GAS PHASE CYCLISATION AND REARRANGEMENT
REATIONS OF AROMATIC FREE RADICALS

by

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Declaration

I declare that this thesis is my own composition, that the work of which it is a record was carried out by myself and that it has not been submitted in any previous application for a higher degree.

This thesis describes the results of research carried out in the Department of Chemistry, University of Edinburgh, under the supervision of Dr. H. McNab since 1st October 1983, the date of my admission as a research student.
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Lecture Courses

The following courses have been attended:

Organic Research Seminars, Edinburgh University Chemistry Department (3 years attendance);

Current Topics in Organic Chemistry (15 Lectures, 3 years attendance), Dr. G. Tennant et al.;

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N-Allylanilines with adjacent substituents were pyrolysed to give aminyl radicals. With 2-anilino substituents the appropriate cyclisation products were obtained in good yields. Labelling studies showed that product formation resulted from a process involving a spirodienyl radical. With 2-benzyl substituents a spirodienyl radical was again involved in product formation.

These reactions were extended to generate thiophenoxyl and benzyl radicals with adjacent 2-benzyl and 2-thiophenoxyl substituents respectively. In both cases the reactions were reasonably clean giving good yields of the cyclisation products, the formation of which occurred exclusively via a spirodienyl radical. On the generation of phenoxy and benzyl radicals, with adjacent 2-benzyl and 2-phenoxy substituent respectively, the major product was, however, a hydroxyfluorene. The mechanism of formation of this rearrangement product was investigated by both deuterium labelling studies and by the generation of phenoxy radicals with adjacent 2-benzoyl substituents. These reactions gave minor products due to cyclisation reactions of phenyl radicals.

These were extended to generate phenyl radicals with 2-phenoxy and 2-thiophenoxyl substituents. Cyclisation of these radical species provided a new synthetic route to dibenzofurans and dibenzothiophenes. These methods were further extended to related hetero-analogues.
## CONTENTS

### INTRODUCTION

A. **Flash Vacuum Pyrolysis**  
   Page 1

B. **Generation of Free Radicals**  
   1. Benzyl and Phenyl Radicals  
      Page 7  
   2. Aminyl Radicals  
      Page 15  
   3. Phenoxyl Radicals  
      Page 17  
   4. Thiophenoxyl Radicals  
      Page 19

C. **Free Radical Rearrangements via a Spirodienyl Intermediate**  
   1. Gas Phase Rearrangement Reactions  
      Page 22  
   2. Rearrangement Reactions in the Solution Phase  
      Page 40

### DISCUSSION

A. **Introduction**  
   Page 64

B. **The Generation and Cyclisation of 2-(Arylamino)phenylaminyl Radicals**  
   Page 70

C. **The Generation and Cyclisation of 2-Thiophenoxylbenzyl and 2-Benzylthiophenoxyl Radicals**  
   Page 88

D. **The Generation and Cyclisation of 2-Benzylaminyl Radicals**  
   Page 106
E. The Generation and Rearrangement of 2-Phenoxybenzyl and 2-Benzylphenoxy Radicals 120

F. Further Investigation of the Mechanism of Hydrogen Abstraction by the Generation of 2-Benzoylphenoxy Radicals and Deuteriated Analogues 146

G. Preparation of Dibenzofurans and Related Hetero-analogues 171

EXPERIMENTAL

A. Symbols and Abbreviations 198

B. Instrumentation 199

C. Pyrolysis Apparatus and General Techniques 202

D. The Generation and Cyclisation of 2-(Arylamino)phenylaminyl Radicals 204

E. The Generation and Cyclisation of 2-Thiophenoxybenzyl and 2-Benzylthiophenoxy Radicals 217

F. The Generation and Cyclisation of 2-Benzylaminyl Radicals 237
G. The Generation and Rearrangement of
2-Phenoxybenzyl and 2-Benzylphenoxyl
Radicals

H. The Generation of 2-Benzoylphenoxyl
Radicals and Related Deuteriated Analogues
to Further Study the Mechanism of Hydrogen
Abstraction

I. Preparation of Dibenzofurans and Related
Hetero-analogues

1. Preparation of Dibenzofurans

2. Preparation of Dibenzothiophenes

3. Attempted Preparation of Carbazoles
   and N-Methylcarbazoles

4. Preparation of Fluorene and Fluorenone

REFERENCES

PUBLICATIONS
INTRODUCTION
INTRODUCTION

A. Flash Vacuum Pyrolysis

Flash vacuum pyrolysis is a convenient method of carrying out many different high temperature reactions. It involves vaporisation of a substrate from an inlet system into a silica furnace tube which is maintained at temperatures of up to 1000°C. The apparatus is usually 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 low concentration of molecules in the hot zone at any one time, tends to lead to intramolecular reactions taking place rather than intermolecular reactions, although radical coupling reactions are observed. There have been many reviews on flash vacuum pyrolysis, the most comprehensive being Brown's recent monograph. General reviews on the subject include those by de Mayo, Seybold, Hagemann and Wiersum, Wentrup, Vogtle and Rossa, Schaden, Wiersum, Karpf and Gajewski.
Flash vacuum pyrolysis has been used in a variety of different ways. Short-lived, reactive species, such as carbenes, nitrenes and free radicals have been generated by this technique which has also been used as a method of investigating reaction mechanisms. Flash vacuum pyrolysis also has a use as a preparative route to a variety of organic compounds.

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.

In the study of concerted reactions, much work has been carried out on the pyrolytic cis elimination reactions, mainly involving esters, and this subject has been reviewed by Depuy and King, Maccoll and Smith and Kelly. The pyrolysis of esters generally results in loss of the ester linkage to give good yields of alkenes by a cyclic concerted process (Scheme 1).

\[
\begin{align*}
\text{COOCH}_3 & \quad \rightarrow \quad \text{COOCH}_3 + \text{OH}\text{-}\text{C-CH}_3 \\
\text{H} & \quad \text{O} \\
\end{align*}
\]

Scheme 1
The Retro-Diels Alder reaction may also occur during flash vacuum pyrolysis. For example, Ardis\(^{17}\) has prepared vinylidene cyanide from 4,4-dicyanocyclohexene \(^{(1)}\) as shown in Scheme 2.

\[
\begin{align*}
\text{NC} & \quad \text{NC} \\
\text{NC} & \quad \text{ON} \\
\text{NC} & \quad \text{ON}
\end{align*}
\]

Scheme 2

The generation and rearrangement of aromatic carbenes and nitrenes, generated in the gas phase by the loss of some small molecule, has been reviewed in considerable detail by Wentrup.\(^{18}\) 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 reaction involving the formation of a carbene is shown in Scheme 3,\(^{19}\) the carbene generated undergoing specific intramolecular cyclisation.
The small molecules eliminated during pyrolysis are thermodynamically highly stable fragments such as CO, CO$_2$, N$_2$ and SO$_2$. The stereoselective synthesis of (E,E) conjugated dienes provides a good example of this, the reaction involving the thermal extrusion of sulphur dioxide$^{20}$ (Scheme 4).
Arynes (2) can also be generated in the gas phase by the elimination of small molecules from precursors with the general structure (3), where x, y and z represent the groups which give stable fragments, e.g. Scheme 5.\textsuperscript{21,22}

\begin{center}
\includegraphics[scale=0.5]{scheme5.png}
\end{center}

Scheme 5

Diazaarynes (4) generated by this method do not however, give azabiphenylenes, the arynes rearranging under flash vacuum pyrolytic conditions to give nitriles as shown in Scheme 6.\textsuperscript{23}

\begin{center}
\includegraphics[scale=0.5]{scheme6.png}
\end{center}

Scheme 6
A third class of reactions undergone during flash vacuum pyrolysis is the generation of free radicals. The formation of radicals in the gas phase, and their subsequent reaction, forms the major part of this thesis and the following section deals with the generation of the types of radicals studied throughout this work.
B. **Generation of Free Radicals**

The generation of free radicals in the gas phase forms the third major class of reactions undergone during flash vacuum pyrolysis. Free radicals are generated by the homolysis of the weakest single bond in the substrate molecule, at a variety of temperatures from 500°C-900°C, thus generating two radical species. The generation of free radicals by flash vacuum pyrolysis has been the subject of a recent review by McNab, Hickson and Cadogan. 24 Throughout this thesis the radical species generated include benzyl, phenyl, aminyl, phenoxyl and thiophenoxyl radicals and the following sections give a summary of the various methods of generating these radicals.

1. **Benzyl and Phenyl Radicals**

Benzyl radicals can be generated from a variety of substrates, one of the most widely used being symmetrical dibenzyl oxalates (5) 25 (Scheme 7).

\[
\text{C}_6\text{H}_4\text{CH}_2\text{O}-\text{C} = \text{C} \quad \text{at } 660^\circ \text{C} \quad \rightarrow \quad \text{C}_6\text{H}_4\text{CH}_2
\]

(5)

**Scheme 7**

One of the advantages of generating benzyl radicals from oxalates is that the substrates are easy to obtain, in high yields, simply by reacting the appropriate benzyl
alcohol with oxalyl chloride at 0°C in a basic solution (Scheme 8). There are examples, however, of this reaction not taking place when a nitrogen atom is present in the alcohol, a thick gum being obtained.

\[
\text{ArCH}_2\text{OH} + \text{Oxalyl chloride} \xrightleftharpoons{\text{NEt}_3, 0^\circ\text{C}} \text{ArCH}_2\text{O}^\text{O}_2\text{C}^+\text{H}_2
\]

Scheme 8

The temperatures required to generate the radicals are moderate, in the range 550-750°C, but the substrates do suffer the disadvantage that they can be rather involatile, especially if the substituents are either large or polar groups. A further disadvantage of the use of oxalates as substrates is the occurrence of competing elimination if an α-H atom is present (e.g. Scheme 9).

\[
\text{Ph-CH-O-C}^+\text{H}_2 \xrightarrow{} \text{Ph-CH=CH-CH}_3
\]

Scheme 9

The use of sulphones (6) to generate benzyl radicals is another widely used and convenient method (Scheme 10).

\[
\text{PhCH}_2\text{SO}_2\text{CH}_2\text{Ph} \xrightarrow{650^\circ\text{C}} \text{PhCH}_2
\]

Scheme 10
Examples of the generation of benzyl radicals from unsymmetrical sulphones have also been reported \(^{28}\) (e.g. Scheme 11).

\[
\begin{array}{c}
\text{Ph} - \text{S} - \text{Ph} \\
\xrightarrow{700^\circ C}
\end{array}
\]

Scheme 11

Pyrolysis temperatures of 700-800\(^\circ\)C are required for complete decomposition of precursors to the appropriate radical and, as for the oxalates, the substrates can be rather involatile if substituents are either bulky or polar groups. The main disadvantage of sulphones over oxalates is their preparation which requires several steps and, in some cases, purification by chromatography as compared to the shorter, quicker oxalate synthesis.

The occasional failure of oxalates and sulphones as benzyl radical precursors has resulted in a search for more volatile starting materials. In recent years selenides (7) have been used as a source of benzyl radicals \(^{29,30}\) (Scheme 12), in some cases where oxalates have proved unsuccessful.

\[
\begin{array}{c}
\text{ArCH}_2\text{SePh} \\
\xrightarrow{600^\circ C}
\end{array}
\]

Scheme 12
Selenide precursors are readily prepared, in high yields, from diphenyl diselenide and the appropriate alkyl halide.\textsuperscript{29} They have the advantage that pyrolyses can be carried out with polar functional groups, thus avoiding the problems with vaporisation, but they have the disadvantage of being very smelly to work with. A further group of precursors that can be used as an alternative benzyl radical generator are the sulfoxides (8)\textsuperscript{31} (Scheme 13).

\[
\text{PhSOCH}_2\text{Ph} \xrightarrow{500^\circ\text{C}} \text{PhCH}_2
\]

\textit{Scheme 13}

Since the sulphoxides are more reactive than the corresponding sulphones pyrolysis can take place at lower temperatures of 500-700°C. Attempts to generate benzyl radicals from the less reactive sulphides,\textsuperscript{31} at temperatures of up to 900°C, have proved unsuccessful, only starting material being recovered.

A variety of other methods which do not have widespread applications have been used to generate benzyl radicals. One example of this is the use of high temperatures to degrade molecules which contain benzyl substituents, the degradation of phenylalanine (9)\textsuperscript{32} and methyl \textit{p}-tolylacetate (10)\textsuperscript{33} being typical examples (Scheme 14).
Phosphoranes (11)$^{34}$ have also been used as a source of benzyl radicals as have phenyl ethers (12)$^{34}$ (Scheme 15).

Phenyl ethers have also been put to use when the presence of a nitrogen atom in a compound complicates the preparation of oxalates$^{35}$ (e.g. Scheme 16).
Benzyl type radicals have been generated by the pyrolysis of the t-butyl peresters of tetralin\(^\text{36}\) (13), the generated radical subsequently rearranging as shown in Scheme 17.

The pyrolysis of \(\text{N-oxides} (14)\)\(^{37}\) with an \(\alpha\)-substituent provides an unusual course of obtaining benzyl radicals as shown in Scheme 18.
Throughout this thesis, however, the method of choice of generating the required benzyl radicals has always been from the appropriate symmetrical dibenzyl oxalate, the radical precursors having no α-H atom thus there being no competing elimination.

Although phenyl radicals are common reaction intermediates there are no well defined and widely applicable methods of generating these radical species in the gas phase. Phenyl radicals have been generated from nitrobenzenes by long contact time pyrolysis (ca. 10 s). However, the generation of phenoxy radicals by C-O bond cleavage competes with the generation of these radical species.\(^{38,39}\) (e.g. Scheme 19).
Just as benzyl radicals can be generated from sulfoxides and sulphones so phenyl radicals can be generated in this way, the radical precursors being symmetrical species \(^{31}\) (Scheme 20).

\[
\begin{align*}
\text{PhSO}_2\text{Ph} & \xrightarrow{700-800^\circ C} \text{Ph}. \\
\text{PhSOPh} & \xrightarrow{700^\circ C} \text{Ph}.
\end{align*}
\]

**Scheme 20**

Phenyl radicals have also been generated by the pyrolysis of diazaprop-2-en-1-ones \(^{40}\) (15). The pyrolysis of these compounds initially results in C-N bond cleavage to generate benzoyl radicals which rapidly lose carbon monoxide to generate the appropriate phenyl radicals (Scheme 21).

\[
\text{Ph-C-O} \xrightarrow{750^\circ C} \text{Ph-C-O} \xrightarrow{750^\circ C} \text{Ph}.
\]

**Scheme 21**

Phenyl radicals have, however, also been generated from allyl esters (16) \(^{41}\) (Scheme 22). This method of generating phenyl radicals was investigated further.
during the work carried out for this thesis and proved to be a useful method of generating these radicals (see Discussion Section).

![Scheme 22]

2. Aminyl Radicals

The generation and reactions of aminyl radicals in the gas phase is a subject which has not been well studied, most of the work being carried out in recent years by McNab et al.\textsuperscript{42,43} Throughout this recent work the aminyl radicals studied have been generated from the appropriate N-allyl derivative (17)\textsuperscript{42} (Scheme 23).

![Scheme 23]
This method of generation is widely applicable to a variety of aromatic systems and provides a good, clean method of generating aminyl radicals at moderate temperatures. The substrates are easily obtained, in reasonable yields, by the reaction of the appropriate amine with allyl bromide in a basic solution, although a small amount of the N,N-diallyl derivative is also generated which can be separated by chromatography (Scheme 24).

Scheme 24

This method of generation cannot, however, be applied to N,N-dialkylamine derivatives, since in these cases fragmentation occurs via a retro-ene mechanism to give the imine which may subsequently cleave to the appropriate benzyl and iminyl radicals (e.g. Scheme 25).

Scheme 25
There have been some isolated examples of dimethylamino radicals which have been generated from tetrazine \(^{44,45}\) (Scheme 26), but this method is much more restricted and is not widely applicable.

\[
\text{Me}_2\text{N}-\text{N}=\text{N}-\text{NMe}_2 \rightarrow 2\text{Me}_2\text{N}^+ + \text{N}_2
\]  
\[(18)\]

Scheme 26

Throughout the work detailed in this thesis the aminyl radical systems of interest have all been generated from the appropriate N-allyl derivatives by pyrolysis at 750°C.

3. Phenoxyl Radicals

Surprisingly, very little work has been carried out on the reactions of phenoxyl radicals in the gas phase, the work detailed in this thesis forming a large part of their study. Consequently, methods of generating these radicals in the gas phase have not been well investigated, although it appears that phenoxyl radicals can be easily obtained from almost any molecule containing this structural unit\(^{46,47}\) (e.g. Scheme 27).

![Scheme 27](image)
Particularly convenient precursors to these species are the aryl allyl ethers (19)\textsuperscript{48,49} (Scheme 28), the oxygen equivalent of the N-allyl derivatives from which aminyl radicals can be generated (see Section 2). As previously described, the substrates are easily obtained, in high yields, and for the phenoxy series require little purification. The radicals are generated by pyrolysis of these precursors at 750°C. Surprisingly, no Claisen rearrangement of these species has ever been observed (Scheme 28).

\begin{align*}
\text{(19)} & \quad \rightarrow \quad \text{phenoxyl radical} + \text{allyl} \\
\end{align*}

Scheme 28

Throughout the phenoxy radical work detailed in this thesis the radicals studied have been generated from the appropriate allyl ether derivative.
4. Thiophenoxyl Radicals

The reactions of thiophenoxyl radicals in the gas phase have not been extensively studied but some work has been done in this area. The generation of these radical species should be analogous to the phenoxyl radical series but in practice, they are obtained by a variety of methods. In the pyrolysis of sulphoxides to prepare sulphenic acids (20), thiophenoxyl radicals are generated as a by-product. However, they can be generated directly by the pyrolysis of thioethers (21) (Scheme 29).

\[
\begin{align*}
&\text{ArS}_2\text{CH}_2\text{CH}_2 \xrightarrow{600^\circ\text{C}} \text{ArSOH} \rightarrow \text{ArS•} \\
&\text{(20)} \\
&\text{ArS•} \xrightarrow{800^\circ\text{C}} \text{ArSCH}_2\text{Ar'} \\
&\text{(21)}
\end{align*}
\]

Scheme 29

Thiophenoxyl radicals have also been generated from sulphoxides via their rearrangement, in the gas phase, to sulphenate esters (22) which subsequently undergo cleavage (Scheme 30).

\[
\begin{align*}
&\text{Ph-S-Ph} \rightarrow \text{PhS-0-Ph} \rightarrow \text{PhS•} \\
&\text{(22)}
\end{align*}
\]

Scheme 30
A considerable amount of preparative work has been carried out by Klemm and co-workers\textsuperscript{51,52} using thioalkoxy radicals. These radical species have been generated directly from the benzyl compound (23) by cleavage of the weak S-benzyl bond (Scheme 31).

\begin{center}
\begin{tikzpicture}
\node (1) at (0,0) {\text{Ph \ \ S\text{\_}Me \ \ Ph}};
\node (2) at (1,0) {\text{Ph \ S\text{\_}Me \ \ Ph}};
\node (3) at (2,0) {\text{Ph \ S\text{\_}Me \ \ Ph}};
\draw[blue, thick, ->] (1) -- (2) node[midway, above] {\text{580\textdegreeCelsius}};
\draw[blue, thick, ->] (2) -- (3) node[midway, above] {\text{580\textdegreeCelsius}};
\end{tikzpicture}
\end{center}

Scheme 31

Similarly, these radicals have been generated directly by the cleavage of the S-methyl bond in sulphides (24) and cleavage of the S-S bond in disulphides (25)\textsuperscript{53} (Scheme 32).

\begin{center}
\begin{tikzpicture}
\node (1) at (0,0) {\text{Ph \ S\text{\_}Me \ \ Ph}};
\node (2) at (1,0) {\text{Ph \ S\text{\_}Me \ \ Ph}};
\node (3) at (2,0) {\text{Ph \ S\text{\_}Me \ \ Ph}};
\draw[blue, thick, ->] (1) -- (2) node[midway, above] {\text{580\textdegreeCelsius}};
\draw[blue, thick, ->] (2) -- (3) node[midway, above] {\text{580\textdegreeCelsius}};
\end{tikzpicture}
\end{center}

Scheme 32

As with the aminyl and phenoxy radicals, thio-phenoxyl radicals have also been generated from the S-allyl
derivatives, the allyl thio ethers (26) \(^{54}\) (Scheme 33). Again, these are readily prepared from the appropriate thiophenol and can be pyrolysed at moderate temperatures, thus they have, again, proved the method of choice for generating the thiophenoxyl radicals studied throughout this thesis.

![Scheme 33](image-url)
C. Free Radical Rearrangements via a Spirodiienyl Intermediate

Once generated, the reactions of aromatic free radicals can follow a variety of courses. One such course is for these species to undergo rearrangement reactions, the remainder of this chapter dealing with rearrangements which occur via a spirodiienyl intermediate. These reactions will be examined firstly in the gas phase then, as a comparison, in solution phase. In addition, the reactions will be examined according to the size of ring observed in the spiro-intermediate, i.e. 3-membered spiro-intermediates up to 7-membered spiro systems.

1. Gas Phase Rearrangement Reactions

Rearrangement reactions can involve the attack of a $\beta$-radical on an aromatic ring to give a spiro-intermediate (27) which can then open in the opposite sense (e.g. the neophyl rearrangement\textsuperscript{55}) (Scheme 34).

\[
\begin{array}{c}
\text{X-CH}_2 \\
\text{X-CH}_2 \\
\text{CH}_2-X^* \\
\end{array}
\]

Scheme 34
The β-radical is usually generated by H shift from a phenyl, benzyl or related radical. This has been demonstrated by Marty and de Mayo⁴¹ where H shift from the o-methoxyphenyl radical (28), followed by spiro-rearrangement to the phenoxy methyl radical (29) gave benzaldehyde as the major product (Scheme 35). This mechanism was confirmed by $^2$H labelling, pyrolysis of the deuterated (OCD$_3$) ether leading to a product totally and specifically labelled at the aldehyde carbon and the position ortho to it. The feasibility of this anisyl radical to aldehyde rearrangement had previously been demonstrated in a static pyrolysis system.⁵⁶

This neophyl rearrangement has also been observed when C-S bond cleavage in 2-t-butylaryl sulphenic acids (30) gives the phenyl radical (31) (cf. Scheme 29). Generation of this species followed by H-shift and rearrangement gives the β-radical from which the products are derived⁵⁷ (Scheme 36).
Much work has been carried out by McNab and co-workers on the reactions of benzyl radicals, with alkyl groups in the ortho position, where there is the possibility of spiro-rearrangement taking place. Generation of the benzyl radical (32), from the appropriate sulphone, phenyl ether or phosphorane, produced as the only pyrolysis product 2-methylbenzaldehyde\textsuperscript{34} (Scheme 37).
The formation of this product is analogous to the formation of 8-hydroxybenzaldehyde obtained by de Mayo. 41

![Scheme 37](image)

Again, further evidence for the mechanism was obtained by labelling studies. The generation of the 2-[$^2\text{H}_3$]methoxybenzyl radical (33) resulted in the label being equally distributed between the aldehyde and methyl groups thus supporting the hydrogen transfer step (Scheme 38).

![Scheme 38](image)
These reactions were extended to examine \( \sigma \)-thio-alkylbenzyl radicals (e.g. 34) when it was expected that they might provide a source of thioaldehydes, a series of compounds not easily obtained. However, these reactions proved more complex than the analogous alkyloxy derivatives, the reactions proceeding in a different manner by the mechanism outlined in Scheme 39.

\[
\begin{align*}
\text{Scheme (39)}
\end{align*}
\]
Generation of the 2-ethyl-thiobenzyl radical (34) led to the formation of the spirodienyl radical (35) by the same sequence outlined previously. However, instead of opening to generate the rearranged radical species, a hydrogen atom is lost to give the closed shell thirane (36). Extrusion of sulphur from this species leads to the major product of the pyrolysis, o-methylstyrene (37) whereas rearrangement gives the minor products, the dihydrothiophenes (38) and (39).

These reactions were further extended to cover benzyl radicals with dialkylamino groups in the ortho position (e.g. 40), generated from the appropriate phenyl ether. The major product of the pyrolysis, obtained only in low yield, was formed by the mechanism outlined in Scheme 40, the mechanism being investigated by deuterium labelling studies.
The benzyl radical (40) initially generated abstracts a hydrogen atom and forms a spiro-intermediate as before, for this system the spiroaziridine ring opening to give an aminyl radical (41). This aminyl radical may tautomerise to the aminoalkyl radical (42) from which cleavage of an imine fragment gives the 2-methylbenzyl radical which dimerises to give di-o-tolylethane (43) as the major product.

The generation of the phenoxyl radical (44), with an adjacent dialkylamino substituent gave, as the major identifiable product, o-cresol. The formation of this compound occurs by a mechanism analogous to Scheme 40 (Scheme 41).

Phenoxy radicals have also been studied where the o-substituent is a thioalkoxy group. The mechanism of product formation is similar to that previously
outlined for benzyl radicals with adjacent thioalkoxy groups (c.f. Scheme 39). In this case formation of the spiro-intermediate is followed by loss of a hydrogen atom to generate the thirane (45) from which products are formed exclusively by the extrusion of sulphur (Scheme 42). No heterocyclic products are obtained by rearrangement of this species, as was observed for the benzyl radicals.

\[
\begin{align*}
\text{Scheme 42} & \\
\text{Attempts to generate and study thiophenoxy} & \\
\text{radicals from the S-allyl compound (46) were unsuccessful} & \\
\text{over a range of conditions.} & \\
\text{Since labile 2-mercapto-} & \\
\text{benzaldehyde was expected as a rearrangement product it} & \\
\text{is possible that only involatile polymeric products were} & \\
\text{obtained.} & 
\end{align*}
\]
In this series of reactions arylaminyl radicals, generated from the N-allyl compound, with o-alkoxy and o-thioalkoxy substituents have also been studied\(^4\) (Scheme 43). The rearrangement of these radicals is similar to that obtained for the corresponding benzyl radicals. The aminyl radicals generated rearrange to form the spiro-intermediate (47) which opens to give the rearranged radical (48) only when \(X=O\), and hence to give the benzaldehyde (49) but only as a minor product (c.f. benzyl radical case). The major product obtained when \(X=O\) is the benzoxazole (51, \(X=O\)) which is formed from the intermediate (50) by C-N bond formation followed by thermal aromatisation of the dihydro compound. A major product obtained when \(X=S\) is the benzothiazole (51, \(X=S\)) which is formed by a similar mechanism. A second product of the thioalkoxy series is 2-aminostyrene (52) which is formed from the intermediate (50) by the extrusion of sulphur as has previously been observed (c.f. Schemes 39 and 42).
Scheme 43

(49)

(48)

(47)

(50)

(51)

(52)
There is evidence that a neophyl type rearrangement can take place even when the β-radical is constrained in a ring. This rearrangement has been demonstrated by the interconversion of the tetralinyl radical (53), generated from the appropriate t-butyl perester, with the indanylmethyl radical (54) (Scheme 44).

Scheme 44

It is speculated that this neophyl-type rearrangement may be involved in the mechanism of formation of 2-quinoline (56) from the radical species (55) as shown in Scheme 45.
Rearrangement reactions have been studied where the spiro-intermediate involves a 5-membered cyclic structure. This type of rearrangement is illustrated by the migration of a phenyl group from phosphorus to carbon as shown in Scheme 46. The radical species is generated from the dihydrophospha-anthracene (57) by homolysis of a t-butyl group. The subsequent 1,4-migration of the phenyl group has been postulated to occur via a spiro-intermediate (58) as outlined in Scheme 46.
However, most of the work on 5-membered spiro-intermediates has been carried out by McNab and co-workers on intermediates with the general structure (59), this work mostly involving iminyl radicals (59, \( X = \text{N}= \)).

The iminyl radicals are generated from the appropriate phenylhydrazones, e.g. (60) and (63). Studies on these systems found that generation of either of the iminyl radicals (61) and (64) led to the formation of the two isomeric quinoxalines (62) and (65), although the ratio of these isomers was not the same from both radicals\(^{60,61}\) (Scheme 47). The position of the methyl substituents in the radical precursors had been specifically designed so as to allow the quinoxaline isomers to be distinguished.

These results suggest that the iminyl radicals (61) and (64) can interconvert via the spirodiienyl radical (66). Further investigations of the reaction mechanism by \( ^{15}\text{N} \) labelling studies\(^{62}\) found that the label was scrambled between both the nitrogen sites of the quinoxalines thus confirming the involvement of the spiro-intermediate.
These labelling studies also showed that equilibration via the spiro-intermediate was incomplete due to the competing direct cyclisation of the iminyl radicals (61) and (64), thus accounting for the differing quinoxaline ratios obtained from each of these radicals.

These reactions were extended to cover systems with two ortho methyl substituents.\textsuperscript{63,64} It was expected that these systems would lead to an efficient synthesis of 5-substituted quinoxalines since two quinoxalines were found to be formed from the o-tolyl compound (67) due to competitive ejection of the hydrogen atom and the methyl group (Scheme 48).

\[ \text{Me} \quad \rightarrow \quad \text{Me} \quad + \quad \text{Me} \]

\textbf{Scheme 48}

However, on generation of the iminyl radicals (68) and (69) it was found that the reaction followed a different course than might have been expected (Scheme 49).

The major product of the pyrolysis was 7-methyl-indole (73) while the two quinoxalines (70) and (71) were only found as minor components. \textsuperscript{15}N labelling studies,
and the formation of the isomeric quinoxalines, confirmed that the spiro-intermediate (74) was involved in product formation. The formation of the indole can be explained by preferential loss of MeCN from (72) to give the nitrile ylide which subsequently cyclises, while the quinoxalines can be formed from the spirodienyl (74) by C-N migration and loss of a methyl group.

These reactions have been extended to arylvinyl-iminyl radicals (76), these being generated by pyrolysis of the O-alkyloxime (75). Cyclisation and rearrangement of the initially generated radical via a spiro-intermediate would be expected to give a mixture of 6- and 7-methyl-quinoline (77) and (78) (Scheme 50).
However, on pyrolysis it was found that only 7-methyquinoline (77) was obtained. This suggests either that direct cyclisation of the radical (76) is taking place or, that on generating the spiro-intermediate (79), C-N bond migration from this species is favoured over C-C migration. In order to determine the mechanism further it would be necessary to generate the vinyl radical directly. Unfortunately a gas-phase method of generating these species is not yet available.

However, in similar systems studied in solution phase it was found that on generation of the vinyl radical (80) the major product was the quinoline (81). The formation of this compound can be explained by rearrangement of the vinyl radical via a spiro-intermediate from which C-N migration is favoured (Scheme 51).
2. **Rearrangement Reactions in the Solution Phase**

The rearrangement of free radicals in the solution phase has been the subject of several texts and reviews including those by Wilt, Walling, Friedlina, Pryor and Nonhebel and Walton. This topic has recently been updated in a further review by Friedlina. Although these radicals usually rearrange by a similar mechanism to that observed in the gas phase, their generation in solution frequently involves chain reactions. A large number of rearrangements covered in these texts involve the 1,2-shift of an aryl group (Scheme 52), i.e. the neophyl rearrangement, this being the first carbon radical rearrangement observed in solution.

\[ \text{Ph} \xrightarrow{\cdot \cdot} \text{Ph} \]

**Scheme 52**

The first neophyl rearrangement was demonstrated by Urry and Kharasch in 1944 who showed that the treatment of neophyl chloride (82) with phenylmagnesium bromide in the presence of cobaltous chloride generated the radical species (83) which subsequently underwent a rearrangement reaction to generate the radical (84) from which the products were derived (Scheme 53).
PhMgBr + CoCl₂ → PhCoCl → Ph₂ + 2CoCl₂ + MgBrCl

CH₃
Ph-CH₂CH₂Cl + CoCl₂ → PhC(CH₃)₂CH₂
CH₃
(82) + CoCl

·C(CH₃)₂CH₂Ph
(84)

H CH₃
PhC≡C-CH₃ + CH₂≡CCH₂Ph + CH(CH₃)₂CH₂Ph
CH₃

Scheme 53

A similar rearrangement was observed by Winstein and Seubold on the decarbonylation of the aldehyde (85), initiated by di-t-butylperoxide, to generate the radical species (86), rearrangement being indicated by the isolation of isobutylbenzene (87) as a product (Scheme 54).

Much of the early work carried out on systems which undergo a neophyl rearrangement was concerned with the activation energy and kinetics of the rearrangement and the effect of substitution in the phenyl ring on the rearrangement rate. However, much of this
work appears to give conflicting values and inconsistent results, and indeed much of the work reviewed more recently by Friedlina is still concerned with the kinetics of the rearrangement. However, a discussion of the rates and energy processes of rearrangement is outwith the scope of this study.

This work has also been concerned with whether the products of the rearrangement are derived directly from the bridged radical (88) formed during the rearrangement i.e. the spiro-intermediate or whether a distinct rearranged radical (89) is generated (Scheme 55).
E.s.r. studies\textsuperscript{72} have failed to observe any indication of the bridged species (88) while work by Rüchardt\textsuperscript{68,73} has shown that decarbonylation of the optically active aldehyde (90) results in the formation of (93) with at least 98\% racemization. This racemization indicates that the bridged radical (91) rearranges to the acyclic radical (92) before the formation of the racemic product (Scheme 56).

The driving force for this rearrangement appears to be the formation of the more stable tertiary radical from a primary radical, the extent of rearrangement depending on the stability of the rearranged and unrearranged radicals. This has been demonstrated by the
Scheme 56

100% rearrangement of a primary radical to a tertiary radical\(^7^4\) compared to only 5% rearrangement of a primary to primary radical\(^7^5\) (Scheme 57).

Scheme 57
Migration of an aryl group via a spiro-intermediate has been observed other than for carbon to carbon rearrangement. Decomposition of triphenylmethyl peroxide (94) to generate the alkoxy radical (96) resulted in rearrangement, via the spiro-intermediate (97), to generate the carbon radical (98) from which the product was obtained by dimerisation.\textsuperscript{76} This rearrangement had previously been observed by Spielman\textsuperscript{77} when the radical (96) was generated by decomposition of triphenylmethyl-hyponitrite (95) (Scheme 58).

\[
\text{Ph}_3\text{COO(\text{CH}_3)_3} \quad \text{(94)}
\]

\[
\begin{array}{c}
\text{Ph-C-Ph} \\
\text{(96)} \\
\text{O-} \\
\text{(97)}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{(98)}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{(95)}
\end{array}
\]

\[
\begin{array}{c}
\text{(Ph)}_3\text{C-O-N=N-O-C(Ph)}_3 \\
\text{(Dimer)}
\end{array}
\]

Scheme 58
A similar rearrangement had been observed by Bartlett and Cotman on the decomposition of p-nitrophenyldiphenylmethyl hydroperoxide (99). They found that during the rearrangement there was preferential migration of the p-nitrophenyl group to the phenyl group (Scheme 59).

However, attempts to carry out this rearrangement in the opposite direction, i.e. where a phenyl group migrates from an oxygen atom to a carbon atom, have so far failed as have attempts to demonstrate a similar rearrangement from a nitrogen atom to a carbon atom.

As with the gas phase, reactions in the liquid phase have also been observed where the rearrangement occurs via a 5-membered spiro-intermediate (100), i.e. a 1,4-migration of the phenyl group. The reactions of these species have been reviewed by Wilt, Friedlina, and Nonhebel and Walton.
Winstein and co-workers observed such a rearrangement on the generation of the radical (101) by the di-t-butylperoxide-induced decarbonylation of 5-methyl-5-phenylhexanal. Rearrangement took place via the spiro-cyclohexadienyl radical (102), resulting in the 1,4-migration of a phenyl group to give the more stable tertiary radical (103) (Scheme 60).
A similar rearrangement was observed on the generation of the acyl radical (104) by treatment of the aldehyde with peroxide at 100°C.\textsuperscript{82} The use of di-t-amyl peroxide at 100°C prevents the decarbonylation of (104) observed in Scheme 60 and allows the rearrangement to take place as shown in Scheme 61.

![Scheme 61](image)

As with the 1,2-migration of a phenyl group, this reaction can occur other than for carbon to carbon migration, the 1,4-migration of a phenyl group from a silicon atom to a carbon atom being known\textsuperscript{83} (Scheme 62). Generation of the alkyl radical (106) by the treatment of
the chloroalkylsilane (105) with tributyltin hydride and peroxide resulted in rearrangement taking place via the spirohexadienyl radical (107) to generate the silyl radical (108).

![Scheme 62]

The rearrangement has also been observed on the generation of oxygen radicals, 1,4 migration of the phenyl group from the carbon atom to the oxygen atom, via a spiro-intermediate, taking place. Thermolysis of both bis-3,3,3-triphenylpropionate (109) and t-butyl-3,3,3-triphenylperpropionate (110) generated the acyloxy radical (111) which subsequently rearranged via the spiro intermediate to give the radical species (112) and hence
phenyl 2,2-diphenylacrylate as product (Scheme 63).

\[
\begin{align*}
\text{(Ph} & {_3CCH_2CO_2)_2} \\
& \text{(109)} \\
\text{Ph} & \text{CCH} \_2 \text{CO}_3 \text{Bu}^+ \\
& \text{(110)} \\
\text{Ph} & \text{C=CHCO}_2 \text{Ph} \rightleftharpoons \text{Ph}_2 \text{CCH}_2 \text{CO}_2 \text{Ph} \\
& \text{(112)}
\end{align*}
\]

Scheme 63

This rearrangement of oxygen-centred radicals is common and is often found to occur during the Hunsdiecker reaction and Kolbe electrolysis. Hunsdiecker reaction\(^86,87\) of silver 3,3,3-triphenyipropionate (113) and electrolysis of 3,3,3-triphenylpropionic acid\(^88\) (114) both led to the generation of the acyloxy radical (115) which subsequently underwent rearrangement \textit{via} the spiro-intermediate (116) (Scheme 64).

That the rearrangement occurred \textit{via} the 5-membered spiro-intermediate (116) was shown by introducing a substituent into the phenyl ring,\(^89\) the retention of the original position of this substituent providing evidence
for a 5-membered spiro-intermediate as opposed to a 6-membered intermediate (117) which was a possibility.
There have been examples reported in the literature where the 1,4 migration of a phenyl group via a spiro-radical results in the intermediate species being trapped. This was demonstrated in the photochemical reaction of 2-phenoxyethanol with mercuric oxide-iodine reagent. Reaction of 2-phenoxyethanol (118) with the mercuric oxide-iodine reagent, followed by irradiation, generates the alkyloxy radical (119) which forms the spiro-intermediate (120). However, this spiro-radical does not re-open to generate a further alkoxy radical but instead forms a carbocation (121), derived from either the radical (120) by oxidation or from the iodide (122). Reaction of this carbocation with an oxygen species, such as HOI or I₂O, followed by elimination would result in the formation of the major product, p-benzoquinone ethylene acetal (123) (Scheme 65).

This reaction has been further studied to investigate the effects of various substituents in the phenyl ring on the course of the reaction.

These types of trapping reactions have also been observed on the generation of amido radicals. Treatment of N-methylbiphenyl-2-carboxamide (124) with lead(IV) acetate-iodine reagent generates the amido radical (125) which subsequently cyclises to form the spiro-intermediate (126). Oxidation of this intermediate with iodine forms
Scheme 65
the carbocation which reacts with acetate in the reaction mixture to give the spirocyclohexadienyl acetates (127) and (128) (Scheme 66). This reaction has also been carried out using t-buty1hypochlorite-iodiđe as reagent in the presence of potassium t-butoxide or t-butyl alcohol to further investigate the reaction mechanism. The effect
of various substituents in the phenyl ring on the course of the reaction have also been studied. A similar reaction to that outlined in Scheme 66 was observed by Forrester and co-workers on the oxidation of N-t-butylibiphenyl-2-carboxamide (129) with persulphate in a hot aqueous solution. Again the amido radical generated formed the spiro-intermediate (130) which was subsequently oxidised to the carbocation. Solvolysis of this cation followed by further oxidation would result in the formation of the spirodienone (131) observed. The major product observed during this reaction was the spirodimer (132) (Scheme 67).
A spirodimer was also the major product observed by Hey et al.$^9$ on the photolysis of 2-iodo-\(N\)-methyl-benzanilide (133) in benzene (Scheme 68). The photolysis of (133) generated the phenyl radical (134) which subsequently cyclised to form the spirocyclohexadienyl radical (135) from which is obtained the spirodimer. A minor product isolated from the photolysis was the spirodiene (136).

\[
\text{Scheme 68}
\]
A further set of reactions which take place via a spiro-intermediate are the 'transannular neophyl' rearrangements. These rearrangements occur only in 6-membered cycles capable of adopting a boat conformation, via the general intermediate (137) to give low yields of rearrangement products.

