STUDIES IN THE CHEMISTRY OF SOME
1,3-BIDENTATE REACTIVE INTERMEDIATES

by

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Thesis presented for the degree of
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To my wife, Helen,

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

This thesis describes results of research carried out in the Department of Chemistry, University of Edinburgh, under the supervision of Professor J.I.G. Cadogan, since the 1st October, 1971, the date of my admission as a research student.

The following courses were attended during the three years of research: Recent Developments in the Theory of Concerted Processes, Dr. A.J. Bellamy (five lectures); Organometallic Reagents in Organic Synthesis, Prof. P.L. Pauson (five lectures); Carbonium Ions, Dr. B. Capon (five lectures); Colloids and Money, Dr. B.A. Pethica and Dr. P. Anderson; Perkin Symposium (1972), Guest Speaker Prof. A. Eschenmoser; E.U. Department Seminars.
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ABSTRACT

The main part of this work is concerned with the study of the thermal decomposition of 2-bromophenoxides and related compounds. The thermal decomposition of sodium 2-bromophenoxides was reinvestigated and evidence for a mechanism involving the intermediacy of a 1,2-ketocarbene intermediate was obtained by trapping reactions with nucleophiles, viz phenols, benzenethiols, and benzamide. The participation of benzoxirene and 1,3-aryne intermediates were excluded on the basis of $^{13}$C F.T. n.m.r. experiments.

Benzoxazoles were formed by thermal decompositions in wet benzonitrile and their formation was shown, by control experiments, to be via nucleophilic attack on the ketocarbene rather than by 1,3-dipolar addition to benzonitrile.

Thermal decomposition of sodium 2-halothiophenoxides gave thianthrene and in contrast to the oxygen analogue, $^{13}$C F.T. n.m.r. suggested the intermediacy of benzthiirene. In accordance with the proposed mechanisms, mixtures of sodium 2-bromophenoxides and 2-bromothiophenoxides gave the corresponding thianthrenes and phenoxythiins. The efficient trapping of ketocarbene intermediates with thiophenoxide was used to provide evidence for a 1,4-ketocarbene from the decomposition of sodium 4-bromophenoxide.
Study of thermal decompositions of sodium 2-bromophenoxide in the presence of other nucleophiles, viz. amines, benzoates and thiobenzoate provided no evidence for nucleophilic attack on the ketocarbene.

The thermal decomposition of sodium 1-bromo-2-naphthoxide was investigated but attempts to prepare 2-bromo-3-hydroxyfluoranthene, in order to investigate the decomposition of its sodium salt, failed.

The remainder of this work is involved with the reinvestigation of the reaction of bromodurene with strong base. "Complex base" was reacted with bromodurene and several solvent systems were investigated. The results provided evidence against a mechanism involving the intermediacy of the bromotrimethylbenzyl anion and were in agreement with a mechanism involving a carbene intermediate.
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# INTRODUCTION

## 1. 1, 3-Bidentate Reactive Intermediates

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INTRODUCTION

1. 1,3-Bidentate Reactive Intermediates

A 1,3-bidentate reactive intermediate is a short-lived species which possesses two concurrent reactive sites; 1,3- indicating the positions of these sites relative to each other in the molecule.

(a) 1,3-Diradicals

1,3-Diradicals belong to this class of reactive intermediates, but pure diradical reactions are rarely encountered, owing to highly-probable, alternative, stepwise radical mechanisms. One of the few reactions which does involve a triplet diradical is the photolysis of 3H-indazoles (1) to benzocyclopropenes (3). The e.s.r. spectrum at 77°K in a pentane glass was unambiguously interpreted by Closs1 to be that of the triplet-state diradical intermediate (2).

![Chemical structure](image)

(b) m-Benzyne

Although 1,2-dehydrobenzene is now a well-known and well-documented species, little is known about its 1,3-bidentate analogue, 1,3-dehydrobenzene or m-benzyne. Evidence has been reported for the transient existence of m-benzyne on several occasions.
Berry and his co-workers\textsuperscript{2} have reported the transient existence of \textsubscript{m}-benzyne in the flash-initiated decomposition of the unstable compound, benzenediazonium-3-carboxylate (4). The products were examined by mass spectrometry and a species with parent mass 76 was observed and identified as \textsubscript{m}-benzyne. Two structures (5 & 6) were suggested for this transient species.

\[
\text{\begin{array}{c}
\text{COO}^- \\
\text{N}_2^+ \\
\text{4} \\
\end{array}} \quad \text{\begin{array}{c}
\text{5} \\
\end{array}} \quad \text{\begin{array}{c}
\text{6} \\
\end{array}}
\]

The formation of 1,2-dehydrobenzene by the photolysis of 1,2-diiodobenzene\textsuperscript{3} prompted Fischer and Lossing to examine the possibility of the formation of \textsubscript{m}-benzyne by thermolysis of 1,3-di-iodobenzene\textsuperscript{4}. Careful examination of the ionisation potentials in the mass spectrometric analysis of the products showed the open chain compound (7) to have been formed rather than the expected \textsubscript{m}-benzyne.

\[
\text{\begin{array}{c}
\text{I} \\
\text{I} \\
\end{array}} \quad \text{\begin{array}{c}
\text{7} \\
\end{array}}
\]

McGriff\textsuperscript{5} attempted the preparation of \textsubscript{m}-benzyne derivatives as
isolable compounds from trisubstituted bicyclo[3,1,0]hexanes (8).

He synthesized cis-2,3-diacetoxybicyclo[3,1,0]hexane-6-carboxylic acid (8, X = OAc, Y = CO₂H) and transformed it into the corresponding primary amine (8, X = OAc, Y = NH₂) and dimethylamine-N-oxide (8, X = OAc, Y = ON(CH₃)₂). Deamination of the amine led to ring-opening and a mixture of triacetoxycyclohexenes was isolated.

Pyrolysis of the dimethylamine-N-oxide also failed to give m-benzyne; tars being the only products. Using a similar precursor (9), Fohlish attempted to prepare the 1,3-bidentate species (10) by thermolysis involving a cis-elimination mechanism. Unfortunately, trans-elimination took place and gave benzene as the only product.
Rossi and his co-workers\textsuperscript{7} claimed the intermediacy of \textit{m}-benzyynes in the thermal decomposition of substituted \textit{m}-carboxybenzenediazonium salts. They examined the solid products obtained, and concluded that their formation was in agreement with a mechanism involving \textit{m}-benzyynes, but they appeared to ignore the more likely possibility of stepwise decomposition.

Recently, Hess and Schaad\textsuperscript{8} examined the possible structures for 1,3-dehydrobenzene:

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{Structures of 1,3-dehydrobenzene}
\end{figure}

They observed that the structures (11) and (13) imply singlet structures, whereas structure (12) can be singlet or triplet. If structure (12) is considered as triplet then all three structures may be considered as resonance forms. They studied the relative energies of the three structures in terms of the concept of "resonance energy per electron" (R.E.P.E.) which they claim to correlate with aromatic character. Compounds with positive R.E.P.E. values are aromatic, those with negative values are antiaromatic and those with R.E.P.E. = 0 are polyolefinic.

Application of this concept to structure (11) gave an R.E.P.E. value of 0.055 which compares with the R.E.P.E. value for benzene.
Hess and Schaad concluded that the structure (11), although apparently under considerable strain, is still a distinct possibility.

(c) **1, 8-Dehydronaphthalene**

1, 8-Dehydronaphthalene may be considered as a 1, 3-bidentate intermediate in which the two reactive centres are formally meta-related. In an analogous reaction to the generation of benzyne by the oxidation of 1-aminobenzotriazole with lead tetra-acetate (L.T.A.), Rees and Storr oxidised 1-amino-naphtho-[1,8-de]triazine (14) with L.T.A., and found that nitrogen was evolved. The products obtained were consistent with dehydrogenation of the amine (14) to generate the nitrene (15), followed by loss of two molecules of nitrogen to give 1,8-dehydronaphthalene (16).

![Chemical structures](image)

Rees and Storr recognised that the peri-dehydro-orbitals are in such a position in 1,8-dehydronaphthalene to allow the possibility of some overlap and stabilisation, as in the case of 1,2-dehydrobenzene. Hoffmann calculated the stabilisation of the species by dehydro-orbital interactions and found it to be only one third of that for 1,2-dehydro-
benzene. Investigation of the reactions of 1,8-dehydronaphthalene by Rees and Storr suggest it to be mainly diradical in character. They trapped 1,8-dehydronaphthalene by 1,2-addition with unsaturated compounds and by the formation of radical abstraction products. On oxidation of the amine (14), using benzene as the solvent, 1-phenylnaphthalene and 6b,10a-dihydrofluoranthenone (17) were obtained. Rees and Storr suggested, from this result, the following mechanism for the general reaction with aromatic hydrocarbons:

```
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
```

Similar 1,2-additions were found to occur with olefins; for example, with tetrachloroethylene, oxidation of the amine (14) with L.T.A. gave tetrachloroacenaphthene and adducts were
formed by 1,2- addition to the double bonds of cyclohexene and cyclooctene. The formation of naphthalene in some of the reactions, by abstraction of benzylic hydrogen atoms, suggested the involvement of radicals.

Rees and Storr\(^9\) also attempted 1,2- addition of 1,8-dehydronaphthalene to azo- compounds and they obtained, for example, a low yield of the adduct (18) with dimethyl azodicarboxylate.

\[
\begin{align*}
\text{CH}_3\text{O}_2\text{C} & - \text{N} & & \text{N} & - \text{CO}_2\text{CH}_3 \\
\text{18}
\end{align*}
\]

Comparison of the reactions of 1,8-dehydronaphthalene with those of benzyne derived by a similar route, suggested it to be much more reactive than benzyne, and, in contrast to benzyne, dimerisation was found not to occur. Radical abstractions were found to take place readily. With carbon tetrachloride, 1,8-dichloronaphthalene was obtained and with bromotrichloromethane, 1,8-dibromonaphthalene and hexachloroethane were produced, providing evidence for abstraction of halogen atoms. No reaction with nucleophiles was observed. For example, with methanol, only hydrogen abstraction took place, giving naphthalene. Rees and Storr studied the stereospecificity of the addition of 1,8-dehydronaphthalene
to cis- and trans- 1, 2-disubstituted olefins and concluded that a singlet diradical intermediate was involved.

(d) 1,3-Dipoles

Undoubtedly, the main group of 1,3-bidentate compounds is the 1,3-dipoles, of which there are a large number of examples. Azides, for instance, classed as 1,3-dipoles with a double bond and octet stabilisation, will readily undergo 1,3-additions to alkynes:

\[
C_6H_5-N-\overset{+}{\equiv}N \leftrightarrow C_6H_5-N-N=\overset{+}{\equiv}N \\
R-C=CCC-H \\
\downarrow \\
C_6H_5-N=\text{N} \text{~N} + C_6H_5-N=\text{N} \text{~N}
\]

Other, well-known members of this class are the diazoalkanes, which have been extensively studied.

\[
\overset{+}{\equiv}N-N-\overset{+}{\equiv}C< \leftrightarrow N=\overset{+}{\equiv}N-\overset{+}{\equiv}C<
\]

Azides and diazoalkanes can be isolated and some of them are thermally stable, but some 1,3-dipoles in this class, such as nitrile ylids, cannot be isolated.

In the work described in this thesis, ketocarbenes,
1, 3-dipoles without octet stabilisation are of particular importance, and are discussed in detail in the next section.

2. Ketocarbenes

Ketocarbenes are obtained almost exclusively by the decomposition of diazoketones by heat, light, and various catalysts. The ketocarbene structure may be written as a resonance hybrid of charged and uncharged canonical forms:

\[
\begin{align*}
\dddot{C} & \equiv \dddot{C} = \dddot{O} & \rightleftharpoons & \dddot{C} = C \equiv \dddot{O}
\end{align*}
\]

On decomposing dicarbonyl diazo compounds in aqueous solution, Wolff \(^{11}\) discovered and isolated products in which the carbon skeleton had been rearranged. Later, when Schroeter \(^{12}\) had obtained diphenylketene by the thermal decomposition of phenylbenzoyldiazomethane, Wolff \(^{13}\) rationalised his products by assuming a similar ketene intermediate (Scheme 1). He recognised that his reaction was analogous to the Curtius degradation of carbonyl azides and further support for his rationalisation came with the preparation of stable ketenes from diazoketones by Staudinger and Hirzel \(^{14}\) and by Gilman and Adams \(^{15}\).

\[
\begin{align*}
R-\text{CO}-\text{CN}_2-R' & \rightarrow R-\text{CO}-\text{C}-R' \rightarrow R-\text{C}=\text{C}=\text{O} \\
& \text{ketene} \\
R'\text{OH} \searrow & \downarrow \text{H}_2\text{O} \\
R'\text{CH-\text{COOR'}} & R'\text{CH-\text{COOH}}
\end{align*}
\]

Scheme 1
The development of efficient syntheses of diazoketones from acid chlorides and diazoalkanes accelerated the interest in the Wolff rearrangement and a systematic study was carried out, notably by Arndt and Eistert.

The migration of alkyl and aryl groups bonded to the carbonyl group of ketocarbenes, to the divalent carbon atom, is still not fully understood and in some cases the carbene intermediate can only be assumed by analogy.

Ketocarbenes are thought to be involved in the reaction of nitrous oxide with acetylene at high pressure and temperature. Buckley and Levy rationalised their results with a scheme involving a 1,2,3-oxadiazole:

\[
\text{PhC≡CPh} + \text{N}_2\text{O} \rightarrow \text{Ph} = \text{C} = \text{C} - \text{Ph} \rightleftharpoons \text{PhCOCN}_2\text{Ph} \]

\[
\downarrow -\text{N}_2
\]

\[
\text{PhCO} - \text{CPh}
\]

\[
\text{Ph} \quad \text{C} = \text{C} = \text{O}
\]

The peroxidation of acetylenes also gives products which can be interpreted by involvement of a ketocarbene intermediate:
According to Suś\textsuperscript{20}, aromatic ketocarbenes, produced by photolysis, are capable of undergoing the Wolff rearrangement, resulting in ring contraction:

\[
\begin{align*}
\text{Nitrene} & \rightarrow \text{Ketocarbene} \\
\text{Ketocarbene} & \rightarrow \text{Aromatic Carbene} \\
\text{Aromatic Carbene} & \rightarrow \text{Aromatic Ketone}
\end{align*}
\]

The size of the ring has little restriction on the applicability of the Wolff rearrangement and a large number of strained cyclic systems have been prepared by ring contraction of diazoketones, for example, benzocyclobutenes\textsuperscript{21} (19) and bicyclo[3.1.1]heptanes (20)\textsuperscript{22}. Reid and Lohwasser\textsuperscript{23} showed 2-diazoacenaphthenone (21) to be one of the few diazoketones in which the Wolff rearrangement could not be achieved.
Scheme 2

\[
\text{22} \xrightarrow{\text{hv}} \text{23} \quad 2\%
\]

\[
\text{C}_6\text{H}_6 \xrightarrow{\text{DDQ}} \text{24} \quad 20\%
\]

\[
\text{22} \xrightarrow{\text{hv}} \text{23}
\]

\[
\text{C}_6\text{H}_6 \xrightarrow{\text{DDQ}} \text{24}
\]

\[
\text{HX}
\]

\[
\text{24} \xrightarrow{\text{HX}} \text{25}
\]

\[
\text{25} \xrightarrow{\text{BR}} \text{26}
\]

\[
\text{26} \xrightarrow{\text{HX}} \text{27}
\]

\[
\text{27} \xrightarrow{\text{HX}} \text{28}
\]

\[
\text{28} \xrightarrow{\text{HX}} \text{29}
\]
On photolysing 9-diazo-10-keto-4,5-methylene phenanthrene (22), Trost\textsuperscript{24} obtained only 2\% of the required ring contracted product (23) in the presence of t-butylamine. Instead, he obtained a 20\% yield of the product (24), formed by a virtually unprecedented reaction between the ketocarbene and the solvent, benzene. From further experiments, Trost was able to conclude that the Wolff rearrangement is only applicable in cases in which the ring strain created in a single step is lower than 50 kcal mol\textsuperscript{-1}. He postulated two mechanisms (Scheme 2) for the formation of the product, one of which involves the novel 1,3-dipolar addition to a simple aromatic compound.

Although 1,3-dipolar addition of ketocarbenes to simple aromatic compounds is virtually unprecedented, many examples are known of 1,3- additions with dipolarophiles possessing a relatively polar or highly strained multiple bond.

A. 1,3 Dipolar Addition Reactions of Ketocarbenes.

(a) Classification of 1,3-dipoles

Huisgen\textsuperscript{25} classifies cycloaddition reactions according to the number of new bonds formed, or according to the size of the ring which is formed. Usually two reactant molecules combine and form a cyclic compound by creation of two new \(\sigma\)-bonds at the expense of two \(\pi\)-bonds.

A 3 + 2 \(\rightarrow\) 5 type cycloaddition giving an uncharged 5-membered ring cannot possibly occur with octet-stabilised reactants
possessing no formal charges. A 1,3-dipole must be defined (a-b-c) such that atom a possesses an electron sextet, i.e., an incomplete valence shell combined with a positive formal charge and that atom c, the negatively charged centre, has an unshared pair of electrons. Combination of such a dipole with a multiple bond system d-e, termed the dipolarophile, is known as 1,3 dipolar cycloaddition. The dipolarophile may be any double or triple bond. The two components coalesce by means of a cyclic displacement of electrons with extinction of the formal charges to give a five-membered ring.

Compounds possessing an electron sextet at a carbon, nitrogen, or oxygen atom, are not stable. The foregoing designation would acquire the physical significance of a mere resonance contributor if the 1,3-dipole were capable of isolation. Stabilisation is possible if an unshared pair of electrons at atom b can relieve electron deficiency at atom a by formation of an additional bond. In the new mesomeric formula all the centres have filled valence shells, atom b now having a positive charge. Such systems are termed 1,3-dipoles with octet stabilisation:

\[ a \equiv b-\stackrel{\cdot}{c} \leftrightarrow a \equiv b-\stackrel{\cdot}{c} \quad b = N \]

\[ a \equiv b-\stackrel{\cdot}{c} \leftrightarrow a \equiv b-\stackrel{\cdot}{c} \quad b = N-R \text{ or } O \]
In the case of ketocarbenes:

\[
\begin{align*}
\overset{+}{\text{C}} & \equiv \overset{-}{\text{C}} - \overset{\cdot}{\text{O}} : & \leftrightarrow & \overset{\cdot}{\text{C}} & \equiv \overset{-}{\text{C}} - \overset{\cdot}{\text{O}} \\
\end{align*}
\]

The centre \(b\) of the 1,3-dipole (\(a-b-c\)) is a carbon atom and internal octet stabilisation is prevented by the lack of an available free electron pair. However, if, as in the case of ketocarbenes, isolation of the 1,3-dipole is relinquished and the intermediates of short life-time are trapped by reaction with the dipolarophile, then the restriction of the 1,3-dipole can be overcome. Such systems are termed 1,3-dipoles without octet stabilisation.

(b) **Addition reactions of aliphatic and alicyclic ketocarbenes**

Loss of nitrogen from a diazoketone results in a ketocarbene intermediate having a singlet state which can best be described by neutral and zwitterionic resonance forms. The resonance form formulated as a 1,3-dipole is capable of cycloaddition. Evidence for the ketocarbene intermediate was initially found by Huisgen and his co-workers\(^{26}\) in the thermolysis of diazoacetophenone (25) in benzonitrile. They obtained products derived from phenylketene, the product of Wolff rearrangement, together with 2,5-diphenyloxazole (27), showing addition of the 1,3-dipole (26) to the dipolarophile to have taken place.
Since Wolff\textsuperscript{13} had found that the addition of silver salts as catalyst increased the rate of decomposition of diazoketones, Huisgen et al.\textsuperscript{26} noted the effect of copper powder and copper salts as catalysts. It was found that nitrogen liberation was enhanced and the Wolff rearrangement was suppressed to give 16% of the adduct (27) with added catalyst, compared with 0.4% without catalyst. Novak et al.\textsuperscript{27} also evidenced the suppression of the Wolff rearrangement in the decomposition of diazoketones with copper in the presence of olefins. Decomposition of 4, 7-dimethyl-2-diazoindan-1-one (28) by photolysis in benzonitrile was found to give 11% and 34% of the condensed oxazole (29) in the absence and presence of copper catalyst, respectively\textsuperscript{25}. Photolysis of the same compound (28) in tetrahydrofuran was shown by Cava\textsuperscript{28} to give the ring-contracted product of the Wolff rearrangement (30).
(c) Addition reactions of ethoxycarbonyl carbenes

Ethyl diazoacetate (31) can lose nitrogen on thermolysis to give ethoxycarbonyl carbene. The mesomeric resonance of the ester might be expected to act in opposition to the 1,3-dipolar activity of the ketocarbene. Ethyl diazoacetate is incapable of undergoing the Wolff rearrangement; decomposition of diazoacetic acid esters in the presence of olefins or aromatic compounds give rise to cyclopropane-carboxylic esters. Surprisingly, however, it was found that thermolysis of ethyl diazoacetate in benzonitrile gave a 42% yield of the adduct, 2-ethoxy-5-phenylxazole (32). Although it might be argued that the ketocarbene initially forms an azirine-3-carboxylic ester on reaction with the nitrile, which then ring expands to give the product,
it is more likely that the product arises directly by 1, 3-dipolar addition.

(d) Addition reactions of aromatic ketocarbenes

In order to trap the short-lived intermediates efficiently, by impeding the Wolff rearrangement, it is necessary to study carefully selected model systems. Benzene-o-diazooxides, intermediate in reactivity between aliphatic diazoketones and aromatic diazonium salts, provide such a system. The intermediate ketocarbene should have a longer lifetime since ring contraction by the Wolff rearrangement results in loss of aromatic resonance energy. It was found\textsuperscript{25} that tetrachlorobenzene-o-diazooxide (33), on thermal decomposition, did not give rearrangement of the ketocarbene and in methanol gave predominantly 2, 3, 4, 5-tetrachloro-6-methylphenol. Huisgen\textsuperscript{26} has shown that the ketocarbene undergoes 1, 3-dipolar addition with numerous nucleophiles; for example, thermolysis in phenylacetylene gave 2-phenyl-4, 5, 6, 7-tetrachloro-benzo[b]furan (34), thermolysis in styrene gave the corresponding 2, 3-dihydro derivative of the furan (34) and in dimethyl acetylenedicarboxylate
a good yield of the adduct (35) was obtained. With benzonitrile, the benzoxazole derivative (36) was obtained.

Huisgen showed that the C = S bond in phenyl isothiocyanate showed a greater dipolarophilic activity than the C = N bond in benzonitrile and a high yield of adduct was obtained with carbon disulphide due to this high dipolarophilic activity of C = S. Photolysis and thermolysis of the diazooxide (33) were found to give almost identical results with the various dipolarophiles.
In contrast to other 1,3-dipolar additions, Huisgen found that reaction of the diazooxide (33) with olefins was not stereospecific and both dimethyl fumarate and dimethyl maleate gave the same trans adduct (37). On following up this work, Huisgen has reported numerous examples of 1,3-dipolar cycloadditions of the diazooxide (33) with alkenes and alkynes; the method allowing the preparation of a great many 5-membered heterocycles.

Further evidence that the ketocarbene is involved in the 1,3-addition is that the rate of decomposition of the diazooxide (33) is only slightly dependent on the solvent, implying that reaction with the dipolarophile only begins after the loss of nitrogen. On the other hand, Huisgen has shown that reaction of the diazooxide (33) with diphenylketene follows a completely different mechanism, nitrogen being liberated below 100° and the adduct (38) being that expected by 1,3-addition. Yates and Robb investigated the reaction of naphthalene-1,2-diazooxide (40) and naphthalene-2,1-diazooxide (39) with ketenes. They found that thermolysis of naphthalene-2,1-diazooxide in boiling xylene in the presence of diphenylketene gave, in addition to the pyrolysis product, a product (41), analogous to that obtained by Huisgen. Yates and Robb followed up the work of Horner, who wrongly assigned the structures of the products obtained by thermal decomposition of the diazooxides (39 & 40). The same product (42) was obtained from both compounds.
Haszeldine and his co-workers synthesized 1-diazotetrafluorobenzene-2-oxide (43) and found that it was even more suitable as a model compound disinclined to undergo the Wolff rearrangement than the corresponding chloro-compound. They studied photochemical and thermal decompositions of the diazooxide (43) in various solvents (Scheme 3). In benzene, nucleophilic substitution by the dipolar ketocarbene was found to occur giving 2,3,4,5-tetrafluoro-6-hydroxybiphenyl in good yield, and the formation of adducts, analogous to those obtained by Huisgen, were obtained with nitriles and isothiocyanate as dipolarophiles. The formation of these adducts was taken as good evidence for the formation of the ketocarbene intermediate (44).
B. **Ketocarbenoids by α-Elimination**

The only source of ketocarbenes for over fifty years has been the decomposition of diazoketones. Recently, however, Scott and Cotton\(^3\) have reported the first example of a ketocarbenoid generated in high yield by α-elimination. Scott and Cotton use the "carbenoid" definition, which describes those carbenes which are not free divalent carbon species; in other words, the species formed by α-elimination are distinct from those produced from diazoketones.

They treated α, α'-dibromocamphor (45) with diethyl zinc in anhydrous benzene, and found that immediate quenching with water led to the formation of endo-α-bromocamphor (46), whereas boiling under
reflux before quenching led to the formation of a tricyclic ketone (47). The formation of the same cyclic ketone by C-H insertion of the ketocarbene derived from the classical diazoketone (48) by Bredt\textsuperscript{34}, indicates a ketocarbenoid intermediate to be present in the $\alpha$-elimination.

\[
\begin{align*}
\text{Et}_2\text{Zn} & \quad \Delta \quad \text{Et}_2\text{Zn} \\
\text{H}_2\text{O} & \quad \text{ZnX}^+ \\
\text{45} & \quad \text{46} \\
\end{align*}
\]

The same result was obtained with zinc dust and with a zinc-copper couple in dimethylformamide and the corresponding $\alpha$-elimination of $\text{HBr}$ from endo-$\alpha$-bromocamphor (46) gave the same ketocarbenoid.

**Trapping of the ketocarbenoids by olefin cycloaddition**

Scott and Cotton\textsuperscript{35} treated $\alpha,\alpha'$-dibromodesoxybenzoin (49) and trans-stilbene with zinc dust in benzene to give the dihydrofuran (50) as the 1:1 adduct.
The adduct (50) is the product of formal dipolar addition of benzoylphenyl carbene to stilbene. Other adducts have been formed; for example, analogous reactions with 1,1-diphenylethylene and diphenylacetylene gave adducts (51) and (52), respectively.

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

51

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

52

The α-elimination from the dibromo compound (49) was induced by zinc to give the intermediate bromoenolate (53), which could then be trapped by olefins.

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \quad \text{Br} \quad \text{Br} \\
\text{Zn or} & \quad \text{Et}_2\text{Zn}
\end{align*}
\]

49

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \quad \text{Zn}^+ \quad \text{X}^{-} \quad \text{Br} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

53

C. Thioketocarbenes

Sulphur analogues of diazoketones lead to the corresponding hetero analogues of ketocarbenes, thioketocarbenes. Replacement of the oxygen atom in diazoketones by sulphur leads to 1,2,3-thiadiazoles, which, although they do not possess a diazo group, are readily decomposed both photochemically and thermally.
By thermolysis of 1, 2, 3-benzothiadiazole (54), Jacobson and Janssen\textsuperscript{36} obtained thianthrene (56) as one of the products, the formation of which is in agreement with a mechanism involving an aromatic thioketocarbene intermediate (55). Kirmse and Horner\textsuperscript{37} obtained derivatives of 1, 3-dithiacyclopentene, called "dithiafulvenes" (59), and in some cases, 1, 4-dithia-2, 5-cyclohexadienes (58) by photolysis of 1, 2, 3-thiadiazoles.

The dithiafulvenes contain a rearranged fragment of the 1, 2, 3-thiadiazole, indicative of 1, 3-addition of thiocarbonyl-carbene (55) and the thioketene (57), which is the product of the Wolff rearrangement.
Compared with the analogous ketocarbene, the thioketocarbene (55) displays slow reactivity. Huisgen\textsuperscript{25} has shown that the thioketocarbene (55) gives preferential dimerisation to thianthrene (56) in the presence of various dipolarophiles, rather than 1, 3-addition products. The only dipolarophiles which successfully undergo 1, 3-addition to the thioketocarbene (55) are those containing the C = S bond. Decomposition of benzothiadiazole with carbon disulphide produced 1, 3-benzodithiol-2-thione (60) which possesses itself a C = S bond, capable of further 1, 3-addition to give the adduct (61).

