-nitronaphthalene.— Treatment of 1-amino-8-nitronaphthalene with phthalic anhydride in hot glacial acetic acid gave 1-phthalimido-8-nitronaphthalene<sup>114</sup> (85%).

1-(N-Acetyl-N-methylamino)-8-nitronaphthalene. — Sodium hydride (100mg., 50% dispersion in oil) was added to 1-acetamido-8-azidonaphthalene (460mg., 2mmole) in dry dimethylformamide (5ml.) Dimethyl sulphate (270mg.) was added and the mixture was stirred for 1hr. and then poured into water. The precipitate was filtered off and washed well with water and crystallised from benzene-petroleum

to give pale yellow needles of 1-(N-acetyl-N-methylamino)-8-nitronaphthalene (35%), m.p. 135-136°; (Found: C, 63.6; H, 4.7; N, 11.8.  $C_{13}H_{12}N_2O_3$  requires: C, 63.9; H, 4.95; N, 11.45%);  $\nu_{\max}$  1645  $cm^{-1}$ ;  $\tau$  1.75-2.9 (m, 6H, aromatic H), 6.8 (s, 3H,  $CH_3$ ), 8.25 (s, 3H,  $COCH_3$ ).

#### 4. Deoxygenations of Nitro Compounds with Triethyl Phosphite. —

The nitro compounds were heated under reflux in triethyl phosphite in an atmosphere of nitrogen. Triethyl phosphite was then removed by distillation under reduced pressure and the residue was chromatographed on silica gel.

1-Benzamido-8-nitronaphthalene after 18hr. gave 9-amino-2-phenylnaphth[1,2 d]oxazole (1%) and 2-phenylperimidine (5%). Control experiments showed that 9-amino-2-phenylnaphth[1,2 d]oxazole and 2-phenylperimidine were recovered after refluxing for 18hr. in triethyl phosphite in (48%) and (44%) yield, respectively.

1-(N-Acetyl-N-methylamino)-8-nitronaphthalene gave after 3hr. 1-acetyl-2-methyl-1,2-dihydrobenz[cd]indazole (15%). A control experiment showed that 1-acetyl-2-methyl-1,2-dihydrobenz[cd]indazole was recovered after refluxing for 3hr. in triethyl phosphite in (72%) yield.

8-Nitro-1-phthalimidonaphthalene after 3hr. gave a precipitate of 12H-isoindolino[2,1-a]perimid-12-one (90%). The residue after evaporation of triethyl phosphite gave more perimidine (98% in all).

#### 5. Miscellaneous Reactions.

2-Phenylnaphth[1,2d]oxazole. — The dibenzoyl derivative of 1-amino-2-naphthol <sup>115</sup> (2g., 5.5 mmole) was added to a refluxing mixture of 10% aqueous sodium hydroxide (50ml) and ethanol (45ml). After refluxing for 1hr. the reaction mixture was cooled and dilute aqueous hydrochloric acid was added slowly until the slurry was just acid to litmus. Dilute aqueous sodium carbonate solution

was added with vigorous agitation until the precipitate just disappeared. The solution was extracted with ether (2 x 50ml.) and the organic layer washed with water and dried over anhydrous magnesium sulphate. The solvent was removed by distillation under reduced pressure and the residue was heated at the melt at 260° for 30 min. Sublimation under reduced pressure gave 2-phenylnaphth[1,2-d]oxazole (300 mg., 23%) which was crystallised from methanol-water as colourless needles m.p. 131-132° (lit.,<sup>110</sup> 131°).

Deamination of 9-Amino-2-phenylnaphth[1,2-d]oxazole. — Sodium nitrite (50mg.) was added to an ice-cold suspension of 9-amino-2-phenylnaphth[1,2-d]oxazole in 5N hydrochloric acid. After 15 min., the filtered solution was poured into aqueous sodium fluoroborate (350mg., in 5ml.) and the resulting diazonium fluoroborate was filtered off and dissolved in dimethylformamide (3ml.). This solution was added to a solution of sodium borohydride (1 g.) in dimethylformamide (5ml.) at 0° and after 5 min. the mixture was poured into ice and dilute hydrochloric acid. The precipitate was collected, washed with a little water, dried and sublimed to give 2-phenylnaphth[1,2-d]oxazole (37%), crystals, m.p. and mixed m.p. 130-131° identical with an authentic specimen.<sup>110</sup>

Similar deamination of 9-amino-2-methylnaphth[1,2-d]oxazole gave 2-methylnaphth[1,2-d]oxazole (20%), identical with an authentic specimen.<sup>116</sup>

Chromatography of naphtho[1,8-cd][1,2,6]thiadiazine. — Naphtho[1,8-cd][1,2,6]thiadiazine was prepared by the method of Beecken<sup>117</sup> (54%, m.p. 138-140°, lit.,<sup>117</sup> 142.5-144°). The thiadiazine in carbon tetrachloride solution was adsorbed on to a neutral alumina column. Elution with ether gave 1,8-diaminonaphthalene (70%) identical with

an authentic sample. Similar adsorption followed by elution with acetone gave 2,2-dimethyl-1,3-dihydroperimidine (86%) m.p. 116-117° (Found: C, 78.6; H, 7.0; N, 14.3.  $C_{13}H_{14}N_2$  requires: C, 78.75; H, 7.1; N, 14.15%);  $\nu_{\max}$ . 3350, 3280  $cm^{-1}$  (N-H);  $\tau$  2.7-3.8 (m, 6H aromatic H), 6.1 (broad s, 2H, NH), 8.75 (s, 6H,  $CH_3$ ). m/e 198, 183, 182 ( $-CH_4$ ). 1,8-Diaminonaphthalene was adsorbed on to neutral alumina. Elution with acetone gave an identical sample of 2,2-dimethyl-1,3-dihydroperimidine (76%).

Attempted preparation of the phthaloyl derivative of 1,8-diaminonaphthalene (14a).

1,8-Diaminonaphthalene (7.9g., 50mmole) and diethyl phthalate (11.1g., 50mmole) were stirred in dimethylformamide (25ml.) at 0-5° for 20 min. Sodium hydride (4.8g., 50% oil dispersion, 100mmole) was added to the solution and the mixture was heated on a steam bath for 1hr. Addition of dilute hydrochloric acid (125 ml.) gave 1,2-di(perimidin-2-yl)benzene which crystallised as orange prisms from dimethylformamide-water, m.p. 300° (decomp.) (Found: C, 81.0; H, 4.6; N, 13.2.  $C_{28}H_{18}N_4$  requires: C, 81.95; H, 4.4; N, 13.85%);  $\nu_{\max}$ . 1635, 1600, 1382, 1345, 1285, 1032, 830, 772, 718 and 700  $cm^{-1}$ ; m/e 410, 242. (m/e required 410).

5-Amino-2-phenylbenzoxazole. — The 2,4-dinitrophenylester of benzoic acid (1.0g., 3.5mmole) was suspended in acetic acid (20ml.) and a solution of stannous chloride (8g.) in hydrochloric acid (20ml.) was added dropwise; the mixture was then stirred at room temperature for 4hr. The mixture was basified by slow addition of aqueous sodium hydroxide solution, keeping the temperature below 30°, and then extracted with ether (2x50ml.). The ether layer was dried over anhydrous sodium sulphate and then evaporated to give 5-amino-2-phenylbenzoxazole (600mg., 83%) which crystallised from ethanol as colourless needles m.p. 150-151° (lit.,<sup>129</sup> 151-152°).

5-Amino-2(4-methoxyphenyl)benzoxazole.— The 2,4-dinitrophenyl ester of anisic acid was reduced in a similar manner to give 5-amino-2(4-methoxyphenyl)benzoxazole (35%) which sublimed under reduced pressure as colourless needles m.p. 146-147°. (Found: C, 69.8; H, 4.9; N, 11.95.  $C_{14}H_{12}N_2O_2$  requires: C, 70.0; H, 5.05; N, 11.65%);  $\nu_{\max}$ . 3430, 3310 ( $NH_2$ )  $cm^{-1}$

2-Phenylbenzoxazole. — Reduction of o-nitrobenzamidobenzene in a similar manner, followed by heating under reflux for 30 min., gave 2-phenylbenzoxazole (87%) which sublimed as colourless needles m.p. 101° (lit.,<sup>118</sup> 101°).

3-Aminobenzanilide.— 3-Azidobenzanilide (1.4g., 5.9mmole) and sodium borohydride (50mg.) in isopropyl alcohol were heated under reflux for 2hr. The solvent was removed by distillation under reduced pressure and the residue partitioned between methylene chloride and water. The organic layer was separated, dried over anhydrous magnesium sulphate, and removed by distillation under reduced pressure to give 3-aminobenzanilide (1.0g., 87%) which crystallised from ethanol as colourless needles m.p. 123-124° (lit., 125°).

3-Amino-p-methoxybenzanilide. — A similar reduction of 3-azido-p-methoxybenzanilide gave 3-amino-p-methoxybenzanilide (77%) which crystallised from ethanol as colourless needles m.p. 101-102°.

1-Benzamido-8-hydroxylaminonaphthalene.— Zinc dust (500mg.) was added to a solution of 1-benzamido-8-nitronaphthalene (205mg., 0.7mmole) and ammonium chloride (500mg.) in water (2ml.) and ethanol (2ml.) and the mixture was stirred for 15min. The unreacted zinc was filtered off to give a solution of 1-benzamido-8-hydroxylaminonaphthalene, (positive test with Tollens reagent).

6. Synthesis of 1,3- and 1,5-Dihydrobenz[cd]indazoles. --

(a) From Dimethyl 1,2-Dihydrobenz[cd]indazole-1,2-dicarboxylate.

A mixture of dimethyl 1,2-dihydrobenz[cd]indazole-1,2-dicarboxylate (500 mg.) and 0.5M ethanolic sodium hydroxide solution (10ml.) was allowed to stand for 3hr. under nitrogen. The resulting purple solution was poured into water (250ml.) and extracted with ether (3x75 ml.). The combined ether extracts were dried ( $MgSO_4$ ) and evaporated to give a mixture of 1,3- and 1,5-dihydrobenzindazoles (71mg., 40%). Sublimation followed by crystallisation from benzene gave needles m.p. 156-158° (sealed tube) (Found C, 77.2; H, 5.2; N, 17.4.  $C_{10}H_8N_2$  requires C, 76.9; H, 5.15; N, 17.95%).

(b) From 5,8-Dihydro-1-naphthylamine. -- Reduction of 1-naphthylamine

in xylene with sodium ethoxide using the method of Pheninger and his co-workers gave 5,8-dihydro-1-naphthylamine hydrochloride.<sup>119</sup> Treatment with acetic anhydride in warm benzene gave 5,8-dihydro-1-acetamidonaphthalene m.p. 161-162° (lit.,<sup>119</sup> 164°).

(i) 5,8-Dihydro-1-naphthylamine hydrochloride (5g., 0.0275 mole) was suspended in acetic acid (50ml.) and amyl nitrite (4ml., 0.0295 mole) was added during 10 min. while keeping the temperature as low as possible. After a further 10 min., cold ether (400 ml. -20°) was added to give a precipitate of the diazonium chloride. The ether was decanted and a solution of triethylamine (2g.) and acetic acid (1.2g.) in chloroform (200ml.), cooled to -20°, was added to the diazonium chloride. The mixture was then allowed to stand in the dark under nitrogen at room temperature for 15hr. The solvent was evaporated and the residue was extracted with 2N hydrochloric acid (2x50 ml.). The acid extracts were neutralised with sodium carbonate and re-extracted with ether.

After drying, evaporation gave an identical mixture of 1,3- and 1,5-dihydrobenzindazoles (12%) (after sublimation).

(ii) 5,8-Dihydro-1-acetamidonaphthalene (5g.) was dissolved in hot acetic anhydride (50ml.) which was then cooled to give a suspension. Dry nitrosyl chloride was passed into the suspension, maintained at 0-5°, until a clear solution was obtained. This was poured into ice-water (500 ml.) to give an oil which solidified to a pale yellow solid after washing with water. This solid was dissolved in benzene (50 ml.) and after drying ( $MgSO_4$ ), the solution was refluxed for 1hr. under nitrogen. The benzene was then evaporated and the residue treated as above to give a mixture of 1,3- and 1,5-dihydrobenzindazoles (11%).

Separation of 1,3- and 1,5-Dihydrobenz[cd]indazoles. — This was carried out by preparative t.l.c. on silica gel under nitrogen. The plate was eluted three times with ether to give a good separation. The separated isomers, in their order of elution, had the following characteristics:-

m.p. 148-151° (decomp)  $\nu_{max.}$  3160  $cm.^{-1}$  (broad NH);  $\lambda_{max.}$  323 (shoulder) ( $\log. \epsilon$  3.81), 310 (3.88), 225 (4.20)  $m\mu$ ;  $\tau$  1.0 (broad s, 1H, NH), 2.5-4.0 (m, 5H, aromatic and vinylic H), 6.1 (broad unresolved m, 2H, allylic H); m/e 156, 155, 128, 127.  
 m.p. 153-156° (decomp.);  $\nu_{max.}$  3160  $cm.^{-1}$  (broad NH);  $\lambda_{max.}$  337 ( $\log. \epsilon$  3.67), 323 (3.76), 311 (3.6), 298 (3.46), 287 (3.34), 225 (3.93)  $m\mu$ ;  $\tau$  0.85 (broad s, 1H, NH), 2.5-4.0 (m, 5H, aromatic and vinylic H) 6.1 (broad unresolved m, 2H, allylic H); m/e 156, 155, 128, 127.

Dihydrobenzindazoles refers to the mixture of 1,3- and 1,5-dihydro-isomers obtained by sublimation of the crude reaction product.

Dimethyl 1,2-Dihydrobenz [cd]indazole-1,2-dicarboxylate.— Methyl chloroformate (310mg., 3.3mmole) in methylene chloride (2.5 ml.) was added dropwise below 5° to a mixture of dihydrobenzindazoles (250 mg., 1.6mmole) and triethylamine (350 mg., 3.5mmole) in methylene chloride (5ml.). The reaction mixture was allowed to warm up to room temperature and to stand for 1.5hr. Evaporation gave a residue which was subjected to preparative t.l.c. on silica gel. Elution with 1:1 ether-petroleum gave dimethyl 1,2-dihydrobenz [cd]indazole-1,2-dicarboxylate (25%) m.p. and mixed m.p. 128-130°. (lit.,<sup>1</sup> 131-132°).

2,3-(1,8-Naphtho)phthalaz-1,4-dione. — A mixture of dihydrobenz [cd]indazoles (135 mg.) and phthaloyl chloride (177 mg.) was maintained at 100° for 1hr. The resulting mixture was chromatographed on silica gel. Elution with 30% ether-petroleum gave 2,3-(1,8-naphtho)phthalaz-1,4-dione (20%), pale yellow needles from ether-petroleum, m.p. 239-240°. (Found: C, 74.8; H, 3.4; N, 9.1.  $C_{18}H_{10}N_2O_2$  requires C, 75.5; H, 3.5; N, 9.8%);  $\nu_{\max}$ . 1670 (C=O), m/e 286 (m/e required 286).

Benzoylation of Dihydrobenz [cd]indazoles. — Benzoyl chloride (150 mg.) was added to a solution of dihydrobenzindazoles (150 mg.) in methylene chloride containing a little pyridine. After 2hr., evaporation, followed by preparative t.l.c. of the residue, gave on elution with 1:1 ether-petroleum 1-benzoyl-1,3(5)dihydrobenz [cd]indazole (20%). This was a single homogeneous product (t.l.c.) m.p. 116-117° (from ether) (Found: C, 78.3; H, 5.00; N, 10.9  $C_{17}H_{12}N_2O$  requires C, 78.45; H, 4.65; N, 10.75%);  $\nu_{\max}$ . 1679 (C=O), m/e 260 (m/e required 260).

Phenacylation of Dihydrobenz [cd]indazoles. — Phenacyl bromide (2.4g., 0.012 mole) in benzene (10ml.) was added dropwise at room

temperature to a mixture of dihydrobenzindazoles (936 mg., 0.006 mole) in benzene (35 ml.) containing pyridine (316 mg.). After 30 min. pyridine hydrobromide was filtered off and the benzene solution was washed with dilute hydrochloric acid to remove unreacted indazoles. Evaporation gave a residue which was chromatographed on silica gel. Elution with 1:1 ether-petroleum gave 1-phenacyl-1,3(5)-dihydrobenz[cd]indazole (17%). This was a single homogeneous product (t.l.c.), plates m.p. 136-137° (from ether-petroleum). (Found: C, 78.2; H, 5.6; N, 10.3.  $C_{18}H_{14}N_2O$  requires C, 78.8; H, 5.15; N, 10.2%);  $\nu_{max}$ . 1685 (C=O);  $\tau$  1.85-4.15 (m, 10H, aromatic and vinylic H), 4.4 (s, 2H, N-CH<sub>2</sub>-CO Ph), 6.25 (broad unresolved m, 2H, allylic H); m/e 274 (m/e required 274).

Diphenylacetylation of Dihydrobenz[cd]indazoles. — Excess of diphenylketene (3mmole) was added to a mixture of dihydrobenzindazoles (156 mg., 1mmole) in methylene chloride. After 3hr. the resulting solution was evaporated onto silica gel for chromatography. Elution with 25% ether-petroleum gave, as a single homogeneous product (t.l.c.), 1-(diphenylacetyl)-1,3(5)dihydrobenz[cd]indazole 203 mg. (50%) cubes from ether-petroleum m.p. 164-166°. (Found: C, 82.2; H, 5.7; N, 7.7.  $C_{24}H_{18}N_2O$  requires C, 82.25; H, 5.2; N, 8.0%);  $\nu_{max}$ . 1695  $cm^{-1}$  (C=O);  $\tau$  1.75-4.0 (m, 16H, aromatic and vinylic H), 6.15 (broad s, 2H, allylic H), m/e 350 (m/e required 350).

Benzylation of Dihydrobenz[cd]indazoles. — A slight excess of benzylbromide (260 mg., 2.2mmole) was added to a mixture of dihydrobenz[cd]indazoles (312 mg., 2.0mmole) in ethanol (5ml.) at 0°. After 1hr. at 20° and 1hr. at 45° the resulting solution was evaporated onto silica gel for chromatography. Elution with 25% ether-petroleum gave, as a single homogeneous product (t.l.c.)

1-benzyl-1,3(5)dihydrobenz[cd]indazole. 10 mg. (4%) cubes from ether m.p. 124-125°. (Unsatisfactory analysis);  $\nu_{\text{max}}$  1641, 1610, 1490, 1350, 1155, 800, 735  $\text{cm.}^{-1}$ ;  $\tau$  2.5-3.45 (m, 10H, aromatic and vinylic H) 4.55 (s, 2H,  $\text{CH}_2\text{-Ph}$ ), 6.2 (broad unresolved m, 2H, allylic H).

1 - Benzoyl-2-methoxycarbonyl-1,3(5)dihydrobenz[cd]indazole.— Methyl chloroformate (250 mg., 2.65 mmole) in methylene chloride (2 ml.) was added dropwise at 0° to a mixture of 1-benzoyl-1,3(5)dihydrobenz[cd]indazole (262 mg., 1.0 mmole) and triethylamine (101 mg., 1.0 mmole) in methylene chloride (15 ml.). The reaction mixture was allowed to warm to room temperature and to stand for 15hr. Evaporation gave a residue which was subjected to preparative t.l.c. on silica gel. Elution with 1:1 ether-petroleum gave 1-benzoyl-2-methoxycarbonyl-1,3(5)dihydrobenz[cd]indazole (21%), vacuum sublimation gave colourless needles m.p. 114-115°;  $\nu_{\text{max}}$  1750 ( $\text{CO}_2\text{CH}_3$ ), 1698  $\text{cm.}^{-1}$  (COPh);  $\tau$  1.8-3.7 (m, 11H, aromatic H), 6.2 (s, 3H,  $\text{CO}_2\text{CH}_3$ ); m/e 318, 223 (-PhCO) (m/e required 318); no satisfactory analysis was obtained due to decomposition to a blue polymeric substance even on standing at 0°.

#### 7. Oxidation of 1,2-Dihydrobenz[cd]indazole.

(a) With lead tetra-acetate.— Lead tetra-acetate (910 mg., 2.05 mmole) was added all at once to a mixture of dihydrobenz[cd]indazoles in methylene chloride at -70°. After stirring for  $\frac{1}{2}$  min., diphenylketene (500 mg., 2.5 mmole) was added and the reaction mixture allowed to warm to 20° and to stand for 15hr. The lead salts were filtered off and the resulting solution was evaporated onto silica gel for chromatography. Elution with 70% ether-petroleum gave an unidentified substance (150mg.) which crystallised as mauve prisms from ether-petroleum m.p. 295° (decomp.); (Found: C, 80.9;

H, 5.65; N, 6.6.  $C_{24}H_{18}N_2O$  requires: C, 82.25; H, 5.2; N, 8.0%);  
 $\nu_{\max}$ . 1700, 1490, 1445, 1370, 1330, 1155, 1110, 800, 745, 695  
 $cm.^{-1}$ ;  $\tau$  2.0-3.1 (m); m/e 350, 320, 232.

Oxidation of dihydrobenzindazoles with lead tetra-acetate in the presence of tetracyclone and 2,3-dimethylbutadiene gave only intractable tars and oils.

(b) With t-butylhypochlorite. — t-Butylhypochlorite (1.1 mmole) was added to a solution at  $-60^\circ$  of dihydrobenzindazoles (156 mg., 1 mmole) in methylene chloride (5.ml.). The reaction mixture was allowed to warm to room temperature and to stand for 15hr. The resulting solution was evaporated on to alumina for chromatography. Elution with 25% ether-petroleum gave an amorphous yellow powder 50 mg., m.p. 159-165°. Elution with 35% ether-petroleum gave an unidentified substance which crystallised from ether-petroleum as yellow plates, (8 mg.) m.p. 117-119°;  $\nu_{\max}$ . 3450, 1625, 1500, 1340, 1115, 950, 910, 792, 735  $cm.^{-1}$ ; m/e 230, 229, 199.

(c) Other oxidising agents. — Oxidation of dihydrobenzindazoles with manganese dioxide, silver oxide, mercuric oxide, N-bromo-succinimide and N-chlorosuccinimide, with and without traps, gave only intractable tars and oils.

#### 8. Deoxygenation of Benz[cd]indazole 1,2-dioxide and Benz[cd]indazole 1-oxide.

Benz[cd]indazole 1,2-dioxide and benz[cd]indazole 1-oxide were prepared by oxidation of 1,8-diaminonaphthalene with m-chloroperbenzoic acid, rather than p-nitroperbenzoic acid, but otherwise using the method of Alder, Naizi and Whiting.<sup>128</sup>

#### Reduction of benz[cd]indazole 1,2-dioxide to the monoxide. —

A solution of benz [cd]indazole 1,2-dioxide (186 mg., 1mmole) in benzene (5 ml.) was heated under reflux for 2hr. A little insoluble polymeric

material was filtered off and the solution evaporated on to alumina for chromatography. Elution with chloroform gave benz[cd]indazole 1-oxide (108 mg., 64%) identical to an authentic specimen.

(a) With phosphorus trichloride. — Phosphorus trichloride (408mg., 3mmole) was added to a solution below 5° of benz[cd]indazole 1-oxide (101 mg., 0.6mmole) and diphenylketene (1g.) in methylene chloride (3 ml.). A trace of polymeric material was filtered off and the solution evaporated on to silica gel for chromatography. Elution with ether gave an unidentified mauve substance (29 mg.) which crystallised from ether-petroleum as mauve prisms m.p. 209–210°, (Found: C, 78.3; H, 4.7; N, 3.7%);  $\nu_{\text{max}}$  1695, 1680, 1380, 1145, 1035, 807, 730, 700  $\text{cm.}^{-1}$ ; m/e 516, 322.

Deoxygenation of benz[cd]indazole 1-oxide with phosphorus trichloride alone and in the presence of 2,3-dimethylbutadiene gave intractable tars and oils.

(b) With other deoxygenating agents. — Deoxygenation of benz[cd]indazole 1-oxide with dichlorocarbene, triethyl phosphite and stannous chloride with and without the presence of traps gave only intractable tars and oils.

ATTEMPTED PREPARATION OF BENZ[cd]INDOLE AND ITS DERIVATIVES.1. Preparation and Decomposition of Methyl 8-Azido-1-naphthoate.

8-Amino-1-naphthoic acid.— Naphthostyryl (1.69g., 10mmole) in 2N aqueous sodium hydroxide solution (50ml.) was heated on a steam bath for 5hr. After cooling, the solution was neutralized to pH 7.0 by careful addition of 2N hydrochloric acid, with external cooling to keep the temperature at about 10°. The precipitate was filtered off and washed with brine (20% w/w) and dried in a desiccator to give 8-amino-1-naphthoic acid (1.3g., 69%)

Methyl 8-Amino-1-naphthoate.— A solution of diazomethane in ether was added dropwise at 0° to a suspension of 8-amino-1-naphthoic acid (1.1g., 6mmole) in ether (20ml.) until no more gas was evolved. The mixture was stirred for 30min. allowing the temperature to rise to 20°. Unreacted 8-amino-1-naphthoic acid was removed by filtration and the solvent was evaporated under reduced pressure to leave methyl 8-amino-1-naphthoate (1.15g., 98%) which crystallised from ethanol as pale yellow needles m.p. 89–90°. (Found C, 71.3; H, 5.3; N, 6.85.  $C_{12}H_{11}NO_2$  requires: C, 71.6; H, 5.5; N, 6.95%);  $\nu_{max}$  3430, 3350 and 1690  $cm^{-1}$ ;  $m/e$  201, ( $m/e$  required 201).

Methyl 8-Azido-1-naphthoate.— Sodium nitrite (260mg., 3.8mmole) in water (2ml.) was added dropwise at 0° to methyl 8-amino-1-naphthoate (702mg., 3.5mmole) in 2N hydrochloric acid (20ml.) and the mixture was stirred for 20min. Sodium azide (1g.) in water (5ml.) was added dropwise over 15min. to the diazonium solution at 0° and the precipitate was filtered off, washed well with water, and dried in a desiccator under reduced pressure to give methyl 8-azido-1-naphthoate (670 mg., 85%) which crystallised

from ether-petroleum as colourless prisms m.p. 77-78°, (Found: C, 64.2; H, 3.95; N, 18.1.  $C_{12}H_9N_3O_2$  requires: C, 63.45; H, 4.0; N, 18.5%);  $\nu_{\max}$ . 2120 ( $N_3$ ) and 1725  $cm^{-1}$  ( $CO_2CH_3$ ).

Decomposition of Methyl 8-Azido-1-naphthoate.

(a) By photolysis. — Methyl 8-azido-1-naphthoate (227mg.) in benzene (100ml.,  $10^{-2}M$  solution) was irradiated at 20° for 15hr. using a pyrex Hanovia medium pressure lamp. The solvent was evaporated on to silica gel for chromatography. Elution with 10% ether-petroleum gave naphtholactam-0-methyl ether (5mg.) as red needles, m.p. 103-104°;  $\nu_{\max}$ . 1630, 1432, 1280, 1200, 1045, 832, 800, 770  $cm^{-1}$ ; m/e 183, 154, 128.

(b) By pyrolysis. — Methyl 8-azido-1-naphthoate (227mg., 1mmole) in 1,2,4-trichlorobenzene (2ml.) was added to refluxing 1,2,4-trichlorobenzene (10ml.) and heated under reflux for a further 5min. The solvent was removed by distillation under reduced pressure and the residue was extracted with warm chloroform (2x5ml.), which was evaporated on to silica gel for chromatography. Elution with 10% ether-petroleum gave red needles of 8,8'-methoxy-carbonyl-1,1'-azonaphthalene (12mg., 6%), (Found: C, 72.15; H, 4.4; N, 7.25.  $C_{24}H_{18}N_2O_4$  requires: C, 72.35; H, 4.55; N, 7.05%);  $\nu_{\max}$ . 1725 (C=O), 1432, 1280, 1200, 832, 800, 768  $cm^{-1}$ , m/e 398, 339, 213, 185, (m/e required 398).

2. Deoxygenation of 8-Nitro-1-naphthylmethylketone and Methyl

8-Nitro-1-naphthoate with Triethyl Phosphite.