Reaction of 4-bromo-1,1-diphenylcyclohexane (138) with tributyltin hydride generates the radical species (139) which is converted to the boat conformer (140) then subsequently rearranges via the spiro-intermediate (141) to give cis and trans-1-phenyl-4-phenylcyclohexane (142) (Scheme 69).
This reaction has also been observed for 4-bromo-methyl-1,1-diphenylcyclohexane (143). Generation of the alkyl radical (144) and subsequent rearrangement must, in this case, involve a 6-membered spiro-intermediate (145), i.e. a 1,5 migration of the phenyl group (Scheme 70).

Further examples of rearrangement via a 6-membered spiro-intermediate have been observed. 1,5 Migration of a phenyl group from carbon to oxygen was observed on the electrolysis of o-benzoylbenzoic acid in methanol, containing sodium methoxide, at 20-30°C. This generated the benzoyloxy radical (146) which rearranged, via a
CO₂H

\[ \text{CO}_2^+ \]  
\[ \text{H}^+ \]

(146)

\[ \text{CO}_2 \]  
\[ \text{Ph} \]

(147)

\[ \text{93°C} \]
\[ \text{CO}_2 \]

(149)

\[ \text{CO}_2 \]  
\[ \text{Ph} \]

(148)

\[ \text{CO}_2 \]  
\[ \text{Ph} \]

Scheme 71
6-membered spiro-intermediate (147), to generate the acyl radical (148) from which the product is derived\(^{98}\) (Scheme 71). Proof of the position of attack of the radical to generate this intermediate is established by the isolation of \(p\)-substituted products from \(o\)-(\(p\)-substituted benzoyl) benzoic acids. However, if the reactions are carried out in a methanol/pyridine mixture at higher temperatures (93 °C) there is decarboxylation of the benzoyloxy radical (146) and the products are derived from the phenyl radical\(^ {98}\) (149) (Scheme 71).

This type of rearrangement has also been observed for the 1,5 migration of a phenyl group from a carbon to a silicon atom.\(^ {99}\) Generation of the silyl radical (151) from the dimethylsilane (150) results in rearrangement taking place, via the spirohexadienyl radical (152), to the alkyl radical (153) (Scheme 72).

\[
\begin{align*}
\text{PhCH}_2(CH_2)_3\text{Si-Me}_2 & \xrightarrow{\text{RO}^-} \text{PhCH}_2(CH_2)_3\text{Si-Me}_2 \\
\text{(150)} & \quad \text{(151)} \\
\end{align*}
\]

Scheme 72

\[
\begin{align*}
\text{Ph-Si(Me)}_2(CH_2)_3\text{CH}_2 \quad \text{Ph-Si(Me)}_2(CH_2)_3\text{CH}_3
\end{align*}
\]

(152)  
(153)
Examples are also known of 1,5-migration of the phenyl group from an oxygen to an oxygen atom and, in one case, from a sulphur atom to an oxygen atom. Cleavage of the peroxide of 2-phenoxybenzoic acid generates the benzoyloxy radical (154) which rearranges to give the phenoxy radical (155) and hence phenyl salicylate as the major product, only 1% decarbonylation taking place\(^{100}\) (Scheme 73).

![Scheme 73](image-url)
In a similar rearrangement the persulphate oxidation\textsuperscript{101} of o-phenoxybenzoic acid generates the radical species (156) which subsequently rearranges via the spiro-intermediate to the phenoxy radical (157) from which dimeric products were isolated (Scheme 74).

![Diagram of chemical reactions]

Scheme 74

In an analogous reaction the persulphate oxidation of o-thiophenoxybenzoic acid follows the same course, the thiophenoxyl radical (158) generated after the rearrangement giving the dimeric product\textsuperscript{102} (Scheme 75).
Scheme 75
A. Introduction

The major part of the work reported in this thesis is concerned with systems of the general type (159) where \( X \) and \( Y \) are a variety of heteroatoms. Once generated, the radical species \( X^\cdot \) could form products by a number of different routes, one such route being direct cyclisation of the radical onto the adjacent aryl ring to give products with the general structure (160) (Scheme 76). However, by comparison with systems examined in the introduction, it can be seen that these radical species have the potential to form a spiro-dienyl intermediate such as (161). Once generated, this intermediate has the potential to rearrange as outlined in Scheme 76.

\[ \begin{align*}
(159) & \quad X,Y = \text{CH}_2\text{NH}, S, O \\
\text{R} & = H, Me \\
(160) & \quad X = \text{aryl ring}, Y = \text{aryl ring} \\
(161) & \quad \text{spiro-dienyl intermediate}
\end{align*} \]

Scheme 76
There is precedent, from work carried out on nitrenes, for rearrangement via a spiro-intermediate occurring in such systems. Cadogan and co-workers\textsuperscript{103,104} found that on deoxygenation of 4-methylphenyl 2-nitrophenyl sulphide (162) with triethylphosphite the major product of the reaction was 3-methylphenothiazine (165). The reaction is believed to involve initial formation of the nitrene (163) followed by generation of the spirodiene intermediate (164). Rearrangement by a 1,2-sigmatropic shift then hydrogen transfer would give 3-methylphenothiazine (165) (Scheme 77).
Messer and Farge\textsuperscript{105} observed the same rearrangement during a study of the synthesis of phenothiazines via thermal or photochemical decomposition of azides.

A further example of rearrangement via a spirodiene intermediate was reported by Kwok and Pranc.\textsuperscript{106} Generation of the nitrene (166) gave as the major product 2,4-dimethoxyacridone. The mechanism of formation of this product is outlined in Scheme 78, the nitrene initially generated forming a spirodiene intermediate. Cleavage of the carbon-carbon bond of this intermediate, followed by ring closure and a hydrogen shift, would result in the formation of the observed product.

![Scheme 78](image-url)
Many more such rearrangement reaction of nitrenes via a spirodiene intermediate have been observed.\textsuperscript{107}

This work has been extended by Hickson\textsuperscript{108} to systems where the reactive species are radicals rather than nitrenes. All the work carried out by Hickson involved the generation of aminyl radicals with a variety of bridging groups, i.e. 159, \( X = \text{NH} \cdot, Y = \text{O}, \text{S}, \text{NH}, \text{CH}_2 \). It was found that on generating the aminyl radical (167) the major product of the pyrolysis, though isolated only in a low yield, was the phenol (169). The fact that both aryl groups are now attached to the nitrogen indicates that rearrangement is taking place via the spiro-intermediate (168) as outlined in Scheme 79.

\begin{center}
\includegraphics[width=\textwidth]{scheme79.png}
\end{center}

Scheme 79
Similarly, on generation of the aminyl radical (170) the major cyclisation product was 3-methylphenothiazine (171) contaminated with a small amount of 2-methylphenothiazine (172). The formation of the 3-methyl isomer as the major product indicates that rearrangement must be taking place, presumably via a spiro-intermediate (Scheme 80).

\[
\text{(170)} \xrightarrow{\text{H}} \text{(171) major} + \text{(172) minor}
\]

Scheme 80

Further examples of the reactions of these systems involved generation of the aminyl radicals (173) and (174), the major products being acridan and phenazine respectively (Scheme 81).
However, in both cases it is not possible to determine if the formation of the major product involves a spiro-intermediate or simply direct cyclisation of the generated radical. Thus, during the course of the work detailed in this thesis both these systems have been re-examined in more detail to determine the extent of involvement of a spirodiényl intermediate in the reaction mechanism.

Scheme 81

(173) \( Y = \text{CH}_2 \)
(174) \( Y = \text{NH} \)
B. The Generation and Cyclisation of 2-(Arylamino)phenylaminyl Radicals

During the work carried out by Hickson the system shown in Scheme 82 was studied. Generation of the aminyl radical led to the formation of phenazine (175) as the major product. Some dihydrophenazine (176) was also detected, although the dihydro compound is known to be readily oxidised to phenazine in the presence of air.

The formation of these products could occur by direct cyclisation of the aminyl radical on the adjacent phenyl ring. However, it is also possible that the mechanism of formation of these compounds involves a spirodienyl intermediate, although for the system outlined in Scheme 82 it is not possible to tell if this is the case. In order to determine if the reaction mechanism involves such an intermediate it would be
necessary to generate a $^{15}$N labelled aminyl radical with a substituent in the mono-substituted phenyl ring, such as (177).

![Diagram](image)

Analysis of the products obtained on generation of (177) by $^{15}$N n.m.r. spectroscopy should determine if the spirodienyl intermediate (178) is involved in the reaction mechanism. Therefore, the system initially studied by Hickson was re-examined and the reaction mechanism further investigated.

The aminyl radicals to be studied were generated from the appropriate N-allyl derivatives (182) and (183). 2-Aminodiphenylamine (180) was commercially available but it was necessary to make the corresponding $p$-substituted amine (181). It was also necessary to prepare the appropriate $^{15}$N labelled compounds (184)-(186). The following sequence of reactions was used for the preparation of the required compounds (Scheme 83).
2-Nitro-4'-methylformanilide (179) was prepared, in 57% yield, by the reaction of 2-nitrochlorobenzene with the anion of 4-methylformanilide as outlined in Scheme 84. The anion was generated by the addition of the formanilide to a molten sodium/toluene mixture. This method was originally used to prepare 4-nitrodiphenyl-amine derivatives but proved to be the method of choice to the required compound (179) since it could be adapted to allow the introduction of a $^{15}$N label on the
bridging NH group. More conventional routes\textsuperscript{110,111} to these compounds required high temperatures, extended reaction times and/or sealed tube conditions which were not amenable to the introduction of the required \textsuperscript{15}N label.

![Chemical reaction equation]

Scheme 84

The corresponding \textsuperscript{[15}N\textsuperscript{]} labelled compound (184) was prepared in a similar reaction, the required labelled formanilide being prepared by the sequence outlined in Scheme 85. The \textsuperscript{15}N label was derived from \textsuperscript{[15}N\textsuperscript{]} ammonium nitrate containing 5.6\% excess of \textsuperscript{15}N (i.e. \textit{ca} 15 times natural abundance). This label was introduced by the
reaction of p-toluoyl chloride with $^{15}$N ammonium nitrate to generate $^{15}$N-p-toluamide. A Hofmann reaction on the toluamide converted it to the corresponding $^{15}$N-p-toluidine from which the required $^{15}$N-4-methylformanilide was prepared.

Scheme 85

The $^{15}$N labelled formanilide was then used to carry out the reaction shown in Scheme 84, although on the smaller scale the reaction was more difficult to control, only a low yield of product being obtained.

The required amines (181) and (185) were prepared by reduction of the nitro-compounds using sodium borohydride and a palladium-charcoal catalyst in a methanol/water mixture. In the preparation of the unlabelled compound problems were encountered due to the insolubility of the starting material, these problems being the cause of the low yield (30%) of product obtained. However, since the reaction of the labelled compound was carried out on a smaller scale these problems were reduced and a considerably higher yield of product was obtained (50%).
Finally, the N-allyl compounds (182), (183) and (186) were readily prepared in 40-50% yield by the reaction of an excess of the appropriate amine (180), (181) or (185) with allyl bromide in dimethylformamide containing potassium carbonate. The proportions of the reactants were optimised to minimise the formation of the N,N-diallyl derivative, the small amount of this compound obtained being separated by column chromatography.

Pyrolysis of the N-allyl compound (182) at 750°C (10⁻³ Torr) gave a mixture of products which could be separated by column chromatography on alumina (Scheme 86). The major product of the pyrolysis was the air sensitive dihydrophenazine (187). This was always accompanied by some phenazine (188) formed either by thermal dehydrogenation or aerial oxidation on work-up. The analysis of the pyrolysate was therefore simplified by allowing the aerial oxidation of the dihydro compound, this taking 2-3 h. at room temperature. The phenazine isolated after chromatography was identical to an authentic sample. A small amount of the amine (189) was also separated and identified.

The third product of the pyrolysis was isolated in only 8% yield and proved more difficult to characterise. The ¹H n.m.r. spectrum showed the presence of seven aromatic signals and additional signals at δH 10.84 (1H)
and δH 5.16 (2H). The $^{13}$C n.m.r. spectrum also showed the presence of seven methine signals, the remaining five carbon atoms of the arylaminyl radical appearing as quaternary signals. This data, together with the molecular ion peak at m/z 182 in the mass spectrum, is consistent with the aminocarbazole structure (190).
The position of the amino substituent was confirmed by both melting point and $^{13}$C n.m.r. spectral data. Literature melting points of the aminocarbazole isomers indicate that the isolated product could be either the 1- or 4-amino isomers (Table 1).

Table 1  Comparison of the observed and Lit. m.p.'s for aminocarbazole isomers

<table>
<thead>
<tr>
<th>Observed m.p.</th>
<th>Lit. m.p.:</th>
<th>1-amino</th>
<th>193°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lit m.p.</td>
<td>1-amino</td>
<td>187-189°C</td>
<td></td>
</tr>
<tr>
<td>2-amino</td>
<td>116</td>
<td>238°C</td>
<td></td>
</tr>
<tr>
<td>3-amino</td>
<td>117</td>
<td>246-248°C (decomp)</td>
<td></td>
</tr>
<tr>
<td>4-amino</td>
<td>118</td>
<td>188-192°C</td>
<td></td>
</tr>
</tbody>
</table>

However, by calculation of the $^{13}$C n.m.r. spectrum using the additivity effect of the amino group, the isomers can be clearly distinguished (Table 2).
Table 2

<table>
<thead>
<tr>
<th>1-</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>C1a</th>
<th>C4a</th>
<th>C5a</th>
<th>C8a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbazole</td>
<td>110.99</td>
<td>125.54</td>
<td>118.54</td>
<td>120.17</td>
<td>120.17</td>
<td>125.54</td>
<td>110.99</td>
<td>139.81</td>
<td>122.51</td>
<td>122.51</td>
<td>139.81</td>
<td></td>
</tr>
<tr>
<td>1-Aminocarbazole (observed)</td>
<td>113.39</td>
<td>109.34e</td>
<td>119.59c</td>
<td>108.35c</td>
<td>119.96</td>
<td>118.10</td>
<td>124.79</td>
<td>110.83d</td>
<td>128.78</td>
<td>123.22</td>
<td>122.71</td>
<td>139.10</td>
</tr>
<tr>
<td>1-Aminocarbazole (calculated)</td>
<td>128.99</td>
<td>112.24</td>
<td>119.44</td>
<td>110.37</td>
<td>120.17</td>
<td>118.54</td>
<td>125.54</td>
<td>110.99</td>
<td>126.51</td>
<td>123.41</td>
<td>122.51</td>
<td>139.81</td>
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<tr>
<td>4-Aminocarbazole (calculated)</td>
<td>101.19</td>
<td>126.44</td>
<td>105.24</td>
<td>138.17</td>
<td>120.17</td>
<td>118.54</td>
<td>125.54</td>
<td>110.99</td>
<td>140.17</td>
<td>109.21</td>
<td>122.51</td>
<td>139.81</td>
</tr>
</tbody>
</table>

a [\textsuperscript{2}H\textsubscript{6}]DMSO solution; b Estimated from the spectrum of carbazole assigned as in reference 121 using the substituent effect of a 1-amino group; c Doublet in \textsuperscript{1}H coupled \textsuperscript{13}C n.m.r. spectrum; d Doublet of doublets in \textsuperscript{1}H coupled \textsuperscript{13}C n.m.r. spectrum as found for carbazole itself; e Assignment may be reversed.
Except in the region of the substituents \([C(1a), C(1)\) and \(C(2)]\) where steric effects are known to reduce the reliability of the method,\textsuperscript{120} the calculated \(^{13}\)C n.m.r. values clearly indicate that the product isolated is the 1-amin6 isomer. The correspondence between the observed and estimated values for this isomer is well within 1 p.p.m., although the absolute assignment may be ambiguous in certain cases (Table 2).

The mechanism proposed for the formation of this compound is outlined in Scheme 87.

\[
\begin{align*}
\text{R} & : \text{H, Me} \\
\text{(190) } R = \text{H}
\end{align*}
\]
The detailed mechanism of this rearrangement to form (190) is not amenable to labelling studies due to the rapid exchange of NH atoms. However, the hydrogen transfer process outlined in Scheme 87 is consistent with results obtained by Hickson$^{108}$ in a related system, the major product in this case being an aminodibenzothiophene.

\[ \text{Me} \]
\[
\begin{array}{c}
\text{NH}_2 \\
\end{array}
\]

The rearrangement mechanism proposed for the formation of these, and related, compounds will be investigated in more detail at a later stage in this work.

Pyrolysis of the substituted N-allyl derivative (183) gave as products the appropriate methyl substituted phenazine (191), after oxidation of the dihydro compound, and the amine (192) (Scheme 88). Attempts to separate these compounds by column chromatography proved unsuccessful, the mixture being separated only after treatment with acetic anhydride to give the N-acetyl compound (193).
An authentic sample of 2-methylphenazine (191) was obtained, for comparison, by the vapour-phase dehydrogenation of its tetrahydro derivative over palladium (0.5%) on alumina at 550°C. Insufficient of the carbazole (194) was obtained for full characterisation, though the location of the methyl group at the 6-position was confirmed by the appearance of the most deshielded aromatic signal in the $^1$H n.m.r. spectrum [H(5)] as a singlet.
In order to determine if a spiro-intermediate was involved in the formation of the products isolated it was necessary to analyse the $^{15}$N n.m.r. spectra of the phenazines (188) and (191) and the diphenylamines (189) and (192). The signals obtained in the $^{15}$N n.m.r. of 2-methylphenazine (191) were assigned by comparison with the chemical shifts of related quinoxalines. These were known by unambiguous synthesis of mono-labelled derivatives, and confirmed by comparison with the $^{13}$C n.m.r. chemical shifts of appropriate anthracenes. The peak assignments for the spectra obtained are shown in Scheme 89.

![Scheme 89](image-url)
Expansion of the peaks for quaternary nitrogen atoms in comparable environments, followed by triangulation, gave a consistent estimate of their relative areas.\(^{61}\) In the present case, the relative areas of the 2-methylphenazine signals at \(\delta N = -59.23\) and \(-61.40\) were 1.03 : 1.00.

The NH and NH\(_2\) signals of the diphenylamines (189) and (192) were identified by two different experiments. A DEPT \(\pi/2\) experiment identified the NH signal, the position of the NH\(_2\) signal being found by a broad band decoupled experiment using chromium tris(acetylacetonate) as relaxation agent. These conditions, unfortunately, produced unreliable values for the relative sizes of the peaks, although the NH signal was generally larger than the NH\(_2\) signal by a factor of 1.5 – 2.0. The peak assignments of the diphenylamines are shown in Scheme 90.

![Chemical structures](image)

Scheme 90

The introduction of a \(\text{p-}\)methyl substituent is known to cause a low frequency shift in the \(^{15}\text{N}\) n.m.r. spectrum of aniline derivatives.\(^{124}\) A DEPT \(\pi/3\) experiment was also
carried out on the labelled derivative (185), this pulse sequence giving equal enhancement to both NH and NH\textsubscript{2} signals. However, only the peak at $\delta$N $-306.86$ was present in the spectrum, this peak corresponding to the labelled NH.

The labelled compound (185) was pyrolysed and the crude pyrolysate left to aerial oxidise before being examined by $^{15}$N n.m.r. spectroscopy. The small amount of labelled carbazole (194) obtained was insoluble in $[^2\text{H}]$chloroform thus could not be analysed under the conditions used. The $^{15}$N n.m.r. spectrum of the mixture showed only four peaks. The peaks observed at $\delta$N $-59.31$ and $-61.57$ were assigned to the labelled phenazine (191), expansion and triangulation indicating that these peaks were in the ratio $1.04 : 1.00$. The peaks at $\delta$N $-306.17$ and $-330.55$ were assigned to the NH and NH\textsubscript{2} of the aminodiphenylamine (192). These peaks were found to be in the ratio ca. $1.5 - 2.7 : 1.00$ but this measurement was very approximate due to the high noise level and low intensity of the NH\textsubscript{2} peak. However, it was obvious that both the NH and NH\textsubscript{2} peaks were labelled.

From the results obtained from the labelling experiment it is possible to determine much more about the mechanism of formation of the isolated products. Scrambling of the $^{15}$N label between both nitrogen atoms of 2-methylphenazine (191) indicates that the spiro-
dienyl intermediate (178) must be involved in the formation of this product (Scheme 91). In addition, since the two sites of 2-methylphenazine are, within experimental error, equally labelled with $^{15}$N (±1%) this product must be formed exclusively via the spiro-intermediate, i.e. there is no competing direct cyclisation of the aminyl radical (177). This is in contrast to the results obtained on the generation of related iminyl radicals$^{61}$ where it was found that direct cyclisation accounted for up to 30% of the reaction pathway.

Additional mechanistic information can also be obtained from the aminodiphenylamine component of the pyrolysate. The incorporation of the label at both sites of the diphenylamine (192) indicates that hydrogen capture by the radical (177) must take place predominantly (if not exclusively) after equilibration via the spiroidienyl (178). This establishes that once the spiro-intermediate is generated it can revert to the ring opened forms (177) and (177') hence setting up the equilibrium shown in Scheme 91.

The results obtained from this labelling experiment do not, however, allow a distinction to be made between the two possible cyclisation mechanisms shown in Scheme 91. Both re-cyclisation of the interconverted aminyl radicals (177) and (177') (route a) and sigmatropic
Scheme 91
migration from the spiro-intermediate itself (route b) would result in scrambling of the $^{15}$N label in 2-methylphenazine. Further work, detailed later in this Discussion Section should help to further clarify this mechanism of cyclisation.
C. The Generation and Cyclisation of 2-Thiophenoxybenzyl and 2-Benzylthiophenoxy Radicals

The radicals generated and studied in the previous section had the general structure (159) where X and Y were both NH. These radical reactions have now been extended to cover systems where the hetero-atoms, X and Y, are different, the following sections examining a number of such systems. The work detailed in this section is concerned with the generation of related benzyl and thiophenoxy radicals i.e. (159) \( X, Y = \text{CH}_2\text{S} \) and their subsequent reactions.

\[
\begin{align*}
\text{(159)} & \\
\text{X, Y = CH}_2\text{S} & \\
\text{R = H, Me} & 
\end{align*}
\]

As in the previous section, it is a possibility that once generated the radical species may form products via a spiro-intermediate. In order to determine if such an intermediate was being invoked it would be necessary to introduce a \( p \)-substituent into the mono-substituted ring. However, in this case, it is also possible that once generated the migration aptitudes of the hetero-atoms from such an intermediate may not be the same. Thus, in order to determine more about the reaction mechanism and migration aptitudes of the hetero-atoms both thiophenoxy
radicals (203) and benzyl radicals (213) were generated and the products in each case identified (Scheme 92).

\[
\begin{align*}
(203) \quad R &= H, Me \\
(201) \quad R &= H \\
(202) \quad R &= Me \\
(204) \quad R &= H, Me \\
(213) \quad R &= H, Me \\
(211) \quad R &= H \\
(212) \quad R &= Me
\end{align*}
\]

Scheme 92

The thiophenoxy radicals (203, R = H, Me) were generated from the appropriate S-allyl derivatives (201) and (202), these being obtained in high yield by the reaction of the thiophenols (199) and (200) with allyl bromide and potassium carbonate in dimethylformamide (Scheme 93).

\[
\begin{align*}
(195) \quad R &= Me \\
(196) \quad R &= H \\
(197) \quad R &= Me \\
(198) \quad R &= H, Me
\end{align*}
\]

Scheme 93
A search of the literature failed to reveal the thiophenols (199) and (200) or any such compounds of similar structure. The synthesis of these compounds was therefore adapted from a method originally used to prepare \textit{m}-thiocresol from \textit{m}-toluidine using potassium ethyl xanthate\textsuperscript{125}, this being extended to \textit{o}-benzyl substituted derivatives. The required 2-benzylaniline (196) was commercially available but it was necessary to prepare the corresponding substituted compound (197). 2-Amino-4'-methylbenzophenone (195) was prepared by Friedel-Crafts reaction\textsuperscript{126} of anthranilic acid, after protection of the amine function with \textit{p}-toluenesulphonyl chloride. Wolff-Kishner reduction\textsuperscript{127} of the benzophenone, using hydrazine hydrate and potassium hydroxide in diethylene glycol gave the substituted aniline in 60\% yield.

Diazotisation of the amines followed by reaction with potassium ethyl xanthate gave the intermediate compound (198). In the preparation of the unsubstituted compound (199) this intermediate was hydrolysed to the thiol using potassium hydroxide. However, this gave the required product in only 5\% yield, and indeed it has been reported that alkaline hydrolysis of hindered xanthates, such as those being generated here, is not very satisfactory, low yields being obtained due to oxidation or incomplete reaction.\textsuperscript{128} It has also been reported that much better yields of 65-90\% can be obtained by reduction of the xanthate with lithium aluminium hydride.\textsuperscript{128,129} This reduction was attempted for the substituted compound (200),
the required product being obtained although only in 15% yield, the reaction conditions not being optimised.

The mass spectra of the S-allyl derivatives (201) and (202) show that the major fragmentation pathway involves loss of the allyl group to give a peak at M-41. Subsequent breakdown involves loss of hydrogen sulphide to give a cluster of peaks at m/z 165-167 and m/z 178-180 corresponding to intermediates such as (205) and (206) (Scheme 94).

\[
\begin{align*}
\text{Scheme 94}
\end{align*}
\]

The mass spectra of the thiols (199) and (200) similarly show loss of a sulphur atom followed by cyclisation to give the same intermediates.

The benzyl radicals (213, R = H, Me) to be studied were generated from the appropriate dibenzyl oxalates (211) and (212). The synthesis of these oxalates is outlined in Scheme 95.
The thiophenoxybenzoic acids (207) and (208) were prepared, in 40-50% yield, by the diazotisation of anthranilic acid followed by reaction of the diazonium salt with the appropriate thiophenol. \textsuperscript{130} Lithium aluminium hydride reduction \textsuperscript{131} of the acids generated the required benzyl alcohols (209) and (210) in 60% yield. Finally, reaction of the alcohols with oxalyl chloride in a triethylamine/ether solution gave the required thiophenoxybenzyl oxalates (211) and (212), in 90% and 65% yields respectively. This method of preparing oxalates had previously been used to generate phenoxybenzyl oxalates. \textsuperscript{132,133}

The mass spectra of these oxalates show cleavage of carbon dioxide, to give (213), followed by the loss of two hydrogen atoms and re-aromatisation giving the structures (214) and (215) (Scheme 96).
The mass spectra of these compounds also show a cluster of peaks at m/z 165-167 and m/z 179-181 corresponding to the intermediates (205) and (206) previously observed in the mass spectra of the S-allyl derivatives. The presence of these intermediates indicates that a spiro-intermediate may be involved in the breakdown pattern of the oxalates as outlined in Scheme 96.

Pyrolysis of the S-allyl compound (201) at 750°C (10^{-3} Torr) gave only one major component which was separated from minor components and impurities by dry-flash chromatography. The \(^1\)H n.m.r. spectrum of this component indicates the presence of eight aromatic protons.
together with a signal at δH 3.86 corresponding to a methylene group. The 13C n.m.r. spectrum, however, shows only four methine peaks together with two quaternary signals and a methylene signal at δC 39.02 thus indicating that this component is symmetrical. The 13C n.m.r. spectrum of an authentic sample of thioxanthene, obtained by diborane reduction of commercially available thioxanthone, showed a methylene signal at δC 39.08 together with four methine and two quaternary signals, the chemical shifts of which were identical to the component isolated. The 1H n.m.r. spectrum of the authentic thioxanthene was also identical to the isolated component thus indicating that the major product of this pyrolysis is thioxanthene (216) (Scheme 97). A further product of the pyrolysis, isolated as only a minor component of the base extract, was identified as 2-mercaptodiphenylmethane (199).

\[
\begin{align*}
\text{S} & \quad \text{S} \\
\text{+} & \quad \text{Z;} \\
\text{SH} & \\
\end{align*}
\]

(201) \quad \xrightarrow{\text{pyrolysis}} \quad (216) \text{ 50\%} \quad + \quad (199) \text{ trace}

Scheme 97

It is of interest to note that no rearrangement product analogous to (190), obtained in the previous chapter on
generation of aminyl radicals as outlined in Scheme 87, was detected in the pyrolysate of the thiophenoxy radicals. It was also noted that no products derived from benzyl radicals were isolated or identified in this pyrolysate e.g. (217).

Pyrolysis of the substituted S-allyl derivative (202) gave a mixture of components which were separated by base extraction followed by dry-flash chromatography. The minor component separated from the pyrolysate was identified as 2-mercapto-4'-methylidiphenylmethane (200) (Scheme 98).

The major component was isolated from the pyrolysate, after chromatography, as a white solid. G.c. of this component showed only one major peak while a mass spectrum indicated a molecular ion peak at m/z 212. However, the $^1$H n.m.r. and $^{13}$C n.m.r. spectra of this solid showed there to be two methyl and two methylene peaks indicating that this component is an isomeric mixture. The $^1$H n.m.r. spectrum shows two methyl peaks at $\delta$H 2.32 and 2.34 and a methylene peak at $\delta$H 3.82 while the $^{13}$C n.m.r. spectrum shows two methylene peaks at $\delta$C 39.15 and 38.63 and a methyl peak at $\delta$C 20.80. The methylene peaks observed for this isomeric mixture have a similar chemical shift to those previously observed for the thioxanthene (216), isolated
from the pyrolysis of the unsubstituted compound (201), indicating that this component is most likely an isomeric mixture of methylthioxanthenes.

An authentic sample of 2-methylthioxanthene (221) was prepared for spectral comparison with the isomeric mixture in an attempt to positively identify the isolated compounds. A mixture of 2-(4-methylthiophenoxy)benzoic acid and sulphuric acid was heated at 100°C to give 2-methylthioxanthone\(^{135}\) which was then reduced with diborane in tetrahydrofuran, as before, to give an authentic sample of 2-methylthioxanthene\(^{134}\) (221).

![n.m.r. spectrum of 2-methylthioxanthene](image)

(221)

The \(^1\)H n.m.r. spectrum of this compound has a methylene peak at \(\delta H 3.85\) and a methyl peak at \(\delta H 2.37\) consistent with those observed for the isolated component but not allowing positive assignment due to the close proximity of the peaks. The \(^{13}\)C n.m.r. spectrum of the authentic sample however shows a methylene peak at \(\delta C 39.08\), which is consistent with the value observed at \(\delta C 39.15\) for the isolated mixture, and a methyl peak at \(\delta C 20.78\), also consistent with the observed value and indicating that one component of the isolated isomeric mixture is 2-methylthioxanthene. However, it still
remains for the position of the methyl group in the remaining isomer to be identified. Identification of this isomer by preparation of further authentic thioxanthenes by the method previously outlined was not possible, a mixture of isomers being expected which would most likely be difficult to separate.

Thus, the position of this methyl group was identified, using the chemical shift of the methylene signal, by comparison with the effect of introducing a methyl group on the methylene chemical shift in dihydroanthracenes and related compounds. The $^{13}$C n.m.r. spectrum of dihydroanthracene (218) shows a signal for the methylene carbon at δC 36.11. The introduction of a methyl group in the 2-position of dihydroanthracene (219) results in two methylene signals being observed at δC 36.08 and 35.67, the effect of this methyl group on the methylene signal chemical shift depends on the proximity to this group. The methylene signal which is meta to the substituent (36.08) is not significantly shifted while the signal para to the substituent (35.67) is shifted to a more shielded position by 0.54 p.p.m. The assignment of these methylene signals was confirmed by the effect of irradiation at the 1-position of 2-methylidihydroanthracene. Using this information the chemical shift of the methylene signal in 2-methylthioxanthene (221) and 3-methylthioxanthene (222) could be calculated.
The expected chemical shift of the methylene signal in 2-methylthioxanthene (221) at δC 39.05 is in agreement with the observed value at δC 39.15, thus confirming both the presence of this isomer in the mixture and the reliability of the method in this series.

The calculated chemical shift of the methylene carbon of 3-methylthioxanthene (222) at δC 38.55 is in very good agreement with the observed value for the as yet unidentified isomer at δC 35.63. The expected chemical shifts of the methylene signal in the 1-methyl and 4-methylthioxanthene, calculated from the chemical shifts in 1-methyldihydroanthracene (220), would be δC 36.34 and δC 39.24 respectively. Clearly, the chemical shift for the 3-methylisomer is in much closer agreement with the observed spectral data than either the 1-methyl or 4-methyl
isomers, thus the isomeric mixture isolated from the pyrolysate is a mixture of 2-methylthioxanthene (221) and 3-methylthioxanthene (222) (Scheme 98). By expanding and accurately integrating the two methyl peaks observed in the $^1$H n.m.r. spectrum, the ratio of the two isomers was found to be 1.00:1.02 i.e. within experimental error 1:1.

![Scheme 98](image)

The presence of the 2- and 3-methyl isomers were confirmed by comparison of the chemical shifts observed for the methine signals in the $^{13}$C n.m.r. of the mixture with the calculated chemical shifts expected for each isomer. The calculated shift values were obtained from the $^{13}$C n.m.r. spectrum of the parent thioxanthene and the additivity effects of introducing a methyl substituent to benzene$^{119}$ (Table 3). For both isomers the correspondence between the estimated and calculated values is well within 1 p.p.m. The chemical shifts for the quaternary signals are not included in Table 3 as these could not be unambiguously assigned due to their close proximity.
<table>
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<th>C2</th>
<th>C3</th>
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<tr>
<td>2-Methylthioxanthene (observed) (^{b})</td>
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<tr>
<td>3-Methylthioxanthene (calculated) (^{a})</td>
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<td>3-Methylthioxanthene (observed) (^{b})</td>
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</table>

\(^{a}\) Estimated from the spectrum of thioxanthene, assigned as in reference 137, using the substituent effect of the methyl group; \(^{b}\) All CDCl\(_3\) solutions; \(^{c}\) Quaternary signal chemical shifts could not be unambiguously assigned.
Pyrolysis of the benzyl oxalate (211) at 750°C (10⁻³ Torr) gave a mixture of components which were separated, after base extraction, by dry-flash chromatography. The major component isolated from the pyrolysate again showed a methylene peak at δH 3.90 and eight aromatic protons in the ¹H n.m.r. spectrum and four methine signals, two quaternary signals and a methylene peak at δC 39.11 in the ¹³C n.m.r. spectrum. This component was identified, by comparison with the authentic sample, as thioxanthene (216) (Scheme 99). The minor component isolated after chromatography was identified as 2-thiophenoxybenzyl alcohol (209). The formation of this compound occurs by competitive breakdown of the oxalate (211) to generate benzyloxy radicals, these species subsequently abstracting a hydrogen atom to give the benzyl alcohol (209) (Scheme 99). This breakdown occurs to only a small extent thus accounting for the alcohol being isolated as only a minor product. No thiol components were isolated or identified in this pyrolysate.

![Scheme 99](image-url)
Pyrolysis of the substituted benzyl oxalate (212) gave one major and one minor component which were again separated by dry-flash chromatography. The minor component isolated from the pyrolysate was identified as 2-(4-methylthiophenoxy)benzyl alcohol (210) by comparison with an authentic sample. The major component was found to have only one major peak when examined by g.c. but the presence of two methyl and methylene peaks, in the $^1$H n.m.r. and $^{13}$C n.m.r. respectively, indicated that an isomeric mixture had again been obtained. Comparison of the chemical shifts of these peaks with those obtained for the isomeric mixture isolated on pyrolysis of the $S$-allyl derivative (202) indicated that the major product obtained from pyrolysis of the oxalate (212) was again an isomeric mixture of 2-methylthioxanthene (221) and 3-methylthioxanthene (222) (Scheme 100). The ratio of the two isomers, determined by expanding and accurately integrating the methyl peaks, was found to be 1:1.02 i.e. within experimental error 1:1.
On generation of both the thiophenoxyland benzyl radicals an isomeric mixture of 2-methyl and 3-methylthioxanthene was isolated. Since direct cyclisation of the thiophenoxy radical (203) would result in the formation of only 3-methylthioxanthene (222), the presence of the 2-methyl isomer indicates that a spirodienyl intermediate such as (204) must be involved in the reaction mechanism. This is also indicated by the isolation of the 3-methyl isomer on generation of the benzyl radical (213) (Scheme 101). However, what is not clear is the mechanism of formation of products from this spiro-intermediate. Thus, the results obtained from these pyrolyses can be explained in terms of setting up an equilibrium between the thiophenoxy radical (203) and the benzyl radical (213) as shown in Scheme 101, the isolated products being obtained by subsequent cyclisation of these species i.e. Route a.
(202) → (203) \[\text{route a}\] \(\text{-H}^+\) → (222)

(204) \[\text{route b}\] \(\text{-H}^+\)

(212) → (213) \[\text{route a}\] \(\text{-H}^+\) → (221)

Scheme 101
However, it is possible that the products obtained may be formed directly from the spiro-intermediate by sigmatropic migration i.e. Route b rather than the intermediate re-opening and subsequently cyclising. Although both these mechanisms would result in the same product mixture, at this stage, the results obtained do not allow a distinction to be made between the two possible cyclisation methods, these possible reaction mechanisms being investigated further at a later stage in this work.

However, on looking at the ratio of the 2-methyl and 3-methyl isomers generated it is found that these products are formed in a 1:1 ratio from both the thiophenoxyl and benzyl radicals. This indicates that direct cyclisation of these radicals is not competing with the formation of the spiro-intermediate i.e. the cyclisation products are formed exclusively via the spiro-radical (204). In addition, the migration aptitudes of both the benzyl and thiophenoxyl radicals from this intermediate must be the same to result in a 1:1 ratio of isomeric products.
D. The Generation and Cyclisation of 2-Benzylaminyl Radicals

The reactions studied in this section are again concerned with systems such as (159), where X and Y are different hetero-atoms. In this case, the study of these reactions involved attempting to generate both aminyl and benzyl radicals i.e. $X, Y = \text{NH, CH}_2$.

$$\begin{align*}
\text{R} \\
\text{H}
\end{align*}$$

\(X, Y = \text{NH, CH}_2\)

Preliminary work on this system previously carried out by Hickson\textsuperscript{108} generated the aminyl radical (223) by pyrolysis of the appropriate N-allyl derivative (Scheme 102). It was found that the major product of this pyrolysis was the acridan (224).

$$\begin{align*}
\text{H} & \text{H} \\
\text{H} & \text{H}
\end{align*}$$

\(159\)

$$\text{R} = \text{H, Me}$$

Since the acridan is formed by direct cyclisation of the generated radical it is possible that a spirodienyl intermediate is involved in product formation. If this is the case then it would be of interest to obtain
information about the migratory aptitudes of the different hetero-atoms from such an intermediate. In order to obtain such information it was again necessary to introduce a $p$-substituent into the mono-substituted benzene ring, in this case a methyl group. Identification of the products obtained on generation of the aminyl radical (226) and the benzyl radical (234) should then provide information on the reaction mechanism of these species (Scheme 103).

![Scheme 103](image)

The aminyl radical (226) was again generated from the N-allyl derivative (225). 2-Amino-4'-'methyldiphenylamine (197), prepared by Wolff-Kishner reduction of the appropriate benzophenone as outlined in the previous section, was reacted with allyl bromide to give the aminyl radical precursor (225) in 50% yield (Scheme 104).
Having prepared the precursor to the aminyl radical (226) the next step was to prepare the precursor to the benzyl radical (234). Benzyl radicals have been generated by the pyrolysis of phenyl ethers. However, by comparison with work previously reported in the literature it is likely that pyrolysis of the phenyl ether (228) would result in the loss of phenol, the required radicals not being generated.

A possible alternative method of generating the benzyl radicals would be from the sulphone ((229). In this case though, it was anticipated that there would be difficulties in the synthetic route to these compounds.
In addition, large bulky sulphones can be rather involatile, decomposition occurring in the inlet system. As outlined in the introduction, the best method of generating benzyl radicals is from the appropriate dibenzyl oxalate. For this system, however, it was anticipated that problems would be encountered with the synthesis since it has been found that these compounds could not be prepared when a nitrogen atom is present, a thick gum being obtained. However, since no other route to the benzyl radical (234) was feasible, the preparation of the dibenzyl oxalate (233) was attempted via the sequence of reactions outlined in Scheme 105.