![Chemical Structure](image)

3. **Oxirenes and their Hetero Analogues**

So far, ketocarbenes have been written as a resonance hybrid of two canonical forms. It is possible, however, to write a third structure, the valence isomer (62), known as the oxirene structure.

\[
\begin{array}{c}
\text{O}^- \\
\overset{\ddagger}{\text{C} = \text{C}} \\
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{O} \\
\overset{\ddagger}{\text{C} = \text{C}} \\
\end{array} \quad \Rightarrow \quad \begin{array}{c}
\text{O} \\
\overset{\ddagger}{\text{C} = \text{C}} \\
\end{array}
\]

\text{62}
The oxirene intermediate and its sulphur and nitrogen analogues, thiirene (63) and 1H-azirine (64), respectively, have recently been subject to closer investigation and their intermediacy established.

\[
\begin{align*}
  &\text{S} \\
  &\text{O} \\
  &\text{C=\text{C}} \\
  &\text{63} \quad \text{64}
\end{align*}
\]

Oxirene intermediates are the family of unsaturated epoxides and the oxirene structure (65) is the simplest oxygen-containing heterocyclic system. The oxirene structure is a potential 4π antiaromatic system\(^{38}\), which, according to quantum mechanical calculations, since it contains 4n π-electrons, ought to be destabilised by resonance. Breslow\(^{39}\) has examined this prediction for the simplest system having 4n π-electrons (n = 1), the cyclopropenyl anion (66). Although isolation of such compounds has never been achieved, kinetic measurements indicate their existence and confirm the predicted properties.

\[
\begin{align*}
  &\text{HC=\text{CH}} \\
  &\text{65} \quad \text{66}
\end{align*}
\]

Calculations by Dewar\(^{40}\) show that antiaromatic heterocyclic analogues of the cyclopropanenyl anion should be stable and
predict that they may occur as stable intermediates,
Hopkinson\textsuperscript{41} computed energies for oxirene (65) and its isomeric formylcarbene and ketene structures. He found that the ketene was more stable than both oxirene and formylcarbene by 70 kcal mol\textsuperscript{-1}, offering an explanation as to why the latter two structures are not physically observable. In contrast to the extended Hückel calculations of Strausz\textsuperscript{59}, which predict ethoxycarbonyl carbenes to be more stable than their corresponding oxirenes, Hopkinson predicted that oxirene and formylcarbene have almost the same energy. Strausz\textsuperscript{42} suggested that oxirene has a singlet ground state with low stability, from molecular orbital calculations.

(a) \textbf{History of oxirenes}

The isolation of these unstable small-ring compounds has been claimed and later withdrawn several times during the last century and their intermediacy has been proposed on a number of occasions.

The first mention of an oxirene was the report\textsuperscript{43} of 2-methyloxirene, resulting from the chromic anhydride oxidation of propyne, just over a hundred years ago. Verification of this result has never been realised and it appears unlikely. Madelung and Overwegner\textsuperscript{44} claimed to have isolated diphenylacetylene epoxide (67) from the pyrolysis of the oxirane (68), which they obtained by reaction of desyl chloride (69) with methanolic sodium ethoxide.
Dauben et al.\textsuperscript{45} repeated this work and showed that the products (67 & 68), claimed to have been isolated were, in fact, both benzoin methyl ether (70) in different states of purity.

Schiubach and Franzen\textsuperscript{46} obtained a compound of molecular formula C\textsubscript{10}H\textsubscript{18}O, by reaction of dibutylacetylene with peracetic acid, which they claimed to be the oxirene (71). Franzen\textsuperscript{47} later refuted his earlier claim and showed the compound to be, in fact, an $\alpha,\beta$-unsaturated ketone (72).

\[
\begin{align*}
\text{C}_4\text{H}_9 - & \equiv \text{C} - \equiv \text{C} - \text{C}_4\text{H}_9 & \xrightarrow{\text{peracetic acid}} & \text{C}_4\text{H}_9 - \equiv \text{C} - \equiv \text{C} - \text{C}_4\text{H}_9 \\
\text{C}_4\text{H}_9 - & \equiv \text{C} - \equiv \text{C} - \text{C}_3\text{H}_7 & & \\
\end{align*}
\]

Scheme 4
Similar reactions of peracids with acetylenes were discussed by other workers in terms of oxirene formation as the first step. Their conclusions were based on the analogy to the formation of epoxides in the peracid oxidation of olefins. McDonald and Schwab discussed the peracid oxidation of phenyl- and diphenylacetylene in this light and assumed electrophilic addition of "singlet" oxygen to the C = C triple bond to form the oxirene (Scheme 4). Stille and Whitehurst discussed the same analogy with equal lack of justifying evidence.

A more detailed investigation of the peroxidation of acetylenes was carried out by Ciabattoni, who studied the reaction of di-t-butylacetylene (73) and cyclodecyne (74) with m-chloroperbenzoic acid and compared the products with those obtained from the decomposition of the structurally related α-diazoketones (75 & 76), respectively.
The remarkable similarity in the ratio of products obtained from the acetylene (73) and the diazoketone (75) suggested a common intermediate \( \alpha \)-ketocarbene (77) to be involved. Vastly different product ratios, however, were obtained from cyclodecyne (74) and the cyclic diazoketone (76), suggesting the absence of such a common intermediate in this case.

The oxirene intermediate (78) was proposed in the cyclodecyne case, which gave a satisfactory explanation for the difference in product ratios by the possibility of a concerted trans-annular reaction. Other possibilities were also discussed, however, after a more recent investigation\textsuperscript{51}.

Japanese workers\textsuperscript{52} studied the kinetics of the peracid oxidation of acetylenes and electrophilic attack on phenylacetylenes. They concluded that electrophilic attack alone takes place and that perbenzoic acid and phenylacetylene react in a 1 : 1 mole ratio, as follows:

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

Kinetic evidence for oxirene participation is also provided by Ciabattoni\textsuperscript{53}, based on correlation of the logarithmic
rates of acetylene oxidation with those of peroxidation of an olefin in a series of solvents of diverse nature. Oxirene has been proposed as an intermediate in the photolysis of trans-1, 4-diphenyl-3, 4-epoxybutan-1-one (79) and in the pyrolytic mass spectrometric decomposition of 1, 2-dinitronaphthalene (80).

\[
\text{Ph} \quad \overset{\text{hv}}{\longrightarrow} \quad \begin{array}{c}
\text{O} \\
\text{H} \\
\text{O} \\
\text{Ph}
\end{array} + \text{Ph} \quad \overset{\text{hv}}{\longrightarrow} \quad \begin{array}{c}
\text{O}
\end{array} \quad \overset{\text{hv}}{\longrightarrow} \quad \text{Ph} \quad \overset{\text{hv}}{\longrightarrow} \quad \text{Ph} \quad \overset{\text{hv}}{\longrightarrow} \quad \begin{array}{c}
\text{O}
\end{array}
\]

Recently, the mechanism of the Wolff rearrangement has been reconsidered in the light of the possibility of oxirene participation. Despite the vast amount of data which has been obtained, many questions remain unanswered, such as whether the Wolff rearrangement involves an intermediate at all, and, if so, what type of intermediate is involved. Thirty years ago Huggett and his co-workers investigated the possibility of oxirene in the Wolff rearrangement of diazoacetophenone, using isotopic labelling technique. They found that no scrambling took place during the rearrangement. Sixteen years later, Franzen studied the photochemical and thermal Wolff rearrangement of \( \alpha \)-diazo-\( \alpha \)-phenylacetophenone (81) in solution, using radioactive labelling technique.
and concluded that oxirene was not an intermediate in the reaction (Scheme 5).

\[
\begin{align*}
\text{Ph} - \text{CO} - \text{CN}_2 - \text{Ph} & \rightarrow [\text{Ph} - \text{CO} - \text{C} - \text{Ph}] \rightarrow \text{Ph}_2\text{CH} - \text{CO}_2\text{H} \\
\end{align*}
\]

Scheme 5

\[
\begin{align*}
\text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 & \rightarrow \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \\
\end{align*}
\]

Scheme 6

Recently, Strausz and his co-workers\textsuperscript{42} re-investigated the Wolff rearrangement in the gas phase with divergent results. The ketenes formed from \textsuperscript{13}C-labelled diazoketones were pyrolysed to yield olefins and carbon monoxide. Both of these products were found
to contain comparable amounts of $^{13}$C and appreciable scrambling was found even with diazoacetone-$2-{^{13}}$C (82), requiring the intervention of a symmetrical oxirene intermediate (Scheme 6). In $^{13}$C-labelled diazoacetophenone (83) the oxirene intermediate was found to ring-open preferentially on the hydrogen side.

An extension of this work to the decomposition of $\alpha$-diazooesters$^{58,59}$, in particular photolysis of $^{13}$C-labelled methyl and ethyl diazoacetate, also showed participation of an oxirene intermediate. Although alkoxy migration was found to be more facile than hydrogen migration, it was found that the latter can effectively compete.

Further extension to the liquid phase$^{60}$ showed over 50% oxirene participation in the photolytic decomposition of $^{13}$C-labelled $\alpha$-diazoo-\(\alpha\)-phenylacetophenone (81), contrary to the result obtained by Franzen$^{57}$. Strausz et al.$^{61}$ concluded that the transient existence of oxirene and its role in the photochemical Wolff rearrangement of $\alpha$-diazo-ketones and $\alpha$-diazooesters can be regarded as being firmly established and that earlier work to the contrary is incorrect. They maintain that the photochemical decomposition involving oxirenes is restricted to excited singlet states, populated upon photoexcitation, and that in thermolysis the Wolff rearrangement takes place without the intervention of oxirenes.

Russell and Rowland$^{62}$ reported the photochemically induced rearrangement of ketene via an oxirene intermediate.
Experiments on the photolysis of $^{14}\text{CH}_2\text{CO}$ showed a pressure dependent yield of $^{14}\text{CO}$, implicating the involvement of an oxirene intermediate (86). They suggest a plausible reaction mechanism (Scheme 7) in which the excited ketene (84) rearranges to the cyclic carbene (85) and the final excited ketene (88) is capable of decomposition or stabilisation. No direct evidence is available for the existence of species (85) and (87).

Montague and Rowland\textsuperscript{63} reported the existence of an oxirene intermediate in the reaction of singlet methylene with carbon monoxide, resulting in isotopic carbon atom exchange and the formation of $^{14}\text{C}$-carbon monoxide. The reaction was shown to proceed via an intermediate capable of stabilisation at high carbon monoxide pressure, the symmetrical nature of which implies the oxirene structure (86).
A simple chemical test for the participation of oxirenes in the decomposition of certain $\alpha$-diazoketones was devised by Matlin and Sammes$^{64}$. This test is based on the fact that keto-carbenes which have adjacent methylene groups undergo hydrogen migration to give an $\alpha,\beta$-unsaturated ketone. If the ketocarbene intermediate can equilibrate with an oxirene, suitable substitution of the starting diazoketone should lead to two isomeric $\alpha,\beta$-unsaturated ketones (Scheme 8).

Scheme 8

Scheme 8 was successfully applied to 3-diazoheptan-4-one (89, $R' = \text{CH}_3$, $R'' = \text{C}_2\text{H}_5$) and other diazoketones, and 86% oxirene participation
was deduced from examination of the products obtained on decomposition. The results obtained were in accordance with, and lent additional support to, those obtained by Strausz. In decompositions catalysed by silver oxide and copper oxide, no oxirene participation was detected. This is in agreement with evidence that copper forms complexes with ketocarbenes and that these complexes inhibit oxirene formation.

Although oxirene formation and participation appears to play an important part in the Wolff rearrangement of open chain \( \alpha \)-diazoketones, such participation appears to be insignificant in a strained polycyclic system. Majerski and Redvanly studied the Wolff rearrangement of \( {^{13}} \text{C} \)-labelled \( \alpha \)-diazohomoadamantane (90) and provided evidence against oxirene participation. Two possible reaction paths are available in this photochemical Wolff rearrangement.

\[
\begin{align*}
\text{90} & \rightarrow [\text{structure} \rightarrow \text{structure}] \rightarrow \text{structure} \\
& \downarrow \text{A} \quad \downarrow \\
\text{structure} & \rightarrow \text{structure} \\
& \rightarrow \text{structure}
\end{align*}
\]
If path B was the preferred reaction path, involving the oxirene intermediate, the product should have 50% of the label at C2 and 50% in the carboxylic group. Less than 2% oxirene participation was, in fact, found, path A being preferred. It was concluded that the oxirene would be under too much strain in the ring system to be able to exist.

(b) **Thiirenes**

Molecular orbital calculations suggest the hypothetical molecule thiirene (63) to be very unstable. As with oxirenes, its instability can be attributed to its antiaromatic character, since with four electrons contributed by the double bond and the lone pair, the ring system is destabilised by resonance. Evidence, however, for the transient existence of thiirenes as intermediates has been obtained.

Japanese workers have reported the formation of the same two products (93 & 94) from the self-condensations of 4-chloro-5-mercapto-3(2H)-pyridazinones (91) and their 5-chloro-4-mercapto isomers (92). The reaction was interpreted in terms of a reversible interconversion of two thioketocarbene intermediates (95 & 96) via a thiirene intermediate (97).
Evidence for the transient existence of the thioketocarbenes was obtained by trapping experiments similar to those carried out by Huisgen\textsuperscript{25} with ketocarbenes. For example, in the presence of phenyl isothiocyanate the adduct (98) was obtained in low yield.
Subsequent work on similar systems gave results which were interpreted in the same way \(^6^8\).

Rees and his co-workers \(^6^9\) recognised that the thiirene ring system is isoelectronic with cyclobutadiene and they attempted to stabilise such systems as tricarbonyl iron complexes \((99)\) analogous to those formed by cyclobutadiene derivatives. A route was chosen involving thioketocarbenes (Scheme 9), such that if isomeric precursors were used, the symmetrical intermediates could be detected by isolation of common products derived from the thioketocarbenes.

A pair of thiadiazoles, with \(R'\) and \(R''\) interchanged, were reacted with nonacarbonyldi-iron, causing elimination of nitrogen and formation of complexes with the resulting thioketocarbenes. The products were analysed by n.m.r., showing the same two iron complexes to have been formed from each of the pair of thiadiazoles;
the minor complex: a "crossover" product in which the sulphur atom is no longer attached to the same carbon atom as in the starting material. Thiirenes, or more correctly, their iron complexes, are thought to be the structures of the symmetrical intermediates, though there is a lack of positive evidence.

Strausz and his co-workers studied the photolysis of 1, 2, 3-thiadiazole and 5-methyl-1, 2, 3-thiadiazole and claimed that a thiirene intermediate was involved. Photolysis in the presence of perfluorobut-2-yn gave good yields of 2, 3-bis (trifluoromethyl) thiophenes. Thiophene is thought to arise from either of the steps 'a' or 'b'. Pathway 'a', however, is impossible if the thiophene is 2,3-disubstituted.

\[
\begin{align*}
\text{C} + \text{C} = \text{S} & \rightarrow \frac{\text{C}}{\text{C}} \rightarrow \left[ \begin{array}{c}
\text{C} \rightarrow \text{C} \\
\text{S} \rightarrow \text{S}
\end{array} \right] \rightarrow \frac{\text{C} = \text{C}}{\text{S} \rightarrow \text{S}} \\
\text{C} = \text{C} + \frac{\text{C}}{\text{C}}
\end{align*}
\]

The same workers also examined the reaction of sulphur atoms with acetylenes using the technique of flash photolysis with kinetic mass spectrometry. Flash photolysis of mixtures of COS and acetylenes gave strong signals for the species \( \text{C}_2\text{H}_2\text{S}, \text{C}_3\text{H}_4\text{S}, \text{C}_4\text{H}_6\text{S} \), etc., for a homologous series of acetylenes. Their evidence points to the thiirene structure for the primary adducts detected.

\[
\text{C}_2\text{H}_2 + \text{S} \rightarrow \text{HC} = \text{CH} \rightarrow \text{CH}_2\text{=CS} \rightarrow \text{CH}_2 + \text{CS}
\]

Japanese workers examined the photolysis of the mesoionic compound, 2, 5-diphenyl-1, 3-dithiol-4-one (100), which
gave tetraphenyl-1,4-dithiin (101), diphenylacetylene and sulphur as products. The formation of diphenylacetylene is strongly suggestive of the possibility of the diphenylthiirene intermediate (102).

\[
\begin{align*}
\text{Ph-C=S-C=Ph} + \text{Ph-C=S-C=Ph} & \rightarrow \text{Ph-C=C=Ph} + \text{S} \\
\text{Ph-C=S-C=O} & \rightarrow \text{PhC=CCPh} \\
\end{align*}
\]

The first strong evidence for the formation of 1'H-azirines, the antiaromatic nitrogen analogues of oxirenes and thiirenes, was for their role as highly reactive intermediates in the cycloaddition of N-phthalimidonitrene to alkynes, where 2'H-azirines were the products isolated. As yet, no 1'H-azirines have been isolated and molecular orbital calculations have confirmed that there is a destabilising interaction between the electrons of the πL-bond and the lone pair on nitrogen. The calculations predict a non-planar structure with unusual high barrier to inversion about nitrogen of 147kJmol⁻¹.
Jacox and Milligan\textsuperscript{74} attempted to prepare \( \text{1}_H \)-azirines by cycloaddition of nitrenes to acetylenes. They found that nitrene, \( \text{NH} \), on treatment with acetylene in a solid argon matrix at \( 40 \text{K} \) gave formylketene imine. Reaction of alkoxy carbonyl nitrenes with acetylenes was found\textsuperscript{75} to give oxazoles and there is a possibility that the first step of the reaction involves the formation of a \( \text{1}_H \)-azirine, which then rearranges to give the product.

\[
\text{RO-CO-} \ddot{\text{N}}: + \text{RC=CR'} \rightarrow \text{COOR} \rightarrow \text{RO-CO-N: + RC=CR'} \rightarrow \text{N} \quad \text{COOR} \rightarrow \text{N} \quad \text{COOR}
\]

Rees et al.\textsuperscript{76} studied the pyrolysis of \( \text{N} \)-phthalimido-1,2,3-triazoles (104) which gave the same products, \( \text{2}_H \)-azirines (107) as those isolated from the oxidation of \( \text{N} \)-aminophthalimide (103) in the presence of alkynes\textsuperscript{72}. Loss of nitrogen from the triazoles is thought to give the same intermediates, \( \text{1}_H \)-azirines (105) as those produced in the oxidation (Scheme 10).
Scheme 11
Further evidence in support of Scheme 10 was obtained by synthesis and pyrolysis of two isomeric triazoles, 4-methyl-5-phenyl-1-phthalimido-1,2,3-triazole (108) and the 5-methyl-4-phenyl compound (109). The formation of identical products from the two triazoles is consistent with the formation of the 1H-azirine intermediate (Scheme 11).

The formation and closure of the intermediate iminocarbene (106, Scheme 10) is analogous to the isomerisation of ketocarbenes. An unexpected feature of the nitrogen analogue
is that equilibrium is apparently complete and other potential iminocarbene reactions, such as the Wolff rearrangement, are not observed. This contrasts with ketocarbene reactions, in which only a small percentage of the products are formed via oxirene intermediates.

4. The Thermal Decomposition of 2-Halophenols and their Salts.

The first report of the thermal decomposition of a salt of a 2-halophenol was made over one hundred years ago by Merz and Weith\(^77\). They obtained a high-melting, crystalline solid which they called "perchlorophenyleneoxide", by heating potassium pentachlorophenoxide at 300\(^0\). They failed, however, to establish the structure of this compound.

A few years later, Zincke\(^78\) found that 2, 2, 3, 4, 4, 5, 6-heptachlorocyclohex-5-enone (110) gave 2, 3, 4, 4, 5, 6-hexachlorocyclohexa-2, 5-dienone (111) on heating to 180\(^0\) and on raising the temperature to over 200\(^0\) he obtained the same product as Merz and Weith. Again, the structure was not assigned for the product, which was undoubtedly octachlorodibenzo-p-dioxin (112).
Although, shortly after this, the thermal decomposition of the alkali salts of 2-chlorophenol was reported\textsuperscript{79} to give dibenzo-\textsubscript{P}-dioxin (113), the mechanism of the reaction and the examination of the structure of "perchlorophenyleneoxide" were disregarded for many years.

\begin{center}
\includegraphics[width=0.3\textwidth]{113}
\end{center}

Hunter\textsuperscript{80} examined the decomposition of the silver salts of 2, 4, 6-trihalophenols and found that on reaction with dry ethyl iodide they formed white amorphous compounds which had the general formula $(C_6H_2X_2O)_n$ and which he called "poly-dihalophenylene oxides". Similar compounds were obtained by decomposition of the silver salts with catalytic amounts of iodine and also by decomposition of the salts in benzene at 60\textdegree. By decomposition of suitably substituted sodium salts containing mixed halogen atoms, Hunter\textsuperscript{81} found that the halogen atoms were removed from the ortho and para positions in the ring and that the order of ease of leaving was: iodine > bromine > chlorine. Hunter\textsuperscript{82} suggested a radical mechanism for the formation of the polymeric oxide. The first step is oxidation of the phenoxy-anion to phenoxy-radical, which explained the role of iodine in the decomposition.
This is followed by loss of a halogen atom leaving a diradical residue (114) and the polymer is then formed by coupling of large numbers of these residues carbon to oxygen, forming a succession of ether linkages, thus:

\[
\begin{align*}
\text{ONa} & \quad \text{I} \quad \text{X} \quad \text{X} \\
\text{X} & \quad \text{X} \\
\text{X} & \quad \text{X} \\
\text{Dewar and James}^{83} & \text{ were dubious about the involvement of diradicals in such a mechanism and suggested an alternative mechanism in which the same phenoxy-radical is initially formed but which then displaces a halogen atom from another molecule of the sodium salt. The halogen atom thus liberated can then oxidise another phenoxy-anion to continue the process.}
\end{align*}
\]
The thermal decomposition of pentachlorophenol and its alkali salts was re-investigated by Sandermann and his co-workers \(^8^4\), who decomposed pentachlorophenol and its sodium salt, separately, and obtained the same two products, hexachlorobenzene and "perchlorophenylene oxide". The latter was identified as octachlorodibenzo-\(p\)-dioxin (112) and they postulated a mechanism explaining its formation in low yield. In this mechanism two simultaneous reactions occur. In one reaction dehydration of two molecules of pentachlorophenol gives decachlorodiphenyl ether (115), which they proposed to undergo cleavage in the presence of hydrogen chloride to give the starting phenol and hexachlorobenzene. The hydrogen chloride is formed in the other reaction in which
elimination of hydrogen chloride gives octachlorodibenzo-p-dioxin directly.

Denivelle\textsuperscript{85} provided evidence against Sandermann's mechanism when he found that the diphenyl ether (115) did not undergo cleavage with hydrogen chloride under the conditions of the decomposition. He confirmed the result obtained by Zincke\textsuperscript{78}, showing that the cyclohexadienone (111) gave octachlorodibenzo-p-dioxin on thermolysis.

Denivelle condensed the cyclohexadienone (111) with a salt of pentachlorophenol to give 2, 3, 4, 5, 6-pentachloro-4-pentachlorophenoxydicyclohexa-2, 5-dienone (116), which underwent several reactions, including formation of octachlorodibenzo-p-dioxin.
Denivelle\textsuperscript{85} also showed that thermolysis of 2, 3, 4, 5-tetrachloro-6-pentachlorophenoxyphenol (117) in quinoline yielded octachlorodibenzo-p-dioxin (112).

Kulka\textsuperscript{86} suggested a route involving a phenoxy radical for the formation of octachlorodibenzo-p-dioxin from the cyclohexadienone (111) or pentachlorophenol. (Scheme 12)

Kulka\textsuperscript{86} obtained octachlorodibenzo-p-dioxin in almost
quantitative yield by treatment of pentachlorophenol with halogens or halogen-producing compounds as oxidants. He found that the best oxidant was the dienone (111) since it not only liberated an oxidant, chlorine, but was itself converted to the dioxin (112) under the same conditions. On repetition of the work of Zincke, Kulka obtained results in agreement with a mechanism involving oxidation of phenol to phenoxy radical, supported by the fact that chlorine itself and, to a lesser extent, bromine and iodine, increased the yield of dioxin (112).

Substituted dibenzo-\(p\)-dioxins, particularly the halogen substituted derivatives, are of considerable biological interest. Some are used in the manufacture of flame retardants and many are useful as chemical intermediates. The thermal decomposition of 2-halophenoxyd oxides provides a good route for the synthesis of symmetrically substituted dibenzo-\(p\)-dioxins. Tomita\(^8\) prepared dibenzo-\(p\)-dioxin by thermal decomposition of potassium 2-bromophenoxydioxide in the presence of copper. He has used the same method in the preparation of substituted dioxins; for example, 2,7-dimethyldibenzo-\(p\)-dioxin\(^8\). Recently, Denivelle and his co-workers\(^9\) have made octafluorodibenzo-\(p\)-dioxin in a similar manner.

Hall\(^10\) studied the decomposition of 2-halophenoxydioxides in the light of the synthetic possibilities and in order to elucidate the mechanism. So far, the mechanism has been considered in terms of
a radical process but it is also possible to consider the formation of a 1,2-ketocarbene intermediate (118).

\[
\begin{align*}
\text{2} & \xrightarrow{\text{X}} \text{118} \\
\text{O} & \rightarrow \text{2} \\
\end{align*}
\]

The formation of dibenzo-\(p\)-dioxin can then be explained by dimerisation of the ketocarbene and the polyphenylene oxides may arise by radical chain processes in which the ketocarbene acts as initiator.

Hall\(^{90}\) attempted to detect the presence of radical intermediates by conducting the decompositions in methyl substituted aromatic solvents, in which reaction with the methyl side-chains could occur. In mesitylene, however, dibenzo-\(p\)-dioxin, alone, was obtained on thermal decomposition of sodium 2-bromophenoxide. An attempt to form a 1,3-cycloaddition product, in a similar manner to those obtained by Huisgen\(^{25}\) with ketocarbenes derived from diazoketones, also proved unsuccessful. Dibenzo-\(p\)-dioxin was the only product from the decomposition of sodium 2-bromophenoxide in the presence of trans-stilbene in t-butylbenzene.

Attention was then turned to chloro-substituted phenoxides.
and thermal decomposition of sodium pentachlorophenoxyde showed attack on the solvent to have taken place to a considerable extent. The expected product, 3,3',5,5'-tetramethylbibenzyl, however, was not formed and its isomer, 2,3',4,5',6-pentamethyldiphenylmethane (119) was obtained instead. 2,3,5,6-Tetrachlorophenol was also produced in this reaction but no octachlorodibenzo-p-dioxin was detected. The latter product was obtained, however, on repetition of the decomposition in t-butylbenzene and no attack on the solvent was detected.

![Chemical structures](image)

Similar decompositions in p-xylene and durene showed formation of diphenylmethanes, trichlorophenol, 2,3,5,6-tetrachlorophenol and 2,3,4,5-tetrachlorophenol. Since 2,3,4,6-tetrachlorophenol was not detected, Hall concluded that chlorine was lost from the ortho and para positions only. A decomposition
carried out in a mixture of p-xylene and t-butylbenzene gave the cross-product (120) as well as 2,4',5-trimethyldiphenylmethane.

Hall concluded that the latter result indicated a two-step mechanism involving initial attack on the methyl substituted aromatic compound to give an intermediate, which will substitute on an aromatic ring to give the diphenylmethanes. The lack of formation of bibenzyl derivatives seemed to rule out the possibility of benzyl radical formation.

Hall proposed three possible mechanisms for the decompositions; none of which fulfilled all the requirements of experimental evidence.

i) **Ketocarbene mechanism**

This mechanism, leading to formation of a benzyl carbonium ion explains the loss of chlorine from **ortho** and **para**
positions but does not explain why the reaction was not observed with sodium 2-bromophenoxide.

ii) **Radical mechanism**

In this case the reaction is initiated by a chlorine atom and the mechanism explains the increased loss of chlorine observed in methylbenzene solvents over that in t-butylbenzene but does not explain the preferential loss from ortho and para positions. Other serious objections to this scheme are that bibenzyl derivatives would be expected by dimerisation of the benzyl radicals and it fails to explain why no attack on the solvent
was detected with sodium 2-bromophenoxide.

iii) Nucleophilic mechanism

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

\[
\begin{align*}
\text{CH}_2 & \quad \text{Cl}. \\
\text{OH} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\]

This mechanism, showing nucleophilic attack on a chlorine atom by the benzyl anion also fails to explain preferential loss of ortho and para chlorine.

Hall finally concluded that more experimental evidence was required to elucidate the mechanism of the decomposition.

5. Reactions of Aryl Halides with Strong Base

Aryl halides in which the aromatic nucleus contains no activating substituents such as nitro groups usually require the use of strong bases and quite forceful conditions for any reaction to occur. Under these conditions, two types of reaction can occur, viz., benzyne formation leading to rearrangement of substituents in the products, and direct nucleophilic substitution leading to unrearranged products.

Before the turn of the century the condensations of amide
and substituted amide ions with aryl halides were studied, but early workers in this field did not attempt to explain the formation of the observed rearranged products. Kym found that reaction of p-dibromobenzene with p-toluidine and soda lime at 350° gave some m-ditoluidinobenzene. Haeussermann did a more extensive study and showed that o-, m- and p-dichlorobenzene all gave the same product, N,N,N',N'-tetraphenyl-m-phenylenediamine on treatment with potassium diphenylamide. Fittig and Mager first recognised that the unexpected product, resorcinol, was obtained from the alkali fusion of both ortho- and para-halogenated phenols.

Other work in this field included that of Bergstrom, who studied the reaction of aryl halides with potassium amide in liquid ammonia, but the phenomenon of the so-called "cine-substitution" was finally solved by Roberts.