Methyl 8-nitro-1-naphthoate. — 1-Naphthoic acid was nitrated by the method of Rule and Barnett<sup>124</sup> and converted into the ester by the method of Koelsch and Hoffmann.<sup>125</sup> Methyl 8-nitro-1-naphthoate (507mg., 2.2mmole) was heated under reflux in triethyl phosphite in an atmosphere of nitrogen for 2hr. The excess of

triethylphosphite was removed by distillation under reduced pressure. The residue was extracted with warm chloroform (2 x 15ml.) and evaporated on to silica gel for chromatography. Elution with 1% ethanol-ether gave naphthostyryl (30mg., 8%) m.p. 180-181° (lit., 181°), having an identical i.r. spectrum to that of an authentic sample. Elution with 5% ethanol-ether gave diethyl N-(1-methoxycarbonyl-8-naphthyl)phosphoramidate (25mg., 3%) as colourless needles m.p. 151-152°, (Found: C, 56.8; H, 6.1; N, 4.25.  $C_{16}H_{20}NO_5P$  requires: C, 56.9; H, 5.95; N, 4.5%);  $\nu_{\max}$ . 3150, 1710, 1450, 1230, 1020, 1000, 965, 790, 762  $cm^{-1}$ ; m/e 337, 309, 281, 263. (m/e required 337).

8-Nitro-1-naphthylmethylketone. — 1-Naphthylamine was nitrated by the method of Derkosch and Spiteller <sup>126</sup> to give a mixture of 8-nitro and 5-nitro-1-naphthylmethylketone. The 8-nitro-1-naphthylmethylketone was separated by fractional crystallisation from glacial acetic acid to give pale yellow needles, m.p. 130-131°, (lit., <sup>126</sup> 130°). Deoxygenation of 8-nitro-1-naphthylmethylketone with triethyl phosphite gave intractable material.

### 3. Preparation of 1,2-Dihydrobenz[cd]indole.

Lithium aluminium hydride (50mg., 13mmole) was added to a solution of naphthostyryl (1g., 5.9mmole) in dioxane (20ml.) at 50-60°. After stirring for 15min. at this temperature the reaction mixture was cooled and water (5ml.) was carefully added. The resulting mixture was poured into 2N sodium hydroxide solution and extracted with ether (2x25 ml.). The combined extracts were washed well with water, dried over anhydrous magnesium sulphate, and evaporated under reduced pressure to give 1,2-dihydrobenz[cd]indole, which sublimed under vacuum as colourless prisms, m.p. 80° (decomp.) having identical i.r. spectra to an authentic

sample<sup>127</sup>;  $\tau$  2.3-3.1 (m, 5H, aromatic H), 3.65 (d, 1H,  $J=3.5$  c.p.s.,  $C_8H$ ), 5.25 (s, 2H,  $CH_2$ ), 5.85 (broad s, 1H, NH).

4. Oxidation of 1,2-Dihydrobenz[cd]indole with Manganese Dioxide.

(a) In benzene. — Dry freshly prepared manganese dioxide (5g.) in dry benzene (50ml.) was heated under reflux in a Dean and Stark apparatus for 1hr. to remove any traces of moisture. 1,2-Dihydrobenz[cd]indole (420mg., 2.7mmole) in dry benzene (5ml.) was added and the mixture was heated under reflux in the Dean and Stark apparatus for 2hr. The insoluble material was removed by filtration and the benzene solution evaporated on to silica gel for chromatography. Elution with 35% ether-petroleum gave di-2-benz[cd]indolyl ether (40mg., 9%) which crystallised from ethanol as red needles, m.p. 284-285°, (Found: C, 82.0; H, 3.6; N, 8.8.  $C_{22}H_{12}N_2O$  requires: C, 82.5; H, 3.8; N, 8.75%);  $\nu_{max}$ . 1655, 1370, 1310, 1248, 1098, 832, 760  $cm^{-1}$ ; m/e 320, 292, 264, 146. Elution with 50% ether-petroleum gave N-(2-benz[cd]indolyl)-naphthostyryl (65mg., 15%) which crystallised from ether-petroleum as straw-coloured needles m.p. 232-233°, (Found: C, 82.7; H, 3.9; N, 8.6.  $C_{22}H_{12}N_2O$  requires: C, 82.5; H, 3.8; N, 8.75%);  $\nu_{max}$ . 1730, 1472, 1450, 1382, 1330, 1260, 1170, 1060, 822, 762  $cm^{-1}$ ; m/e 320, 292, 264, 146. Elution with 1% ethanol-ether gave naphthostyryl (60mg., 13%) m.p. 179-180°.

Manganese dioxide (5g.) and benzene (50ml.) were thoroughly dried by the method used above. 1,2-Dihydrobenz[cd]indole (420mg., 2.7mmole) in dry benzene (5ml.) was added immediately followed by dry methanol (10ml.) and the mixture heated under reflux for 2hr. The insoluble material was filtered off and the solution evaporated onto silica gel for chromatography. Elution with 35% ether-petroleum gave di-2-benz[cd]indolyl ether (2%) m.p. 284-285°.

Elution with 50% ether-petroleum gave N-(2-benz[cd]indolyl)-naphthostyryl (7%) m.p. 230-232°. Elution with 1% ethanol-ether gave naphthostyryl (100 mg., 22%) m.p. 178-179°.

(b) In methanol. — A mixture of 1,2-dihydrobenz[cd]indole (420 mg., 2.7mmole), freshly prepared dry manganese dioxide (5g.), anhydrous magnesium sulphate (5g.) in anhydrous methanol was heated under reflux for 12hr. with rapid agitation. The insoluble material was filtered off and the methanol solution was evaporated onto silica gel for chromatography. Elution with 20% ether-petroleum gave an unidentified substance (20mg.) which crystallised from ether-petroleum as orange needles m.p. 157-158° (Found: C, 79.0; H, 3.8; N, 8.05.  $C_{22}H_{12}N_2O_2$  requires: C, 78.55; H, 3.6; N, 8.35%);  $\nu_{max}$ . 1510, 1490, 1395, 1350, 1222, 1085, 1000, 818, 790, 778, 761, 751  $cm^{-1}$ ; m/e 336, 321, 306. m/e required for  $C_{22}H_{12}N_2O_2$  336.

ROUTES TO AZABENZOCYCLOBUTADIENE.1. Preparation of Hydrazones.

o-Aminobenzaldehyde. — o-Nitrobenzaldehyde was reduced by the method of Mann and Wilkinson<sup>132</sup> to give o-aminobenzaldehyde which was purified by steam distillation to give pale-yellow leaflets m.p. 38–39° (lit.,<sup>132</sup> 39–40°).

o-Aminobenzaldehyde hydrazone.— o-Aminobenzaldehyde (1g., 8.25mmole) in ether (5ml.) was added dropwise to hydrazine hydrate (10ml.) at 10° with agitation. The mixture was then warmed to 45° allowing the ether to evaporate off. After 30min. at this temperature the reaction mixture was cooled to 15° and the precipitate of o-aminophenylketazine (25mg., 2%) m.p. 246–248° (lit.,<sup>133</sup> 248°) filtered off. The filtrate was poured into water (50ml.) and the precipitate filtered off, washed well with cold water and dried in a desiccator to give o-aminobenzaldehyde hydrazone (600 mg., 49%) which crystallised from benzene-petroleum as pale-yellow leaflets m.p. 59–60° (lit.,<sup>133</sup> 62°).

o-Aminoacetophenone-hydrazone. — o-Aminoacetophenone hydrochloride (1.5g., 11mmole) was added to glacial acetic acid (8ml.) and hydrazine hydrate (10ml.) and the mixture was heated under reflux for 1hr. After cooling the precipitate was filtered off to give o-aminophenylmethylketazine (25mg., 1%) which crystallised from ethanol as yellow leaflets m.p. 161–162°, (Found: C, 72.0; H, 7.0; N, 20.8.  $C_{16}H_{18}N_4$  requires: C, 72.15; H, 6.8; N, 21.05%);  $\nu_{\max}$  3350, 1610, 1580, 1250, 1357, 740  $cm^{-1}$ ; m/e 266, 251, 235, 133 (m/e required 266). The filtrate was poured into water (75ml.) and the product extracted with ether (2 x 20ml.). The ether solution was dried over anhydrous magnesium sulphate and the

solvent removed by distillation under reduced pressure to give *o*-aminoacetophenone hydrazone (1.2g., 73%) as a straw coloured oil. (Found C, 63.8; H, 7.2; N, 28.45. Calculated for  $C_8H_{11}N_3$  C, 64.4; H, 7.45; N, 28.15%);  $\nu_{\max}$ . 3340, 3380, 3290  $cm^{-1}$ ; m/e 149, 133, 118, 91, (m/e required 149).

*o*-Aminobenzophenone hydrazone.— Similar treatment of *o*-aminobenzophenone with hydrazine hydrate in glacial acetic acid gave *o*-aminobenzophenone hydrazone (62%), which crystallised from ethanol as colourless prisms m.p. 141–142°, (Found: C, 73.4; H, 6.0; N, 19.45.  $C_{13}H_{13}N_3$  requires: C, 73.9; H, 6.2; N, 19.9%);  $\nu_{\max}$ . 3450, 3360, 3270  $cm^{-1}$ ; m/e 211, 181, 165 (m/e required 211).

## 2. Oxidation of the Hydrazones with Lead Tetra-acetate.

*o*-Aminoacetophenone hydrazone. — Lead tetra-acetate (3.9g., 8.8mmole) was added to a stirred solution of *o*-aminoacetophenone hydrazone (596mg., 4mmole) in methylene chloride (30ml.) at 20°. (Some gas was evolved). After stirring for 2hr. the lead salts were filtered off and washed with methylene chloride (10ml.). The combined filtrate and washings were evaporated on to basic alumina for chromatography. Elution with 25% ether-petroleum gave a yellow oil (30mg.);  $\nu_{\max}$ . 1735, 1612, 1445, 1365, 1235, 1040, 750  $cm^{-1}$ ; m/e 177, 162, 148, 135, 120, 92. (No analysis was obtained). Elution with ether gave a yellow-orange oil (125mg.)  $\nu_{\max}$ . 3450, 3330, 1650, 1610, 1582, 1450, 1340, 1310, 1300, 1240, 1160, 950, 750  $cm^{-1}$ , m/e 234, 198, 180, 165, 152, 138. (No analysis was obtained). Elution with 2% ethanol-ether gave a dark brown amorphous powder (200 mg.) which decomposed on heating. (A recent examination of this oxidation<sup>134</sup> has shown

that elution with 50% ethyl acetate-ether gives 4-methylbenzo-1,2,3-triazine (35%). ).

Similar oxidations at lower temperatures in the absence and presence of cyclopentadiene gave only intractable tars and oils.

o-Aminobenzophenone hydrazone. — A similar oxidation of o-aminobenzophenone hydrazone with lead tetra-acetate, but with chromatography on silica gel, gave on elution with ether 4-phenylbenzo-1,2,3-triazine (72%) which crystallised from ethanol as colourless needles m.p. 155-156°, (Found: C, 75.5; H, 4.6; N, 20.25.  $C_{13}H_9N_3$  requires: C, 75.35; H, 4.4; N, 20.3%);  $\nu_{\max}$ . 1610, 1565, 1390, 1362, 930, 780, 704  $cm^{-1}$ ;  $\lambda_{\max}$ . 206 (log.  $\epsilon$  3.86), 232 (4.1), 293 (2.95)  $\mu$ ; m/e 207, 179, 152. (m/e required 207).

Similar oxidations in the presence and absence of cyclopentadiene at -30° gave 4-phenylbenzo-1,2,3-triazine in (86%) and (78%) yield respectively.

Oxidation of o-aminobenzophenone hydrazone with only 1 mole/mole of lead tetra-acetate gave 4-phenylbenzo-1,2,3-triazine (20%).

o-Aminobenzaldehyde hydrazone.— Oxidation at -30° of o-aminobenzaldehyde hydrazone with 2.2 mole/mole of lead tetra-acetate in methylene chloride gave only intractable material.

### 3. Oxidation of o-Aminobenzophenone hydrazone with Nickel Peroxide.

Nickel peroxide (400 mg.) was added to a solution of o-aminobenzophenone hydrazone (400 mg., 1.9mmole) in methylene chloride at 0° and the temperature allowed to warm to 20° and stirred for a further 48hr. The inorganic material was filtered off and washed with methylene chloride (5ml.). The filtrate and washings were combined and evaporated onto silica gel for chromatography. Elution with

70% ether-petroleum gave an unidentified substance (80mg.) which crystallised from ether-petroleum as yellow prisms m.p. 82-84°, (Found: C, 82.25; H, 6.4%);  $\nu_{\max}$  3360 (broad), 1618, 1600, 1580, 1500, 1450, 1310, 1250, 1155, 1025, 749, 698  $\text{cm.}^{-1}$ ; m/e 381, 364, 196. Elution with 85% ether-petroleum gave a mixture of the unidentified substance and *o*-aminobenzophenone hydrazone, (100mg.). Elution with 90% ether-petroleum gave a mixture of *o*-aminobenzophenone hydrazone and 4-phenylbenzo-1,2,3-triazine (100mg.). Elution with ether gave 4-phenylbenzo-1,2,3-triazine (78mg., 20%) m.p. 153-154°, mixed m.p. 153-154°.

#### 4. Preparation of Azides.

All the azides were prepared in a similar way. Sodium nitrite (665mg., 9.6mmole) in water (5ml.) was added dropwise to a solution at 0° of *o*-aminoacetophenone hydrochloride (1.51g., 9mmole) in 0.5N hydrochloric acid (20ml.) and the mixture was stirred for 15min. Sodium azide (1.14g., 17.5mmole) in water (10ml.) was added dropwise to the diazonium solution and the resulting mixture was extracted with ether (2 x 25ml.). The combined extracts were dried over anhydrous magnesium sulphate and the solvent was removed by distillation under reduced pressure to give *o*-azidoacetophenone (1.2g., 85%) as a straw coloured oil. (Found: C, 59.8; H, 4.45; N, 25.7. Calculated for  $\text{C}_8\text{H}_7\text{N}_3\text{O}$ : C, 59.6; H, 4.4; N, 26.1%);  $\nu_{\max}$  2120, 1680  $\text{cm.}^{-1}$ ; m/e 161, 133. (m/e required 161).

*o*-Aminobenzophenone gave *o*-azidobenzophenone (62%) as a straw coloured oil, (Found: C, 70.1; H, 4.0; N, 19.15. Calculated for  $\text{C}_{13}\text{H}_9\text{N}_3\text{O}$ : C, 69.95; H, 4.05; N, 18.85%);  $\nu_{\max}$  2120, 1665  $\text{cm.}^{-1}$ ; m/e 223, 195, 167. (m/e required 223).

o-Aminobenzaldehyde gave o-azidobenzaldehyde as straw coloured prisms from ether-petroleum m.p. 32-34° (lit.,<sup>135</sup> 37.5°), (35%).

o-Aminophenylmethylketazine gave o-azidophenylmethylketazine (45%) as a straw coloured oil. (Found: C, 60.8; H, 4.7; N, 34.3. C<sub>16</sub>H<sub>14</sub>N<sub>8</sub> requires: C, 60.35; H, 4.45; N, 35.2%),  $\nu_{\max}$  2120 cm.<sup>-1</sup>; m/e 318. (m/e required 318).

##### 5. Attempted preparation of the azidohydrazones.

o-Azidoacetophenone (1g., 5.7mmole) in glacial acetic acid (5ml.) and hydrazine hydrate (6ml.) was heated under reflux for 30min. The solution was cooled and poured into water (75ml.) and extracted with chloroform (2 x 20ml.). The chloroform extracts were washed well with water and dried over anhydrous magnesium sulphate. Evaporation under reduced pressure gave 3-methylindazole (80%) as pale-yellow needles m.p. 102-103°. Crystallisation from ether-petroleum gave colourless needles m.p. 108-109° (lit.,<sup>136</sup> 113°)  $\nu_{\max}$  3150 cm.<sup>-1</sup>;  $\lambda_{\max}$  218 (log E 3.96), 255 (3.57), 289 (3.74), 293 (3.73), 302 (3.71) $\mu$ ; m/e 132, (m/e required 132); picrate m.p. 197° (lit.,<sup>136</sup> m.p. 199°).

Similar treatment of o-azidophenylmethylketazine gave intractable material containing no 3-methylindazole (t.l.c.).

o-Azidobenzophenone was treated in glacial acetic acid with hydrazine hydrate in a similar manner to above, but with an increased reaction time of 10hr. The final extraction with ether gave 3-phenylindazole (92%), which crystallised from ether-petroleum as colourless needles m.p. 107-108°, (lit.,<sup>137</sup> 107-108°).

o-Azidobenzaldehyde was treated in glacial acetic acid with hydrazine hydrate in a similar manner, with a reaction time of 4hr.

The final extraction with chloroform gave indazole (87%) which crystallised from ether-petroleum as colourless needles m.p. 142-144°, mixed m.p. 143-145°, (lit., 146.5°).

6. Amination of Indazoles with Hydroxylamine-0-sulphonic acid.

3-Phenylindazole. — Ethanol was added to a stirred suspension of 3-phenylindazole (lg., 5.15mmole) in water (5ml.) at 60° until all the crystals had dissolved. Solid potassium hydroxide (4.0g.) was added followed by hydroxylamine-0-sulphonic acid<sup>104</sup> (4.0g.) at such a rate as to maintain the temperature between 55-60°. The solution was stirred at 60° for 20min. and the excess of ethanol was then removed by evaporation under reduced pressure. Just sufficient water was added to dissolve the precipitate of potassium sulphate and the solution was extracted with chloroform (3 x 20ml.). The combined extracts were washed well with water, dried over anhydrous sodium sulphate and evaporated onto alumina for chromatography. Elution with 90% methylene chloride-petroleum gave 2-amino-3-phenylindazole (80%) which crystallised from ether-petroleum as colourless needles m.p. 112-113°, (Found: C, 74.9; H, 5.3; N, 19.65.  $C_{13}H_{11}N_3$  requires: C, 74.6; H, 5.3; N, 20.1%);  $\bar{\nu}_{\max.}$  3330, 3180 ( $NH_2$ )  $cm^{-1}$ ;  $\lambda_{\max.}$  219 ( $\log \epsilon$  4.15); 249 (3.69); 312 (3.8)  $m\mu$ ;  $\tau$  2.4-3.4 (m, 9H, aromatic H), 3.85 (broad s, 2H,  $NH_2$ ); m/e 209, (m/e required 209). Anisylidene derivative, m.p. 126-127° (colourless needles from ethanol), (Found: C, 77.05; H, 5.3; N, 12.95.  $C_{21}H_{17}N_3O$  requires: C, 77.05; H, 5.25; N, 12.85%);  $\bar{\nu}_{\max.}$  1605, 1250, 1150, 1105, 1070, 1022, 952, 742  $cm^{-1}$ .

3-Methylindazole. — A similar amination of 3-methylindazole with hydroxylamine-0-sulphonic acid, gave on elution with

methylene chloride, 1-amino-3-methylindazole (45%), m.p. 116-117° (colourless needles from ether-petrol); (Found: C, 65.35; H, 6.2; N, 28.75.  $C_8H_9N_3$  requires C, 65.3; H, 6.15; N, 28.55%),  $\bar{\nu}_{\max}$ . 3310, 3280,  $(NH_2)$   $cm^{-1}$ ;  $\lambda_{\max}$ . 220 ( $\log \epsilon$  4.03), 258 (3.37), 300 (3.66) $\mu$ ;  $\tau$  2.4-3.2 (m, 4H, aromatic H), 4.7 (s, 2H,  $NH_2$ ), 7.6 (s, 3H,  $CH_3$ ); m/e 147, 132, 104. (m/e required 147). Anisylidene derivative, m.p. 102-103° (colourless needles from ethanol); (Found: C, 72.4; H, 5.85; N, 15.8;  $C_{16}H_{15}N_3O$  requires C, 72.45; H, 5.7; N, 15.85%);  $\bar{\nu}_{\max}$ . 1608, 1500, 1248, 1160, 1070, 1025, 830, 738  $cm^{-1}$ ; Elution with 15% ethyl acetate-methylene chloride gave 2-amino-3-methylindazole (30%), m.p. 154° (colourless plates from ether-petroleum); (Found: C, 65.1; H, 6.2; N, 28.4;  $C_8H_9N_3$  requires: C, 65.3; H, 6.15; N, 28.55%);  $\bar{\nu}_{\max}$ . 3300, 3160  $(NH_2)$   $cm^{-1}$ ;  $\lambda_{\max}$ . 220, ( $\log \epsilon$  4.0), 278 (3.4), 300 (3.5) $\mu$ ;  $\tau$  2.2-3.15 (m, 4H, aromatic H), 4.35 (s, 2H,  $NH_2$ ), 7.45 (s, 3H,  $CH_3$ ); m/e 147, 132, 117 (m/e required 147). Anisylidene derivative, m.p. 115-116° (colourless needles from ethanol); (Found: C, 72.3; H, 5.75; N, 15.7.  $C_{16}H_{15}N_3O$  requires: C, 72.45; H, 5.7; N, 15.85%);  $\bar{\nu}_{\max}$ . 1600, 1258, 1161, 1028, 832, 748  $cm^{-1}$ .

Indazole. — A similar amination of indazole gave 1-aminoindazole (50%) and 2-aminoindazole (33%), identical in all respects to authentic samples. <sup>138</sup>

3-Phenylindazole. — Amination with hydroxylamine-O-sulphonic acid at different temperatures and pH gave only the 2-amino-3-phenylindazole.

Amination of 3-phenylindazole with chloramine. —

3-Phenylindazole (lg., 5.15mmole) and sodium hydride (260 mg., 50% dispersion in oil, 5.2mmole) in ether (100ml.) were heated

under reflux for 15hr. A solution of chloramine in ether <sup>139</sup> (5.5mmole) was added at  $-10^{\circ}$  and the reaction mixture allowed to warm to  $20^{\circ}$  and to stand for 15hr. The sodium chloride was filtered off and the ether solution evaporated on to alumina for chromatography. Elution with 90% methylene chloride-petroleum gave 2-amino-3-phenylindazole (62%) m.p.  $113-115^{\circ}$ .

#### 7. Oxidation of the Aminoindazoles with Lead Tetra-acetate.

##### (a). In methylene chloride.

2-Amino-3-phenylindazole. — Lead tetra-acetate (2.54g., 5.75mmole) was added to a solution of 2-amino-3-phenylindazole (1g., 4.8mmole) in methylene chloride at  $20^{\circ}$ . After stirring for 1hr. the lead salts were removed by filtration and washed with a little methylene chloride (5ml.). The combined filtrate and washings were evaporated on to silica gel for chromatography. Elution gave 4-phenylbenzo-1,2,3-triazine (80%) m.p.  $153-154^{\circ}$ , mixed m.p.  $153-154^{\circ}$ .

1-Amino-3-methylindazole. — A similar oxidation of 1-amino-3-phenylindazole with lead tetra-acetate gave, on elution with 35% ethyl acetate-methylene chloride, 4-methylbenzo-1,2,3-triazine (71%), which sublimed under vacuum as colourless prisms, m. p.  $120-121^{\circ}$ ; (Found: C, 66.45; H, 5.05; N, 28.7.  $C_8H_7N_3$  requires: C, 66.2; H, 4.85; N, 28.95%);  $\nu_{\max.}$  1608, 1570, 1250, 1208, 1141, 1018, 916, 825, 800, 762, 711  $cm.^{-1}$ ;  $\lambda_{\max.}$  207 ( $\log \epsilon$  3.58), 227, (4.0), 275 (2.83) $\mu$ ;  $\tau$  1.45-2.2 (m, 4H, aromatic H), 6.95 (s, 3H,  $CH_3$ ); m/e 145, 117 (m/e required 145).

2-Amino-3-methylindazole. — A similar oxidation of 2-amino-3-methylindazole with lead tetra-acetate gave, on elution with 35% ethyl acetate-methylene chloride, 4-methylbenzo-1,2,3-triazine (60%)

m.p. 118-120°, mixed m.p. 118-120°.

1-Aminoindazole.— A similar oxidation of 1-aminoindazole (735mg., 5mmole) at -30° with lead tetra-acetate gave a brown oil (130mg.). Sublimation gave o-acetamidobenzaldehyde, 65 mg. (8%), identical to an authentic sample. Similarly 2-aminoindazole gave o-acetamidobenzaldehyde (5%).

(b) In dimethyl sulphoxide.

2-Amino-3-phenylindazole.— Lead tetra-acetate (2.54g., 5.75mmole) was added to a solution of 2-amino-3-phenylindazole (1g., 4.8mmole) in dimethyl sulphoxide (25ml.) at 20°. After stirring for 1hr. the mixture was poured into water (100ml.) and extracted with ether (3 x 25ml.). The combined extracts were washed well with water and dried over anhydrous magnesium sulphate. The ether solution was evaporated onto alumina for chromatography. Elution with (70%) ether-petroleum gave an unidentified substance (35mg.) which crystallised from ethanol as yellow needles m.p. 230-231°. (Found: C, 73.45; H, 4.4; N, 19.5%);  $\bar{\nu}_{\max}$  1370, 1305, 1290, 1222, 1146, 1111, 1065, 780, 768, 741, 698  $\text{cm.}^{-1}$ ; m/e 194, 193, 165, 149. Elution with ether gave 4-phenylbenzo-1,2,3-triazine (10%) m.p. 152-154°, mixed m.p. 151-153°.

1-Amino-3-methylindazole.— A similar oxidation of 1-amino-3-methylindazole (500mg., 3.4 mmole) in dimethyl sulphoxide gave on elution with 25% methylene chloride-petroleum an unidentified substance (40 mg.) as a yellow oil,  $\bar{\nu}_{\max}$  3450, 3330, 1610, 1580, 1480, 1449, 1358, 1290, 1240, 1160, 1022, 951, 749  $\text{cm.}^{-1}$ ; m/e 252, 209, 135. Elution with 50% ethyl acetate-petroleum gave 4-methylbenzo-1,2,3-triazine (10%), m.p. 118-120°, mixed m.p. 117-119°.

2-Amino-3-methylindazole. — A similar oxidation of 2-amino-3-methylindazole (400 mg. 2.7 mmole) in dimethyl sulphoxide gave on elution with 25% methylene chloride-petroleum an unidentified substance (10mg.) as a rapidly decomposing oil,

$\nu_{\max}$ . 2115, 1675, 1590, 1440, 1255, 1050, 800, 750  $\text{cm.}^{-1}$

Elution with 40% ethyl acetate-methylene chloride gave an unidentified substance (40 mg.) as a brown oil,  $\nu_{\max}$ .

1640, 1520, 1435, 1270, 1040, 949, 800, 749  $\text{cm.}^{-1}$

Elution with 5% ethanol-ethyl acetate gave an unidentified substance

(50 mg.) as a straw coloured oil,  $\nu_{\max}$ . 3005, 2920, 1620, 1305,

1360, 1210, 1150, 1116, 1030, 950, 821, 740, 686  $\text{cm.}^{-1}$ ;  $m/e$

223, 194, 177, 163, 149.

(c) In dimethylformamide.

1-Amino-3-methylindazole. — Lead tetra-acetate (1.25g., 2.8mmole) was added to a solution of 1-amino-3-methylindazole (294mg., 2.0mmole) in dimethylformamide (10ml.) and stirred for 2hr. The reaction mixture was drowned into water (50ml.) and extracted with ethyl acetate (2 x 25ml.). The combined extracts were washed well with water and dried over anhydrous magnesium sulphate. The ethyl acetate solution was evaporated on to silica gel for chromatography. Elution with 30% methylene chloride-petroleum gave an unidentified substance as a dark brown oil. Elution with 50% ethyl acetate-methylene chloride gave 4-methylbenzo-1,2,3-triazine (8%) m.p. 120-121°.

8. Decomposition of 4-Phenylbenzo-1,2,3-triazine.

4-Phenylbenzo-1,2,3-triazine (103mg., 0.5mmole) was pyrolysed in the vapour phase by sublimation through a quartz tube at 400° at 0.2mm. pressure. The products condensed on separate areas of

the cold portions of the tube to give biphenylene (6mg., 16%), m.p. 110°, (lit., 110°) having an identical i.r. spectrum to that of an authentic sample and benzonitrile (10mg., 20%) having an identical i.r. spectrum to that of an authentic sample.

Irradiation of 4-phenylbenzo-1,2,3-triazine in dry benzene for 24hr. at 20° using a Hanovia medium pressure quartz lamp gave recovered starting material (92%). A similar irradiation in acetonitrile gave only polymeric material.