Scheme 105

The substituted anthranilic acid (230) was prepared, in high yield, by the reaction of o-chlorobenzoic acid with p-toluidine. In an attempt to obtain the benzyl alcohol (232), the methyl ester (231) was first prepared
by reaction of the acid (230) with methanol and concentrated sulphuric acid. Subsequent lithium aluminium hydride reduction\(^{139}\) of the ester to the required benzyl alcohol was, however, unsuccessful, a black tar being obtained. A search of the literature revealed that carboxylic acids had previously been reduced to benzyl alcohols using 1M diborane in tetrahydrofuran.\(^{141}\) This method was applied to the system outlined here and the required benzyl alcohol (232) was isolated in 40% yield. The final step of the sequence, reaction of the alcohol with oxalyl chloride, gave, however, a brown sticky oil on work-up, the required product not being generated even on successive attempts. Thus, the benzyl radical (234) could not be generated in the gas phase since a suitable radical precursor was not available. The aminyl radical precursor (225) was however pyrolysed.

Pyrolysis of the N-allyl derivative at 750°C gave a dark pyrolysate which was dissolved in deuteriochloroform. The components of this pyrolysate were not separated but were examined and identified by n.m.r. spectroscopy. G.c. of the pyrolysate showed one major peak which was found, by g.c.m.s., to have m/z 193, consistent with this component being a methyl-substituted acridan. The \(^{13}\)C n.m.r. spectrum, however, showed there to be two methyl and methylene peaks indicating that the major product of the pyrolysis is an isomeric mixture of methylacridans. The \(^1\)H n.m.r. spectrum provided no information useful for
identification of the isomers, the two methyl and the
two methylene peaks being co- incidental.

For n.m.r. spectral comparison an authentic sample
of 2-methylacridan (235) was prepared.\textsuperscript{142} N-Phenyl-
(4'-methyl)anthranilic acid (230) was cyclised to give
2-methylacridone (234) by heating with concentrated
sulphuric acid. The acridone was then heated under
reflux with amyl alcohol and sodium to give authentic
2-methylacridan (235) in 30\% yield\textsuperscript{143} (Scheme 106).

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {\includegraphics[scale=0.5]{scheme106.png}};
  \node at (-1.5,0.5) {\textbf{Scheme 106}};
\end{tikzpicture}
\end{center}

The $^{13}$C n.m.r. spectrum of this compound shows a
methyl peak at $\delta$C 21.53 and a methylene peak at $\delta$C 31.24.
The $^{15}$N n.m.r. spectrum of this compound shows an NH
signal at $\delta$N -289.91. These chemical shifts are
consistent with those observed at $\delta$C 21.53 and $\delta$C 31.23
in the $^{13}$C n.m.r. spectrum of the pyrolysate, attributed
to the methyl and methylene peaks respectively. The
$^{15}$N n.m.r. spectrum is also consistent with the peak
observed at $\delta$N -288.95 in the $^{15}$N n.m.r. spectrum of the
pyrolysate thus confirming the presence of 2-methylacridan
(235) as the major isomer present in the pyrolysate.

The remaining isomer present in the pyrolysate could
not be identified by preparation of an authentic sample by the method previously outlined since an isomeric mixture of products would be expected, problems with the separation of these isomers being anticipated. Thus, the remaining isomer was identified, by $^{13}$C n.m.r. spectroscopy, using the effect of a methyl group on the chemical shift of the methylene signal, $^{136}$ as previously outlined in the preceding section for the dihydroantracenes and the thioxanthene systems, and the position of the methylene signal in 2-methylacridan. The chemical shifts of the methylene signal expected for the remaining isomers are shown in Table 4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C9</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methyl (observed)</td>
<td>31.24</td>
</tr>
<tr>
<td>unsubstituted</td>
<td>31.28</td>
</tr>
<tr>
<td>1-methyl</td>
<td>29.54</td>
</tr>
<tr>
<td>3-methyl</td>
<td>30.83</td>
</tr>
<tr>
<td>4-methyl</td>
<td>31.34</td>
</tr>
</tbody>
</table>

The remaining methylene peak observed in the $^{13}$C n.m.r. spectrum of the pyrolysate at δC 30.83 can be assigned only to the 3-methyl isomer, the 1- and 4-methyl isomers having the wrong chemical shift. The peak
observed at δN -290.08 in the $^{15}$N n.m.r. spectrum of the pyrolysate must therefore be assigned to the 3-methyl isomer. Thus, the major product obtained on generation of the aminyl radical (226) is an isomeric mixture of 2-methylacridan (235) and 3-methylacridan (236) (Scheme 107). From the $^{13}$C n.m.r. and $^{15}$N n.m.r. spectra of the pyrolysate the ratio of 2-methylacridan : 3-methylacridan was found to be 2:1.

\[
\begin{array}{c}
\text{(266)} \\
\text{N}^* \\
\text{Me} \\
\end{array} \quad \xrightarrow{\text{Me}} \quad \begin{array}{c}
\text{(235)} \\
\text{N} \\
\text{Me} \\
\end{array} \quad \text{Me} \\
\begin{array}{c}
\text{(236)} \\
\text{N} \\
\text{Me} \\
\end{array}
\]

Scheme 107

It is of interest to note that the positions of the NH signals in the $^{15}$N n.m.r. spectrum of the 2- and 3-methylacridan isomers are reversed to that observed in the case of the phenazines dealt with previously.
For the acridans, the NH signal para to the methyl group (235) is shifted to a more shielded position by 1.4 p.p.m., the signal meta to the methyl group remaining virtually unchanged (236). In contrast, for the unsaturated nitrogens of phenazine the signal para to the methyl group is shifted to a more shielded position by only 1.9 p.p.m., while the signal meta to the methyl group is more shielded by 4 p.p.m. The $^{15}\text{N}$ n.m.r. spectrum of the acridans can be compared to the spectra obtained for aniline derivatives. The introduction of a para methyl group into aniline results in the NH signal being shifted to a more shielded position to the extent of 2.6 p.p.m., a meta methyl group causing a similar shift of 0.9 p.p.m.
Although the magnitude of the shift is greater for the aniline derivatives, the effect of introducing a methyl group into the meta and para positions causes a low frequency shift of the NH signal for both the aniline and acridan isomers.

Several smaller methyl peaks were evident in the $^{13}$C n.m.r. spectrum of the pyrolysate but these could not be unambiguously assigned due to the close proximity of the peaks and a lack of authentic samples for spectral comparison. However, from the products identified in the pyrolysate more information can be obtained about the reaction mechanism of these species. The presence of the two isomeric acridans (235) and (236) in the pyrolysate of the substituted radical (226) indicates that the spiro-intermediate (227) must be involved in product formation. In addition, the presence of the rearranged product, 2-methylacridan (235), as the major isomer in the mixture indicates that on generation of the spirodienyl intermediate carbon-carbon migration must be favoured over carbon-nitrogen migration. (Scheme 108).
This appears to be in contrast to work previously reported involving aryliminyl radicals. On generation of the iminyl radical (237) the only product isolated was 7-methylquinoline (239) (Scheme 109). None of the 6-methyl isomer (241) was detected. The formation of (239) as the only product suggests either that this product is formed by direct cyclisation of the generated radical, although the reactions of similar systems (238) have been shown to involve a spiro-intermediate, or that on generation of the spirodiényl (240) carbon-nitrogen migration is favoured over carbon-carbon migration.
In similar systems studied in solution phase, it was also found that on generation of the spiro-intermediates (242) and (243) carbon-nitrogen migration was favoured over carbon-carbon migration in both cases.
From the results obtained from the system studied it is not possible to determine if direct cyclisation of the aminyl radical (226) is competing with the formation of the spiro-intermediate (227). Indeed, it could be the case that carbon-carbon migration occurs exclusively from this intermediate and that the 3-methyl isomer (236) is being formed only by direct cyclisation of the initially generated radical. In order to clarify this situation, the benzyl radical (230) would have to be generated directly by pyrolysis of a suitable radical precursor. Thus, further clarification of this mechanism awaits a reliable gas phase method of generating the required benzyl radical. In addition, it is also not possible to determine if, on formation of the spiro-intermediate, this
species re-opens to generate the radicals (226) and (234) or whether the acridan isomers are obtained by sigmatropic migration of the spirodienyl itself (Scheme 108).
E. The Generation and Rearrangement of 2-Phenoxybenzyl and 2-Benzylphenoxy Radicals

This section again deals with the reactions of systems such as (159), in this case the reactions studied involve the generation of phenoxy and benzyl radicals i.e. 159 $X, Y = CH_2, O$.

![Chemical structure](image)

As in the preceding sections we are interested in determining if the reactions of these species involve a spiro-intermediate such as (250) and thus the migratory aptitudes of the hetero-atoms from such an intermediate (Scheme 110). The phenoxy radicals (249) and the benzyl radicals (257) were generated and the pyrolysis products isolated and identified.
The phenoxy radicals (249, R=H, Me) were generated from the appropriate O-allyl derivatives (247) and (248), this being the best method of generating these species as previously outlined in the introduction. The preparation of these precursors is shown in Scheme 111. The unsubstituted hydroxydiphenylmethane (245) was commercially available but it was necessary to make the corresponding p-substituted derivative (246). Friedel-Crafts reaction\textsuperscript{146} of O-anisic acid and toluene gave the benzophenone (244) which was reduced to the corresponding diphenylmethane (246) by Wolff-Kishner reaction.\textsuperscript{126} The allyl derivatives (247) and (248) were again prepared by reaction of the phenol with allyl bromide in dimethylformamide to give the required products in 80% yield.

The mass spectra of these allyl derivatives show the major fragmentation pathway to involve loss of an allyl group to give a peak at M-41. Subsequent loss of water gives a cluster of peaks at m/z 165-163 and m/z 183-181 to give the structures shown in Scheme 112.
The mass spectral breakdown pattern of these compounds is identical to that previously observed for the analogous S-allyl compounds (c.f. Scheme 94).

The required benzyl radicals (257, R=H, Me) were again generated from the appropriate benzyl oxalates (255) and (256), these compounds being prepared, in 60% yield, by the reaction of the benzyl alcohols (253) and (254) with oxalyl chloride and triethylamine at 0°C (Scheme 113). The benzyl alcohols were themselves obtained by lithium aluminium hydride reduction \(^\text{147}\) of the 2-phenoxybenzoic acids. The unsubstituted acid (251) was commercially available, the \(p\)-substituted compound being prepared. \(^\text{148}\) Reaction of the potassium salt of \(o\)-chlorobenzoic acid with \(p\)-cresol in a sodium methoxide solution, with copper bronze as catalyst, gave the required 2-(4-methylphenoxy) benzoic acid (252) in 50% yield.
The unsubstituted allyl derivative (247) was pyrolysed at 750°C and the pyrolysate extracted with base to separate any phenolic components. The products isolated in the base extract were separated by column chromatography on alumina. Two major components were separated, the first component isolated being identified, by g.c. and g.c.m.s. comparison with an authentic sample, as 2-hydroxydiphenylmethane (245) (Scheme 114). The n.m.r. spectra obtained for this component were also identical to those of an authentic sample.
The second major component was more difficult to identify. The $^1$H n.m.r. spectrum shows two $^1$H doublets, with long range coupling, at $\delta$H 7.80 and 7.57, a 4$^1$H multiplet between $\delta$H 7.26 and 7.55 and a further $^1$H doublet with long range coupling ($^3J = 7.1$Hz, $^4J = 0.7$Hz) in a more shielded environment at $\delta$H 6.78. The spectrum also shows a methylene peak at $\delta$H 3.84 and a broad singlet at $\delta$H 5.25 attributed to an OH group. The $^{13}$C n.m.r. spectrum confirms the presence of seven methine signals, the remaining five carbon atoms of the phenoxy radical appearing as quaternary signals. A methylene signal is also evident in the $^{13}$C n.m.r. spectrum. A molecular ion peak is observed in the mass spectrum of m/z 182 (100%) which, together with the n.m.r. data, is consistent with component being the hydroxyfluorene (258). The mechanism of formation of this component will be dealt with at a later stage in this section.
The position of the hydroxyl-substituent was determined by both melting point and $^{13}$C n.m.r. data. Literature melting-point data indicated that the isolated product could only be the 1-hydroxy isomer (Table 5).

Table 5

<table>
<thead>
<tr>
<th>Isomers</th>
<th>Observed m.p.</th>
<th>Lit. m.p.'s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Hydroxy</td>
<td>118-120°C</td>
<td>119-120°C</td>
</tr>
<tr>
<td>2-Hydroxy</td>
<td></td>
<td>169-171°C</td>
</tr>
<tr>
<td>3-Hydroxy</td>
<td></td>
<td>136-137°C</td>
</tr>
<tr>
<td>4-Hydroxy</td>
<td></td>
<td>109-110°C</td>
</tr>
</tbody>
</table>

The position of the hydroxyl group was confirmed by calculation of the $^{13}$C n.m.r. spectrum of this isomer using the additivity effect of the hydroxyl group, initially determined for benzene, and the $^{13}$C n.m.r. spectrum for fluorene (Table 6). The correspondence between the observed and estimated values for this isomer are well within 1 p.p.m., except for the quaternary signal C1a, adjacent to the hydroxy substituent, where the reliability of this method can be reduced by steric effects. In the case of the signals for C6 and C7
Table 6

Observed and Estimated $^{13}$C n.m.r. Chemical Shifts of 1-Hydroxyfluorene

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>C9</th>
<th>C1a</th>
<th>C4a</th>
<th>C5a</th>
<th>C8a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorene</td>
<td>124.93</td>
<td>126.63</td>
<td>126.63</td>
<td>119.81</td>
<td>119.81</td>
<td>126.63</td>
<td>126.63</td>
<td>124.93</td>
<td>36.82</td>
<td>143.16</td>
<td>141.67</td>
<td>141.67</td>
<td>143.16</td>
</tr>
<tr>
<td>1-Hydroxyfluorene (calculated)</td>
<td>151.83</td>
<td>113.93</td>
<td>128.03</td>
<td>112.51</td>
<td>119.81</td>
<td>126.63</td>
<td>126.63</td>
<td>124.93</td>
<td>-</td>
<td>130.46</td>
<td>143.07</td>
<td>141.67</td>
<td>143.16</td>
</tr>
<tr>
<td>1-Hydroxyfluorene (observed)</td>
<td>152.01</td>
<td>113.41</td>
<td>128.41</td>
<td>112.83</td>
<td>120.06</td>
<td>126.61</td>
<td>126.78</td>
<td>124.93</td>
<td>33.41</td>
<td>128.23</td>
<td>143.79</td>
<td>141.50</td>
<td>142.75</td>
</tr>
</tbody>
</table>

$^a$ Estimated from the spectrum of fluorene assigned as in reference 153 using the substituent effect of a 1-hydroxy group; $^b$ CDCl$_3$ solution; $^c$ Doublet in $^1$H-coupled $^{13}$C n.m.r. spectrum; $^d,e$ Assignments may be reversed.
and the quaternary signals C4a and C8a the absolute assignments may be ambiguous.

The only minor product of the pyrolysis that could be identified was isolated from the neutral fraction of the pyrolysate. The $^1$H n.m.r. spectrum of this component showed eight aromatic protons and a methylene peak at $\delta$H 4.05 while the $^{13}$C n.m.r. spectrum showed only four methine peaks and two quaternary peaks as well as the methylene peak at $\delta$C 27.78. By g.c., g.c./m.s. and spectral comparison with an authentic, this component was identified as the cyclisation product Axanthene (259). This product was isolated in only 4% yield of material which was still impure.

Pyrolysis of the substituted allyl derivative (248), followed by base extraction of pyrolysate, resulted in two major components being isolated from the basic solution after column chromatography on alumina. The $^1$H n.m.r. spectrum of the first component showed eight aromatic protons together with methyl, methylene and OH signals. Both the $^1$H n.m.r. and $^{13}$C n.m.r. spectra were consistent with those of an authentic sample of 2-hydroxy-4'-methyldiphenylmethane (246) thus confirming the presence of this compound in the pyrolysate (Scheme 115).
The $^{13}$C n.m.r. spectrum of the second component isolated after chromatography showed six methine peaks, six quaternary signals and methyl and methylene peaks at $\delta$C 21.35 and 33.00 respectively. G.c. showed there to be only one peak while the mass spectrum showed a molecular ion peak at m/z 196. This is consistent with this compound being 1-hydroxyfluorene, as previously isolated, but with a methyl substituent. However, it is necessary to determine the position of this methyl substituent. The $^1$H n.m.r. spectrum shows a methyl peak at $\delta$H 2.47 and a methylene peak at $\delta$H 3.79. In the aromatic region the spectrum shows a shielded $^1$H doublet with long range coupling ($^3$J = 7.8Hz, $^4$J = 0.8Hz) at $\delta$H 7.75. This doublet was observed for the unsubstituted hydroxyfluorene (258) previously isolated and is attributed to the proton at C2 adjacent to the hydroxyl substituent. The $^1$H n.m.r. spectrum also shows a further doublet at $\delta$H 7.14, a triplet at $\delta$H 7.77, two doublets superimposed at $\delta$H 7.38-7.46 and
a singlet at $\delta H$ 7.59.

The presence of only one singlet in this spectrum indicates that the methyl substituent is in the unsubstituted ring (260), substitution in the ring containing the hydroxyl group at either the 3- or 4-position being expected to show either two singlets or no single peaks respectively. In addition, $^1$H decoupling by irradiation at the doublet observed at $\delta H$ 6.75, attributed to C2, resulted in the triplet collapsing to a doublet, indicating that these two hydrogens are adjacent.

The presence of the singlet in the $^1$H n.m.r. spectrum indicates that the methyl group must be in the 6- or 7-position of the hydroxyfluorene. To determine the exact position of the methyl group the $^{13}$C n.m.r. spectrum must be examined. A comparison of this spectrum with that obtained for the unsubstituted compound (258) indicates that the chemical shifts of the signals attributed to carbons 2-4 remain unchanged, confirming the presence of the substituent in the other ring system. The position of the methyl group was determined by comparison of the observed $^{13}$C n.m.r. spectrum with the spectra calculated
Table 7

Observed and Estimated $^{13}$C n.m.r. Chemical Shifts for 6-Methyl and 7-Methyl 1-hydroxyfluorene

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>C1a</th>
<th>C4a</th>
<th>C5a</th>
<th>C8a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound Isolated from Pyrolysate$^a$</td>
<td>152.03</td>
<td>113.32</td>
<td>128.35</td>
<td>112.73</td>
<td>120.67</td>
<td>136.26</td>
<td>127.77</td>
<td>124.64</td>
<td>143.88</td>
<td>141.68</td>
<td>139.86</td>
<td></td>
</tr>
<tr>
<td>1-Hydroxy-6-methyl fluorene$^b$</td>
<td>152.01</td>
<td>113.41</td>
<td>128.41</td>
<td>112.06</td>
<td>120.76</td>
<td>135.51</td>
<td>127.48</td>
<td>124.83</td>
<td>143.79</td>
<td>141.40</td>
<td>139.85</td>
<td></td>
</tr>
<tr>
<td>1-Hydroxy-7-methyl fluorene$^b$</td>
<td>152.01</td>
<td>113.41</td>
<td>128.41</td>
<td>119.96</td>
<td>127.31</td>
<td>135.68</td>
<td>125.63</td>
<td>128.73</td>
<td>143.79</td>
<td>138.60</td>
<td>142.65</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ CDCl$_3$ solution; $^b$ Estimated from the observed spectrum of 1-hydroxyfluorene, assigned as in Table 6, using the substituent effect of a methyl group
for the 6- and 7-methyl isomers (Table 7). The calculated spectra were obtained using the additivity effect of the methyl group\textsuperscript{119} and the observed assigned spectrum of 1-hydroxyfluorene (see Table 6).

The correspondence between the observed spectrum and the spectra calculated for the 6- and 7-methyl isomers is within 1 p.p.m. for all the methine signals. It is only by comparison of the quaternary signals for C5a and C8a (Table 7) that the isomers can be distinguished, these indicating that the product isolated is 1-hydroxy-6-methylfluorene (261) (Scheme 115). The mechanism of formation of this compound will be examined in detail at the end of this section.

The only minor product identified in the pyrolysate, only 6% of impure material being isolated, was again found in the residue remaining after base extraction. G.c. of this component showed there to be one major peak although a number of smaller peaks were observed for impurities which could not be separated. However, the \textsuperscript{13}C n.m.r. spectrum showed there to be two methyl peaks at \(\delta C 20.90\) and 20.47 and two methylene peaks at \(\delta C 27.77\) and 27.44 indicating that this component was an isomeric mixture of products. The \textsuperscript{1}H n.m.r. also showed two methyl peaks at \(\delta H 2.39\) and 2.36 and a methylene peak at \(\delta H 4.04\). G.c./m.s. shows this component to have \(m/z 196\) which is consistent with this being an isomeric mixture of methylxanthenes.

An authentic sample of 2-methylxanthene (263) was
prepared by Wolff-Kishner reduction\(^{126}\) of 2-methylxanthone (262) (Scheme 116). The xanthone itself was prepared from 2-(4-methylphenoxy)benzoic acid (252), cyclisation occurring when the acid was heated to 100°C with concentrated sulphuric acid.\(^{154}\)

\[
\begin{align*}
\text{(252)} & \xrightarrow{\text{MeSO}_4, 100^\circ C} \text{(262)} \\
\text{(262)} & \xrightarrow{\text{Me}} \text{(263)}
\end{align*}
\]

Scheme 116

The \(^{13}\)C n.m.r. spectrum of the authentic xanthene shows a methylene peak at \(\delta C 27.73\) and a methyl peak at \(\delta C 20.46\). These values are consistent with those observed at \(\delta C 27.77\) and 20.47 in the \(^{13}\)C n.m.r. of the isolated isomeric mixture indicating that one component of this mixture is 2-methylxanthene (263) (Scheme 115). The \(^1\)H n.m.r. spectrum of the authentic 2-methyl isomer shows a methyl peak at \(\delta H 2.31\), this signal being too close to the peaks observed in the \(^1\)H n.m.r. spectrum of the mixture to be unambiguously assigned to either isomer.

The method used for preparing 2-methylxanthene could not be extended to prepare an authentic sample of 3-methylxanthene since an isomeric mixture of the 1- and 3-methyl products would be obtained which would probably be difficult to separate. Instead, the remaining isomer was identified by \(^{13}\)C n.m.r. spectroscopy using the effect
of introducing a methyl group on the chemical shift of xanthene (259) as outlined in previous sections.

Using this effect, 3-methylxanthene (264) would be expected to show a methylene signal at δ27.22 in the $^{13}$C n.m.r. spectrum. This is consistent with the signal observed at δC 27.44 in the $^{13}$C n.m.r. spectrum of the isomeric mixture. The expected values for the 1-methyl isomer, at δC 24.99, and the 4-methyl isomer at δC 27.89 are clearly not consistent with the observed value. Thus, the second component of the isomeric mixture is confirmed as 3-methylxanthene (264) (Scheme 115). The ratio of 2-methylxanthene : 3-methylxanthene for this pyrolysis was found to be 1:1.

The reactions of the unsubstituted benzyl radicals (257, R=H) had previously been studied by Trahanovsky et al.\textsuperscript{155}, these radicals being generated by pyrolysis of the benzyl oxalate (255). The main product of the pyrolysate, although found in only 12% yield, was identified as xanthene, the total yield of products identified from the pyrolysate by Trahanovsky being less than 20%. Thus, in the light of the reactions previously detailed in this section, it was
of interest to look at these reactions again and try to identify the remaining 80% of products.

Pyrolysis of the benzyl oxalate (255) at 750°C gave a mixture of components which were separated by column chromatography on alumina. Only one major product was isolated from the pyrolysate although three minor products were also identified (Scheme 117). The major product of the pyrolysate was identified, by comparison of the $^1$H n.m.r. and $^{13}$C n.m.r. spectra with those previously obtained, as 1-hydroxyfluorene (258) (Scheme 117).

\[
\begin{align*}
\text{(257)} & \quad \xrightarrow{\text{Pyrolysis}} \quad \text{(245)} \quad 5\% \\
\text{(253)} & \quad \text{(258)} \quad 36\% \\
\text{(259)} & \quad 9\%
\end{align*}
\]

Scheme 117

After repeated attempts at purification, the first minor product isolated was still contaminated with minor impurities. However, by comparison of the $^1$H n.m.r. and $^{13}$C n.m.r. spectra of this component with those of an authentic sample this product was identified as the cyclisation product xanthene (259). The second minor
product isolated after chromatography was identified, also by spectral and g.c. comparison with an authentic sample, as 2-hydroxydiphenylmethane (245).

The final pyrolysis product, present in only trace amounts, was identified as 2-phenoxybenzyl alcohol (253). The formation of this compound is due to the competitive breakdown of the oxalate to generate alkoxy radicals, as has previously been outlined, this process occurring to only a small extent. The products isolated and identified in this pyrolysate do, however, account for a 50% yield recovery compared to less than 20% identified by Trahanovsky.

Pyrolysis of the substituted oxalate (256), at 750°C, also gave a mixture of products which were separated by column chromatography on alumina. The major product separated after chromatography was isolated as a brown solid. The $^{13}$C n.m.r. spectrum of this solid showed aromatic and quaternary signals with methyl and methylene peaks at $\delta$C 21.37 and $\delta$C 33.02 respectively. The position of these peaks was consistent, as was the $^1$H n.m.r. spectrum, with this component being 1-hydroxy-6-methylfluorene (261) (Scheme 118). This was confirmed by comparison of the spectra with those obtained for this compound on generation of the phenoxy radical.
The first minor component isolated after chromatography again proved difficult to purify, this component still being contaminated with minor impurities even after repeated attempts at purification. G.c. analysis of this component showed there to be only one major peak. However, $^{13}$C n.m.r. spectroscopy indicated the presence of two methyl and two methylene peaks suggesting that this component was an isomeric mixture of products. The position of the methyl peaks at δC 27.67 and 27.33 and the methylene peaks at δC 20.88 and 20.45 is consistent with this component being an isomeric mixture of 2-methyIxanthene (263) and 3-methyIxanthene (264) as was previously observed. The ratio of the 2-methyl : 3-methyl isomer was found to be 2.5:1 on generation of the benzyl radicals (Scheme 118).

The second minor component isolated was identified
by comparison of its $^{1}H$ n.m.r. and $^{13}C$ n.m.r. spectra with those of an authentic compound. This component was thus identified as 2-hydroxy-4'-methylidiphenylmethane (246). The final component identified in the pyrolysate, present in only trace amounts, was identified as 2-(4-methylphenoxy)benzyl alcohol (254), the formation of this compound again being due to competitive breakdown of the oxalate.

It is of interest to note that the major product isolated on the generation of both the unsubstituted and substituted benzyl radicals is indeed derived by rearrangement from phenoxy radicals, one of the minor products also being derived from these radical species. The products derived from both the phenoxy and benzyl radical pyrolysates indicate that the reaction mechanisms of these species are more complex than those previously encountered. The formation of the hydroxydiphenylmethanes (245) and (246) on generation of the benzyl radicals (257, $R = H, Me$) indicates that a spiro-intermediate such as (250, $R = H, Me$) must be involved in product formation (Scheme 119). The isolation of these compounds also provides evidence that once formed, this intermediate must re-open to generate the phenoxy radicals (249, $R = H, Me$) i.e. rearrangement via the spiro-intermediate (250) must be taking place (Scheme 119).
This is in contrast to the results obtained on generation of the benzyl and thiophenoxy radicals previously studied where no evidence was obtained that the spiro-intermediate was re-opening to generate the localised radical species. However, on examining the products isolated from this pyrolysis there is no evidence to suggest that this intermediate re-opens in the opposite direction to generate the benzyl radical (257, R = H, Me) and so establish the equilibration shown in Scheme 119.

The formation of the minor products, the methylxanthene isomers (263) and (264) provides further evidence that a spiro-intermediate is involved in product formation. However, whether these species are formed directly from the spirodienyl by a sigmatropic migration or from the free radical species still cannot be determined from the experimental evidence. These compounds were isolated with difficulty, in only low yields of products which
could not be completely purified. However, on looking more closely at these products it can be seen that the isomeric ratio is different on generation of the phenoxy radicals than from the benzyl radicals (Scheme 120).

This suggests that equilibration of the radicals via the spiro-intermediate is incomplete. Thus, some other mechanism must be competing with the formation of this intermediate, the most likely explanation being competing direct cyclisation on initial generation of the radical species. In addition, due to this difference in the isomeric ratio there is insufficient evidence to determine any information about the migratory aptitudes of the different hetero-atoms.

However, the xanthenes are only the minor products isolated in the pyrolysates. The major products obtained on generation of both the radical species are derived from hydrogen abstraction reactions of the phenoxy radicals (249, \( R = H, Me \)). No major products are derived from the benzyl radicals (257, \( R = H, Me \)). Thus, the bias of the
equilibrium outlined in Scheme 119 favours the phenoxy radicals, perhaps for thermodynamic reasons although a more likely explanation is that the phenoxy radicals are more reactive. It is clear from the products obtained that these species are very good hydrogen abstractors, the main products being derived from this type of reaction. This is clearly in contrast to the reactions of benzyl radicals. The phenoxytoluene derivative (265) which would be obtained from hydrogen abstraction by the benzyl radical (257) has not been isolated in these pyrolysates. Indeed, in all the systems studied so far the product (266) which would be derived by hydrogen abstraction of these species has never been isolated thus suggesting that benzyl radicals are very poor at hydrogen abstraction.

\begin{align*}
\text{(265)} \quad & R = \text{H, Me} \\
\text{(266)} \quad & Y = \text{S, NH} \\
& R = \text{H, Me}
\end{align*}

On looking more closely at the hydroxydiphenylmethanes (245) and (246), isolated on generation of both the phenoxy and benzyl radicals, it can be seen that the yields of these compounds are much higher from the phenoxy radicals.
A possible explanation for this difference in yield is that on direct generation of the phenoxy radical, by pyrolysis of the O-allyl derivatives, H abstraction by the radical species to give the hydroxy compound is competing with formation of the spiro-intermediate.

The major product isolated on generation of both the benzyl and phenoxy radicals was identified as a hydroxy-fluorene (258, \( R = H \); 261, \( R = \text{Me} \)), the formation of which must occur by some rearrangement process.

<table>
<thead>
<tr>
<th></th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>(258) ( R = H )</td>
<td>From ( \text{CH}_2 ) 36% 48%</td>
</tr>
<tr>
<td>(261) ( R = \text{Me} )</td>
<td>From ( \text{O}^* ) 30% 26%</td>
</tr>
</tbody>
</table>

A similar compound (267) had previously been observed by Hickson,\textsuperscript{108} on generation of aminyl radicals when the bridging group was sulphur. It was thought at the time
that the formation of this compound could in some way be due to the sulphur atom which can expand its valence shell to possibly form a radical intermediate such as (268).

![Chemical Structures]

(267) $X = S$
(194) $X = NH$

(268)

However, the formation of the aminocarbazole (194), previously observed to a small extent on the generation of aminyl radicals with a bridging NH, and the hydroxyfluorene observed here rules out such a mechanism since the formation of an intermediate by valence shell expansion is no longer possible. However, the mechanism outlined in Scheme 121 is equally plausible for the rearrangement products (194) and (267) previously observed and the hydroxyfluorenes (258) and (261) isolated from the pyrolysates outlined in this chapter.
This proposed rearrangement mechanism is however very unusual and unexpected. The phenoxy radical (249) is highly resonance stabilised due to delocalisation of the free radical in the phenyl ring. Hydrogen abstraction by this species from the adjacent ring generates a localised phenyl radical (269) which cannot gain additional resonance stabilisation. In addition, this hydrogen abstraction must be an endothermic reaction. However, having generated the phenyl radical the cyclisation and re-aromatisation steps shown result in formation of the isolated product.

However, the mechanism outlined in Scheme 121 is not the only mechanism which can be proposed for the formation of the isolated products. The reaction sequence outlined in Scheme 122 can also explain the formation of the
rearrangement products. In this case the first step is cyclisation of the phenoxy radical to generate (270) which can subsequently re-open in the opposite direction to generate the phenyl radical (271). However, if the reaction sequence is followed through this mechanism results in both the substituents being in the same ring.

\[
\begin{align*}
\text{R=H,Me} & \quad \quad (270) \\
\Rightarrow & \\
\text{(271)}
\end{align*}
\]

Since close examination of the \(^{13}\text{C}\) n.m.r. spectra showed that the hydroxy and methyl substituents were in different ring systems, as were the substituents when this rearrangement was previously observed, this proposed mechanism does not result in the formation of the observed, isolated products.

A further mechanism proposed to explain the isolated rearrangement products involves the bridging hydrogen atoms in the reaction mechanism as outlined in Scheme 123. In this case the stabilised phenoxy radical abstracts a
hydrogen atom from the bridging CH$_2$ to generate a carbon radical which can still be stabilised by delocalisation. However, if this is the mechanism of formation of these rearrangement products it cannot explain the dibenzothiophene (267) isolated when the bridging group was a sulphur atom. In this case an alternative mechanism would have to be involved although it seems most likely that such unusual rearrangement products would be formed via a unique mechanism.

\[
\begin{align*}
&\text{Scheme 123} \\
&\text{R} = \text{H, Me}
\end{align*}
\]

The proposed mechanisms are however amenable both to labelling studies and to further investigation using systems which have no bridging hydrogen atoms. Thus the reaction mechanisms outlined in Schemes 121 and 123 will be examined and investigated in more detail in the following section.
F. Further Investigation of the Mechanism of Hydrogen Abstraction by the Generation of 2-Benzoylphenoxyl Radicals and Deuteriated Analogues

Pyrolysis to generate benzyl and phenoxy radicals, as detailed in the previous section, led to the isolation of unusual rearrangement products (258) and (261) from both the radical species generated.

\[
\begin{align*}
(258) & \quad R=H \\
(261) & \quad R=\text{Me}
\end{align*}
\]

The mechanism of formation of these compounds is of great interest and various mechanisms can be proposed. The first of these, outlined in detail in Scheme 121, involves the first step being hydrogen abstraction by the phenoxy radical from the adjacent phenyl ring to give the phenyl radical (269) (Scheme 124).

\[
\begin{align*}
\text{Scheme 124}
\end{align*}
\]

The occurrence of such a process is most unusual since the radical produced is of higher energy than the
reacting radical. A further possible mechanism can be proposed, outlined in Scheme 123, which avoids this endothermic step.

The first step in this alternative mechanism involves abstraction of a hydrogen atom from the bridging CH\textsubscript{2} to generate a stabilised carbon radical (272) (Scheme 125).

\[
\text{O}^\bullet \begin{array}{c} \text{R} \\ \text{H} \end{array} \rightarrow \text{O}^\bullet \begin{array}{c} \text{OH} \\ \text{H} \end{array} \rightarrow \text{product}
\]

\[ R=\text{H, Me} \]

Scheme 125

Thus, this mechanism was further investigated by a deuterium labelling experiment. The bridging hydrogen atoms were replaced by deuterium and the pyrolysate from generation of the labelled phenoxy radicals (273), obtained from the O-allyl derivatives as before, examined by n.m.r. spectroscopy.

\[
\begin{array}{c} \text{O}^\bullet \\ \text{D} \end{array} \begin{array}{c} \text{D} \\ \text{D} \end{array}
\]

(273)

If the rearrangement mechanism does involve the bridging atoms, as shown in Scheme 125, then one of the deuterium labels should be replaced by hydrogen. If however, the first step involves the generation of a phenyl
radical, as shown in Scheme 124, the labelled site should remain intact. Thus, this labelling experiment should help to distinguish the two alternative mechanisms.

This rearrangement mechanism could also be further investigated if the bridging hydrogen atoms were replaced by a carbonyl group. If the rearrangement does involve the step shown in Scheme 125, generation of the phenoxy radical (274) should not result in formation of the rearranged fluorenone (275) (Scheme 126).

The required deuteriated O-allyl derivative (277) was prepared by reduction of the benzophenone (276) (Scheme 127). This compound was prepared by reaction of o-hydroxybenzophenone, which is commercially available, with allyl bromide as outlined before. The reduction of this compound to the labelled deuterium derivative was carried out, in 30% yield using lithium aluminium deuteride-aluminium chloride reagent in ether at 25°C. This method had previously been used to reduce a variety of aromatic ketones to the corresponding hydrocarbons, a range of reaction conditions being investigated.156
The O-allyl derivative (276) prepared during this reaction sequence is also the precursor for generation of the phenoxy radical (274) which can be used to further investigate the rearrangement mechanism.

The deuteriated O-allyl derivative (277) was pyrolysed at 750°C, and the entire pyrolysate dissolved in deuteriochloroform. This pyrolysate was examined by $^1$H and $^{13}$C n.m.r. spectroscopy only for the presence of 1-hydroxyfluorene (258), this compound when previously isolated showing methylene peaks at $\delta$H 3.84 and $\delta$C 33.41. The $^1$H and $^{13}$C n.m.r. spectra both show triplets at $\delta$H 3.85 and $\delta$C 33.15, these peaks being assigned to 1-hydroxy-9-$[^1$H]$[^2$H]fluorene (279) where one deuterium has been replaced by hydrogen. These n.m.r. spectra also both show single peaks at $\delta$H 3.86 and $\delta$C 33.45 which can be assigned to the methylene signals of 1-hydroxyfluorene (258) itself.
However, from these spectra it is not possible to determine if any of the doubly deuteriated fluorenol (278) is present in the pyrolysate. The presence of this compound was determined by expansion and accurate integration of a single aromatic proton observed at $\delta H 6.75$ in the 360MHz $^1H$ n.m.r. spectrum. This signal was previously assigned as the C2 proton in 1-hydroxy-fluorene. $^2D$ irradiation also collapsed the triplet at $\delta H 3.85$ to a singlet which could be accurately integrated. Comparison of the integral values for the two single peaks at $\delta H 3.85$ and 3.86 with the integral of the aromatic signal indicated that a substantial amount of the deuteriated fluorenol (278) must be present in the pyrolysate. From these integrals the relative amounts of $CD_2 : CHD : CH_2$ was found to be $4.6 : 4.4 : 1$.

The results obtained from this labelling study are not what would be expected from either of the proposed rearrangement mechanisms! The identification of the doubly deuteriated compound (278) provides evidence for the mechanism where the first step involves hydrogen abstraction to
generate a phenyl radical (Scheme 124). However, the identification of the hydroxyfluorene (279), where one deuterium is replaced by a hydrogen atom, is in agreement with the mechanism involving the bridging CH$_2$ (Scheme 125). Thus, the presence of these two products in the pyrolysate would perhaps initially suggest that both mechanisms were occurring in competition with each other, although neither mechanism can account for the unlabelled hydroxyfluorene (258).

However, on looking at the first mechanism proposed (Scheme 121) in more detail it is possible that this rearrangement reaction can account for formation of the singly deuteriated fluorene (279) (Scheme 128).

![Scheme 128](image)

Generation of the phenyl radical, by hydrogen abstraction, followed by cyclisation as previously outlined (Scheme 121) would result in the formation of the radical
species (280). Once generated this species can react in two ways. Loss of a hydrogen radical would give the deuteriated hydroxyfluorene (278) but product formation could also occur by loss of a deuterium radical to give (281) which would subsequently undergo a hydrogen transfer reaction to give (279). Thus this mechanism can account for the two major labelled compounds isolated from the pyrolysate, although it still cannot explain the formation of the unlabelled compound (258). The alternative route to product formation proposed in Scheme 128 could be verified by generation of the phenyl radical (282) (Scheme 129). Subsequent cyclisation and re-aromatisation of this species would be expected to give a mixture of (283) and (284), in the same ratio as previously observed, if the reaction mechanism involved loss of both hydrogen and deuterium radicals. Attempts have been made to prepare a radical precursor from which the phenyl radical (282) could be generated. However, these have so far proved unsuccessful. Additionally, deuterium scrambling in the product (283) would have to be excluded.

Scheme 129
The results obtained from this labelling study have not provided conclusive evidence for either of the mechanisms proposed for the formation of the rearranged products. Thus, further work was carried out to investigate the reaction mechanism by generating the phenoxy radicals (274) with a carbonyl group in the bridging position.