Roberts provided evidence for an intermediate species, dehydrobenzene, or benzyne (122), by reaction of 14C-labelled chlorobenzene (121) with potassium amide in liquid ammonia. He obtained almost equal amounts of the unrearranged and rearranged products (123 & 124, respectively).
Huisgen\textsuperscript{97} confirmed benzyne to be the intermediate in these nucleophilic substitutions by reaction of aryl halides with phenyl lithium and its existence was placed beyond doubt when Wittig\textsuperscript{98}, visualising it to act as a dienophile, succeeded in trapping benzyne with furan as the Diels-Alder adduct (125).

\[
\begin{align*}
\text{benzyne} & \quad + \quad \text{furan} \\
\rightarrow & \\
\text{adduct} (125)
\end{align*}
\]

Anthracene has also been used in a similar manner to trap benzyne as the adduct, triptycene (126) and reactions of this type are commonly used for the detection and trapping of benzyynes\textsuperscript{99}.

\[
\begin{align*}
\text{benzyne} & \quad + \quad \text{anthracene} \\
\rightarrow & \\
\text{adduct} (126)
\end{align*}
\]

(a) **Mechanism and scope of reactions involving the generation of benzyne from aryl halides.**

Scheme 13 represents the complete equation for the
formation of benzyne by reaction of an aryl halide with a strong base.

\[
\begin{align*}
    & \text{Ph}^- + B^- & \frac{k_1}{k_1} & \text{Ph}^- + BH \quad \text{(i)} \\
    & \text{Ph}^- & \frac{k_2}{k_2} & \text{Ph}^- + X^- \quad \text{(ii)}
\end{align*}
\]

Scheme 13

Although Roberts\textsuperscript{100} suggested this mechanism to be valid only for the amination of chlorobenzene, whereas that of bromobenzene does not require the anion (127) as an intermediate, it can be used to account for all such reactions provided that suitable values are chosen for \(k_1\), \(k_1\), \(k_2\) and \(k_2\).

The mechanism must account for the change in order of reactivity for different aryl halides on metalation in different solvent systems. For amination in protic solvents, such as liquid ammonia, the order of reactivity of phenyl halides with sodamide is PhBr>PhI>PhCl, and fluorobenzene is not aminated at all under these conditions\textsuperscript{94}. With an aprotic system, lithium piperidide in ether, however, the order PhF>PhBr>PhCl>PhI is observed\textsuperscript{101}.

Hoffmann\textsuperscript{102} explained this difference in reactivities as follows. The sequence F>Cl>Br>I would be the expected order
of reactivity for the metalation of aryl halides if $k_1$ is rate determining, as is the case with aprotic solvents. In protic solvents, however, step (i) (Scheme 13) becomes reversible and the order of reactivity to reprotonation is $F > Cl > Br > I$. Fluorobenzenes in protic media are reprotonated rapidly and never have a chance to take part in step (ii). In protic solvents $k_2$ can become the rate determining factor giving the order of reactivity $I > Br > Cl > F$, but the order of reactivity actually observed: $Br > I > Cl >>> F$ is obtained by superimposition of these two reaction sequences. The concentration of the base controls the extent to which one sequence predominates and almost any sequence of reactivity can be achieved by varying the strength of the base.

Substituents have a pronounced effect on the rate of halide loss from the anion (127). Halide ion is lost together with its bonding electrons and substituents which can stabilise the negative charge by their inductive effect will tend to reduce the loss of halide ion and strengthen the $C - X$ bond.

Electron-withdrawing substituents will assist step (i) but retard step (ii) and electron-donating groups will destabilise the anion (127) (Scheme 13). It has been shown that 1,3-dihalo and polyhalobenzenes can be readily metalated by potassium anilide in liquid ammonia, and methanolic sodium methoxide, conditions under which monohalobenzenes are not attacked$^{102}$. Step (ii), however, becomes so retarded as to preclude halide loss by reprotonation.
The inductive effect of methyl groups is shown in the amination of 3-halotoluenes with potassium amide in liquid ammonia\(^\text{103}\) (Scheme 14). In the bromo-compound loss of bromide is fast and the metalation is irreversible, giving rise to a 2 : 3 ratio of the benzyynes (130) and (131), respectively and, hence, the same ratio of anions (128) and (129). In the chloro-compound the same ratio of metalation can be assumed but the metalation step is reversible in this case. The observed products arise from the benzyynes (130) and (131) in the ratio 4 : 1, respectively, showing the inductive effect of the methyl group \textit{ortho} to the negative charge to have increased the loss of chloride and hence increased the amount of benzyne formed.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{X} & \quad \text{X} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\downarrow & \\
\text{130} & + \quad \text{128} \quad \text{129} \\
\text{X=Cl} & \quad 80\% \quad 40\% \quad 60\% \\
\text{X=Br} & \quad 40\% \quad 20\%
\end{align*}
\]

\textbf{Scheme 14}
Although substituents in the aromatic ring affect the formation of the benzyne, which is no longer symmetrical, the ratio of products formed by its further reaction should be the same, independent of the base system in which it was produced. Good agreement has been found in the ratios of isomeric products obtained when substituted aryl halides have been treated with sodamide in liquid ammonia\textsuperscript{103} and with potassium t-butoxide in t-butylbenzene\textsuperscript{99}.

\[
\begin{align*}
\text{R} - \text{X} & \quad \xrightarrow{\text{N \BH RQB}} \quad \text{R} [\text{B}] \quad \xrightarrow{\text{BH}} \quad \text{R} [\text{B}] + \text{R} [\text{B}]
\end{align*}
\]

(b) **Reactions involving direct nucleophilic substitution of aryl halides by strong bases**

In many cases, particularly when the metalating agent is a good nucleophile, direct nucleophilic substitution of the aryl halide by the addition/elimination mechanism\textsuperscript{95, 104} takes place. Benzyne formation and competing direct nucleophilic substitution
Two routes are available for the formation of the unrearranged product (132). It may be formed as the single product of direct nucleophilic substitution or as one of the two products resulting from benzyne participation. Obviously, lack of formation of the rearranged product is indicative of direct nucleophilic substitution having occurred. The nature of the base determines which of the two routes is followed. A fairly weak base, which is a good nucleophile, tends towards direct nucleophilic substitution, for example, lithium diphenylphosphide reacts with aryl bromides by direct nucleophilic substitution only. Reaction of bromonaphthalene with piperidine at 230° leads to a single product formed by direct nucleophilic substitution, whereas the use of a stronger base, sodium piperidide leads to the formation of two products, formed exclusively by the benzyne route.
In the reaction of aryl halides with sodium hydrazide\textsuperscript{107} only the aryl fluorides give direct substitution. This result has been explained in terms of a cyclic intermediate (133); \textit{N, N}-dimethylhydrazide reacts only via the benzyne route since it cannot form such an intermediate.

Liveris and Miller\textsuperscript{108} have reported that aryl halides react with sodium methoxide only by direct nucleophilic substitution above 100\degree and that fluorobenzene reacts one hundred times faster than chlorobenzene at 200\degree. A similar behaviour has also been reported for the reaction of aryl halides with potassium t-butoxide in dimethyl sulfoxide\textsuperscript{109}. In contrast to this, the order of reactivity \text{ArI}>\text{ArBr}>\text{ArCl}>\text{ArF} has been suggested\textsuperscript{110} for the direct substitution of aryl halides with aqueous sodium hydroxide at 250\degree. The difference in order of reactivity of halogen depends on which step of the addition/elimination mechanism is rate-determining and cannot, therefore, be used to detect participation of direct nucleophilic substitution.

(c) \textbf{Novel reactions of aryl halides with strong base}

The highly acidic nature of the hydrogen atoms ortho to
halogens in aromatic systems has been demonstrated by Roberts et al.\textsuperscript{111}, who showed that fluorobenzene-2-d exchanged hydrogen isotope a thousand times faster than deuteriobenzene. The effect of the para fluorine is even weaker than the meta. The ease of formation of o-halophenyl anions is exemplified by the cleavage of o-halobenzophenones by potassium amide in liquid ammonia\textsuperscript{112}.

\[
\text{Ph-C} = \text{O} \xrightarrow{\text{KNH}_2, \text{liq NH}_3} \text{Ph-}X \xrightarrow{\text{KHN-C} = \text{O}} \text{Ph} + \text{H}_X
\]

Nucleophilic attack can also take place on the halogen atom. The unexpected product, 1,4-dibromobenzene was obtained by reaction of 1,2,4-tribromobenzene with potassium t-butoxide in a 50:50 mixture of t-butylalcohol and dimethylsulphoxide\textsuperscript{112}.

\[
\text{Br-Br} \xrightarrow{\text{KOBu}^+, \text{Bu}^+\text{OH, DMSO}} \text{Br} \text{Br} + \text{Br}^-
\]

Bunnett and Victor\textsuperscript{113} explained this effect, which took place more readily with the iodo-compound and not at all with the chloro-compound, as a nucleophilic attack by the methanesulphinyl anion (134).

\[
\text{Bu}^+\text{O}^- + \text{CH}_3\text{SOCH}_3 \rightleftharpoons \text{Bu}^+\text{OH} + \text{CH}_3\text{SOCH}_2^- \quad (134)
\]

\[
\text{CH}_3\text{SOCH}_2^- + \text{ArX} \rightarrow \text{Ar}^- + \text{CH}_3\text{SOCH}_2\text{X}
\]

\[
\text{Ar}^- + \text{Bu}^+\text{OH} \rightarrow \text{ArH} + \text{Bu}^+\text{O}^-
\]
Treatment of the 5- and 6-iodopseudocumenes (135 and 136, respectively), separately, with potassium amide in liquid ammonia would be expected to form the same aryne intermediate (137) and hence the same proportions of amine products (138 and 139) (Scheme 15). Each of the iodo compounds, however, was found to give preferentially the unrearranged product\textsuperscript{112}, suggesting a competing direct nucleophilic substitution reaction. Nucleophilic substitution of this type, however, is unlikely and no examples are known under these conditions.
Evidence for a radical mechanism to explain this result was obtained by addition of a radical scavenger, tetraphenyldiazin, to the system, which increased the yield of rearranged product.

Furthermore, addition of potassium metal to the system promoted substitution without rearrangement, and Bunnett\textsuperscript{112} proposed the following mechanism of radical substitution:

\[
\text{electron donor} + \text{ArI} \rightarrow \text{ArI}^- + \text{residue} \\
\text{ArI}^- \rightarrow \text{Ar}^+ + \text{I}^- \\
\text{Ar}^+ + \text{NH}_2^- \rightarrow \text{ArNH}_2^- \\
\text{ArNH}_2^- + \text{ArI} \rightarrow \text{ArNH}_2 + \text{ArI}^- \\
\text{termination steps}
\]

Although potassium metal in liquid ammonia provides an excellent electron donor, without the metal the identity of the electron donor is obscure. Bunnett termed this mechanism "substitution, radical-nucleophilic, unimolecular" (SRN\textsubscript{1}). Addition of potassium metal to the reaction of o-bromoanisole with potassium amide in liquid ammonia, normally a classic benzyne reaction, gave
\( \text{o-anisidine as the sole product.} \)

In 1959, Wotiz and Huba\textsuperscript{114} noticed, to their surprise, that 1,2,4-tribromobenzene (140) on treatment with sodamide in liquid ammonia, gave the isomeric product (141). Moyer and Bunnett\textsuperscript{115} later found that potassium anilide caused this isomerisation more readily. Other products included small amounts of \( m \)- and \( p \)-dibromobenzene caused by disproportionation, tetrabromobenzenes (142 and 143) and larger amounts of the benzyne derived products (144 and 145). (Scheme 16).

\[ \begin{align*}
\text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{C}_6\text{H}_5\text{NH}_2 & \quad \text{NH}_3 \\
\text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} \\
140 & & 141 & & & \\
\text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{NH}_2 & \quad \text{NH}_2 \\
142 & & 143 & & 144 & & 145
\end{align*} \]

\textbf{Scheme 16}

Bunnett\textsuperscript{112} suggested a positive halogen transfer mechanism (Scheme 17) to explain the formation of the observed products. The cryl
anion (146) causes displacement of another aryl anion (147) by nucleophilic attack on bromine in the tribromobenzene (142). The net result is transfer of a positive bromine from one carbon to another.

Scheme 17

The disproportionation products may be explained, for example, by formation of the aryl anion (148).
(d) **Reaction of bromodurene with strong base**

It has been shown\textsuperscript{96, 116} that blocking of the *ortho* positions of aryl halides does not lead to substitution with bases under normal conditions. Although 1,2 loss of hydrogen halide is prevented in such systems as the substituted benzene (149), the possibility of 1,4 loss was considered if the conditions were forceful enough.

\[ R_2\text{C}_{\text{ortho}}X \xrightarrow{-HX} R_2\text{C}_{\text{ortho}} \]

Hall\textsuperscript{90} examined the reaction of bromodurene (150) with potassium t-butoxide at elevated temperatures and found that hydrogen bromide was eliminated. The products of the reaction at 220\textdegree C were durene (151), t-butanol, hexamethylbibenzyl (152), bromohexamethylbibenzyl (153) and dibromohexamethylbibenzyl (154) (Scheme 18).
Scheme 19
A radical mechanism (Scheme 19) was postulated for this reaction since the formation of the bibenzyl products suggested the involvement of benzyl radicals. The initial attack by the base produces a benzyl anion, which loses bromide ion to give the
Scheme 20
vinylcarbene (155). Hall suggested this carbene to have a triplet structure since a singlet structure would be expected to product aryl t-butyl ethers (157) or diphenylmethanes (158) by reaction of its dipolar resonance form with other anions.

Hall doubted that the yield of durene obtained (22%) could all have arisen by transfer of hydrogen from bromodurene to the benzyl radical (156). A second mechanism (Scheme 20) was, therefore, suggested in which the benzyl anion (159) and bromodurene react by nucleophilic displacement of bromine to give the substituted benzyl bromide (160), and an aryl anion (161). Abstraction of a proton from the solvent by the aryl anion (161) then gives rise to durene. Bibenzyl formation is shown by other anionic steps in Scheme 20. The objection to this scheme, however, was the lack of formation of t-butyl ether (163), since nucleophilic attack by the t-butoxide ion on the benzyl bromide (160) would be
expected to produce the ether (163). This objection was substantiated when Hall reacted bromodurene with potassium t-butoxide in the presence of an isomeric mixture of the bromotrimethylbenzyl bromides (160 and 162) and isolated the corresponding isomeric t-butyl ethers (163 and 164).

\[
\begin{align*}
160 + \text{ButO}^- & \rightarrow 163 \\
162 & \rightarrow 164
\end{align*}
\]

The latter result suggested the ether (163) to be stable under the reaction conditions and Hall discounted Scheme 20. Robertson, however, cast doubt on this result when he reinvestigated the reaction of bromodurene in the presence of the isomeric benzyl bromides (160 and 162), and concluded that the ethers (163 and 164), if formed, were destroyed under the reaction conditions. On this contradictory evidence the question of the anionic mechanism, therefore, was placed in the balance.

(e) "Complex bases"

Whilst studying the condensation of bromobenzene with various nucleophiles in the presence of sodamide and tetrahydrofuran,
Caubère and Loubinoux noticed that the addition of t-butoxide to the reaction mixture greatly increased the yields of the condensation products. Some of the arynic condensations were found to take place only in the presence of sodamide and t-butoxide; no reaction occurring with sodamide alone. The enhancement of the strength of the basic medium was proposed by Caubère and Loubinoux to arise from the equilibrium:

\[
\text{NaOBu}^+ + \text{NaNH}_2 \rightleftharpoons \text{BuO}^- + \text{NH}_2\text{Na}^-
\]

The charged species (165) was called the "complex base" and the increase in base strength was attributed to the ability of the "complex base" to increase the solubility and ionisation of sodamide. The heterogeneous medium, in which the equilibrium exists between the solid phase and the solution, was studied by its reaction with triphenylmethane, which gave an immediate red colouration due to the formation of the triphenylmethyl anion. The red colouration was removed by condensation of the anion with benzyl chloride and its disappearance taken as indicative of completion of the condensation in the presence of excess base. In this way, the strengths of the basic media obtained using a variety of alkoxides were determined and the following order found:

\[\text{i-PrONa} > \text{t-BuONa} > \text{PhONa} > \text{cyclohexylONa}\]
The results obtained by Caubere and Loubinoux were not very reproducible, and were dependent to a large extent on the purity of the tetrahydrofuran.

6. Programme of Research

Attempts to elucidate the mechanism of the thermal decomposition of sodium 2-halophenoxides by Hall\textsuperscript{90} have been described in the Introduction. Little previous work has been carried out in this field, although radical mechanisms have been suggested to explain the formation of polymeric oxides and dibenzo-p-dioxins resulting from decompositions of some halophenols and their salts. Hall\textsuperscript{90} suggested three mechanisms, \textit{viz.} a mechanism involving radicals, a mechanism involving nucleophilic attack on the halogen atom, and a mechanism involving a ketocarbene intermediate. None of these mechanisms proved entirely satisfactory in explaining experimental observations, and it was concluded that further experimental evidence was required to clarify the picture.

Since the 1,3-dehydrobromination of bromodurene has been shown to proceed via a mechanism involving a vinylcarbene\textsuperscript{168}, a mechanism involving the formation of a ketocarbene in the decomposition of sodium 2-halophenoxides, was attractive.

Thermal decompositions of sodium 2-bromophenoxides and related compounds were, therefore, studied with a view to finding
evidence for a 1,2-ketocarbene mechanism.

The successful use of "complex base" by Caubère and Loubinoux in arylic condensations with bromobenzene led to the use of this system to study the reaction of bromodurene with strong base. Hall studied the reaction of bromodurene with potassium t-butoxide at 220° in an autoclave and postulated two possible mechanisms to explain the products obtained, viz., a radical mechanism and a mechanism involving nucleophilic displacement of bromine. Since evidence for both mechanisms was conflicting, an attempt was made to clarify the situation by carrying out the reactions under the less forceful conditions required by "complex bases".
A. Preparation of Starting Materials

1. Preparation of Diphenyl Ethers

(a) 2-Nitrophenyl phenyl ether
(b) 2-Chlorophenyl 2-nitrophenyl ether
(c) 3-Chlorophenyl 2-nitrophenyl ether
(d) 2-Aminophenyl phenyl ether
(e) 2-Aminophenyl 2-chlorophenyl ether
(f) 2-Aminophenyl 3-chlorophenyl ether
(g) 2-Bromophenyl phenyl ether
(h) 2-Chlorophenyl 2-hydroxyphenyl ether
(i) 3-Chlorophenyl 2-hydroxyphenyl ether
(j) 2-(3-Chlorophenoxy)benzenediazonium fluoroborate

2. Preparation of Phenols

(a) 5-Methyl-2-nitrophenol
(b) 4-Methyl-2-nitrophenol
(c) 2-Amino-4-methylphenol
(d) 2-Bromo-5-methylphenol
(e) 2-Bromo-4-methylphenol
(f) 2-Bromo-5-methoxyphenol
(g) 2-Bromo-4-methoxyphenol

3. Preparation of Benzenethiols

(a) 2-Bromobenzenethiol
(b) 2-Iodobenzenethiol
(c) 2-Bromo-4-methylbenzenethiol

(a) 2-Azido-4-methylphenol 97
(b) 2-Azido-5-methylphenol 97
(c) 2-Azido-4-methylphenyl benzoate 97
(d) 2-Azido-5-methylphenyl benzoate 97
(e) 5-Methyl-2-phenylbenzoxazole 97
(f) 6-Methyl-2-phenylbenzoxazole 98

5. Preparation of Fluoranthene Compounds:

Attempted Preparation of 2-Bromo-3-hydroxyfluoranthene 98

(a) 3-Nitrofluoranthene 98
(b) 3-Acetamidofluoranthene 98
(c) 3-Acetamido-2-bromofluoranthene 99
(d) 3-Amino-2-bromofluoranthene 99
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b.p. boiling point
m.p. melting point
g.l.c. gas-liquid chromatography
g.l.c./m.s. gas-liquid chromatography coupled with mass spectrometry
t.l.c. thin layer chromatography
n.m.r. nuclear magnetic resonance
i.r. infrared
s singlet
d doublet
c complex
h.s.l.c. high speed liquid chromatography
m/e mass to charge ratio
m/100m moles per 100 moles of starting material
M molarity
M\(^+\) mass of molecular ion
w/v weight/volume ratio

In accordance with common usage, 1,2,4,5-tetramethylbenzene is referred to by its trivial name, durene, and is represented by the symbol
Instrumentation and General Techniques

Gas-Liquid Chromatography

All g.l.c. analyses were carried out on Pye Series 104 chromatographs with flame ionisation detectors using 1.5 m x 4 mm i.d. packed columns. The carrier gas was nitrogen in all cases, and the flow rates were those recommended by the manufacturers. Quantitative measurements were made using the internal standard technique: calibration graphs were drawn of peak area ratio against molar ratio using standard solutions containing known weights of the internal standard and the compound for which the yield in the reaction mixture is required. Stationary phases, supported on 100-120 mesh celite included neopentylglycol succinate (NGPS), polyethylene glycol (CAR), silicone elastomer (SE 30) and Apiezon L grease (APL).

High Speed Liquid Chromatography was carried out by Dr. J. N. Done using a Du Pont model 820 liquid chromatograph. Operating conditions and columns are described where appropriate in the experimental section. 1 m x 2 mm packed columns and a u.v. photometer detector were used.

Column Chromatography

The alumina used was Laporte Industries Ltd., activated aluminium oxide, type H, supplied by Fisons Scientific Apparatus (Brockman Activity 1-2).

Thin Layer Chromatography

Thin layer chromatograms were obtained on 0.33 mm layers of alumina (Merck, aluminium oxide G) on glass plates.
Components were detected by development in iodine vapour or by their fluorescence in u.v. light.

**Infrared Spectroscopy**

Spectra were recorded on a Perkin Elmer 157G grating spectrometer, liquid and low-melting solid samples being examined as films and solid samples as nujol mulls. A polystyrene film was used as reference at 1603 cm\(^{-1}\).

**Nuclear Magnetic Resonance Spectroscopy**

Routine spectra were recorded on a Perkin Elmer R-10 spectrometer and a Varian EM 360 spectrometer, operating at a frequency of 60 MHz. High resolution spectra were recorded on a Varian H.A. 100 spectrometer operating at 100 MHz. Chemical shifts are recorded as \(\tau\) (\(\tau\)) values in parts per million, tetramethylsilane (\(\tau = 10.0\)), being used as internal reference. Unless otherwise stated, for reasons of solubility, spectra were determined in 10 - 15% w/v solutions in deuteriochloroform.

Carbon-13 nuclear magnetic resonance spectra were obtained using a Varian XL-100 instrument using the pulse and Fourier transform technique at 25.16 MHz. The deuterium signal from the solvent (CDCl\(_3\) or C\(_2\)D\(_6\)CO) was used for field frequency lock and signals were recorded in parts per million from tetramethylsilane (positive for low field).

**Mass Spectroscopy**

Mass spectra and exact mass measurements were
recorded on an A. E. I. MS-902 mass spectrometer.

**Mass Spectroscopy/Gas Liquid Chromatography**

Reaction mixtures were examined on an A. E. I. MS-20 spectrometer or on a Micromass 12 spectrometer, both being coupled to a Pye Series 104 chromatograph using helium as carrier gas.

**Elemental Analyses**

Microanalyses were carried out by Mr. J. Grunbaum on a Perkin Elmer 240 Elemental Analyser.

**Melting Points**

The melting points of new compounds were determined by using a Kofler hot stage apparatus.

**Solvents and Reagents**

Unless otherwise stated, petroleum refers to the fraction b.p. 40 - 60°. Mesitylene, t-butylbenzene, petroleum, and other common solvents were purified by distillation and stored over sodium.

"Superdry"methanol was prepared by the method of Vogel\(^{119}\).

Dioxan was purified by passage through an alumina column and stored over sodium.

Tetrahydrofuran was passed through a column of alumina, distilled from potassium hydroxide pellets and stored over sodium.

1, 2-Dimethoxyethane was boiled under reflux over
calcium hydride (BDH commercial grade) under dry nitrogen for ten hours and allowed to stand over calcium hydride. This was then freshly distilled as required from calcium hydride under nitrogen.

"Superdry" benzonitrile and acetonitrile were distilled from phosphorous pentoxide and stored over activated molecular sieve.

Aniline, pyridine, and cyclohexylamine were dried over potassium hydroxide pellets, distilled under an atmosphere of dry nitrogen, and stored over potassium hydroxide pellets.

Nitrobenzene was purified by distillation and fractional freezing.

Potassium t-butoxide was sublimed; block temperature 210°/0.1 mm.

Sodamide (May & Baker) was used without purification.

Sodium salts of phenols, benzenethiols, and carboxylic acids were prepared using sodium methoxide. The residues, after removal of the methanol under vacuum, were dried for twenty-four hours in a drying pistol at 120° under high vacuum and were used without further purification.

Other reagents were purified by distillation or crystallisation.
A. Preparation of Materials

1. Preparation of Diphenyl Ethers

(a) 2-Nitrophenyl phenyl ether was prepared by the method of Wright and Jorgensen\textsuperscript{120} by heating 2-chloro-nitrobenzene and phenol with potassium hydroxide pellets in dimethyl sulphoxide. Extraction with ether gave an oil, which was fractionally distilled to give 2-chloronitrobenzene, b.p. 46-50°/0.02 mm and 2-nitrophenyl phenyl ether, b.p. 119-123°/0.02 mm (lit., 121 183-185°/8 mm).

(b) 2-Chlorophenyl 2-nitrophenyl ether was prepared by the method of Henley\textsuperscript{122} by heating 2-chloronitrobenzene and 2-chlorophenol with potassium hydroxide and a little water at 200°. Extraction with chloroform and distillation as in (a) gave the product, b.p. 160°/0.3 mm, m.p. 47-48° (lit., 123 m.p. 48°) (46%).

(c) 3-Chlorophenyl 2-nitrophenyl ether was prepared as described in (b), b.p. 144°/0.1 mm (lit., 123 b.p. 204°/8 mm) (82%).

(d) 2-Aminophenyl phenyl ether was prepared by the method of Lim\textsuperscript{124} by reduction of 2-nitrophenyl phenyl ether with iron powder and dilute hydrochloric acid. The product was distilled, b.p. 96-97°/0.1 mm and on recrystallisation from alcohol had m.p. 43.5-44° (lit., 125 41.5°) (40%).

(e) 2-Aminophenyl 2-chlorophenyl ether was prepared by the method described in (d) from the corresponding nitro-compound (b) and distilled, b.p. 110-112°/0.1 mm. On recrystallisation from
petroleum (60-80°) the product had m.p. 43-44° (lit., 123 44-45°) (97%).

(f) 2-Aminophenyl 3-chlorophenyl ether was prepared as described in (d) from the corresponding nitro-compound (c) and distilled, b.p. 110°/0.1 mm (lit., 123 195°/13 mm) (85%).

(g) 2-Bromophenyl phenyl ether was prepared from the corresponding amine (d) by the method of Vogel119 with the exception that the distillate obtained by steam-distillation was extracted with ether, the ethereal solution dried over magnesium sulphate and the ether removed under vacuum to give a white solid. The solid, 2-bromophenyl phenyl ether, was recrystallised from petroleum and had m.p. 43-44°. (22%)

(Found: C, 58.0; H, 3.6. Calc. for C12H9BrO: C, 57.9; H, 3.6%)

(h) 2-Chlorophenyl 2-hydroxyphenyl ether

2-Aminophenyl 2-chiorophenyl ether (4.4 g, 0.02 mol) was dissolved in concentrated sulphuric acid (3.5 ml) and water (10 ml) added. The solution was stirred and cooled with the addition of ice (10 g) to a temperature between 0 and 5°. A solution of sodium nitrite (1.66 g, 0.023 mol) in water (5 ml) was added dropwise to the stirred solution, maintaining the temperature between 0 and 5°. After the addition was complete, cold water (15 ml) and ice (15 g) were added together with urea (0.1 g) and the solution allowed to warm slowly to room temperature. Anhydrous sodium sulphate (7.5 g) and concentrated sulphuric acid (5 g) were added and the mixture boiled for one hour. The brown oil which separated was
extracted into ether, the ethereal solution dried over magnesium sulphate, filtered and the ether removed under vacuum. Distillation of the residual oil gave a colourless liquid, 2-chlorophenyl 2-hydroxyphenyl ether (0.4 g), b.p. 88°/0.01 mm, i.r. ν 3440 (broad, OH) 1600, 1580, 1260, 1095, 1055, 880, 740 cm⁻¹. The mass spectrum gave the correct parent ion: m/e; 220/222. Addition of a catalytic amount of copper bronze to the aqueous solution and further boiling for 3 h gave a further 0.1 g of the product.

(i) 3-Chlorophenyl 2-hydroxyphenyl ether was prepared by the method described in (h) with the exception that the corresponding amine precursor (f) required boiling in concentrated sulphuric acid to ensure that the amine sulphate was formed. The product was distilled, b.p. 100-110°/0.02 mm (0.2 g), i.r. ν 3380 (broad, OH), 1587, 1264, 1210, 910, 750 cm⁻¹. The mass spectrum showed the correct parent ion: m/e; 220/222.

(j) 2-(3-Chlorophenoxy)benzenediazonium fluoroborate

2-Aminophenyl 3-chlorophenyl ether (0.55 g, 2.5 mmol) was dissolved in a mixture of concentrated hydrochloric acid (2 ml) and concentrated sulphuric acid (1 ml) by boiling for several minutes. Water (2 ml) was added, the solution cooled to a temperature of between 0 and 5° and whilst stirring continuously the amine salt separated as coarse granules. A solution of sodium nitrite (0.18 g, 2.6 mmol) in water (1 ml) was added dropwise, followed by dropwise addition of a solution of sodium tetrafluoroborate (0.4 g, 3.6 mmol) in water (1 ml). The mixture was stirred for a further 30 mins, maintaining the temperature between 0 and 5°, after the addition was complete. The precipitate was filtered off, washed once with a cold 10% aqueous solution
of sodium tetrafluoroborate (3 ml), twice with ethanol (2 ml portions) and several times with a large quantity of ether. The product was purified by dissolving it in the minimum volume of acetone and adding ether to re-precipitate the solid, 2-(3-chlorophenoxy)benzenediazonium fluoroborate (0.6 g), m.p. 134-135° (decomp.), i.r. ν 2275 (N₂⁺), 1050 (BF₄⁻) cm⁻¹ (Found: C, 45.0; H, 2.4. C₁₂H₈BClF₄N₂O requires C, 45.2; H, 2.5%).

