DEHYDRO-INTERMEDIATES IN NAPHTHALENE CHEMISTRY

By

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STATEMENT

The work described in this thesis was carried out by the author in the Departments of Chemistry of the University of London, King's College and the University of Leicester under the supervision of Professor C. W. Rees. No part of it is concurrently being submitted for any other degree.

October 1964 - June 1967

Signed R C Storr

(R. C. Storr)

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Professor C. W. Rees for his invaluable advice and encouragement throughout the course of the work presented in this thesis.

I should also like to thank the University of Leicester and University of London King's College for providing research facilities, and the Science Research Council for the award of a Research Studentship.

ABSTRACT

The extension of benzyne chemistry to non ortho-dehydroarenes is discussed. The generation and reactions of the "meta"-dehydroarene, 1,8-dehydronaphthalene, are described and attempts made to correlate its properties with the possible electronic structures of dehydroaromatic intermediates.

1,8-Dehydronaphthalene was generated by oxidation of 1-aminonaphtho[1,8-de]triazine and was shown to be a highly reactive species, readily undergoing radical abstraction reactions and 1,2-addition to a variety of unsaturated systems such as olefins, acetylenes, aromatic hydrocarbons and azo compounds. The stereospecificity of 1,2-addition to olefins was carefully investigated in an attempt to determine the singlet-triplet nature of 1,8-dehydronaphthalene.

1-Aminonaphtho[1,8-de]triazine was prepared by direct amination of naphtho[1,8-de]triazine with hydroxylamine-O-sulphonic acid which also gave 8-azido-1-naphthylamine rather than the expected 2-aminonaphtho[1,8-de]triazine. However amination of the naphthotriazine with chloramine gave both 1- and 2-aminonaphthotriazines, and the 2-amino isomer was shown to rearrange readily to 8-azido-1-naphthylamine under the alkaline conditions of the hydroxylamine-O-sulphonic acid amination, although it was stable to acid. In contrast 1-aminonaphthotriazine was stable to alkali but underwent an interesting acid catalysed

rearrangement to the same azide. Other possible, but unsuccessful, routes to 1,8-dehydronaphthalene were briefly investigated.

Since 1,8-dehydronaphthalene was very different from benzyne generated similarly, 1,2-and 2,3-naphthyne were prepared by oxidation of the appropriate aminonaphthotriazole, to provide a more direct comparison. These two naphthynes closely resembled benzyne and were again significantly different from 1,8-dehydronaphthalene. Their dimerisation in the absence of aryne "traps," and their crossed coupling with each other and with benzyne proved an attractive route to the dibenzo- and monobenzo-biphenylenes.

The new heterocyclic system, benz[cd]indazole, was of interest as a possible product in the oxidations of 1- and 2-aminonaphtho[1,8-de]triazines and as a possible precursor to 1,8-dehydronaphthalene. Various attempts to obtain this and its dihydro derivative failed; however dimethyl dihydrobenz[cd]-indazole-1,2-dicarboxylate was formed by addition of 1,8-dehydronaphthalene to dimethyl azodicarboxylate. A novel oxazole synthesis is also described.

Anomalies in the amination of benzotriazole with chloramine and hydroxylamine-O-sulphonic acid compared with similar amination of naphtho[1,8-de]triazine led to the isolation of 1-chlorobenzotriazole, which proved to be a reactive positive halogen compound and a convenient new oxidant.

CONTENTS

INTRODUCTION

The preparation and reactions of ortho- dehydroarene intermediates are now well established, especially following the intensive studies of the last decade. However, although there are many reviews on these ortho- arynes,[1-10] at the outset of our work (1964) no successful attempts to prepare non ortho- dehydroaromatic intermediates had been reported. This was probably due to two factors: a) the inherent difficulty in the formation of these intermediates, and b) the problem of detecting any such new type of species. Nevertheless the prospect of a whole 'new chemistry' of non ortho- dehydroarenes comparable with that of the ortho- arynes, together with the associated theoretical interest, provided a great stimulus for research into such intermediates.

A dehydroarene may be defined as an arene from which two hydrogen atoms have formally been removed;* that is an arene

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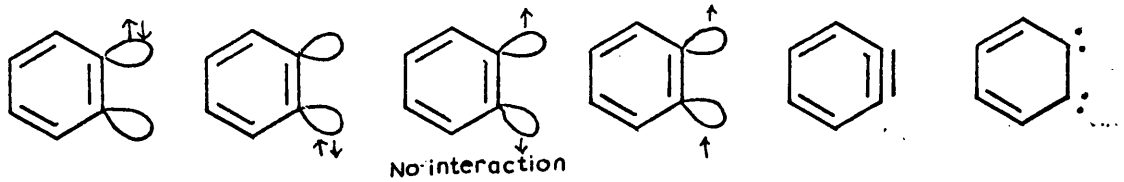
* Hydrogen atoms can formally be removed from the meta or para positions of the same benzene nucleus to give 1,3-dehydrobenzene or 1,4-dehydrobenzene directly, or they can be removed from polycyclic aromatic systems in such a way that the reactive centres can be effectively related 'meta' and 'para' although they are in different rings, e.g. the peri-positions of naphthalene and the 2,2'-positions of biphenyl respectively.

with two available sp^2 orbitals between which two electrons are distributed. Different distributions of these two electrons lead to different electronic states of the dehydroarene. The possible states for o-dehydrobenzene, benzyne (1), are given below, the extension to non ortho cases being obvious.

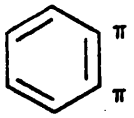


a b c d e f

(1)

Although there is experimental evidence to suggest that o-dehydrobenzene generated in different ways is the same intermediate,[11] the precise electronic structure is still a matter for conjecture and several different views have been advanced.

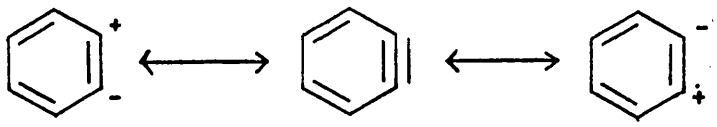
Ingold[12] first suggested that benzyne was a cis-bent acetylene. It is now generally accepted that the removal of two ortho- hydrogen atoms leaves the aromatic system of the nucleus relatively undisturbed since the sp^2 orbitals concerned are, to a first approximation, independent of the aromatic π system. Since these sp^2 orbitals diverge at an angle of 60°, any overlap must be small and Huisgen[3a] has suggested that although the symmetry qualities are not those of a true π bond, benzyne should be represented by the structure:-



(2)

Since the extra electrons can only contribute to the energy of formation in spin coupled states the possibility of triplet[13] or triplet-singlet[14] states was excluded. The failure of attempts to trap benzyne with nitric oxide possibly gives some experimental support to this.[15] Huisgen does concede that limiting polar formulae may contribute to a small extent to the ground state of benzyne.

Wittig[16] considers that benzyne is best represented as a resonance hybrid of the canonical forms:-



(3)

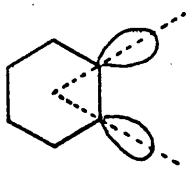
He suggests that overlap is small due to ring strain giving a weak "dehydro-bond" which explains the high reactivity of benzyne. Wittig ruled out the bis-carbene structure (1f) on the basis of failure to trap the intermediate with the known carbene trap isobutene,[17] and he also dismissed the possibility of a triplet diradical.[15]

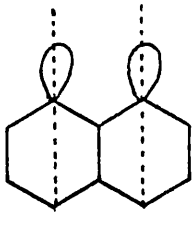
Simmons[18] assumed that there is no ring deformation and showed from rough calculations that the diradical structure produced when two ortho- hydrogen atoms are removed from benzene is much more stable than the two polar resonance forms (1a) and (1b). He also showed that if interaction is allowed in the diradical to give (1e), the extra energy required for conversion of (1e) to the polar forms is estimated to be 100 K cals. On this

basis the ionic type structures are less significant than the acetylenic structure and, assuming that the hexagonal geometry is distorted so that exchange interaction of the sp^2 orbitals becomes more negative, then they become relatively even less significant. Thus from these calculations it appears that benzyne is best considered as a truly aromatic hydrocarbon with one multiple bond of high energy content whose reactivity resembles that of a very strained olefin rather than that of a polar species.

In view of this confusion the study of non ortho-dehydroarenes could be very valuable in shedding light on the problem of the electronic nature of o-dehydrobenzene. For instance if stabilisation of the intermediate by interaction of the sp^2 orbitals does in fact occur, one would expect that dehydroarenes in which such interaction is impossible would have very different properties, such as lifetime and reactivity.

On this basis m-dehydrobenzene would be very different from o-dehydrobenzene but a species such as 1,8-dehydronaphthalene, although formally a meta-dehydroarene, might be expected to show some similarity by virtue of interaction of the peri-orbitals which, although further apart than in o-dehydrobenzene, are more favourably orientated.





On the other hand if there is no stabilisation by interaction in benzyne, as in a diradical species, one would expect meta- and para- dehydroarenes to be of comparable stability.

The remainder of the introduction to this thesis is an attempt to review critically the possible routes to non ortho- dehydroarenes and the success which has so far been achieved. The problems involved in detecting these intermediates are also briefly considered. In order to present the problem systematically, the methods of generating ortho- dehydroarenes will be mentioned and their possible extension to non ortho cases discussed.

1. Generation from dihalo compounds.

The high reactivity of,and low temperature required for the formation of o-haloaryl-lithium compounds and o-haloaryl Grignard reagents compared with their meta and para analogues can be explained by the 1,2-elimination of lithium or magnesium halide to form o-dehydrobenzene. Thus p-chlorophenyl-lithium[19] can be obtained in 90% yield at room temperature but attempts to prepare o-chlorophenyl-lithium at 0° and -30° have failed. In order to obtain comparable yields it was necessary to cool to -90°.[20] Similarly although m-bromophenylmagnesium bromide[21] was obtained in 70% yield, only 30% of o-bromophenylmagnesium bromide[22] was given under the same conditions. All o-halogenorganometallic compounds are highly labile, and complex products are obtained from reactions of o-dihalo compounds which are not obtained with the other isomers. The stability of the m- and p-halogenorganometallic

compounds suggests that this method cannot be extended to give meta- or para- elimination. Treatment of 1,8-dibromonaphthalene with lithium butyl at room temperature gave 85% of 1,8-dilithionaphthalene, no elimination being noted.[23]

Günther[24] found that benzyne was formed in small amounts in solution and to a greater extent in the gas phase, by the action of zinc on o-diiodobenzene. No parallel work appears to have been carried out for non ortho cases.

Kampmeier and Hoffmeister[25] studied the photolysis of 1,2-diiodobenzene in dilute solution in the hope that, since carbon-iodine bond cleavage takes place easily to give aryl radicals, some benzyne might be formed. They obtained products derived largely from o-iodophenyl radicals but using tetracyclone were able to trap benzyne in yields of up to 10%.

Fisher and Lossing[26] extended this decomposition to the gas phase and studied the products mass spectrometrically. Thermal decomposition of o-diiodobenzene at 960° gave iodine atoms, iodophenyl radicals, phenyl iodide, phenyl radicals, benzene, a product of parent mass 76 and one of mass 152. The latter two were assigned to benzyne and biphenylene respectively. Other structures for the species of mass 76 were ruled out on the basis of its ionisation potential. They also examined the thermal decomposition of 1,4- and 1,3- diiodobenzene. 1,4-Diiodobenzene produced iodophenyl radicals, benzene and a compound of mass 76, no peak for mass 152 being detected. The ionisation potential for the

species of mass 76 was in good agreement with that expected for (5).

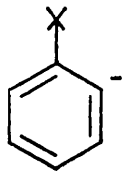
H—C≡C.CH=CH.C≡CH (5)

Similarly, in the decomposition of the meta-isomer a product of mass 76, with the same ionisation potential, was observed, to which structure (5) was again assigned. As before no mass peak 152 was obtained. The authors did not suggest the possible formation of 1,3- or 1,4-dehydrobenzene as did Berry, Clardy and Schafer[27] in the decomposition of benzenediazonium-3- and -4-carboxylates (see below). Photolysis of 1,3- and 1,4- diiodobenzenes in solution has not been reported and this method of generation of dehydro-species has not been extended to other non ortho cases such as 1,8-diiodonaphthalene.

The photolysis of 1,2-diiodobenzene has recently been reinvestigated by Kharasch and Sharma[28] in order to confirm that the tetracyclone adduct obtained by Kampmeier and Hoffmeister arose by way of benzyne rather than by a two step radical addition. The formation of anisole in good yield by photolysis of 1,2-diiodobenzene in methanol was taken to be conclusive evidence for benzyne formation, since this product could only arise by reaction of benzyne with the alcohol, not by a radical abstraction mechanism. However whether the benzyne arose by a concerted elimination of two iodine atoms or by a two step process via the 2-iodophenyl radical is not yet known.

2. Generation by base catalysed elimination from aryl halides.

The generation of o-dehydrobenzene by the action of strong bases on aryl halides is well known. The elimination of hydrogen halide cannot be extended to the meta and para cases and indeed where there is no hydrogen atom ortho to the halogen, aryne formation does not take place. Thus bromodurene and bromomesitylene are not aminated by sodium amide in liquid ammonia, although this could perhaps be explained by deactivation of the hydrogen atoms by the methyl groups. In certain cases the elimination is concerted but it is mostly considered to go via a stepwise mechanism involving the anion (6), which can pick up a proton or



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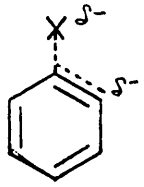


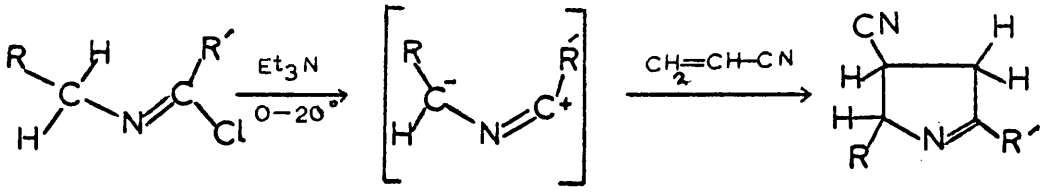
(7)

lose X^- to give the aryne. Bunnett[29] suggested that loss of X^- could be explained in terms of an aryne-like transition state (7) and if this is so it is not surprising that loss of X^- does not result from meta- or para- anions. The cleavage of o-halobenzophenones by potassamide in liquid ammonia is presumably similar. A stepwise mechanism has been proved in the case of 2-chloro-4-methylbenzophenone. The base catalysed fragmentation of o-bromophenylazo compounds was shown by Hoffmann to proceed via the

o-bromophenyl anion which could either lose the bromide ion to form benzyne, or capture a proton to form bromobenzene.[30]

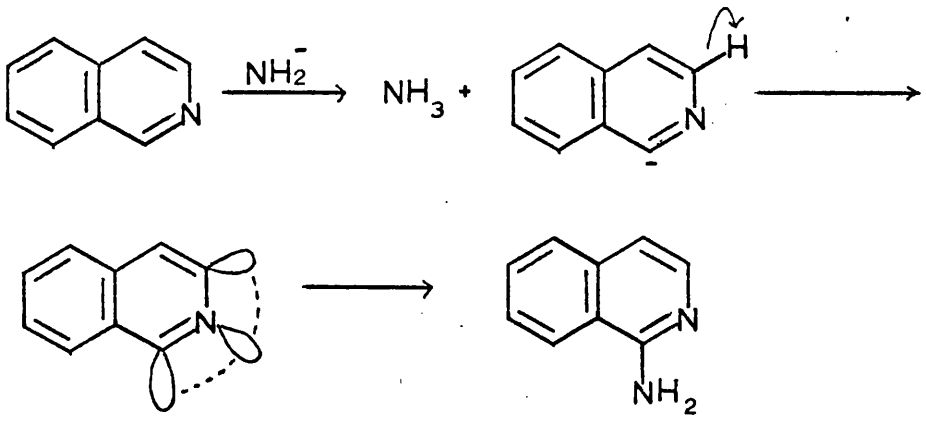
The need for intervention of 1,4-dehydronaphthalene generated by the action of lithium piperidide in piperidine-ether on halonaphthalenes has been ruled out since 1-halo-4-methyl- and 2-halo-4-methylnaphthalene gave identical mixtures of 28% 1- and 72% 2-piperidine-4-methylnaphthalene.[31]

According to Kauffmann,[3,9] o-dehydroaromatic compounds can exist only because of the energy lowering overlap of the orbitals of the extra electrons. Owing to the possibility of overlap between the orbitals of the extra electrons and those of the lone electrons on the nitrogen in hypothetical 2,6-dehydropyridine, it appears that such compounds may be capable of existence.[9] Slight evidence for the 2,6-elimination of hydrogen halide from 2-chloropyridine by lithium piperidide in boiling ether, was the formation of resinous products, less than 1% of the expected 2-piperidinopyridine and none of the 3-isomer.[32] Lithium diethylamide and lithium dicyclohexylamide gave the same result. Resinification did not occur when the 6-position of the 2-halogenopyridine was blocked, e.g. in 2-chloro-6-methylpyridine or 2-chloroquinoline. Further support for the existence of 2,6-dehydropyridine came from the fact that the analogous open chain compounds readily eliminate hydrogen halide on treatment with base.[33]



(8) (9)

Jones and Beveridge[34] suggested that 2,6-dehydropyridine (8) should be even more stable than 2,3-dehydropyridine (9) which they proposed as an intermediate in the Tschitschibabin reaction, both dehydropyridines being stabilised by the lone pair effect. They similarly explained the exclusive formation of 1-aminoisoquinoline in the amination of isoquinoline by the formation of a 1,3-dehydroarene intermediate (10).

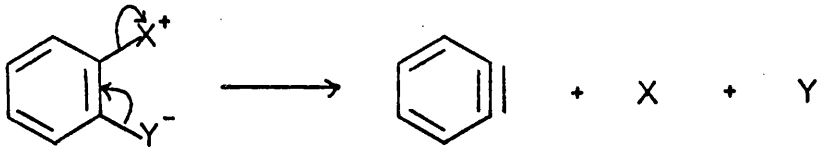


(10)

They also suggested that 2,3-dehydropyridine (9) should be more stable than 3,4-dehydropyridine, a fact which was not immediately in accord with the formation of only 3,4-dehydropyridine from 3-chloropyridine. This however has been explained by a consideration of the rates of exchange of the hydrogens in the 2- and 4-positions, the 4-hydrogens exchanging very much more readily than the 2-hydrogens.[35] However, the intermediacy of 2,3-dehydropyridine and 2,6-dehydropyridine has now been ruled out for the Tschitschibabin reaction.[36]

3. Generation by elimination of stable molecules from disubstituted arenes.

These reactions are of the form:-

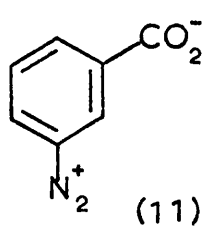


This type of generation of arynes, first introduced by Stiles[37] in 1960, greatly extended the scope of benzyne chemistry since it allowed the generation of the intermediate without the use of strong base or of metals. Benzenediazonium-2-carboxylate ($X = N_2$, $Y = CO_2$) was isolated and decomposed by warming in organic solvents to give rapid loss of nitrogen, somewhat slower loss of carbon dioxide, and benzyne. It was later found that isolation of the unstable betaine was unnecessary and that benzyne could be produced in situ by diazotisation of anthranilic acid.[38] The

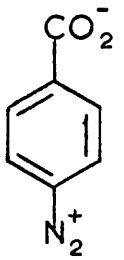
decomposition of benzenediazonium-2-carboxylate in the gas phase was studied by Berry, Spokes and Stiles[39,40] using flash photolysis techniques. The products of decomposition were examined spectroscopically and the formation of biphenylene was observed. Spectra taken soon after photolysis (20-80 μsec) showed a strong, transient broad continuum with a maximum at ca. 2420 Å which did not correspond to biphenylene. This absorption decayed with the formation of biphenylene and was assigned to benzyne. Photolysis of di-o-iodophenyl mercury gave the same transient spectrum.

In 1964 Berry, Clardy and Schafer,[41] extending the work of Fisher and Lossing,[26] introduced time of flight mass spectrometry to the study of gaseous benzyne. Preliminary experiments showed that when benzene-diazonium-2-carboxylate was flash photolysed and the products observed by a time of flight mass spectrometer, the initial products were nitrogen, carbon dioxide and a species of mass 76. The mass peak 76 diminished in intensity with time but a peak corresponding to biphenylene, mass 152, increased in intensity.

These same authors in 1965 published similar evidence for the existence of 1,3- and 1,4-dehydrobenzene[27] produced by flash photolysis of benzenediazonium-3- and -4-carboxylate, (11) and (12). Benzenediazonium-4-carboxylate was decomposed and the



(11)

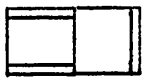


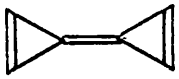
(12)

products were observed using optical and time of flight mass spectrometry.

The time resolved mass spectrum was the most useful means of identifying the reaction species. Fragmentation to give nitrogen, carbon dioxide and a species of mass 76 accounted for over 90% of the fragment intensities. In addition a peak at mass 94 was ascribed to phenol and one at 92 was probably due to a dehydrophenoxy triplet. The most surprising fact was that the species of mass 76 was not transient but persisted for up to two minutes. There were no peaks corresponding to the possible dimer or trimer of species mass 76. The authors considered that the species of mass 76 was either (13) or (14), (13) being slightly favoured by its closer similarity to the precursor.

(13)





(14)

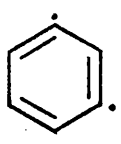
$HC{\equiv}C.CH{=}CH.C{\equiv}CH$

(5)

Structure (5) was eliminated by its known mass spectrum, although it was suggested by Fisher and Lossing[26] as the species of mass 76 obtained by thermal decomposition of p-diiodobenzene. Hexa-1-en-3,5-diyne was ruled out by its known ultra violet spectrum and 3-methylene-penta-1,4-diyne by its mass spectrum. Finally benzyne and its meta-dehydro isomer were excluded by their known mass

spectra, and a variety of cumulene and highly strained ring systems by the requirement of hydrogen shifts and strain energies. The variation of the mass spectrum with time was probably due to isomerisation of (13) to (14), or to intersystem crossing from a singlet to a triplet state, or to vibrational relaxation by collisions in the sample tube. The continuous absorption in the ultra violet spectrum could not be attributed to the species of mass 76 since the same bands were obtained from the meta-isomer which gave a very different mass spectrum.

In a similar decomposition of benzenediazonium-3-carboxylate (11) a transient parent mass peak 76 was again observed for times up to approximately 400 μsec after photolysis. Large peaks for masses 28 and 44 were also present. A broad transient peak for mass 152, presumably a dimer of species mass 76, was also observed. Possible structures for the initial transient intermediate were the three hexaendiynes or 1,3-dehydrobenzene. The former were ruled unlikely by a consideration of the fragmentation patterns although one optical spectrum, taken at 1800 μsec after the initial flash, indicated that such species might have been formed later by slow rearrangement. Thus 1,3-dehydrobenzene was considered to be the most likely form of the species, represented as either (15) or (16).



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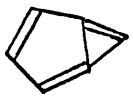
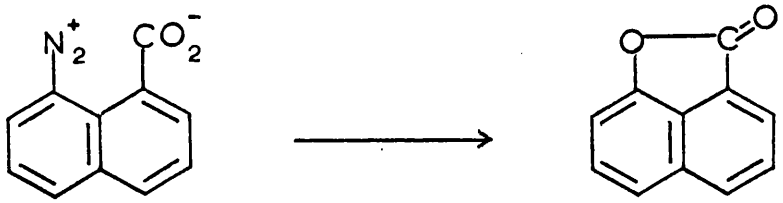


(16)

The species of mass 76 from the diazonium carboxylates were clearly different from those obtained by decomposition of the diiodobenzenes for which structure (5) was suggested.

Although the use of benzenediazonium-2-carboxylate as a source of o-dehydrobenzene in solution is now well known, similar attempts with the meta- and para- isomers have not so far been made. An attempt to extend the method to the formation of 1,8-dehydronaphthalene failed,[42] possibly due to ring closure after initial loss of nitrogen. This type of ring closure might



be expected to be a drawback in the preparation of multicyclic dehydroarenes where such processes are sterically favourable.

In this type of elimination nitrogen is not the only possible leaving group. LeGoff[43] has generated benzyne in good yield by the pyrolysis of diphenyl-iodonium-2-carboxylate. A relatively high temperature was required (ca. 160°) and this suggests that non ortho- elimination may be prohibitively difficult. No such attempts to generate non ortho-dehydroarenes have yet been reported.

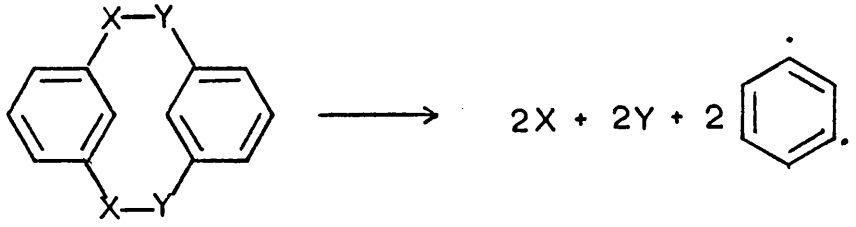
Beringer[44] found that high temperatures were required for the elimination from aryliodoniobenzoates and that at lower temperatures rearrangement to aryl-2-iodobenzoates predominated.

Again no extensions of this method have been made.

4. Generation by fragmentation of fused ring systems.

In the concerted fragmentation of a ring system to give stable molecules, leaving a dehydroaromatic species, the greater the number of fragments, the more likely it is that elimination would not be simple or complete. For steric reasons the spanning of meta- and para-positions in benzene by normal sized rings (5 or 6 membered) is not likely to be practicable. Thus any bridging systems large enough to span meta- or para- positions directly are unlikely to fragment in a concerted and complete manner. Two possible ways round this problem exist.

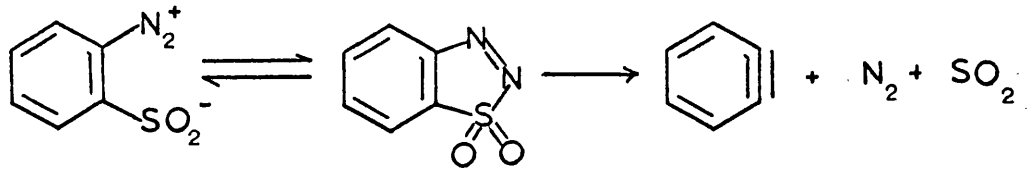
a) The meta- or para-bridging of two aromatic rings by two bridges so that fragmentation could lead to two aryne molecules.



b) The bridging across positions related meta and para to each other but not in the same ring:

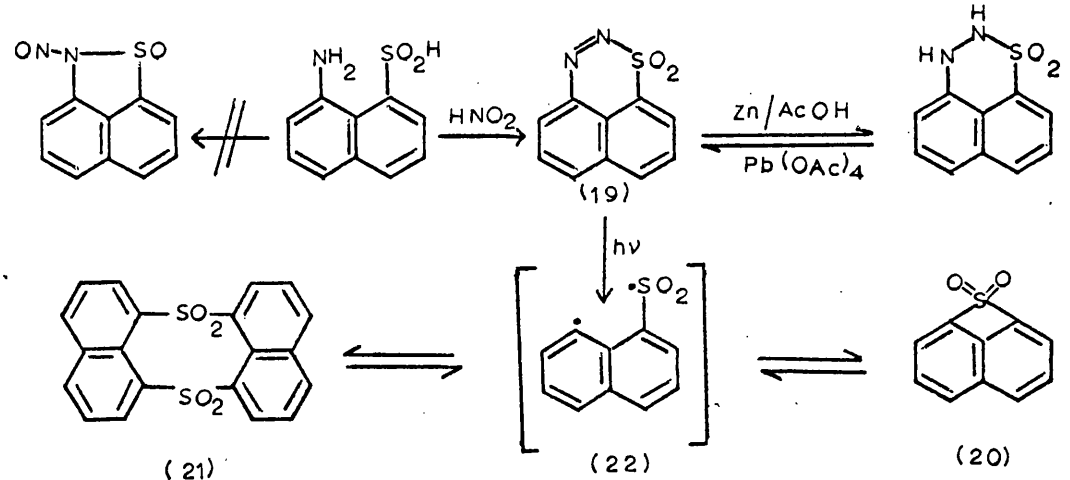
The second of these two alternatives appears to be the simpler and is the only one which has so far found any practical application.

Following the generation of benzyne from benzenediazonium-2-carboxylate, Wittig tried the related compound with a sulphinite group in place of the carboxylate.[45] This compound was found to exist in the ring closed form, 1,2,3-benzothiadiazole-1,1-dioxide (17) rather than in the Zwitterionic form (18).



(18) (17)

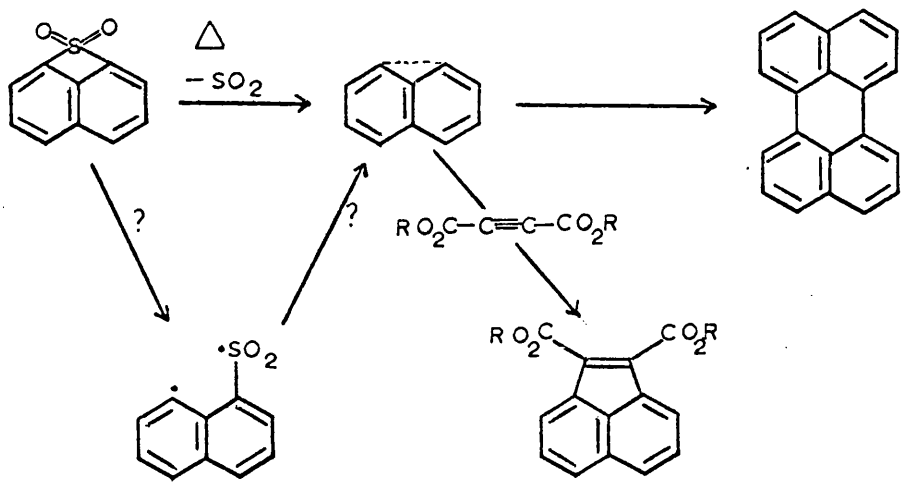
Mild thermolysis gave nitrogen, sulphur dioxide and a good yield of benzyne. Hoffmann[46] extended this type of ring system to span the peri-positions of naphthalene in the synthesis of 1,2,3-thiadiazino[4,5,6-ij] naphthalene-1,1-dioxide (19) as a possible precursor for 1,8-dehydronaphthalene. However, this compound was considerably more stable than the benzene analogue



(21) (22) (20)

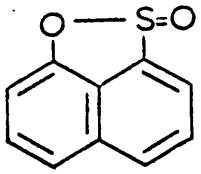
and did not release sulphur dioxide or nitrogen until heated above 200°, when the pigment naphthothiamyl blue was formed.[47] Similarly, photolysis for 36 hours at 15° gave naphthothiamyl blue as the major product, but simultaneous loss of nitrogen gave 25% thieto[2,3,4-ij] naphthalene-1,1-dioxide (20) and 3% dinaphtho-[1,8-bc:1',8'-fg]-1,5di-thiocin-1,1-5,5-tetroxide (21). Irradiation of (20) in ethanol gave up to 54% (21) while similar treatment of (21) gave 20% (20) possibly via the diradical (22).

Both compounds (19) and (20) were possible precursors of 1,8-dehydronaphthalene. Pyrolysis of (20) at 240° gave only impure carbonyl compounds and up to 0.02% perylene, the dimer of 1,8-dehydronaphthalene. When the pyrolysis was performed in the presence of copper the yield rose to 0.4%. Attempts to trap the 1,8-dehydronaphthalene with tetracyclone failed. Similar attempts with maleic anhydride, diethyl fumarate, benzene and tetrachloroethylene also failed but with diethylacetylenedicarboxylate the adduct (23) was isolated in 0.15% yield.[48]



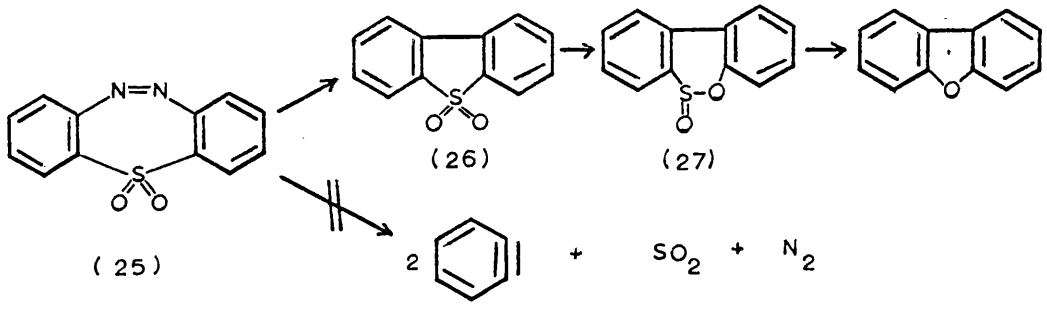
(23)

Thus it appeared that pyrolysis of (20) gave 1,8-dehydronaphthalene in only very small yield. The main course of pyrolysis led to polymer and it was thought that vapour phase pyrolysis in vacuo would reduce this. Such pyrolysis led to the discovery of the rearrangement of (20) to (24), for which mass spectral data indicated the loss of sulphur monoxide rather than sulphur dioxide (cf. Fields[50] work on dibenzothiophen-1,1-dioxide) so that 1,8-dehydronaphthalene was not formed.



(24)

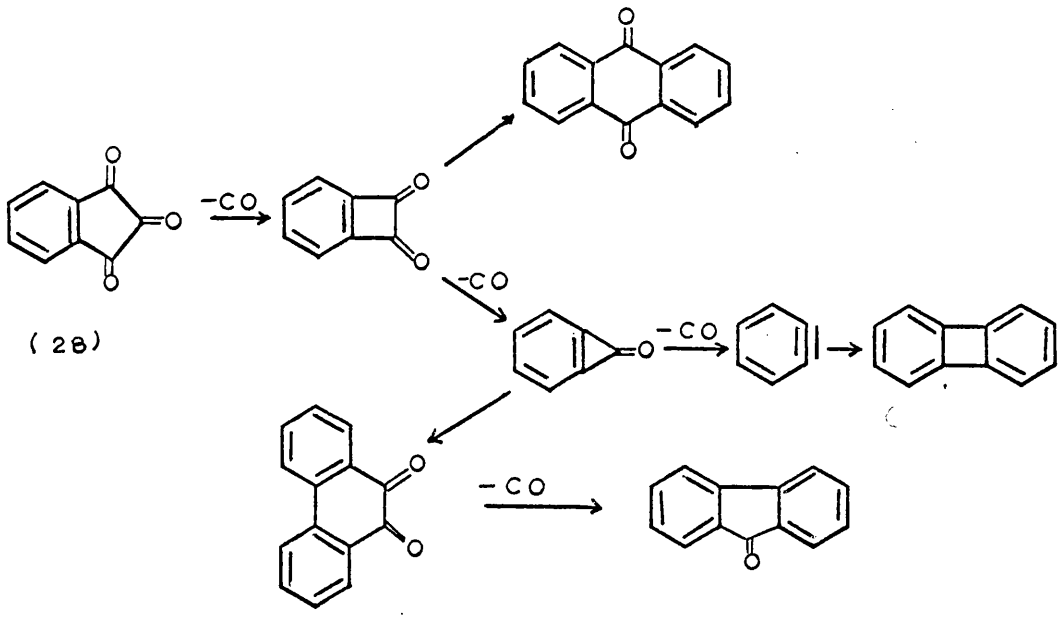
In the pyrolysis of 2,3:6,7-dibenzo-1-thia-4,5-diazacycloheptatriene-1,1-dioxide (25) at 700°, only dibenzothiophene-1,1-dioxide (26) was isolated, in 10% yield.[49]



In attempting to generate biphenylene from the sulphone (26) by pyrolysis at 690°, Fields[50] found that it ring expanded to the internal sulphinate (27) which then eliminated sulphur monoxide to give dibenzofuran and some dibenzothiophen rather than

2,2'-dehydrobiphenyl or biphenylene.

Much work has been done, particularly by Brown,[51] on the correlation between the breakdown of molecular ions in mass spectral analysis and the decomposition in high temperature pyrolysis. Pyrolysis of indantrione (28) mixed with benzene or chlorobenzene gave products arising from addition of benzyne to the aromatic nuclei. Pyrolysis alone at 600°/0.7 mm. gave biphenylene and at lower temperatures, 500°/0.3 mm., biphenylene and a variety of carbonyl containing compounds. Their formation is explained by the scheme below.

