GAS PHASE REACTIONS OF AMINYL AND RELATED RADICALS

by

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ABSTRACT

Flash vacuum pyrolysis of *N*-alkyl-*N*-allylanilines gives imines by a free radical process with initial cleavage of the allyl group followed by loss of a hydrogen atom or alkyl radical from the α-carbon of the alkyl group. *N*-Allyl-*N*,*N*-dialkylamines also give rise to imines on pyrolysis but by a concerted retro-ene process. *N*-Alkyl-*N*-propargylanilines decompose thermally by a retro-ene process, resulting in different products from the corresponding *N*-allyl compounds.

N-Allylanilines and *O*-allylphenols have been used to generate anilino and/or phenoxy radicals with 2-alkylthio, 2-alkoxy and 2-dialkylamino substituents. The corresponding 2-dialkylamino benzyl radical was generated by pyrolysis of its phenyl ether. Intramolecular rearrangement was observed in all cases, with hydrogen transfer from the 2-substituent to the initial radical site thought to be the first step. Some direct rearrangement to give aldehydes from the 2-alkoxy compounds and styrenes from the 2-alkylthio derivatives was observed. The other main reaction of these radicals was cyclisation followed by aromatisation to give five membered heterocycles. However no heterocycles containing both oxygen and sulphur were observed. Some products are thought to arise from initial cleavage of the 2-alkyl rather than the allyl group. Almost complete loss of nitrogen from the 2-dialkylamino compounds occurred to give products derived from the corresponding aryl-2-alkyl radical.

N-Allylanilines with adjacent aryl substituents were pyrolysed. With 2-benzyl, 2-benzoyl or 2-anilino substituents the reactions were reasonably clean giving rise to good yields

of the appropriate cyclisation product. With 2-aryloxy and 2-thioaryloxy substituents the products in both cases resulted from a process involving a spirodienyl radical. Surprisingly in the sulphur case the major product was a dibenzothiophene.

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INTRODUCTION

A. Flash Vacuum Pyrolysis

Flash vacuum pyrolysis is a convenient method of carrying out many different high temperature reactions. It involves vaporisation of the substrate from an inlet system into a silica furnace tube, which can be maintained at temperatures up to 1000°C. The apparatus is kept under a vacuum of 10^{-2}-10^{-3} Torr and the products are collected in a liquid nitrogen trap situated at the exit point of the furnace. A diagram of the apparatus and further details of the method may be found in the experimental section of this thesis.

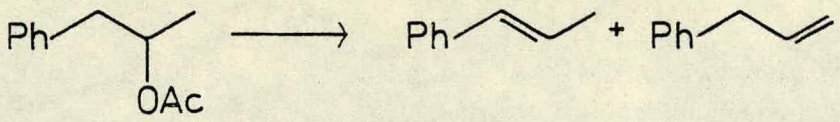
This technique ensures that the material has only a very short contact time in the hot zone - estimated to be in the order of 1-10 milliseconds. This, coupled with the very low concentration of molecules in the hot zone at any one time, tends to result in intramolecular rather than intermolecular reactions taking place, although radical coupling reactions are observed. There have been many reviews on flash vacuum pyrolysis, the most comprehensive being Brown's recent monograph[1]. General reviews on the subject include those by de Mayo[2], Seybold[3], Hageman and Wiersum[4], Wentrup[5], Vogtle and Rossa[6], Schaden[7] and Wiersum[8-10].

There are several types of reaction that may occur during flash vacuum pyrolysis. These include generation of transient species such as free radicals, arynes, carbenes, nitrenes etc, elimination reactions and fragmentation reactions. Any of these may be followed by thermal rearrangement of the resulting

molecule. The subject of thermal isomerisation of hydrocarbons has been well documented by Gajewski.[11]

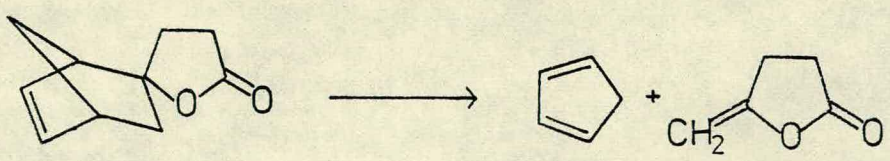
The two major classes of reaction undergone during flash vacuum pyrolysis are concerted reactions and those involving loss of a small molecule to give either carbene type species or diradicals.

Much work has been carried out on pyrolytic cis elimination reactions, mainly involving esters, and this subject has been reviewed by DePuy and King,[12] Maccoll[13] and Smith and Kelly.[14] Pyrolysis of esters generally results in loss of the ester linkage to give good yields of alkenes by a concerted retro-ene process (Scheme 1).[15]



Scheme 1

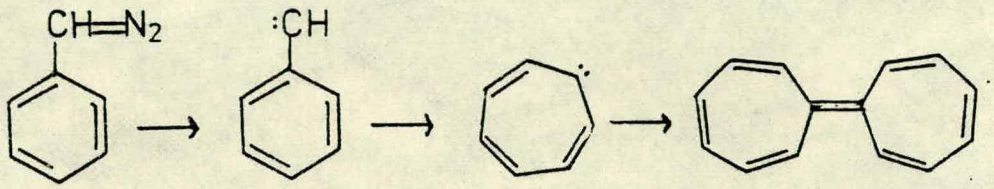
The Retro-Diels Alder reaction may also occur during flash vacuum pyrolysis (e.g. scheme 2).[16]



Scheme 2

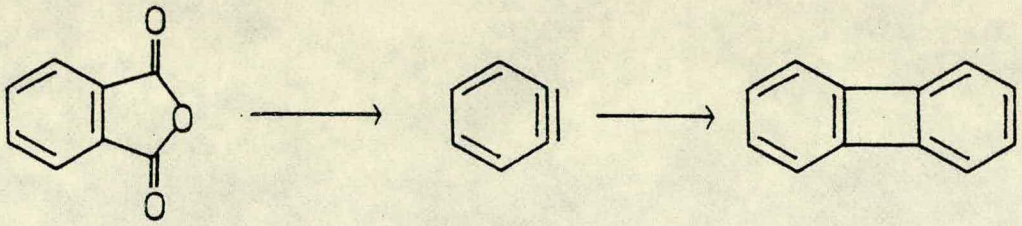
Generation of transient species by flash vacuum pyrolysis is useful in that intramolecular reactions tend to occur and the possibility of the reactive species interacting with any

coordinated species or with the solvent, as may occur in solution, is ruled out. A typical reaction involving formation of a carbene is shown in scheme 3.[17]



Scheme 3

Elimination of small molecules from cyclic structures can also take place (scheme 4).[18,19]



Scheme 4

Although the majority of flash vacuum pyrolyses involve concerted or diradical mechanisms, there is a third class of reactions, which involves the formation of radicals.

Formation of radicals using flash vacuum pyrolysis forms the major part of this thesis and the rest of this chapter reviews methods of generating these radicals and the various types of reactions which they undergo. Only thermal gas phase reactions involving flow systems are considered; however not all the reactions studied have been carried out under vacuum.

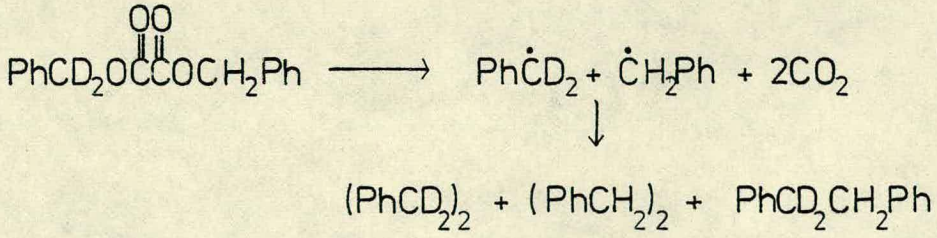
B. Generation of Free Radicals

1. Carbon Centred Radicals

The generation and reactions of carbon radicals has been reviewed by Kochi;[20] however few of these involve pyrolytic generation of the radical.

Pyrolytic generation of carbon centred radicals has been carried out using many different precursors. These include oxalates,[21-28] sulphones,[22,29] selenides,[30] ethers,[22] esters,[31,32] phosph(v)oles[22] and nitro compounds.[33-36] Carbon diradicals are formed by fragmentation of cyclic structures[1,37-41] and these are discussed in more detail at the end of this section.

Oxalates and sulphones both afford clean routes to benzyl radicals, the by-products being CO_2 and SO_2, respectively. Oxalates have the advantage over sulphones in that their preparation is generally easier. Pyrolysis of several benzyl oxalates has been carried out by Trahanovsky and his co-workers. Yields of bibenzyls from 40-90% were obtained. The involvement of benzyl radicals was confirmed by the pyrolysis of unsymmetrical benzyl oxalates.[21] The mixture of bibenzyls expected from random coupling reactions of the radicals was found (Scheme 5).



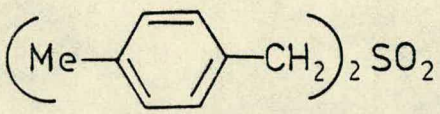
Scheme 5

Pyrolysis of oxalates has also been used to generate radicals for the measurement of ionisation potentials.[28]

A similar process to Trahanovsky's was observed on pyrolysis of dibenzylsulphones by Leonard.[29] Again the mechanism involves cleavage to benzyl radicals, this time with elimination of SO_2. Further evidence for this mechanism was obtained by Husband *et al.*,[22] who found that on co-pyrolysis of the sulphones (1) and (2), the expected mixture of coupled products was obtained.

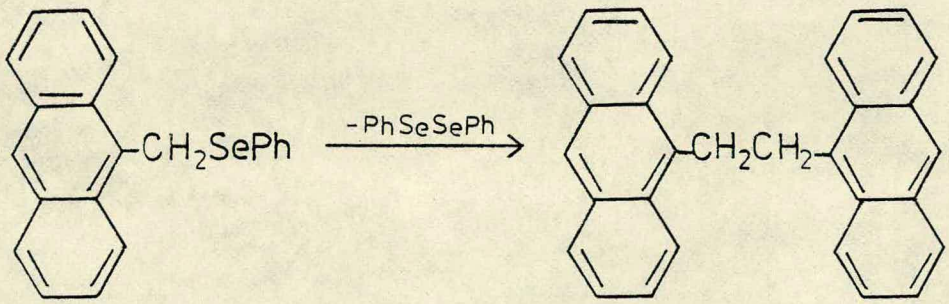
$(PhCH_2)_2SO_2$

(1)



(2)

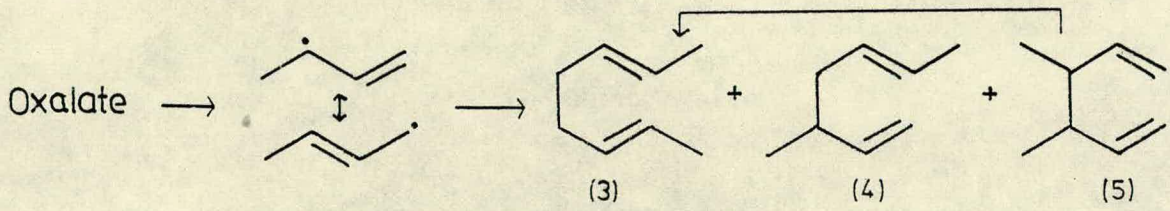
Bibenzyls have also been formed in the gas phase from arylmethyl phenyl selenides[30] (e.g. Scheme 6). Although unpleasant to handle these precursors have one advantage in that derivatives with polar groups on the ring system tend to be more readily vaporised than the corresponding oxalates or sulphones, which may decompose in the inlet system.



Scheme 6

Trahanovsky has studied the pyrolysis of di-allyl, disubstituted allyl and other related radicals. Diallyl oxalate gives biallyl in yields of 40-60%, via allyl radicals.[23] Allyl radicals generated by flash vacuum pyrolysis have been isolated in an argon matrix and identified spectroscopically by Maier *et al.*[42]

If a similar mechanism to that of the benzyl radicals is in operation then di-*trans* crotyl oxalate would be expected to give the radical coupling products shown in scheme 7.

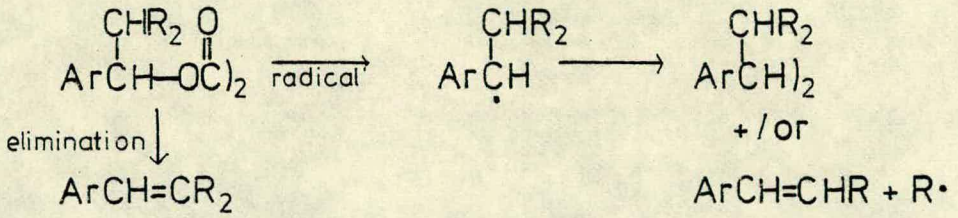


Scheme 7

However, only products (3) and (4) are formed in equal quantities. It is suggested that (5), after formation is converted to (3) which is more stable. Therefore statistical coupling of the initially formed radicals occurs to give the olefins in a 1:2:1 ratio.

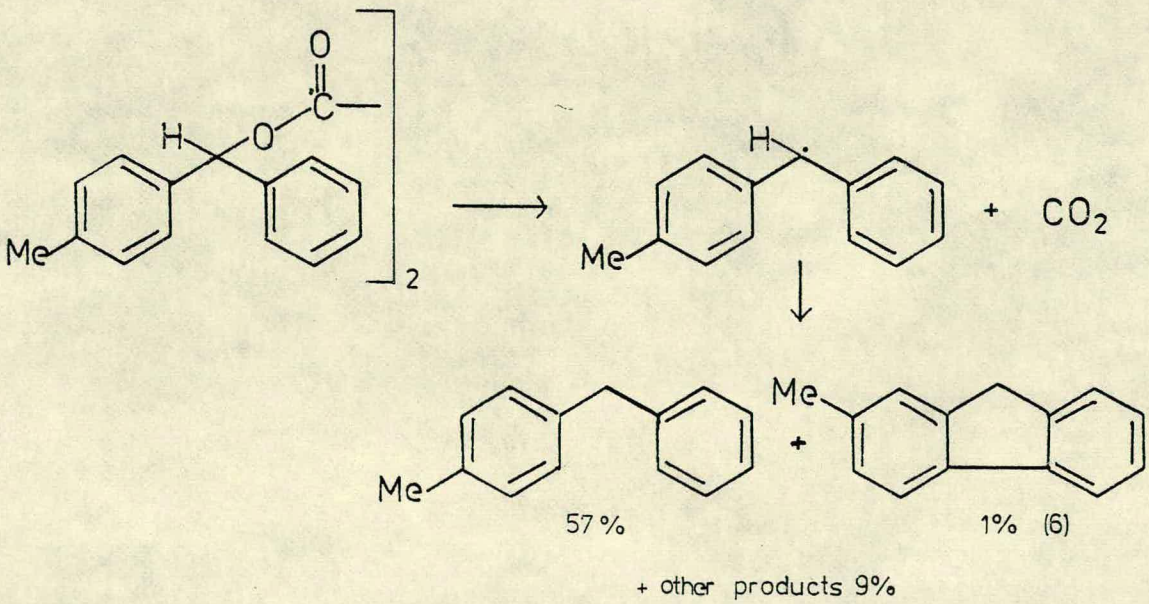
In all the examples so far coupling has been the major reaction undergone by the radicals. On pyrolysis of di(α-substituted) benzyl oxalates Trahanovsky found that concerted elimination was the dominant reaction.[24] Some formation of an α-alkyl substituted benzyl radical does occur but coupling only takes place if R is a methyl group. If R is an ethyl or isopropyl group then β-scission is the main reaction of the alkyl radical (Scheme 8). It has been found that, in general, during flash vacuum pyrolysis loss of an alkyl radical takes

precedence over loss of a hydrogen atom.[22] This is partially due to the high heat of formation of a hydrogen atom and also because the C-C bond is relatively weak compared to the C-H bond.



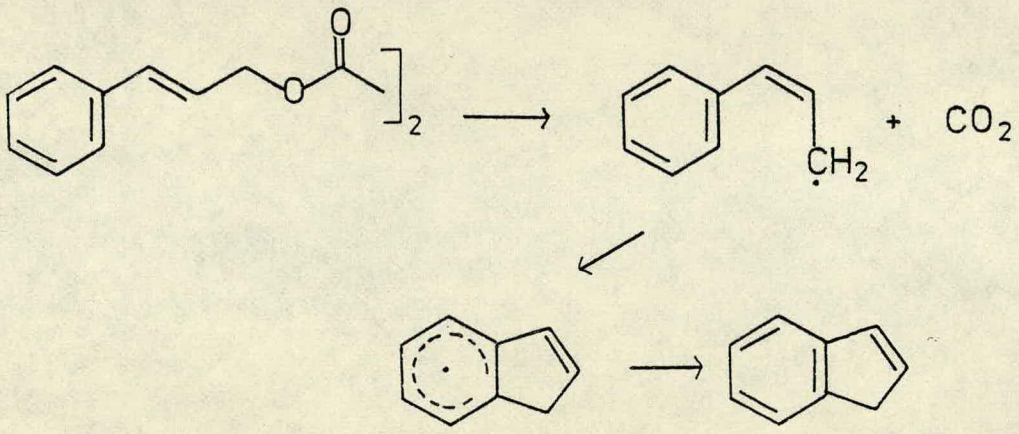
Scheme 8

A further example of pyrolysis of a substituted benzyl oxalate is that of bis[phenyl(*p*-tolyl)methyl] oxalate by Lehr and Wilson.[25] Various radical derived products were obtained, but Lehr also obtained (6) which must be formed by a carbene rearrangement mechanism (scheme 9). He goes on to suggest that several of the minor products in previously reported oxalate pyrolyses may arise from carbene rather than radical pathways.



Scheme 9

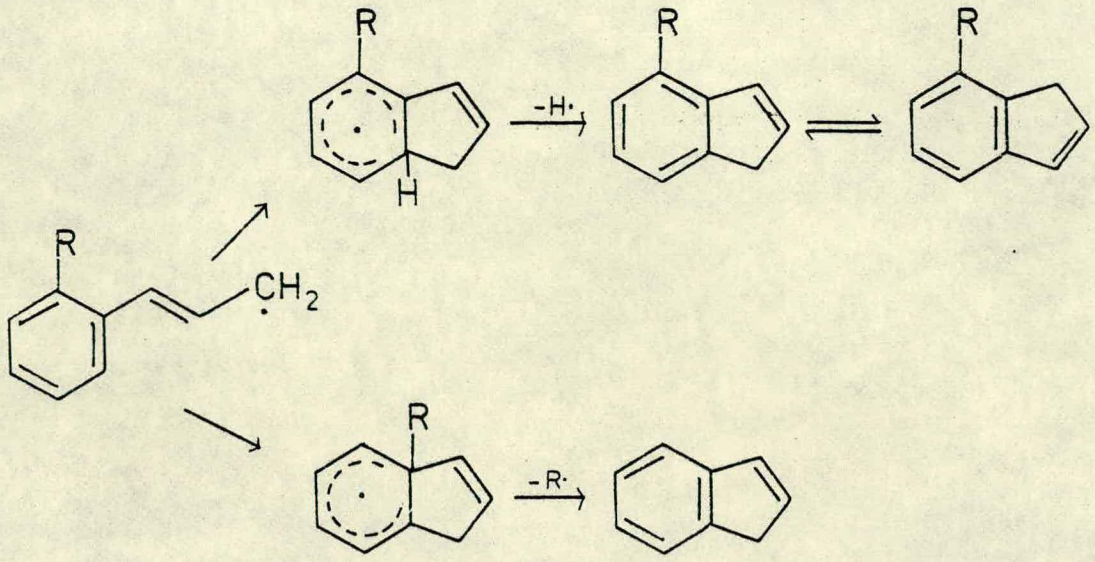
Most of the above examples involve intermolecular reactions, however, as would be expected, there are many carbon-centred radicals which undergo intramolecular reactions. Again much of this work has been carried out by Trahanovsky. On pyrolysis of di-*trans*-cinnamyl oxalate[23,26] the major product was indene, indicating that cyclisation of the cinnamyl radical is favoured over coupling. Minor products were *trans*-β-methylstyrene and allylbenzene formed by hydrogen capture of the cinnamyl radical and traces of toluene and styrene. The proposed mechanism for the formation of indene is shown in scheme 10.



Scheme 10

The mechanism of this reaction has been further investigated by the pyrolysis of *o*-methyl- and *o*-trifluoromethyl-cinnamyl oxalates.[27] There are now two possible sites for cyclisation to occur at and these give rise to different products (scheme 11).

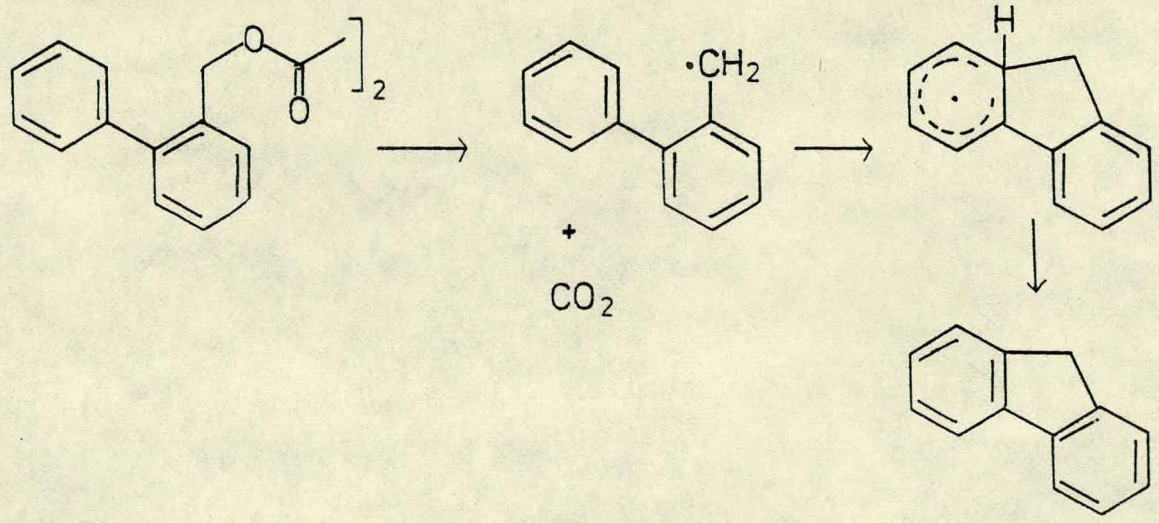
It was found that the ratio of products was very dependent on the substituent R. When R is a methyl group, a 23% yield



Scheme 11

of indene and only a 12% yield of 4- and 7-methylindenes was found. However when R is a trifluoromethyl group no indene was detected and a 59% yield of 4- and 7-methylindenes was determined. This is probably due to the fact that a trifluoromethyl radical is less stable than a methyl radical.

Several other *o*-substituted benzyl oxalates have been pyrolysed, all of which undergo similar free radical cyclisation reactions. Di-*o*-phenylbenzyl oxalate gives fluorene.[23,26] (Scheme 12).

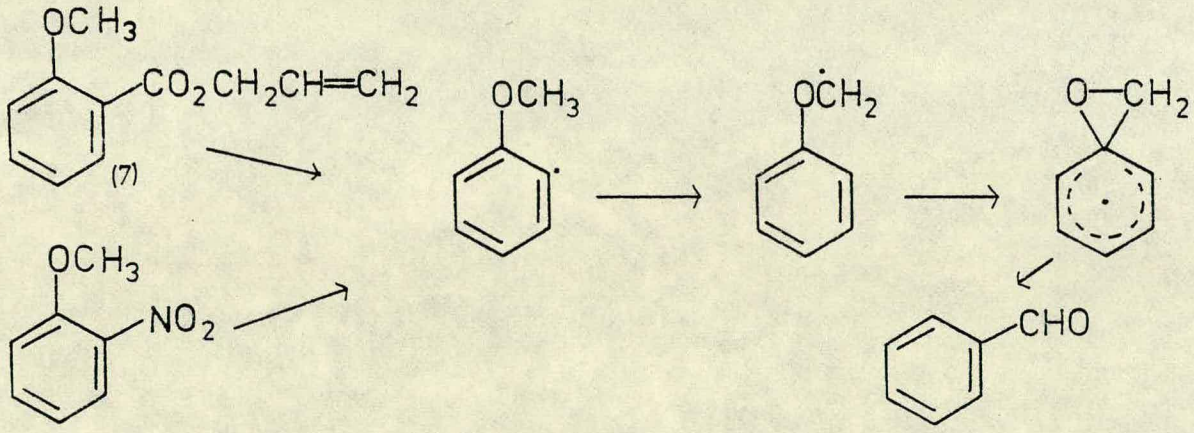


Scheme 12

Similarly di-*o*-phenoxybenzyl oxalate gives xanthene and di-*o*-benzylbenzyloxalate gives 9,10-dihydroanthracene.[23] The driving force for these reactions is the formation of conjugated systems and it is suggested that the hydrogen atoms lost are transferred to polymeric material on the furnace tube.

The above examples of radical cyclisation all involve addition of the initially generated radical to a π-system. However, when adjacent alkyl groups are present cyclisation is not possible. Instead hydrogen transfer, followed by rearrangement takes place.

It was found by Marty and de Mayo[31] that pyrolysis of nitroanisole, or the allyl ester (7), gave benzaldehyde as the major product. The mechanism proposed is shown in scheme 13.

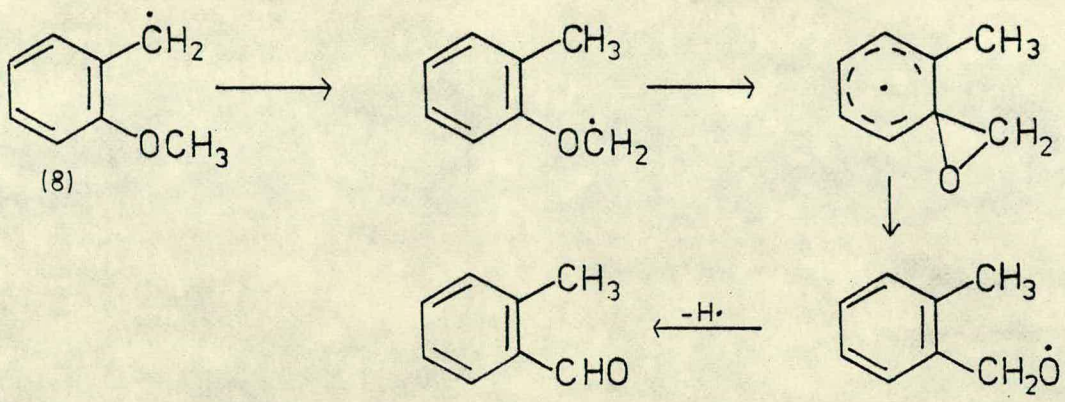


Scheme 13

Rearrangement to the aldehyde must be rapid as no anisole is formed. The ester (7) is an unusual choice of precursor as no previous pyrolyses of compounds of this type had been reported.

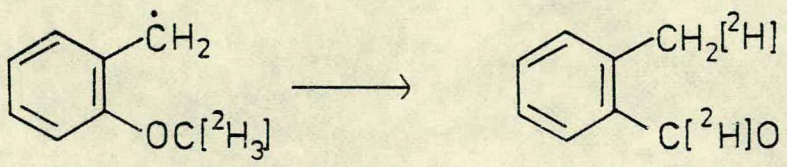
Further work on similar rearrangements has been carried out by Husband *et al.*[22] The intramolecular reactions of *o*-alkoxy- and *o*-alkylthio benzyl radicals, generated from

phosph(v)oles, ethers or sulphones, were studied. *o*-Tolualdehyde was obtained from the benzyl radical (8). Formation of this product can be rationalised by a scheme similar to that of Marty and de Mayo (scheme 14).



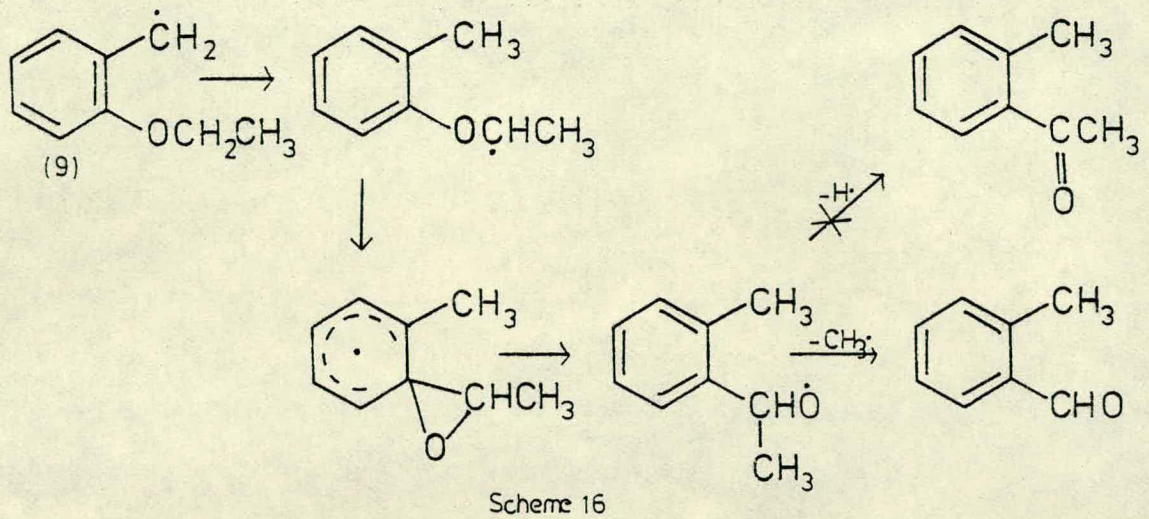
Scheme 14

Further evidence for this mechanism was obtained by generating the 2-[$^2H_3$]-methoxybenzyl radical. A study of the crude pyrolysate by ^2H n.m.r. spectroscopy showed one deuterium atom present in the aldehyde function and one in the methyl group (Scheme 15).



Scheme 15

Also, on generation of the *o*-ethoxybenzyl radical (9), the product formed is *o*-tolualdehyde not acetophenone (scheme 16).

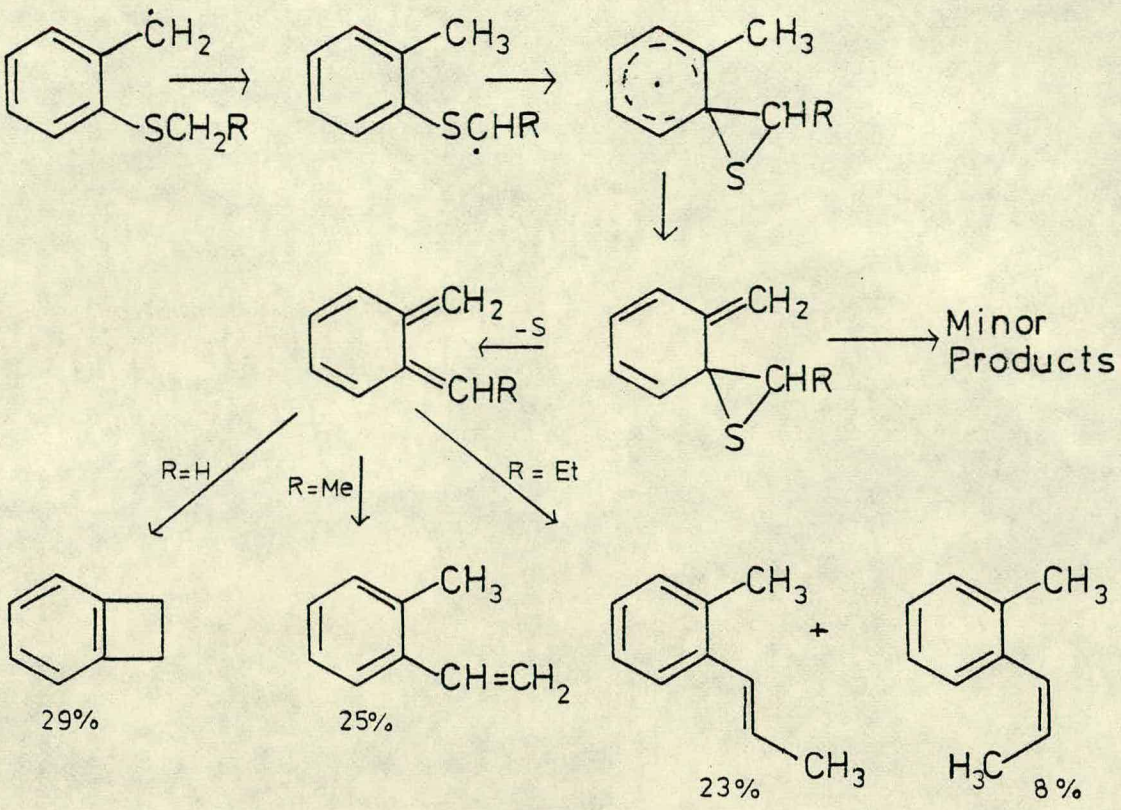


Scheme 16

In the final stage of this reaction a methyl radical, rather than a hydrogen atom, is lost. It has been found that, in general, in the gas phase loss of a methyl radical takes precedence over loss of a hydrogen atom.[43]

It was hoped that this intramolecular reaction process could be applied to the synthesis of thioaldehydes. However the pyrolysates were much more complex than with the alkoxy derivatives and neither thioaldehydes, their trimers or radical coupling products were detected. The major volatile products were hydrocarbons, formed via an intermediate spiro-episulphide. The proposed pathway for the formation of the major products is shown in scheme 17.

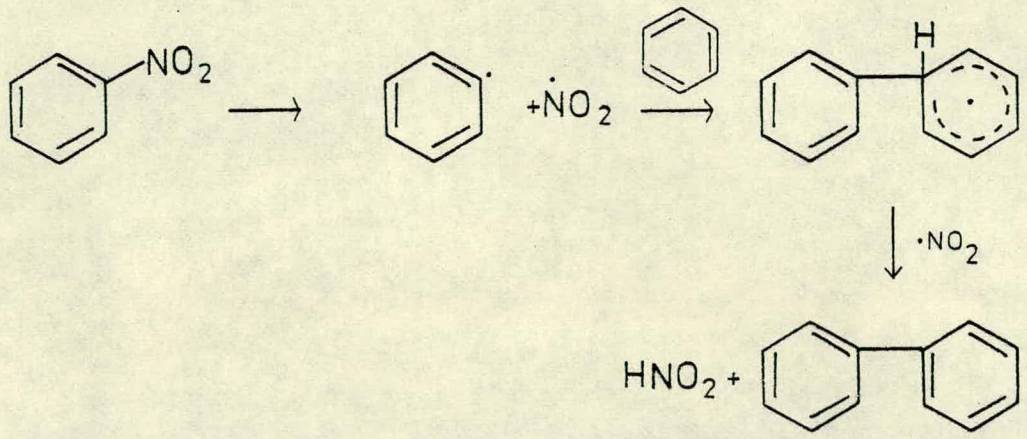
A reaction scheme such as this can be used to explain some of the results obtained in this thesis and this scheme is further discussed and expanded in the discussion section.



Scheme 17

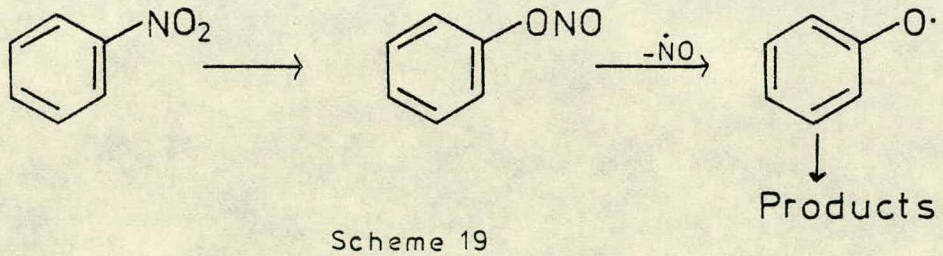
Work on the generation of aromatic radicals by pyrolysis of nitro compounds has been carried out by several groups. Marty and de Mayo[31] used *o*-nitroanisole to generate an aryl radical (scheme 13). Earlier work by Fields and Meyerson[33,34] had shown that the nitroarene bond in aromatic nitro compounds breaks above 400°C to give aromatic radicals. It was thought that this could be used as a method of arylating aromatic and heterocyclic compounds by co-pyrolysis of aromatics and nitro-aromatics (scheme 18).

However it seems unlikely that this process is of any synthetic value, as pyrolysis of nitrobenzene alone gave sixteen different products, the three major ones being phenol, biphenyl and dibenzofuran. The biphenyl is formed by dimerisation of phenyl radicals, which appears to be their major reaction as



Scheme 18

very little benzene is formed. The mechanism proposed for the formation of phenol and dibenzofuran is slightly different as rearrangement of the nitro group to a nitrite group and subsequent loss of •NO to give a phenoxy radical must occur (scheme 19). This type of reaction is discussed in more detail in the section on oxygen radicals.

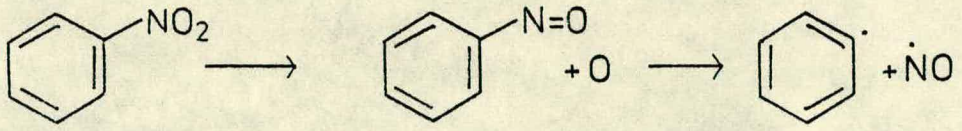


Scheme 19

Pyrolysis of nitrobenzene with benzene and d^6-benzene also led to a wide variety of products.

Further work on the pyrolysis of aromatic nitro compounds has been carried out by Hand *et al.*[35] using a pyrolyser coupled directly to a g.c./m.s. system. Several products derived from phenyl radicals were detected but no evidence supporting direct fission to phenyl and nitro radicals was found. A similar set of products was found on pyrolysis of nitrosobenzene and

the following mechanism was suggested (scheme 20). No phenol, the major product in Field and Meyersons' pyrolysis, was detected under these conditions.



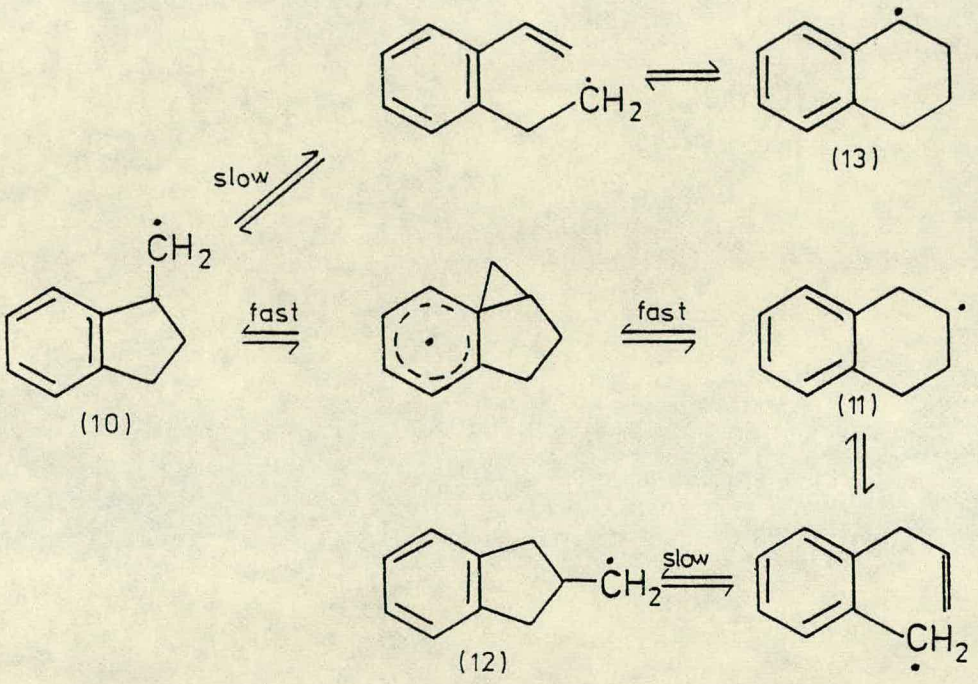
Scheme 20

More recently, McCarthy and O'Brien[36] pyrolysed nitrobenzene in a flow system and obtained products similar to those found by Fields and Meyerson. In contrast to the previous two studies some NO_2 was detected, though this could arise from a secondary rather than a primary process. The authors suggest that consideration should still be given to the possibility of direct arene-nitrogen bond cleavage.

Another type of reaction undergone by carbon radicals is ring expansion or contraction. Work has been carried out by various groups on radicals derived from indans,[32] tetralins[32,44] and heterocycles such as indoles[45] and pyrroles.[46]

In a study related to the thermal production of radicals during the dissolution of coal, Franz and Cannaloni investigated radicals (10) to (13) formed by flash vacuum pyrolysis of the t-butyl peresters of tetralins and methylindans.[32] The use of these esters results in the required alkyl radical being generated in the presence of methyl radicals from the t-butoxy group. The products formed resulted, in general, from initial decomposition of the ester to give an alkyl radical, which could then rearrange. The reaction is

terminated by the alkyl radical coupling either with another alkyl radical, a hydrogen atom or a methyl radical. Scheme 21 shows the possible interactions between the various tetralin and methylindan radicals. In general the major products from any one of the four initial precursors are tetralin, dihydronaphthalenes and methyltetralin, although the product distribution depends to some extent on the substrate.



Scheme 21

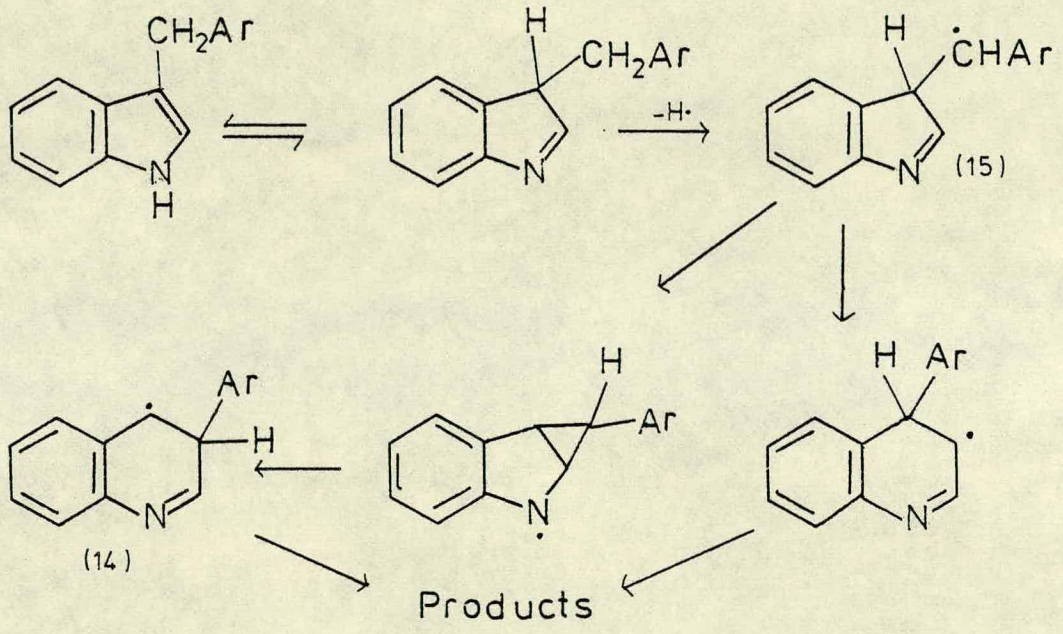
The product distribution from precursors to (10) and (11) is similar, indicating that interconversion between the two is rapid relative to radical depletion reactions. However, with radicals (12) and (13) β-scission is a relatively slow process and product distributions are different from (10) and (11).

These results show that the radical induced isomerisation from tetralin to methylindan occurs readily by a reverse 1,2-aryl migration from (11) to (10).

In a related study Trahanovsky and Swenson[44] pyrolysed

tetralin and various mono- and di-alkyltetralins. They obtained indene as one of the products, presumably by a similar mechanism to that described above.

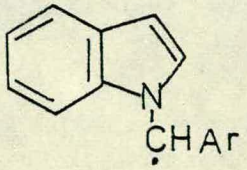
Ring expansion via free radicals has also been observed by Patterson *et al*[45] in the formation of quinolines from benzyl indoles. The proposed mechanism is shown in scheme 22. It is interesting to note the initial loss of a hydrogen atom, as it would be expected that the more stable benzyl radical would be cleaved.



Scheme 22

The radical (14) could also be formed by β-scission of (15) in a similar manner to the conversion of (10) to (13) (scheme 21).

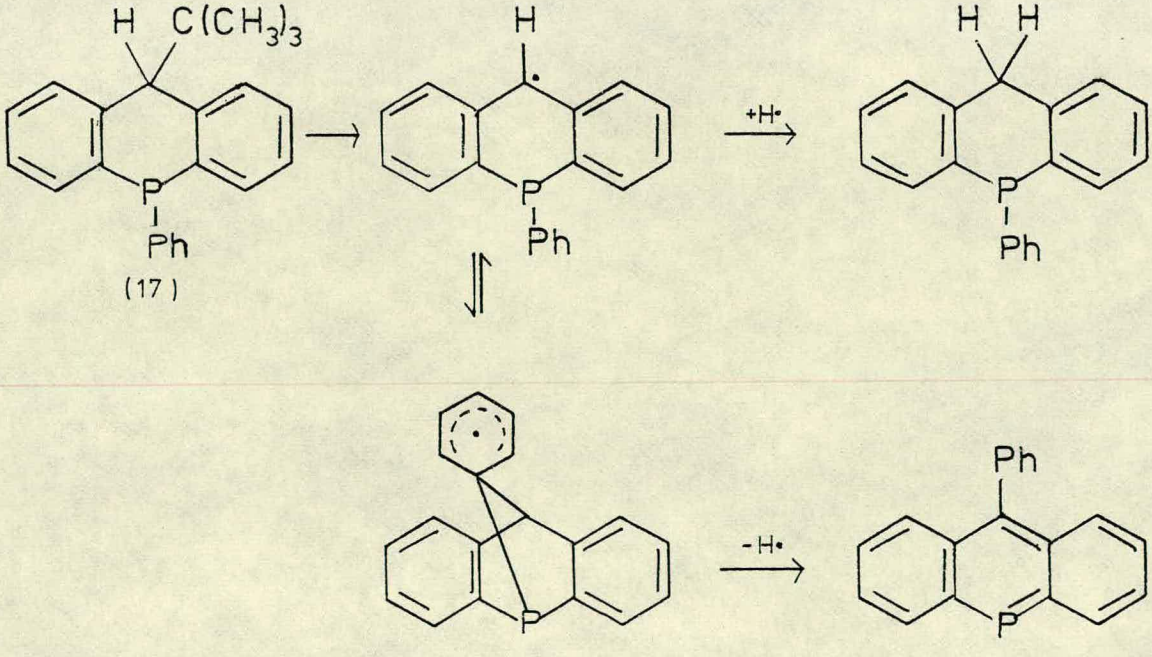
The *N*-benzylindole follows a similar pathway, however the yields of phenylquinolines and quinolines are higher than on pyrolysis of the 3-benzylindoles. This may be due to the fact that the radical (16) derived from the *N*-benzylindole has greater stability than radical (15) in scheme 22.[47-49]



(16)

Earlier work by Patterson[46] showed that pyridine was formed in yields of 1.6-4% on pyrolysis of N-methyl pyrrole. Although no mechanism is suggested it is likely that a similar mechanism to those described above is in operation.

There is one isolated example in the literature of a thermally induced 1,4-aryl migration from phosphorus to carbon involving a carbon radical[50]. Scheme 23 shows the mechanism for the formation of the two major products on pyrolysis of 9-phenyl-10-t-butyl-9,10-dihydro-9-phospha-anthracene (17).