An attempt to prepare 3-chlorophenyl 2-hydroxyphenyl ether from 2-(3-chlorophenoxy)benzenediazonium fluoroborate by the method of Lewin and Cohen¹²⁶, using cuprous oxide as catalyst and cupric nitrate as additive in 0.1 M sulphuric acid, failed to give the desired product.

2. Preparation of Phenols

(a) 5-Methyl-2-nitrophenol was prepared by the method of Staedel and Kolb¹²⁷ by low-temperature nitration of m-cresol in glacial acetic acid. The product was purified by steam-distillation and recrystallised from ethanol, m.p. 56° (lit.,¹²⁷ m.p. 56°).

(b) 4-Methyl-2-nitrophenol was prepared by the method of Nolting and Wild¹²⁸ by diazotisation and nitration of 4-methylaniline. The product was recrystallised from alcohol, m.p. 32-33° (lit.,¹²⁸ m.p. 33.5°).

(c) 2-Amino-4-methylphenol was prepared by a modification of the method of Vogel¹¹⁹, by reduction of the corresponding nitro-compound (b) with tin and hydrochloric acid. The tin complex was broken down by passage of hydrogen sulphide through the warm acidic solution. The solution was neutralised with concentrated ammonia solution, boiled, filtered whilst hot and the cooled filtrate extracted
with ether. Removal of the ether under vacuum gave the product, m.p. 135° (lit., 129 m.p. 135°) (40%).

(d) **2-Bromo-5-methylphenol**

5-Methyl-2-nitrophenol (a) was reduced to the amine hydrochloride by the method of Vogel\(^{119}\), with the following modifications. The acid solution was concentrated to half the volume by removal of water under reduced pressure and the hydrochloride allowed to crystallise. The salt was filtered off, dissolved in the minimum quantity of hot water and an equal volume of 48% hydrobromic acid solution was added. On cooling, a crystalline solid was obtained, which was filtered off and the latter treatment with hydrobromic acid repeated to give the amine hydrobromide as pale yellow needles. The amine hydrobromide was diazotised and brominated by the method of Huston and Peterson\(^{130}\) to give 2-bromo-5-methylphenol, b.p. 88°/10 mm (lit., 130 81-82°/4 mm), n.m.r. (CDCl\(_3\)): \(\tau\) 2.6-3.5 (c, 3H, aromatic), \(\tau\) 4.6 (s, 1H, OH), \(\tau\) 7.75 (s, 3H, CH\(_3\)). The mass spectrum showed the correct parent ion: m/e; 186/188.

(e) **2-Bromo-4-methylphenol**

The precursor for this compound, 4-amino-3-bromotoluene, was prepared by the method of Johnson and Sandborn\(^{131}\), b.p. 67-72°/0.5 mm (lit., 131 b.p. 92-94°/3 mm), m.p. 16-17° (lit., 131 m.p. 17-18°). Diazotisation and subsequent hydrolysis of the resulting diazonium salt by the method of Ungnade and Orwoll\(^{132}\) gave the product, b.p. 102-104°/20 mm (lit., 132 b.p. 102-104°/20 mm), n.m.r. (CDCl\(_3\)): \(\tau\) 2.6-3.1 (c, 3H, aromatic), \(\tau\) 4.65 (s, 1H, OH), \(\tau\) 7.80 (s, 3H, CH\(_3\)).
(f) **2-Bromo-5-methoxyphenol**

Methylation of 4-bromoresorcinol by the method of Rice\textsuperscript{133} gave 2-bromo-5-methoxyphenol, which was purified by distillation on a Fischer Spaltrohr (concentric column) distillation unit, b. p. 68-71°/0.5 mm (lit.,\textsuperscript{133} 152°/15 mm), n. m. r. (CDCl\textsubscript{3}): \(\tau\) 2.65-3.73 (c, 3H, aromatic), \(\tau\) 4.45 (s, 1H, OH), \(\tau\) 6.29 (s, 3H, OCH\textsubscript{3}).

(g) **2-Bromo-4-methoxyphenol**

Methylation of quinol by the method of Robinson and Smith\textsuperscript{134} gave 4-methoxyphenol, m. p. 53-54° (lit.,\textsuperscript{134} m. p. 53°), which on bromination in carbon disulphide according to Irvine and Smith\textsuperscript{135} gave 2-bromo-4-methoxyphenol, m. p. 44-45° (lit.,\textsuperscript{135} m. p. 44-45°).

3. **Preparation of Benzenethiols**

(a) **2-Bromobenzenethiol** was prepared by the method of Schwarzenbach and Egli\textsuperscript{136} from 2-bromoaniline by diazotisation and treatment with potassium ethyl xanthate. The product was distilled, b. p. 53-54°/0.1 mm (lit.,\textsuperscript{136} 96-98°/11 mm), n. m. r. (CDCl\textsubscript{3}): \(\tau\) 2.4-3.3 (c, 4H, aromatic), \(\tau\) 6.10 (s, 1H, SH), i. r. \(\nu\) 2563 (SH) cm\textsuperscript{-1}.

(b) **2-Iodobenzenethiol** was prepared from 2-iodoaniline in a similar manner to (a) by the method of Suter and Hansen\textsuperscript{137}, b. p. 82-84°/0.1 mm (lit.,\textsuperscript{135} 119.5°/11 mm), n. m. r. (CDCl\textsubscript{3}): \(\tau\) 2.15-3.45 (c, 4H, aromatic), \(\tau\) 5.90 (s, 1H, SH), i. r. \(\nu\) 2550 (SH) cm\textsuperscript{-1}.

(c) **2-Bromo-4-methylbenzenethiol** was prepared as described in (b) from 4-amino-3-bromotoluene [A, 2 (e)]. The product was distilled, b. p. 128-133°/15 mm (lit.,\textsuperscript{138} 61-62°/0.5 mm), n. m. r. (CDCl\textsubscript{3}): \(\tau\) 2.3-3.3 (c, 3H, aromatic), \(\tau\) 6.15 (s, 1H, SH), \(\tau\) 7.76 (s, 3H, CH\textsubscript{3}), i. r. \(\nu\) 2568 (SH) cm\textsuperscript{-1}.
4. **Preparation of Azides and their Reductive Cyclisation to Benzoxazoles**

(a) **2-Azido-4-methylphenol** was prepared by the method of Smith et al.\(^{139}\) by diazotisation of 2-amino-4-methylphenol \([A, 2(c)]\) in sulphuric acid and treatment with sodium azide. The product was extracted as a dark oil and was not purified, \(\text{i.r. } \nu 3400 (\text{OH, broad}), 2100 (N_3) \text{ cm}^{-1}\).

(b) **2-Azido-5-methylphenol** was prepared by a modification of the method of Smith et al.\(^{139}\) The hydrochloride of 2-amino-5-methylphenol \([A, 2(d)]\) in water was treated with two equivalents of concentrated hydrochloric acid and diazotised as described in (a). The brown solid product was not purified, \(\text{i.r. } \nu 3400 (\text{OH, broad}), 2130 (N_3) \text{ cm}^{-1}\).

(c) **2-Azido-4-methylphenyl benzoate**

2-Azido-4-methylphenol (a) was benzoylated by the Schotten-Baumann reaction as described by Vogel\(^{119}\). The product was washed with water and dried under vacuum, \(\text{i.r. } \nu 2100 (N_3), 1735 (C = 0) \text{ cm}^{-1}\), n.m.r. \((\text{CDCl}_3)\): \(\tau 1.4-3.0 (c, 8\text{H, aromatic}), \tau 7.65 (s, 3\text{H, CH}_3)\).

(d) **2-Azido-5-methylphenyl benzoate** was obtained by benzoylation of 2-azido-5-methylphenol (b) as described in (c), \(\text{i.r. } \nu 2122 (N_3), 2090 (N_3), 1735 (C = 0) \text{ cm}^{-1}\), n.m.r. \((\text{CDCl}_3)\): \(\tau 1.7-3.1 (c, 8\text{H, aromatic}), \tau 7.65 (s, 3\text{H, CH}_3)\).

(e) **5-Methyl-2-phenylbenzoxazole** was prepared by reductive cyclisation of 2-azido-4-methylphenyl benzoate (c) with triethyl phosphite using the method of Saunders\(^{140}\). After removal of the solvent by distillation at atmospheric pressure, the residue was chromatographed on
alumina to give the product (80%). On recrystallisation from ethanol
the product had m. p. 104-105° (lit., 141 m. p. 104°), n. m. r. (CDCl₃):
\( \tau 1.6-3.0 \) (c, 8H, aromatic), \( \tau 7.52 \) (s, 3H, CH₃). (Found: C, 80.3;
H, 5.5; N, 6.5. Calc. for C₁₄H₁₁NO: C, 80.4; H, 5.3; N, 6.7%).
The mass spectrum showed the correct parent ion: m/e; 209.

(f) 6-Methyl-2-phenylbenzoxazole was prepared in 80% yield
from (d) by the same method as (e) and after recrystallisation from
ethanol, had m. p. 90-91° (lit., 142 92.5°), n. m. r. (CDCl₃): \( \tau 1.7-3.0 \)
(c, 8H, aromatic), \( \tau 7.54 \) (s, 3H, CH₃). (Found: C, 80.2; H, 5.3;
N, 6.4. Calc. for C₁₄H₁₁NO: C, 80.4; H, 5.3; N, 6.7%). The mass
spectrum showed the correct parent ion: m/e; 209.

5. Preparation of Fluoranthene Compounds: Attempted
   Preparation of 2-Bromo-3-hydroxyfluoranthene

(a) 3-Nitrofluoranthene was prepared by nitration of fluor-
anthene according to the method of Kloetzel et al. 143, m. p. 162-163°
(lit., 144 162-163°).

(b) 3-Acetamidofluoranthene

3-Nitrofluoranthene (23.5 g, 0.1 mol) was dissolved in hot glacial acetic
acid (500 ml) and a solution of stannous chloride dihydrate (200 g) in
concentrated hydrochloric acid (200 ml) added dropwise. After boiling
the mixture for a few minutes the dark-yellow precipitate was filtered
off, dried under vacuum and boiled for 15 mins in a solution of potassium
hydroxide (100 g) in water (250 ml) giving a bright yellow precipitate.
The solid was filtered off, dissolved in benzene (500 ml) and the
benzene solution dried over magnesium sulphate. The solution was
filtered and the filtrate concentrated to half its volume by removal
of benzene under vacuum. Acetic anhydride (12.5 g, 0.12 mol) was added with stirring and the yellow precipitate which formed was filtered off, washed with petrol and dried to give 3-acetamido-fluoranthene, 13.5 g (52%), m.p. 239-242° (lit., 143 m.p. 242-245°).

(c) 3-Acetamido-2-bromofluoranthene was prepared according to Charlesworth and Blackburn145 by bromination of 3-acetamido-fluoranthene (b) in pyridine. The product was recrystallised from a mixture of pyridine and water and had m.p. 266-267° (lit., 145 266-267°).

(d) 3-Amino-2-bromofluoranthene was prepared by boiling 3-acetamido-2-bromofluoranthene (c) in a mixture of methanol, pyridine and sodium hydroxide as described by Charlesworth and Blackburn145. The product was obtained as yellow needles, m.p. 175-176° (lit., 145 m.p. 176-177°).

(e) Attempted preparation of 2-bromo-3-hydroxyfluoranthene via 2-bromofluoranthene-3-diazonium fluoroborate

3-Amino-2-bromofluoranthene (0.59 g, 2 m mol) in hot glacial acetic acid (8 ml) was treated with concentrated hydrochloric acid (1.5 ml) and water (2 ml) to give a pink precipitate. The mixture was stirred and cooled to a temperature between 0 and 5°, and a solution of sodium nitrite (0.2 g) in water (2 ml) added dropwise over 20 mins. The resulting red solution was stirred for a further 30 mins whilst maintaining the temperature below 5°. The solid material was filtered off, washed with a large quantity of ether and purified by boiling in acetone, filtering the hot solution and reprecipitating by addition of ether. The solid, 2-bromofluoranthene-3-diazonium fluoroborate was filtered
off, and dried under vacuum, i.r. 2225 (N₂⁺), 1060 (BF₄⁻, broad), 1035 (BF₄⁻, broad) cm⁻¹.

The fluoroborate (0.65 g), without further purification, was treated with a mixture of anhydrous potassium carbonate and trifluoroacetic acid according to the method of Horning et al.¹⁴⁶ in an attempt to decompose it and produce the phenol, 2-bromo-3-hydroxyfluoranthene. A dark-brown solid was filtered off from the reaction mixture and washed with water, leaving an orange solid. The orange solid was filtered off, dried under vacuum and shown to be a diazonium salt from the i.r. spectrum 2200 (N₂⁺) cm⁻¹. The substance was not the starting material, 2-bromofluoranthene-3-diazonium fluoroborate since no absorptions were shown for BF₄⁻ in the i.r. spectrum. No phenolic product was obtained from the reaction mixture and the orange substance did not decompose to produce the required product on boiling in dilute sulphuric acid (0.1 M) for 12 h.

(f) Attempted preparation of 2-bromo-3-methoxyfluoranthene via the zinc chloride double salt of 2-bromofluoranthene-3-diazonium chloride.

2-Bromofluoranthene-3-diazonium chloride was prepared from 3-amin-2-bromofluoranthene (1.43 g, 5 mmol) as described in (e). A 20% excess of the theoretical amount of zinc chloride was added to the mixture to give the zinc chloride double-salt according to the method of Hodgson and Foster¹⁴⁷. The brick-red precipitate was filtered off, washed with a mixture of ether and a little methanol and dried under vacuum to give a 95% yield of the zinc chloride double salt of 2-bromofluoranthene-3-diazonium chloride, m.p. 175-178⁰ (decomp.), i.r. 2200 cm⁻¹.
(N₂⁺) (Found: C, 46.5; H, 1.8; N, 6.9. C₃₂H₁₈Br₂Cl₄N₄Zn requires C, 46.7; H, 1.9; N, 6.8%). The zinc chloride double salt was boiled under reflux in methanol as described by Hodgson and Foster¹⁴⁷. The solvent was removed under vacuum to leave a black, tarry residue which gave seven spots on examination by t.l.c. Chromatography on alumina gave a yellow solid (0.54 g) on elution with benzene. The solid was identified as a mixture of 2-bromofluoranthene, 2-bromo-3-chlorofluoranthene and a trace of 2-bromo-3-methoxyfluoranthene from its mass spectrum, which showed three parent ions: m/e; 314/316; 280/282; 310/312, and n.m.r. (CDCl₃) which gave mainly aromatic signals: τ 1.8-3.0 and a small signal at τ 6.12 (OMe). Further elution with more polar solvents gave tars only.

6. Preparation of Miscellaneous Aromatic Compounds

(a) 4-Methylphenyl 2-nitrophenyl sulphone

Sodium p-toluenesulphinate was prepared according to the method of Whitmore¹⁴⁸ by reaction of p-toluenesulphonyl chloride with zinc dust and sodium carbonate. Following the method of Hoffmann¹⁴⁹, 4-methylphenyl 2-nitrophenyl sulphone was prepared by reaction of sodium p-toluenesulphinate and 2-chloronitrobenzene in boiling dimethylformamide. After recrystallisation from methanol the product had m.p. 155-156°C (lit., ¹⁴⁹ m.p. 155-156°C).

(b) 2-Aminophenyl 4-methylphenyl sulphone was prepared by hydrogenation of the corresponding nitro-compound (a) following the method of Hoffmann¹⁴⁹ using Raney nickel in ethanol. The product had m.p. 120°C (lit., ¹⁴⁹ m.p. 120°C) (85%)
(c) 2-Hydroxyphenyl 4-methylphenyl sulphone was prepared by diazotisation of the corresponding amine (b) and conversion of the amino-group to hydroxyl as described in [A, 1(h)]. The crude product was obtained as an oil, which was extracted with sodium hydroxide solution (10%). The product was liberated by treatment of the alkaline solution with sulphuric acid (10%), extracted into chloroform, the chloroform solution dried over magnesium sulphate and filtered. Removal of the solvent under vacuum gave the product which on recrystallisation from ethanol/water had m.p. 121.5-122° (lit., 150 m.p. 121°).

(d) 1-Bromo-2-naphthol was prepared by bromination of 2-naphthol in glacial acetic acid by the method of Hazlet\textsuperscript{151}. On recrystallisation from petrol : benzene (3 : 1) the product had m.p. 82-83° (lit., 151 m.p. 84°).

(e) Bromodurene was prepared using the method of Smith and Moyle\textsuperscript{152} by bromination of durene in carbon tetrachloride. On recrystallisation from ethanol the product had m.p. 60-60.5° (lit., 152 m.p. 60.5°).

(f) Bromomesitylene was prepared by bromination of mesitylene according to Smith\textsuperscript{153} and had b.p. 104-105°/10 mm.

(g) 3,5,3',5'-Tetramethylbibenzyl was prepared from mesitylene and di-t-butyl peroxide by the method of Hall\textsuperscript{90} and on recrystallisation from ethanol had m.p. 72° (lit., 90 72-73°).

Pure samples of 2, 4, 5, 2', 4', 5'-hexamethylbibenzyl and bromo-2, 4, 5, 2', 4', 5'-hexamethylbibenzyl for use as g.l.c. standards were provided by Dr. J.A.K. Hall.
(h) Isomeric mixture of 2-bromo-3,4,6-trimethylbenzyl bromide and 3-bromo-2,4,5-trimethylbenzyl bromide

The mixture of isomers was prepared from bromodurene and N-bromosuccinimide in carbon tetrachloride by the method described by Hall. The mixture was distilled, b.p. 92-96°C/0.1 mm (lit., 90 b.p. 92-96°C/0.1 mm), n.m.r. (CDCl₃): δ 3.00, 3.12 (2 x s, 1H, aromatic), δ 5.30, 5.55 (2 x s, 2H, CH₂), δ 7.6-7.8 (C, 9H, CH₃).

(i) 2,2'-Dichlorodiphenyl disulphide

2-Chlorobenzenethiol was oxidised with alcoholic iodine as described by Wilson and Tarbell and the residue, after removal of the solvent, was recrystallised from alcohol to give 2,2'-dichlorodiphenyl disulphide as white needles, m.p. 89-90°C (lit., 155 m.p. 89-90°C).

(j) Diphenyl disulphide was prepared from benzenethiol as described above (i) and had m.p. 60-61°C (lit., 156 60°C).

(k) p-Toluamide was prepared according to McMaster and Langreck by oxidation of p-tolunitrile with 10% hydrogen peroxide solution. The product was recrystallised from ethanol and had m.p. 158-160°C (lit., 157 155°C).

(l) 3,4-benzocoumarin was prepared following the method outlined by Gringauz and Tosh, from 9-fluorenone (10 g). The mixture was stirred for twelve hours and the dark-brown solution was washed once with water (25 ml), twice with 10% w/v potassium bicarbonate solution (50 ml portions) and once again with water (25 ml). The organic layer was separated, dried over magnesium sulphate and concentrated to one third of the volume. Elution with methylene chloride on a short alumina column gave the product, which was recrystallised from methanol, m.p. 92-94°C (lit., 158 93-94°C) (85%).
B. Thermal Decomposition of Sodium 2-Bromophenoxides and Related Compounds

Unless otherwise stated, all these reactions were carried out by the following general method. The reactants, in a suitable solvent, were placed in an autoclave which was evacuated after freezing the contents by immersing it in liquid nitrogen. The contents were then allowed to decompose at 260° and removed from the autoclave by washing with a mixture of ether and water through a sintered-glass funnel to collect any insoluble material. The aqueous layer was separated, extracted several times with ether, acidified with dilute nitric acid (2 M) and halide ion determined gravimetrically as silver halide. The combined ether extract was dried over magnesium sulphate, filtered, and the ether removed under vacuum. Halide ion is recorded as moles per 100 moles of the sodium salt and the amorphous solids collected in the sintered-glass funnel were not examined.

1. Thermal Decomposition of Sodium 2-Bromophenoxides

(a) Thermal decomposition of sodium 2-bromophenoxide in mesitylene.

Sodium 2-bromophenoxide (2.0 g, 10.25 mmol) in mesitylene (25 ml) was decomposed for six days as described previously. The mesitylene was removed under high vacuum and the residue distilled to give a white solid, dibenzo-\(p\)-dioxin (0.42 g, \(22\) m/100 m), b.p. 90-92°/0.02 mm, which on recrystallisation from petroleum had m.p. 118° (lit.,\(^{159}\) 120-121°). The mass spectrum showed the correct parent ion: m/e; 184.
Thermal decomposition of sodium 2-bromo-4-methylphenoxide in mesitylene

Sodium 2-bromo-4-methylphenoxide (2.40 g, 11.5 mmol) in mesitylene (25 ml) was decomposed for seven days as described previously. The mesitylene was removed under vacuum and the residue distilled to give a white solid, 2,7-dimethyldibenzop-dioxin (0.20 g, 3.2 mmol/100 ml), b.p. 94°/0.05 mm, which on recrystallisation from petroleum had m.p. 115-116° (lit., 88 116°), n.m.r. (CDCl₃): \( \gamma \) 3.26-4.43 (c, 6H, aromatic), \( \tau \) 7.80 (s, 6H, CH₃) (Found: C, 79.3; H, 5.7). Calc. for C₁₄H₁₂O₂: C, 79.3; H, 5.7%). The mass spectrum showed the correct parent ion: m/e; 212.

Thermal decomposition of sodium 2-bromo-5-methylphenoxide in mesitylene

Sodium 2-bromo-5-methylphenoxide (2.0 g, 9.6 mmol) in mesitylene (25 ml) was decomposed for three days as described previously. Bromide ion (88 m/100 m) was determined gravimetrically. Examination by g.l.c./m.s. (2% NPGS, 204°) showed four peaks: m/e; 108, 238, 212, 214. The peak m/e; 212 was found to have an identical mass spectrum to that of 2,7-dimethyldibenzop-dioxin from (b). The yield of this compound (1.2 mmol/100 ml) was determined by g.l.c. (2% NPGS, 200°) using biphenyl as internal standard. The peak: m/e; 108 was found to have an identical mass spectrum to that of an authentic sample of m-cresol. The mesitylene was removed under vacuum and the residue chromatographed on alumina.

Elution with petroleum gave a low-melting white
solid (0.05 g), identified as a mixture of 2,3', 4,5',6-pentamethyl-
diphenylmethane and 3,3',5,5'-tetramethylbibenzyl from its n.m.r.
spectrum (CDCl₃): τ 2.8-3.4 (C aromatic), τ 6.1 (s, diphenylmethane
CH₂), τ 7.2 (s, bibenzyl CH₂), τ 7.7 (s, CH₃), τ 7.8 (s, CH₃).

(d) **Thermal decomposition of sodium 2-bromo-5-methyl-
phenoxide in t-butylbenzene**

Sodium 2-bromo-5-methylphenoxide (6.2 g, 30 mmol) in t-butylbenzene
(50 ml) was decomposed for three days as described previously. Bromide
ion (70 m/100 m) was determined gravimetrically. Examination by g.l.c./
m.s. (5% CAR, 205°) showed three peaks: m/e; 108, 212, 214. The
peaks: m/e; 108, 212 had identical mass spectra to those of authentic
samples of m-cresol and 2,7-dimethyldibenzo-p-dioxin, respectively.
The t-butylbenzene was removed under high vacuum and the residue
(1.3 g) chromatographed on alumina. Elution with petroleum: ether
(90:10) gave a white solid, 2,7-dimethyldibenzo-p-dioxin (0.04 g,
0.6 m/100 m), identified by its proton noise-decoupled ¹³C n.m.r.
spectrum (CDCl₃) which gave signals at: 20.6, 115.8, 116.7, 123.7,
133.3, 139.8, 141.7 p.p.m. On recrystallisation from petroleum
the compound had m.p. 115-116°, and on mixing with 2,7-dimethyldibenzo-p-dioxin from (b) had m.p. 115-116°.

Elution with ether: methanol (100:2) gave a brown liquid
(0.42 g), which on examination by g.l.c. (5% CAR, 220°) was found to
contain m-cresol and 2-hydroxy-4-methylphenyl 3-methylphenyl ether.
The yield of 2-hydroxy-4-methylphenyl 3-methylphenyl ether (3 m/100 m)
was estimated by g.l.c. (5% CAR, 220°) from peak area ratios.

Elution with more polar solvents gave tars only.
Thermal decomposition of sodium 2-bromo-4-methylphenoxide in t-butylbenzene

Sodium 2-bromo-4-methylphenoxide (2.0 g, 9.6 mmol) in t-butylbenzene (25 ml) was decomposed for two days as described previously. Bromide ion (71m/100m.) was determined gravimetrically. Examination by g.l.c./m.s. (5% CAR, 200°) showed three peaks: m/e; 108, 212, 214, which had identical mass spectra to those of authentic samples of p-cresol, 2,7-dimethyldibenzo-p-dioxin and 2-hydroxy-5-methylphenyl 4-methylphenyl ether, respectively. The t-butylbenzene was removed under high vacuum and the residue (0.3 g) chromatographed on alumina.

Elution with petroleum : ether (100 : 1) gave a white solid, 2,7-dimethyldibenzo-p-dioxin (0.19 g, 9m/100m), identified by its proton noise-decoupled n.m.r. spectrum (CDCl₃) which gave signals at: 20.6, 115.9, 116.8, 123.8, 133.5, 139.9, 141.9 p.p.m. On recrystallisation from petroleum the compound had m.p. 115-116°, and on mixing with an authentic sample from (b) had m.p. 115-116°.

Elution with ether : methanol (100 : 1) gave a brown oil (0.18 g), which on examination by g.l.c. (5% CAR, 200°) was shown to contain p-cresol and 2-hydroxy-5-methylphenyl 4-methylphenyl ether. The yield of 2-hydroxy-5-methylphenyl 4-methylphenyl ether (0.3m/100m) was estimated by g.l.c. (5% CAR, 200°) from peak area ratios.

Elution with more polar solvents gave tars only.

Thermal decomposition of a mixture of sodium 2-bromo-4-methylphenoxide and sodium 2-bromo-5-methylphenoxide
Sodium 2-bromo-4-methylphenoxide (2.0 g, 9.6 mmol) and sodium 2-bromo-5-methylphenoxide (2.0 g, 9.6 mmol) in t-butylbenzene (45 ml) were decomposed for two days as described previously. Bromide ion (67 m/100 m) was determined gravimetrically and examination by g.l.c./m.s. (5% CAR, 200°) showed three peaks: m/e; 108, 212, 214.

Removal of the t-butylbenzene under vacuum gave a black residue (1.4 g) which was chromatographed on alumina. Elution with petroleum : ether (100 : 2) gave a white solid (0.26 g, 7 m/100 m), identified as a mixture of 2, 7-dimethyldibenzo-\(p\)-dioxin and 2, 8-dimethyldibenzo-\(p\)-dioxin from the proton noise-decoupled \(^{13}\)C n.m.r. spectrum (CDCl\(_3\)), which gave signals at: 20.6, 115.9, 116.8, 123.8, 133.4, 133.7, 139.9, 141.8, 141.9 p.p.m. and the \(^{13}\)C n.m.r. spectrum (C\(_2\)D\(_6\)CO) which gave signals at: 20.6, 116.5, 117.5, 124.9, 125.0, 134.4, 134.5, 140.6, 140.7, 142.4, 142.6 p.p.m. Proton n.m.r. (CDCl\(_3\)): \(\tau\) 3.0-4.8 (\(\delta\), 6H, aromatic), \(\tau\) 7.8 (\(\delta\), 6H, CH\(_3\)).

Thermal decomposition of sodium 2-bromo-4-methoxyphenoxide in t-butylbenzene

Sodium 2-bromo-4-methoxyphenoxide (2.0 g, 8.9 mmol) in t-butylbenzene (25 ml) was decomposed for two days as described previously. Bromide ion (97 m/100 m) was determined gravimetrically and examination by g.l.c./m.s. (5% CAR, 200°) showed a single peak: m/e; 124, which had an identical mass spectrum to that of an authentic sample of 4-methoxyphenol. The solution was extracted with dilute sodium hydroxide (0.5 M), acidified with dilute sulphuric acid (0.5 M) and extracted with ether. The
ether solution was dried over magnesium sulphate, filtered and the ether removed under vacuum to give a red oil, 4-methoxyphenol (0.5 g, 45m/100m), i.r. indistinguishable from that of an authentic sample. Examination of the reaction mixture by t.l.c. and by g.l.c. using various columns (1% SE30, 2% NPGS, 2% APL) gave no indication of further products.