![Phenoxy radical structure](274)

If the mechanism of product formation involves the bridging hydrogen atoms, the isolation of rearrangement products from the reactions of these radical species would not be anticipated. The Q-allyl derivative (276) was pyrolysed at 750°C, the entire pyrolysate dissolved in solvent and extracted with base. The components of the basic fraction were separated by dry-flash chromatography on silica, two compounds being isolated from this fraction. The $^1$H n.m.r. spectrum of the first component isolated showed the presence of nine aromatic protons and a single peak at δH 12.03 attributed to an OH group. By comparison of this spectrum and the $^{13}$C n.m.r. spectrum with an authentic sample this component was identified as 2-hydroxybenzophenone (285). The second component of this base extract was isolated as a yellow crystalline solid.
The $^1$H n.m.r. spectrum of this compound shows a single peak at $\delta$H 8.41 attributed to an OH signal, a 1H doublet with long range coupling ($^3J = 7.3$Hz, $^4J = 1.0$Hz) at $\delta$H 7.58, and a further six aromatic protons. The $^{13}$C n.m.r. spectrum confirms the presence of seven methine signals, the remaining five carbon atoms of the phenoxy radical appearing as quaternary signals plus an additional quaternary signal due to the carbonyl group. The spectral data and melting point obtained for the isolated solid are consistent with this component being 1-hydroxyfluorenone (275) (Scheme 130). This was confirmed by calculation of the expected $^{13}$C n.m.r. spectrum for this compound using the additivity effect of the hydroxyl group, initially determined for benzene, and the $^{13}$C n.m.r. spectrum for fluorenone (Table 8). Except in the region of the substituent where, as previously outlined, steric effects can occur the correspondence between the observed and calculated chemical shifts was within 1 p.p.m.

\[ \begin{align*}
(276) & \rightarrow (285) + (275) \\
& + (277) + (276)
\end{align*} \]

Scheme 130
Table 8

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>C9</th>
<th>C1a</th>
<th>C4a</th>
<th>C5a</th>
<th>C8a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorenone</td>
<td>124.8</td>
<td>129.1</td>
<td>134.7</td>
<td>120.3</td>
<td>120.3</td>
<td>134.7</td>
<td>129.1</td>
<td>124.3</td>
<td>193.7</td>
<td>134.2</td>
<td>144.5</td>
<td>144.5</td>
<td>134.2</td>
</tr>
<tr>
<td>1-Hydroxyfluorenone (calculated)</td>
<td>151.2</td>
<td>116.4</td>
<td>136.1</td>
<td>113.0</td>
<td>120.3</td>
<td>134.7</td>
<td>129.1</td>
<td>124.3</td>
<td>195.1</td>
<td>121.5</td>
<td>145.9</td>
<td>144.5</td>
<td>134.2</td>
</tr>
<tr>
<td>1-Hydroxyfluorenone (observed)</td>
<td>157.25</td>
<td>118.01</td>
<td>137.22</td>
<td>112.59</td>
<td>120.80</td>
<td>134.44</td>
<td>128.89</td>
<td>123.85</td>
<td>196.07</td>
<td>117.28</td>
<td>143.69</td>
<td>143.99</td>
<td>134.11</td>
</tr>
</tbody>
</table>

a Estimated from the spectrum of fluorenone assigned as in reference 157 using the substituent effect of a 1-hydroxy group; b CDCl₃ solution; c Assignments may be reversed
The pyrolysate residue remaining after base extraction was found to contain two components, these being separated by dry-flash chromatography on silica. The $^1$H n.m.r. spectrum of the first compound isolated indicated the presence of only eight aromatic protons between $\delta$H 7.63 and 7.96. The $^{13}$C n.m.r. spectrum showed only four methine signals and two quaternary signals, neither of the quaternary peaks being attributed to a carbonyl group. This compound was identified as dibenzofuran (276) by comparison of the $^{13}$C n.m.r. spectrum obtained with an authentic literature spectrum$^{158}$ (Table 9).

Table 9

<table>
<thead>
<tr>
<th></th>
<th>C1,8</th>
<th>C2,7</th>
<th>C3,6</th>
<th>C4,5</th>
<th>C4a,5a</th>
<th>C1a,8a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibenzofuran</td>
<td>121.1</td>
<td>123.4</td>
<td>127.6</td>
<td>112.0</td>
<td>156.7</td>
<td>124.6</td>
</tr>
<tr>
<td>(Literature)$^{a}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td>120.51</td>
<td>122.57</td>
<td>127.00</td>
<td>111.55</td>
<td>156.14</td>
<td>124.15</td>
</tr>
<tr>
<td>(Observed)$^{b}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{a}$ Assigned as in reference 158; $^{b}$ CDC$_3$ solution

The correspondence between the observed and literature values in the $^{13}$C n.m.r. spectra of this isolated compound is within 1 p.p.m. confirming the presence of dibenzofuran.
The final component separated by chromatography, isolated as a white crystalline solid, was identified by mixed m.p. and comparison of the $^1$H and $^{13}$C n.m.r. spectra with those of an authentic sample as the cyclisation product xanthone (277).

From the results obtained from this pyrolysis we can clarify the mechanism for formation of the rearrangement product. Isolation of the hydroxyfluorenone (275) from the pyrolysate indicates that bridging hydrogen atoms are not required in the mechanism of formation of this compound. Thus, the only mechanism so far proposed which can account for the formation of this, and the other rearranged products previously observed, and result in the observed substitution pattern is that shown in Scheme 131. The mechanism previously outlined in Scheme 123 can now be discounted in this case.

![Scheme 131]
However, in addition to clarifying the rearrangement mechanism, the isolation of dibenzofuran (276) from this pyrolysis may provide more information on the way in which products are formed on generation of a spirodiienyl intermediate. The unexpected formation of dibenzofuran is thought to involve the spiro-intermediate (278) (Scheme 132). If on generation this species opens in the direction to generate the radical (279), there is precedent from work previously carried out\(^4\) that such a species would quantitatively decarbonylate to give a phenyl radical (280) even when favourable intramolecular reactions are possible. Subsequent cyclisation of this radical would give dibenzofuran (276) (Scheme 132).

The formation of dibenzofuran simply by decarbonylation of xanthone was ruled out by pyrolysis of xanthone at temperatures of up to 900°C, only starting material being recovered. The formation of this compound could, however,
Scheme 133
be used to probe the mechanism of reaction of the spiro-
intermediate by the introduction of a p-methyl group in
the unsubstituted right-hand ring.

Thus, if the formation of the cyclisation products
isolated in this, and all the previous pyrolysates, is
taking place directly from the spiro-intermediate by a
sigmatropic migration (route b, Scheme 133) then an isomeric
mixture of products (282) and (283) would be expected. If
however the intermediate is re-opening to generate the free
radical species (route a, Scheme 133) only the isomer (282),
obtained by direct cyclisation, would be expected since
generation of (281) should result in decarbonylation and
hence no cyclisation product.

Thus, in order to investigate further the mode of
reaction from the spiro-intermediate, the phenoxyl radical
(285) was generated by pyrolysis of the O-allyl derivative
(284) at 750°C. This precursor was prepared by reaction
of the hydroxydiphenylmethane (244), previously described
in Scheme 111, with allyl bromide (Scheme 134) to give the
required compound in 90% yield.

\[ 
\begin{align*}
\text{OH} & \\
\text{Me} & \\
\text{C} & \\
\text{O} & \\
\text{Me} & \\
\end{align*}
\]

(244)  (284)  (285)

Scheme 134
The entire pyrolysate was again extracted with base to remove any phenolic components, these being separated by dry-flash chromatography on silica. Two products were isolated from this extract, the first being obtained as a yellow solid. By comparison of the $^1$H and $^{13}$C n.m.r. spectra with those of an authentic sample this component was identified as 2-hydroxy-4'-methylbenzophenone (244). The second product of the extract was isolated as fine yellow needles. The $^1$H n.m.r. spectrum of this compound shows a singlet at $\delta$H 8.42 attributed to an OH group, a $^1$H doublet at $\delta$H 7.46, a $2^1$H multiplet between $\delta$H 7.24 and 7.33, a $1^1$H multiplet at $\delta$H 7.04 and two further $1^1$H doublets, both with long range coupling, at $\delta$H 6.94 and 6.71. The spectrum also shows a methyl peak at $\delta$H 2.36. The $^{13}$C n.m.r. spectrum shows six methine peaks and seven quaternary signals, one of these attributed to a carbonyl peak, as well as a methyl signal at $\delta$C 21.90. This n.m.r. spectral data is consistent with this component being a methyl substituted hydroxyfluorenone. The $^{13}$C n.m.r. chemical shifts for the isolated compound are consistent with the spectrum expected for 1-hydroxy-6-methylfluorenone (286) (Scheme 136) calculated from the observed $^{13}$C n.m.r. spectrum for 1-hydroxyfluorene, assigned as in Table 7, using the known substituent effect of a methyl group (Table 10). The calculated and observed values correspond to within 1 p.p.m. except for the quaternary signals C4a and C5a where slight variations were previously observed.
Table 10

<table>
<thead>
<tr>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>C9</th>
<th>C1a</th>
<th>C4a</th>
<th>C5a</th>
<th>C8a</th>
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<tbody>
<tr>
<td>157.06</td>
<td>117.88</td>
<td>136.89</td>
<td>112.39</td>
<td>121.72</td>
<td>143.59</td>
<td>129.37</td>
<td>123.77</td>
<td>195.84</td>
<td>117.68</td>
<td>145.63 C</td>
<td>144.36 C</td>
<td>131.69</td>
</tr>
<tr>
<td>1-Hydroxy-6-methyl fluorenone</td>
<td>157.25</td>
<td>118.01</td>
<td>137.22</td>
<td>112.59</td>
<td>121.50</td>
<td>143.34</td>
<td>129.59</td>
<td>123.75</td>
<td>196.07</td>
<td>117.28</td>
<td>143.99</td>
<td>143.59</td>
</tr>
</tbody>
</table>

| Compound isolated from Pyrolysate\textsuperscript{a} | 157.06 | 117.88 | 136.89 | 112.39 | 121.72 | 143.59 | 129.37 | 123.77 | 195.84 | 117.68 | 145.63 C | 144.36 C | 131.69 |
| 1-Hydroxy-6-methyl fluorenone (calculated)\textsuperscript{b} | 157.25 | 118.01 | 137.22 | 112.59 | 121.50 | 143.34 | 129.59 | 123.75 | 196.07 | 117.28 | 143.99 | 143.59 | 131.21 |

\textsuperscript{a} CDCl\textsubscript{3} solution; \textsuperscript{b} Estimated from the observed spectrum of 1-hydroxyfluorenone, assigned as in Table 8, using the substituent effect of a methyl group. \textsuperscript{c} Assigned by comparison with the calculated values of 1-hydroxyfluorene given in Table 7.
The components remaining in the pyrolysate after base extraction were also separated by dry-flash chromatography on silica. The $^1$H n.m.r. spectrum of the first component isolated showed the presence of only seven aromatic protons and a methyl group while a DEPT $^{13}$C n.m.r. spectrum also shows seven methine and one methyl signal. The n.m.r. spectral data is consistent with this compound being a methyl substituted dibenzofuran. The position of the substituent was determined by comparison of the observed $^1$H and $^{13}$C n.m.r. chemical shifts for the isolated compound with the expected chemical shifts of the possible dibenzofuran isomers (Table 11).

Table 11

<table>
<thead>
<tr>
<th>Oberved value</th>
<th>1-Methyl</th>
<th>2-Methyl</th>
<th>3-Methyl</th>
<th>4-Methyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.52</td>
<td>2.80</td>
<td>2.56</td>
<td>2.86</td>
<td>2.61</td>
</tr>
<tr>
<td>21.18</td>
<td>15.09</td>
<td>21.20</td>
<td>19.60</td>
<td>21.70</td>
</tr>
</tbody>
</table>

This data indicates that the isolated compound is most likely 2-methyldibenzofuran (287) (Scheme 136) although
the chemical shifts are not vastly different from the 4-methyl isomers. These two isomers were distinguished by calculating the expected methine $^{13}\text{C}$ n.m.r. chemical shifts using methyl group additivity effects\textsuperscript{119} and the assigned $^{13}\text{C}$ n.m.r. spectrum of dibenzofuran\textsuperscript{158} (Table 12). These calculated spectra indicate that the isolated compound is indeed the 2-methyl isomer, this being the expected isomer from the proposed mechanism of formation of this compound (Scheme 135).

The final component isolated from the pyrolysate was obtained as a colourless solid. The aromatic signals observed in the $^{13}\text{C}$ n.m.r. spectrum and the presence of two methyl peaks at $\delta^{C} 21.73$ and 20.60 suggests this component is an isomeric mixture of methylxanthones. The $^{1}\text{H}$ n.m.r. spectrum also shows two methyl peaks at $\delta^{H} 2.50$ and 2.39. The $^{13}\text{C}$ n.m.r. spectrum of an authentic sample of 2-methylxanthone (262), previously generated in Scheme 116.
Table 12

<table>
<thead>
<tr>
<th>Compound Isolated from Pyrolysate\textsuperscript{a}</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methyldibenzofuran (calculated)\textsuperscript{b}</td>
<td>121.8</td>
<td>132.3</td>
<td>128.3</td>
<td>111.9</td>
<td>112.0</td>
<td>127.6</td>
<td>123.4</td>
<td>121.1</td>
</tr>
<tr>
<td>4-Methyldibenzofuran (calculated)\textsuperscript{b}</td>
<td>118.9</td>
<td>123.3</td>
<td>128.3</td>
<td>120.9</td>
<td>112.0</td>
<td>127.6</td>
<td>123.4</td>
<td>121.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} CDCl\textsubscript{3} solution; \textsuperscript{b} Estimated from the spectrum of dibenzofuran, assigned as in reference 158, using the effect of a methyl group; \textsuperscript{c} Quaternary signals
by cyclisation of 2-(4-methylphenoxy)benzoic acid, has a methyl peak at δC 20.57 which is consistent with the peak observed in the isolated isomeric mixture at δC 20.60, the methine signals of this authentic sample also corresponding to those observed in the isolated component. The presence of the 3-methyl isomer as the second component of the mixture could not, in this case, be confirmed using the effect of the methyl group used in the previous sections since there is no bridging methylene group. Instead, the presence of this isomer was confirmed by calculation of the expected chemical shifts for the methine signals using the 13C n.m.r. spectrum of xanthone159 and the methyl group substituent effect used previously (Table 13).

Table 13

<table>
<thead>
<tr>
<th>Compound</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Methylxanthone</td>
<td>126.4</td>
<td>125.17</td>
<td>-</td>
<td>117.7</td>
<td>117.49</td>
<td>134.36</td>
<td>123.5</td>
<td>126.46</td>
</tr>
<tr>
<td>(calculated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Observed and Expected 13C n.m.r. Methine Chemical Shifts for 3-Methylxanthone
The calculated and observed chemical shifts for this isomer are well within 1 p.p.m. thus confirming that this component is a mixture of 2-methylxanthone (262) and 3-methylxanthone (288) (Scheme 136).

\[
\begin{align*}
&\text{(285)} \\
\xrightarrow{\text{C}} &\text{(244)} \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me}
\end{align*}
\]

\[
\begin{align*}
&\text{(286)} \\
\xrightarrow{\text{C}} &\text{(262)} \\
\text{OH} &\text{Me} \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me}
\end{align*}
\]

\[
\begin{align*}
&\text{(287)} \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me} \\
\text{Me} &\text{Me}
\end{align*}
\]

Scheme 136

A series of small scale pyrolysis experiments, to generate the phenoxy radical (285) were carried out at various temperatures. From the pyrolysates, the ratio of 2-methylxanthone : 3-methylxanthone was determined at each temperature by comparison of the carbonyl groups observed in the $^{13}$C n.m.r. spectrum, these being the only peaks which could be clearly distinguished. The ratio of the xanthone isomers : dibenzofuran was also determined at each temperature by g.c. analysis. The results of these experiments are given in Table 14.
Table 14

Product Ratios Determined by $^{13}$C n.m.r. Spectroscopy and G.C. at Various Temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>2-Methyl : 3-Methyl</th>
<th>2- and 3-Methyl : 2-Methyl dibenzofuran</th>
</tr>
</thead>
<tbody>
<tr>
<td>750°C</td>
<td>1 : 1</td>
<td>1 : 0.32</td>
</tr>
<tr>
<td>850°C</td>
<td>1 : 1</td>
<td>1 : 0.35</td>
</tr>
<tr>
<td>950°C</td>
<td>1 : 1</td>
<td>1 : 0.48</td>
</tr>
</tbody>
</table>

The isolation of only 2-methyldibenzofuran (287) from the pyrolysate indicates that this product is formed by the mechanism outlined in Scheme 135, generation of the benzoyl radical resulting in decarbonylation. The isolation of the methylxanthone isomers indicates that the formation of the cyclisation products most likely occurs directly from the spiro-intermediate by a sigmatropic rearrangement. However, it is possible that at 750°C decarbonylation of the radical (290) (Scheme 137) is not complete and that formation of the rearranged xanthone (262) can occur by cyclisation of this species. In order to determine if this was the case the series of small scale pyrolyses were carried out at 750°C-950°C and the products examined (Table 14). On increasing the temperature the amount of 2-methyldibenzofuran increases by a small, but consistent, amount while the ratio of xanthone isomers remains constant. Had the amount of
rearranged xanthone (262) decreased as the amount of
dibenzo[2,3]furan isomer increased this would have indicated
that the formation of 2-methylxanthone (262) could occur
by cyclisation of the benzoyl radical (290). However,
since the ratio of 2-methylxanthone : 3-methylxanthone
remains unchanged we can conclude that the formation of
these compounds probably occurs directly from the spiro-
intermediate (289) by a sigmatropic migration (Scheme 137)
and that at 750°C decarbonylation of the radical (290) is
complete. Such a migration is suprafacially allowed with
inversion of configuration at the migrating centre.

From the results obtained, however, it is not possible
to determine anything about the migratory aptitudes of the
two radical species from the spiro-intermediate or if the
unrearranged xanthone (288) is also being generated by
competing direct cyclisation of the phenoxy radical (285).
The increase in the amount of 2-methyl dibenzofuran observed
on increasing the pyrolysis temperature can possibly be
attributed to the increased energy of the system re-opening
the spiro-intermediate to generate the rearranged radical
(290) to a greater extent.
G. Preparation of Dibenzofurans and Related Hetero-analogues

During the course of the investigation of the rearrangement mechanism, outlined in the preceding chapter, it was observed that on generating phenyl radicals these species will form cyclisation products. In the preceding chapter, generation of the phenyl radical (280) resulted in formation of dibenzofuran (276), though only in low yield since this was a minor pathway of the reaction mechanism (Scheme 138).

Thus, if phenyl radicals could be generated directly, by pyrolysis of an appropriate radical precursor, this cyclisation reaction could provide a general route to the preparation of dibenzofurans. This system could also be extended to other compounds, such as dibenzothiophenes, simply by changing the bridging hetero-atom (Scheme 139).
Both dibenzofurans and dibenzothiophenes have previously been prepared by a variety of routes. The most widely used methods of generating dibenzofurans involves diphenyl ethers or biphenyls. One of the oldest methods of preparing these compounds is from \(o\)-aminodiphenyl ethers. Diazotisation of the amine followed by warming in 50% sulphuric acid for several hours yields the ring closure product. Although the yield for this reaction is not generally high, a number of derivatives substituted in the 2-, 3- and 4-positions have been prepared by this method e.g. (Scheme 140).
acid or trifluoroacetic acid, has given dibenzofurans in good yield, an intermediate of the type (291) being suggested for the reaction.  

\[
\text{L-Pd-L}
\]

This method has been applied to a range of substituted diphenyl ethers and particularly to chlorinated compounds, product yields varying between 35 and 55%. Irradiation of a dilute solution of diphenyl ether in cyclohexane in the presence of an equimolar amount of iodine as oxidant produces dibenzofuran. A conrotatory electrocyclisation producing the carbonyl ylide intermediate (292) is probably involved, the intermediate then undergoing oxidation by iodine to produce dibenzofuran (Scheme 141).

\[
\begin{align*}
\text{hv} > & \\
\text{Oct} & \\
\end{align*}
\]

\[
(292)
\]

Scheme 141

This reaction has been used to synthesise a range of alkyldibenzofurans, yields of 35-55% usually being
obtained, although yields as low as 20% have been observed for \textit{i-Pr} and \textit{t-Bu} substituents. This reaction fails when the product would be subject to the severe steric hindrance of two bulky alkyl groups in the 1- and 9-positions.

The use of biphenyls in the preparation of dibenzofurans has been widely used, most especially the use of 2,2'-bi-phenyldiols (293).

These compounds undergo dehydration when treated with a variety of acidic reagents, the most common being hydrobromic acid, phosphoric acid and pyridinium chloride or bromide.\textsuperscript{166, 167} The mechanism of the reaction has been investigated by labelling studies\textsuperscript{168} and was found to involve intramolecular nucleophilic attack of the 2'-hydroxy group on C-2 of the adjacent ring activated by protonation (Scheme 142).
This method has been used to prepare mostly hydroxyl substituted dibenzofurans and a few alkyl substituted systems in yields of 60-80%, although yields of 20% have been observed. The major drawback of this method is the lability of some functional groups, such as carboxylic acids, under the acidic conditions of the reaction. Dibenzofurans have also been synthesised by intramolecular reaction as shown in Scheme 143.

A number of these types of syntheses, with X a variety of leaving groups, have been carried out under basic
conditions. This method has been applied to the synthesis of 2-hydroxydibenzofurans\textsuperscript{169} e.g. Scheme 144.

\begin{equation}
\begin{align*}
\text{Cl} & \quad \text{OH} & \quad \text{OH} \\
\uparrow & \quad \downarrow & \quad \downarrow \\
\text{aq KOH} & \quad \text{NaHSO}_3 \\
100-230^\circ C & \quad 12-23\text{ atm} \\
7\text{ h} & \\
\end{align*}
\end{equation}

Scheme 144

Dibenzothiophene (294) has been prepared by a wide variety of methods, the best of these involving the action of sulphur on biphenyl in the presence of aluminium halides\textsuperscript{170} (Scheme 145).

\begin{equation}
\begin{align*}
\text{C} & \quad \text{C} \\
\uparrow & \quad \downarrow \\
\text{AlX}_3 & \quad \text{S} \\
9\text{ h} & \\
\end{align*}
\end{equation}

Scheme 145

Deoxygenation of dibenzothiophene-5-oxide (295) by treatment of (295) with hydrochloric acid and tin chloride\textsuperscript{171} gives dibenzothiophene in high yield (Scheme 146).

\begin{equation}
\begin{align*}
\text{S} & \quad \text{O} \\
\uparrow & \quad \downarrow \\
\text{HCl} & \quad \text{SnCl}_2 \\
\end{align*}
\end{equation}

Scheme 146
A new route to dibenzothiophene which has been extensively studied\(^1\)\(^2\),\(^1\)\(^3\) involves the condensation of thiophenol with 2-chlorocyclohexanone (Scheme 147).

\[
\begin{align*}
\text{Cl} & \quad \text{HS-} \\
\text{O} & \quad \text{C} \\
\end{align*}
\]

This reaction has been extended to substituted systems where good yields were obtained for thiophenols with electron releasing substituents but low yields or no reaction was observed for electron donating substituents. This reaction system, however, could be extended to give substitution in both rings. Dibenzothiophenenes have also recently been synthesised from allylbenzo(b)thiophenes to give products which are substituted only in the 1-, 1,3-, or 3-positions in high yields\(^1\)\(^4\) e.g. Scheme 148.

\[
\begin{align*}
\text{Scheme 147} \\
\end{align*}
\]
Finally, phenyl radicals generated from N-nitrosoacetanilides, at room temperature in ethyl acetate, have been found to attack 1,2,3-benzothiadiazole to yield derivatives of dibenzothiophene as shown in Scheme 149.\textsuperscript{175}

\begin{equation}
\text{Scheme 148}
\end{equation}

The preparative methods for generating dibenzofurans and dibenzothiophenes outlined here are by no means exhaustive. A large number of other methods have been
used to prepare these systems, often for a specifically substituted system, these being adequately reviewed in detail.\textsuperscript{176-179} From the methods examined, however, it is clear that no one method can prepare a wide range of substituted compounds. Thus, the direct generation of phenyl radicals of the type (296) could provide a new route to the preparation of dibenzofurans, dibenzothiophenes and possibly related systems.

\[
\text{R=O,S}
\]

(296)

As previously outlined in the introduction, one method of generating phenyl radicals is from the appropriate allyl ester, this proving the method of choice for the work of this thesis. The preparation of the radical precursors from which dibenzofurans could be generated is outlined in Scheme 150.
Reaction of the potassium salt of o-chlorobenzoic acid with the appropriate phenol in sodium methoxide solution gave the substituted benzoic acids (297) in yields of 45-75%. Reaction of the benzoic acids with an excess of allyl bromide in a potassium carbonate/dimethylformamide solution gave the required radical precursors in high yields. The compounds prepared by this method and the yields obtained are shown in Table 15.

Table 15 Yields of Prepared Derivatives

<table>
<thead>
<tr>
<th>R</th>
<th>297</th>
<th>298</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-†</td>
<td>80</td>
</tr>
<tr>
<td>p-Me</td>
<td>50</td>
<td>63</td>
</tr>
<tr>
<td>p-COMe</td>
<td>45</td>
<td>44</td>
</tr>
<tr>
<td>p-OMe</td>
<td>78</td>
<td>73</td>
</tr>
<tr>
<td>p-Cl</td>
<td>65</td>
<td>81</td>
</tr>
<tr>
<td>m-Me</td>
<td>53</td>
<td>82</td>
</tr>
<tr>
<td>m-COMe</td>
<td>45</td>
<td>44</td>
</tr>
<tr>
<td>o-Me</td>
<td>72</td>
<td>82</td>
</tr>
</tbody>
</table>

(† commercially available)
With the exception of special effects due to the substituent, the mass spectra of these compounds show a peak at M-57 due to the loss of an O-allyl fragment.

The preparation of the radical precursors from which dibenzothiophenes could be generated is outlined in Scheme 151.

\[
\begin{align*}
\text{HCl} & \quad \text{HCl} \\
\text{NaNO}_2 \quad \text{NaNO}_2 & \quad \text{NaNO}_2 \\
\end{align*}
\]

Diazotisation of anthranilic acid (299) followed by reaction of the diazonium salt with the appropriate thio-phenol gave the substituted thiophenoxybenzoic acids. Reaction of the acids with an excess of allyl bromide as before gave the appropriate radical precursors. The compounds prepared by this route and the yields obtained are outlined in Table 16.
Table 16 Yields of Prepared Derivatives

<table>
<thead>
<tr>
<th>R=</th>
<th>300</th>
<th>301</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>50</td>
<td>75</td>
</tr>
<tr>
<td>p-Me</td>
<td>44</td>
<td>48</td>
</tr>
<tr>
<td>p-Cl</td>
<td>49</td>
<td>20</td>
</tr>
<tr>
<td>m-Me</td>
<td>54</td>
<td>52</td>
</tr>
<tr>
<td>o-Me</td>
<td>48</td>
<td>57</td>
</tr>
</tbody>
</table>

The mass spectra of the allyl ether derivatives (301) also show the major fragmentation pathway to involve loss of an O-allyl fragment to give a peak at M-57 (Scheme 152).

![Scheme 152](image)

Generation of phenyl radicals by pyrolysis of the allyl esters has the advantage that a wide range of substituted precursors can be easily prepared in high yields, these requiring little purification. However, on pyrolysis of these allyl ester derivatives it was found that furnace temperatures of 750°C and 850°C were not adequate to generate the required radicals, a furnace temperature of 900°C being required to completely cleave the ester group. Pyrolysis of the unsubstituted allyl derivatives (298) and (301) at this higher temperature did indeed result in the
formation of dibenzofuran and dibenzothiophene in good yield. Thus, these pyrolyses were extended to the substituted allyl ester derivatives.

Pyrolysis of the p-substituted radical precursors (302) and (303) gave as the pyrolysis product the appropriate 2-substituted dibenzofurans (304) and dibenzothiophenes (305) (Scheme 153). The crude pyrolysate was purified by chromatography and recrystallisation or sublimation.

![Scheme 153](image)

The pyrolysate of the substituted dibenzofurans always contained a small amount of the dibenzofuran itself, usually <10%, which was removed during purification. In the case of the p-methoxy substituent, the pyrolysate consisted only of a number of small degradation products indicating that this group was unstable at the pyrolysis temperature. The presence of the required products was confirmed by melting point data and comparison of the n.m.r. spectra with those of an authentic or literature spectrum. The 2-substituted
derivatives prepared by this method, and the yields of pure, isolated material are given in Table 17.

Table 17
Yields of Isolated and Purified 2-Substituted Dibenzofuran and Dibenzothiophene Derivatives

<table>
<thead>
<tr>
<th>R</th>
<th>X=O</th>
<th>X=S</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>49</td>
<td>63</td>
</tr>
<tr>
<td>Me</td>
<td>38</td>
<td>56</td>
</tr>
<tr>
<td>COMe</td>
<td>35</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>56</td>
<td>36</td>
</tr>
</tbody>
</table>

The preparation of these compounds was extended to the m-substituted precursor systems (306) and (307). In these cases a mixture of 1- and 3-methyl substituted compounds was anticipated (Scheme 154), although some selectivity in the cyclisation site was expected thus favouring the formation of one isomer.

Scheme 154
However, as can be seen from the yields given in Table 18 such selectivity was not observed, the generated radical giving almost equal amounts of each isomer. In addition, only the 1- and 3-acetyldibenzofuran isomers could be separated, repeated attempts to separate the methyl isomers of both dibenzofuran and dibenzothiophene proving unsuccessful. The yield of each isomer was obtained by $^1$H n.m.r. spectroscopy.

Table 18

Yields of 1- and 3-Substituted Dibenzofuran and Dibenzothiophene Derivatives

<table>
<thead>
<tr>
<th></th>
<th>1-Me</th>
<th>3-Me</th>
<th>1-COMe</th>
<th>3-COMe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X=O$</td>
<td>42</td>
<td>37</td>
<td>27</td>
<td>29</td>
</tr>
<tr>
<td>$X=S$</td>
<td>37</td>
<td>31</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Finally, the preparation of these compounds was extended to radical precursors with an o-methyl substituent (308) and (309). It was expected that pyrolysis of these derivatives would provide a route to 4-methyldibenzofuran (310) and 4-methyldibenzothiophene (311) (Scheme 155).
On pyrolysis of the allyl esters (308) and (309) the major components isolated from the pyrolysates were indeed 4-methyldibenzofuran (310) and 4-methyldibenzothiophene (311) respectively, isolated in 35% and 52% yields. However, minor components isolated from the pyrolysate of (308) were identified as 1-hydroxyfluorene (316) and xanthene (313) while a minor component in the pyrolysate of (309) was found to be thioxanthene (314). The mechanism proposed for the formation of these compounds is outlined in Scheme 156.
The phenyl radical generated on pyrolysis of the precursors can abstract a hydrogen atom from the methyl group so generating the benzyl radical (312). The formation of products from this species follows the course previously outlined (c.f. Sections C and E), the radical generating a spiro-intermediate from which xanthene (313) and thioxanthene (314) can be formed directly by sigmatropic migration. In the case where $X=O$, the intermediate will open in the opposite direction to generate the phenoxy radical (315) from which 1-hydroxyfluorene (316) is obtained by the rearrangement mechanism previously outlined (c.f. Scheme 121).
In the case of the dibenzofuran preparations these radicals were extended to a system where the substituent was in the same ring as the generated radical. The generation of phenyl radicals such as (317) is a potential route to the formation of compounds with substituents in both ring systems. However, by comparison with the mechanism proposed for the formation of the rearrangement products such as (316), these radical species have the potential to abstract a hydrogen atom from the adjacent ring so generating the radical (318) and setting up the equilibrium shown in Scheme 157.

![Scheme 157](image)

If such an abstraction was taking place this would have repercussions on the synthetic viability of this route since, in most cases, the substituent pattern could not be specifically designed. Thus, by examining and identifying the products the occurrence of this equilibrium can be investigated.

The preparation of the radical precursor is outlined in Scheme 158.
Diazotisation of 3-chloro-p-toluidine followed by reaction with cuprous cyanide generated 3-chloro-p-toluonitrile$^{180,181}$ (319) which was hydrolysed to the acid (320) by refluxing in potassium hydroxide solution.$^{182}$ Reaction of the acid with phenol, as previously outlined, followed by allylation generated the radical precursor (321).

Pyrolysis of this precursor at 900°C led to the formation of an isomeric mixture of 1-methyl and 3-methyl-dibenzofuran, in 25% and 75% yield respectively, thus indicating that the equilibrium shown in Scheme 157 is being established, the isolated products being generated as shown in Scheme 159.
The formation of 1-methyldibenzofuran (325) and 3-methyldibenzofuran (324) in the ratio 1:3 indicates that the radical species must be completely equilibrated since on direct generation of (323) a 1:1 mixture of the two isomers is obtained. With (322) generating 50% of 3-methyldibenzofuran and (323) generating 25% 3-methyl-dibenzofuran and 25% 1-methyldibenzofuran a ratio of 25% :75% 1-methyl : 3-methyldibenzofuran would be obtained. This pyrolysis was also carried out at 850°C, 950°C and 1000°C to determine if the equilibration would be affected by the temperature increase but in each case the product ratio of 3:1 remained unaltered.
Having successfully used the generation of phenyl radicals as a preparative method of obtaining substituted dibenzofurans and dibenzothiophenes it was attempted to extend this method to other similar systems such as carbazoles (326), fluorenes (327) and fluorenones (328).

The substituted phenylaminobenzoic acid (329) was readily available from work previously carried out so was reacted with allyl bromide in dimethylformamide, as previously described, to generate the phenyl radical precursor (330) in a high yield (Scheme 160).

However, on pyrolysis of this precursor at 900°C the major product isolated and identified was not 2-methyl-
carbazole as expected but 2-methylcocridone (331). The mechanism of formation of the isolated compound is outlined in Scheme 161, a search of the literature indicating that such a rearrangement had previously been observed by Boekelheide on pyrolysis of similar compounds.

Thus, this route cannot be used as a preparative method of obtaining substituted carbazoles. If, however, the bridging NH could be replaced by NMe then this route might be used to obtain N-methylcarbazoles. The preparation of the radical precursors required to generate these compounds is shown in Scheme 162.
The anthranilic acid derivatives (332) and (333), readily available from previous work, were refluxed with methyl iodide and potassium hydroxide in an aqueous solution for 60h. The mixture of N-methylated derivatives and starting material obtained was separated by column chromatography to give the N-methylated esters (334) and (335) but only in low yields. Hydrolysis of these derivatives to the corresponding acids followed by reaction of the acids with allyl bromide again gave the radical precursors in high yields. Pyrolysis of these precursors again did not give the expected product, the compounds isolated from the pyrolysis being shown in Scheme 163.
The N-methylcarbazoles (338) and (339) were isolated from the pyrolysate in only 5% and 6% yields respectively, however the carbazoles (340) and (341) were isolated from the pyrolysates, both in 26% yield. Pyrolysis of an authentic sample of N-methylcarbazole (338) at 900°C results in the major product of the pyrolysis being carbazole (340), contaminated with a small amount of (338), thus accounting for the formation of the carbazole derivatives (340) and (341). A third product isolated from both pyrolysates were the acridone derivatives (342) and (343) isolated in 32% and 30% yields respectively. The most likely mechanism of formation of these compounds is cleavage of the N-methyl group in the starting material. In agreement with this, pyrolysis of an authentic sample of N-methylacridone at 900°C gave only acridone as the isolated product thus establishing the instability of the N-methyl group under the pyrolysis conditions and accounting for the formation of the isolated products.
The product mixture obtained on pyrolysis of (336) and (337) were very messy, a large number of minor impurities being obtained. Due to solubility problems with the products obtained, the product mixtures were also difficult to separate thus the pyrolysis of compounds such as (336) and (337) is not a viable method of preparation of either carbazole or N-methylcarbazole derivatives.

Finally, these reactions were extended to try and prepare fluorene (348) and fluorenone (349) by the generation of phenyl radicals. The benzoic acids (344) and (345) were commercially available so the radical precursors (346) and (347) were readily obtained by the usual reaction (Scheme 164).

![Scheme 164](image)

On pyrolysis of (346) only one product was obtained which was isolated and identified as fluorene (348). The crude isolated material was purified by column chromatography to give the pure material in 72% yield.
However, pyrolysis of (347) gave a mixture of two products which could not be completely separated, these compounds being identified as fluorenone (349) and benzophenone (350).

![Fluorenone and Benzophenone](image)

(349)  (350)

After column chromatography and recrystallisation the sample of fluorenone, isolated in 43% yield, was still contaminated with benzophenone (10%). This is the only system so far studied where one of the isolated, identified products has been obtained by the generated phenyl radical scavenging a hydrogen atom. However, minor unidentified products formed by such a mechanism may be present in previous pyrolysates. The difference in this pyrolysate is that the bridging group is now of an electron-withdrawing
nature, the change in the reaction profile possibly being connected with this. However, further examples would be required to study this further.

Although only the unsubstituted system has so far been examined it is likely that these reactions could be extended as a preparative method to substituted fluorene derivatives to give the required products in high yields. The viability of this method as a preparation of fluorenones would depend on the extent of formation of the benzophenone derivatives and the development of a method of separating these compounds from the pyrolysate mixture.
EXPERIMENTAL
A. **Symbols and Abbreviations**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>b.p.</td>
<td>boiling point</td>
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<td>m.p.</td>
<td>melting point</td>
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<tr>
<td>t.l.c.</td>
<td>thin layer chromatography</td>
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<tr>
<td>g.c.</td>
<td>gas-liquid chromatography</td>
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<td>g.c./m.s.</td>
<td>gas-liquid chromatography/mass spectrometry</td>
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<td>n.m.r.</td>
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<td>t</td>
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<td>q</td>
<td>quaternary (in $^{13}$C n.m.r. spectra)</td>
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<td>m</td>
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<td>δ</td>
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<td>i.r.</td>
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<td>v</td>
<td>wavenumber</td>
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<td>m.s.</td>
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<td>$M^+$</td>
<td>mass of molecular ion</td>
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B. **Instrumentation**

**Mass Spectrometry**

Mass spectra were recorded by Mr. D. Thomas, Mr. A. Thomson and Miss E. Stevenson on an A.E.I. MS902 mass spectrometer and latterly by Mr. A. Thomson on a Kratos MS50TC instrument. Exact mass measurements were recorded by Mr. A. Thomson on a Kratos MS50TC spectrometer.

**Nuclear Magnetic Resonance Spectroscopy**

(i) $^1$H n.m.r. spectra were recorded by Mr. L.H. Bell and Dr. H. McNab on a Bruker WP80 spectrometer.

(ii) $^2$H n.m.r. spectra were recorded by Dr. D. Reed on a Bruker WH360 spectrometer.

(iii) $^{13}$C n.m.r. spectra were recorded by Mr. J.R.A. Millar and Dr. H. McNab on a Bruker WP200 spectrometer and by Miss E. Stevenson, Mr. J.R.A. Millar and Dr. H. McNab on a Varian CFT20 spectrometer.

All n.m.r. spectra were recorded in deuteriochloroform solutions unless otherwise stated. Chemical shifts ($\delta_C$, $\delta_H$) were measured in parts per million relative to tetramethylsilane ($\delta = 0.0$).
Chromatography

(i) Qualitative and preparative gas-liquid chromatography was carried out on a Carlo Erba Strumentazione Fractovap 2450 instrument. Some qualitative work was carried out using a Pye series 204 chromatograph. Both instruments were fitted with a flame ionisation detector and nitrogen was used as a carrier gas. Most samples were run on a 1.5 m x 4.5 mm column of 5% SE30 on Gas-chrom (80-100 mesh), although some samples were run on 5% Carbowax on Gas-chrom (80-100 mesh). Preparative g.c. was performed on a 0.85 m x 12 mm column of 10% SE30 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.

(ii) Thin-layer chromatography was carried out using glass plates coated with aluminium oxide (0.3 mm, Merck, 60G, type E) containing Woelm fluorescent green indicator (0.5%) or pre-coated plastic sheets (0.25 mm silica gel or 0.2 mm aluminium oxide) with UV fluorescent indicator from Macherey-Nagel.