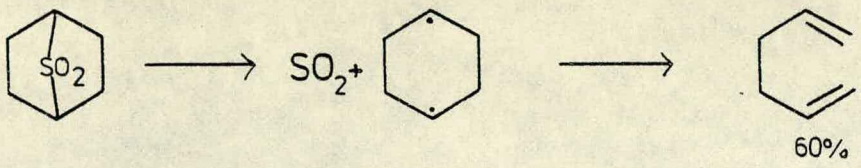


(17)

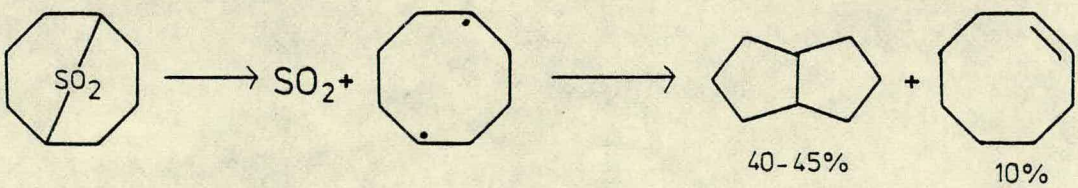
Scheme 23

All the pyrolyses studied so far have involved cleavage of a bond to give two separate radicals. The final part of this section will deal with carbon diradicals. Only systems in which the two radical sites are remote will be considered. Diradicals are formed by the fragmentation of cyclic structures and two of the most important methods of formation are from sulphones[6,37] or by cleavage of small ring systems,[38-40] mainly cyclobutanes.

Bridged cyclic sulphones generate diradicals with elimination of SO_2. These diradicals may then either fragment (Scheme 24) or cyclize to bicyclic products[37] (Scheme 25).



Scheme 24

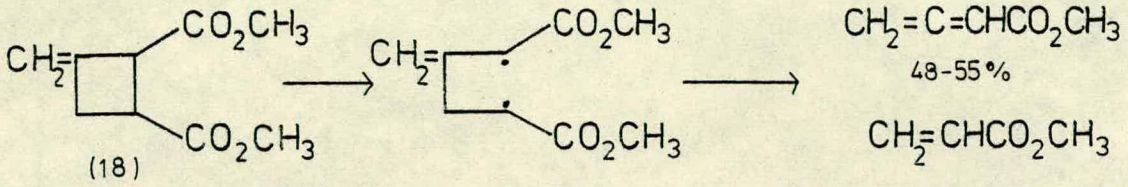


Scheme 25

The synthetic use of sulphone pyrolyses in the preparation of cyclophanes has been reviewed by Vogtle and Rossa.[6]

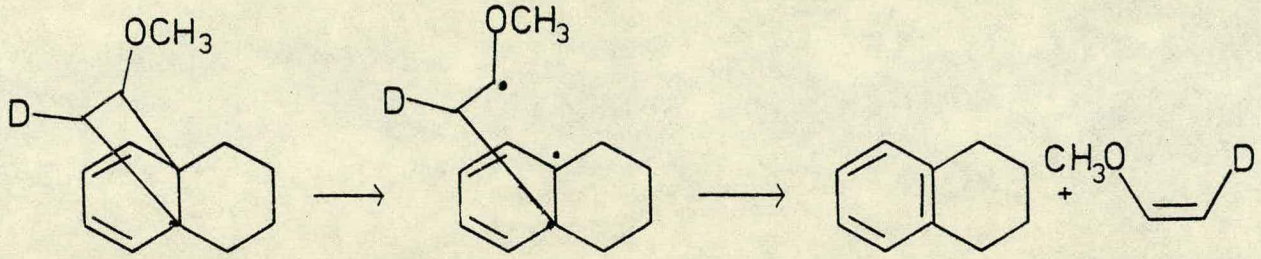
Several examples of the pyrolysis of compounds containing a cyclobutane ring have been reported. One synthetic application is the pyrolysis of the cycloadduct (18) to give an allenic ester, methyl-2,3-butadienoate[38] (Scheme 26). Homolysis

of the C-C bond between the two ester groups occurs as this leads to the most stable diradical.



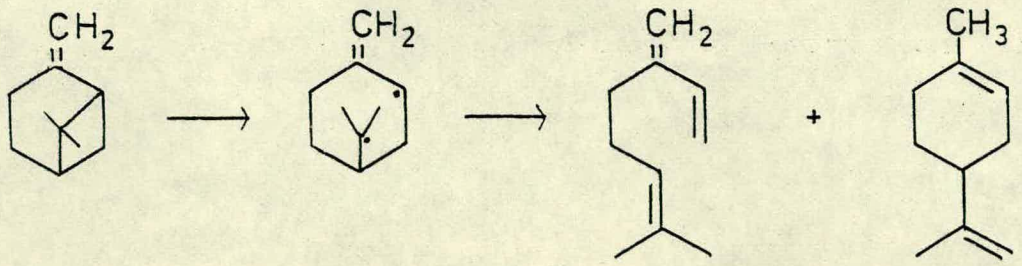
Scheme 26

This fragmentation of the cyclobutane ring appears to be stereoselective in some cases, as shown by Paquette and Thomson's pyrolysis of [4.4.2]Propella-2,4-dienes.[39] This indicates that cleavage to the product occurs much faster than rotation of the D-C-$COCH_3$ bond (Scheme 27)



Scheme 27

Much work has been carried out on the thermolysis of pinanes and related terpenes. Pyrolysis of these compounds again generally results in cleavage of the four membered ring to give a diradical, which then either undergoes a 1,6-hydrogen shift or a bond breaking reaction. This is shown in Goldblatt and Palkin's pyrolysis of β-pinene[40] (Scheme 28).



Scheme 28

Rearrangements of pinane derivatives have been reviewed by Banthorpe and Whittaker.[41] Many more examples of pyrolyses of this type and examples of formation of other diradicals may be found in chapter 6 of Brown's book.[1]

2. Nitrogen Centred Radicals

General reviews on nitrogen radicals include those by Nelsen[51] and Forrester *et al.*[52] A review on the chemistry of aminyl and ammoniumyl radicals has been published by Ogawa and Nomura.[53]

There are two types of nitrogen radicals that occur during flash vacuum pyrolysis. Very little previous work has been carried out on the generation of aminyl radicals $R\dot{N}R'$ and the work reported in this thesis appears to be the only major study of these radicals in gas phase flow pyrolysis systems. Previous reports[54,55] involve the formation of the dimethylamino radical on pyrolysis of tetramethyltetrazen. The major reactions of the dimethylamino radical are coupling or disproportionation (Scheme 29).

McNab generated the anilino radical $Ph\dot{N}H$ as a by-product in one of his pyrolyses and found that aniline and azobenzene were formed from it.[56]

$$Me_2N\text{-}N{=}N\text{-}NMe_2 \longrightarrow 2Me_2\dot{N} + N_2 \longrightarrow Me_2NH + Me_2NNMe_2 + CH_2{=}NMe \rightarrow \text{trimer}$$

Scheme 29

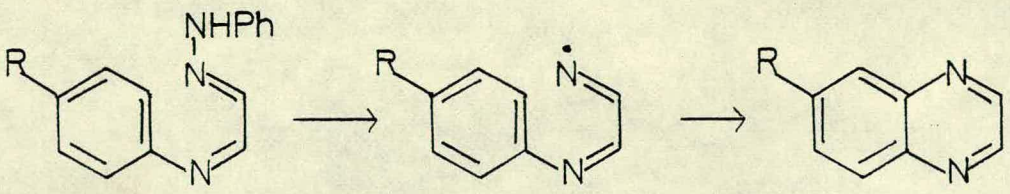
The generation and reactions of aminyl radicals as determined by the author are studied in detail in the discussion section of this thesis.[57]

Unlike aminyl radicals, there are several reports in the literature on the generation and reactions of iminyl radicals $RCR^1{=}N\cdot$. Precursors to iminyl radicals in the gas phase include azines,[58-60] hydrazones,[56,61-64] oxime esters,[65] oxime ethers,[64,66] oximes[67] and nitrimines.[68]

The reactions of iminyl radicals in the gas phase can be divided into two main groups. The pyrolyses of simple azines, oxime esters, oximes and nitrimines result in the formation of nitriles (e.g. scheme 30), whilst pyrolysis of polyazapentadienes, carried out by McNab *et al* generally results in cyclisation of the iminyl radical to give quinoxalines (e.g. Scheme 31).

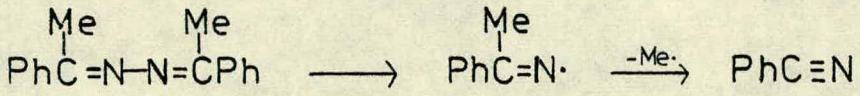
$$PhCH{=}N\text{-}N{=}CHPh \longrightarrow PhCH{=}\dot{N} \longrightarrow PhC{\equiv}N + H$$

Scheme 30



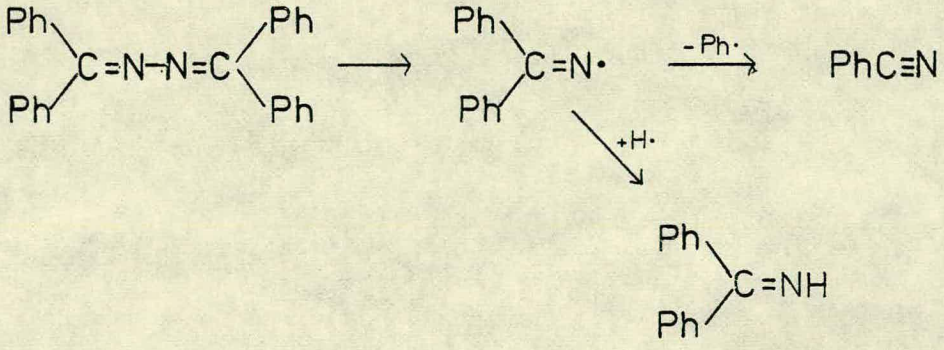
Scheme 31

Gas phase pyrolyses of several azines have been carried out by Crow and his co-workers.[58,59] Both aryl aldehyde and aryl ketone azines give aryl cyanides in varying yields.[58] In general high yields were obtained using ketone azines (e.g. scheme 32), as would be expected because it is known that alkyl radicals are better leaving groups than hydrogen atoms.



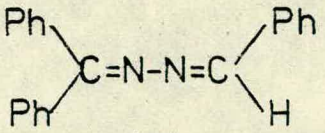
Scheme 32

Flash pyrolysis of aromatic azines has also been carried out by Hirsch using a direct pyrolyser → g.c. system.[60] He found that benzophenone azine decomposed by a free radical mechanism to give the products shown in scheme 33.



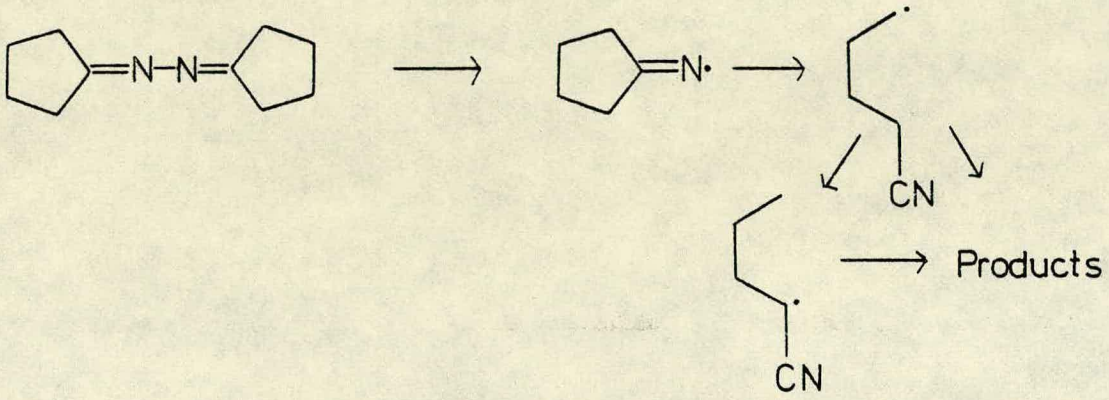
Scheme 33

However, on pyrolysis of benzhydrylidene benzylidene azine (19), Hirsch found not only the above products but also N_2 and triphenylethylene. This suggests that both free radical and molecular mechanisms participate in the reaction.



(19)

Crow has also carried out work on cyclic iminyl radicals.[59] The iminyl radical formed on pyrolysis of cyclopentanone azine undergoes fragmentation of the ring system to give ω-cyanoalkyl radicals which readily isomerise to α-cyanoalkyl radicals (scheme 34).

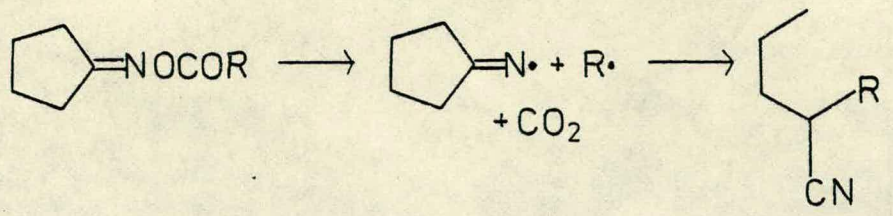


Scheme 34

These cyanoalkyl radicals undergo various fragmentation and coupling reactions. Many different nitrile products are obtained, including C_6 and C_7 nitriles which must occur as a result of radical coupling reactions at the α- and ω-carbons of the nitrile. An even larger variety of nitriles was obtained from cyclohexanone azine as there are more possibilities for H-atom transfer, followed by fragmentation and coupling reactions. These pyrolyses therefore have no synthetic application as complicated mixtures of nitriles are obtained.

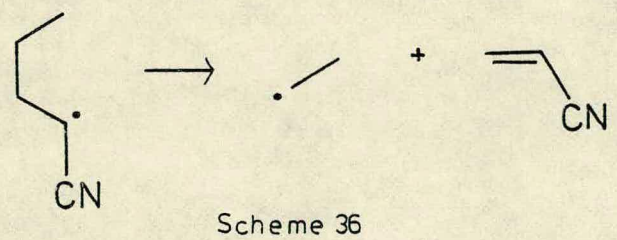
Cyclopentanone and cyclohexanone iminyl radicals have been generated from oxime esters.[65] This results in the co-formation

of a high concentration of a single alkyl radical which can then couple with the α-cyano radical formed from the iminyl (Scheme 35).



Scheme 35

In general these reactions are much cleaner than the azine pyrolyses. The propionate ester of cyclopentanone oxime gives only two nitriles, pentanenitrile and 2-ethyl-pentanenitrile, on pyrolysis. However, specific alkylation of the α-cyano radical is not possible as some fragmentation to give ethyl radicals, which can compete in the coupling reaction, still occurs (Scheme 36).

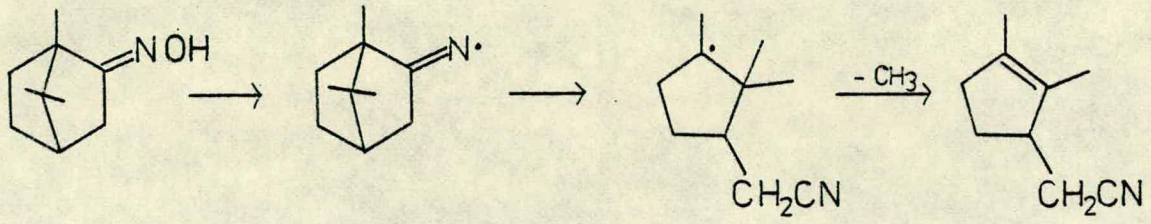


Scheme 36

Unlike the azine pyrolyses no products derived from ω-cyanoalkyl radicals are observed and it is suggested that the rate of isomerisation to α-cyanoalkyl radicals is high due to the increase in pressure because of the presence of CO_2.

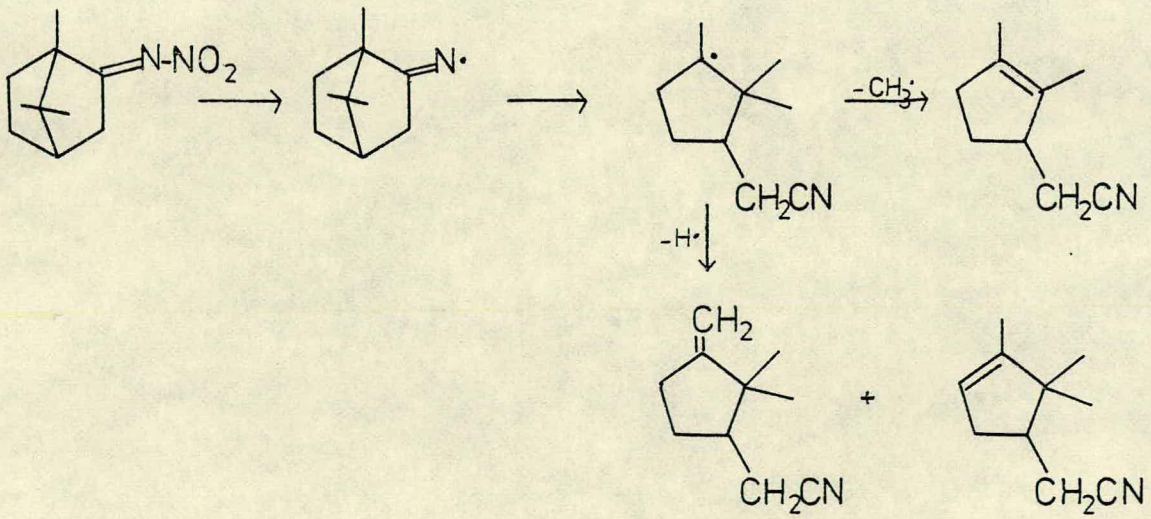
A further example of a cyclic iminyl radical undergoing ring fragmentation is found in the pyrolysis of camphor oxime.[67] Initial homolysis of the N-O bond is followed by ring cleavage

and isomerisation of the resulting cyano radical. Finally a methyl radical is lost to give the major product (Scheme 37).



Scheme 37

On pyrolysis of camphor nitrimine a similar reaction sequence is observed.[68] Initial cleavage of the N-NO_2 bond occurs, followed by ring cleavage. The NO_2 radicals produced can abstract hydrogen atoms to give HNO_2 and so products resulting from loss of a hydrogen atom from the initially formed cyano radical (20) are also observed as well as those obtained by loss of a methyl radical (Scheme 38).

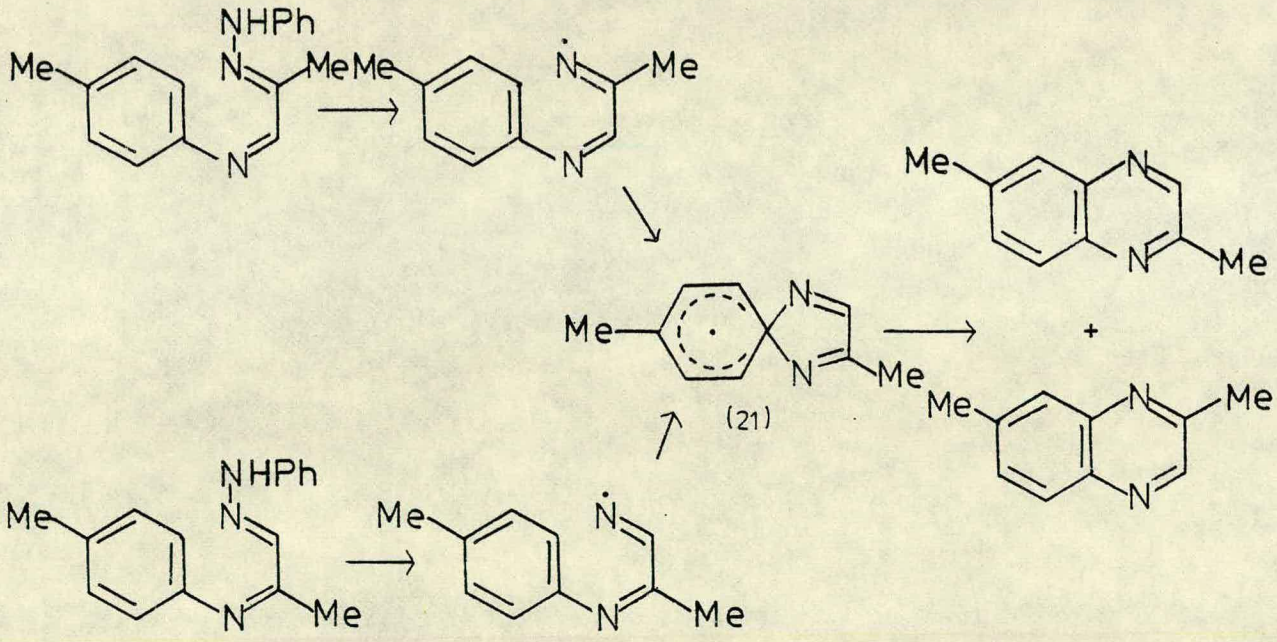


Scheme 38

The mechanistic and synthetic applications of iminyl radicals formed on pyrolysis of hydrazones and oxime ethers of polyazapentadienes have been studied by McNab and his co-

workers. The carbocyclic quinoxaline ring formed in scheme 31 has been found to be derived from the 5-aryl group as the methyl substituted compound gives rise to 6-methylquinoxaline.[56]

Further work[61] has confirmed that the reaction does proceed via an iminyl radical, in contrast to 1,5-diazapentadienes[69] and that isomeric iminyl radicals can interconvert via a spirodienyl radical (21). Substitution of a methyl group at the 3 or 4 position of the 1,2,5-triazapentadiene system results in a mixture of both possible isomeric quinoxalines (Scheme 39).

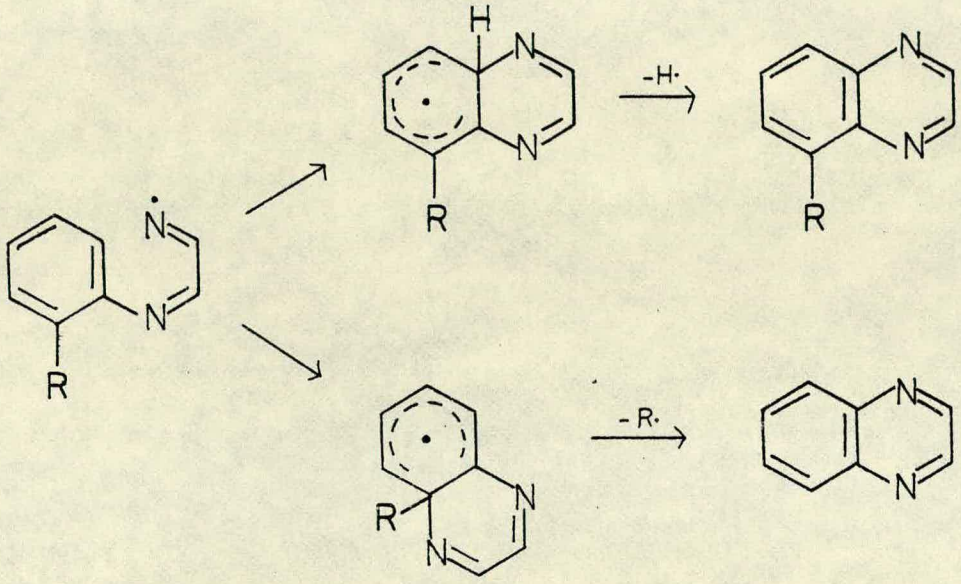


Scheme 39

The ratio of products depends on the structure of the starting material so the spiro-dienyl radical mechanism must compete with direct cyclisation of the iminyl radical.

In both this and the previous example[56] minor products are formed by stepwise loss of HCN from the iminyl radical, followed by various radical coupling reactions.

If an *o*-substituent is present in the 5-aryl ring,[62] 5-substituted quinoxalines are formed, but these are contaminated with the parent compound. This is explained by the fact that the iminyl radical can attack at either ortho position. The proposed mechanism is shown in scheme 40. This process is similar to that observed by Trahanovsky on the pyrolysis of *o*-substituted cinnamyl oxalates[27] (Scheme 11).



Scheme 40

However in this case we might expect the parent quinoxaline to be the major product as an alkyl radical should be lost more readily than a hydrogen atom. Table I shows the results obtained by McNab with various R groups and also Trahanovsky's results.

Although most of these results can be explained by the respective authors' arguments, the ratios obtained with a methyl substituent are not consistent. This may be due to the fact that Trahanovsky's examples involve formation of a 5- rather

Table I

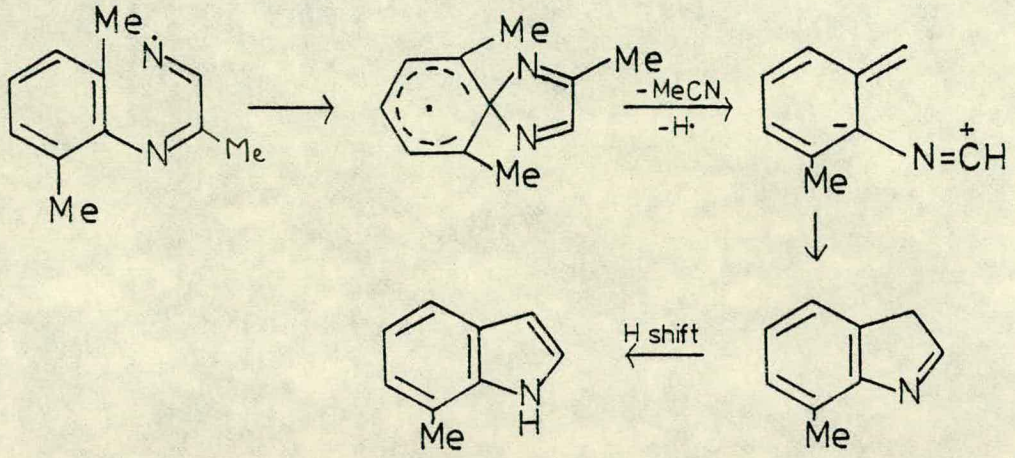
	R	parent compd.	substituted compd.
o-substituted cinnamyl oxalates	Me	23%	12%
	CF_3	-	59%
o-substituted polyazapentadienes	Me	12%	25%
	OMe	11%	2%
	Cl	9%	18%

than a 6-membered ring, and proceed via a benzyl rather than an iminyl radical.

McNab has also studied the effects of substituents in the *p*- and *m*-positions in the 5-aryl ring. *p*-Substitution results in the formation of 6-methylquinoxaline only, as both possible sites for cyclisation are identical. *m*-Substitution again results in a mixture of substituted quinoxalines by a mechanism similar to that of the *o*-substituted compounds. However in this case the ratio of products is very dependent on the nature of the substituent. Attack at the position *ortho* to the substituent is favoured by alkyl substituents, whilst *para*-attack is favoured by electron donating or withdrawing groups.

Returning to the pyrolysis of the *o*-substituted compound, it was thought that if two *ortho*-substituents were present then a synthesis of 5-substituted quinoxalines might be achieved.[63] However, on pyrolysis of the appropriate hydrazones only low yields of quinoxalines were obtained and the major product was 7-methylindole. The proposed mechanism for this reaction again

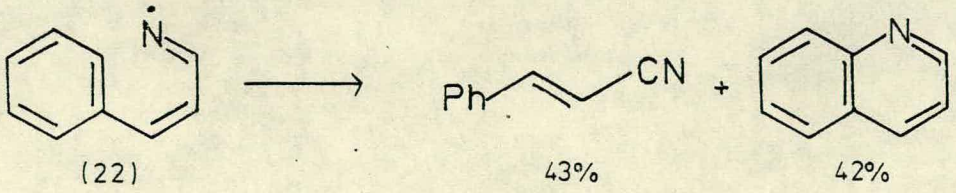
involves a spirodienyl radical (Scheme 41).



Scheme 41

Further confirmation of the intermediate spirodienyl radical in these reactions was obtained by the use of ^{15}N-labelled precursors analysed by n.m.r. spectroscopy.

There is one example in McNab's work on pyrolysis of polyazapentadienes in which a nitrile is one of the major products. Although nitriles had been detected in quinoxaline pyrolysates they were only minor products. Previous work by the author has shown that the iminyl radical (22), formed on pyrolysis of the hydrazone or oxime ether, gives E-cinnamonitrile in similar quantities to the quinoline[64] (Scheme 42).

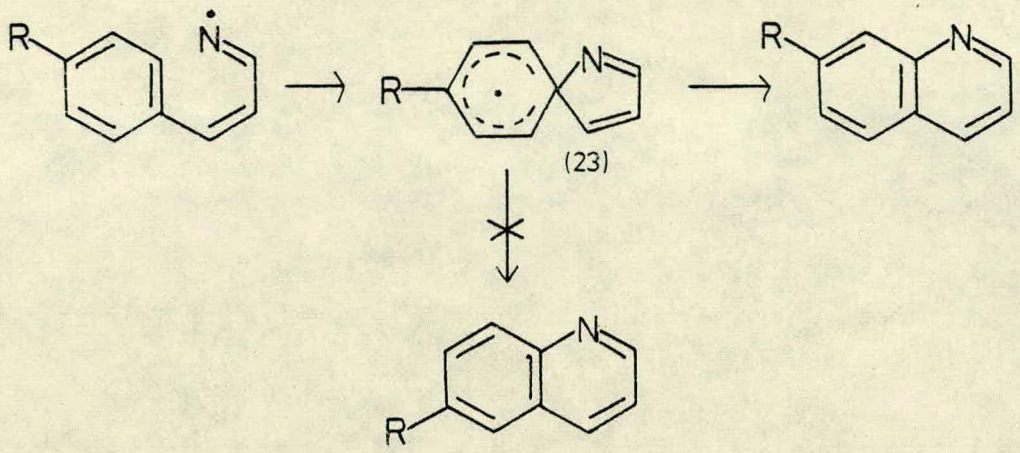


(22) 43% 42%

Scheme 42

If a *p*-substituent is introduced into the 5-aryl ring then only one quinoline isomer is formed (Scheme 43). The

mechanism for this reaction is therefore not clear. Either direct cyclisation of the iminyl radical takes place or C-N migration from the spirodienyl radical (23) is favoured over C-C migration.[70,71]

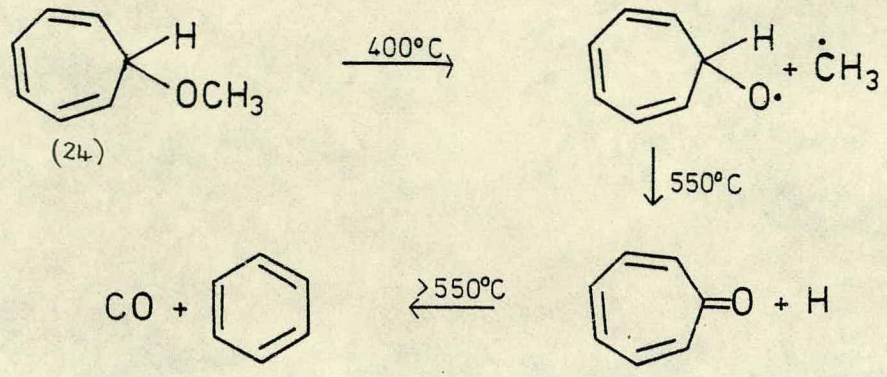


Scheme 43

This reaction appears to be the best synthetic route to 7-substituted quinolines.

Another useful synthetic reaction involving iminyl radicals is the formation of thieno- and furo-[3,2-b]pyridines from oxime ethers.[66] Unlike the reactions involving hydrazones, no basic side products are formed on pyrolysis of oxime ethers. Although the yields of products were low, no evidence was found for rearrangement of the iminyl radicals. It is probable that nitriles are formed in these reactions but only the basic fraction was studied. The proposed mechanism for the reaction is shown in scheme 44.

further decomposed to a cyclopentadienyl radical and carbon monoxide. The various radicals were "observed" by mass spectroscopy using a pyrolysis system coupled directly to a mass spectrometer. The tropenyl methyl ether (24) was found to undergo an analogous thermal decomposition to give benzene (Scheme 45).



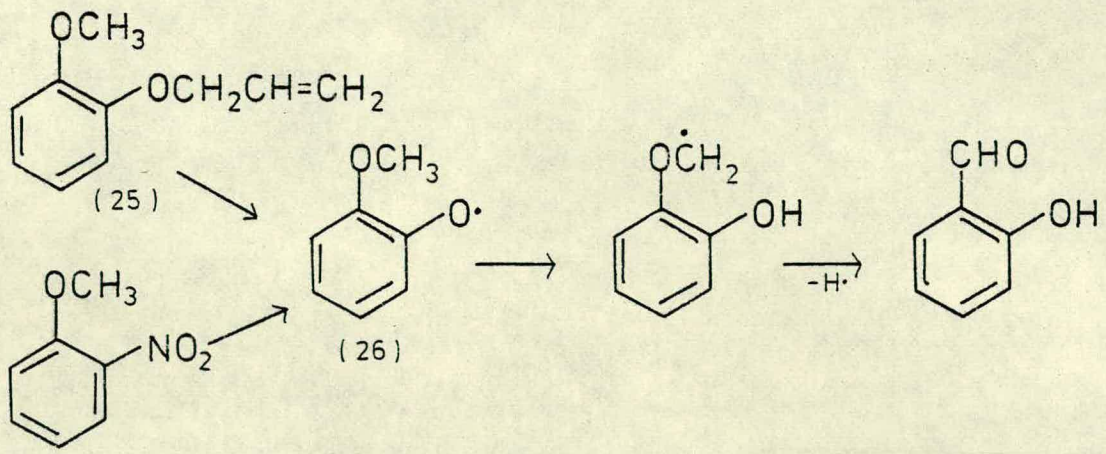
(24)

Scheme 45

Lossing[78] found that phenylallyl ether decomposed thermally in a similar manner to anisole, to give first a phenoxy radical, which then lost CO to give a cyclopentadienyl radical. The final products from this pyrolysis are not reported but pyrolysis of the same ether by Hedaya and McNeil,[79] in a similar system gave rise to biallyl, allylcyclopentadiene and phenol as the major products.

Another example of the thermal cleavage of a phenyl allyl ether is the pyrolysis of (25) carried out by Marty and de Mayo[31] (Scheme 46).

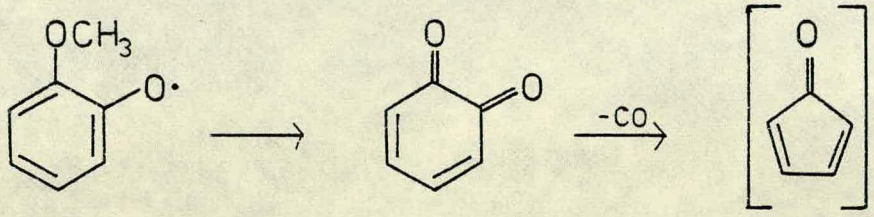
This reaction is analogous to that in scheme 13 in which H transfer from the methyl group to an aromatic carbon occurs. The same product is also obtained from *o*-nitroanisole by



Scheme 46

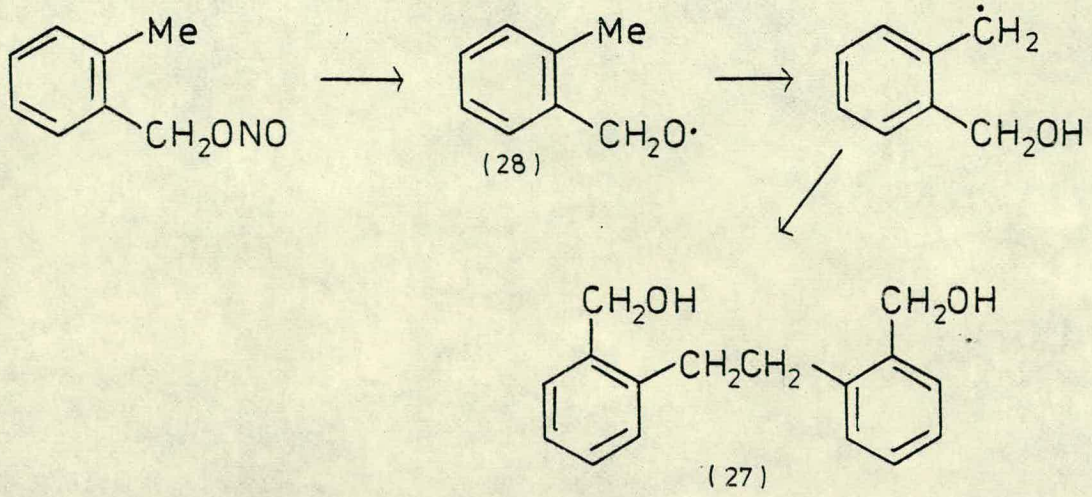
rearrangement of the nitro group to the nitrite, followed by loss of NO· to give radical (26).

Although loss of the allyl group is the major reaction of the ether (25) it is possible that some cleavage of the methyl group also occurs as the following scheme is presented in de Mayo's paper (Scheme 47).



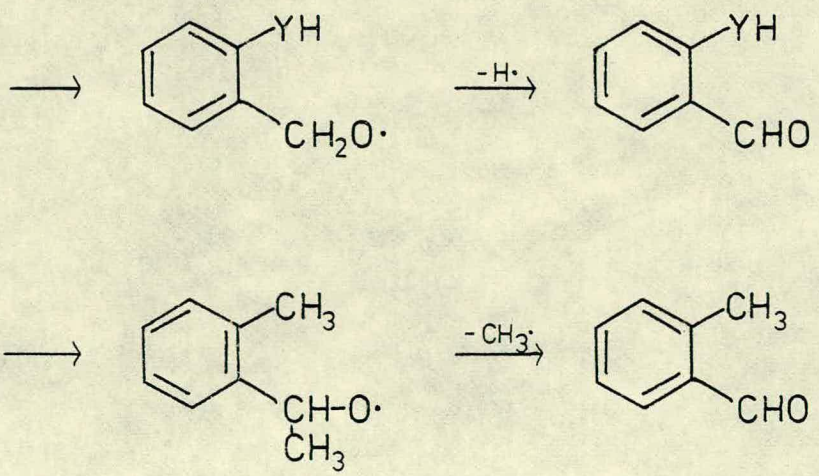
Scheme 47

Some earlier, related work has been carried out by Barton *et al* who pyrolysed various nitrite esters.[73] On pyrolysis of *o*-tolylmethyl nitrite they obtained the dimer (27). This is thought to arise via an intramolecular hydrogen transfer process to give benzyl radicals which then dimerise (Scheme 48).



Scheme 48

It is interesting to note that the radical (28) undergoes intramolecular hydrogen transfer from the methyl group to the oxygen. In both de Mayo's work[31] (scheme 46) and more recent work by Husband *et al*[22] (scheme 49) loss of a hydrogen atom or a methyl radical from the alkoxy radical to give an aldehyde is observed.

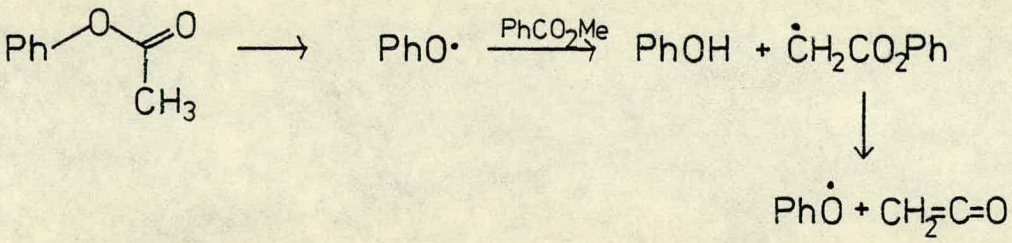


Scheme 49

To show that this hydrogen transfer was intramolecular rather than involving attack of the initially formed alkoxy

radical on any undecomposed nitrite, Barton pyrolysed *p*-tolylmethylnitrite. No dimer was obtained, since hydrogen transfer from the methyl group is not possible in this case. The major products were *p*-tolualdehyde and *p*-tolylmethanol, formed by disproportionation of the initially formed alkoxy radical. Neither de Mayo nor Husband reported co-formation of alcohols with the aldehydes they obtained.

Only one example of pyrolysis of an aromatic ester was found in the literature. Phenylacetate undergoes thermal decomposition to give phenol and keten. Hurd and Blunk first carried out this pyrolysis in 1938 and suggested a radical chain mechanism[80] (Scheme 50).

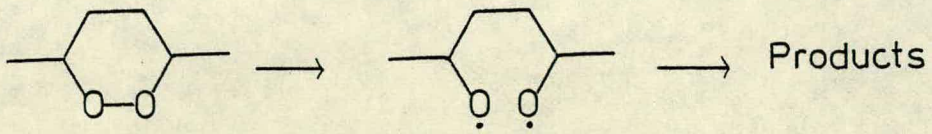


Scheme 50

Meyer and Hammond photolysed phenylacetate and their results led them to suggest a concerted mechanism for the thermal process.[81]

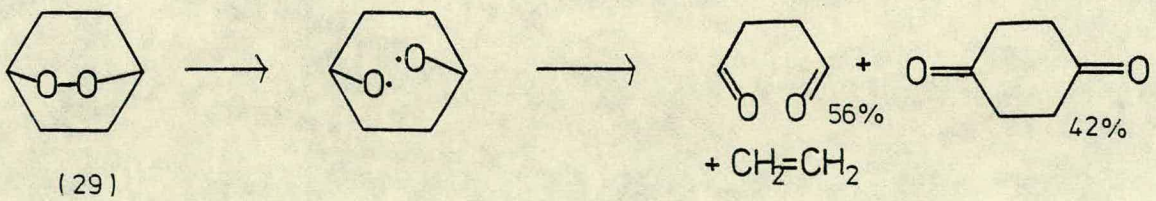
More recently Barefoot and Carroll[82] pyrolysed phenyl 2,2,2-trideuterioacetate in a flow system and found that no significant amount of *o*-deuteriophenol was obtained. This indicates a radical rather than a concerted mechanism and the presence of minor products such as *o*- and *p*-cresols and *o*-phenoxyphenol also points to a radical pathway.

As mentioned previously little work has been carried out on the gas phase pyrolysis of peroxides. The majority of this work has been carried out recently by Bloodworth and his co-workers[74,75] on pyrolysis of cyclic and bicyclic peroxides. Pyrolysis of cyclic peroxides results in cleavage of the oxygen-oxygen double bond to give oxygen diradicals (e.g. scheme 51).



Scheme 51

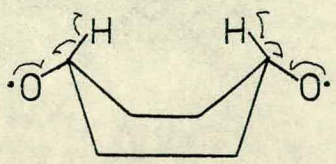
The bicyclic peroxide (29) gives succindialdehyde, ethylene and cyclohexane-1,4-dione on pyrolysis, via a similar oxygen diradical (Scheme 52).



(29)

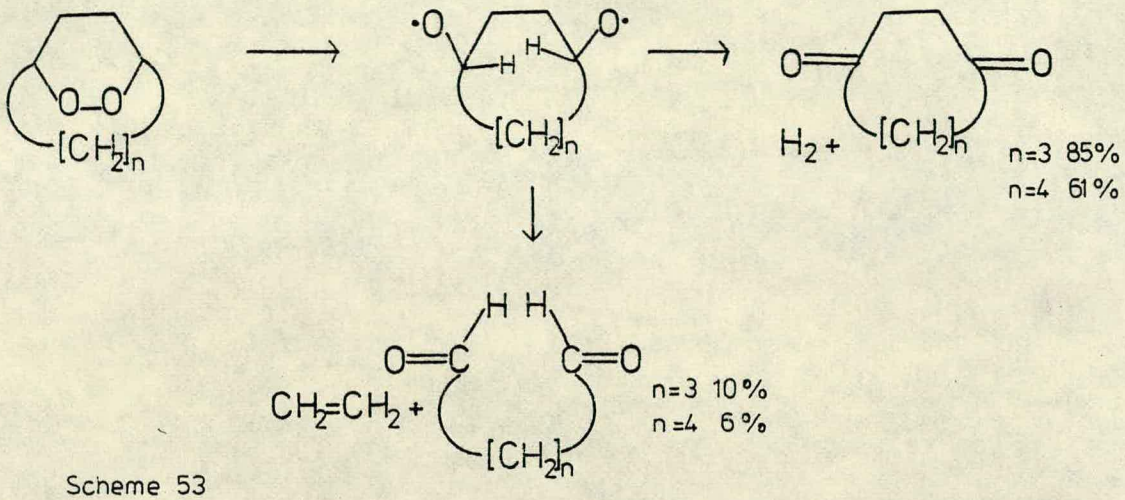
Scheme 52

The diradical must lose either H_2 or ethylene to give the two major products. Bloodworth suggests that the dehydrogenation reaction may involve a boat like transition state (30). Loss of ethylene may also occur by a concerted process.



(30)

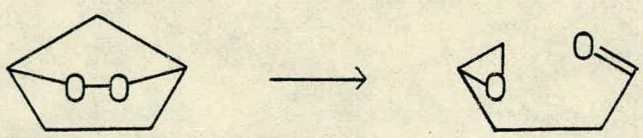
However, on pyrolysis of [n.2.2]peroxyalkanes elimination of hydrogen occurs to a much greater extent than loss of ethylene from the diradical (Scheme 53).[75]



Scheme 53

This is because of the conformational constraints on the 1,6-diradical due to the presence of the cycloalkane ring.

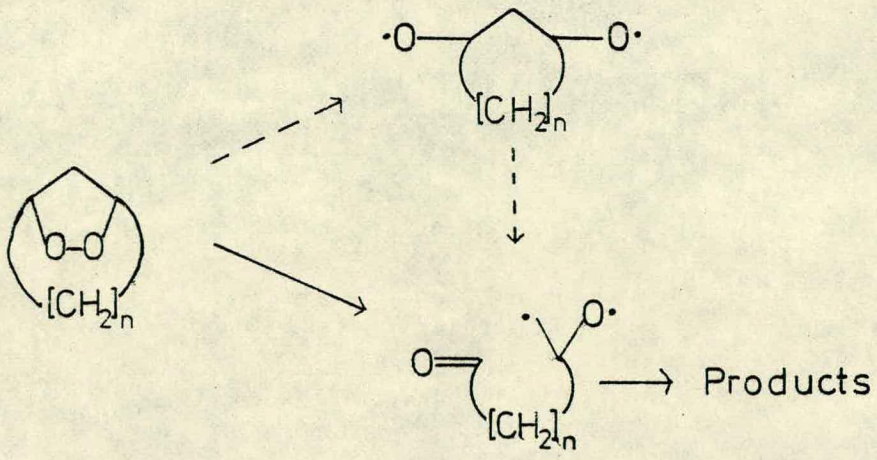
Bloodworth has also studied cyclic peroxides with a one carbon bridge. On pyrolysis of these compounds no diketones are formed. The bicyclic peroxide (31) gave 4,5-epoxypentanal as the only major product (Scheme 54).[74]



(31)

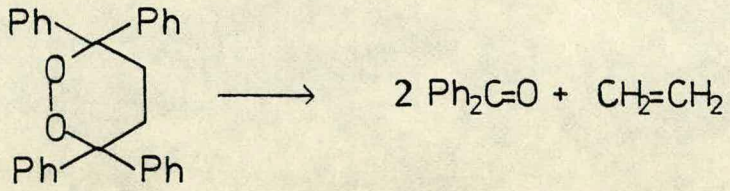
Scheme 54

Further work on [n.2.1]peroxides has lead Bloodworth to suggest a concerted two bond fission to give a 1,3-diradical rather than the expected cycloalkanedioxyl radical[75] (Scheme 55).



Scheme 55

A further example of the gas phase thermal fragmentation of cyclic peroxides is Haynes[76] pyrolysis of (32) to give ethylene and benzophenone as the major products (Scheme 56).



(32)

Scheme 56

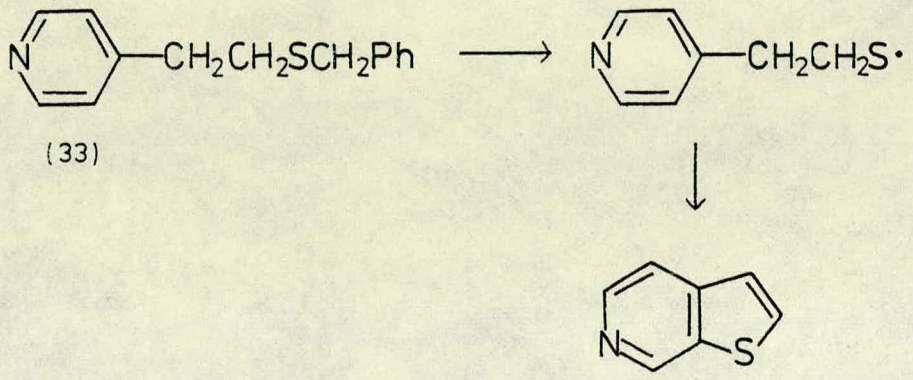
Presumably this reaction follows a pathway similar to that of Bloodworth's peroxides - cleavage of the oxygen-oxygen bond to give the diradical which then eliminates ethylene to give two moles of the ketone. It is also possible that a concerted mechanism is in operation.