(h) **Thermal decomposition of sodium 2-bromo-5-methoxyphenoxide in t-butylbenzene**

Sodium 2-bromo-5-methoxyphenoxide (1.90 g, 8.44 mmol) in t-butylbenzene (25 ml) was decomposed for two days as described previously. Bromide ion (96m/100m) was determined gravimetrically and an amorphous, dark-grey solid (0.75 g) was collected. Examination by g.l.c./m.s. (5% CAR, 208°) showed a single peak: m/e; 124, which had an identical mass spectrum to that of an authentic sample of 3-methoxyphenol. Extraction as described above (g) gave a red oil, 3-methoxyphenol (0.33 g, 32m/100m), i.r. indistinguishable from that of an authentic sample. Further examination by t.l.c. and g.l.c. as above (g) gave no indication of other products.

2. **Thermal Decompositions Involving Halodiphenyl Ethers.**

(a) **Thermal decomposition of the sodium salt of 2-chlorophenyl 2-hydroxyphenyl ether in mesitylene**

The sodium salt of 2-chlorophenyl 2-hydroxyphenyl ether (0.60 g, 2.47 mmol) in mesitylene (10 ml) was decomposed for seven days as previously described. The mesitylene was removed under vacuum and the residue distilled to give a white solid, dibenzo-p-dioxin (0.40 g, 88m/100m), b.p. 80°/0.1 mm, which on recrystallisation from petroleum had m.p. 118°, and on mixing with a sample of dibenzo-p-
dioxin from [B, 1(a)] had m.p. 118°. The mass spectrum showed the correct parent ion: m/e; 184.

(b) **Thermal decomposition of the sodium salt of 3-chloro-phenyl 2-hydroxyphenyl ether in t-butylbenzene.**

The sodium salt of 3-chlorophenyl 2-hydroxyphenyl ether (0.20 g, 0.8 mmol) in t-butylbenzene (10 ml) was decomposed for two days as described previously. Bromide ion (100m/100m) was determined gravimetrically and examination by g.l.c./m.s. (5% CAR, 212°) gave a single peak: m/e; 184 which had an identical mass spectrum to that of an authentic sample of dibenzo-p-dioxin from [B, 1(a)] and the addition of an authentic sample of dibenzo-p-dioxin to a portion of the reaction mixture gave peak enhancement on examination by g.l.c. (5% CAR, 212°). The yield of dibenzo-p-dioxin (18m/100m) was determined by g.l.c. (5% CAR, 200°), using phenanthrene as internal standard.

(c) **Attempted reaction of sodium phenoxide with 2-bromophenyl phenyl ether in t-butylbenzene**

Sodium phenoxide (0.58 g, 5 mmol) and 2-bromophenyl phenyl ether (1.25 g, 5 mmol) in t-butylbenzene (25 ml) were heated in the autoclave for two days as described previously. No bromide ion was detected on treatment with silver nitrate solution and removal of the t-butylbenzene under vacuum gave a quantitative recovery of 2-bromophenyl phenyl ether, which on recrystallisation from petroleum had m.p. 43-44°.

(d) **Attempted reaction of sodium 2-methoxyphenoxide with 2-bromophenyl phenyl ether in t-butylbenzene**

Sodium 2-methoxyphenoxide (0.44 g, 3 mmol) and 2-bromophenyl phenyl
ether (0.75 g, 3 mmol) in t-butylbenzene (15 ml) were heated in the autoclave for two days as described previously. No bromide ion was detected on treatment with silver nitrate solution and removal of the t-butylbenzene under vacuum gave a quantitative recovery of 2-bromo-phenyl phenyl ether, m.p. 43-44°.


(a) Thermal decomposition of sodium 2-bromophenoxide in benzonitrile

Sodium 2-bromophenoxide (2.0 g, 10.25 mmol) in benzonitrile (25 ml) was decomposed for 36 h as described previously. Examination by g.l.c./m.s. (5% CAR, 203°) showed six peaks: m/e; 94, 184, 198, 186, 195, and 121, having mass spectra identical to those of authentic samples of phenol, dibenzo-p-dioxin, phenyl benzoate, 2-hydroxyphenyl phenyl ether, 2-phenylbenzoxazole and benzamide, respectively. Peaks: m/e; 198, 186, and 121 were shown to be present in trace amounts only by g.l.c. (5% CAR, 200°) examination. The benzonitrile was removed under vacuum to give a dark-brown residue (1.3 g) which was chromatographed on alumina.

Elution with petroleum : ether (100 : 5) gave a white solid, dibenzo-p-dioxin (0.15 g, 8 m/100m) which on recrystallisation from petroleum had m.p. 118°, and on mixing with a sample of dibenzo-p-dioxin from [B, 1(a)] had m.p. 118°.

Elution with petroleum : ether (3 : 1) gave a pale-yellow solid, which on recrystallisation from alcohol gave a white solid,
2-phenylbenzoxazole (0.22 g, 11 mmol), m.p. 103°, mixed m.p. 103° with an authentic sample of 2-phenylbenzoxazole.

A pale-grey crystalline solid (0.08 g) was collected in the sintered-glass funnel and after recrystallisation from toluene was identified as 2,4,6-triphenyl-s-triazine, m.p. 232° (lit., 160-232°), m/e; 309 (M⁺), 206, 103.

(b) **Thermal decomposition of sodium 2-bromo-4-methyl-phenoxide in benzonitrile**

Sodium 2-bromo-4-methylphenoxide (2.0 g, 9.6 mmol) in benzonitrile (25 ml) was decomposed for six days as described previously. Bromide ion (74 mmol) was determined gravimetrically and a pale-grey solid (2 g) was collected, which was identified as above (a), as 2,4,6-triphenyl-s-triazine.

Examination by g.l.c./m.s. (5% CAR, 210°) showed four peaks: m/e; 108, 212, 121, 209, which had identical mass spectra to those of authentic samples of p-cresol, 2,7-dimethyldibenzo-p-dioxin, benzamide and 5-methyl-2-phenylbenzoxazole, respectively. The benzonitrile was removed under vacuum to give a dark-brown solid residue (0.9 g) which was chromatographed on alumina.

Elution with petroleum gave a white solid, 2,7-dimethyldibenzo-p-dioxin (0.11 g, 6 mmol), which on recrystallisation from petroleum had m.p. 115-116°, and on mixing with 2,7-dimethyldibenzo-p-dioxin from [B, 1(b)] had m.p. 115-116°.

Elution with petroleum : ether (100 : 2) gave a pale-yellow solid, 5-methyl-2-phenylbenzoxazole (0.035 g, 1.3 mmol), which on
examination by h.s.l.c. on alumina (Spherisorb AX 20/4) using a 15% solution of (50% water-saturated methylene chloride) in n-hexane had identical retention time to that of an authentic sample. Further h.s.l.c. examination under the same conditions showed enhancement of the peak corresponding to 5-methyl-2-phenylbenzoxazole on addition of an authentic sample to a portion of the reaction mixture. Recrystallisation from alcohol gave the compound as a white solid, m.p. 104-105° (lit., 141° 104°), mixed m.p. 104-105°.

Elution with petroleum ether (50:50) gave a yellow oil (0.1 g) which on examination by g.l.c. (5% CAR, 200°) was shown to contain p-cresol.

Elution with ether: methanol (100:2) gave a white solid, benzamide (0.22 g) which on recrystallisation from hot water had m.p. 130° (lit., 119° 130°) and on mixing with an authentic sample of benzamide had m.p. 130°. The i.r. was indistinguishable from that of an authentic sample.

Further elution with more polar solvents gave tars only. 
(c) **Thermal stability of 5-methyl-2-phenylbenzoxazole in t-butylbenzene**

5-Methyl-2-phenylbenzoxazole (0.31 g, 1.5 mmol) in t-butylbenzene (10 ml) was heated in the autoclave for three days at 260° under vacuum. The t-butylbenzene solution was examined by g.l.c. (2\% NPGS, 210°), which showed a single peak with retention time corresponding to that of the starting material. Removal of the solvent under vacuum led to a quantitative recovery of 5-methyl-2-phenylbenzoxazole, which on recrystallisation from ethanol had m.p. 104-105°.
Thermal decomposition of sodium 2-bromo-4-methylphenoxide in the presence of 5-methyl-2-phenylbenzoxazole in t-butylbenzene

Sodium 2-bromo-4-methylphenoxide (0.62 g, 3.0 mmol) and 5-methyl-2-phenylbenzoxazole (0.31 g, 1.5 mmol) in t-butylbenzene (15 ml) were decomposed for two days as described previously. Bromide ion (70m/100m) was determined gravimetrically and examination by g.l.c./m.s. (5% CAR, 210°) showed three peaks: m/e; 108, 212, 209, with mass spectra identical to those of authentic samples of m-cresol, 2,7-dimethyl-p-dioxin and 5-methyl-2-phenylbenzoxazole, respectively. Addition of an authentic sample of benzamide to a portion of the reaction mixture gave a new peak on examination by g.l.c. under the same conditions.

Thermal stability of 6-methyl-2-phenylbenzoxazole in t-butylbenzene.

6-methyl-2-phenylbenzoxazole (0.31 g, 1.5 mmol) in t-butylbenzene (10 ml) was heated in the autoclave for three days at 260° under vacuum. Examination of the t-butylbenzene solution by g.l.c. (5% CAR, 210°) showed a single peak with retention time corresponding to that of the starting material. Removal of the solvent under vacuum led to a quantitative recovery of the starting material, which on recrystallisation from ethanol had m.p. 90-91°.

Thermal decomposition of sodium 2-bromophenoxide and p-tolunitrile in t-butylbenzene

Sodium 2-bromophenoxide (0.975 g, 5 mmol) and p-tolunitrile (1.17 g,
10 mmol) in t-butylbenzene (25 ml) were decomposed for two days as described previously. Bromide ion (70m/100m) was determined gravimetrically. Examination by g.l.c./m.s. (5% CAR, 204°) showed two peaks: m/e; 117, 184, with mass spectra identical to those of authentic samples of p-tolunitrile and dibenzo-p-dioxin, respectively. Addition of an authentic sample of 2-p-tolylbenzoxazole to a portion of the reaction mixture gave a new peak on examination by g.l.c. (5% CAR, 204°).

(g) **Thermal decomposition of sodium 2-bromophenoxide in "superdry" benzonitrile**

Sodium 2-bromophenoxide (2.0 g, 10.25 mmol) in "superdry" benzonitrile (25 ml) was decomposed for two days as described previously. Bromide ion (96m/100m) was determined gravimetrically and examination by g.l.c. (2% NPGS, 206°; 5% CAR, 210°) showed a single product with retention time identical to that of dibenzo-p-dioxin. Examination by g.l.c./m.s. (5% CAR, 210°) showed a peak: m/e; 184, with mass spectrum identical to that of an authentic sample of dibenzo-p-dioxin. The yield of dibenzo-p-dioxin (11m/100m) was determined by g.l.c. (5% CAR, 208°) using phenanthrene as internal standard.

(h) **Thermal decomposition of sodium 2-bromophenoxide and "superdry" benzonitrile in t-butylbenzene**

Sodium 2-bromophenoxide (1.46 g, 7.5 mmol) and "superdry" benzonitrile (1.55 g, 15 mmol) in t-butylbenzene (25 ml) were decomposed for two days as described previously. Bromide ion (91m/100m) was determined gravimetrically and a black, amorphous solid (0.1 g) was
collected. Examination by g.l.c. (5% CAR, 210°) showed the peak: m/e; 184, with retention time identical to that of an authentic sample of dibenzo-p-dioxin. The yield of dibenzo-p-dioxin (8 m/100m) was determined as above (g).

(i) **Thermal decomposition of sodium 2-bromophenoxide and benzamide in t-butylbenzene**

Sodium 2-bromophenoxide (1.95 g, 10 mmol) and benzamide (1.21 g, 10 mmol) in t-butylbenzene (25 ml) were decomposed for two days as described previously. A black, amorphous solid (0.29 g) was collected and bromide ion (70 m/100m) was determined gravimetrically. Examination by g.l.c./m.s. (5% CAR, 208°) showed four product peaks: m/e; 184, 186, 195, and 121, with mass spectra identical to those of authentic samples of dibenzo-p-dioxin, 2-hydroxyphenyl phenyl ether, 2-phenylbenzoxazole and benzamide, respectively. 2-Hydroxyphenyl phenyl ether was present in trace amount only. The t-butylbenzene was removed under vacuum and the residue (0.55 g) chromatographed on alumina.

Elution with petroleum ether gave a white solid, dibenzo-p-dioxin (0.025 g, 13 m/100m) which on recrystallisation from petroleum had m.p. 118°, mixed m.p. 118°.

Elution with petroleum : ether (4 : 1) gave a white solid, 2-phenylbenzoxazole (0.045 g, 2.3 m/100m) which on recrystallisation from alcohol had m.p. 104°, mixed m.p. 104°.
(j) **Thermal decomposition of sodium 2-bromophenoxide and benzamide in "superdry" benzonitrile**

Sodium 2-bromophenoxide (1.88 g, 9.6 mmol) and benzamide (1.17 g, 9.6 mmol) in "superdry" benzonitrile (25 ml) were decomposed for two days as described previously. Bromide ion (84m/100m) was determined gravimetrically and a dark-grey, amorphous solid (0.28 g) was collected. Examination by g.l.c./m.s. (5% CAR, 202°) showed four peaks: m/e; 184, 198, 195, 121, with mass spectra identical to those of authentic samples of dibenzo-p-dioxin, phenyl benzoate, 2-phenylbenzoxazole, and benzamide, respectively. The benzonitrile was removed under high vacuum and the residue (1.8 g) chromatographed on alumina. Dibenzo-p-dioxin (0.062 g, 38m/100m) and 2-phenylbenzoxazole (0.58 g, 31m/100m) were eluted and identified as described above (i).

4. **Thermal Decomposition of Sodium 2-Bromophenoxide with p-Toluamide: Attempted Trapping in Various Solvents**

(a) **Thermal decomposition of sodium 2-bromophenoxide with p-toluamide in "superdry" benzonitrile**

Sodium 2-bromophenoxide (1.88 g, 9.6 mmol) and p-toluamide (1.35 g, 10 mmol) in "superdry" benzonitrile (25 ml) were decomposed for two days as described previously. Bromide ion (93m/100m) was determined gravimetrically and a dark, amorphous solid (0.33 g) was collected. Examination by g.l.c./m.s. (5% CAR, 203°) showed eight peaks: m/e; 103, 117, 94, 184, 195, 121, 209, 135, with mass spectra identical to those of authentic samples of benzonitrile, p-tolunitrile, phenol, dibenzo-p-dioxin, 2-phenylbenzoxazole, benzamide, 2-p-toly benzoxazole and
p-tolualide, respectively. The t-butylbenzene was removed under vacuum and the residue (3.0 g) chromatographed on alumina.

Elution with petroleum gave a white solid (0.39 g) which in ether was shown by g.l.c. (5% CAR, 203°) to be a mixture of benzonitrile, p-tolunitrile and dibenzo-p-dioxin. The yield of dibenzo-p-dioxin (4.7 m/100 m) was determined by g.l.c (5% CAR, 208°) using phenanthrene as internal standard.

Elution with petroleum : ether (100 : 5) gave a white solid (0.48 g) which in ether was shown to be a mixture of 2-phenylbenzoxazole (22 m/100 m) and 2-p-tolylbenzoxazole (4 m/100 m). The yields were estimated from peak area ratios on examination by g.l.c. (5% CAR, 203°).

Elution with ether : methanol (100 : 5) gave a brown oil (0.12 g), which on examination by g.l.c. (5% CAR, 200°) was found to contain phenol.

Elution with ether : methanol (90 : 10) gave a white solid (0.85 g) which in chloroform was shown to be a mixture of benzamide (0.37 g) and p-toluamide (0.48 g), estimated from peak area ratios on examination by g.l.c. (5% CAR, 203°).

Elution with more polar solvents gave tars only.

(b) Thermal decomposition of sodium 2-bromophenoxide with p-toluamide in nitrobenzene

Sodium 2-bromophenoxide (1.88 g, 9.6 mmol) and p-toluamide (1.35 g, 10 mmol) in nitrobenzene (25 ml) were decomposed for two days as described previously. Bromide ion (85 m/100 m) was determined
gravimetrically and a black, amorphous solid (0.85 g) was collected. Examination by g.l.c./m.s. (5% CAR, 206°) showed four peaks: m/e; 123, 182, 209, 135. Peaks: m/e; 123, 209, and 135 had mass spectra identical to those of authentic samples of nitrobenzene, 2-p-tolylbenzoxazole, and p-toluamide, respectively.

The nitrobenzene was removed under vacuum to give a red-brown residue (1.7 g) which was chromatographed on alumina. Elution with petroleum gave a trace of white solid, shown to be 2-p-tolylbenzoxazole by comparison of its retention time with that of an authentic sample on examination by g.l.c. (5% CAR, 206°).

Elution with petroleum : ether (100 : 5) gave an orange solid, azobenzene (0.24 g), which on recrystallisation from ethanol had m.p. 68° (lit., 119 m.p. 68°) and on mixing with an authentic sample had m.p. 68°.

Elution with ether : methanol (100 : 1) gave a trace of brown oil, which was not identified.

Elution with ether : methanol (90 : 10) gave a white solid, p-toluamide (0.47 g) which on recrystallisation from ethanol had m.p. 158-160 (lit., 157 m.p. 155°), and on mixing with an authentic sample had m.p. 158-160°.

Elution with more polar solvents gave tars only.

(c) **Thermal decomposition of sodium 2-bromophenoxide with p-toluamide in acetonitrile**

Sodium 2-bromophenoxide (1.90 g, 9.7 mmol) and p-toluamide (1.35 g, 10 mmol) in acetonitrile (25 ml) were decomposed for two days as described previously. Bromide ion (96m/100m) was determined gravi-
metrically and a black, amorphous solid (0.9 g), insoluble in ether, water, benzene, methanol, acetone or chloroform was collected.

The acetonitrile was removed under vacuum to give an orange liquid 1.7 g) which on examination by g.l.c./m.s. (5% CAR 200°) showed four peaks: m/e; 117, 94, 199, and 184, respectively. Peaks: m/e; 117, 94, and 184 had mass spectra identical to those of authentic samples of p-tolunitrile, phenol, and dibenzo-p-dioxin, respectively. The yield of dibenzo-p-dioxin (24m/100m) was determined by g.l.c. (5% CAR, 208°), using phenanthrene as internal standard.

An ethereal solution of the residue was extracted with dilute sodium hydroxide (0.5M), washed with water and the combined aqueous extract acidified with dilute hydrochloric acid (0.5M).

The acidified aqueous extract was extracted with ether, the ethereal solution dried over magnesium sulphate, filtered and the ether removed under vacuum to give a brown oil, (0.32 g), which on examination by g.l.c. (5% CAR, 200°) was found to contain phenol.

The component: m/e; 199, with peak area of equal magnitude to that of dibenzo-p-dioxin on the g.l.c. trace, was not isolated and its structure not confirmed. Mass spectrum: m/e; 199 (M⁺), 117, 82.

5. **Thermal Decomposition of Sodium 2-Halothiophenoxides:**

**Synthesis of Thianthrenes**

(a) Thermal decomposition of sodium 2-chlorothiophenoxide in t-butylbenzene

Sodium 2-chlorothiophenoxide (2.20 g, 13 mmol) in t-butylbenzene (25 ml) was heated for two days as described previously. No chloride ion
was detected on treatment of the aqueous extract with silver nitrate solution and examination by g.l.c. (5% CAR, 210°, 1% SE 30, 200°) showed no product peaks. The acidified aqueous solution was then extracted with ether, the ethereal solution dried over magnesium sulphate, filtered and the ether removed to give a white solid (1.2 g), 2,2'-dichlorodiphenyl disulphide, which on recrystallisation from alcohol gave white needles, m.p. 88-89° (lit., 155 m.p. 89-90°). The mass spectrum showed the correct parent ion: m/e; 286/288/290.

Thermal decomposition of sodium 2-bromothiophenoxide in t-butylbenzene

Sodium 2-bromothiophenoxide (2.11 g, 10 mmol) in t-butylbenzene (25 ml) was decomposed for two days as described previously. Bromide ion (48m/100m) was determined gravimetrically and examination by g.l.c. (5% CAR, 205°) showed a single product. The t-butylbenzene was removed under vacuum to give a brown residue (0.55 g) which was chromatographed on a short alumina column.

Elution with petroleum gave a white solid, thianthrene (0.44 g, 20m/100m), which on recrystallisation from ethanol had m.p. 158-159° (lit., 161 m.p. 160°). The mass spectrum showed the correct parent ion: m/e; 216 (Found: C, 66.6; H, 3.9. Calc. for C₁₂H₈S₂: C, 66.7; H, 3.7%)

Thermal decomposition of sodium 2-iodothiophenoxide in t-butylbenzene

Sodium 2-iodothiophenoxide (2.30 g, 8.9 mmol) in t-butylbenzene (25 ml) was decomposed for two days as described previously. Iodide ion (97m/100m) was determined gravimetrically and examination by g.l.c. (5%
CAR, 200\textdegree) followed by chromatography as above (b) gave thianthrene (0.67 g, 36\textpercent/100m), which on recrystallisation from ethanol had m.p. 158-159\textdegree and on mixing with thianthrene from (b) had m.p. 158-159\textdegree.

(d) Thermal decomposition of sodium 2-bromo-4-methylthiophenoxide in t-butylbenzene

Sodium 2-bromo-4-methylthiophenoxide (2.08 g, 10 mmol) in t-butylbenzene (25 ml) was decomposed for two days as described previously. Bromide ion (89\textpercent/100m) was determined gravimetrically and examination by g.l.c. (5\% CAR, 212\textdegree) showed a single peak. Most of the t-butylbenzene was removed by distillation under atmospheric pressure and the remaining liquid (2.8 g) was transferred to a small-scale distillation apparatus. After removal of the remaining solvent, b.p. 40-45\textdegree/0.02 mm, a pale-yellow liquid was obtained (0.71 g, 27\textpercent/100m), b.p. 134\textdegree/0.02 mm, identified as a mixture of 2,7-dimethyl-thianthrene and 2,8-dimethylthianthrene from the proton noise-decoupled $^{13}$C n.m.r. spectrum (CDCl$_3$) which gave signals at: 20.8, 128.3, 129.1, 132.0, 132.3, 135.4, 135.7, 137.5 p.p.m. Proton n.m.r. (CDCl$_3$): $\tau$ 2.6-3.15 (c, 6H, aromatic), $\tau$ 7.75 (s, 6H, CH$_3$). The mass spectrum showed the correct parent ion: m/e; 244.

6. Thermal Decompositions in the Presence of Sodium Phenoxides and Thiophenoxides: Formation of Diphenyl Ethers and Diphenyl Sulphides

(a) Thermal decomposition of sodium 2-bromophenoxide and sodium phenoxide in t-butylbenzene

Sodium 2-bromophenoxide (1.88 g, 9.6 mmol) and sodium phenoxide (1.16 g, 10 mmol) in t-butylbenzene (25 ml) were decomposed for two
days as described previously. Bromide ion (85 m/100m) was determined gravimetrically, and examination by g.l.c./m.s. (5% CAR, 202°) showed three peaks: m/e; 94, 184, 186. The peaks: m/e; 94, 184 had mass spectra identical to those of authentic samples of phenol and dibenzo-p-dioxin, respectively. The t-butylbenzene solution was extracted with dilute sodium hydroxide (0.5 M), washed with water and the combined aqueous extract acidified with dilute hydrochloric acid (0.5 M), forming a brown precipitate. The precipitate was filtered off, washed with water and dried under vacuum. The solid, 2-hydroxyphenyl phenyl ether (0.59 g, 33m/100m) was recrystallised once from petroleum (80-100°) and twice from ethanol, m.p. 105-105.5° (lit., 162 m.p. 105-106°), i.r. ν 3420 (OH, broad), 1605, 1590, 1240, 1103, 750 cm⁻¹, n.m.r. (CDCl₃); δ 2.5-3.4 (c, 9H, aromatic), τ 4.35 (s, 1H, OH).

The t-butylbenzene solution, after extraction of the phenolic material, was dried over magnesium sulphate, filtered and the t-butylbenzene removed under vacuum to give dibenzo-p-dioxin (0.13 g, 7.5m/100m), which on recrystallisation from petroleum had m.p. 118°.

(b) Thermal decomposition of sodium 2-bromophenoxide and sodium thiophenoxide in t-butylbenzene

Sodium 2-bromophenoxide (1.88 g, 9.6 mmol) and sodium thiophenoxide (1.30 g, 9.8 mmol) in t-butylbenzene (25 ml) were decomposed for two days as described previously. Bromide ion (100m/100m) was determined gravimetrically and examination by g.l.c./m.s. (5% CAR, 204°) showed four peaks: m/e; 94, 186, 218, and 202. The peaks: m/e; 94, 186, and
had mass spectra identical to those of authentic samples of phenol, diphenyl sulphide and diphenyl disulphide, respectively. Examination by g.l.c. (5% CAR, 204°) showed phenol and diphenyl disulphide to be present in trace amounts only and addition of authentic samples of diphenyl sulphide and diphenyl disulphide to a portion of the reaction mixture showed enhancement of the respective peaks corresponding to these compounds.

The t-butylbenzene solution was extracted with dilute sodium hydroxide (0.5 M) and washed with water. The combined aqueous extract was acidified with dilute hydrochloric acid (0.5 M) causing separation of a brown oil. The oil was extracted into ether, the ethereal solution dried over magnesium sulphate, filtered and the ether removed under vacuum. The residual oil was distilled using a small-scale cold finger distillation unit to give a colourless liquid, 2-hydroxyphenyl phenyl sulphide (0.85 g, 44m/100m), 155-160° (bath)/1 mm (lit., 163 b.p. 140°/3 mm), i.r. ν 3425 (OH, broad), 1580, 1472, 1190, 1028, 758, 740 cm⁻¹, n.m.r. (CDCl₃): τ 2.7-3.3 (6, 9H, aromatic), τ 3.52 (6, 1H, OH).

The t-butylbenzene solution after extraction of the phenolic material was dried over magnesium sulphate, filtered and the yield of diphenyl sulphide (3.5 m/100m) determined by g.l.c. (5% CAR, 205°) using phenanthrene as internal standard.

(c) Thermal decomposition of sodium 4-bromophenoxide and sodium thiophenoxide in t-butylbenzene

Sodium 4-bromophenoxide (1.85 g, 9.5 mmol) and sodium thiophenoxide (1.30 g, 9.8 mmol) in t-butylbenzene (25 ml) were decomposed for three days as described previously. The ether/water mixture, which was
used to remove the contents of the autoclave, formed an emulsion. This was removed by addition of a few drops of dilute sulphuric acid. Bromide ion (64 m/100 m) was determined gravimetrically and examination by g.l.c./m.s. (5% CAR, 200°) showed four peaks: m/e; 94, 186, 218, 202. The peaks: m/e; 94, 186 and 218 had mass spectra identical to those of authentic samples of phenol, diphenyl sulphide and diphenyl disulphide, respectively. Addition of authentic samples of diphenyl sulphide and diphenyl disulphide to portions of the reaction mixture showed enhancement of the corresponding peaks on g.l.c. examination (5% CAR, 200°).

The t-butylbenzene solution was extracted with dilute sodium hydroxide (0.5 M) and acidified with dilute hydrochloric acid (0.5 M). The liberated oil was extracted with ether, the ethereal solution dried over magnesium sulphate, filtered and the ether removed to give a brown oil (0.9 g). The oil was distilled as above (b) and gave a phenolic fraction (0.27 g) 80-85° (bath)/1 mm and a second colourless fraction, 4-hydroxyphenyl phenyl sulphide (0.47 g, 24 m/100 m), 170-180° (bath)/0.4 mm (lit., 163 b.p. 164-165/3 mm), i.r. ν 3410, (OH, broad), 1580, 1470, 1190, 830, 739 cm⁻¹, n.m.r. (CDCl₃): δ 2.4-3.45 (aromatic and OH). The p-nitrobenzoyl derivative was prepared according to Vogel and had m.p. 73-74° (lit., 163 m.p. 74-75°).

The t-butylbenzene solution was then washed with water, dried over magnesium sulphate, filtered and the yields of diphenyl sulphide (3.1 m/100 m) and diphenyl disulphide (15 m/100 m) determined by g.l.c. (5% CAR, 210°) using thianthrene as internal standard.
(d) Thermal decomposition of sodium 2-bromo-4-methylphenoxide and sodium 4-methylphenoxide in t-butylbenzene

Sodium 2-bromo-4-methylphenoxide (2.02 g, 9.7 mmol) and sodium 4-methylphenoxide (1.30 g, 10 mmol) in t-butylbenzene (25 ml) were decomposed for two days as described previously. Bromide ion (100m/100m) was determined gravimetrically and examination by g.l.c./m.s. (5% CAR, 208°) showed three peaks: m/e; 108, 212, 214. The peaks: m/e; 108, 212 had mass spectra identical to those of authentic samples of p-cresol and 2,7-dimethyldibenzo-p-dioxin, respectively. The t-butylbenzene solution was extracted as described above (c) to give a brown oil (0.95 g), which was distilled as in (c). Distillation gave p-cresol (0.1 g) 40-50° (bath)/0.02 mm, i.r. indistinguishable from that of an authentic sample, and a second fraction, 2-hydroxy-5-methylphenyl 4-methylphenyl ether (0.62 g, 30m/100m), 100-120° (bath)/0.02 mm (lit., 164 172°/12 mm), i.r. ν 3500 (OH, broad), 3028, 2922, 2882, 1600, 1505, 1275, 1220, 1110, 948, 815 cm⁻¹, n.m.r. (CDCl₃): τ 2.7-3.45 (c, 7H, aromatic), τ 4.78 (s, 1H, OH), τ 7.70 (s, 3H, CH₃), τ 7.83 (s, 3H, CH₃).