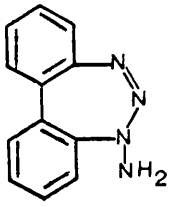


(28)

o-Dehydrobenzene has also been obtained from the pyrolysis of phthaloyl peroxide[49] and phthalic anhydride.[52] Fields[53] pyrolysed a selection of anhydrides in pyridine at 690° and analysed the products by mass spectrometry or a combination of mass spectrometry

and gas chromatography. Pyrolysis of 1,8-naphthalic anhydride was found to be more difficult than that of the 2,3-isomer. In the former case 1,8-dehydronaphthalene was trapped as its insertion product, naphthylpyridine; the latter also gave naphthylpyridine.

Oxidation of 1-aminobenzotriazole with lead tetraacetate[54] has recently proved to be a mild method for generating benzyne in high yields. The extension of this method to oxidation of other aminotriazole or triazine systems, fused meta and para, is obvious, e.g. (29) and (30).



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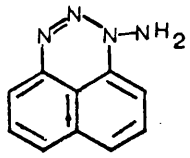
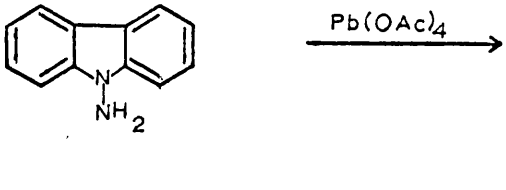


(30)

It is to this problem that the major part of this thesis is devoted.

The oxidation of N-aminocarbazole (31), a possible precursor of 2,2'-dehydrobiphenyl has already been reported.[55] Oxidation with lead tetraacetate in acetonitrile gave the tetrazene (32) without loss of nitrogen.



(31) (32)

Formally any aryl diradical can be considered as a dehydroarene and indeed the concept of diradical states of dehydroarenes has already been introduced. However, the independent generation of two separate radical centres is unlikely to lead to an intermediate in which the two radical sites exist simultaneously, a condition which must be satisfied for a dehydroarene. Thus decomposition of a lithium aryl or an aryl Grignard reagent with transition metal chlorides gives the aryl radical but no evidence for the existence of free o-dehydrobenzene was obtained in the similar decomposition of o-dilithiobenzene.[56] The products obtained were a variety of open chain o-polyphenyls, particularly biphenyl, and o-phenylene compounds, particularly triphenylene, presumably formed by stepwise processes. Similar decomposition of 2,2'-dilithiobiphenyl[57] led to the same type of reaction. However, as previously mentioned, the attempted formation of the o-phenylene diradical by photolysis of o-diiodobenzene did give benzyne.[25,28]

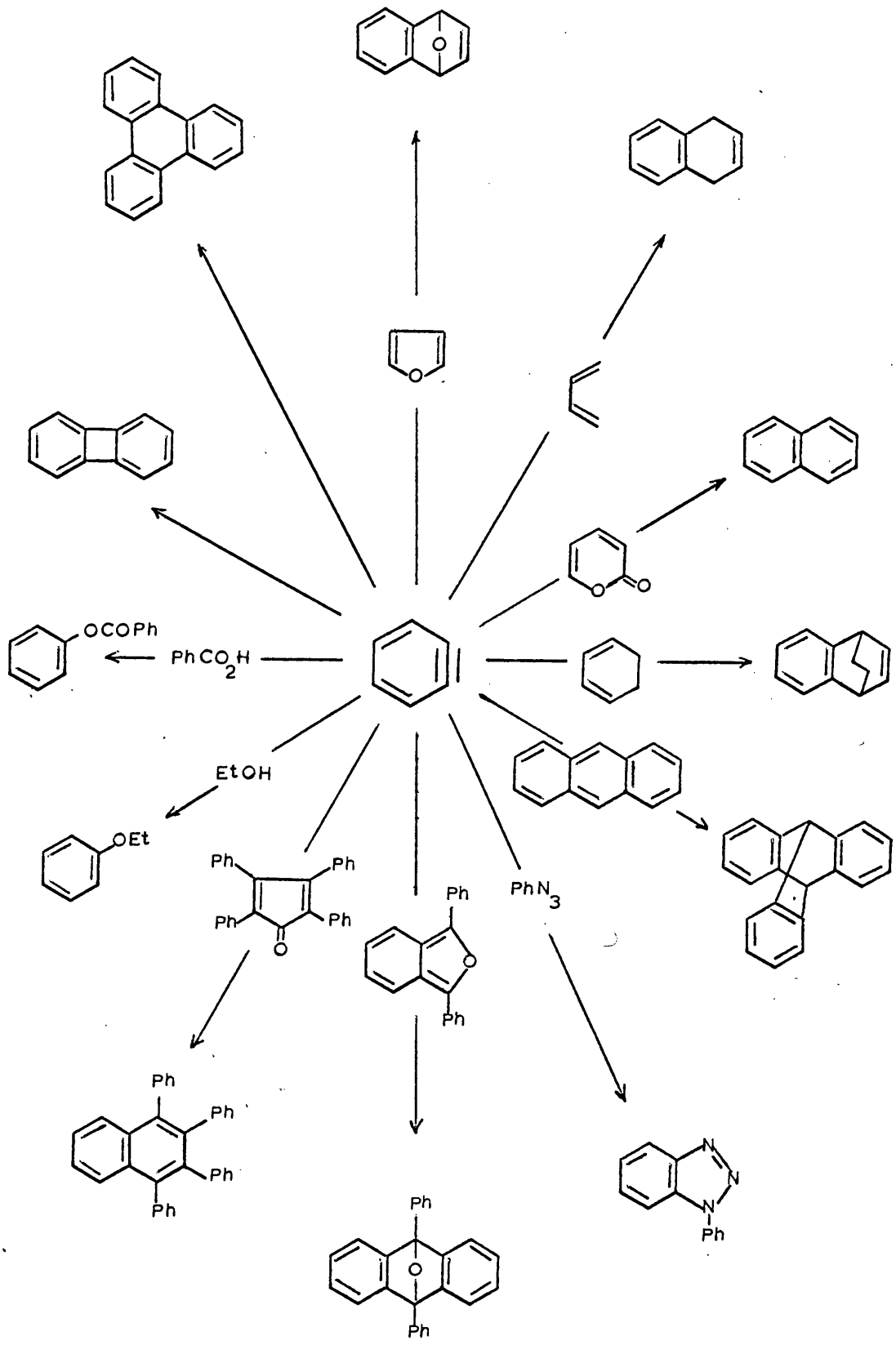
Detection of Dehydroarenes.

The existence of o-dehydrobenzene has been demonstrated in many ways. The occurrence of cine substitution is usually a good indication of a mechanism involving benzyne. This is, however, not invariably the case as for example in the von Richter reaction. The production of biphenylene by dimerisation, and the occurrence of mass spectral fragments have also been used

as evidence. Because of its considerable dienophilic character, one of the most valuable means of intercepting the intermediate involves the use of dienes. These and other reactions used to characterise the formation of benzyne and other o-dehydroarene intermediates are shown in the chart.

The detection of non ortho-dehydroarenes is at the present time speculative owing to the limited information available.

The assignment of mass spectral peaks has been used elegantly by Berry, Clardy and Schafer[27] in their decomposition of benzenediazonium-3- and -4-carboxylates. However the problems of chemical detection are more complex, for although all o-dehydroarenes are closely related sterically, this is not necessarily the case for the non-ortho analogues. Thus 1,3-dehydrobenzene is very different from 1,8-dehydronaphthalene and their reactions might be expected to reflect this steric difference. For example, it is difficult to imagine simple dimerisation of m-dehydrobenzene but the formation of perylene from 1,8-dehydronaphthalene is readily envisaged. In fact, the formation of perylene has already been noted[46,48] whereas in the decomposition of benzenediazonium-3-carboxylate there was evidence of a transient dimer only.[27] Similarly 1,8-dehydronaphthalene might be expected to add in a concerted fashion to olefins or even to 1,3-dipoles but the possibility of m-dehydrobenzene undergoing such reactions seems remote. Hoffmann has reported the adduct of 1,8-dehydronaphthalene with diethyl acetylene dicarboxylate in very small yield.[44]


OCOPh
PhCO2H
EtOH
OEt
Ph
PhN3
N
N
N
Ph

In those dehydro-species where the reactive centres are so placed that simple concerted cycloadditions are ruled out one might expect to find radical abstraction or polymer formation. Formation of resins has been tentatively put forward as evidence of the formation of 2,6-dehydropyridine on treatment of 2-chloropyridine with base.[31] Insertion reactions are also possible and indeed it was found by Fields that the 1,8-dehydronaphthalene, produced by pyrolysis of naphthalic anhydride, inserted in the carbon-hydrogen bond of pyridine to give naphthyl pyridine.[53]

In addition to steric considerations, the electronic characters of the various non ortho-dehydroarenes may be very different from those of each other and from that of o-dehydrobenzene. As previously pointed out, since differences in electronic character will be reflected in the reactions of the particular species, a study of such reactions should be very valuable in attempts to elucidate the nature of o-dehydrobenzene or other dehydroarenes. Thus an investigation of the stereospecificity of the possible addition of a species such as 1,8-dehydronaphthalene to olefins should give an indication as to the singlet or triplet nature of the intermediate.

The effect of a hetero-atom has already been discussed in the case of the dehydropyridines.

It is important therefore to emphasise that the chemistry of the non ortho-dehydroarenes will depend on the

particular stereochemistry and electronic nature of the species considered, and that correlation will probably only be possible between closely related types.

1,8-DEHYDRONAPHTHALENE

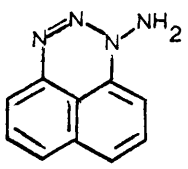
1. PREPARATION AND NON-OXIDATIVE REACTIONS OF AMINONAPHTHO[1,8-de]TRIAZINES

Initial attempts to prepare 1-aminonaphtho[1,8-de]-triazine (1) involved direct amination of naphtho[1,8-de]triazine (2) with hydroxylamine-O-sulphonic acid.[58]

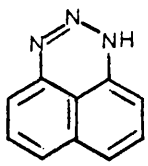
Naphtho[1,8-de]triazine was first prepared in moderate yield by the method of Waldmann and Back[59] by diazotisation of 1,8-diaminonaphthalene in aqueous acetic acid with sodium nitrite. The product was however extremely crude and a somewhat cleaner sample was obtained by Soxhlet extraction with ethanol. Pure naphtho[1,8-de]triazine was obtained by passing an ethanolic solution of the Soxhlet extracted triazine through a short basic alumina column, followed by final crystallisation from ethanol. The Soxhlet extracted triazine proved quite satisfactory for amination reactions but the very crude triazine gave low yields. A more convenient method, giving an initially purer product in higher yield, was found to be diazotisation by amyl nitrite in ethanolic acetic acid. The melting point of the pure naphtho-triazine was ca. 235° (decomp.) (Waldmann and Back report 236-237°[59]). However, the melting point seemed to be a poor criterion of purity since the very crude triazine melted at ca. 230°. Recently, pure naphtho[1,8-de]triazinehas been obtained almost quantitatively by heating freshly distilled 1,8-diaminonaphthalene in benzene with diphenylnitrosamine and

acetic acid, a melting point of 260-263° being reported.[60]

Direct amination of benzotriazole with hydroxylamine-O-sulphonic acid in aqueous base gave both 1- and 2-aminobenzotriazoles,[13] the reaction paralleling the basically similar methylation with dimethyl sulphate in alkaline solution.[61] Perkins treated naphtho[1,8-de]triazine with dimethyl sulphate and obtained two isomers, red 1-methylnaphtho[1,8-de]triazine (3) and blue 2-methylnaphtho[1,8-de]triazine (4). However, naphtho[1,8-de]triazine with hydroxylamine-O-sulphonic acid gave red 1-aminonaphtho[1,8-de]triazine (1) together with a colourless isomer 8-azido-1-naphthylamine (5), rather than the expected blue 2-aminonaphtho[1,8-de]triazine (6). Since 1-aminonaphtho[1,8-de]triazine is stable under the amination conditions, 8-azido-1-naphthylamine arose presumably by rearrangement of the initially formed 2-aminotriazine.



(1)



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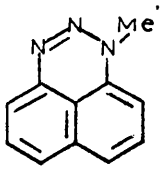

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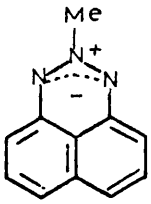

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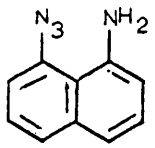

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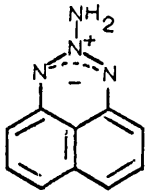
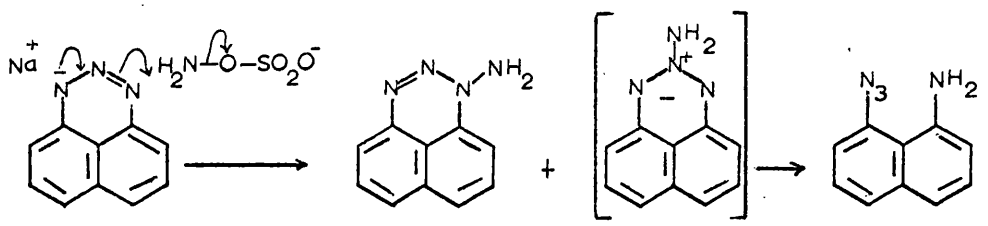


(6)

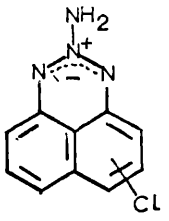
The structure of 8-azido-1-naphthylamine was supported by its i.r. spectrum which showed peaks corresponding to a primary aromatic amine (3500, 3380 $cm.^{-1}$) and an azide (2110 $cm.^{-1}$), by the formation of an azo dye when diazotised and coupled with β-naphthol, and finally by its reduction to 1,8-diaminonaphthalene. The p.m.r. spectrum and analysis provided further confirmation.

Spectral properties of 1-aminonaphtho[1,8-de]triazine were as expected; in particular the u.v. spectrum showed close similarity to that of 1-methylnaphthotriazine.[61] A satisfactory analysis was obtained and the structure was finally confirmed by deamination to give naphtho[1,8-de]triazine. The deamination was most conveniently effected by the use of diphenylnitrosamine, a reagent shown by Campbell[62] to be particularly effective for deamination of N-amino compounds, and recently used as a diazotising agent.[60]

The optimum conditions for the amination are described in the Experimental section. Yields were found to depend on the particular batch of hydroxylamine-O-sulphonic acid used, and aminations in ethanol and dimethylformamide were less satisfactory than those in aqueous solution. 1-Aminonaphthotriazine could not be freed from troublesome traces of naphtho[1,8-de]triazine by recrystallisation and it was necessary to rechromatograph carefully on basic alumina.



Since the potentially interesting 2-aminonaphtho[1,8-de]-triazine was not stable under the vigorous conditions of the hydroxylamine-O-sulphonic acid amination, a milder method was tried. Treatment of the sodium salt of naphtho[1,8-de]triazine with a small excess of chloramine in ether gave a slightly improved yield of 1-aminonaphtho[1,8-de]triazine together with small amounts of two blue compounds. Analyses and mass spectra indicated that these blue compounds were 2-aminonaphtho[1,8-de]-triazine (6) and a chloro-2-aminonaphtho[1,8-de]triazine (7). The ratio of chloro2-aminonaphthotriazine to 2-aminonaphthotriazine



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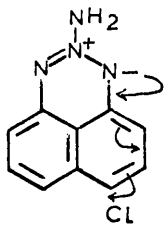
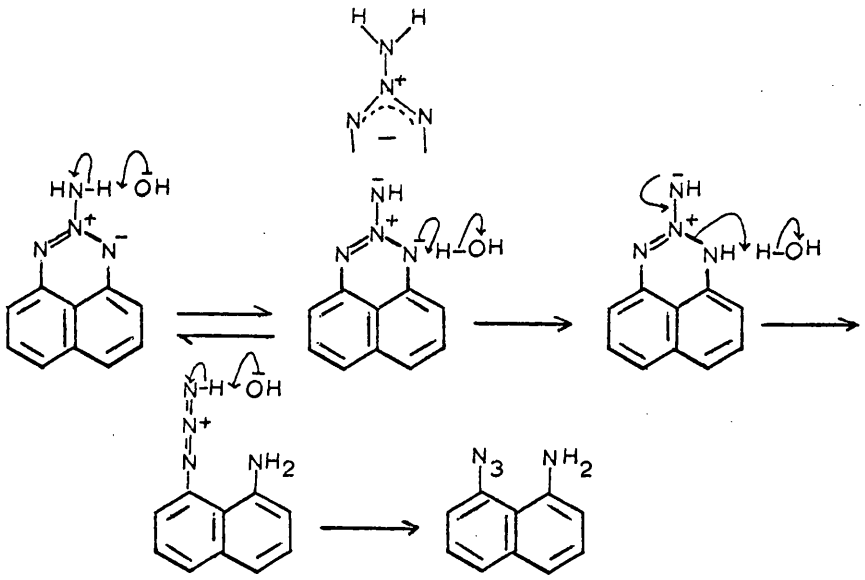


increased with increasing strength of chloramine solution. The u.v. spectra of both blue compounds closely resembled the u.v. spectrum of the blue 2-methylnaphtho[1,8-de]triazine, and the chlorine in chloro-2-aminonaphthotriazine was shown to be in the naphthalene nucleus since the i.r. spectra of the two compounds were very similar in the N-H region but differed markedly in the aromatic region. Since chloramine can act as a source of NH_2^+ and Cl^+, the introduction of chlorine into the naphthalene nucleus is in accord with its expected increasedactivity to electro-philic attack caused by the 2-substituted triazine system.

Perkins[61] has shown that 2-methylnaphtho[1,8-de]triazine readily forms a tetrabromo derivative. Alternatively this nucelar chlorination product could have been formed by an Orton-type rearrangement of an N-chloramino compound formed from dichloramine impurity in the chloramine. Small scale deamination of 2-amino-naphtho[1,8-de]triazine with diphenylnitrosamine was not very satisfactory but did give some naphtho[1,8-de]triazine (T.L.C.).

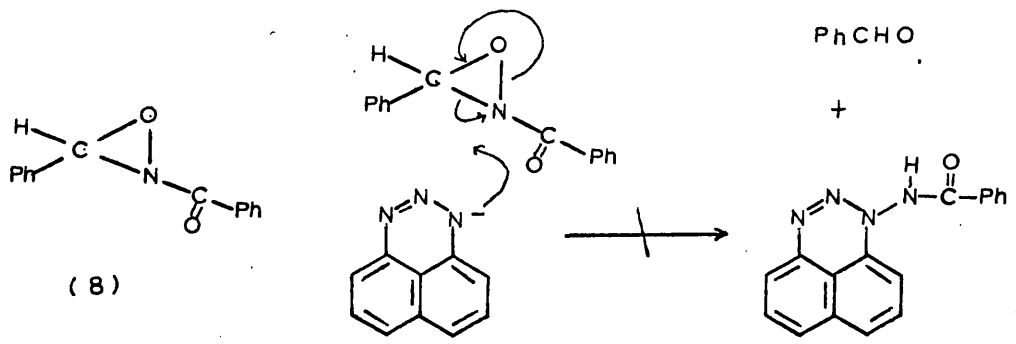
It was shown that 2-aminonaphtho[1,8-de]triazine could have been the initial intermediate in the formation of 8-azido-1-naphthylamine in the hydroxylamine-O-sulphonic acid amination, since when treated with aqueous base under similar conditions it rearranged to the aminoazide. The amino hydrogen atoms of 2-amino-naphtho[1,8-de]triazine are presumably more acidic than those in 1-aminonaphthotriazine due to the electronic structure, and hence are more easily removed by base. This would explain the ease of the base catalysed rearrangement to the aminoazide in which the electronic strain of the 2-substituted system is relieved.



On the other hand since naphtho[1,8-de]triazine is known to react as a 'masked' diazonium compound, e.g. refluxing with hydrobromic acid gives 8-bromo-1-naphthylamine,[63] and since diazonium compounds are known to react with hydroxylamine-O-sulphonic acid to give azides,[64] 8-azido-1-naphthylamine may have been formed directly. However this would seem unlikely under basic conditions and indeed 1-methylnaphthotriazine, which could presumably behave similarly, was completely unchanged under the same conditions.

Treatment of naphtho[1,8-de]triazine itself, rather than its sodium salt, with chloramine failed to give any amino derivatives.

A further direct amination attempt using 2-benzoyl-3-phenyl oxaziridine[65] (8) failed with both naphtho[1,8-de]triazine and benzotriazole.

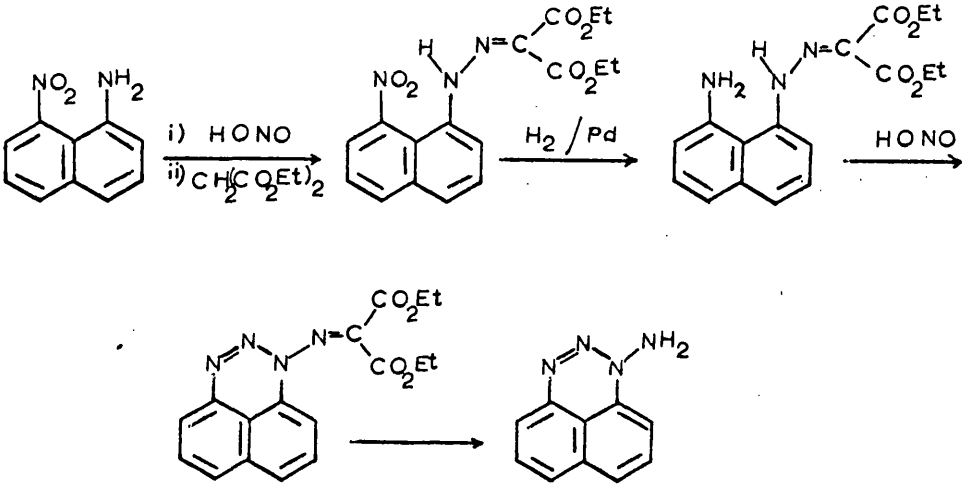


(8)

An attempted nitrosation of naphtho[1,8-de]triazine using nitrosyl chloride in ether gave an extremely complex mixture of highly coloured products (T.L.C.) and so was abandoned.

Nitrosation of benzotriazole has so far also been unsuccessful.

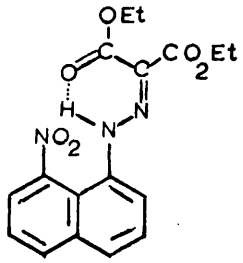
An alternative route to 1-aminonaphtho[1,8-de]triazine from 8-nitro-1-naphthylamine using Campbell's[62] modification of the method of Trave and Bianchetti[66] was investigated.



8-Nitro-1-naphthylamine was prepared from 1-naphthylamine by the method of Hodgson and Ratcliffe[67] by protection of the amino group with phthalic anhydride, followed by nitration, removal of the protecting group and separation of the isomers. The compound was also obtained by direct nitration of 1-naphthylamine.[68]

Diazotisation of 8-nitro-1-naphthylamine and coupling with diethyl malonate gave the required diethyl mesoxalate-8-nitro-1-naphthylhydrazone (9) in low yield. However, appreciable amounts of 1-nitronaphthalene and diethyl-8-nitro-1-naphthyl malonate (10) were also formed, arising from the 8-nitro-1-naphthyl radical by hydrogen abstraction and combination with the

stabilised diethyl malonate radical produced by the abstraction. The nitronaphthyl radical itself may also be stabilised by the steric effect of the peri-nitro group.



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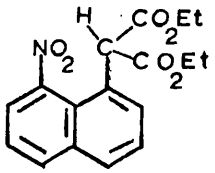

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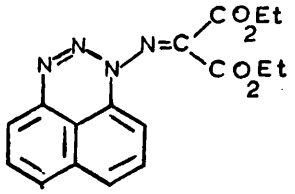


(11)

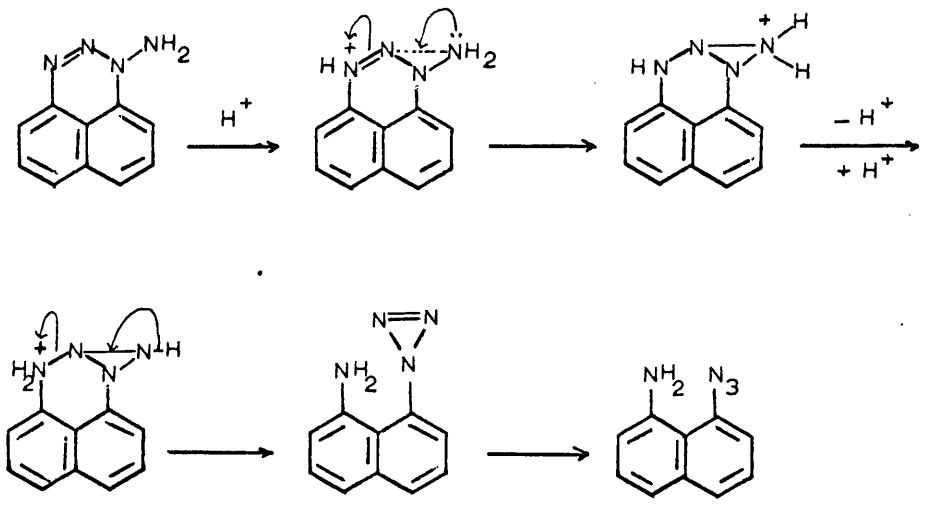
The structuresof (9) and (10) were confirmed by analysis and i.r. and p.m.r. data. In particular p.m.r. of (10) showed a single proton at 4.9τ and two equivalent ethyl groups; i.r. showed one carbonyl stretching frequency at 1729 cm.$^{-1}$ P.m.r. of (9) indicated one proton at -2.75τ and two non-equivalent ethyl groups, presumably due to hydrogen bonding of one of the carbonyls. The i.r. spectrum supported this showing carbonyl absorptions at 1730 cm.$^{-1}$ and 1680 cm.$^{-1}$ In the case of o-nitroaniline[62] no products analogous to nitronaphthalene and (10) were observed; however the large steric peri-interaction in the 8-nitro-1-naphthyl diazonium compound results in ready loss of nitrogen to give the 8-nitro-1-naphthyl radical.

The low yield and difficulty in isolation of the diethyl mesoxalate-8-nitro-1-naphthylhydrazone from the first stage in this series of preparations, together with the discovery at this time that 1-aminonaphtho[1,8-de]triazine readily rearranged

to 8-azido-1-naphthylamine under acid conditions, led us to abandon this approach since the final stage would have involved hydrolysis of (naphtho[1,8-de]triazin-1-yl)imino malonate (11) with concentrated hydrochloric acid.

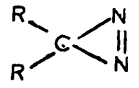
The rearrangement of 1-aminonaphtho[1,8-de]triazine proceeded rapidly on warming in dilute mineral acid giving 8-azido-1-naphthylamine in high yield. The acid catalysed rearrangement explains the unsatisfactory deamination of 1-amino-naphthotriazine in acid with sodium nitrite.

2-Aminonaphtho[1,8-de]triazine was insoluble in dilute mineral acid and did not rearrange under these conditions. Thus the 1-aminotriazine system is readily opened by a protonation mechanism, the amino hydrogens being inert to base whereas the 2-aminotriazine system is inert to acid but rearranges readily by removal of a proton in base. The following mechanism is tentatively proposed for the acid catalysed rearrangement.



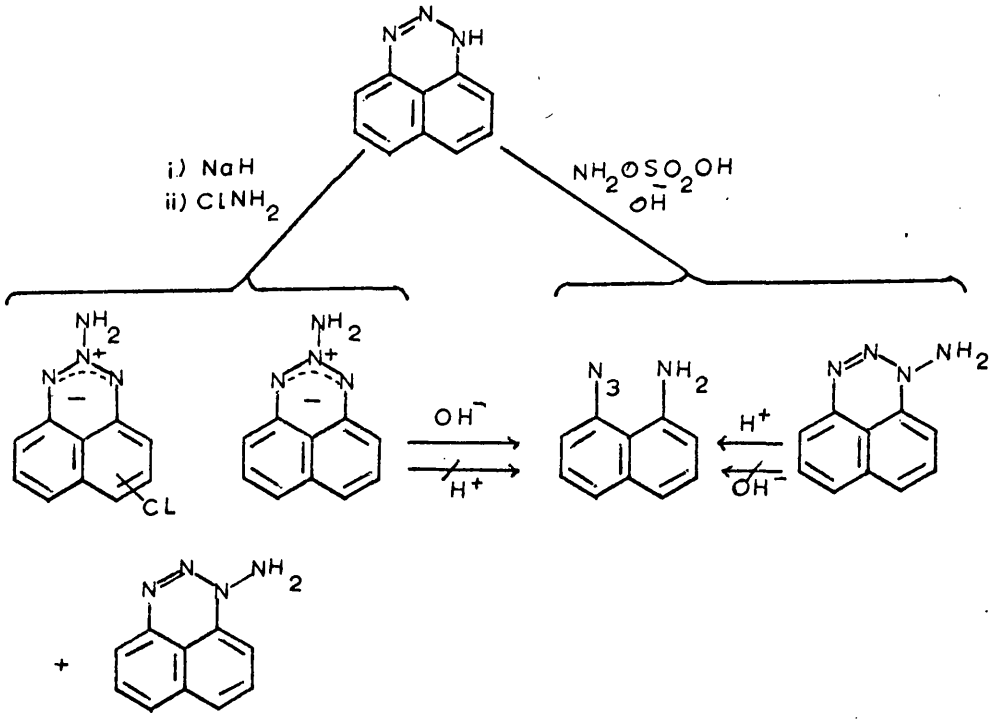
(12)

It is interesting to note that the cyclic azide structure c.f.(12) was initially proposed by Fischer[69] as the structure for the azide group but was later ruled out when X-ray analysis became available. A parallel situation occurred with aliphatic diazo compounds where a cyclic structure (13) was initially proposed, but was later replaced by a linear structure. However compounds of structure (13) are now known to be stable[70] so that the intermediate (12) may be capable of existence.



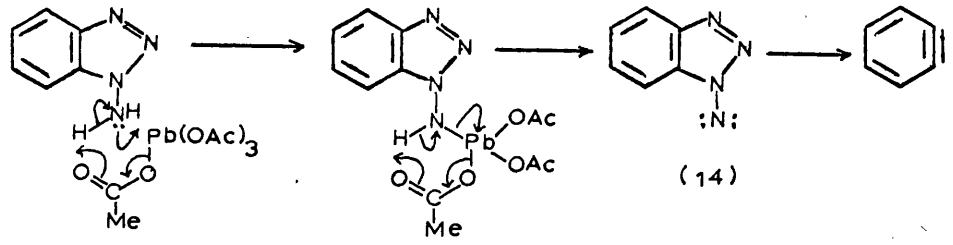
(13)

The above reactions may be summarised:



2. OXIDATIONS OF 1-AMINONAPHTHO[1,8-de]TRIAZINE

Oxidation of 1-aminobenzotriazole with lead tetra-acetate gave rapid evolution of nitrogen and formed benzyne in high yield.[54] The formation of benzyne occurred by fragmentation of the initially formed nitrene (14) and it was thought that similar oxidation of 1-aminonaphtho[1,8-de]triazine would give an analogous nitrene (15), fragmentation of which would lead to 1,8-dehydronaphthalene (16).

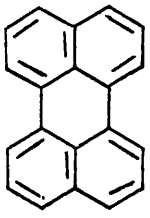


When 1-aminonaphtho[1,8-de]triazine was treated with lead tetra-acetate or other oxidants in a solvent, rapid evolution of nitrogen occurred and products were formed which could only be explained by the intermediacy of 1,8-dehydro-naphthalene. The 1,8-dehydronaphthalene did not dimerise, unlike benzyne generated similarly, but could be trapped by 1,2-addition to a variety of unsaturated compounds and by the formation of

radical abstraction products. No truly inert solvent was found and trapping was most effective. when the trap itself was used as the solvent. Dilution, except for the most efficient traps, led to considerably lower yields of adducts. In few cases were products isolated in yields greater than 50%, the formation of varying amounts of intractable oils, tars and polymeric material accounting for the rest of the reaction.

Oxidations in Aromatic Solvents.

In the oxidation of 1-aminobenzotriazole with lead tetra-acetate in benzene in the absence of a trap, the benzyne generated dimerised in high yield to give biphenylene.[54] Similar oxidation of 1-aminonaphthotriazine in benzene gave, not the 1,8-dehydronaphthalene dimer perylene (17), but products arising from attack of the 1,8-dehydronaphthalene on the benzene solvent. Thus 1-phenylnaphthalene (18), 6b, 10a-dihydrofluoranthene (19)



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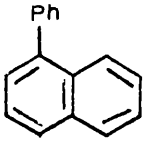

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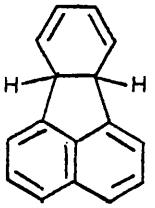

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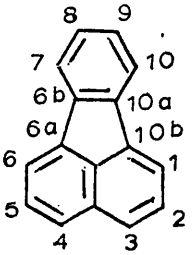
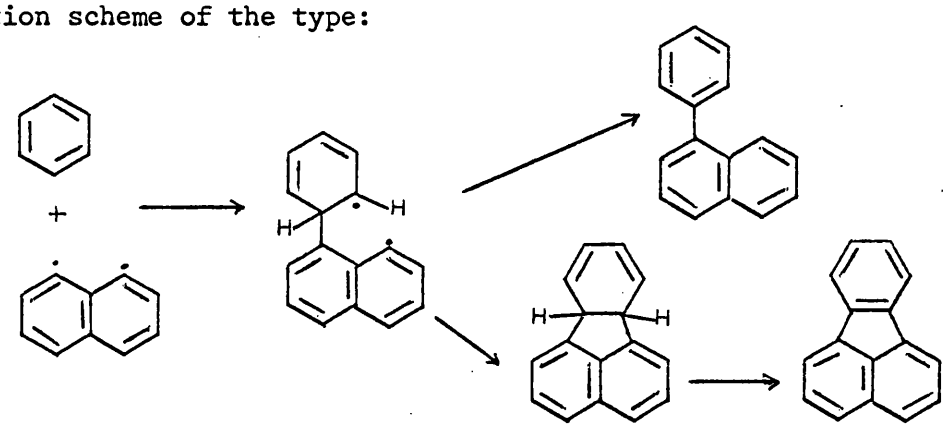


(20)

and fluoranthene (20) were isolated. Initially, owing to the small scale of the reactions and difficulty in separation of products, only the solid fluoranthene was identified. This was easily characterised by its fluorescence and by comparison with

an authentic specimen. However the u.v. spectrum of the crude fluoranthene was not entirely consistent with that of a purified sample and when larger amounts of starting material became available 1-phenylnaphthalene was isolated from the product mixture. Fluoranthene presumably arose by 1,2-addition of 1,8-dehydronaphthalene to benzene with further oxidation of the intermediate dihydrofluoranthene. Attempts to analyse the 1-phenylnaphthalene-fluoranthene mixture by u.v. spectroscopy and gas-liquid chromatography indicated the presence of a third compound when the initial excess of lead tetra-acetate was small. Careful chromatography led to the isolation of dihydrofluoranthene as a colourless crystalline solid which readily decolourised potassium permanganate in acetone. Analysis, i.r., u.v. and p.m.r. spectral data were consistent with the structure which was finally confirmed by mass spectrometry which indicated a molecular weight of 204. However large peaks occurred for P-1 and P-2 (intensity P-2 > P-1 > P) presumably since the molecular ion derived from stable fully aromatic fluoranthene was readily formed by fragmentation.

The formation of these products can be explained by a reaction scheme of the type:



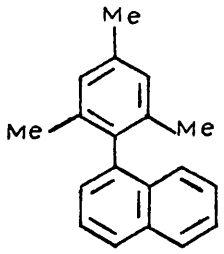
The proposed intermediacy of dihydrofluoranthene in the formation of fluoranthene is supported by the fact that when 1-amino-naphthotriazine was oxidised with lead tetra-acetate in benzene containing a compound which destroys lead tetra-acetate competitively, no fluoranthene was formed. Thus in the presence of tetrakis-triphenylphosphine platinum (0) (used in an attempt to isolate a platinum complex incorporating 1,8-dehydronaphthalene) excess of lead tetra-acetate was destroyed and 1-phenylnaphthalene and dihydrofluoranthene only were formed.