4. Sulphur, Silicon and Phosphorus Centred Radicals

Few reactions involving gas phase, flow pyrolysis generation of sulphur radicals have been reported. All of

these involve formation of a styrylthiyl or related radical, followed by intramolecular cyclisation to give a sulphur containing ring system.

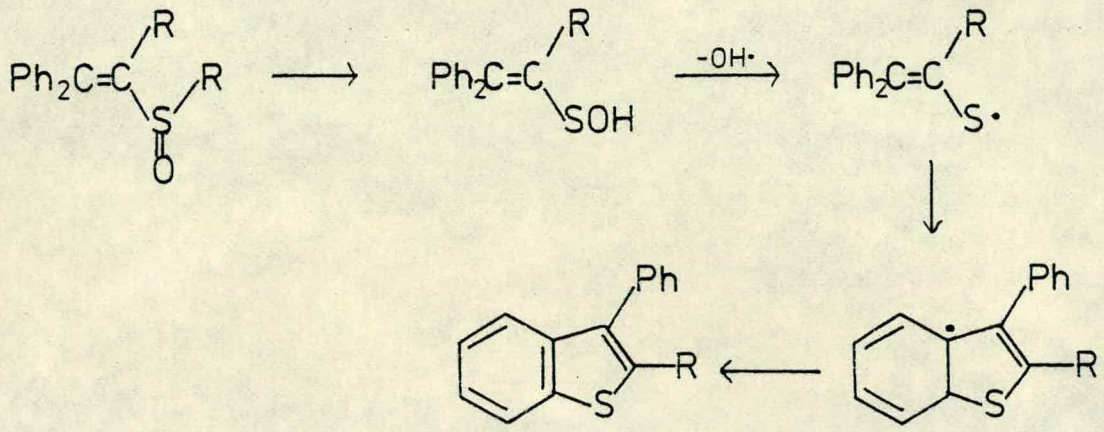
Klemm and his co-workers[83] pyrolysed 2- and 4-vinyl pyridines and obtained thieno[3.2-b]- and [2,3-c]pyridines[84] respectively. They suggest that cleavage of the $PhCH_2$-S bond in (33) occurs, followed by cyclisation and dehydrogenation of the resultant pyridylethyl thiyl radical (Scheme 57).



(33)

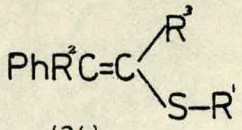
Scheme 57

More recently Ando *et al*[85] have pyrolysed a series of styryl sulphoxides, styryl sulphides and styryl disulphides in a similar nitrogen flow system but in an excess of benzene. They obtained benzothiophenes in good yields. A mechanism similar to Klemm's is suggested. However, in the case of the sulphoxides Ando suggests that the initial step is formation of a sulphenic acid, which then cleaves resulting in formation of styrylthiyl and hydroxyl radicals (Scheme 58).



Scheme 58

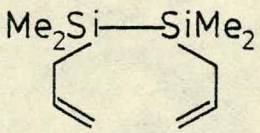
The alkyl styryl sulphides and styryl disulphides react in the same manner as Klemm's compounds, for example, cleavage of the S-R^1 bond in (34) occurs.



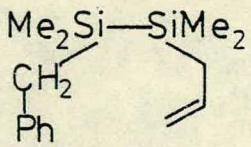
(34)

There are again few examples of gas phase flow pyrolyses resulting in silicon radicals. In 1967 Fritz[86] pyrolysed various methyl and chloromethyl silanes and obtained over forty products. A free radical chain mechanism was proposed for their formation.

Barton and Jacobi[87] have carried out pyrolysis of 1,2-diallyl-1,1,2,2-tetramethyldisilane (35) and 1-allyl-2-benzyl-1,1,2,2-tetramethyldisilane (36).

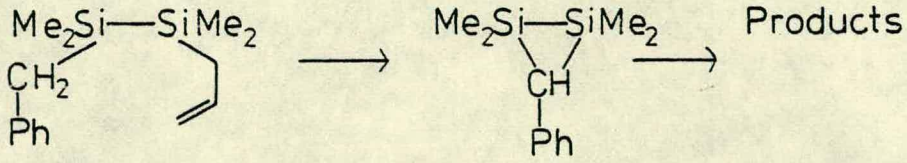


(35)



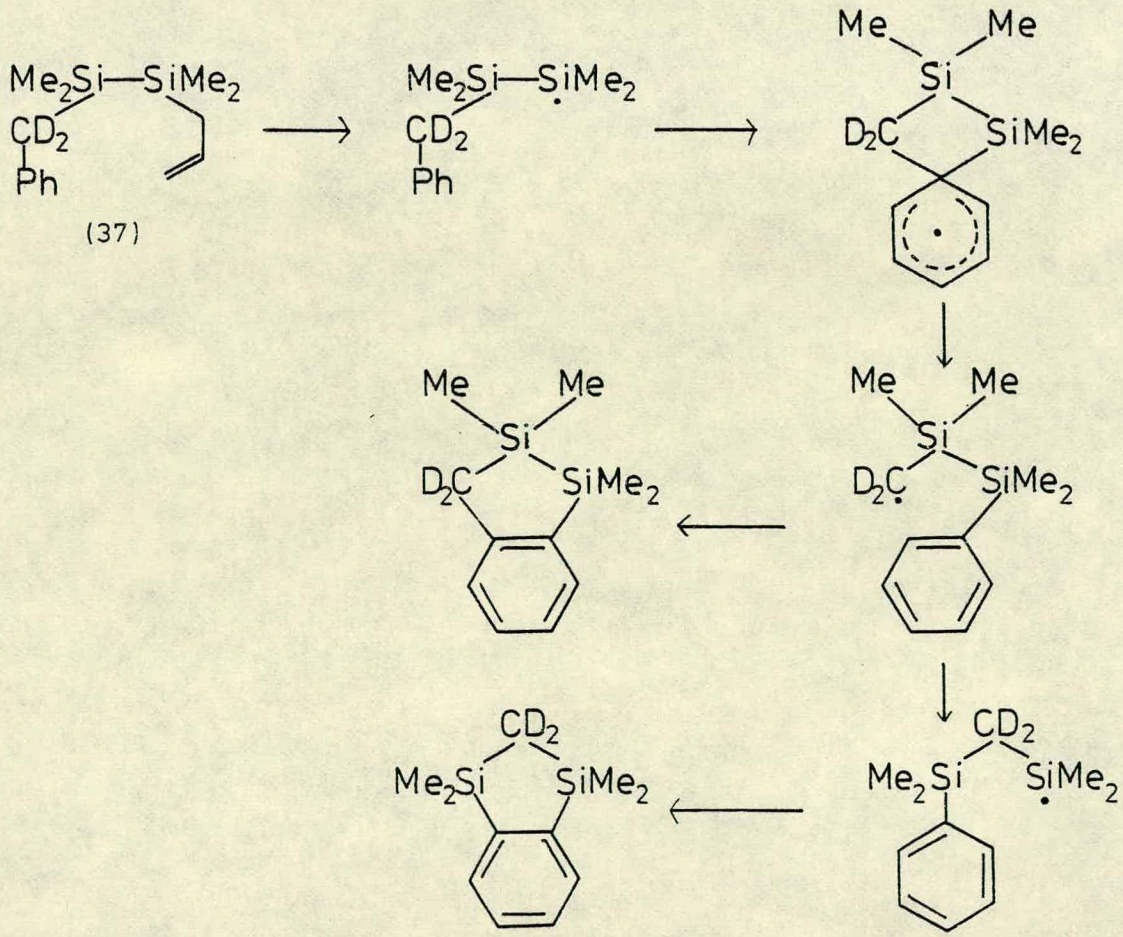
(36)

It was thought at first that the mechanism of the reaction involved initial homoretroene elimination of propene (Scheme 59).



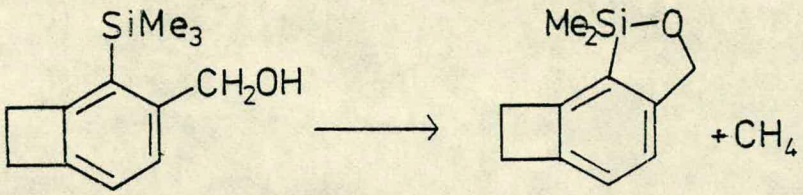
Scheme 59

This mechanism has, however, been shown to be incorrect by the use of deuterium labelling. On pyrolysis of the 1-allyl-2-benzyl compound (37), one deuterium would be lost if the above mechanism is in operation. No significant loss of deuterium was observed. The proposed mechanism is shown in scheme 60.



Scheme 60

Another pyrolysis reaction for which the mechanism is in doubt is Hillard and Vollhardt's[88] pyrolysis of (38) resulting in formation of the cyclic product (39) (Scheme 61).

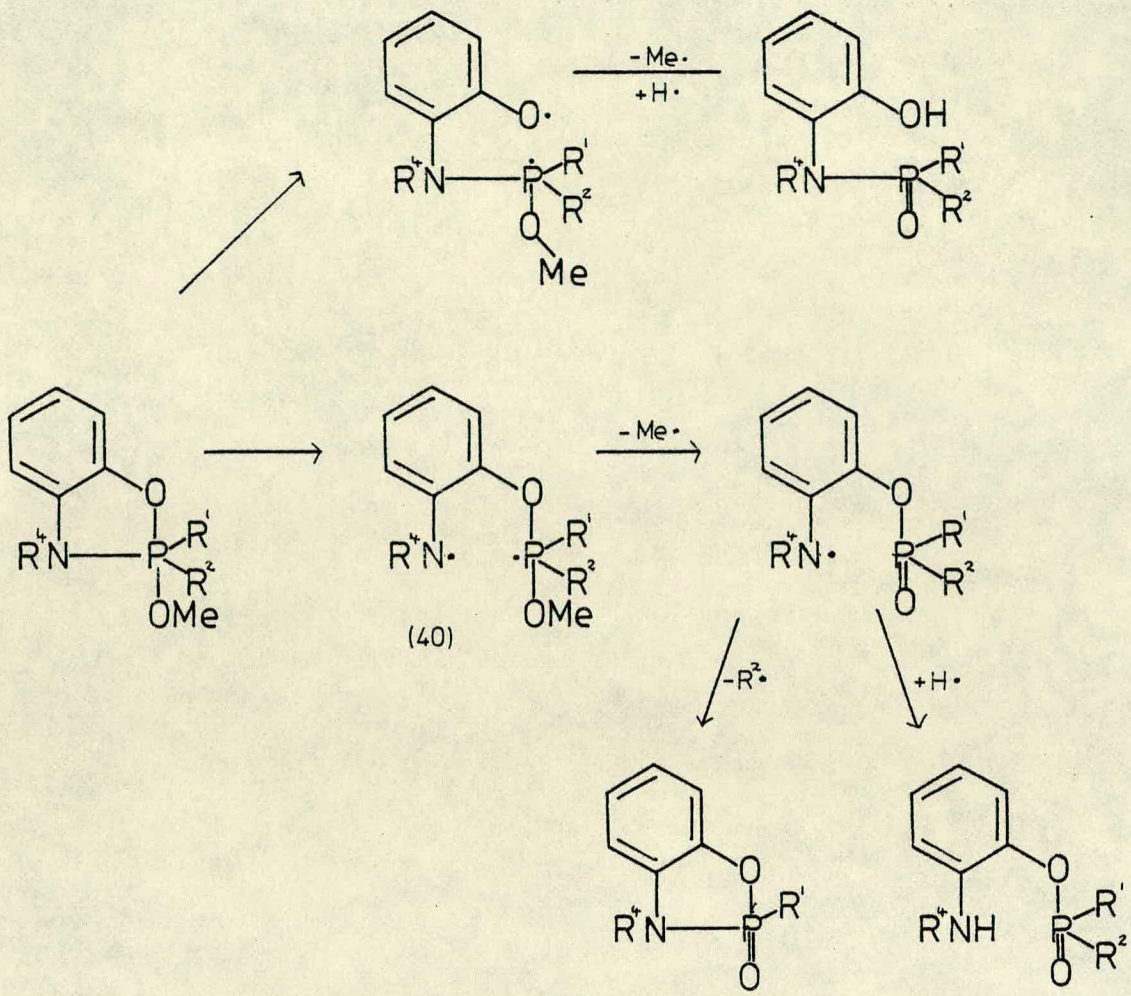


(38) Scheme 61 (39)

The mechanism suggested is nucleophilic attack of the hydroxy group on the silicon, followed by methane extrusion. However, a more likely mechanism might be initial loss of a methyl radical followed by cyclisation.

Although much work has been carried out on radical reactions of silanes these are all solution reactions.[89]

Only one example of generation of phosphorus radicals in a gas phase flow system was found. On pyrolysis of the 3-aryl- and 3-alkyl-2,3-dihydro-1,3,2-benzoxaphosph(v)oles cleavage of the oxazaphosph(v)ole ring system to give di-radicals was observed.[90] Cleavage of either the O-P or N-P bond is thought to occur depending on the nature of the substituent R^4. If R^4=Ar then cleavage of the N-P bond to give radical (40) tends to occur, but if R^4= alkyl then cleavage of the O-P bond is the major process (Scheme 62).



Scheme 62

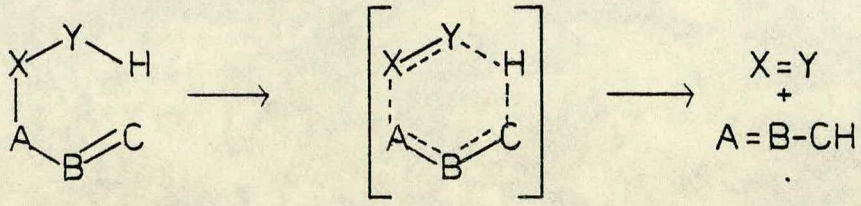
The added driving force for P-N bond cleavage to give (40) is that when R^4=Ar delocalisation of the aminyl radical into two aromatic rings is possible.

DISCUSSION

A. Reactions which Involve *N*-Allylanilines, *N*-Allylamines and *N*-Propargylamines

There are a few examples of the pyrolysis of *N*-allylamines in the literature, but most of these involve kinetic studies in gas phase, static reactors.[91-94] Under these conditions thermal decomposition is found to occur *via* a retro-ene mechanism.

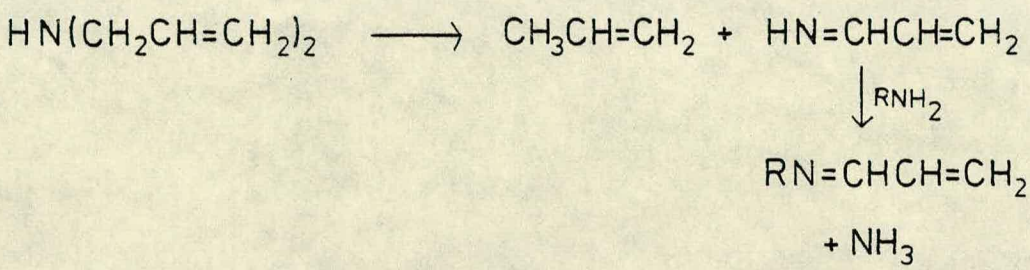
The retro-ene reaction[95] involves 3,4-cleavage of a compound with a double bond and a hydrogen in the 5-position, resulting in allylic shift of the double bond and hydrogen transfer *via* a six-membered transition state (Scheme 63).



Scheme 63

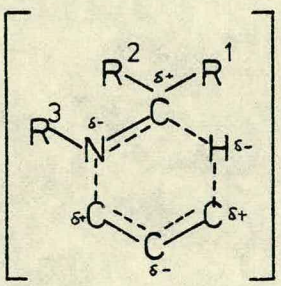
Y is generally a carbon atom, A,B,C and X may be carbon or heteroatoms. As mentioned in the introduction the most common use of this reaction is the preparation of alkenes by pyrolysis of esters[12-14] or xanthate esters.[12,13] The retro-ene reaction is also readily adapted to the formation of carbon-heteroatom multiple bonds. There are several examples involving oxygen,[96-100] sulphur[101] or silicon[102-104] as the heteroatom X. Pyrolytic retro-ene reactions involving nitrogen as this heteroatom are less common and these are now considered in detail.

Egger and Vitins carried out kinetic studies on the thermal decomposition of a series of *N*-allylalkylamines. The major products were propene and the expected imine, with some polymeric material also being formed. In general it was necessary to trap the unstable imine with an alkylamine to give an isolable product. Scheme 64 shows the products obtained on pyrolysis of *N*,*N*-diallylamine.[94]



Scheme 64

Substituents bound to the carbon atom carrying the hydrogen to be transferred had a pronounced effect on the activation energy of the process.[91-94] This led Egger and Vitins to suggest a non-synchronous mode of bond breaking with significant charge separation in the transition state (41).

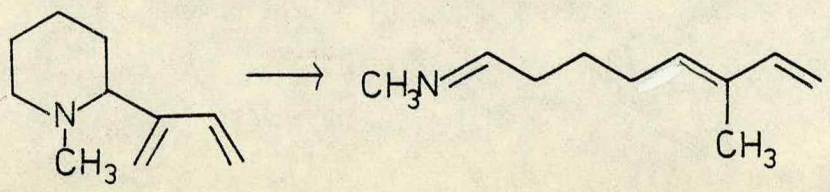


(41)

It was also noted that the presence of the heteroatom lowers the activation energy of the process which further supports the proposal of a polar transition state.

All of the aliphatic *N*-allylamines studied by Egger and Vitins were found to decompose thermally *via* a retro-ene route.

More recently a study of the thermal decomposition of *N*-allyl- and *N*-propargylamines, in a flow system similar to ours, has been made by Earl and Vollhardt.[105] Good yields of the appropriate imine, together with propene, were obtained in all cases. *N*-Propargylamines were found to give higher yields of imines than *N*-allylamines. Earl and Vollhardt had hoped that the retro-ene reaction undergone by these compounds could be used to generate α,ω-iminodienes which are potential Diels-Alder substrates. However, on pyrolysis of (42), secondary proton abstraction occurred at C6, leading to the iminodiene (43), which did not undergo cyclisation.



(42) (43)

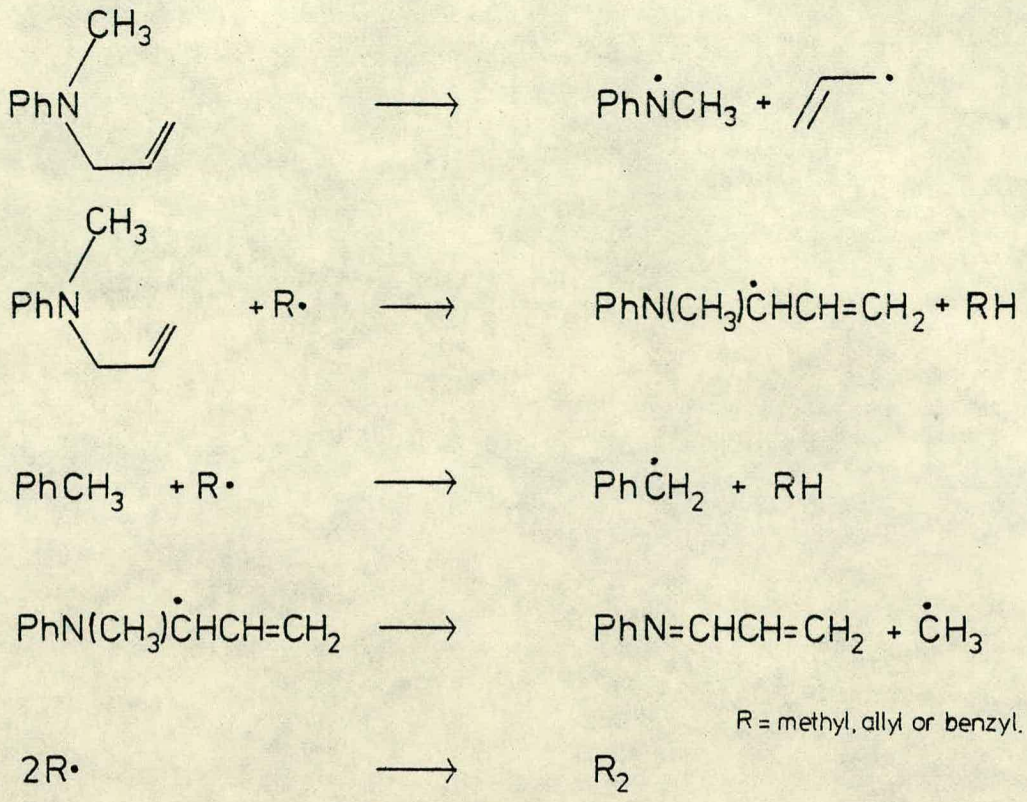
A series of propargylamines with phenyl and/or alkyl substituents have been pyrolysed in a flow system by Viola *et al*,[106,107] who found that the retro-ene mechanism was the major pathway in most cases. Again substitution at the carbon attached to the migrating hydrogen affects the rate of reaction. It is suggested that faster rates in general for amines implies that the dissociation energy of the bonds that must break is less than for other compounds.

On pyrolysis of *N*,*N*-dibenzylpropargylamine and *N*-methyl-*N*

phenylpropargylamine a large number of products were obtained and it was thought that some radical decomposition might be occurring.[106] The reason suggested for this is that the phenyl substituents further weaken the bonds that must break, to the point where homolytic processes can compete with the retro-ene reaction.

A compound with a phenyl group attached to the nitrogen has also been pyrolysed by Egger and Vitins, in a static system.[108] *N*-Allyl-*N*-methylaniline should give propene and formaldehyde anil if a retro-ene process occurs. However the major component of the pyrolysate, after the addition of toluene as a hydrogen donor, was *N*-methylaniline with hexa-1,5-diene, ethane, but-1-ene and 4-phenylbut-1-ene also being formed. This compound, therefore, appears to decompose *via* a radical rather than a retro-ene mechanism. A radical chain mechanism (Scheme 65) is proposed by Egger and Vitins, involving initial formation of allyl and *N*-methylanilino radicals. This scheme however, does not account explicitly for the formation of *N*-methylaniline and does not account at all for the formation of aniline, another major product. In addition no products obviously derived from the acrolein anil were obtained.

Egger and Vitins rationalised a radical, rather than a retro-ene process by again involving the proposed charged transition state (41). It is suggested that the phenyl group reduces the C-N bond strength making a radical process competitive with the retro-ene pathway.



Scheme 65

From these results it seems that the presence of a phenyl ring can promote free radical rather than retro-ene reactions. However there are only two isolated examples in the literature and no systematic study of *N*-allylamines containing an aromatic ring has been made. The following section discusses a series of *N*-allyl and *N*-propargyl compounds that have been prepared and pyrolysed in order to further study the mechanism of their thermal decomposition.

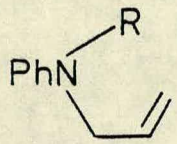
1. Preparation of *N*-Allylamines, *N*-Allylanilines and *N*-Propargylanilines

These compounds were prepared by reaction of the appropriate secondary amine with allyl or propargyl bromide. In some cases it was necessary to first make the secondary amine.

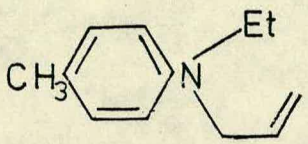
To obtain reasonable yields of the *N*-allyl- and *N*-propargyl-

amines it was generally found necessary to repeat the reaction with the appropriate bromide two or three times, except with some of the more reactive di-alkylamines. The products were purified by column chromatography and/or distillation. As their ^{1}H n.m.r. spectra were complicated it was difficult to determine the extent of reaction and so ^{13}C n.m.r. spectroscopy was used to monitor the purity of the product.

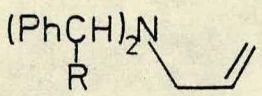
The following compounds were prepared [(44) to (61)].



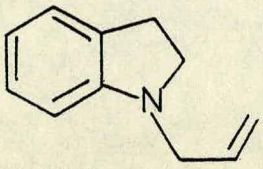
(44) R = Me
(45) R = Et
(46) R = Pr^{i}
(47) R = Bu^{t}
(48) R = CH_2Ph
(49) R = $CH_2CH{=}CH_2$



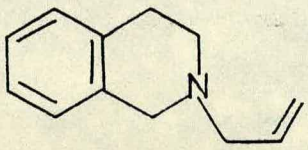
(50)



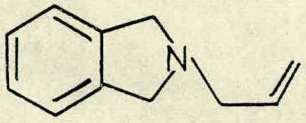
(51) R = H
(52) R = Me



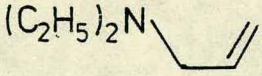
(53)



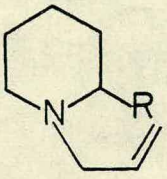
(54)



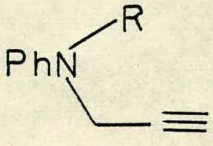
(55)



(56)

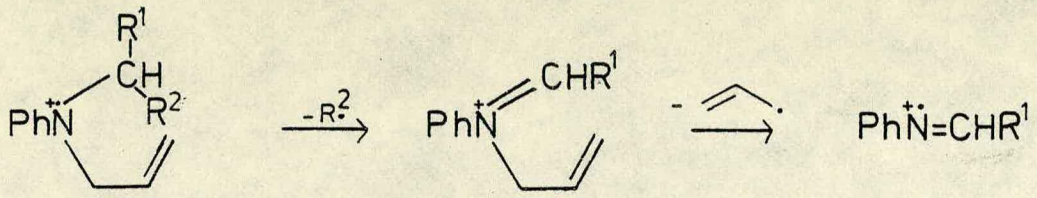


(57) R = H
(58) R = Me



(59) R = Me
(60) R = Et
(61) R = Pr^{i}

The mass spectra of these compounds show two major fragmentation pathways, neither of which corresponds to the expected thermal breakdown. Only the *N*-methyl-*N*-propargylaniline (59) shows initial cleavage of the C_3 fragment. Cleavage of a C_2H_3 fragment from the allyl group is the major process for the *N*-allyl-*N*-methylaniline (44) and the cyclic compounds (53-55), and a minor pathway for (48), (51), (57) and (58). The major fragmentation for these and (45), (46), (47), (60) and (61) involves cleavage of the substituent at a position α to the nitrogen followed by loss of the allyl group (scheme 66).



Scheme 66

Apart from the *N*-methyl derivatives the allyl and propargyl compounds show similar mass spectra.

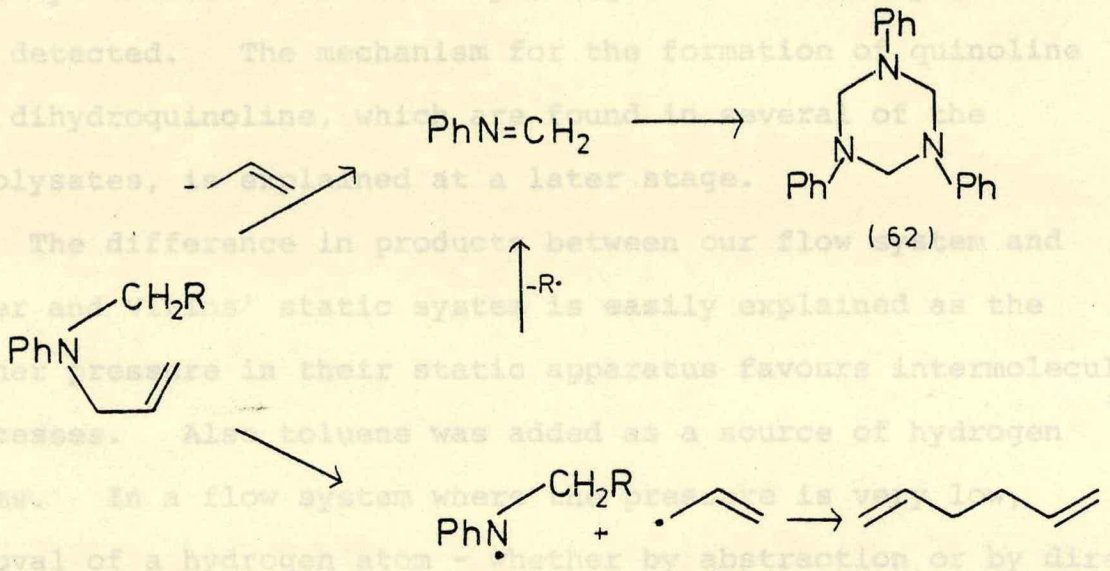
2. Pyrolysis of *N*-Allylamines, *N*-Allylanilines and *N*-Propargylanilines

As previously stated *N*-allyl-*N*-methylaniline has been pyrolysed in a gas phase, static system and gives *N*-methylaniline as the major product.[108] Thermolysis of the same compound in solution results in the formation of *o*-allyl-*N*-methylaniline by a Claisen-type rearrangement.[109]

On pyrolysis of *N*-allyl-*N*-methylaniline (44) under low

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pressure conditions in a gas phase flow system, neither of the aforementioned products was obtained. The major product, formed in 19% yield, was hexahydro-1,3,5-triphenyl-1,3,5-triazine (62). This is the well known trimer[110] of formaldehyde anil and can be prepared by reaction of aniline and formaldehyde in solution. The mechanism for its formation in this pyrolysis could be either a radical or a retro-ene reaction (Scheme 67, R=H).

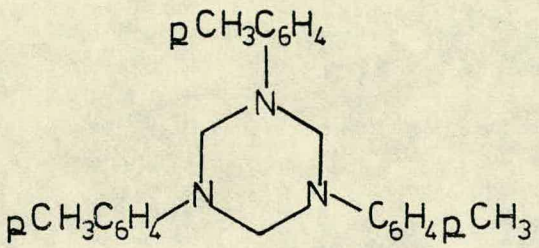


Scheme 67

However the presence of hexa-1,5-diene, presumably formed from two allyl radicals, indicates that a radical mechanism is taking place. It is difficult to determine exact yields of hexa-1,5-diene as it is fairly volatile and may evaporate during work-up of the pyrolysate. Minor products identified in the pyrolysate were aniline (8%) and formaldehyde anil, *N,N*-dimethylaniline, quinoline and dihydroquinoline which were present in smaller quantities. The presence of these minor products, coupled with the low yields of major product also

occurs more readily than loss of a hydrogen atom in gas phase radical reactions. This pyrolysate was much cleaner than that obtained from the *N*-methyl compound and fewer minor products were obtained. Trace amounts of aniline, formaldehyde anil and *N*-ethylaniline were detected. These can all be explained as being derived from an *N*-ethylanilino radical.

On pyrolysis of *N*-allyl-*N*-ethyl-*p*-toluidine (50) an identical pathway was followed resulting in the formation of hexahydro-1,3,5-tri-*p*-tolyl-1,3,5-triazine (63) in 42% yield.



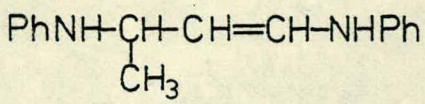
(63)

No attempt was made to characterise minor products in the pyrolysate as these were again present only in trace amounts.

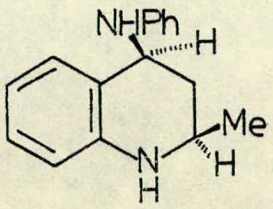
On the basis of the above results, one would expect acetaldehyde anil to be generated by pyrolysis of *N*-allyl-*N*-isopropylaniline (46). However, pyrolysis of this compound resulted in a complex pyrolysate and no major product was obtained. The ^{1}H n.m.r. spectrum of the crude pyrolysate showed only broad, unresolved signals. T.l.c. showed mainly base line material suggesting polymeric products. Reaction of acetaldehyde and aniline in solution under neutral conditions does not give rise to acetaldehyde anil or its trimer.[111,112] Instead the so-called Eckstein's and Eibner's bases are formed.

For many years the structures of these compounds were thought to be (64) and (65) respectively,[110,113] but they are now known to be the tetrahydroquinolines (66) and (67).[114]

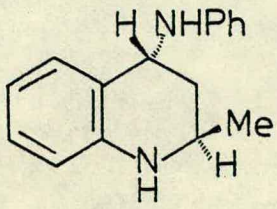
(64) Trans



(65) Cis



(66)



(67)

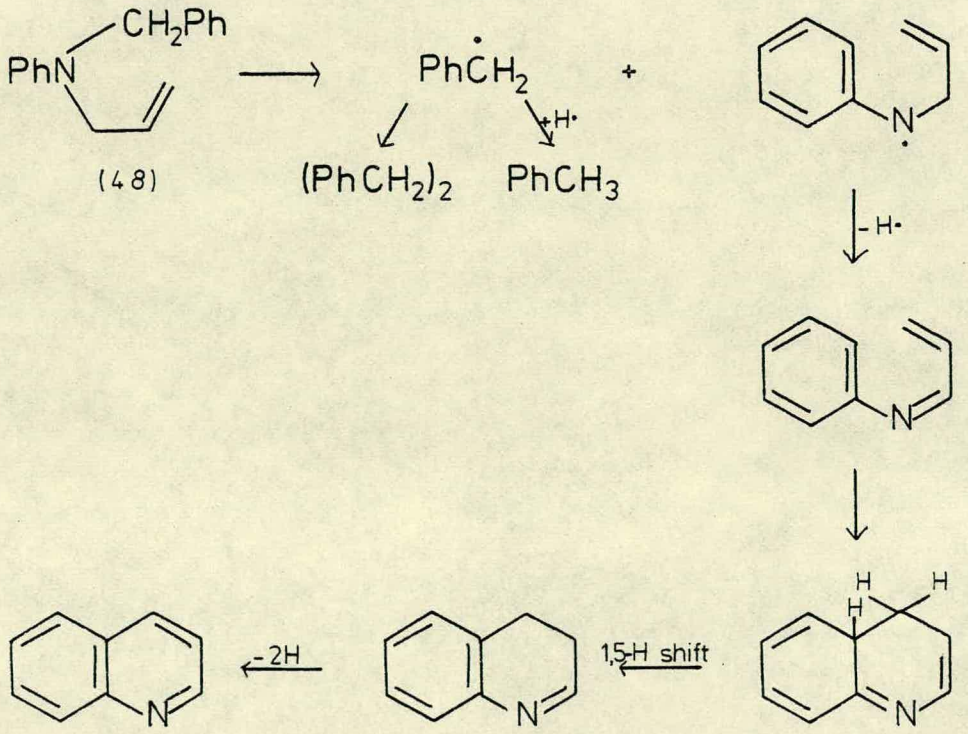
The formation of these tetrahydroquinolines in solution does not necessitate acetaldehyde anil as an intermediate.

A trace of acetaldehyde anil was detected in the crude pyrolysate by g.c./m.s., indicating that this imine is formed initially, by a mechanism similar to that of scheme 67, and then probably reacts further to form polymeric products. A trace of acetone anil [$PhN=C(Me)_2$] was also detected. This results from loss of a hydrogen atom rather than a methyl radical from the initially formed *N*-isopropylanilino radical. Aniline and *N*-isopropylaniline must also be formed from this radical. The formation of styrene and quinoline, believed to involve the allyl function, are discussed at a later stage.

In contrast to these previous examples, *N*-allyl-*N*-t-butylaniline (47), should generate a stable imine, acetone anil

$PhN=C(Me)_2$], on pyrolysis. Indeed, this compound is formed in 36% yield. This yield is a minimum value since, on exposure to air, some hydrolysis of the imine to give aniline and acetone is known to occur. This explains the high yield of aniline (23%) found in the crude pyrolysate. The minor products detected were styrene, quinoline, dihydroquinoline and *N*-t-butylaniline.

N-Allyl-*N*-benzylaniline (48), should also give a stable imine on pyrolysis. As expected the major product was benzylidene aniline PhN=CHPh (45%). The presence of hexa-1,5-diene (16%) and a compound thought to be 4-phenylbut-1-ene point to a radical mechanism. In this case an alternative, minor route is direct cleavage of a benzyl radical giving rise to small quantities of toluene, bibenzyl, quinoline and dihydroquinoline (Scheme 68).



Scheme 68

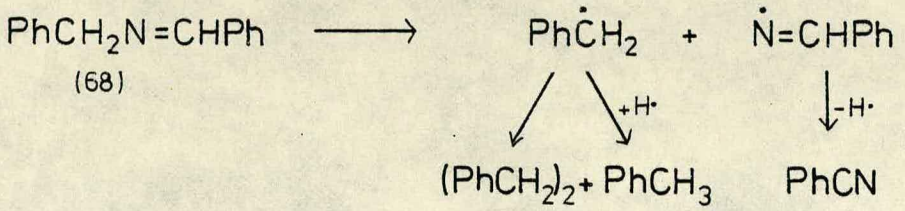
In order to determine if this proposed mechanism for the formation of quinoline was feasible, pyrolysis of *N*,*N*-diallylaniline (49) was carried out. A 12% yield of quinoline was calculated, which is significantly higher than in any of the previously studied pyrolysates. At least eight other components were present in yields of <1%, including aniline, styrene and dihydroquinoline. The proposed mechanism for the formation of quinoline seems viable and it also seems likely that trace amounts of styrene may arise from the allyl group.

The source of aniline in most of these pyrolysates is not clear. It was thought that it could arise by dealkylation of the appropriate *N*-alkylanilino radical, however on pyrolysis of *N*-ethylaniline at a higher than usual temperature, a 45% recovery of starting material was obtained and only trace quantities of aniline were detected. It is most likely that the aniline is formed from highly vibrationally excited molecules in the gas phase which lose their alkyl substituents to give the most thermodynamically stable product. The possibility that trace quantities of aniline were present in the starting materials, although unlikely, cannot be entirely ruled out from all the examples.

The results from these pyrolyses show that the thermal decomposition of *N*-allylanilines occurs *via* radical cleavage rather than the retro-ene reaction. This is probably because the arylamino radical is stabilised by resonance with the aromatic ring system.

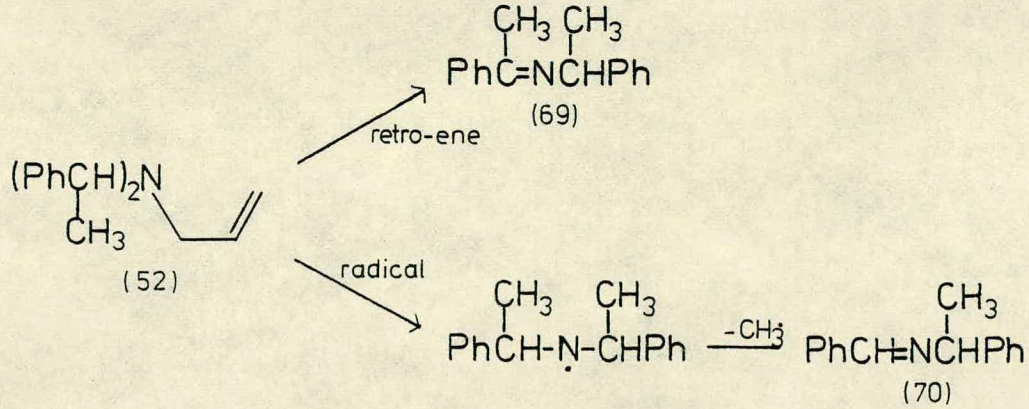
The effect of an aryl group at a more remote site in the molecule has also been studied by the pyrolysis of several *N*-allylamines.

On pyrolysis of *N*,*N*-dibenzylamine (51), the major product was benzaldehyde-*N*-benzylimine (68) in 28% yield. Since no hexa-1,5-diene was detected it seems likely that the allyl group is lost as propene indicating a retro-ene mechanism. Minor products obtained were toluene, bibenzyl and benzonitrile, indicating formation of benzyl radicals at some stage. That these products could result from breakdown of the imine was shown by the pyrolysis of an authentic sample (scheme 69). Radical products were also thought to arise on pyrolysis of *N*,*N*-dibenzylpropargylamine[106].



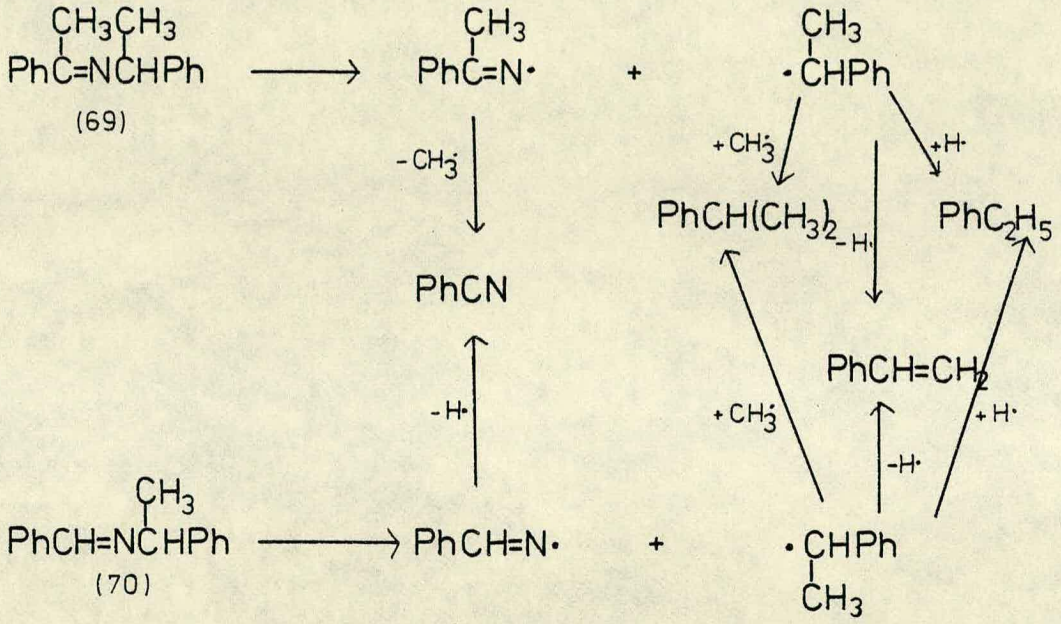
Scheme 69

An experiment was devised that should clearly indicate the mechanism of this pyrolysis. The methyl labelled dibenzyl compound (52) would be expected to give rise to different imines depending on whether a retro-ene or radical mechanism was in operation (scheme 70).



Scheme 70

However, on pyrolysis of (52) no imines could be detected in the pyrolysate and the major products were benzonitrile (34%) and styrene (60%), with smaller quantities of ethylbenzene and isopropylbenzene. It was thought that these products must result from breakdown of the initially formed imine. Independant pyrolyses of the proposed intermediate imines (69) and (70) indeed led to the same set of products (scheme 71).



Scheme 71

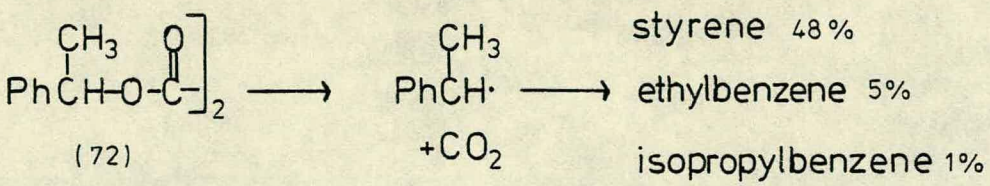
The yields of products from pyrolyses of both of the imines (69) and (70), the *N*-allyl compound (52) and its parent secondary amine (71) are shown in Table II.

Table II

	% Yield			
	Benzonitrile	Styrene	Ethylbenzene	Isopropylbenzene
(52)	34	60	7	7
(69)	58	39	4	12
(70)	56	44	6	2
(71)	20	42	4	7

The much lower level of isopropylbenzene from (70) is not significant since the formation of benzonitrile from the *N*-allyl compound (52) would generate methyl radicals in a comparable amount to those formed from (69).

It was surprising that no coupling products were formed from the α-methylbenzyl radicals. However, generation of these radicals from the oxalate (72) led to the same set of products (scheme 72).



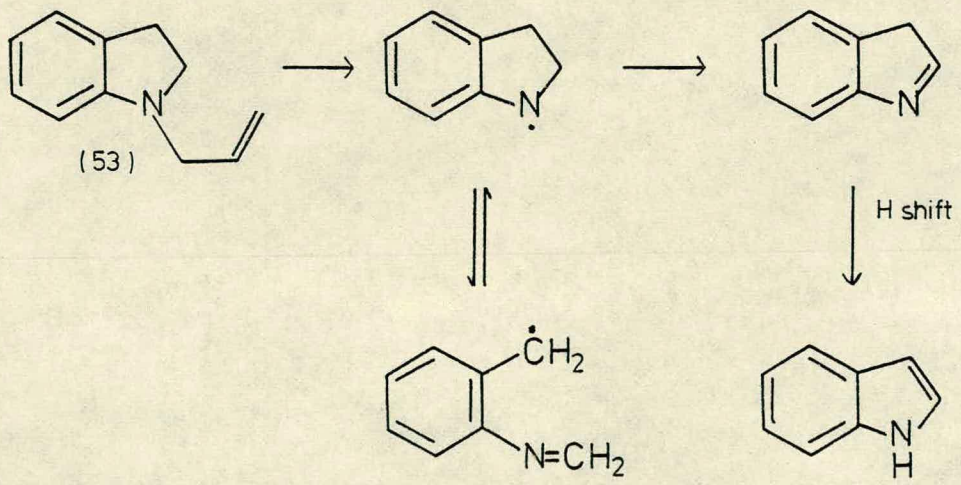
Scheme 72

It is possible that the styrene is formed by a concerted elimination reaction as this was proposed by Trahanovsky to be the dominant reaction for di-(α-substituted)benzyl oxalates.[24] However, the ethylbenzene and isopropylbenzene can only be explained as being formed from radical coupling reactions and indeed Trahanovsky observed some radical coupling products.

Finally, the possibility of direct cleavage of an α-methylbenzyl radical from the *N*-allyl compound (52) cannot be ruled out since pyrolysis of the parent secondary amine (71) resulted in a similar set of products (Table II).

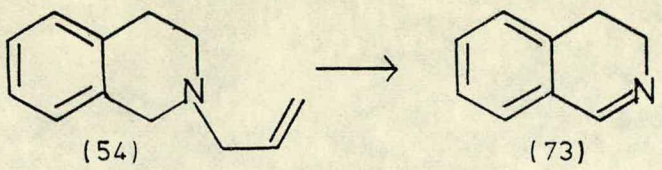
Some examples where the nitrogen atom is part of a ring system were studied next. If a radical mechanism is in operation, then some ring cleavage might be expected.

On pyrolysis of *N*-allylindoline (53) a 61% yield of indole was obtained after purification of the crude pyrolysate by column chromatography and distillation. However, hexa-1,5-diene was detected in the crude pyrolysate indicating a radical route. This is not surprising as this *N*-allyl compound (53) is formally a substituted aniline, with the nitrogen connected directly to the phenyl ring. The proposed mechanism for the formation of indole is shown in scheme 73. What is surprising is that very little ring cleavage is observed, although some must occur to give rise to the minor products - styrene, toluene and *o*-toluonitrile. It is possible that in cyclic cases such as this, these ring opening reactions may well be reversible.



Scheme 73

Again a high yield of product was obtained on pyrolysis of *N*-allyl-1,2,3,4-tetrahydroisoquinoline (54). A 61% yield of 3,4-dihydroisoquinoline (73), characterised by conversion to its picrate salt, was calculated (scheme 74). Trace quantities of styrene, tetralin and isoquinoline were also detected in the crude pyrolysate. The high yield of major product, in addition to the lack of minor products and the absence of any hexa-1,5-diene indicates that a concerted retro-ene process is occurring rather than a radical reaction. The only radical reaction in which a high yield of major product was obtained was that of *N*-allylindoline and that is explained by the high stability of the end product, indole.