#### 9. Preparation and Oxidation of 4-Hydrazinobenzo-1,2,3-triazine.

4-Hydrazinobenzo-1,2,3-triazine was prepared using a modification to the method of Parnell.<sup>140</sup> Hydrazine hydrate (3ml.) was added to a solution of 4-mercaptobenzo-1,2,3-triazine (1.63g., 1mmole) in ethanol (25ml.) and the mixture was stirred at room temperature for 48hr. The precipitate was filtered off and washed with a little ice-cold ethanol to give 4-hydrazinobenzo-1,2,3-triazine (82%) which crystallised from methanol as buff coloured needles, m.p. 185-186° (lit.,<sup>140</sup> 188°).

Oxidation with manganese dioxide. — Freshly prepared manganese dioxide (2.5g.) was added to 4-hydrazinobenzo-1,2,3-triazine (600mg., 3.75mmole) in benzene (50ml.) and the mixture stirred vigorously and heated under reflux for 5hr. The inorganic material was filtered off and washed with a little benzene. The combined filtrate and washings were evaporated on to silica gel for chromatography. Elution with ether-petroleum gave benzonitrile (110mg., 29%), having an identical i.r. spectrum to that of an authentic sample.

Oxidation with silver oxide. — The above treatment of 4-hydrazinobenzo-1,2,3-triazine was repeated using silver oxide

instead of manganese dioxide. Separation of the products by chromatography on silica gel gave benzonitrile (45mg., 12%) and on elution with 75% ether-petroleum gave an unidentified substance, which crystallised from ether-petroleum as yellow prisms, 12mg., m.p. 151°, (Found: C, 68.8; H, 5.9; N, 24.3%)  $\nu_{\text{max}}$  1520, 1410, 1315, 1240, 1050, 935, 815, 730, 690  $\text{cm}^{-1}$ . m/e 411, 310.

"5-NITRENO-1,4-DIPHENYL-1,2,3-TRIAZOLE".

1. Decomposition of 5-Azido-1,4-diphenyl-1,2,3-triazole.

5-Azido-1,4-diphenyl-1,2,3-triazole was prepared by the method of Smith, Krbecek and Resemann,<sup>130</sup> m.p. 70° (lit.,<sup>131</sup> 70°).

(a) In petrol. — A suspension of 5-azido-1,4-diphenyl-1,2,3-triazole (2g., 7.5mmole) in petroleum (150 ml., b.p. 60-80°) was heated under reflux for 2hr. Some insoluble material was removed from the hot petrol by filtration and the solvent was then removed by distillation under reduced pressure. The residue was crystallised from petroleum (b.p. 60-80°) to give compound A (1.4g., 80%) as dark red prisms m.p. 112-114°, (lit.,<sup>130</sup> 115-116°).

(b) In cyclohexene. — A similar decomposition of 1,4-diphenyl-5-azido-1,2,3-triazole in refluxing cyclohexene gave compound A (72%) as dark red prisms m.p. 114-115°.

(c) In dimethyl sulphoxide. — 5-Azido-1,4-diphenyl-1,2,3-triazole (524 mg., 2mmole) in dimethyl sulphoxide (5 ml.) was heated at 45-50° for 15hr. The solution was then poured into water (25 ml.) and extracted with chloroform (2 x 15 ml.). The chloroform solution was washed well with water, dried over anhydrous magnesium sulphate and evaporated on to silica gel for chromatography. Elution with 10% ether-petroleum gave compound A (28%) m.p. 112-114°. Elution with 95% ether-petroleum gave 5-amino-1,4-diphenyl-1,2,3-triazole (9%) m.p. 168-170° (lit.,<sup>131</sup> m.p. 169-171°) which had an identical i.r. spectrum to that of an authentic sample.

2. Oxidation of 5-Amino-1,4-diphenyl-1,2,3-triazole with Lead Tetra-acetate.

(a) In methylene chloride. — Lead tetra-acetate (2.8g., 6.4mmole) was added to a solution of 5-amino-1,4-diphenyl-1,2,3-

triazole (1g., 4.25mmole) in methylene chloride (20ml.) at 5-10°. (Some gas was evolved). After stirring for 1hr. the lead salts were removed by filtration and washed with a little methylene chloride (5ml.). The combined filtrate and washings were evaporated on to silica gel for chromatography. Elution with 10% ether-petroleum gave compound A (38%), m.p. 69-70°, mixed m.p. 69-70°. Elution with 35% ether-petroleum gave an unidentified substance as yellow prisms (2 mg.) m.p. 121-124°. Elution with 55% ether-petroleum gave azo-1,4-diphenyl-1,2,3-triazole (7%) which crystallised from ether-petroleum as red prisms m.p. 228-229°; (Found C, 71.4; H, 4.5.  $C_{28}H_{20}N_8$  requires: C, 71.8; H, 4.3%);  $\nu_{\max.}$  1590, 1540, 1490, 1362, 1070, 980, 765, 715, 690  $cm^{-1}$  m/e 468, 248 (m/e required 468). Elution with ether gave an unidentified substance (100 mg.) which crystallised from ether-petroleum as colourless needles m.p. 163-165°; (Found: C, 71.65; H, 5.3; N, 10.3);  $\nu_{\max.}$  3150, 1738, 1680, 1490, 1450, 1335, 1235, 1210, 960, 810, 720  $cm^{-1}$ ; m/e 266, 250, 161.

(b) In cyclohexene. — Lead tetra-acetate (2.8g., 6.3mmole) was added to a solution of 5-amino-1,4-diphenyl-1,2,3-triazole (1.0g., 4.25mmole) in methylene chloride (15ml.) and cyclohexene (15ml.) at 0°. The mixture was stirred for 1hr. at 0° and then 2hr. at 20°. The lead salts were filtered off and washed with methylene chloride (5ml.) and the combined filtrate and washings were dried over anhydrous magnesium sulphate and evaporated on to silica gel for chromatography. Elution with 10% ether-petroleum gave compound A (34%) m.p. 70-71°. Elution with 95% ether-petroleum gave an unidentified substance (30mg.) which crystallised from ethanol as colourless needles, m.p. 166-167°; (Found: C, 69.4;

H, 4.8; N, 5.0%);  $\nu_{\text{max}}$  1730, 1675, 1488, 1360, 1265, 1230, 962, 840, 768, 712, 700  $\text{cm}^{-1}$ ;  $m/e$  239, 225, 197.

(c) In methyl acrylate.— A similar oxidation to (b) above of 5-amino-1,4-diphenyl-1,2,3-triazole in methyl acrylate (10ml.) and methylene chloride (25ml.) gave on elution with 10% ether-petroleum compound A (40%). Elution with 95% ether-petroleum gave an unidentified substance (80mg.) which crystallised from ethanol as colourless needles m.p. 164-166°, and had an identical i.r. spectrum to the compound m.p. 166-167° isolated in (b) above.

(d) In dimethyl sulphoxide. — Lead tetra-acetate (2.9g., 6.5mmole) was added to 5-amino-1,4-diphenyl-1,2,3-triazole (1g., 4.25mmole) in dimethyl sulphoxide (10ml.) at 10° and stirred at 20° for 4hr. The reaction mixture was poured into water (100ml.) and extracted with chloroform (2 x 50ml.) The combined extracts were washed well with water, dried over anhydrous magnesium sulphate and evaporated to silica gel for chromatography. Elution with 10% ether-petroleum gave compound A (45%) m.p. 70-71°. Elution with 35% ether-petroleum gave an unidentified substance (10mg.). Crystallisation from ether-petroleum gave colourless needles m.p. 121-122°, (Found: C, 73.6; H, 4.45; N, 11.9%);  $\nu_{\text{max}}$  2225, 1725, 1490, 1280, 1260, 1065, 755, 725, 690  $\text{cm}^{-1}$ ;  $m/e$  222, 206, 197.

Attempted Preparation of 5-Acetamino-1,4-diphenyl-1,2,3-triazole.

Acetic anhydride (510mg., 5mmole) was added to a solution of 5-amino-1,4-diphenyl-1,2,3-triazole (1g., 4.25mmole) in pyridine (4ml.) and the mixture heated on a steam bath for 30min. After cooling the reaction mixture was poured into water (30ml.) and the precipitate filtered off and washed with water. Crystallisation

from ethanol gave 5-diacetylamino-1,4-diphenyl-1,2,3-triazole as colourless prisms, m.p. 176-177°; (Found: C, 67.0; H, 5.05; N, 17.2.  $C_{18}H_{16}N_4O_2$  requires: C, 67.5; H, 5.05; N, 17.5%);  $\nu_{\max}$ . 1740, 1720  $cm^{-1}$ ;  $\tau$  2.0-2.8 (m, 10H, aromatic H), 7.75 (s, 6H,  $COCH_3$ ); m/e 320, 250, 209, (m/e required 320).

Further attempts to mono-acetylate with acetic anhydride and acetyl chloride in pyridine and dilute sodium hydroxide solution gave only 5-diacetylamino-1,4-diphenyl-1,2,3-triazole.

### 3. Preparation of 1,4-Diphenyl-5-triphenylphosphinimino-1,2,3-triazole.

Triphenylphosphine (1g., 3.8mmole) was added to a solution of 5-azido-1,4-diphenyl-1,2,3-triazole (1g., 3.8mmole) in benzene (20 ml.) and the mixture was stirred for 1hr. at 20°. (Slow gas evolution). The mixture was then heated under reflux for 15min., cooled and the solvent removed by distillation under reduced pressure. The residue was crystallised from ethanol to give 1,4-diphenyl-5-triphenylphosphinimino-1,2,3-triazole (600 mg., 32%) as colourless needles, m.p. 208-209°; (Found: C, 77.15; H, 5.1; N, 11.5.  $C_{32}H_{25}N_4P$  requires: C, 77.4; H, 5.05; N, 11.3%);  $\nu_{\max}$ . 1598, 1550, 1495, 1262, 1110, 971, 722, 690  $cm^{-1}$ ; m/e 496, 468, 379, 288, 262, 234 (m/e required 496).

Irradiation of 1,4-diphenyl-5-triphenylphosphinimino-1,2,3-triazole in a quartz Hanovia medium pressure lamp for 15hr. at 20° in the absence and presence of cyclohexene gave only triphenylphosphine and triphenylphosphine oxide. No compound A was detected (t.l.c.).

A mixture of compound A and triphenylphosphine in benzene was heated under reflux for 15hr. There was no reaction and no

trace of 1,4-diphenyl-5-triphenylphosphinimino-1,2,3-triazole (t.l.c.).

#### 4. Reaction of Compound A with Amines.

(a) Diethylamine.— Diethylamine (4.0g., 5.5mmole) was added to a solution of compound A (1g., 4.8mmole) in benzene (20ml.) and the mixture stirred for 1hr. at 20°. The solvent was removed by distillation under reduced pressure. Crystallisation from ether gave an unidentified substance (175mg., 13%) as colourless prisms, m.p. 137–138°; (Found C, 72.0; H, 7.2; N, 17.75%);

$\nu_{\text{max}}$  3470, 3340, 1660, 1640, 1590, 1545, 1359, 1230, 1165, 1050, 825, 770, 709, 690  $\text{cm.}^{-1}$ ;  $\tau$  1.95–3.4 (m, 10H, aromatic H), 4.95 (broad s, 2H), 7.15 (q, 4H,  $J=4$  c.p.s.), 1.15 (t, 6H,  $J=6.5$  c.p.s.); m/e 306, 279, 264, 235. The ether filtrate from the

above crystallisation was adsorbed onto basic alumina for chromatography. Elution with 95% ether-petroleum gave an unidentified compound (500mg., 61%) which crystallised from ether-petroleum as yellow needles, m.p. 109–110°, (Found: C, 72.85; H, 7.4; N, 19.9%);

$\nu_{\text{max}}$  1540, 1420, 1345, 1195, 1110, 985, 915, 770, 690  $\text{cm.}^{-1}$ ;

$\tau$  2.3–2.95 (m, 10H, aromatic H), 6.15 (q, 2H,  $J=5$  c.p.s.), 6.85 (q, 2H,  $J=5$  c.p.s.), 8.35–9.15 (overlapping t, 6H); m/e 193, 164, 136, 121.

(b) Aniline. — Aniline (3.7g., 4.0mmole) and compound A (702mg., 3mmole) in benzene (25ml.) were heated under reflux for 10hr. The solution was evaporated on to basic alumina for chromatography. Elution with 10% ether-petroleum gave phenylglyoxylonitrile anil (60%) which crystallised from ether-petroleum as pale-yellow prisms, m.p. 69–70°, (lit.,<sup>130</sup> 71°). Elution with 1% ethyl acetate-ether gave an unidentified substance contaminated with

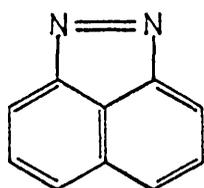
aniline. The aniline was removed by washing with ether and crystallisation from ethanol gave pale-yellow prisms (50mg., 6%), m.p. 163-164°; (Found: C, 70.9; H, 5.2; N, 17.3%);  $\nu_{\text{max}}$  1530, 1462, 1420, 1095, 1065, 750, 690  $\text{cm.}^{-1}$ ; m/e 299, 270, 271, 195, 194.

D I S C U S S I O N   O F   R E S U L T S.

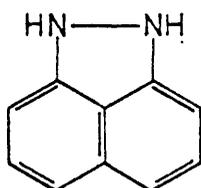
## Section I.

PREPARATION OF DIHYDROBENZ[cd]INDAZOLE AND ITS  
DERIVATIVES AND ATTEMPTED PREPARATION OF  
BENZ[cd]INDAZOLE.

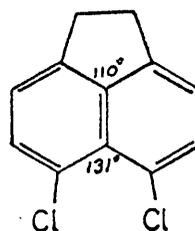
Benz[cd]indazole (1), the aza analogue of acenaphthylene, is of interest to us as an example of a simple, yet unreported, heterocyclic system. Its thermolysis or photolysis might lead to different electronic states of the meta-dehydroaromatic species, 1,8-dehydronaphthalene. There are only a few references in the literature to benz[cd]indazole and its dihydroderivatives. Peri-substituted naphthalene compounds have been reviewed by



(1)



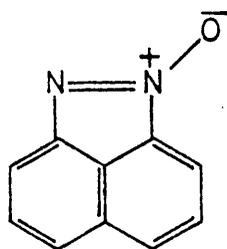
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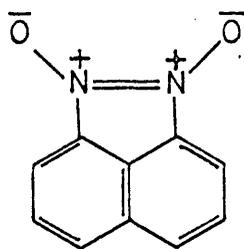
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Balasubramaniyan<sup>141</sup> and it would appear that the strain in such molecules as (1) and (2) might not be prohibitive. In some acenaphthene derivatives the distortion of the naphthalene nucleus can be considerable; e.g. 5,6-dichloroacenaphthene (3).

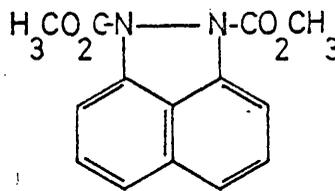
Ekstrand<sup>142</sup> first suggested a benz[cd]indazole type of structure as a possibility for a product of partial reduction of 4,5-dinitro-1-naphthoic acid. However the only authenticated



(4)



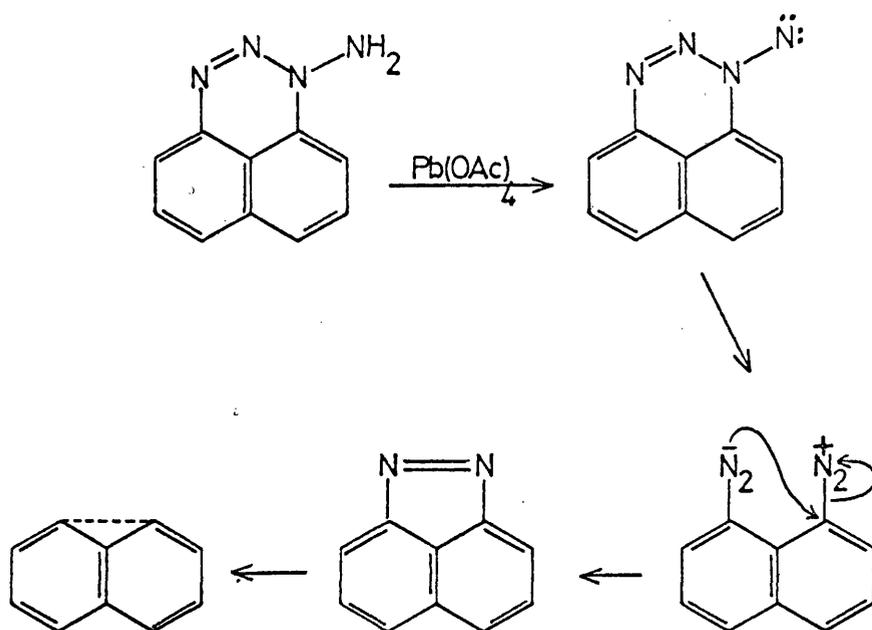
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(6)

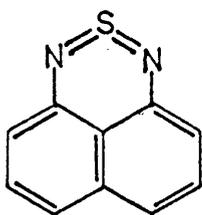
examples of the benz[cd]indazole system are of the mono and di-N-oxides (4) and (5) very recently reported by Alder, Niazi

and Whiting.<sup>128</sup> The N-oxides were obtained from pyrolysis of 1-azido-8-nitronaphthalene and from peracid oxidation of 1,8-diaminonaphthalene. A 1,2-disubstituted dihydrobenz[cd]indazole derivative was formed on addition of 1,8-dehydronaphthalene to dimethyl azodicarboxylate to give dimethyl dihydrobenzindazole-dicarboxylate (6) in low yield.<sup>1</sup> The dehydro intermediate was generated by oxidation of 1-aminonaphtho[1,8 deltriazine with lead tetra-acetate. The loss of nitrogen may be concerted or stepwise via benz[cd]indazole.

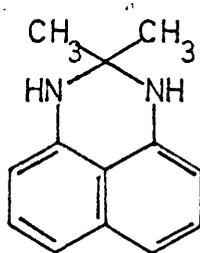


1,2-Dihydrobenz[cd]indazole has been reported by Vorozhtsov and Koslov<sup>143</sup> in the hydrogen sulphide-ammonia reduction of 1,8-dinitronaphthalene in aniline. However considerable doubt exists about the exact nature of the product they obtained. We were unable to repeat the Russian work and Hoffmann<sup>144</sup> has also been unable to repeat this reaction and he also reports that other routes involving reduction of 1,8-dinitronaphthalene failed.

Beecken,<sup>145</sup> however, claimed to have obtained a product which was identical to that reported by Vorozhtsov and Koslov, by eluting (7) with acetone <sup>from</sup> neutral alumina. We repeated Beecken's experiment and obtained a product identical in all respects to that reported by Beecken. However, the n.m.r. spectrum showed the presence of two methyl groups. Analysis of this product was consistent with the structure of 2,2-dimethyl-1,3-dihydroperimidine (8). This product was obtained by elution with



(7)

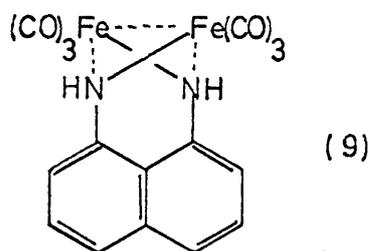


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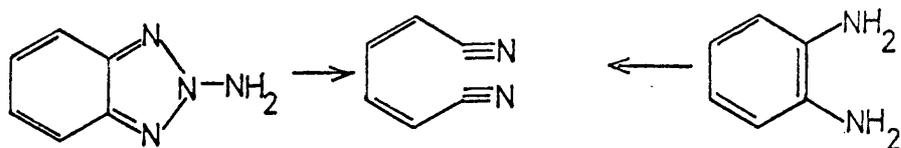
acetone from neutral alumina. However, we found that 1,8-diaminonaphthalene was always the primary product in Beecken's reaction in the absence of acetone. Adsorption of 1,8-diaminonaphthalene on neutral alumina and elution with acetone gives the perimidine (8) in very good yield. Since the dimethyldihydroperimidine (8) is formed rapidly from 1,8-diaminonaphthalene and acetone it would seem that Beecken's product almost certainly arose in this way. This has been confirmed independently by Hoffmann.<sup>144</sup>

Other attempts to prepare benz[cd]indazole have been reported, but without success. Recently an attempt to prepare (1) by reduction of 1,8-dinitronaphthalene with carbon monoxide and iron pentacarbonyl (reagents which normally give very good yields of

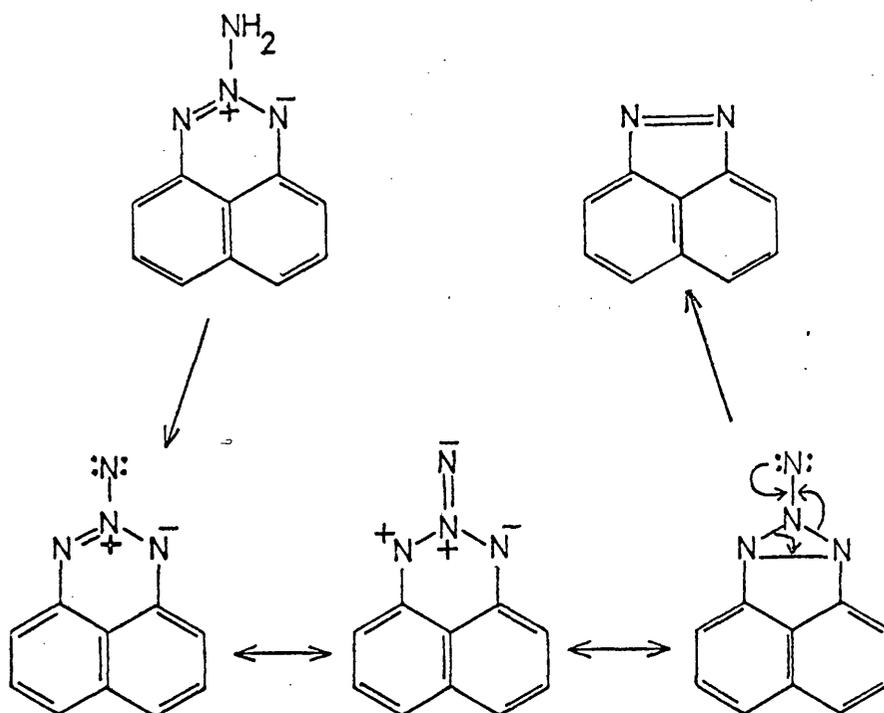
azo compounds) failed.<sup>146</sup> The action of iron pentacarbonyl on 1-amino-8-azidonaphthalene and 1,8-diazidonaphthalene gave the complex (9).<sup>147</sup> A similar complex prepared from 2,2'-diazido-biphenyl gave a good yield (70%) of benzo[c]cinnoline on oxidation with ferric chloride, but a similar oxidation of the complex (9) failed to give benz[cd]indazole.<sup>148</sup>



Oxidation of 2-aminobenzotriazole<sup>75</sup> leads to the loss of only one molecule of nitrogen leaving the other two nitrogen atoms in the form of a ring opened dicyano compound. A similar oxidation of the appropriate diamino compound gives the same dicyano compound.<sup>25</sup> It was thought<sup>105</sup> that benz[cd]indazole

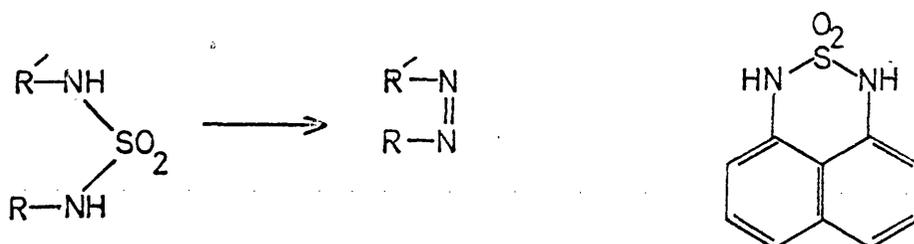


could be a product in the oxidation of 2-aminonaphtho[de]triazine with lead tetra-acetate, since loss of one molecule of nitrogen could not lead to a dicyano compound. However although nitrogen was evolved no characterisable product was isolated. Similar oxidations of 1,8-diaminonaphthalene and 1-amino-8-azidonaphthalene



were found to give intractable material. Oxidation of 2,2'-diaminodiphenyl with manganese dioxide gave benzo[c]cinnoline in 55% yield,<sup>150</sup> but a similar oxidation of 1,8-diaminonaphthalene gave only 8,8'-diamino-1,1'-azonaphthalene.<sup>151</sup>

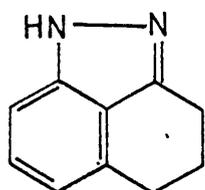
Dialkyl sulphamides have been found to give azoalkanes in good yield on oxidation with aqueous sodium hypochlorite in sodium hydroxide.<sup>152</sup> However a similar oxidation of naphtho-[1,8-cd][1,2,6]thiadiazine-2,2-dioxide (10) by Forster<sup>133</sup> in an



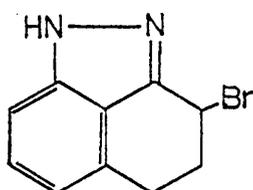
(10)

attempt to form benz[cd]indazole gave only polymeric products.

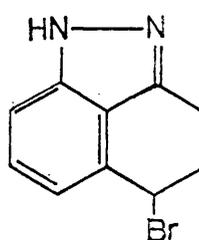
The indazole (11) was prepared by the method of Vesely from N-nitroso-1-acetylamino-tetralin.<sup>153</sup> Previous attempts at dehydrogenation with 1,2-dichloro-4,5-dicyanobenzoquinone and oxidation with N-bromosuccinimide and lead tetra-acetate had been unsuccessful.<sup>150</sup>



(11)



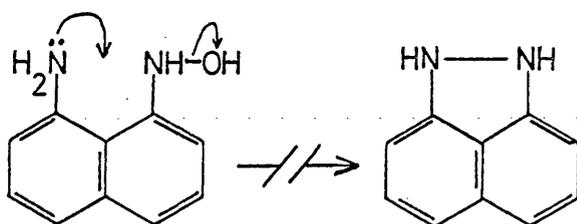
(12)



(13)

Our attempts at dehydrogenation gave no dihydrobenz[cd]indazole. Crystallisation of the residue from ethanol gave a small amount of a substance, m.p. 195-199°, which showed two spots on t.l.c. but could not be separated on chromatography. The infrared spectrum showed NH and the mass spectrum gave a molecular weight of 237 showing the incorporation of bromine. This indicated the material was possibly a mixture of brominated indazoles with structures such as (12) and (13).

Reduction of 1-amino-8-nitronaphthalene with zinc and ammonium chloride gave a solution of 1-amino-8-hydroxylamino-naphthalene. However cyclodehydration attempts with acid failed to

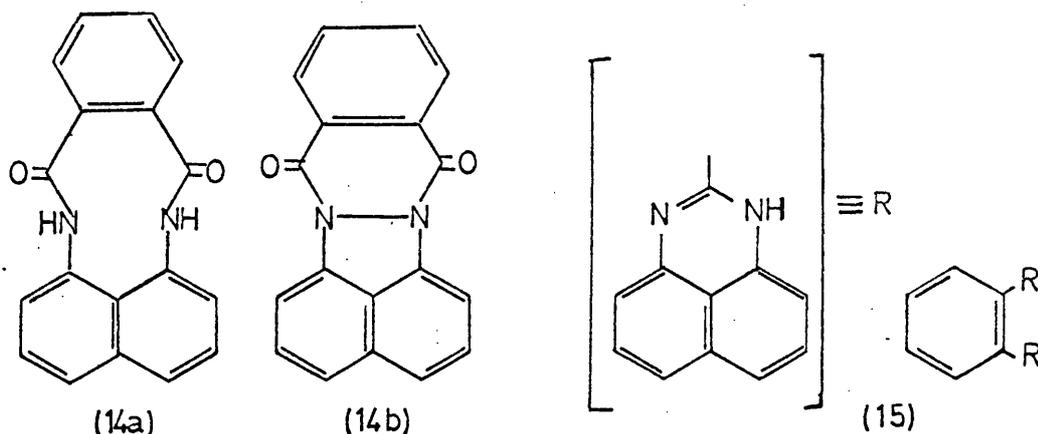


give dihydrobenz[cd]indazole.

Flossman<sup>154</sup> has removed sulphur from thiadiazenes to give azo compounds by treatment with sodium in an inert solvent, but initial attempts of similar treatment of naphtho[1,8-cd][1,2,6]thiadiazine gave only polymeric material.