6b,10a-Dihydrofluoranthene has not been reported previously and cannot be obtained by hydrogenation of fluoranthene which is reported to give 1,2,3,10b-tetrahydrofluoranthene, possibly via 2,3-dihydrofluoranthene, 1,2,3,6b,7,8,9,10,10a,10b-decahydro-fluoranthene and perhydrofluoranthene in successively more vigorous hydrogenations.[71] Recently however, reduction of fluoranthene by sodium hydrazide has given 50% of a dihydrofluoranthene m.p. 80-81°[72] for which no further details were given. 6b,10a-Dihydro-fluoranthene had m.p. 76° and therefore these two dihydro compounds could be identical. 2,3-Dihydrofluoranthene is reported to have m.p. 63-65°.[73]

Addition of 1,8-dehydronaphthalene to aromatic hydrocarbons appears to be a general reaction. Thus with p-xylene, 7,10-dimethyl-fluoranthene was obtained together with a trace of naphthalene and an oily product which was presumably 1-(2,5-dimethylphenyl)-naphthalene. 7,10-Dimethylfluoranthene gave the expected analytical,

spectral and mass spectral data; in particular the u.v. spectrum was very similar to that of fluoranthene itself. The trace of naphthalene, presumably formed by abstraction of the benzilic hydrogens by the dehydronaphthalene, suggests that the reaction is radical in nature.

In mesitylene, 1,8-dehydronaphthalene might be expected to give 1-(2,4,6-trimethylphenyl)naphthalene (21) or 6b,8,10-trimethyl-6b,10a-dihydrofluoranthene (22) which should be stable to further oxidation. However only (21) and naphthalene were isolated from the reaction. The structure of (21) was confirmed by analytical and spectral data and by the non-decolourisation of



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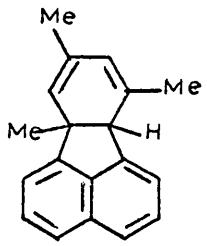
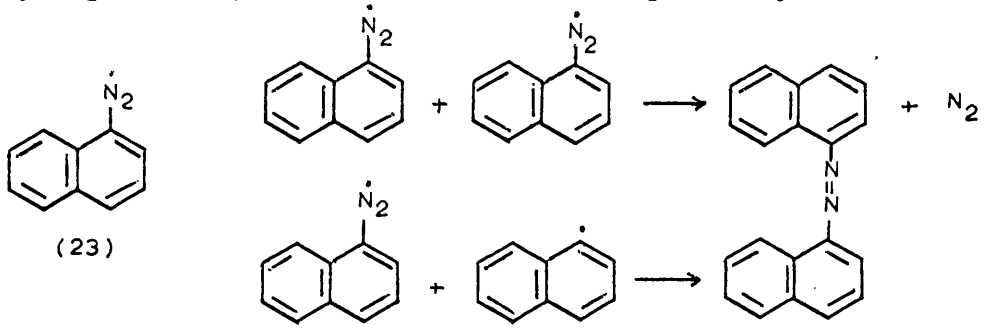


(22)

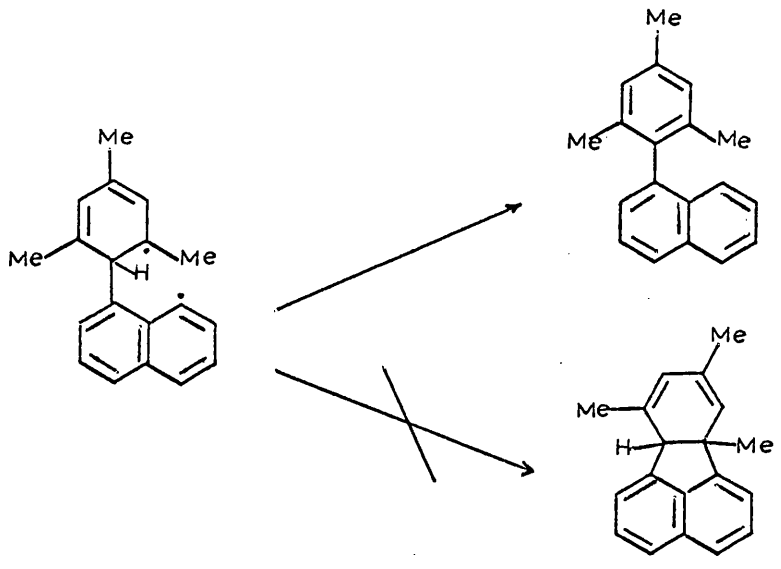
potassium permanganate in acetone. The mass spectrum showed large peaks at m/e 119 (trimethyl-phenyl), and 128 (naphthyl + 1). P.m.r. indicated two equivalent methyl groups at 8.17τ and a different methyl at 7.64τ. The shielding of the two equivalent methyls relative to the other methyl is surprising since from a consideration of steric peri-interactions and the electronic effects of the naphthalene nucleus, relative deshielding would be expected. Finally the compound was prepared by the arylation procedure of Cadogan[74] by heating α-naphthylamine and amyl nitrite in mesitylene.

The reaction did not proceed as cleanly as reported for simpler cases but a small amount of 1-(2,4,6-trimethylphenyl)naphthalene, identical in all respects to that obtained from 1,8-dehydronaphthalene, was obtained. In addition, naphthalene and an appreciable amount of 1,1'-azonaphthalene were isolated, presumably having arisen from side reactions involving ready abstraction of the mesitylene hydrogen atoms, and the radical (23) respectively.



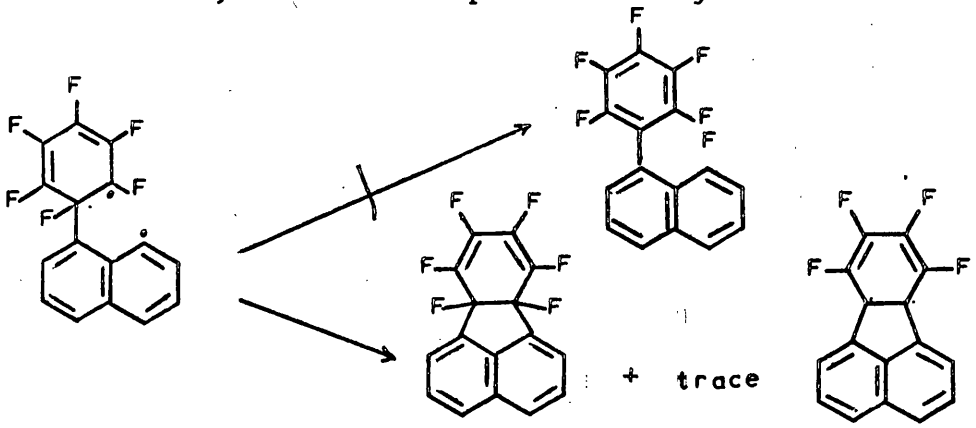
(23)

The formation of only (21) in the oxidation of 1-amino-naphthotriazine can be rationalised by initial attack of the 1,8-dehydronaphthalene at the least hindered position of the mesitylene ring, followed by hydrogen atom transfer rather than sterically unfavourable ring closure. On the other hand the



1,8-dehydronaphthalene may have first abstracted hydrogen to give a naphthyl radical, which then substituted homolytically in mesitylene.

Hexafluorobenzene was initially used as a trap, before the isolation of dihydrofluoranthene from reaction in benzene, in the hope that the analogue of dihydrofluoranthene would in this case be stable. 6b,7,8,9,10,10a-Hexafluorofluoranthene (24) was in fact the major product although the stability of the fluoranthene system was reflected in the formation of a trace of material which had the characteristic fluorescence and u.v. spectrum of a fluoranthene and which was presumably 7,8,9,10-tetrafluorofluoranthene (25). Hexafluorofluoranthene had the expected analysis and spectral properties. The mass spectrum showed P-38 > P-19 > P, cf. the mass spectrum of dihydrofluoranthene.

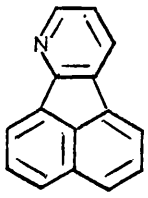


(24) (25)

In this case, transfer of a fluorine in the intermediate diradical is highly improbable and only the ring closed product is formed.

In the oxidation of 1-aminonaphtho[1,8-de]triazine in pyridine, isolation of products by chromatography proved unsatisfactory

due to their polarity. The most convenient method was evaporation of the pyridine under reduced pressure followed by extraction of the basic products with dilute acid. This gave a small amount of an oily substance, possibly 7-azafluoranthene (26), which formed a picrate m.p. 273-274°. The picrate of 7-azafluoranthene is reported to have m.p. 272°.[75] The u.v. of the initial



(26)

oil showed close similarity to the u.v. of fluoranthene. Fields[53] has obtained naphthylpyridines by pyrolysis of 1,8-naphthalic anhydride in pyridine at 690°, presumably via 1,8-dehydronaphthalene. However under his conditions, any 7-azafluoranthene may have been converted into naphthylpyridine. We obtained no evidence for naphthylpyridines.

The oxidation of 1-aminonaphtho[1,8-de]triazine in benzene solution with oxidants other than lead tetra-acetate was also studied.

Lead tetra-isobutyrate gave a greater yield of mixed hydrocarbon products than lead tetra-acetate, the mixture consisting of 1-phenylnaphthalene and fluoranthene. Iodobenzene diacetate oxidised 1-aminonaphthotriazine rapidly in warm benzene giving a mixture of 1-phenylnaphthalene and fluoranthene in somewhat lower yield than lead tetra-acetate. Both nickel peroxide and manganese

dioxide were less effective than lead tetra-acetate, giving only trace amounts of product. In the case of nickel peroxide, some dihydrofluoranthene was isolated in addition to 1-phenylnaphthalene and fluoranthene. Thus these other oxidants although varying in their effectiveness, did not significantly change the course of reaction. In the oxidation of 1-aminobenzotriazole, lead tetra-acetate was unique in giving the benzyne dimer biphenylene, other oxidants giving none (with the exception of nickel peroxide which gave a trace[62]). In the case of 1-aminonaphthotriazine no oxidant gave detectable amounts of the 1,8-dehydronaphthalene dimer perylene for which T.L.C. was a very sensitive test. Control experiments showed that a 3µl sample of a solution containing 1 mg. perylene/100 ml. was sufficient for detection.

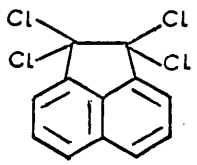
N-Bromosuccinimide oxidised 1-aminonaphthotriazine rapidly in warm benzene after a brief induction period. No products derived from attack on benzene were observed however; 1,8-dibromonaphthalene and 1,4,5-tribromonaphthalene were isolated in moderate yield. 1,8-Dibromonaphthalene presumably arose by preferential attack of 1,8-dehydronaphthalene on the excess of N-bromosuccinimide or elementary bromine in the system, and the tribromonaphthalene from further bromination of 1,8-dibromonaphthalene.

Oxidations in Olefins and other 1,2-unsaturated systems

The initial isolation of fluoranthene arising by 1,2-addition of 1,8-dehydronaphthalene to benzene led us to

investigate the addition to other 1,2-unsaturated systems. This was found to be a general reaction.

Oxidation of 1-aminonaphtho[1,8-de]triazine with lead tetra-acetate in tetrachloroethylene gave a small amount of 1,1,2,2-tetrachloroacenaphthene[76] (27). The compound was not



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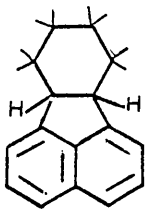


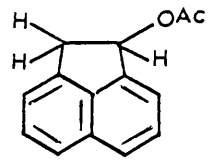
(28)

compared with an authentic specimen but it had the expected spectral properties and the melting point agreed with the literature.

In cyclohexene, 1,8-dehydronaphthalene gave naphthalene, by radical abstraction of the allylic hydrogen atoms of cyclohexene, and 6b,7,8,9,10,10a-hexahydrofluoranthene (28) in low yield, by 1,2-addition. The structure of (28) was supported by i.r., u.v. and mass spectroscopy, but because of the low yield no analysis was possible. This addition of 1,8-dehydronaphthalene to cyclohexene is interesting since 6b,7,8,9,10,10a-hexahydrofluoranthene cannot be obtained by direct hydrogenation of fluoranthene.

Oxidation of 1-aminonaphthotriazine in vinyl acetate gave 1-acetoxyacenaphthene (29) in good yield. This was identical with an authentic specimen obtained by acetoxylation of acenaphthene with lead tetra-acetate.[77] Hydrolysis gave 1-hydroxyacenaphthene,

again identical with an authentic specimen.



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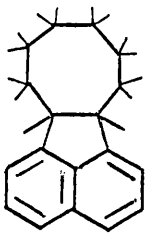


(30)

In cyclooctene, naphthalene was again formed together with the adduct, cyclo-octaacenaphthene (30). The structure (30) was supported by analysis and by i.r. and mass spectrometry. P.m.r. indicated six aromatic protons, two benzilic protons, considerably split, 6.5τ, and a complex multiplet of twelve aliphatic protons, 7.8-8.6τ.

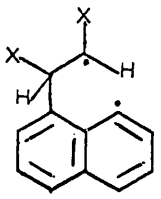
The use of a cis-trans olefin pair would make possible the study of the stereochemistry of the 1,8-dehydronaphthalene addition to olefins, thereby giving an insight into the electronic state of the intermediate. The relation between stereospecificity of addition and the singlet-triplet nature of the intermediate is well known in carbene chemistry[78] and is based on Skell's[79] hypothesis that σ bond rotation is more rapid than spin inversion. Thus the observed non-stereospecific addition of triplet carbene is attributed to bond rotations in the intermediate triplet 1,3-diradical prior to the relatively slow spin inversion which is required before ring closure can occur. In singlet carbene, spin inversion is not necessary for ring closure, which is therefore concerted. Recently experimental support for Skell's hypo-

thesis has been obtained from a study of the ring closure of singlet and triplet 1,3-diradicals produced by methods not involving carbene addition.[80] It has been shown that reactive intermediates, e.g. carbenes and nitrenes, generated initially in a singlet state, which adds stereospecifically, can decay to a triplet ground state which adds non-stereospecifically,[81] thus complicating the simple case. The isomerisation of products once formed could also lead to apparent non-stereospecific addition, but this is usually easily checked by suitable control experiments. It is also possible that a triplet diradical intermediate may ring close stereospecifically because steric or other factors prevent free rotation or because one product is highly favoured thermodynamically.

With these reservations, the application of Skell's hypothesis to the 1,5-diradical (31) produced by the first addition step of 1,8-dehydronaphthalene to an olefin would seem valid. Thus singlet dehydronaphthalene should give a cis-disubstituted acenaphthene with a cis-1,2-disubstituted olefin, and a trans-disubstituted acenaphthene with a trans-olefin. Triplet dehydronaphthalene would be expected to give a mixture of cis- and trans-disubstituted acenaphthenes in either case.

The availability and physical properties of cis- and trans- dichloroethylenes made them suitable for such a study. Preliminary experiments indicated that 1,8-dehydronaphthalene added to both olefins in relatively good yield in a largely

stereospecific manner. Authentic samples of cis- and trans-dichloroacenaphthene were prepared by the method of Cristol.[82] The cis compound (31) was obtained by direct chlorination of acenaphthene in benzene in the absence of light. Some difficulty was initially experienced due to overchlorination but the product was easily isolated when the flow of chlorine was stopped immediately the calculated quantity had been absorbed. It was found that the reaction was completed much more quickly than Cristol reported. trans-Dichloroacenaphthene (33) was prepared by chlorination of



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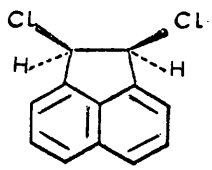

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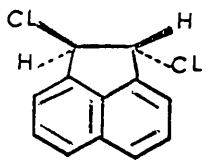


(33)

acenaphthene with iodobenzene dichloride in the presence of 1,3,5-trinitrobenzene (radical inhibitor).

The p.m.r. spectrum of cis-dichloroacenaphthene in deuteriochloroform showed a singlet at 4.18τ due to the benzilic protons; trans-dichloroacenaphthene showed a similar singlet at 4.27τ. This difference in chemical shift for the protons in the cis- and trans-compounds, although small, was sufficient to make analysis of mixtures of the two possible. It was shown that 5% of one isomer in 95% of the other was easily detected. Carbon tetrachloride was not a suitable solvent since the difference in the chemical shift of the protons concerned was considerably reduced.

Oxidations were first carried out in the standard way by dropwise addition of 1-aminonaphthotriazine in the olefin to a slight excess of lead tetra-acetate in the olefin. Filtration was followed by evaporation on to silica gel and rapid chromatography. The combined cis-trans-dichloroacenaphthene fraction was collected, dissolved in deuteriochloroform, and a p.m.r. spectrum was run. In all experiments with trans-dichloroethylene, less than 5% of cis-dichloroacenaphthene could be observed in the mixture. In almost all experiments with cis-dichloroethylene less than 5% of the trans-isomer was observed, but in isolated instances appreciable amounts of the trans-compound (40:60 trans:cis) were detected. Control experiments indicated that cis- and trans-dichloroacenaphthene were not isomerised under the reaction conditions but that they were destroyed by adsorption on to silica gel with unchanged lead tetra-acetate.

In order to have the mildest possible oxidation conditions, a very slight excess of lead tetra-acetate was added as a solid to 1-aminonaphthotriazine in the olefin. Immediately the reaction was complete, a drop of glycerol was added to destroy the excess of lead tetra-acetate and the reaction mixture was evaporated. The dichloroacenaphthenes were then extracted, almost pure, with ether, from the polymeric residue and p.m.r. spectra were run. In all cases, for both cis- and trans-dichloroethylene, the addition was found to be more than 95% stereospecific. When generated in an equimolar mixture of cis- and trans-dichloroethylenes,

1,8-dehydronaphthalene added equally to each giving an almost 1:1 mixture of cis- and trans-dichloroacenaphthenes.

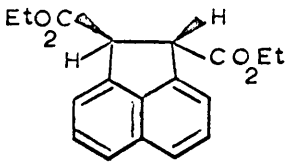
These observations are most simply explained by considering that the 1,8-dehydronaphthalene is generated in a singlet state and adds in a concerted manner to the olefins. The trace of non-stereospecific isomer may be due to relaxation to a triplet state or to the fact that ring closure is not enormously faster than bond rotation. The isolated cases of non-stereospecific addition to cis-dichloroethylene cannot be explained simply; however in the vast majority of cases the addition was fully stereospecific. The anomaly found with certain batches of lead tetra-acetate with regard to dimerisation of benzyne (see Section II) may have some connection with the isolated non-stereospecific additions, perhaps by assisting relaxation to a triplet state or by the initial generation of a triplet.

Since the dichloroethylenes proved to be good traps for 1,8-dehydronaphthalene, dilution with the relatively inert methylene chloride was studied. The yield of adduct fell from 38% in pure trans-dichloroethylene to 28% in 1:1 dichloroethylene-methylene chloride and to 25% in 1:10 dichloroethylene-methylene chloride. T.L.C. indicated that the reaction was largely stereospecific even in the most dilute solution. Thus the dehydronaphthalene did show some degree of selectivity. However, the dilution was not sufficient to indicate a marked increase in relaxation of a possible singlet to triplet state. Dilution with the more reactive solvent, chloro-

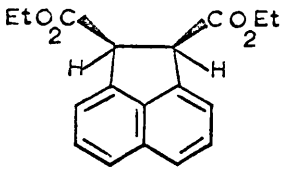
form (1:10) reduced the yield of adduct to 11%. Oxidation in trans-dichloroethylene with nickel peroxide, as expected, gave a lower yield of adduct which appeared to be largely trans.

In the absence of another more suitable pair of cis-trans olefins, the oxidation of 1-aminonaphthotriazine was carried out in diethyl fumarate and diethyl maleate. The p.m.r. spectra of the two isomers showed that the olefinic protons in diethyl fumarate absorb at lower field than those of diethyl maleate and hence the benzilic protons in diethyl trans-acenaphthene-1,2-dicarboxylate (34) should absorb at lower field than those of the corresponding cis-isomer (35). The relatively large difference in chemical shift between the olefinic protons (30 c.p.s.) in diethyl maleate and fumarate should also be reflected in the adducts. In the dichloroethylenes the protons in the cis-olefin and cis-adduct absorbed at the lower field.

Oxidation in diethyl fumarate by the second method used for the dichloroethylenes gave a semi-solid product shown by p.m.r. to be largely diethyl trans-acenaphthene-1,2-dicarboxylate (34), having a singlet due to the two benzilic protons at 4.9τ. However the presence of a small amount (<10%) of a second isomer, showing a singlet at 5.19τ, assumed to be the cis-adduct, was observed. This was not isolated. The structure of diethyl trans-acenaphthene-1,2-dicarboxylate was fully supported by analytical



(34)

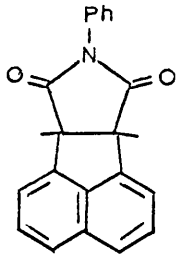


(35)

and spectral data, the trans configuration being considered the more likely from the p.m.r. chemical shifts and the mode of formation. With diethyl maleate, similar procedure gave the same products in the same ratio but in lower yield.

The formation of largely the trans-adduct in both cases, rather than the expected stereospecific isomers may have been due to isomerisation of the cis- to the trans-adduct under the reaction and work up conditions which were necessarily more vigorous than for the dichloroethylenes. However, this would seem unlikely in the absence of base, and alternative explanations are discussed in a consideration of the structure of 1,8-dehydronaphthalene.

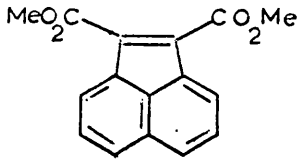
It is of interest that Hoffmann,[48] generating 1,8-dehydronaphthalene by our method, has obtained the adduct (36) with N-phenylmaleimide in low yield.



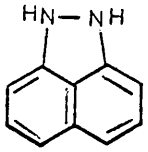
(36)

1,2-Addition by 1,8-dehydronaphthalene has been extended to acetylenes. Thus oxidation of 1-aminonaphthotriazine in dimethyl acetylenedicarboxylate gave dimethyl acenaphthylene-1,2-dicarboxylate (37) in relatively good yield. The structure was confirmed by analytical, mass spectral and other spectral data. The generality of addition to acetylenes was confirmed by reaction with diphenylacetylene in methylene chloride solution. A small amount of product was isolated having the same colour and melting point reported for 1,2-diphenylacenaphthylene.[83] T.L.C. also indicated a trace of material having the characteristic fluorescence of a fluoranthene under u.v. light, possibly indicating some attack on the phenyl rings of the diphenylacetylene. The low yield of diphenylacenaphthylene was due to the dilute solution used and to the expected inefficiency of the trap.

Since 1,2-additions to unsaturated carbon compounds were general, the addition to unsaturated systems containing atoms other than carbon was investigated. Addition to azo-compounds might be expected to give derivatives of the interesting dihydrobenz[cd]indazole (38) system (see Section III). Oxidation of 1-aminonaphthotriazine in dimethyl azodicarboxylate gave a low yield of unstable colourless solid assumed to be dimethyl 1,2-dihydrobenz[cd]indazole-1,2-dicarboxylate (39) on the basis



(37)



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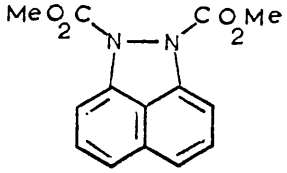


(39)

of its i.r., p.m.r. and mass spectra. Because of its explosive nature the dimethyl azodicarboxylate was diluted with methylene chloride and after the oxidation the excess of azo ester was not removed by distillation but was destroyed by stirring overnight in an aqueous buffer. Analysis of (39) was not attempted because of its instability and the difficulty of obtaining a pure sample from the small amount available. The i.r. spectrum showed no N-H absorption but carbonyl peaks occurred at 1756, 1723, 1710 $cm.^{-1}$ together with ester C-O peaks at 1293 and 1243 $cm.^{-1}$ Aromatic absorptions at 793, 740, 723 $cm.^{-1}$ indicated the presence of the naphthalene nucleus in the molecule. P.m.r. showed six aromatic protons and two equivalent methyl groups at 6.06τ. Finally mass spectroscopy gave the molecular weight 272 with fragmentation peaks at m/e 213 ($-CO_2Me$), 169 ($-CO_2-CO_2Me$), 126 ($-MeO_2C-N-N-CO_2Me$).

Unfortunately, because of the small amount of material available no reactions could be attempted such as hydrolysis and decarboxylation to give the parent dihydrobenz[cd]indazole. In spite of much effort, this would appear to be the first example of the system and as such may be worthy of further investigation.

Although 1,8-dehydronaphthalene had added successfully to C=C and N=N systems an attempted addition to the C=N system of ethylidene ethylamine (40) failed. Nickel peroxide was used as oxidant since lead tetra-acetate rapidly destroyed ethylidene ethylamine, but none of the expected adduct (41) was obtained, traces of naphthalene being the only product isolated.

(40)

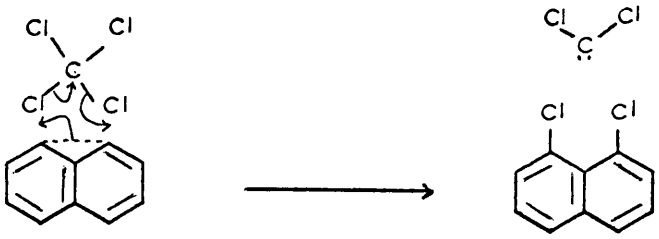
(41)

Oxidations in Chlorinated Hydrocarbon Solvents.

Early in our study of 1,8-dehydronaphthalene, much effort was directed to the detection of the dimer perylene. Several solvents were used for the lead tetra-acetate oxidation of 1-aminonaphthotriazine but perylene was never detected, even in reactions carried out at temperatures as low as -70°.

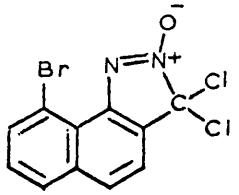
One of these solvents was carbon tetrachloride which it was assumed would be inert to the dehydronaphthalene. However this was not so, and a moderate yield of 1,8-dichloronaphthalene, identified by comparison with an authentic specimen,[84] was obtained together with a further unidentified product. This contained chlorine and its i.r. spectrum indicated that it was an acetoxy compound. 1,8-Dichloronaphthalene presumably arose by radical abstraction of chlorine atoms by the dehydronaphthalene. However, none of the expected hexachloroethane was detected, but this was hardly surprising in view of its high volatility and the small amount which would have been formed.

A similar oxidation was carried out in bromotrichloromethane in order to rule out an alternative mechanism in which both chlorine atoms in the 1,8-dichloronaphthalene came from the same molecule of carbon tetrachloride, forming dichlorocarbene.



The analogy is, however, not strictly correct since in bromotrichloromethane the C-Br bond is much weaker than the C-Cl bond.

This oxidation gave a good yield of 1,8-dibromonaphthalene and hexachloroethane, no 1-bromo-8-chloronaphthalene, which would be expected from the second mechanism, being detected. In addition a third compound was isolated but not identified. This was yellow and analysed for $C_{11}H_5BrCl_2N_2O$, the mass spectrum confirming this molecular formula. The presence of nitrogen is particularly interesting since this was the only product isolated from oxidations of 1-aminonaphthotriazine in which some of the nitrogen of the initial nitrene was retained. A possible structure



(42)

may be (42) but, in the absence of sufficient material to study the chemistry of the compound, this must remain speculative.

The use of methylene chloride as a relatively inert solvent has already been mentioned. Initially it was used since, unlike most other solvents, it readily dissolved lead tetra-acetate, and had been shown to be satisfactory for reactions of benzyne generated by lead tetra-acetate oxidations of 1-amino-benzotriazole. Methylene chloride was not however completely inert and small amounts of naphthalene and 1-chloronaphthalene were formed by radical abstraction. Hoffmann[48] has reported

the formation of up to 0.5% of perylene by oxidations in methylene chloride but we were unable to observe any.

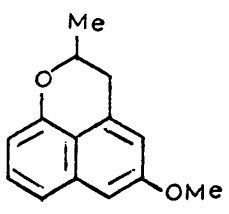
As expected, the hydrogen atom in chloroform proved to be more easily abstracted. Thus in chloroform, 1,8-dehydronaphthalene gave largely naphthalene but a small amount of chloronaphthalene was also formed, indicating the relatively low degree of selectivity. Hexachloroethane was also formed.

Oxidation of 1-aminonaphthotriazine occurred slowly with an excess of iodine in methylene chloride, giving 1,8-diiodonaphthalene.

Miscellaneous Oxidations.

Since benzyne adds readily to phenylazide[85] giving 1-phenylbenzotriazole, it was thought that 1,8-dehydronaphthalene may give 1-phenylnaphtho[1,8-de]triazine; however none was observed when 1-aminonaphtho[1,8-de]triazine was oxidised in phenylazide.

The synthesis of (±)xanthorrhoein[86] (43) has recently been reported and an attempt was made to obtain the basic ring system (44) by reaction of 1,8-dehydronaphthalene with propylene oxide. This was unsuccessful, however.



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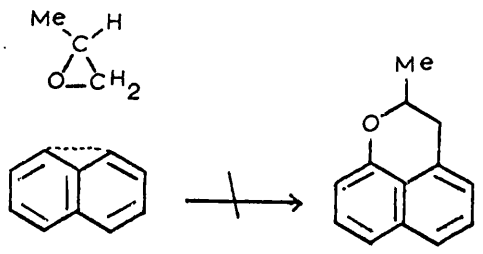
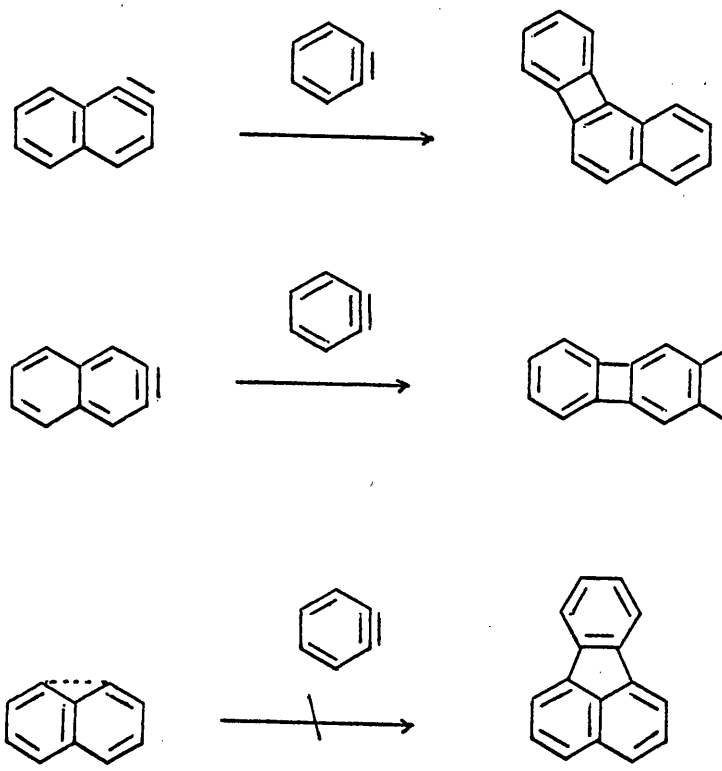


(44)

Generation of 1,2- and 2,3-dehydronaphthalene in the presence of benzyne gave good yields of the mixed biphenylenes (Section II) but similar generation of 1,8-dehydronaphthalene in the presence of benzyne gave no trace of fluoranthene, suggesting that the two intermediates have very different life times.



3. ATTEMPTED ROUTES TO 1,8-DEHYDRONAPHTHALENE

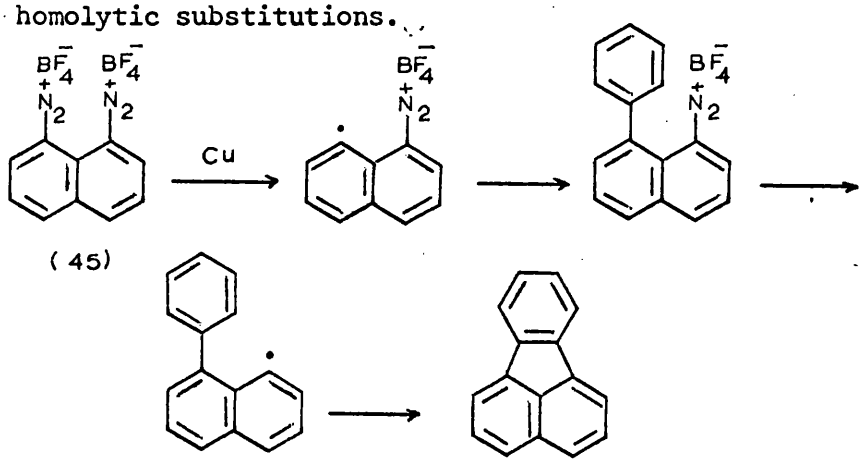
Since 1,8-dehydronaphthalene had many properties consistent with those of the 1,8-naphthylene diradical, attempts were made to generate the latter and to compare its properties with those of 1,8-dehydronaphthalene generated in a concerted manner by oxidation of 1-aminonaphthotriazine.

The treatment of Grignard reagents with anhydrous cobaltous chloride, to give aryl radicals, has been well known since its discovery by Kharasch.[87] However the cobaltous chloride catalysed decomposition of o-dilithiobenzene[56] failed to give any free benzyne, giving instead a variety of open chain polyphenyls and closed chain o-phenylene compounds by a stepwise process. A similar type of reaction occurred with 2,2'-dilithiobiphenyl.[57] Our results from the cobaltous chloride decomposition of 1,8-dilithionaphthalene,[23] from which only perylene was isolated, support this type of stepwise mechanism. The formation of perylene was in marked contrast to its complete absence in the reactions of free 1,8-dehydronaphthalene.

Since the copper catalysed decomposition of aryl diazonium fluoroborates gives rise to aryl radicals, the decomposition of naphthalene-1,8-tetrazonium fluoroborate (45) was investigated. Clean tetrazotisation of 1,8-diaminonaphthalene proved difficult, the most convenient method found being that described in the Experimental Section. The dry tetrazonium fluoroborate was decomposed with freshly prepared copper under a variety of conditions. Thus in benzene-acetone,

1,1'-azonaphthalene was the main product, although in low yield. Decomposition in pure refluxing benzene gave only a trace of azonaphthalene but a small amount of fluoranthene was isolated. In cis- and trans- dichloroethylene the presence of some acetone was required for decomposition to proceed smoothly. T.L.C. indicated a trace of azonaphthalene together with other unidentified products. No cis- and trans- dichloroacenaphthene was detected in either case.

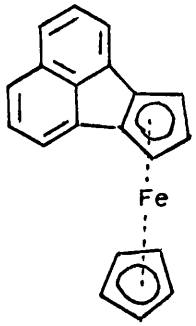
The formation of azonaphthalene in all cases suggests a stepwise decomposition of the two diazonium groups. In refluxing benzene the formation of fluoranthene rather than dihydrofluoranthene, the expected product of concerted 1,2-addition, again suggests a stepwise decomposition, the fluoranthene being formed by two separate homolytic substitutions.



(45)

The non-formation of the normal dehydronaphthalene adduct with the dichloroolefins also argues against the formation of free 1,8-dehydronaphthalene in this decomposition.

Little[88] has reported the formation of (46) by decomposition



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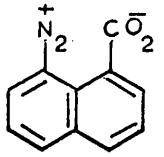
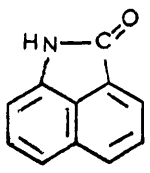


(47)

of naphthalene-1,8-tetrazonium fluoroborate in the presence of ferrocene.

Benzenediazonium-2-carboxylate has been widely used for the generation of benzyne, and the formation of 1,3- and 1,4-dehydrobenzene by decomposition of the appropriate diazonium carboxylate has already been described. An attempt to generate 1,8-dehydronaphthalene from naphthalene-1,8-diazonium carboxylate (47) is reported to have failed,[42] but in view of our experience with the detection of 1,8-dehydronaphthalene, the decomposition of this diazonium carboxylate was reinvestigated. 8-Amino-1-naphthoic acid was obtained by alkaline hydrolysis of naphthostyril (48) and was not purified because of its tendency to revert to (48).