The t-butylbenzene solution was then dried over magnesium sulphate, filtered and the t-butylbenzene removed under vacuum to give a brown residue (0.5 g). The residue was chromatographed on alumina, elution with petroleum giving 2,7-dimethyldibenzo-p-dioxin (0.15 g, 8°m/100m), which on recrystallisation from petroleum had m.p. 115-116° and on mixing with an authentic sample had m.p. 115-116°.

Elution with more polar solvents gave tars only.
7. Thermal Decompositions of Mixtures of Sodium Phenoxides and Sodium Thiophenoxides

(a) Thermal decomposition of sodium 2-bromophenoxide and sodium 2-bromothiophenoxide in t-butylbenzene

Sodium 2-bromophenoxide (0.975 g, 5 mmol) and sodium 2-bromothiophenoxide (2.11 g, 10 mmol) in t-butylbenzene (25 ml) were decomposed for two days as described previously. The t-butylbenzene was removed under vacuum to give a brown residue (1.6 g) which was chromatographed on alumina.

Elution with petroleum : ether (100 : 1) gave a white solid (0.7 g) which on examination by g.l.c./m.s. (5% CAR, 212°) showed two peaks: m/e; 200, 216, the latter with mass spectrum identical to that of an authentic sample of thianthrene.

Further elution with more polar solvents gave tars only.

The mixture of the two components obtained was then chromatographed on a long, thin column of alumina in an attempt to separate them. Elution with petroleum gave poor separation but amongst the fractions were samples of each of the two components. The compound: m/e; 200 was recrystallised from methanol to give fine white needles of phenoxythiin, m.p. 58-59° (lit., 165 m.p. 58°) (Found: C, 72.1; H, 4.0). Calc. for C₁₂H₈O₂S: C, 72.0; H, 4.0%). The compound: m/e; 216 was recrystallised from ethanol to give thianthrene, m.p. 157-158°, which on mixing with a sample of thianthrene from [B, 5(b)] had m.p. 157-158°.

The yields of phenoxythiin (28m/100m) and thianthrene (8m/100m) were determined by g.l.c. (5% CAR, 209°) using phenanthrene as internal standard.
Thermal decomposition of sodium 2-bromo-4-methylphenoxide and 2-bromothiophenoxide in t-butylbenzene

Sodium 2-bromo-4-methylphenoxide (1.30 g, 6.2 mmol) and sodium 2-bromothiophenoxide (1.30 g, 6.2 mmol) in t-butylbenzene (25 ml) were decomposed for two days as described previously. Examination by g.l.c./m.s. (5% CAR, 208°) showed four peaks: m/e; 108, 212, 214, 216. Peaks: m/e; 108, 212, 216 had mass spectra and retention times identical to those of authentic samples of p-cresol, 2,7-dimethyl-dibenzo-p-dioxin and thianthrene, respectively. The t-butylbenzene was removed under vacuum to give a brown residue (1.2 g) which was chromatographed on alumina.

Elution with petroleum : ether (90 : 10) gave mainly mixtures of the components: m/e; 212, 214, 216 but a pure sample of the single component: m/e; 214 was obtained from one of the fractions and identified as 2-methylphenoxathiin, m.p. 36-37° (lit., 166 m.p. 38-39°). (Found: 214.04553. Calc. for C_{13}H_{10}OS: 214.04534). A total weight of 0.63 g of 2,7-dimethyl-dibenzo-p-dioxin, 2-methylphenoxathiin and thianthrene was obtained from these fractions. The yields of 2,7-dimethyl-dibenzo-p-dioxin (3.5 m/100m), 2-methylphenoxathiin (31 m/100m) and thianthrene (k2 m/100m) were estimated from their peak area ratios by g.l.c. (5% CAR, 208°).

Elution with ether : methanol (100 : 5) gave a brown oil (0.1 g) which on examination by g.l.c. (5% CAR, 200°) was found to contain p-cresol.

Elution with more polar solvents gave tars only.
Thermal Decompositions of Sodium 2-Bromophenoxide with Amines as Added Nucleophiles

(a) Thermal decomposition of sodium 2-bromophenoxide and aniline in t-butylbenzene

Sodium 2-bromophenoxide (1.75 g, 8.9 mmol) and aniline (0.93 g, 10 mmol) in t-butylbenzene (25 ml) were decomposed for two days as described previously. Bromide ion (99m/100m) was determined gravimetrically and a brown, amorphous solid (0.41 g) was collected. Examination by g.l.c./m.s. (5% CAR, 200°C) showed four peaks: m/e; 93, 94, 184, 186, with mass spectra identical to those of authentic samples of aniline, phenol, dibenzo-p-dioxin and 2-hydroxyphenyl phenyl ether, respectively. Examination by g.l.c. (1% SE 30, 150°C) showed no further product peaks; addition of a pure sample of 2-anilinophenol to a portion of the reaction mixture showed a new peak when examined under these g.l.c. conditions.

The t-butylbenzene solution was extracted with dilute sodium hydroxide (0.5 M), washed with water and the combined aqueous extract acidified with dilute hydrochloric acid (0.5 M) to give a brown precipitate. The precipitate was filtered off, washed with water and dried in a vacuum-desiccator to give 2-hydroxyphenyl phenyl ether (0.095 g, 5.7 mmol/100 m), which on recrystallisation from petroleum (80-100°C) had m.p. 105°C and on mixing with 2-hydroxyphenyl phenyl ether from [B, 6(a)] had m.p. 105°C.

The t-butylbenzene solution was then extracted with hydrochloric acid (10% w/v), washed with water and basified with sodium hydroxide solution (10% w/v). The liberated basic material was extracted
into ether, the ethereal solution dried over magnesium sulphate, filtered and the ether removed under vacuum to give a red liquid, aniline (0.80 g), i.r. indistinguishable from that of an authentic sample. The yield of dibenzo- \( \text{p} \)-dioxin \((\text{\%m}/100\text{m})\) was determined by g.l.c. (5% CAR, 208\(^{\circ}\)) using phenanthrene as internal standard in a sample of the t-butylbenzene solution.

(b) **Thermal decomposition of sodium 2-bromophenoxide and aniline in "superdry" benzonitrile**

Sodium 2-bromophenoxide (1.80 g, 9.2 mmol) and aniline (0.93 g, 10 mmol) in "superdry" benzonitrile (25 ml) were decomposed for two days as described previously. Bromide ion \((98\text{m}/100\text{m})\) was determined gravimetrically and a black, amorphous solid (0.1 g) was collected. Examination by g.l.c./m.s. (5% CAR, 204\(^{\circ}\)) showed five peaks: \( \text{m/e} \); 93, 94, 184, 186, 195 with mass spectra identical to those of authentic samples of aniline, phenol, dibenzo- \( \text{p} \)-dioxin, 2-hydroxyphenyl phenyl ether and 2-phenylbenzoxazole, respectively. The yield of dibenzo- \( \text{p} \)-dioxin \((\text{\%m}/100\text{m})\) was determined by g.l.c. (5% CAR, 208\(^{\circ}\)) using phenanthrene as internal standard and the yields of 2-hydroxyphenyl phenyl ether \((4\text{m}/100\text{m})\) and 2-phenylbenzoxazole \((5\text{m}/100\text{m})\) were estimated by g.l.c. (5% CAR, 208\(^{\circ}\)) from peak area ratios. Examination by g.l.c. (1% SE 30, 150\(^{\circ}\)) as above (a) showed 2-anilinophenol to be absent.

(c) **Thermal decomposition of sodium 2-bromophenoxide and cyclohexylamine in "superdry" benzonitrile**

Sodium 2-bromophenoxide (2.0 g, 10.25 mmol) and cyclohexylamine
(0.99 g, 10 mmol) in "superdry" benzonitrile (25 ml) were decomposed for two days as described previously. On opening the autoclave a smell of ammonia was detected. Bromide ion (94m/100m) was determined gravimetrically and a grey crystalline solid (0.37 g) was collected and identified as 2,4,6-triphenyl-s-triazine as described in \[B, 3(a)\].

Examination by g.l.c./m.s. (5% CAR, 202°) showed eight peaks: m/e; 94, 175, 184, 187, 186, 195, 203, 262. The products: m/e; 187 and 262 were present in trace amount only and the remainder were present in low yields. The peaks: m/e; 94, 184, 186, 195 had mass spectra identical to those of authentic samples of phenol, dibenzo-p-dioxin, 2-hydroxyphenyl phenyl ether and 2-phenylbenzoxazole, respectively. Further examination by g.l.c./m.s. (1% SE 30, 150°) showed a further product in low yield: m/e; 181. The yields of dibenzo-p-dioxin (~5m/100m), 2-hydroxyphenyl phenyl ether (~2.5m/100m) and 2-phenylbenzoxazole (~6m/100m) were determined as described above (b).

The t-butylbenzene solution was extracted with hydrochloric acid (10% w/v) as described in (a) and a red liquid (0.5 g) obtained, which on examination by g.l.c. (1% SE 30, 50° and 150°) was shown to contain cyclohexylamine and the products: m/e; 181, 187. The latter two basic compounds were tentatively identified as dicyclohexylamine and N-phenylcyclohexylamine from the characteristic loss of the fragment of mass 43 in their mass spectra. The non-basic product: m/e; 203 was tentatively identified as N-cyclohexylbenzamide from its mass spectrum: m/e; 203(M⁺), 160, 122, 105, 77.
Thermal Decomposition of Sodium 2-Bromophenoxide with Benzoates and Thiobenzoate as Added Nucleophiles

Sodium 2-bromophenoxide (1.88 g, 9.6 mmol) and sodium 2-bromobenzoate (2.16 g, 9.7 mmol) in t-butylbenzene (25 ml) were decomposed for two days as described previously. A dark-grey, amorphous solid (0.4 g) was collected, and examination by g.l.c./m.s. (5% CAR, 204°C) showed six product peaks: m/e; 94, 170, 184, 248/250, 186, 196 with mass spectra identical to those of authentic samples of phenol, diphenyl ether, dibenzo-p-dioxin, 2-bromophenyl phenyl ether, 2-hydroxyphenyl phenyl ether and xanthone, respectively. Addition of authentic samples of diphenyl ether, 2-bromophenyl phenyl ether and xanthone to portions of the reaction mixture showed enhancement of the respective peaks on examination by g.l.c. (5% CAR, 204°C). Addition of an authentic sample of 3, 4-benzocoumarin to a portion of the reaction mixture gave a new peak on g.l.c. examination under these conditions.

The t-butylbenzene solution was extracted with dilute sodium hydroxide (0.5 M), washed with water and the combined extract acidified with dilute hydrochloric acid (0.5 M). The liberated oil was extracted into ether, the ethereal solution dried over magnesium sulphate, filtered and the ether removed under vacuum to give a dark-brown oil (0.23 g). Examination of the oil by g.l.c. (5% CAR, 204°C) showed phenol and a trace of 2-hydroxyphenyl phenyl ether to be present by comparison of the retention times with those of authentic samples.
The t-butylbenzene solution was then dried over magnesium sulphate and the yields of dibenzo-\(p\)-dioxin (2.7 m/100 m), diphenyl ether (3.0 m/100 m) and 2-bromophenyl phenyl ether (10 m/100 m) were determined by g. l. c. (5% CAR, 208°) using phenanthrene as internal standard. The yields of 2-hydroxyphenyl phenyl ether (1.3 m/100 m) and xanthone (2.0 m/100 m) were estimated from peak area ratios.

(b) Thermal decomposition of sodium 2-bromophenoxide and sodium benzoate in t-butylbenzene

Sodium 2-bromophenoxide (1.92 g, 9.8 mmol) and sodium benzoate (1.44 g, 10 mmol) in t-butylbenzene (25 ml) were decomposed for two days as described previously. The contents of the autoclave were removed as usual by washing with a mixture of ether and water, and a brown, amorphous solid (0.19 g) was collected. The aqueous layer was separated, acidified with dilute nitric acid (2 M) and again extracted, several times with ether. The combined ether extract of the acidified aqueous layer was dried over magnesium sulphate, filtered and the ether removed under vacuum to give a white solid, benzoic acid (1.20 g) which on recrystallisation from water had m. p. 122° (lit., 119 m. p. 122°) and on mixing with an authentic sample had m. p. 122°. Bromide ion (93 m/100 m) was determined gravimetrically.

The ether was removed under vacuum from the original ether extract of the aqueous layer and the t-butylbenzene solution was examined by g. l. c. /m. s. (5% CAR, 203°), which showed the product peak: m/e; 184, with mass spectrum identical to that of an authentic sample of dibenzo-\(p\)-dioxin. The yield of dibenzo-\(p\)-dioxin (20 m/100 m) was
determined by g.i.c. (5% CAR, 208°) using phenanthrene as internal standard.

(c) **Thermal decomposition of sodium 2-bromophenoxide and sodium thiobenzoate in t-butylbenzene**

Sodium 2-bromophenoxide (1.30 g, 6.7 mmol) and sodium thiobenzoate (1.02 g, 6.4 mmol) in t-butylbenzene (25 ml) were allowed to decompose for two days as described previously. A few drops of dilute sulphuric acid (2 M) were added to the ether/water mixture used to remove the contents from the autoclave and bromide ion (100m/100m) was determined gravimetrically. The ether extract of the acidified aqueous layer was dried over magnesium sulphate, filtered and the ether removed under vacuum.

On standing for two days a brown precipitate was formed in the t-butylbenzene solution. This was filtered off, dried and identified as sulphur, m.p. 119°, the i.r. spectrum showing no absorptions.

Examination by g.i.c./m.s. (5% CAR, 200°) showed three peaks: m/e; 94, 198, 122, with mass spectra identical to those of authentic samples of phenol, phenyl benzoate and benzoic acid, respectively. The phenyl benzoate was present in trace amount only.

The t-butylbenzene solution was extracted with sodium bicarbonate solution (10% w/v) and the extract acidified with dilute hydrochloric acid (2 M) to give a white precipitate. The precipitate was extracted into chloroform, the chloroform extract dried over magnesium sulphate and filtered. Removal of the chloroform under vacuum gave a white solid, benzoic acid (0.63 g), which on recrystallisation from
water had m.p. 122° (lit., 119 m.p. 122°) and mixed m.p. 122°.

The t-butylbenzene solution was then extracted with dilute sodium hydroxide (0.5M) and the extract acidified with dilute hydrochloric acid (0.5M), liberating a brown oil. The oil was extracted into ether, the ethereal solution dried over magnesium sulphate, filtered and the ether removed under vacuum to give phenol (0.31 g, 49m/100m), i.r. indistinguishable from that of an authentic sample.

10. Miscellaneous Decompositions

(a) Thermal decomposition of the sodium salt of 2-hydroxyphenyl 4-methylphenyl sulphone in t-butylbenzene

The sodium salt of 2-hydroxyphenyl 4-methylphenyl sulphone (0.65 g, 2.4 mmol) in t-butylbenzene (10 ml) was heated for two days as described previously. Examination of the t-butylbenzene solution by g.l.c. (5% CAR, 200°, 1% SE 30, 200°) showed no product peaks. The aqueous solution was acidified with dilute sulphuric acid (2 M) and extracted continuously for 6 h with chloroform. The chloroform layer was separated, dried over magnesium sulphate, filtered and the chloroform removed under vacuum to give 2-hydroxyphenyl 4-methylphenyl sulphone (0.58 g), which on recrystallisation from ethanol/water had m.p. 120-122° (lit., 150° m.p. 121°).

(b) Thermal decomposition of sodium 1-bromo-2-naphthoxide in t-butylbenzene

Sodium 1-bromo-2-naphthoxide was prepared in the usual manner from 1-bromo-2-naphthol and sodium methoxide and dried at 100° under vacuum for 24 h. The salt, after drying, had a grey-green appearance and some decomposition appeared to have occurred.
\( \text{i) Examination of the dried salt} \)

A sample of the dried salt (1.85 g) was warmed in water (30 ml) and the insoluble material filtered off and dried in a vacuum-desiccator to give a yellow solid (0.3 g). The yellow solid was soluble in chloroform and examination by g.l.c. (1% SE 30, 200\( ^0 \)) showed no product peaks. Examination by t.l.c. showed seven spots using benzene as the eluant.

The filtrate was acidified with dilute sulphuric acid (0.5 M), extracted with chloroform, the chloroform solution dried over magnesium sulphate and filtered. Removal of the chloroform under vacuum gave a white solid, 1-bromo-2-naphthol (1.15 g), m.p. 82-83\( ^0 \) (lit., 151 m.p. 84\( ^0 \)). The aqueous layer was treated with silver nitrate solution (10% w/v) and bromide ion (29m/100m) was determined gravimetrically.

\( \text{ii) Thermal decomposition of the dried salt} \)

The dried salt (1.60 g) was boiled under reflux in t-butylbenzene (25 ml) in an atmosphere of dry nitrogen for two days. The contents of the flask were removed with a mixture of ether and water, which was passed through a sintered-glass funnel and a dark-grey amorphous solid (0.15 g) collected. The aqueous layer was separated from the filtrate and bromide ion (90m/100m) determined gravimetrically. The ether layer was dried over magnesium sulphate, filtered and the ether removed under vacuum. The t-butylbenzene solution which remained was dark-brown with a green fluorescence and examination by g.l.c. (1% SE 30, 180\( ^0 \)) showed two peaks: m/e; 144, 286. The peak: m/e; 144 had an identical mass spectrum to that of 2-naphthol. On examination by t.l.c. the solution
showed at least seven spots using benzene as the eluant.

The t-butylbenzene solution was extracted with dilute sodium hydroxide (0.5 M) and the alkaline extract acidified with dilute sulphuric acid (0.5 M), liberating a small amount of brown oil. The oil was extracted into ether, the ethereal extract dried over magnesium sulphate, filtered and the ether removed under vacuum to give a brown solid (0.35 g). Fractional crystallisation of the solid from a mixture of ether and cyclohexane gave a light-brown crystalline solid, 1,1'-bis (2-naphthol) (12 mg), m.p. 216-217° (lit., 167 m.p. 216°), n.m.r. (CDCl₃): δ 1.9-3.0 (c, 12H, aromatic), δ 4.95 (s, 2H, OH) (Found: 286.097887. Calc. for C₂₀H₁₄O₂: 286.099373).

(c) Thermal decomposition of sodium 2-iodothiophenoxide and benzamide in "superdry" benzonitrile

Sodium 2-iodothiophenoxide (2.28 g, 9.2 mmol) and benzamide (1.21 g, 10 mmol) in "superdry" benzonitrile (25 ml) were decomposed for two days as described previously. Iodide ion (92m/100m) was determined gravimetrically and examination by g.l.c./m.s. (5% CAR, 200°) showed three peaks: m/e; 186, 121, 216, which had mass spectra identical to those of authentic samples of diphenyl sulphide, benzamide and thianthrene, respectively. Diphenyl sulphide was present in trace amount only and the yield of thianthrene (26m/100m) was determined by g.l.c. (5% CAR, 208°) using phenanthrene as internal standard.

T.l.c. examination showed the absence of 2-phenylbenzothiazole from the reaction products.
(d) **Thermal decomposition of sodium 2-bromophenoxide in the presence of the sodium salt of benzyl alcohol**

2-Bromophenol (1.73 g, 10 mmol) was added to a solution of sodium (0.46 g, 20 mmol) in dry benzyl alcohol (25 ml) and the solution allowed to decompose for two days as previously described. On opening the autoclave a strong smell of almonds was detected. The aqueous layer from the ether/water washings was acidified with a few drops of dilute nitric acid (2 M) before further extraction with ether. Bromide ion (100 m/100 m) was determined gravimetrically and examination by g.l.c./m.s. (5% CAR, 200°) showed two product peaks: m/e; 106, 122, which had mass spectra identical to those of authentic samples of benzaldehyde and benzoic acid, respectively. T.l.c. examination and further g.l.c. (1% SE 30, 150° and 200°) examination showed no further products.

The benzyl alcohol solution was extracted with sodium bicarbonate solution (10% w/v) and the aqueous extract acidified with dilute hydrochloric acid (2 M), giving a white precipitate. The precipitate was extracted into chloroform, the chloroform solution dried over magnesium sulphate, filtered and the chloroform removed under vacuum to give a white solid, benzoic acid (1.1 g), which on recrystallisation from water had m.p. 122° (lit., 119° m.p. 122°), mixed m.p. 122°.

C. **Reactions of Bromodurene with "Complex Base"**

The following series of reactions of bromodurene with "complex base" (a mixture of potassium t-butoxide and sodamide) in various solvents was carried out according to the general method exemplified by the
reaction in tetrahydrofuran (a).

In all cases, the products included durene, 2,4,5,2',4',5'-hexamethylbibenzyl and bromo-2,4,5,2',4',5'-hexamethylbibenzyl. Other products, identified by their mass spectra from g.l.c/m.s. examination are described where appropriate. The yields of durene were determined by g.l.c. (2% NPGS, 100°) using bromomesitylene as internal standard and the yields of 2,4,5,2',4',5'-hexamethylbibenzyl and bromo-2,4,5,2',4',5'-hexamethylbibenzyl were determined by g.l.c. (2% NPGS, 200°) using 3,5,3',5'-tetramethylbibenzyl as internal standard. Yields are recorded as moles per 100 moles of the "complex base".

(a) Reaction of bromodurene with "complex base" in tetrahydrofuran

Bromodurene (16.0 g, 75.1 mmol), potassium t-butoxide (1.50 g, 13.4 mmol) and sodamide (0.50 g, 12.8 mmol) in tetrahydrofuran (35 ml) were boiled under reflux for 18 h in an atmosphere of dry nitrogen. The product mixture was washed with water (100 ml) and bromide ion (59 mmol/100 ml) determined gravimetrically as silver bromide. Examination of the tetrahydrofuran solution by g.l.c./m.s. (2% NPGS, 80° for 10 min, programmed at 16°/min to 225°) showed four peaks: m/e; 134, 212/214, 266, 344/346, with mass spectra identical to those of authentic samples of durene, bromodurene, 2,4,5,2',4',5'-hexamethylbibenzyl and bromo-2,4,5,2',4',5'-hexamethylbibenzyl, respectively. The yields of durene (22 mmol/100 ml), 2,4,5,2',4',5'-hexamethylbibenzyl (3.4 mmol/100 ml) and bromo-2,4,5,2',4',5'-hexamethylbibenzyl (3.1 mmol/100 ml) were determined as described previously.
(b) Reaction of bromodurene with "complex base" in various solvents

Reactions were carried out using the same quantities of reactants as above (a). The yields of products are shown in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Reaction Time</th>
<th>Bromide Ion (m/100m)</th>
<th>Durene m/100m</th>
<th>Hexamethylbibenzyl (m/100m)</th>
<th>Bromohexamethylbibenzyl (m/100m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>18h</td>
<td>69</td>
<td>22</td>
<td>3.4</td>
<td>3.1</td>
</tr>
<tr>
<td>THF*</td>
<td>7 days</td>
<td>74</td>
<td>19</td>
<td>5.9</td>
<td>7.0</td>
</tr>
<tr>
<td>Dioxan</td>
<td>5 days</td>
<td>75</td>
<td>24</td>
<td>1.7</td>
<td>8.5</td>
</tr>
<tr>
<td>DME</td>
<td>40h</td>
<td>61</td>
<td>15</td>
<td>2.7</td>
<td>12.8</td>
</tr>
<tr>
<td>50:50 THF:DME</td>
<td>40h</td>
<td>62</td>
<td>20.5</td>
<td>2.9</td>
<td>10.2</td>
</tr>
</tbody>
</table>

THF tetrahydrofuran
DME dimethoxyethane

* Examination by g.l.c./m.s. (2% NPGS, 200°) showed two small peaks immediately after bromodurene, each with parent ion: m/e; 204. The first was tentatively identified as 2-(2,4,5-trimethylbenzyl)tetrahydrofuran from its mass spectrum which had base peak: m/e; 71, indicating fission α to the oxygen atom of the tetrahydrofuran. The second was tentatively identified as the isomer, 3-(2,4,5-trimethylbenzyl)tetrahydrofuran from its mass spectrum.
Reaction of bromodurene with "complex base" in tetrahydrofuran in the presence of added isomeric bromotrimethylbenzyl bromides

Bromodurene (16.0 g, 75.1 mmol), potassium t-butoxide (1.5 g, 13.4 mmol), sodamide (0.5 g, 12.8 mmol) and isomeric bromotrimethylbenzyl bromides (2.0 g, 6.8 mmol) in tetrahydrofuran (35 ml) were allowed to react as described previously. Examination by g.l.c./m.s. (2% NPGS, 160°) showed two new peaks, each with parent ion: m/e; 284/286, identified as 3-bromo- and 2-bromo-2,4,5-trimethylbenzyl t-butyl ethers by comparison of their mass spectra with those obtained by Hall. The yields of the t-butyl ethers were not determined. The yields of durene (2.2 m/100 m), 2,4,5,2',4',5'-hexamethylbibenzyl (1.6 m/100 m) and bromo-2,4,5,2',4',5'-hexamethylbibenzyl (1.3 m/100 m) were determined as described previously.
DISCUSSION

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A. Thermal Decomposition of Sodium 2-Bromophenoxides and Related Compounds

1. Evidence for the Intermediacy of Ketocarbenes in the Thermal Decomposition of Sodium 2-Bromophenoxides and the Exclusion of Benzoxirene Participation

(a) Mechanism of dioxin formation

In agreement with results obtained by other workers 79, 87, 90, the thermal decomposition of sodium 2-bromophenoxide in mesitylene at 260° in the autoclave resulted in the formation of dibenzo-\( \beta \)-dioxin (22m/100m). A possible mechanism (Scheme 21) for the formation of the dioxin (169) is the decomposition of the bromophenoxide ion (166) to give the 1,2-ketocarbene intermediate (167), followed by dimerisation of the dipolar resonance form (168) of the ketocarbene.

\[
\begin{align*}
166 & \rightarrow [167 \rightleftharpoons 168] \\
2 & \rightarrow 169
\end{align*}
\]

Scheme 21
There is a precedent for Scheme 21 in the work of Huisgen\textsuperscript{25}, who has accounted for the formation of the sulphur analogue of the dioxin (169), thianthrene (171) as the main product from the thermal decomposition of 1,2,3-benzothiadiazole by dimerisation of the dipolar resonance form (170) of the corresponding thioketocarbene intermediate.

Another possible route to the dioxin (169) can be envisaged, involving nucleophilic attack by the 2-bromophenoxide ion (166) at the electron-deficient centre of the ketocarbene (167) (Scheme 22).

Experiments were carried out with a view to providing
evidence for Scheme 22. The intermediate (172), formed by nucleophilic attack, is thought to give the dioxin (169) by an intramolecular mechanism. Although none of the hydroxydiphenyl ether (173) was obtained after the aqueous work-up, evidence for involvement of the intermediate (172) was provided by the separate thermal decompositions of the 2- and 3-chlorophenoxides (174 and 175), which both gave the dioxin (169) as the only product.

The latter results suggested the involvement of a common aryne intermediate (177), which in the case of the 3-chlorophenoxide (175) could result from attack on the ortho hydrogen atom to give the carbanion (176), followed by loss of chloride ion (Scheme 23).

A possible mechanism for the formation of the dioxin from the aryne involves nucleophilic attack by the oxygen lone pair to give the
betaine (178) which then leads to the product by proton transfer.\[\text{102}\]

Of course, there is the possibility that the betaine (178) is not involved and that the dioxin results from a concerted mechanism. A possible objection to the aryne route is the absence of products derived via attack on the aryne by other nucleophiles in the system, such as the bromophenoxide ion (166), although the intramolecular nature of the reaction may preclude this.

Formation of the same aryne (177) from the 2-chlorophenoxide (174), by a similar intramolecular mechanism, is inconceivable since the hydrogen atom ortho to the chlorine atom is too far removed to allow attack by the phenoxide ion. It is conceivable, however, that the aryne may be formed by an intermolecular route, involving attack by another phenoxide ion, and control reactions were carried out to test this possibility. A compound of similar structure to the 2-chlorophenoxide (174), 2-bromophenyl phenyl ether, was heated in the presence of sodium phenoxide and products formed by nucleophilic attack on the aryne were sought. A quantitative recovery of 2-bromophenyl phenyl ether from the reaction mixture, however, showed no aryne formation to have taken place and repetition of the experiment with sodium 2-methoxyphenoxide as the nucleophile gave the same result. Since the stronger nucleophile,
2-methoxyphenoxide, also gave no aryne formation, the possibility of intermolecular aryne formation as a possible route to dibenzo-p-dioxin was discounted.

The considerable difference in the yields of dioxin (169) obtained from the 2-chlorophenoxide (174) (88m/100m) and the 3-chlorophenoxide (175)(12m/100m) suggested different mechanisms for the two decompositions and another possible route to the formation of the dioxin (169) from the 2-chlorophenoxide (174) in good yield was sought. A route involving intramolecular nucleophilic displacement of chloride ion was discounted since such reactions are only known when activating substituents, such as nitro groups, are present in the aromatic ring. A well-known example of the latter is the reaction of phenoxide ion with p-chloronitrobenzene.

\[
\begin{align*}
\text{Cl} & \quad + \quad \text{O} \\
\text{NO}_2 & \quad \rightarrow \\
\end{align*}
\]

It is possible to write a mechanism for the formation of dibenzo-p-dioxin from the 2-chlorophenoxide ion (174) via intramolecular formation of a 1,3-aryne intermediate (179) (Scheme 24). Although little evidence has been found for the intermediacy of 1,3-dehydrobenzene,
Hess and Schaad\textsuperscript{8} consider its formation to be possible on the basis of "resonance energy per electron" calculations.