Azo compounds are formed when aromatic amines in ether are treated with chloramine<sup>155</sup> or sodium hypochlorite.<sup>156</sup> Attempts to form an intramolecular azo linkage with 1,8-diaminonaphthalene gave only a mixture of chlorinated 1,8-diaminonaphthalenes with chloramine, and intractable material with sodium hypochlorite.

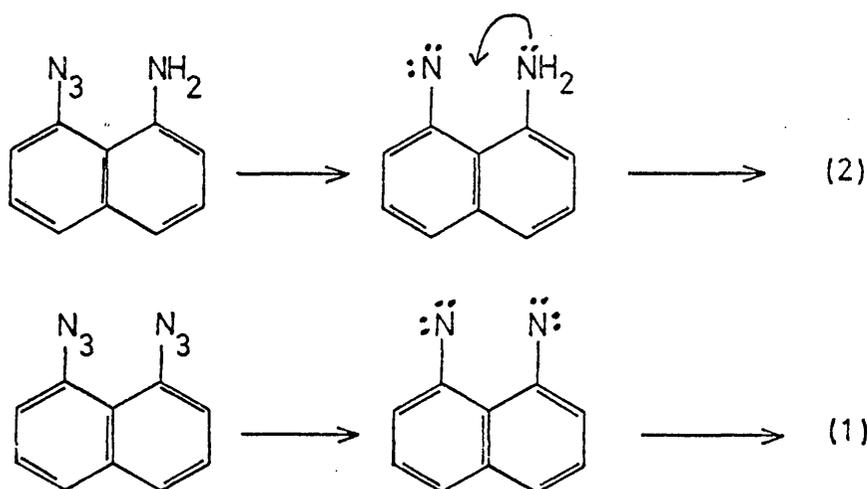
Attempts were made to prepare the phthaloyl derivative of 1,8-diaminonaphthalene (14a) using the method of Paudler and Zeiler<sup>157</sup> in the hope that treatment with sodium hypochlorite would give 2,3-(1,8-naphtho)phthalaz-1,4-dione (14b), a derivative of dihydrobenz[cd]indazole. However the reaction of 1,8-diaminonaphthalene with diethyl phthalate in dimethylformamide below 5° gave only orange prisms of 1,2-di(perimid-2-yl)benzene (15), the structure of which was confirmed by spectral and analytical data.



The mass spectrum gave a molecular weight of 410 with the loss of 168 (perimidine (R) - H) and also the infrared spectrum was almost identical with that of 3-phenylperimidine.<sup>108</sup>

A good route to benz[cd]indazole and its dihydro derivative seemed to be generation of an electrophilic nitrene

peri to a nucleophilic nitrogen. This could be accomplished by pyrolysis or photolysis of 1-amino-8-azidonaphthalene and 1,8-diazidonaphthalene. Pyrolysis and photolysis of aryl azides is generally accepted to give aryl nitrenes which often dimerise (Introduction, page 11). Thus 1-amino-8-azidonaphthalene might be expected to give (2) by intramolecular hydrogen abstraction and ring closure, while 1,8-diazidonaphthalene may give (1) by intramolecular "dimerisation" of the peri-nitrene.

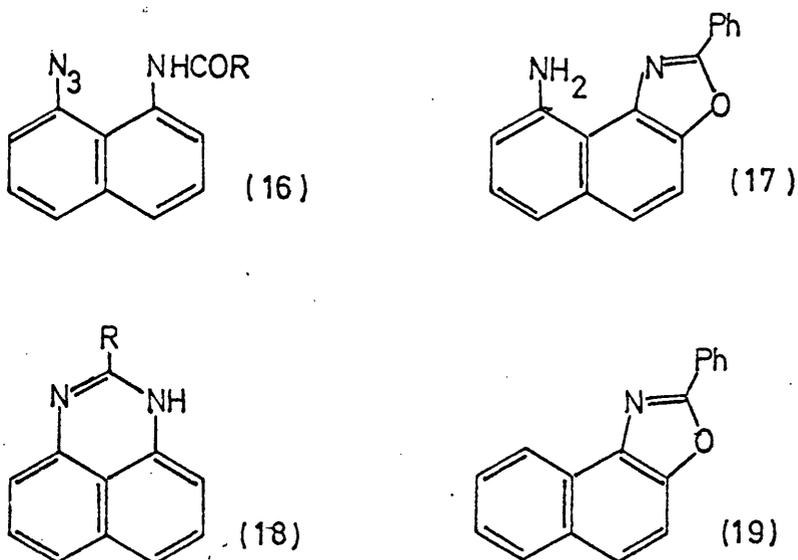


Preliminary investigation of these reactions by Storr<sup>105</sup> failed to give any of the required products. He found that pyrolysis of 1-amino-8-azidonaphthalene and 1,8-diazidonaphthalene gave 1,8-diaminonaphthalene, presumably by hydrogen abstraction from the solvent and photolysis of 1-amino-8-azidonaphthalene gave 1,8-diaminonaphthalene together with the intermolecular dimer 8,8'-diamino-1,1'-azonaphthalene. 1-Amino-8-azidonaphthalene was prepared by a modification of the method of Rees and Storr.<sup>139</sup> Diazotisation of 1-amino-8-azidonaphthalene and treatment of the diazonium solution with sodium azide gave 1,8-diazidonaphthalene. The thermolysis reactions were confirmed and only 1,8-diaminonaphthalene

was isolated. No benz[cd]indazole (1) or 1,2-dihydrobenz[cd]indazole (2) could be found. If benz[cd]indazole was formed it could lose nitrogen under the conditions employed to give 1,8-dehydronaphthalene. However, thermolysis of 1,8-diazidonaphthalene in carbon tetrabromide and mesitylene failed to give any 1,8-dibromonaphthalene of 1-(2,4,6-trimethylphenyl)naphthalene. The failure to obtain benz[cd]indazole by this method is analogous to the non-formation of the known, stable benzo[c]cinnoline from 2,2'-diazidobiphenyl.<sup>158</sup>

Storr found<sup>105</sup> that pyrolysis and photolysis of 1-acetamido-8-azidonaphthalene gave 2-methylperimidine and, very surprisingly, 9-amino-2-methylnaphth[1,2-d]oxazole. This intriguing reaction was confirmed and further investigation revealed that the formation of 2-substituted perimidines and 9-amino-2-substituted naphthoxazoles was a general reaction on decomposition of 1-amino-8-azidonaphthalene derivatives. The acyl and aroyl derivatives of 1-amino-8-azidonaphthalene were prepared directly by treatment of the amino compound with the appropriate acid chloride or anhydride in pyridine. They were all obtained in good yield as colourless crystalline solids readily identified by examination of their infrared spectra which showed a secondary amine, an azide and a carbonyl group. Preparation of the acylamino azides from monoacyl derivatives of 1,8-diaminonaphthalene was not considered since such peri-substituted naphthalenes spontaneously ring close to perimidines.<sup>141</sup> Decomposition of the aroyl derivatives proceeded much more cleanly and enabled the scope of this reaction to be studied in more detail. Pyrolysis of the benzamido derivative (16, R=Ph) in refluxing 1,2,4-trichlorobenzene gave, after chromatography on silica gel, 9-amino-2-

phenylnaphth[1,2-d]oxazole (17, R=Ph), and 2-phenylperimidine (18, R=Ph) (10%). The structure of the phenylperimidine was confirmed by comparison with an authentic sample prepared by the reaction of

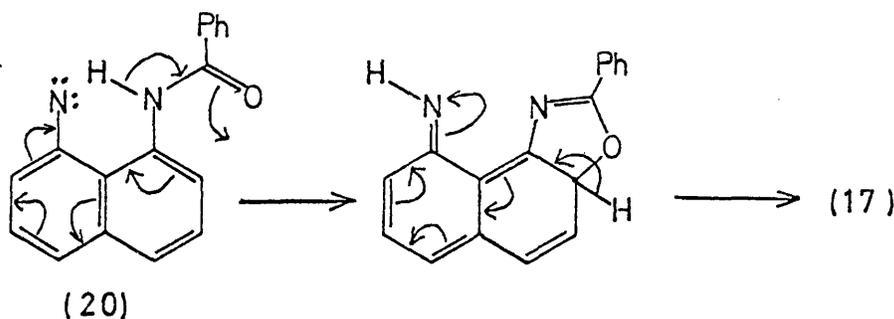


1,8-diaminonaphthalene with benzoyl chloride in benzene. 108, 109

Initially it was thought that formation of the perimidine in this reaction arose from the nitrene by hydrogen abstraction from the solvent to give the amine followed by cyclodehydration. This seemed a reasonable mechanism because hydrogen abstraction nearly always occurs in nitrene formation by decomposition of azides, and monoacyl derivatives of 1,8-diaminonaphthalene are known to cyclodehydrate spontaneously to perimidines.<sup>141</sup> The structure of the amino oxazole was supported by its infrared spectrum which indicated a primary amine but no carbonyl, and confirmed by deamination. Because of the difficulty in devising a simple route to 9-aminonaphthoxazoles direct comparison with an independently prepared specimen was not attempted. The infrared spectrum was very similar to that of 2-phenylnaphth[1,2-d]oxazole (19) obtained by cyclodehydration of the N-benzoyl derivative of

1-amino-2-naphthol.<sup>110</sup> The structure of (17) was verified experimentally by deamination to 2-phenylnaphthoxazole which was identical with the authentic specimen. Deamination was effected by reduction of the diazonium fluoroborate with sodium borohydride in dimethylformamide. The *p*-methoxy derivative (16, R=*p*OMe Ph) gave the corresponding oxazole and perimidine in similar yields and the *p*-nitro derivative (16, R=*p*NO<sub>2</sub>Ph) gave the analogous products in a somewhat lower yield. The propionyl derivative like the acetyl gave only small amounts of naphthoxazole and perimidine.

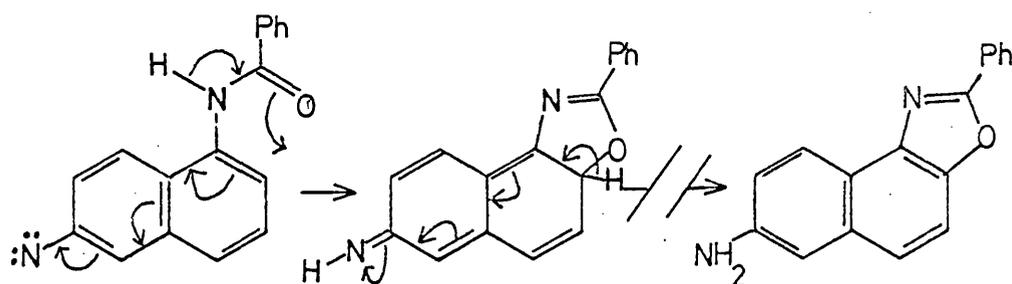
We can envisage several possible mechanisms for the formation of the amino oxazole. The first involves decomposition of the azide to give a nitrene (20) and nucleophilic attack on C<sub>2</sub> by the amide oxygen under the electron withdrawing influence of the electrophilic centre at C<sub>8</sub> (Scheme 1). If this type of mechanism is operative then we would expect any meta-amido aryl



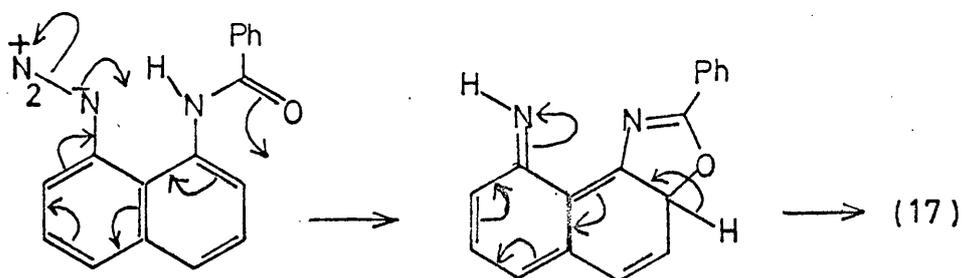
( Scheme 1 )

azide to decompose similarly into an amino oxazole. 1,3-Dinitro-naphthalene was reduced with sodium sulphide,<sup>111</sup> and acetylated with acetic anhydride to give 1-acetamido-3-nitronaphthalene and 1,3-diacetamido naphthalene. Reduction with iron in glacial acetic acid gave 1-acetamido-3-aminonaphthalene. 1,6-Dinitronaphthalene was reduced with stannous chloride in hydrochloric acid<sup>111</sup> to give

1-amino-6-nitronaphthalene which was treated in pyridine with benzoyl chloride to give the benzamido derivative. Reduction with Pd/C under hydrogen (1 atmos) gave 6-amino-1-benzamidonaphthalene. 1-Acetamido-3-aminonaphthalene and 6-amino-1-benzamidonaphthalene were diazotised in dilute hydrochloric acid and sodium azide added to the diazonium solutions to give 1-acetamido-3-azidonaphthalene and 6-azido-1-benzamidonaphthalene respectively. Treatment of *m*-azidoaniline with benzoyl chloride in pyridine gave *m*-azidobenzanilide. However pyrolysis of *m*-azidobenzanilide, 1-acetamido-3-azidonaphthalene and more significantly 6-azido-1-benzamidonaphthalene did not give naphthoxazoles and only small amounts of amines were found. 6-Azido-1-benzamidonaphthalene is at least as well set up as 1-azido-8-benzamidonaphthalene for decomposition by Scheme 1 and only lacks the *peri*-interaction required by other possible mechanisms.



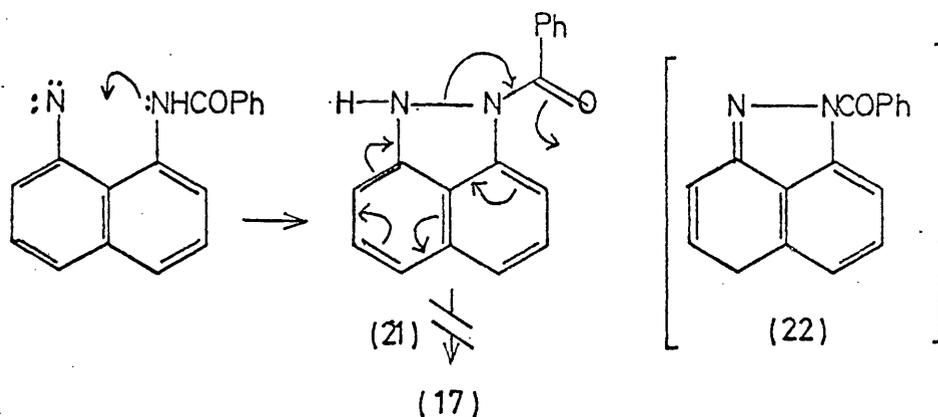
A second possible mechanism involves the sterically favoured intramolecularly acid-catalysed decomposition of the azide with concerted nucleophilic attack by the amide oxygen on the aromatic ring (Scheme 2). (This mechanism is somewhat analogous to that for the formation of substituted anilines by decomposition of phenyl azide in aqueous acid <sup>159</sup>). Some evidence for this mechanism is that the *peri*-substituted azides decomposed smoothly at about 140°, but significantly the other azides were thermally more



( Scheme 2 )

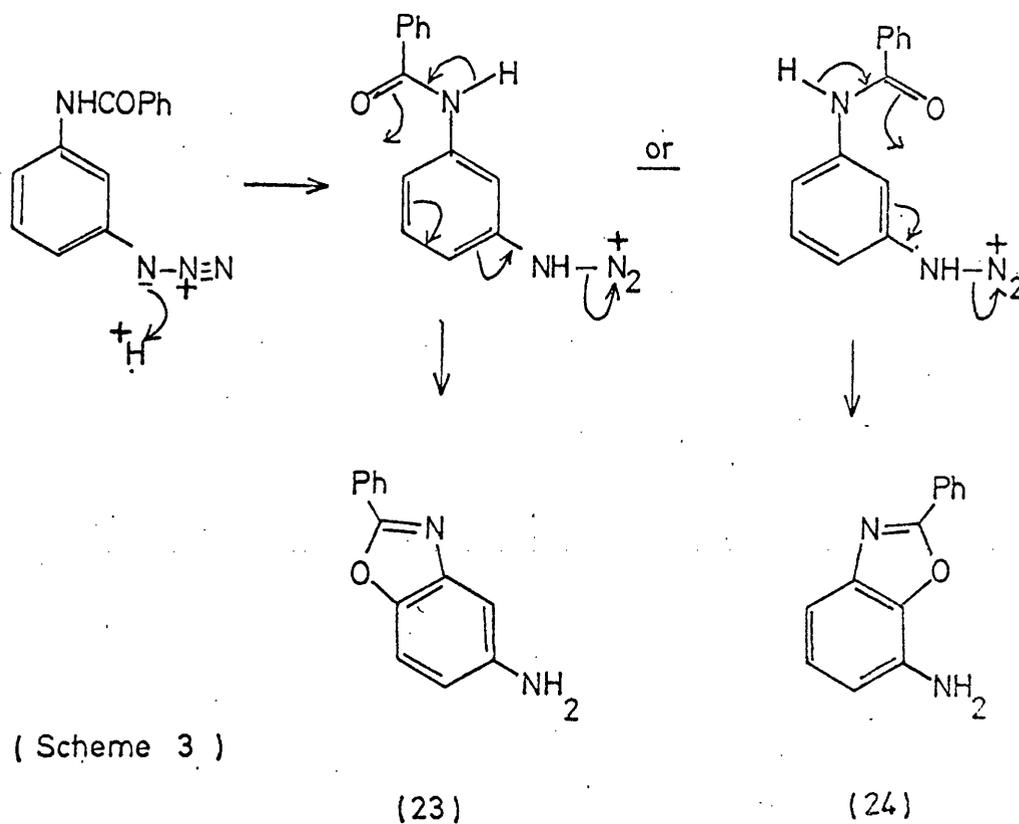
stable and decomposed slowly at about  $180^{\circ}$  to give the corresponding amino compound, presumably by hydrogen abstraction. Slow pyrolysis of 1-azido-8-benzamidonaphthalene at  $110^{\circ}$  gave only the amino naphthoxazole and no perimidine was formed. This suggests that the intermediate in the formation of the oxazole and perimidine is different and that the perimidine has a higher energy intermediate.

A further mechanism involving a derivative of the desired 1,2-dihydrobenz[cd]indazole system was initially considered. 1-Aroyl-1,2-dihydrobenz[cd]indazole, initially formed by direct nitrene insertion into the NH bond could rearrange to give the amino oxazole. Such an initial step was subsequently shown to be reasonable by a mechanism similar to that discussed later for the formation of the methyl acyl indazole from 1 azido-8-methyl acetamidonaphthalene. However this is unlikely since such an intermediate should rearrange to or be in equilibrium with its tautomer (22). The indazole (22) was obtained independently (see later) and shown to be stable and not to rearrange to the



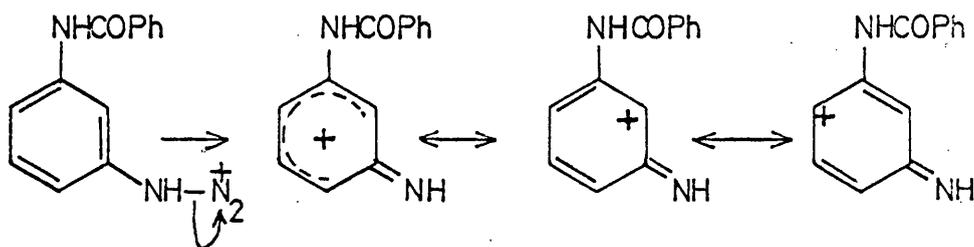
amino oxazole under the pyrolysis conditions.

Possible support for the mechanism involving the intramolecular acid catalysis (Scheme 2) is provided by the formation of 5-amino-2-phenylbenzoxazole (23) (48%) on treatment of a chloroform solution of *m*-azidobenzanilide with cold concentrated sulphuric acid. Electrophilic attack (by  $H^+$ ) at the substituted azido nitrogen to give a protonated azide could lead to loss of nitrogen and concerted nucleophilic attack by the amide oxygen at the ortho or para positions of the aryl ring (Scheme 3).



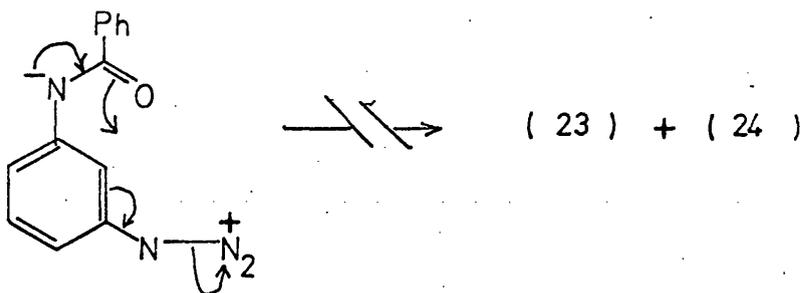
Formation of the 5-amino rather than the 7-amino isomer presumably reflects the greater stabilisation of the para than the ortho quinonoid transition state usually observed in nucleophilic aromatic substitution.

Alternatively loss of nitrogen from the protonated azide may give the nitrenium ion which would also facilitate nucleophilic attack at the ortho and para positions of the aryl ring.



5-Amino-2(4-methoxyphenyl)benzoxazole was isolated on decomposition of 2-azido-4-methoxybenzanilide in acid, but oxazoles could not be isolated from 2-azidoacetanilide, 1-acetamido-3-azidonaphthalene, or 6-azido-1-benzamidonaphthalene in cold concentrated sulphuric acid. 1-Azido-8-benzamidonaphthalene gave only a trace of the amino oxazole under these conditions.

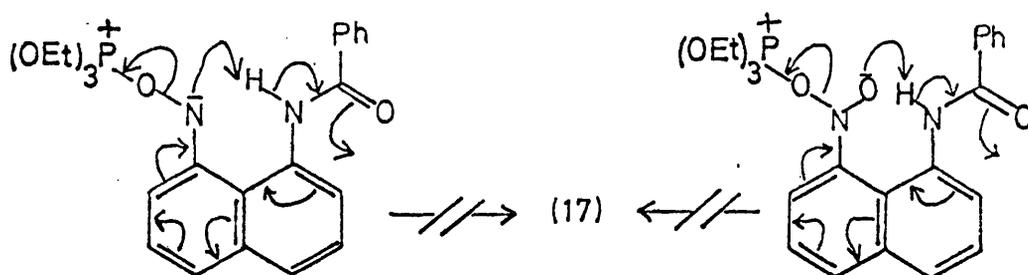
Decomposition of *m*-azidobenzanilide in base gave only intractable material.



The proposed mechanism (Scheme 2) for amino oxazole formation is unusual in that it involves intramolecular nucleophilic aromatic substitution by an amide oxygen, activated through both

rings of the naphthalene system by thermal decomposition of an azide group. It is possible that the whole process is facilitated by being concerted as shown, the proton transfer activating both the nucleophilic and electrophilic centres.

Deoxygenation of the corresponding nitro compound might be expected to give an analogous reaction with similar neighbouring group participation.



1-Benzamido-8-nitronaphthalene was prepared and treated with triethyl phosphite; this gave only a trace of the oxazole and a little 2-phenylperimidine.

This difference between the azide decomposition and nitro compound deoxygenation suggests that there is not a common intermediate.

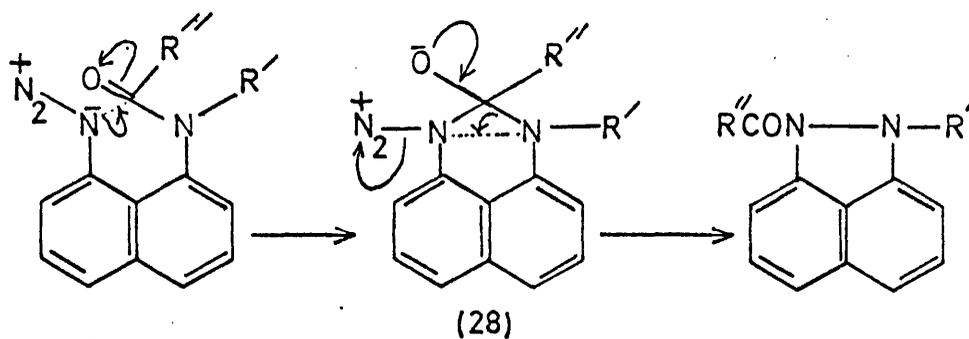
The lower decomposition temperature of 1-amido-8-azido-naphthalenes is attractively explained by the acid catalysis mechanism. However, steric destabilisation of the azide group by the bulky peri-substituent is an alternative explanation for the lower decomposition temperature of these compounds compared with other aryl azides. In order to check this the pyrolysis of the more hindered disubstituted amido azides were investigated.

Methylation of 1-acetamido-8-azidonaphthalene with dimethyl sulphate in acetone and aqueous sodium hydroxide solution



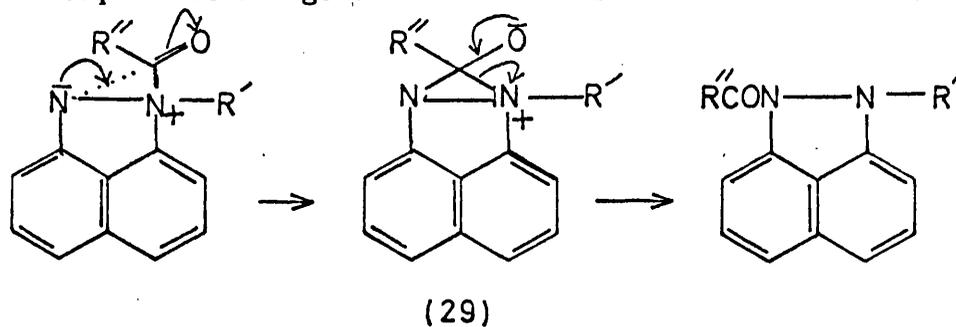
spectrum showed an acetyl group, a methyl group, and six aromatic protons (one of which was a singlet at lower field and presumably was the proton at C<sub>3</sub> deshielded by the N-acetyl in the indazole). The methylated benzamide (26, R' = Me, R'' = C<sub>6</sub>H<sub>5</sub>) gave an analogous product (27, R' = Me, R'' = C<sub>6</sub>H<sub>5</sub>) in lower yield. No N-methylated perimidines were formed in either case. Addition of 1-amino-8-azidonaphthalene to refluxing acetic anhydride gave the diacetylamino derivative (26, R' = R'' = COCH<sub>3</sub>) which on thermolysis gave the diacetylidazole (27, R' = R'' = COCH<sub>3</sub>); again no N-acetyl perimidine was isolated. Direct comparison of these 1,2-disubstituted benzindazoles was not possible. Treatment of 1-amino-8-azidonaphthalene with methyl chloroformate in the presence of triethylamine gave 1-azido-8-methoxycarbonylamino-naphthalene (16, R = OCH<sub>3</sub>). Addition of methyl chloroformate to the sodium salt of 1-azido-8-methoxycarbonylamino-naphthalene in dry dimethylformamide gave 1-azido-8-di(methoxycarbonyl)amino-naphthalene (26, R' = R'' = CO<sub>2</sub>CH<sub>3</sub>). This compound gave on pyrolysis the known 1,2-dihydrobenz[cd]indazole derivative (27, R' = R'' = CO<sub>2</sub>CH<sub>3</sub>), which was identical in all respects to the adduct formed by addition of 1,8-dehydronaphthalene to dimethyl azodicarboxylate.