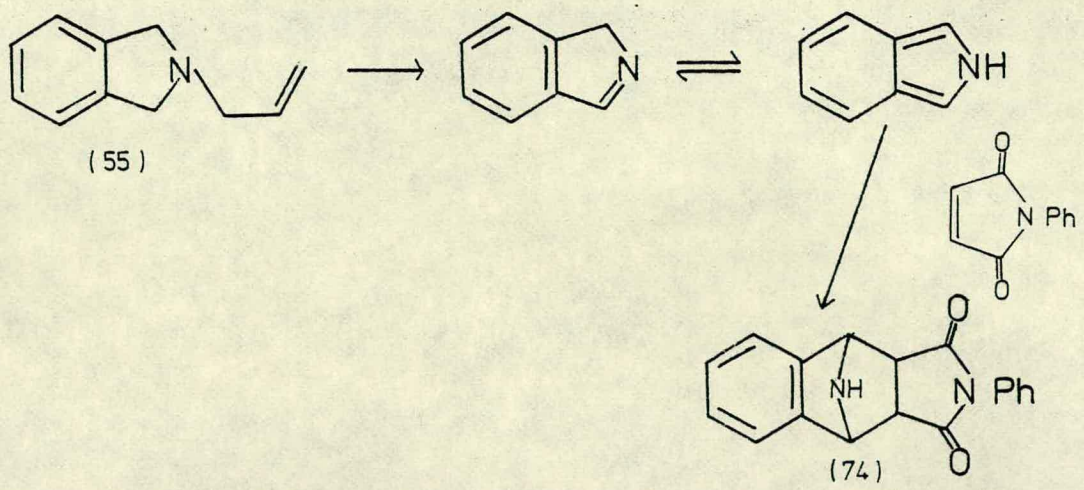


(54) (73)

Scheme 74

On the basis of the above results it was hoped that pyrolysis of *N*-allyldihydroisoindole (55) could be used as a method of generating isoindole[115] (scheme 75). This reaction should proceed *via* a retro-ene process as the nitrogen is not directly attached to the phenyl ring.

As isoindole is known to be unstable at room temperature an attempt was made to trap it at low temperatures, using *N*-phenylmaleimide in an effort to prepare the adduct (74).[116] However, this proved unsuccessful and the only product from this pyrolysis was a brown resin, suggesting that polymerisation



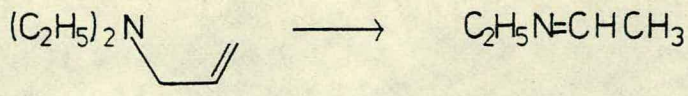
(55) (74)

Scheme 75

had occurred prior to the isoindole reaching the trap.[115,116] Several minor products were present, but only in minute quantities (<<1%) and were therefore not characterised.

In view of the previous work that had been carried out only a very limited study of pyrolysis of *N*-allyldialkylamines was carried out.

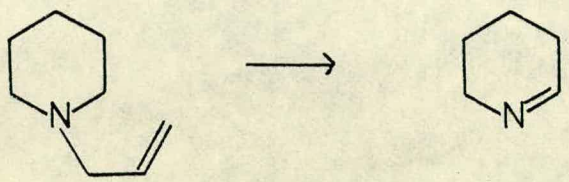
N-Allyl-*N*,*N*-diethylamine (56) gave rise to a complex pyrolysate from which the only product identified was acetaldehyde *N*-ethylimine (75). This imine was identified by comparison of the chemical shift values in the ^{1}H n.m.r. spectrum of the crude pyrolysate with literature values,[117] though the earlier assignment of minor coupling constants requires revision (see experimental section).



(56) (75)

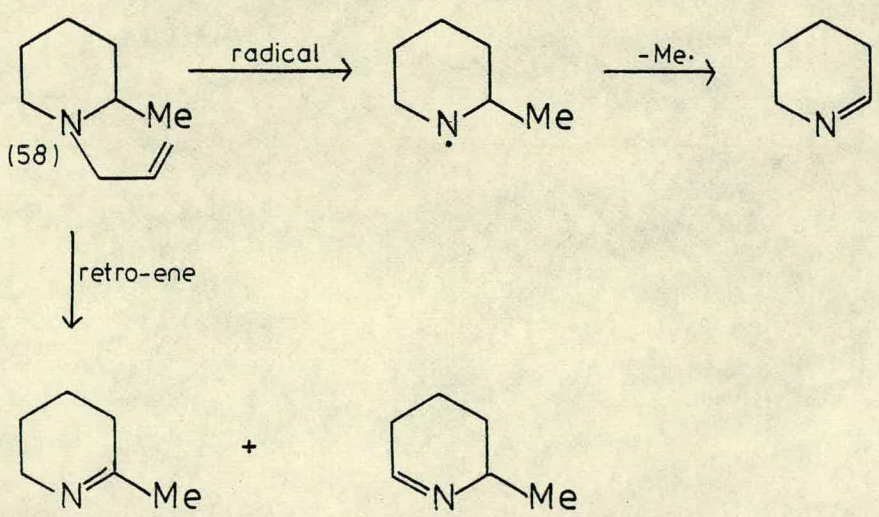
No hexa-1,5-diene was detected and no evidence for loss of a methyl group was found suggesting a retro-ene process, as would be expected.

Pyrolysis of *N*-allylpiperidine (57) again resulted in a complex pyrolysate. 3,4,5,6-Tetrahydropyridine (76) was detected by g.c./m.s. but no other products were identified.



(57) (76)

This product could be formed by either a radical or retro-ene process, although the absence of hexa-1,5-diene indicates a retro-ene pathway. If, however, a methyl group is introduced on to the 2-position of the piperidine ring then different products would be obtained depending on the mechanism in operation (scheme 76).



Scheme 76

On pyrolysis of (58), g.c./m.s. of the crude pyrolysate indicated the presence of two isomeric tetrahydropicolines, with no trace of any tetrahydropyridine. Therefore it is clear that this reaction proceeds *via* a retro-ene pathway.

It seems then that pyrolysis of *N*-allylanilines results in radical cleavage reactions, whilst *N*-allylamines undergo retro-ene reactions.

In addition to the *N*-allylamines, Earl and Vollhardt[105] also pyrolysed several *N*-propargylamines and found that these also underwent retro-ene reactions. Viola *et al*[106] also found that *N*-propargylamines decomposed *via* a retro-ene process but suggested that radical cleavage may play a part in the decomposition of *N*,*N*-dibenzylpropargylamine and *N*-methyl-*N*-propargylaniline.

It was therefore of interest to pyrolyse a series of *N*-propargylanilines, in view of the above results and the fact that the retro-ene reaction is more readily undergone by propargyl than by allyl derivatives.

Pyrolysis of *N*-methyl-*N*-propargylaniline (59) resulted in the formation of hexahydro-1,3,5-triphenyl-1,3,5-triazine (62, 17%) and aniline (22%) as the major products. The mechanism for the formation of the trimer is not clear as it could be formed by a radical or retro-ene process. The aniline is presumably formed by a high energy process but it is difficult to explain why such a large amount is obtained in this case. The presence of several minor products including toluene, indene, quinoline and benzylidene aniline indicates that some radical cleavage must be occurring.

The *N*-ethyl-*N*-propargyl compound (60) gave a complex pyrolysate, reminiscent of the pyrolysate obtained from *N*-allyl-

N-isopropylaniline (46), with no major product. This, coupled with the fact that a trace of the anil PhN=CHMe was detected, indicates a retro-ene mechanism. However a trace of formaldehyde anil ($PhN=CH_2$) was also detected by g.c./m.s. and again large quantities of aniline (20%) were obtained. Minor products obtained were *N*-ethylaniline, quinoline and benzylidene aniline. The quinoline is presumably formed by a mechanism similar to that proposed for the *N*-allylanilines (scheme 68). Formation of the benzylidene aniline is not clear but probably involves the propargyl group as it is present in all the *N*-propargylaniline pyrolysates.

Finally, pyrolysis of the *N*-isopropyl-*N*-propargylaniline gave acetone anil $PhN=C(Me)_2$ in 19% yield. This must result from a retro-ene reaction. Again a high yield of aniline (16%) was obtained. The only minor products detected were quinoline and benzylidene aniline.

These results indicate that *N*-alkyl-*N*-propargylanilines decompose thermally by a retro-ene route. However, the low yields and the presence of large quantities of aniline implies that other processes must also be occurring (see page 47/48).

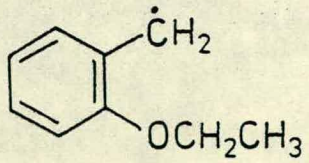
B. Reactions which Involve Generation of 2-Substituted Thiophenoxy, Anilino and Benzyl Radicals

In the introduction it was seen that on pyrolytic generation of 2-substituted benzyl or phenoxy radicals, hydrogen transfer from the substituent occurred, followed by rearrangement of the resulting alkyl radical. Husband *et al*[22] found that aldehydes were formed from (2-alkoxy)benzyl radicals (scheme 14) but that the analogous sulphur compounds gave rise to mixtures of products, the major ones resulting from elimination of the sulphur.

In order to study the influence of both the nature of the initially generated radical, and the heteroatom in the 2-position, a series of precursors to carbon and heteroatom radicals with an alkoxy, alkylthio or dialkylamino substituent in the 2-position have been prepared and pyrolysed. There are no previous examples involving initial generation of a substituted anilino radical, presumably because no suitable precursors to this radical had been found. However by using *N*-allylanilines (c.f. section A) it was found possible to generate radicals of this type.

1. Generation of Anilino and Thiophenoxy Radicals with a 2-Alkoxy Substituent

A study of these compounds was made first as reasonably clean reactions had been observed by Husband[22] on generation of the benzyl analogues such as (9), (Scheme 16).

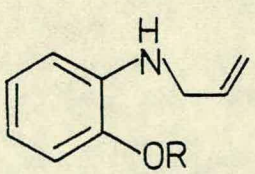


(9)

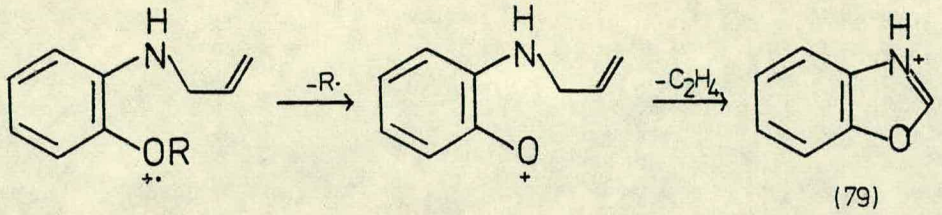
Some difficulty was experienced in preparing the appropriate 2-alkoxy-*N*-allylanilines. Specific alkylation of 2-hydroxyaniline could provide a route to these compounds and also to 2-(alkylamino)-*O*-allylphenols. It was found, though, that it was not possible to selectively alkylate the oxygen without first protecting the amine function. However, after acylation of the amine group alkylation of the oxygen atom proved to be difficult. Low yields of the required product were obtained and in an attempt to prepare the methoxy compound, migration of the acyl group from the nitrogen to the oxygen was observed.

Eventually the *N*-allyl compounds (77) and (78) were prepared by the simpler route of reaction of *o*-anisidine and *o*-phenetidine respectively, with allyl bromide in dimethylformamide containing potassium carbonate. This method results in a mixture of starting material, product and the *N*,*N*-diallyl compound as, once formed, the mono allyl compound is very readily allylated. The mixture was separated by column chromatography to give the required product.

(77) R=Me
(78) R=Et



The mass spectra of these compounds show initial loss of the alkyl group followed by loss of 28 mass units from the allyl group, presumably to give a protonated structure (79) (Scheme 77).



(79)

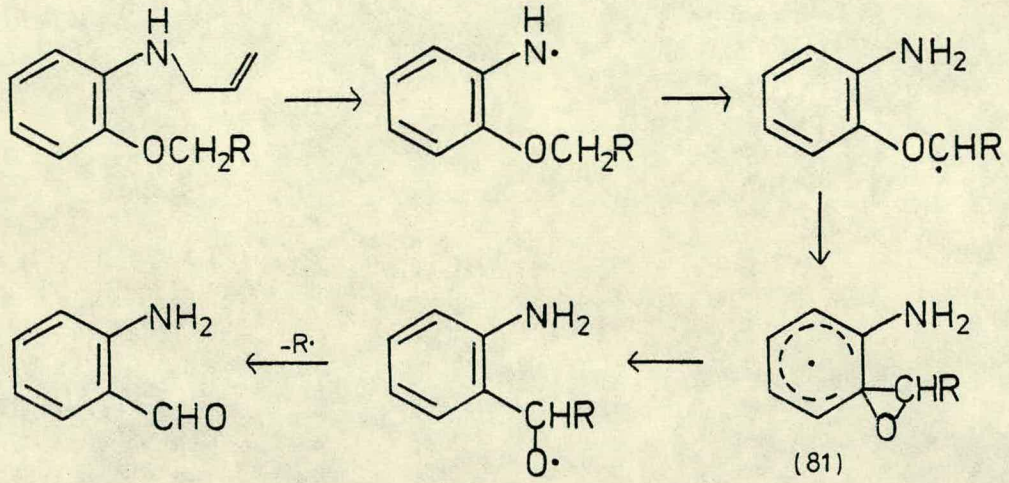
Scheme 77

Pyrolysis of (77) and (78) both resulted in a mixture of products, the major one in each case being benzoxazole (80). The major products, along with the yields are shown in Table III. Minor products were present only in trace quantities and are not further discussed.

Table III

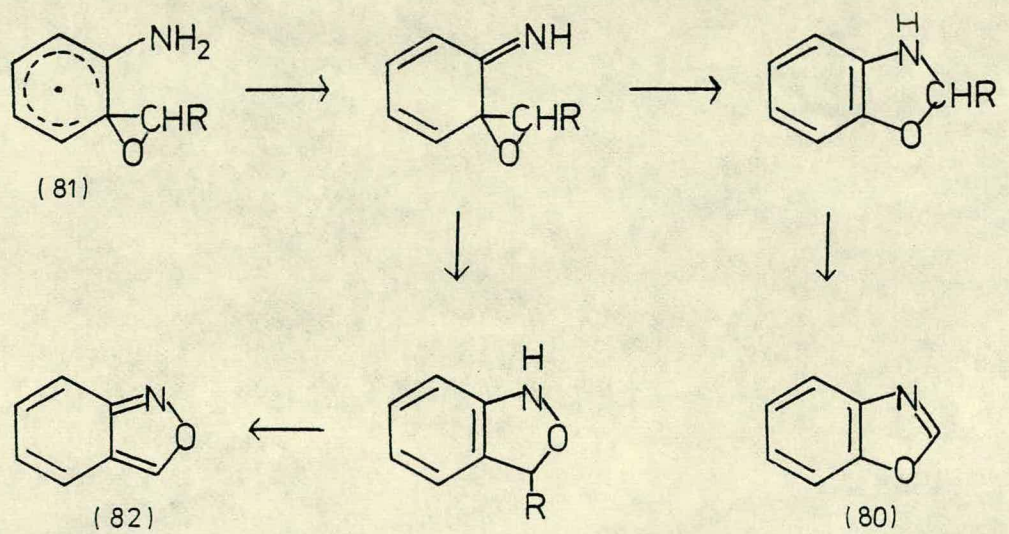
	2-methoxy (77)	2-ethoxy (78)
benzoxazole	52	56
1,2-benzisoxazole	10	7
2-aminobenzaldehyde	12	7
aniline	10	3

The 2-aminobenzaldehyde is almost certainly formed by the route shown in scheme 78, which is analogous to that observed by Husband *et al*[22] (scheme 16).



Scheme 78

The benzoxazole may also be formed from an intermediate such as (81). However, if this is the case then we would also expect some anthranil (82) to be formed (scheme 79). All three isomers of benzoxazole were separable by g.l.c. and it was clear that no anthranil was present in the pyrolysate.

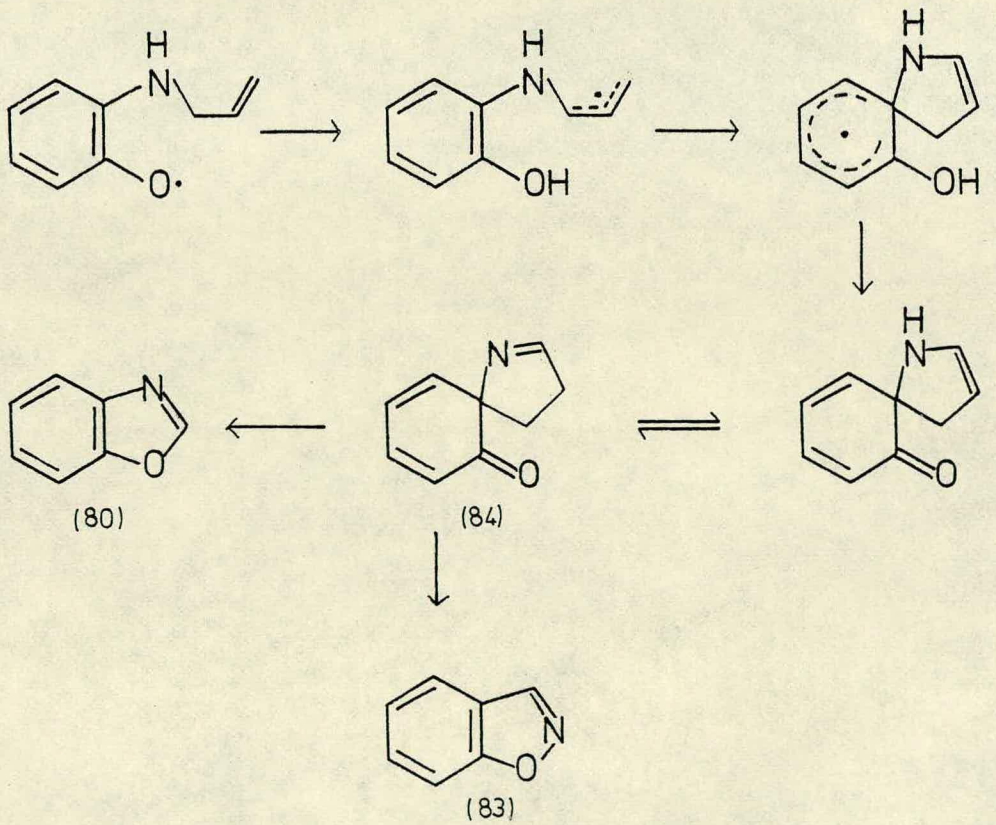


Scheme 79

The absence of any anthranil in the pyrolysate is explained by the fact that it is unstable under our pyrolysis conditions. Pyrolysis of anthranil resulted in formation of a tarry pyrolysate which contained neither anthranil, nor its isomers.[118]

It is interesting to note that Husband did not report the formation of any heterocycles in the *o*-alkoxybenzyl radical series.

The pathway shown in scheme 79 does not explain the formation of 1,2-benzisoxazole (83). If however, some cleavage of the alkoxy, rather than the allyl group occurred initially then an intermediate such as (84) could be formed which can then form either benzoxazole or 1,2-benzisoxazole (scheme 80).



Scheme 80

This mechanism for the formation of benzoxazole may be supported by the fact that approximately equal ratios of these two products are obtained in both pyrolysates. It is surprising that no ethyl substituted derivatives are obtained (see later). Formation of a five membered ring intermediate is more likely than a three membered aziridine ring due to strain factors. Also we might expect nitrogen to be extruded from a three membered ring [c.f. section B (3)].

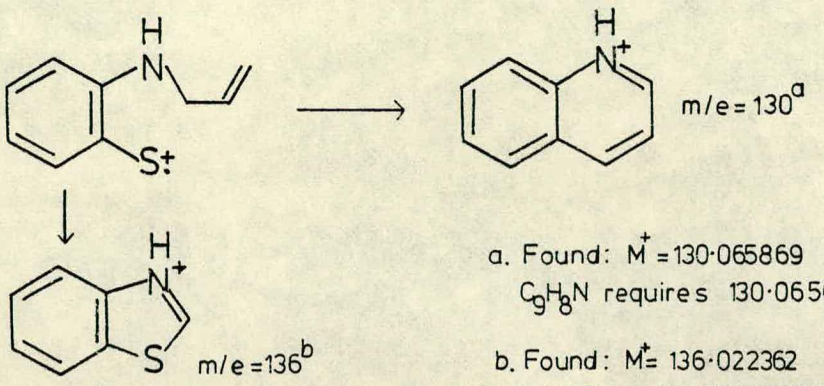
The aniline formed in these pyrolysates is surprising and again probably results from very highly excited molecules produced under these conditions.

One example of an *S*-allyl compound with a 2-alkoxy substituent was prepared and pyrolysed. In this case selective alkylation of the sulphur, followed by alkylation of the oxygen was possible [see section B (2)].

The mass spectrum of this compound was similar to those of the *N*-allyl-2-alkoxyanilines with a peak at m/e 137 being obtained, corresponding to the sulphur analogue of (79).

It was thought that these compounds with their weak sulphur-carbon bond would be a good source of thiophenoxy radicals, however on pyrolysis of *S*-allyl-2-ethoxythiophenol (85) a complex pyrolysate was obtained with no major product. A lower pyrolysis temperature resulted in an even more complex mixture. It was obvious that either this compound was not a good source of thiophenoxy radicals or that these radicals, once formed, underwent complex reactions.

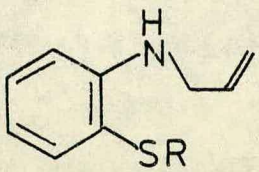
or cleavage of part of the allyl group to give a benzothiazolium ion, *m/e* = 136.



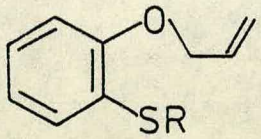
a. Found: M^+ = 130·065869
C_9H_8N requires 130·065671

b. Found: M^+ = 136·022362
C_7H_6NS requires 136·022095

The *O*-allyl compounds again show loss of the *S*-alkyl group but cleavage of the allyl group is the major fragmentation pathway of the ethyl compound (91).

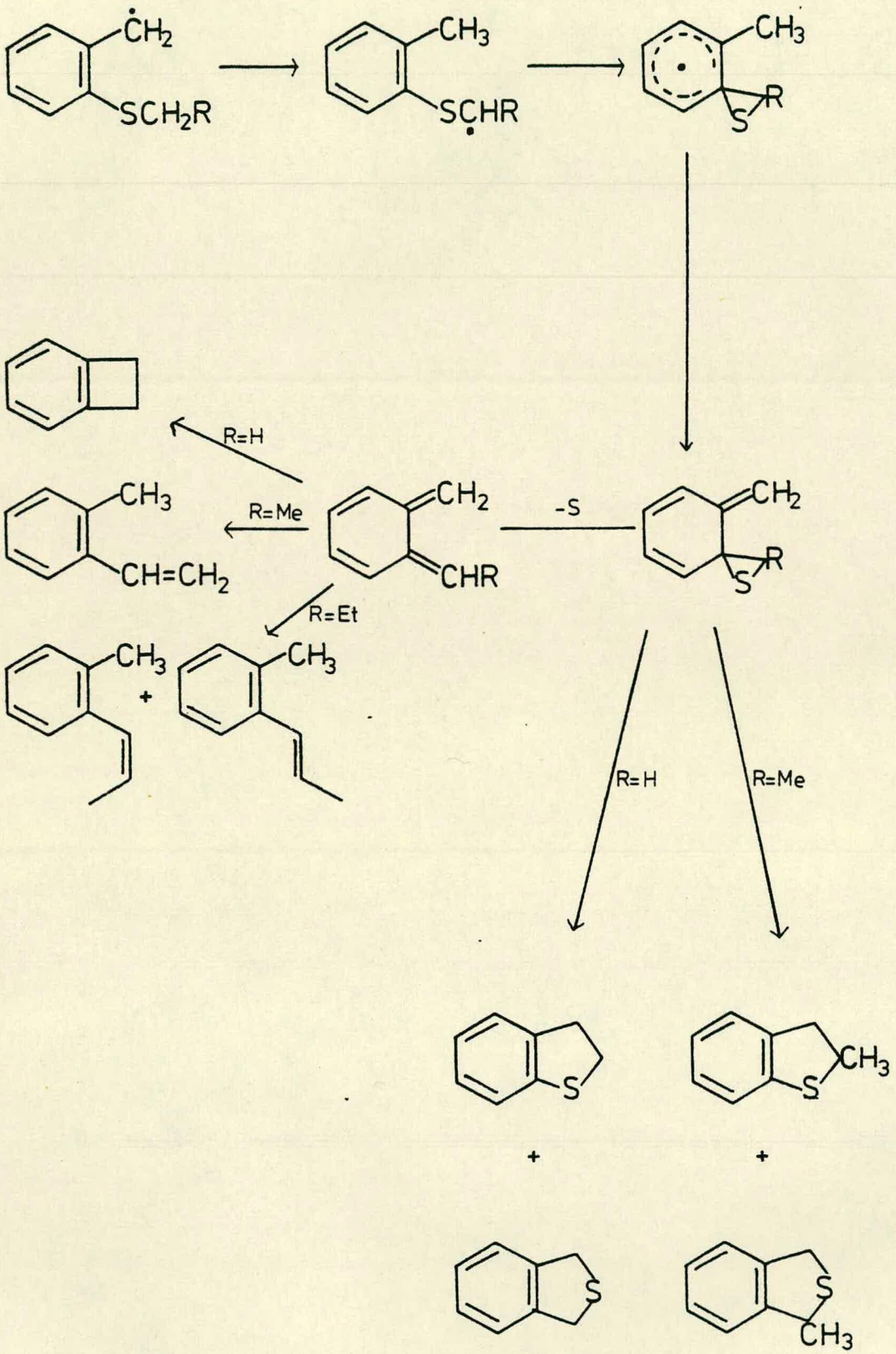


(86) R=Me
(87) R=Et
(88) R=Pr
(89) R=Pr^i
(90) R=Allyl



(91) R=Et
(92) R=Pr

On pyrolysis of the *N*-allyl compounds the major products were aminostyrenes and benzothiazole. Small quantities of 2-ethylbenzothiazole were also detected in all the pyrolysates. Table IV shows the yields of products obtained in each case. The overall accountance of product yield is significantly lower than with the *N*-allyl-2-alkoxyaniline pyrolyses.


CH2
SCH2R
CH3
SCHR
CH3
R
S
R=H
CH3
R=Me
CH=CH2
CH2
CHR
-S
CH2
R
S
R=Et
CH3
+
CH3
R=H
R=Me
S
+
S
CH3
+
S
S
CH3

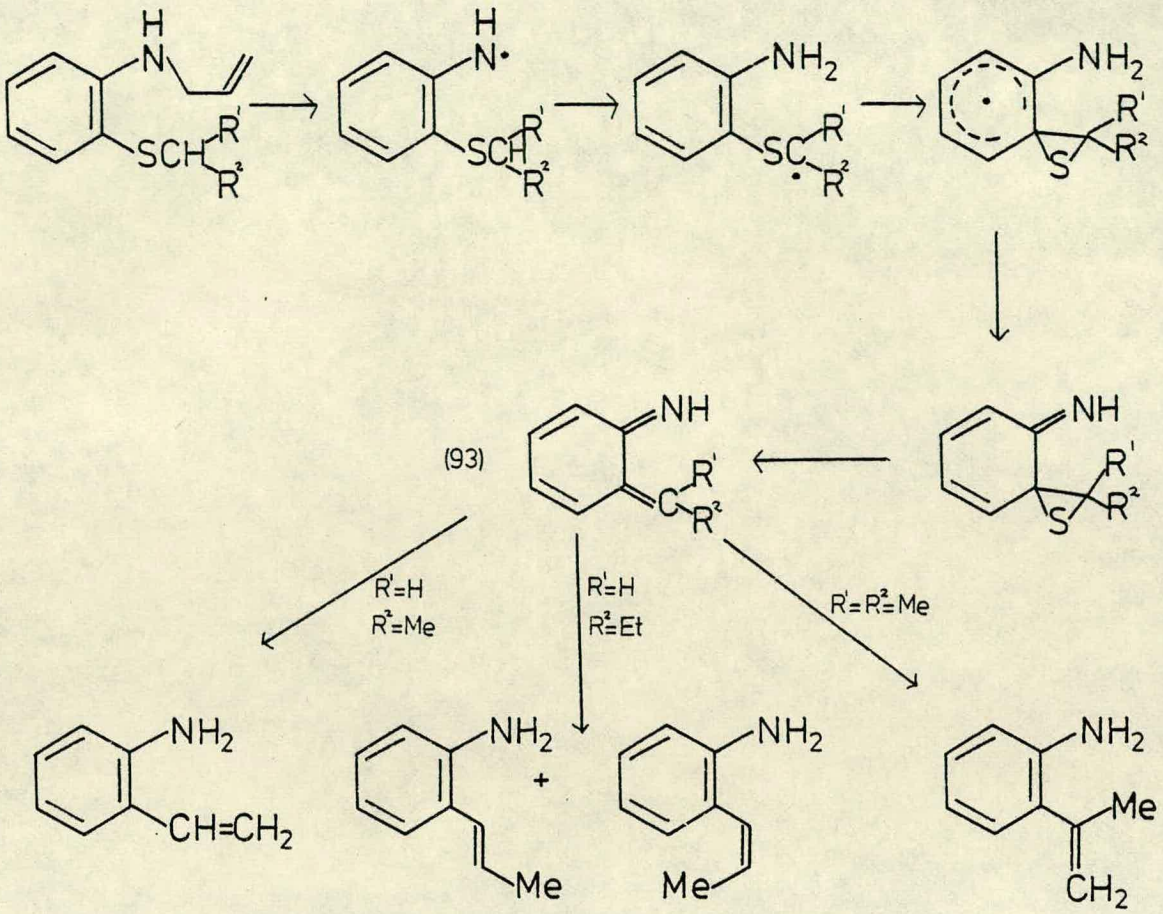
Scheme 81

Table IV

	R					
	Me	Et	Pr	Pr^i	Allyl	
Benzothiazole	7	10	21	17	49	%
2-Aminostyrene(s)	-	21	cis 6 trans 12	7	-	%
2-Ethylbenzothiazole	2	2	4	4	trace	%
Others (total % yield)	5	3	-	-	trace	%

Scheme 81 shows the mechanisms for the formation of the various products obtained by Husband[22] on pyrolytic generation of 2-thioalkylbenzyl radicals. It can be seen that the formation of the above 2-aminostyrenes can take place by a similar mechanism (scheme 82). However no nitrogen analogue of benzocyclobutene was formed. It has been suggested by Storr *et al*[120] that in general azaxylylenes do not ring close to benzazetidines.

It is therefore possible that the methylthio compound (86) undergoes a similar reaction, but gives rise to polymeric products, as the total percentage yield obtained from this pyrolysate was very low. This compound does, however, give rise to a 4% yield of 2-methylthioaniline presumably by addition of a hydrogen atom to the initially formed 2-(methylthio)-anilino radical.

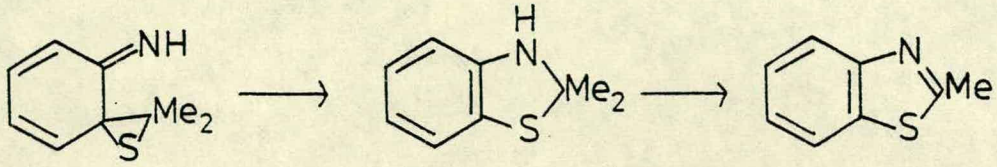


Scheme 82

The low yield of α-methyl-2-aminostyrene obtained on pyrolysis of the *N*-allyl compound (89) is explained by the ease of loss of the isopropyl group under our pyrolysis conditions. On pyrolysis of 2-(isopropylthio)aniline no evidence of an isopropyl group was found among the products, the major of which was 2-mercaptoaniline.

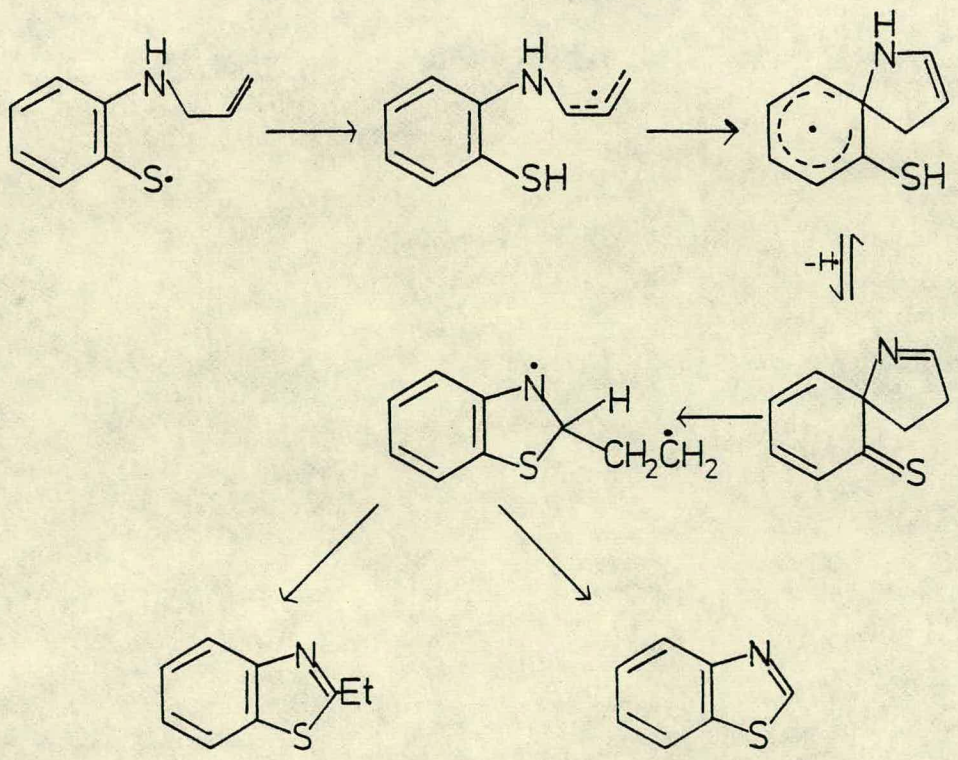
The 2-ethylbenzothiazole and at least some of the benzothiazole again probably result from loss of the alkyl rather than the allyl group. If the benzothiazole was formed *via* an analogous route to that proposed by Husband for formation of dihydrobenzothiophenes, then a methyl substituted benzothiazole must be formed on pyrolysis of the 2-isopropylthio

compound (89) (Scheme 83), but none was detected.



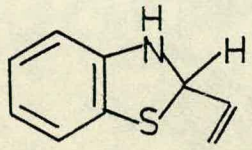
Scheme 83

Further evidence for the initial loss of an alkyl radical results from the fact that pyrolysis of the 2-allylthio compound (90) gives rise to a much higher yield of benzothiazole than any of the other pyrolysates. Again a mechanism involving a spiro-dienyl radical with a 5-membered ring intermediate is proposed (Scheme 84).



Scheme 84

Although only speculative this mechanism accounts for the transfer of two hydrogen atoms in a stepwise manner to form the ethyl group of the 2-ethylbenzothiazole. If a three membered ring intermediate was involved then (93) would be obtained which would require unprecendented transfer of two hydrogen atoms to give 2-ethylbenzothiazole.



(93)

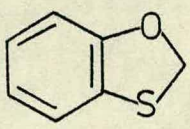
The only factor not explained by this mechanism is the very low yield of 2-ethylbenzothiazole obtained from pyrolysis of *N*-allyl-2-allylthioaniline (90). In all the other pyrolysates the ratio of benzothiazole : 2-ethylbenzothiazole is approximately equal. One method of determining if this mechanism is infact in operation would be to substitute a deuterium for the hydrogen initially attached to the nitrogen. This should then appear in the CH_2 part of the ethyl group.

The oxygen analogues of these compounds also give rise to two major products on pyrolysis (Table V). Surprisingly no sulphur containing products are formed in significant quantities.

Table V

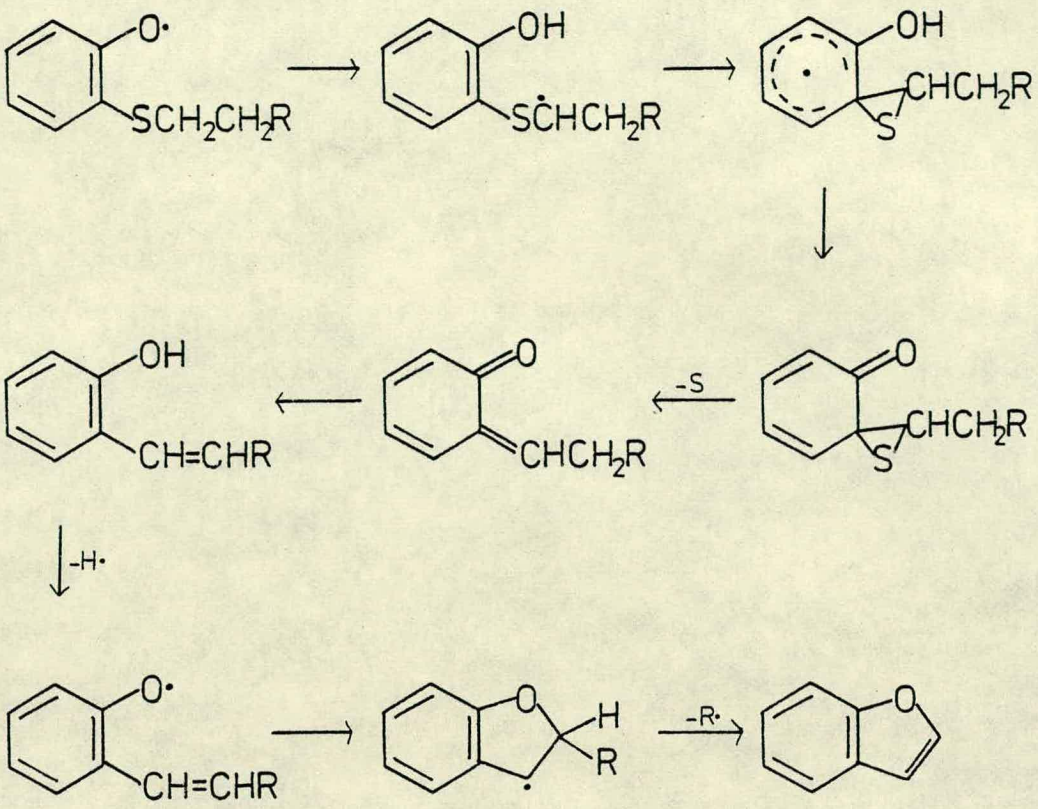
	R		
	Et (91)	Pr (92)	
Benzofuran	26	12	%
o-Hydroxystyrene(s)	48	9 cis 15 trans	%

Benzoxathioles (94), the sulphur analogues of the dihydrobenzothiazole intermediates are known [121] but nothing is known of their stability under pyrolysis conditions.



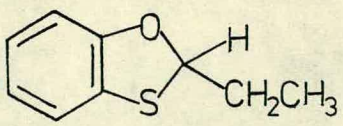
(94)

However, as the reactions are clean, particularly in the case of the ethyl compound (91), with only one minor product being detected in trace quantity, it seems likely that the reaction follows only the pathway shown in scheme 85. The benzofuran is probably formed by cyclisation of the *o*-hydroxystyrene, as it is known that 2-methylstyrene gives rise to indene under similar pyrolysis conditions.[118]



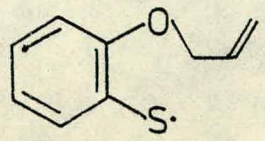
Scheme 85

The crude pyrolysate of the propyl compound (92) also contained a trace of methylbenzofuran which could be obtained by loss of a hydrogen atom rather than a methyl radical in the final step of scheme 85. Several other minor products were detected in the crude pyrolysate of (92), including trace quantities of styrene, phenyl allyl ether and a compound with the correct molecular ion for a structure such as (95).



(95)

Since both the oxygen and sulphur atoms have C_3 units attached, (95) could arise from either *S*-alkyl or *O*-allyl cleavage. The lower yields of product found in the pyrolysate point to some other reaction pathway occurring. On the basis of previous results a radical such as (96) would be expected to give (95) and benzoxathiole as the products.



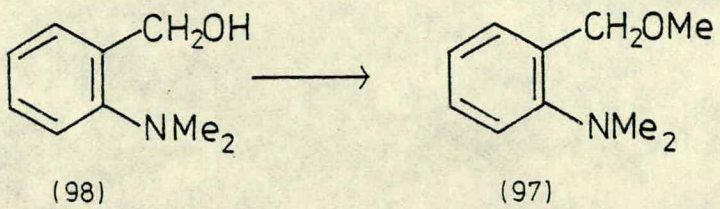
(96)

However attempts at generating sulphur radicals with 2-alkoxy substituents resulted in a complex mixture of products (see section 1).

3. Generation of Benzyl and Phenoxy Radicals with a 2-Dialkylamino Substituent

Husband[122] tried several methods of preparing a suitable precursor to 2-(alkylamino)benzyl radicals. Several different routes to the appropriate oxalates or sulphones were attempted but none proved successful.

In the present study an attempt was made to generate the 2-(dimethylamino)benzyl radical by pyrolysis of methyl 2-(*N*,*N*-dimethylamino)benzyl ether (97). The benzyl alcohol (98) was easily prepared by the method used by Husband *et al.*[122] This compound was then alkylated by reaction with methyl iodide in tetrahydrofuran containing sodium hydride.

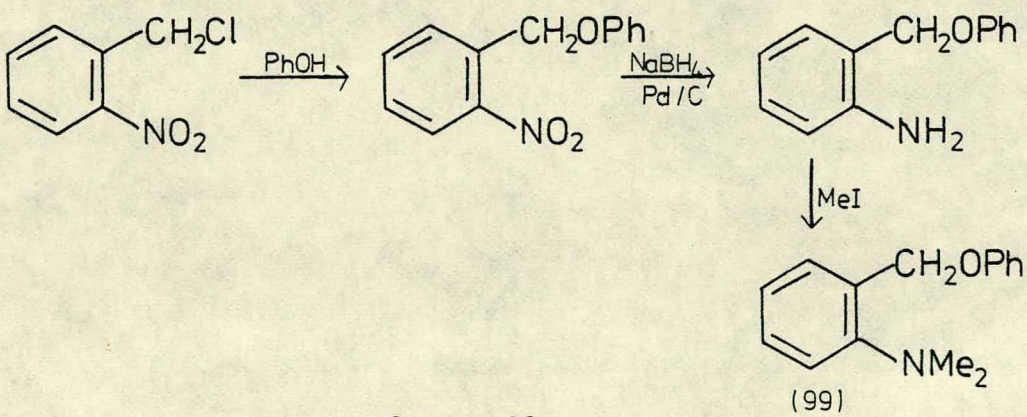


(98) (97)

However, on pyrolysis of (97) no major product was obtained and at least twelve minor products were detected. It was obvious that a better leaving group, such as a phenoxy radical, was necessary to generate the benzyl radical.

An attempt was made to convert the alcohol (98) to the benzyl chloride which could then be reacted with phenol. However an attempt to prepare the chloro compound was unsuccessful.

Eventually the following sequence of reactions was devised for preparation of the phenyl ether of 2-(*N*,*N*-dimethylamino)benzyl alcohol (99) (Scheme 86).



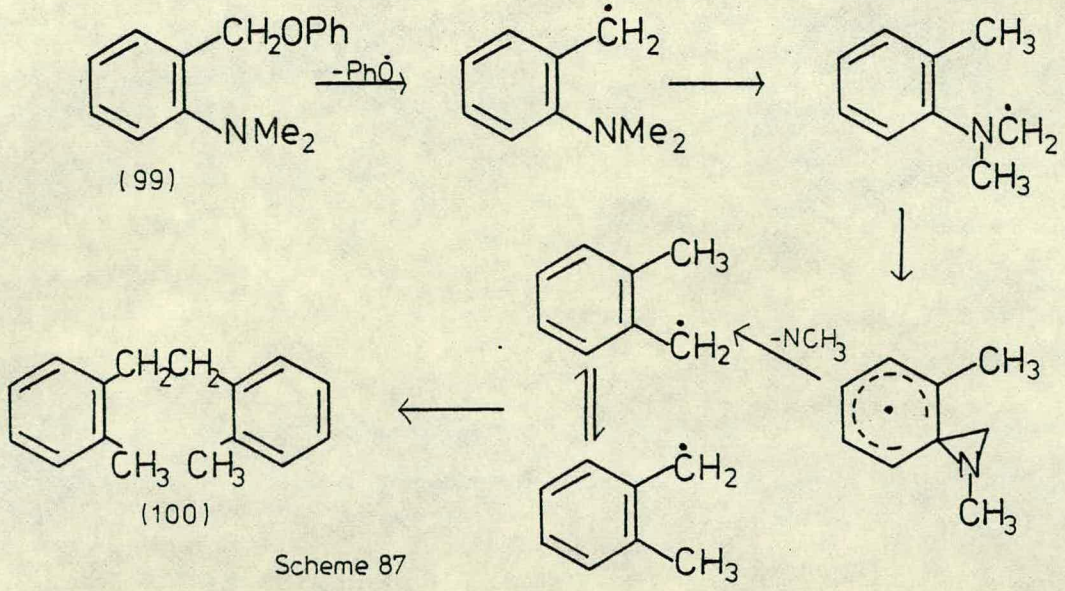
(99)

Scheme 86

Reaction of 2-nitrobenzyl chloride with phenol in dimethylformamide containing potassium carbonate gave phenyl

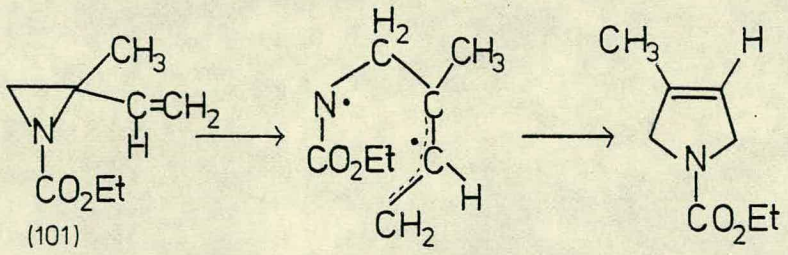
2-(nitro)benzyl ether. The next step involved reduction of the nitro-compound to the amine, and this was carried out using sodium borohydride and palladium charcoal in a water/methanol mixture.[123] Finally alkylation of phenyl 2-(amino)-benzyl ether was carried out using methyl iodide in dimethyl-formamide containing potassium carbonate to give the required product (99). This compound shows only one major fragmentation in its mass spectrum, that is, loss of the phenoxy group.

On pyrolysis of this phenyl ether (99), the major product, apart from the phenol derived from the phenoxy radicals, was di-*o*-tolylethane (100). In order to form this product nitrogen must be lost at some stage in the reaction. A mechanism similar to that observed with the 2-alkylthiobenzyl radicals[22] (scheme 17) is proposed (scheme 87). By using deuterium labelled methyl groups it was possible to show that this route is feasible as deuterium is then found in both the CH_2 (δ^2H 2.90) and CH_3 (δ^2H 2.36) groups of the di-*o*-tolylethane. Complete scrambling in the *o*-methylbenzyl radical would give a predicted integral ratio of methylene to methyl of 1:2 and the observed ratio was 1:2.3 which is probably within experimental error.