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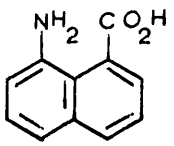

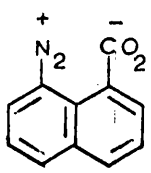

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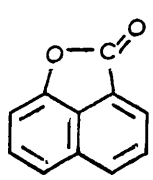


(49)

Aprotic diazotisation with amyl nitrite gave very crude naphthalene-1,8-diazonium carboxylate which was not purified because of its possible explosive nature. On addition of (47) to refluxing benzene, nitrogen was evolved and 1,8-naphtholactone (49) was the only product isolated, there being no evidence for the formation of 1,8-dehydronaphthalene. Higher temperature decomposition in dimethyl acetylenedicarboxylate gave no trace of dimethyl acenaphthylenedicarboxylate, again only 1,8-naphtholactone being isolated. Thus it would appear that initial loss of nitrogen is followed or accompanied by ring closure to give the stable lactone.

Attempted oxidative decarboxylation of 1,8-naphthalic anhydride with lead tetra-acetate also failed. However, Fields[53] has obtained 1,8-dehydronaphthalene from 1,8-naphthalic anhydride by pyrolysis at 690°.

Since benzyne has been produced by photolysis of, and the action of zinc on o-diiodobenzene, the formation of dehydronaphthalene from 1,8-diiodonaphthalene was briefly considered. However the action of zinc on 1,8-diiodonaphthalene caused only partial decomposition to 1-iodonaphthalene, no dehydronaphthalene products being detected. In view of this failure and the small amount of benzyne reported by photolysis of o-diiodobenzene,[25] similar photolysis of the less favourable 1,8-diiodonaphthalene was not attempted. However the recent demonstration by Kharasch and Sharma[28] that

photolysis of o-diiodobenzene does give benzyne in good yield suggests that photolysis of 1,8-diiodonaphthalene should be investigated.

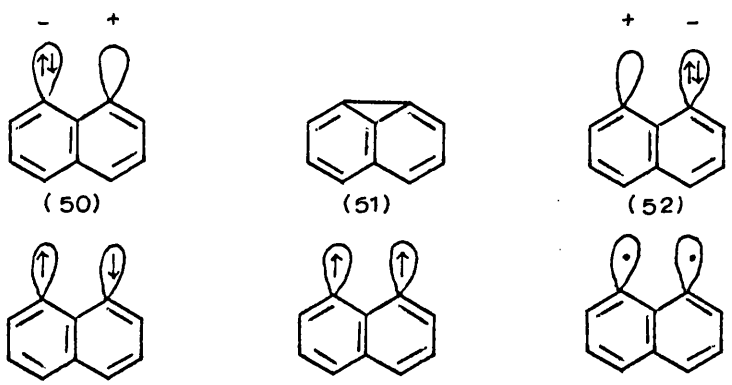
The oxidation of 1-aminonaphtho[1,8-de]triazine is so far the only synthetically useful way of generating 1,8-dehydronaphthalene. Of the other methods reported, pyrolysis of naphthalic anhydride at 690° is impractical, and the formation of dehydronaphthalene from 1,2,3-thiadiazino[4,5,6-ij]naphthalene-1,1-dioxide and thieto[2,3,4-ij]naphthalene-1,1-dioxide[48] is not only doubtful but certainly of no value in synthesis. The ready 1,2-addition of 1,8-dehydronaphthalene forms an attractive route to fluoranthenes, particularly their hydrogenated derivatives, acenaphthenes and acenaphthylenes which might otherwise be difficult to prepare. However the need for a large excess of the unsaturated compound is a limiting factor. As already mentioned, the formation of the dihydrobenzindazole system is particularly interesting.

4. STRUCTURE OF 1,8-DEHYDRONAPHTHALENE

As initially pointed out in the Introduction, a study of 1,8-dehydronaphthalene, apart from its synthetic value, should give information concerning the structure of dehydroaromatic species.

The basic premise, that we are dealing with free 1,8-dehydronaphthalene in oxidations of 1-aminonaphtho[1,8-de]-triazine, is supported by consistent failure, with only one exception, to isolate or detect products with any of the nitrogen retained. Also, where the 1,8-naphthylene diradical has been generated in a stepwise process e.g. by cobaltous chloride catalysed decomposition of 1,8-dilithionaphthalene or copper catalysed decomposition of naphthalene-1,8-tetrazonium fluoroborate, the products of reaction were very different from those of oxidation of 1-aminonaphthotriazine.

If we formally remove two hydrogen atoms from the peri-positions of naphthalene, the following distributions of the two remaining electrons in the two dehydro-orbitals must be considered:



(50) (51) (52)

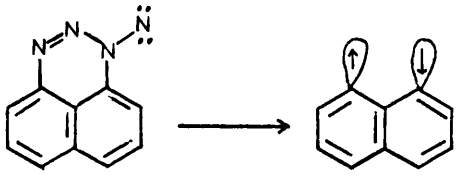
Singlet (53) Triplet (54) No interaction (55)

The analogue of the bis-carbene structure for benzyne (56) will not be significant for 1,8-dehydronaphthalene since the dehydro-centres are not conjugated.

(56)

Species such as (50) or (52) should undergo polar reactions, the vacant orbital promoting electrophilic character. A resonance hybrid involving canonical forms (50), (51) and (52), analogous to Wittig's formulation of benzyne, should behave similarly. However the contribution from (51) should be much less than from the corresponding canonical form for benzyne. The distinction between (51) and (53) is one of degree, (53) perhaps best being considered as an excited (51). Species such as (53), (54) and (55) would be largely radical in character but should differ in their reactions with olefins. Assuming that Skell's[79] hypothesis can be extended to this problem, one would expect (53) to undergo concerted stereospecific addition, while (54) should add in a non-stereospecific manner. In an intermediate such as (55) where no interaction is assumed, relative spin has no significance and since both electrons are of the same energy, spin inversion must be extremely rapid. It is difficult to predict the reactions of a species such as (55) apart from its obviously basic radical character. Addition to olefins may be possible but should not be stereospecific.

The reactions of 1,8-dehydronaphthalene, e.g. the abstraction of hydrogen and halogen, suggest that it is largely radical in character, supporting the diradical structures (53), (54) and (55) rather than the polar structures (50) and (52). The ready 1,2-addition to olefins, aromatic hydrocarbons, and acetylenes is also in accord with the diradical forms (53), (54) and (55). However the concerted stereospecific addition to the dichloroethylenes is most simply explained by a singlet species (53). This implies appreciable interaction between the two electrons involved and that fragmentation of the nitrene (15) occurs to give initially a singlet diradical.



(15)

It is difficult to rule out a completely non-interacting diradical (55) on the basis of experimental data butintuitively the absence of any interaction in this species would seem most unlikely. In benzyne, it is generally accepted that interaction between the two dehydrocentres occurs although the nature of this interaction is poorly understood. The commonly accepted picture is that of direct weak 'sideways' overlap between the two sp^2 orbitals concerned, leading to a highly reactive olefinic type of intermediate. The overlap integral S for benzyne has been calculated as 0.1-0.125,[18,89] compared with 0.25 for a normal

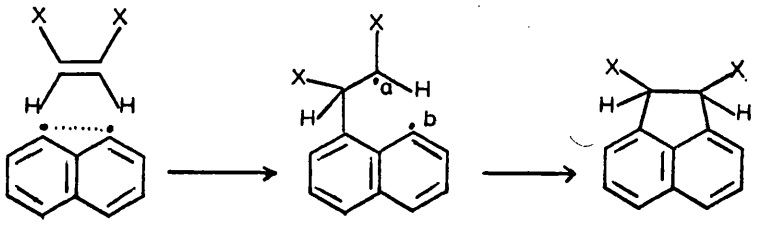
π bond in benzene.

Since in 1,8-dehydronaphthalene the dehydro-positions are not conjugated, one might expect no interaction other than that through space, and an extreme view would be that of the pure diradical with no interaction at all. However Hoffmann[48] has pointed out that, assuming an undistorted naphthalene nucleus, the separation of the dehydro-orbitals is 2.4 A° whichfrom a consideration of Slater overlap integrals for pπ pπ bonds leads to a value of 0.04 for S. Any distortion would increase S. Thus, on the simple basis of direct overlap, 1,8-dehydronaphthalene should not be a simple diradical but should show some slight similarity to benzyne, the reduced overlap leading to a shorter lifetime, less selectivity and greater radical character.

This is borne out experimentally by the difference between 1,8-dehydronaphthalene and benzyne generated similarly. This difference is over and above that demanded by the steric requirements of the two species. Thus benzyne is very selective, dimerising in high yield and being trapped effectively by dienes even in dilute solution. 1,8-Dehydronaphthalene does not dimerise, readily undergoes radical abstraction reactions and trapping is only efficient with a vast excess of the mono-ene. The dilution experiments with dichloroethylene in methylene chloride do suggest some degree of stability however.

We have tentatively suggested that 1,8-dehydronaphthalene

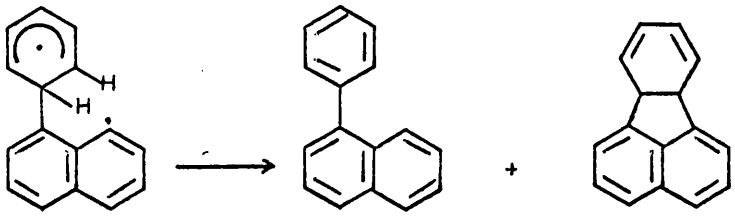
generated by oxidation of 1-aminonaphthotriazine is initially in a singlet state. However the non-stereospecific addition to diethyl fumarate and maleate apparently contradicts this. This anomaly can perhaps be rationalised by considering the intermediate diradical (35) in the addition of 1,8-dehydronaphthalene to an olefin.



(35)

Following Skell's hypothesis, it is assumed that if the electron spins in (35) are anti-parallel (singlet), then ring closure is fast and the stereochemistry of the olefin is preserved inthe adduct. This applies for the dichloroethylenes. However, if electron 'a' can be stabilised in the intermediate (35), ring closure could be retarded, allowing time for bond rotation and leading to non-stereospecific products. Now in the addition to diethyl fumarate and maleate, electron 'a' can be markedly stabilised by delocalisation and non-stereospecific addition could therefore result. This concept may also be applied to the reaction of 1,8-dehydronaphthalene with benzene where one would expect only dihydrofluoranthene from a singlet species. Stabilisation of electron 'a' by delocalisation again slows down ring closure, making possible the formation of 1-phenylnaphthalene by the

competing process of hydrogen transfer.



On the other hand it could reasonably be argued that such stabilisation is more likely to be important in the addition of a triplet dehydronaphthalene, where a definite intermediate 1,5-diradical must be invoked, than in the concerted addition of a singlet dehydronaphthalene. Thus triplet dehydronaphthalene adds to the dichloroolefins in a stereospecific manner because spin inversion in this case is faster than bond rotation, but non stereospecific addition occurs with diethyl maleate and fumarate because stabilisation now slows down the ring closure process. The stereospecific addition to the dichloroolefins would then be in contradiction to Skell's hypothesis but as has frequently been pointed out[78,90] this has no firm basis, and although there is experimental support from carbene addition to olefins, the factors involved may be more finely balanced in the addition of a 1,3-diradical to an olefin.

A final explanation of the difference between these additions to the dichloroethylenes and to the esters could be spin inversion in 1,8-dehydronaphthalene from an initially formed singlet to a more stable triplet state. This would seem reasonable in view of the relatively small interaction between the two electrons,

but it is difficult to see why addition to the dichloroethylenes should be more rapid and occur through a singlet state while addition to the olefinic esters should be slower and occur through a triplet state. However this could be checked by suitable competition reactions. Such singlet-triplet decay should be concentration dependent i.e. dilution of the dichloroethylenes should lead to an increase in non-stereospecific product since more time is allowed for the decay to occur before reaction. However our very limited dilution study did not indicate any striking effect, and further investigation of this would be desirable. Such an explanation would also apply to the reaction with benzene, the 1-phenylnaphthalene arising from the triplet state dehydronaphthalene, after relaxation.

Although the observed reactions of 1,8-dehydronaphthalene indicate some degree of interaction between the dehydro- centres and are in qualitative agreement with what one might predict on the simple basis of direct overlap, the isolated comparison between benzyne and 1,8-dehydronaphthalene in no way supports the fundamental concept that stabilisation in dehydroarenes is a result of direct overlap interaction. Indeed recent calculations by Hoffmann[91] suggest that direct overlap may not even be the major contribution to interaction. Moreover, our observed reactions of 1,8-dehydronaphthalene are in striking agreement with his predictions which also rationalise the differences between benzyne and dehydronaphthalene.

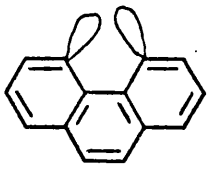
The removal of two hydrogen atoms from an aromatic system leaves two orbitals, n_1 and n_2, which are commonly considered as sp^2, although this is not strictly correct. The difference in energy between the symmetric combination S ($n_1 + n_2$) and antisymmetric combination A ($n_1 - n_2$) is a measure of the interaction between the orbitals. Depending on the type of interaction, either S or A can be the lower energy combination, and this is crucial to the subsequent reactions of the species, since from molecular orbital arguments it follows that a species with two electrons in a lower S level should add thermally (stereospecifically) 1,4: 1,8: 1,12 .... to polyenes while a species with two electrons in a lower A level should add 1,2; 1,6 ....

From his calculations Hoffmann[91] has shown that the interaction between the orbitals depends only on the orientation of the σ bonds between the orbitals and on the orientation of the orbitals themselves, and that the interactions can be split up into contributions from direct (through space) interaction and indirect (through bond) interaction. As expected, o-benzyne shows a large direct interaction with the S level lower in energy than the A level. m-Dehydrobenzene again has S of lower energy than A, the interaction being greater than expected. For p-dehydrobenzene the direct interaction over 2.8 Å is almost non-existent and if direct interaction were all that mattered, the difference between A and S should be correspondingly small.

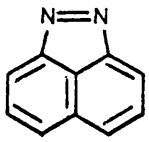
However the splitting is very large with the anti-symmetric combination A at lower energy than S. In its lowest energy singlet state, o-benzyne should resemble an olefin and, from the selection rules[92] for concerted cyclo-addition reactions, should add 1,4 in a concerted manner.

Calculations[91] for 1,8-dehydronaphthalene indicate an A level lower than S, therefore predicting concerted 1,2-addition, as observed experimentally with the dichloroethylenes. The difference between m-dehydrobenzene and 'meta' 1,8-dehydronaphthalene illustrates the steric dependence of the interaction. The relatively low difference in energy (0.4 ev.) between the A and S levels for 1,8-dehydronaphthalene would indicate a high degree of radical character and a possible triplet ground state. Apart from the mechanism of interaction this molecular orbital picture of 1,8-dehydronaphthalene is essentially the same as the valence bond picture discussed previously.

Thus our limited number of experiments with 1,8-dehydronaphthalene indicate that interaction between the dehydro-centres in dehydroarenes is important and point the way to a possible determination of the nature of the interaction. For example the Hoffmann[91] predictions form a working hypothesis which could be further investigated by other examples of 1,3-diradicals or by investigation of species such as 4,5-dehydrophenanthrene (59) which should undergo concerted 1,4-addition.



(59)



(60)

Since the singlet-triplet nature of 1,8-dehydronaphthalene is still uncertain the preparation of benz[cd]indazole (60) is of interest because photolysis of this compound under different conditions could lead to 1,8-dehydronaphthalene in the different electronic states. Low temperature photolysis in a frozen glass might make an electron spin resonance study possible.

INSTRUMENTATION AND EXPERIMENTAL TECHNIQUES

The following general points apply to the whole Thesis except where noted.

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

   The method of purification of specific solvents is given with the details of the particular experiment. Petrol refers to petroleum spirit b.p. 40-60°.

2. Lead tetra-acetate (B.D.H.) was freed from acetic acid by filtration and stored *in vacuo* over concentrated sulphuric acid.

3. Thin layer chromatography (T.L.C.) was widely used as a guide to the composition of reaction mixtures and as a means of testing the purity of compounds. Samples were eluted with suitable solvent mixtures on glass plates coated with a 250μ layer of Kieselgel G. (E. Merck). The plates were observed under ultraviolet light or developed by spraying with iodine.

4. Column chromatography was carried out using basic alumina (Spence type H), neutral alumina (Woelm) or silica gel (B.D.H. or Hopkin & Williams M.F.C.). The alumina columns

were packed under petrol and the eluent was gradually replaced by ether and then by methanol. Silica gel columns were either packed and eluted by the wet column method or by the dry column technique of Loev and Snader.[93] In all cases, samples for chromatography were dissolved in a suitable solvent and the resulting solutions were evaporated on to a small amount of adsorbent which was then packed on to the top of the column. Chromatographic fractions containing insignificant amounts of material are not recorded.

5. Infrared (i.r.) spectra were recorded in the range 4000-650cm^{-1} on a Perkin-Elmer 237 Spectrophotometer. Solid samples were run as nujol mulls and liquids as thin films, both between rock salt plates. The absorption peaks of new compounds were corrected using polystyrene as reference.
6. Ultraviolet (u.v.) spectra were recorded in the range 200-450 mμ on a Unicam SP800 spectrophotometer. Absolute ethanol was used as solvent.
7. Proton magnetic resonance spectra (p.m.r.) were recorded on a Perkin-Elmer R.10 60 Mc/s or a Varian A60 instrument. Deuteriochloroform and carbon tetrachloride were used as solvents with tetramethylsilane as internal reference.
8. Mass spectra were recorded on an Associated Electrical Industries M.S.9 spectrometer.
9. Melting point (m.p.) determinations were carried out in an electrically heated block apparatus, using corrected

thermometers, the sample being contained in a capillary tube.

10. Where possible, compounds were characterised by comparison of their melting points and mixed melting points (m.m.p.) and i.r. spectra with those of authentic specimens. Literature m.p. and b.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 (3rd and 4th Editions).

SECTION I EXPERIMENTAL

1. PREPARATION AND NON-OXIDATIVE REACTIONS OF AMINONAPHTHO[1,8-de]TRIAZINES

A. Preparation of 1-Aminonaphtho[1,8-de]triazine by Amination of Naphtho[1,8-de]triazine.

Naphtho[1,8-de]triazine

1,8-Diaminonaphthalene (40 g.) in ethanol and glacial acetic acid was stirred at 0° while amyl nitrite (27 g.) was added dropwise over several hours. After standing overnight the resulting precipitate was collected and washed thoroughly with ether to give crystalline naphtho[1,8-de]triazine (31 g., 72%), m.p. ca. 230°. (Lit., m.p. 236-237°,[59] 260-263°[60]).

Elution with ethanol from basic alumina followed by crystallisation from ethanol (charcoal) gave a very pure product in the form of lustrous red plates, m.p. ca. 235°

a) Amination with Hydroxylamine-O-sulphonic Acid.

Hydroxylamine-O-sulphonic acid was prepared by the method of R. Gösl and A. Meuwsen.[58]

Naphtho[1,8-de]triazine (10 g., 0.06 mole) suspended in aqueous potassium hydroxide (14 g., 0.24 mole in 200 ml.) was stirred at 70-80° while solid hydroxylamine-O-sulphonic acid (7 g., 0.06 mole) was added in small portions. More solid potassium hydroxide (14 g.) was then added followed by more

hydroxylamine-O-sulphonic acid (14 g.). The total addition was complete after about 4 hr. After cooling, the mixture was filtered and the residue was thoroughly washed with aqueous potassium hydroxide and then water. The residue was extracted with ether until the colouration indicated that no more red 1-aminonaphtho[1,8-de]triazine was present. The ether extracts were then dried, evaporated on to silica gel and chromatographed on a dry column.

Elution with 50% ether-petrol gave 1-azido-8-naphthylamine (2.9 g., 26%) which crystallised from petrol as very pale buff needles, m.p. 79-80°.

$\lambda_{max.}$ 232(log ε 4.20); 252.5(4.19); 346 mμ(3.94). $\nu_{max.}$ 3500, 3380, 2110, 1594, 1578, 1300, 810, 750 $cm.^{-1}$ τ2.15-2.85 (Complex multiplet, 5H); τ3.3(quartet, 1H; J=3 c.p.s.); τ4.60 (broad singlet, 2H). (Found: C, 65.6; H, 4.4; N, 29.6. $C_{10}H_8N_4$ requires: C, 65.2; H, 4.3; N, 30.4%).

Acetyl derivative, needles from ethanol, m.p. 147-148°. (Found: C, 64.2; H, 4.7; N, 24.3. $C_{12}H_{10}N_4O$ requires: C, 63.7; H, 4.4; N, 24.8%).

Elution with ether gave 1-aminonaphtho[1,8-de]triazine (4 g., 37%) contaminated with a small amount of naphtho[1,8-de]-triazine. Further chromatography on basic alumina using ether as eluent gave pure 1-aminonaphtho[1,8-de]triazine which crystallised from ethanol or ether as red needles, m.p. 154.5-155.5°.

$\lambda_{max.}$ 232.5 ($\log \varepsilon$ 4.42); 339 mμ(4.01). $\nu_{max.}$ 3415, 3205, 1630, 1584, 842, 772, 757 $cm.^{-1}$ (Found: C, 65.3; H, 4.3; N, 30.6. $C_{10}H_8N_4$ requires: C, 65.2; H, 4.3; N, 30.4%).

Benzylidene derivative, dark red needles from ethanol, m.p. 151-152°. (Found: C, 74.8; H, 4.6; N, 20.7. $C_{17}H_{12}N_4$ requires: C, 75.0; H, 4.4; N, 20.6%).

Treatment of 1-Methylnaphtho[1,8-de]triazine[61] with Hydroxylamine-O-sulphonic acid.

Hydroxylamine-O-sulphonic acid (1.3 g.) was added portionwise over 1 hr. to a mixture of 1-methylnaphtho[1,8-de]-triazine (1 g.) and potassium hydroxide (1.34 g.) maintained at 60-70°. Thin layer chromatography indicated only 1-methylnaphtho-[1,8-de]triazine. Addition of more hydroxylamine-O-sulphonic acid failed to produce any reaction.

b) Amination with chloramine

Ethereal Chloramine

Powdered ammonium chloride (27 g., 0.5 mole) was suspended in ether (1 l.) and cooled to -10°. Concentrated aqueous ammonia (42 ml., 0.67 mole) was added to the mixture which was then vigorously stirred while commerical aqueous sodium hypochlorite (250 ml. of 1.8 N solution, iodometric estimation; 0.45 mole) was added in small portions over 5-10 min., keeping the internal temperature between -15° and -10°. The ethereal layer was separated, washed once with saturated aqueous sodium chloride

solution (250 ml.) and dried over granulated calcium chloride for 1 hr. at -15°. After filtering the ethereal chloramine could be stored for several hours at -10° or below.

Estimation of Chloramine.

Potassium iodide (10 g.) dissolved in water (150 ml.) containing concentrated hydrochloric acid (2 ml.) was treated with a 10 ml. aliquot of ethereal chloramine. After shaking for 20 min., the ether was removed from the mixture by warming and the cooled solution was then made up to 250 ml. This solution was titrated against 5 ml. or 10 ml. aliquots of standard N/10 sodium thiosulphate solution using starch as indicator. The ethereal chloramine solutions were normally in the range 0.15 to 0.25 molar.

Amination with Chloramine.

Naphtho[1,8-de]triazine (5 g., 30 mmole) and sodium hydride (820 mg., 34 mmole) were refluxed overnight in dry ether. Chloramine in ether (430 ml. of 0.085 M solution, 36.5 mmole) was then added and the mixture stirred overnight. The resulting mixture was filtered, evaporated on to silica gel and chromatographed (dry column).

Elution with 50% ether-petrol gave a blue solid fraction (293 mg.) contaminated with a red oil. Further elution gave 1-aminonaphtho[1,8-de]triazine (2.33 g., 43%) contaminated with a little naphtho[1,8-de]triazine. Final purification of

1-aminonaphtho[1,8-de]triazine was effected by chromatography on basic alumina.

The blue solid fraction was rechromatographed carefully on silica gel. Elution with 20% ether-petrol gave an unidentified red oil (17 mg.) followed by 2-amino-6(?)-chloronaphtho[1,8-de] triazine (35 mg., corresponding to an overall yield of 0.72%), which crystallised from ether-petrol as blue needles, m.p. 197-198°. $\lambda_{max.}$ 235.5 (log ε 4.50); 270 (3.85); 350 mμ (4.02). $\nu_{max.}$ 3360, 3180, 3140, 1635, 1575, 1363, 1322, 1180, 818, 810 cm.$^{-1}$ (Complex of less intense peaks between 900-700 cm.$^{-1}$) m/e 220, 218, 181, 179, (Cl pattern) 155, 139, 127, 126. (Found: C, 55.1; H, 3.1; N, 25.5. $C_{10}H_7ClN_4$ requires: C, 54.9; H, 3.2; N, 25.6%).

Elution with 30% ether-petrol gave 2-aminonaphtho[1,8-de]-triazine (100 mg., 1.8%), blue needles from ether-petrol, m.p. 179-181°. $\lambda_{max.}$ 233.5 (log ε 4.50); 272 (3.85); 350 mμ (4.06). $\nu_{max.}$ 3300, 3140, 1620, 1580, 1374, 1255, 1187, 810, 750, 745 cm.$^{-1}$ m/e 184, 155, 140, 127. (Found: C, 64.9; H, 4.6; N, 30.1. $C_{10}H_8N_4$ requires: C, 65.2; H, 4.3; N, 30.4%).

Reaction of Chloramine with Naphtho[1,8-de]triazine directly.

Naphtho[1,8-de]triazine in dimethoxyethane in the presence of triethylamine (2 mole) was stirred with chloramine in ether for 2 days. Thin layer chromatography indicated no reaction

B. Attempted Preparation of 1-aminonaphtho[1,8-de]triazine from 8-Nitro-1-naphthylamine.

8-Nitro-1-naphthylamine (2.5 g.) and concentrated hydrochloric acid (4 ml.) were mixed to a paste which was diluted by the addition of water (9 ml.). Sodium nitrite (1.04 g.) in water (2.5 ml.) was added below 5° to give a dark red solution whichwas then added dropwise to a rapidly stirred suspension of diethyl malonate (2.1 ml.) in water (10 ml.). The mixture was kept alkaline during this process by the addition of sodium carbonate (4.5 g.). The product separated as an oily solid which was extracted with chloroform. After drying, the chloroform extract was evaporated on to silica gel for chromatography.

Elution with 20% ether-petrol gave 1-nitronaphthalene (400 mg., 17.5%), yellow needles from ethanol m.p. 59° (Lit., m.p. 61.5°).

Picrate m.p. 69-70° (Lit., m.p. 71°)

Further elution gave diethyl 8-nitro-1-naphthyl malonate (360 mg., 8%), yellow crystals from ethanol m.p. 94-5°. $\lambda_{max.}$ 217 (log ε 4.63); 242 (4.06); 335 mμ (3.50). $\nu_{max.}$ 1729, 1513, 1325, 1315, 1228, 1200, 1172, 1150, 1025, 890, 870, 848, 743 $cm.^{-1}$ τ1.1-2.43 (multiplet, 6H); τ4.9 (singlet, 1H); τ5.54 (quartet, 4H, J = 7.8 c.p.s.); τ8.67 (triplet, 6H, J = 7.8 c.p.s.). (Found: C, 61.5; H, 5.1. $C_{17}H_{17}NO_6$ requires: C, 61.6; H, 5.1%).

Continued elution gave diethyl mesoxalate-8-nitro-1-naphthylhydrazone (1 g., 21%), pale orange crystals from ethanol

m.p. 90-1°. $\lambda_{max.}$ 208 (log ε 4.53); 239 (4.32); 351 mμ(4.21). νmax. 1730; 1680; 1525; 1349; 1310; 1263; 1205; 1114; 1094; 1027; 837; 803; 760 cm.$^{-1}$ τ-2.75 (singlet 1H); τ1.65-2.32 (multiplet, 6H); τ5.39 (quartet, 2H, J = 7.8 c.p.s.); τ5.52 (quartet, 2H, J = 7.8 c.p.s.); τ8.52 (triplet, 3H, J = 7.8 c.p.s.); τ8.57 (triplet, 3H, J = 7.8 c.p.s.). (Found: C, 56.2; H, 5.1; N, 11.4. $C_{17}H_{17}N_3O_6$ requires: C, 56.8; H, 4.7; N, 11.7%).

C. Non-oxidative reactions of aminonaphtho[1,8-de]triazines.

a) Deamination of 1-Aminonaphtho[1,8-de]triazine.

1-Aminonaphtho[1,8-de]triazine (184 mg., 1mmole) and diphenyl nitrosamine (198 mg., 1 mmole) were refluxed in dry benzene for 3 hr. On cooling naphtho[1,8-de]triazine (120 mg.) m.p. 225-30°, separated and was filtered off. The filtrate was evaporated and the residue was chromatographed on silica gel to give diphenylamine (144 mg., 85%), m.p. 50-51°, (Lit.,m.p. 54°) followed by a further fraction of naphtho[1,8-de]triazine (24 mg., total 85%).

b) Deamination of 2-Aminonaphtho[1,8-de]triazine

A small amount of 2-aminonaphtho[1,8-de]triazine was treated similarly. Thin layer chromatography indicated diphenylamine and naphtho[1,8-de]triazine together with other unidentified products.

c) Treatment of 1-Aminonaphtho[1,8-de]triazine with Acid.

1-Aminonaphtho[1,8-de]triazine (100 mg.) was dissolved

in 2N sulphuric acid and warmed to 60° for several minutes. After cooling, the solution was made alkaline and extracted with ether. The ether extract was washed with water, dried and adsorbed on to silica gel. Chromatography on elution with 50% ether-petrol gave 8-azido-1-naphthylamine (88 mg., 88%) m.p. and m.m.p. 78-9°. Further elution gave a small amount of tarry material.

Similar treatment of 1-aminonaphtho[1,8-de]triazine with 2N hydrochloric acid gave 8-azido-1-naphthylamine, (80%).

d) Treatment of 2-Aminonaphtho[1,8-de]triazine with Base.

2-Aminonaphtho[1,8-de]triazine (33 mg.) was warmed with aqueous potassium hydroxide on a steam bath for 5 min. After cooling, the mixture was extracted with ether, the extract being washed with water, dried and finally adsorbed on to silica gel. Chromatography gave 8-azido-1-naphthylamine (22 mg., 66%) m.p. and m.m.p. 78-80°.

e) Reduction of 8-Azido-1-naphthylamine.

8-Azido-1-naphthylamine (1 g.) in 50% hydrochloric acid was stirred for several hours with granulated tin. The mixture was then made alkaline and extracted with ether. The ether extract was washed with water, dried and evaporated to give 1,8-diaminonaphthalene (826 mg. 96%) as a discoloured oil. Distillation gave a colourless solid, m.p. and m.m.p. 60° (Lit., m.p. 66.5°).

Trinitrobenzene addition compound, m.p. 223° (Lit., m.p. 225°)

2. OXIDATIONS OF 1-AMINONAPHTHO[1,8-de]TRIAZINE.

A. Oxidation of 1-aminonaphtho[1,8-de]triazine with lead tetra-acetate in aromatic solvents.

The oxidations were carried out under standard conditions and basically the same procedure was adopted for each experiment.

1-Aminonaphtho[1,8-de]triazine (184 mg., 1 mmole), in the aromatic solvent (20 ml.), was added dropwise to an excess of lead tetra-acetate (666 mg., 1.5 mmole) suspended in the same solvent (5 ml.) and stirred vigorously under nitrogen. Nitrogen was rapidly evolved and stirring was continued for several minutes after the reaction appeared to be complete. Lead salts were separated by filtration and the solvent was removed by distillation under reduced pressure. The products were finally separated by chromatography on basic alumina or silica gel by elution with petrol. More polar solvents gave small amounts of intractable oils and tars.

a) Benzene

From 1-aminonaphtho[1,8-de]triazine (500 mg.) with final chromatography on basic alumina was obtained:

i) 1-Phenylnaphthalene (39 mg., 7%) as a colourless oil having an identical i.r. spectrum to an authentic specimen.

ii) 6b,10a-Dihydrofluoranthene (15 mg., 2.2%), colourless needles from petrol m.p. 76°, decomposing in air. $\lambda_{max.}$ 225 mμ (log ε 4.64). $\nu_{max.}$ 1620, 1593, 1470, 1083, 829,

785, 780, 735 cm.$^{-1}$

τ2.3-2.9 (multiplet, 6H); τ4.28 (multiplet, 4H); τ5.5 (multiplet, 2H). m/e 204, 203, 202 (Intensity 202>203>204), 103, 88. (Found: C, 94.1; H, 6.1. $C_{16}H_{12}$ requires: C, 94.1; H, 5.9%).

iii) Fluoranthene (65 mg., 11.6%), colourless-very pale yellow needles from ethanol m.p. and m.m.p. 108°. (Lit., m.p. 110°)

2,4,7-Trinitrofluorenone addition complex, yellow needles from ethanol m.p. and m.m.p. 208°-209°. (Lit.,[94] m.p. 215.4-216°).

b) p-Xylene

From 1-aminonaphtho[1,8-de]triazine (368 mg., 2 mmole) with final chromatography on basic alumina was obtained:

i) Naphthalene (3 mg., 1.2%) m.p. and m.m.p. 80°.

ii) 1-(2,5-Dimethylphenyl)naphthalene (51 mg., 11%), colourless oil contaminated with fraction iii).

iii) 7,10-Dimethylfluoranthene (82 mg., 18%) needles from ethanol m.p. 202°.

$\lambda_{max.}$ 239 (log ε 4.56); 261 (4.19); 279.5 (4.05); 286 (3.85); 290.5 (3.95); 322 (3.77); 352 (3.88); 370 mμ(3.85).

$\nu_{max.}$ (KCl disc) 3064, 2995, 2941, 2880, 1492, 1464, 1439, 835, 813, 785 cm.$^{-1}$

$\nu_{max.}$ (nujol mull) 810, 790, 760 cm.$^{-1}$ m/e 230, 215, 202, 105, 103. (Found: C, 93.6; H, 6.2. $C_{18}H_{14}$ requires: C, 93.9; H, 6.1%).

c) Mesitylene

From 1-aminonaphtho[1,8-de]triazine (368 mg., 2 mmole)

with final chromatography on basic alumina was obtained:

i) 1-(1,3,5-trimethylphenyl)naphthalene (112 mg., 22.7%), colourless oil, slowly solidifying. Crystallisation from ethanol gave needles m.p. 63°-64°.

$\nu_{max.}$ 855, 800, 780 $cm.^{-1}$

τ2.0-3.1 (multiplet, 8H); τ7.64 (singlet, 3H); τ8.17 (singlet, 6H). m/e 246, 238, 231, 217, 215, 128, 119 (v. intense)

(Found: C, 92.5; H, 7.4. $C_{19}H_{18}$ requires: C, 92.7; H, 7.3%).

ii) Unidentified yellow oil (32 mg.).

Independent preparation of 1-(1,3,5-Trimethylphenyl)-naphthalene.

1-Naphthylamine (2 g.) and amyl nitrite (3 g.) were refluxed in mesitylene (50 ml.) for 3 hr. Mesitylene and other volatile products were then removed by distillation under reduced pressure and the residue was chromatographed on basic alumina. Elution with petrol gave:

i) Naphthalene (21 mg., 1.2%) m.p. and m.m.p. 80°.

ii) 1-(1,3,5-trimethylphenyl)naphthalene (220 mg., 6.4%) m.p. 63-64° (from ethanol) m.m.p. 63-64°.

Elution with 5% ether-petrol gave:

iii) 1,1′-azonaphthalene (520 mg., 26.5%), needles from petrol m.p. and m.m.p. 190°.(Lit., m.p. 190°).

More polar solvents gave a variety of unidentified red oils and solids (800 mg.).

d) Hexafluorobenzene

Hexafluorobenzene was obtained from the Imperial Smelting Corporation and was used as supplied.

From 1-aminonaphtho[1,8-de]triazine (368 mg., 2 mmole) with final chromatography on silica gel was obtained:

i) 7,8,9,10-Tetrafluorofluoranthene (1 mg., 0.2%).

$\lambda_{max.}$ 236.5, 275.5, 282, 286, 308, 323, 352, 370 mμ

ii) 6b,7,8,9,10,10a-Hexafluorofluoranthene (115 mg., 18.4%), needles from ethanol m.p. 129-130°.

$\lambda_{max.}$ 222 (log ε 4.74); 289 m (3.83). $\nu_{max.}$ 1650; 1600; 1495; 1470; 1100; 1082; 945; 877; 830; 784; 770 $cm.^{-1}$ m/e 312, 293, 174, 243.

(Found: C, 61.4; H, 2.0. $C_{16}H_6F_6$ requires: C, 61.5, H, 1.9%).

e) Pyridine

The pyridine was refluxed for several hours over potassium hydroxide, distilled and stored over potassium hydroxide.