A possible mechanism for the formation of 1,2-disubstituted benz[cd]indazoles is catalysis by electrophilic attack of the amide carbonyl group, in the absence of more efficient intramolecular catalysis of the azide decomposition by an amide proton, to give the tetrahedral intermediate (28) which then collapses to the indazole (Scheme 4). However loss of nitrogen to give a nitrene



( Scheme 4 )

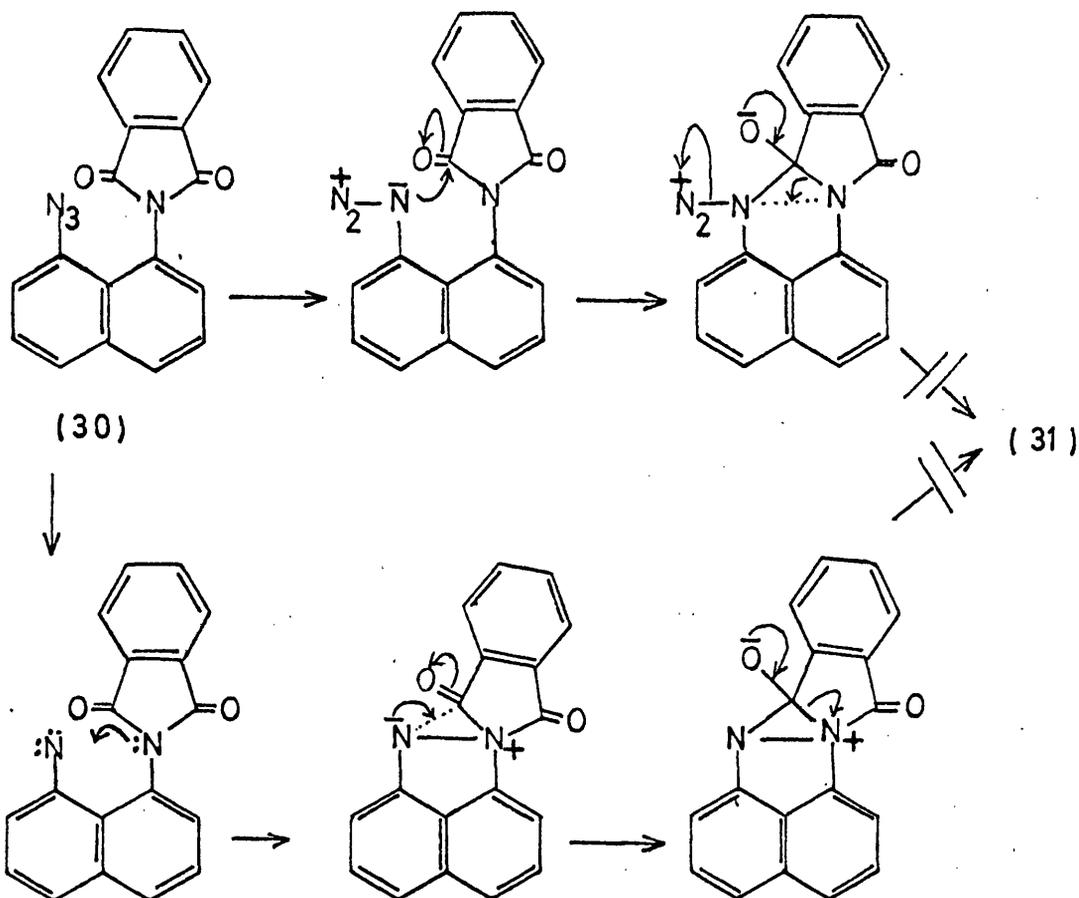
followed by nucleophilic attack by the adjacent nitrogen (Scheme 5) and subsequent rearrangement to the indazole cannot be ruled out.



( Scheme 5 )

This is very unlikely however because of the strain in such an intermediate as (29) and nitrene insertions into C-N bonds are unknown.

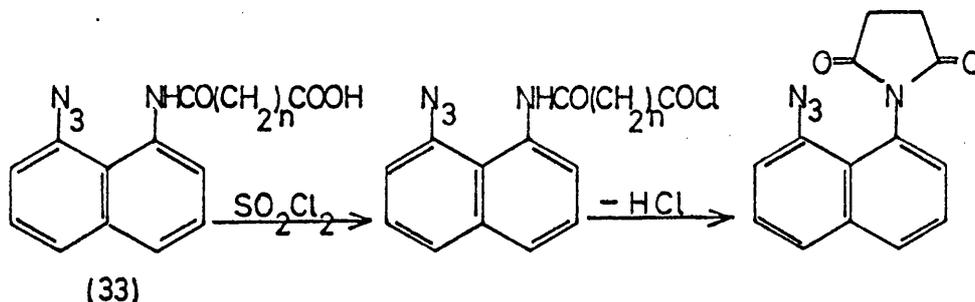
In contrast to the disubstituted amido azides, the phthalimido azide (30) gave no 1,2-benz[cd]indazole derivative (31), although some might have been expected if the above mechanisms operated. Instead the perimidine (32) was obtained in relatively high yield. Perimidine formation in the thermolysis of the mono-substituted amido azides was initially assumed to be the result of spontaneous cyclodehydration of 1-amido-8-aminonaphthalenes,



these amines arising by hydrogen abstraction by the initially formed nitrene. However, although this route very likely contributes to perimidine formation in solution an alternative mechanism must also be involved. This follows from the fact that perimidine formation also occurs on pyrolysis on dry sand and in the vapour phase when hydrogen abstraction is highly unlikely.

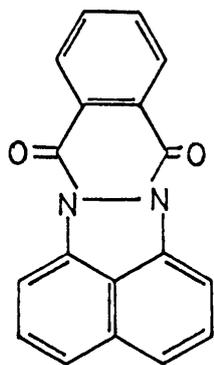
1-Azido-8-phthalimidonaphthalene and the maleimide analogue were prepared by treatment of 1-amino-8-azidonaphthalene with the appropriate anhydride in glacial acetic acid. Succinic and glutaric anhydride however gave only the mono substituted amido acids (33,  $n=2$  and 3 respectively). Treatment of the amido acid (33,  $n=2$ ) with thionyl chloride and subsequent heating resulted

in cyclisation and formation of the succinimido azide. However

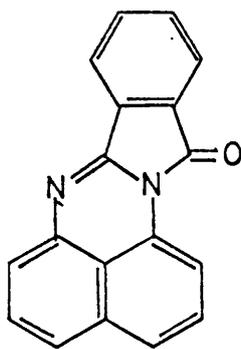


initial attempts to similarly cyclize the amino acid (33,  $n=3$ ) failed.

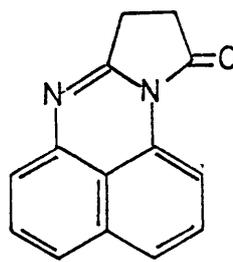
Pyrolysis of the phthalimido azide (30) gave the perimidine (32) (30%) in refluxing 1,2,4-trichlorobenzene. The yield was increased in tetralin, a better source of hydrogen atoms, to 60%. But when the phthalimido azide was decomposed on dry sand a quantitative yield of perimidine was obtained. Quantitative hydrogen abstraction is inconceivable under these conditions. Mass spectral examination of the gas evolved indicated that it was nitrogen rather than nitrous oxide. The succinimido azide did not



(31)



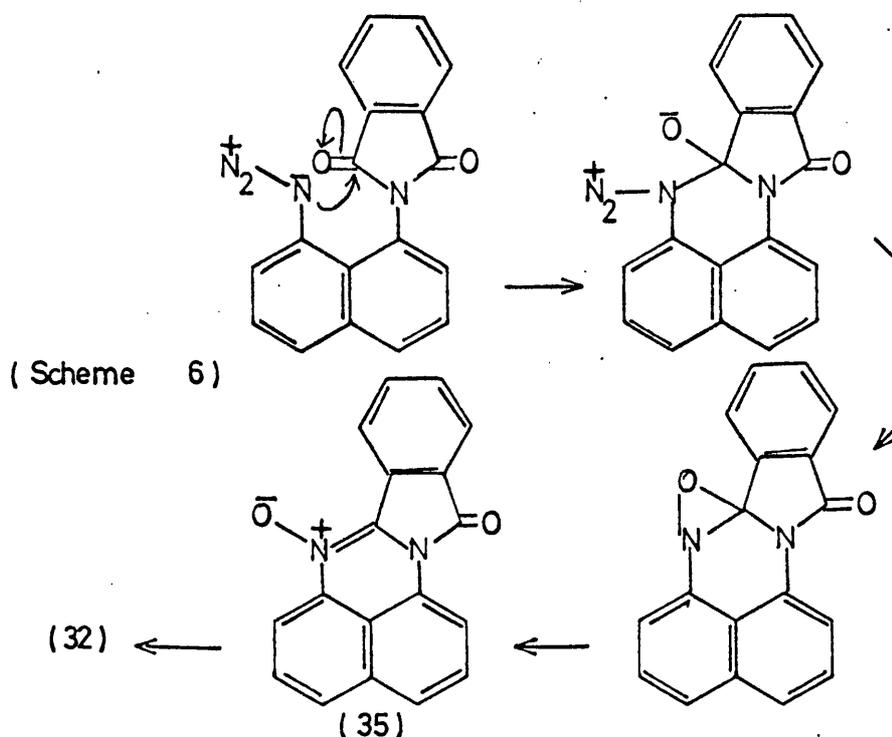
(32)



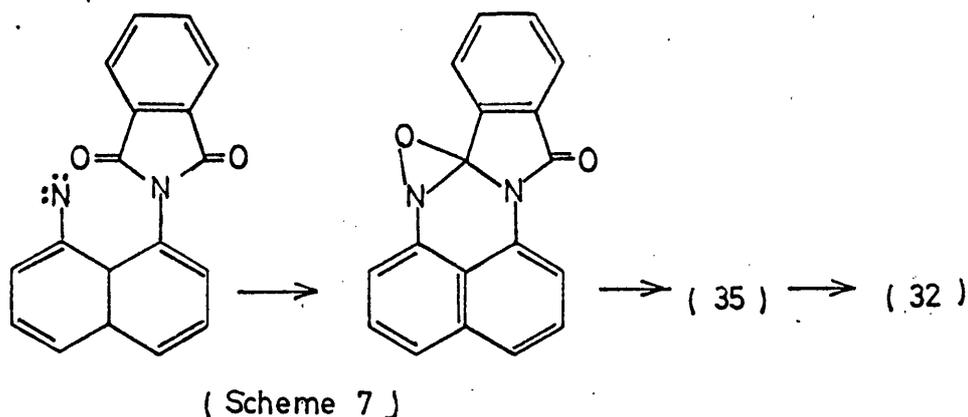
(34)

decompose as cleanly and gave only 60% yield of the perimidine (34) on dry sand, and 10% yield on thermolysis in 1,2,4-trichlorobenzene. The structure of the perimidines was confirmed by comparison with independently prepared authentic samples.<sup>109</sup> The perimidines could possibly arise from the same type of intermediate suggested

for indazole formation (Scheme 4), by an alternative mode of breakdown (Scheme 6) through a perimidine N-oxide (35) which would



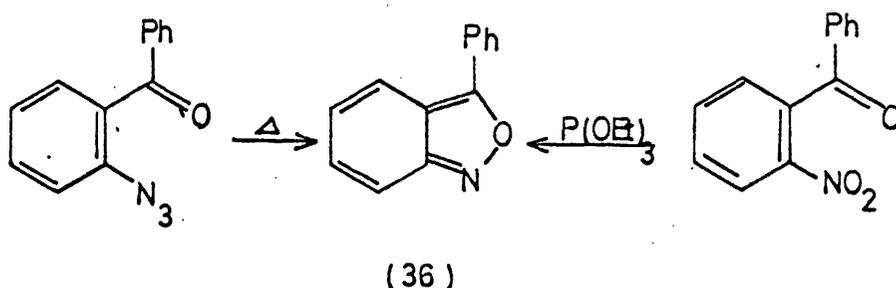
be expected to deoxygenate under the conditions of the reaction. Alternatively the oxaziridine (Scheme 7) could arise directly by addition of the corresponding nitrene to the carbonyl group. Attempts to isolate the postulated perimidine N-oxide (35) from



the azide pyrolysis and by independent preparation from the perimidine (32) by treatment with per-acids failed. However photolysis of the azide did give a product with spectral data consistent with the perimidine N-oxide and which on heating was converted to perimidine. The mass spectrum showed a molecular

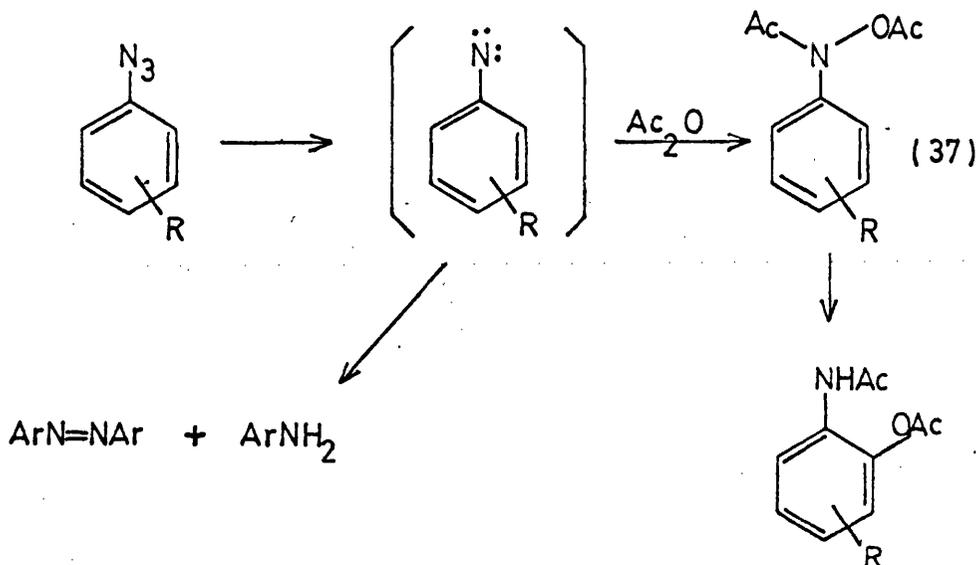
weight of 286 with the loss of 16 ( $-O$ ) and the infrared spectrum was almost identical to that of the perimidine but had in addition a strong peak at  $1240\text{cm.}^{-1}$  ( $N-O$ ). Attempts to purify this compound and to obtain satisfactory analysis failed.

Interaction of nitrenes or nitrene precursors with a  $C=O$  bond has been proposed by other workers. Thermolysis of o-azidobenzophenone<sup>158</sup> and deoxygenation of o-nitrobenzophenone<sup>160</sup> gave the anthranil (36). An apparent intermolecular insertion

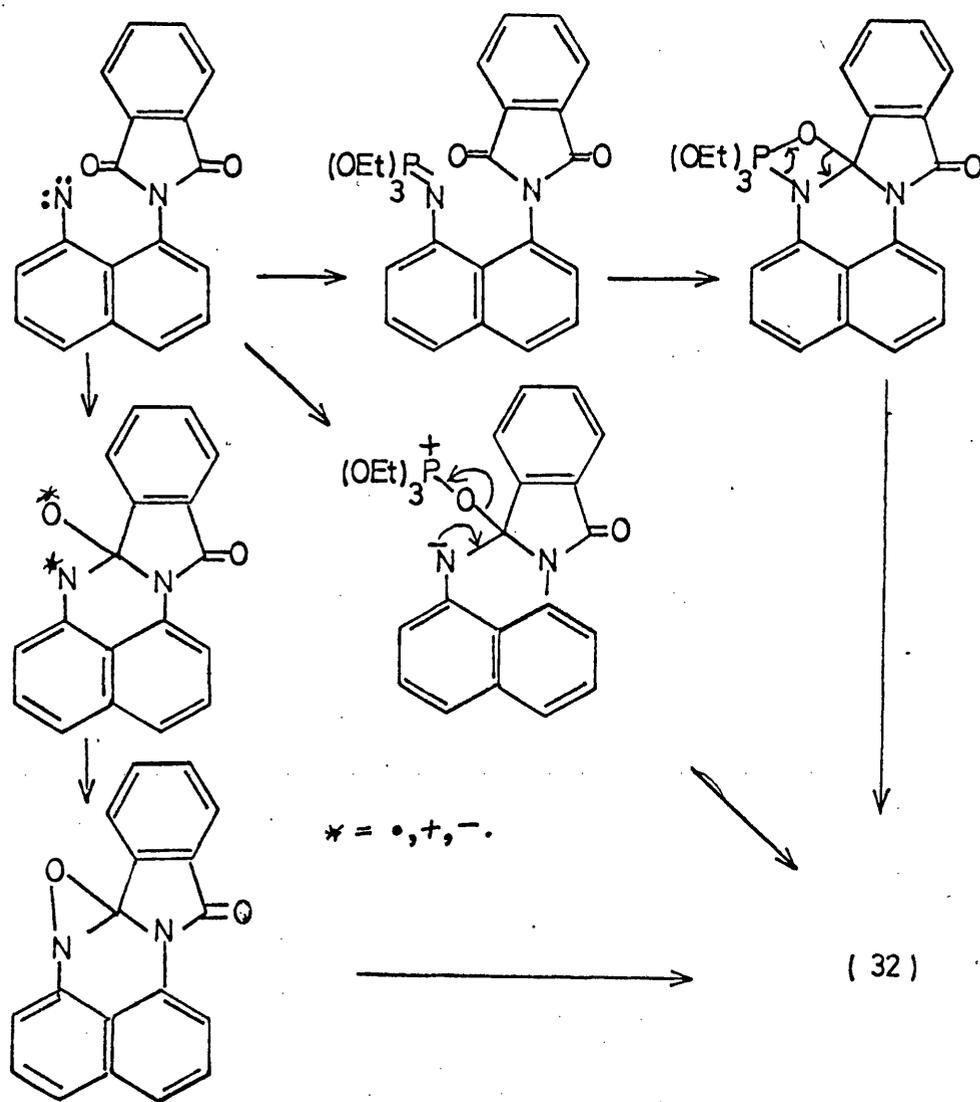


into a  $C-O$  bond was observed in the decomposition of aryl azides in refluxing acetic anhydride to give acetylated o-aminophenols.<sup>161</sup>

The N-acetoxyacetanilides (37), which could arise from nitrene insertion into acetic anhydride, are known to rearrange to o-acetoxyacetanilides.

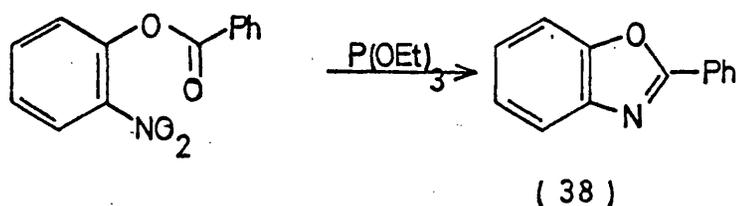


Until recently no examples of nitrenes (or nitrene precursors) reacting with suitably oriented carbonyl groups leading to products from stoichiometric loss of an oxygen atom had been reported. The formation of oxaziridines, by addition of the nitrene to a carbonyl group, has been suggested by Kametani<sup>53-57</sup> in the deoxygenation of suitable nitro compounds with triethyl phosphite. Significantly, deoxygenation of the corresponding nitro compound in our series (nitro in place of azide) with triethyl phosphite, led to indazole and perimidine formation, (but gave only traces of oxazoles). If initial reduction of the nitro group to a nitrene is assumed, several possible mechanisms can be envisaged. Both decomposition of the azide (30) and the corresponding nitro



compound give the perimidine suggesting the possibility that a similar intermediate is involved in perimidine formation.

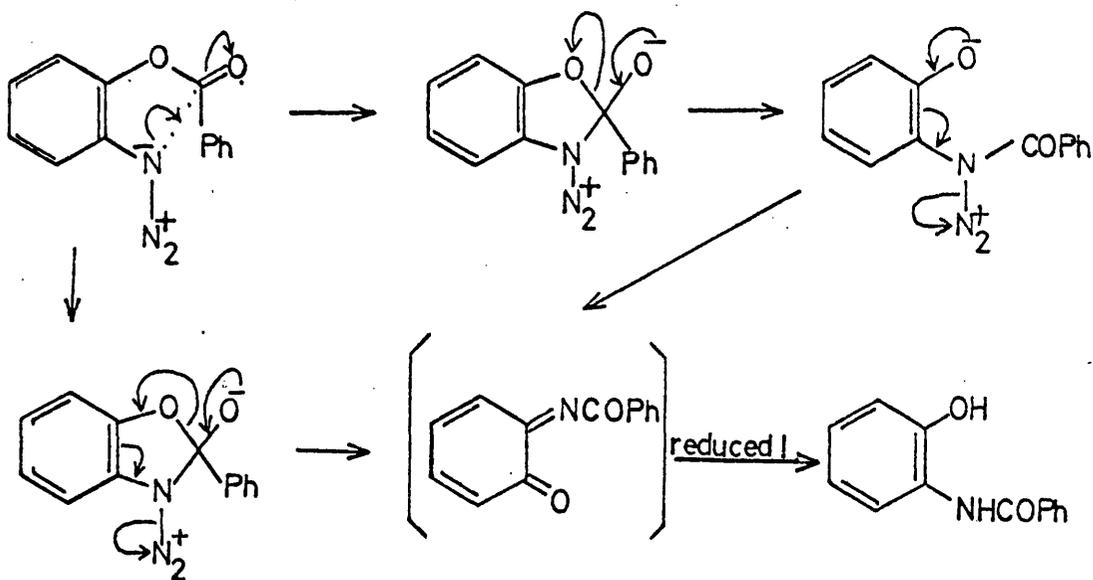
In a recent communication<sup>162</sup> a simpler example of reductive cyclisation has been reported. Treatment of o-nitrophenyl benzoate with triethyl phosphite gave 2-phenylbenzoxazole (38). This is an apparent nitrene addition to the C=O bond of the o-nitrophenyl ester with loss of one atom of oxygen, leading to formation of the oxazole. We confirmed this observation.



However, when the nitrene was generated by decomposition of the corresponding azide, the reaction took an entirely different course. o-Azidophenyl benzoate was easily prepared by the action of benzoyl chloride on o-azidophenol.<sup>106</sup> Thermolysis of o-azidophenyl benzoate in refluxing 1,2,4-trichlorobenzene gave o-hydroxybenzanilide (39) (10%) as the only isolable product. Surprisingly only a trace of the oxazole could be detected (t.l.c.). A control reaction showed that 2-phenylbenzoxazole was stable under the reaction conditions. We have therefore a markedly different mode of reaction for an azide decomposition and for a nitro compound deoxygenation. If indeed nitrenes are involved in both cases it would appear that the presence of triethyl phosphite is necessary for the subsequent formation of the oxazole. One obvious possibility is the formation of (40) by nucleophilic attack by phosphorus on the nitrene, and that this is the species which leads to oxazole

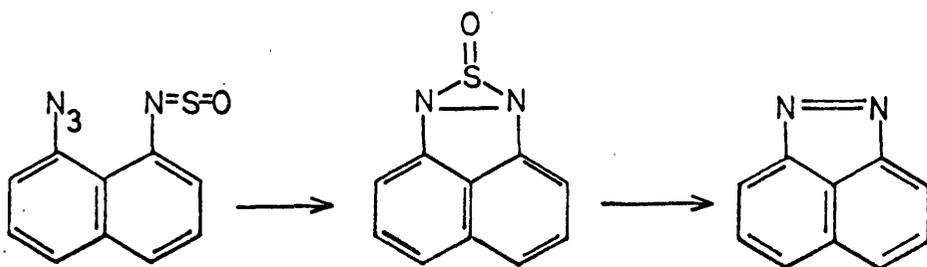


A nitrene intermediate may not be involved and a concerted mechanism can be envisaged to account for the formation of the phenol (Scheme 9).



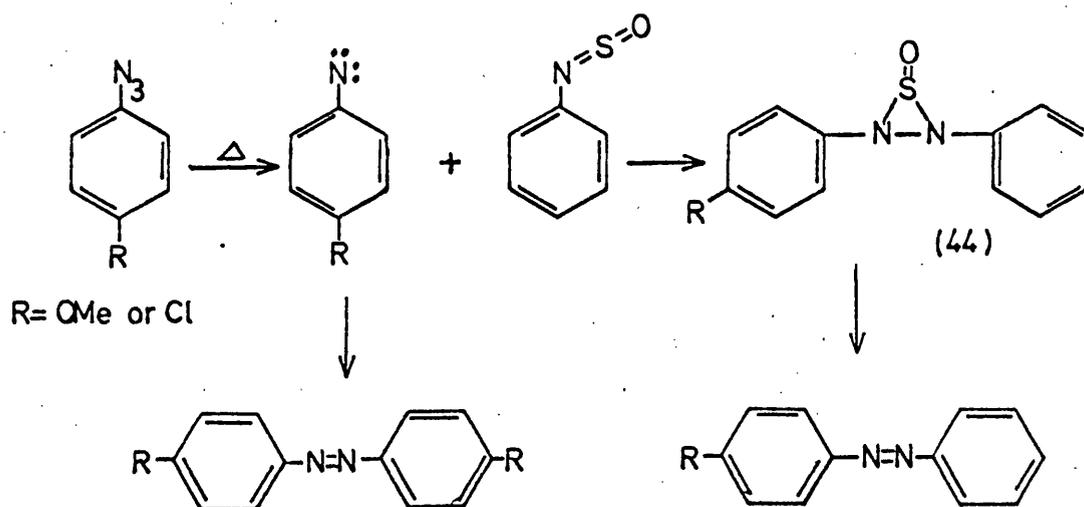
( Scheme 9 )

Photolysis of diphenyldiazomethane and N-sulphonylaniline gave amongst other products N-diphenylmethyleaniline, which can be explained by addition of the carbene to the nitrogen sulphur double bond and subsequent extrusion of  $\text{SO}$ .<sup>163</sup> An extension of this to the addition of a nitrene to a sulphonylamino group could lead to the formation of azo compounds. This could possibly be applied to the synthesis of benz[cd]indazole.



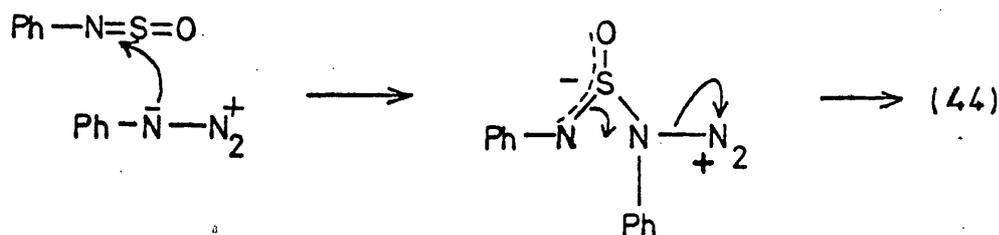
(45)

This reaction was first attempted with more simple systems. N-Sulphonylaniline was made by the reaction of thionyl chloride with aniline,<sup>164</sup>. Diazotization of aniline and treatment of the diazonium solution with sodium azide gave phenyl azide. Pyrolysis of phenyl azide in refluxing N-sulphonylaniline gave azobenzene. This product could of course arise by reaction of the nitrene with the N=S bond or by dimerisation (see Introduction, section 3b). However, para-methoxy and para-chlorophenylazide on thermolysis in N-sulphonylaniline gave the "mixed" unsymmetrical azo compound ( as well as the symmetrical dimerization product in the para-methoxy case). This is not a clean reaction and only



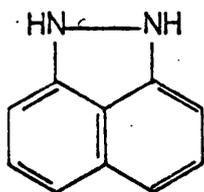
goes in low yield but constitutes a new route to "mixed" azo compounds. This is the only example of addition of a nitrene to a N=S bond. Photolysis of the azide in the presence of N-sulphonylaniline gave only trace amounts of the azo compound.

A nitrene may not be involved. Initial attack may involve the azide as shown in formation of the thiadiazene (44):

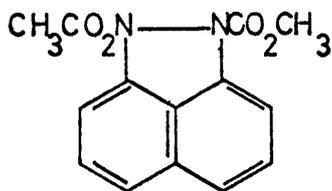


This possible route to benz[cd]indazole was abandoned since attempts to prepare 1-azido-8-sulphinylaminonaphthalene (45) by treatment of 1-amino-8-azidonaphthalene with both N-sulphinyl-p-toluensulphonamide and thionyl chloride failed.

Another possible route to benz[cd]indazole would be oxidation of its dihydro derivative (2). This system has been reported in the literature but we had shown earlier the assigned structure was incorrect. The N,N-diester (6) of 1,2-dihydrobenz[cd]indazole would be an ideal precursor to the dihydro derivative.