Another possible intramolecular mechanism, which cannot be discounted, is nucleophilic attack on the halogen atom by the phenoxide ion. In a mechanism involving similar attack, Bunnett and Victor\textsuperscript{113} have accounted for the debromination of 1,2,4-tribromobenzene with potassium t-butoxide in a mixture of t-butanol and dimethyl sulfoxide. Scheme 25 shows formation of the hypochlorite (180) by nucleophilic attack on the chlorine atom, with subsequent attack by the carbanion giving the dioxin (169).

\textbf{Scheme 24}

\textbf{Scheme 25}
It was thought that mechanisms such as Scheme 24 and Scheme 25 may be favourable under the forceful conditions of the decompositions in the autoclave.

(b) **The role of benzoxirene**

Conclusive evidence 42, 60, 61, has recently been reported for the participation of oxirenes in the photochemical decomposition of diazoketones and subsequent Wolff rearrangement. It was shown that oxirenes do not take part in the thermal Wolff rearrangement and Majerski and Redvanly 65 have provided evidence against the participation of an oxirene intermediate in cyclic systems. From the latter evidence, the possibility of the involvement of an oxirene intermediate in the thermal decomposition of 2-halophenoxides seemed remote, but participation of the benzoxirene structure (181), a valence isomer of the ketocarbene intermediate (167), was considered.

\[
\begin{align*}
\text{167} & \quad \text{181} \\
& \equiv \quad & \equiv
\end{align*}
\]

The mechanism involving nucleophilic attack by the bromophenoxide ion at the electron-deficient centre of the ketocarbene (Scheme 22) provides a chemical test for the participation of the benzoxirene by use of a suitably substituted phenoxide. For example, sodium 2-bromo-4-methylphenoxide would lead to formation of an isomeric mixture of
2,7- and 2,8-dimethyldibenzo-\(p\)-dioxin (186 and 187, respectively) if the benzoxirene (184) was involved. (Scheme 26). The two isomers result from attack by the phenoxide ion (182) on the two different ketocarbene intermediates (183 and 185), interconverted via the benzoxirene (184).

Clearly, thermal decomposition of sodium 2-bromo-5-methylphenoxide (188) would lead to the same pair of isomers (186 and 187) by the same mechanism. Thermal decompositions of sodium 2-bromo-5-methylphenoxide and sodium 2-bromo-4-methylphenoxide, separately, and a control experiment involving thermal decomposition of a mixture of the two phenoxides (182 and 188), were carried out.
$^{13}\text{C}[^1\text{H}] \text{n.m.r. spectrum of}$

from sodium 2-bromo-4-methylphenoxide

fig. 1

$^{13}\text{C}[^1\text{H}] \text{n.m.r. spectrum of}$

from mixture of 2-bromo-5-methyl- and 2-bromo-4-methylphenoxide

fig. 2
The control experiment must give an isomeric mixture of the dioxins (186 and 187) regardless of the involvement of benzoxirene (184) and a physical method of distinguishing between them was required. The reaction mixture of the control experiment was analysed by g.l.c. and showed, not surprisingly, no separation of the two isomers. An attempt to separate them by column chromatography of the reaction mixture resulted only in the separation of the unresolved isomeric mixture from the other products. Proton n.m.r. also failed to distinguish between the isomers but, finally, the problem was solved using $^{13}$C Fourier transform n.m.r. The corresponding dioxin products were separated from the reaction mixtures of the separate decompositions by column chromatography and the products from all three reaction mixtures were analysed by $^{13}$C proton noise-decoupled n.m.r. The spectra of the dioxin products obtained from the separate decompositions of sodium 2-bromo-4-methylphenoxide and sodium 2-bromo-5-methylphenoxide were found to be the same (fig. 1), whereas that of the product from the control experiment showed differences (fig. 2).

Interpretation of the spectra and assignment of the peaks

Since the chemical shift values of neither of the isomers (186 and 187) is available in the literature, the values for a model compound of similar structure to the two isomers, 4-methyl-2-phenoxyphenyl phenyl ether, are calculated. This is done, as follows, by making the appropriate changes of chemical shifts for the substituents added stepwise to diphenyl ether, for which the chemical shifts are
The chemical shift changes for a phenoxy group are readily obtained, knowing the chemical shift of benzene (128.6 p.p.m.), in the same solvent, deuteriochloroform:

\[
\begin{array}{cccc}
\text{C - 1} & \text{ortho} & \text{meta} & \text{para} \\
\text{PhO} & +29.4 & -9.6 & +1.4 & -5.6 \text{ p.p.m.}
\end{array}
\]

Adjustments are then made for an ortho phenoxy substituent in diphenyl ether:

Finally, the appropriate adjustments are made for the known chemical shift changes of a methyl group from the literature. Adjustments for a methyl group in the para position gives the chemical shifts for the carbon atoms of the model compound:

\[
\begin{array}{cccc}
\text{C - 1} & \text{ortho} & \text{meta} & \text{para} \\
\text{CH}_3 & +8.9 & +0.7 & -0.1 & -2.9 \text{ p.p.m.}
\end{array}
\]
The theoretical values thus obtained are compared with those obtained in the $^{13}$C n.m.r. spectra of the dimethyldibenzo-p-dioxins from the thermal decompositions of sodium 2-bromo-4-methylphenoxide, sodium 2-bromo-5-methylphenoxide and the mixture of the two phenoxides, as shown in Table 2. The peak of chemical shift 20.6 p.p.m. in each of the three spectra is obviously due to the carbon atoms of the methyl groups, since it is the only peak in this characteristic region.

![Chemical structure of dimethyldibenzo-p-dioxins]

Table 2

Assignment of Peaks in $^{13}$C n.m.r. Spectra of Dimethyldibenzo-p-dioxins

<table>
<thead>
<tr>
<th></th>
<th>C$_1$</th>
<th>C$_2$</th>
<th>C$_3$</th>
<th>C$_4$</th>
<th>C$_5$</th>
<th>C$_6$</th>
<th>C$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>product from sodium 2-bromo-4-methylphenoxide</td>
<td>115.8</td>
<td>123.7</td>
<td>133.3</td>
<td>116.7</td>
<td>141.7</td>
<td>139.8</td>
<td>20.6</td>
</tr>
<tr>
<td>product from sodium 2-bromo-5-methylphenoxide</td>
<td>115.9</td>
<td>123.8</td>
<td>133.5</td>
<td>116.8</td>
<td>141.9</td>
<td>139.9</td>
<td>20.6</td>
</tr>
<tr>
<td>product from mixture (control)</td>
<td>115.9</td>
<td>123.8</td>
<td>133.4</td>
<td>116.8</td>
<td>141.8</td>
<td>139.9</td>
<td>20.6</td>
</tr>
<tr>
<td>model compound (4-methyl-2-phenoxyphenyl phenyl ether)</td>
<td>120.4</td>
<td>125.4</td>
<td>133.4</td>
<td>121.4</td>
<td>148.4</td>
<td>145.4</td>
<td></td>
</tr>
</tbody>
</table>


The calculated values of the chemical shifts for the model compound, although slightly high, enable the chemical shifts of the products to be assigned to the appropriate carbon atoms. The spectrum of the product from the control experiment shows pairs of peaks for C3 and C5 and since both 2,7- and 2,8-dimethyl dibenzo-p-dioxin should be formed in this experiment it is obvious that these pairs of peaks must arise by overlap of their two very similar spectra. The $^{13}$C n.m.r. spectrum of the same product in deuterioacetone showed pairs of peaks for C2, C3, C5 and C6, due to the solvent effect, indicating more clearly the slight differences detected in the symmetry of the two compounds by this technique.

The spectra of the products from the other two thermal decompositions are both attributed to isomerically pure 2,7-dimethyldibenzo-p-dioxin and on this evidence the possibility of benzoxirene participation is discounted.

(c) The role of the 1,3-aryne

The thermal decomposition of sodium 2-bromo-5-methylphenoxide, resulting in the formation of isomerically pure 2,7-dimethyldibenzo-p-dioxin, as shown by $^{13}$C n.m.r., discounts the possibility of 1,3-aryne participation, postulated in Scheme 24. The formation of the 1,3-aryne (191) from the intermediate (190), resulting from nucleophilic attack by the 2-bromo-5-methylphenoxide ion on the keto-carbene (189), should lead to the formation of two isomeric products, 2,7-dimethyldibenzo-p-dioxin and 1,8-dimethyldibenzo-p-dioxin (192) (Scheme 27).
Scheme 24, therefore, may be discounted as a possible route to the dioxin (169) from the intermediate (172) since the 1,8-isomer (192) was not obtained.

(d) Further reactions of the ketocarbenes: formation of phenolic products.

The formation of 2,7-dimethyldibenzo-p-dioxin in the
thermal decompositions of sodium 2-bromo-4-methylphenoxide and sodium 2-bromo-5-methylphenoxide is accompanied by formation of cresols and hydroxydiphenyl ethers. The products obtained in these decompositions are shown in Table 3.

**Table 3**

Thermal Decomposition of Bromomethylphenoxides in t-Butylbenzene

<table>
<thead>
<tr>
<th>Phenoxide</th>
<th>Products</th>
<th>Yield (m/100m)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure" /></td>
<td><img src="image2" alt="Structure" /></td>
<td>0.9</td>
</tr>
<tr>
<td><img src="image3" alt="Structure" /></td>
<td><img src="image4" alt="Structure" /></td>
<td>0.3</td>
</tr>
<tr>
<td><img src="image5" alt="Structure" /></td>
<td><img src="image6" alt="Structure" /></td>
<td>0.6</td>
</tr>
<tr>
<td><img src="image7" alt="Structure" /></td>
<td><img src="image8" alt="Structure" /></td>
<td>3</td>
</tr>
</tbody>
</table>

The higher yield of the dioxin in the thermal decomposition of the 2-bromo-4-methylphenoxide may be due to the inductive effect of the methyl group para to the oxygen atom. This electron-donating effect may enhance nucleophilic attack at the electron-deficient centre of the ketocarbene, whereas the methyl group in the meta position in
the 2-bromo-5-methylphenoxide will have no such effect. The overall low yields of products in these tarry reaction mixtures may be due to the highly probable Wolff rearrangement as an alternative reaction of the aromatic ketocarbenes. Süss²⁰ has shown that aromatic ketocarbenes readily undergo the Wolff rearrangement to give ketenes and in this case the ketocarbene (183) should react to give the ketene (193) which will undoubtedly lead to tar formation by further reaction.

\[
\begin{align*}
\text{CH}_3\text{O} & \quad \rightarrow \quad \text{CH}_3\text{C}=\text{O} \\
183 & \quad \rightarrow \quad \text{tars}
\end{align*}
\]

A possible source of the cresols obtained in these decompositions is also via an alternative reaction of the ketocarbene intermediates. The ketocarbene (183) may be written as the dipolar resonance form (194) or as the radical structure (195). Either or both of the latter structures may, possibly, react with the solvent, t-butylbenzene, resulting in the formation of \( p \)-cresol (Scheme 28).

The dipolar resonance form (194) may abstract a hydride ion from a methyl group of the solvent to give a phenoxide ion (196) which on aqueous work-up will give \( p \)-cresol. Alternatively, the dipolar structure (195) may abstract a hydrogen atom from the solvent giving the phenyl radical (197), which on abstraction of a second hydrogen atom from the solvent gives \( p \)-cresol. Similarly, Scheme 28 accounts for the formation of \( m \)-cresol from the ketocarbene derived by thermal decomposition of sodium 2-bromo-5-methylphenoxide.
A possible objection to this scheme, however, is the absence of other products derived from the solvent. Abstraction of a hydride ion will produce a carbonium ion which should give products arising by reaction with other anions (182 or 196) and abstraction of hydrogen atoms should lead to formation of dimers of the solvent. It may be that some of these products are, in fact, formed but were not detected or that polymeric materials or tars are formed instead. Another possible source of hydrogen atoms or radicals is from the presence of water in the reaction, although rigorous precautions were taken in an attempt to avoid this.

The formation of the hydroxydiphenyl ether (198) adds support to the mechanism involving nucleophilic attack on the ketocarbene (Scheme 22). Attack on the ketocarbene (183) by the phenoxide...
ion (196) will result in formation of the hydroxydiphenyl ether (198) by a similar mechanism (Scheme 29).

Scheme 29

Thermal decomposition of sodium 2-bromo-5-methylphenoxide in mesitylene rather than t-butylbenzene gave, in addition to the products derived from the solvent, viz. m-cresol, 2-hydroxy-4-methylphenyl 3-methylphenyl ether, and 2,7-dimethyldibenzo-p-dioxin, two products derived from the solvent, viz. 2,3',4,5',6-pentamethyldiphenylmethane (200) and 3,3',5,5'-tetramethylbibenzyl (201). The latter two products were obtained as a mixture and identified by the n.m.r. spectrum which showed a signal at $\tau$ 6.1, the characteristic chemical shift of diphenylmethane methylene protons and a signal at $\tau$ 7.2, the characteristic chemical shift of bibenzyl methylene protons. The formation of the latter two compounds gives support to a radical abstraction mechanism for the formation of m-cresol by reaction of the diradical derived from the ketocarbene with the solvent, mesitylene (Scheme 30).
Abstraction of a hydrogen atom from one of the methyl groups in mesitylene gives a benzyl radical (199) which may dimerise to give the bibenzyl (201) or substitute on to the aromatic ring of a second molecule of mesitylene to give the diphenylmethane (200). An alternative possibility for the formation of the benzyl radical (199), from the presence of traces of peroxides in the solvent, seems unlikely since passage of the mesitylene through a column of alumina immediately before use failed to prevent formation of products derived from the solvent. Since the latter complicated the separation of the products obtained from the phenoxides, further thermal decompositions were carried out in t-butylbenzene.
Thermal decomposition of sodium 2-bromo-4-methoxyphenoxide and sodium 2-bromo-5-methoxyphenoxide, separately, in t-butylbenzene led to the formation of 4-methoxyphenol and 3-methoxyphenol, respectively, as the only products.

(e) The halide leaving group

The importance of halide ion as the leaving group in the thermal decompositions is suggested by the thermal stability of the sodium salt of 2-hydroxyphenyl 4-methylphenyl sulphone (202) under the conditions of the decomposition. Replacement of the bromine atom of sodium 2-bromophenoxide by the p-toluenesulphonyl group, which is known to be a good leaving group, led to a quantitative recovery of 2-hydroxyphenyl 4-methylphenyl sulphone, showing no decomposition to have occurred.

\[
\begin{align*}
\text{OH} & \quad \text{CH}_3 \\
\text{SO}_2 & \\
\end{align*}
\]

2. Nucleophilic Attack by Benzamide in the Formation of Benzoxazoles

1,3-Dipolar additions have often been used to provide evidence for involvement of ketocarbene intermediates. Haszeldine\textsuperscript{32} and Huisgen\textsuperscript{25} have both made use of benzonitrile in particular as a dipolarophile to trap ketocarbene intermediates, derived from the decomposition of tetrahalobenzene-o-diazooxides, to form benzoxazoles.
An attempt to form benzoxazoles in a similar manner was, therefore, the next logical step to provide evidence for the existence of ketocarbene intermediates in the thermal decomposition of sodium 2-bromophenoxides. The initial thermal decomposition of sodium 2-bromophenoxide in benzonitrile as solvent gave the encouraging result of the formation of 2-phenylbenzoxazole (203, \(11\text{m}/100\text{m}\)), suggesting a 1,3-dipolar addition to have occurred. (Scheme 31).

![Scheme 31](image)

This result gave a second means of testing for the participation of the benzoxirene intermediate in the decomposition, again by use of a suitably substituted phenoxide. Thermal decomposition of sodium 2-bromo-4-methylphenoxide in benzonitrile should lead to the formation of an isomeric mixture of 5- and 6-methyl-2-phenylbenzoxazoles (205 and 206, respectively) if the benzoxirene intermediate (204) is involved. (Scheme 32).

When the decomposition was carried out, however, isomerically pure 5-methyl-2-phenylbenzoxazole (205) was formed. Proof of its isomeric purity was obtained by high speed liquid chromatography. A mixture of authentic samples of 5- and 6-methyl-2-phenylbenzoxazole gave good separation of peaks on examination by h.s.l.c. and the peak corresponding to the 5-methyl isomer (205) had identical retention time to that of the benzoxazole product in the reaction mixture.
Table 4
Thermal Decomposition of 2-Bromophenoxides in Benzonitrile

<table>
<thead>
<tr>
<th>Phenoxide</th>
<th>Products</th>
<th>Yield (m/100m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td><img src="attachment" alt="Phenoxide branching" /></td>
<td>8</td>
</tr>
<tr>
<td>Br</td>
<td><img src="attachment" alt="Phenoxide branching" /></td>
<td>11</td>
</tr>
<tr>
<td><img src="attachment" alt="Phenoxide branching" /></td>
<td><img src="attachment" alt="Phenoxide branching" /></td>
<td>207</td>
</tr>
<tr>
<td><img src="attachment" alt="Phenoxide branching" /></td>
<td><img src="attachment" alt="Phenoxide branching" /></td>
<td>1.8</td>
</tr>
<tr>
<td><img src="attachment" alt="Phenoxide branching" /></td>
<td><img src="attachment" alt="Phenoxide branching" /></td>
<td>6</td>
</tr>
</tbody>
</table>
Addition of an authentic sample of the 5-methyl isomer (205) to the reaction mixture gave enhancement of the corresponding benzoxazole peak and addition of an authentic sample of the 6-methyl isomer (206) gave a new peak on examination by h.s.1.c., showing the latter to be absent in the reaction mixture. To rule out the possibility that the 6-methyl isomer (206) was initially formed, together with the 5-methyl isomer (205), but was thermally unstable under the decomposition conditions, an authentic sample of the 6-methyl isomer (206) was heated in t-butylbenzene under the same conditions. A quantitative recovery of the benzoxazole (206) confirmed it to be thermally stable under these conditions and benzoxirene participation in Scheme 31 was discounted on the above evidence.

The products obtained from these decompositions in benzonitrile are shown in Table 4.

In addition to the six products obtained on thermal
decomposition of sodium 2-bromophenoxide (Table 4), a trimer of benzonitrile, 2, 4, 6-triphenyl-1,3,5-triazine (208) was obtained on filtering the ether/water mixture used to remove the product mixture from the autoclave.

Bengelsdorf studied the reactions of aromatic nitriles under high pressure and temperature and obtained good yields of the triazine (208) from benzonitrile. Even at the moderate pressure of 255 p.s.i. he recorded a 2.5% yield of the triazine (208) at 360° after 14 h. The 0.1% yield of the triazine (208) obtained from the autoclave at 260° is, therefore, not surprising.

The unexpected formation of benzamide in these reactions suggested the presence of water, but alternative possibilities for its formation were considered since precautions were taken to keep the system dry. A possible source of benzamide by thermal decomposition of the benzoxazoles was considered, but 6-methyl-2-phenylbenzoxazole was shown to be thermally stable, as described previously and an authentic sample of the 5-methyl isomer (205) heated in t-butylibenzene under the conditions of the decomposition was also thermally stable. The possibility of benzamide formation via attack on the benzoxazole by the phenoxide ion was then considered, but thermal decomposition of
sodium 2-bromo-4-methylphenoxide in the presence of 5-methyl-2-phenylbenzoxazole, in t-butylbenzene, failed to give any benzamide. The presence of water in the reaction, therefore, remained the only reasonable explanation for the formation of benzamide. Further evidence for the presence of water was the formation of phenols, since it is unlikely for hydrogen atoms or hydride ions to be extracted from the solvent, benzonitrile, in this case. The formation of the hydroxy-diphenyl ether (207) is in accordance with the mechanism involving attack on the ketocarbene (167) by phenoxide ion (Scheme 29) and the presence of phenoxide ion can easily account for the trace of phenyl benzoate obtained by nucleophilic attack on benzamide (Scheme 33).

Thermal decomposition of sodium 2-bromophenoxide in the presence of p-tolunitrile failed to give the expected product, 2-p-tolylbenzoxazole, casting doubt on the mechanism of 1,3-dipolar addition (Scheme 31), for the formation of benzoxazoles in benzonitrile.
Repetition of the original trapping experiment by decomposition of sodium 2-bromophenoxide in "superdry" benzonitrile gave a high yield of dibenzo-p-dioxin (22m/100m) and no trace of 2-phenylbenzoxazole, casting further doubt on the 1,3-dipolar addition mechanism. Similarly, no benzoxazole was obtained when sodium 2-bromophenoxide was decomposed in the presence of "superdry" benzonitrile with t-butylbenzene as the solvent. These results pointed to an alternative mechanism (Scheme 34) for the formation of the benzoxazole, involving nucleophilic attack by the nitrogen lone pair of benzamide at the electron-deficient centre of the ketocarbene (167). Attack by the resulting phenoxide ion, intramolecularly, on the carbonyl carbon atom, results in ring closure and subsequent dehydration gives the product.

\[
\begin{align*}
\text{Scheme 34}
\end{align*}
\]
Decomposition of sodium 2-bromophenoxide in the presence of benzamide in t-butylbenzene, however, gave only a low yield of the benzoazole (2.3m/100m), but decomposition of sodium 2-bromophenoxide in the presence of an equimolar amount of benzamide in benzonitrile gave a high yield of 2-phenylbenzoxazole (31m/100m), giving strong support for Scheme 34.

It appears that the weak nucleophile, benzamide, requires the more polar solvent, benzonitrile, for the reaction to take place readily, whereas the stronger nucleophile, the phenoxide ion (166) gives identical yields (22m/100m) of dibenzo-γ-dioxin in both benzonitrile and t-butylbenzene, suggesting the solvent to have little effect in the latter case.

It is obvious that Scheme 34 requires the presence of only a catalytic amount of water for benzoxazole formation. Initial hydrolysis of benzonitrile to benzamide is followed by nucleophilic attack, ring closure and elimination of water, which can restart the cycle by further hydrolysis of benzonitrile. This observation raises the possibility that some of the 1,3-dipolar additions of benzonitrile which have been reported in the literature may, in fact, involve nucleophilic attack by benzamide in a similar manner.

The dipolar additions carried out by Huisgen\textsuperscript{25} and Haszeldine\textsuperscript{32} differ significantly from those attempted in the decomposition of sodium 2-bromophenoxides. They both studied 1,3-dipolar additions of tetrahaloketocarbenes which are known to be more stable than the unsubstituted aromatic ketocarbenes and are
less prone to undergo the alternative Wolff rearrangement, giving high yields of products. Decompositions of 2-bromophenoxides are never clean reactions, products being accompanied by tars, presumably resulting from rearrangement of the ketocarbenes at the high temperature involved. The decompositions of the tetrahalodiazooxides take place at much lower temperatures than the thermal decompositions of the 2-bromophenoxides and no alternative reaction to 1,3-dipolar addition is available for the tetrahaloketocarbenes, whereas the mechanism of nucleophilic attack (Scheme 22) may preclude 1,3-addition in the thermal decomposition of sodium 2-bromophenoxides. In agreement with the latter, Hall\(^90\) has shown that no adduct, similar to those formed with tetrahalodiazooxides, is formed when sodium 2-bromophenoxide is decomposed in the presence of trans stilbene.

Attempts were made to extend the proposed mechanism of nucleophilic attack by benzamide on ketocarbenes to form 2-phenylbenzoxazoles with substituents in the 2-phenyl group, by using substituted benzamides. Decomposition of sodium 2-bromophenoxide and p-toluamide in "superdry" benzonitrile, however, gave a poor yield of the expected product, 2-p-tolylbenzoxazole (4m/100m) together with, surprisingly, 2-phenylbenzoxazole (22m/100m). Since benzamide and p-tolunitrile were also amongst the products it is apparent that an equilibrium exchange between the amides and nitriles exists at 260°.
Dehydration of p-toluamide to give p-tolunitrile and hydration of benzonitrile to give benzamide, and the reverse reactions, gives a satisfactory explanation for the formation of the observed products. The greater yield of 2-phenylbenzoxazole suggests the forward reaction of the equilibrium to predominate, and some of the water produced by dehydration of the amides may be used in the formation of phenol, as described previously.

In an attempt to overcome this problem, nitrobenzene was used as a possible suitable, polar solvent and a similar decomposition carried out. Nitrobenzene, however, proved to be unsatisfactory, giving a very tarry reaction mixture containing only a trace of the expected 2-p-tolylbenzoxazole. The formation of azobenzene in this reaction showed that nitrobenzene had acted as an oxidising agent, resulting, presumably, in tar formation. Azobenzene is commonly obtained as a result of the reduction of nitrobenzene; for example, Evans and Fry\textsuperscript{172} have reported a 90\% yield of azobenzene by reduction of nitrobenzene with magnesium amalgam and ethanol below 45\°.

Finally, the decomposition was carried out in acetonitrile in an attempt to form 2-p-tolylbenzoxazole and possibly 2-methylbenzoxazole via similar equilibration of the nitriles and amides as obtained in benzonitrile. The reaction mixture was again very tarry and a considerable amount of a black, amorphous solid was obtained on filtering the ether/water mixture used to remove the product mixture from the autoclave. Apart from phenol and dibenzo-p-dioxin,
the only other product detected by g.l.c. was a compound of parent
mass 199, which was not identified, though its mass spectrum
suggested it to contain two molecules of acetonitrile (m/e; 82) and
one of p-tolunitrile (M⁺; 117) and is, possibly, an s-triazine.
Although the latter suggests the dehydration of some p-toluamide, no
evidence for the hydration of acetonitrile was obtained.

3. Thermal Decompositions Involving Sodium Thiophenoxides:
   Evidence for Attack by Strong Nucleophiles
   (a) Formation of thianthrenes by thermal decomposition of
      sodium 2-halothiophenoxides

   After studying the formation of dibenzo-p-dioxins by thermal
decomposition of sodium 2-bromophenoxides via the mechanism believed
to involve nucleophilic attack on the ketocarbene by phenoxide ion,
attention was turned to the sulphur analogues, sodium 2-halothiophenoxides.
The latter were expected to give the analogous sulphur-containing
products, thianthrenes, in greater yields than the corresponding
dibenzo-p-dioxins, since the thiophenoxide ion is a better nucleophile
than the phenoxide ion. Gravimetric halide determinations in the thermal
decomposition of a series of 2-halothiophenoxides containing different
halogen atoms showed a classic example of the relative ease of leaving
of halide, in the order I > Br > Cl. Sodium 2-chlorophenoxide was
completely stable at 260°, the iodo- compound decomposed almost
completely and the bromo- compound gave intermediate decomposition.
The latter two decompositions proceeded cleanly to give thianthrene
(171) as the only product. The results of this series of decompositions
are shown in Table 5.
Table 5

Thermal Decomposition of Sodium 2-Halo thiophenoxides in t-Butylbenzene

<table>
<thead>
<tr>
<th>Thiophenoxide</th>
<th>Bromide Ion (m/100m)</th>
<th>Thianthrene (m/100m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-chloro-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2-bromo-</td>
<td>48</td>
<td>20</td>
</tr>
<tr>
<td>2-iodo-</td>
<td>97</td>
<td>35</td>
</tr>
</tbody>
</table>

The aqueous layer of the ether/water mixture used to remove the reaction products of the thermal decomposition of sodium 2-chlorothiophenoxide from the autoclave was separated, acidified with dilute nitric acid and, after a negative test for chloride ion, extracted with ether. On removal of the ether by rotary evaporation in a warm water-bath, 2, 2'-dichlorodiphenyl disulphide (209) was obtained, rather than the expected compound, 2-chlorobenzenethiol. Since benzenethiols readily undergo oxidation to diphenyl disulphides the disulphide (209) obviously resulted by oxidation of 2-chlorobenzenethiol, presumably with the nitric acid.
The successful formation of thianthrene in these decompositions of thiophenoxides suggested an analogous mechanism (Scheme 35) to that applied in the phenoxide case (Scheme 22).

![Scheme 35](image)

In Scheme 35 decomposition of the thiophenoxide (210) gives the thiketocarbene (211), which is attacked nucleophilically by a second molecule of the thiophenoxide ion (210) to give the intermediate (212). The final stage, involving formation of thianthrene from the intermediate (212) is possibly of an intramolecular nature. Considering that in the case of sodium 2-bromothiophenoxide only 48% is decomposed, then the yield of thianthrene (20m/100m) is actually 85% of the reacted salt. Comparison of the latter figure with the yield of dibenzo-p-dioxin (22m/100m), in the thermal decomposition of the analogous 2-bromophenoxide is in accordance with the mechanism involving nucleophilic attack at the electron-deficient centre, since the better nucleophile leads to a greater yield of the product.
$^{13}\text{C}[^1\text{H}]$ n.m.r. spectrum of

\[ \text{from sodium 2-bromo-4-methylthiophenoxide} \]
Scheme 36 allows for the possibility of participation of a benzothiirene intermediate (215) and interconversion of two thioketocarbenes (214 and 216). Attack on the thioketocarbene (214) by the thio-phenoxide ion (213) gives 2,7-dimethylthianthrene (217) and attack on the other thioketocarbene (216) similarly gives 2,8-dimethylthianthrene (218).

\[ \text{Scheme 36} \]

Thermal decomposition of the suitably substituted 2-bromo-thiophenoxide (213) should, therefore, give an isomeric mixture of 2,7- and 2,8-dimethylthianthrene in the event of benzothiirene participation. Sodium 2-bromo-4-methylthiophenoxide (213) was decomposed and the product examined by \(^{13}\text{C}\) proton noise-decoupled n.m.r. in a similar manner to the corresponding oxygen case discussed earlier. The \(^{13}\text{C}\) n.m.r. spectrum (fig. 3) shows signals at: 20.8, 128.3, 129.1, 132.0, 132.3, 135.4, 135.7, and 137.5 p.p.m.