(iii) Gravity column chromatography was carried out using alumina (Laporte Industries, type H) deactivated to 6% by the addition of water. Dry-flash column chromatography was carried out, by the method of Harwood, using Merck silica gel, grade 60 (230-400 mesh, 60 μ).
Elemental Analysis

Microanalyses were obtained using a Perkin-Elmer 204 elemental analyser operated by Mr. J. Grunbaum or by Mrs E. McDougal on a Carlo Erba Elemental Analyser model 1106.

Infra-red Spectroscopy

Spectra were recorded, as liquid films or nujol mulls, on a Perkin Elmer 781 spectrometer.

Solvents

Commercially available solvents were used without further purification, except for light petroleum which was distilled. All light petroleum used had b.p. 40-60°C unless otherwise stated. Dry ether was prepared by heating sodium dried ether under reflux with lithium aluminium hydride for 2 h then distilling off the ether. Dry tetrahydrofuran was prepared by heating tetrahydrofuran under reflux with calcium hydride then collecting by distillation.
C. Pyrolysis Apparatus and General Techniques

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 Figure 1. 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 600-1000°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 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.

Figure 1
Small scale pyrolyses were generally carried out with sample sizes of 0.1-1.0 mmol. The entire pyrolysate was dissolved in deuteriochloroform and analysed by $^1$H n.m.r., g.c. and in some cases g.c./m.s. Products were characterised by comparison with authentic samples. In most cases two independent methods of identification were used: comparison with an authentic sample by g.c. and comparison with the $^1$H n.m.r. spectrum of an authentic sample. In some cases comparison of m.s. breakdown patterns was also used. 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.c., after calibration of the detector response, using an internal standard. Relative yields were obtained by g.c. in some cases.

For preparative scale experiments sample sizes of 0.2 - 2 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.
D. The Generation and Cyclisation of 2-(Arylamino)-phenylaminyl Radicals

1. Preparation of 2-Amino-4'-methyldiphenylamine

(a) 4-Methylformanilide. A mixture of formamide (18 g, 0.4 mol), p-toluidine (32.1 g, 0.3 mol) and acetic acid (45 g, 1.8 mol) was heated on an oil bath at 60°C. The reaction was followed by t.l.c. (alumina, ether) and after 1 h no p-toluidine remained. The reaction mixture was allowed to cool before it was added to water (300 ml). The mixture was then washed with a 10% ammonium carbonate solution (300 ml) and was extracted with methylene chloride (4 x 100 ml). The organic layer was separated, dried (MgSO$_4$) and the solvent was evaporated to leave a brown oil which crystallised on trituration with ether. Recrystallisation from benzene/cyclohexane (20:80) gave the required product (22.7 g, 56%), m.p. 48-50°C (lit., 53°C).

(b) 2-Nitro-4'-methyldiphenylamine. This compound was prepared by a modification of the method of Rondestvedt. Toluene (25 ml) was heated, under nitrogen, in an oven-dried round bottom flask fitted with a dropping funnel, mechanical stirrer (glass blade) and a condenser. Sodium (0.8 g, 35 mmol) was added in large pieces, with vigorous stirring, then with the pot temperature above 100°C molten 4-methylformanilide (5.0 g, 37 mmol) was added via the
dropping funnel. While still hot, the apparatus was re-assembled for distillation, and a solution of 2-nitrochlorobenzene (5.0 g, 31.7 mmol) in dimethylformamide (5 ml) was added in one portion and the temperature was raised so that the toluene distilled off. The temperature rose to about 150°C, whereupon the reaction became exothermic, but was controlled by removing the heating mantle when necessary. The temperature was maintained at 150-155°C for 2 h after which the dimethylformamide was removed by distillation and sodium hydroxide solution (30%, 5 ml) was added to the warm residue. The hydrolysis of the excess formanilide was completed during steam distillation (ca. 50 ml distillate collected), to remove p-toluidine and unreacted 2-nitrochlorobenzene. The cooled residue was extracted with methylene chloride (2 x 50 ml), the combined organic layers were washed with water (50 ml), dried (MgSO\textsubscript{4}), and the solvent was removed in vacuo. The black oil obtained was purified by bulb-to-bulb distillation to give the required nitro-compound as a red solid (4.15 g, 57%), m.p. 64-65°C (lit., 186.69°C), δH 9.42 (1H, br.s), 8.19 (1H, dd), 6.0-7.45 (6H, m), 6.72 (1H, m) and 2.37 (3H, s); δC 143.51(q), 135.78(q), 135.46, 132.70(q), 130.13, 126.43, 124.62, 116.90, 115.78 and 20.81 (one quaternary signal is not apparent).
(c) 2-Amino-4'-methyldiphenylamine.

Palladium charcoal (5%, 300 mg) was suspended in water (25 ml) and a solution of sodium borohydride (4.0 g, 0.11 mol) was added. A slow stream of nitrogen was bubbled through the mixture, and a solution of 2-nitro-4'-methyldiphenylamine (4.10 g, 18 mmol) in the minimum amount of methanol (ca. 200 ml) was added dropwise. The reaction mixture was stirred overnight at room temperature and was filtered to remove catalyst. The filtrate was acidified to destroy any excess of sodium borohydride, and was finally made basic (NaOH). It was then extracted with ether (3 x 200 ml), and the organic extracts were dried (MgSO₄) and concentrated to leave the amine (1.07 g, 31%), b.p. 123 °C (0.3 Torr), which was not, however, obtained in crystalline form [m.p. (lit.¹¹⁰) 77 °C], δH 6.5-7.5 (8H, m), 5.0 (1H, br.s), 3.5 (2H, br.s) and 2.27 (3H, s); δC 142.59(q), 141.21(q), 129.62, 128.68(q), 124.92, 123.75, 119.01, 116.00, 115.67 and 20.31 (one quaternary signal is not apparent).

2. Preparation of 2-(Allylamino)diphenylamines

The following general method was used: the appropriate amine (0.02 mol) was dissolved in dimethylformamide (50 ml) containing potassium carbonate (0.15 mol). Allyl bromide (0.015 mol) was added dropwise, with stirring, and the
mixture was stirred at room temperature for the time stated. The excess of potassium carbonate was filtered through celite, water (100 ml) was added to the filtrate, and the solution was extracted with ether (3 x 100 ml). The combined organic layers were washed with water (3 x 100 ml), dried (MgSO₄) and the solvent was removed in vacuo. The resulting mixture of starting material, N-allyl compound and a small amount of N,N-diallyl derivative was separated by column chromatography on alumina using 20% ether in light petroleum as eluant. Fractions from the column were monitored by g.c. The fractions containing the required product were combined, the solvent was removed and the remaining material was purified by distillation. The following compounds were prepared by this method:

2-(Allylamino)diphenylamine (stirred for 23 h) (53%), b.p. 148-150°C (0.5 Torr) (Found: C, 80.35; H, 6.95; N, 12.4 C₁₅H₁₆N₂ requires C, 80.3; H, 7.2; N, 12.5%); δH 6.64-7.35 (9H, m), 6.00 (1H, m), 5.0-5.5 (3H, m), 4.23 (1H, br.s.) and 3.85 (2H, m); δC 145.72(q), 143.86(q), 135.32, 129.15, 128.09(q), 126.09, 124.96, 119.15, 117.25, 115.89, 115.13, 111.29 and 46.17; m/z 224 (M⁺, 63%), 195 (88), 183 (59), 182 (100), 105 (31) and 77 (38).

2-(Allylamino)-4'-methyldiphenylamine (stirred for 48 h) (48%), b.p. 175-178°C (0.3 Torr) (Found: M⁺ 238.1484; C₁₆H₁₈N₂ requires M⁺ 238.1470); δH 6.55-6.9 (4H, m), 7.0-7.25 (4H, m), 6.0 (1H, m), 5.05-5.45 (2H, m),...
5.0 (1H, br.s), 4.18 (1H, br.s), 3.82 (2H, m) and 2.32 (3H, s); δC 143.38(q), 143.06(q), 135.35, 129.66, 128.97(q), 128.67(q), 125.53, 124.04, 117.31, 115.91, 115.64, 111.29, 46.24 and 20.38; m/z 238 (M⁺, 50%), 209 (68), 194 (21) and 182 (100).

3. Preparation of an Authentic Sample of 2-Methylphenazine

(a) 2-Methyl-5,6,7,8-tetrahydrophenazine

A mixture of 3,4-diaminotoluene (3.6 g, 29.5 mmol), cyclohexane-1,2-dione (3.3 g, 29.5 mmol), sodium acetate (5 g, 61 mmol) and glacial acetic acid (15 ml) was heated under reflux for 2 h. The solution was poured into water and was made alkaline. The mixture was then extracted with ether (3 x 50 ml), the combined organic extracts were washed with water (3 x 50 ml), dried (MgSO₄), the solvent was removed in vacuo and the remaining oil was distilled, b.p. 110-114°C (0.4 Torr). The product slowly crystallised (1.90 g, 32%), m.p. 79-80°C (lit. 78°C), δH 7.79 (1H, d), 7.70 (1H, s), 7.43 (1H, dd), 3.02-3.19 (4H, m), 2.52 (3H, s) and 1.90-2.07 (4H, m); δC 153.67(q), 152.83(q), 141.06(q), 139.44(q), 138.96(q), 130.92, 127.60, 127.00, 32.89, 22.60 and 21.49 (signal corresponds to two carbons at 22.60).
(b) **2-Methylphenazine**

2-Methyl-5,6,7,8-tetrahydrophenazine was dehydrogenated using a gas phase technique. The central part of a silica pyrolysis tube (35 x 2.5 cm) was packed with pellets of palladium (0.5%) on alumina, which were conditioned under vacuum at 550°C for 3 h. 2-Methyl-5,6,7,8-tetrahydrophenazine (0.92 g, 5 mmol) was distilled (140°C, 0.01-0.6 Torr) through the furnace tube (2.5 h) to give a yellow crystalline pyrolysate (0.51 g). 2-Methylphenazine was separated from unreacted tetrahydro-compound by column chromatography (alumina, chloroform) and was recrystallised from light petroleum to give the product as yellow needles (0.5 g, 53%), m.p. 114-115°C (lit. 187, 117°C), δH 8.1-8.3 (3H, m), 7.99 (1H, s), 7.75-7.9 (2H, m), 7.67 (1H, d.d.) and 2.65 (3H, s); δC 143.51(q), 143.36(q), 142.88(q), 142.21(q), 141.01(q), 133.34, 130.11, 129.71, 129.48, 129.41, 128.98, 127.55 and 22.07.

4. **Preparation of [1-\textsuperscript{15}N]-2-(Allylamino)-4'-methylidiphenylamine**

(a) **[\textsuperscript{15}N]-4-Methylformanilide**

p-Toluoyl chloride was prepared by heating under reflux a mixture of thionyl chloride (18 ml) and p-toluic acid until the evolution of gases had ceased (1.5 h). The resulting oil was purified by distillation to give
p-toluoyl chloride (17.45 g, 92%), b.p. 96°C (12 Torr) [lit.\textsuperscript{188}, 102°C (15 Torr)].

\[^{15}\text{N}\]-\(p\)-Toluamide was prepared using the \(p\)-toluoyl chloride generated above. A solution of ammonium nitrate (3.92 g; 5.6% \(^{15}\text{NH}_4\text{NO}_3\)) in water was cooled in ice and a solution of sodium hydroxide (4.13 g, 0.1 mol) in water (35 ml) was added. The mixture was shaken for 1 h. with a solution of \(p\)-toluoyl chloride (7 g, 0.05 mol) in chloroform (400 ml). The chloroform layer was separated and the aqueous layer was extracted with ether (3 x 30 ml). The ether extracts were combined with the chloroform layer, dried (MgSO\(_4\)) and the solvents were removed \textit{in vacuo}. The resulting solid was washed with light petroleum and was filtered to give the required \[^{15}\text{N}\]-\(p\)-toluamide (6.1 g, 98%), \(\delta\)H 7.70 (2H, d), 7.21 (2H, d), 5.90 (2H, br.s) and 2.38 (3H, s).

\[^{15}\text{N}\]-\(p\)-Toluamide was converted to \[^{15}\text{N}\]-\(p\)-toluidine via a Hofmann reaction. A solution of sodium hypobromite was prepared, at 0°C, by the addition of bromine (2.7 g, 0.02 mol) to a solution of sodium hydroxide (10.8 g, 0.27 mol) in water (90 ml). \[^{15}\text{N}\]-\(p\)-toluamide (6 g, 0.04 mol) was added and the mixture was shaken until solution was complete. The mixture was heated to 70°C, this temperature was maintained for 20 min then the solution was subjected to steam distillation for 45 min. The amine was extracted from the distillate
with ether (3 x 45 ml), the extracts were dried (MgSO₄) and the solvent was removed in vacuo to give the required \[^{15}\text{N}]\text{-p-toluidine} (2.19 g, 51%), \delta H 7.0 (2H, d), 6.62 (2H, d), 3.50 (2H, br.s) and 2.24 (3H, s), which was used without further purification.

Finally \[^{15}\text{N}]\text{-4-methylformanilide} was prepared from formamide (1.09 g, 24 mmol), \[^{15}\text{N}]\text{-p-toluidine} (2.2 g, 18.6 mmol) and acetic acid (3.24 g, 54 mmol) as previously described in section 1(a). The crude material was recrystallised from benzene/cyclohexane (20:80) to give the required \[^{15}\text{N}]\text{-4-methylformanilide} (2.55 g, 91%), m.p. 46-49°C (lit. 185, 53°C).

(b) \[^{1-15}\text{N}]\text{-2-Nitro-4'-methylidiphenylamine}

This reaction was carried out using the formanilide from (a), on exactly one half of the scale described for the unlabelled compound in 1(b). The reaction was more difficult to control on a small scale and very impure product was obtained which could not be purified by distillation. However, column chromatography on alumina with ether/light petroleum (50:50) as eluant gave the pure \[^{1-15}\text{N}]\text{-2-nitro-4'-methylidiphenylamine} (0.46 g, 13%).
(c) \textit{[1-^{15}N]-2-Amino-4'-methyldiphenylamine}

Reduction of the nitro compound (0.38 g, 1.7 mmol) from (b) using NaBH$_4$/Pd/C was more efficient than described for the unlabelled compound in 1(c), probably because the solubility problems were less on the smaller scale. The yield of \textit{[1-^{15}N]-2-amino-4'-methyldiphenylamine}, which was used without further purification, was (0.17 g, 50%).

(d) \textit{[1-^{15}N]-2-(Allylamino)-4'-methyldiphenylamine}

The amino compound (0.15 g, 0.74 mmol) from (c) was reacted with allyl bromide (0.73 g, 0.6 mmol) in dimethylformamide (10 ml) containing potassium carbonate (0.83 g, 6.6 mmol) as previously described for the unlabelled compound in 2. Column chromatography, as before, gave \textit{[1-^{15}N]-2-(allylamino)-4'-methyldiphenylamine} (0.07 g, 40%).

5. Pyrolysis of \textit{2-(Allylamino)diphenylamines}

(a) \textit{2-(Allylamino)diphenylamine}

0.071 g (0.320 mmol), 70°C, 750°C, 1 x 10\textsuperscript{-3} Torr, 60 min: phenazine (57%); 2-aminodiphenylamine (7%); 1-aminocarbazole (8%). [Yields obtained by g.c. comparison (5% SE30) with authentic (or isolated) samples]. On a preparative scale the amine (1.494 g, 6.67 mmol) was distilled at 1 x 10\textsuperscript{-3} Torr into a furnace at 750°C over a period of 2 h. The entire pyrolysate was suspended in chloroform and was set aside for 2 h to allow aerial oxidation of the insoluble dihydrophenazine.
The entire pyrolysate was chromatographed on a column of alumina and eluted with ether (50%) in light petroleum. The first component to be eluted was the major product phenazine (crude wt. = 0.265 g). This crude material was recrystallised from acetic acid to give pure phenazine (0.195 g, 16%), m.p. 174-175°C, mixed m.p. 175-176°C (lit. 189-175-176°C), δH 8.14-8.31 (4H, m) and 7.24-7.92 (4H, m); δC 143.28(q), 130.19 and 129.46. These 1H n.m.r. and 13C n.m.r. chemical shifts were identical to those of an authentic sample of phenazine: δH 8.12-8.29 (4H, m) and 7.25-7.90 (4H, m); δC 143.29(q), 130.19 and 129.47. The second component was 2-amino-diphenylamine (0.10 g, 7%), b.p. 106-108°C (0.4 Torr) which could not be obtained in a crystalline form; δH 6.65-7.31 (9H, m), 5.2 (1H, br.s) and 3.75 (2H, br.s); δC 145.25(q), 141.83(q), 129.18, 128.43(q), 125.58, 124.79, 119.18, 119.01, 116.01 and 115.09. However, the 1H n.m.r. and 13C n.m.r. spectra were identical to those of an authentic sample; δH 6.55-7.38 (9H, m), 5.16 (1H, br.s) and 3.42 (2H, br.s); δC 145.23(q), 141.83(q), 129.15, 128.39(q), 125.57, 124.78, 119.14, 118.97, 116.00 and 115.06. Further elution of the column with methanol gave 1-aminocarbazole (0.19 g, 15%), m.p. 187-189°C (lit. 115, 193°C), δH ([2H₆]DMSO), 10.84 (1H, s), 8.00 (1H, d), 7.50 (1H, d), 7.34 (2H, m), 7.11 (1H, t), 6.92 (1H, t), 6.67 (1H, d) and 5.16 (2H, br.s);
(b) 2-(Allylamino)-4'-methyldiphenylamine

0.012 g (0.09 mmol), 100°C, 750°C, 1 x 10⁻³, 40 min:

2-Methyiphenazine (40%); 2-amino-4'-methyldiphenylamine (11%); 1-amino-6-methylcarbazole (10%). On a larger scale the amine (0.27 g, 1.13 mmol) was pyrolysed (750°C, 1 x 10⁻³ Torr) over a period of 2.25 h. The entire pyrolysate was suspended in chloroform and was set aside for 2 h to allow aerial oxidation of the insoluble dihydrophenazine. The solvent was removed and column chromatography of the residue on alumina, with light petroleum/ether (60:40) as eluant, gave a mixture of 2-methyiphenazine and 2-amino-4'-methyldiphenylamine which could not be further separated by chromatography on either alumina or silica. Further elution of the column with methanol gave a small amount of impure 1-amino-6-methylcarbazole (0.015 g, 7%), b.p. 89-92°C (0.3 Torr) (Found M⁺ 196.1000; C₁₃H₁₂N requires M⁺ 196.1000); δH (acetone) 7.87 (1H, s), 7.76 (1H, d), 7.37 (1H, d), 7.18 (1H, d), 7.09 (1H, t), 6.67 (1H, d) and 2.47 (3H, s); m/z 196 (M⁺, 100%), 182(31), 122(15) and 89(60).
Separation of the mixture of the phenazine and diphenylamine (0.157 g) was effected by acetylation of the diphenylamine using acetic anhydride (0.4 ml) at 100°C (5 min). The cooled mixture was diluted with water (10 ml), was basified (NaOH), and was extracted with methylene chloride (3 x 10 ml). The extracts were dried (MgSO₄), concentrated and chromatographed on alumina, using chloroform as eluant, to give 2-methylphenazine (0.12 g) as the first component. This crude material was purified by sublimation, 88-90°C (0.3 Torr), to give pure 2-methylphenazine (0.093 g, 42%), m.p. 114-116°C [from light petroleum], mixed m.p. 112-114°C (lit. 187, 117°C), δH 8.16-8.25 (2H, m), 8.10 (1H, d), 7.96 (1H, s), 7.73-7.83 (2H, m), 7.63 (1H, dd) and 2.62 (3H, s); δC 143.59(q), 143.44(q), 142.95(q), 142.28(q), 141.04(q), 133.38, 130.12, 129.73, 129.56, 129.46, 129.04, 127.63 and 22.05. The ¹H n.m.r. and ¹³C n.m.r. spectra are identical to those of the authentic sample previously quoted. The second component from the column consisted of impure 2-acetylaminod-4'-methyldiphenylamine (0.024 g, 9%) (Found: M⁺ 240.1262; C₁₅H₁₆N₂O requires M⁺ 240.1262); δH 6.6-7.8 (10H, m), 2.26 (3H, s) and 2.08 (3H, s); m/z 240 (M⁺, 95%), 222(100), 198(40) and 182(45%).
6. Pyrolysis of [1-$^{15}$N]$^{-2}$-(Allylamino)-4'-methyl-
diphenylamine

0.079 g (0.33 mmol), 100°C, 750°C, $1 \times 10^{-3}$ Torr,
75 min; the pyrolysate was suspended in [$^2$H] chloroform
and set aside in air until the solid had dissolved.
This solution was used for $^{15}$N n.m.r. spectra, without
further purification; the results are reported in
the Discussion section.
E. The Generation and Cyclisation of 2-Thiophenoxybenzyl and 2-Benzylthiophenoxy Radicals

1. Preparation of 2-Mercaptodiphenylmethane
(a) (2-Benzylphenyl)ethyl xanthate

In a round bottom flask, equipped with a stirrer and thermometer, was placed concentrated hydrochloric acid (10 ml) and crushed ice (10 g) and the flask was immersed in an ice-bath. 2-Benzylaniline (0.1 g, 0.05 mol) was added slowly, with stirring, and the mixture was cooled to 0 ° C. A cold solution of sodium nitrite (3.7 g, 0.05 mol) in water (8.5 ml) was added, the temperature being kept below 4 ° C. After an additional 30 min at this temperature to ensure complete decomposition, the red oily layer was separated and the aqueous layer was extracted with ether (2 x 10 ml). The combined oil and ether extracts were washed with sodium hydroxide solution (10%, 10 ml) and then with water until the water washings were neutral to litmus. The ether solution was dried (MgSO₄) and the solvent was removed in vacuo to give the required (2-benzylphenyl)ethyl xanthate.
(b) 2-Mercaptodiphenylmethane

The crude ethyl xanthate was dissolved in ethanol (150 ml) and the solution was heated until boiling. The source of heat was removed and potassium hydroxide pellets (12 g) were added to the hot solution at such a rate that it kept boiling. The mixture was then heated overnight under reflux by which time successive aliquots were completely soluble in water. Most of the ethanol was removed under vacuum, water (40 ml) was added and the aqueous solution was extracted with ether (3 x 30 ml). The aqueous mixture was acidified by the addition of hydrochloric acid then the mixture was extracted with ether (3 x 100 ml), the ether solution was dried (MgSO₄) and the solvent was removed in vacuo. A brown oil was obtained which partially solidified (crude wt. 2.38 g). On triturating the oily mixture with light petroleum the required product was obtained as a pale brown solid (0.52 g, 5%), m.p. 44-47°C (from light petroleum) (Found: C, 78.2; H, 6.05 C₁₃H₁₂S requires C, 78.0; H, 6.0%); δH 7.13-7.50 (9H, m), 4.19 (2H, s) and 3.39 (1H, s); δC 139.27(q), 139.05(q), 131.05, 130.83(q), 130.49, 128.77, 128.39, 126.90, 126.11 and 40.35 (two signals are co-incidental); m/z 200 (M⁺, 96%), 165(50) and 122(100).
2. Preparation of 2-Mercapto-4'-methyldiphenyl-methane

(a) 2-Amino-4'-methylbenzophenone

A mixture of sodium carbonate (29 g, 0.27 mol) and water (165 ml) was placed in a round bottom flask equipped with a mechanical stirrer and while the mixture was warmed anthranilic acid (15 g, 0.12 mol) was added. The temperature was raised to 70°C to effect complete solution then the mixture was cooled to 60°C and p-toluenesulphonyl chloride (25.3 g, 0.13 mol) was added, with stirring, in five portions over a period of 20 min. When all the p-toluenesulphonyl chloride had been added the reaction mixture was maintained at 60-70°C for an additional 20 min. The temperature was raised to 85°C and charcoal (1.1 g) was added then the solution was filtered. Hydrochloric acid (12M, 30 ml) and water (30 ml) were placed in a beaker (500 ml) equipped with a stirrer which could operate above the liquid level to break the foam. The filtrate obtained previously was cooled to 50°C and was added to the hydrochloric acid at such a rate that the mixture did not foam over. The mixture was filtered and was washed with dilute hydrochloric acid (7 ml of 10M HCl diluted to 30 ml) then with water (60 ml). The solid was dried to give p-toluenesulphonylanthranilic acid (15.3 g, 48%).
A mixture of dry \( p \)-toluenesulphonylanthranilic acid (30 g, 0.1 mol), phosphorus pentachloride (23.8 g, 0.11 mol) and toluene (300 ml) was placed in a dry round bottom flask equipped with a mechanical stirrer and connected to a hydrogen chloride trap. The stirred solution was heated to 50°C for 30 min then was cooled to 20-25°C and aluminium chloride (60 g, 0.45 mol) was added in four portions. The resulting mixture was stirred at 80-90°C for 4 h, then was cooled to room temperature and poured onto a mixture of ice (100 g) and hydrochloric acid (12M, 8 ml). Toluene was removed in vacuo and the grainy brown product was filtered. It was washed thoroughly with dilute hydrochloric acid, water, then with sodium carbonate solution (5%, 2 x 100 ml) and finally with water (3 x 100 ml). The crude sulfonamide was dissolved in concentrated sulphuric acid (300 ml) and was warmed on a steam bath for 15 min. The acid solution was divided into two equal portions, for ease of neutralisation, each being placed in a 1 1 beaker, and the beakers were cooled in ice. Ice (320 g) was slowly added with stirring then charcoal (10 g total) was added, and the solution was filtered. The filtrates were poured onto ice and were neutralised separately by the addition, with stirring, of ammonia (d. 0.88). The yellow solid was filtered off and dried to give 2-amino-4'-methyl-benzophenone (7.81 g, 31%), m.p. 90-92°C (lit. 126°C, 90-92°C), \( \delta \)H 7.17-7.62 (6H, m), 6.50-6.77 (2H, m), 5.74 (2H, br.s) and 2.42 (3H, s).
(b) 2-Amino-4'-methyldiphenylmethane

This compound was prepared by modification of the method described in Vogel. 127 A mixture of 2-amino-4'-methylbenzophenone (7.5 g, 35.5 mmol), hydrazine hydrate (4.5 ml) and potassium hydroxide pellets (5.38 g, 96 mmol) in diethylene glycol (65 ml) was heated under reflux for 1 h. The condenser was then removed and the flask was fitted for distillation. The mixture was distilled until the temperature of the liquid rose to 190°C then the mixture was heated under reflux for a further 3 h. The solution was cooled, added to water (50 ml) and was extracted with ether (3 x 30 ml). The ether extracts were washed with water, dried (MgSO₄) and the solvent was removed in vacuo. The light brown solid obtained was purified by sublimation, 156-158°C (0.2 Torr) to give the pure product as a yellow solid (4.5 g, 61%), m.p. 56-60°C (from hexane) (Found: C, 85.0; H, 7.85; N, 7.05 C₁₄H₁₅N requires C, 85.3; H, 7.6; N, 7.1%); δH 6.66-7.25 (8H, m), 3.91 (2H, s), 3.42 (2H, br.s) and 2.37 (3H, s); δC 144.53(q), 136.10(q), 135.68(q), 130.66, 129.19, 128.22, 127.41, 125.18(q), 118.54, 115.73, 37.52 and 20.83; m/z 197 (M⁺, 100%), 182(29), 164(35) and 106(21).

(c) 2-Mercapto-4'-methyldiphenylmethane

2-Amino-4'-methyldiphenylmethane (4.5 g, 23 mmol) was diazotised then was reacted with potassium ethyl
xanthate (4.38 g, 23 mmol), as previously described in 1(a). The ethyl xanthate obtained was dissolved in dry ether (45 ml) then reduced to the appropriate thiol using lithium aluminium hydride since the potassium hydroxide method used previously gave a very poor yield. The ethereal solution of ethyl xanthate was added dropwise to a stirred slurry of lithium aluminium hydride (0.95 g, 25 mmol) in dry ether (45 ml) at such a rate that the ether refluxed gently. The mixture was stirred at room temperature for 1.5 h after the addition was complete. The excess of lithium aluminium hydride was destroyed by the dropwise addition of water (7 ml), with rapid stirring since the mixture became thick. The solid was destroyed by the addition of sulphuric acid (10%, 25 ml), then the ether layer was separated and the aqueous layer was extracted with ether (3 x 40 ml). The required product was isolated from the ether solution but was found to be contaminated with minor impurities. The oily mixture was dissolved in methylene chloride and extracted with sodium hydroxide solution (1M, 80 ml). The basic solution was neutralised, extracted with methylene chloride, dried (MgSO₄) and the solvent was removed in vacuo to leave an orange oil (crude wt. 0.86 g). The crude product was purified by distillation, b.p. 128–134°C (0.1 Torr) to leave 2-mercapto-4'-methylidiphenylmethane as a pale yellow liquid which crystallised on cooling (0.72 g, 15%). A small amount was further
purified, for characterisation, by dry-flash chromatography eluting with methylene chloride/hexane (30:70). The clear oil isolated was distilled, b.p. 140-142°C (0.1 Torr), to give the pure product, on cooling, as a colourless solid, m.p. 39-41°C (from light petroleum) (Found: C, 78.8; H, 6.65 \( \text{C}_{14}\text{H}_{14}\text{S} \) requires C, 78.5; H, 6.55%); δH 7.09-7.31 (8H, m), 4.04 (2H, s), 3.30 (1H, s) and 2.33 (3H, s); δC 139.31(q), 136.22(q), 135.66(q), 131.02, 130.92(q), 130.51, 129.19, 128.73, 126.90, 126.11, 40.03 and 20.95; m/z 214 (M\(^+\), 94%), 197(24), 181(19), 165(59) and 122(100).

3. **Preparation of 2-(Allyl mercapto)diphenyl-methanes**

The appropriate thiophenol (1.9 mmol) was reacted with allyl bromide (2 mmol) in dimethylformamide (7 ml) containing potassium carbonate (2 mmol) as previously described in Section D2. The reaction mixture was stirred overnight at room temperature and the product was purified by distillation. The following compounds were prepared by this method: 2-(Allyl mercapto)diphenylmethane (71%), b.p. 140°C (0.1 Torr) (Found: C, 79.8; H, 6.75 \( \text{C}_{16}\text{H}_{16}\text{S} \) requires C, 80.0; H, 6.65%); δH 7.19-7.52 (9H, m), 5.72-6.02 (1H, m), 5.07-5.31 (2H, m), 4.28 (2H, s) and 3.55 (2H, d); δC 141.11(q), 140.32(q), 135.22(q), 133.37, 130.11, 128.90, 128.20, 126.65, 126.28, 125.86, 117.52, 39.54 and 37.15 (two peaks co-incidental at
2-(Allylmercapto)-4'-methyldiphenylmethane (55%), b.p. 140°C (0.1 Torr). The isolated oil was further purified by dry-flash chromatography, with methylene chloride/hexane (30:70) as eluant, to give the required product as a clear oil, b.p. 151°C (0.1 Torr) (Found: C, 80.6; H, 7.2; C_{17}H_{18}S requires C, 80.3; H, 7.1%); δH 7.39-7.43 (1H, d), 7.14-7.26 (7H, m), 5.91 (1H, m), 5.09-5.22 (2H, m), 4.18 (2H, s), 3.53 (2H, d) and 2.37 (3H, s); δC 141.32(q), 137.22(q), 135.30(q), 135.21(q), 133.41, 130.01, 129.98, 128.93, 128.79, 126.57, 126.23, 117.52, 39.11, 37.11 and 20.87; m/z 254 (M^+, 83%), 214(47), 213(100), 211(82), 197(61), 178(35), 165(74) and 112(31).

4. Preparation of Related 2-Thiophenoxybenzoic acids

Anthranilic acid (11.6 g, 85 mmol) was added to a mixture of concentrated hydrochloric acid (19 ml) and water (50 ml) and the mixture was swirled until the amine had dissolved. The solution was cooled to 2-5°C and sodium nitrite (3.14 g, 43 mmol) in water (15 ml) was added dropwise. (Note: the quantity of sodium nitrite used in these preparations was accidentally, exactly one half that which was actually required, hence yields of products will be calculated from the molar quantity of the nitrite actually used).
A mixture of the appropriate thiophenol (90 mmol), sodium hydroxide (17.4 g, 0.44 mol) and water (85 ml) was heated to 45-50°C, on a water bath, and the diazonium salt prepared above was added from a dropping funnel in a slow stream. The alkaline solution became red and nitrogen was evolved. The mixture was warmed on a water bath for 1 h, or until all the nitrogen had evolved, then the mixture was cooled, acidified and the precipitated acid was filtered. The acid was dissolved in sodium carbonate solution and the phenyldisulphide which precipitated was filtered off. The solution was re-acidified and the solid obtained was separated by filtration, washed with water then with light petroleum to remove excess thiophenol, and dried. The following compounds were prepared by this method: 2-thiophenoxybenzoic acid (4.93 g, 50%), m.p. 159-160°C (from methanol) (lit.130, 160°C), δH 9.80 (1H, br.s), 8.13 (1H, d), 7.56-7.71 (2H, m), 7.41-7.47 (3H, m), 7.10-7.32 (2H, m) and 6.82 (1H, d): 2-(4-methylthiophenoxy)benzoic acid (4.61 g, 44%), m.p. 210-212°C (from methanol) (lit.190, 215-216°C), δH ([2H₆]DMSO): 7.90 (1H, d), 7.13-7.44 (6H, m), 6.70 (1H, d), 3.36 (1H, br.s) and 2.36 (3H, s).

5. Preparation of Related 2-Thiophenoxybenzyl alcohols131

A solution of the appropriate benzoic acid (16 mmol) in dry ether (100 ml) was slowly added to a stirred slurry of lithium aluminium hydride (16 mmol) in dry ether (40 ml).
The mixture was heated under reflux for 4.5 h then allowed to cool. Excess hydride was destroyed by the addition of wet ether (5 ml) then water (10 ml) and finally dilute hydrochloric acid (20 ml). The mixture was filtered through celite, the ether layer was separated and the aqueous layer was extracted with ether (2 x 50 ml). The ether solution was washed with sodium carbonate solution (10%, 2 x 50 ml), dried (MgSO$_4$) and the solvent was removed in vacuo. The crude product was purified by distillation. The following compounds were prepared by this method: 2-thiophenoxybenzyl alcohol (1.99 g, 58%), b.p. 131-133°C (0.2 Torr) to give a colourless oil which solidified on cooling, m.p. 41-43°C (lit. $^{13}$1, 44°C), $\delta$H 7.17-7.46 (9H, m), 4.77 (2H, s) and 2.25 (1H, br.s); $\delta$C 142.44(q), 136.04(q), 133.92, 132.43(q), 129.44, 129.13, 128.36, 126.51 and 63.46 (three signals co incidental at 128.36): 2-(4-methyl-thiophenoxy)benzyl alcohol (60%), b.p. 145-148°C (0.15 Torr) [lit. $^{19}$1, 185-188°C (5 Torr)], $\delta$H 7.0-7.57 (8H, m), 4.78 (2H, s), 2.70 (1H, br.s) and 2.35 (3H, s); $\delta$C 141.31(q), 136.77(q), 133.48(q), 132.33, 131.48(q), 130.48, 129.83, 127.98, 127.50, 63.64 and 20.77 (signals correspond to two carbon atoms at 130.48, 129.83 and 127.98).
6. **Preparation of Related Bis[2-(thiophenoxy)benzyl] Oxalates**

Symmetrical dibenzyl oxalates were prepared by the general method of Trahanovsky et al.\(^{132,133}\) A solution of oxalyl chloride (4 mmol) in dry ether (9 ml) was added dropwise over a period of ca. 5 min to a stirred, ice-cold solution of the appropriate benzyl alcohol (9 mmol) and triethylamine (12 mmol) in dry ether (90 ml) and the mixture was stirred, at room temperature, for 2 h. A white precipitate formed immediately. At the end of the reaction water was added until the precipitate had dissolved and the ether layer was separated. The aqueous layer was extracted with ether (2 x 40 ml), the combined organic layers were dried (MgSO\(_4\)) and the solvent was removed in vacuo. The crude isolated product was purified by recrystallisation. The following compounds were prepared by this method:

- **Bis[2-(thiophenoxy)benzyl] oxalate** (2.10 g, 98%), m.p. 117-120°C (from ethanol)
  
  (Found: C, 68.8; H, 4.5 \(\text{C}_{26}\text{H}_{22}\text{O}_4\text{S}_2\) requires C, 69.15; H, 4.55%); \(\delta \text{H} 7.49 \text{ (3H, m)}, 7.16-7.41 \text{ (15H, m) and 5.44 \text{ (4H, s)}}\); \(\delta \text{C} 157.04 \text{ (C=O), 135.82(q), 135.62(q), 134.20(q), 133.93, 129.81, 129.41, 129.11, 128.18, 126.67 and 66.40 (signals correspond to two carbon atoms at 129.81, 129.41 and 129.11); m/z 486 (M\(^+\), 67%); 197(100), 184(17), 165(21) and 104(17):**

- **Bis[2-(4-methylthiophenoxy)benzyl] oxalate** (63%), m.p. 130-132°C (from acetonitrile) (Found: C, 69.5; H, 5.1 \(\text{C}_{30}\text{H}_{26}\text{O}_4\text{S}_2\cdot 0.25\text{H}_2\text{O}\) requires C, 69.45; H, 5.4%) (analyses consistently
with 0.25 mol water); \( \delta H \) 7.45-7.51 (2H, m), 7.04-7.34 (14H, m), 5.48 (4H, s) and 2.32 (6H, s); \( \delta C \) 157.13 (C=O), 137.10(q), 135.48(q), 134.97(q), 132.70, 131.37(q), 130.96, 129.92, 129.19, 127.47, 66.30 and 20.81 (signals correspond to two carbon atoms at 130.96, 129.92 and 129.19); m/z 514 (M\(^+\), 61%), 392(27), 302(23), 211(100), 181(7%) and 91(36).

7. Preparation of Authentic Samples for Comparison with Pyrolysates

Preparation of Thioxanthene 134

Thioxanthone (1.5 g, 7 mmol) was dissolved in dry tetrahydrofuran (30 ml) and the stirred solution was cooled to 0°C. The mixture was treated with 1M diborane in tetrahydrofuran (14 ml) and was allowed to warm to room temperature. The reaction was monitored by g.c. (5% SE30) and after stirring at room temperature for 1.5 h no xanthone was present. The mixture was cooled to 0°C and excess diborane was destroyed by the addition of small ice chips. The mixture was diluted with an equal amount of water and tetrahydrofuran was removed in vacuo whereupon thioxanthene crystallised from the reaction mixture. The solid was filtered and purified by recrystallisation from methanol to leave the pure product as a colourless crystalline solid (0.70 g, 50%), m.p. 128-130°C (lit.\(^1\)92, 130°C), \( \delta H \) 7.17-7.56 (8H, m) and 3.90 (2H, s); \( \delta C \) 136.06(q), 133.79(q), 127.78, 126.71, 126.44, 126.38 and 39.08.
Preparation of 2-Methylthioxanthene

(a) 2-Methylthioxanthone  A mixture of 2-(4-methylthiophenoxy)benzoic acid (0.70 g, 2.9 mmol) and concentrated sulphuric acid (5 ml) was heated on a water bath at 100°C for 1 h. The mixture was cooled and was poured into water (100 ml). The aqueous mixture was extracted with chloroform (3 x 40 ml), washed with water (3 x 30 ml), dried (MgSO₄) and the solvent was removed in vacuo. The crude material was recrystallised from ethanol to give the required product as a colourless solid (0.35 g, 54%), m.p. 119-122°C (lit. 135, 125-127°C) δH 8.58-8.63 (1H, d), 8.41 (1H, s), 7.41-7.59 (5H, m) and 2.47 (3H, s); δC (D.E.P.T.) 133.48, 131.88, 129.69, 129.45, 125.89, 125.78, 125.67 and 21.01.

(b) 2-Methylthioxanthene 2-Methylthioxanthone (0.353 g, 1.56 mmol) was treated with 1M diborane (10 ml) in tetrahydrofuran (7 ml) as previously described for the unsubstituted system. The mixture was stirred overnight at room temperature. After work up and recrystallisation from ethanol the product was obtained as a yellow solid (0.138 g, 42%), δH 7.17-7.52 (6H, m), 7.04 (1H, d), 3.85 (2H, s) and 2.37 (3H, s); δC 136.24(q), 136.06(q), 134.19(q), 130.34(q), 128.57, 127.73, 127.12, 126.69, 126.50, 126.28, 39.08 and 20.78 (two signals coincidental at 126.28; two quaternary signals coincidental at 136.24). (This compound appears to be
more unstable than the equivalent unsubstituted system
and as a precautionary measure was stored at -20°C).