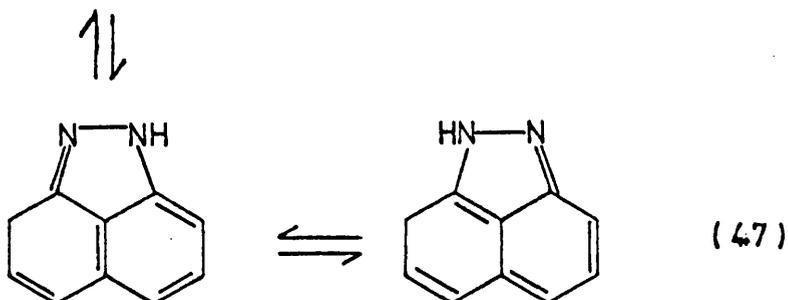
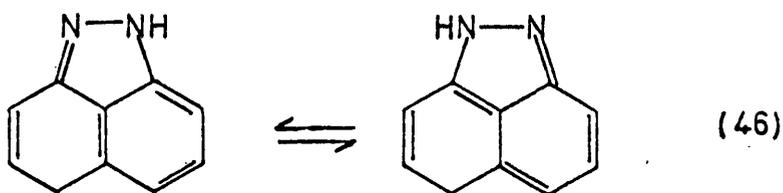


(2)



(6)

Although only small amounts of the diester (6) were available, from the reaction of 1,8-dehydronaphthalene and dimethylazodicarboxylate, its hydrolysis and decarboxylation should lead to the parent dihydrobenz[cd]indazole. Treatment of the colourless diester (6) with ethanolic potassium hydroxide rapidly gave a deep purple solution from which two colourless isomeric compounds,  $\text{C}_{10}\text{H}_8\text{N}_2$ , were isolated.

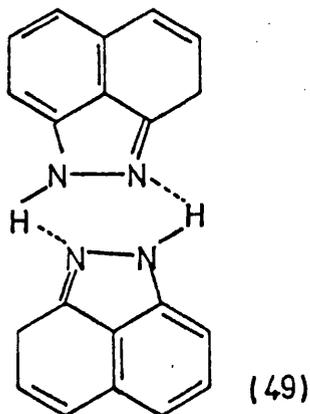
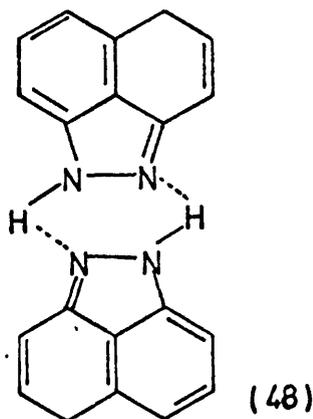


These isomers were separated by preparative t.l.c., but interconverted slowly on standing, and rapidly on heating or in the presence of base. The infrared, n.m.r. and mass spectral data for both isomers were very similar. The mass spectrum gave a molecular weight of 156, with loss of 1 (-H) followed by 28 (-N<sub>2</sub>). The n.m.r. spectrum showed a multiplet of five protons, assigned as aromatic and vinylic H, two allylic protons, and a broad singlet assigned as NH. The solid phase infrared spectrum (K Br disc) showed a very broad NH at 3160 cm.<sup>-1</sup> Solution infrared showed a broad NH at 3160 cm.<sup>-1</sup> which gave on dilution a sharp peak, and osmometric molecular weight determination in non-polar solvents

	dihydrobenz[cd] indazole			indazole 166b	
	0.0223	0.068	0.123	0.055	0.494
molar concentration	0.0223	0.068	0.123	0.055	0.494
apparent molecular weight	158	184	198	-	-
association of monomer	1.0	1.2	1.3	1.2	1.5

indicated association typical of indazoles;

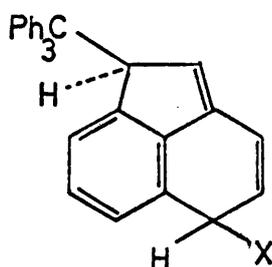
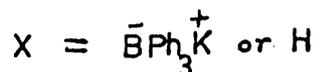
such as (48) and (49).<sup>166</sup>



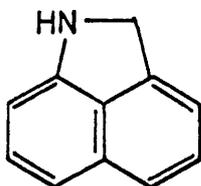
However, the u.v. spectra of the two isomers were significantly different, the least polar isomer showing much more fine structure. However it was not possible to differentiate between the two isomers.

Compounds (46) and (47) are only moderately stable and decomposed, particularly in solution, to give intensely coloured polymers; indeed the formation of a deep purple colour was diagnostic of the presence of (46) and (47). Alder, Niazi and Whiting<sup>128</sup> obtained a very similar mixture, which they could not separate, of the dihydroindazoles by reduction of the N-oxides (4) and (5). It would appear therefore that dihydrobenz[cd]indazole prefers to exist in the thermodynamically more stable tautomeric forms which have an aromatic indazole system rather than a naphthalene system. This possibly reflects the differences in strain between the 10  $\pi$  aromatic systems with five- or six-membered 'peri'-bridges, and the differences in resonance energy between indazole and naphthalene. An analogous carbocyclic example<sup>165</sup>

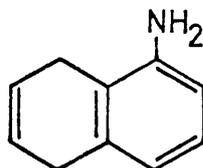
which exists as (50) suggests that strain may be the dominant factor. We can speculate that this type of tautomerism is general in 1,8-bridged naphthalene systems. However the n.m.r. spectrum (see following section) of 1,2-dihydrobenz[cd]indole (51) indicates that it exists in the form shown although perhaps significantly it



(50)



(51)



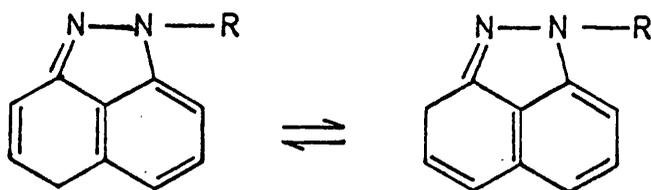
(52)

readily decomposes to purple polymers as do the benzindazoles.

Further support for the structure of (46) and (47) came from the formation of an identical mixture by diazotisation of 5,8-dihydro-1-naphthylamine (52) in a standard type of indazole preparation. 5,8-Dihydro-1-naphthylamine was easily made by reduction of 1-aminonaphthalene with sodium ethoxide in xylene.<sup>119</sup> The best procedure found was to allow the diazonium chloride to decompose slowly in chloroform containing equimolar amounts of triethylamine and glacial acetic acid at room temperature for 24hr. Unfortunately the yields were low and variable but the directness of approach made this the most convenient source of (46) and (47).

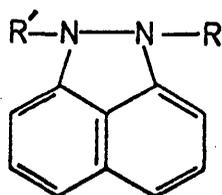
In view of the possible mobile tautomeric equilibrium  $2 \rightleftharpoons 46 \rightleftharpoons 47$  attempts were made to convert the indazoles (46)

and (47) into the N,N-disubstituted derivatives of form (2). Treatment of (46) and (47) with excess of methyl chloroformate in the presence of triethylamine gave dimethyl 1,2-dihydrobenz[cd]indazole-1,2-dicarboxylate (6), identical in all respects to that obtained by addition of 1,8-dehydronaphthalene to dimethyl azodicarboxylate. The N,N-disubstituted derivative (31) was obtained in low yield by treatment of (46) and (47) with phthaloyl chloride. 1,2-Dihydrobenz[cd]indazole derivatives can thus be prepared from 1-aminonaphthalene although the overall yield is very low. Other attempts at N,N-disubstitution were less successful. Thus benzoyl chloride, phenacyl bromide and benzyl bromide gave only the mono N-substituted derivatives



(53)

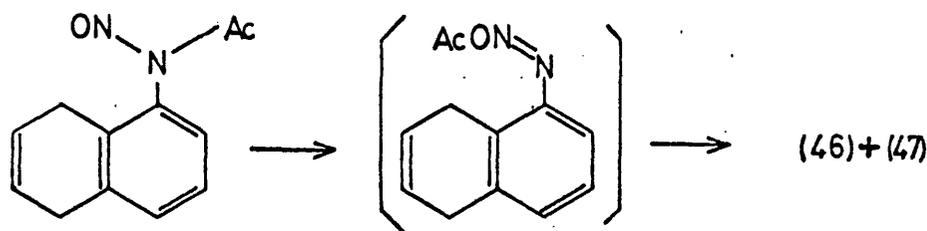
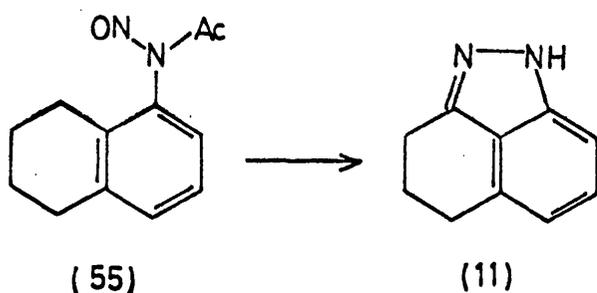
(53, R-PhCO, PhCOCH<sub>2</sub>, PhCH<sub>2</sub> respectively). The mono N-substituted dihydrobenz[cd]indazoles were similar to the parent compound in preferring structure (53) to the tautomeric naphthalene structure



(54)

(54, R' = H). This was readily shown by two allylic protons in the n.m.r. spectrum; significantly these compounds also decomposed slowly to a blue polymer. The N,N-disubstituted derivative (54, R' = PhCO, R = CO<sub>2</sub>Me) was obtained by treatment of 1-N-benzoyl-1,2-dihydrobenz[cd]indazole with methyl chloroformate in the presence of triethylamine. Further attempts to add a second N-substituent to the mono-N-derivatives were unsuccessful. The simple alkyl derivatives of the indazoles (46) and (47) could not be isolated. Attempts at methylation with dimethyl sulphate failed and neither mono nor dimethyl derivatives were isolated. Reduction of the diester (6) and N-methyl-N-acetylbenz[cd]indazole (54, R' = CH<sub>3</sub>, R = COCH<sub>3</sub>) with both lithium aluminium hydride and diborane also failed. 1-N-Aminonaphthotriazine was oxidised with lead tetra-acetate in azotertiarybutane, in the hope that addition of 1,8-dehydronaphthalene to the N=N bond would give N,N-di-*t*-butylbenz[cd]indazole (54, R' = R = *t*-butyl) but only yellow gums which could not be purified were obtained. Attempts to prepare the methyl iodide quaternary salt of the indazole (46) and (47) and to stabilize the benzindazole system by forming a cuprous chloride complex were also unsuccessful.

Decomposition of N-nitroso-1-acetamidotetralin (55) gives the indazole (11) in reasonable yield.<sup>154</sup> In an attempt to improve the yield of the indazoles (46) and (47) from 5,8-dihydro-1-naphthylamine, the acetyl derivative was nitrosated with nitrous fumes and decomposed in a similar manner. However only low yields of the dihydrobenzindazoles (46) and (47) were obtained.



Finally a very satisfactory method for converting 1-amino-8-azidonaphthalene to the dihydrobenzindazoles (46) and (47) was found in the later stages of this work. Although all attempts in solution had failed, pyrolysis carried out by sublimation of 1-amino-8-azidonaphthalene through a hot tube gave the dihydrobenz[cd]indazoles in good yield. The optimum conditions were found to be a sublimation temperature of  $120^{\circ}$  and a hot tube temperature of  $300^{\circ}$  at 0.04mm. Hg pressure giving a yield of 80%. The conditions of the reaction were critical and the yield is decreased on lowering the sublimation temperature and on raising or lowering the tube temperature. The nitrene formed from the azide could give the indazoles by intramolecular hydrogen abstraction and ring closure, or indeed at this temperature the nitrene probably inserts directly into the adjacent NH bond, followed by isomerisation. Pyrolysis of the amino azide in solution gave no trace of the required product and since the dihydrobenzindazoles would have survived the solution pyrolysis

conditions this is a striking example of the advantages of high-temperature, low-pressure, gas phase decomposition compared to lower temperature decomposition in a solvent.

Although 1,2-dihydrobenz[cd]indazole (2) itself was not available it seemed possible that oxidation of the indazole tautomers (46) and (47) could lead to benz[cd]indazole. However oxidation (with lead tetra-acetate, mercuric oxide, silver oxide, and manganese dioxide) and dehydrogenation (with N-bromosuccinimide, dichlorodicyano-o-benzoquinone, and palladium in p-xylene) under a variety of conditions gave no isolable, stable product. Oxidation with t-butylhypochlorite at  $-60^{\circ}$  gave an unidentified substance as yellow plates in low yield. The infrared spectrum showed a peak at  $3450\text{ cm.}^{-1}$  (OH or NH) and the mass spectrum gave a molecular weight of 230. This is consistent with a 1:1 adduct of the dihydrobenzindazole and t-butyl alcohol. However attempts to purify this compound and obtain satisfactory analysis failed. Attempts to trap benz[cd]indazole assuming it to be a strained reactive cis-azo compound also failed. Thus no adduct was isolated from oxidation in the presence of 2,3-dimethylbutadiene with which cis-azobenzene will form an adduct but trans-azobenzene will not.<sup>167</sup> No 2+2 adduct was obtained from oxidation in the presence of diphenylketene, another cis azo compound trap.<sup>167</sup> Addition of diphenylketene to (46) and (47) in methylene chloride gave an immediate reaction. Chromatography on silica gel gave 1-N-diphenyl-acetyl-1,2-dihydrobenz[cd]indazole (53,  $R=\text{Ph}_2\text{CHCO}$ ) as well as diphenylketene polymer and diphenylacetic acid. However oxidation of the dihydroindazoles (46) and (47) at  $-70^{\circ}$  with lead tetra-acetate followed by addition of diphenylketene did not give the

mono N-substituted indazole but an isomeric compound. The infrared spectrum showed a carbonyl group and the mass spectrum gave a molecular weight of 350. The n.m.r. spectrum showed only aromatic protons. Attempts to purify this compound also failed.

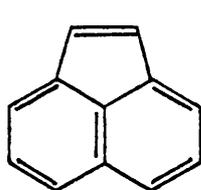
The mono and di-N-oxides (4) and (5) of benz[cd]indazole have recently been reported.<sup>128</sup> These appear to be ideal precursors and deoxygenation should give benz[cd]indazole. The mono and di-N-oxides (4) and (5) were prepared by m-chloroperbenzoic acid oxidation of 1,8-diaminonaphthalene. Attempts to isolate or trap benz[cd]indazole in the deoxygenation of (4) and (5) with phosphorus trichloride, triethyl phosphite and dichlorocarbene (generated by decomposition of phenyltrichloromethyl mercury) in the presence of diphenylketene, phenyl sydnone and 2,3-dimethylbutadiene all failed. Attempts at reduction of the N-oxides (4) and (5) with stannous chloride in acetic acid, and Raney nickel and hydrogen gave no isolable product. The di-N-oxide was easily deoxygenated to the mono N-oxide by refluxing in benzene. This is surprising as such thermal deoxygenations usually require much higher temperatures.

The mono N-oxide is a 1,3-dipole and as such should be trapped by 1,3-dipolarophiles. However attempts to effect such a reaction with dimethyl fumarate, allyl alcohol, or nitrosobenzene failed.

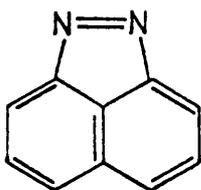
**Section II.**

ATTEMPTED PREPARATION OF BENZ[cd]INDOLE AND  
ITS DERIVATIVES.

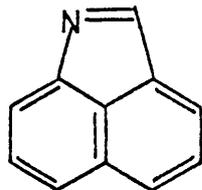
Acenaphthylene (1) is a known stable compound; benz[cd]indazole (2) however is unknown and we have shown earlier that it could not be isolated. Very little is known about benz[cd]indole (3) the compound intermediate between the two. The parent compound(3)



(1)



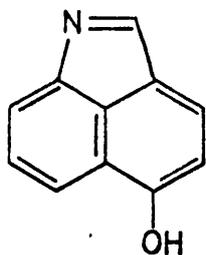
(2)



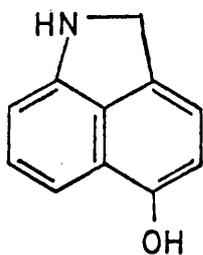
(3)

has never been described and only a few derivatives of this system have been reported in the open literature. However several derivatives of benz[cd]indole are referred to in patents, although the structures assigned to some of these compounds seem doubtful.

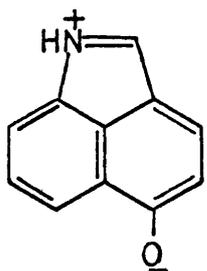
5-Hydroxybenz[cd]indole<sup>167</sup> (4) is readily available from 1,2-dihydro-5-hydroxybenz[cd]indole (5) by alkaline oxidation, which occurs rapidly with such reagents as potassium ferricyanide, persulphate or hypiodite.<sup>168</sup> The hydroxy compound (4) has been formulated



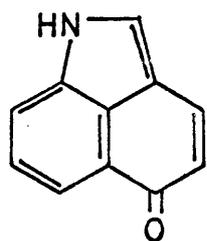
(4)



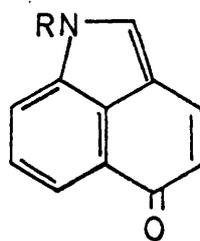
(5)



(6A)



(6B)

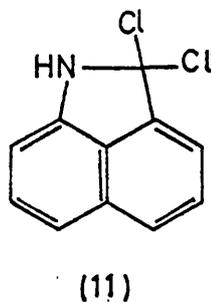
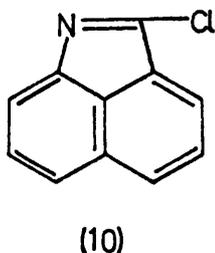
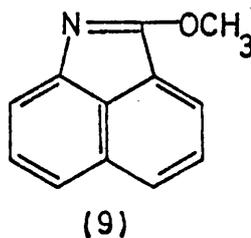
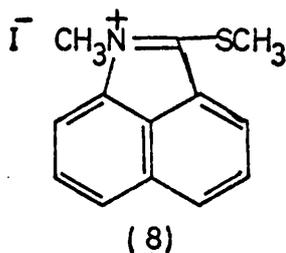


(7)

as the resonance hybrid  $6A \leftrightarrow 6B$ ; reactions such as acetylation and methylation occur readily at the nitrogen<sup>169, 170</sup> giving compounds (7,  $R=COCH_3$ ) and (7,  $R=CH_3$ ) respectively.

Quaternary salts of the benz[cd]indole system have been suggested for several compounds,<sup>171, 172</sup> a simple example being the salt (8) described by Russian workers.<sup>173</sup> The methosulphate is less stable than the iodide.

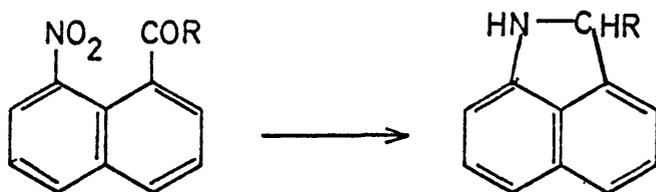
The simplest derivatives of benz[cd]indole appear to be naphtholactam-0-methyl ether (9) and the chlorobenz[cd]indole (10).<sup>174</sup> However although the ether (9) is mentioned in patents



and appears to be used in large quantities, its preparation and characterisation are not described. The intermediacy of the chloro compound (10) has only been implied and is assumed to arise in high temperature reactions by loss of HCl from 2-dichloro-1,2-dihydrobenz[cd]indole (11), which itself is prepared by heating naphthostyryl with phosphorus oxychloride. Compounds (9) and (10) react with compounds containing active methylene groups to give dyestuffs of the type (12).

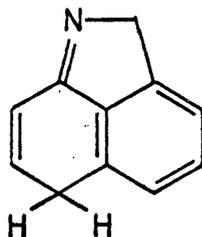


1,2-Dihydrobenz[cd]indole is obtained by catalytic reduction of 8-nitro-1-naphthaldehyde.<sup>178</sup> This presumably involves reduction to the amino compound followed by ring cyclization by elimination of water to give benz[cd]indole, which then undergoes additional reduction. Similar reduction of 8-nitronaphthylketones<sup>126</sup> gave 2-substituted 1,2-dihydrobenz[cd]indoles.

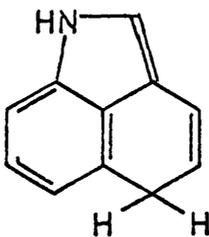


Our interest in benz[cd]indole was to compare its stability with that of benz[cd]indazole and acenaphthylene. Irradiation or thermolysis of this system could lead to 1,8-dehydronaphthalene by the loss of R-C≡N.

1,2-Dihydrobenz[cd]indole was prepared by lithium aluminium hydride reduction of naphthostyryl using a modification of the method of Stoll.<sup>127</sup> This compound was unstable and decomposed to a purple polymer suggesting that it could exist in tautomeric forms such as (18) and (19) analogous to those previously described for 1,2-dihydrobenz[cd]indazole. The n.m.r.



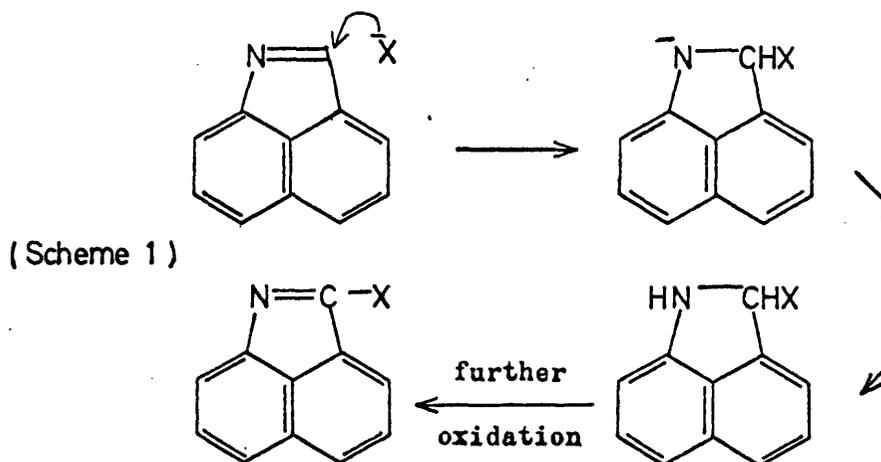
(18)



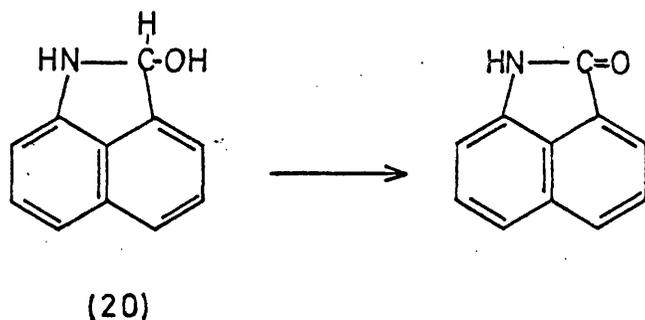
(19)

spectrum showed a broad singlet, 1 proton (NH), a sharp singlet, 2 protons ( $\text{CH}_2$ ) and 6 protons as a multiplet. No allylic protons were detected. On addition of  $\text{D}_2\text{O}$  the broad singlet disappeared, but addition of NaOD had no further effect; thus no D was incorporated at a carbon atom. We can assume therefore that 1,2-dihydrobenz[cd]indole has in fact structure (15).

Mild oxidation of 1,2-dihydrobenz[cd]indole should lead to benz[cd]indole. Since we could expect benz[cd]indole to be susceptible to nucleophilic attack (Scheme 1) the oxidations were

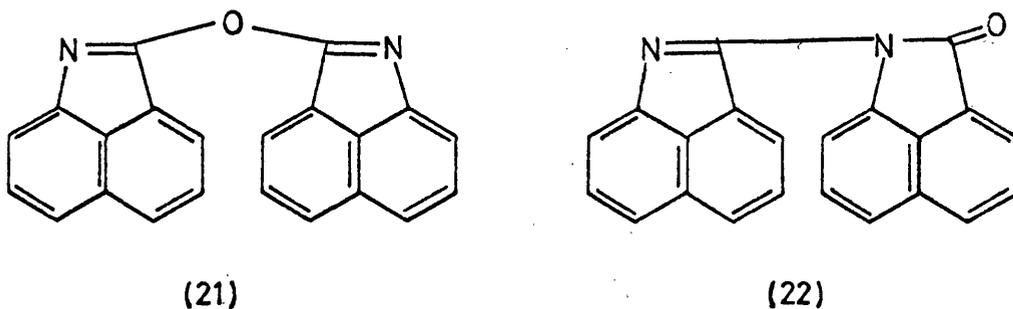


carried out under anhydrous conditions. Unfortunately since water is produced in the reaction we would expect any benz[cd]indole formed to give the hydrate (20) which would probably be quickly oxidised to naphthostyryl. The oxidations in benzene with manganese

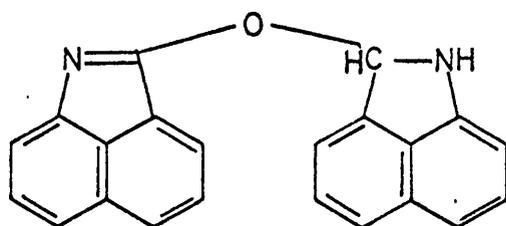


dioxide were carried out in a Dean and Stark apparatus to remove any traces of moisture formed as quickly as possible. Naphthostyryl

was the major product together with two minor ones which were separated by chromatography on silica gel and tentatively assigned the structures di-2-benz[cd]indolyl ether (21) and N (2-benz[cd]indolyl)-naphthostyryl (22). The first compound

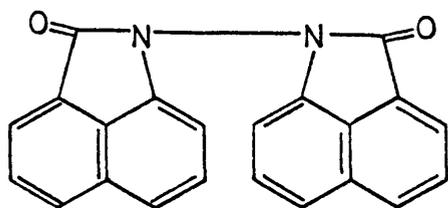


was eluted from the column as red crystals,  $C_{22}H_{12}N_2O$ . The infrared spectrum showed no NH and no carbonyl group. The mass spectrum gave a molecular weight of 320, showing that the structure was made up of naphthostyryl minus one hydrogen and benz[cd]indole minus one hydrogen. A conceivable structure which fits all the physical data is the ether (21). The second compound,  $C_{22}H_{12}N_2O$ , was straw-coloured. Its infrared spectrum was very similar to that of naphthostyryl and showed a carbonyl group at  $1730\text{ cm}^{-1}$  but no NH peak. The mass spectrum gave a molecular weight of 320. The most plausible structure is that of N (2-benz[cd]indolyl)naphthostyryl (22). The mass spectrum breakdown pattern of the two compounds (21) and (22) were identical showing distinct similarity in their structures. Both products can be rationalised by nucleophilic attack by naphthostyryl on benz[cd]indole, with further oxidation of the dihydro species produced. Attack by O would give the ether (21) and attack by N the compound (22). An alternative mechanism is attack by the hydrate (20) to give the ether (23) which would be

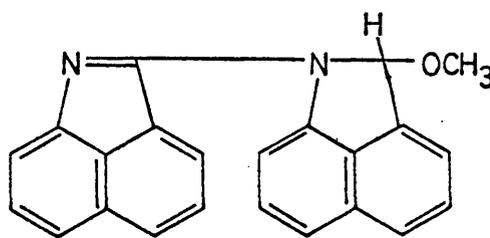


(23)

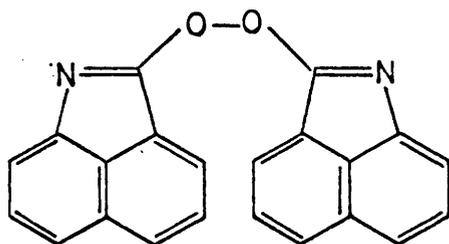
oxidised further to give (22). Attempts were made to trap benz [cd]indole using methanol as a nucleophile. Anhydrous methanol was added to the above reaction. However the same products were obtained, and surprisingly no naphtholactam-O-methyl ether was detected. Manganese dioxide oxidation in dry methanol however gave on elution with 20% ether-petroleum from silica gel an unidentified substance as orange crystals in addition to compound (22), although di-2-benz[cd]indolyl ether (21) was not isolated. The mass spectrum showed a molecular weight of 336 which is consistent with any of the structures (24) to (27). The analysis



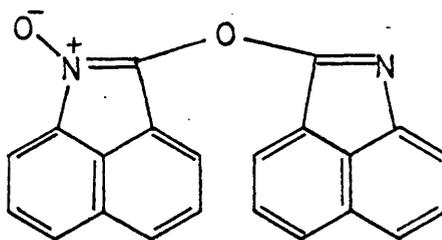
(24)



(25)



(26)



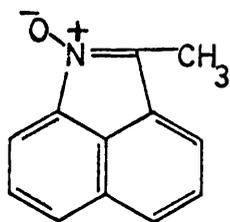
(27)

was consistent with  $C_{22}H_{12}N_2O_2$  (24, 26, or 27) thus ruling out structure (25). The infrared spectrum showed the absence of

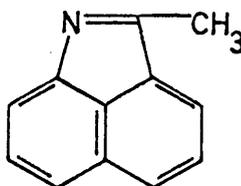
a carbonyl group ruling out naphthostyryl dimer (24). The peroxide (26) is unlikely and a peak at  $1222\text{ cm.}^{-1}$  could be assigned to an N-oxide, thus leaving (27) as the most plausible structure.