Scheme 87

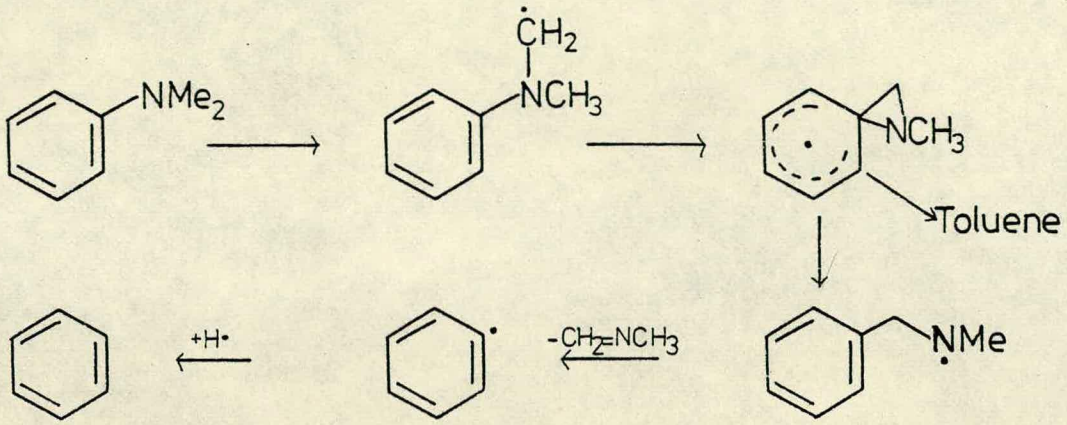
However, unlike the analogous loss of sulphur from episulphides which is well known,[124] there is no precedence for loss of the nitrogen function on thermolysis of aziridines. Thermolysis of the aziridine (101) in a g.c. inlet system resulted in ring expansion occurring to give a 5-membered nitrogen containing ring.[125] The proposed mechanism involves cleavage of just one carbon-nitrogen bond to give a di-radical[126] (scheme 88).



Scheme 88

There is one isolated example in the literature in which loss of nitrogen by a similar mechanism to ours is proposed. On pyrolysis of *N*,*N*-dimethylaniline in a static reactor in the presence of hydrogen,[127] benzene and toluene were formed, as well as various nitrogen containing products. The proposed

mechanism for the formation of benzene is shown in scheme 89. The toluene may be formed from the spiro intermediate by a process similar to ours.



Scheme 89

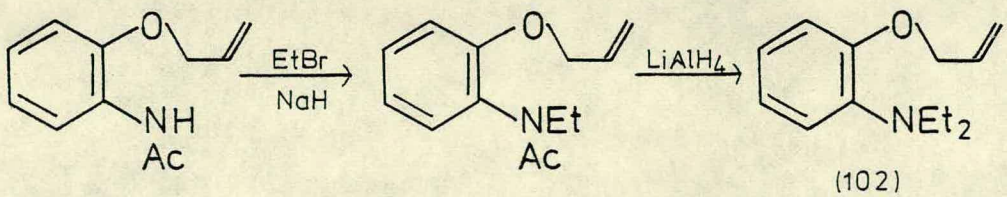
It is therefore not clear how the nitrogen function is lost from these compounds during pyrolysis. Two possible explanations are that it is lost as a nitrene or, more likely, that ring opening, followed by isomerisation occurs, allowing it to be lost as an imine.

Returning to the pyrolysate of phenyl 2-(*N*,*N*-dimethylamino)benzyl ether (99), most of the minor products did not contain nitrogen either. The minor products detected were *o*-ethyltoluene, *o*-tolualdehyde, *N*-methylindole, *o*-toluidine, *o*-xylene and anisole. The *o*-ethyltoluene and *o*-xylene are probably formed from the *o*-(methyl)benzyl radical by addition of a methyl radical or hydrogen atom respectively. The anisole must arise from coupling of phenoxy and methyl radicals. *o*-Tolualdehyde must result from initial cleavage of a phenyl rather than a phenoxy radical, followed by hydrogen transfer and loss of the $N\text{-}CH_3$ fragment. Of the two nitrogen containing products, both present in very low yields (∿1%), the *N*-methyl

indole must result from cyclisation of the initially formed 2-(*N*,*N*-dimethylamino)benzyl radical. The *o*-toluidine is presumably formed *via* some high energy molecules similar to the formation of aniline in section A.

As this was the only example of a radical with a nitrogen in the 2-position, some precursors to phenoxy, rather than benzyl radicals of this type were prepared.

Again it proved difficult to prepare these compounds as it was not possible to specifically alkylate the oxygen without first protecting the nitrogen from attack (c.f. section 1). After protection of the amino function with an acetyl group it was then possible to allylate the oxygen using allyl bromide as previously described. The acetyl group was then removed by refluxing the compound in acid and an attempt was made to prepare the dialkyl and/or monoalkylamino compounds. Reaction of the amino compound with an excess of the appropriate alkyl halide resulted in a mixture of mono- and di-alkylated products which could not be separated by column chromatography. Eventually the following scheme, in which the protecting group is incorporated directly into the required product, was devised for the preparation of the diethyl compound, (102), (Scheme 90).



(102)

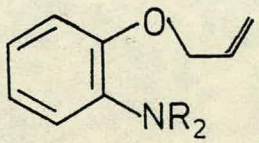
Scheme 90

The *N*-acetyl-*O*-allyl compound was reacted with ethyl bromide in tetrahydrofuran containing sodium hydride to give *N*-acetyl-2-allyloxy-*N*-ethylaniline. The acetyl group was then reduced to an ethyl group using lithium aluminium hydride[128] to give the required *N*,*N*-diethyl compound (102).

The *N*,*N*-dimethyl compound (103) was prepared in a similar manner using a formyl rather than an acetyl protecting group and methyl iodide in the alkylation step. The only major fragmentation pathway in the mass spectra of these compounds is loss of the allyl group.

Attempts to prepare the mono-ethyl- and mono-methyl-*O*-allyl compounds by reduction of *N*-acetyl-2-allyloxyaniline and *N*-formyl-2-allyloxyaniline respectively, proved unsuccessful.

On pyrolysis of (102) and (103) the major products again did not contain nitrogen.



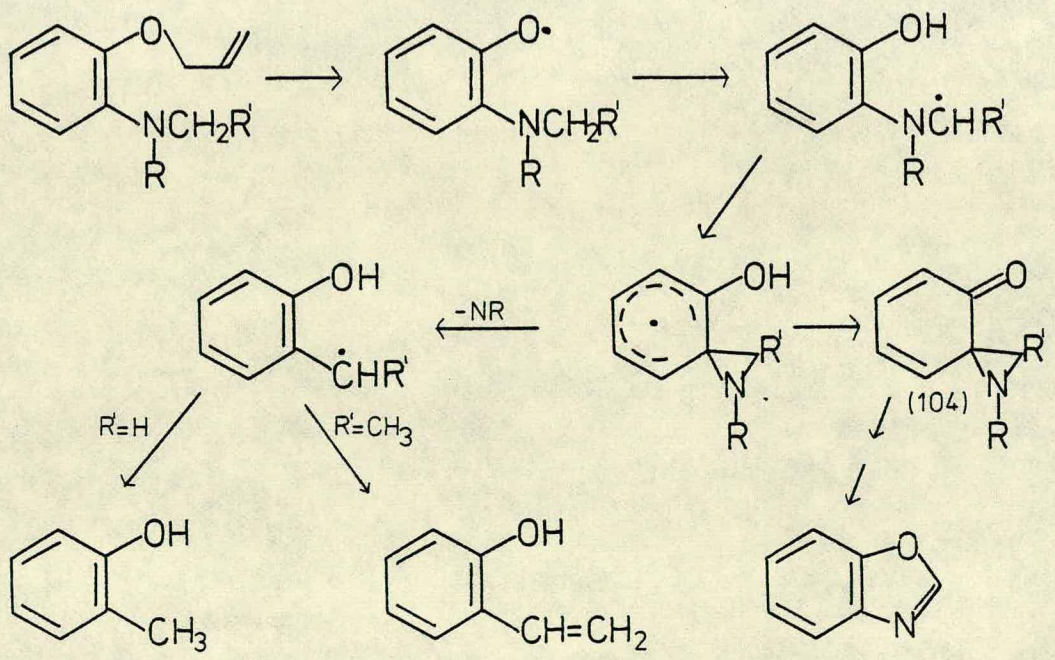
(102) R=Et
(103) R=Me

The products obtained, along with the approximate yields of minor products are shown in Table VI.

Table VI

	R	
	Me (102)	Et (103)
o-Cresol	19	- %
o-Hydroxystyrene	4	10 %
o-Ethylphenol	4	6 %
Benzofuran	3	3 %
Phenol	-	3 %
Benzoxazole	2	2 %
2-Methylbenzoxazole	trace	-

The following scheme is proposed for the formation of the major products, again involving loss of nitrogen *via* a 3-membered ring (Scheme 91).



Scheme 91

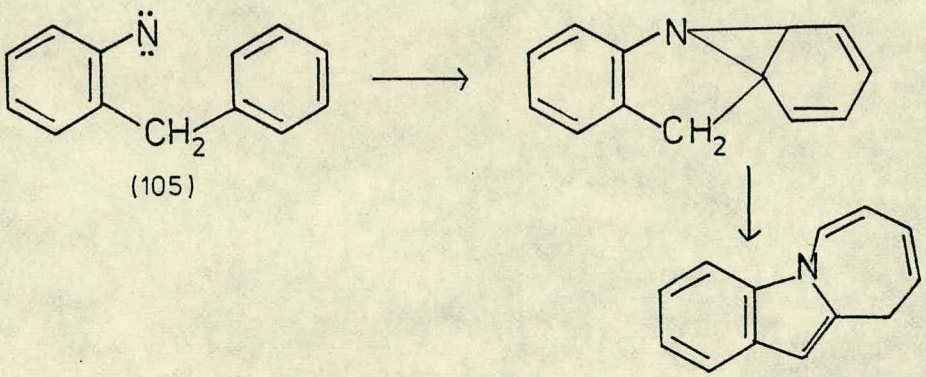
The *o*-ethylphenol formed from the dimethyl compound presumably arises from coupling of the benzyl radical with a methyl radical (c.f. page 85), with some dehydrogenation then occurring to give *o*-hydroxystyrene. In both pyrolyses the benzofuran is explained as being derived from the *o*-hydroxystyrene (scheme 85). The benzoxazole arises logically from cyclisation of the intermediate (104) (c.f. Scheme 79), although it is surprising that 2-methylbenzoxazole is found in the pyrolysate from the dimethyl rather than the diethyl compound. The mechanism for the formation of phenol must involve a high energy process resulting in loss of the entire diethylamino function.

C. Reactions which Involve *N*-Allyl-2-aminodiphenylmethane and Related Heteroanalogues

In the previous section the interaction of radicals with alkyl groups was studied. We now turn to the interaction of anilino radicals with adjacent aryl groups. There is only one paper in the literature on gas phase reactions of this type. Trahanovsky[23] has shown that pyrolysis of di-*o*-arylbenzyl oxalates generates *o*-arylbenzyl radicals which result in the formation of cyclic products. For example di-*o*-benzylbenzyl oxalate gives rise to 9,10-dihydroanthracene.

However, most of the previous interest in this type of reaction involves the behaviour of nitrenes and carbenes, with adjacent aryl groups, often in solution.

Krbechek and Takimoto[129] found that the nitrene (105) generated from the azide, inserted into the π-system of the adjacent phenyl ring to give a ring expanded product (scheme 92).

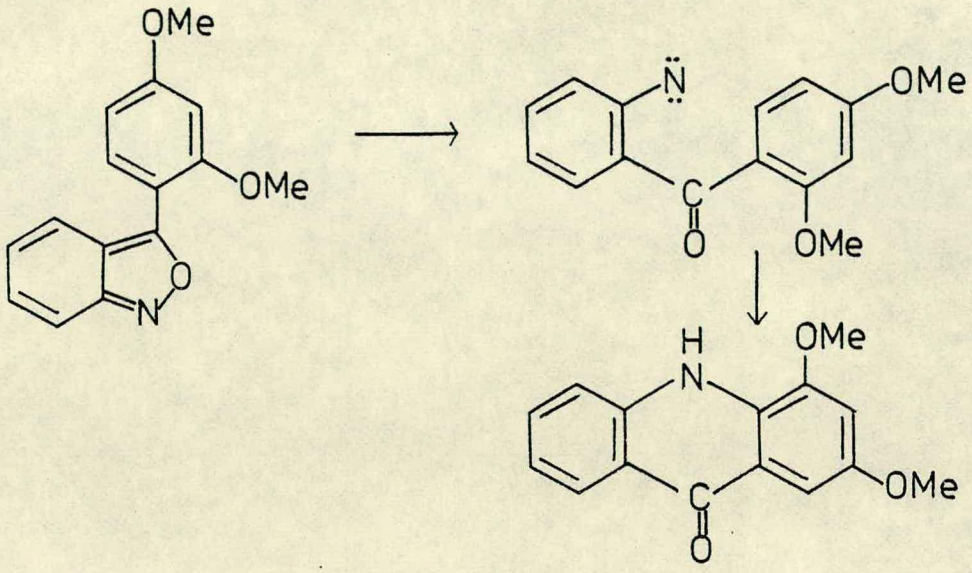


(105)

Scheme 92

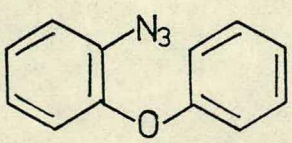
This reaction has been studied and extended by G. Jones and his co-workers.[130] In contrast, Crow and McNab[131] found that the corresponding carbene underwent direct cyclisation to give 9,10-dihydroanthracene and anthracene.

Kwok and Pranc[132] generated nitrenes with substituted acyl rings and found that rearrangement of the substituents was observed in the products (scheme 93). The possible mechanism for this rearrangement is discussed at a later stage.



Scheme 93

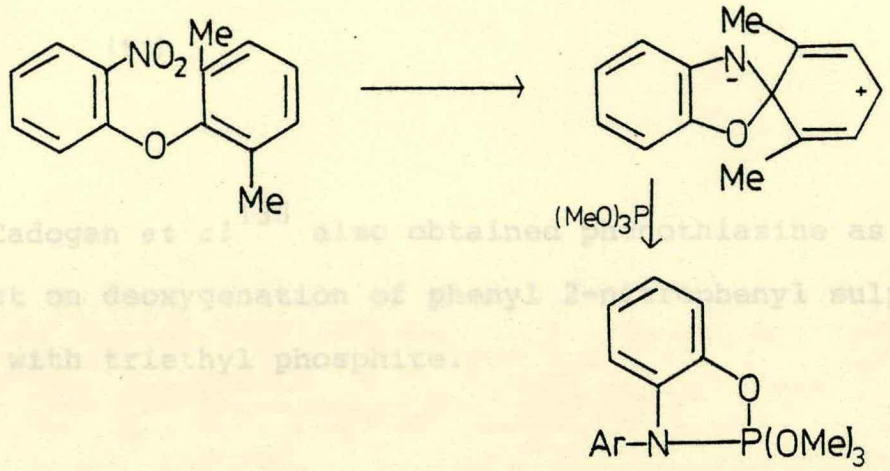
Several groups have studied nitrenes and carbenes with adjacent *O*-aryl groups. Smith *et al*[133] hoped to obtain phenoxazine by photolysis or thermolysis of the azide (106), but both methods proved unsuccessful.



(106)

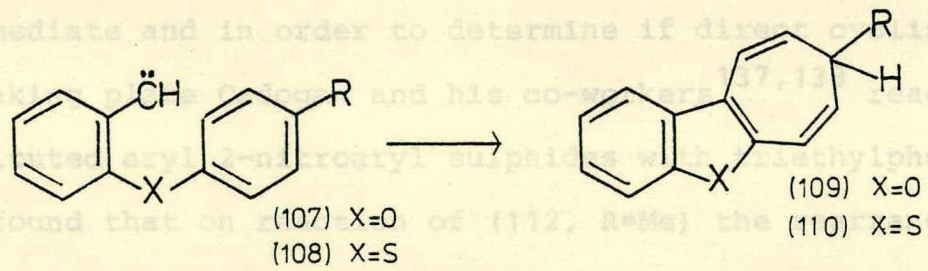
Cadogan *et al*[134] did manage to prepare some phenoxazines by thermolysis of azides with blocked *o*-positions on the adjacent aryl ring. However generation of the nitrenes by deoxygenation of the nitro compounds with trimethyl phosphite, a method that

had proved successful with the analogous sulphur compounds, resulted in the formation of phosphoranes (scheme 94) in preference to the expected phenoxazines.[135]

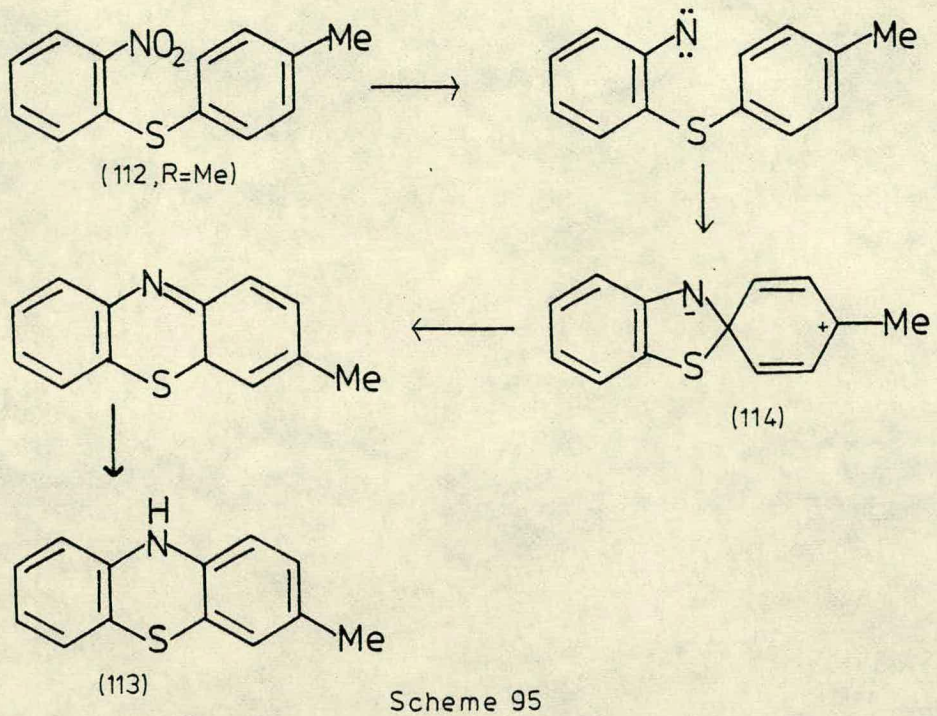


Scheme 94

On generation of the carbene (107), Crow and McNab[131] observed formation of a ring expanded product (109) due to π-insertion into the adjacent phenyl ring.



The corresponding sulphur containing ring expanded product (110) was similarly formed. In the nitrene series direct cyclisation takes place rather than formation of a ring expanded product. In contrast to the oxygen example, Smith *et al*[133] found that phenothiazine was formed on thermolysis or photolysis of the azide (111).



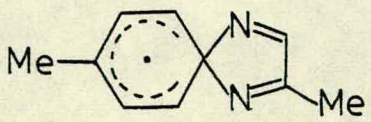
Scheme 95

Cadogan *et al* also reinvestigated the work of Smith and found that the thermolysis or photolysis of azides resulting in phenothiazines proceeds *via* an analogous route. However, lower yields are obtained than by deoxygenation of the appropriate nitro compounds.

Concurrently, and independently of this work, Messer and Farge[139] studied the thermal decomposition reactions of azides and observed similar rearrangements.

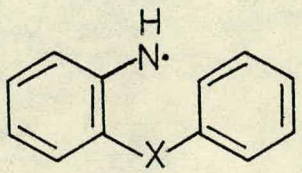
Spirodiene structures similar to (114) have also been postulated in gas phase free radical chemistry. It was proposed by McNab[61] that iminyl radicals give rise to rearranged products *via* a spirodienyl radical (21) (see scheme 39).

In this example two products are obtained as either C-N bond can migrate. Cadogan *et al*[138] found only one product formed from the spirodiene intermediate (114). This suggests that the product(s) formed depends on the relative migratory tendencies of the two bonds involved.



(21)

It is therefore of interest to generate radicals of the type (115) in order to investigate the mechanism for reaction of these species.



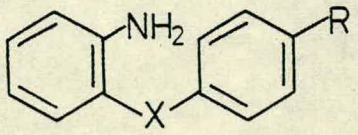
X= CH_2, C=O, NH, O or S.

(115)

As the derivatives with X=CH_2, C=O and NH were most readily prepared they were pyrolysed to determine if cyclisation to give a six membered ring, or ring expansion to give a five and a seven membered ring was observed. Methyl substituted oxygen and sulphur analogues were then prepared and the mechanism of these pyrolyses was studied in more detail.

The appropriate radicals (115) were generated by pyrolysis of the *N*-allyl derivatives. In order to prepare the *N*-allyl compounds it was first necessary to make the appropriate secondary amines (116) to (120).

2-Aminobenzophenone (116) was available commercially and this was converted to 2-aminodiphenylmethane (117) in good yield by a Wolff-Kischer reduction. This method appears to be better



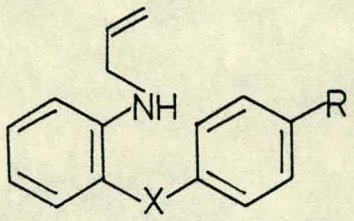
	X	R
(116)	C=O	H
(117)	CH_2	H
(118)	NH	H
(119)	O	Me
(120)	S	Me

than any of the literature preparations for this compound. The nitrogen analogue (118) was prepared by reduction of the nitro compound, available commercially, with sodium borohydride and palladium charcoal in methanol/water[123]. In the cases of the oxygen and sulphur compounds (119) and (120) it was necessary to prepare the nitro compound by reaction of 2-chloronitrobenzene with the appropriate phenol or thiophenol and so the *p*-methyl substituted substrates were used.

The amine (119) was prepared by reduction of the nitro compound in the same manner as used for the nitrogen analogue (118). However this proved unsuccessful for the sulphur compound (120), which was finally prepared by direct hydrogenation of an ethanolic solution of the nitro compound using a palladium charcoal catalyst.

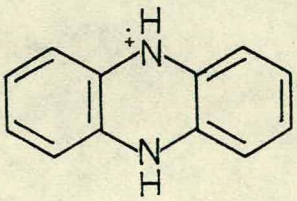
The *N*-allyl compounds (121-125) were prepared by reaction of the amine with allyl bromide in dimethylformamide containing potassium carbonate. It was found, as before, that the *N*-allyl compound, once formed, alkylated readily to give the diallylamine and so an excess of the secondary amine was used. The mixture of starting material, product and *N*,*N*-diallyl compound was separated by column chromatography. In general yields of 40-50% of purified products were obtained, but a very low yield

was found for (*N*-allyl-2-amino)diphenylamine (123).

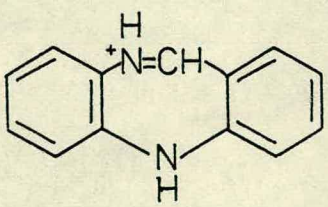


	X	R
(121)	C=O	H
(122)	CH_2	H
(123)	NH	H
(124)	O	Me
(125)	S	Me

The mass spectra of these compounds all showed slightly different breakdown patterns, although, with only one exception, the major fragmentation pathway generally involved loss of the allyl group. In the case of (121) cleavage occurred adjacent to the carbonyl group resulting in two fragments with *m/e* = 132 and *m/e* = 105. Both (122) and (123) gave a peak at M-41 resulting from loss of the allyl group but (123) also gave a large peak at M-42. This probably arises by cyclisation followed by loss of a hydrogen atom to give a structure such as (126). Compound (123) also gives a large peak at M-29 corresponding to an intermediate such as (127).



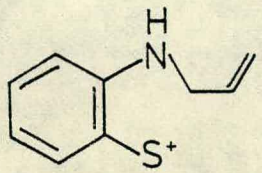
(126)



(127)

Finally the oxygen and sulphur compounds (124) and (125) fragment with cleavage of the entire allylamine function to

give a peak at M-56. The sulphur compound also fragments with loss of the aryl group to give an intermediate, (128), the same as that found on loss of the alkyl group from *N*-allyl-2-alkythioanilines [section B(2)]. As before this results in the two structures with *m/e* = 130 and *m/e* = 136.

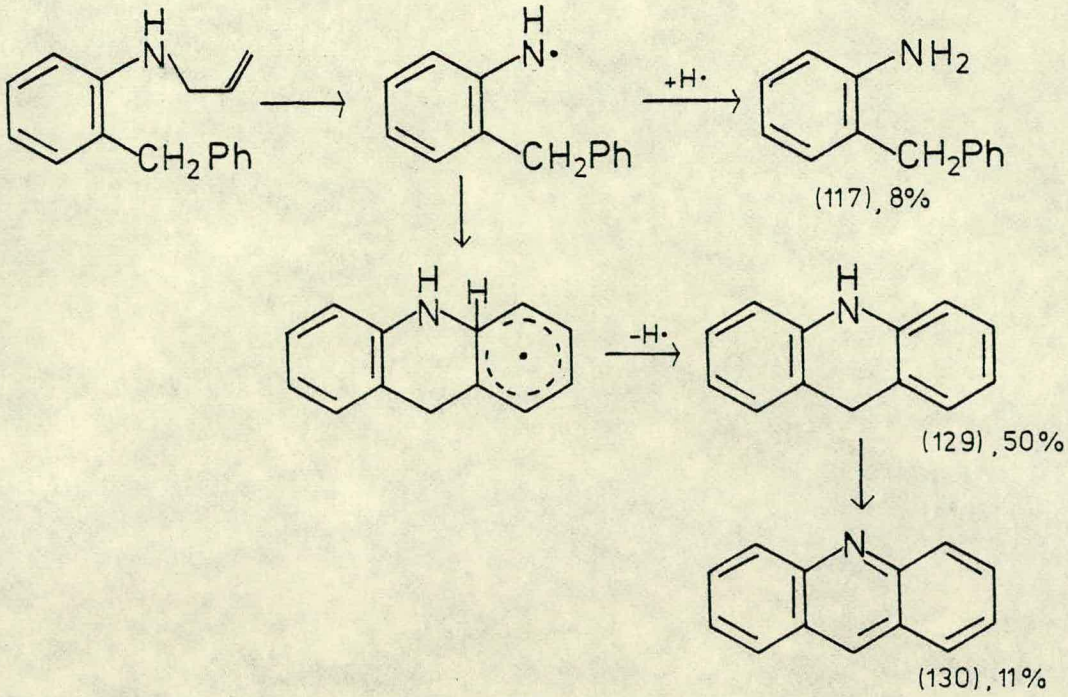


(128)

The oxygen compound (124) undergoes a similar fragmentation to give peaks at *m/e* = 131 and *m/e* = 120.

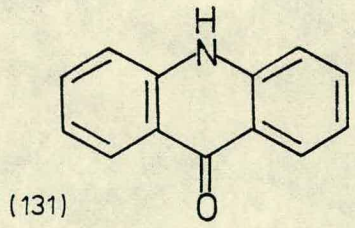
Pyrolysis of *N*-allyl-2-aminodiphenylmethane (122) and *N*-allyl-2-aminobenzophenone were carried out first in order to determine if direct cyclisation would occur (c.f. scheme 94) or if ring expanded products (c.f. scheme 95) would be formed.

Pyrolysis of (122) resulted mainly in the formation of acridan (129), although some acridine (130) was also detected. It is possible, though, that the acridine is formed by dehydrogenation of acridan on the g.l.c. column.[131] The only other product was the secondary amine (117). The proposed mechanism for the formation of these products is shown in scheme 96.



Scheme 96

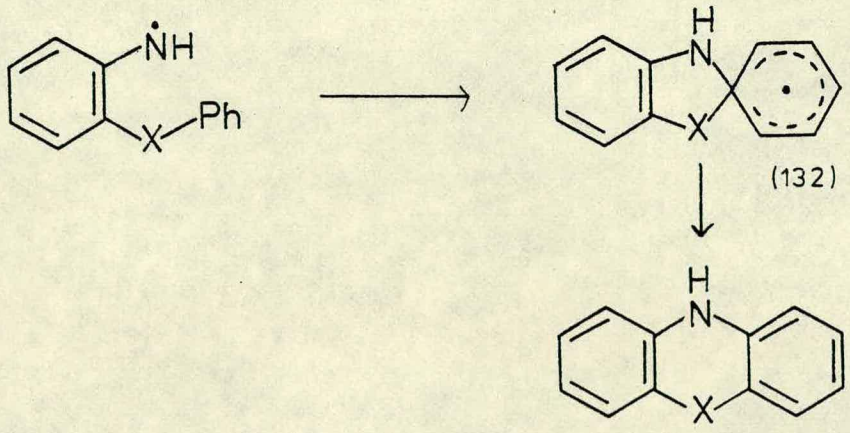
Similarly *N*-allyl-2-aminobenzophenone (121) underwent a very clean reaction to give almost pure acridone (131). Minor products were found to be present only in trace amounts and were not characterised.



(131)

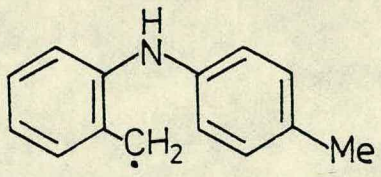
It is obvious, then, that these radical reactions do not result in any ring expansion products as observed with nitrenes 129,130.

However it is not possible to tell if the reactions are occurring *via* direct cyclisation or by a spirodienyl radical (132) (scheme 97) as observed with the sulphur containing nitrene analogues (scheme 92).



Scheme 97

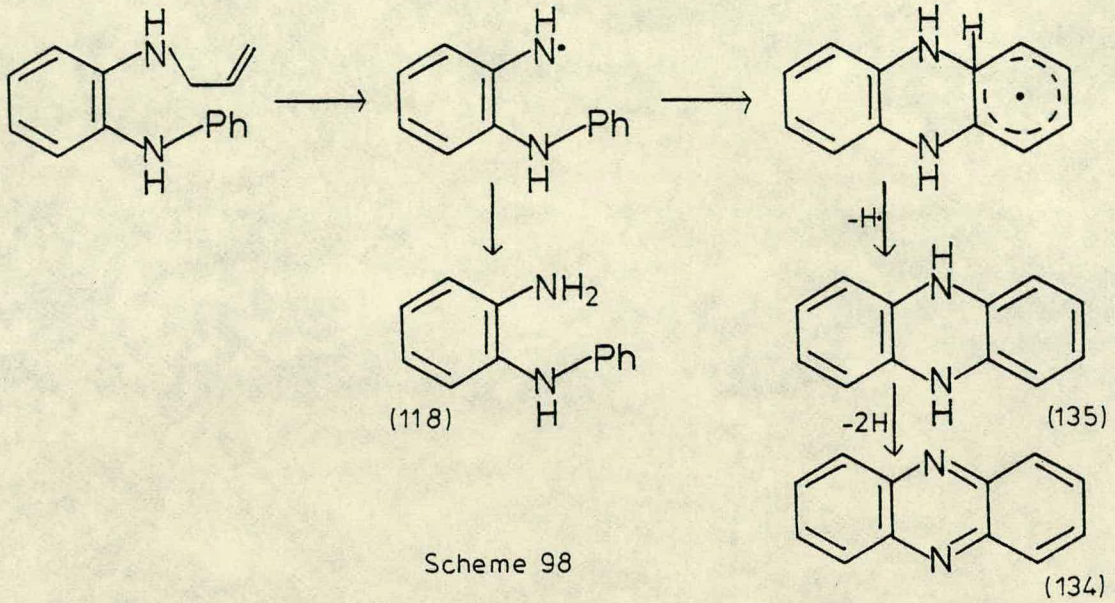
In order to determine the mechanism it would be necessary to introduce a methyl group on to the mono-substituted phenyl ring. However, it has been found that in similar systems, C-N migration is favoured over C-C migration,[70,71] and this would lead to the same product as formed by direct cyclisation of the anilino radical. One possible way of overcoming this problem would be to generate the radical (133), which should give rise to a rearranged product if a spirodienyl intermediate is involved.



(133)

No examples of simple nitrenes[140] with 2-amino substituents were found in the literature and so pyrolysis of (*N*-allyl-2-amino)diphenylamine (123) was carried out in order to determine if direct cyclisation or ring expansion reactions occurred. The major product was phenazine (134) with small quantities of

5,10-dihydrophenazine (135) and 2-aminodiphenylamine (118) being detected (scheme 98).

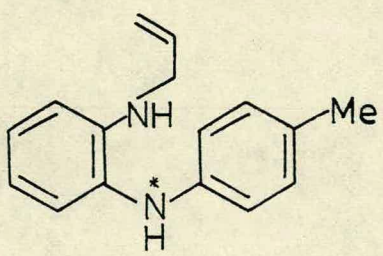


Scheme 98

The dihydro compound[141] (135) is known to be readily oxidised to phenazine in the presence of air.

The phenazine was obtained as a black powdery solid, characterised by mixed m.p., g.l.c., and ^{1}H n.m.r. spectroscopy.

In order to determine the mechanism for this cyclisation reaction it would be necessary to use a ^{15}N labelled compound with a methyl substituent such as (136).



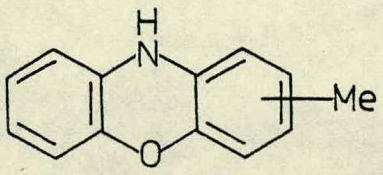
(136)

If a spiro-dienyl mechanism is in operation then the ratios of isomers could be determined by ^{15}N n.m.r. spectroscopy.

Pyrolysis of the methyl labelled compounds (124) and (125)

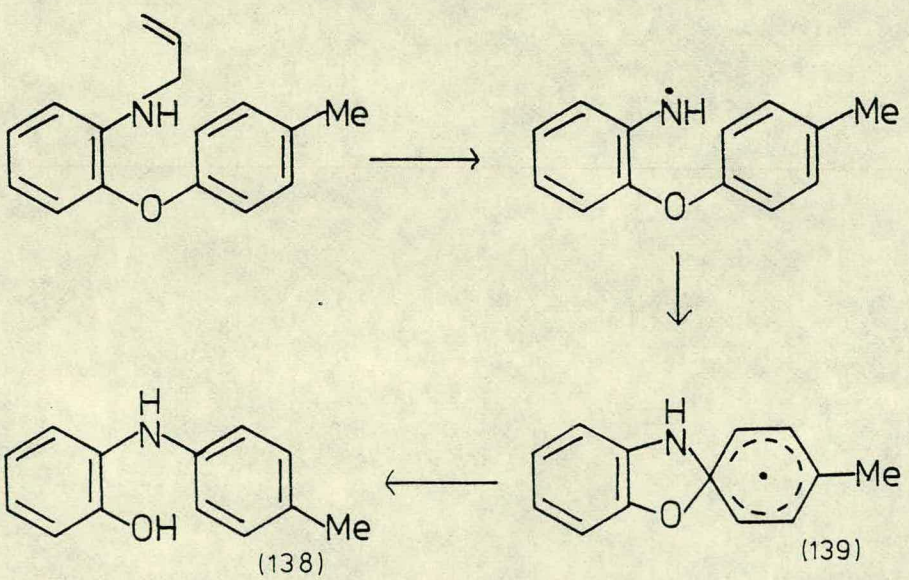
should indicate if the radical reactions proceed in a similar manner to those observed with nitrenes.[138]

Pyrolysis of *N*-allyl-2-amino-*p*-tolyl ether (124) resulted in a much less clean reaction than the previous examples. A compound with the correct molecular ion corresponding to a methylphenoxazine (137) was detected in small quantities by g.c./m.s. but it was not possible to distinguish the 2- or 3-substituted isomers.



(137)

Surprisingly, the major product was found to be 2-*p*-toluidinophenol (138). The fact that the aryl group is now attached to the nitrogen suggests formation of a spirodienyl radical (139) (Scheme 99).



(138) (139)

Scheme 99

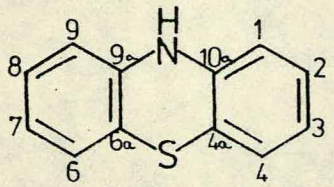


Table VII

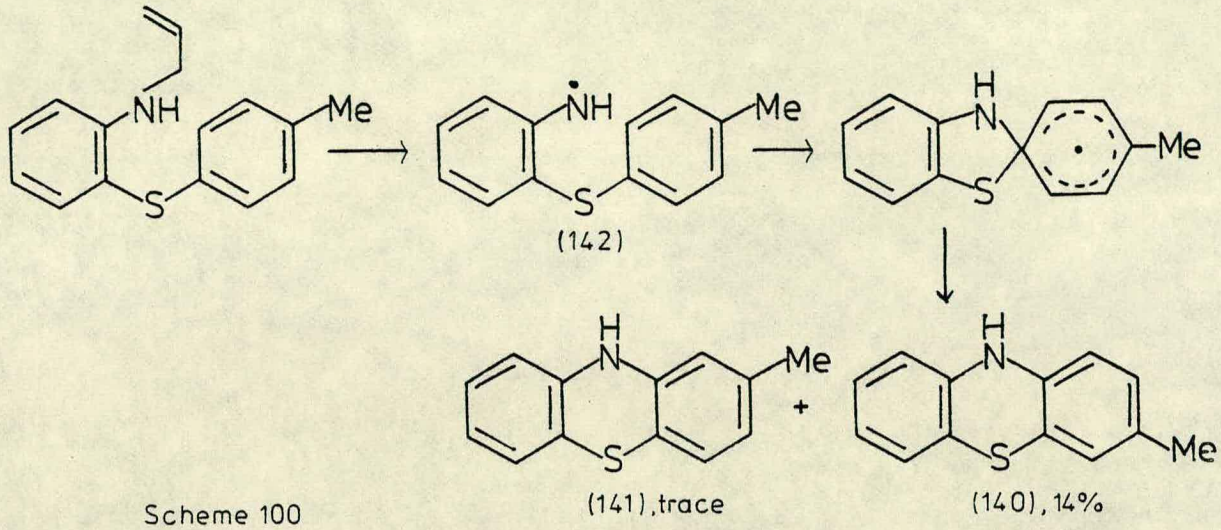
^{13}C N.m.r. chemical shifts in d^6 DMSO

	C1	C2	C3	C4	C4a(q)	C6	C6a(q)	C7	C8	C9	C9a(q)	C10a(q)
3-methylphenothiazine authentic expt.values	114.30	126.48	130.66	127.42	116.38	126.21	116.38	121.42	127.93	114.30	142.42	139.59
Major component of isolated fraction	114.28	126.45	130.68	127.42	116.26	126.19	116.26	121.42	127.94	114.28	142.36	139.56
2,7-dimethyl phenothiazine (authentic expt.values)	115.00	136.79	122.18	126.01	113.00	127.85	116.16	130.54	126.48	114.32	139.68	142.35
Minor component of isolated fraction	115.11	136.88	122.47	126.01	112.71	as major component						142.02
2-methylphenothiazine (calculated values)[144]	115.1	136.6	122.4	126.0	113.3	126.0	116.2	121.6	127.3	114.3	142.0	142.0

A sample of 2-*p*-toluidinophenol (138) was isolated by preparative g.l.c. and was characterised by comparison of its ^{1}H n.m.r. spectrum with that of an authentic sample.[142] The only minor product detected was a trace of *o*-toluidine.

Pyrolysis of *N*-allyl-2-aminophenyl-*p*-tolyl sulphide (125) resulted in a complex pyrolysate. Two major products were present, along with several minor products, some of which could not be identified. The presence of trace amounts of *p*-thiocresol, 2-aminophenyl-*p*-tolyl sulphide and starting material were confirmed. The two major products were isolated by column chromatography and purified by sublimation. Surprisingly only one was found to be a phenothiazine (14%). This compound was identified as 3-methylphenothiazine (140) by comparison of the ^{1}H n.m.r. and ^{13}C n.m.r. spectra with those of an authentic sample.[138] This product was contaminated with a small quantity of a compound believed to be 2-methylphenothiazine (141). The identity of this compound was determined by comparison of the ^{13}C n.m.r. spectrum of the mixture with calculated chemical shift values for both 2- and 3-methylphenothiazines and also a ^{13}C n.m.r. spectrum of 2,7-dimethylphenothiazine[143] (Table VII). These ^{13}C n.m.r. shift values were calculated by taking the known values for the parent compound and altering these depending on their relationship to the appropriate substituent. The ^{13}C substituent effects were those determined for benzene[144] but were considered to be accurate enough for this purpose. Thus the ^{13}C n.m.r. spectrum of this sample isolated from the pyrolysate shows small peaks corresponding to the expected values for 2-methylphenothiazine as well as the major peaks corresponding to 3-methylphenothiazine.

The presence of 3-methylphenothiazine (140) indicates that rearrangement must occur, presumably *via* the spirodienyl intermediate (scheme 100).



Scheme 100

(141), trace

(140), 14%

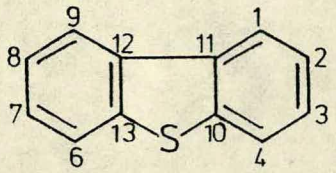
It is possible that the trace of (141) is formed by direct cyclisation of the anilino radical (142). It was noted by Cadogan *et al*[138] that C-S migration was favoured over C-N migration in similar reactions involving nitrenes (scheme 92).

The other major product from this pyrolysate, found in a much higher yield (34%) had an identical molecular weight to a methylphenothiazine. The structure of this compound was determined by ^{1}H n.m.r. and ^{13}C n.m.r. spectroscopy.

The ^{1}H n.m.r. spectrum of this compound indicates the presence of six aromatic protons, a methyl group and an amino substituent. This implies a structure with two tri-substitued benzene rings, which from its molecular weight could be a di-substituted dibenzothiophene (142).

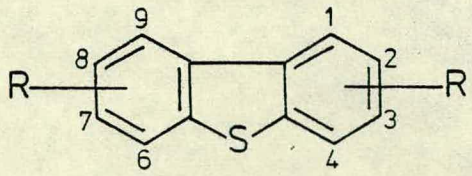
The ring containing the methyl substituent can be identified as some three bond coupling from the adjacent ring protons to the methyl group is observed. The three protons in this ring

Table VIII



^{13}C N.m.r. chemical shifts[145]

	C1	C2	C3	C4	C6	C7	C8	C9	C10	C11	C12	C13
Compound isolated from pyrolysate	111.88	125.51	112.34	140.86	122.44	128.02	134.09	122.11	125.94	136.53	135.64	136.53
4-amino-8-methyl dibenzothiophene	111.5	124.9	113.0	140.4	122.4	127.1	133.3	122.1	126.0	136.2	135.3	136.4
4-amino-7-methyl dibenzothiophene	118.4	124.0	125.5	131.7	123.3	113.0	142.0	108.0	140.1	135.3	136.2	129.5
1-amino-8-methyl dibenzothiophene	112.0	124.8	126.3	119.5	109.1	144.3	110.7	122.2	139.3	136.1	125.5	138.4
1-amino-7-methyl dibenzothiophene	139.3	110.7	127.2	112.6	123.6	135.6	124.8	121.3	126.0	136.2	132.4	139.3



(142)

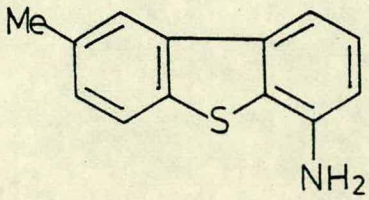
appear as a finely coupled apparent quintet (^4J = 0.8Hz), and a broad doublet (^3J = 8.1Hz), which is coupled to a multiplet which overlaps with another peak in the spectrum. Spin decoupling experiments confirmed this data which is consistent with a methyl substituent in the 7 or 8 position of the dibenzothiophene.

The ring containing the amino substituent shows two protons occurring as doublets of doublets (^3J = 7.7Hz, J^4= 1.0Hz) and one as a triplet (^3J = 7.7Hz). This implies that all these hydrogens must be adjacent and so the amine substituent must be in the 1 or 4 position of the dibenzothiophene.

There are therefore four possible structures *viz* 1-amino-7-methyl-, 1-amino-8-methyl-, 4-amino-7-methyl- and 4-amino-8-methyldibenzothiophene. These ambiguities can be resolved by ^{13}C n.m.r. spectroscopy.

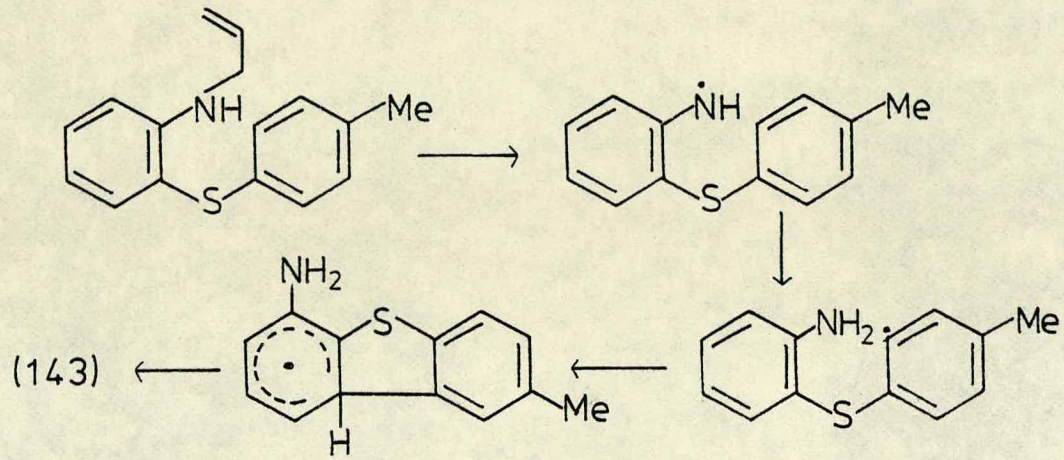
Table VIII shows the ^{13}C n.m.r. chemical shift values for the unknown product and the values for the four possible structures, which were calculated as before.

Therefore the structure of this compound is proved to be 4-amino-8-methyldibenzothiophene (143).



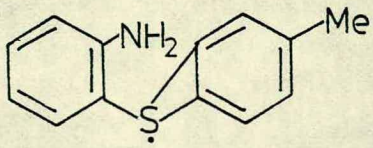
(143)

The proposed mechanism for the formation of (143) is shown in scheme 101.



Scheme 101

The step involving hydrogen abstraction from the aryl ring is unusual and there are several possible explanations why this might occur. Unlike oxygen, sulphur is able to expand its valence shell and may possibly form a radical intermediate such as (144).



(144)

However this intermediate (144) can be ruled out as it should give rise to two isomers in equal quantity and only one is formed.

However the most likely explanation involves geometric rather than electronic factors. As carbon-sulphur bonds are longer than carbon-carbon bonds the 7-membered transition state required to transfer the hydrogen may be more readily achieved.

EXPERIMENTAL

A. Symbols and Abbreviations

b.p.	boiling point
m.p.	melting point
t.l.c.	thin layer chromatography
g.l.c.	gas-liquid chromatography
g.c./m.s.	gas-liquid chromatography/mass spectrometry
n.m.r.	nuclear magnetic resonance
s	singlet
d	doublet
t	triplet
q	quartet
m	multiplet
J	coupling constant
δ	chemical shift
i.r.	infra-red
ν	wavenumber
M^+	mass of molecular ion
m/e	mass to charge ratio
m^*	metastable peak
h	hours
min	minutes
mol	moles
mmol	millimoles

B. Instrumentation

Mass Spectroscopy. Mass spectra and exact mass measurements were recorded by Mr. D. Thomas on an AEI MS902 mass spectrometer.

Nuclear Magnetic Resonance Spectroscopy

(i) ^{1}H n.m.r. spectra were recorded by Mr. J.R.A. Millar on a Varian HA100 or Bruker WP200 spectrometer. Some spectra were recorded by Mr. L.H. Bell on a Bruker WP80 instrument. Chemical shifts (δ_H) are measured in p.p.m. relative to tetramethylsilane (δ = 0.0) or chloroform (δ = 7.25).

(ii) ^{2}H n.m.r. spectra were recorded by Dr. D. Reed on a Bruker WH360 instrument. Chemical shifts (δ_D) are measured in p.p.m. relative to tetramethylsilane (δ = 0.0).

(iii) ^{13}C n.m.r. spectra were recorded by Mr. J.R.A.Millar on a Varian CFT20 spectrometer.