The oxidation was carried out in the standard way with final chromatography on silica gel. Elution with ether-methanol gave traces of oil.

$\lambda_{max.}$ 235, 273, 284, 318, 347, 360 mμ

The reaction was repeated and the residue, after removal of pyridine by distillation under reduced pressure, was extracted with dilute hydrochloric acid. The acid extract was basified and re-extracted with ether. Evaporation gave a small amount of residue which formed a picrate, which after two recrystallisations

from acetone gave yellow needles m.p. 273-274° (Lit.,[75] m.p. for 7-azafluoranthene, 272°).

f) Benzene in the presence of Tetrakistriphenylphosphine platinum (0).[95]

1-Aminonaphtho[1,8-de]triazine (184 mg., 1 mmole) and tetrakistriphenylphosphine platinum (0) (1243 mg., 1 mmole) were stirred in benzene and solid lead tetra-acetate (666 mg., 1.5 mmole) was added. After stirring for 0.5 hr. the mixture was filtered and the residue washed with benzene. The bulk of the combined filtrate and washings was reduced to 10 ml. and ether was added. Bisacetylbistriphenylphosphine platinum (0)[96] separated and was filtered off. The filtrate was evaporated on to basic alumina and chromatographed to give 1-phenylnaphthalene (32 mg., 15.7%) and dihydrofluoranthene (64 mg., 31%) m.p. 76°. No fluoranthene was detected.

B. Oxidation of 1-Aminonaphtho[1,8-de]triazine in benzene with other oxidants.

a) Lead Tetraisobutyrate

Oxidation of 1-aminonaphtho[1,8-de]triazine (1 mmole) with lead tetraisobutyrate under the conditions used for lead tetra-acetate gave a hydrocarbon fraction (87 mg., 42.8%). Careful sublimation showed this to be 1-phenylnaphthalene and crystalline fluoranthene. No dihydrofluoranthene was isolated.

b) Nickel peroxide

1-Aminonaphtho[1,8-de]triazine (552 mg., 3 mmole) in benzene was added dropwise to a stirred suspension of nickel peroxide (2.5 g.) under nitrogen. After stirring for several hours the resulting solution was filtered and evaporated on to basic alumina and chromatographed. Elution with petrol gave 1-phenylnaphthalene (20 mg., 3.3%), dihydrofluoranthene (15 mg., 2.5%) and fluoranthene (10 mg., 1.6%).

c) Iodobenzenediacetate.

1-Aminonaphtho[1,8-de]triazine (184 mg., 1 mmole) in dry benzene was added dropwise to a solution of iodobenzenediacetate (322 mg., 1 mmole) in benzene maintained at 70° (to keep it in solution). The mixture was cooled after 1 hr. but stirring was continued overnight. After filtration, the filtrate was evaporated to dryness to remove iodobenzene and the residue was chromatographed on silica gel. Elution with petrol gave a mixture of 1-phenylnaphthalene and fluoranthene (30 mg., 15%).

d) Manganese Dioxide.[97]

1-Aminonaphtho[1,8-de]triazine in benzene was added dropwise to a suspension of manganese dioxide in refluxing benzene. The reaction was complete after 4 hr. refluxing. Chromatography of the benzene solution on silica gel gave a trace of a mixture of 1-phenylnaphthalene and fluoranthene.

e) N-Bromosuccinimide.

1-Aminonaphtho[1,8-de]triazine (184 mg., 1 mmole) in

benzene was added dropwise to a suspension of N-bromosuccinimide (374 mg., 2.1 mmole) in refluxing benzene. After refluxing for 1 hr. the benzene solution was cooled and filtered, leaving a dark residue which was extracted with boiling chloroform to give impure succinimide on evaporation. The filtrate was evaporated and the residue chromatographed on neutral alumina. Elution with petrol gave:

i) 1,4,5-tribromonaphthalene (36 mg., 10%) m.p. 83-84° (after sublimation) (Lit., m.p. 86°).

ii) 1,8-dibromonaphthalene (54 mg., 19%) m.p. and m.m.p. 108-109° (Lit., m.p. 109-110°).

C. Oxidation of 1-aminonaphtho[1,8-de]triazine with lead tetra-acetate in olefinic solvents.

The oxidations were carried out using the following method:

1-Aminonaphtho[1,8-de]triazine (184 mg., 1 mmole) in the olefin (20 ml.) was added dropwise to a rapidly stirred suspension of lead tetra-acetate (532 mg., 1.2 mmole) in the olefin (5 ml.). When nitrogen evolution had ceased the solution was filtered and the residue was washed thoroughly with chloroform. The combined washings and filtrate were evaporated to dryness under reduced pressure and the resulting residue was adsorbed on to basic alumina or silicagel for chromatography.

a) Vinyl Acetate.

Vinyl acetate (Hopkin and Williams) contained hydro-

quinone (5 p.p.m.) as a stabiliser and was not purified before use.

From 1-aminonaphtho[1,8-de]triazine (368 mg., 2 mmole) elution with 10% ether-petrol from silica gel in the final chromatography gave 1-acetoxyacenaphthene (193 mg., 47%), a pale yellow oil having an identical i.r. spectrum to that of an authentic specimen.[77]

1-Acetoxyacenaphthene (40 mg.) was refluxed for 2 hr. in methanol (1 ml.) and water (1 ml.) with sodium hydroxide (20 mg.). After cooling, the resulting yellow solid was recrystallised from benzene to give 1-hydroxyacenaphthene (30 mg., 93%) colourless needles m.p. and m.m.p. 147° (Lit.,[77] m.p. 148°).

b) Cyclohexene.

Cyclohexene (B.D.H.) was distilled before use.

From 1-aminonaphtho[1,8-de]triazine (368 mg; 2 mmole) with final chromatography on basic alumina was obtained on elution with petrol:

i) Naphthalene (39 mg., 15%) m.p. and m.m.p. 80°.

ii) 6b,7,8,9,10,10a-Hexahydrofluoranthene (38 mg., 9.1%), colourless oil.

$\nu_{max.}$ 1605, 820, 778 cm.$^{-1}$ m/e 208, 178, 165.

c) Cyclooctene.

Cyclooctene (Koch Light) was redistilled.

From 1-aminonaphtho[1,8-de]triazine (368 mg., 2 mmole)

with final chromatography on basic alumina was obtained on elution with petrol:

i) Naphthalene (10 mg., 5%), m.p. and m.m.p. 80°.

ii) 1,2-Cyclooctaacenaphthene (87 mg., 18.4%) colourless needles from petrol m.p. 116-117°.

$\nu_{max.}$ 1600; 1260; 1018; 968; 830; 818; 792; 765 cm.$^{-1}$

τ2.4-3.0 (complex multiplet, 6H); τ6.5 (broad complex multiplet, 2H); τ7.8-8.6 (Complex multiplet, 12H). m/e 236; 221; 203; 194; 179; 165; 154; 153; 141. (Found: C, 91.4; H, 8.6. $C_{18}H_{20}$ requires: C, 91.5; H, 8.5%).

d) Tetrachloroethylene

From 1-aminonaphtho[1,8-de]triazine (184 mg., 1 mmole) with final chromatography on basic alumina was obtained on elution with 5% ether-petrol:

i) 1,1,2,2-tetrachloroacenaphthene (21 mg., 7.2%), which sublimed to give a colourless solid m.p. 99-100° (Lit.,[76] m.p. 101.5-102.5°).

$\lambda_{max.}$ 227.5 (log ε 4.71); 285 (4.01); 296 (4.05); 305 mμ(3.94).

$\nu_{max.}$ 1118; 1030; 922; 785; 763; 755; 719 cm.$^{-1}$

e) cis- and trans-Dichloroethylene

cis-1,2-Dichloroethylene (Koch Light) was fractionally distilled on a spinning band column (Buchl Drehband Kolonne System Dr. Abegg; 30 theoretical plates). The fraction used was b.p. 61.5-62° and was shown by gas-liquid chromatography to contain

none of the trans-isomer.

trans-1,2-Dichloroethylene (Koch Light) was similarly treated and the fraction b.p. 47.8-47.9°, shown by gas-liquid chromatography to be free from the cis-isomer, was used.

1-Aminonaphtho[1,8-de]triazine was oxidised in the olefin by the following methods:

(1) The method already described, chromatography being carried out on silica gel and elution with 5% ether-petrol giving the dichloroacenaphthenes

(2) 1-Aminonaphtho[1,8-de]triazine (184 mg., 1 mmole) in the olefin (20 ml.) was added dropwise to a stirred suspension of lead tetra-acetate (532 mg., 1.2 mmole) in the olefin. The excess of lead tetra-acetate was destroyed by the addition of a few drops of glycerol. The solution was filtered and evaporated to dryness. Extraction with ether left a polymeric residue, the ether extract was washed with water, dried ($MgSO_4$), and, after treatment with activated charcoal, was evaporated to give the dichloroacenaphthenes.

(3) Lead tetra-acetate (532 mg., 1.2 mmole) was added portionwise to 1-aminonaphtho[1,8-de]triazine (184 mg., 1 mmole) in the olefin (20 ml.). Excess of lead tetra-acetate was destroyed by the addition of glycerol and the work up was completed as in method (2).

cis-1,2-Dichloroethylene.

Oxidation of 1-aminonaphtho[1,8-de]triazine (368 mg.,

2 mmole) by method (1) gave impure cis-1,2-dichloroacenaphthene (228 mg., 50%), shown by T.L.C. to contain a small amount of trans-1,2-dichloroacenaphthene. Recrystallisation from ethanol gave pure cis-1,2-dichloroacenaphthene, needles m.p. and m.m.p. 114-116° (Lit.,[82] m.p. 116°) τ2.1-2.6 (Complex multiplet, 6H); τ4.18 (singlet, 2H).

Several oxidations using methods (2) and (3) gave slightly impure cis-1,2-dichloroacenaphthene (29-37%). In each case the total dichloroacenaphthene fraction was dissolved in deuteriochloroform and the p.m.r. spectrum indicated that it contained more than 95% cis-1,2-dichloroacenaphthene, a trace of the trans-isomer being observed.

trans-1,2-Dichloroethylene.

Oxidation of 1-aminonaphtho[1,8-de]triazine (368 mg., 2 mmole) by method (1) gave impure trans-1,2-dichloroacenaphthene (180 mg., 40%), shown by T.L.C. to contain a small amount of cis-1,2-dichloroacenaphthene. Recrystallisation from ethanol gave pure trans-1,2-dichloroacenaphthene, needles m.p. and m.m.p. 66-67° (Lit.,[82] m.p. 67-68°).
τ2.0-2.55 (Complex multiplet, 6H); τ4.27 (singlet, 1H);

Several oxidations using methods (2) and (3) gave slightly impure trans-1,2-dichloroacenaphthene (27-40%). The total dichloroacenaphthene fraction was dissolved in deuterio-chloroform and the p.m.r. spectrum indicated that it was more

than 95% trans-1,2-dichloroacenaphthene, a trace of the cis-isomer being observed.

1:1 Mixture of cis- and trans-1,2-Dichloroethylene

Oxidation of 1-aminonaphtho[1,8-de]triazine in a 1:1 mixture of cis- and trans-1,2-dichloroethylene by method (3) gave a mixed dichloroacenaphthene fraction (48%) shown on analysis by p.m.r. to contain cis-1,2-dichloroacenaphthene (55%) and trans-1,2-dichloroacenaphthene (45%).

trans-1,2-Dichloroethylene and Methylene Chloride

Oxidation of 1-aminonaphtho[1,8-de]triazine in pure trans-1,2-dichloroethylene, 1:1 and 1:10 (molar) dichloroethylene-methylene chloride by method (1) gave trans-1,2-dichloroacenaphthene (38%, 28%, 25% respectively). Small amounts of naphthalene and 1-chloronaphthalene were also obtained in the last two experiments. T.L.C. indicated very little cis-1,2-dichloroacenaphthene.

trans-1,2-Dichloroethylene and Chloroform

Oxidation of 1-aminonaphtho[1,8-de]triazine in 1:10 trans-1,2-dichloroethylene-chloroform gave trans-1,2-dichloroacenaphthene (11%) together with a mixture of hexachloroethane, naphthalene and 1-chloronaphthalene.

Oxidation of 1-Aminonaphtho[1,8-de]triazine in trans-1,2-Dichloroethylene with Nickel Peroxide.

1-Aminonaphtho[1,8-de]triazine (184 mg., 1 mmole) in trans-1,2-dichloroethylene was added dropwise to a suspension of

nickel peroxide (1 g.) in the same solvent. When nitrogen evolution had ceased, the mixture was filtered and evaporated to dryness. The residue was extracted with ether, the extract was dried ($MgSO_4$), treated with charcoal and evaporated to give almost pure trans-1,2-dichloroacenaphthene (30 mg., 13.5%) containing a trace of the cis-isomer (T.L.C.).

f) Diethyl Fumarate and Diethyl Maleate.

Diethyl Fumarate

Diethyl fumarate (B.D.H.) was redistilled and no diethyl maleate could be detected by p.m.r.

1-Aminonaphtho[1,8-de]triazine (368 mg., 2 mmole) in diethyl fumarate was oxidised as in method (3) for dichloroethylenes, to give diethyl trans-acenaphthene-1,2-dicarboxylate (210 mg., 35%) as a colourless oil slowly solidifying. Recrystallisation from petrol gave needles, m.p. 70.5-71°.

$\nu_{max.}$ 1737, 1378, 1277, 1258, 1210, 1187, 1040, 871, 828, 793 $cm.^{-1}$

τ2.17-2.76 (Complex multiplet, 6H); τ4.9 (singlet, 2H); τ5.73 (quartet, 4H, J = 7.1 c.p.s.); τ8.70 (triplet, 6H, J = 7.1 c.p.s.).

(Found: C, 72.6; H, 5.9. $C_{16}H_{14}O_4$ requires: C, 72.5; H, 6.0%).

P.m.r. investigation of the initial crude fraction indicated the presence of a small amount of impurity, possibly the cis-isomer (ca. 10%).

τ2.15-2.75 (complex multiplet); τ5.19 (singlet); τ5.80 (quartet, J = 7 c.p.s.); τ8.77 (triplet, J = 7 c.p.s.).

Diethyl Maleate

Diethyl maleate (B.D.H.) was redistilled and p.m.r. indicated the presence of approximately 1% of diethyl fumarate.

The oxidation was carried out exactly as for diethyl fumarate and gave crude diethyl trans-acenaphthene-1,2-dicarboxylate (18.7%), shown by p.m.r. to contain the same impurity in the same ratio as in the case of diethyl fumarate.

D. Oxidation of 1-Aminonaphtho[1,8-de]triazine with Lead Tetra-Acetate in Acetylenic Solvents.

a) Dimethyl Acetylenedicarboxylate.[98]

1-Aminonaphtho[1,8-de]triazine (368 mg., 2 mmole) was oxidised as in the standard method for olefinic solvents. Final chromatography on silica gel on elution with 40% ether-petrol gave dimethyl acenaphthylene-1,2-dicarboxylate (163 mg., 30%), yellow plates from petrol, m.p. 99-100°.

$\lambda_{max.}$ 233 (log ε 4.63); 253 (4.33); 337 (4.45); 363 mμ (4.26).

$\nu_{max.}$ 1720, 1630, 1535, 1350, 1277, 1230, 1150, 1135, 1075, 1032, 820, 760, 720 $cm.^{-1}$

τ1.86-2.55 (multiplet, 6H); τ6.09 (singlet, 6H). m/e 268, 237, 207, 194, 150, 138, 103, 75.

(Found: C, 71.5; H, 4.5. $C_{16}H_{12}O_4$ requires: C, 71.6; H, 4.5%).

b) Diphenylacetylene.

1-Aminonaphtho[1,8-de]triazine (184 mg., 1 mmole) was oxidised by the standard method for olefinic solvents in a mixture of diphenylacetylene (1 g., 5.6 mmole) and methylene

chloride (10 ml.). Final chromatography on basic alumina gave on elution with petrol:

i) Almost quantitative recovery of diphenylacetylene.

Elution with 5% ether-petrol gave:

ii) 1,2-diphenylacenaphthylene (15 mg., 5%), yellow plates from petrol m.p. 158-161° (Lit.,[83] m.p. 159-161°).

E. Oxidation of 1-Aminonaphtho[1,8-de]triazine in Dimethyl Azodicarboxylate.

1-Aminonaphtho[1,8-de]triazine (368 mg., 2 mmole) suspended in dimethyl azodicarboxylate[99] was stirred in an ice bath while lead tetra-acetate (1.33 g., 3 mmole) in methylene chloride (10 ml.) was added dropwise. After filtering, the methylene chloride was removed from the filtrate by evaporation under reduced pressure. The remainder of the filtrate was stirred overnight at room temperature with aqueous sodium acetate solution and the resulting mixture was extracted with ether. The ether extract was dried ($MgSO_4$), and the residue was chromatographed on silica gel. Elution with 20% ether-petrol gave dimethyl 1,2-dihydrobenz[cd]indazole-1,2-dicarboxylate (40 mg., 7.4%), as a slightly discoloured oil slowly solidifying. Sublimation gave a colourless solid, m.p. 122° (decomp.), which decomposed on standing.

$\lambda_{max.}$ 237 (log ε 4.60); 325 (4.06); 335 mμ(4.05).

$\nu_{max.}$ 1756, 1723, 1710, 1586, 1362, 1293, 1243, 1183, 1158, 1043, 978, 793, 740, 723 $cm.^{-1}$

τ2.4-2.75 (Complex multiplet, 6H); τ6.06 (Singlet, 6H). m/e 272, 213, 169, 126, 106, 59.

F. Oxidation of 1-Aminonaphtho[1,8-de]triazine in Ethylidene Ethylamine.

Ethylidene ethylamine was prepared by condensation of ethylamine and acetaldehyde, and was fractionally distilled, b.p. 47°.

Ethylidene ethylamine was rapidly attacked by lead tetra-acetate and therefore nickel peroxide was used as oxidant.

1-Aminonaphtho[1,8-de]triazine in ethylidene ethylamine was added dropwise to a suspension of nickel peroxide in the anil under nitrogen. The mixture was filtered and evaporated to give a dark coloured, evil smelling oil. Chromatography on basic alumina gave a trace of naphthalene, m.p. and m.m.p. 80°,and traces of intractable oils.

G. Oxidation of 1-Aminonaphtho[1,8-de]triazine with Lead Tetra-Acetate in Chlorinated Hydrocarbon Solvents.

Oxidations were carried out as described in the standard method for oxidations in olefinic solvents.

a) Carbon Tetrachloride.

Carbon tetrachloride was dried by stirring over phosphorus pentoxide for 24 hr., followed by distillation, b.p. 76.5-77.5°.

From 1-aminonaphtho[1,8-de]triazine (1 g., 5.4 mmole)

with final chromatography on silica gel was obtained:

On elution with petrol:

i) 1,8-dichloronaphthalene (263 mg., 24.5%), needles from ethanol m.p. and m.m.p. 88°. (Lit.,m.p. 89-89.5°).

Elution with 5% ether-petrol:

ii) pale yellow gum (130 mg.) which was sublimed to give a colourless solid m.p. 137-142°.

$\nu_{max.}$ 1692, 1507, 1300, 1222, 1202, 1107, 827, 769, 762. $cm.^{-1}$

More polar solvents gave small amounts of intractable tars.

b) Chloroform

Chloroform (A.R.) was washed with water, dried over calcium chloride and redistilled, b.p. 61.5°.

Oxidation by the standard procedure gave on elution with petrol from silica gel:

i) hexachloroethane (i.r., smell)

ii) naphthalene contaminated with a small amount of 1-chloronaphthalene (i.r. and T.L.C.), recrystallised from ethanol to give pure naphthalene, m.p. and m.m.p. 80°.

1-Aminonaphtho[1,8-de]triazine (34 mg.) was added portionwise to lead tetra-acetate (150 mg.) in chloroform (1 ml.). The resulting mixture was examined by gas-liquid chromatography on a Perkin Elmer F 11 gas chromatograph using a Carbowax 1500, 25% on Celite column. The column temperature was 220° and the injection block was maintained at 350°. Naphthalene (60%) and 1-chloronaphthalene (8%) were found in the reaction mixture by

reference to standard solutions of the two compounds in chloroform.

c) Methylene Chloride.

From 1-aminonaphtho[1,8-de]triazine (368 mg., 2 mmole), final chromatography on basic alumina gave naphthalene contaminated with a small amount of 1-chloronaphthalene (i.r.) (10 mg., 4%).

Addition of a solution of lead tetra-acetate in methylene chloride to a solution of 1-aminonaphtho[1,8-de]triazine in the same solvent gave the same result.

d) Bromotrichloromethane.

Bromotrichloromethane (Eastman Kodak) was dried over magnesium sulphate and fractionally distilled through a 3 ft. Fenske column packed with helices. The apparatus was protected from light. Fraction used b.p. 103.5°.

From 1-aminonaphtho[1,8-de]triazine (368 mg., 2 mmole) with final chromatography on basic alumina was obtained:

On elution with petrol:

i) Hexachloroethane (ca. 150 mg.) (i.r.).

ii) 1,8-Dibromonaphthalene (272 mg., 47.5%), plates from ethanol m.p. and m.m.p. 109-110°. (Lit., m.p. 109-110°).

Elution with 5% ether-petrol gave:

iii) Yellow solid, $C_{11}H_5BrCl_2N_2O$, (176 mg., 26.5%), plates from ethanol or petrol, m.p. 105.5-106.5°.

$\nu_{max.}$ 1655, 1560, 1317, 1294, 977, 959, 850, 807, 766 cm.$^{-1}$

m/e 334, 332, 330, 299, 297, 295, 289, 287, 253, 251.

(Found: C, 40.0; H, 1.7; Br, 23.9; Cl, 20.8; N, 8.8. $C_{11}H_5BrCl_2N_2O$

requires: C, 39.5; H, 1.5; Br, 24.0; Cl, 21.3; N, 8.4%).

e) Oxidation of 1-Aminonaphtho[1,8-de]triazine with Iodine in Methylene Chloride.

1-Aminonaphtho[1,8-de]triazine (368 mg., 2 mmole) in methylene chloride was added dropwise to a stirred solution of iodine (3.05 g., 12 mmole) in methylene chloride and the mixture was refluxed for 5 hr. After cooling, the methylene chloride solution was washed with sodium thiosulphate solution, water, and then dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel. Elution with 4% ether-petrol gave 1,8-diiodonaphthalene (152 mg., 21%), plates from ethanol, m.p. and m.m.p. 108-109° (Lit., m.p. 109°).

1-Aminonaphtho[1,8-de]triazine (20 mg.) was recovered.

3. ATTEMPTED ROUTES TO 1,8-DEHYDRONAPHTHALENE

A. From 1,8-Dilithionaphthalene[23]

Butyl-lithium solution in ether (15 ml., 0.6M; 9 mmole) was added quickly to 1,8-dibromonaphthalene (1 g., 3.3 mmole) stirred under nitrogen in dry ether at room temperature. Stirring was continued for 45 min. to give a clear pale yellow solution. The dilithionaphthalene solution was transferred under nitrogen to a suspension of cobaltous chloride* (0.5 g., 3.3 mmole) in dry ether, cooled by an external Drikold-acetone bath. The mixture was allowed to warm up to room temperature and stirring was continued for 24 hr. Water was added under nitrogen, followed by benzene. The layers were separated and the residues were Soxhlet extracted with benzene. The combined benzene extracts were dried ($MgSO_4$), evaporated, and chromatographed on basic alumina.

Elution with petrol gave an unidentified oily solid (120 mg.). Elution with 5% ether-petrol gave perylene (84 mg., 19%, based on 1,8-dibromonaphthalene), bright yellow cubes m.p. and m.m.p. 273-274° (Lit., m.p. 273-274°).

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* Anhydrous cobaltous chloride was prepared by heating the hexahydrate under vacuum for several hours at temperatures above 180°. The required quantity was then weighed quickly and used immediately.

B. Naphthalene-1,8-tetrazonium Fluoroborate.

Recrystallised 1,8-diaminonaphthalene (10 g.) in ether was converted into its hydrochloride by passing in hydrogen chloride. The hydrochloride was suspended in dilute hydrochloric acid, cooled to -5°, and solid sodium nitrite was added quickly. Stirring was continued below 0° for 15 min. and the mixture was then quickly filtered through a celite pad into a cooled receiver containing a saturated solution of sodium fluoroborate. The resulting naphthalene-1,8-tetrazonium fluoroborate was filtered off, washed with cold water, acetone and finally ether. Drying in vacuo over phosphorus pentoxide gave pale buff needles (6 g.). $\nu_{max.}$ 2260, 1530, 1498, 1342, 1060 (v. broad), 942, 833, 730 $cm.^{-1}$

Naphthalene-1,8-tetrazonium fluoroborate (1.5 g.) was decomposed with copper powder (3 g.) as follows:

a) Stirring overnight in 1:1 acetone-benzene. The resulting solution was filtered, evaporated to dryness and reextracted with ether. T.L.C. indicated 1,1'-azonaphthalene, a trace of fluoranthene, and possibly a trace of 1-phenylnaphthalene. Recrystallisation of the mixture from petrol gave 1,1'-azonaphthalene (75 mg., 13%) m.p. and m.m.p. 191° (Lit.,m.p. 190).

b) In refluxing benzene for 4 hr. Evaporation of the solution followed by chromatography on basic alumina gave fluoranthene (10 mg.,1%) m.p. and m.m.p. 109° (Lit., m.p. 110°), and a trace of 1,1'-azonaphthalene. No 1-phenylnaphthalene or dihydrofluoranthene were detected.

c) Stirring in cis-dichloroethylene-acetone. After evaporation and reextraction with ether, T.L.C. indicated a trace of 1,1'-azonaphthalene together with traces of other products. No cis- or trans-dichloroacenaphthene was detected.

d) Stirring in trans-dichloroethylene-acetone. T.L.C. indicated a trace of 1,1'-azonaphthalene together with traces of other products. No cis- or trans-dichloroacenaphthene was detected.

C. Decomposition of Naphthalene-1,8-diazonium carboxylate.

Amyl nitrite (2.2 ml.) was added dropwise to a stirred suspension of crude 8-amino-1-naphthoic acid (1.9 g.) in dry tetrahydrofuran (25 ml.) containing a trace of trichloroacetic acid. After stirring for 1 hr. at 0°, crude naphthalene-1,8-diazonium carboxylate was filtered off from the dark red solution. The dark brown solid was washed quickly with ether and divided into two equal portions.

Portion (1) was added to refluxing benzene, nitrogen being evolved. After refluxing for 2 hr. the solution was evaporated and the residue chromatographed on silica gel. Elution with 40% ether-petrol gave 1,8-naphtholactone (ca. 100 mg.), m.p. and m.m.p. 108° (Lit., m.p. 108°). More polar eluents gave traces of intractable tars. No phenylnaphthalene, dihydrofluoranthene or fluoranthene were detected.

Portion (2) was added to dimethyl acetylenedicarboxylate maintained at 130°. After 1 hr. the solvent was removed by

distillation under reduced pressure. T.L.C. of the residue indicated 1,8-naphtholactone as the only product. No dimethyl acenaphthylene-1,2-dicarboxylate was detected.

D. Oxidative Decarboxylation of Naphthalic Anhydride with Lead Tetra-acetate.

Naphthalic anhydride and lead tetra-acetate were refluxed in i) benzene, ii) p-xylene and iii) p-xylene-pyridine 1:1 mixture. T.L.C. indicated no formation of fluoranthenes.

E. Reaction of 1,8-diiodonaphthalene with Zinc.

1,8-Diiodonaphthalene (1 g., 2.6 mmole) was refluxed for 24 hr. in benzene with activated zinc. The mixture was filtered and the filtrate was evaporated on to basic alumina for chromatography. Elution with petrol gave 1-iodonaphthalene (110 mg., 16.5%), colourless oil.

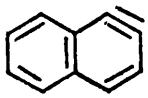
Picrate m.p. 127° (Lit., m.p. 127°) from ethanol.

Elution with 5% ether-petrol gave recovered 1,8-diiodonaphthalene (600 mg., 60%).

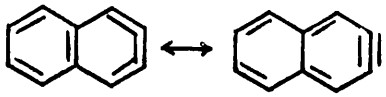
1,2- and 2,3- DEHYDRONAPHTHALENE

Since there is a great difference between 1,8-dehydronaphthalene and benzyne generated similarly, particularly with regard to dimerisation, it was thought that a more direct comparison between 1,2- and 2,3-dehydronaphthalene and 1,8-dehydronaphthalene would be desirable.

Until recently, generation of naphthynes has always involved base catalysed elimination from 1- and 2-halonaphthalenes. Thus although the exclusive formation of 1,2-naphthyne from 1-halonaphthalene has been possible, similar exclusive formation of 2,3-naphthyne has not. Oxidation of the appropriate aminonaphthotriazole would give specifically either 1,2- or 2,3-naphthyne. Thus a comparison of the potentially very different naphthynes (1) and (2) becomes possible. It has been shown that



(1)

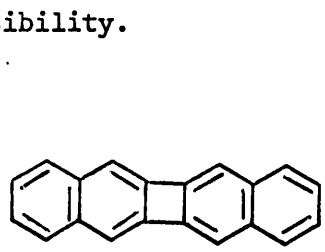


(2)

the increased bond energy resulting from a decreased bond distance gives greater selectivity in an aryne intermediate.[100] This should be reflected by differences between (1) and (2). The specific generation of 2,3-dehydronaphthalene has recently been reported in the pyrolysis of 2,3-naphthalic anhydride[53] and from naphthalene-2-diazonium-3-carboxylate.[101]

The possibility of dimerisation of the naphthynes is

synthetically interesting since the dibenzobiphenylenes (3), (4) and (5) are extremely difficult to prepare. Similarly 'crossed' naphthyne coupling for the formation of the hitherto unknown dibenzo[ah]biphenylene (6) or 'crossed' benzyne naphthyne coupling to give the two monobenzobiphenylenes (7) and (8) is also a possibility.



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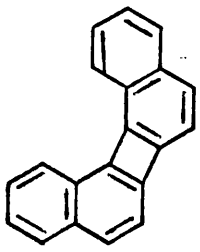

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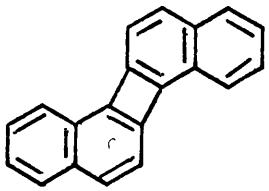

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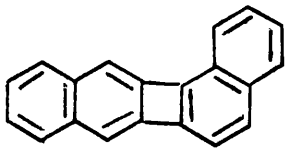

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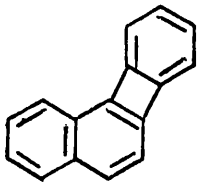
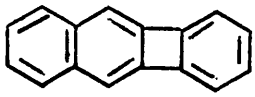


(7)



(8)

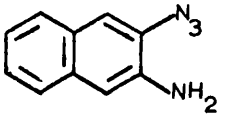
2,3-Naphthyne has already been postulated as an intermediate in the formation of traces of dibenzo[bh]biphenylene (3) by heating 2-bromo-3-iodonaphthalene with copper in dimethyl formamide[102] although a stepwise Ullman reaction is perhaps more likely.

The generation of 1,2- and 2,3-naphthyne, by oxidation of aminonaphthotriazoles, as a synthetic route to these biphenylenes has been independently investigated by Barton,[103] and in view of this our work on the problem was abandoned prematurely. Where appropriate, our results are compared with Barton's.

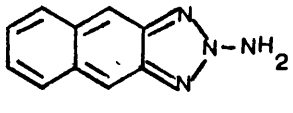
1. PREPARATION OF THE AMINOTRIAZOLES

Naphtho[2,3-d]triazole and naphtho[1,2-d]triazole were prepared by diazotisation of 2,3-diaminonaphthalene and 1,2-diaminonaphthalene respectively.[104,105] Amination was carried out with hydroxylamine-O-sulphonic acid in aqueous alkali at 70° and as expected the products paralleled those of methylation with dimethyl sulphate.[106,107]

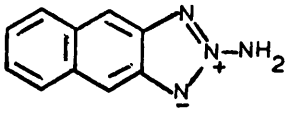
Naphtho[2,3-d]triazole gave largely the 1-aminotriazole but a small amount of 3-azido-2-naphthylamine (9) was also formed, presumably by rearrangement of the 2-aminotriazole (10) under the reaction conditions as in the case of 2-aminonaphtho[1,8-de]-triazine. This rearrangement presumably results from the high reactivity of the 2-amino derivative (10), for which only o-quinonoid (10 a) or charged (10 b) structures can be written, as with 2-aminonaphtho[1,8-de]triazine. Significantly 2-amino-benzotriazole does not undergo this base-catalysed rearrangement to o-azidoaniline.



(9)



(10a)

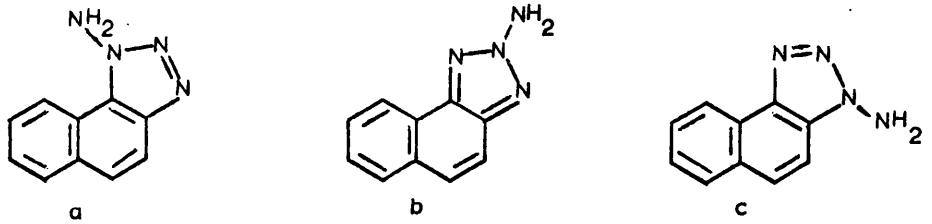


(10b)

The structures of the two amination isomers were supported by analytical and spectral data. It is interesting to

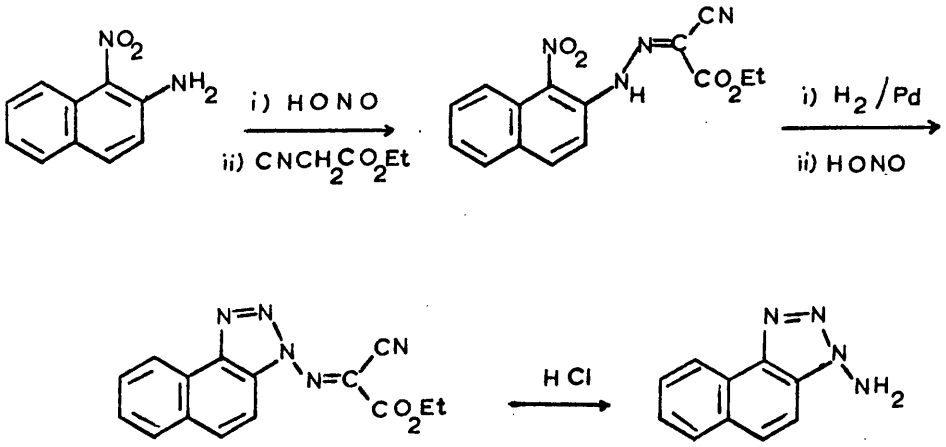
note that whereas naphtho[2,3-d]triazole shows a strong blue fluorescence in daylight or under ultra violet light, this fluorescence is completely absent in the 1-amino derivative. This could possibly be due to a small proportion of the triazole existing in the 2-H form; comparison with the 2-amino derivative was not possible because of the above rearrangement.

Similar amination of naphtho[1,2-d]triazole gave three products (T.L.C.) as expected, but only 2-aminonaphtho[1,2-d]-triazole (11b) (3%) and 1-aminonaphtho[1,2-d]triazole (11c) (18%) could be isolated, the third product, presumably 3-aminonaphtho-[1,2-d]triazole (11a), being an impurity in the 1-aminonaphtho-[1,2-d]triazole before recrystallisation. Barton,[103] by a similar amination at room temperature followed by warming to 80°, obtained approximately equal amounts of the 1- and 2-isomers together with a trace of a third product. His overall reaction yield (12%) was however lower and a considerable amount of unchanged naphtho[1,2-d]triazole was recovered.



(11)

Barton confirmed the structure of 1-aminonaphtho[1,2-d]-triazole by an alternative unambiguous synthesis from 1-nitro-2-naphthylamine, using the method of Trave and Bianchetti.[66]



Analytical and spectral data for 1- and 2-amino-naphtho-[1,2-d]triazole were as expected and their structures were confirmed by their oxidation (discussed later) which paralleled those of 1- and 2-aminobenzotriazole. With 2-aminonaphtho[1,2-d]triazole, where electronic strain involves only one of the rings, as in 2-aminobenzotriazole, there was no tendency to rearrange to an amino azide.

2. OXIDATION OF THE AMINONAPHTHOTRIAZOLES.

Oxidation of 1-aminonaphtho[1,2-d]triazole and 1-aminonaphtho[2,3-d]triazole with lead tetra-acetate gave rapid evolution of nitrogen and formed the respective naphthyne which could be trapped in good yield.