Initial attempts to oxidise 1,2-dihydrobenz[cd]indole with N-bromosuccinimide were unsuccessful.

Reductive cyclisation of methyl 8-nitro-1-naphthylketones has been reported to give the 2-methyldihydrobenzindole presumably via the benz[cd]indole which is further reduced. Deoxygenation of 8-nitro-1-naphthylmethylketone was attempted with triethyl phosphite. By analogy to the deoxygenation of 8-nitro-1-phthalimidonaphthalene, discussed in the previous section, we could expect this reaction to give the N-oxide (28) which would deoxygenate under the conditions employed to give 2-methylbenz[cd]indole (29). However no trace of the indole (29) or N-oxide (28) were detected. Methyl 8-nitro-1-naphthoate was prepared by



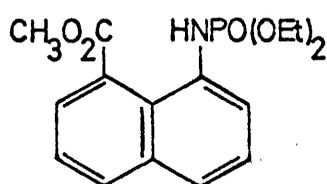
(28)



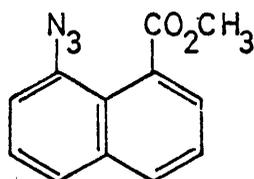
(29)

nitration of 1-naphthoic acid and the methyl ester was treated similarly with triethyl phosphite. Chromatography on silica gel gave naphthostyryl and diethyl N-(1-methoxycarbonyl-8-naphthyl) phosphoramidite (30), a type of product commonly obtained in triethyl phosphite deoxygenation of nitro compounds; see Introduction Section 2b. Again no 2-substituted benz[cd]indole was obtained.

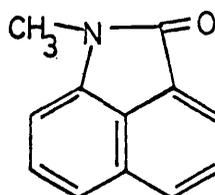
8-Amino-1-naphthoic acid was prepared by treatment of naphthostyryl with aqueous sodium hydroxide. Addition of diazomethane to a suspension of the acid in ether gave an almost quantitative yield of methyl 8-amino-1-naphthoate. Diazotisation and treatment of the resulting diazonium solution with sodium azide gave methyl 8-azido-1-naphthoate (31). Irradiation of this azide in benzene gave red needles of a compound, m.p. 103-104°, in very low yield. The infrared spectrum showed no characteristic peaks. The mass spectrum gave a molecular weight of 183. The possible products with this molecular weight are (9) (28) and



(30)



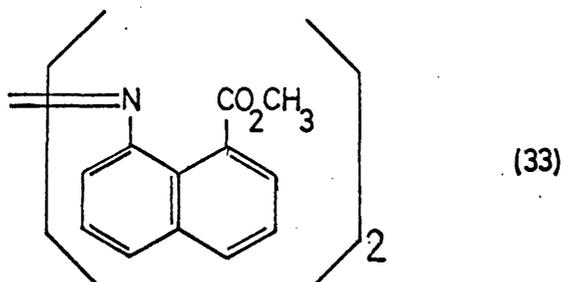
(31)



(32)

(32). Compound (32) would show a carbonyl group in its infrared spectrum and in fact is a known compound,<sup>179</sup> m.p. 77-79°. Since there is no loss of 16 in the mass spectrum the N-oxide structure is considered unlikely. This therefore leaves the ether (9), a known but not described compound (see earlier) as a possible structure. Attempts to prepare (9) unambiguously by methylation of naphthostyryl failed.

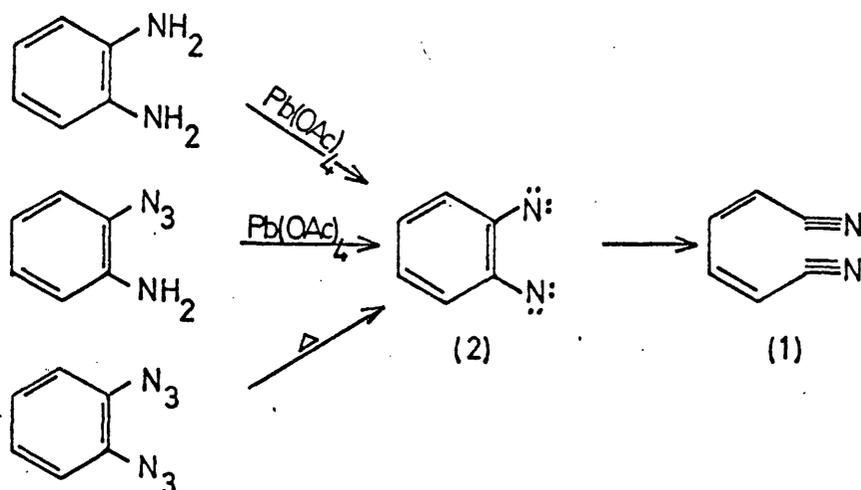
Pyrolysis of methyl 8-azido-1-naphthoate in refluxing 1,2,4-trichlorobenzene gave red needles of 8,8'-methoxycarbonyl-1,1'-azonaphthalene (33), the normal dimerisation product found in azide decompositions. The infrared spectrum indicated a carbonyl group but no amine. The mass spectrum gave a molecular weight of 398, with losses of 59 ( $\text{CO}_2\text{CH}_3$ ), 126 ( $\text{C}_{10}\text{H}_6$ ) and 28 ( $\text{N}_2$ ).



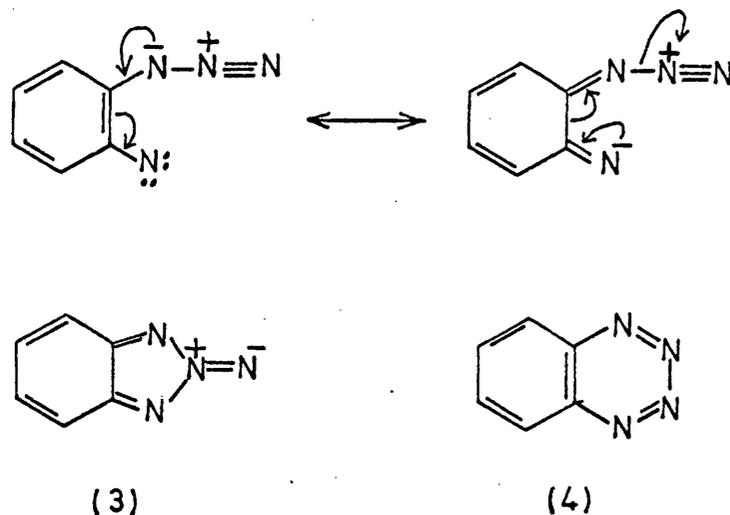
Our attempts to prepare the parent benz[cd]indole were thus unsuccessful. However products were obtained that could be explained by very rapid nucleophilic attack on this compound by naphthostyryl. Naphthostyryl itself probably arises from benz[cd]indole by covalent hydration, which occurs in the presence of manganese dioxide. Generation of a nitrene peri to a carbonyl group in this naphthalene system does not readily lead to formation of the peri C=N bond. This possibly reflects the difference between a 5 or 6 ring peri nitrene-carbonyl interaction.

**Section III.****ROUTES TO AZABENZOCYCLOBUTADIENE.**

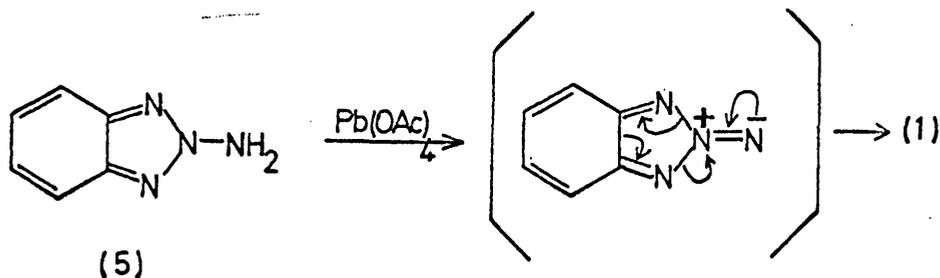
Thermolysis of o-diazidobenzene<sup>182</sup> and oxidation of o-phenylenediamine<sup>25</sup> and o-azidoaniline<sup>183</sup> all give 1,4-dicyano-1,3-butadiene (1). These reactions can all be envisaged as proceeding via the dinitrene (2), although this seems most unlikely.



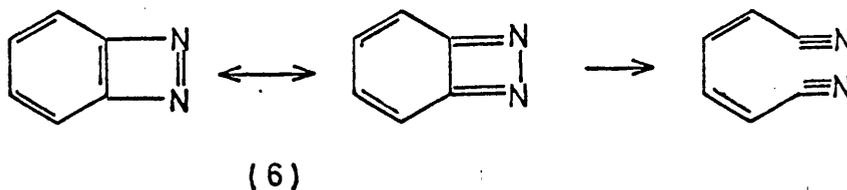
In the case of the azido compounds the mono azidonitrene could lose a molecule of nitrogen in concert with ring cleavage. There is also the possibility that interaction of the nitrene with the adjacent azido group leads to unstable heterocyclic systems such as (3) or (4) which fragment (possibly in a symmetry allowed concerted process) with the loss of one molecule of nitrogen. Support for the intermediate (3) is found in the lead tetra-acetate oxidation



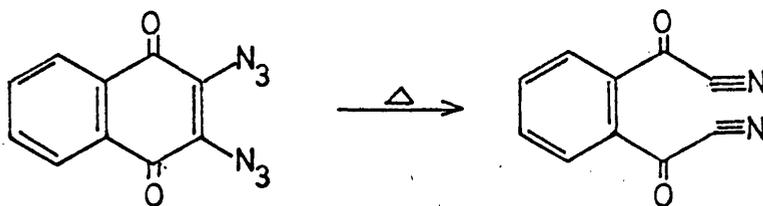
of 2-aminobenzotriazole (5) with formation of the dicyano compound (1).<sup>75</sup> There is also the intriguing, but perhaps less likely



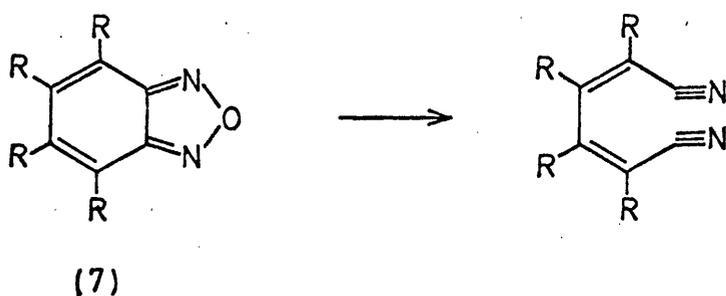
possibility, that the reaction proceeds through an unstable diazabenzocyclobutadiene (6).



This ring cleavage is a general reaction and 2,3-diazido-1,4-naphthoquinone gives phthaloyl cyanide on thermolysis in toluene.<sup>184</sup>

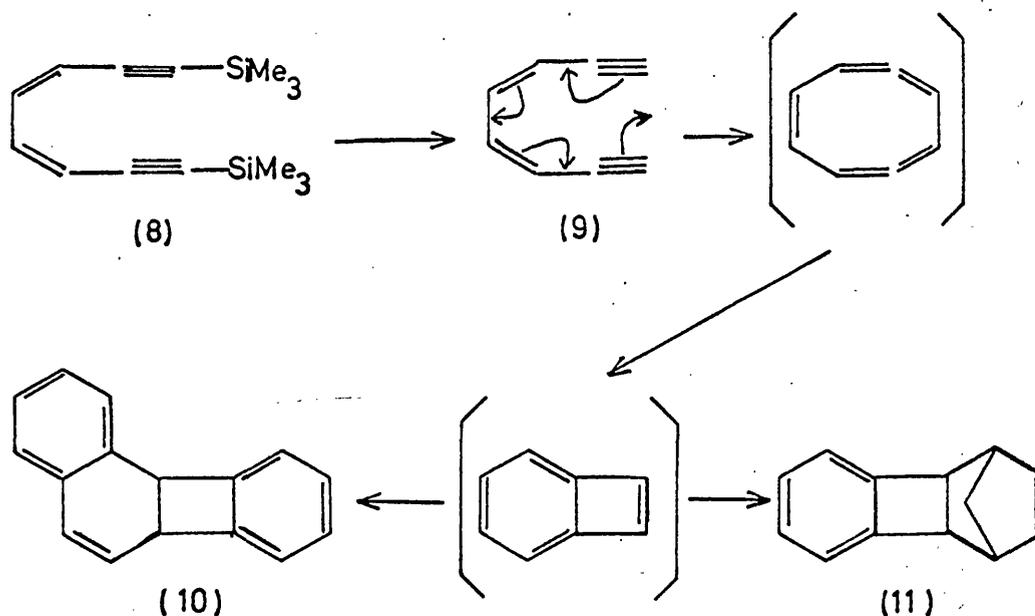


Another possible example illustrating the general tendency of species with the stoichiometry of (2) to cleave to the corresponding dicyano compound is the deoxygenation of the furazan (7) by irradiation



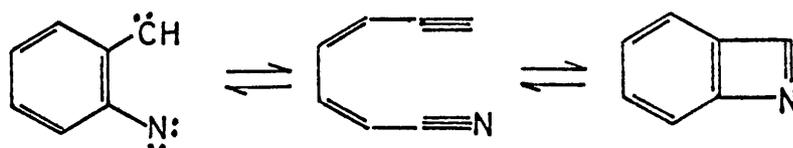
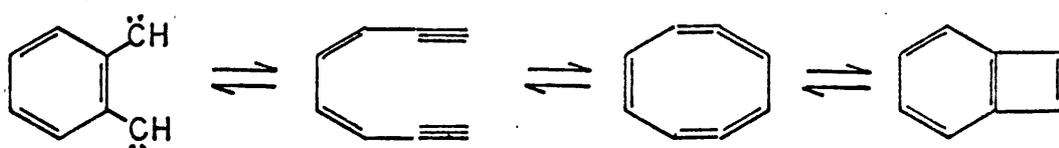
in the presence of triethyl phosphite.<sup>21</sup> However in this case cleavage of the ring may precede deoxygenation.

In view of the above reactions, where ring opening is observed, we were surprised by a recent communication by Sondheimer.<sup>185</sup> Hydrolysis of the bis (trimethylsilyl) compound (8) in ethanol with aqueous sodium hydroxide was found to give cis, cis-3,5-octadiene-1,7-diyne (9). This was detected spectroscopically, but was an unstable compound, which is rapidly converted into the known benzocyclobutadiene dimer (10) in high yield. Hydrolysis of the silyl derivative (8) in the presence of cyclopentadiene gave the adduct (11) of benzocyclobutadiene.



Since the formal dinitrene ring-opens to the dicyano compound, whereas the corresponding diacetylene ring closes to give the unstable benzocyclobutadiene, we thought that it would be interesting to study the following systems.<sup>†</sup> We decided to examine o-nitrenophenylcarbene (12) first, since this would be easier, and since it was intermediate between the dinitrene and the dicarbene. From the nitreno-carbene (12) we could expect to get the

<sup>†</sup> See page 144.

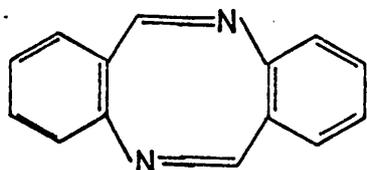


(12)

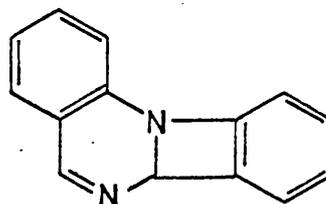
(13)

(14)

cyanoacetylene (13) or products derived from azabenzocyclobutadiene (14) such as the dimers (15) or (16).

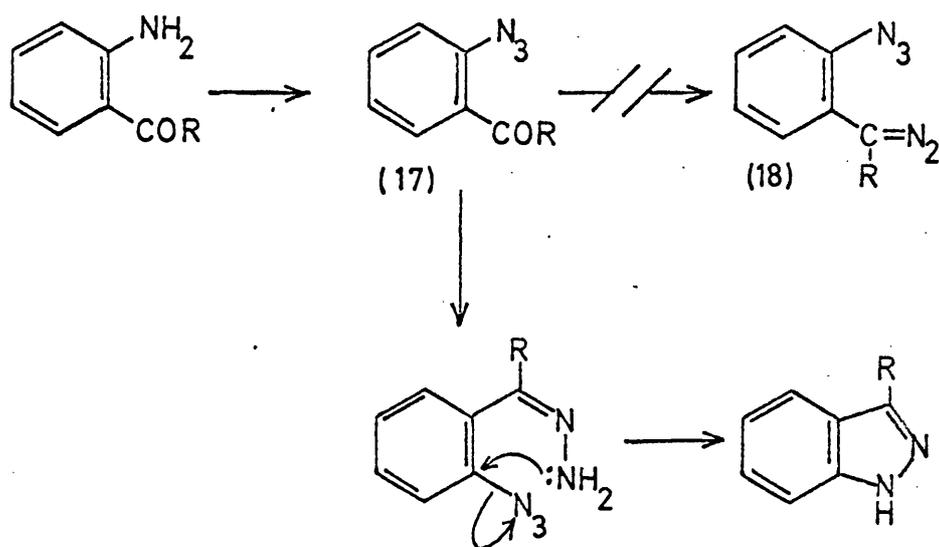


(15)

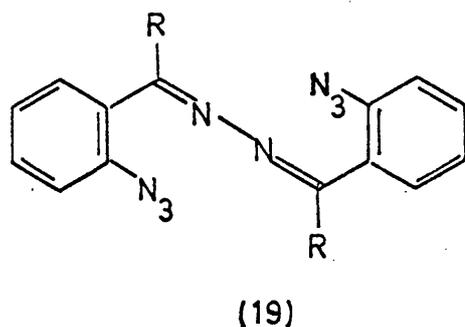


(16)

The obvious precursor to (12) would be the *o*-azidodiazoo compound (18, R=H). Since non-terminal acetylenes may be more stable than a terminal acetylene, attempts were made to prepare the substituted *o*-azidodiazoo compounds (18, R=Me or Ph). Treatment of the azidoaldehyde (17, R=H) or azidoketones (17, R=Me or Ph) with hydrazine hydrate did not give the hydrazone but gave the corresponding indazole in high yield.

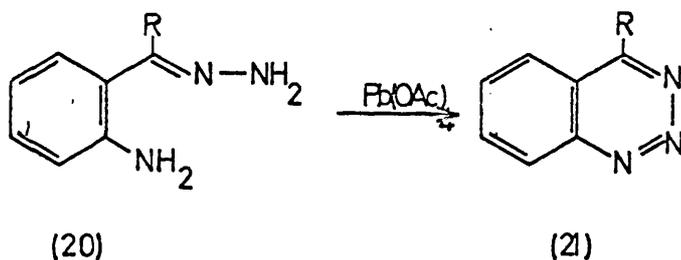


The indazoles probably arise by intramolecular nucleophilic displacement of the azido group in the first formed azidohydrazone. This is known for *o*-bromoketones and *o*-nitroketones with hydrazine but more forcing conditions are required. Thus 3-phenylindazole can be obtained in 45% yield by heating *o*-bromobenzophenone with hydrazine hydrate at 200° for 12hr.<sup>186</sup> Our conditions are much milder and it is perhaps surprising that the azide group is such a good leaving group; relatively few examples of nucleophilic displacement of aromatic azide groups have been reported.<sup>187</sup> Therefore we considered the possibility of a ketazine intermediate. The ketazine of *o*-aminoacetophenone was prepared and converted into

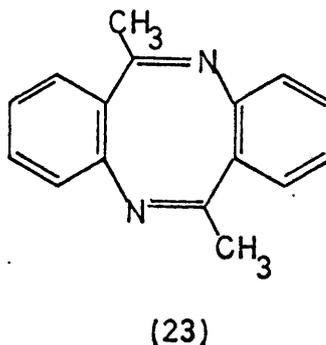
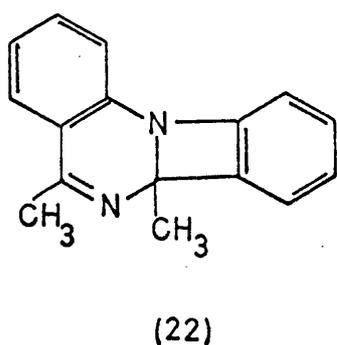


the azidoketazine (19) by diazotisation and treatment with sodium azide. However decomposition of this compound under the normal reaction conditions gave no trace of 3-methylindazole.

Since an *o*-azidodiazo compound was not readily available, oxidation of the *o*-aminohydrazone was considered. This should lead to the *o*-aminodiazo compound and then to the *o*-nitrenocarbene by analogy with the oxidation of *o*-azidoaniline. However oxidation of *o*-aminobenzophenone hydrazone (20, R=Ph) with lead tetra-acetate gave a good yield (86%) of a colourless crystalline solid,  $C_{13}H_{12}N_3$ . The infrared spectrum showed no functional groups, and the mass spectrum gave a molecular weight of 207. The compound was therefore assigned the 4-phenyl-1,2,3-benzotriazine structure (21, R=Ph). The 4-methyl analogue (21, R=Me) was obtained in lower yield on

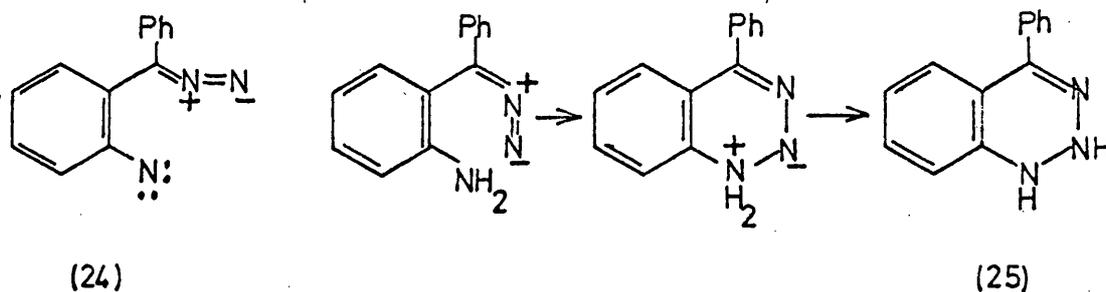


oxidation of *o*-aminoacetophenone hydrazone (20, R=Me) together with an unidentified oil, the molecular weight of which showed it to consist of 2 units of azabenzocyclobutadiene. However, the infrared spectrum which showed  $NH_2$  ruled out a simple dimer (analogous to a

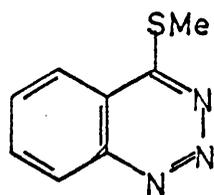


benzocyclobutadiene dimer) such as (22) or (23). Similar oxidation of the *o*-aminobenzaldehyde hydrazone (20, R=H) did not give the parent benzotriazine (21, R=H). Therefore either this is unstable or the reaction takes a different course. No trace of the cyanoacetylene (13) or products which could have arisen from azabenzocyclobutadiene were found. Oxidation of *o*-aminobenzophenone hydrazone with  $\text{NiO}_2$  gave the benzotriazine (21, R=Ph) as well as an unidentified substance ( $m/e$  381) which showed a broad peak at  $3360 \text{ cm.}^{-1}$  in the infrared.

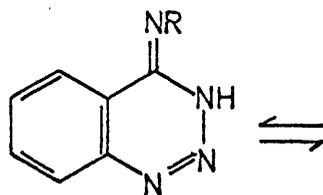
The benzotriazine (21) could be formed from the diazonitrene (24), but more likely arises from the diazo group interacting with the amino group to give the cyclic hydrazine (25), which would be rapidly oxidised further.



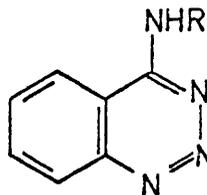
The parent compound (21, R=H) has not yet been described. Previous attempts to synthesise it have been unsuccessful.<sup>188</sup> No 4-aryl or 4-alkyl substituted derivatives of this system have been reported, although some 4-substituted derivatives are known, e.g.  $=\text{O}$ <sup>189</sup>,  $=\text{S}$ ,  $-\text{NHR}$ ,  $-\text{NHNH}_2$ <sup>188</sup>. Triazinones are well known, as are the benzotriazine N-oxides, but the only unambiguous triazine is the thiomethyl derivative (26).<sup>190</sup> Tautomerism of the type  $27 \rightleftharpoons 28$  is possible for all other reported 4-substituted benzotriazines.<sup>191, 192</sup>



(26)

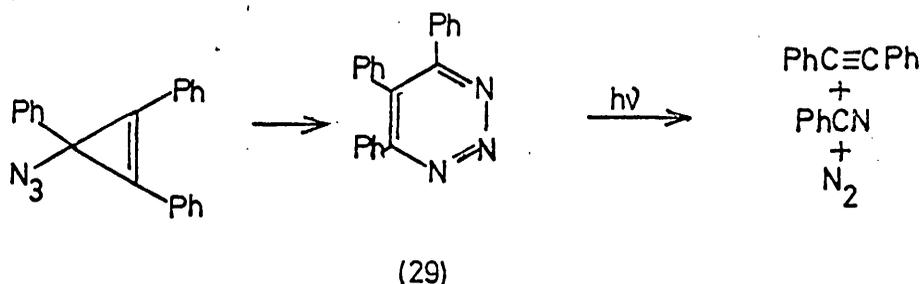


(27)

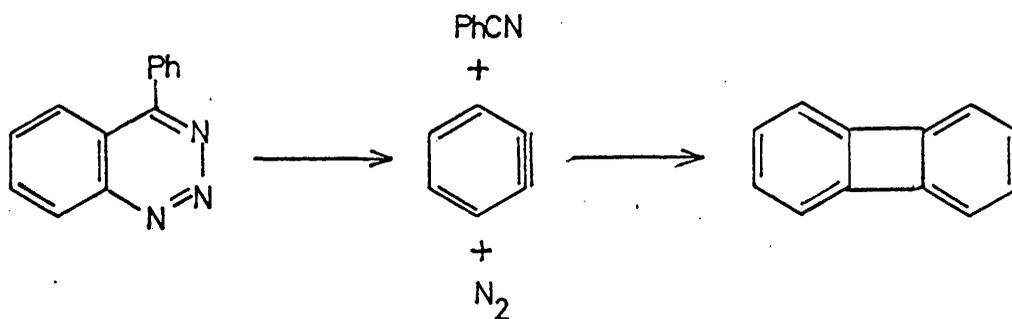


(28)

The only monocyclic triazine known is 4,5,6-triphenyl-1,2,3-triazine (29). This readily decomposes on irradiation in benzene to give diphenylacetylene, phenyl cyanide and nitrogen.<sup>193</sup> 4-Phenylbenzo-1,2,3-triazine was found to be photolytically stable



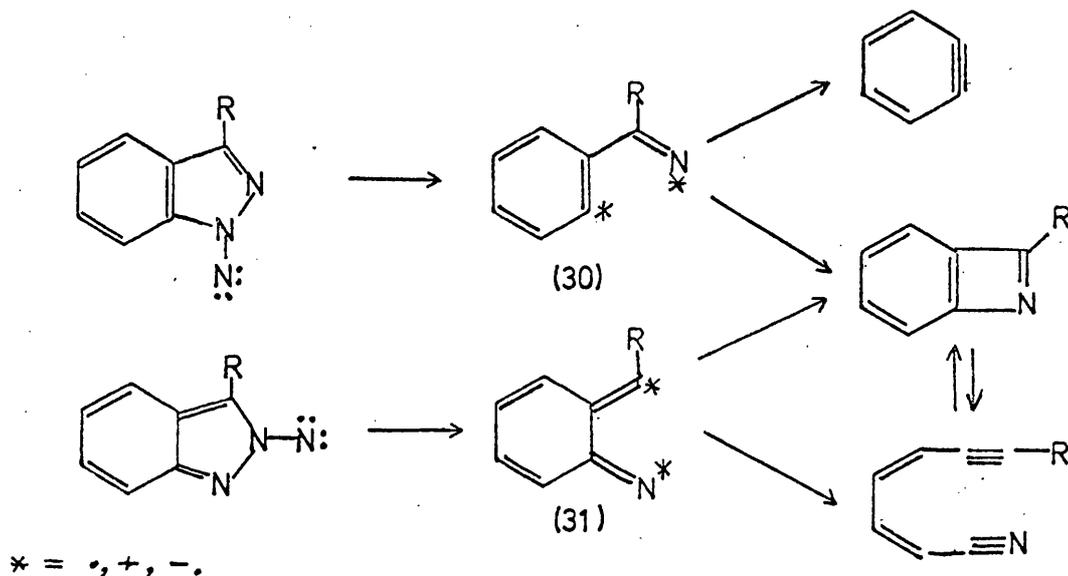
in benzene, but decomposed to polymeric material in acetonitrile. Photolysis in acetonitrile in the presence of furan in an attempt to trap benzyne gave no 1-naphthol after acid work up. However thermolysis in a hot tube (400°, 0.2 mm) did give biphenylene (16%) and phenyl cyanide (20%). The reaction may be stepwise with initial



loss of nitrogen followed by loss of phenyl cyanide or it could be a

concerted process. The phenylbenzotriazine is therefore a new benzyne precursor and this fragmentation provides further support for its structure. Initial experiments have shown that the 4-methyl analogue is less stable than the 4-phenyl and a more refined vapour phase pyrolysis apparatus would probably give better yields of benzyne.