Gas-liquid chromatography. Qualitative and preparative g.l.c were carried out on a Carlo Erba Strumentazione Fractovap 2450 instrument. Some qualitative g.l.c was carried out using a Pye series 204 chromatograph . Both instruments were fitted with a flame ionisation detector and nitrogen was used as the carrier gas. Most samples were run on a 2m x 4.5mm column of 5% Carbowax 20M on Chromosorb W (80-100 mesh), although high temperature work was carried out using SE 30 on Gas-chrom (80-100 mesh). Preparative g.l.c was performed on a 0.85m x 12 mm column of 10% Carbowax 20M, or 10% SE 30, on Chromosorb W (40-60 mesh). G.c./m.s. results were obtained from a Pye

series 104 chromatograph coupled to a VG Micromass 12 spectrometer operated by Miss E. Stevenson.

Thin-layer Chromatography. Analytical chromatograms were developed on 0.3mm layers of alumina (Merck, neutral aluminium oxide 60G, type E), containing Woelm fluorescent green indicator (0.5%). The components were observed under ultra-violet light. Preparative t.l.c. was carried out on 20 x 20 cm plates coated with a 1 mm layer of alumina. The components were observed by ultra-violet light, the relevant bands were scraped off and the products removed by washing the alumina with 5% methanol in chloroform.

Column Chromatography. Alumina (Laporte Industries, Type H) was deactivated by addition of water (6%).

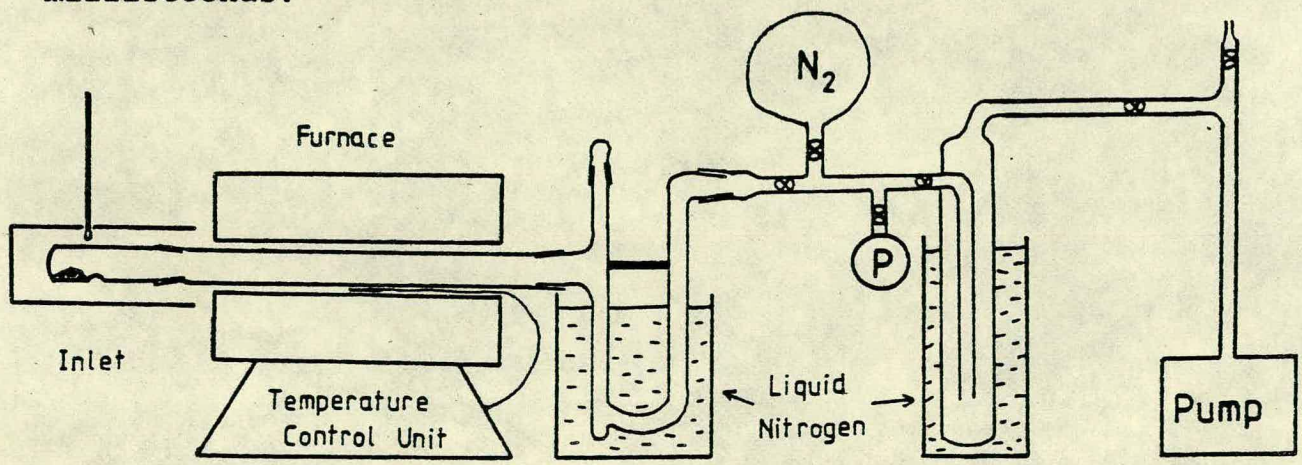
Elemental Analysis. Microanalyses were obtained using a Perkin-Elmer 204 elemental analyser operated by Mr. J. Grunbaum.

Melting Points. Melting points of some new compounds were recorded on a Kofler hot stage microscope. All other melting points were recorded on Gallenkamp or Electrothermal apparatus.

Solvents. In general commercially available solvents were used without further purification. Light petroleum, however, was distilled before use, e.g. light petroleum (40:60) refers to the fraction boiling at 40-60^{o}C. Dry ether was prepared by refluxing ether (previously dried over sodium) with lithium aluminium hydride for 4 h and then distilling off the ether. Dry ether was stored over 4 Å molecular sieve.

C. Pyrolysis Apparatus and General Technique

Flash vacuum pyrolysis was carried out on apparatus based on the design of W.D. Crow, Australian National University. The important features of this apparatus are shown in scheme 102. The sample was volatilised from a horizontal inlet tube, heated by a Buchi Kugelrohr oven, into a silica furnace tube (30 x 2.5 cm). This was maintained at temperatures in the range 600-900°C by a Stanton Redcroft laboratory tube furnace LM8100, the temperature being measured by a platinum/platinum 13% rhodium thermocouple situated at the centre of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen and situated at the exit point of the furnace. The apparatus was evacuated to 10^{-2}-10^{-3}Torr by an Edwards Model ED100 high capacity rotary oil pump, the pressure being measured by a McLeod gauge situated between the trap and the pump. Under these conditions the contact time in the hot zone was estimated to be in the range 1-10 milliseconds.



Scheme 102

Small scale pyrolyses were generally carried out with sample sizes of 0.5-2.0 mmol. The entire pyrolysate was dissolved in deuteriochloroform and analysed by ^{1}H n.m.r., g.l.c. and g.c./m.s. Products were characterised by comparison with authentic samples. In most cases two independent methods of comparison were used; comparison with an authentic sample by g.l.c. and comparison of g.c./m.s. breakdown patterns. In some cases ^{1}H n.m.r. was also used. "Tentative" identification of minor products generally refers to the presence of the correct molecular ion in the g.c./m.s. Absolute yields were obtained from the ^{1}H n.m.r. spectra by addition of cyclohexane (5 μℓ) as an integral calibrant (yields calculated by this method are estimated to be correct to ±5%) or in some cases by g.l.c. using an internal standard. Relative yields were normally obtained by g.l.c. after calibration of the detector response.

For preparative scale experiments sample sizes of 0.5-1.5 g were used.

In the sections which deal with pyrolysis experiments the conditions are quoted as follows: substrate, quantity pyrolysed, inlet temperature, furnace temperature, pressure range, pyrolysis time and products (generally in order of molecular weight).

D. Reactions which Involve N-Allyl and N-Propargyl Amines

1. Preparation of Reagents

a) N-Alkylanilines were prepared by the method described by Vogel.[146] The relevant bromo or chloro compound (0.2 mol) was heated under reflux with the appropriate amine (0.6 mol) for 12-16 h. The mixture was then cooled, made alkaline with sodium hydroxide solution (ca.1M) and a solution of zinc chloride (27.2 g, 0.22 mol) in water (40 ml) was added whilst the mixture was cooled in an ice bath and stirred. After 6-12 hours the thick paste which had formed was filtered off, washed with water and drained. The filtrate was extracted with light petroleum (60:80). The paste was extracted with light petroleum (60:80) (250 ml) using a soxhlet apparatus. This petrol extract was combined with the petrol extract of the aqueous zinc chloride washings. These extracts were washed with water (2 x 100 ml) and with dilute ammonia (1 x 100 ml). The extracts were dried ($MgSO_4$), the solvent was removed in vacuo and the remaining oil was distilled. The following compounds were prepared; N-isopropylaniline (74%), b.p. 45-50°C (10^{-1}Torr) (lit.,[147] 206-208°C); N-benzyl aniline (35%), b.p. 144-146°C (1 Torr) (lit.,[148] 306-307°C); N-ethyl-p-toluidine (5%), b.p. 68-72°C (0.8Torr) (lit.,[149] 220°C); di-α-phenylethylamine (after stirring for 16 hours the mixture was heated to 100°C for 4 hours) (44%), b.p. 125-135°C (0.2Torr) [lit.,[150] 169-171°C (18 Torr)].

b) N-t-Butylaniline was prepared as follows by the method of Nef[151]. Aniline (45 g, 0.48 mol) and t-butyl iodide (30 g,

0.16 mol) were stirred at room temperature for 24 hours. The solution was made alkaline with sodium hydroxide solution (ca 1M) and extracted with ether (3 x 100 ml). The combined extracts were dried ($MgSO_4$), the solvent was removed in vacuo and the mixture was distilled b.p. 44-49°C (10^{-1}Torr). The distillate was cooled and treated with two volumes of acetic anhydride to remove any unreacted aniline. The mixture was filtered and water was added to remove any excess anhydride. The solution was then made alkaline with sodium hydroxide solution (ca.1M) and extracted with ether (3 x 50 ml). The ether fraction was extracted with dilute sulphuric acid (ca.1M). The acid layer was basified and extracted with ether (3 x 50 ml). The combined ether extracts were dried ($MgSO_4$), the solvent was removed in vacuo and the remaining oil was distilled to give the product (1.86 g, 8%), b.p. 104-106°C (0.2Torr) (lit.,[151] 205-210°C).

2. Preparation of N-Alkyl-N-allylanilines

A mixture of allyl bromide (12.1 g, 0.1 mol) and the appropriate secondary amine (0.05-0.1 mol) was heated on a water bath for the length of time indicated. The mixture was then basified with sodium hydroxide (ca.1M), and was extracted with methylene chloride (3 x 50 ml). The combined extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. If the secondary amine was found to be still present the above treatment was repeated, or the mixture was separated by chromatography on a column of 6% deactivated alumina eluted with light petroleum (40:60). The following compounds were prepared by this method; N-Allyl-N-methylaniline (heated

for 1.5 h), (44%), b.p. 105-110°C (10^{-1}Torr) [lit.,[152] 214-216°C], δ_H ($CDCl_3$): 7.10-7.30 (2H, complex), 6.60-6.80 (3H, complex), 5.82 (1H, m), 5.00-5.32 (2H, complex), 3.87 (2H, m) and 2.88 (2H, s); m/e 147 (M^+, 61%), 146 (25), 132 (11), 131 (8), 130 (10), 121 (17), 120 (100), 106 (13), 105 (17), 104 (19), 91 (13), and 77 (46); δ_C ($CDCl_3$): 149.25 (q), 134.64, 128.86, 115.84, 115.64, 112.22, 54.99 and 37.69.

N-Allyl-N-ethylaniline (heated for 1.5 h), (44%), b.p. 105-110°C (10^{-1}Torr) (lit.,[153] 227-229°C), δ_H ($CDCl_3$): 7.00-7.30 (2H, complex), 6.50-6.70 (3H, complex), 5.83 (1H, m), 5.00-5.30 (2H, complex), 3.85 (2H, m), 3.34 (2H, q) and 1.12 (3H, t); m/e 161 (M^+, 57%), 146 (100), 134 (32), 118 (12), 106 (24), 105 (24), 104 (40), 91 (12) and 77 (62); δ_C ($CDCl_3$) 148.04 (q), 134.35, 128.98, 115.64, 115.57, 111.93, 52.46, 44.51 and 12.13.

N-Allyl-N-isopropylaniline (heated for 2 x 1.5 h), (46%), b.p. 105-115°C (0.5 Torr) (lit.,[152] 223-227°C), δ_H ($CDCl_3$): 7.00-7.30 (2H, complex), 6.50-6.80 (3H, complex), 5.83 (1H, m), 5.00-5.30 (2H, complex), 4.07 (1H, septet), 3.73 (2H, m) and 1.12 (6H, d); m/e 175 (M^+, 30%), 160 (100), 119 (28), 118 (17), 106 (13), 104 (19) and 77 (38); δ_C ($CDCl_3$): 148.84 (q), 136.62, 128.84, 115.62, 115.01, 112.79, 47.69, 46.58 and 19.66.

N-Allyl-N-t-butylaniline (heated for 2 x 3 h) (purified by chromatography), (41%), b.p. 130-135°C (12 Torr), δ_H ($CDCl_3$): 7.00-7.31 (5H, complex), 5.65 (1H, m), 4.80-5.16 (2H, complex), 3.73 (2H, m) and 1.12 (9H, s); m/e 189 (M^+, 20%), 175 (14), 174 (100), 133 (33), 132 (22), 118 (25), 106 (25), 77 (20)

and 58 (20); δ_C ($CDCl_3$) 148.56 (q), 137.88, 129.58, 127.67, 124.36, 115.04, 55.07, 51.35 and 28.02. (Found: C, 82.35; H, 10.35; N, 7.45. $C_{13}H_{19}N$ requires C, 82.5; H, 10.1; N, 7.4%); N-Allyl-N-benzylaniline (heated for 2 x 4 h), (54%), b.p. 130-135°C (10^{-1}Torr) [lit.,[154] 184-185°C (15 Torr)], δ_H ($CDCl_3$): 7.00-7.40 (7H, complex), 6.50-6.80 (3H, complex), 5.79 (1H, m), 5.00-5.20 (2H, complex), 4.45 (2H, s) and 3.90 (2H, m); m/e 223 (M^+, 60%), 196 (16), 173 (47), 146 (58), 132 (21), 130 (21), 105 (18), 104 (31), 91 (100) and 77 (50); δ_C ($CDCl_3$): 148.71 (q), 138.71 (q), 133.48, 128.91, 128.34, 126.56, 126.36, 116.35, 116.05, 112.20, 53.72 and 52.18; N,N-Diallylaniline (heated for 2.5 h), (76%), b.p. 80-86°C (0.2 Torr) (lit.,[155] 243-245°C), δ_H ($CDCl_3$): 7.00-7.30 (2H, complex), 6.50-6.80 (3H, complex), 5.96 (2H, m), 5.00-5.30 (4H, complex) and 3.89 (4H, m); m/e 173 (M^+, 100%), 146 (86), 144 (21), 130 (36), 105 (32), 104 (46) and 77 (64); δ_C ($CDCl_3$) 148.56 (q), 133.92, 128.89, 116.18, 115.79, 112.23 and 52.87. N-Allyl-N-ethyl-p-toluidine (heated for 2.5 h), (41%), b.p. 82-85°C (0.2 Torr) (lit.,[156] 238°C), δ_H ($CDCl_3$): 7.03 (2H, d), 6.03 (2H, d), 5.91 (1H, m), 5.00-5.30 (2H, complex), 3.85 (2H, m), 3.34 (2H, q), 2.25 (3H, s) and 1.12 (3H, t); m/e 175 (M^+, 84%); 161 (10), 160 (100), 148 (32), 120 (23), 119 (35), 118 (29) and 91 (29); δ_C ($CDCl_3$) 146.07 (q), 134.73, 129.51, 124.98 (q), 115.54, 112.50, 52.79, 44.70, 20.03, and 12.13.

3. Preparation of N-Allyl-N,N-dialkylamines

The following compounds were made by the method described above for the aniline derivatives: N-Allyl dibenzylamine

(heated for 3 x 1.5 h), (34%), b.p. 135-140°C (0.5 Torr) [lit.,[157] 168-170°C (10 Torr)], δ_H ($CDCl_3$): 7.00-7.40 (10H, complex), 5.90 (1H, m), 5.00-5.30 (2H, complex), 3.58 (4H, s) and 3.06 (2H, m); m/e 237 (M^+, 16%), 210 (9), 187 (11), 160 (25), 149 (19), 106 (8), 105 (9), 100 (9), 92 (17), 91 (100), 77 (12) and 65 (12); δ_C ($CDCl_3$): 139.44 (q), 135.78, 128.56, 128.01, 126.65, 117.14, 57.60 and 56.15. N-Allyl-N,N-di-α-phenylethylamine (heated for 3 x 4 h) (purified by chromatography), (12%), b.p. 154-158°C (0.2 Torr), δ_H ($CDCl_3$): 7.15-7.70 (10H, complex), 5.83 (1H, m), 4.90-5.20 (2H, complex), 4.05 (2H, m), 3.23 (2H, m) and 1.41 and 1.28 (6H, 2d); m/e 265 (M^+, 14%), 250 (43), 146 (59), 105 (100), 84 (17) and 77 (17); δ_C ($CDCl_3$) two isomers (minor in parenthesis where appropriate): 145.46 (144.96), 139.78 (139.44), 127.94, 127.84, 127.63, 127.37, 126.34, 114.50 (114.63), 57.47 (57.04), 49.70 (48.87) and 17.17 (18.29). (Found: C, 85.9; H, 8.9; N, 5.1. $C_{19}H_{23}N$ requires C, 86.0; H, 8.75; N, 5.3%).

As certain amines reacted vigorously under these conditions the following method was used to prepare all other N-allyl-dialkylanilines. The amine (0.05-0.1 mol), either as a neat liquid, or in solution in ethanol, was cooled to 0°C, while allyl bromide (12.1 g, 0.1 mol) was added dropwise with stirring. The mixture was then allowed to warm to room temperature and was stirred for the stated length of time. The solvent was removed if necessary and the mixture was treated as described in section D(2) to give the amine. The following compounds were prepared by this method: N-Allyl-piperidine (stirred for 1 h), (30%), b.p. 75-85°C (15 Torr) (lit.,[158] 155-156°C), δ_H ($CDCl_3$): 5.90 (1H, m), 5.00-5.30

(2H, complex), 2.94 (2H, m), 2.30-2.50 (4H, complex) and 1.50-1.80 (6H, complex); m/e 125 (M^+, 48%), 124 (77), 110 (21), 98 (100), 85 (11), 84 (27), 83 (17), 82 (17), 55 (23), 42 (27) and 41 (38); δ_C ($CDCl_3$): 135.35, 117.08, 62.38, 54.18, 25.70 and 24.08. N-Allyl-2-methylpiperidine (stirred for 1 h), (31%), b.p. 100-110°C (10 Torr), δ_H ($CDCl_3$): 5.90 (1H, m), 5.00-5.30 (2H, complex), 1.20-3.50 (11H, complex) and 1.05 (3H, d); m/e 139 (M^+, 12%), 125 (9), 124 (100), 112 (6), 96 (8), 84 (17), and 82 (6); δ_C ($CDCl_3$): 134.83, 116.82, 57.05, 55.60, 51.98, 34.46, 25.84, 23.80 and 18.85. This compound was characterised as the picrate, m.p. 108°C (from ethanol) (Found: C, 48.9; H, 5.55; N, 15.4. $C_{15}H_{20}N_4O_7$ requires C, 48.9; H, 5.5; N, 15.2%).

N-Allyl-1,2,3,4-tetrahydroisoquinoline (stirred for 1 h in ethanol) [Purified by chromatography using 1:1 ether:light petroleum (40:60) as eluent], (31%), b.p. 102-108°C (0.2 Torr), δ_H ($CDCl_3$): 6.90-7.10 (4H, complex), 5.93 (1H, m), 5.10-5.30 (2H, complex), 3.57 (2H, s), 3.12 (2H, m) and 2.60-3.00 (4H, complex); m/e 173 (M^+, 61%), 172 (100), 146 (28) and 104 (54); δ_C ($CDCl_3$): 135.12 (q), 134.53 (q), 133.98, 128.37, 126.29, 125.83, 125.29, 117.50, 61.22, 55.75, 50.33 and 28.85. (Found: C, 83.2; H, 8.7; N, 7.9. $C_{12}H_{15}N$ requires C, 83.2; H, 8.75; N, 7.9%). N-Allyldiethylamine (stirred for 16 h, then heated for 2 h on a water bath), (9%), b.p. 105-110°C (lit.,[159] 110-111°C), δ_H ($CDCl_3$): 5.90 (1H, m), 4.85-5.30 (2H, complex), 3.10 (2H, m), 2.55 (4H, q) and 1.15 (6H, t); m/e 113 (M^+, 29%), 112 (9), 99 (9), 98 (100), 86 (31), 58 (19), 56 (33), 42 (24) and 41.67; δ_C ($CDCl_3$): 135.79, 116.69,

56.04, 46.41 and 11.43. N-Allylindoline (stirred for 16 h), (26%), b.p. 140-145°C (35 Torr), δ_H ($CDCl_3$): 6.90-7.10 (2H, complex), 6.40-6.80 (2H, complex), 5.87 (1H, m), 5.00-5.40 (2H, complex), 3.63 (2H, m), 2.80-3.50 (4H, complex); m/e 159 (M^+, 47%), 158 (33), 132 (53), 119 (59), 118 (100), 117 (41), 91 (53), 86 (70) and 84 (100); δ_C ($CDCl_3$): 151.97 (q), 134.03, 129.98 (q), 127.02, 124.21, 117.47, 117.00, 107.11, 52.99, 51.92 and 28.32. (Found: C, 82.95; H, 8.25; N, 8.8. $C_{11}H_{13}N$ requires C, 82.75; H, 7.95; N, 8.9%). N-Allyldihydroisoindole (stirred for 16 h in a 1:1 mixture of ethanol:chloroform), (38%), b.p. 145°C (10 Torr) [lit.,[160] 125°C (17 Torr)], δ_H ($CDCl_3$): 7.15 (4H, s), 6.00 (1H, m), 5.00-5.40 (2H, complex), 3.90 (4H, s) and 3.34 (2H, m); m/e 159 (M^+, 56%), 158 (100), 144 (8), 132 (19), 131 (10), 130 (8), 118 (15), 117 (29), 116 (12) and 105 (15); δ_C ($CDCl_3$): 139.89 (q), 135.69, 126.36, 121.96, 116.66 and 58.53.

4. Preparation of N-Alkyl-N-propargylanilines

The following N-propargylanilines were prepared by the method previously described for the corresponding N-allyl compounds (Section D2): N-Methyl-N-propargylaniline (heated for 2 x 4 h, purified by chromatography), (14%), b.p. 95-100°C (10^{-1}Torr) [lit.,[161] 125-130°C (13 Torr)], δ_H ($CDCl_3$): 7.10-7.40 (2H, complex), 6.70-6.90 (3H, complex), 3.98 (2H, d), 2.94 (3H, s) and 2.14 (3H, t); m/e 145 (M^+, 83%), 144 (75) and 77 (100); δ_C ($CDCl_3$): 148.79 (q), 128.88, 118.08, 114.04, 79.11 (q), 71.84, 42.18 and 38.29; N-Ethyl-N-propargylaniline (heated for 4 h), (61%), b.p. 110-115°C (0.2 Torr) [lit.,[162] 119-120°C (15 Torr)], δ_H ($CDCl_3$): 7.10-7.40 (2H, complex),

6.50-6.90 (3H, complex), 3.96 (2H, d), 3.42 (2H, q), 2.15, (1H, t) and 1.18 (3H, t); m/e 159 (M^+, 49%), 144 (100), 106 (35), 105 (22), 104 (27) and 77 (48); δ_C ($CDCl_3$): 147.69 (q), 128.95, 117.51, 113.71, 80.14 (q), 71.43, 45.27, 39.31 and 12.17. N-isoPropyl-N-propargylaniline (heated for 2 x 4 h), (63%), b.p. 85-93°C (10^{-1}Torr), δ_H ($CDCl_3$): 7.10-7.40 (2H, complex), 6.60-7.00 (3H, complex), 4.10 (1H, septet), 3.90 (2H, d), 2.12 (1H, t) and 1.20 (6H, d); m/e 173 (M^+, 37%) 169 (13), 159 (13), 158 (100), 143 (17), 130 (20), 119 (17), 104 (23) and 77 (47); δ_C ($CDCl_3$): 147.94 (q), 128.90, 117.33, 113.87, 82.03 (q), 70.79, 48.49, 33.57 and 19.87. (Found: C, 83.1; H, 8.4; N, 7.9. $C_{12}H_{15}N$ requires C, 83.2; H, 8.7; N, 8.1%).

5. Pyrolysis of N-Allyl and N-Propargylamines

(i) Pyrolysis of N-alkyl-N-allylanilines

(a) N-Allyl-N-methylaniline. 0.182 g (1.24 mmol), 40°C 700°C, 1-5 x 10^{-3}Torr, 10 min: hexa-1,5-diene (2.5%), aniline (8%), m/e 93 (M^+, 100%), 66 (38) and 65 (23); formaldehyde anil (trace), m/e 105 (M^+, 100%), 104 (79) and 77 (99); N,N-dimethylaniline (1.5%), m/e 121 (M^+, 75%), 120 (75) and 77 (100); quinoline (trace); m/e 129 (M^+, 100%), 102 (30), and 73 (34); dihydroquinoline (tentative, trace); m/e 131 (M^+, 81%), 130 (55), 89 (32) and 45 (100) and unreacted starting material (5%). The major product was hexahydro-1,3,5-triphenyl-1,3,5-triazine (19%), and was identified by comparison of the ^1H n.m.r. spectrum of the pyrolysate with

that of an authentic sample.

(b) N-Allyl-N-ethylaniline. 0.176 g (1.09 mmol), 80°C, 700°C, 10^{-3}Torr, 15 min: aniline (trace), m/e 93 (M^+, 100%), 66 (33) and 65 (19); formaldehyde anil (trace), m/e 105 (M^+, 100%), 104 (78) and 77 (98) and N-ethylaniline (trace), m/e 121 (M^+, 37%), 106 (100) and 77 (31). The major product was shown by ^{1}H n.m.r. to be hexahydro-1,3,5-triphenyl-1,3,5-triazine. On a preparative scale the amine (0.51 g, 3.2 mmol) was distilled into the furnace set at 700°C over a period of 30 min. The crude pyrolysate was recrystallised from hexane to give hexahydro-1,3,5-triphenyl-1,3,5-triazine (0.14 g, 42%), m.p. and mixed m.p. 135-136°C (lit.,[110] 141°C), δ_H ($CDCl_3$): 6.8-7.4 (15H, complex) and 4.86 (6H, s); m/e 315 (M^+, 3%), 210 (12), 106 (19), 105 (100), 104 (88), 77 (97) and 51 (40); δ_C ($CDCl_3$): 148.51 (q), 129.03, 120.77, 117.52 and 68.43.

(c) N-Allyl-N-isopropylaniline. 0.146 g (0.83 mmol), 60°C, 700°C, 1-5 x 10^{-3}Torr, 15 min: aniline (8%), m/e 93 (M^+, 100%), 66 (31) and 65 (17); styrene (trace), m/e 104 (M^+, 100%), 103 (38) and 78 (45); acetaldehyde anil (trace), m/e 119 (M^+, 67%), 104 (73), 77 (100) and 51 (36); quinoline (2%), m/e 129 (M^+, 100%), 102 (25) and 77 (25); acetone anil (2%), m/e 133 (M^+, 37%), 118 (92) and 77 (100); N-isopropylaniline (trace), m/e 135 (M^+, 25%), 120 (100) and 77 (26) and methylquinoline (2%), m/e 143 (M^+, 100%), 128 (15) and 115 (17). No major product was detected in this pyrolysate and t.l.c. [alumina, 10% ether in light petroleum (40:60)] showed mainly base line material.

(d) N-Allyl-N-t-butylaniline. 0.139 g (0.74 mmol), 30°C, 700°C, 1-5 x 10^{-3} Torr, 20 min: aniline (23%), m/e 93 (M^+, 100%), 66 (34) and 65 (21); styrene (6%), m/e 104 (M^+, 100%), 103 (39) and 78 (41); quinoline (3%), m/e 129 (M^+, 100%), 102 (26) and 76 (14); dihydroquinoline (tentative, trace), m/e 131 (M^+, 100%) 130 (68) and 77 (15); acetone anil (36%), m/e 133 (M^+, 39%) 118 (100) and 77 (95); N-t-butylaniline (trace), m/e 149 (M^+, 28%), 134 (100) and 77 (42) and acetone (>7%). The acetone and aniline are known to be formed by hydrolysis of acetone anil.

(e) N-Allyl-N-benzylaniline. 0.171 g (0.77mmol), 80°C, 700°C, 1-5 x 10^{-3} Torr, 20 min: hexa-1,5-diene (16%); toluene (7%), m/e 92 (M^+, 80%) and 91 (100); aniline (14%), m/e 93 (M^+, 100%), 66 (32) and 65 (18); styrene (9%), m/e 104 (M^+, 100%), 103 (40) and 78 (46), ethyl benzene (2%), m/e 106 (M^+, 28%), 92 (14) and 91 (100); quinoline (6%), m/e 129 (M^+, 100%), 128 (19) and 102 (31); dihydroquinoline (tentative, trace), m/e 131 (M^+, 100%), 129 (47) and 102 (13); 4-phenylbut-1-ene (tentative, trace), m/e 132 (M^+, 17%), 91 (100) and 65 (13), benzylideneaniline (45%), m/e 181 (M^+, 100%), 180 (94) and 77 (92) and bibenzyl (3%), m/e 182 (M^+, 18%), 91 (100) and 65 (14).

(f) N-Allyl-N-ethyl-p-toluidine. 0.076 g (0.43 mmol), 40°C, 700°C, 10^{-3} Torr, 20 min: the major product was identified as hexahydro-1,3,5-tri-p-tolyl-1,3,5-triazine (42%), δ_H ($CDCl_3$): 6.5-7.1 (12H, complex), 4.74 (6H, s) and 2.24 (9H, s), by comparison with an authentic sample.

(g) N,N-Diallylaniline. 0.213 g (1.230 mmol), 40°C, 800°C, 10^{-3} Torr, 15 min: quinoline (12%), m/e 129 (M^+, 100%), and 102 (26); 8 other components all in yields of <1%, were present.

(ii) Pyrolysis of N-allyl-N,N-dialkylamines

(a) N-Allyl-N,N-dibenzylamine. 0.114 g (0.48 mmol), 60°C, 700°C, 10^{-3}Torr, 15 min: toluene (6%), m/e 92 (M^+, 78%), 91 (100) and 65 (16); aniline (3%), m/e 93 (M^+, 100%), 66 (35) and 65 (22); benzonitrile (17%), m/e, 103 (M^+, 100%), 76 (37) and 50 (19); bibenzyl (12%), m/e 182 (M^+ 16%), 92 (18) and 91 (100) and benzaldehyde-N-benzylimine (28%), m/e 195 (M^+, 21%), 92 (30) and 91 (100).

(b) N-Allyl-N,N-di-α-phenylethylamine. 0.121 g (0.46 mmol) 80°C, 800°C, 1-5 x 10^{-3}Torr, 20 min: aniline (2%), m/e 93 (M^+, 100%), 66 (44) and 65 (33); benzonitrile (34%), m/e 103 (M^+, 100%), 76 (49) and 50 (50); styrene (60%), m/e 104 (M^+, 69%), 103 (25) and 78 (52); ethylbenzene (7%), m/e 106 (M^+, 21%), 91 (79) and 78 (10) and cumene (7%), m/e 120 (M^+, 25%), 105 (100) and 77 (29).

(c) N-Allylpiperidine. 0.153 g (1.22 mmol), 20°C, 850°C, 10^{-2}Torr, 30 min: g.c./ms. showed the correct peak for 3,4,5,6-tetrahydropyridine m/e 83 (M^+, 48%), 82 (21) and 55 (100). No attempt was made to identify other products from this pyrolysate.

(d) N-Allyl-2-methylpiperidine. 0.192 g (1.10 mmol) 20°C, 800°C, 1-5 x 10^{-3}Torr, 30 min: g.c./ms. showed the correct peaks for the two isomeric tetrahydropicolines, m/e 97 (M^+, 55%), 69 (62) and 68 (18) and m/e 97 (M^+, 27%), 69 (52) and 68 (15).

(e) N-Allyl-1,2,3,4-tetrahydroisoquinoline. 0.181 g (1.05 mmol), 50°C, 750°C, 1-5 x 10^{-3}Torr, 20 min: styrene

(trace), m/e 104 (M^+, 100%), 103 (36) and 78 (40); isoquinoline (trace), m/e 129 (M^+, 100%), 128 (18) and 102 (29); 3,4-dihydroisoquinoline (61%), m/e 131 (M^+, 100%), 130 (89), 104 (31) and 103 (33) and tetralin (trace), m/e 132 (M^+, 95%), 104 (91) and 103 (86). On a preparative scale the amine (0.86 g, 5 mmol) was distilled at 10^{-2}Torr into a furnace at 775°C over a period of 30 min. The crude pyrolysate (0.7 g) was added to a solution of picric acid (0.75 g, excess) in acetone (5 ml) to give 3,4-dihydroisoquinolinium picrate, which was recrystallised from ethanol, m.p.185-187°C (lit.,[163] 174-176°C) (Found: C, 49.95; H, 3.15; N, 15.35. $C_{15}H_{12}N_4O_7$ requires C, 50.0; H, 3.35; N, 15.5%).

(f) N-Allyldiethylamine. 0.203 g (1.80 mmol), 25°C, 800°C, 1-20 x 10^{-3}Torr, 15 min: The only product identified from this complex pyrolysate was acetaldehyde N-ethylimine characterised by the following peaks in the ^{1}H n.m.r. spectrum[117]: δ7.34 (1H, q of t, ^{3}J5.0, ^{4}J0.25Hz), 3.01 (2H, quartet of quintets, ^{3}J7.5, $^4J \doteqdot {}^5J$=0.25 Hz), 1.57 (3H, d of t, ^{3}J5.0, ^{5}J0.2Hz) and 0.83 (3H, t, ^{3}J7.5Hz).

(g) N-Allylindoline. 0.237 g (1.49 mmol), 30°C, 800°C, 5-10 x 10^{-3}Torr, 15 min: hexa-1,5-diene (5%); toluene (trace), m/e 92 (M^+, 80%), 91 (87) and 65 (29); styrene (trace), m/e 104 (M^+, 16%), 103 (8) and 78 (12); o-toluonitrile (trace), m/e 117 (M^+, 36%), 116 (14) and 90 (17) and indole (73%), m/e 117 (M^+, 84%), 90 (46) and 89 (34). On a preparative scale the amine (1.59 g, 10 mmol) was distilled at 2-5 x 10^{-2} Torr into a furnace at 825°C over a period of 30 min. The crude pyrolysate (0.98 g) was chromatographed on 6% deactivated

alumina using a 50:50 mixture of ether and light petroleum (40:60) as eluent. After removal of the solvents, the residue was distilled to give indole (0.71 g, 61%), b.p. 95-105°C (0.3 Torr) [lit.,[164] 253-254°C].

(h) N-Allyldihydroisoindole. 0.227 g (1.43 mmol), 30°C, 750°C, 5-10 x 10^{-3}Torr, 15 min: The only product obtained was a brown polymeric resin[115]. Minor products were present only in trace amounts (<<1%) and were not characterised.

(iii) Pyrolysis of N-alkyl-N-propargylanilines

(a) N-Methyl-N-propargylaniline. 0.149 g (1.03 mmol), 30°C, 750°C, 5-10 x 10^{-3}Torr, 15 min: toluene (2%), m/e 92 (M^+, 80%) and 91 (96); aniline (22%), m/e 93 (M^+, 100%), 66 (34) and 65 (20); indene (3%), m/e 116 (M^+, 100%), 66 (34) and 65 (20); formaldehyde anil (trace); m/e 105 (M^+, 80%), 104 (61) and 77 (100); quinoline (3.5%); m/e 129 (M^+, 100%) and 102 (28); benzylideneaniline (4%), m/e 181 (M^+, 100%), 180 (88) and 77 (96) and recovered starting material (1%). The major product was hexahydro-1,3,5-triphenyl-1,3,5-triazine (17%), which was identified by comparison of the ^{1}H n.m.r. spectrum of the pyrolysate with that of an authentic sample.

(b) N-Ethyl-N-propargylaniline. 0.193 g (1.21 mmol), 50°C, 700°C, 1-5 x 10^{-3}Torr, 20 min: aniline (20%), m/e 93 (M^+, 100%), 66 (41) and 65 (25); formaldehyde anil (trace), m/e 105 (M^+, 85%), 104 (66) and 77 (100); acetaldehyde anil (trace), m/e 119 (M^+, 46%), 104 (58) and 77 (100);

N-ethylaniline (18%), m/e 121 (M^+, 28%), 106 (100) and 77 (76); quinoline (trace), m/e 129 (M^+, 100%), 102 (31) and 77 (23) and benzylideneaniline (trace), m/e 181 (M^+, 83%), 180 (71) and 77 (100).

(c) N-isoPropyl-N-propargylaniline. 0.157 g (0.91 mmol), 40°C, 700°C, 10^{-3}Torr, 20 min: aniline (16%), m/e 93 (M^+, 100%), 66 (45) and 65 (27); quinoline (7%), m/e 129 (M^+, 100%) and 102 (25); acetone anil (19%), m/e 133 (M^+, 29%), 118 (71) and 77 (100); benzylideneaniline (trace), m/e 181 (M^+, 85%), 180 (71) and 77 (100) and acetone (≥3%).

6. Preparation of Authentic Samples for Comparison with Pyrolysates

Preparation of Hexahydro-1,3,5-triazines

A solution of the amine (0.1 mol) in water (100 ml) was cooled to 5°C and an aqueous solution of formaldehyde (40%, 8 ml) was added dropwise with stirring. The solution was allowed to stand for the length of time stated, the solid was filtered off and a small sample was recrystallised from ethanol. The following compounds were prepared by this method: Hexahydro-1,3,5-triphenyl-1,3,5-triazine (stirred for 6 h, left to stand for 16 h), m.p.135-136°C (lit.,[110] 141°C), δ_H ($CDCl_3$): 6.75-7.50 (15H, complex) and 4.90 (6H, s); m/e 315 (M^+, 8%), 210 (26), 105 (100), 104 (32) and 77 (35); δ_C ($CDCl_3$): 148.51 (q), 129.03, 120.77, 117.52 and 68.43.

Hexahydro-1,3,5-tri-p-tolyl-1,3,5-triazine (left to stand for 3 h), m.p. 123-124°C (lit.,[110] 127°C), δ_H ($CDCl_3$): 6.80-7.14 (12H, complex), 4.72 (6H, s) and 2.28 (9H, s); m/e 357 (M^+, 4%), 238 (8), 119 (82), 118 (100), 91 (83) and 77 (20); δ_C ($CDCl_3$): 146.22, 130.18, 129.54, 117.83, 69.34 and 20.35.

Acetone anil. A solution of aniline (18.6 g, 0.2 mol) and acetone (11.6 g, 0.2 mol) in cyclohexane (150 ml) was heated for 1 h at 60-65°C in the presence of 4Å molecular sieve [previously dried at 600°C (0.5 Torr) for 1 h]. The solution was then filtered and the cyclohexane was removed under vacuum. The remaining oil was distilled to give the product, contaminated by a small amount of aniline (14.45 g, 53%), b.p. 88-90°C (10 Torr) (lit.,[165] 227-229°C), δ_H ($CDCl_3$): 6.54-7.40 (complex), 2.14 (3H, s) and 1.76 (3H, s); m/e 133 (M^+, 68%), 118 (100) and 77 (64). On exposure to air some of the product hydrolysed to give acetone and aniline.

Benzaldehyde-N-benzylimine. Benzylamine (10.7 g, 0.1 mol) was added dropwise to a stirred solution of benzaldehyde (10.6 g, 0.1 mol) in ether. The solution became warm and water soon formed in droplets, after which the mixture was heated under reflux for 0.5 h on a water bath. The solution was dried ($MgSO_4$) and the solvent was removed under vacuum. The remaining oil was distilled to give the required product (10.66 g, 55%), b.p. 135-145°C (0.2 Torr) [lit.,[166] 200-202°C (10 Torr)], δ_H ($CDCl_3$): 8.45 (1H, s), 7.25-8.30 (10H, complex) and 4.80 (2H, s); m/e 195 (M^+, 52%), 194 (34), 117 (15), 106 (15), 105 (17), 92 (54), 91 (100), 77 (19) and 65 (20).

Benzaldehyde N-α-methylbenzylimine. Benzaldehyde (5.30 g, 0.05 mol) in ether (10 ml) was added dropwise to a stirred solution of α-methylbenzylamine (6.05 g, 0.05 mol) in ether (20 ml) containing acetic acid (0.5 ml). The mixture was heated under reflux for 0.5 h. The solution was then dried ($MgSO_4$), the solvent was removed under vacuum and the remaining oil was distilled to give the product (8.76 g, 84%), b.p. 135-140°C (0.3 Torr) [lit.,[167] 273-275°C (14 Torr)], δ_H ($CDCl_3$): 8.24 (1H, s), 7.10-7.80 (10H, complex), 4.48 (1H, q) and 1.05 (3H, d); m/e 209 (M^+, 7%), 194 (21), 106 (22), 105 (100), 104 (12), 103 (11), 79 (15) and 77 (25).

Acetophenone N-α-methylbenzylamine. Acetophenone (6.0 g, 0.05 mol) in ethanol (10 ml) was added dropwise to a stirred solution of α-methylbenzylamine (6.05 g, 0.05 mol) in ethanol (20 ml) containing acetic acid (0.5 ml). The mixture was heated under reflux for 3 h over 4Å molecular sieve (previously dried at 200°C for 2 h). The solution was then filtered and the solvent was removed under vacuum. The remaining oil was distilled to give the product (3.08 g, 28%), b.p. 140-145°C (0.1 Torr) [lit.,[168] 106°C (0.4 Torr)], δ_H ($CDCl_3$): 7.24-7.86 (10H, complex), 4.88 (1H, q), 2.24 (3H, s) and 1.51 (3H, d); m/e 224 (M+1, 7%), 223 (M^+, 34%), 222 (22), 208 (22), 106 (16), 105 (100), 104 (26), 103 (16), 79 (14) and 77 (25).

Generation of Benzaldimine. Gaseous ammonia was passed through a solution of benzaldehyde (2 g) in refluxing benzene (100 ml) containing *p*-toluenesulphonic acid (0.1 g), and the reaction was monitored by g.c./m.s. After 30 min a small but reproducible peak was observed, m/e 105 (M^+, 100%), 104 (91), 78 (38) and 77 (50). The breakdown pattern was clearly

different to the peak of m/e 105 obtained in the g.c./m.s. traces of certain of the pyrolysates.

Generation of Acetaldehyde anil. Equimolar quantities of acetaldehyde and aniline were dissolved in benzene. After a few minutes at room temperature, molecular sieve was added and the reaction was monitored by g.c./m.s. A trace of the anil, m/e 119 (M^+, 45%), 104 (55), 77 (100) and 51 (42) was detected.

Formaldehyde anil. Hexa-1,3,5-triphenyl-1,3,5-triazine was dissolved in ether and a g.c./m.s. trace of the solution showed a small peak m/e 105 (M^+, 100%), 104 (91) and 77 (50).

Di-α-phenylethyloxalate. This compound was prepared by the method of Trahanovsky[21]: oxalyl chloride (2.7 ml, 0.03 mol) was added dropwise to a stirred solution of α-phenylethanol (4.48 g, 0.04 mol) and triethylamine (8 ml, 0.06 mol) in dry ether (100 ml). After 10 min at room temperature, water was added and the ether layer was separated off. The aqueous layer was extracted with ether (2 x 100 ml), and the combined organic extracts were dried (Na_2SO_4). The solvent was removed in vacuo and the remaining oil was distilled to give the oxalate (3.90 g, 65%), b.p. 145-150°C (0.1 Torr), δ_H ($CDCl_3$): 7.2-7.5 (10H, complex), 6.03 (2H, q) and 1.67 (3H, d); m/e 298 (M^+, 0.2%), 106 (46), 105 (100), 104 (35), 103 (25), 79 (28), 78 (23) and 77 (49); δ_C ($CDCl_3$): 157.04 (q), 139.85 (q), 128.38, 128.14, 125.96, 75.24 and 21.68. (Found: C, 72.4; H, 6.2. $C_{18}H_{18}O_4$ requires C, 72.5; H, 6.1%).

7. Pyrolysis of Authentic Samples

(a) Benzaldehyde N-benzylimine. 0.139 g (0.71 mmol), 80°C, 750°C, 10^{-3}Torr, 20 min: toluene (32%), m/e 92 (M^+, 77%), 91 (100) and 65 (18); benzonitrile (84%), m/e 103 (M^+, 100%), 76 (35) and 75 (9); bibenzyl (32%), m/e 182 (M^+, 17%), 91 (100) and 65 (13) and recovered starting material (3%).

(b) Benzaldehyde N-α-methylbenzylimine. 0.216 g (1.03 mmol), 100°C, 800°C, 5-10 x 10^{-3}Torr, 30 min: benzonitrile (56%), m/e 103 (M^+, 100%), 76 (39) and 50 (23); styrene (44%), m/e 104 (M^+, 100%), 103 (37), 78 (39) and 77 (21); ethylbenzene (6%), m/e 106 (M^+, 28%) and 91 (100) and cumene (2%), m/e 120 (M^+, 27%), 105 (100) and 77 (17).

(c) Acetophenone N-α-methylbenzylimine. 0.227 g (1.02 mmol), 130°C, 800°C, 5 x 10^{-3}Torr, 25 min: benzonitrile (58%), m/e 103 (M^+, 100%), 76 (73) and 75 (34); styrene (39%), m/e 104 (M^+, 88%), 103 (32) and 78 (100); ethylbenzene (4%), m/e 106 (M^+, 30%) and 91 (100) and cumene (12%), m/e 120 (M^+, 18%), 105 (100) and 77 (75).

(d) N-Ethylaniline. 0.192 g (1.59 mmol), 25°C, 900°C, 10^{-2}Torr, 15 min: a 45% yield of starting material was obtained. A variety of minor products were obtained in yields $<<$1%, none of which were identified.

(e) Di-α-phenylethylamine. 0.192 g (0.85 mmol), 100°C, 800°C, 5 x 10^{-3}Torr, 20 min: benzonitrile (20%), m/e 103 (M^+, 100%), 76 (52) and 50 (74); styrene (42%), m/e 104

(M^+, 45%), 103 (20) and 78 (31); ethylbenzene (4%), m/e 106 (M^+, 30%) and 91 (68%) and cumene (7%), m/e 120 (M^+, 22%), 106 (52) and 105 (100).

(f) Di-α-phenylethyloxalate. 0.289 g (0.97 mmol), 140-170°C, 750°C, 5 x 10^{-2}Torr, 45 min: styrene (48%), m/e 104 (M^+, 100%), 103 (39), 78 (30) and 77 (21); ethylbenzene (5%), m/e 106 (M^+, 32%), 92 (21) and 91 (100) and cumene (1%), m/e 120 (M^+, 22%), 106 (59) and 105 (100).