8. Pyrolysis of Related 2-(Allylmercapto)-
diphenylmethanes

(a) 2-(Allylmercapto)diphenylmethane

0.014 g (0.058 mmol), 100-110°C, 750°C, 1 x 10^-3 Torr, 35 min
thioxanthene (50%); 2-mercaptodiphenylmethane (trace).

On a larger scale the substrate (0.086 g, 0.36 mmol) was
distilled at 5 x 10^-3 Torr into a furnace at 750°C over
a period of 1.5 h. The entire pyrolysate was dissolved
in methylene chloride and was extracted with sodium
hydroxide solution. The remaining methylene chloride
solution was dried (MgSO₄), the solvent was removed in
vacuo and the residue was purified by dry-flash chromato-
graphy, using methylene chloride/hexane (50:50) as eluant.
The major component of the residue was thioxanthene
(crude wt. = 0.036 g). The crude product was recrystallised
from methanol to give pure thioxanthene (0.016 g, 23%),
m.p. 129-130°C, mixed m.p. 129-130°C (lit.¹⁹², 128-130°C),
δH 7.40-7.48 (2H, m), 7.26-7.34 (2H, m), 7.14-7.25 (4H, m)
and 3.86 (2H, s); δC 136.01(q), 133.71(q), 127.72,
126.66, 126.38, 126.11 and 39.02. The ¹H n.m.r. and ¹³C
n.m.r. spectra are identical to those of the authentic
sample previously quoted. The remainder of the residue
consisted of small components, isolated in less than 5%,
which were not identified.
The base extract from the pyrolysate was acidified, extracted with methylene chloride (3 x 15 ml), dried (MgSO₄) and the solvent was removed in vacuo. The residue (isolated wt. = 8 mg), was shown by g.c. to be 2-mercapto-diphenylmethane, contaminated with impurities, which was not purified further.

(b) 2-(Allylmercapto)-4'-methyldiphenylmethane

0.016 g (0.063 mmol), 110-120°C, 750°C, 1 x 10⁻³, 40 min:
2-methylthioxanthene (29.5%) and 3-methylthioxanthene (29.5%); 2-mercapto-4'-methyldiphenylmethane (6%). The pyrolysis was carried out on a larger scale, the substrate (0.173 g, 0.68 mmol) being distilled (1 x 10⁻³ Torr) through the furnace tube (750°C) over a period of 120 min. The entire pyrolysate was dissolved in methylene chloride and extracted with sodium hydroxide solution (1M, 50 ml). The methylene chloride was dried (MgSO₄) and the solvent was removed in vacuo. The components of the residue were separated by dry-flash chromatography with methylene chloride /hexane (70:30) as eluant. The major component was a mixture of 2-methylthioxanthene and 3-methylthioxanthene, obtained as a white crystalline solid which was found to be very pure (0.033g, 23%). The mixture of isomers could not be further separated. The ¹H n.m.r. spectrum shows two methyl peaks at 2.32 and 2.34, which were tentatively assigned to the 2-methyl and 3-methyl isomers respectively,
a peak at 3.82 attributed to the methylene signals for the two compounds and aromatic signals between 6.99 and 7.46. The $^{13}$C n.m.r. spectrum shows two methylene peaks at 39.15 and 38.63, assigned to the 2-methyl and 3-methyl isomers respectively (see Discussion section), and a signal at 20.80 attributed to the methyl signals of the isomers. The remainder of the signals in the aromatic region could be assigned to the respective isomers:

2-methylthioxanthene: 136.32 (2 x q), 136.14 (q), 134.25 (q), 130.40 (q), 128.61, 127.78, 127.17, 126.75, 126.56 and 126.33 (two signals co-incidental at 126.33): 3-methylthioxanthene: 133.94 (q), 133.59 (q), 133.07 (q), 127.78, 127.59, 127.29, 127.21, 126.75 and 126.33 (the remainder of the quaternary signals could not be unambiguously assigned; two signals co-incidental at 126.33). The $^{13}$C n.m.r. spectrum for the 2-methyl isomer is compatible with that previously quoted for the authentic compound. The remainder of the components separated by chromatography were isolated in less than 5% and were not identified.

The base extract was neutralised, extracted with methylene chloride (3 x 25 ml), dried, and the solvent was removed. The residue was identified by g.c. and $^1$H n.m.r. spectroscopy, as 2-mercapto-4'-methylidiphenylmethane contaminated with impurities (crude wt. = 0.026 g). The crude material was not purified further:
δH 7.03-7.34 (8H, m), 4.02 (2H, s), 3.29 (1H, s) and 2.32 (3H, s). The 1H n.m.r. spectrum is identical to that obtained for the authentic compound.

9. Pyrolysis of Related Bis[2-(thiophenoxy)benzyl] oxalates

(a) Bis[2-(thiophenoxy)benzyl] oxalate

0.024 g (0.049 mmol), 140-230°C, 750°C, 5x10⁻³ Torr, 140 min: thioxanthene (53%); 2-thiophenoxybenzyl alcohol (5%). On a preparative scale the oxalate (0.992 g, 2.04 mmol) was distilled at 1 x 10⁻³ Torr into a furnace at 750°C over a period of 250 min. The entire pyrolysate was dissolved in methylene chloride and was extracted with sodium hydroxide solution (1M, 50 ml). After extraction the methylene chloride was dried (MgSO₄), the solvent was removed in vacuo and the residue was separated by dry-flash chromatography, using methylene chloride/hexane (70:30) as eluant. The following components were isolated: Thioxanthene (crude wt. = 0.470 g). The crude material was recrystallised from methanol to give pure thioxanthene (0.15 g, 18%), m.p. 125-126°C, mixed m.p. 126-128°C (lit. 192, 128-130°C), δH 7.40-7.58 (2H, m), 7.31-7.38 (2H, m), 7.18-7.29 (4H, m) and 3.90 (2H, s); δC 136.05 (q), 133.76 (q), 127.78, 126.71, 126.44, 126.38 and 39.11. The 1H and 13C n.m.r. spectra are identical to those previously quoted for the authentic compound: 2-thiophenoxybenzyl alcohol
(0.58 g, 13%), contaminated with minor impurities which could not be separated. This component was not obtained in crystalline form, b.p. 135-136°C (0.2 Torr) (lit. m.p., 44°C), δH 7.15-7.58 (9H, m), 4.77 (2H, s) and 2.30 (1H, br.s); δC 142.36(q), 135.98(q), 133.84, 132.35(q), 129.37, 129.05, 128.30, 126.44 and 63.35. The 1H and 13C n.m.r. spectra are identical to those previously quoted for the authentic sample.

The base extract from the pyrolysate was neutralised, extracted with methylene chloride (3 x 15 ml), dried (MgSO₄) and the solvent was removed. The residue (crude wt. = 0.011 g) was examined by t.l.c. and g.c. and was found to contain a number of small components which could not be separated or identified.

(b) Bis[2-(4-methyliithiophenoxy)benzyl] oxalate

0.029 g (0.056 mmol), 220-230°C, 750°C, 1 x 10⁻³ Torr, 40 min: 2-methylthioxanthene (25%) and 3-methylthio-
xanthene (25%): 2-(4-methyliithiophenoxy)benzyl alcohol (8%). On a preparative scale the oxalate (0.713 g, 1.39 mmol) was pyrolysed at 750°C, 1 x 10⁻³ Torr over a period of 165 min. The components of the pyrolysate were separated by dry-flash chromatography, using methylene chloride/hexane (50:50) as eluant. The major component isolated was a mixture of 2-methylthioxanthene and 3-methylthioxanthene, isolated as a white solid contaminated with some minor impurities which were not further separated.
The mixture of isomers could not be further separated. The $^1$H n.m.r. spectrum shows two methyl peaks at 2.41 and 2.42 which could not be unambiguously assigned, a peak at 3.90 attributed to the methylene signals for the two isomers and aromatic signals between 7.07 and 7.56. The $^{13}$C n.m.r. spectrum shows two methylene peaks at 39.17 and 38.65 assigned to the 2-methyl and 3-methyl isomers respectively and a peak at 20.94 attributed to the methyl peaks for the two isomers. The remainder of the peaks in the aromatic region could be assigned to each isomer: 2-methylxanthene δC (D.E.P.T.) 128.68, 127.86, 127.22, 126.80, 126.60 and 126.39 (two signals co- incidental at 126.39); 3-methylthioxanthene δC (D.E.P.T.) 127.86, 127.65, 127.35, 127.27, 126.80 and 126.39 (two signals co- incidental at 126.39). The $^{13}$C n.m.r. spectrum for the 2-methyl isomer is compatible with that previously quoted for the authentic compound: 2-(4-methylthiophenoxy)benzyl alcohol (0.05 g, 15%), contaminated with minor impurities, isolated as a yellow oil, b.p. 154-155°C (0.5 Torr) [lit. $^{191}$, 185-188°C (5 Torr)], δH 7.08-7.46 (8H, m), 4.79 (2H, s), 2.34 (3H, s) and 2.27 (1H, br.s); δC 141.50(q), 136.89(q), 133.69(q), 132.64, 131.67(q), 130.53, 129.91, 128.25, 128.16, 127.66, 63.37 and 20.82. The $^1$H n.m.r. and $^{13}$C n.m.r. spectra are identical to those of the authentic sample previously quoted.
The remainder of the components separated by chromatography were isolated in less than 5% yield and were not identified.
F. The Generation and Cyclisation of 2-Benzylaminyl Radicals

1. Preparation of 2-(Allylamino)-4'-methyl-diphenylmethane

2-Amino-4'-methyldiphenylmethane (12 mmol) (previously prepared in Section E2) was reacted with allyl bromide (12 mmol) in dimethylformamide (30 ml) containing potassium carbonate (12 mmol) as previously described in Section D2. The reaction mixture was stirred at room temperature for 72 h. After work-up and column chromatography on alumina with ether/light petroleum (20:80) as eluant, the crude product was purified by distillation to give 2-(allylamino)-4'-methylidiphenylmethane as a yellow oil (0.77 g; 52%), b.p. 160-162°C (0.5 Torr) (Found: C, 85.9; H, 7.95; N, 5.7; C_{17}H_{19}N requires C, 86.05; H, 8.0; N, 5.9%); δH 7.15-7.49 (6H, m), 6.73-6.96 (2H, m), 5.75-6.25 (1H, m), 5.12-5.35 (2H, m), 3.99 (2H, s), 3.80-3.86 (2H, m), 3.78 (1H, br.s) and 2.46 (3H, s); δC 145.76(q), 136.00(q), 135.71(q), 135.17, 130.39, 129.17, 128.15, 127.51, 124.82(q), 117.05, 115.63, 110.78, 46.06, 37.57 and 20.86; m/z 237 (M⁺, 37%), 210(48), 196(100), 181(20) and 180(26).
2. Preparation of Methyl 2-(4-methylphenylamino)-benzoate

(a) N-Phenyl-(4'-methyl)anthranilic acid

A mixture of p-toluidine (88.81 g, 0.83 mol), o-chlorobenzoic acid (20.5 g, 0.13 mol), potassium carbonate (20.5 g, 0.15 mol) and copper oxide (0.5 g) was heated under reflux for 2 h, in a round bottom flask fitted with an air condenser, using an oil bath. The mixture was steam distilled to remove excess p-toluidine, then charcoal (10 g) was added to the brown residual solution. The mixture was filtered and the filtrate was added, with stirring, to a mixture of hydrochloric acid (30 ml, concentrated) and water (60 ml). The precipitated acid was filtered and dried to leave the required product as a colourless solid (25.39 g, 86%), m.p. 194-197°C (lit. 194, 191-195°C), δH 9.57 (1H, br.s), 8.03 (1H, d), 7.04-7.35 (6H, m), 6.71 (1H, t), 2.35 (3H, s) and 1.43 (1H, s).

(b) Methyl 2-(4-methylphenylamino)benzoate

A mixture of N-phenyl-(4'-methyl)anthranilic acid (19 g, 85 mmol), methanol (380 ml) and concentrated sulphuric acid (19 ml) was heated under reflux for 19 h. The mixture was cooled and methanol was removed in vacuo. Sodium carbonate solution was added to neutralise the reaction mixture and the resulting solution was extracted with ether (3 x 100 ml). The ether extracts were washed with a sodium carbonate solution (10%, 2 x 100 ml),
dried \((\text{MgSO}_4)\) and the solvent was removed in vacuo to give the required product as a brown crystalline solid which was used without further purification (20.24 g, 79%), m.p. 45-48°C (lit. 195°C, 48.5°C), \(\delta\)H 9.38 (1H, br.s), 7.96 (1H, m), 7.07-7.30 (6H, m), 6.69 (1H, m), 3.90 (3H, s) and 2.35 (3H, s).

3. Preparation of 2-(4-Methylphenylamino)benzyl alcohol

An attempt was made to prepare this compound by the reduction of methyl 2-(4-methylphenylamino)benzoate (10 g, 41 mmol) using lithium aluminium hydride (2.6 g, 69 mmol) in dry ether (50 ml). After heating the reaction mixture under reflux for 3 h then stirring overnight at room temperature, a black oil was obtained on work-up. This oil could not be distilled, the \(^1\)H n.m.r. spectrum of the reaction mixture indicating that the required product was not present.

An alternative method of preparing this compound was tried. \(^{196}\) \(N\)-Phenyl-(4'-methyl)anthranilic acid (5.0 g, 22 mmol) was dissolved in dry tetrahydrofuran (7 ml) and the stirred mixture was cooled to 0°C under an atmosphere of dry nitrogen. Diborane in tetrahydrofuran (1M solution, 75 ml) was added to the mixture, via a septum, over a period of 15 min and the resulting yellow solution was stirred at room temperature for 4.5 h.
The mixture was then cooled to 0°C and sodium hydroxide solution (1M, 6 ml) was slowly added to destroy excess hydride. The reaction mixture was stirred overnight at room temperature to hydrolyse the amine-borane complex, then the pH of the resulting solution was adjusted to 11.0 by the addition of a sodium hydroxide solution. The aqueous phase was saturated with potassium carbonate, the tetrahydrofuran phase was separated and the aqueous phase was extracted with ether (4 x 50 ml). The combined tetrahydrofuran and ether layers were dried (Na₂SO₄) and the solvent was removed in vacuo. A brown oil was obtained which was shown by ¹H n.m.r. spectroscopy to contain a large quantity of water. The oil was dissolved in methylene chloride (100 ml), washed with water (2 x 50 ml), dried (MgSO₄) and the solvent was removed. The crude product was purified by distillation to give 2-(4-methylphenylamino)benzyl alcohol as a yellow oil (1.93 g, 41%), b.p. 130-132°C (0.5 Torr) (Found: C, 78.65; H, 6.95; N, 6.55. C₁₄H₁₅NO requires C, 78.85; H, 7.05; N, 6.55%). δH 6.74-7.35 (10H, m), 4.71 (2H, s) and 2.32 (3H, s); δC 143.72(q), 140.16(q), 130.63(q), 129.70, 129.36, 129.02, 127.75(q), 119.69, 119.01, 116.10, 64.43 and 20.52; m/z 213 (M⁺, 42%), 194(62), 183(46), 180(46), 74(58), 59(100) and 45(75).
4. **Reaction of 2-(4-Methylphenylamino)benzyl alcohol with Oxalyl Chloride**

Attempts were made to prepare the appropriate benzyl oxalate by the reaction of the benzyl alcohol with oxalyl chloride as previously described in Section E6. On removing the solvent after work-up a thick, sticky oil was obtained. An i.r. spectrum of this oil indicated that no carbonyl groups were present thus the required product had not been obtained.

5. **Preparation of Authentic Samples for Comparison with Pyrolysates**

**Preparation of 2-Methylacridan**

(a) **2-Methylacridone** A mixture of N-phenyl-(4'-methyl)anthranilic acid (6.02 g, 26 mmol) and concentrated sulphuric acid (15 ml) was heated on a boiling water bath for 1 h then was carefully poured into boiling water (150 ml). The resulting solution was boiled for 5 min and the yellow precipitate was filtered. The solid obtained was boiled for 5 min with a solution of sodium carbonate (4.3 g, 40 mmol) in water (60 ml) then was filtered and washed well with water. The required product was isolated as a yellow solid (4.41 g, 81%), m.p. 335-338°C (lit. 338°C), δH ([^2]H_DMSO): 11.63 (1H, br.s), 8.22 (1H, d), 8.02 (1H, s), 7.31-7.81 (4H, m), 7.20 (1H, m) and 2.42 (3H, s).
(b) 2-Methylacridan  A mixture of 2-methylacridone (4.0 g, 19 mmol) and amyl alcohol (160 ml) was heated under reflux and sodium (12 g, 0.52 mol) was added in six equal portions at 5 min intervals. The mixture was cooled, cautiously diluted with water (160 ml) then the amyl alcohol was removed by steam distillation. After the removal of amyl alcohol, 2-methylacridan was precipitated as a brown solid which was isolated by filtration. The crude product was recrystallised from methanol to give 2-methylacridan as a pale brown solid (1.13 g, 31%), m.p. 167-170°C (lit. \(143°\), \(157°C\)), δH 7.06 (2H, m), 6.78-6.91 (3H, m), 6.60 (2H, m), 5.88 (1H, br.s), 4.01 (2H, s) and 2.26 (3H, s); δC 140.29(q), 137.59(q), 129.71(q), 128.98, 128.46, 127.33, 126.79, 120.19, 119.79(q), 113.19, 21.23 and 20.45 (two signals co-incidental at 113.19; two quaternary signals co-incidental at 119.79).

6. Pyrolysis of 2-(Allylamino)-4'-methyl-diphenylmethane

0.060 g (0.253 mmol), 750°C, 1 x 10^{-3} Torr, 40 min. The crude pyrolysate was dissolved in chloroform and analysed, by n.m.r. spectroscopy, for the presence of acridans. The \(^{13}C\) n.m.r. spectrum shows two methylene peaks at 31.23 and 30.83 and two methyl peaks at 21.53 and 22.08 assigned to 2-methylacridan and 3-methylacridan respectively (authentic 2-methylacridan shows
methylenes and methyl peaks at δC 31.24 and 21.53). The $^1$H n.m.r. spectrum shows a methyl peak at 2.28 and a methylene peak at 4.02 attributed to the methylacridan isomers. A $^{15}$N n.m.r. spectrum of the pyrolysate indicates two NH signals at δN -290.08 and -288.95 (authentic 2-methylacridan shows a peak at δN -289.91). From the n.m.r. spectra obtained, the ratio of 2-methylacridan:3-methylacridan was found to be 2:1. The $^1$H n.m.r. spectrum obtained also indicated the presence of acridines in the pyrolysate, the aromatic signals being spread over the range 6.46-8.69 and a single peak being observed at 2.57 (authentic 2-methylacridine has a methyl resonance at δH 2.60). The minor components of the pyrolysate were not identified.
G. The Generation and Rearrangement of 2-Phenoxybenzyl and 2-Benzylphenoxy Radicals

1. Preparation of 2-Hydroxy-4'-methylidiphenylmethane

(a) 2-Hydroxy-4'-methylbenzophenone

A mixture of o-anisic acid (20.0 g, 0.13 mol) and thionyl chloride (18 g, 0.15 mol) was heated under reflux for 30 min and then excess thionyl chloride was removed under vacuum. The acid chloride was dissolved in toluene (80 ml) and aluminium chloride (20.0 g, 0.15 mol) was added in small portions to the stirred mixture, with cooling if necessary. The mixture was heated on a water bath for 1.5 h until the reaction had ceased. The reaction mixture was cooled and poured onto a mixture of ice (50 g) and dilute hydrochloric acid (5 ml). The toluene layer was separated, washed with water (3 x 50 ml) then with dilute ammonia (3 x 30 ml) and dried (Na₂SO₄). Toluene was removed in vacuo. The crystalline solid obtained was washed with light petroleum to give the required product as a yellow solid (4.63 g, 17%), m.p. 56-59°C (lit. 146, 61.5°C), δH 12.02 (1H, s), 6.75-7.65 (8H, m) and 2.45 (3H, s); δC 190.72 (C=O), 163.03(q), 142.58(q), 135.93, 135.11(q), 133.36, 129.33, 128.87, 119.19(q), 118.40, 118.22 and 21.44.
(b) 2-Hydroxy-4'-methyldiphenylmethane

This compound was prepared by Wolff-Kishner reduction of the benzophenone (3.5 g, 16.5 mmol) as described in Section E2. The crude, isolated product was purified by distillation to give the pure product as a colourless oil (3.28 g, 99%); b.p. 148-150 °C (0.4 Torr) [lit. 198, 73-76 °C (0.05 Torr)], δH 6.80-7.36 (8H, m), 4.56 (1H, br.s), 4.09 (2H, s) and 2.42 (3H, s); δC 153.64(q), 136.54(q), 135.81(q), 130.78, 129.26, 128.43, 127.65, 127.06(q), 120.79, 115.65, 35.90 and 20.87.

2. Preparation of Related 2-(Allyloxy)diphenylmethanes

The appropriate phenol (1.9 mmol) was reacted with allyl bromide (2 mmol) in dimethylformamide (7 ml) containing potassium carbonate (2 mmol) as previously described in Section D2. The reaction mixture was stirred overnight at room temperature and the product was purified by distillation. The following compounds were prepared by this method: 2-(Allyloxy)diphenylmethane (83%), b.p. 138-140 °C (0.5 Torr) (Found: C, 85.65; H, 7.05 C_{16}H_{16}O requires C, 85.7; H, 7.15); δH 7.0-7.54 (9H, m), 6.22 (1H, m), 5.36-5.72 (2H, m), 4.70 (2H, m) and 4.28 (2H, s); δC 156.15(q), 140.89(q), 133.35, 130.29, 129.89(q), 128.83, 128.05, 127.16, 125.59, 120.52, 116.75, 111.59, 68.58 and 35.91; m/z 224 (M^+ 56%), 183(100), 165(30), 155(22), 130(37), 117(59), 107(13), 91(70), 77(50) and 41(60).
2-(Allyloxy)-4'-methyldiphenylmethane (83%), b.p. 156-158°C (0.6 Torr) (Found: C, 85.55; H, 7.3 \( \text{C}_{17}\text{H}_{18}\text{O} \) requires C, 85.7; H, 7.55%); \( \delta \text{H} \) 6.82-7.31 (8H, m), 6.15 (1H, m), 5.20-5.57 (2H, m), 4.58 (2H, m), 4.04 (2H, s) and 2.37 (3H, s); \( \delta \text{C} \) 156.30(q), 137.92(q), 135.01(q), 133.54, 130.30, 129.24(q), 128.80, 127.09, 120.63, 116.76, 111.82, 68.81, 35.47 and 20.83 (2 signals co-incidental at 128.80); m/z 238 (M\(^+\), 81%), 198(33), 197(100), 181(30) and 131(26).

3. Preparation of 2-Phenoxybenzyl alcohol

A solution of 2-phenoxybenzoic acid (10.0 g, 46.7 mmol) in dry ether (100 ml) was slowly added to a stirred suspension of lithium aluminium hydride (1.8 g, 47 mmol) in dry ether (50 ml). The mixture was stirred under reflux for 5 h then allowed to cool. Excess hydride was destroyed by the addition of wet ether (15 ml) then water (15 ml) and finally hydrochloric acid (10%, 15 ml). The mixture was filtered through celite and the ether layer was separated. The aqueous layer was extracted with ether (2 x 100 ml), the combined ether extracts were dried (MgSO\(_4\)) and the solvent was removed in vacuo. The remaining oil was distilled to give the product as a colourless oil (6.46 g, 69%), b.p. 130-133°C (0.1 Torr) [lit.\(^{147}\), 140-145°C (0.4 Torr)].
δH 6.83-7.56 (9H, m), 4.74 (2H, s) and 2.86 (1H, s);
δC 157.04(q), 154.51(q), 131.85(q), 129.70, 129.06, 128.83, 123.65, 123.16, 118.50, 118.22 and 60.95.

4. **Preparation of 2-(4-Methylphenoxy)benzyl alcohol**

   (a) **2-(4-methylphenoxy)benzoic acid**

   The potassium salt of o-chlorobenzoic acid was prepared by the following method: potassium hydroxide pellets (1 mol) were dissolved in methanol. o-Chlorobenzoic acid (1 mol) was dissolved in the solution and the solvent was removed in vacuo to give the salt as a white solid.

   p-Cresol (14.0 g, 0.13 mol) was dissolved in sodium methoxide [from sodium (1.18 g) in methanol (26 ml)] then the potassium salt of o-chlorobenzoic acid (10 g, 0.05 mol) and copper bronze (0.1 g) were added. The methanol was removed by distillation and the reaction mixture was heated to 170-200°C on an oil bath. This temperature was maintained for 15-20 min and then the reaction mixture was allowed to cool. The entire mixture was dissolved in water (200 ml), sodium carbonate (10%, 100 ml) was added and the mixture was filtered. The filtrate was extracted with ether (3 x 50 ml) to remove excess p-cresol and the aqueous
layer was acidified to give 2-(4-methylphenoxy)benzoic acid (6.10 g, 53%), m.p. 123-127°C [from light petroleum (b.p. 80-100°C)] (lit. 148, 118.5°C), δH 10.14 (1H, br.s), 8.06-8.18 (1H, dd), 6.78-7.55 (7H, m) and 2.34 (3H, s); δC 166.20 (C=O), 157.56(q), 152.05(q), 135.16(q), 134.61, 133.30, 130.62, 123.21, 120.04, 117.18 and 20.66 (one quaternary signal is not apparent, possibly beneath the peak at 130.62).

(b) 2-(4-Methylphenoxy)benzyl alcohol

This compound was prepared by lithium aluminium hydride reduction of the acid as previously described in 3. The crude material was purified by distillation to give the pure product as a colourless oil (70%), b.p. 163-165°C (0.4 Torr) [lit. 147, 125-127°C (0.1 Torr)], δH 7.32-7.51 (1H, m), 7.00-7.28 (4H, m), 6.77-6.96 (3H, m), 4.75 (2H, s), 3.16 (1H, br.s) and 2.34 (3H, s); δC 155.16(q), 154.54(q), 132.86(q), 131.44(q), 130.18, 129.03, 128.79, 123.23, 118.45, 117.85, 61.19 and 20.52.

5. Preparation of Benzyl oxalates

Symmetrical dibenzyl oxalates were prepared by the general method of Trahanovsky et al previously described in Section E6. The following compounds were prepared by this method: Bis [2-(phenoxy)benzyl] oxalate (61%), m.p. 94-96°C
(from ethanol) (lit.\textsuperscript{133}, 94-96°C), \(\delta\)H 6.80-7.51 (18H, m) and 5.39 (4H, s); \(\delta\)C 157.35(q), 156.83(q), 155.34(q),
130.45, 130.19, 129.68, 125.36(q), 123.38, 118.63,
118.48 and 63.71 (two carbon signals co- incidental at
129.68, 123.38 and 118.63). Bis[2-(4-methylphenoxy)-
benzyl] oxalate (61%), m.p. 78-81°C (from ethanol (Found:
C, 74.45; H, 5.35 \(\text{C}_{30}\text{H}_{26}\text{O}_{6}\) requires C, 74.7; H, 5.4%);
\(\delta\)H 6.76-7.50 (16H, m), 5.41 (4H, s) and 2.31 (6H, m);
\(\delta\)C 157.36(q), 155.80(q), 154.33(q), 152.94(q), 130.26,
130.11, 124.93(q), 122.89, 118.79, 117.72, 63.70 and
20.50 (two signals are co- incidental); m/z 482 (M\textsuperscript{+} 46%),
286(46), 242(24), 198(100) and 182(23).

6. Preparation of Authentic 2-Methylxanthene

(a) 2-Methylxanthone

A stirred mixture of 2-(4-methylphenoxy)benzoic acid (previously prepared in section G4: 7.0 g, 0.03 mol)
and concentrated sulphuric acid (100 ml) was heated at
100°C for 30 min. The reaction was terminated by pouring
the mixture onto cold water (100 ml). The precipitate
was collected and was washed with sodium bicarbonate
(5%, 100 ml) and then with water (100 ml). The crude
product was dissolved in chloroform (150 ml) and insoluble
materials were removed by filtration. The solvent was
removed in vacuo to leave the required product as a pale
brown solid (2.19 g, 35%), m.p. 119-120°C (lit. 154, 120-121°C), δH 8.20-8.25 (1H, d), 7.99 (1H, s), 7.57 (1H, t), 7.20-7.40 (4H, m) and 2.35 (3H, s); δC 175.80 (C=O), 154.93(q), 153.13(q), 134.71, 133.28, 132.38(q), 125.45, 124.75, 122.41, 120.63(q), 120.26(q), 116.69, 116.48 and 19.54.

(b) 2-Methylxanthene

This compound was prepared by treating the xanthone (2.0 g, 9.47 mmol) with hydrazine hydrate and potassium hydroxide as previously described in section E2(b). A mixture of xanthone and xanthene was obtained which was separated by column chromatography on alumina, eluting with ether/light petroleum (20:80). The isolated product was recrystallised from hexane to leave pure 2-methylxanthene as a colourless solid (0.365 g, 20%), m.p. 92-94°C (lit. 199, 96°C), δH 6.88-7.25 (7H, m), 4.00 (2H, s) and 2.31 (3H, s); δC 152.02(q), 149.73(q), 132.09(q), 129.08, 128.78, 128.05, 127.40, 122.59, 120.43(q), 120.02(q), 116.28, 116.01, 27.73 and 20.46.
7. **Pyrolysis of Allyldiphenylmethanes**

(a) **2-(Allyloxy)diphenylmethane**

0.089 g (0.397 mmol), 130-140°C, 750°C, \(1 \times 10^{-3}\) Torr, 20 min: 2-hydroxydiphenylmethane (33%), \(m/z\) 184 (\(M^+\), 100%), 182(27), 165(29) and 106 (53); 1-hydroxyfluorene (30%), \(m/z\) 182 (\(M^+\), 100%), 181(67), 152(32) and 149(23); xanthene (2%), \(m/z\) 182 (\(M^+\), 57%), 181(100) and 152(23).

On a preparative scale the phenol (2.164 g, 9.66 mmol) was distilled at \(5 \times 10^{-3}\) Torr into a furnace at 750°C over a period of 2 h. The entire pyrolysate was chromatographed on a column of alumina, using ether/light petroleum (50:50) as eluant. The following components were isolated: 2-hydroxydiphenylmethane (0.30 g, 17%), b.p. 119°C-120°C (0.5 Torr) which could not be obtained in crystalline form, \(\delta\)H 6.74-7.43 (9H, m), 5.06 (1H, br.s) and 4.07 (2H,s); \(\delta\)C 153.50(q), 139.78(q), 130.83, 128.54, 128.46, 127.66, 126.91(q), 126.16, 120.82, 115.57 and 36.12. However, the \(^1\)H n.m.r. and \(^{13}\)C n.m.r. were identical to those of an authentic sample; \(\delta\)H 6.73-7.36 (9H, m), 4.84 (1H, s) and 4.06 (2H, s); \(\delta\)C 153.51(q), 139.75(q), 130.83, 128.65, 128.56, 127.68, 126.87(q), 126.18, 120.84, 115.58 and 36.14; 1-hydroxyfluorene (crude wt = 0.127 g).

The crude isolated material was purified by distillation, b.p. 130-132°C (0.5 Torr) to give the pure product as a brown solid (0.095 g, 6%), m.p. 118-120°C (from water (lit. 149, 119-120°C), \(\delta\)H 7.80 (1H, d), 7.57 (1H, d),
7.26-7.55 (4H, m), 6.78 (1H, d), 5.25 (1H, br.s) and 3.84 (2H, s); \( \delta C \) 152.01(q), 143.79(q), 142.75(q), 141.50(q), 128.41, 128.23(q), 126.78, 126.61, 124.98, 120.06, 113.41, 112.83 and 33.41; \( m/z \) 182 (M\(^+\), 100%), 165(38), 152(86), 91(41) and 77(46). However, g.c./m.s. showed that a minor product of the pyrolysis was xanthene, yet no xanthene had been isolated from the pyrolysate during chromatography. A further preparative scale pyrolysis was carried out, the phenol (1.489 g, 6.65 mmol) being pyrolysed at 750°C, 1 x 10\(^{-3}\) Torr over a period of 1.5 h. The entire pyrolysate was dissolved in methylene chloride and was extracted with sodium hydroxide (1M, 100 ml) to remove the phenolic components. The methylene chloride was dried (\( \text{Na}_2\text{SO}_4 \)) and the solvent was removed in vacuo. The residue was chromatographed on a column of alumina eluting with light petroleum. The xanthene isolated from the column was purified by recrystallisation from ethanol to give a yellow solid which was still impure (0.05 g, 4%), \( \delta H \) 7.01-7.49 (8H, m) and 4.05 (2H, s); \( \delta C \) 151.00(q), 128.78, 127.50, 122.83, 120.48(q), 116.34 and 27.78. The \(^1\)H n.m.r. and \(^13\)C n.m.r. were compatible with those of an authentic sample: \( \delta H \) 7.00-7.23 (8H, m) and 4.05 (2H, s); \( \delta C \) 151.88(q), 128.77, 127.50, 122.81, 120.45(q), 116.34 and 27.76.
(b) **2-(allyloxy)-4'-methyldiphenylmethane**

0.129 g (0.542 mmol), 120-130°C, 750°C, 1 x 10^{-3} Torr, 25 min: 2-hydroxy-4'-methyldiphenylmethane (22%), m/z 198 (M⁺, 100%), 196(13), 183(68) and 166(30);

1-hydroxy-6-methylfluorene (26%), m/z 196 (M⁺, 100%), 195(35), 181(91) and 152(25); 2-methylxanthene (2%) and 3-methylxanthene (2%), m/z 196 (M⁺, 61%), 195(100) and 181(39). On a larger scale the phenol (1.534 g, 6.43 mmol) was pyrolysed at 750°C, 2 x 10^{-3} Torr over a period of 1.5 h. The entire pyrolysate was dissolved in methylene chloride and was extracted with sodium hydroxide (1M, 100 ml). The base extract was neutralised, extracted with methylene chloride, dried (MgSO₄) and the solvent was removed in vacuo. The residue was chromatographed on a column of alumina, with ether/light petroleum (50:50) as eluant. The following components were isolated: 2-hydroxy-4'-methyldiphenylmethane (0.10 g, 8%), b.p. 174-176°C (0.7 Torr), [lit.¹ 198, 73-76°C (0.05 Torr)], δH 6.77-7.31 (8H, m), 5.07 (1H, br.s), 4.06 (2H, s) and 2.43 (3H, s); δC 153.64(q), 136.55(q), 135.78(q), 130.79, 129.24, 128.44, 127.65, 127.08(q), 120.79, 115.66, 35.89 and 20.86. The ¹H n.m.r. and ¹³C n.m.r. spectra are identical to those of the authentic sample previously quoted in 1(b); 1-hydroxy-6-methylfluorene (crude wt. = 0.139 g).
The crude product was purified by sublimation, 173-
175°C (0.7 Torr), to give the pure product as a light
brown solid (0.121 g, 10%), m.p. 119-121°C (Found:
C, 85.55; H, 6.3 C\textsubscript{14}H\textsubscript{12}O requires C, 85.7; H, 6.1%);
\(\delta\)H 7.60 (1H, s), 7.30-7.50 (2H, m), 7.08-7.27 (2H, m),
6.75 (1H, d), 5.07 (1H, s), 3.79 (2H, s) and 2.47 (3H, s);
\(\delta\)C 152.03(q), 143.88(q), 141.68(q), 139.86(q), 136.26(q),
128.62(q), 128.35, 127.77, 124.64, 120.67, 113.32,
112.73, 33.00 and 21.35; m/e 196 (M\textsuperscript{+}, 90%), 181(100),
165(21) and 152(29).

After base extraction the methylene chloride layer
was dried (MgSO\textsubscript{4}) and the solvent was removed in vacuo.
The residue consisted of a mixture of both 2-methyl-
xanthene and 3-methylxanthene but was contaminated with
a large number of impurities (crude wt. = 0.90 g). The
two isomers could not be separated but attempts were made
to separate the isomers from the impurities. However,
even after column chromatography on alumina and dry-
flash chromatography, using light petroleum and methylene
chloride/hexane (40:60), respectively, as eluants, the
isomeric mixture was still impure. A pale yellow oily
solid was isolated which could not be further purified
(0.081 g, 6%). The \(^1\text{H}\) n.m.r. spectrum of the mixture
shows two methyl peaks at \(\delta\)H 2.36 and 2.39 and a
peak at 4.04 corresponding to the methylene protons.
The corresponding spectrum of authentic 2-methylxanthene
shows a methyl peak at δH 2.31 but since the chemical shifts of the methyl protons are so close a positive assignment of the signals to the two isomers is not possible. However, assignments can be made using data from the $^{13}$C n.m.r. spectrum. This shows two methyl peaks at δC 20.90 and 21.36 and two methylene peaks at δC 27.43 and 27.77. Using the chemical shift of the methylene carbon in xanthene and known substitution effects the peak at δC 27.43 can be assigned to 3-methylxanthene and the peak at δC 27.77 can be assigned to 2-methylxanthene [Authentic 2-methylxanthene shows a peak due to the methylene carbon at δC 27.75] (see Discussion section). This assignment allows the yields of the isomers to be calculated.

For these pyrolyses absolute yields could not be obtained by the methods previously outlined. The co-incidence of peaks in both the $^1$H n.m.r. spectrum and the g.c. traces resulted in absolute yields being obtained from $^1$H n.m.r. and $^{13}$C n.m.r. spectral data. The absolute yield of the appropriate fluorene could be obtained from the $^1$H n.m.r. spectrum, by the addition of cyclohexane as previously outlined, and the relative yields of the isolated products could be obtained from the $^{13}$C n.m.r. spectrum. From a combination of this n.m.r. data the absolute yields of each product could be obtained.
8. **Pyrolysis of Benzyl oxalates**

(a) **Bis[2-(phenoxy)benzyl] oxalate**

0.108 g (0.238 mmol), 140-160°C, 750°C, 1 x 10⁻³ Torr, 40 min: 2-hydroxydiphenylmethane (5%), m/z 184 (M⁺, 100%), 182(27), 165(28) and 106(51); 1-hydroxyfluorene (36%), m/z 182 (M⁺, 100%), 181(56) and 152(32); xanthene (9%), m/z 182 (M⁺, 55%), 182(100) and 152(16); 2-phenoxybenzyl alcohol (trace), m/z 200 (M⁺, 27%), 182(32) and 181(100).

On a preparative scale the benzyl oxalate (2.064 g, 4.54 mmol) was distilled at 5 x 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 eluting with ether/light petroleum (50:50). The following components were isolated: 2-hydroxydiphenylmethane (0.19 g, 11%), b.p. 120-121°C (0.5 Torr) which could not be obtained in crystalline form, δH 6.72-7.38 (9H, m), 4.90 (1H, br.s) and 4.03 (2H, s); δC 153.61(q), 139.81(q), 130.84, 128.51, 127.67, 126.91(q), 126.19, 120.78, 115.59 and 36.17 (two peaks co-incidental at 128.51).