Oxidation of 1-aminonaphtho[1,2-d]triazole in methylene chloride solution in the presence of an excess of tetracyclone gave 1,2,3,4-tetraphenylphenanthrene (86%). Similar oxidation of 1-aminonaphtho[2,3-d]triazole as a suspension in methylene chloride containing an excess of tetracyclone gave 1,2,3,4-tetraphenylanthracene (55%). The somewhat lower yield of adduct in this case was almost certainly due to inefficient stirring of the suspension and indeed oxidation in furan gave the expected 1,4-epoxy-1,4-dihydroanthracene in improved yield (78%). Satisfactory analytical, spectral and mass spectral data were obtained for the three naphthyne adducts. The cycloaddition of 2,3-naphthyne generated from naphthalene-2-diazonium-3-carboxylate to 3,4-diphenyl-2,5-dodecamethylene cyclopentadienone has been used in the preparation of fused ring derivatives of [12]paracyclophane.[101]

Oxidation in the absence of traps

Initial oxidations of 1-aminonaphtho[1,2-d]triazole with lead tetra-acetate in benzene or methylene chloride gave no trace of dibenzo[ag]biphenylene[108] (5) or dibenzo[ai]biphenylene[109] (4), even when oxidations were carried out at -70°. A red colour, which

faded rapidly, was observed on the addition of each drop of aminobenzotriazole solution to the lead tetra-acetate. This was probably due to the formation of the dibenzobiphenylenes which quickly decomposed. The only products isolated were oily solids shown by infra red to contain acetyl or acetoxy groups.

Similar treatment of 1-aminonaphtho[2,3-d]triazole gave traces of dibenzo[bh]biphenylene (3) confirmed by its melting point and by comparison of its u.v. spectrum with that recorded in the literature.[110] In methylene chloride, especially at low temperature, the major product was 2-acetoxynaphthalene (35%) confirmed by comparison with an authentic specimen.

Using a different batch of lead tetra-acetate to oxidise a 1:1 mixture of 1-aminobenzotriazole and 1-aminonaphtho-[1,2-d]triazole, biphenylene (33%) and benzo[a]biphenylene (7) (26%) were obtained, the products being isolated by chromatography on basic alumina. Benzo[a]biphenylene was identical to the compound described in the literature.[109] Similar oxidation of a 1:1 mixture of 1-aminobenzotriazole and 1-aminonaphtho[2,3-d]-triazole with the new batch of lead tetra-acetate gave biphenylene (40%), benzo[b]biphenylene (8) (38%) and a trace of dibenzo[bh]-biphenylene. Using an excess of 1-aminobenzotriazole (4:1), the yield of benzo[b]biphenylene rose to 63%. This compound agreed closely with that described in the literature.[111]

In view of this discrepancy between oxidations with different samples of lead tetra-acetate, control oxidations of

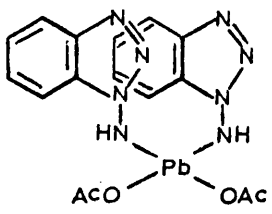
1-aminobenzotriazole were carried out. Using samples of the initial lead tetra-acetate, biphenylene was obtained in yields up to 37% only (Campbell[62] reports 83%), but samples of the lead tetra-acetate used for the crossed oxidations gave biphenylene consistently in over 70% yield.

Barton[103] has independently carried out a similar series of oxidations. From 1-aminonaphtho[1,2-d]triazole he obtained dibenzo[ag]biphenylene (5) (30%) and dibenzo[ai]biphenylene (4) (13%). 1-Aminonaphtho[2,3-d]triazole gave dibenzo[bh]-biphenylene (75%). Crossed oxidation of 1-aminobenzotriazole and 1-aminonaphtho[1,2-de]triazole (2:1) gave benzo[a]biphenylene (36%) and similar crossed oxidation of 1-aminobenzotriazole and 1-aminonaphtho[2,3-d]triazole gave benzo[b]biphenylene (65%). In addition the new dibenzo[ah]biphenylene (6) was obtained by co-oxidation of 1-aminonaphtho[1,2-d]triazole and 1-aminonaphtho-[2,3-d]triazole. In all his oxidations, Barton used only a very small excess of lead tetra-acetate which was destroyed by the addition of glycerol. The more unstable biphenylenes (4), (5), (6) and (7) were isolated as their 2,4,7-trinitrofluorenone complexes, and the stable ones (3) and (8) by fractional crystallisations.

Our initial failure to isolate the biphenylenes must be attributed to some peculiarity of the lead tetra-acetate, and indeed when 'good' lead tetra-acetate was used in the crossed oxidations, our yields of the benzobiphenylenes agreed closely

with Barton's. This was confirmed by a further oxidation of 1-aminonaphtho[2,3-d]triazole, closely following the method of Barton, which gave dibenzo[bh]biphenylene (58%). The instability of the dibenzo[ag] and [ai] biphenylenes probably made their isolation by our method less likely since this involved a greater excess of lead tetra-acetate which was not destroyed, and chromatographic work up rather than isolation of the 2,4,7-trinitrofluorenone complexes.

The mechanism of dimerisation of arynes obtained by lead tetra-acetate oxidation of aminotriazoles is obscure. In the case of 1-aminobenzotriazole, the benzyne generated dimerises in yields up to 86%, considerably greater than with benzyne from any other source. Oxidants other than lead tetra-acetate (with the exception of nickel peroxide which gives 2% biphenylene) give no biphenylene. From our results certain samples of lead tetra-acetate give little or no dimerisation although the aryne is formed effectively, as shown by trapping with tetracyclone. Campbell[62] has suggested that the high degree of dimerisation may be caused by coordination of two molecules of 1-aminobenzotriazole to the lead salt as in (12), followed by fragmentation in such a way as to generate two benzyne molecules in close proximity to each other, but this seems unlikely.



(12)

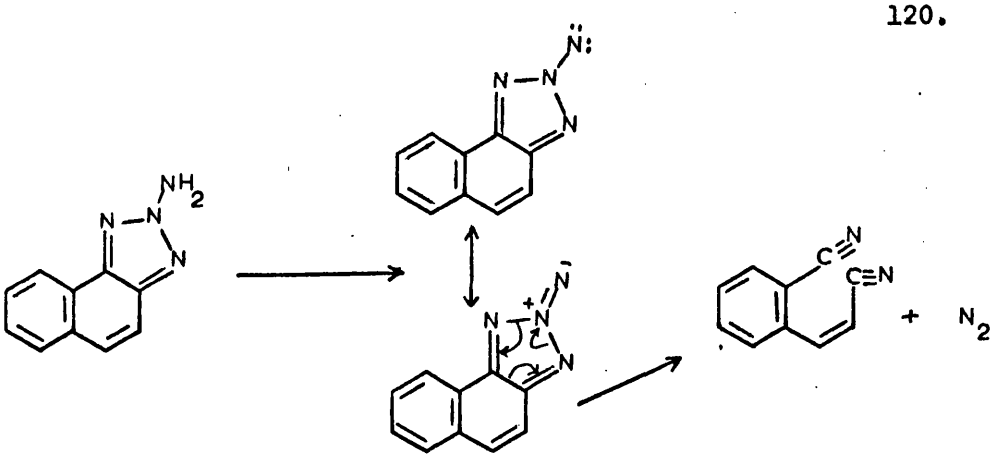
The difference between lead tetra-acetate and other oxidants may be due to the formation of a lead salt-benzyne complex since Friedman[112] has recently shown that the reactions of benzyne generated from benzene diazonium-2-carboxylate depend greatly on the presence of silver salt impurities and he has explained this in terms of an unstable silver salt-benzyne complex. The variation in products with different samples of lead tetra-acetate could depend on varying degrees of coordination of the lead tetra-acetate to benzyne due to the presence of varying amounts of acetic acid or water, also capable of coordination, or to the presence or absence of particular lead salt impurities which form such complexes. In an initial attempt to determine whether dimerisation of benzyne is affected by the presence of lead salts, benzenediazonium-2-carboxylate was decomposed in refluxing methylene chloride in the presence and absence of lead diacetate and lead tetra-acetate. Biphenylene was formed in very low yield in their absence but in their presence no biphenylene could be detected. In this case, therefore, the lead salts are certainly not assisting the dimerisation of benzyne if indeed it is initially formed.

From our work it would appear that 1,2- and 2,3-naphthynes, from the oxidation of the aminotriazoles, have very different properties from similarly generated 1,8-dehydronaphthalene and, as expected, these 'benzobenzynes' closely resemble parent benzyne. Also from the limited number of reactions carried out,

1,2- and 2,3-naphthynes seem to be very similar and the relative yields of dibenzobiphenylenes, crossed dibenzobiphenylene and benzobiphenylene indicate that the two naphthynes and benzyne must have similar reactivities and lifetimes. The fact that no evidence was obtained for any very significant difference between the two benzobenzynes (1) and (2) would appear to support the idea that in such arynes the aromaticity of the parent system is very little disturbed. Our route to 1,2- and 2,3-naphthyne provides a convenient basis for further, more carefully designed, competition experiments which could shed further light on this problem.

Oxidation of 2-Aminonaphtho[1,2-d]triazole

Lead tetra-acetate oxidation of 2-aminonaphtho[1,2-d]-triazole in methylene chloride solution gave o-cyanocinnamonitrile (58%) with rapid evolution of nitrogen, thus paralleling oxidation of 2-aminobenzotriazole which gave cis,cis-mucononitrile.[13] The o-cyanocinnamonitrile was identical to that obtained in lower yield (40%) by lead tetra-acetate oxidation of 1,2-diaminonaphthalene in ether,[113] and was assumed to have the cis configuration by analogy with the cis,cis-mucononitrile. The observed coupling constant for the olefinic protons of 12.5 c.p.s. supports this assignment.[114] The formation of o-cyanocinnamonitrile from 2-aminonaphtho[1,2-d]triazole can be explained by the following scheme:



Oxidation of o-phenylenediamine with lead tetra-acetate[113] or with nickel peroxide[115] and pyrolysis of o-diazidobenzene[116] have also given cis,cis-muconononitrile, possibly all by a substantially similar mechanism.

SECTION II EXPERIMENTAL

1. PREPARATION OF AMINOTRIAZOLES

A. Amination of naphtho[2,3-d]triazole

Naphtho[2,3-d]triazole (3 g.) in potassium hydroxide solution (8 g. in 100 ml. water) was stirred at 70° while solid hydroxylamine-O-sulphonic acid (4 g.) was added in small portions over 1.5 hr. The resulting cooled mixture was extracted with ether (10 x 100 ml.) and after washing with aqueous potassium hydroxide and then water, the combined ether extracts were dried ($MgSO_4$) and evaporated, and chromatographed on basic alumina. Elution with ether gave 3-azido-2-naphthylamine (70 mg., 2%), pale buff needles from petrol m.p. 103-104°.

$\lambda_{max.}$ 257 (log ε 4.46); 355 mμ(3.57).

$\nu_{max.}$ 3390, 3275, 3160, 2093, 1625, 1506, 1284, 851, 730 $cm.^{-1}$

m/e 184, 158, 156, 155, 130, 129, 128, 102. (Found: C, 65.3; H, 4.5; N, 30.5. $C_{10}H_8N_4$ requires: C, 65.2; H, 4.3; N, 30.4%).

Elution with 5% methanol-ether gave 1-aminonaphtho[2,3-d]-triazole (900 mg., 27%) which crystallised from ethanol as lustrous plates m.p. 207-208°

$\lambda_{max.}$ 238 (log ε 4.44); 310 (3.51); 324 (3.69); 356 mμ(3.62).

$\nu_{max.}$ 3319, 1250, 1094, 944, 854, 725 $cm.^{-1}$

(Found: C, 65.1; H, 4.4; N, 30.2. $C_{10}H_8N_4$ requires: C, 65.2; H, 4.3; N, 30.4%).

B. Amination of Naphtho[1,2-d]triazole

Naphtho[1,2-d]triazole (12.8 g.) was aminated by the method used for the [2,3-d]isomer. Chromatography was carried out on silica gel. Elution with 50% ether-petrol gave 2-aminonaphtho[1,2-d]triazole (375 mg., 3%), colourless needles from ethanol m.p. 165-166°.

$\lambda_{max.}$ 227 (log ε 4.33); 255(4.41); 3.15 (3.71); 329 mμ(3.80)

$\nu_{max.}$ 3257, 3120, 1172, 804, 742, 697 $cm.^{-1}$

(Found: C, 65.0; H, 4.5; N, 30.3. $C_{10}H_8N_4$ requires: C, 65.2; H, 4.3; N, 30.4%).

Elution with ether gave 1-aminonaphtho[1,2-d]triazole (2.5 g. 18%), which crystallised from ethanol as colourless needles m.p. 151-152°.

$\lambda_{max.}$ 226 (log.ε 4.34); 245 (4.29); 275 (3.87); 286 (3.88); 310 (3.41); 324 mμ (3.47).

$\nu_{max.}$ 3297, 3180, 1644, 1628, 1254, 1107, 997, 806, 747, 714, 705 $cm.^{-1}$ [Found: C, 65.4; H, 4.5; N, 30.6. $C_{10}H_8N_4$ requires: C, 65.2; H, 4.3; N, 30.4%].

2. OXIDATION OF AMINONAPHTHOTRIAZOLES

A. Oxidation of 1-Aminonaphtho[2,3-d]triazole

a) Oxidation in the absence of a trap.

Oxidations were carried out using the following two methods.

i)* 1-Aminonaphtho[2,3-d]triazole (100 mg., 0.54 mmole) in dry ethyl acetate (10 ml.) was added dropwise to a rapidly stirred suspension of lead tetra-acetate (270 mg., 0.61 mmole) in dry benzene (50 ml.). When nitrogen evolution had ceased, a drop of glycerol was added and stirring was continued for 10 min. The reaction mixture was filtered, concentrated in vacuo and then petrol was added. Dibenzo[b,h]biphenylene (40 mg., 58%) crystallised and was sublimed under reduced pressure to give yellowish grey plates m.p. (sealed tube) 375-377°. (Lit.,[110] m.p. 376±2°).

ii) 1-Aminonaphtho[2,3-d]triazole (184 mg., 1 mmole) suspended in methylene chloride (50 ml.) was added dropwise to a stirred solution of lead tetra-acetate (666 mg., 1.5 mmole) in the same solvent. When the reaction was complete, the solution was filtered, evaporated, and the residue was chromatographed on basic alumina. Eluents up to the polarity of ether gave only a trace of dibenzo[b,h]biphenylene.

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* See Section II, 2D, p.127

Similar results were obtained when methylene chloride was replaced by benzene. The reaction was also carried out at -70°, followed by chromatography on silica gel. Elution with 10% ether-petrol gave a trace of dibenzo[b,h]biphenylene followed by 2-acetoxy naphthalene (35 mg., 35%) m.p. and m.m.p. 72° (Lit., m.p. 72°).

b) Oxidation in the presence of 1-aminobenzotriazole*

1-Aminonaphtho[2,3-d]triazole (184 mg., 1 mmole) and 1-aminobenzotriazole (134 mg., 1 mmole) in warm benzene were oxidised as in a) (ii). Elution with petrol from basic alumina gave:

i) biphenylene (30 mg., 40%), needles from ethanol m.p. and m.m.p. 109-110° (Lit., m.p. 110°),

followed by

ii) benzo[b]biphenylene (75 mg., 38%) which was sublimed to give a colourless solid m.p. 240-241° (Lit.,[111] m.p. 242-243°).

More polar solvents gave a trace of dibenzo[b,h]-biphenylene. Similar oxidation of a mixture of 1-aminonaphtho-[2,3-d]triazole (100 mg., 0.5 mmole) and 1-aminobenzotriazole (268 mg., 2 mmole) gave biphenylene (84 mg., 57%) and benzo[b]biphenylene (69 mg., 63%).

c) Oxidation in the presence of tetracyclone.

1-Aminonaphtho[2,3-d]triazole (184 mg., 1mmole) was oxidised as in a) (ii) by dropwise addition to a solution of

tetra-acetate (666 mg., 1.5 mmole) in methylene chloride containing tetracyclone (1.9 g., 5 mmole). Elution from basic alumina with 20% ether-petrol gave 1,2,3,4-tetraphenylanthracene (256 mg., 55%) which crystallised from ethanol-benzene as colourless needles m.p. 293-294°.

$\lambda_{max.}$ 269 (log ε 4.88); 360(3.73); 379(3.86); 400 mμ(3.78).

$\nu_{max.}$ 1071, 1027, 887, 741, 712, 702, 697 $cm.^{-1}$

m/e 482, 404, 78. (Found: C, 94.5; H, 5.5 $C_{38}H_{26}$ requires: C, 94.6; H, 5.4%).

More polar eluents gave recovered tetracyclone.

d) Oxidation in furan.

Furan (B.D.H.) was dried over sodium wire and distilled before use.

1-Aminonaphtho[2,3-d]triazole (184 mg., 1 mmole) suspended in furan was added dropwise to a stirred suspension of lead tetra-acetate (666 mg., 1.5 mmole) in furan under nitrogen. The reaction mixture was filtered and, after washing with sodium bicarbonate solution and water, the filtrate was dried ($MgSO_4$), evaporated on to silica gel and quickly chromatographed on a short dry column. Elution with ether gave 1,4-epoxy-1,4-dihydroanthracene (152 mg., 78%) which crystallised from petrol as colourless needles m.p. 164-165°.

$\lambda_{max.}$ 236(log ε 4.48); 260 (3.89); 268(3.78); 276 mμ(3.53).

$\nu_{max.}$ 1277, 972, 885, 861, 839, 746 $cm.^{-1}$

m/e 194, 178, 168, 166, 165, 139, 126, 115.

(Found: C, 86.8; H, 5.3. $C_{14}H_{10}O$ requires: C, 86.6; H, 5.2%).

B. Oxidation of 1-Aminonaphtho[1,2-d]triazole

a) Oxidation in the absence of a trap.

Oxidation of 1-aminonaphtho[1,2-d]triazole by the method A a) (ii) as used for 1-aminonaphtho[2,3-d]triazole gave only small amounts of oily solids which showed carbonyl absorptions in their i.r. spectra. Dibenzo[ag]biphenylene ahd dibenzo[ai]-biphenylene were not detected.

b) Oxidation in the presence of 1-Aminobenzotriazole*

Oxidation of 1-aminonaphtho[1,2-d]triazole (184 mg., 1 mmole) and 1-aminobenzotriazole (134 mg., 1 mmole) was carried out exactly as for the mixture 1-aminonaphtho[2,3-d]triazole and 1-aminobenzotriazole.

Similar chromatography gave:

i) biphenylene (33 mg., 43%), needles from ethanol m.p. and m.m.p. 109-110°.

followed by:

ii) benzo[a]biphenylene (155 mg., 26%) m.p. 66-67° (Lit.,[108] m.p. 72°), 2,4,7-trinitrofluorenone complex, dark needles from benzene, m.p. 201-203° (Lit.,[108] m.p. 201.5-202°).

c) Oxidation in the presence of Tetracyclone

Oxidation of 1-aminonaphtho[1,2-d]triazole (150 mg., 0.8 mmole) by the method used for 1-aminonaphtho[2,3-d]triazole gave 1,2,3,4-tetraphenylphenanthrene (344 mg., 86%) which crystallised from ethanol-benzene m.p. 214° (rapid heating)

243-245° (slow heating).

$\lambda_{max.}$ 269(log ε 4.68); 307 mμ(4.16).

$\nu_{max.}$ 1580, 1075, 1028, 833, 755, 733, 711, 696 $cm.^{-1}$

m/e 482, 405, 363, 327, 326.

(Found: C, 94.5; H, 5.6. $C_{38}H_{26}$ requires: C, 94.6; H, 5.4%).

C. Oxidation of 2-Aminonaphtho[1,2-d]triazole.

2-Aminonaphtho[1,2-d]triazole (142 mg., 0.77 mmole) in methylene chloride was added dropwise to a stirred solution of lead tetra-acetate (450 mg., 1 mmole) in the same solvent. After filtering, the resulting solution was evaporated on to silica gel for chromatography. Elution with 30% ether-petrol gave o-cyano-cis-cinnamonitrile (84 mg., 58%) which was sublimed at 120°/2 mm. to give a colourless solid, m.p. and m.m.p. 69-70°. (Lit.,[115] m.p. 70-70.5°).

$\nu_{max.}$ 2213, 806, 786, 769, 720 $cm.^{-1}$

τ1.5-2.7 (Complex multiplet, 4H); τ2.53 (Doublet, 1H, J = 12.5 c.p.s.)

τ4.28 (Doublet, 1H, J = 12.5 c.p.s.).

D. Control Oxidation of 1-Aminobenzotriazole.

Oxidation of 1-aminobenzotriazole by method 2a) (ii), using the same batch of lead tetra-acetate as that used for most of the oxidations in this section, gave biphenylene in yields of up to 37% only. A different batch of lead tetra-acetate gave biphenylene (73%); reactions in which this lead tetra-acetate was used are marked with an asterisk(*).

E. Decomposition of Benzenediazonium-2-Carboxylate.

Benzenediazonium-2-carboxylate was prepared by diazotisation of anthranilic acid with amyl nitrite in tetrahydrofuran. The product was filtered and washed with methylene chloride. Aliquots (2 g.) of the methylene chloride-moist solid were quickly weighed out and decomposed in refluxing methylene chloride for 1-5 hr. under the following conditions:

a) Pure refluxing methylene chloride.

b) Refluxing methylene chloride containing lead tetraacetate.

c) A suspension of lead diacetate in refluxing methylene chloride.

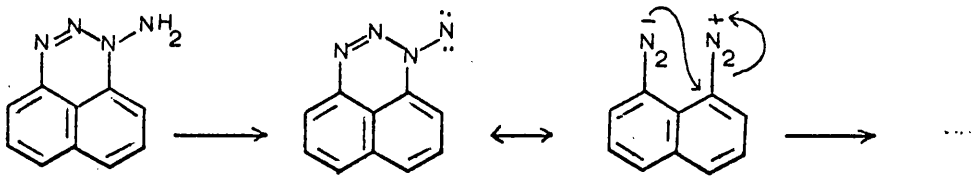
The resulting solutions were filtered and evaporated on to basic alumina for chromatography.

a) gave biphenylene (31 mg., approx. 3%).

b) and c) gave no biphenylene.

BENZ[cd]INDAZOLE

Benz[cd]indazole (1) was initially of interest to us as a possible product in the oxidation of 1-aminonaphtho[1,8-de]-triazine, by loss of only one molecule of nitrogen from the nitrene (2), and also as a potential precursor to 1,8-dehydro-naphthalene by photolysis or pyrolysis.



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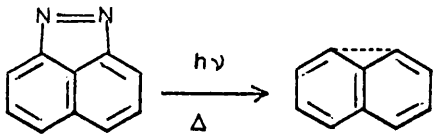
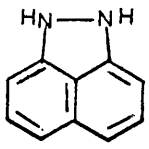


(1)

There are only obscure references in the literature to benz[cd]indazole and its dihydro derivative (3), although the tetrahydro system (4) is well authenticated. Peri-substituted naphthalene compounds have recently been reviewed by Balasubramaniyan[117] and it would appear that the strain in such molecules



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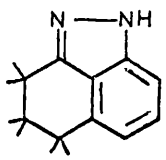

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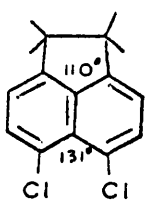


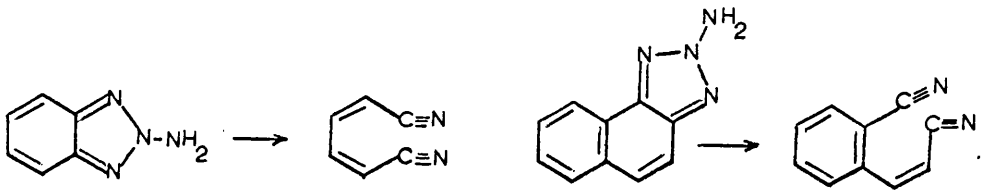
(5)

as (1) and (3) might not be prohibitive. In certain acenaphthene derivatives the distortion of the naphthalene nucleus can be considerable; e.g. 5,6-dichloroacenaphthene (5).

Ekstrand[118] first suggested a benz[cd]indazole type structure as a possibility for a product of partial reduction of 4,5-dinitro-1-naphthoic acid. More recently an attempt to prepare (1) by reduction of 1,8-dinitronaphthalene with carbon monoxide and iron pentacarbonyl (reagents which normally give good yields of azo compounds) failed.[119]

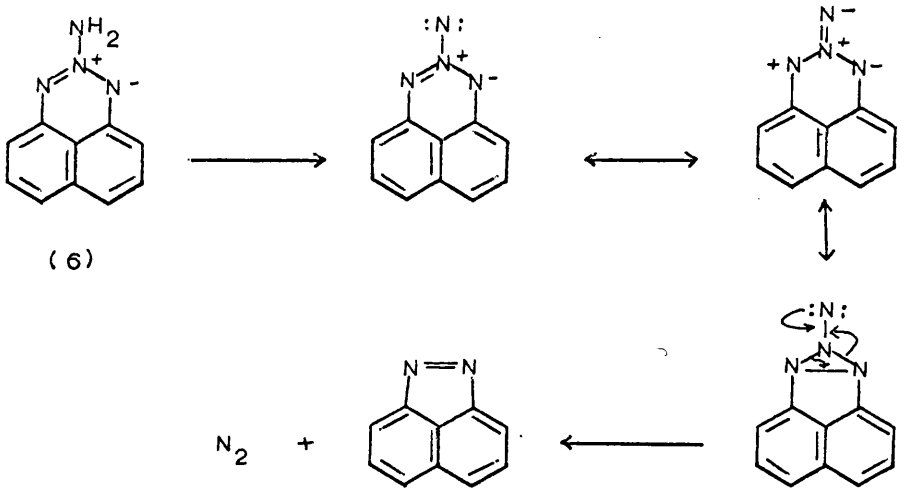
Vorozhtsov and Kozlov[120] reported the formation of dihydrobenzindazole (3) by hydrogen sulphide-ammonia reduction of 1,8-dinitronaphthalene in aniline, but Hoffmann[48] has been unable to repeat this work and also reports that other routes from 1,8-dinitronaphthalene failed.

Oxidation of 2-aminotriazoles, e.g. 2-aminobenzotriazole[62] and 2-aminonaphtho[1,2-d]triazole (section II p. 119) leads to loss of only one molecule of nitrogen leaving the other two nitrogen atoms in the form of a ring opened dicyano compound.



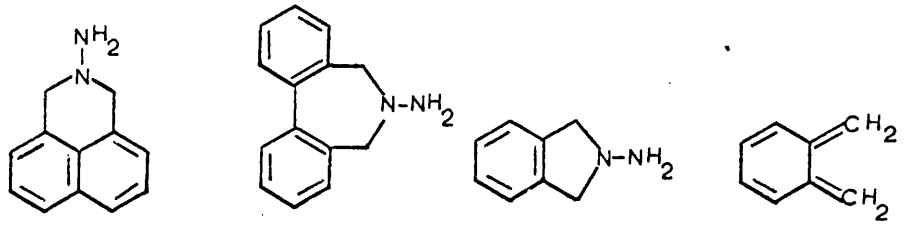
Loss of one molecule of nitrogen after oxidation of 2-aminonaphtho[1,8-de]triazine (6) cannot lead to a dicyano

compound, and it was thought that benzindazole would be the product of such an oxidation.



(6)

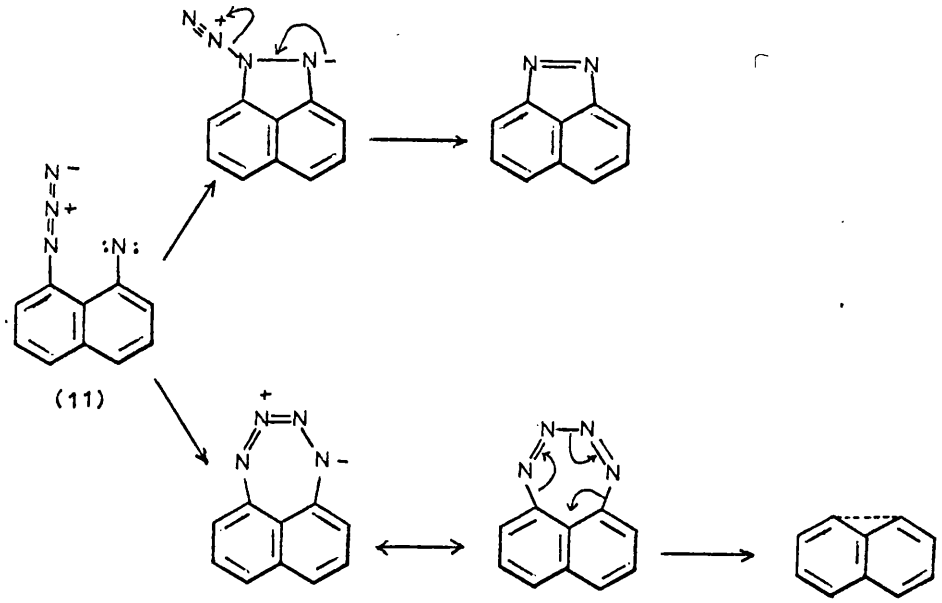
Oxidation of 2-aminonaphthotriazine with lead tetra-acetate did give evolution of nitrogen but left a complex mixture of products from which nothing could be isolated due to the necessary small scale of the reaction. Carpino[121] found a similar situation in the oxidation of 2-amino-2,3-dihydro-1H-benz[de]isoquinoline (7), which gave no acenaphthene in contrast to (8) and (9) which gave 9,10-dihydrophenanthrene and benzocyclobutene respectively. This difference was rationalised by



(7) (8) (9) (10)

postulating o-quinodimethanes, e.g. (10), as intermediates for (8) and (9) which is impossible for (7). On the other hand since acyclic analogues such as 1,1-dibenzylhydrazine gave dibenzyl it may have been the result of a simple steric effect.

Since oxidation of the appropriate diamino compound[113,115] has given the same dicyano compound as oxidation of the 2-amino-triazole, a similar lead tetra-acetate oxidation of 1,8-diamino-naphthalene was carried out, but this gave only complex intractable mixtures. Oxidation of 8-azido-1-naphthylamine should lead to the nitrene (11) which could lose one or two molecules of nitrogen to give benzindazole or dehydronaphthalene. However, this



(11)

oxidation again gave intractable mixtures, no trace of benzindazole or dehydronaphthalene products being observed.

The ready availability of 8-azido-1-naphthylamine

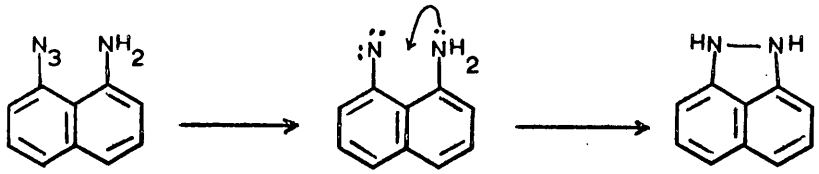
suggested the possible formation of dihydrobenzindazole (3) from a nitrene intermediate. Pyrolysis and photolysis of aryl azides is generally accepted to give nitrenes which normally react in the following ways:[122,123]

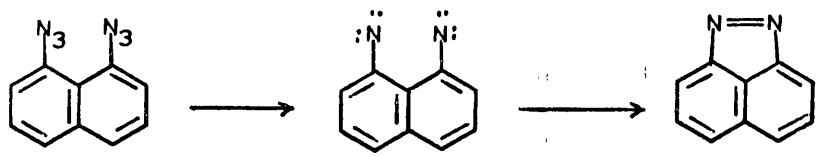
i) by intermolecular hydrogen abstraction (e.g. from the solvent) to give a primary amine.

ii) or preferably, where possible, by intramolecular hydrogen abstraction and ring closure to give a five membered ring.

iii) by dimerisation.

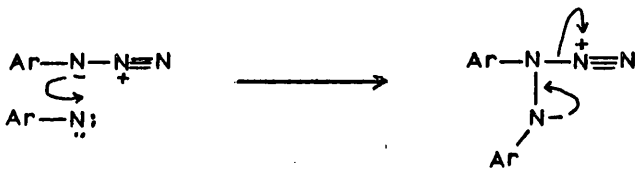
Thus 8-azido-1-naphthylamine might be expected to give (3) by intramolecular hydrogen abstraction and ring closure, while 1,8-diazidonaphthalene should give (1) by intramolecular 'dimerisation' of the peri-nitrenes. The formation of azo





compounds from pyrolyses and photolyses of aryl azides are usually said to arise from dimerisation of the nitrenes; however a more likely mechanism is attack of the nitrene on an unchanged

azide molecule to give the azo compound after loss of nitrogen. This type of mechanism should favour the formation of benzindazole

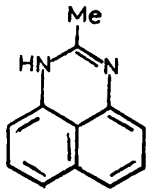


from 1,8-diazidonaphthalene.

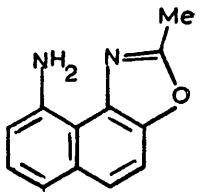
Pyrolysis of 8-azido-1-naphthylamine gave, apart from polymeric material, only 1,8-diaminonaphthalene by hydrogen abstraction from the solvent, even in 1,2,4-trichlorobenzene. Photolysis again gave 1,8-diaminonaphthalene together with the intermolecular nitrene dimer 8,8'-diamino-1,1'-azonaphthalene. A large amount of polymer was again formed. 8,8'-Diamino-1,1'-azonaphthalene was identical to the product obtained in low yield by manganese dioxide oxidation of 1,8-diaminonaphthalene, and the structure was confirmed by i.r. and mass spectrometry. A satisfactory analysis was not obtained.

Pyrolysis and photolysis of the acetyl derivative of 8-azido-1-naphthylamine proved very interesting, giving two products. One of these was readily shown to be 2-methylperimidine (12) by comparison with authentic specimens prepared by reduction of 1-acetylamino-8-nitronaphthalene and by treatment of 1,8-diaminonaphthalene with acetic anhydride.[124] This product presumably arose by the hydrogen abstraction reaction giving the unstable 8-acetylamino-1-naphthylamine which readily ring closed. The

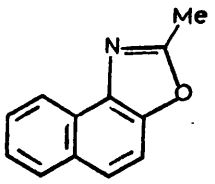
second product, which was eluted first from a silica gel column,



(12)



(13)

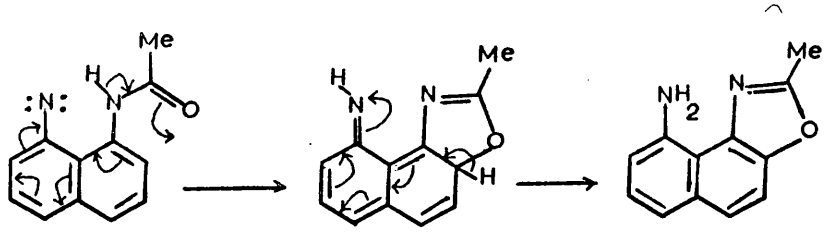


(14)

was a low melting colourless solid, $C_{12}H_{10}N_2O$. The i.r. spectrum indicated a primary amine with no carbonyl group. The presence of the amine group was confirmed by coupling with β-naphthol on diazotisation, to give an azo dye; and by the formation of a hydrochloride with dilute hydrochloric acid. The mass spectrum gave the molecular weight 198 and p.m.r. showed only five aromatic protons, two primary aromatic amine protons and a methyl group. Thus the only possible structure appeared to be the amino oxazole (13). Direct comparison with an independently prepared specimen was not possible but a sample of 2-methylnaphtho-[1,2-d]oxazole (14) was obtained from β-naphthol by coupling with diazotised sulphanilic acid, reduction to the amine and treatment of amine hydrochloride with acetic anhydride.[125] Comparison with the amino oxazole showed similarity in the i.r. spectra and in the chemical shift of the oxazole methyl group. In 2-methyl-naphthoxazole a very low field proton occurred which was absent in the amino-2-methylnaphthoxazole. This was presumably the peri- proton deshielded by the nitrogen of the oxazole ring. In

addition the amino oxazole showed a high field proton absent in the oxazole and this was assumed to be the proton ortho to the amine group. Final confirmation of the structure of 9-amino-2-methylnaphthoxazole was obtained by small scale deamination, by reduction of the diazonium chloride with hypophosphorous acid. This gave a trace of 2-methylnaphthoxazole identical to the authentic specimen, (T.L.C. in several eluent systems). Nitration of 2-methylnaphthoxazole followed by reduction was unsatisfactory.