E. Reactions which Involve 2-(Alkylthio)-N-allylanilines and 2-Alkoxy-N-allylanilines

1. Preparation of 2-(Alkylthio)anilines. These were prepared by the method described by Pederson[119] for the alkylation of 2-mercaptophenols as follows: 2-mercaptoaniline (0.05 mol) was dissolved in methanol (50 ml) and sodium hydroxide (0.05 mol) was added. The mixture was then heated on a water bath until all the solid had dissolved. The solution was cooled to room temperature and the appropriate alkyl halide was added dropwise, with stirring. The mixture was then heated under reflux for 1 h. The solvent was removed in vacuo and water was added to dissolve any salts present. The aqueous solution was extracted with ether (3 x 75 ml), the combined extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. The following compounds were prepared by this method: 2-(Methylthio)aniline (59%),

b.p. 85-95°C (0.1 Torr) [lit.,[169] 133-134°C (15 Torr)], δ_H ($CDCl_3$): 6.58-7.40 (4H, complex), 4.22 (2H, s), 2.32 (3H, s); m/e 139 (M^+, 100%), 125 (8), 124 (83) and 80 (32), δ_C ($CDCl_3$): 146.73 (q), 132.91, 128.46, 119.78 (q), 118.27 114.50 and 17.24. 2-(Ethylthio)aniline. (77%), b.p. 90-95°C (0.3 Torr) [lit.,[170] 144°C (15 Torr)], δ_H ($CDCl_3$): 6.40-7.35 (4H, complex), 4.15 (2H, s), 2.70 (2H, q) and 1.25 (3H, t); m/e 153 (M^+, 82%), 125 (48), 124 (100), 97 (16), 93 (18), 80 (54) and 65 (15); δ_C ($CDCl_3$): 148.01 (q), 135.50, 129.23, 118.09, 117.58, 114.55 (q), 28.54 and 14.62. 2-(Propylthio)aniline[171] (66%), b.p. 100-110°C (0.1 Torr); δ_H ($CDCl_3$): 6.96-7.44 (2H, complex), 6.50-6.72 (2H, complex), 4.26 (2H, s), 2.70 (2H, t), 1.60 (2H, m) and 0.94 (3H, t); m/e 167 (M^+, 61%), 125 (100), 124 (37), 109 (11), 95 (13), 93 (17), 81 (19) and 80 (24); δ_C ($CDCl_3$): 147.92 (q), 135.37, 129.12, 118.10, 114.55, 36.57, 22.70 and 13.03 (one quaternary carbon signal is not apparent). 2-(isoPropylthio)aniline[171] (52%), b.p. 85-95°C (0.1 Torr), δ_H ($CDCl_3$): 6.54-7.44 (4H, complex), 4.36 (2H, s), 3.20 (1H, septet) and 1.24 (6H, d); m/e 167 (M^+, 46%), 126 (12), 125 (100), 124 (17), 93 (17) and 80 (21); δ_C ($CDCl_3$): 148.73 (q), 136.91, 129.63, 117.91, 117.03 (q), 114.51, 38.56 and 23.04. 2-(Allylthio)-aniline. (73%), b.p. 122-124°C (6 Torr) [lit.,[172] 84-86°C (0.4 Torr)], δ_H ($CDCl_3$): 7.03-7.45 (2H, complex), 6.59-6.80 (2H, complex), 5.88 (1H, m), 4.84-5.10 (2H, complex), 4.30 (2H, br s) and 3.37 (2H, m); m/e 165 (M^+, 53%), 125 (21), 124 (100) and 80 (24); δ_C ($CDCl_3$): 148.18 (q), 136.08, 133.69, 129.54, 118.06, 117.03, 114.59 and 37.68 (one quaternary carbon signal is not apparent).

and 109 (34); δ_C ($CDCl_3$): 148.85 (q), 135.95, 135.03, 129.70, 117.36 (q), 116.57, 115.79, 110.17, 46.03, 28.84 and 14.73. (Found: M^+ = 193.092249. $C_{11}H_{15}NS$ requires M^+ = 193.092517). 2-Propylthio-N-allylaniline (62%), b.p. 115-120°C (0.2 Torr), δ_H ($CDCl_3$): 7.15-7.45 (2H, complex), 6.55-6.70 (2H, complex), 5.95 (1H, m), 5.10-5.40 (2H, complex), 3.85 (2H, m), 2.70 (2H, t), 1.60 (2H, m) and 1.00 (3H, t); m/e 207 (M^+, 100%), 164 (90), 149 (25), 136 (82), 130 (80) and 124 (60); δ_C ($CDCl_3$): 148.78 (q), 135.83, 135.04, 129.62, 117.81 (q), 116.62, 115.85, 110.19, 46.09, 36.95, 22.83 and 13.16 (Found: C, 69.55; H, 8.05; H, 6.85. $C_{12}H_{17}NS$ requires C, 69.5; H, 8.25; N, 6.75%). 2-isoPropylthio-N-allylaniline (40%), b.p. 95-100°C (0.1 Torr), δ_H ($CDCl_3$): 7.39 (1H, m), 7.20 (1H, m), 6.57-6.66 (2H, complex), 5.95 (1H, m), 5.13-5.33 (2H, complex), 3.81 (2H, m), 3.16 (1H, septet) and 1.23 (6H, d); m/e 207 (M^+, 100%), 166 (14), 165 (14), 164 (93), 162 (14), 140 (17), 136 (65), 131 (24), 130 (59), 125 (45), 124 (93) and 109 (24); δ_C ($CDCl_3$): 149.52 (q), 137.18, 135.08, 130.06, 116.95 (q), 116.45, 115.78, 110.19, 46.07, 38.62 and 23.19 (Found: C, 69.25; H, 8.0; N, 7.0. $C_{12}H_{17}NS$ requires C, 69.5; H, 8.25; N, 6.75%). 2-Allylthio-N-allylaniline (20%), b.p. 110-120°C (0.2 Torr), δ_H ($CDCl_3$): 7.07-7.45 (2H, complex), 6.52-6.72 (2H, complex), 5.88 (2H, m), 4.84-5.42 (4H, complex), 4.70 (1H, br s), 3.83 (2H, m) and 3.33 (2H, m); m/e 205 (M^+, 70%), 164 (81), 136 (100), 130 (93), 124 (63) and 109 (37); δ_C ($CDCl_3$): 148.98 (q), 136.48, 134.97, 133.78, 130.01, 117.10, 116.80 (q), 116.57, 115.86, 110.25, 46.06 and 38.05 (Found: C, 70.1;

H, 7.6; N, 7.05. $C_{12}H_{15}NS$ requires C, 70.2; H, 7.35; N, 6.8%).

2-Ethylthio-N,N-diallylaniline. This compound was prepared by reaction of 2-(ethylthio)aniline (0.01 mol) with allyl bromide (0.06 mol) by the method described above. The mixture was stirred at room temperature for 4 days. After standard work-up and distillation the aniline was obtained as a pale yellow oil (48%) b.p. 105-110°C (0.1 Torr), δ_H ($CDCl_3$): 6.90-7.26 (4H, complex), 5.83 (2H, m), 4.96-5.28 (4H, complex), 3.66 (4H, m), 2.89 (2H, q) and 1.36 (3H, t); m/e 233 (M^+, 19%), 204 (12), 192 (100), 136 (81), 131 (19), 130 (52), 109 (24), 77 (14) and 65 (14). (Found: M^+ = 233.123899. $C_{14}H_{19}NS$ requires M^+ = 233.123815).

2-Ethylthio-N-allyl-N-methylaniline. 2-Ethylthio-N-allylaniline was alkylated by reaction with methyl iodide for 36 h in dimethylformamide containing potassium carbonate as described above. G.l.c. and g.c./m.s. showed the product to be contaminated with a small amount of 2-ethylthio-N,N-diallylaniline. The N-allyl compound was obtained in 69% yield, b.p. 105-110°C (0.5 Torr), δ_H ($CDCl_3$): 6.25-7.44 (4H, complex), 5.78 (1H, m), 4.74-5.30 (2H, complex), 3.56 (2H, m), 2.78 (2H, q), 2.58 (3H, s) and 1.24 (3H, t); m/e 207 (M^+, 45%), 206 (64), 193 (56), 192 (56), 178 (83), 164 (68), 136 (100) and 109 (37). Due to the known contamination this compound was characterised by an accurate mass measurement. (Found: M^+ = 207.108104. $C_{12}H_{17}NS$ requires M^+ = 207.108166).

3. Pyrolysis of 2-Alkylthio-N-allylanilines.

(a) 2-Methylthio-N-allylaniline. 0.180 g (1.01 mmol), 60°C, 750°C, 1-5 x 10^{-3}Torr, 20 min: o-toluidine (trace), m/e 107 (M^+, 92%), 106 (100) and 77 (27); 2-(methylthio)-aniline (4%), m/e 139 (M^+, 96%), 124 (100) and 80 (71); quinoline (trace), m/e 129 (M^+, 69%) and 102 (22); benzothiazole (7%), m/e 135 (M^+, 100%), 108 (37) and 69 (27) and 2-ethylbenzothiazole (2%), m/e 163 (M^+, 36%), 162 (46) and 135 (61).

(b) 2-Ethylthio-N-allylaniline. 0.111 g (0.575 mmol), 50°C, 750°C, 10^{-3}Torr, 15 min: indole (1%), m/e 117 (M^+, 100%), 90 (39) and 89 (25); 2-aminostyrene (21%), m/e 119 (M^+, 100%), 117 (63) and 91 (32); benzothiazole (10%), m/e 135 (M^+, 100%), 108 (38) and 69 (27); 2-methylbenzothiazole (trace), m/e 149 (M^+, 35%), 135 (15) and 108 (15); 2-ethylbenzothiazole (2%), m/e 163 (M^+, 84%), 162 (100) and 148 (19) and recovered starting material (2%), m/e 193 (M^+, 38%), 164 (49) and 136 (21).

(c) 2-Propylthio-N-allylaniline. 0.178 g (0.859 mmol), 60°C, 750°C, 1-5 x 10^{-3}Torr, 25 min: cis-β-methyl-2-aminostyrene (6%), m/e 133 (M^+, 78%), 132 (41), 118 (59) and 117 (34); trans-β-methyl-2-aminostyrene (12%), m/e 133 (M^+, 97%), 132 (45), 118 (74) and 117 (42); benzothiazole (21%), m/e 135 (M^+, 100%), 108 (38) and 69 (32) and 2-ethylbenzothiazole (4%), m/e 163 (M^+, 32%) and 162 (39). The cis and trans-β-methyl-2-aminostyrenes were identified by comparison of the ^{1}H n.m.r. spectra with the literature values.[173]

(d) 2-isoPropylthio-N-allylaniline. 0.143 g (0.691 mmol), 60°C, 750°C, 1-5 x 10^{-3}Torr, 15 min: α-methyl-2-aminostyrene (7%), m/e 133 (M^+, 100%), 132 (58), 118 (53) and 91 (53); benzothiazole (17%), m/e 135 (M^+, 100%), 108 (39) and 69 (31) and 2-ethylbenzothiazole (4%), m/e 163 (M^+, 15%), 162 (100), 135 (21) and 108 (19).

(e) 2-Allylthio-N-allylaniline. 0.102 g (0.497 mmol), 100°C, 750°C, 10^{-3}Torr, 15 min: benzothiazole (49%), m/e 135 (M^+, 100%), 108 (31) and 69 (18); 2-methylbenzothiazole (trace); m/e 149 (M^+, 100%), 148 (32), 135 (72) and 108 (51) and 2-ethylbenzothiazole (trace), m/e 163 (M^+, 162 (100), 148 (14) and 135 (20).

(f) 2-Ethylthio-N,N-diallylaniline. 0.134 g (0.575 mmol), 60°C, 750°C, 10^{-3}Torr, 25 min: quinoline (3%), m/e 129 (M^+, 100%) and 102 (32) and benzothiazole (5%), m/e 135 (M^+, 100%), 108 (40) and 69 (33). Several other minor components were present but no attempt was made to identify them.

(g) 2-Ethylthio-N-allyl-N-methylaniline. 0.075 g (0.362 mmol), 60°C, 750°C, 1-5 x 10^{-3}Torr, 20 min: 2-aminostyrene (7%), m/e 119 (M^+, 100%), 117 (28) and 91 (36) and benzothiazole (13%), m/e 135 (M^+, 100%), 108 (38) and 69 (34). Several other minor components were present but none of these were identified.

(h) 2-(isopropylthio)aniline. 0.075 g (0.449 mmol), 40°C, 750°C, 1 x 10^{-3}Torr, 20 min: g.l.c. of the pyrolysate showed only two products, one of which was shown to be 2-mercapto-aniline by comparison with an authentic sample. The ^{1}H n.m.r. spectrum showed that no starting material was present.

4. Preparation of (2-Alkoxy)-N-allylanilines

These were prepared by reaction of the corresponding 2-alkyloxyaniline with allyl bromide by the method described in section E2. The product was purified on a column of 6% deactivated alumina using ether (5%) in light petroleum (40:60) as eluent. The following compounds were prepared by this method: 2-Methoxy-N-allylaniline (45%), b.p. 90-100°C (0.1 Torr) [lit.,[174] 80-100°C (0.01 Torr)], δ_H ($CDCl_3$): 6.65-7.02 (4H, complex), 6.10 (1H, m), 5.19-5.49 (2H, complex), 4.42 (1H, br s), 3.92 (3H, s) and 3.87 (2H, m); m/e 163 (M^+, 100%), 148 (38), 136 (23), 121 (15), 120 (40), 105 (23), 92 (19) and 78 (19); δ_C ($CDCl_3$): 146.72 (q), 137.88 (q), 135.45, 121.09, 116.39, 115.77, 110.00, 109.32, 55.22 and 46.10. 2-Ethoxy-N-allylaniline (74%), b.p. 85-95°C (0.1 Torr) [lit.,[175] 110°C (2 Torr)], δ_H ($CDCl_3$): 6.61-7.04 (4H, complex), 6.03 (1H, m), 5.13-5.47 (2H, complex), 4.46 (1H, br s), 4.12 (2H, q), 3.86 (2H, m) and 1.49 (3H, t); m/e 177 (M^+, 100%), 148 (95) and 120 (53); δ_C ($CDCl_3$): 145.07 (q), 138.01 (q), 135.57, 120.98, 116.34, 115.64, 110.38, 110.03, 63.56, 46.11 and 14.78.

5. Pyrolysis of 2-Alkoxy-N-allylanilines

(a) 2-Methoxy-N-allylaniline. 0.160 g (0.982 mmol), 70°C, 750°C, 2×10^{-2} - 1×10^{-3} Torr, 15 min: aniline (ca 10% from g.l.c. trace), m/e 93 (M^+, 100%), 66 (35) and 65 (19); N-methylaniline (trace), m/e 107 (M^+, 78%), 106 (100) and 77 (43); o-toluidine (trace), m/e 107 (M^+, 93%), 106 (100)

and 77 (19); benzoxazole (52%), m/e 119 (M^+, 100%), 91 (28) and 64 (40); 1,2-benzisoxazole (ca.10% from g.l.c. trace), m/e 119 (M^+, 100%) and 91 (63); 2-aminobenzaldehyde (12%), m/e 121 (M^+, 81%); 120 (31) and 93 (100); quinoline (trace), m/e 129 (M^+, 100%) and 102 (26) and methylquinoline (tentative, trace), m/e 143 (M^+, 100%), 133 (14) and 115 (36).

(b) 2-Ethoxy-N-allylaniline. 0.183 g (1.034 mmol), 70°C, 750°C, 1-5 x 10^{-3}Torr, 15 min: aniline (ca.3%), m/e 93 (M^+, 100%), 66 (37) and 65 (23); benzoxazole (56%), m/e 119 (M^+, 100%), 91 (36) and 64 (46); 1,2-benzisoxazole (ca.7% from g.l.c. trace), m/e 119 (M^+, 100%) and 91 (65); 2-amino-benzaldehyde (7%), m/e 121 (M^+, 73%), 120 (26), and 93 (90); quinoline (trace), m/e 129 (M^+, 100%), 128 (18) and 102 (25) and methylquinoline (tentative, trace), m/e 143 (M^+, 100%), 142 (26) and 115 (35).

F. Reactions which Involve 2-Allyloxy-S-alkylthiophenols, 2-Ethoxy-S-allylthiophenol, 2-Allyloxy-N,N-dialkyl-anilines and 2-Allyloxy-N-alkylanilines

1. Preparation of 2-Hydroxy-S-alkylthiophenols. These compounds were prepared from o-mercaptophenol by the method of Pederson[119] as previously described in Section E1. The following compounds were prepared: 2-Hydroxy-S-ethylthiophenol (57%), b.p. 75-80°C (0.3 Torr) [lit.,[119] 97°C (10 Torr)], δ_H ($CDCl_3$): 6.50-7.40 (5H, complex), 2.68 (2H, q) and 1.22 (3H, t); m/e 154 (M^+, 69%), 153 (46), 126 (61) and 105 (100);

δ_C ($CDCl_3$): 156.93 (q), 135.92, 130.89, 120.53, 115.16 (q), 114.54, 30.64 and 14.76. 2-Hydroxy-S-propylthiophenol (62%), b.p. 75-85°C (0.1 Torr) [lit.,[119] 109-110°C (10 Torr)], δ_H ($CDCl_3$): 6.68-7.54 (5H, complex), 2.66 (2H, t), 1.62 (2H, m) and 0.94 (3H, t); m/e 168 (M^+, 85%), 139 (27), 126 (100) and 97 (30); δ_C ($CDCl_3$): 156.71 (q), 135.70, 130.68, 120.47, 115.11 (q), 114.51, 38.51, 22.76 and 12.93. 2-Hydroxy-S-allylthiophenol (61%), b.p. 75-80°C (0.1 Torr) [lit.,[176] 110°C (19 Torr)], δ_H ($CDCl_3$): 6.50-7.42 (4H, complex), 5.70 (1H, m), 4.54-5.46 (2H, complex)and 3.16 (2H, m); m/e 166 (M^+, 100%), 165 (23), 137 (43), 134 (25), 133 (20), 132 (27), 131 (18), 126 (43), 125 (67), 97 (72) and 94 (25); δ_C ($CDCl_3$): 156.84 (q), 136.12, 132.88, 130.98, 120.43, 117.93, 115.11 (q), 114.56 and 39.48.

2. Preparation of 2-Allyloxy-S-alkylthiophenols. These compounds were prepared by the method previously described in Section E2 for the allylation of 2-alkythio-N-allylanilines. Thus the appropriate thiophenol was reacted with allylbromide in dimethylformamide, containing potassium carbonate, for 48 h. However, it was not necessary to purify the products by column chromatography. The following compounds were prepared by this method: 2-Allyloxy-S-ethylthiophenol (80%), b.p.100-110°C (0.5 Torr), δ_H ($CDCl_3$): 6.74-7.34 (4H, complex), 6.06 (1H, m), 5.18-5.56 (2H, complex), 4.60 (2H, m), 2.91 (2H, q) and 1.26 (3H, t); m/e 194 (M^+, 81%), 165 (50), 154 (27), 153 (100), 125 (88), 97 (92), 94 (46) and 91 (65); δ_C ($CDCl_3$): 155.84 (q), 132.81, 128.51, 126.23, 120.94, 117.03, 114.44 (q), 111.76, 68.98, 25.53 and 13.79. (Found: C, 67.95; H, 7.0.

$C_{11}H_{14}OS$ requires C, 68.0; H, 7.25%). 2-Allyloxy-S-propylthiophenol (68%), b.p. 100-105°C (0.1 Torr), δ_H ($CDCl_3$): 6.74-7.34 (4H, complex), 6.02 (1H, m), 5.18-5.60 (2H, complex), 4.58 (2H, m), 2.84 (2H, t), 1.70 (2H, m) and 1.00 (3H, t); m/e 208 (M^+, 48%), 167 (24), 165 (18), 137 (16), 125 (100), 124 (22) and 97 (29); δ_C ($CDCl_3$): 155.94 (q), 132.86, 128.62, 126.21, 120.97, 117.07, 114.48 (q), 111.80, 69.03, 33.63, 22.10 and 13.31 (Found: C, 69.4; H, 7.6. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.75%).

3. Preparation of 2-Ethoxy-S-allylthiophenol. 2-Ethoxy-S-allylthiophenol was prepared by reaction of 2-hydroxy-S-allylthiophenol with ethylbromide in dimethylformamide containing potassium carbonate as described above. The required thiophenol was obtained as a pale yellow oil (60%), b.p. 85-95°C, 0.1 Torr, δ_H ($CDCl_3$): 6.72-7.46 (4H, complex), 5.89 (1H, m), 4.94-5.26 (2H, complex), 4.08 (2H, q), 3.05 (2H, m) and 1.49 (3H, t); m/e 194 (M^+, 100%), 165 (17), 137 (34), 132 (20), 12 (21), 124 (45) and 97 (38); δ_C ($CDCl_3$): 156.83 (q), 133.63, 130.12, 127.14, 120.62, 117.24, 111.46, 64.00, 35.15 and 14.63 (one quaternary carbon signal is not apparent). (Found: M^+ = 194.075831. $C_{11}H_{14}OS$ requires M^+ = 194.076532).

4. Pyrolysis of 2-Allyloxy-S-alkylthiophenols and 2-Ethoxy-S-allylthiophenol .

(a) 2-Allyloxy-S-ethylthiophenol. 0.118 g (0.608 mmol), 60°C, 750°C, 1 x 10^{-3}Torr, 20 min: benzofuran (ca. 26%), m/e 118 (M^+, 100%), 90 (38) and 89 (34) and o-hydroxystyrene

(48%), m/e 120 (M^+, 100%), 92 (25) and 91 (84). The yields of both these compounds were calculated from the ^1H n.m.r. spectrum. G.l.c. showed one minor product present (trace, m/e = 134) but this component was not identified.

(b) 2-Allyloxy-S-propylthiophenol. 0.103 g (0.495 mmol), 60°C, 750°C, 1 x 10^{-3}Torr, 20 min: styrene (trace), m/e 104 (M^+, 100%), 103 (42) and 78 (63); benzofuran (ca. 12% from g.l.c. trace), m/e 118 (M^+, 100%), 90 (29) and 89 (28); methylbenzofuran (tentative, trace), m/e 132 (M^+, 53%), 131 (100) and 77 (29); phenylallyl ether (tentative, trace), m/e 134 (M^+, 100%), 133 (36) and 91 (69); cis-β-methyl-2-hydroxystyrene (9%), m/e 134 (M^+, 65%), 91 (38) and 66 (41); trans-β-methyl-2-hydroxystyrene (15%), m/e 134 (M^+, 100%), 119 (41) and 91 (53); three other trace components which could not be identified were present. cis- and trans-β-Methyl-2-hydroxystyrenes were identified by comparison with literature ^1H n.m.r. values[177].

(c) 2-Ethoxy-S-allylthiophenol. 0.165 g (0.850 mmol), 50°C, 750°C, 1-5 x 10^{-3}Torr, 20 min: a complex mixture was obtained with no major products. Nine minor products were shown to be present in varying amounts by g.l.c. The yields were thought to be very low. The following components were identified: phenol, m/e 94 (M^+, 100%), 66 (54) and 65 (34); styrene, m/e 104 (M^+, 100%), 103 (43) and 78 (64); benzofuran, m/e 118 (M^+, 100%), 90 (30) and 89 (28); acetophenone, m/e 120 (M^+, 28%), 105 (100) and 77 (93) and o-thiocresol, m/e 124 (M^+, 100%) and 91 (76). The ^1H n.m.r. spectrum of the

pyrolysate showed a peak at δ=9.82 which may have been due to 2-mercaptobenzaldehyde, however no peak corresponding to the correct molecular weight was found in the g.c./m.s. data. 2-Mercaptobenzaldehyde is known to be unstable[178] and the ^{1}H n.m.r. spectrum has not been reported. As sulphur-carbon bonds are relatively weak, the pyrolysis was repeated with a furnace temperature of 600°C. At this lower temperature an even more complex pyrolysate was obtained; g.l.c. showed at least fourteen different products and the ^{1}H n.m.r. spectrum was extremely complicated. With a furnace temperature of 450°C the pyrolysate consisted almost entirely of starting material.

5. Preparation of 2-Allyloxy-N,N-dialkylanilines and 2-Allyloxy-N-alkylanilines.

2-Allyloxyaniline. An attempt was made to prepare this compound by direct alkylation of 2-hydroxyaniline with allyl bromide in methanol containing sodium hydroxide, as described in Section E1. The resulting oil was shown by ^{13}C n.m.r. to be a mixture of compounds. It was found that in order to specifically alkylate the oxygen it was first necessary to protect the amino group.

N-Acetyl-2-hydroxyaniline. This compound was prepared from 2-hydroxyaniline by the standard method described in Vogel[179]. An 85% yield was obtained m.p. 208-210°C (lit.,[180] 207-210°C).

N-Acetyl-2-allyloxyaniline. The alkylation was carried out by the method quoted in section E2. Thus N-acetyl-2-hydroxyaniline was reacted with allyl bromide in dimethyl-

formamide containing potassium carbonate. The mixture was stirred for 21 h and the product was obtained in 64% yield m.p. 50-51°C (lit.,[181] 50-51°C). The crude product was used for the next stage.

2-Allyloxyaniline. This was prepared from N-acetyl-2-allyloxyaniline by heating it under reflux in dilute hydrochloric acid (6M) for 60 min. The O-allyl compound was a pale yellow oil (58%), b.p. 85-95°C (0.1 Torr) [lit.,[182] 129-130°C (10 Torr)].

Preparation of 2-Allyloxy-N,N-diethylaniline.

(i) Reaction of 2-allyloxyaniline with ethyl bromide in dimethylsulphoxide containing potassium hydroxide[183] gave both the mono- and di-alkylated products. However, it was found that these could not be separated by chromatography.

(ii) N-Acetyl-2-allyloxy-N-ethylaniline. Sodium hydride (50% suspension in oil) was added slowly to a stirred solution of N-acetyl-2-allyloxyaniline (3.82 g, 0.02 mol) in tetrahydrofuran (50 ml) until the evolution of hydrogen had ceased. Ethyl bromide (4.36 g, 0.04 mol) was added dropwise and the mixture was heated under reflux for 4.5 h. Methanol (20 ml) was added to the cooled solution to destroy any excess hydride. Water (60 ml) was then added and the mixture was extracted with ether (3 x 100 ml). The combined extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. The remaining oil was distilled to give N-acetyl-2-allyloxy-N-ethylaniline (70%), b.p. 125-130°C (0.1 Torr), δ_H ($CDCl_3$): 6.79-7.36 (4H, complex), 5.93 (1H, m), 5.10-5.45 (2H, complex), 4.50 (2H, m), 3.63 (2H, m), 1.72 (3H, s) and 1.10 (3H, t);

m/e 219 (M^+, 19%), 162 (20), 137 (11), 136 (100), 120 (16), 108 (9) and 43 (25). (Found: C, 71.05; H, 8.05; N, 6.15. $C_{13}H_{17}NO_2$ requires C, 71.2; H, 7.8; N, 6.4%).

2-Allyloxy-N,N-diethylaniline. This was prepared by reduction[128] of the N-acetyl compound as follows: a mixture of lithium aluminium hydride (1.14 g, 0.03 mol) and dry ether (200 ml) was placed in a three necked flask fitted with a mechanical stirrer. The system was kept under nitrogen and a solution of N-acetyl-2-allyloxy-N-ethylaniline (2.00 g, 0.09 mol) was added at such a rate as to produce a gentle reflux. The mixture was heated under reflux for a further 1.5 h and was then cooled in ice. Wet ether, followed by water was added to destroy any excess hydride. A solution of potassium sodium tartrate (20%, 200 ml) was added and the ether layer was separated off. The aqueous layer was extracted twice with ether (150 ml), the combined extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. The remaining oil was distilled to give the aniline (71%), b.p. 95-100°C (0.5 Torr), δ_H ($CDCl_3$): 6.81-7.25 (4H, complex), 6.07 (1H, m), 5.15-5.51 (2H, complex), 4.59 (2H, m), 3.18 (2H, q) and 1.03 (3H, t); m/e 205 (M^+, 34%), 165 (16), 164 (100), 150 (14), 149 (18), 148 (27), 136 (36), 134 (14), 120 (41), 93 (11), 92 (16), 91 (14) and 77 (18); δ_C ($CDCl_3$): 152.56 (q), 139.64 (q), 133.72, 122.13, 121.75, 120.69, 116.84, 113.61, 69.08, 45.77 and 12.07. This compound was characterised as the picrate salt, m.p. 94-95°C (from ethanol), which appeared to be hygroscopic (Found: C, 52.15; H, 5.35; N, 13.1. $C_{19}H_{22}N_4O_7.H_2O$ requires C, 52.3; H, 5.5; N, 13.1%).

Attempted Preparation of 2-Allyloxy-N-ethylaniline.

(i) 2-Hydroxy-N-ethylaniline (supplied by J.B. Husband[122]) was reacted with allyl bromide in dimethylformamide containing potassium carbonate. The mixture was stirred for 2.5 days and the work up was carried out as described in Section E.2. The only product was a black tar which showed broad unresolved signals in the ^{1}H n.m.r. spectrum.

(ii) An attempt was made to prepare 2-allyloxy-N-ethylaniline by lithium aluminium hydride reduction of N-acetyl-2-allyloxy-aniline using the method described on the previous page. This, however, was unsuccessful and the ^{1}H n.m.r. spectrum of the crude product showed mainly aliphatic protons.

(iii) Finally an attempt was made to prepare the required product from N-acetyl-2-allyloxy-N-ethylaniline by acid hydrolysis of the acetyl group: the amide was heated under reflux in dilute hydrochloric acid (6M) for 2 h. After work-up the ^{1}H n.m.r. of the crude product showed this to be mainly starting material. A small scale experiment was then carried out; the amide was heated under reflux in D_2O/D_2SO_4 and the reaction was monitored by ^{1}H n.m.r. spectroscopy. It was found, however, that under these conditions the allyl group was removed preferentially to the acetyl group.

Preparation of 2-Allyloxy-N,N-dimethylaniline. This compound was prepared in a similar manner to the di-ethyl compound as follows:

N-Formyl-2-hydroxyaniline. Formylation of 2-hydroxyaniline was carried out by the method described by Vogel[184]. A mixture of 2-hydroxyaniline (10.9 g, 0.1 mol) and formic acid (90%,

60 ml) was heated under reflux for 30 min. The hot solution was poured into water (100 ml) and the mixture was cooled in ice. Solid sodium chloride was added until precipitation of the product occurred. The product was filtered off, washed with water and was dried *in vacuo*. The amide was obtained in 43% yield, m.p. 129-130°C (lit.,[180] 129-129.5°C). The crude product was used without further purification.

2-*Allyloxy*-N-*formylaniline*. Allylation of *N*-formyl-2-hydroxyaniline was carried out by reaction with allyl bromide in dimethylformamide containing potassium carbonate as described in Section E2. 2-*Allyloxy*-N-*formylaniline* was obtained in 67% yield, b.p. 135-140°C (0.1 Torr), δ_H ($CDCl_3$): 8.39 (1H, d), 8.20 (1H, br s), 6.73-7.90 (3H, complex), 6.00 (1H, m), 5.14-5.46 (2H, complex) and 4.49 (2H, m); m/e 177 (M^+, 89%), 136 (82), 120 (18), 109 (25), 108 (100), 84 (21) and 80 (96). (Found: C, 67.5; H, 6.5; N, 7.7. $C_{10}H_{11}NO_2$ requires C, 67.8; H, 6.25; N, 7.9%).

2-*Allyloxy*-N-*formyl*-N-*methylaniline*. Alkylation of 2-allyloxy-*N*-formylaniline was carried out by reaction with methyl iodide in tetrahydrofuran containing sodium hydride as described on page 144. The *N*-methyl compound was a colourless oil (69%), b.p. 125-135°C (0.2 Torr), δ_H ($CDCl_3$); 8.15 (1H, s), 6.90-7.30 (4H, complex), 5.96 (1H, m), 5.21-5.40 (2H, complex), 4.53 (2H, m) and 3.18 (3H, s); *m/e* 191 (M^+, 51%), 134 (32), 123 (19), 122 (100), 95 (21), 94 (53), 77 (28) and 65 (19). (Found: C, 68.95; H, 7.1; N, 7.1. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.85; N, 7.3%).

2-Allyloxy-N,N-dimethylaniline. This was prepared by lithium aluminium hydride reduction of 2-allyloxy-N-formyl-N-methylaniline following the method described earlier in this section (p.145). The product was obtained in 64% yield b.p. 85-95°C (0.2 Torr), δ_H ($CDCl_3$): 6.85-6.96 (4H, complex), 6.11 (1H, m), 5.24-5.49 (2H, complex), 4.62 (2H, m) and 2.82 (6H, s) [lit., δ_H ($CDCl_3$): 2.78 (6H, s)]; m/e 177 (M^+, 28%), 137 (21), 136 (100), 120 (19), 108 (19) and 65 (17); δ_C ($CDCl_3$): 150.94 (q), 142.50 (q), 133.40, 121.76, 120.90, 117.86, 116.94, 112.66, 68.79 and 42.99.

Attempted Preparation of 2-Allyloxy-N-methylaniline.
An attempt was made to prepare this compound by lithium aluminium hydride reduction of 2-allyloxy-N-formylaniline by the method described on page 145. The ^1H n.m.r. spectrum of the crude reaction mixture showed that none of the expected product was present. Most of the peaks were in the aliphatic region of the spectrum.

6. Pyrolysis of 2-Allyloxy-N,N-dialkylanilines.

(a) 2-Allyloxy-N,N-diethylaniline. 0.135 g (0.658 mmol), 70°C, 750°C, 10^{-2}-10^{-3}Torr, 10 min: the major product was o-hydroxystyrene (10%), m/e 120 (M^+, 100%) and 91 (66). No yields were determined for the minor products but these were thought to be present in yields of 1-6% from the g.l.c. peak heights. The minor products were phenol (ca. 3%), m/e 94 (M^+, 100%), 66 (21) and 65 (20); benzofuran (ca. 3%), m/e 118 (M^+, 100%), 90 (39) and 89 (28); benzoxazole (ca. 2%), m/e 119 (M^+, 100%) and 91 (30); o-ethylphenol (ca. 6%),

m/e 122 (M^+, 42%), 108 (47) and 107 (100).

(b) 2-Allyloxy-N,N-dimethylaniline. 0.213 g (1.203 mmol), 60°C, 750°C, 10^{-2}-10^{-3}Torr, 10 min: the major product from this pyrolysis was o-cresol (19%), m/e 108 (M^+, 100%), 107 (67) and 79 (23). The yields of minor products were approximated by measurement of g.l.c. peak heights and comparison with the peak corresponding to o-cresol. The minor products obtained were: benzofuran (ca. 3%), m/e 118 (M^+, 100%), 90 (28) and 89 (25); benzoxazole (ca. 2%), m/e 119 (M^+, 100%) and 91 (31); o-hydroxystyrene (ca. 4%), m/e 120 (M^+, 100%), 119 (22) and 91 (68); o-ethylphenol (ca. 4%), m/e 122 (M^+, 41%), 107 (100) and 77 (21) and 2-methylbenzoxazole (trace), m/e 133 (M^+, 75%), 132 (100) and 78 (33).

G. Reactions which Involve Methyl and Phenyl Ethers of 2-(N,N-Dimethylamino)benzyl Alcohol

1. Preparation of Methyl 2-(N,N-dimethylamino)benzyl Ether.

Methyl N,N-dimethylanthranilate was prepared by the method of Edsall and Wyman[185]. Dimethyl sulphate (95 g, 0.75 mol) was reacted at room temperature with anthranilic acid (20.6 g, 0.15 mol) dissolved in water (100 ml) containing potassium hydroxide (12 g). After work up and distillation the required product was obtained as a colourless liquid (5.88 g, 22%), b.p. 115-120°C (0.4 Torr) [lit.,[185] 139°C (16 Torr)].

2(N,N-Dimethylamino)benzyl alcohol was prepared by lithium aluminium hydride reduction of methyl N,N-dimethylanthranilate by the method described in Section F5. The product was obtained as a colourless liquid (66%), b.p. 110-120°C (0.1 Torr) [lit.,[186] 115°C (8 Torr)].

Methyl 2-(N,N-dimethylamino)benzyl ether

This was prepared by reaction of 2-(N,N-dimethylamino)benzyl alcohol with methyl iodide in tetrahydrofuran containing sodium hydride. The method used was that previously described for the alkylation of 2-allyloxy-N-acetyl aniline. The product was obtained in 80% yield, b.p. 95-105°C (0.2 Torr), δ_H ($CDCl_3$): 6.88-7.48 (4H, complex), 4.50 (2H, s), 3.36 (3H, s) and 2.64 (6H, s). This product was not further characterised.

2. Preparation of the Phenyl Ether of 2-(N,N-Dimethylamino)benzyl alcohol

Phenyl 2-(nitro)benzyl ether. This was prepared by the standard method of alkylation described in Section E2. 2-Nitrobenzyl chloride (4.72 g, 0.0275 mol) was reacted at room temperature with phenol (2.59 g, 0.0275 mol) in dimethylformamide (50 ml) containing potassium carbonate (7.6 g, 0.055 mol). After work-up the product was recrystallised from ethanol. A 50% yield of product was obtained, m.p. 58-59°C (lit.,[187] 63°C), δ_H ($CDCl_3$): 6.78-8.28 (9H, complex) and 5.48 (2H, s); m/e 229 (M^+, 11%), 137 (9), 136 (100), 123 (20), 121 (11), 94 (18), 89 (11) and 78 (41).

Phenyl 2-(amino)benzyl ether. Palladium charcoal (10%, 100 mg) was suspended in water (15 ml) and a solution of sodium borohydride (1.52 g, 0.024 mol) in water (50 ml) was added[123]. A slow stream of nitrogen was bubbled through the mixture and a solution of phenyl 2-nitrobenzyl ether (4.58 g, 0.012 mol) in methanol (300 ml) was added dropwise. The mixture was then stirred at room temperature for 2 h. After filtration the solution was acidified to remove any sodium borohydride remaining, rebasified, and the methanol was removed in vacuo. The remaining solution was extracted with ether (3 x 150 ml), the extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. The product was obtained in 68% yield after recrystallisation from ethanol, m.p. 70-71 °C (lit.,[187] 81-82°C), δ_H ($CDCl_3$): 6.60-7.55 (9H, complex), 5.05 (2H, s) and 3.87 (2H, br s); m/e 199 (M^+, 97%), 136 (93), 107 (99), 106 (100), 105 (31), 104 (58), 94 (97), 93 (23), 91 (30), 79 (90), 78 (96), 77 (97) and 65 (92).

Phenyl 2-(N,N-dimethylamino)benzyl ether. The phenyl ether of 2-(amino)benzyl alcohol (0.398 g, 0.002 mol) was reacted with methyl iodide (0.852 g, 0.006 mol) in dimethylformamide (10 ml) containing potassium carbonate (0.552 g, 0.004 mol) as described in Section E2. After work-up and distillation the required product was obtained as a pale yellow oil (61%) b.p. 155-157°C (0.2 Torr), δ_H ($CDCl_3$): 6.70-7.75 (9H, complex), 5.20 (2H, s) and 2.75 (6H, s); m/e 227 (M^+, 9%), 135 (12), 134 (100), 119 (7), 118 (21), 91 (18) and 65 (15); δ_C ($CDCl_3$): 158.88 (q), 152.43 (q), 131.03 (q), 129.44, 129.26, 128.48, 123.04, 120.54, 118.84, 114.73, 65.84 and

45.05. (Found: C, 79.45; H, 7.35; N, 6.25. $C_{15}H_{17}NO$ requires C, 79.25; H, 7.55; N, 6.15%).

Phenyl 2-([$^2H_6$] N,N-dimethylamino)benzyl ether.
Prepared as above using [$^2H_3$] methyl iodide, this ether was obtained in 57% yield, b.p. 115-125°C (0.05 Torr), δ_H ($CDCl_3$): 6.84-7.60 (9H, complex) and 5.17 (2H, s); m/e 233 (M^+, 12%), 141 (12), 140 (100), 121 (9), 120 (7), 93 (7) and 65 (6).

3. Attempted Preparation of Phenyl 2-(N-Methylamino)benzyl Ether. The phenyl ether of 2-(amino)benzyl alcohol (0.398 g, 0.002 mol) was reacted with methyl iodide (0.284 g, 0.002 mol) by the method described above. After work-up, the ^1H n.m.r. spectrum showed a mixture of the required product and the dimethylated compound. It was not found possible to separate these by column chromatography.

4. Attempted Preparation of Phenyl 2-(N-isoPropylamino)-benzyl Ether. An attempt was made to prepare this compound by the above method, using a three times excess of isopropyl bromide. After stirring for 5 days only starting material was obtained on work-up.

5. Pyrolysis of the Methyl and Phenyl Ethers of 2-(N,N-Dimethylamino)benzyl alcohol

(a) Methyl 2-(N,N-dimethylamino)benzyl ether 0.209 g (1.27 mmol), 60°C, 850°C, 1 x 10^{-2}-5 x 10^{-3} Torr, 15 min: ^1H n.m.r. and g.l.c. showed at least twelve minor products including ethylbenzene, o-xylene, isopropylbenzene,

benzonitrile and indoline. No major products were present in the pyrolysate. On repeating the pyrolysis at a lower temperature, (750°C) the ^1H n.m.r. spectrum showed starting material (10%) to be present in the crude pyrolysate.

(b) Phenyl 2-(N,N-dimethylamino)benzyl ether. 0.060 g (0.264 mmol), 130°C, 700°C, 1-5 x 10^{-3}Torr, 10 min: phenol (65%), m/e 94 (M^+, 100%), 73 (24) and 65 (35); o-xylene (trace), m/e 106 (M^+, 56%), 105 (21) and 91 (100); o-toluidine (1%), m/e 107 (M^+, 99%), 106 (100) and 77 (24); anisole (trace), m/e 108 (M^+, 100%), 78 (72) and 71 (24); o-ethyltoluene (3%), m/e 120 (M^+, 27%), 106 (29) and 105 (100); o-tolualdehyde (2%), m/e 120 (M^+, 69%), 119 (68) and 91 (100); N-methylindoline (1%), m/e 133 (M^+, 76%), 132 (100), 117 (35); di-o-tolylethane (24%), m/e 210 (M^+, 11%), 105 (76) and 73 (50). The [$^2H_6$] compound gave deuteriated o-tolylethane (p.83).

6. Preparation of an Authentic Sample of Di-o-tolylethane.

o-Methylbenzyl oxalate. This compound was prepared by the method of Trakanovsky[21] as previously described in Section D6. o-Methylbenzyl alcohol (2.44 g, 0.02 mol) was reacted with oxalyl chloride (0.9 ml, 0.0103 mol) in dry ether (100 ml) containing triethylamine (4 ml, 0.03 mol). The required oxalate was obtained as white needles, m.p. 62-64°C (from ethanol), δ_H ($CDCl_3$): 7.08-7.54 (8H, complex), 5.30 (4H, s) and 2.34 (6H, s); m/e 298 (M^+, 13%), 209 (31), 208 (96), 121 (65), 105 (100) and 91 (83). (Found: C, 72.3; H, 6.15. $C_{18}H_{18}O_4$ requires C, 72.45; H, 6.1%).

Pyrolysis of o-methylbenzyl oxalate. 0.936 g (3.14 mmol) 140°C, 775°C, 1 x 10^{-2}-1 x 10^{-3}Torr, 2h. The solid fraction

obtained (0.48 g) was recrystallised from ethanol to give di-o-tolylethane (0.336 g, 51%), m.p. 55-57°C (lit.,[188] 66.5°C), δ_H ($CDCl_3$): 7.26 (8H, s), 2.98 (4H, s) and 2.43 (6H, s).

H. Reactions which Involve N-Allyl-2-aminodiphenylmethane and Related Hetero-analogues

1. Preparation of Reagents

(a) 2-Nitrophenyl-p-tolyl ether. The method of Wright and Jorgensen[189] was used. Reaction of 2-chloronitrobenzene (23.7 g, 0.15 mol) with p-cresol (19.5 g, 0.18 mol) in dimethylsulphoxide (200 ml) in the presence of potassium hydroxide (8.4 g, 0.15 mol) at 90°C under nitrogen gave the required product (10.4 g, 30%) as pale yellow crystals, m.p. 48-49°C (from methanol) (lit.,[190] 48°C).

(b) 2-Nitrophenyl-p-tolyl sulphide was supplied by Dr. H. McNab.

(c) 2-Aminophenyl-p-tolyl ether. This compound was prepared by reduction of the nitro compound using sodium borohydride and 10% Pd/C in methanol/water as previously described in Section G2. After work up and distillation the product was obtained as a pale yellow oil (77%), b.p. 110-120°C (0.1 Torr) [lit.,[191] 195°C (15 Torr)], δ_H ($CDCl_3$): 6.62-7.25 (8H, complex), 3.66 (2H, br s) and 2.34 (3H, s); m/e 199 (M^+, 100%) 108 (24), 91 (11), 91 (12), 80 (11) and 65 (11).

(d) 2-Aminodiphenylamine. This compound was prepared by reduction of the nitro compound as described in Section G2.

The crude material was recrystallised from ethanol to give the product as light brown needles (53%), m.p. 77-79°C (lit.,[192] 79-80°C), δ_H ($CDCl_3$): 6.50-7.30 (9H, complex) and 4.34 (3H, s); m/e 184 (M^+, 100%), 183 (37), 182 (15) and 169 (26).

(e) 2-Aminophenyl-p-tolyl sulphide. 2-Nitrophenyl-p-tolyl sulphide (4.90 g, 0.02 mol) was suspended in ethanol (200 ml) and palladium charcoal (5%, 1 g) was added. The mixture was hydrogenated for 20 h at a pressure of 70 lb H_2. The solution was then filtered through celite, the solvent was removed in vacuo and the remaining oil was distilled, b.p. 148-154°C (0.2 Torr). The product crystallised on standing (3.14 g, 73%), m.p. 48-49°C (lit.,[193] 49°C), δ_H ($CDCl_3$): 7.45-7.68 (1H, m), 7.40 (1H, m), 7.25 (4H, s), 6.91-6.99 (2H, complex), 4.46 (2H, br s) and 2.49 (3H, s); m/e 215 (M^+, 100%), 214 (15), 200 (18), 199 (9), 167 (13), 91 (11), 89 (9) and 65 (11).

(f) 2-Aminodiphenylmethane. This compound was prepared from 2-aminobenzophenone by a modification of the method described in Vogel[194]. A mixture of 2-aminobenzophenone (9.85 g, 0.05 mol), hydrazine hydrate (6 ml) and potassium hydroxide pellets (6.67 g, 0.17 mol) in diethylene glycol (100 ml) was heated under reflux for 1 h. The condenser was then removed and the flask was fitted for distillation. The mixture was then distilled until the temperature of the liquid rose to 190°C. The mixture was heated under reflux for a further 3 h, by which time it had become pale yellow. The solution was cooled, added to water (250 ml) and was extracted with ether (3 x 100 ml). The ether extracts were washed with water, dried ($MgSO_4$) and the solvent was removed in vacuo.

The remaining oil was distilled to give the product as a pale yellow oil (6.26 g, 68%), b.p. 135-145°C (0.2 Torr) [lit.,[195] 173°C (12 Torr)], δ_H ($CDCl_3$): 6.58-7.54 (9H, complex), 3.90 (2H, s) and 3.49 (2H, br s); m/e 183 (M^+, 100%), 181 (48), 167 (14), 165 (33) and 106 (38).

2. Preparation of N-Allyl-2-aminodiphenylmethane and Related Hetero-analogues

The appropriate amine (0.02 mol) was reacted with allyl bromide (0.015 mol) in dimethylformamide (50 ml), containing potassium carbonate (0.015 mol) as previously described in Section E2. The reaction was monitored by g.l.c. and stirring was carried out for the length of time stated. The resulting mixture of starting material, N-allyl compound and a small amount of the N,N-diallyl derivative were separated by chromatography on 6% deactivated alumina using 20% ether in light petroleum (40:60) as eluent. Fractions from the column were monitored by g.l.c. The fractions containing the required product were combined, the solvent was removed and the remaining material was purified by distillation or recrystallisation. The following compounds were prepared by this method: N-Allyl-2-aminodiphenylmethane (stirred for 16 h) (43%), b.p. 130-135°C (0.2 Torr), δ_H ($CDCl_3$): 7.05-7.35 (7H, complex), 6.63-6.78 (2H, complex), 5.84 (1H, m), 5.05-5.15 (2H, complex), 3.92 (2H, s), 3.72 (2H, m) and 3.70 (1H, br s); m/e 223 (M^+, 36%), 194 (9), 183 (15), 182 (100), 180 (18), 167 (9), 165 (15) and 91 (15); δ_C ($CDCl_3$): 145.73 (q), 139.14 (q), 135.09, 130.45, 128.45, 128.35, 127.60, 126.21, 124.52 (q), 117.06, 115.61, 110.78, 45.99 and 37.97.