However, the ¹H n.m.r. and ¹³C n.m.r. were identical to those of an authentic sample; δH 6.73-7.36 (9H, m), 4.84 (1H, br.s) and 4.06 (2H, s); δC 153.51(q), 139.75(q), 130.83, 128.50, 127.68, 126.87(q), 126.18, 120.78, 115.58 and 36.14; 1-hydroxyfluorene (crude wt. = 0.39 g). The crude material was purified by distillation, b.p. 132-134°C (0.5 Torr), to give the pure product as a pale brown solid (0.15 g, 10%), m.p. 118-120°C (from
(b) Bis[2-(4-methylphenoxy)benzyl] oxalate

0.078 g (0.161 mmol), 170-200°C, 750°C, 1 x 10⁻³ Torr, 50 min: 2-hydroxy-4'-methyldiphenylmethane (6%), m/z 198 (M⁺, 100%), 196(15) and 183(66); 1-hydroxy-6-methylfluorene (48%), m/z 196 (M⁺, 100%), 195(29), 181(89) and 152(25); 2-methylxanthene (14%) and 3-methylxanthene (5%), m/z 196 (M⁺, 61%), 195(100) and 181(40); 2-(4-methylphenoxy)benzyl alcohol (trace), m/z 214 (M⁺, 44%), 195(48), 182(48) and 181(100). The oxalate (1.082 g, 2.24 mmol) was pyrolysed on a larger scale at 750°C.
and $3 \times 10^{-3}$ Torr over a period of 2.5 h. The components of the pyrolysate were separated by column chromatography on alumina, using light petroleum/ether (50:50) as eluant. The following components were isolated: 2-hydroxy-4'-methyl-diphenylmethane (0.064 g, 7%), b.p. 161°C (0.6 Torr) [lit. 198, 73-76°C (0.05 Torr)], δH 6.72-7.38 (8H, m), 3.98 (2H, s) and 2.36 (3H, m); δC 153.73(q), 136.59(q), 135.78(q), 130.78, 129.25, 128.44, 127.64, 127.07(q), 120.73, 115.65, 35.90 and 20.87. The $^1$H n.m.r. and $^{13}$C n.m.r. spectra were identical to those of the authentic sample previously quoted in 1(b). The $^1$H n.m.r. and $^{13}$C n.m.r. spectra of this component of the pyrolysate also shows additional peaks at δH 4.79 and 2.34 and δC 61.31 and 20.53 respectively. These peaks correspond to the values expected for the methyl and methylene signals of 2-(4-methylphenoxy)benzyl alcohol; δH 4.75 and 2.34; δC 61.19 and 20.52.

1-hydroxy-6-methyl-fluorene (crude wt. = 0.160 g). The crude material was purified by sublimation, 159-162°C (0.7 Torr) to give the pure material as a light brown solid (0.121 g, 10%). The sublimed material had m.p. 118-120°C; δH 7.61 (1H, s), 7.28-7.49 (2H, m), 7.08-7.27 (2H, m), 6.75 (1H, d), 5.07 (1H, br.s), 3.79 (2H, s) and 2.47 (3H, s); δC 152.09(q), 143.92(q), 141.73(q), 139.86(q), 136.32(q), 128.59(q), 128.39, 127.81, 124.69, 120.69, 113.33, 112.75, 33.02 and 21.37. The $^1$H n.m.r. and $^{13}$C n.m.r. spectra are identical to those obtained for the same compound isolated from the
pyrolysis in section 7(b): 2-methylxanthene and 3-methylxanthene isolated in a mixture contaminated with a large number of impurities (crude wt. = 0.139 g). Attempts to purify the mixture, both by distillation and preparative t.l.c., were again unsuccessful, the impure mixture being isolated as a yellow oily solid (0.054 g, 6%). The $^{13}$C n.m.r. spectrum of the mixture shows two large peaks at $\delta$C 27.67 and 20.45 assigned to the methylene and methyl resonances of 2-methylxanthene, the major xanthene isomer in this pyrolysis [authentic 2-methylxanthene has peaks at $\delta$C 27.73 and 20.46]. The spectrum also shows two smaller peaks at $\delta$C 27.33 and 20.88 assigned to 3-methylxanthene. In the $^1$H n.m.r. spectrum positive identification of the methyl peaks was not possible due to the number of impurity peaks.

Absolute yields of these pyrolysis products were obtained using both $^{13}$C n.m.r. and $^1$H n.m.r. spectral data as previously outlined in 7(b).
H. The Generation of 2-Benzoylphenoxy Radicals and Related Deuteriated Analogues to Further Study the Mechanism of Hydrogen Abstraction

1. Preparation of 2-(Allyloxy)benzophenones

The appropriate phenol (1.9 mmol) was reacted with allyl bromide (2 mmol) in dimethylformamide (7 ml) containing potassium carbonate (2 mmol) as previously described in Section D2, the reaction mixture being stirred overnight at room temperature. The required product was purified by distillation. The following compounds were prepared by this method: 2-( Allyloxy)-benzophenone (90%), b.p. 145-147°C (0.2 Torr) (Found C, 81.1; H, 5.85 \(C_{16}H_{14}O_2\) requires C, 80.7; H, 5.9%); \(\delta H\) 7.73-7.89 (2H, m), 7.24-7.68 (5H, m), 6.86-7.10 (2H, m), 5.67 (1H, m), 4.88-5.09 (2H, m) and 4.35-4.44 (2H, m); \(\delta C\) 196.06 (C=O), 156.21(q), 138.05(q), 132.39, 132.21, 131.59, 129.43, 129.30, 127.87, 120.61, 116.59, 112.77 and 68.86 (one quaternary is signal not apparent); m/z 238 (M+, 19%), 223(16), 208(19), 198(69), 197(100), 181(40), 121(94), 105(97) and 77(91): 2-(Allyloxy)-4'-methylbenzophenone (from 2-hydroxy-4'-methylbenzophenone previously prepared in Section G1) (90%), b.p. 140-142°C (0.2 Torr) (Found: C, 81.2; H, 6.35 \(C_{17}H_{16}O_2\) requires C, 80.95; H, 6.35%); \(\delta H\) 7.63-7.76 (2H, m), 7.23-7.55 (4H, m), 6.84-7.14 (2H, m), 5.73 (1H, m), 4.89-5.15 (2H, m), 4.38-4.48 (2H, m) and 2.37 (3H, s); \(\delta C\) 156.09(q),
143.31(q), 135.44(q), 132.39, 131.34, 129.64, 129.31, 128.66, 120.60, 116.63, 112.81, 68.93 and 21.37 (one quaternary signal is not apparent); m/z 252 (M⁺, 30%), 237(34), 222(21), 211(51), 209(27), 208(29), 181(45), 121(64), 120(33), 119(100) and 91(78).

2. Preparation of 2-(Allyloxy)diphenyl[²H₂]methane

A solution of 2-(allyloxy)benzophenone (2.5 g, 0.01 mol) in dry ether (30 ml) was added dropwise to a stirred suspension of lithium aluminium deuteride (0.410 g, 0.01 mol) in dry ether (30 ml). After 40 min. a solution of aluminium chloride (1.40 g, 0.01 mol) in dry ether (20 ml) was added via the dropping funnel. The mixture was stirred at room temperature and monitored by g.c. After 5 h most of the starting material had reacted so the reaction was worked-up. Water (15 ml) was added to the reaction mixture followed by sulphuric acid (6M, 15 ml). The ether layer was separated and the aqueous layer was extracted with ether (3 x 20 ml). The combined ethereal solutions were dried (MgSO₄) and the solvent was removed in vacuo. The required product was isolated as an oil contaminated with minor impurities (crude wt. = 1.06 g), b.p. 130-132°C (0.2 Torr). The minor impurities were separated by dry-flash chromatography, using methylene chloride/hexane (50:50) as eluant, to give the required deuteriated product as a colourless oil (0.738 g, 31%), b.p. 133-135°C (0.2 Torr), δ²H (CHCl₃): 3.91.
3. Pyrolysis of 2-(Allyloxy)benzophenone

These pyrolyses were carried out on a preparative scale only, the yields quoted being for the isolated and purified compound. After pyrolysis, the entire pyrolysate was dissolved in methylene chloride and was extracted with sodium hydroxide solution (2M, 300 ml). The base extract was neutralised, extracted with methylene chloride (3 x 100 ml), dried (MgSO₄) and the solvent was removed. The residual mixture was separated by dry-flash chromatography, eluting with the solvent system stated. After base extraction the remaining methylene chloride solution was dried (MgSO₄) and the components of the residue were separated by dry-flash chromatography, again eluting with the solvent system stated. The following compounds were treated in this way.

(a) 2-(Allyloxy)benzophenone

0.452 g (1.9 mmol), 130-140°C, 750°C, 1 x 10⁻³ Torr, 120 min: 2-hydroxybenzophenone (8%); 1-hydroxyfluorenone (9%); xanthone (14%), dibenzofuran (6%). The following components were separated from the base extract, eluting with methylene chloride/hexane (50:50): 2-hydroxybenzophenone (0.030 g, 8%), b.p. 124-126°C (0.2 Torr) [lit.²⁰⁰, 175°C (14 Torr)], δH 12.03 (1H, s), 7.45-7.70 (7H, m), 7.07 (1H, d) and 6.87 (1H, t); δC 201.42 (C=O), 163.10(q), 137.82(q), 136.09, 133.39, 131.69, 128.95, 128.14, 119.03(q), 118.42 and 118.25. The ¹H n.m.r. and ¹³C n.m.r. spectra
are identical to those of an authentic sample: \( \delta H \ 12.07 \) (1H, s), 7.44-7.69 (7H, m), 7.06 (1H, d) and 6.86 (1H, t); 
\( \delta C \ 201.42 \) (C=O), 163.12(q), 137.79(q), 136.13, 133.42, 131.74, 129.00, 128.17, 119.02(q), 118.47 and 118.24: 1-hydroxyfluorenone (crude wt. = 0.05 g). The crude solid was recrystallised from aqueous ethanol to give 1-hydroxyfluorenone as a yellow crystalline solid (0.034 g, 9%), m.p. 115-117°C (lit. 201 \( \delta H \ 8.41 \) (1H, s), 7.58 (1H, d), 7.44 (2H, m), 7.21-7.36 (2H, m), 6.97 (1H, d) and 6.72 (1H, d); \( \delta C \ 196.07 \) (C=O), 157.25(q), 143.99(q), 143.69(q), 137.22, 134.44, 134.11(q), 128.89, 123.85, 120.80, 118.01, 117.28(q) and 112.59. The \( ^1H \) n.m.r. and \( ^{13}C \) n.m.r. spectra are consistent with those expected for this compound. After base extraction the following components were separated from the residue, eluting with methylene chloride/hexane (50:50): dibenzofuran (0.02 g, 6%), m.p. 72-74°C (from methanol) (lit. 202, 83-84°C), \( \delta H \ 7.96 \) (2H, d) and 7.28-7.63 (6H, m); 
\( \delta C \ 156.14(q), 127.00, 124.15(q), 122.57, 120.51 \) and 111.55. The \( ^1H \) n.m.r. and \( ^{13}C \) n.m.r. spectra are identical to those obtained for this compound when isolated from a preparative pyrolysis (see Section 14): xanthone (crude wt. = 0.068 g). The crude solid was recrystallised from ethanol to give xanthone as fine white needles (0.052 g, 14%), m.p. 174-175°C, mixed m.p. 174.5-176°C (lit. 203, 173-174°C), \( \delta H \ 8.29 \) (2H, d), 7.68 (2H, m) and 7.29-7.45 (4H, m); \( \delta C \ 176.89 \) (C=O), 155.98(q),
264

134.55, 126.52, 123.68, 121.70(q) and 117.76. The \(^1\)H n.m.r. and \(^{13}\)C n.m.r. are identical to those of an authentic sample; \(\delta\)H 8.28 (2H, d), 7.67 (2H, m) and 7.28-7.44 (4H, m); \(\delta\)C 176.87 (C=O), 155.95(q), 134.53, 126.50, 123.66, 121.69(q) and 117.74.

(b) 2-(Allyloxy)-4'-methylbenzophenone

0.568 g (2.25 mmol), 120-160°C, 750°C, 5 x \(10^{-3}\) Torr, 130 min: 2-hydroxy-4'-methylbenzophenone (5%); 1-hydroxy-6-methylfluorenone (9%); 2-methyl dibenzofuran (3%); 2-methylxanthone and 3-methylxanthone (18%). The following components were isolated from the base extract, eluting with methylene chloride/hexane (70:30): 2-hydroxy-4'-methylbenzophenone (crude wt. = 0.028 g). The orange oil obtained was triturated with light petroleum to give the product as a yellow solid (0.016 g, 5%), m.p. 54-57°C (lit.\(^{146}\), 61.5°C), \(\delta\)H 12.02 (1H, s), 6.75-7.67 (8H, m) and 2.45 (3H, s); \(\delta\)C 197.41 (C=O), 163.09(q), 142.56(q), 135.90, 135.19(q), 133.36, 129.33, 128.89, 119.29(q), 118.38, 118.26 and 21.43. The \(^1\)H n.m.r. and \(^{13}\)C n.m.r. spectra are identical to those obtained for this compound when prepared previously: 1-hydroxy-6-methylfluorenone (crude wt. = 0.08 g). The crude solid was recrystallised from ethanol to give 1-hydroxy-6-methylfluorenone as fine yellow needles (0.041 g, 9%), m.p. 104-106°C (from ethanol) (Found: C, 79.40; H, 4.75 \(\text{C}_{14}\text{H}_{10}\text{O}_{2}\) requires C, 80.00; H, 4.75%); (Found: \(\text{M}^+\) 210.0677 \(\text{C}_{14}\text{H}_{10}\text{O}_{2}\) requires \(\text{M}^+\) 210.0681); \(\delta\)H 8.42 (1H, s), 7.46 (1H, d), 7.24-7.33 (2H, m).
2.50 (3H, s); δC (D.E.P.T.) 134.36, 126.46, 126.41, 125.17, 123.50, 117.70, 117.49 and 21.73: 2-methylxanthone, δH 8.27 (1H, m), 8.03 (1H, s), 7.58-7.67 (1H, m), 7.07-7.46 (4H, m) and 2.39 (3H, s); δC (D.E.P.T.) 135.79, 134.28, 126.25, 125.76, 123.45, 117.70, 117.49 and 20.60. The ¹H n.m.r. and ¹³C n.m.r. spectra for this isomer are identical to those obtained for an authentic sample; δH 8.23 (1H, d), 7.98 (1H, s), 7.57 (1H, m), 7.20-7.40 (4H, m) and 2.35 (3H, s); δC (D.E.P.T.) 135.74, 134.32, 126.39, 125.69, 123.40, 117.67, 117.46 and 20.57.

A series of small scale pyrolyses were carried out at various furnace temperatures. For the peaks observed at 177.10 and 176.82 in the ¹³C n.m.r. spectra of the crude pyrolysate, attributed to the carbonyl group in each isomer, the ratio of 2-methylxanthone:3-methylxanthone was obtained at each temperature and from the g.c. traces of the crude pyrolysate the ratio of dibenzofuran:xanthone isomers was also obtained. The pyrolysis conditions are quoted below. For the results obtained from these experiments see the Discussion Section: 0.054 g (0.214 mmol), 130-160°C, 750°C, 1 x 10⁻³ Torr, 30 min; 0.048 g (0.19 mmol), 130-140°C, 850°C, 1 x 10⁻³ Torr, 40 min; 0.099 g (0.393 mmol), 140-150°C, 950°C, 1 x 10⁻³ Torr, 40 min.

(c) Pyrolysis of Xanthone

0.055 g (0.284 mmol), 120-140°C, 750°C, 5 x 10⁻³ Torr, 45 min. The crude pyrolysate was dissolved in chloroform and examined by g.c. The only product of the pyrolysis was xanthone. No dibenzofuran was present. 0.040 g (0.206 mmol), 130-140°C, 950°C, 1 x 10⁻³ Torr, 35 min. The only product of
the pyrolysis was identified as xanthone. Again no dibenzofuran was present.

4. **Pyrolysis of 2-(Allyloxy)diphenyl[\(\text{H}_2\)]methane**

0.108 g (0.478 mmol), 100-120°C, 750°C, 1 x 10^{-3} Torr, 35 min. The entire pyrolysate was dissolved in deuteriochloroform and analysed, from the \(^1\text{H}\) n.m.r. and \(^{13}\text{C}\) n.m.r. spectra, for its hydroxyfluorene content. The \(^1\text{H}\) n.m.r. spectrum shows a triplet at \(\delta\text{H} 3.85\), indicating that one of the deuterium labels has been replaced by hydrogen, and a singlet at \(\delta\text{H} 3.86\) corresponding to the methylene peak of 1-hydroxyfluorene (authentic 1-hydroxyfluorene shows a methylene peak at \(\delta\text{H} 3.84\)). The \(^{13}\text{C}\) n.m.r. spectrum shows a triplet at \(\delta\text{C} 33.15\), again indicating that a deuterium label has been replaced, and a methylene peak at \(\delta\text{C} 33.45\) corresponding to 1-hydroxyfluorene (authentic 1-hydroxyfluorene shows a methylene peak at \(\delta\text{C} 33.41\)). From these spectra it is not possible to determine if any 1-hydroxy-9-[\(\text{H}_2\)]fluorene is present in the pyrolysate.

The relative amounts of the hydroxyfluorene components were obtained from a 360 mHz \(^1\text{H}\) n.m.r. spectrum, sharpened by \(^2\text{H}\) irradiation. By accurate integration of the observed peaks for the unlabelled fluorene and the 1-hydroxy-9-[\(^1\text{H}\)][\(\text{H}_2\)]fluorene components relative to a doublet at \(\delta\text{H} 6.72\), known to correspond to one aromatic proton of 1-hydroxyfluorene, the relative amount of the 1-hydroxy-9-[\(\text{H}_2\)]fluorene was obtained by difference.
A $^2$H n.m.r. spectrum showed no peaks at $\delta H$ 6.72 in the region of the doublet. The relative amounts of 1-hydroxy-9-$^{[2H]}$fluorene:1-hydroxy-9-$^{[1H][2H]}$fluorene:1-hydroxy-fluorene were found to be 4.6:4.4:1.
I. PREPARATION OF DIBENZOFURANS AND RELATED HETERO-ANALOGUES

PREPARATION OF DIBENZOFURANS

1. Preparation of Reagents

(a) 3-Chloro-p-toluenitrile

A cuprous chloride solution was first prepared. A solution of copper sulphate (50 g, 0.2 mol) and sodium chloride (12.99 g, 0.22 mol) in hot water (160 ml) was prepared and an alkaline solution of sodium sulphite [from sodium bisulphite (10.6 g) and sodium hydroxide (7 g) in water (80 ml)] was added, with stirring, over a period of 5 min. The mixture was cooled to room temperature and washed by decantation. The cuprous chloride was obtained as a white solid which would, however, darken on exposure to air. The cuprous chloride was suspended in cold water (80 ml) and a solution of sodium cyanide (25.5 g, 0.52 mol) in water (40 ml) was added, with stirring. The cuprous chloride dissolved with considerable evolution of heat to give a solution of cuprous cyanide.

3-Chloro-p-toluidine (14 g, 0.1 mol) was added to a mixture of hydrochloric acid (d. 1.19, 40 ml), water (20 ml) and ice (80 g) and the mixture was stirred until the solid had dissolved. The solution was cooled to 0-5°C and a solution of sodium nitrite (7 g, 0.1 mol)
in water (23 ml) was added dropwise, the temperature being kept in the range 0-5°C. This diazonium solution was quickly added, with stirring, to the boiling cuprous cyanide solution and the resulting mixture was boiled for 10 min. The mixture was then steam distilled, the distillate was extracted with ether (3 x 30 ml), dried (MgSO₄) and the solvent was removed in vacuo. An orange oil was obtained which was found to be a mixture of starting material and product. This material was dissolved in ether, washed with dilute acid, dried (MgSO₄) and the solvent removed to give the required product as a pale brown solid (1.54 g, 10%), m.p. 58-60°C (from ethanol) (lit.¹⁸¹, 60-61°C), δH 7.53 (1H, d), 7.31 (1H, s), 7.14 (1H, dd) and 2.39 (3H, s).

(b) 2-Chloro-4-methylbenzoic acid

The nitrile (1.3 g, 8.58 mmol) was hydrolysed to the corresponding acid by heating under reflux with potassium hydroxide solution (2M, 150 ml) for 5 h. The reaction mixture was cooled, extracted with ether (2 x 20 ml) and was then acidified. The required product was obtained as a white solid (1.33 g, 91%), m.p. 152-154°C (lit.¹⁸², 155-155.5°C), δH 7.92 (1H, d), 7.29 (1H, s), 7.12 (1H, d) and 2.37 (3H, s).
2. **Preparation of Substituted 2-Phenoxybenzoic acids**

The appropriate phenol (63 mmol) was reacted with the potassium salt of o-chlorobenzoic acid (25 mmol) and copper bronze (0.1 g), in methanolic sodium methoxide [from sodium (25 mmol) in methanol (15 ml)] as previously described in Section G4. After work-up the required product was purified by recrystallisation from the appropriate solvent. The following compounds were prepared by this method: 2-(4-acetylphenoxy)benzoic acid (2.86 g, 45%), m.p. 184-185°C [from methanol/water (70:30)] (lit.204, 182°C), δH ([^2^H_6]DMSO): 7.75 (1H, d), 7.35-7.6 (2H, m), 7.20 (1H, d), 6.81-6.92 (4H, s), 6.79 (1H, s) and 3.68 (3H, s);
δC ([^2^H_6]DMSO): 195.43 (C=O), 166.11(C=O), 162.08(q), 153.40(q), 134.08, 131.81, 131.37(q), 130.66, 125.50, 125.17(q), 122.77, 116.28 and 26.56: 2-(4-chlorophenoxy)benzoic acid (4.03 g, 65%), m.p. 110-111°C (from aqueous ethanol) (lit.205, 114-115°C), δH ([^2^H_6]DMSO): 7.83 (1H, d), 7.27-7.69 (4H, m) and 6.78-7.19 (3H, m); δC ([^2^H_6]DMSO): 166.25 (C=O), 156.68(q), 154.29(q), 133.71, 131.50, 129.63, 126.45(q), 124.75(q), 124.60, 121.56 and 118.96: 2-(4-methoxyphenoxy)benzoic acid (4.70 g, 78%), m.p. 140-141°C [from light petroleum/xylene (50:50)] (lit.204, 144°C), δH ([^2^H_6]-DMSO) 7.75 (1H, dd), 7.05-7.58 (3H, m), 6.79-6.91 (4H, s) and 3.63 (3H, s); δC ([^2^H_6]DMSO) 166.87 (C=O), 156.33(q), 155.46(q), 150.29(q), 133.28, 132.94, 123.78(q), 123.00,
119.93, 119.16, 115.11 and 55.53: 2-(3-methylphenoxy)-benzoic acid (3.00 g, 53%), m.p. 91-93°C [from methanol/water (80:20)] (lit. 148, 95°C), δH ([2H6]DMSO): 7.85 (1H, dd), 7.55 (1H, t), 7.03-7.34 (3H, m), 6.94 (1H, s), 6.64-6.85 (2H, m) and 2.27 (3H, s); δC ([2H6]DMSO): 167.65 (C=O), 157.28(q), 155.11(q), 140.32(q), 134.51, 133.01, 129.64, 120.50, 123.19, 120.26, 119.97(q), 118.31, 116.59 and 21.15:

2-(3-acetylphenoxy)benzoic acid (2.82 g, 44%), m.p. 105-107°C [from methanol/water (70:30)] (Found: C, 68.6; H, 4.55 C15H12O4.0.33H2O requires C, 68.7; H, 4.85%) (consistently analyses with 0.33 mol water); δH([2H6]-DMSO): 7.85 (1H, dd), 7.26-7.71 (5H, m), 7.00-7.19 (2H, m) and 2.50 (3H, s); δC ([2H6]DMSO): 184.45 (C=O), 166.34 (C=O), 158.14(q), 154.23(q), 138.56(q), 133.82, 131.61, 130.38, 124.92(q), 124.77, 122.97, 122.09, 121.75, 115.86 and 26.83: m/z 256 (M+, 44%), 241(49), 152(20), 139(29) and 136(100): 2-(2-methylphenoxy)benzoic acid (4.08 g, 72%), m.p. 133.5-134°C [from benzene/light petroleum (50:50)] (lit. 148, 133.5°C), δH 9.74 (1H, br.s), 8.16 (1H, dd), 6.91-7.53 (6H, m), 6.69(1H, d) and 2.23 (3H, s); δC 167.35 (C=O), 157.44(q), 152.37(q), 134.58, 133.26, 131.75, 130.19(q), 127.45, 125.50, 122.66, 120.48, 118.85(q), 116.16 and 15.88:

2-phenoxy-4-methylbenzoic acid (55%), m.p. 130-133°C (from acetonitrile) (Found: C, 73.7; H, 5.25 C14H12O3 requires C, 73.7; H, 5.25%); δH 8.03 (1H, s), 7.38 (2H, m), 7.20 (1H, m), 7.02 (3H, m), 6.66 (1H, s) and 2.29 (3H, s);
3. Preparation of Allyl 2-phenoxybenzoates

The appropriate benzoic acid (0.01 mol) was reacted with allyl bromide (0.02 mol) in dimethylformamide (25 ml) containing potassium carbonate (0.02 mol) as previously described in Section D2. The reaction mixture was stirred overnight at room temperature and the product was purified by distillation. The following compounds were prepared by this method: **allyl 2-phenoxybenzoate** (1.90 g, 80%), b.p. 134-136°C (0.4 Torr) (Found: C, 75.7; H, 5.55; \( C_{16}H_{14}O_3 \) requires C, 75.6; H, 5.5%); \( \delta H \) 7.95 (1H, dd), 7.10-7.54 (5H, m), 6.85-7.03 (3H, m), 5.86 (1H, m), 5.07-5.43 (2H, m) and 4.70 (2H, d); \( \delta C \) 165.18 (C=O), 157.48(q), 155.95(q), 133.39, 131.83, 131.69, 129.50, 123.33, 123.19(q), 122.84, 120.78, 117.91 and 65.44 (two signals co-incidental at \( \delta \)117.91); m/z 254 (M', 45%), 197(100) and 115(21): **allyl 2-(4-methylphenoxy)benzoate** (1.84 g, 63%), b.p. 141-143°C (0.4 Torr) (Found: C, 76.5; H, 6.0; \( C_{17}H_{16}O_3 \) requires C, 76.1; H, 5.95%); \( \delta H \) 7.94 (1H, dd), 7.38 (1H, td), 6.81-7.21 (6H, m), 5.90 (1H, m),
5.09-5.46 (2H, m), 4.74 (2H, m) and 2.31 (3H, s);
δC 165.37 (C=O), 156.68 (q), 154.98 (q), 133.33, 132.61 (q),
131.97, 131.64, 130.06, 122.85, 120.02, 118.30,
117.86, 65.45 and 20.50 (one quaternary signal not
apparent); m/z 268 (M^+, 68%), 211(65), 192(27), 151(30),
155(100), 121(49), and 120(46): allyl 2-(4-acetyl-
phenoxy)benzoate (1.26 g, 44%), b.p. 139-141°C (0.2 Torr)
(Found: C, 73.4; H, 5.5  C_{18}H_{16}O_4 requires C, 73.0;
H, 5.4%); δH 7.81-8.04 (3H, m), 6.83-7.56 (5H, m), 5.50-6.25 (1H, m), 5.06-5.36 (2H, m), 4.61 (2H, m) and 2.53 (3H, s);
δC 196.18 (C=O), 164.45 (C=O), 162.09 (q), 154.14 (q),
133.72, 131.96, 131.61, 130.29, 124.81, 124.00 (q), 122.41,
118.03, 116.23, 65.47 and 26.04 (one quaternary signal
not apparent); m/z 296 (M^+, 50%), 281(100) and 197(34):
allyl 2-(4-chlorophenoxy)benzoate (2.3.4 g, 81%), b.p. 150-
153°C (0.1 Torr) (Found: C, 67.0; H, 4.5  C_{16}H_{13}ClO_3
requires C, 66.55; H, 4.5%); δH 7.93 (1H, dd), 7.25 -
7.56 (4H, m), 6.74-7.14 (3H, m), 5.84 (1H, m), 5.07-5.38
(2H, m) and 4.68 (2H, m); δC 164.84 (C=O), 156.34 (q),
155.41 (q), 133.55, 131.83, 131.75, 129.44, 127.76 (q),
123.91, 123.39 (q), 121.09, 118.86, 118.03 and 65.50;
m/z 290 (27%), 288 (M^+, 75), 246(25), 231(100) and
197(40): allyl 2-(4-methoxyphenoxy)benzoate (2.08 g, 73%),
b.p. 107-109°C (0.3 Torr) (Found: C, 71.6; H, 5.65
C_{17}H_{16}O_4 requires C, 71.85; H, 5.65%); δH 7.81-7.93
(1H, m), 6.71-7.46 (7H, m), 5.75-6.20 (1H, m), 5.09-5.43
(2H, m), 4.74 (2H, m) and 3.71 (3H, s); δC 165.38 (C=O)
157.37 (q), 155.68 (q), 150.34 (q), 133.23, 131.94, 131.54, 122.36, 122.17 (q), 120.02, 118.94, 117.81, 114.69, 65.39 and 55.47; m/z 284 (M+ , 2%), 192 (20) and 135 (100): allyl 2-(3-methylphenoxy)benzoate (2.21 g, 82%), b.p. 130–133°C (0.3 Torr) (Found: C, 76.3; H, 5.95%); δH 7.94 (1H, dd), 6.72–7.56 (7H, m), 5.83 (1H, m), 5.10–5.43 (2H, m), 4.73 (2H, d) and 2.31 (3H, s); δC 165.23 (C=O), 157.38 (q), 156.16 (q), 139.68 (q), 133.32, 131.93, 131.64, 129.21, 128.19 (q), 123.73, 123.14, 120.65, 118.74, 117.82, 115.03, 65.42 and 21.18; m/z 268 (M+, 35%), 212 (88), 211 (82), 197 (23), 180 (35), 151 (41) and 105 (100): allyl 2-(3-acetylphenoxy)benzoate (1.56 g, 56%), b.p. 142°C (0.4 Torr); a white crystalline solid was obtained, m.p. 32–34°C (from light petroleum) (Found C, 72.9; H, 5.35%); δH 7.92 (1H, dd), 7.60 (1H, d), 7.21–7.49 (3H, m), 7.05–7.18 (2H, d), 6.96 (1H, d), 5.80 (1H, m), 5.19 (2H, m), 4.64 (2H, m) and 2.49 (3H, s); δC 194.71 (C=O), 164.83 (C=O), 158.12 (q), 155.21 (q), 138.71 (q), 133.69, 131.97, 131.77, 129.72, 124.15, 123.51 (q), 122.66, 122.16, 121.34, 118.06, 116.94, 65.52 and 26.51; m/z 296 (M+, 59%), 239 (50), 221 (43), 211 (32), 197 (68), 161 (84), 135 (64) and 121 (100): allyl 2-(2-methylphenoxy)benzoate (2.20 g, 82%), b.p. 111–113°C (0.4 Torr) (Found: C, 75.7; H, 6.0%); C17H16O3 requires C, 76.1; H, 5.95%); δH 7.96 (1H, dd), 7.02–7.52 (5H, m), 6.75–6.98 (2H, m), 5.93 (1H, m), 5.12–5.49 (2H, m), 4.78 (2H, m) and 2.30 (3H, s); δC 165.64 (C=O), 156.70 (q), 154.61 (q),
2.75

133.28, 132.00, 131.74, 131.27, 129.28(q), 126.92, 123.66, 122.31, 121.98(q), 118.50, 118.37, 117.84, 65.40 and 15.99; m/z 268 (M⁺, 85%), 211(62), 197(23), 191(31), 183(65), 162(61), 139(88) and 135(100): allyl 2-phenoxy-5-methylbenzoate (69%), b.p. 141-143°C (0.2 Torr)

(Found: C, 75.9; H, 6.0  C₁₇H₁₆O₃ requires C, 76.1; H, 5.95%); δH 7.87 (1H, d), 7.30 (2H, m), 6.92–7.09 (4H, m), 6.81 (1H, s), 5.85 (1H, m), 5.13–5.35 (2H, m), 4.70 (2H, m) and 2.31 (3H, s); δC 165.02 (C=O), 157.77(q), 155.96(q), 144.58(q), 132.06, 131.76, 129.43, 124.36, 122.60, 121.54, 120.45(q), 117.74, 117.62, 65.19 and 21.23; m/z 268 (M⁺, 53%), 211(100), 175(29) and 119(29).

4.(a) Preparation of Dibenzofuran and 2-Substituted Dibenzofurans by Pyrolysis of Allyl 2-phenoxybenzoates

The appropriate allyl 2-phenoxybenzoate was distilled at 10⁻² - 10⁻³ Torr into a furnace at 900°C. Minor components of the pyrolysate were removed either by sublimation and recrystallisation or by chromatography followed by recrystallisation. The yields quoted are for the isolated and purified compound. The pyrolysis details are reported as [allyl 2-phenoxybenzoate derivative (amount pyrolysed), inlet temperature, pyrolysis time]. The following dibenzofurans were made by this method: dibenzofuran (0.28 g, 49%), sublimed, 125-128°C (0.3 Torr), to give a yellow solid, m.p. 80-81°C (from
methanol) (lit. 82-83°C), δH 7.92-8.05 (2H, m) and 7.26-7.72 (6H, m); δC 156.12(q), 126.92, 124.12(q), 122.49, 120.42 and 111.47; [from allyl 2-phenoxybenzoate (0.866 g, 3.41 mmol), 150-160°C, 1h]: 2-methyldibenzofuran (0.26 g, 38%), sublimed, 103-105°C (0.4 Torr), to give a yellow solid, m.p. 38-40°C (from ethanol) (lit. 44-45.5°C), δH 7.96 (1H, d), 7.78 (1H, s), 7.29-7.64 (5H, m) and 2.56 (3H, s); δC 156.36(q), 154.43(q), 132.03(q), 128.06, 126.99(q), 126.78, 124.13(q), 122.38, 120.48, 120.41, 111.50, 111.01 and 21.18; [from allyl 2-(4-methylphenoxy)benzoate (1.00 g, 3.73 mmol), 140-160°C, 90 min]: 2-acetyldibenzofuran (0.15 g, 35%) by column chromatography on alumina with ether/light petroleum (20:80) as eluant to give a white solid, m.p. 77-79°C (from methanol) (lit. 81°C), δH 8.54 (1H, s), 7.92-8.14 (2H, m), 7.32-7.61 (4H, m), and 2.68 (3H, s); δC 194.81 (C=O), 158.79(q), 156.75(q), 132.43(q), 127.83, 124.46(q), 123.63(q), 123.25, 121.44, 120.80, 111.81, 111.43 and 26.60 (two signals co-incidental at δ 127.83); [from allyl 2-(4-acetylphenoxy)benzoate (0.665 g, 2.25 mmol), 150-170°C, 160 min]: 2-chlorodibenzofuran (0.30 g, 56%) by column chromatography on alumina eluted with ether/light petroleum (50:50) to give a white solid, m.p. 100-101°C (from methanol) (lit. 100°C), δH 7.88-7.93 (2H, m) and 7.31-7.59 (5H, m); δC 156.68(q), 154.38(q), 128.10(q), 127.73, 127.00, 125.53(q), 123.23(q), 122.86, 120.66, 120.33, 112.50 and 111.72; [from allyl 2-(4-chlorophenoxy)benzoate (0.750 g, 2.60 mmol), 140-160°C, 105 min]: 2-methoxydibenzofuran was not obtained on
pyrolysis of the appropriate benzoate. G.c. showed the pyrolysate to have many minor components indicating the methoxy group was unstable to pyrolysis at this temperature. The same result was obtained when the pyrolysis was attempted at 800°C.

4. (b) Pyrolysis of Substituted Allyl 2-phenoxybenzoates

Excluding 4'-Substituted Derivatives

Allyl 2-(3-methylphenoxy)benzoate

0.069 g (0.57 mmol), 130-140°C, 900°C, 5 x 10⁻³ Torr, 35 min: 1-methyldibenzofuran (42%); 3-methyldibenzofuran (37%).

On a preparative scale the benzoate (0.645 g, 2.40 mmol) was distilled at 1 x 10⁻³ Torr into a furnace at 900°C over a period of 90 min. The crude pyrolysate was washed down a column of alumina, with ether as eluant, to give a mixture of 1-methyldibenzofuran and 3-methyldibenzofuran, separated from minor impurities. The mixture was partially separated using the different physical characteristics of the isomers, since the 3-methyl isomer crystallised on cooling the liquid 1-methyl isomer could be removed by pipette:

1-methyldibenzofuran (0.164 g, 37%) (contaminated with some 3-methyldibenzofuran), δH 8.05 (1H, d), 7.38-7.59 (5H, m), 7.17-7.26 (1H, t) and 2.86 (3H, s); δC 156.18(q), 156.08(q), 133.43(q), 126.79, 126.39, 124.83(q), 123.82, 122.48, 122.21, 111.38, 108.91 and 19.61 (one quaternary signal not apparent): 3-methyldibenzofuran (0.127 g; 29%) (contaminated with some 1-methyldibenzofuran), δH 7.96-8.00
(2H, m), 7.69 (2H, t), 7.39-7.59 (2H, m), 7.17-7.26 (1H, t), and 2.61 (3H, s); δC 156.60(q), 156.15(q), 137.48(q), 126.35, 124.31(q), 123.77, 122.40, 121.59(q); 120.11, 119.97, 111.79, 111.38 and 21.70. (A lit.209, 1H n.m.r. spectrum shows the 3-methyl isomer in the more shielded position at δH 2.40 with the 1-methyl isomer at δH 2.65. This corresponds to the results obtained for this pyrolysis, the 3-methyl isomer being the more shielded at δH 2.61 and the 1-methyl isomer at δH 2.86).

Allyl 2-(3-acetylphenoxy)benzoate
0.054 g (0.176 mmol), 130-160°C, 900°C, 5 x 10⁻³ Torr, 65 min: 1-acetyldibenzofuran (27%); 3-acetyldibenzofuran (29%). The pyrolysis was carried out on a preparative scale, the benzoate (0.634 g, 2.10 mmol) being pyrolysed at 900°C, 5 x 10⁻³ Torr over a period of 3 h. The components of the crude pyrolysate were separated by dry-flash chromatography, using methylene chloride/hexane (50:50) as eluant. The following components were separated: 1-acetyldibenzofuran (0.027 g, 6%), b.p. 157-159°C (0.3 Torr)210 isolated as a pale yellow oil, δH 8.80 (1H, dd), 7.24-7.95 (6H, m) and 2.75 (3H, s); δC 199.04 (C=O), 156.98(q), 156.81(q), 133.60(q), 128.24, 126.35, 126.03, 124.84, 123.04(q), 122.94(q), 122.72, 115.82, 110.98 and 28.24; 3-acetyldibenzofuran (0.028 g, 6%), m.p. 145-147°C (from methanol) (lit.211 144°C) isolated as a white solid, δH 8.15 (1H, s), 7.93-8.05 (3H, m), 7.37-7.60 (3H, m) and 2.69 (3H, s); δC 196.97 (C=O), 157.56(q), 155.87(q), 136.15(q), 128.45,
123.23(q), 123.05, 122.97, 121.27, 120.25, 119.02(q), 
111.88, 111.64, and 26.59.

**Allyl 2-(2-methylphenoxy)benzoate**

0.095 g (0.354 mmol), 110-120°C, 900°C, 1 x 10⁻³ Torr, 
40 min: 4-methyldibenzofuran (35%); 1-hydroxyfluorene (10%); 
xanthene (6%). On a preparative scale the benzoate (0.907 g, 
3.36 mmol) was distilled at 1 x 10⁻³ Torr into a furnace 
at 900°C over a period of 2 h. The entire pyrolysate was 
chromatographed on a column of alumina and eluted with 
ether (30%) in light petroleum. The following components 
were isolated: 4-methyldibenzofuran (crude wt. = 0.371 g). 
The crude isolated material was shown, by G.C. and spiking 
experiments to be contaminated with xanthene which could 
not be separated by further chromatography. The mixture 
was partly separated by distillation to give impure 
4-methyldibenzofuran as a yellow oil (0.202 g, 33%), b.p. 
106-108°C (0.2 Torr) [lit.²⁰⁶ 105°C (0.2 Torr)], 
δH 8.08 (1H, dd), 7.93 (1H, m), 7.80 (1H, m), 7.40-7.66 (4H, 
m) and 2.80 (3H, s); δC 155.96(q), 127.98, 126.76, 
124.51(q), 123.51(q), 122.50, 122.42, 121.73(q), 120.56, 
117.86, 111.50 and 15.09 (one quaternary signal not 
apparent). The ¹³C n.m.r. spectrum also shows peaks at δC 
128.76, 127.49, 122.79 and 116.32 (quaternary signals could 
not be unambiguously assigned) which are co-incidental 
to those observed for the authentic sample of xanthene 
previously quoted; 1-hydroxyfluorene (crude wt. = 0.062 g).
The crude oil obtained was purified by distillation, 146-148°C (0.4 Torr), to give 1-hydroxyfluorene as a yellow solid (0.045 g, 7%), m.p. 114-116°C (from water) (lit.149, 119-120°C), δH 7.79 (1H, d), 7.55 (1H, d), 7.23-7.47 (4H, m), 6.78 (1H, d), 5.10 (1H, br. s) and 3.84 (2H, s); δC 152.32(q), 143.90(q), 142.91(q), 141.71(q), 128.05, 126.81, 126.66, 125.04, 120.11, 113.61, 112.81 and 33.54 (one quaternary signal not apparent). The 1H n.m.r. and 13C n.m.r. spectra are identical to those obtained for the same compound when previously isolated (see Section G7).