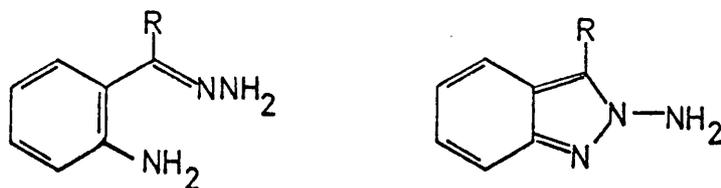
Over the past few years, Rees and his group have systematically studied N-nitrenes obtained by oxidation of heterocyclic N-amino compounds. During the course of this work Horwell<sup>138</sup> examined the oxidation of 1- and 2-aminoindazoles. The expected reactions of the nitrenes derived from oxidation of the N-aminoindazoles are shown in Scheme 1. Since these are



(Scheme 1 )

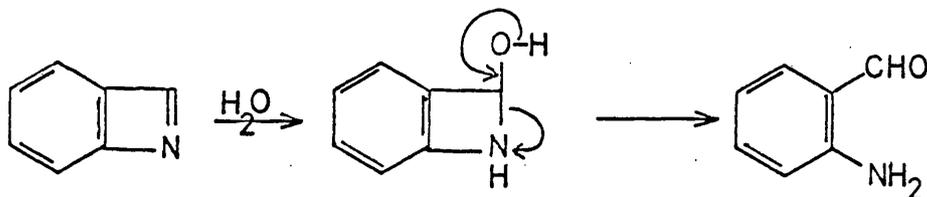
N-nitrenes with an adjacent nitrogen atom, fragmentation would be expected to lead to species of stoichiometry (30) and (31) in a similar manner to the very ready loss of nitrogen on oxidation of N-aminobenzotriazole. In principle (30) could lose RCN to give benzyne or ring close to give 2-substituted azabenzocyclobutadiene which may cleave to give cyanoacetylene. It would be instructive, therefore, to compare the products obtained by

oxidation of N-aminoindazoles with those of the hydrazones described above. Oxidation of 2-aminoindazoles is especially



relevant in the study of the nitrenocarbene problem.

Horwell examined the lead tetra-acetate oxidation of 1- and 2-aminoindazoles and his results are summarised in Table 1. He explained the formation of the acetamidoaldehyde and the anils in terms of azabenzocyclobutadiene which would be highly susceptible to nucleophilic attack. o-Acetamidobenzaldehyde is probably not the major product and subsequent re-investigation <sup>194</sup> of this reaction has shown that it is in fact o-aminobenzaldehyde. o-Aminobenzaldehyde is readily explained by attack of water. In vigorously dried solvents

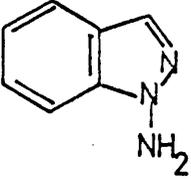
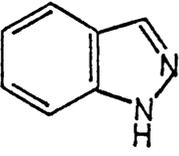
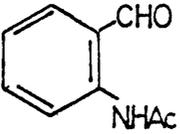
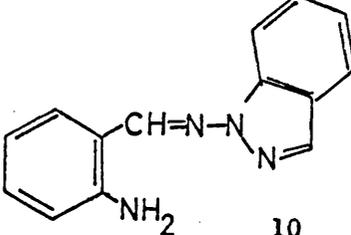
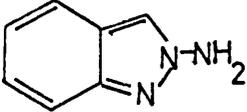
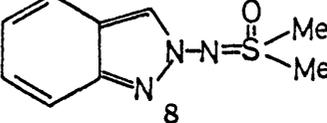
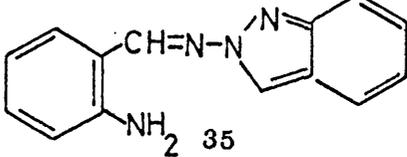


the yield of o-aminobenzaldehyde falls considerably and significantly the yield is greatest from oxidation in dimethylformamide ( a solvent particularly hard to dry).

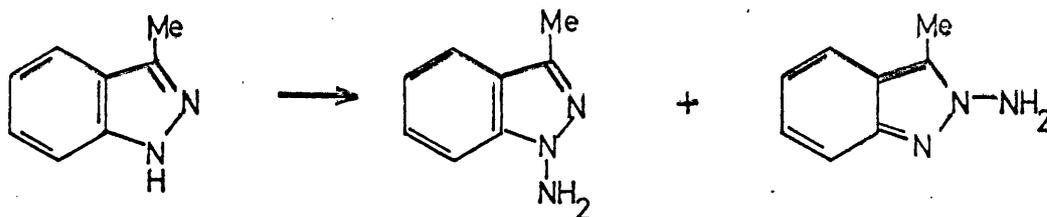
Horwell also isolated, in small yield, two compounds which appeared to be the dimers of azabenzocyclobutadiene (15) and (16).

Both 1- and 2-aminoindazoles were obtained by the method of Horwell. 3-Methylindazole was aminated in alkaline solution with hydroxylamine-o-sulphonic acid to give the 1-N-amino and 2-N-amino-3-methylindazoles. These isomeric structures are easily

Table 1.

Indazole and solvent	Products and yields %		
			others.
methylene chloride	20	5	-
dimethyl sulphoxide	15	20	-
dimethylformamide	0	70	-
ethanol (-70°)	5	0	 10
			
methylene chloride	0	15	-
dimethyl sulphoxide	0	20	 8
methylene chloride and cyclopentadiene	0	0	 35

distinguished by examination of their u.v. spectra and comparison



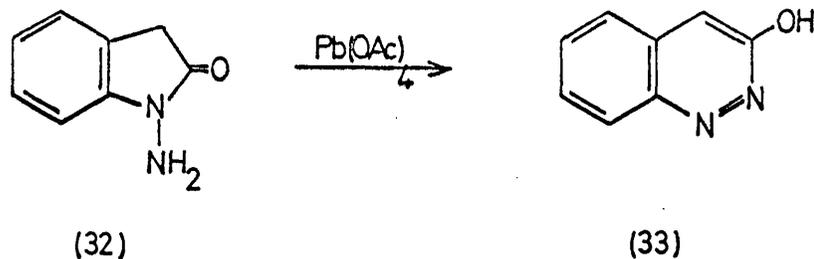
with those of 1- and 2-methylindazoles<sup>195</sup> and 1- and 2-aminobenzo-  
triazoles.<sup>183</sup> In all these cases the u.v. spectrum of the

1-N-substituted compound was very similar to that of the unsubstituted parent. In the case of 3-phenylindazole, various attempts to aminate with hydroxylamine-O-sulphonic acid at different pH and temperature and with chloramine in ether gave only the 2-amino-3-phenylindazole. 1-Amino-3-phenylindazole was not isolated.

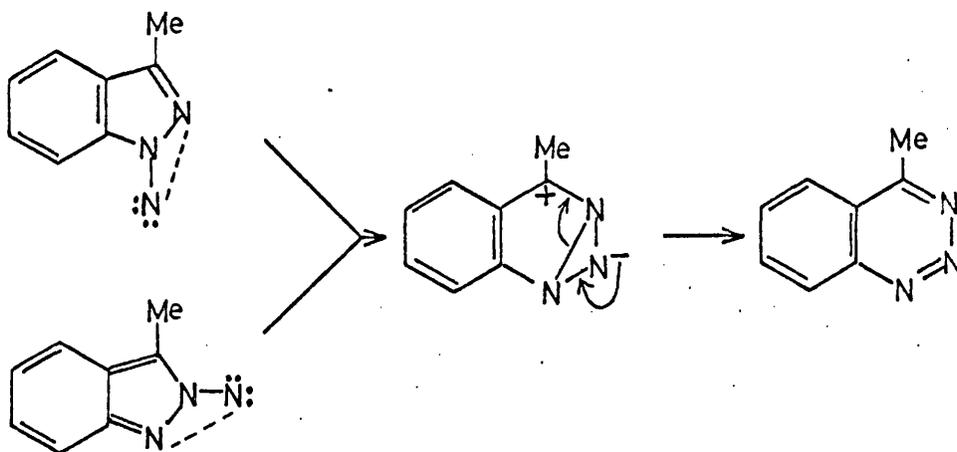
Oxidation of 2-amino-3-phenylindazole in methylene chloride with lead tetra-acetate gave, surprisingly, a high yield (80 %) of 4-phenylbenzo-1,2,3-triazine. No products arising from formation of azabenzocyclobutadiene could be detected. Both 1-amino and 2-amino-3-methylindazole on oxidation gave 4-methylbenzo-1,2,3-triazine (71 % and 60 % respectively), in lower yield than in the phenyl case. Similar oxidation of 1- and 2-N-aminoindazole in methylene chloride gave low yields of o-acetamidobenzaldehyde; no triazine could be found.

This conversion of indazoles into triazines is a very intriguing reaction. There are no other examples of ring expansion on oxidation of N-amino compounds with an adjacent nitrogen atom in the ring. Nitrenes thus formed usually fragment. Ring expansion has been observed<sup>196</sup> on oxidation of 1-aminooxindole (32) to give cinnolin-3-ol (33).

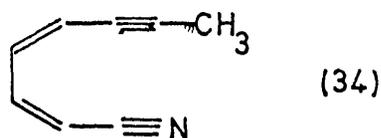
Both the 1-amino and 2-amino-3-methylindazoles on oxidation give the same product, 4-methylbenzo-1,2,3-triazine.



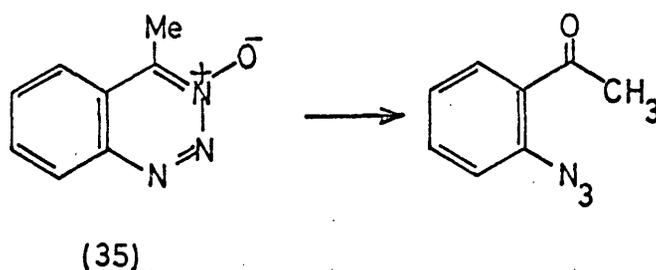
If "ring insertion" of the nitrene does occur in this reaction, it is possibly into the N-N bond to give the same intermediate in both cases; although insertion into a C-N bond cannot be excluded.



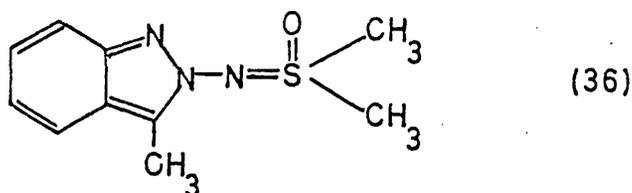
The amino indazoles were also oxidised in dimethyl sulphoxide in the hope that the nitrene would be trapped as the sulphoximine. Oxidation of 2-amino-3-phenylindazole gave a low yield of the triazine as well as an unidentified yellow crystalline solid. The infrared spectrum of the yellow substance showed no characteristic peaks and the mass spectrum gave a molecular weight of 194 (though not 2- or 3-phenylindazole). 2-Amino-3-methylindazole on similar oxidation gave a rapidly decomposing oil which showed a doublet in the infrared spectrum at  $2115 \text{ cm.}^{-1}$ . This could be the sought after cyanoacetylene (34). The possibility that this oil was *o*-azidoacetophenone was considered. The



benzotriazine oxide (35) is known to rearrange to *o*-azidoacetophenone.<sup>197</sup>



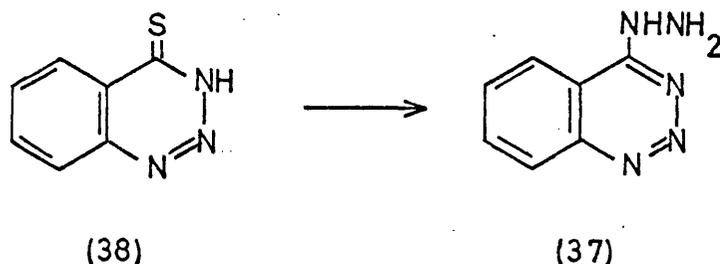
However, the oil obtained had a different infrared spectrum to *o*-azidoacetophenone, and decomposed much faster than the azide. Closer examination of this oxidation revealed an oil which could be the dimethylsulphoximine (36). Horwell isolated the dimethyl sulphoxide adduct from 2-aminoindazole but was unable to detect the isomeric adduct in the oxidation of 1-aminoindazole. The mass spectrum of the oil gave a molecular weight of 223 which corresponds to compound (36). The infrared showed a peak at  $1030\text{cm.}^{-1}$  ( $\text{S}=\text{O}$ )



characteristic of a sulphoximine. However it would not crystallise and no satisfactory analysis was obtained. No triazine was isolated in dimethyl sulphoxide. 1-Amino-3-methylindazole in dimethyl sulphoxide did, however, give a low yield of 4-methylbenzotriazine

and also an unidentified yellow oily substance which showed NH in the infrared and had a molecular weight of 252, (mass spectrum).

4-Hydrazinobenzo-1,2,3-triazine (37) was prepared using a modification of a literature method<sup>140</sup> by treatment of 4-mercapto-benzo-1,2,3-triazine (38) with hydrazine hydrate.



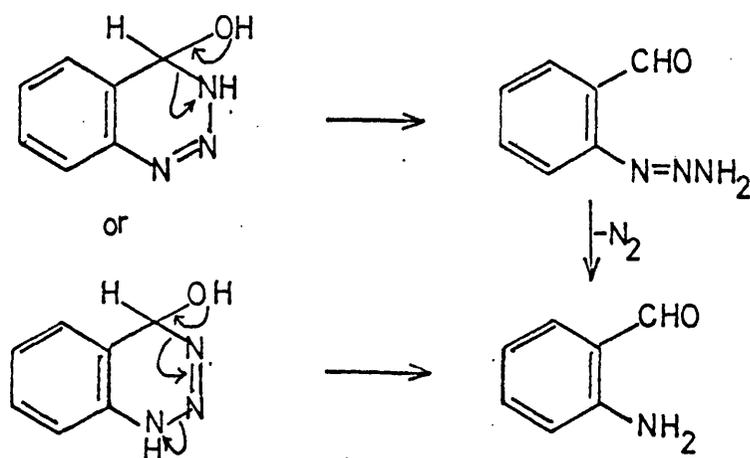
The hydrazine (37) was oxidised in benzene in an attempt to form the parent benzotriazine (21, R=H). Alternatively since arylhydrazines have been oxidised in aromatic hydrocarbons to give diaryls,<sup>198</sup> oxidation of hydrazine (37) in benzene could give 4-phenylbenzo-1,2,3-triazine. However oxidation with manganese dioxide gave benzonitrile (29%). The parent benzotriazine could well have been formed, but decomposed as shown, via the diazonium compound. Such a decomposition is not available to the 4-substituted benzotriazines.



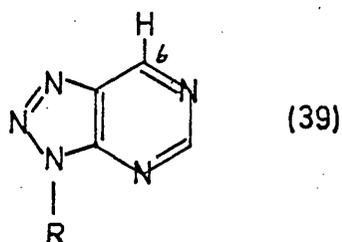
Silver oxide also gave benzonitrile, but in lower yield (12%), together with an unidentified crystalline substance.

The formation of benzotriazines in the oxidation of the 3-substituted indazoles throws considerable doubt on Horwell's suggestion that azabenzocyclobutadiene is formed in the oxidation of 1- and 2-aminoindazole. The possibility that the products obtained

in those reactions arose from the unsubstituted triazine must be seriously considered. This would also explain the similarity of products from both the 1- and 2-aminoindazole. It seems unreasonable that there should be such a vast difference in modes of reaction on oxidation of 3-substituted and 3-unsubstituted indazoles. It is probable, therefore, that in the unsubstituted case, the triazine is first formed. The triazine would be susceptible to nucleophilic attack and the products of Horwell can be explained on this basis.



The 4-substituted triazine might well be stable. A rather similar situation has been found by Albert<sup>199</sup>; 6-substituted azapurines are stable but the unsubstituted azapurine (39) is susceptible to covalent hydration. This is probably due to both steric and electronic factors.

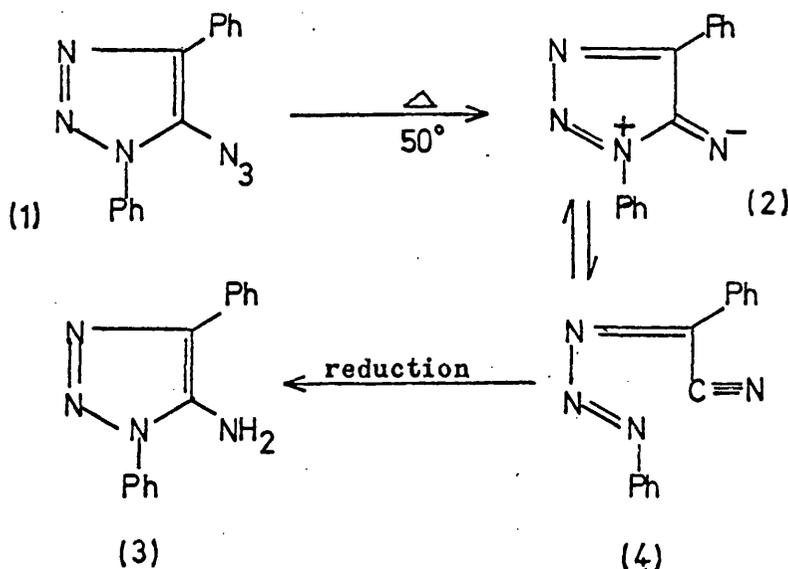


It is still possible, though unlikely, that the products obtained on oxidation of the aminoindazoles could arise by different mechanisms. The two modes of breakdown of the indazole nitrene may be affected by the indazole 3-substituent. 3-Phenyl-2-aminoindazole gives on oxidation a good yield of the benzotriazine. The 3-methylaminoindazoles give much lower yields of the benzotriazine and this could possibly be due to some breakdown of the first formed nitrene to give the unstable substituted azabenzocyclobutadiene. The aminoindazoles themselves do not give the benzotriazine, but give products which could arise from the intermediacy of either azabenzocyclobutadiene or benzotriazine. A distinction between these possibilities awaits further investigation.

## Section IV.

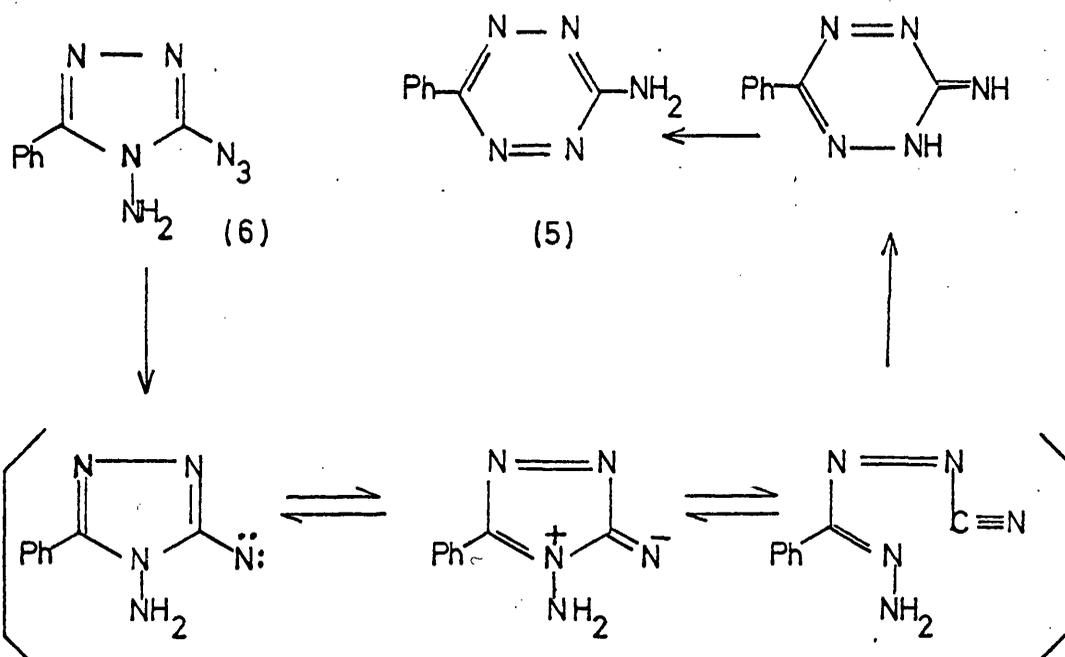
"5-NITRENO-1,4-DIPHENYL-1,2,3-TRIAZOLE".

Smith and his co-workers<sup>130</sup> have decomposed 5-azido-1,4-diphenyl-1,2,3-triazole (1) at low temperature (50°) to obtain a red product which they claim to be a stable nitrene. On the basis of chemical reactions, they concluded that this compound had the nitrene structure (2). Reduction of their product, catalytically and with butyl mercaptan gave the amine (3). However since it also absorbed weakly in the infrared at 2200 cm.<sup>-1</sup> it was necessary to postulate that it was in equilibrium with the ring opened form (4). None of the expected reactions

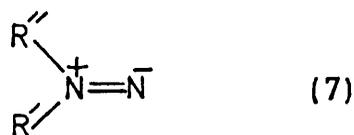


of a nitrene, such as dimerisation, hydrogen abstraction, rearrangement, or insertion were reported. A similar intermediate has been proposed<sup>180</sup> to account for the formation of compound (5) on the decomposition of 4-amino-3-azido-5-phenyl-1,2,4-triazole (6).

The structure suggested by Smith is a highly stabilised nitrene and is thus similar to a stabilised singlet N-nitrene of type (7). We were intrigued by the product (2) or (4) which posed a



perplexing problem. Even though the structure proposed was a "stable nitrene" no attempt had been made to prove this by reaction



with established nitrene traps. Since this structure is comparable to a stabilised singlet N-nitrene the compound (2) should undergo normal N-nitrene reactions. Therefore with olefins we would expect to observe addition reactions and isolate the appropriate aziridine, and with dimethyl sulphoxide we should get the sulphoximine.

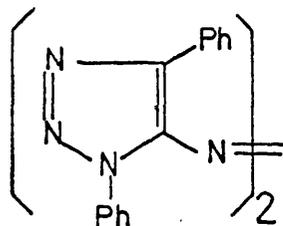
Diazotisation of 1-amino-1,4-diphenyl-1,2,3-triazole and addition of sodium azide to the diazonium solution gave 1-azido-1,4-diphenyl-1,2,3-triazole. Decomposition of the azide gave the compound<sup>†</sup> reported by Smith in good yield. However decomposition in cyclohexene also gave compound A in good yield and no aziridine was

†

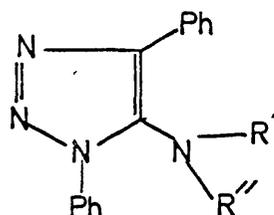
Hereafter referred to as compound A.

isolated. Decomposition of the azide in dimethyl sulphoxide gave a lower yield of compound A, together with a small amount of the amino compound which could have arisen by hydrogen abstraction by the nitrene. Heating compound A with diethyl acetylenedicarboxylate in refluxing xylene did not trap the nitrene.

Oxidation of N-amino compounds to give the N-nitrene is well established. Oxidation of C-amino compounds to give nitrenes is relatively unknown. o-Phenylenediamine gives muconitrile on oxidation, which could possibly arise by the involvement of a nitrene. Oxidation of 5-amino-1,4-diphenyl-1,2,3-triazole (3) with lead tetra-acetate gave compound A in 38% yield, the formal nitrene dimer (8) in 9% yield, together with an unidentified substance. Dimerisation is fairly common in reactions



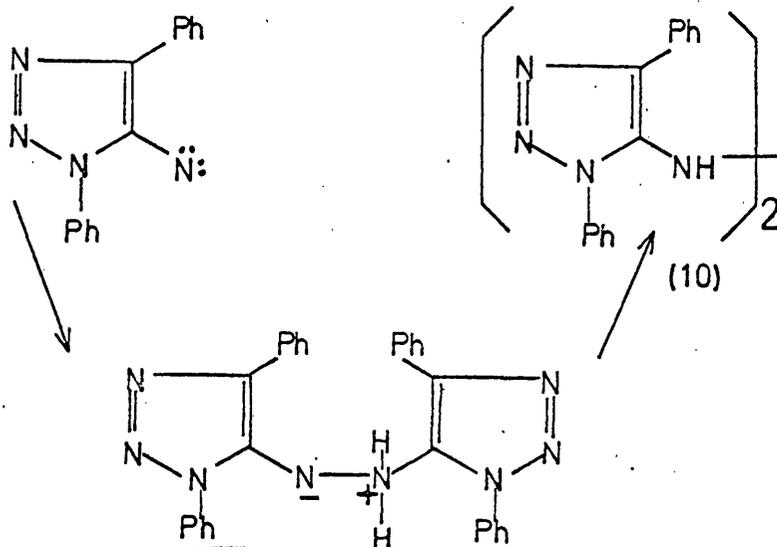
(8)



(9)

which are used to generate nitrenes (See Introduction, Section 3b).

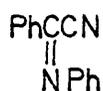
The nitrene, produced on oxidation, probably attacks unoxidised amino compound to give the hydrazine (10) which is further oxidised to the



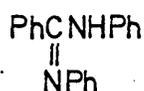
azo compound. The unidentified substance was isolated as colourless needles. The infrared spectrum showed a secondary amine and a carbonyl group and at first it was thought to be the mono-acetyl derivative of the amine (9,  $R' = H, R'' = COCH_3$ ). Attempts to prepare the mono-acetyl derivative of 5-amino-1,4-diphenyl-1,2,3-triazole by reaction with acetic anhydride failed and only the diacetyl derivative (9,  $R' = R'' = COCH_3$ ), which was identified readily by analytical and spectral data, was isolated. However the mass spectrum of the unknown substance gave a molecular weight of 266 ( $m/e$  required 278). Oxidation of the amino compound in cyclohexene and in methyl acrylate gave the compound A in 34% and 40% yield respectively, together with an unidentified cyanide. No aziridine could be found in either case.

Another possible precursor of the nitrene (2) was prepared. Treatment of the azide with triphenyl phosphine gave 1,4-diphenyl-5-triphenylphosphinimino-1,2,3-triazole (9,  $-N=PPh_3$  for  $-NRR''$ ). However this compound was stable to photolysis and gave no trace of the red compound A.

Compound (2) should react with amines to give hydrazines. Smith found it reacted with aniline to give N,N-diphenylbenzamidine (11). However he found compound A decomposed on heating to phenylglyoxylonitrile anil (12) and this was shown to be an intermediate in the formation of (11). We confirmed this reaction and also isolated an unidentified substance which had a molecular



(12)



(11)

weight of 299 (consistent with compound A less  $N_2$  plus aniline). Reaction of the so called "stable nitrene" with diethylamine in an attempt to get the N-diethylhydrazine gave two unidentified compounds which could not be explained by the intermediacy of a nitrene.

A compound with structure (2) should undergo normal nitrene reactions. Our investigation of this compound gave no products that could be explained by this structure. We must conclude from our inability to get nitrene products that in fact the compound does not have structure (2) and this is not in equilibrium with (4). In a very recent paper<sup>181</sup> Smith has stated that his former evidence is "neutralised," that the electronically stabilised nitrene has only a minor part in the equilibrium and that the compound mainly exists as shown in (4). However if the nitrene (2) were there, even in small quantities, it should be trapped and it seems that (2) plays no part at all in the equilibrium proposed.

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