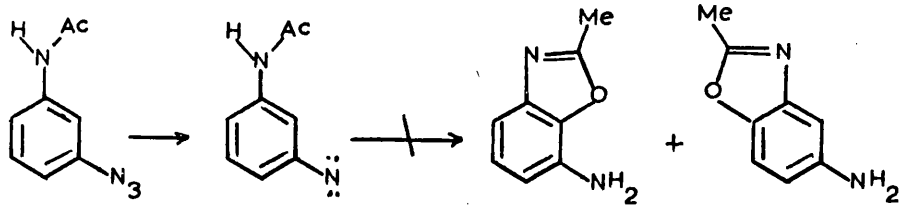
A possible mechanism for the formation of 9-amino-2-methylnaphth[1,2-d]oxazole involves a novel nucleophilic substitution due to the electron withdrawing effect of the electron deficient nitrene (15).



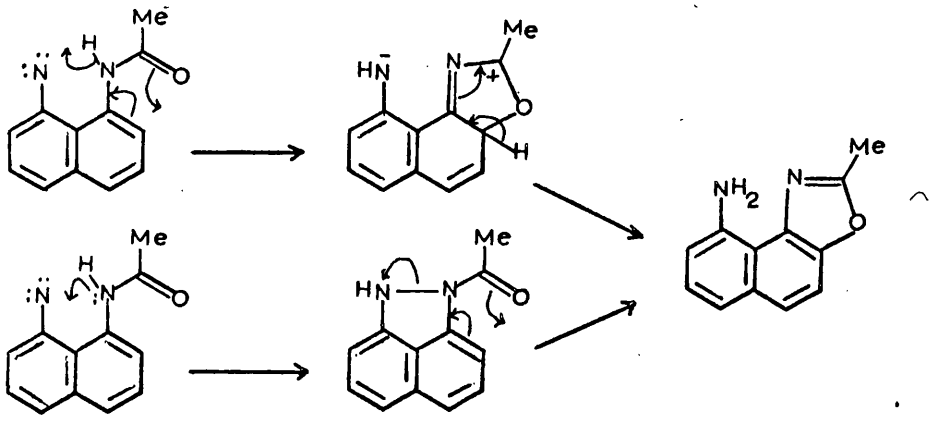
(15)

If this type of mechanism is operative, the reaction should extend to m-azidoacetanilide. This was prepared from m-nitroaniline by acetylation, reduction, diazotisation and treatment of the diazonium solution with sodium azide. However m-azidoacetanilide proved to be surprisingly stable, only partially decomposing on pyrolysis for 15 min. at 200°, and no

amino oxazole formation was observed. This difference between



the benzene and naphthalene cases may suggest alternative mechanisms involving hydride shift or perhaps even the formation of the acetyl derivative (16) of the long sought benzindazole, as shown.

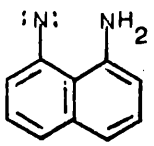


(16)

The formation of oxazoles by pyrolysis of azides in polyphosphoric-acetic acid has recently been reported.[126] However, in this case the nitrene nitrogen from the azide is incorporated into the oxazole ring.

Nitrenes have been suggested as intermediates in the deoxygenation with triethylphosphite of nitro compounds.[127] However treatment of 8-nitro-1-naphthylamine with triethylphosphite,

as a route to the aminonitrene (17), gave only intractable tars.



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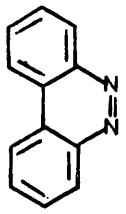

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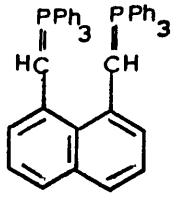

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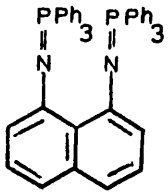
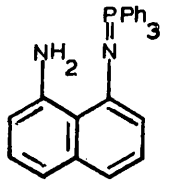


(20)

1,8-Diazidonaphthalene was prepared from 8-azido-1-naphthylamine and 1,8-diaminonaphthalene by treatment of the respective diazonium and tetrazonium solutions with sodium azide. Pyrolysis of the diazide gave largely polymeric material, but a small amount of 1,8-diaminonaphthalene was also formed, indicating that intermolecular hydrogen abstraction was again preferred to a ring closure reaction. Photolysis was complicated by the formation of polymer on the surface of the vessel which inhibited further irradiation. Apart from polymer, the only product isolated was a trace of 8-azido-1-naphthylamine. The failure to obtain benzindazole by this method is analogous to the non-formation of the known, stable benzo[c]cinnoline (18) from 2,2'-diazidobiphenyl.[122,128]

It has recently been shown that treatment of the bisphosphorane (19) in dimethyl sulphoxide with oxygen gave a good yield of acenaphthylene,[129] and it was thought that similar treatment of the corresponding bisiminophosphorane (20) might give benzindazole, although iminophosphoranes are less reactive than their carbon analogues.

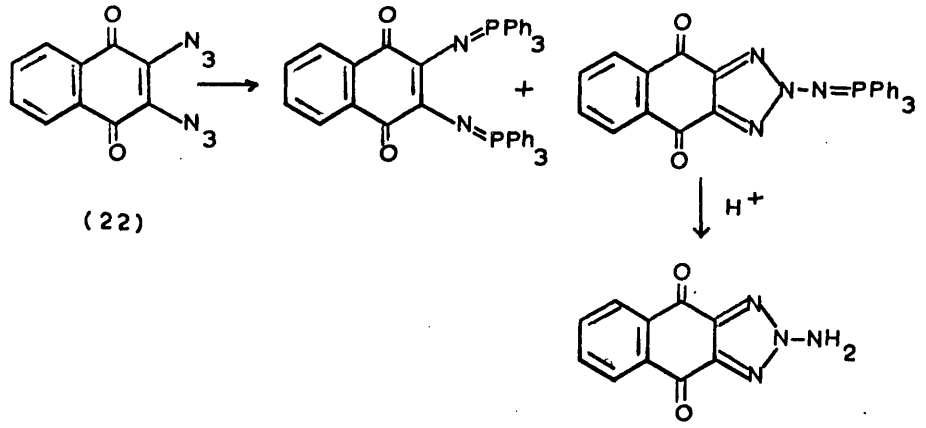
Compound (20) was prepared by treatment of triphenylphosphinedichloride with 1,8-diaminonaphthalene.[130] The crude product could not be purified by chromatography since hydrolysis of one of the iminophosphorane groups occurred to give the amino-iminophosphorane (21). The structure of this compound was



(21)

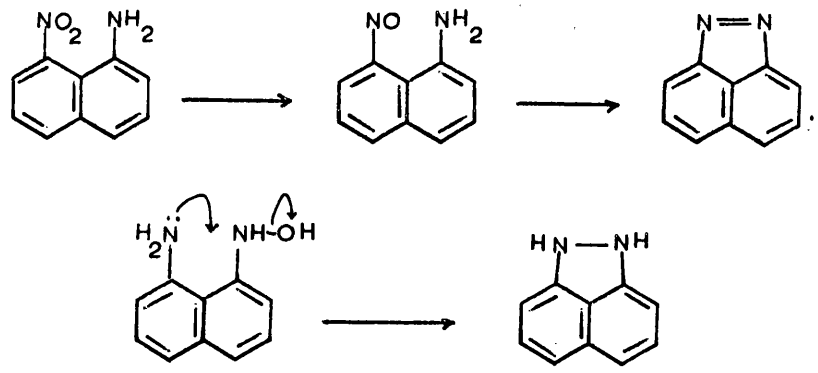
confirmed by comparison with that prepared by treatment of 8-azido-1-naphthylamine with triphenylphosphine. This reaction of an azide with triphenylphosphine is general[131] and the bisimino-phosphorane (20) was also obtained by this method from 1,8-diazido-naphthalene. This route was of special interest since Mosby and Silva[132] have shown that 2,3-bisazidonaphthoquinones (22) gave 2-aminotriazole derivatives, and a similar reaction in this case would lead to derivatives of 2-aminonaphtho[1,8-de]triazine. However although a considerable amount of blue material was produced in addition to the required bisiminophosphorane, its hydrolysis with concentrated hydrochloric acid gave no trace of 2-aminonaphthotriazine, and it was assumed to be polymeric. The bisiminophosphorane (20) was recovered quantitatively from treatment with oxygen in dimethyl sulphoxide.

Some attempts were made to prepare 8-nitroso- and 8-hydroxylamino-1-naphthylamine, in the hope that cyclodehydration



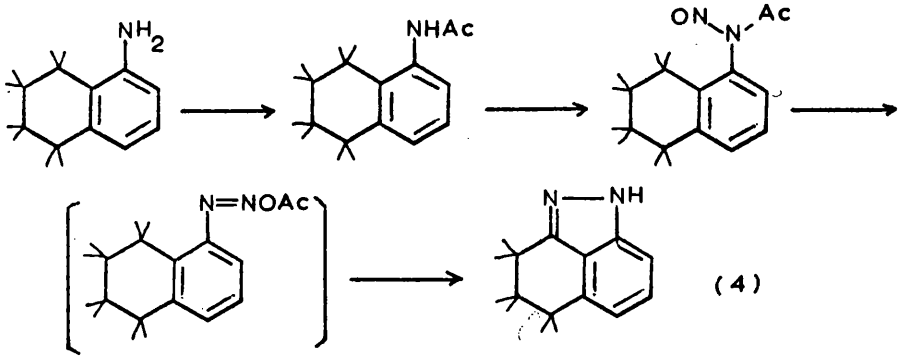
(22)

would give the required indazoles. However these reactions gave only intractable tarry products.



Since approaches to benzindazole and dihydrobenzindazole involving coupling of two nitrogens in the naphthalene peri-positions appeared unpromising, an attempt was made starting with the basic ring system intact. Tetrahydronaphthopyrazole (4)

was prepared by the method of Vesely[133] from N-nitroso-1-acetylamino-tetralin, but dehydrogenation attempts proved unsuccessful. Thus 1,2-dichloro-4,5-dicyanobenzoquinone (D.D.Q.) gave a black



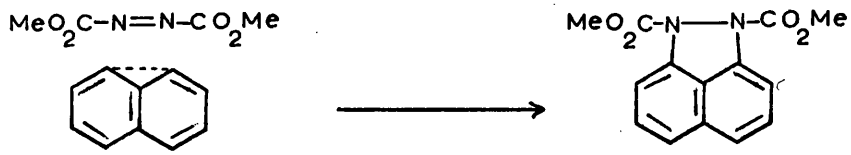
(4)

insoluble solid, possibly a molecular complex since D.D.Q. is known to form complexes with basic nitrogen compounds.[134] N-Bromosuccinimide oxidation gave only a high melting N-H compound and lead tetra-acetate oxidation was also unsuccessful.

Since N-nitroso-1-acetylaminotetralin ring closes to give (4), decomposition of the fully aromatic analogue was attempted. However N-nitroso-1-benzoylaminonaphthalene gave only a trace of naphthalene, 1-phenylnaphthalene, and an unidentified product shown not to be benzindazole. 1-Phenylnaphthalene was the expected product since decomposition of N-nitrosoarylamides is a standard method for the production of aryl radicals.

The final, and only successful attempt to prepare the benzindazole system involved the formation of the two aryl C-N bonds, the N-N bond being already formed. Addition of 1,8-dehydronaphthalene to dimethyl azodicarboxylate gave dimethyl dihydrobenzindazole dicarboxylate (23) in low yield, the evidence for its formation having already been discussed (Section I).

Unfortunately sufficient of this compound was not available for hydrolysis and decarboxylation to dihydrobenzindazole and its



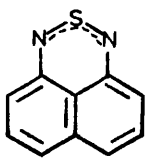
(23)

subsequent oxidation to benzindazole. However in the absence of other success, this route would seem the most promising for obtaining (1) and (3), although the low yield and practical difficulties involved make it by no means attractive.

Failure to isolate (1), especially in some of the pyrolytic and photolytic experiments may have been due to its instability. However, no dehydronaphthalene products were ever detected and since dehydronaphthalene is the most likely decomposition product of (1), it is probable that the indazole was never formed. Also, the formation of 1,8-diaminonaphthalene and 8-amino-2-methylnaphtho[1,2-d]oxazole from 8-azido-1-naphthylamine and 1-acetylamino-8-azidonaphthalene respectively rather than the dihydrobenzindazoles suggests that the expected favourable nucleophilic attack of the amino- and acetylamino- groups on the electron deficient nitrene cannot occur for steric reasons.

Since the completion of this work it has been reported by Beecken[135] that dihydrobenzindazole (3) can be obtained in good yield from naphtho[1,8-cd][1,2,6]thiadiazine (24) by adsorption

on activated alumina or by reduction with zinc and acetic acid. The product was identical to a specimen prepared by the method of Vorozhtsov and Kozlov[120] although, as reported above, this preparation could not be repeated by Hoffmann.[48] Attempts to obtain benzindazole (1) by oxidation of (3) with lead (IV) oxide in ether at 20° gave a very unstable orange solution from which (1) could not be isolated, even as a Diels Alder adduct. The instability of (1) in part explains our failure to isolate it, since if formed, it would certainly have decomposed under our conditions. However, the stability of (3) makes its non-formation by apparently favourable methods, such as decomposition of 8-azido-1-naphthylamine, intriguing.



(24)

SECTION III EXPERIMENTAL

ATTEMPTED PREPARATION OF BENZ[cd]INDAZOLE AND DIHYDROBENZ[cd]INDAZOLE

1. Oxidation of 2-Aminonaphtho[1,8-de]triazine

2-Aminonaphtho[1,8-de]triazine (55 mg., 0.3 mmole) in methylene chloride was added dropwise to a stirred solution of lead tetra-acetate (150 mg., 0.34 mmole) in the same solvent. Nitrogen was evolved and the blue colour was discharged. One drop of glycerol was added and stirring was continued for several minutes. The resulting solution was filtered leaving a black insoluble residue. The yellow filtrate was washed with sodium bicarbonate solution, water and then dried ($MgSO_4$). Evaporation under reduced pressure gave a trace of oil shown by T.L.C. to contain at least four compounds. The small scale made isolation of any products impossible.

2. Oxidation of 1,8-Diaminonaphthalene.

1,8-Diaminonaphthalene was stirred overnight in ether under dry nitrogen with lead tetra-acetate (2.1 equiv.). T.L.C. indicated a very complex mixture from which only small amounts of intractable tars were isolated by chromatography on silica gel. A similar result was obtained when the reaction was carried out in refluxing benzene.

3. Oxidation of 8-Azido-1-naphthylamine

Identical treatment of 8-azido-1-naphthylamine gave similar results.

4. Pyrolysis and Photolysis of 8-Azido-1-naphthylamine

A. Pyrolysis

8-Azido-1-naphthylamine (500 mg.) in dry decalin was added dropwise to refluxing decalin over 5 min. and the mixture was refluxed for a further 10 min. On cooling, a dark polymeric solid (230 mg.) separated and was filtered off. Decalin was removed from the filtrate by distillation under reduced pressure leaving an oily residue shown by T.L.C. to be largely 1,8-diaminonaphthalene. Extraction with dilute hydrochloric acid followed by basification of the acid extract and re-extraction with ether gave 1,8-diaminonaphthalene (150 mg., 35%) as a colourless oil. Distillation gave solid 1,8-diaminonaphthalene which crystallised as needles from petrol, m.p. and. m.m.p. 62-63° (Lit., m.p. 66.5°).

B. Photolysis

8-Azido-1-naphthylamine (290 mg.) in dry benzene was exposed in glass apparatus to a 100W Hanovia medium pressure mercury lamp for 20 hr., the heat of the lamp being allowed to reflux the solution. Polymeric material (80 mg.) was filtered off and the filtrate was evaporated on to basic alumina for chromatography. Elution with ether gave:

i) 8,8'-diamino-1,1'-azonaphthalene (50 mg., 20%) which crystallised as orange needles from benzene-petrol, m.p. 275-276° (decomp.). m/e 312, 168, 115. (Found: C, 77.8; H, 5.0. $C_{20}H_{16}N_4$ requires: C, 76.9; H, 5.2%).

ii) 1,8-diaminonaphthalene (80 mg., 32%); vacuum distillation and crystallisation from petrol gave colourless needles, m.p. and m.m.p. 62-63° (Lit., m.p. 66.5°).

5. Pyrolysis and Photolysis of 1-Acetylamino-8-azidonaphthalene

1-Acetylamino-8-azidonaphthalene was prepared quantitatively from 8-azido-1-naphthylamine by acetylation with acetic anhydride in pyridine. It crystallised from ethanol as colourless needles m.p. 147-148°. (See Section I p.79)

A. Pyrolysis

1-Acetylamino-8-azidonaphthalene (500 mg.) dissolved in a small volume of 1,2,4-trichlorobenzene was added dropwise to refluxing trichlorobenzene (50 ml.). After 10 min. the mixture was cooled and the trichlorobenzene was removed by distillation under reduced pressure. The residue was extracted with hot chloroform and the solution was evaporated on to silica gel. Elution with 20% ether-petrol gave 9-amino-2-methylnaphtho[1,2-d]-oxazole (59 mg., 13.5%) which sublimed to give a colourless solid, m.p. 78°.

$\nu_{max.}$ 3430, 3325, 1617, 1591, 1581, 1560, 1448, 1403, 1364, 1353, 1296, 1279, 1219, 1034, 1008, 973, 942, 810, 783, 749, 693 $cm.^{-1}$

τ2.4-2.9 (Complex multiplet, 4H); τ3.37 (quartet, 1H); τ4.43 (broad singlet, 2H); τ7.42 (singlet, 3H).

m/e 198, 183, 169, 129, 102.

[Found: C, 73.6; H, 5.2. $C_{12}H_{10}N_2O$ requires: C, 72.6; H, 5.1%].

Picrate, from ethanol m.p. 195°.

Acetyl derivative m.p. 151-153° (unrecryst.)

$\nu_{max.}$ 3280, 1700, 1603, 1583, 1560, 1304, 833, 775, 770, 750, 725 $cm.^{-1}$.

m/e 240, 225, 198, 183, 169, 129, 102.

Elution with methanol gave very discoloured 2-methylperimidine (150 mg., 37%) (i.r. and T.L.C.).

B. Photolysis

1-Acetylamino-8-azidonaphthalene (380 mg.) in benzene (100 ml.) was photolysed under nitrogen in quartz apparatus for 3 hr. using a 450 W Hanovia medium pressure mercury lamp. The resulting solution was evaporated on to silica gel and chromatographed. Elution with 20% ether-petrol gave 9-amino-2-methylnaphtho[1,2-d]oxazole (30 mg., 9%). Elution with methanol gave impure 2-methyl perimidine (120 mg., 39%).

Deamination of 9-Amino-2-methylnaphtho[1,2-d]oxazole.

9-Amino-2-methylnaphtho[1,2-d]oxazole (ca. 50 mg., 0.25 mmole) in dilute hydrochloric acid (2 ml.) was diazotised with sodium nitrite (18 mg., 0.25 mmole). Ice cold hypophosphorous acid (1 g.) was added and the mixture was maintained at 0-5° for 24 hr. Extraction with ether gave a trace of oily material, shown by T.L.C. to contain 2-methylnaphtho[1,2-d]oxazole by comparison with an authentic specimen in several eluent systems.

6. Pyrolysis and Photolysis of m-Azidoacetanilide.

A. Preparation of m-Azidoacetanilide.

m-Nitroacetanilide was prepared quantitatively by

acetylation of m-nitroaniline with acetic anhydride in pyridine.

m-Nitroacetanilide (10 g.) in ethanol-ethyl acetate was hydrogenated over 10% Pd/C catalyst. After absorption of 3 moles of hydrogen, the mixture was filtered and the solvent was removed. The resulting amine was suspended in dilute hydrochloric acid and cooled to 0°. Sodium nitrite (4.25 g.) in a small volume of water was added dropwise and the resulting solution was treated with excess of sodium azide. m-Azidoacetanilide (7.5 g., 75%) was filtered off and recrystallised from ethanol or ether-petrol to give colourless needles, m.p. 123-124°.

$\nu_{max.}$ 3260, 2125, 1663, 1595, 1555, 1305, 1286, 1264, 865, 804 $cm.^{-1}$

(Found: C, 54.7; H, 4.7; N, 32.0. $C_8H_8N_4O$ requires: C, 54.6; H, 4.5; N, 31.8%).

B. Pyrolysis

Pyrolysis of m-azidoacetanilide for 15 min. in 1,2,4-trichlorobenzene at 200° gave some recovered m-azidoacetanilide together with resinous products. No amino-benzoxazoles were detected.

C. Photolysis

Photolysis was complicated by the insolubility of the azide in benzene and hexane, and again some m-azidoacetanilide was recovered unchanged. No trace of amino-benzoxazoles was found.

7. De-oxygenation of 8-Nitro-1-naphthylamine

8-Nitro-1-naphthylamine (500 mg.) was refluxed for 6 hr. under nitrogen in freshly distilled triethyl phosphite. After

removal of triethyl phosphite by vacuum distillation, T.L.C. indicated a complex mixture from which only intractable tars were obtained by chromatography on silica gel.

8. Pyrolysis and Photolysis of 1,8-Diazidonaphthalene

A. Preparation of 1,8-Diazidonaphthalene from 8-Azido-1-naphthylamine

8-Azido-1-naphthylamine (552 mg., 3 mmole) in ether solution was cooled to 0° and the amine hydrochloride was precipitated by passing in hydrogen chloride. This was filtered off, washed with ether and suspended in dilute hydrochloric acid (30 ml., N/10, 3 mmole). Sodium nitrite (2.1 g., 3 mmole) in water (10 ml.) was added dropwise and the resulting solution was treated with sodium azide (2.6 g., 4 mmole) in a small volume of water. After stirring for 30 min. the precipitate was recrystallised from ether-petrol to give 1,8-diazidonaphthalene (450 mg., 81%), as colourless needles, m.p. 127° (decomp.).

$\lambda_{max.}$ 228 (log ε 4.47); 260(3.76); 323(4.07); 337 mμ(3.96).

$\nu_{max.}$ 2110, 2080, 1610, 1560, 1300, 1283, 950, 800, 742, 677 $cm.^{-1}$

Analysis was not attempted because of the unstable nature of the diazide.

B. Preparation from 1,8-Diaminonaphthalene.

1,8-Diaminonaphthalene (5 g., 31.5 mmole) was converted into its hydrochloride whichwas suspended in dilute hydrochloric acid (45 ml., 2N, 9 mmole) and the mixture was cooled to -5°. Solid sodium nitrite (5 g., 72 mmole) was added quickly and the mixture was stirred for 15 min. The resulting solution was filtered

into a cooled receiver and stirred at 0° while sodium azide (6.5 g., 100 mmole) in a small volume of water was added. After 30 min. the precipitate was recrystallised from ether-petrol to give 1,8-diazidonaphthalene (2 g., 30%). 1,8-Diazidonaphthalene was very unstable to light but could be stored for long periods in the cold and dark.

C. Pyrolysis of 1,8-Diazidonaphthalene

Pyrolysis of 1,8-diazidonaphthalene (1 g.) in 1,2,4-trichlorobenzene, by the method used for 8-azido-1-naphthylamine gave polymeric material (650 mg.) and 1,8-diaminonaphthalene (60 mg., 7.9%).

Attempted pyrolysis of the solid diazide under reduced pressure resulted in an explosion.

D. Photolysis of 1,8-Diazidonaphthalene

Photolysis of 1,8-diazidonaphthalene by the method used for 8-azido-1-naphthylamine was unsatisfactory owing to the formation of polymeric material on the surface of the vessel which prevented further irradiation. Thus after 24 hr. 1,8-diazidonaphthalene (1 g.) gave, in addition to polymeric material, unchanged starting material (580 mg., 58%) and a trace of 8-azido-1-naphthylamine (i.r. T.L.C.). These compounds were isolated, after removal of solvent, by chromatography on silica gel in the dark.

Photolysis in benzene solution for 10 hr. using a 450W Hanovia medium pressure mercury lamp with a quartz filter gave

only amorphous polymeric solid and unchanged 1,8-diazidonaphthalene. Similar results were obtained using hexane as solvent.

9. Oxidation of Naphthalene-1,8-bistriphenyl-phosphineimine

A. Preparation of Naphthalene-1,8-bistriphenylphosphineimine from 1,8-Diaminonaphthalene.

Triphenylphosphine (13.1 g.) 50 mmole) in dry benzene (140 ml.) was stirred at 0° while a solution of bromine (8 g., 50 mmole) in benzene (20 ml.) was added under nitrogen. Triethylamine (10.1 g., 100 mmole) in benzene (20 ml.) was added at 0-5° followed by 1,8-diaminonaphthalene (3.95 g., 25 mmole). The mixture was heated to 80° for 20 min., cooled and then filtered. The residue was warmed with 2N sodium hydroxide solution at 40-50° for 5 min. causing the grey solid to turn yellow. The naphthalene-1,8-bistriphenylphosphineimine was filtered off, washed and dried (14 g., 82%). Recrystallisation was unsatisfactory; reprecipitation from chloroform solution by ether gave a greenish yellow solid, m.p. 275-280° (decomp.).

$\nu_{max.}$ 1555, 1438, 1350, 1310, 1134, 1102, 1052, 813, 746, 715, 695 $cm.^{-1}$

(Found: C, 81.2; H, 5.5; N, 4.0. $C_{46}H_{36}N_2P_2$ requires: C, 81.4; H, 5.3; N, 4.1%).

B. Preparation from 1,8-Diazidonaphthalene

Triphenylphosphine (3.75 g., 14.3 mmole) in benzene (40 ml.) was added dropwise to 1,8-diazidonaphthalene (1.5 g., 7,1 mmole) in benzene (50 ml.). The mixture was then refluxed for

15 min. On cooling a dark purple solid separated (750 mg.). Addition of ether to the filtrate gave naphthalene-1,8-bistriphenylphosphineimine (1 g., 21%), crystallising as a greenish yellow solid, m.p. ca. 280° (decomp.).

The initial purple solid was refluxed for several hours with acetic acid containing concentrated hydrochloric acid. No trace of 2-aminonaphtho[1,8-de]triazine or 8-azido-1-naphthylamine was observed. The mother liquor, after filtration of the naphthalene-1,8-bistriphenylphosphineimine, was evaporated and the residue was treated in the same way as the purple solid. Again no trace of 2-aminonaphtho[1,8-de]triazine or 8-azido-1-naphthylamine was observed.

Adsorption of naphthalene-1,8-bistriphenylphosphineimine on basic alumina, followed by elution with chloroform gave 8-triphenylphosphineimino-1-naphthylamine, a yellow solid m.p. 150-155°.

$\nu_{max.}$ 3450, 3230, 1608, 1565, 1440, 1398, 1320, 1280, 1135, 112, 1090, 1070, 945, 812, 758, 747, 721, 695, 684 $cm.^{-1}$

(Found: C, 80.6; H, 5.7; N, 6.5. $C_{28}H_{23}N_2P$ requires: C,80.4; H, 5.5; N, 6.7%).

C. Preparation of 8-Triphenylphosphineimino-1-naphthylamine

Triphenylphosphine (830 mg., 3.19 mmole) in benzene was added dropwise to 8-azido-1-naphthylamine (580 mg., 3.15 mmole) in benzene. The mixture was refluxed for 15 min. and on cooling 8-triphenylphosphineimino-1-naphthylamine (1 g., 77%) crystallised m.p. and m.m.p. 150-155°.

D. Oxidation of Naphthalene-1,8-bistriphenylphosphineimine

Naphthalene-1,8-bistriphenylphosphineimine (2 g.) was suspended in dry dimethylsulphoxide maintained at 70° while dry oxygen was bubbled through for 36 hr. Starting material was recovered quantitatively, no trace of triphenylphosphine oxide being observed.

10. Dehydrogenation of Tetrahydronaphth[1,8-]pyrazole.

A. Attempted Dehydrogenation with 1,2-Dichloro-4,5-dicyano-benzoquinone.

Tetrahydronaphtho[1,8]-pyrazole (158 mg.) and 1,2-dichloro-4,5-dicyanobenzoquinone (500 mg.) were refluxed overnight in benzene (5 ml.). The black solid (300 mg.) which separated was insoluble in all solvents and did not melt below 360°.

B.. Attempted Dehydrogenation with N-Bromosuccinimide.

Dehydrogenation with N-bromosuccinimide following the method of Barnes[136] gave a gum which was sublimed to give an unidentified colourless solid, m.p. 195-200°.

$\nu_{max.}$ 3000 (v. broad), 1617 (weak), 1340, 1310, 940 $cm.^{-1}$

C. Oxidation with Lead Tetra-acetate.

Tetrahydronaphtho[1,8]pyrazole (474 mg., 3 mmole) in methylene chloride was added dropwise to lead tetra-acetate (3.1 g., 7 mmole) in the same solvent. The solution was filtered and evaporated on to basic alumina. Elution with ether gave an unidentified colourless solid, (40 mg.) recrystallised from ether-

petrol, m.p. 213-215°.

$\nu_{max.}$ 1630, 1612, 1515, 1391, 1380, 1259, 826, 781, 764, 758 $cm.^{-1}$

The p.m.r. spectrum was very complex in the aliphatic proton region.

12. Decomposition of N-Nitroso-1-benzoylaminonaphthalene

1-Benzoylaminonaphthalene was prepared from 1-naphthylamine by treatment with benzoyl chloride in pyridine.

A. Preparation of N-Nitroso-1-benzoylaminonaphthalene.

1-Benzoylaminonaphthalene (5 g.) in acetic acid-acetic anhydride was cooled to 1-4° and nitrous fumes were passed in for 3.5 hr. The resulting solution was poured into ice-water to give a yellow oily solid. This was dissolved in acetone at 0° and carefully reprecipitated with ice water to give N-nitroso-1-benzoylaminonaphthalene as a yellow crystalline solid, m.p. 88-89° after drying quickly between filter papers.

B. Decomposition of N-nitroso-1-benzoylaminonaphthalene.

The nitroso compound was immediately dissolved in benzene, dried quickly ($MgSO_4$) and left to decompose overnight at room temperature. Evaporation on to basic alumina followed by chromatography gave on elution with petrol

i) naphthalene (trace) m.p. and m.m.p. 80°

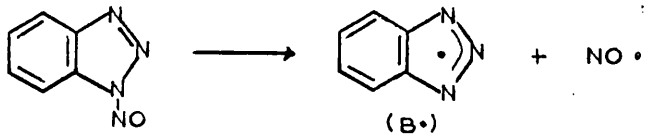
ii) 1-phenylnaphthalene (200 mg.) (i.r.)

Elution with5% ether-petrol gave:

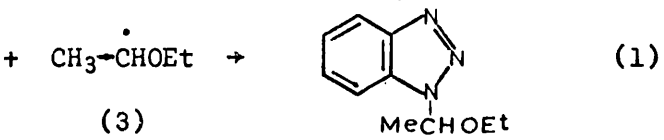
iii) unidentified yellow solid (90 mg.), recrystallised from ethanol, m.p. 129-130°. m/e 249, 229, 202.

1-CHLOROBENZOTRIAZOLE

Both naphtho[1,8-de]triazine and benzotriazole are readily aminated by hydroxylamine-O-sulphonic acid, but although amination with ethereal chloramine is satisfactory for the triazine no success has been obtained with the triazole. In an attempt to N-nitrosate benzotriazole with nitrosyl chloride in ether, Campbell[62] obtained 1-(1-ethoxyethyl)benzotriazole (1) and no trace of the nitroso compounds. He explained the formation of 1-(1-ethoxyethyl)benzotriazole by the following scheme.

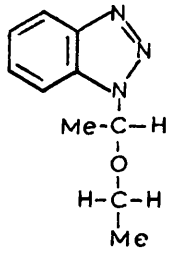


B• + CH_3–CH_2OEt → BH + CH_3–$\dot{C}H$–OEt



We reinvestigated the amination reaction and found that when benzotriazole in ether was treated with chloramine, 1-(1-ethoxyethyl)benzotriazole was again a product, together with benzotriazole hydrochloride. Some unchanged benzotriazole remained. Since chloramine can behave either as a chlorinating or aminating agent and since 1-aminobenzotriazole is known to be stable in ether solution, the possibility that 1-chlorobenzotriazole was the reactive intermediate was further investigated. When benzotriazole was treated with chlorine in ether, a colourless

crystalline solid immediately separated, followed by a further amount when the mixture was left to stand; 1-(1-ethoxyethyl)-benzotriazole was obtained from the filtrate. The colourless solid dissolved readily in water to give an acid solution and was identical with benzotriazole hydrochloride produced by passing hydrogen chloride into ethereal benzotriazole.[137] Although analysis was not entirely satisfactory, probably due to the nature of the compound, it did support the structure. 1-(1-Ethoxyethyl)benzotriazole was characterised by Campbell[62] on the basis of its mass spectral fragmentation and its p.m.r. spectrum. It is interesting to note that the non-equivalence of the two secondary hydrogen atoms of the ethoxy group, due to the asymmetric centre,[138] causes the ethyl quartet to be split into a decet.



(1)

The formation of these products can be explained by a free radical reaction scheme involving 1-chlorobenzotriazole.

$$B\text{-}Cl \rightarrow B\cdot + Cl\cdot \qquad (i)$$

$$Cl\cdot + Et_2O \rightarrow Me\dot{C}HOEt + HCl \qquad (ii)$$

$$Me\dot{C}HOEt + BCl \rightarrow B\text{-}\underset{\displaystyle Me}{\underset{|}{C}}H\text{-}OEt + Cl\cdot \qquad (iii)$$

$$Me\dot{C}HOEt + BCl \quad B\cdot + Me\underset{\displaystyle Cl}{\underset{|}{C}}H\cdot OEt \qquad (iv)$$

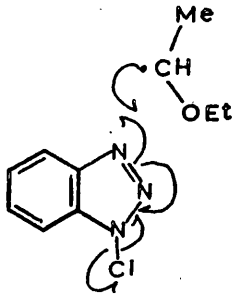
$B\cdot + Et_2O \rightarrow BH + MeCHOEt$ (v)

$B\cdot + HCl \rightarrow BH + Cl\cdot$ (vi)

$BCl + HCl \quad BH + Cl_2$ (vii)

This type of mechanism is to be preferred to that proposed by Campbell which involves a combination of the two radicals (2) and (3), rather than the more likely chain mechanism. The non-formation of any dibenzotriazole, B-B, also argues against his mechanism.

The dissociation of 1-chlorobenzotriazole is the initiation stage and the halogen radical is proposed as the main chain carrier as has been shown for N-halogeno compounds such as N-bromo- and N-chlorosuccinimide.[139] Stage (iii) is perhaps the least attractive stage and is best considered as a radical displacement:



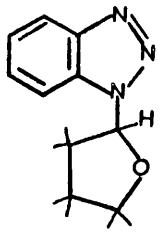
The expected abstraction of chlorine by step (iv) no doubt also occurs but any chloroether (4) would not have been detected. Reactions such as (v) (vi) and (vii) account for the formation of benzotriazole.

In view of its interest as an intermediate, and since no N-halogeno derivatives of benzotriazole have been reported,

attempts were made to isolate 1-chlorobenzotriazole. Treatment of a suspension of benzotriazole in carbon tetrachloride with excess of chlorine gave a solution containing 1-chlorobenzotriazole. After filtration from benzotriazole hydrochloride and unchanged benzotriazole, evaporation of the solution gave 1-chlorobenzotriazole contaminated with benzotriazole. Several recrystallisations gave a pure sample which had the expected analytical, spectral and mass spectral data. This method was unsatisfactory because of the inevitable formation of a large amount of benzotriazole hydrochloride and the fact that the benzotriazole impurity was difficult to remove. Treatment of benzotriazole with chlorine in the presence of triethylamine, to remove the hydrogen chloride produced, was also unsatisfactory. N-Halogeno compounds have frequently been prepared by the action of sodium hypochlorite on acidified solutions of the parent N-H compounds and when benzotriazole in aqueous acetic acid was so treated, almost pure 1-chlorobenzotriazole separated quantitatively. One recrystallisation from methylene chloride-petrol gave the pure compound which could be stored indefinitely in the dark.