**Allyl 2-phenoxy-5-methylbenzoate**

0.073 g (0.27 mmol), 130-140°C, 900°C, 5 x 10⁻³ Torr, 35 min: 1-methyldibenzofuran (25%); 3-methyldibenzofuran (75%) (relative yields are quoted). On a larger scale the benzoate (0.134 g, 0.50 mmol) was distilled at 1 x 10⁻³ Torr into a furnace at 900°C over a period of 45 min. The crude pyrolysate was purified by dry-flash chromatography, eluting with methylene chloride/hexane (30:70) to give a mixture of 1-methyldibenzofuran and 3-methyldibenzofuran (0.069 g, 76%). This mixture was not separated further, however the 1H n.m.r. and 13C n.m.r. spectra were identical to those previously obtained for the mixture. A series of small scale pyrolyses, at various temperatures, were also carried out. From the 1H n.m.r. spectra of the crude pyrolysates the relative
yields of the 1-methyl isomer, at 62.81, and the 3-methyl isomer, at 62.55, were obtained for each temperature:

0.035 g (0.131 mmol), 130-140°C, 850°C, 5 x 10^{-3} Torr, 60 min; 1-methyldibenzofuran (26%); 3-methyldibenzofuran (74%): 0.029 g (0.108 mmol), 130-140°C, 950°C, 1 x 10^{-3} Torr, 60 min; 1-methyldibenzofuran (25%); 3-methyldibenzofuran (75%): 0.033 g (0.123 mmol), 140-150°C, 950°C (packed with silica wool), 5 x 10^{-3} Torr, 60 min; 1-methyldibenzofuran (24%); 3-methyldibenzofuran (76%): 0.034 g (0.127 mmol), 140-150°C, 1000°C, 5 x 10^{-3} Torr, 45 min; 1-methyldibenzofuran (25%); 3-methyldibenzofuran (75%).

PREPARATION OF DIBENZOTHIOPHENES

5. Preparation of Substituted 2-Thiophenoxybenzoic acids

The appropriate thiophenol (0.09 mol) was reacted with diazonium salt of anthranilic acid in sodium hydroxide solution as previously described in Section E4, yields again being calculated from the sodium nitrite. After work-up the required product was washed with light petroleum then purified by sublimation or recrystallisation. The following compounds were prepared by this method:

2-(4-chlorothiophenoxy)benzoic acid (5.91 g, 49%), m.p. 222-226°C (from aqueous ethanol) (lit.212, 239-242°C),
δH ([2H_6]DMSO): 7.90 (1H, d), 7.34-7.86 (5H, m), 7.25 (1H, m) and 6.76 (1H, d); δC ([2H_6]DMSO): 167.25 (C=O), 140.18(q), 136.15, 133.95(q), 132.29, 131.74(q), 130.66, 129.86, 128.58(q), 127.53 and 125.12: 2-(3-methylthiophenoxy)benzoic acid (5.9 g, 54%), purified by sublimation, 136-138°C (0.15 Torr), to leave the required product as a white crystalline solid, m.p. 174-176°C (from ethanol) (Found: C, 67.9; H, 5.0 C_{14}H_{12}O_2S requires C, 67.6; H, 5.0%) (analyses consistently with 0.25 mol H_2O); δH 8.12 (1H, d), 7.25-7.40 (5H, m), 7.17 (1H, t), 6.82 (1H, d) and 2.37 (3H, s); δC ([2H_6]DMSO): 167.28(q), 141.44(q), 139.39(q), 135.18, 132.06, 131.85, 130.63, 129.77, 129.66, 128.01(q), 127.06, 124.54 and 20.65 (one quaternary signal not apparent); m/z 244 (M+, 100%), 184(28), 149(22) and 137(44): 2-(2-methylthiophenoxy)benzoic acid (4.95 g, 48%), purified by sublimation, 138-140°C (0.2 Torr), to leave the required product as a white powdery solid, m.p. 171-173°C (from ethanol) (Found: C, 68.6; H, 4.75 C_{14}H_{12}O_2S requires C, 68.85; H, 4.9%); δH ([2H_6]DMSO): 7.94 (1H, d), 7.52 (1H, d), 7.37 (2H, m), 7.25-7.33 (2H, m), 7.16 (1H, m), 6.52 (1H, d) and 2.25 (3H, s); δC ([2H_6]DMSO): 167.29 (C=O), 142.11(q), 140.90(q), 136.29, 132.20, 131.08, 130.98, 129.81, 127.62(q), 127.34, 125.85, 125.68(q), 124.34 and 19.94; m/z 244 (M+, 100%), 226(24), 197(32), 193(45), 149(56), 137(23) and 91(59).
6. **Preparation of Allyl 2-thiophenoxybenzoates**

The appropriate benzoic acid (5 mmol) was reacted with allyl bromide (10 mmol) in dimethylformamide (15 ml) containing potassium carbonate (10 mmol) as previously described in Section D2. The reaction mixture was stirred overnight at room temperature and the product was purified by distillation. The following compounds were prepared by this method: **allyl 2-thiophenoxybenzoate** (75%), b.p. 179-181°C (0.4 Torr) (Found: C, 71.6; H, 5.25 C_{16}H_{14}O_{2}S requires C, 71.1; H, 5.15%); δH 7.97 (1H, m), 7.31-7.62 (5H, m), 7.07-7.25 (2H, m), 6.93 (1H, m), 6.04 (1H, m), 5.19-5.55 (2H, m) and 4.85 (2H, m); δC 165.91 (C=O), 143.09(q), 135.34, 132.55(q), 132.17, 132.02, 130.89, 129.58, 128.89, 127.43, 126.79(q), 124.20, 118.39 and 65.68; m/z 270 (M^+, 25%), 213(51), 184(37), 146(35), 138(31), 118(90), 109(26) and 91(100): **allyl 2-(4-methyl-thiophenoxy)benzoate** (48%), purified by sublimation, 157-159°C (0.3 Torr) to give a yellow solid, m.p. 60-62°C (from methanol) (Found: C, 71.9; H, 5.75 C_{17}H_{16}O_{2}S requires C, 71.85; H, 5.65%); δH 8.02 (1H, dd), 7.98 (2H, d), 7.04-7.46 (4H, m), 6.81 (1H, d), 6.05 (1H, m), 5.26-5.49 (2H, m), 4.85 (2H, m) and 2.38 (3H, s); δC 165.76 (C=O), 143.79(q), 139.12(q), 135.48, 131.99, 130.80, 130.33, 128.62(q), 126.89, 126.31(q), 123.81, 118.23, 65.50 and 21.05; m/z 284 (M^+, 94%), 246(22), 227(100) and 184(44): **allyl 2-(4-chlorothiophenoxy)-**
benzoate (20%), purified by distillation, 160-162°C (0.1 Torr), to give the required product, on cooling, as a yellow solid, m.p. 58-61°C (from methanol) (Found: C, 63.1; H, 4.25; N, 0.45 \( \text{C}_{16}\text{H}_{13}\text{ClO}_2\text{S}\). 0.1 mol HCON(CH₃)₂ requires C, 62.8; H, 4.4; N, 0.45%) (consistently analyses with 0.1 mol dimethylformamide); \( \delta \text{H} 8.02 \) (1H, dd), 7.29-7.99 (4H, m), 7.09-7.27 (2H, m), 6.81 (1H, d), 6.04 (1H, m), 5.25-5.48 (2H, m) and 4.84 (2H, m); \( \delta \text{C} 165.76 \) (C=O), 142.07(q), 136.24, 135.12(q), 132.19, 131.92, 131.42(q), 130.91, 129.73, 129.27(q), 127.62, 124.57, 118.38 and 65.67; \( m/z \) 306 (37%), 304 (100), 247(90), 184(46), 143(22) and 108(35): allyl 2-(3-methylthiophenoxy)benzoate (52%), b.p. 175-178°C (0.2 Torr) (Found: C, 71.7; H, 5.65 \( \text{C}_{17}\text{H}_{16}\text{O}_2\text{S} \) requires C, 71.8; H, 5.6%); \( \delta \text{H} 8.04 \) (1H, m), 7.01-7.97 (6H, m), 6.83 (1H, m), 6.05 (1H, m), 5.20-5.56 (2H, m), 4.85 (2H, m) and 2.36 (3H, s); \( \delta \text{C} 165.73 \) (C=O), 143.16(q), 139.31(q), 135.71, 132.21, 132.09(q), 132.00, 131.93, 130.72, 129.61, 129.26, 127.32, 126.65(q), 123.97, 118.19, 65.49 and 20.97; \( m/z \) (284 (M⁺, 83%), 264(38), 227(100) and 184(25): allyl 2-(2-methylthiophenoxy)benzoate (51%), b.p. 155-157°C (0.1 Torr) (Found: C, 72.0; H, 5.65 \( \text{C}_{17}\text{H}_{16}\text{O}_2\text{S} \) requires C, 71.85; H, 5.65%); \( \delta \text{H} 7.98 \) (1H, m), 7.31-7.57 (1H, m), 7.21-7.27 (2H, m), 7.01-7.18 (3H, m), 6.59 (1H, m), 6.02 (1H, m), 5.16-5.51 (2H, m), 4.82 (2H, m) and 2.30 (3H, s); \( \delta \text{C} 165.72 \) (C=O), 142.79(q), 142.54(q), 136.65, 132.12, 131.99, 131.23(q), 131.00, 130.74, 129.53, 126.95, 126.45(q), 126.22, 123.78, 118.14, 65.44 and 20.29; \( m/z \) 284 (M⁺, 74%), 246(63), 227(50), 197(37), 164(29), 149(29), 137(32) and 123(100).
7.(a) **Preparation of Dibenzothiophene and 2-Substituted Dibenzothiophenes by Pyrolysis of Allyl 2-thiophenoxybenzoates**

The appropriate allyl 2-thiophenoxybenzoate was distilled at $10^{-2} \text{ - } 10^{-3}$ Torr into a furnace at 900°C. The crude pyrolysate was dissolved in methylene chloride and was washed with sodium carbonate solution (10%, 50 ml). The residue was then separated from minor impurities by dry-flash chromatography, using methylene chloride/hexane (50:50) as eluant. The yields quoted are for the isolated, pure compound. The pyrolysis details are reported as [allyl 2-thiophenoxybenzoate derivative (quantity pyrolysed), inlet temperature, pyrolysis time]. The following dibenzothiophenes were made by this method: dibenzothiophene (0.201 g, 63%), m.p. 96-98°C (from ethanol), mixed m.p. 98-100°C (lit.; \textsuperscript{202}99.7°C), δH 8.18 (2H, m), 7.88 (2H, m) and 7.48 (4H, m); δC 139.34(q), 135.44(q), 126.49, 124.15, 122.61 and 121.37. The \textsuperscript{1}H n.m.r. and \textsuperscript{13}C n.m.r. spectra are identical to those of an authentic sample: δH 8.19 (2H, m), 7.90 (2H, m) and 7.50 (4H, m); δC 139.25(q), 135.34(q), 126.40, 124.06, 122.50 and 121.31; [from allyl 2-thiophenoxybenzoate (0.467 g, 1.73 mmol), 140-170°C, 95 min]: 2-methyldibenzothiophene (0.088 g, 56%), m.p. 80-83°C (from ethanol) (lit.; \textsuperscript{213}86°C), δH 8.13 (1H, m), 7.97 (1H, s), 7.85 (1H, m), 7.75 (1H, d), 7.45 (2H, m), 7.28 (1H, d) and 2.55 (3H, s); δC 139.79(q), 136.40(q),
135.66(q), 135.39(q), 133.98(q), 128.08, 126.38, 124.06, 122.69, 122.29, 121.65, 121.33 and 21.30; [from allyl 2-(4-methylthiophenoxy)benzoate (0.225 g, 0.79 mmol), 140-160°C, 85 min]: 2-chlorodibenzothiophene (0.046 g, 36%), m.p. 122-123°C (from ethanol) (lit. 213, 125-126°C), δH 7.94-8.07 (2H, m), 7.60-7.88 (2H, m) and 7.30-7.53 (3H, m); δC 140.03(q), 137.36(q), 136.73(q), 134.38(q), 130.50(q), 127.12, 126.70, 124.41, 123.52, 122.69, 121.56 and 121.27; [from allyl 2-(4-chlorothiophenoxy)benzoate (0.180 g, 0.59 mmol), 130-160°C, 1.5 h].

7.(b) Pyrolysis of Allyl 2-(2-methylthiophenoxy) and 2-(3-methylthiophenoxy)benzoates

Allyl 2-(3-methylthiophenoxy)benzoate

0.039 g (0.137 mmol), 150-170°C, 900°C, 5 x 10⁻³ Torr, 35 min: 1-methyldibenzothiophene (37%); 3-methyldibenzothiophene (31%). On a preparative scale the benzoate (0.488 g, 2.46 mmol) was distilled at 1 x 10⁻³ Torr into a furnace at 900°C over a period of 75 min. The entire pyrolysate was dissolved in methylene chloride and was washed with sodium carbonate solution (10%, 50 ml). The residue was purified by dry-flash chromatography eluting with methylene chloride/hexane (50:50) to leave a clean mixture of 1-methyldibenzothiophene and 3-methyldibenzothiophene (0.234 g, 48%) which could not be further separated. The ¹H n.m.r. spectrum showed two methyl peaks at δH 2.99 and 2.59, the peak at 2.99 being assigned to the 1-methyl
isomer (lit. chemical shift, $^{214}\delta$ 2.82) and the peak at 2.59 being assigned to the 3-methyl isomer (lit. chemical shift $^{215}\delta$ 2.45). The $^{13}$C n.m.r. spectrum showed methyl peaks at $\delta$C 22.24 and 21.35, assigned to the 1-methyl and 3-methyl isomers respectively. The remainder of the peaks in the $^{13}$C n.m.r. spectrum could not be unambiguously assigned, a small group of quaternary carbon signals being observed between 139.02 and 139.58 and a further group of quaternary carbon signals evident between 133.04 and 136.54. A group of peaks attributed to the methine signals was observed between 120.23 and 126.74.

**Allyl 2-(2-methylthiophenoxy)benzoate**

0.104 g (0.366 mmol), 130-150°C, 900°C, $1 \times 10^{-3}$ Torr, 60 min: 4-methyl dibenzothiophene (52%); thioxanthene (22%).

The benzoate (0.546 g, 1.92 mmol) was pyrolysed on a preparative scale at 900°C, $2 \times 10^{-3}$ Torr over a 140 min. period. The pyrolysate was purified by dry-flash chromatography using methylene chloride/hexane (30:70) as eluant to give 4-methyl dibenzofuran, separated from minor impurities as a yellow crystalline solid. The crude isolated material was shown by g.c. to be contaminated with thioxanthene which could not be separated by further chromatography. Attempts to separate the mixture by both distillation and recrystallisation proved unsuccessful, the isolated sample of 4-methyl dibenzofuran remaining contaminated with thioxanthene (isolated wt. = 0.221 g);
4-methyldibenzofuran, $\delta$H 8.06-8.23 (2H, m), 7.79-7.99 (2H, m), 7.30-7.58 (3H, m) and 2.61 (3H, s); $\delta$C 139.49(q), 139.14(q), 135.29(q), 132.11(q), 127.16(q), 126.88, 126.41, 124.59, 124.21, 122.70, 121.66, 118.93 and 20.34. The $^1$H n.m.r. spectrum shows a single peak at $\delta$H 3.92 which is coincidental with the methylene signal in authentic thioxanthene which appears at $\delta$H 3.90. The $^{13}$C n.m.r. spectrum also shows peaks which are coincidental with those observed for authentic thioxanthene as previously quoted; $\delta$C 136.10(q), 133.78(q), 127.80, 126.73, 126.52, 126.41 and 39.06.
ATTEMPTED PREPARATION OF CARBAZoles AND N-METHYL-CARBAZoles

8. Preparation of Reagents

(a) N-Methyl-N-Phenylanthraniolic acid

A mixture of N-phenylanthraniolic acid (5.00 g, 23 mmol), sodium hydroxide (1.0 g, 25 mmol), methyl iodide (10 g, 70 mmol) and water (30 ml) was heated under reflux for 60 h, the reaction being monitored by t.l.c. After this time the reaction seemed to proceed no further so excess methyl iodide was removed on the vacuum pump. The mixture was extracted with ether (3 x 50 ml), washed with water (3 x 50 ml), dried (MgSO₄) and the solvent was removed in vacuo. The product mixture was separated by dry-flash chromatography, using chloroform/hexane (40:60) as eluant, to give the methyl ester of the required product. The ester (0.37 mmol) was heated under reflux with sodium hydroxide solution (20%, 15 ml) for 1 h., the mixture was diluted with water (100 ml) and was then acidified. The required product was isolated as a yellow solid (0.906 g, 13%), m.p. 102-103°C [from light petroleum/ether (50:50)] (lit.¹⁸³, 104-104.5), δH 8.37 (1H, m), 6.86-7.60 (8H, m) and 3.21 (3H, s). [Note: (1) When the reaction was first attempted the mixture of methyl esters was hydrolysed then attempts were made to separate the mixture of acids, which proved unsuccessful; (2) When carrying out this reaction, a
double surface condenser must be used to prevent loss of methyl iodide. It may also be necessary to add additional amounts of methyl iodide for the reaction to continue further.

(b) N-Methyl-N- (4-methylphenyl)anthranilic acid

A mixture of N-phenyl-(4'-methyl)anthranilic acid (5 g, 0.023 mol) (previously prepared in Section F2), sodium hydroxide (1 g, 0.025 mol), methyl iodide (11 g, 0.080 mol) and water (30 ml) was reacted, as previously described for the unsubstituted system. The methyl ester of the required product was isolated, after dry-flash chromatography, with chloroform/hexane (60:40) as eluant, and the ester was hydrolysed to the required acid as previously described. On acidifying the reaction mixture a sticky brown oil was obtained so the mixture was extracted with ether (3 x 50 ml), dried (MgSO₄) and the solvent was removed in vacuo. An oily solid was thus obtained which was recrystallised from light petroleum/ether (50:50) to give the required product as a yellow crystalline solid (0.673 g, 12%), m.p. 86-88°C (Found: C, 74.6; H, 6.25; N, 5.9 \( \text{C}_{15}\text{H}_{16}\text{NO}_2 \) requires C, 74.7; H, 6.2; N, 5.8%); δH 12.65 (1H, br.s), 8.32 (1H, dd), 7.44 (2H, m), 7.08 (3H, m), 6.81 (2H, m), 3.16 (3H, m) and 2.26 (3H, s); δC 166.06 (C=O), 150.98(q), 145.66(q), 134.67, 132.91(q), 132.26, 129.78, 127.64, 126.61, 125.95(q), 118.66, 42.05 and 20.38; m/z 241 (M⁺, 100%), 196(29), 194(19); 181(33) and 180(29).
9. Preparation of Allyl 2-(4-methylphenylamino)benzoate and Related N-Methyl Derivatives

The appropriate benzoic acid (3 mmol) was reacted with allyl bromide (6 mmol) in dimethylformamide (10 ml) containing potassium carbonate (6 mmol) as previously described in Section D2. The reaction mixture was stirred overnight at room temperature and purified by distillation. The following compounds were prepared by this method:

- **allyl 2-(4-methylphenylamino)benzoate (90%)**, b.p. 153-155°C (0.2 Torr) (Found: C, 76.6; H, 6.25; N, 5.3)

  \[ C_{17}H_{17}NO_2 \] requires C, 76.4; H, 6.4; N, 5.25%)

  \( \delta H \) 8.11 (1H, dd), 7.28 (6H, m), 7.25 (1H, br.s), 6.79 (1H, t), 6.16 (1H, m), 5.35-5.57 (2H, m), 4.91 (2H, m) and 2.44 (3H, s); \( \delta C \) 167.97 (C=O), 148.66 (q), 137.84 (q), 134.00, 133.36 (q), 132.27, 131.44, 129.78, 123.15, 117.88, 116.42, 113.58, 111.18 (q), 64.94 and 20.71; m/z 267 (M⁺, 74%), 209(100), 180(22) and 167(17).

- **allyl N-methyl-N-phenylanthranilate (89%)**, b.p. 168-170°C (0.2 Torr) (Found: M⁺ 267.1247; \[ C_{17}H_{16}NO_2 \] requires M⁺ 267.1259)

  \( \delta H \) 7.87 (1H, m), 7.45-7.64 (1H, m), 7.06-7.36 (4H, m), 6.60-6.86 (3H, m), 5.69 (1H, m), 5.08-5.37 (2H, m), 4.52 (2H, m) and 3.31 (3H, s); \( \delta C \) 166.22 (C=O), 148.99 (q), 147.87 (q), 132.91, 131.89, 131.10, 129.59 (q), 128.93, 128.56, 125.04, 117.87, 117.62, 113.93, 65.33 and 40.00; m/z 267 (M⁺, 100%), 226(21), 210(25), 208(25), 179(50), 180(54), 177(21) and
allyl N-methyl-N-(4-methylphenyl)anthranilate (93%), b.p. 177-179°C (0.3 Torr) (Found: C, 77.2; H, 6.7
C18H19NO2 requires C, 76.9; H, 6.75%); δH 7.82 (1H, m), 7.49 (1H, m), 7.32 (1H, s), 6.95-7.24 (4H, m), 6.61 (1H, m), 5.80 (1H, m), 5.11-5.38 (2H, m), 4.51 (2H, m), 3.30 (3H, s) and 2.27 (3H, s); δC 166.76 (C=O), 164.78(q), 148.38(q), 147.01(q), 132.90, 132.03, 131.13, 129.28, 128.14, 127.33(q), 124.48, 118.06, 114.88, 32.54, 40.46 and 20.20; m/z 281 (M+, 100%), 224(21), 222(27), 210(27), 195(27), 194(42) and 180(36).

10. Preparation of Authentic Samples for Comparison with Pyrolysates

Preparation of N-Methylcarbazole

Methyl iodide (3.19 g, 22.5 mmol) was added dropwise, with stirring, to a mixture of carbazole (2.5 g, 15 mmol), benzyldriethylammonium chloride (0.103 g, 0.45 mmol) and sodium hydroxide solution (50%, 10 ml), with benzene (5 ml) as solvent. The mixture was stirred at room temperature for 2 h. then poured into hot water (50 ml) and left overnight at room temperature. The precipitated solid was filtered and was washed well with water. The crude isolated material was found to be a mixture of starting material and product so the solid was dissolved in chloroform and filtered to remove the insoluble carbazole. The required N-methylcarbazole was isolated as a pale brown
solid (1.20 g, 44%), m.p. 85-86°C (from ethanol) (lit. 88-89°C), δH 8.17 (2H, m), 7.20-7.66 (6H, m) and 3.83 (3H, s); δC 140.93(q), 125.52, 122.72(q), 120.12, 118.71, 108.26 and 28.73.

Preparation of N-Methylacridone
Methyl iodide (1.92 g, 13.5 mmol) was added dropwise to a mixture of acridone (1.7 g, 8.75 mmol), benzyltriethylammonium chloride (0.06 g, 0.26 mmol) and sodium hydroxide solution (50%, 7 ml) with ethyl methyl ketone (7 ml) as solvent. The mixture was stirred at 55-60°C for 3 h. then was poured into hot water and left overnight at room temperature before the precipitated solid was filtered and washed well with water. The required N-methylacridone was isolated as a yellow solid (1.54 g, 83%), m.p. 200-201°C (from ethanol) (lit. 200-201°C), δH 8.49 (2H, m), 7.69 (2H, m), 7.56 (1H, s), 7.11-7.46 (3H, m) and 3.78 (3H, s); δC 177.74 (C=O), 142.39(q), 133.42, 127.48, 122.40(q), 120.91, 114.46, and 33.25.

11. Pyrolysis of Allyl 2-(4-methylphenylamino)benzoate and Related N-methyl Derivatives
Allyl 2-(4-methylphenylamino)benzoate
0.106 g (0.397 mmol), 140-160°C, 650°C, 1 x 10⁻³ Torr, 45 min: 2-methylacridone (24%), m/e 209 (M⁺, 86%), 181 (36%), 180(43), 122(43) and 105(100). A yellow solid formed round the entrance to the trap which was scraped out and
recrystallised from ethanol. The product isolated from the pyrolysis was not 2-methylcarbazole but was identified as 2-methylacridone (0.02 g, 24%), m.p. 318-320°C (lit.)

338°C), δH ([2H6]DMSO): 11.61 (1H, br.s), 8.16-8.28 (1H, m), 8.01 (1H, s), 7.30-7.72 (4H, m), 7.10-7.28 (1H, m) and 2.40 (3H, s); δC ([2H6]DMSO): 176.58 (C=O), 140.81(q), 139.00(q), 134.84, 133.14, 130.59(q), 126.00, 125.06, 120.66, 120.41(q), 117.24 and 20.54 (two signals co-incidental at 117.24 and two quaternary signals co-incidental at 120.41). The 13C n.m.r. spectrum is identical with that of an authentic sample; δC ([2H6]DMSO): 176.62 (C=O), 140.86(q), 139.06(q), 134.96, 133.26, 130.13(q), 126.08, 125.14, 120.76, 120.44(q), 117.33 and 20.65 (co-incidental signals as above).

**Allyl N-methyl-N-phenylantranilate**

0.085 g (0.318 mmol), 120-150°C, 900°C, 1 x 10⁻³ Torr, 40 min: acridone; carbazole; N-methylcarbazole [absolute yields could not be obtained for this pyrolysis]. On a preparative scale the benzoate (0.192 g, 0.719 mmol) was distilled at 5 x 10⁻³ Torr into a furnace at 900°C over a period of 100 min. The trap was washed through with chloroform to remove the components of the pyrolysate which were soluble in this solvent, an insoluble yellow solid being left in the trap. The solid was scraped out and identified as acridone (0.045 g, 32%), m.p. 326-330°C (decomp.), mixed m.p. 332-335°C (decomp) (lit.)

140, 344-346°C),
$\delta H \left( [^2\text{H}_6] \text{DMSO} \right): \ 8.23 \ (2\text{H}, \text{d}), \ 7.72 \ (2\text{H}, \text{m}), \ 7.54 \ (2\text{H}, \text{d})$
and $7.25 \ (2\text{H}, \text{t})$. The $^1\text{H}$ n.m.r. spectrum is identical to that of an authentic sample; $\delta H \left( [^2\text{H}_6] \text{DMSO} \right): \ 11.72 \ (1\text{H}, \text{br.s}), \ 8.23 \ (2\text{H}, \text{d}), \ 7.72 \ (2\text{H}, \text{m}), \ 7.54 \ (2\text{H}, \text{d})$ and $7.24 \ (2\text{H}, \text{t})$. The remainder of the pyrolysate was chromatographed by dry-flash chromatography, with chloroform/hexane (30:70) as eluant. The following components were isolated: N-methylcarbazole (0.006 g, 5%), m.p. 80-82°C (lit.\textsuperscript{183} 88-89°C), $\delta H \ 8.09 \ (2\text{H}, \text{d})$, 7.37-7.48 (6H, m) and 3.85 (3H, s). The $^1\text{H}$ n.m.r. spectrum is identical to that of the authentic sample previously quoted: carbazole (0.031 g, 26%) as a white solid after sublimation [174-176°C (0.3 Torr)], m.p. 238-240°C, mixed m.p. 240-243°C (lit.\textsuperscript{217, 245°C}), $\delta H \ 8.00-8.14 \ (2\text{H}, \text{m})$ and 7.11-7.49 (6H, m). The $^1\text{H}$ n.m.r. is identical to that of an authentic sample; $\delta H \ 8.01-8.13 \ (2\text{H}, \text{m})$ and 7.11-7.45 (6H, m). Absolute yields could not be obtained for the pyrolysis products since the carbazole peaks were co-incidental in g.c. and no common solvent could be found for n.m.r. work.

\textbf{Allyl N-methyl-N-(4-methylphenylamino)anthranilate}

0.0379 (0.132 mmol), 130-150°C, 900°C, $1 \times 10^{-3}$ Torr, 50 min: 2-methylacridone; 2-methylcarbazole; N-methyl-2-methylcarbazole [absolute yields could not be obtained for this pyrolysis]. On a larger scale the benzoate (0.240 g, 0.854 mmol) was pyrolysed at 900°C, $1 \times 10^{-3}$ Torr
over a period of 110 min. The trap was washed through with chloroform to remove the components of the pyrolysate which were soluble in this solvent, an insoluble yellow solid being left in the trap. The solid was scraped out and identified as 2-methylacridone (0.052 g, 30%), m.p. 325-328°C (lit.143, 335°C), δH ([2H₆DMSO]: 11.62 (1H, br.s), 8.23 (1H, d), 8.02 (1H, s), 7.30-7.74 (4H, m), 7.13-7.24 (1H, m) and 2.42 (3H, s). The ¹H n.m.r. spectrum is identical to that of an authentic sample; δH ([2H₆DMSO]: 11.63 (1H, br.s), 8.22 (1H, d), 8.02 (1H, s), 7.31-7.81 (4H, m), 7.20 (1H, m) and 2.40 (3H, s).

The remainder of the pyrolysate was chromatographed by dry-flash chromatography, with chloroform/hexane (30:70) as eluant. The following components were isolated: N-methyl-2-methylcarbazole (0.009 g, 6%) (Found: M⁺ 195.1052 C₁₄H₁₃N requires M⁺ 195.1048); δH 8.06 (1H, d), 7.89 (1H, s), 7.13-7.45 (5H, m), 3.82 (3H, s) and 2.54 (3H, s); m/z 195 (M⁺, 100%), 194(52), 44(38) and 40(33): 2-methylcarbazole (0.039 g, 26%), m.p. 200-201°C (from methanol) (lit.218, 199-203°C), δH 8.07 (1H, d), 7.87 (1H, s), 7.36-7.44 (2H, m), 7.17-7.33 (3H, m) and 2.53 (3H, s). The ¹H n.m.r. spectrum is identical to that of an authentic sample; δH 8.03 (1H, d), 7.86 (1H, s), 7.19-7.40 (5H, m) and 2.52 (3H, s).
N-Methylacridone

0.053 g (0.253 mmol), 140-180°C, 900°C, 1 x 10⁻³ Torr, 1 h. The only product obtained from the pyrolysis was acridone, isolated as a yellow solid. No N-methyl-acridone was isolated. δH ([²H₆]DMSO): 11.69 (1H, br.s), 8.23 (2H, m), 7.73 (2H, m), 7.52 (2H, m) and 7.23 (2H, t). The ¹H n.m.r. spectrum is identical to that of the authentic sample previously quoted.

N-Methylcarbazole

0.030 g (0.166 mmol), 130-140°C, 900°C, 5 x 10⁻³ Torr, 20 min. The solid obtained from the pyrolysis was identified as carbazole contaminated with a small amount of N-methyl-carbazole (approx. 20%), m.p. 200-205°C (lit. 217, 245°C), δH 8.02-8.17 (2H, m) and 7.13-7.51 (6H, m). The ¹H n.m.r. spectrum is identical to that of the authentic sample quoted previously.
12. **Preparation of Allyl 2-benzylbenzoate**

Allyl bromide (2.28 g, 17 mmol) was added dropwise to a stirred mixture of 2-benzylbenzoic acid (2.11 g, 9.9 mmol) in dimethylformamide (20 ml) containing potassium carbonate (2.06 g, 17 mmol) and the mixture was stirred overnight at room temperature. The work-up was carried out as previously described in Section D2. The crude product was purified by distillation to give the required product as a colourless oil (2.21 g, 88%), b.p. 138-140°C (0.1 Torr) (Found: C, 80.9; H, 6.6 C_{17}H_{16}O_{2} requires C, 80.95; H, 6.35%); δH 7.99 (1H, d), 7.44 (1H, m), 7.09-7.35 (7H, m), 5.99 (1H, m), 5.26-5.43 (2H, m), 4.78 (2H, d) and 4.44 (2H, s); δC 167.09 (C=O), 142.12(q), 140.78(q), 132.10, 131.85, 131.45, 130.55, 129.97(q), 128.83, 128.19, 126.12, 125.81, 118.13, 65.36 and 39.44; m/z 252 (M^+, 8%), 211(100), 193(24), 194(44), 165(52) and 133(58).

13. **Preparation of Allyl 2-benzoylbenzoate**

Allyl bromide (0.02 mol) was added dropwise to a stirred mixture of 2-benzoylbenzoic acid (0.02 mol) in dimethylformamide (25 ml) containing potassium carbonate (0.02 mol). The mixture was stirred overnight at room temperature and the reaction mixture was worked-up as previously described in Section D2. The crude isolated product was purified by distillation to give the
required **allyl 2-benzoylbenzoate** as a white oil (2.60 g, 97%), b.p. 145-147°C (0.2 Torr) (Found: C, 77.0; H, 5.25 \( \text{C}_{17}\text{H}_{14}\text{O}_{3} \) requires C, 76.7; H, 5.25%); \( \delta \) H 8.03 (1H, m), 7.22-7.77 (8H, m), 5.45-5.92 (1H, m), 4.97-5.25 (2H, m) and 4.41-4.50 (2H, m); \( \delta \) C 195.13 (C=O), 165.33 (C=O), 141.51(q), 136.98(q), 132.82, 132.19, 131.11, 129.90, 129.36, 129.16, 128.23, 127.56, 118.36 and 65.78 (one quaternary signal not apparent); m/z 266 (M+, 13%), 210(88), 209(67), 105(79), 77(60) and 41(100).

14. **Pyrolysis of Allyl 2-benzylbenzoate**

0.103 g (0.409 mmol), 120-140°C, 900°C, 1 x 10^{-3} Torr, 30 min.: fluorene (72%). On a preparative scale the benzoate (0.527 g, 2.09 mmol) was distilled at 5 x 10^{-3} Torr into a furnace at 900°C over a period of 105 min. The main component of the pyrolysate was separated from minor impurities by dry-flash chromatography with methylene chloride/hexane (50:50) as eluant to isolate fluorene (crude wt. = 0.193 g). The crude material was purified by recrystallisation, from ethanol, to give pure fluorene as a pale yellow crystalline solid (0.139 g, 40%), m.p. 110-112°C, mixed m.p. 111-112°C (lit.\(^{219}\), 115-116°C), \( \delta \) H 7.81 (2H, d), 7.56 (2H, d), 7.28-7.44 (4H, m) and 3.92 (2H, s); \( \delta \) C 143.06(q), 141.58(q), 126.52, 124.82, 119.67 and 36.76 (two signals co-incident at 126.52). The \( ^1\)H n.m.r. and \( ^{13}\)C n.m.r. spectra are identical to those of an authentic sample; \( \delta \) H 7.81 (2H, m), 7.56 (2H, m),
7.25-7.42 (4H, m) and 3.91 (2H, s); δC 143.11(q), 141.62(q), 126.58, 124.89, 119.73 and 36.81 (two signals co- incidental at 126.58).

15. **Pyrolysis of Allyl 2-benzoylbenzoate**

This pyrolysis was carried out only on a preparative scale. The benzoate (0.630 g, 2.37 mmol) was distilled at 5 × 10⁻³ Torr into a furnace at 900°C over a period of 2 h. The pyrolysate appeared to consist of two components, a crystalline solid being formed round the entrance to the trap with a more impure component formed further into the trap. However both components were found to be a mixture of fluorenone and the minor product benzophenone. Attempts to separate benzophenone by column chromatography on alumina, with light petroleum/ether (50:50) as eluant, proved unsuccessful as did repeated recrystallisation from ethanol. The sample of fluorenone isolated was shown, by g.c., to be contaminated with a small amount of benzophenone (10%); fluorenone (0.181 g, 43%), m.p. 76-79°C (lit.²²⁰, 85°C). A clean sample of each compound was obtained by preparative g.c., using a 10% SE30 column: fluorenone; δC (D.E.P.T.) 134.48, 128.90, 124.14 and 120.12. The ¹³C n.m.r. spectrum is identical to that of an authentic sample; δC (D.E.P.T.) 134.46, 128.85, 124.06 and 120.10: benzophenone; δC (D.E.P.T.) 132.19, 129.86 and 128.08. The ¹³C n.m.r. spectrum is identical to that of an authentic sample; δC (D.E.P.T.) 132.16, 129.79 and 128.05.
References


122. D. Leaver, Unpublished Work.


197. Dr. H. McNab, Unpublished results.
New Gas Phase Reactions of Substituted Benzyl, Phenylaminyl, and Phenoxy Radicals: Rearrangements to Fused 5- and 6-Membered Heterocyclic Systems

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Flash vacuum pyrolysis studies of substituted benzyl, phenylaminyl, and phenoxy radicals have revealed three new classes of reactions: formation of five-membered ring products via intramolecular abstraction of an aromatic hydrogen atom, formation of six-membered rings via spirodienyl radical intermediates, and isomerisation of o-phenoxybenzyl into o-benzylphenoxy radicals and vice versa.

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New Gas Phase Reactions of Substituted Benzyl, Phenylaminyl, and Phenoxyl Radicals. Rearrangements to Fused 5- and 6-Membered Heterocyclic Systems

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Flash vacuum pyrolysis studies of substituted benzyl, phenylaminyl, and phenoxyl radicals have revealed three new classes of reactions: formation of five-membered ring products via intramolecular abstraction of an aromatic hydrogen atom, formation of six-membered rings via spirodienyl radical intermediates, and isomerisation of o-phenoxybenzyl into o-benzylphenoxyl radicals and vice versa.

Studies of gas phase reactions of radicals of intermediate size, e.g., those containing more than one aromatic ring, have been rare, in contrast to those of reactions carried out in solution. In exploring this new ground we have observed several new reactions including an intramolecular abstraction of an aromatic hydrogen atom, which appears to be unprecedented in both solution and the gas phase.

Thus, generation of the arminyl radical (2) by flash vacuum pyrolysis (f.v.p.) of the o-allyl precursor (1) gave 6-amino-2-methylbenzothiophene (3: 34%) and a mixture of 2- (4: trace) and 3-methylphenothiazine (5: 14%). This suggests reaction as in Scheme 1 via novel internuclear hydrogen transfer followed by cyclisation to give the five-membered thiophene ring (3). In competition with this are cyclisation of the radical (2) to give 2-methylphenothiazine (4) and, via a spirodienyl radical, rearrangement to give 3-methylphenothiazine (5).

Reaction of the corresponding CO and CH₂ bridged arminyl radicals proceeded only by cyclisation to give six-membered rings in high yield (Scheme 2).

Although the formation of fused six-membered heterocycles from arynitrenes via rearrangement through spirodienyl type intermediates is well established, the corresponding reaction of radicals is without precedent in the gas phase, and there is only one report of direct radical internuclear cyclisation: that of the formation of xanthene (11) in low yield from the o-phenoxphenyl radical (7) by f.v.p. In the light of our results using allyl precursors, it was of interest to attempt the preparation of this o-phenoxphenyl radical by f.v.p. of allyl o-benzylphenyl ether (9). This reaction also gave a low yield of xanthene, but the major products were 1-hydroxyfluorene (13) and o-benzylphenol (12). In our hands, repetition of the earlier experiments with the oxalate (6) gave the same set of major products. The formation of (13) in both cases (Scheme 3) not only points to intramolecular hydrogen transfer followed by cyclisation to give a five-membered ring i.e. analogous to the reaction in Scheme 1 but also to interconversion of the o-phenoxphenyl and o-benzylphenoxyl radicals via the spirodienyl radical (8). Such isomerisations have not been observed before. Xanthene can result from direct cyclisation of the radicals (7) and (10).

In all cases, mixtures were separated by column chromatography on alumina; new compounds were characterised by spectra and by elemental analysis. Analysis of product ratio was made by ¹H and ¹³C n.m.r. spectroscopy of crude pyrolysates.
and/or via direct rearrangement of the spirodieneyl radical. As a test of this, we examined the methylxanthene fraction from the methyl labelled radicals (14) and (16) (Scheme 4) in the expectation that direct cyclisation should lead only to xanthenes [(17) from (14)] and [(18) from (16)] while equilibration through the spirodieneyl (15) should give the same mixture of both xanthenes in each case. In practice, mixtures were formed in each experiment, though in different ratios. We conclude, therefore, that under our conditions, equilibration is incomplete, and reaction via the spirodieneyl (15) competes with direct cyclisation.

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References