(Found: C, 86.15; H, 7.7; N, 6.15. $C_{16}H_{17}N$ requires C, 86.05; H, 7.65; N, 6.25%). N-Allyl-2-aminobenzophenone (stirred for 64 h) (49%), m.p. 53°C (from ethanol), δ_H ($CDCl_3$): 8.75 (1H, br s), 7.25-7.69 (7H, complex), 6.44-6.82 (2H, complex), 5.99 (1H, m), 5.13-5.48 (2H, complex) and 3.95 (2H, m); m/e 237 (M^+, 100%), 236 (36), 167 (18), 132 (36), 105 (30), 91 (15) and 77 (45); δ_C ($CDCl_3$): 199.14 (q), 151.42 (q), 140.32 (q), 135.25, 134.69, 134.09, 130.53, 128.78, 127.80, 117.23 (q), 116.02, 113.76, 111.68 and 44.97. (Found: C, 81.05; H, 6.25; N, 6.05. $C_{16}H_{15}NO$ requires C, 81.0; H, 6.35; N, 5.9%). (N-Allyl-2-amino)diphenylamine (stirred for 16 h) (12%), b.p. 195-200°C (0.4 Torr), δ_H ($CDCl_3$): 7.07-7.26 (4H, complex), 6.68-6.86 (5H, complex), 5.93 (1H, m), 5.09-5.29 (2H, complex) and 3.79 (2H, d); m/e 224 (M^+, 54%), 196 (19), 195 (92), 183 (50), 182 (100), 181 (23) and 77 (27); δ_C ($CDCl_3$): 145.68 (q), 143.83 (q), 135.27, 129.13, 128.01 (q), 126.08, 124.92, 119.11, 117.21, 115.89, 115.08, 111.25 and 46.12. (Found: C, 80.35; H, 6.95; N, 12.4. $C_{15}H_{16}N_2$ requires C, 80.3; H, 7.2; N, 12.5%). N-Allyl-2-aminophenyl-p-tolyl ether (stirred for 18 h) (53%), b.p. 140-145°C (0.4 Torr), δ_H ($CDCl_3$): 6.68-7.25 (8H, complex), 5.95 (1H, m), 5.12-5.39 (2H, complex), 4.45 (1H, br s), 3.85 (2H, m) and 2.39 (3H, s); m/e 239 (M^+, 100%), 183 (29), 132 (16), 131 (33), 130 (23), 120 (35), 105 (25), and 91 (20); δ_C ($CDCl_3$): 155.04 (q), 143.41 (q), 139.95 (q), 135.17, 132.04 (q), 129.98, 124.33, 118.51, 117.34, 116.57, 115.83, 111.40, 45.87 and 20.43. (Found: C, 80.15; H, 7.1; N, 5.95. $C_{16}H_{17}NO$ requires C, 80.3; H, 7.15; N, 5.85%). N-Allyl-2-amino-

phenyl-p-tolyl sulphide (30 h) (36%), b.p. 150-155°C (0.2 Torr), δ_H ($CDCl_3$): 7.18-7.54 (2H, complex), 7.02 (4H, s), 6.59-6.78 (2H, complex), 5.91 (1H, m), 4.99-5.27 (2H, complex), 3.82 (2H, m) and 2.28 (3H, s); m/e 255 (M^+, 100%), 226 (36), 199 (36), 136 (72), 130 (36), 109 (22), 91 (22), 77 (19) and 65 (21); δ_C($CDCl_3$): 148.98 (q), 137.19, 135.14 (q), 134.71, 133.04 (q), 130.90, 129.58, 126.71, 116.34, 115.71, 114.64 (q), 110.68, 45.75 and 20.75. (Found: C, 75.2; H, 6.5; N, 5.3. $C_{16}H_{17}NS$ requires C, 75.25; H, 6.7; N, 5.5%).

3. Pyrolysis of N-Allyl-2-aminodiphenylmethane and Related Hetero-analogues

(a) N-Allyl-2-aminodiphenylmethane. 0.158 g (0.708 mmol) 110°C, 750°C, 1 x 10^{-3}Torr, 15 min: 2-aminodiphenylmethane (8%), m/e 183 (M^+, 100%), 165 (28) and 106 (40); acridine (11%), m/e 179 (M^+, 100%) and 151 (10); acridan (50%), m/e 181 (M^+, 62%), 179 (100) and 151 (9). On a preparative scale the amine (0.75 g, 3.36 mmol), was distilled at 1 x 10^{-3}Torr into a furnace at 775°C over a period of 1 h. The crude pyrolysate (0.71 g) was recrystallised from ethanol to give a pure sample of acridan (0.329 g, 54%), m.p. 170-172°C, mixed m.p. 169-172°C (lit.,[196] 168°C), δ_H ($CDCl_3$): 6.59-8.50 (8H, complex), 5.93 (1H, br s) and 4.05 (2H, s); δ_C ($CDCl_3$): 140.00 (q), 128.47, 126.87, 120.50, 119.89 (q), 113.29, and 31.24. The ^1H n.m.r. and ^{13}C n.m.r. spectra were identical to those of an authentic sample of acridan.[197]

(b) N-Allyl-2-aminobenzophenone. 0.332 g (1.401 mmol), 160°C, 750°C, 1 x 10^{-3}Torr, 20 min: the only product isolated

was a yellow solid which formed at the exit point of the furnace. It had m.p. 348-350°C (darkens above 300°C). On a preparative scale the amine (1.362 g, 5.7 mmol) was distilled at 1 x 10^{-3}Torr into a furnace at 775°C over a period of 50 min. The crude pyrolysate (0.877 g) was recrystallised from dimethylformamide to give acridone (0.441 g, 40%), m.p. and mixed m.p. >350°C (decomposition occurs above 340°C) (lit.,[198] 354°C) δ_H [$(CD_3)_2SO$]: 8.18-8.31 (2H, complex), 7.14-7.84 (6H, complex) and 3.43 (1H, br s); δ_C [$(CD_3)_2SO$]: 176.80 (q), 140.91 (q), 133.44, 126.03, 121.00, 120.55 (q), and 117.33. The ^1H n.m.r. and ^{13}C n.m.r. spectra were identical to those of an authentic sample.

(c) (N-Allyl-2-amino)diphenylamine. 0.047 g (0.210 mmol), 120°C, 750°C, 1-5 x 10^{-3}Torr, 15 min: phenazine m/e 180 (M^+, 100%), 153 (7) and 152 (5); 5,10-dihydrophenazine m/e 182 (M^+, 100%), 169 (36) and 80 (16); 2-aminodiphenylamine, m/e 184 (M^+, 100%), 180 (77) and 169 (38). On a preparative scale the amine (0.169 g, 0.754 mmol) was distilled at 1 x 10^{-3} Torr into a furnace at 750°C over a period of 30 min. The solid which formed at the furnace exit (53 mg) was scraped out and an attempt was made to recrystallise it from ethanol. A black powdery solid was obtained which was shown by mixed m.p., g.l.c. and ^1H n.m.r. to be phenazine (18.6 mg, 14%) m.p. and mixed m.p. 164-170°C (lit.,[199] 169°C), δ_H ($CDCl_3$): 8.21-8.29 (4H, complex) and 7.80-7.88 (4H, complex). The remainder of the pyrolysate was dissolved in ether and chromatographed by preparative t.l.c. on alumina eluted with 30% ether in petrol (40:60). The required bands were

scraped off and eluted with 10% methanol in chloroform. The following components were isolated by this method: phenazine (3.1 mg, 2%), m.p. 165-170°C; 2-aminodiphenylamine (13 mg, 9%), δ_H ($CDCl_3$): 6.70-7.23 (9H, complex).

(d) N-Allyl-2-aminophenyl-p-tolyl ether. 0.106 g (0.443 mmol), 100°C, 750°C, 1 x 10^{-3}Torr, 15 min: o-toluidine (trace), m/e 107 (M^+, 100%), 106 (70) and 77 (21); 2- and/or 3-methylphenoxazine (14%), m/e 197 (M^+, 100%), 181 (9) and 168 (10) and 2-p-toluidinophenol (20%), m/e 199 (M^+, 100%), 183 (28) and 182 (28). A sample of 2-p-toluidinophenol was isolated by preparative g.l.c. (240°C, SE 30), δ_H ($CDCl_3$ +1% dithionite in D_2O): 6.66-7.17 (8H, complex) and 2.26 (3H, s) [lit.,[142] δ_H ($CDCl_3$): 6.4-7.4 (8H, complex) and 2.25 (3H, s)].

(e) N-Allyl-2-aminophenyl-p-tolylsulphide. 0.123 g (0.482 mmol), 100°C, 750°C, 1 x 10^{-3}Torr, 15 min: p-thiocresol, m/e 124 (M^+, 95%) and 91 (100); 3-methylphenothiazine (14%), m/e 213 (M^+, 100%) and 180 (44); 4-amino-8-methyldibenzothiophene (34%), m/e 213 (M^+, 100%) and 180 (6); 2-aminophenyl-p-tolyl sulphide, m/e 215 (M^+, 46%) and starting material (trace), m/e 255 (M^+, 53%), 199 (33) and 136 (63). No yields were calculated for the p-thiocresol or 2-aminophenyl-p-tolyl sulphide but these were thought to be present in yields of ca.3-5% from the g.l.c. trace. There were two minor components of this pyrolysate, m/e = 179 and m/e = 182 which were not identified. On a preparative scale the amine (0.859 g, 3.37 mmol) was distilled at 10^{-3}Torr into a furnace at 750°C over a period of 1.5 h. The entire pyrolysate was chromatographed on a column of alumina and eluted with ether (20%) in

light petroleum (40:60). The following components were isolated: 3-methylphenothiazine (crude wt = 0.236 g). This crude material was purified by sublimation to give 3-methylphenothiazine (0.078 g, 10%), probably contaminated with a small amount of the 2-methyl compound. The sublimed material had m.p. 150-153°C (3-methylphenothiazine, lit.,[200] 166-168°C, 2-methylphenothiazine lit.,[138] 184-186°C), δ_H [$(CD_3)_2SO$] 8.42 (1H, br s), 6.51-7.12 (complex) and 2.12 (3H, m); δ_C [$(CD_3)_2SO$]: 142.36 (q), 139.56 (q), 130.68, 127.94, 127.42, 126.45, 126.19, 121.42, 116.26 (q, 2C's), 114.28 and 19.94. These ^1H n.m.r. and ^{13}C n.m.r. chemical shifts were identical to those of an authentic sample of 3-methylphenothiazine: δ_H [$(CD_3)_2SO$]: 8.41 (1H, br s), 6.52-7.08 (7H, complex) and 2.12 (3H, s); δ_C [$(CD_3)_2SO$]: 142.42 (q), 139.59 (q), 130.66 (q), 127.93, 127.42, 126.48, 126.21, 121.42, 116.38 (q, 2C's), 114.30 and 19.96. The ^1H n.m.r. spectrum of this fraction of the pyrolysate also had a peak at δ_H [$(CD_3)_2SO$]: 2.15 which may be due to the presence of 2-methylphenothiazine. The ^{13}C n.m.r. spectrum showed peaks corresponding to the calculated values for 2-methylphenothiazine as well as several impurity peaks (see discussion section). Comparison of the ^{13}C n.m.r. spectrum with that of an authentic sample of 2,7-dimethylphenothiazine[143] also indicated the presence of 2-methylphenothiazine;

4-Amino-8-methyldibenzothiophene (crude wt. = 0.217 g). The crude material was purified by sublimation to give the product (0.110 g, 15%), m.p. 103-105°C, δ_H ($CDCl_3$): 7.92 (1H, m), 7.74 (1H, d), 7.62 (1H, dd), 7.25-7.33 (2H, complex), 6.79 (1H, dd), 3.88 (2H, br s) and 2.52 (3H, s): δ_C ($CDCl_3$): 140.86 (q), 136.53 (q, 2C's), 135.64 (q), 134.09 (q), 128.02, 125.94 (q), 125.51, 122.44, 122.11, 112.34, 111.88 and 21.30.

(Found: C, 73.05; H, 5.35; N, 6.65. $C_{13}H_{11}NS$ requires C, 73.2; H, 5.2; N, 6.55%); a sample of the unknown compound with m/e 182 was also isolated from the column (crude wt. = 0.105 g). The crude material was purified by sublimation to give a compound with m.p. 75°C, δ_H ($CDCl_3$): 6.83-7.27 (complex), 5.60 (br s) and 1.25 (s).

An authentic sample of 3-methylphenothiazine was supplied by S. Kulik.

PUBLICATIONS

The Pyrolysis of *N*-Allyl Compounds: Free-radical and Retro-ene Mechanisms

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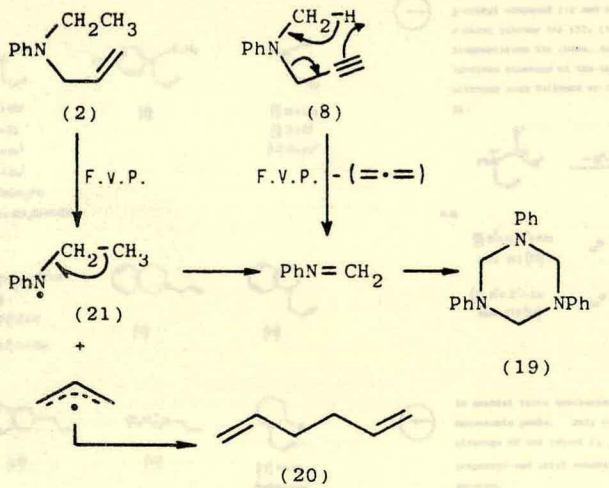
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We have established that the thermolyses of corresponding *N*-allyl- and *N*-propargyl-anilines in the gas phase take place by free-radical and retro-ene mechanisms, respectively, which can lead to different sets of products.

Earlier work has shown that allyl- and propargyl-amines generally give imines on pyrolysis, although the latter precursors are more efficient.[11] The reactions are known to be concerted retro-ene processes:[9] the sole exception is *N*-methyl-*N*-allylaniline, whose thermolysis in the gas phase in a static reactor generates *N*-methylaniline by a free-radical mechanism.[10]

As expected, flash vacuum pyrolysis (F.V.P.) of *N*-methyl-*N*-propargylaniline (8) generates formaldehyde anil, which was identified as its well known trimer (19) (17%).[15] Surprisingly, the *same* product is formed *more efficiently* (42%) by pyrolysis of the *N*-allyl-*N*-ethyl analogue (2). This is best explained by free-radical cleavage to give the stabilised phenylaminyl (21), which exclusively loses a methyl group rather than a hydrogen atom[16] (Scheme 1). In addition, hexa-1,5-diene (20) was



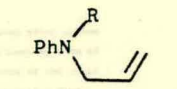
Scheme 1

detected in the pyrolysate, which provides confirmatory evidence for the co-production of allyl radicals and provides a convenient monitor of the mechanism.

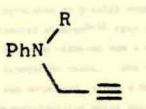
Similarly both (4) and (10) gave the stable imine (25), although generation of acetaldehyde anil (22) by the radical or retro-ene route from (3) or (9), respectively, only gave polymeric products.

Resonance stabilisation of the aminyl is a requirement of the free-radical mechanism. In the formation of imines from the benzylaniline (5) and the related dibenzylamine (11), hexa-1,5-diene is found only in the first case, which suggests that the dialkylamine decomposes by the retro-ene route. Subsequent cleavage of the imine (29) leads to minor products (Scheme 2); such reactions dominate the pyrolysis of the methylated analogue (12), although the precise sequence of their formation remains ambiguous.

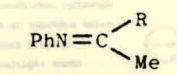
The cleavage reactions of *N*-allyl compounds may be useful in synthesis. Thus 3,4-dihydroisoquinoline (35) (61%) is formed regiospecifically by a retro-ene process,



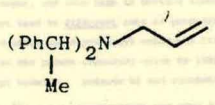
(3) R = Pr^i
(4) R = Bu^t
(5) R = CH_2Ph



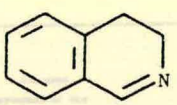
(9) R = Et
(10) R = Pr^i



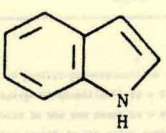
(22) R = H
(25) R = Me



(12)



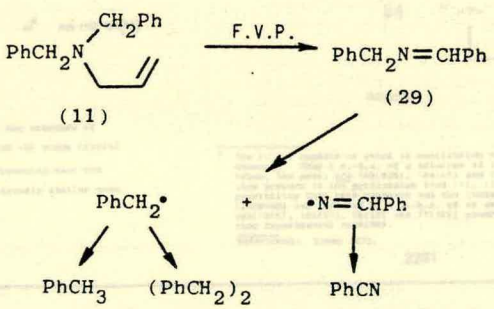
(35)



(36)

while indole (36) (61%) is obtained by a free-radical mechanism from the corresponding *N*-allyl precursors.

In conclusion, the present study, together with the earlier work, has established that radical cleavage is the dominant reaction for *N*-allylanilines, while *N*-allyl-*N*,*N*-dialkylamines fragment by a concerted retro-ene process. Where possible, all *N*-propargyl derivatives thermolyse *via* a retro-ene pathway.



Scheme 2

We are grateful to Miss E. Stevenson for the g.c.–mass spectrometry results, and to the British Petroleum Company Ltd. for an Extra-Mural Research Award.

Techniques used: N.m.r. (^{13}C and ^{1}H), flash vacuum pyrolysis, g.c.–mass spec.

References: 38

Paper: E/098/83 Received: 7th June 1983

References cited in this synopsis:

[9]*e.g.*, K. W. Egger and P. Vitins, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1289.
[10]K. W. Egger and P. Vitins, *Helv. Chim. Acta.*, 1974, **57**, 214.
[11]R. A. Earl and K. P. C. Vollhardt, *Heterocycles*, 1982, **19**, 265, and references therein.
[15]J. G. Miller and E. C. Wagner, *J. Am. Chem. Soc.*, 1932, **54**, 3698.
[16]J. I. G. Cadogan, J. B. Husband, and H. McNab, *J. Chem. Soc., Perkin Trans. 2*, 1983, 697, and references therein.

*To receive any correspondence.

19. H. Funabashi, H. Iwakawa and J. Yoshimura, Bull. Chem. Soc. Jpn., 1969, 42, 2885.
20. R. Bonnett and S.A. Worth, Adv. Heterocycl. Chem., 1981, 29, 341.
21. R. Colebourne, R.G. Foster and E. Robson, J. Chem. Soc.,(C), 1967, 685.
22. cf 'Vogel's Textbook of Practical Organic Chemistry' 4th Edition ed. B.S. Furniss et al, Longmans, London, 1978, p 670.
22a. Reference 22, p 201.
23. J. von Braun, Chem. Ber., 1900, 33, 2728.
24. E. Wedekind, Liebigs Ann. Chem., 1901, 318, 90.
25. E. Wedekind, Chem. Ber., 1899, 32, 517.
26. A. Sandor, Liebigs Ann. Chem., 1882, 214, 138.
27. E. Wedekind and F. Oberheide, Chem. Ber., 1904, 37, 2717.
28. J. von Braun, E. Pinnegger and H. Kuhn, Liebigs Ann. Chem., 1925, 445, 201.
29. J. von Braun, H. Kuhn and S. Siddiqui, Chem. Ber., 1926, 59, 1081.
30. J. von Braun and E. Schwarz, Chem. Ber., 1902, 35, 1279.
31. E. Borlem and E. Eneisel, Chem. Ber., 1906, 39, 1429.
32. J. Meisenheimer, E. Greeske and A. Willmersdorf, Chem. Ber., 1922, 55, 513.
33. J. von Braun, Chem. Ber., 1910, 43, 1357.
34. E. Ramab, J. Chem. Soc., Perkin Trans. 1, 1980, 2208.
35. H. Decker, W. Kropp, E. Boyer and F. Becker, Liebigs Ann. Chem., 1913, 395 299.
36. A.T. Nasos and G.R. Winder, J. Chem. Soc., 1894, 65, 191.
37. C. Overberger, N.P. Marullo and R.G. Hiskey, J. Am. Chem. Soc., 1961, 83, 1374.
38. M. Kana and J. Tafel, Chem. Ber., 1894, 27, 2366.

yield: 1.80 g (33%); b.p. 129–131 °C/16 torr (Ref.[3], 107–108 °C/10 torr); purity: 96% (G. L. C. on 5% Carbowax 20 M at 180 °C).

C_7H_5NS (135.1)

M.S.: *m/e* (relative intensity) = 135 (M^+, 100), 108 (12), 91 (9), 82 (7), 63 (7), 45 (9).

^{1}H-N.M.R.[3] ($CDCl_3$): δ = 8.61 (1 H, dd); 8.04 (1 H, d of q); 7.62 (1 H, d); 7.48 (1 H, dd); 7.09 ppm (1 H, dd).

^{13}C-N.M.R. ($CDCl_3$): δ = 155.68 (C-3a); 146.86 (C-5, $^1J_{CH}$ = 178.4 Hz, $^2J_{CH}$ = 3.8 Hz, $^3J_{CH}$ = 6.7 Hz); 132.69 (C-7a); 130.19, 129.98 (C-2 and C-7, non-first-order coupling pattern); 124.75 (C-3, $^1J_{CH}$ = 172.2 Hz, $^2J_{CH}$ = 3.7 Hz); 118.19 ppm (C-6, $^1J_{CH}$ = 165.8 Hz, $^2J_{CH(5)}$ = 9.2 Hz).

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* Address for correspondence.

1 L. H. Klemm, D. Reed, *J. Org. Chem.* **25**, 1816 (1960).
2 L. H. Klemm, J. Shabtai, D. R. McCoy, W. K. T. Kiang, *J. Heterocycl. Chem.* **5**, 883 (1968).
3 S. Gronowitz, C. Westerlund, A. B. Hörnfeldt, *Acta Chem. Scand. Ser. B* **29**, 233 (1975).
4 L. H. Klemm et al., *J. Org. Chem.* **34**, 347 (1969).
5 Cf. H. McNab, *J. Chem. Soc. Perkin Trans. 1* **1980**, 2200.
6 A. R. Forrester, M. Gill, R. H. Thomson, *J. Chem. Soc. Perkin Trans. 1* **1979**, 616.
7 K. J. Bird, A. W. K. Chan, W. D. Crow, *Aust. J. Chem.* **29**, 2281 (1976).
8 W. D. Crow, H. McNab, J. M. Philip, *Aust. J. Chem.* **29**, 2299 (1976).
9 H. McNab, *J. Chem. Soc. Chem. Commun.* **1980**, 422.
10 W. König, *Ber. Dtsch. Chem. Ges.* **58**, 2559 (1925).
11 H. Keskin, R. E. Miller, F. F. Nord, *J. Org. Chem.* **16**, 199 (1951).

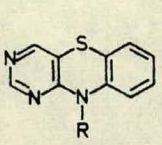
A Convenient Method for Indole *N*-Alkylation in Substituted Pyrazino[2′,1′:6,1]pyrido[3,4-*b*]indoles[1]

Shiv K. Agarwal, Anil K. Saxena*, Nitya Anand

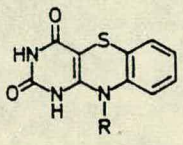
Division of Medicinal Chemistry, Central Drug Research Institute, Lucknow 226001, India

The indole *N*-alkylation in polyfunctional condensed indoles is a field of considerable interest because of the biological activity exhibited by many of these compounds[2–6]. The difficulty encountered in indole *N*-alkylation in substituted 1,2,3,4,6,7,12,12a-octahydropyrazino[2′,1′:6,1]pyrido[3,4-*b*]indoles **1** by the classical method of generating an anion with sodium hydride or thallium(II) ethoxide followed by alkyl halide treatment, namely the simultaneous quaternisation at N-5, led to a search for alternative methods.

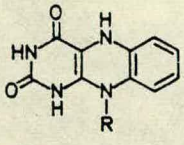
We now report a convenient method for the synthesis of the *N*-alkylindole derivatives **3**, by the reaction of **1** with 1-methyl-2,2-dialkoxypyrrolidine[7] (**2**) in dry tetrahydrofuran.



1

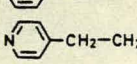
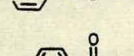
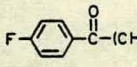
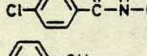
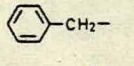
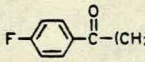
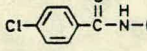
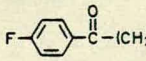
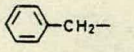


2



3

Table 1. 2,7-Disubstituted 1,2,3,4,6,7,12,12a-Octahydropyrazino[2′,1′:6,1]pyrido[3,4-*b*]indoles **3**

Substrate **1** No.	R[1]	R[2] in **2**	Product No.	Yield [%]	m.p. [°C] (solvent)	Molecular formula[a]	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. (solvent) δ [ppm]
1a		CH_3	**3a**	88	see experimental procedure and Ref.[2]			
1b		CH_3	**3b**	72	203° ($CHCl_3$/CH_3OH)	$C_{22}H_{26}N_4$ (346.5)	2950–2800, 1610, 760	(CF_3COOH): 2.6–4.7 (m, 18 H); 6.4–7.1 (m, 4 H); 7.5–7.7 (m, 2 H); 8.1–8.3 (m, 2 H)
1c		CH_3	**3c**	90	174–176° ($CHCl_3$/CH_3OH)	$C_{25}H_{28}FN_3O$ (405.5)	2970–2760, 1680, 1600, 840, 750	($DMSO$-d_6): 2.2–4.2 (m, 20 H); 6.8–7.2 (m, 6 H); 7.7–8.2 (m, 2 H)
1d		CH_3	**3d**	83	144–145° ($CHCl_3$/ether)	$C_{24}H_{27}ClN_4O$ (423.0)	2930–2800, 1640, 745	($CDCl_3$): 2.1–3.6 (m, 18 H); 6.7–7.6 (m, 8 H)
1a		C_2H_5	**3e**	79	198° ($CHCl_3$/CH_3OH)	$C_{23}H_{27}N_3$ (345.5)	3000–2850, 1630, 755, 710	($CDCl_3$/$DMSO$-d_6): 1.10 (t, 3 H); 2.2–4.1 (m, 15 H); 6.7–7.4 (m, 9 H)
1c		C_2H_5	**3f**	85	180° ($CHCl_3$/CH_3OH)	$C_{26}H_{30}FN_3O$ (419.5)	2970–2800, 1675, 1600, 700	($CDCl_3$/$DMSO$-d_6): 1.15 (t, 3 H); 1.7–6.0 (m, 19 H); 6.8–7.3 (m, 6 H); 7.7–8.0 (m, 2 H)
1d		C_2H_5	**3g**	80	155° ($CHCl_3$/ether)	$C_{25}H_{29}ClN_4O$ (437.0)	2950, 2300, 1640, 745	($CDCl_3$): 1.20 (t, 3 H); 2.3–4.0 (m, 17 H); 6.9–7.9 (m, 8 H)
1c		n-C_3H_7	**3h**	90	186° ($CHCl_3$/CH_3OH)	$C_{27}H_{32}FN_3O$ (433.6)	2900–2800, 1680, 1600, 745	($DMSO$-d_6): 1.10 (t, 3 H); 1.8–4.2 (m, 21 H); 6.7–7.5 (m, 6 H); 7.7–7.9 (m, 2 H)
1a		n-C_3H_7	**3i**	90	222° ($CHCl_3$/CH_3OH)	$C_{24}H_{29}N_3$ (359.5)	2960–2800, 1610, 755, 710	(CF_3COOH); 0.9 (t, 3 H); 2.5–5.0 (m, 17 H); 6.8–7.2 (m, 9 H)
1b		n-C_3H_7	**3j**	74	215° ($CHCl_3$/CH_3OH)	$C_{24}H_{30}N_4$ (374.5)	2950–2800, 1615, 755	(CF_3COOH): 1.10 (t, 3 H), 2.3–4.8 (m, 19 H), 6.3–6.8 (m, 4 H); 7.2–7.4 (m, 2 H); 7.8–8.1 (m, 2 H)

[a] Satisfactory microanalyses obtained: C ±0.47, H ±0.37, N ±0.32.

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References

1. R.F.C. Brown, 'Pyrolytic Methods in Organic Chemistry,' Academic Press, New York, 1980.
2. P. de Mayo, Endeavour, 1972, 31, 135.
3. G. Seybold, Angew.Chem.Int.Ed.Engl., 1977, 16, 365.
4. H.J. Hageman and U.E. Wiersum, Chem.Br., 1973, 9, 206.
5. C. Wentrup, Chimia, 1977, 31, 258.
6. F. Vögtle and L. Rossa, Angew.Chem.Int.Ed.Engl., 1979, 18, 515.
7. G. Schaden, J.Anal.Appl.Pyrol., 1982, 4, 83.
8. U.E. Wiersum, Recl.Trav.Chim.Pays-Bas, 1982, 101, 317.
9. U.E. Wiersum, Recl.Trav.Chim.Pays-Bas, 1982, 101, 365.
10. U.E. Wiersum, Aldrichimica Acta, 1981, 14, 53.
11. J.J. Gajewski, 'Hydrocarbon Thermal Isomerisations' Academic Press, New York, 1981.
12. C.H. DePuy and R.W. King, Chem.Rev., 1960, 60, 431.
13. A. Maccoll in 'The Chemistry of Alkenes,' ed. S. Patai, Wiley, New York, 1964, p.203.
14. G.G. Smith and F.W. Kelly, 'Progress in Physical Organic Chemistry,' ed. A. Streitwieser and R.W. Taft, Wiley, New York, 1971, vol.8, p.75.
15. W.J. Bailey and C. King, J.Org.Chem., 1956, 21, 858.
16. J. Haslouin and F. Rouessac, Tetrahedron Lett., 1976, 4651.
17. P. Schissel, M.E. Kent, D.J. McAdoo, and E. Hedaya, J.Am.Chem.Soc., 1970, 92, 2147.
18. M.P. Cava, M.J. Mitchell, D.C. DeJongh, and R.Y. Van Fossen, Tetrahedron Lett., 1966, 2947.

19. R.F.C. Brown, D.V. Gardner, J.F.W. McOmie, and R.K. Solly, Aust.J.Chem., 1967, 20, 139.

20. 'Free Radicals,' ed. J.K. Kochi, Wiley, New York, 1973, Vol.I and Vol.II, parts II and III.

21. W.S. Trahanovsky, C.C. Ong, and J.A. Lawson, J.Am.Chem. Soc., 1968, 90, 2839.

22. J.I.G. Cadogan, J.B. Husband, and H. McNab, J.Chem.Soc., Perkin Trans.2, 1983, 697.

23. W.S. Trahanovsky and C.C. Ong, J.Am.Chem.Soc., 1970, 92, 7174.

24. W.S. Trahanovsky, C.C. Ong, J.G. Pataky, F.L. Weitl, P.W. Mullen, J.C. Clardy, and R.S. Hansen, J.Org.Chem., 1971, 36, 3575.

25. R.E. Lehr and J.M. Wilson, J.Chem.Soc., Chem.Commun., 1971, 666.

26. W.S. Trahanovsky and C.C. Ong, Tetrahedron Lett., 1968, 3627.

27. W.S. Trahanovsky and P.W. Mullen, J.Chem.Soc., Chem. Commun., 1971, 102.

28. T. Koenig, W. Snell, and J.C. Chang, Tetrahedron Lett., 1976, 4569.

29. E.C. Leonard, Jr., J.Org.Chem., 1962, 27, 1921.

30. H. Higuchi, Y. Sakata, S. Misumi, T. Otsubo, F. Ogura, and H. Yamaguchi, Chem.Lett., 1981, 627.

31. R.A. Marty and P. de Mayo, J.Chem.Soc., Chem.Commun., 1971, 127.

32. J.A. Franz and D.M. Camaioni, J.Org.Chem., 1980, 45, 5247.

33. E.K. Fields and S. Meyerson, J.Am.Chem.Soc., 1967, 89, 724.

34. E.K. Fields and S. Meyerson, J.Am.Chem.Soc., 1967, 89, 3224.

35. C.W. Hand, C. Merritt, Jr., and C. DiPietro, J.Org.Chem., 1977, 42, 841.

36. E. McCarthy and K. O'Brien, J.Org.Chem., 1980, 45, 2086.

37. E.J. Corey and E. Block, J.Org.Chem., 1969, 34, 1233.

38. J.J. Drysdale, H.B. Stevenson, and W.H. Sharkey, J.Am. Chem.Soc., 1959, 81, 4908.

39. L.A. Paquette and G.L. Thompson, J.Am.Chem.Soc., 1972, 94, 7127.

40. L.A. Goldblatt and S. Palkin, J.Am.Chem.Soc., 1941, 63, 3517.

41. D.V. Banthorpe and D. Whittaker, Chem.Soc.Rev., 1966, 20, 373.

42. G. Maier, H.P. Reisenauer, B. Rohde, and K. Dehnicke, Chem.Ber., 1983, 116, 732.

43. M.F.R. Mulcahy, B.G. Tucker, D.J. Williams, and J.R. Wilmshurst, Aust.J.Chem., 1967, 20, 1155.

44. W.S. Trahanovsky and K.E. Swenson, J.Org.Chem., 1981, 46, 2985.

45. J.M. Patterson, C.F. Mayer, and W.T. Smith, Jr., J.Org. Chem., 1975, 40, 1511.

46. J.M. Patterson and P. Drenchko, J.Org.Chem., 1962, 27, 1650.

47. D. Griller, J.A. Howard, P.R. Marriott, and J.C. Scaiano, J.Am.Chem.Soc., 1981, 103, 619.

48. D. Griller and F.P. Lossing, J.Am.Chem.Soc., 1981, 103, 1586.

49. J.D. Goddard, Can.J.Chem., 1982, 60, 1250.

50. C. Jongsma, R. Lourens, and F. Bickelhaupt, Tetrahedron, 1976, 32, 121.

51. S.F. Nelson in 'Free Radicals,' ed. J.K. Kochi, Wiley, New York, 1973, Vol.II, p.527.

52. A.R. Forrester, J.M. Hay, and R.H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, London, 1968.

53. K. Ogawa and Y. Nomura, Yuki Gosei Kagaku Kyokai Shi, 1978, 36, 342.

54. F.O. Rice and C.J. Grelecki, J.Am.Chem.Soc., 1957, 79, 2679.

55. J.S. Watson, J.Chem.Soc., 1956, 3677.

56. H. McNab, J.Chem.Soc., Perkin Trans.1, 1980, 2200.

57. J.I.G. Cadogan, C.L. Hickson, and H. McNab, J.Chem.Res., 1983 (S), 243; (M) 2247.

58. K.J. Bird, A.W.K. Chan, and W.D. Crow, Aust.J.Chem., 1976, 29, 2281.

59. W.D. Crow and A.N. Khan, Aust.J.Chem., 1976, 29, 2289.

60. S.S. Hirsch, J.Org.Chem., 1967, 32, 2433.

61. H. McNab, J.Chem.Soc., Chem.Commun., 1980, 423.

62. H. McNab, J.Chem.Soc., Perkin Trans.1, 1982, 1941.

63. H. McNab and G.S. Smith, J.Chem.Soc., Chem.Commun., 1982, 996.

84. C.L. Hickson and H. McNab, J.Chem.Soc., Perkin Trans.1, in the press.

65. W.D. Crow, H. McNab, and J.M. Philip, Aust.J.Chem., 1976, 29, 2299.

66. C.L. Hickson and H. McNab, Synthesis, 1981, 464.

67. T. Obase and H. Sato, Tetrahedron Lett., 1967, 1633.

68. L.J. Winters, J.F. Fischer, and E.R. Ryan, Tetrahedron Lett., 1971, 129.

69. J.C. Jutz, Top.Curr.Chem., 1978, 73, 125.

70. D.H. Hey, G.M. Jones, and M.J. Perkins, J.Chem.Soc., Perkin Trans.1, 1972, 105.

71. D.H. Hey, G.H. Jones, and M.J. Perkins, J.Chem.Soc., Perkin Trans.1, 1972, 118.

72. J.K. Kochi in 'Free Radicals,' ed. J.K. Kochi, Wiley, New York, 1973, Vol.II, p.665.

73. D.H.R. Barton, G.C. Ramsay, and D. Wege, J.Chem.Soc.(C), 1967, 1915.

74. A.J. Bloodworth and D.S. Baker, J.Chem.Soc., Chem.Commun., 1981, 547.

75. A.J. Bloodworth, D.S. Baker, and H.J. Eggelte, J.Chem.Soc., Chem.Commun., 1982, 1034.

76. R.K. Haynes, M.K.S. Probert, and I.O. Wilmot, Aust.J.Chem., 1978, 31, 1737.

77. A.G. Harrison, L.R. Honnen, H.J. Dauben, Jr., and F.P. Lossing, J.Am.Chem.Soc., 1960, 82, 5594.

78. F.P. Lossing and J.C. Traegar, J.Am.Chem.Soc., 1975, 97, 1579.

79. E. Hedaya and D. McNeil, J.Am.Chem.Soc., 1967, 89, 4213.

80. C.D. Hurd and F.H. Blunk, J.Am.Chem.Soc., 1938, 60, 2419.

81. J.W. Meyer and G.S. Hammond, J.Am.Chem.Soc., 1972, 94, 2219.

82. A.C. Barefoot and F.A. Carroll, J.Chem.Soc., Chem.Commun., 1974, 357.

83. L.H. Klemm, J. Shabtai, D.R. McCoy, and W.K.T. Kiang, J. Heterocycl.Chem., 1968, 5, 883.

84. L.H. Klemm, Heterocycles, 1981, 15, 1285.

85. W. Ando, T. Oikawa, K. Kishi, T. Saiki, and T. Migita, J.Chem.Soc., Chem.Commun., 1975, 704.

86. G. Fritz, Angew.Chem.,Int.Ed.Engl., 1967, 6, 677.

87. T.J. Barton and S.A. Jacobi, J.Am.Chem.Soc., 1980, 102, 7981.

88. R.L. Hillard and K.P.C. Vollhardt, Tetrahedron, 1980, 36, 2435.

89. J.W. Wilt in 'Reactive Intermediates,' ed. R.A. Abramovitch, Plenum Press, New York, 1983, Vol. 3 , p.113.

90. J.I.G. Cadogan, J.B. Husband, and H. McNab, J.Chem.Soc., Perkin Trans.1, 1983, 1489.

91. K.W. Egger, J.Chem.Soc., Perkin Trans.2, 1973, 2007.

92. K.W. Egger and P. Vitins, Helv.Chim.Acta, 1974, 57, 17.

93. K.W. Egger and P. Vitins, Int.J.Chem.Kinet., 1974, 6, 371.

94. K.W. Egger and P. Vitins, J.Chem.Soc., Perkin Trans.2, 1974, 1289.

95. H.M.R. Hoffmann, Angew.Chem., Int.Ed.Engl., 1969, 8, 556.

96. C.S. Marvel and C.W. Hinman, J.Am.Chem.Soc., 1954, 76, 5435.

97. R.C. Cookson and S.R. Wallis, J.Chem.Soc.(B), 1966, 1245.

98. R.T. Arnold and G. Smolinsky, J.Org.Chem., 1960, 25, 129.

99. J.M. Conia and J.P. Barnier, Tetrahedron Lett., 1969, 2679.

100. K.W. Egger and P. Vitins, J.Chem.Soc., Perkin Trans.2, 1974, 1292.

101. H.G. Giles, R.A. Marty, and P. de Mayo, Can.J.Chem., 1976, 54, 537.

102. B. Solouki, P. Rosmus, H. Bock, and G. Maier, Angew. Chem., Int.Ed.Engl., 1980, 19, 51.

103. H. Bock, R.A. Bowling, B. Solouki, T.J. Barton, and G.T. Burns, J.Am.Chem.Soc., 1980, 102, 429.

104. C.L. Kreil, O.L. Chapman, G.T. Burns, and T.J. Barton, J.Am.Chem.Soc., 1980, 102, 841.

105. R.A. Earl and K.P.C. Vollhardt, Heterocycles, 1982, 19, 265.

106. A. Viola, J.J. Collins, and N. Filipp, Prepr.Div.Pet. Chem., Am.Chem.Soc., 1979, 24, 206.

107. A. Viola, J.J. Collins, and N. Filipp, Tetrahedron, 1981, 37, 3765.

108. K.W. Egger and P. Vitins, Helv.Chim.Acta, 1977, 60, 978.

109. S. Jolidon and H.-J. Hansen, Helv.Chim.Acta, 1977, 60, 978.

110. J.G. Miller and E.C. Wagner, J.Am.Chem.Soc., 1932, 54, 3698.

111. M.M. Sprung, Chem.Rev., 1940, 26, 297.

112. R.W. Layer, Chem. Rev., 1963, 63, 489.

113. A. Eibner, Justus Liebigs Ann.Chem., 1901, 318, 58.

114. M. Funabashi, M. Iwakawa, and J. Yashimura, Bull.Chem. Soc.Jpn., 1969, 42, 2885.

115. R. Bonnett and S.A. North, Adv.Heterocycl.Chem., 1981, 29, 341.

116. R. Bonnett and R.F.C. Brown, J.Chem.Soc., Chem.Commun., 1972, 393.

117. N. Colebourne, R.G. Foster, and E. Robson, J.Chem. Soc.(C), 1967, 685.

118. H. McNab, unpublished results.

119. A.O. Pedersen, G. Schroll, S.-O. Lawesson, W.A. Laurie, and R.I. Reed, Tetrahedron, 1970, 26, 4449.

120. R.D. Bowen, D.E. Davies, C.W.G. Fishwick, T.O. Glasbey, S.J. Noyce, and R.C. Storr, Tetrahedron Lett., 1982, 23, 4501.

121. S. Cabiddu, A. Maccioni, and M. Secci, Synthesis, 1976, 797, and references therein.

122. J.B. Husband, Ph.D. Thesis, University of Edinburgh, 1982.

123. T. Neilson, H.C.S. Wood, and A.G. Wylie, J.Chem.Soc., 1962, 371.

124. D.D. Reynolds and D.L. Fields in 'Heterocyclic Compounds with Three- and Four-membered Rings Part 1, ed. A. Weissberger, Wiley, New York, 1964.

125. A. Mishra, S.N. Rice, and W. Lwowski, J.Org.Chem., 1968, 33, 481.

126. R.S. Atkinson and C.W. Rees, J.Chem.Soc., Chem.Commun., 1967, 1232.

127. V.I. Stenberg, V.R. Srinivas, R.J. Baltisberger, and N.F. Woolsey, J.Org.Chem., 1983, 48, 1107.

128. R.F. Nystrom and W.G. Brown, J.Am.Chem.Soc., 1948, 70, 3738.

129. L. Krbechek and H. Takimoto, J.Org.Chem., 1968, 33, 4286.

130. G.R. Cliff and G. Jones, J.Chem.Soc.(C), 1971, 3418.

131. W.D. Crow and H. McNab, Aust.J.Chem., 1981, 34, 1037.

132. R. Kwok and P. Pranc, J.Org.Chem., 1968, 33, 2880.

133. P.A.S. Smith, B.B. Brown, R.K. Putney, and R.F. Reinisch, J.Am.Chem.Soc., 1953, 75, 6335.

134. J.I.G. Cadogan and P.K.K. Lim, J.Chem.Soc., Chem.Commun., 1971, 1431.

135. J.I.G. Cadogan, D.S.B. Grace, P.K.K. Lim, and B.S. Tait, J.Chem.Soc., Chem.Commun., 1972, 520.

136. J.I.G. Cadogan, R.K. Mackie, and M.J. Todd, J.Chem.Soc., Chem.Commun., 1966, 491.

137. J.I.G. Cadogan, S. Kulik, and M.J. Todd, J.Chem.Soc., Chem.Commun., 1968, 736.

138. J.I.G. Cadogan, S. Kulik, C. Thomson, and M.J. Todd, J.Chem.Soc.(C), 1970, 2437.

139. M. Messer and D. Farge, Bull.Soc.Chim.Fr., 1968, 2832.

140. See however Y. Maki, T. Hosokami, and M. Suzuki, Tetrahedron Lett., 1971, 3509.

141. G.A. Swan and D.G.I. Felton in 'Phenazines,' ed. A. Weissberger, Wiley, New York, 1957.

142. D.S.B. Grace, Ph.D. Thesis, University of Edinburgh, 1974.

143. K. Brown, Ph.D. Thesis, University of Edinburgh, 1983.

144. J.D. Memory and N.K. Wilson, 'NMR of Aromatic Compounds,' Wiley, New York, 1982.

145. T.N. Huckerby, J.Mol.Struct., 1979, 54, 95.

146. A.I. Vogel, 'Textbook of Practical Organic Chemistry,' Longmans, London, 1978, p.670.

147. A. Pictet and P. Crépieux, Chem.Ber., 1888, 21, 1106.

148. K. Brand, Chem.Ber., 1909, 42, 3460.

149. E.C. Wagner, J.Am.Chem.Soc., 1933, 55, 724.

150. M. Busch and L. Leefhelm, J.Prakt.Chem., 1907, 77, 1.

151, J.U. Nef, Justus Liebigs Ann.Chem., 1899, 309, 126.

152. J. v. Braun, Chem.Ber., 1900, 33, 2728.

153. E. Wedekind, Justus Liebigs Ann.Chem., 1901, 318, 90.

154. E. Wedekind, Chem.Ber., 1903, 36, 3791.

155. A. Zander, Justus Liebigs Ann.Chem., 1882, 214, 138.

156. E. Wedekind and F. Oberheide, Chem.Ber., 1904, 37, 2712.

157. J. v Braun and R. Schwarz, Chem.Ber., 1902, 35, 1279.

158. H. Hörlein and R. Kneisel, Chem.Ber., 1906, 39, 1429.

159. J. Meisenheimer, H. Greeske, and A. Willimersdorf, Chem.Ber., 1922, 55, 513.

160. J. v. Braun, Chem.Ber., 1910, 43, 1353.

161. J. v. Braun, R. Fussgänger, and M. Kühn, Justus Liebigs Ann.Chem., 1925, 445, 201.

162. J. v. Braun, M. Kühn, and S. Siddiqui, Chem.Ber., 1926, 59, 1081.

163. H. Decker, W. Kropp, H. Hoyer, and P. Becker, Justus Liebigs Ann.Chem., 1913, 395, 299.

164. G. Ciamician and C. Zatti, Chem.Ber., 1889, 22, 1976.

165. P. Riehm, Justus Liebigs Ann.Chem., 1887, 238, 1.

166. A.T. Mason and G.R. Winder, J.Chem.Soc., 1894, 65, 191.

167. M. Kann and J. Tafel, Chem.Ber., 1894, 27, 2306.

168. C. Overberger, N.P. Marullo, and R.G. Hiskey, J.Am. Chem.Soc., 1961, 83, 1374.

169. Th. Zineke and G. Siebert, Chem.Ber., 1915, 48, 1242.

170. K. Brand and H. Stein, J.Prakt.Chem., 1924, 108, 19.

171. D.G. Foster and E.E. Reid, J.Am.Chem.Soc., 1924, 46, 1936.

172. C.S. Davis, G.L. Jenkins, A.M. Knevel, and C. Paget, J.Pharm.Sci., 1962, 51, 840.

173. A. Padwa and S. Nahm, J.Org.Chem., 1981, 46, 1402.

174. S. Blechert, R. Gericke, and E. Winterfeldt, Chem.Ber., 1973, 106, 355.

175. F.A. Hussein and S.Y. Kazandji, J.Indian Chem.Soc., 1966, 43, 663.

176. S. Ishida, S. Asaka, Y. Kawamura, and M. Omori, Jap.P. 6524/64.

177. P. Golborn and F. Scheinmann, J.Chem.Soc., Perkin Trans.1, 1973, 2870.

178. D. Leaver, J. Smolicz, and W.H. Stafford, J.Chem.Soc., 1962, 740.

179. Reference 146, p.684.

180. E. Bamberger, Chem.Ber., 1903, 36, 2042.

181. B.D. Tiffany, J.Am.Chem.Soc., 1948, 70, 592.

182. J. v. Braun and O. Braunsdorf, Chem.Ber., 1921, 54, 685.

183. R.A.W. Johnstone and M.E. Rose, Tetrahedron, 1979, 35, 2169.

184. Reference 146, p.1131.

185. J.T. Edsall and J. Wyman, Jr., J.Am.Chem.Soc., 1935, 57, 1964.

186. H.F. Hudson and G.F. Smith, J.Chem.Soc., 1957, 3544.

187. J. Thiele and O. Dimroth, Justus Liebigs Ann.Chem., 1899, 305, 102.

188. C. Moritz and R. Wolffenstein, Chem.Ber., 1899, 32, 2531.

189. J. Wright and E.C. Jorgensen, J.Org.Chem., 1968, 33, 1245.

190. J.I.G. Cadogan, D.S.B. Grace, P.K.K. Lim, and B.S. Tait, J.Chem.Soc., Perkin Trans.1, 1975, 2376.

191. F. Mayer and W. Krieger, Chem.Ber., 1922, 55, 1659.

192. M. Schöpff, Chem.Ber., 1890, 23, 1839.

193. H. Gilman and H.S. Broadbent, J.Am.Chem.Soc., 1947, 69, 2053.

194. Reference 146, p.605.

195. P. Carré, Bull.Soc.Chim.Fr., 1909, [4], 5, 119.

196. A. Bernthsen and F. Bender, Chem.Ber., 1883, 16, 1971.

197. This material was provided by Dr. H. McNab.

198. C. Graebe and K. Lagodzinski, Justus Liebigs Ann.Chem., 1903, 276, 35.

199. J.S. Morley, J.Chem.Soc., 1952, 4008.

200. H. Gilman and D.A. Shirley, J.Am.Chem.Soc., 1944, 66, 888.