The possible intermediacy of 1-chlorobenzotriazole in the formation of 1-(1-ethoxyethyl)benzotriazole was confirmed by allowing it to react with ether. After an induction period of several hours benzotriazole hydrochloride separated leaving 1-(1-ethoxyethyl)benzotriazole and benzotriazole in solution. This type of reaction was shown to be general by the formation

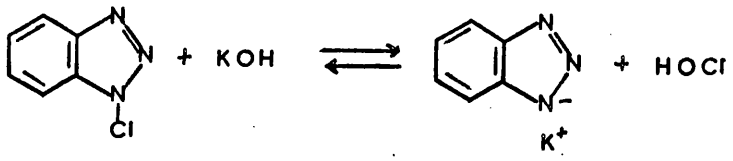
of 1-(2-tetrahydrofuryl)benzotriazole (5) when ether was replaced by tetrahydrofuran. The higher yield in the latter case, and the long induction period followed by a rapid reaction, support the radical mechanism proposed. In the treatment of ethereal benzotriazole with chlorine, immediate T.L.C. indicated the presence of 1-chlorobenzotriazole before the formation of any 1-(1-ethoxyethyl)benzotriazole.



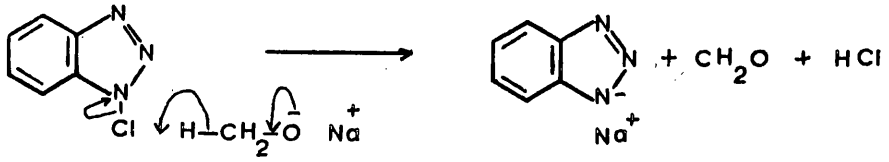
(5)

In view of the ready availability of 1-chlorobenzotriazole, the possibility of nucleophilic replacement of the chlorine to give 1-substituted benzotriazoles was investigated e.g. replacement by amide ion could give an attractive route to 1-aminobenzotriazole. However the chlorine atom proved to be inert to such reactions and the chemistry of N-chlorobenzotriazole was consistent with that of a positive halogen compound.

1-Chlorobenzotriazole dissolved readily in dilute sodium hydroxide solution but was reprecipitated in high yield on acidification. After refluxing for several hours in 10% aqueous potassium hydroxide, unchanged chlorobenzotriazole (35%) was recovered. Some decomposition to give benzotriazole (42%) had occurred but no 1-hydroxybenzotriazole was detected.



Treatment of 1-chlorobenzotriazole in cold dry methanol with sodium methoxide in methanol gave a rapid exothermic reaction which required two moles of sodium methoxide for completion. No 1-methoxybenzotriazole was detected, only benzotriazole being produced. Thus oxidation of the methoxide ion had occurred, rather than nucleophilic displacement of chlorine.



The oxidising nature was further supported by the liberation of iodine when cold ethanolic 1-chlorobenzotriazole was added to aqueous potassium iodide. Ethanolic solutions which had been warmed gave no iodine, the 1-chlorobenzotriazole having been destroyed in oxidising the ethanol.

1-Chlorobenzotriazole has been shown to be a general positive halogen oxidising agent. We have studied the oxidation by it of a variety of 1,2-disubstituted hydrazines, 1,1-disubstituted hydrazines and alcohols. The oxidations were easily carried out

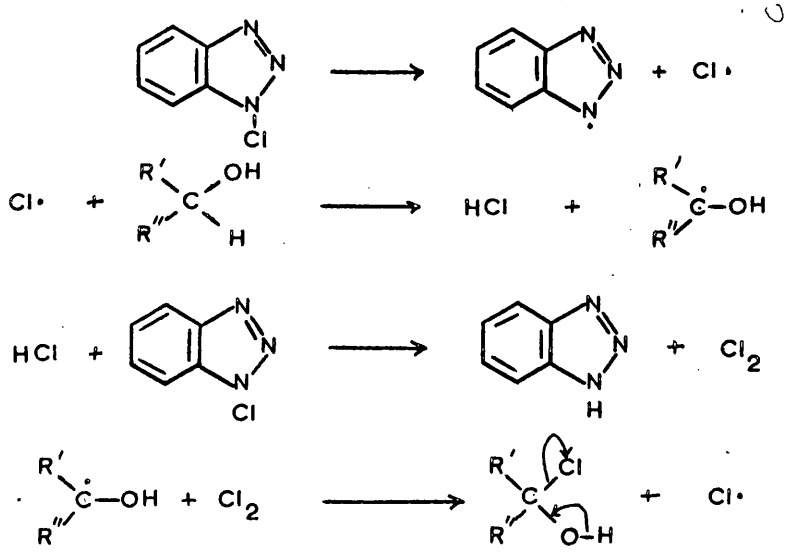
by mixing equimolar amounts of 1-chlorobenzotriazole and the compound to be oxidised in an inert solvent such as carbon tetrachloride or methylene chloride at room temperature. Mild warming was necessary in the case of alcohols. In all cases the other oxidation products, benzotriazole and hydrogen chloride formed benzotriazole hydrochloride which could be removed by filtration, leaving the required compound in solution. This product was invariably contaminated with a small amount of benzotriazole which could be removed by washing with dilute sodium hydroxide solution. Evaporation then gave the pure oxidation product.

Until very recently there has been no convenient method for the oxidation of alcohols to aldehydes or ketones under mild conditions at room temperature, and with its low temperature and mild method for removal of by-products the 1-chlorobenzotriazole oxidation must compare favourably with other current methods. 4-Phenyl-1,2,4-triazolin-3,5-dione has recently been shown to oxidise alcohols at room temperature over a few hours, under truly neutral conditions, but this reagent is not so readily prepared as ours.[140] Diethyl azodicarboxylate has also been used to oxidise alcohols in boiling benzene, although less effectively.[141]

Oxidation of alcohols in carbon tetrachloride solution with 1-chlorobenzotriazole required no initiator and on warming to ca. 50° the 1-chlorobenzotriazole dissolved and a rapid exothermic reaction occurred. After benzotriazole hydrochloride

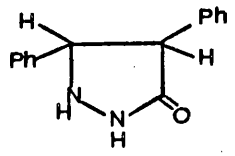
had been removed, addition of 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of the carbonyl compound, which was compared with an authentic specimen. When solutions of 1-chlorobenzotriazole in the alcohol itself were warmed, oxidation again occurred rapidly but benzotriazole hydrochloride did not separate.

In all these reactions the induction period and the evolution of a little chlorine support a free radical chain mechanism of the type proposed for N-chlorosuccinimide, which is now accepted to involve chlorine atoms as a chain carrier.



The oxidation of hydrazobenzene in methylene chloride solution occurred instantaneously, but similar treatment of dimethyl hydrazodicarboxylate gave the azo compound slowly. This is perhaps not surprising since, as mentioned above, diethyl azodicarboxylate has itself been used as an oxidising agent. trans-4,5-Diphenyl-3-pyrazolidinone[142] (6) was oxidised with rapid evolution of nitrogen and carbon monoxide leaving benzotriazole

hydrochloride and trans-stilbene. Thus the 1-chlorobenzotriazole oxidation of 4,5-diphenyl-3-pyrazolidinone paralleled the lead tetra-acetate oxidation[143a] in which the intermediate α-carbonylazo compound lost both nitrogen and carbon monoxide to form the olefin.

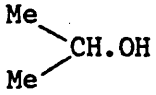
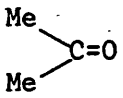
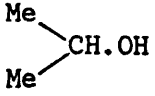
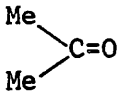
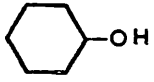
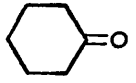
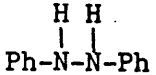
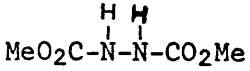
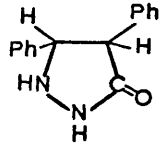
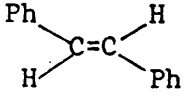


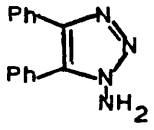
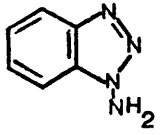
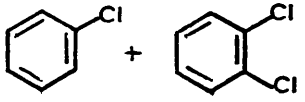
(6)

N-Aminotriazoles were readily oxidised by 1-chlorobenzotriazole giving rapid evolution of nitrogen. Thus 1-amino-4,5-diphenyl triazole gave diphenylacetylene in good yield, again paralleling similar lead tetra-acetate oxidation. However oxidation of 1-amino-4,5-diphenyltriazole with an excess of N-bromosuccinimide has given 1,2-dibromostilbene.[143b] 1-Aminobenzotriazole with 2 moles of 1-chlorobenzotriazole gave a mixture of chlorobenzene and o-dichlorobenzene, presumably by attack of the initially formed benzyne on the hydrogen chloride and chlorine present.

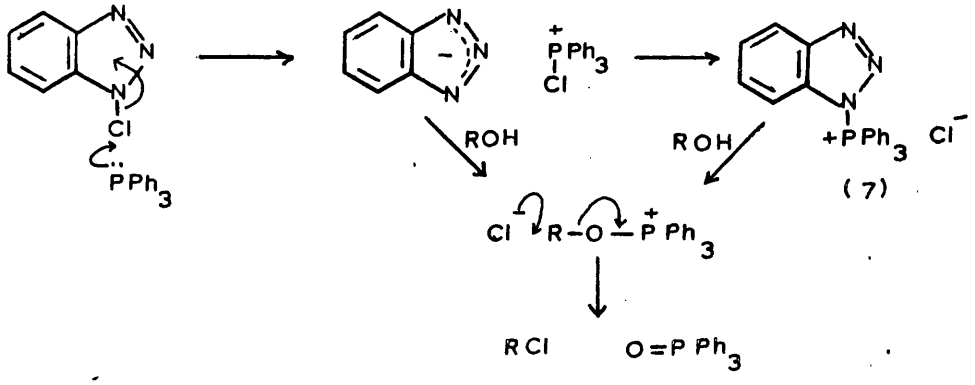
Diethyl azodicarboxylate has recently been used to oxidise phenylhydroxylamine[144] to nitrosobenzene. 1-Chlorobenzotriazole gave the nitroso compound cleanly and instantaneously in methylene chloride solution.

The oxidations involving 1-chlorobenzotriazole are summarised in the Table:

Starting Material	Solvent	Product	% Yield	% Yield of Benzotriazole Hydrochloride
$PhCH_2OH$	-	PhCHO	81	-
	-		44	-
$PhCH_2OH$	CCl_4	PhCHO	60	47
	CCl_4		30	73
	CCl_4		46	66
	CH_2Cl_2	Ph-N=N-Ph	89	70
	CH_2Cl_2	MeO_2C-N=N-CO_2Me	-	-
	CH_2Cl_2		75	70

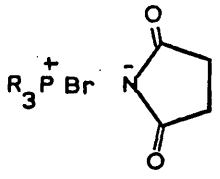
Starting Material	Solvent	Product	% Yield	% Yield of Benzotriazole Hydrochloride
	CH_2Cl_2	Ph-C≡C-Ph	75	80
	CH_2Cl_2		19 + 44	-
PhNHOH	CH_2Cl_2	PhNO	-	70

On mixing equimolar solutions of 1-chlorobenzotriazole and triphenyl phosphine in dry methylene chloride, a rapid exothermic reaction occurred giving a deep red colour which faded to yellow. Addition of dry ether to this solution caused the separation of a colourless oil, presumably the quaternary salt (7). Addition of moist ether gave rapid precipitation of benzotriazole hydrochloride (91%) leaving triphenylphosphine oxide in solution. When dry methanol was used in place of water for the decomposition, benzotriazole and triphenyl phosphine oxide were the only products isolated. No hydrogen chloride was detected. These facts can be explained by the following mechanism:

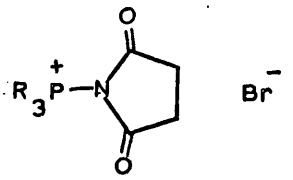


In the case of decomposition by benzyl alcohol the formation of benzyl chloride by an Arbusov type[145] of reaction was confirmed by G.L.C.

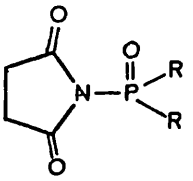
The reaction of N-haloimides with tervalent phosphorus compounds, although not widely studied, has been shown to proceed by nucleophilic displacement by phosphorus at the halogen.[146] Thus N-bromosuccinimide gave (8) which could rearrange to the isomeric ion pair (9).



(8)



(9)

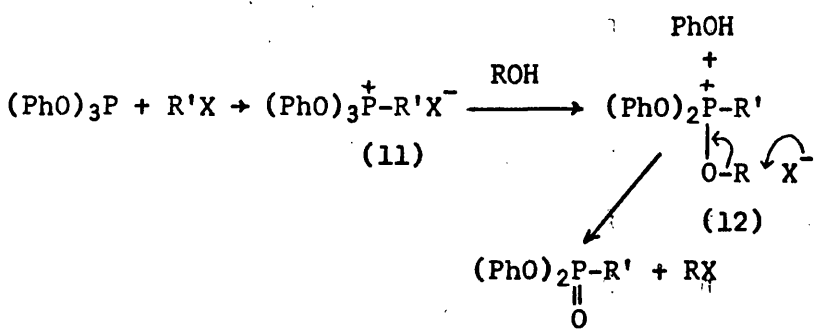


(10)

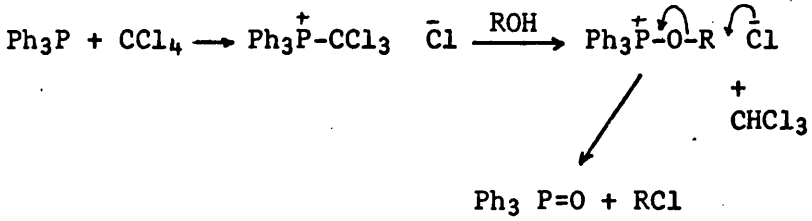
When R was alkoxyl, further reaction occurred by nucleophilic attack of the halide ion in (9) on the α-carbon of the alkoxy group to give N-(dialkoxylphosphoro)succinimide (10) and the corresponding alkyl halide.

When R was phenyl, hydrolysis gave triphenylphosphine oxide succinimide and hydrogen bromide,[146] treatment with ethanol gave triphenyl phosphine oxide, succinimide and ethyl bromide.[147]

The conversion of alcohols to halides by the Rydon[148] method is well known. Triphenyl phosphite when treated with methyl iodide, benzyl bromide or benzyl chloride gives a quaternary salt (11) which on treatment with the alcohol gives a second quaternary salt (12) which undergoes the Arbusov reaction to give the required halide.



Recently Lee and Downie,[149,150] having found the Rydon method unsatisfactory for the conversion of certain sensitive hydroxyesters to chloroesters, obtained the chloro compound by heating the alcohol with a tertiary phosphine in carbon tetrachloride at 80° for a short time. They propose a basically similar mechanism.



Although we have not exploited the conversion of alcohols to chlorocompounds with 1-chlorobenzotriazole-triphenylphosphine, ~~with~~ its apparent ease and mildness ~~it~~ suggests that it may well have synthetic possibilities.

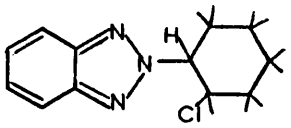
Treatment of 1-chlorobenzotriazole with ammonia in the hope of isolating the hydrochloride of 1-aminobenzotriazole, by analogy with the quaternary salt with triphenylphosphine, gave only ammonium chloride and benzotriazole, suggesting that the 1-chlorobenzotriazole had again oxidised the ammonia.

In view of the commercial importance of 1,1'-dibenzotriazole[151] and the difficulty of its preparation, attempts were made to obtain it from the readily available 1-chlorobenzotriazole. Treatment of 1-chlorobenzotriazole with activated zinc in methylene chloride gave only an amorphous solid, the

infra red of which indicated that it was a zinc salt of benzotriazole. Fusion gave the characteristic zinc oxide residue.

When the sodium salt of benzotriazole was treated with 1-chlorobenzotriazole no reaction occurred although similar reaction of 1-chloroaziridine and 1-lithium aziridine to give 1,1'-bisaziridine has been reported.[152]

When 1-chlorobenzotriazole was allowed to react with cyclohexene the only product isolated, apart from benzotriazole and a variety of carbonyl- and hydroxyl-containing oils, was 2-(2-chlorocyclohexyl)benzotriazole (13). The structure was

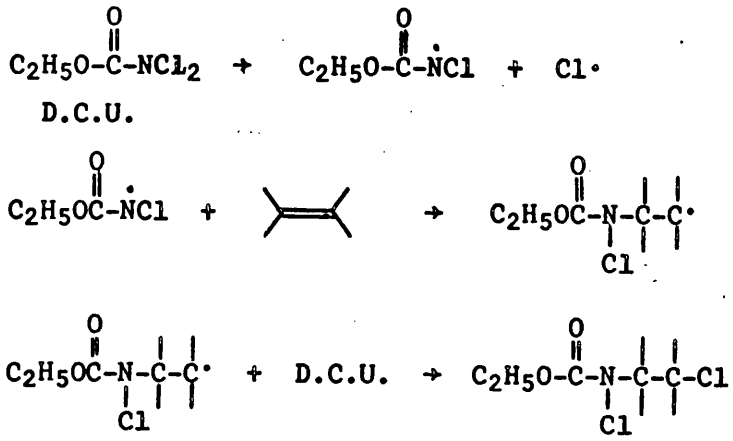


(13)

confirmed by its analysis, mass spectrum and p.m.r. spectrum which showed the characteristic aromatic A_2X_2 system of 2-substituted benzotriazoles.

Swern in attempting to prepare compounds containing C-N bonds directly by the addition of pseudohalogens containing nitrogen to unsaturated systems has used iodine isocyanate,[153,154] nitrosyl acetate,[155] and more recently N,N-dichlorourethan[156] (D.C.U.). D.C.U. with a variety of olefins gave rapid anti-Markovnikov addition to give the β-chlorocarbamate in high yield (60-80%). With cyclohexene the β-chlorocarbamate was formed in lower yield together with allylic chlorination products. The rapid reaction

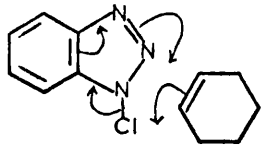
after an induction period, anti-Markovnikov, non-stereospecific addition, and the fact that the yield of urethan increases with the number of allylic hydrogen atoms in the olefin, support the proposed radical mechanism.



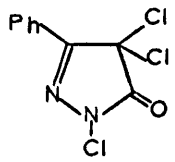
If a radical mechanism involving the benzotriazolyl radical operates in the case of the addition of 1-chlorobenzotriazole to cyclohexene, one would expect the formation of two isomers. Although no 1-(2-chlorocyclohexyl)benzotriazole was isolated this did not preclude its formation since it may have been masked by the larger amounts of cyclohexene decomposition products. However, if in fact no 1-(2-chlorocyclohexyl)-benzotriazole is formed it must mean that the benzotriazolyl radical reacts, surprisingly, only as the 2-benzotriazolyl radical. In all the previous reactions where we have proposed a benzotriazolyl radical, products have been derived by hydrogen abstraction and the isolation of 1-H benzotriazole would of course be explained by the ready rearrangement of 2-H benzotriazole to the 1-H isomer. An ionic reaction should also give two

isomers unless the leaving chlorine sterically directs substitution at the 2-position. On the other hand a concerted mechanism[13a] would explain the exclusive formation of the 2-isomer. Further investigation of this reaction would therefore be desirable.

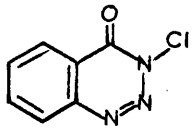
Most positive halogen compounds have the halogen on nitrogen α to at least one carbonyl group. Since the three nitrogen triazole system of 1-chlorobenzotriazole also activates the halogen it was thought that a halogen on a triazole system which is also adjacent to a carbonyl group might be even more reactive. Carpino has reported that the trichloropyrazole (14) vigorously oxidised ethanol to acetaldehyde,[157] therefore the related 3-chloro-1,2,3-benzotriazin-4-one (15) was considered.



(13a)



(14)



(15)

1,2,3-Benzotriazin-4-one was prepared from anthranilamide by diazotisation and ring closure.[158] This was converted quantitatively to the N-chloro-derivative by treatment of the triazinone in aqueous acetic acid with sodium hypochlorite. The structure of 3-chloro-1,2,3-benzotriazinone was supported by analysis and spectral data.

The oxidising properties were shown to be similar to those of 1-chlorobenzotriazole. Thus alcohols were oxidised

slowly in the cold and rapidly on warming to give the aldehyde or ketone and benzotriazinone. In refluxing carbon tetrachloride solution the alcohols were readily oxidised without an initiator and on cooling benzotriazinone crystallised out. However 3-chloro-1,2,3-benzotriazin-4-one did not have any obvious advantage over 1-chlorobenzotriazole.

SECTION IV EXPERIMENTAL

1. Reaction of benzotriazole with chloramine

Benzotriazole (8 g., 67.2 mmole) was stirred overnight with ethereal chloramine (375 ml., 0.2 M solution, 75 mmole). Benzotriazole hydrochloride (5 g., 47.6%) was filtered off and the filtrate was evaporated on to silica gel for chromatography. Elution with 20% ether-petrol gave 1-(1-ethoxyethyl)benzotriazole[62] (i.r., p.m.r.) (2.3 g., 17.7%), as a colourless oil, followed by benzotriazole (2 g., 25%), needles from benzene, m.p. and m.m.p. 94-96°. (Lit., m.p. 100°).

Benzotriazole hydrochloride

Hydrogen chloride was passed into an ethereal solution of benzotriazole and benzotriazole hydrochloride was filtered off. Recrystallisation from ethanol-ether gave colourless needles, m.p. 160-180° (decomp.), readily soluble in water giving an acid solution.

$\nu_{max.}$ 3,300 (broad), 2,300 (broad), 1,775 (broad), 1610, 1395, 1284, 1235, 1116, 1000, 976, 917, 888, 773, 755, 745 $cm.^{-1}$

(Found: C, 47.0; H, 3.7; N, 27.4; Cl, 21.6. Calc. for $C_6H_6N_3Cl$: C, 46.3; H, 3.9; N, 27.0; Cl, 22.8%).

2. Reaction of benzotriazole with chlorine

Chlorine was passed into a solution of benzotriazole (1 g.) in ether until a yellow colour persisted. Benzotriazole hydrochloride (300 mg.) precipitated immediately and on standing

more hydrochloride (400 mg., total 53%) separated. The filtrate, which contained only 1-(1-ethoxyethyl)benzotriazole and benzotriazole (T.L.C.), was washed with 2N sodium hydroxide solution, followed by water, and after drying ($MgSO_4$) was evaporated to give 1-(1-ethoxyethyl)benzotriazole (100 mg., 6.1%).

3. Preparation of 1-chlorobenzotriazole

A. Benzotriazole (10 g.) suspended in carbon tetrachloride was treated with excess of chlorine in the same solvent and the mixture was stirred for 2 hr. Benzotriazole hydrochloride (5 g., 38%) and benzotriazole (3 g., 30%) were filtered off. Evaporation of the filtrate gave impure 1-chlorobenzotriazole (3.5 g., 26%). Five recrystallisations from petrol gave colourless needles, m.p. 103-105°.

$\lambda_{max.}$ 207(log ε 3.84); 252(3.72); 257(3.71); 275 mμ(3.60).

$\nu_{max.}$ 1610, 1588, 1490, 1442, 1255, 1234, 1147, 1060, 1046, 774, 759, 745 $cm.^{-1}$

m/e 155, 153, 127, 125, 119, 91.

(Found: C, 47.2; H, 2.7; N, 27.4. $C_6H_4N_3Cl$ requires: C, 46.9; H, 2.6; N, 27.4%).

B. Sodium hypochlorite solution (50 ml., 2M, 100 mmole) was added dropwise at room temperature to a stirred solution of benzotriazole (10 g., 8 mmole) in aqueous acetic acid (1:1). 1-Chlorobenzotriazole separated immediately and was recrystallised once from methylene chloride-petrol to give the pure compound (13 g., 90%), m.p. 103-105°.

4. Reaction of 1-chlorobenzotriazole with ether

1-Chlorobenzotriazole (850 mg.) was stirred in dry redistilled ether for several hours. After an induction period of approximately 2 hr., benzotriazole hydrochloride (340 mg., 40%) separated and was filtered off. The filtrate was evaporated on to silica gel for chromatography. Elution with 10% ether-petrol gave 1-(1-ethoxyethyl)benzotriazole (52 mg., 5%) followed by benzotriazole (250 mg., 32%).

5. Reaction of 1-chlorobenzotriazole with tetrahydrofuran

1-Chlorobenzotriazole (1 g.) was stirred for several hours in dry redistilled tetrahydrofuran. Benzotriazole hydrochloride (160 mg., 16%) was filtered off and the filtrate was evaporated to dryness and redissolved in ether. After washing with sodium hydroxide solution, followed by water, the ethereal solution was dried ($MgSO_4$) and evaporated to give 1-(2-tetrahydrofuryl)benzotriazole as a slightly discoloured oil (560 mg., 35%). Distillation gave a colourless oil b.p. 150°/~5 mm.

$\nu_{max.}$ 2960, 2940, 2870, 1610, 1490, 1450, 1290, 1274, 1187, 1151, 1141, 1070, 1030, 940, 925, 780, 765, 745 $cm.^{-1}$

τ1.9-2.9 (Complex multiplet, 4H); τ3.5 (broad multiplet 1H); τ6.1 (triplet, 2H, J = 6.5 cp.s.); τ6.9-8.5 (broad multiplet, 4H).

(Found: C, 63.3; H, 5.8; N, 22.1. $C_{10}H_{11}N_3O$ requires: C, 63.5; H, 5.8; N, 22.2%).

6. Reaction of 1-chlorobenzotriazole with potassium hydroxide.

1-Chlorobenzotriazole (500 mg.) was dissolved in potassium hydroxide solution (20ml., 2N). Neutralisation of the solution gave recovered 1-chlorobenzotriazole (405 mg., 81%).

1-Chlorobenzotriazole (400 mg.) was refluxed in potassium hydroxide solution (10%) for 5 hr. Acidification gave recovered 1-chlorobenzotriazole (140 mg., 35%) which was filtered off. Extraction of the filtrate with ether gave impure benzotriazole (130 mg., 42%). No 1-hydroxybenzotriazole was detected.

7. Reaction of 1-chlorobenzotriazole with sodium methoxide.

1-Chlorobenzotriazole (1.53 g., 10 mmole) was suspended in dry methanol and sodium methoxide solution (15 ml. of solution containing sodium (1 g.) in methanol (50 ml.), 13.1 mmole) was added. The 1-chlorobenzotriazole dissolved immediately and sodium chloride was precipitated in an exothermic reaction. T.L.C. indicated some unchanged 1-chlorobenzotriazole and further sodium methoxide solution (15 ml.) was added. Sodium chloride was filtered off and the mother liquor was concentrated, acidified, and extracted with ether to give benzotriazole (800 mg., 67%). No 1-methoxybenzotriazole was observed.

8. Oxidations with 1-chlorobenzotriazole

A. Alcohols

Addition of cold ethanolic 1-chlorobenzotriazole to

aqueous potassium iodide caused the liberation of iodine. Addition of warmed ethanolic 1-chlorobenzotriazole failed to give this reaction.

a) Oxidation of the pure alcohol.

Benzyl alcohol.

1-Chlorobenzotriazole (306 mg., 2 mmole) was warmed in benzyl alcohol (10 ml.). The colour of the solution darkened and chlorine was evolved. A solution of 2,4-dinitrophenylhydrazine was added to give an immediate precipitate of benzaldehyde-2,4-dinitrophenylhydrazone (470 mg., 81%), m.p. 247°. (Lit., m.p. 247°).

Isopropanol.

Similar oxidation of isopropanol gave acetone estimated as its 2,4-dinitrophenylhydrazone (44%) m.p. 128° (Lit., m.p. 128°).

b) Oxidation of the alcohol in carbon tetrachloride solution

1-Chlorobenzotriazole (1.5 g., 10 mmole) and a slight excess of the alcohol were warmed in carbon tetrachloride solution (25 ml.). The colour of the solution darkened, a little chlorine was evolved, and an immediate precipitate of benzotriazole hydrochloride separated. This was filtered off and the filtrate was treated with 2,4-dinitrophenylhydrazine solution to give the 2,4-dinitrophenylhydrazone of the carbonyl compound, as follows:

	Benzotriazole hydrochloride	Carbonyl Compound
Benzyl alcohol	47%	60%
Isopropanol	73%	30%
Cyclohexanol	66%	46%

Further oxidations were carried out in the manner given below for hydrazobenzene, only variations in detail are described thereafter.

B. Hydrazobenzene

Hydrazobenzene was recrystallised from ethanol to give colourless plates, m.p. 126-127° (Lit.,m.p. 126-127°).

1-Chlorobenzotriazole (306 mg., 2 mmole) in methylene chloride was added to hydrazobenzene (368 mg., 2 mmole) in the same solvent. Benzotriazole hydrochloride (220 mg., 70%) separated immediately and was filtered off. The filtrate was washed with 2N sodium hydroxide solution, then water and,after drying ($MgSO_4$), evaporation of the solvent gave azobenzene (325 mg., 89%), m.p. and m.m.p. 66-67° (Lit.,m.p. 68°).

C. Dimethyl hydrazodicarboxylate

Benzotriazole hydrochloride crystallised slowly. The filtrate contained dimethyl azodicarboxylate and a trace of benzotriazole (T.L.C.).

D. 4,5-Diphenyl-3-pyrazolidinone

4,5-Diphenyl-3-pyrazolidinone[142] (238 mg., 1 mmole) and

1-chlorobenzotriazole (154 mg., 1mmole) gave benzotriazole hydrochloride (110 mg., 70%). The filtrate was evaporated on to basic alumina and chromatographed. Elution with petrol gave trans-stilbene (125 mg., 75%) which crystallised from ethanol m.p. and m.m.p. 124° (Lit., m.p. 124°).

E. 1-Amino-4,5-diphenyltriazole

1-Amino-4,5-diphenyltriazole (118 mg., 0.5 mmole) and 1-chlorobenzotriazole (80 mg., 0.5 mmole) gave benzotriazole hydrochloride (60 mg., 80%). The filtrate was evaporated on to basic alumina for chromatography. Elution with petrol gave diphenylacetylene (71 mg., 75%), m.p. and m.m.p. 61-62° (Lit., m.p. 62.5°).

F. 1-Aminobenzotriazole

1-Aminobenzotriazole (50 mg., 0.37 mmole) was treated with 1-chlorobenzotriazole (120 mg., 0.75 mmole) in methylene chloride. The resulting solution was made up to 5 ml. and examined by gas-liquid chromatography using an R6 Gas Chromatograph fitted with a 2 metre x ¼" O.D. 10% Carbowax 1500 on 90/110 Celite column maintained at 130°. Comparison with standard solutions of chlorobenzene and o-dichlorobenzene indicated the presence of both compounds (19%) and (44%) respectively.

G. Phenylhydroxylamine

Phenylhydroxylamine (218 mg., 2 mmole) and 1-chlorobenzotriazole (306 mg., 2 mmole) gave, on mixing in methylene

chloride, an immediate blue colour and a precipitate of benzotriazole hydrochloride (216 mg., 70%). The filtrate contained nitrosobenzene and a trace of benzotriazole only (T.L.C.).

9. Reaction of 1-Chlorobenzotriazole with Triphenylphosphine

1-Chlorobenzotriazole (1.53 g., 10 mmole) in dry methylene chloride was added to triphenylphosphine (2.62 g., 10 mmole) in the same solvent. Heat was evolved and a transient red colour, fading to yellow, was observed. On the addition of dry ether a colourless oil separated. Moist ether caused the oil to dissolve with the immediate precipitation of benzotriazole hydrochloride (1.4 g., 91%) which was filtered off. The filtrate was washed with base, water, and then dried ($MgSO_4$). Concentration, followed by the addition of petrol, gave triphenylphosphine oxide (2.3 g., 83%). m.p. and m.m.p. 155-156° (Lit., m.p. 156°).
1-Chlorobenzotriazole (1.53 g., 10 mmole) and triphenylphosphine (2.62 g., 10 mmole) were mixed in methylene chloride and the yellow colour was discharged by the addition of dry methanol. T.L.C. indicated only triphenylphosphine oxide and benzotriazole; in particular no 1-methyl- or 1-methoxy-benzotriazole could be detected. The solution was washed with water which then showed neutral pH. Benzotriazole (600 mg., 50%) was removed from the solution by base extraction. The solution was then dried ($MgSO_4$), concentrated and the addition of petrol gave triphenylphosphine oxide (2.4 g., 86%) m.p. 156°.

The triphenylphosphine/1-chlorobenzotriazole complex

was decomposed by the addition of benzyl alcohol. The solution was examined by gas-liquid chromatography using a Perkin Elmer F11 instrument fitted with a Carbowax 1500 on Celite column. Benzyl chloride was foundto be present in the solution, by comparison with an authentic specimen.

10. Reaction of 1-chlorobenzotriazole with ammonia

1-Chlorobenzotriazole (1 g.) in dry methylene chloride was cooled to 0° and dry ammonia was bubbled through slowly. Ammonium chloride separated and was filtered off. The filtrate was evaporated under reduced pressure and the residue was extracted with ether to give benzotriazole (600 mg., 77%).

11. Reaction of 1-chlorobenzotriazole with zinc.

1-Chlorobenzotriazole was stirred in methylene chloride with an excess of zinc. A white solid was gradually deposited and was separated by decantation from the heavier zinc. The amorphous powder did not melt below 360° and could not be crystallised. Ignition gave the characteristic zinc oxide residue. $\nu_{max.}$ 1500, 1278, 1210, 1150, 986, 937, 789, 775, 755, 741 $cm.^{-1}$

12. Treatment of 1-Chlorobenzotriazole with the sodium salt of Benzotriazole

1-Chlorobenzotriazole was stirred with a suspension of the sodium salt of benzotriazole (equimolar quantities) in methylene chloride. No reaction was observed after one week.

13. Reaction of 1-Chlorobenzotriazole with cyclohexene

1-Chlorobenzotriazole (1 g.) was stirred in cyclohexene

(40 ml.) overnight. The mixture was then evaporated on to basic alumina and chromatographed. Elution with 25% ether/petrol gave 2-(2-chlorocyclohexyl)benzotriazole (154 mg., 10%), which crystallised from petrol as colourless needles, m.p. 90°.

$\lambda_{max.}$ 211 (log ε 4.20); 272(4.04); 277(4.07); 284 mμ(4.00).

$\nu_{max.}$ 1320, 1277, 749, 741, 732 cm.$^{-1}$

τ2.2 (quartet, 2H, J = 6.5 c.p.s., 3 c.p.s.); τ2.74 (quartet, 2H, J = 6.5 c.p.s., 3 c.p.s.); τ5.2 (broad unresolved multiplet, 2H); τ7.35-8.85 (Complex multiplet, 8H).

m/e 237, 235, 200, 120.

(Found: C, 61.3; H, 6.0. $C_{12}H_{14}ClN_3$ requires: C, 61.1; H, 6.1%).

More polar eluents gave a variety of oils which showed hydroxyl and carbonyl absorptions in their i.r. spectra.

14. 3-Chloro-1,2,3-benzotriazin-4-one

Aqueous sodium hypochlorite (20 ml., 2.2 M, 44 mmole) was added dropwise to 1,2,3-benzotriazin-4-one[158] (4 g., 30 mmole) in aqueous acetic acid. Water was added and 2-chloro-1,2,3-benzotriazin-4-one crystallised. Recrystallisation from methylene chloride/petrol gave colourless needles (4 g., 81%), m.p. 110° (decomp.).

$\nu_{max.}$ 1690 (broad); 1329, 1285, 1240, 1131, 985, 937, 852, 785, 773, 730, 709 cm.$^{-1}$

(Found: C, 46.0; H, 2.2; N, 23.1. $C_7H_4ClN_3O$ requires: C, 46.3; H, 2.2; N, 23.1%).

15. Oxidations with 3-chloro-1,2,3-benzotriazin-4-one

i) 3-Chlorobenzotriazinone (900 mg.) and benzyl alcohol (500 mg.) were refluxed in carbon tetrachloride under nitrogen for 30 minutes. On cooling benzotriazinone (650 mg., 85%) m.p. and m.m.p. 213-214° (Lit., m.p. 212-213°) crystallised. The filtrate was treated with 2,4-dinitrophenylhydrazine to give benzaldehyde 2,4-dinitrophenylhydrazone (538 mg. 60%), m.p. 247° (Lit., m.p. 247°).

ii) 3-Chlorobenzotriazinone was warmed gently in the alcohol. A rapid reaction occurred, and on cooling benzotriazinone, m.p. and m.m.p. 213-4° (Lit., m.p. 212-213°) separated. Addition of 2,4-dinitrophenylhydrazine to the filtrate gave the 2,4-dinitrophenyl-hydrazone of the carbonyl compound:

Ethanol	-	74% triazinone
Isopropanol	30% acetone	83% triazinone
Benzyl alcohol	70% benzaldehyde	80% triazinone

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