The signals were not assigned as in the corresponding
oxygen case due to lack of information in the present literature. The signal at 20.8 p.p.m., however, is obviously due to the carbon atoms of the methyl groups and the signal at 128.3 p.p.m. is assumed to be due to two aromatic carbon atoms, since it is considerably larger than the other peaks in the spectrum. The two pairs of small peaks (132.0, 132.3 and 135.4, 135.7 p.p.m.) suggest the presence of an isomeric mixture of 2,7- and 2,8-dimethyl-thianthrene, in which there is a slight overlap of their very similar spectra.

This evidence suggests the participation of a benzthiirenne intermediate in the thermal decomposition of sodium 2-bromothiophenoxides, although it is not possible, on this evidence, to estimate the degree of its participation. The apparent contrast in the mechanisms of the thermal decompositions of sodium 2-bromophenoxides and sodium 2-bromothiophenoxides is presumably due to the greater size and polarisability of the sulphur atom compared to oxygen.

The transient existence of a benzthiirenne intermediate in the thermal decomposition of sodium 2-halothiophenoxides is in agreement with the report of the participation of a thiirenne (221) in the self-condensation of 4-chloro-5-mercapto-3(2H)-pyridazinones (219) which gives rise to two isomeric products (223 and 224) by a similar interconversion of thioketocarbenes (220 and 222).
### Table 6

Thermal Decomposition of Mixtures of 2-Bromophenoxides and 2-Bromothiophenoxides in t-Butylbenzene

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Product</th>
<th>Yield (m/100m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) 5 mmol 2-Bromophenoxide + 10 mmol 2-Bromothiophenoxide</td>
<td><img src="image1" alt="Products" /></td>
<td>28</td>
</tr>
<tr>
<td>(ii) 6.2 mmol 2-Bromophenoxide + 6.2 mmol 2-Bromothiophenoxide</td>
<td><img src="image2" alt="Products" /></td>
<td>35</td>
</tr>
</tbody>
</table>

Scheme 37
(b) Thermal decomposition of mixtures of sodium 2-bromophenoxides and sodium 2-bromothiophenoxides

The products obtained by thermal decomposition of mixtures of sodium 2-bromophenoxides and sodium 2-bromothiophenoxides can also be rationalised by the mechanism involving nucleophilic attack on ketocarbene and thioketocarbene intermediates. The products obtained from decompositions of these mixtures are shown in Table 6.

The formation of the products obtained can be explained as shown in Scheme 37.

The ketocarbene (226) and thioketocarbene (227) result from decomposition of the phenoxide (225) and thiophenoxide (228), respectively. Nucleophilic attack by the phenoxide (225) on the ketocarbene (226) gives rise to the dibenzio-p-dioxin (229) and similar attack by the phenoxide (225) on the thioketocarbene (227) gives rise
to the phenoxathiin (230). The phenoxathiin (230) also results by nucleophilic attack of the thiophenoxide (228) on the ketocarbene (226) and attack by the same nucleophile (228) on the thiketocarbene (227) gives thianthrene (171). The relative amounts of the products obtained in decompositions (i) and (ii) (Table 6) are in agreement with Scheme 37. In (i), using excess sodium 2-bromothiophenoxide, no dibenzo-p-dioxin (229, X = H) was formed due to preferential attack by the stronger nucleophile, 2-bromothiophenoxide, which precludes attack by the phenoxide ion (225, X = H) on the ketocarbene (226, X = H). Phenoxathiin (230, X = H) and thianthrene (171) result from attack by 2-bromothiophenoxide (228) on the ketocarbene (226, X = H) and thiketocarbene (227), respectively.

In (ii), using an equimolar ratio of the phenoxide (225, X = CH₃) and thiophenoxide (228), a low yield of the dioxin (229, X = CH₃) was obtained by attack of the weaker nucleophile (225, X = CH₃) on the ketocarbene (226, X = CH₃). 3-Methylphenoxathiin (230, X = CH₃) results, presumably, mainly by attack of the thiophenoxide (228) on the ketocarbene (226, X = CH₃), although attack by the weaker nucleophile (225, X = CH₃) on the thiketocarbene (227) will give the same product (230, X = CH₃).

(c) Thermal decomposition of sodium 2-bromophenoxides with phenoxides and thiophenoxides as added nucleophiles

The formation of hydroxy diphenyl ethers in the decomposition of sodium 2-bromophenoxides was accounted for by a mechanism involving nucleophilic attack of the debrominated phenoxides on the ketocarbone intermediates (Scheme 29). In order to find evidence for
### Table 7

Thermal Decompositions in the Presence of Sodium Phenoxides and Sodium Thiophenoxides in t-Butylbenzene

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Yield (m/100m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td><img src="Image1" alt="Reactant 1" /> + <img src="Image2" alt="Reactant 2" /></td>
<td><img src="Image3" alt="Product 1" /></td>
</tr>
<tr>
<td></td>
<td><img src="Image3" alt="Product 1" /></td>
<td><img src="Image4" alt="Product 2" /></td>
</tr>
<tr>
<td>(ii)</td>
<td><img src="Image5" alt="Reactant 3" /></td>
<td><img src="Image6" alt="Product 3" /></td>
</tr>
<tr>
<td></td>
<td><img src="Image6" alt="Product 3" /></td>
<td><img src="Image7" alt="Product 4" /></td>
</tr>
<tr>
<td></td>
<td><img src="Image7" alt="Product 4" /></td>
<td><img src="Image8" alt="Product 5" /></td>
</tr>
<tr>
<td>(iii)</td>
<td><img src="Image9" alt="Reactant 6" /> + <img src="Image10" alt="Reactant 7" /></td>
<td><img src="Image11" alt="Product 6" /></td>
</tr>
<tr>
<td></td>
<td><img src="Image11" alt="Product 6" /></td>
<td><img src="Image12" alt="Product 7" /></td>
</tr>
</tbody>
</table>
this mechanism, thermal decompositions in the presence of sodium phenoxides and sodium thiophenoxides were carried out and the products obtained are shown in Table 7.

The formation of hydroxydiphenyl ethers and hydroxydiphenyl sulphides, in good yields, is in accordance with Scheme 38, providing good evidence for the overall mechanism involving nucleophilic attack.

![Chemical Structure]

**Scheme 38**

Attack by the nucleophile (232) on the ketocarbene (226) gives the phenoxide ion (233), which on treatment with water gives the product (234). The greater yield of the sulphide (234, \( X = H, Z = S \), 44%) obtained with sodium thiophenoxide compared with the ether (234, \( X = H, Z = O \), 33%) obtained with sodium phenoxide, is consistent with enhanced attack on the ketocarbene (226, \( X = H \)) by the stronger nucleophile, thiophenoxide. This is further substantiated by the absence of dibenzo-\( \beta \)-dioxin in (ii) since attack on the ketocarbene by the stronger nucleophile, thiophenoxide, will preclude attack by the weaker nucleophile, 2-bromophenoxide. In both (i) and (iii) the yields
of dioxin obtained are less than those of the diphenyl ethers, presumably since 2-bromophenoxide is a weaker nucleophile than phenoxide itself, due to the electron-withdrawing inductive effect of the ortho bromine atom.

The other products in (ii), diphenyl sulphide and diphenyl disulphide (231) presumably arise from the thiophenoxide. Diphenyl sulphide has been obtained by pyrolysis of sodium thiophenoxide\textsuperscript{173} and it is possible that the same product may be formed under the decomposition conditions in the autoclave. Disulphides are formed by oxidation of thiophenoxides with molecular oxygen and such oxidations in water are commonly used for the conversion of thiols to disulphides\textsuperscript{174}.

\[
\text{RS}^- + \dot{O}_2 \rightarrow \text{RS}^* + \dot{O}_2^-
\]

\[
2\text{RS}^* \rightarrow \text{RSSR}
\]

The thiophenoxide reacts with molecular oxygen by an electron-transfer mechanism to give the thiyl radical and peroxide ion. The disulphide is then formed by dimerisation of the thiyl radicals.

Some air will, undoubtedly, be present in the decomposition reaction mixture, since the contents of the autoclave are frozen prior to evacuation and air will be trapped in the frozen mixture. It may be possible, therefore, that a similar electron-transfer reaction takes place under the decomposition conditions.

(d) Evidence for a 1,4-ketocarbene in the thermal decomposition
Since sodium thiophenoxide proved to be an efficient nucleophile for attack at the electron-deficient centre of a 1,2-ketocarbene, an attempt was made to make and trap the corresponding 1,4-ketocarbene in a similar manner.

Thus, sodium 4-bromophenoxide was decomposed in the presence of sodium thiophenoxide in t-butylbenzene and isolation of 4-hydroxyphenyl phenyl sulphide (24m/100m) provides good evidence for the intermediacy of the 1,4-ketocarbene (236) as shown in Scheme 39.

![Scheme 39](image)

Decomposition of the 4-bromophenoxide ion (235) leads to formation of the 1,4-ketocarbene (236) in a similar manner to the
formation of the 1, 2-ketocarbene from 2-bromophenoxide (Scheme 21). Nucleophilic attack by the thiophenoxide ion at the electron-deficient centre of the 1, 4-ketocarbene gives the phenoxide (237) which on treatment with water gives the product, 4-hydroxyphenyl phenyl sulphide (238). The other products, diphenyl sulphide and diphenyl disulphide (231) may arise from sodium thiophenoxide, as described above.

(e) Attempted formation of 2-phenylbenzothiazole by nucleophilic attack of benzamide on a 1, 2-thioketocarbene

The above decompositions show inhibition of attack by the weaker nucleophiles, phenoxides, on ketocarbene and thioketocarbene intermediates in the presence of the stronger nucleophiles, thiophenoxides. This tendency is also exemplified in the attempt to prepare the sulphur analogue of 2-phenylbenzoxazole, 2-phenylbenzothiazole (239) by thermal decomposition of sodium 2-iodothiophenoxide and benzamide in benzonitrile. Under these conditions with sodium 2-bromophenoxide, 2-phenylbenzoxazole is formed in good yield as described previously, but the only products obtained in the sulphur case are thianthrene (26m/100m) and diphenyl sulphide. The thiophenoxide, being a much stronger nucleophile than benzamide completely precludes nucleophilic attack by the latter on the thioketocarbene.

\[\text{239}\]
4. Thermal Decompositions in the Presence of Other Nucleophiles

(a) Thermal decomposition of sodium 2-bromophenoxide in the presence of amines as added nucleophiles

Since it has previously been shown that the ketocarbene intermediates are attacked by the weak nucleophile, benzamide, resulting in the formation of 2-phenylbenzoxazoles, decompositions were carried out in the presence of stronger nucleophiles, amines, to seek evidence for nucleophilic attack. With aniline, nucleophilic attack on the ketocarbene derived by decomposition of sodium 2-bromophenoxide was expected to give 2-anilinophenol (240), according to Scheme 40.

\[
\begin{align*}
\text{C}_{6}\text{H}_{5}\text{CO}& \quad \text{H}_{2}\text{N} \quad \text{C}_{6}\text{H}_{5} \\
& \quad \text{C}_{6}\text{H}_{5} \quad \text{H}_{2}\text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{C}_{6}\text{H}_{5}\text{C}\text{O} & \quad \text{H}_{2}\text{N} \quad \text{C}_{6}\text{H}_{5} \\
& \quad \text{C}_{6}\text{H}_{5} \quad \text{H}_{2}\text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{C}_{6}\text{H}_{5}\text{C}\text{O} & \quad \text{H}_{2}\text{N} \quad \text{C}_{6}\text{H}_{5} \\
& \quad \text{C}_{6}\text{H}_{5} \quad \text{H}_{2}\text{N} \\
\end{align*}
\]

Scheme 40

Initially the decomposition was carried out in t-butylbenzene and no trace of the expected product was found. Addition of an authentic sample of 2-anilinophenol to a portion of the reaction mixture
gave a new peak on examination by g.l.c., showing its absence in the original mixture. The decomposition was then carried out in benzonitrile, since this solvent was previously found to be necessary for nucleophilic attack by benzamide to take place. 2-Anilinophenol, however, was similarly shown to be absent and the products obtained from these two decompositions are shown in Table 8.

Table 8

Thermal Decompositions of Sodium 2-Bromophenoxide in the Presence of Aniline

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Products</th>
<th>Yield (m/100m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-butylbenzene</td>
<td><img src="image1" alt="Structure" /></td>
<td>6</td>
</tr>
<tr>
<td></td>
<td><img src="image2" alt="Structure" /></td>
<td>6</td>
</tr>
<tr>
<td>benzonitrile</td>
<td><img src="image3" alt="Structure" /></td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td><img src="image4" alt="Structure" /></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td><img src="image5" alt="Structure" /></td>
<td>4.5</td>
</tr>
</tbody>
</table>
The formation of phenol in the decomposition in t-butylbenzene can be accounted for by abstraction of hydride ion from the solvent by the dipolar resonance form of the ketocarbene or by abstraction of hydrogen atoms by the diradical structure as described earlier (Scheme 28). In the decomposition in "superdry" benzonitrile the formation of phenol suggested the aniline to be wet. This is also evidenced by the formation of 2-phenylbenzoxazole, previously shown to result by hydrolysis of benzonitrile to benzamide and subsequent nucleophilic attack by benzamide on the ketocarbene intermediate (Scheme 34). The similar, low yields of dibenzo-p-dioxin in both decompositions suggest inhibition of attack by the 2-bromophenoxide ion on the ketocarbene, possibly due to the presence of aniline, and the formation of 2-hydroxyphenyl phenyl ether can be attributed to nucleophilic attack by phenoxide ion on the ketocarbene, according to the mechanism shown earlier (Scheme 29).

It is conceivable that the absence of 2-anilinophenol in the reaction mixtures is due to its decomposition under the reaction conditions or that polymeric oxidation products are produced, possibly in the form of tars, since 2-anilinophenol is known to oxidise very readily. On the other hand, it may simply be that aniline is too weak a nucleophile to attack the ketocarbene and that nucleophilic attack in the case of benzamide is energetically favourable due to ring closure to form the benzoxazole by subsequent attack on the carbonyl group. The stronger nucleophile, cyclohexylamine, was then added to sodium 2-bromophenoxide and the decomposition carried out in benzonitrile.
A tarry reaction mixture was obtained and the smell of ammonia was detected on opening the autoclave. On filtering the ether/water mixture used to remove the product mixture from the autoclave some of the benzonitrile trimer, 2,4,6-triphenyl-s-triazine (208) was collected. The formation of phenol, 2-hydroxyphenyl phenyl ether (2.5m/100m) and 2-phenylbenzoxazole (6m/100m) suggested the cyclohexylamine to be wet and a low yield of dibenzo-p-dioxin (5m/100m) was obtained, as in the decompositions in the presence of aniline.

Nine products in all were detected on examination by g.l.c. All products were present in low yield and none of them was found to have the correct parent ion at m/e; 191, on examination by g.l.c. coupled with high-resolution mass spectrometry, for the expected product (241) resulting from nucleophilic attack by the lone pair of cyclohexylamine at the electron-deficient centre of the ketocarbene.

Extraction of the reaction mixture with dilute acid gave two products, tentatively identified as dicyclohexylamine (242) and N-phenyl-cyclohexylamine (243) from their mass spectra, which show the correct parent ions and both give the characteristic loss of the fragment of mass 43, peculiar to cyclohexylamines. Budzikiewicz, Djerassi
and Williams\textsuperscript{175} account for this characteristic loss by the following rearrangement:

\[
\begin{align*}
&\text{X} \\
\text{+NH} &\rightarrow \text{+NH} \\
\text{CH}_2 &\rightarrow \text{CH}_2 + \text{CH}_3 + \text{CH}_2 = \text{CH}_2 \\
\text{m;43}
\end{align*}
\]

The mass spectrum of the amine (243) also shows the fragment of m/e 77, giving evidence for the presence of a phenyl group.

The mass spectrum of the neutral compound with molecular ion at m/e 203, also showing loss of the fragment of mass 43, suggests it to be $N$-cyclohexylbenzamide (244). The loss of the fragment of mass 43 is often encountered in the mass spectra of cycloalkyl amides, though the breakdown processes are generally more complex\textsuperscript{175}. The fragment of m/e 105 in the mass spectrum evidences the presence of PhCO in the molecule.

\[
\text{244}
\]

A possible route to $N$-cyclohexylbenzamide is nucleophilic
attack by the cyclohexylamine lone pair at the carbonyl group of benzamide, followed by loss of ammonia (Scheme 41).

![Scheme 41](image)

This accounts for the detection of ammonia on opening the autoclave and gives a possible explanation for the lack of detection of benzamide as one of the reaction products. The formation of dicyclohexylamine and N-phenylcyclohexylamine cannot be simply explained. It is conceivable that the expected product (241) is unstable under the reaction conditions and results in the formation of the latter two products on decomposition.

(b) **Thermal decomposition of sodium 2-bromophenoxide in the presence of benzoates and thiobenzoate as added nucleophiles**

The ability of benzamide to attack ketocarbene intermediates nucleophilically, with subsequent ring closure, led to the choice of other nucleophiles, in which the possibility of ring closure exists once the
Table 9

Thermal Decomposition of Sodium 2-Bromophenoxide in the Presence of Sodium 2-Bromobenzoate in t-Butylbenzene

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (m/100m)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure 1" /></td>
<td>2.7</td>
</tr>
<tr>
<td><img src="image2" alt="Chemical Structure 2" /></td>
<td>3.0</td>
</tr>
<tr>
<td><img src="image3" alt="Chemical Structure 3" /></td>
<td>1.0</td>
</tr>
<tr>
<td><img src="image4" alt="Chemical Structure 4" /></td>
<td>1.2</td>
</tr>
<tr>
<td><img src="image5" alt="Chemical Structure 5" /></td>
<td>2.0</td>
</tr>
</tbody>
</table>
ketocarbene has been attacked.

In the presence of sodium 2-bromobenzoate the expected reaction path is attack by the 2-bromobenzoate anion (245) on the ketocarbene produced by decomposition of sodium 2-bromophenoxide to give a phenoxyde (246), which ring closes to form the lactone (247) (Scheme 42). The final ring closure step may be similar to the proposed intramolecular, final step in the formation of dibenzo-p-dioxin (Scheme 22).

![Scheme 42]

The products actually obtained from this thermal decomposition are shown in Table 9.

Phenol, dibenzo-p-dioxin and 2-hydroxyphenyl phenyl ether are the usual, expected products from the thermal decomposition of sodium 2-bromophenoxide in t-butylbenzene. The formation of the other three products viz., diphenyl ether, 2-bromophenyl phenyl ether
and xanthone (248), can be explained by attack of various nucleophiles in the system on benzyne: the latter derived by thermal decomposition of 2-bromobenzoic acid. McNeilis\textsuperscript{176} has provided evidence for the intermediacy of benzyne in the thermal decomposition of 2-bromo- benzoates at 300-315\degree by trapping experiments with tetracyclone (249) to give 1, 2, 3, 4-tetraphenylnaphthalene (250).

\[ \begin{array}{c}
\text{Ph} \\
\text{Br} \\
\text{COO}^- \\
+ \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{O} \\
\text{249} \\
\rightarrow \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{250} \\
\text{Co} + \text{CO}_2 + \text{Br}^- \\
\end{array} \]

In the thermal decomposition of alkali-metal 2-halobenzoates, xanthone is usually obtained as the major product. McNeilis\textsuperscript{176} has provided evidence for the formation of benzyne by decarboxylation and elimination of halide ion. He proposed a mechanism (Scheme 43) for the formation of xanthone by nucleophilic attack on benzyne by a second molecule of the 2-halobenzoate (251).

The final stage of this mechanism, involving displacement of the halide ion, is reminiscent of the final stage of Scheme 22 in the formation of dibenzo-p-dioxin, but McNeilis merely describes it as an unexceptional displacement.
The formation of diphenyl ether and bromophenyl phenyl ether can be accounted for by nucleophilic addition of phenoxide and 2-bromophenoxide ions, respectively, to benzyne. Such addition of alkoxides to benzyne is well-known\textsuperscript{102}.

Mc Nelis\textsuperscript{176} has also isolated 3, 4-benzocoumarin (252) from the thermal decomposition of 2-bromo- and 2-iodobenzoates. To check for this product, an authentic sample of 3, 4-benzocoumarin was added to a portion of the reaction mixture from the thermal decomposition of the mixture of sodium 2-bromophenoxide and sodium
2-bromobenzoate, but the appearance of a new peak on g.l.c. examination showed it to be absent.

McNelis' report of the formation of 3,4-benzocoumarin suggests that 2-halophenyl anions are not involved in the thermal decomposition of 2-halobenzoates and a cycloaddition mechanism has been postulated\(^\text{102}\) (Scheme 44). In this scheme xanthone arises by reaction of benzyne with the ketoketene \((253)\).

To avoid benzyne formation, the thermal decomposition of a mixture of sodium 2-bromophenoxide and sodium benzoate was carried out and evidence sought for nucleophilic attack by the benzoate anion on the ketocarbene. A quantitative recovery of sodium benzoate as benzoic acid, and a good yield of dibenzo-\(p\)-dioxin \((2O\text{m}/100\text{m})\), however, showed no nucleophilic attack by the benzoate ion to have occurred.
Since it appears from the latter result that sodium benzoate is too weak a nucleophile, the decomposition was carried out using sodium thiobenzoate in an attempt to effect nucleophilic attack. Extraction of the reaction mixture with sodium bicarbonate solution to give benzoic acid and the precipitation of sulphur from the reaction mixture suggested dibenzoyl disulphide (254) to have been formed. Dibenzoyl disulphide is formed by mild oxidation of sodium thiobenzoates and is known to decompose to give benzoic acid and sulphur\textsuperscript{177}.

\[
\text{Ph-C-S-S-C-Ph} \\
\bar{\text{O}} \quad \bar{\text{O}} \\
254
\]

No evidence was found for nucleophilic attack on the ketocarbene by the thiobenzoate anion.

(c) Thermal decomposition of sodium 2-bromophenoxide in the presence of the sodium salt of benzyl alcohol

Although complete loss of bromide ion from sodium 2-bromophenoxide occurred, the only products detected were benzoic acid and benzaldehyde. Since benzoic acid and benzaldehyde are the oxidation products of benzyl alcohol, which was used as the solvent in this case, their formation suggests that any other products may have been reduced, possibly to tars, under the conditions of the decomposition.
5. Thermal Decomposition of 1,2-Bromohydroxypolyycyclic Compounds.

(a) Attempted preparation of the sodium salt of 2-bromo-3-hydroxyfluoranthene

The report by Trost\textsuperscript{24}, that photolysis of 9-diazo-10-keto-4,5-methylenephenanthrene (255) does not lead to formation of the product of the Wolff rearrangement, since the strain involved in ring contraction is too great, was interesting. It suggested that thermal decomposition of the salt of the corresponding 9-bromo-10-hydroxy compound (257) should give a good yield of products resulting from nucleophilic attack on the ketocarbene intermediate (256). Normally, the Wolff rearrangement is thought to be a facile, alternative reaction of ketocarbenes, rather than their undergoing attack by nucleophiles at the electron-deficient centre.

\[ \text{255} \rightarrow \text{256} \leftarrow \text{257} \]

Since serious problems were envisaged in the synthesis of the diazoketone (255), it was decided to attempt the synthesis of the sodium salt of 2-bromo-3-hydroxyfluoranthene (258), which on thermal decomposition should give a ketocarbene (259) similarly
The precursor, 3-amino-2-bromofluoranthene, was readily synthesized but attempts to convert it to the hydroxy compound, via the diazonium salt, failed. Horning et al.\textsuperscript{146} have recently reported a method for converting the diazonium salts of aromatic amines to phenols with considerable ease using trifluoroacetic acid and potassium carbonate. They have carried out such transformations in cases for which all other known methods have failed.

The diazonium fluoroborate was prepared as required by the method, but it failed to decompose and form the product.

Hasan\textsuperscript{178} made many unsuccessful attempts to prepare 2-bromo-3-hydroxyfluoranthene from diazonium salts, which proved to be extraordinarily resistant to decomposition in the usual manner. He prepared the diazonium sulphate of 3-amino-2-bromofluor anthene by the method of Charlesworth\textsuperscript{145} and attempted to convert it to the phenol by numerous methods. Heating with dilute acid of various concentrations for various intervals of time, with and without the passage
of steam through the solution, did not cause decomposition of the
diazonium salt and addition of various metallic salts, and sodium
sulphate, well-known methods of decomposing stable diazonium
salts, also failed. In all cases Hasan observed tar formation and
after similar failures using diazonium salts prepared by other methods
he reverted to more drastic measures. He heated 3-amino-2-bromo-
fluoranthene in sealed tubes in the presence of dilute hydrochloric or
sulphuric acid at various temperatures, but succeeded only in forming
high-melting residues. An attempt to decompose and hydrolyse the
diazonium fluoroborate, by boiling with alkali, resulted in the formation
of an impure oil and in an attempt to prepare 2-bromo-3-methoxyfluor-
anthene, by boiling the diazonium sulphate in methanol, Hasan obtained
2-bromofluoranthene as the only product.

It was decided to attempt the preparation of 2-bromo-3-
methoxyfluoranthene by a method which Hasan had not tried, via the
zinc chloride double salt of the diazonium chloride, by boiling with
methanol as described by Hodgson and Foster\textsuperscript{147}. Although the zinc
chloride double salt was successfully prepared, decomposition in
methanol gave mainly 2-bromofluoranthene, together with 2-bromo-
3-chlorofluoranthene and a trace of the required methoxy- compound.
The formation of 2-bromofluoranthene is not surprising, since Hodgson\textsuperscript{147}
has pointed out that an electrophilic substituent, in this case bromine,
favours hydrogen rather than methoxy replacement. Attack by the
chloride ion of the zinc chloride complex, in this case giving rise to
2-bromo-3-chlorofluoranthene, has also been mentioned by Hodgson\textsuperscript{179}. 
Since this method proved to be unsuccessful, no further attempt was made to prepare 2-bromo-3-hydroxyfluorantheene.

(b) **Thermal decomposition of sodium 1-bromo-2-naphthoxide**

Smith\(^{180}\) reported that 1-bromo-2-naphthol decomposes readily at 130\(^\circ\)C giving off fumes of hydrogen bromide and forming a sublimate of 2-naphthol on further heating. From this observation it was thought that sodium 1-bromo-2-naphthoxide (260) might decompose readily to give the dioxin (261).

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
260 & \quad \rightarrow \\
\text{261}
\end{align*}
\]

The sodium salt (260) was prepared and found to undergo considerable decomposition even on drying in the vacuum pistol at 100\(^\circ\)C, with 29% loss of bromide ion after 24 hours. After treatment of the partly-decomposed salt with water, a yellow solid was filtered off, which on dissolving in chloroform gave seven spots on t.l.c. examination. The solid was not examined further.

The products obtained by extraction with sodium hydroxide solution, after thermal decomposition of a sample of the partly-decomposed salt by boiling in t-butylbenzene, were 2-naphthol and 1,1'-bis (2-naphthol) (262).
The reaction mixture had a green fluorescence and after extraction with dilute sodium hydroxide showed at least seven spots on t.l.c. examination. The expected dioxin (261) was not detected by g.l.c. examination. Since 1,1'-bis (2-naphthol) was detected by g.l.c., the dioxin (261) was assumed to be absent, since it should give a peak with shorter retention time than 1,1'-bis (2-naphthol) under the same g.l.c. conditions. Hinsberg\textsuperscript{167} reported the formation of 1,1'-bis (2-naphthol) by heating 1-bromo-2-naphthol with copper powder at 230° and also by warming a mixture of 2-naphthol and 1-bromo-2-naphthol with sodium methoxide in methanol. By treatment of 1-bromo-2-naphthol, alone, with sodium methoxide in warm methanol he did not obtain the same product but isolated instead a bright-yellow, alkali-insoluble solid, which he did not investigate further.

1,1'-Bis (2-naphthol) is known to be readily formed in good yield by oxidative coupling of 2-naphthol\textsuperscript{181}, suggesting that its formation in the thermal decomposition of sodium 1-bromo-2-naphthoxide is by a mechanism initially involving loss of a bromine atom. This may be
explained by formation of the ketocarbene intermediate (263),
followed by abstraction of a hydrogen atom from the solvent to give
the naphthoxy radical (264), which can then undergo carbon-carbon
ortho-ortho-coupling (Scheme 45). Abstraction of a second hydrogen
atom from the solvent, by the radical (264), explains the formation
of 2-naphthol.

B. Reaction of Bromodurene with "Complex Base"

The reaction of bromodurene with "complex base" (an
equimolar mixture of potassium t-butoxide and sodamide) in boiling
tetrahydrofuran gave results similar to those obtained by Hall from
the reaction of bromodurene with potassium t-butoxide in an autoclave
at 220°C. Thus, "complex base" enabled the reaction to be carried out
under milder conditions than those used by Hall.
Although Caubre and Loubinoux suggested the use of tetrahydrofuran as the solvent in "complex base" reactions they gave no indication that other, similar solvents should not be employed. Reactions were carried out in various solvents viz. dioxan, dimethoxyethane and a mixture of tetrahydrofuran and dimethoxyethane, and the results were compared. The yields of durene, 2,4,5,2',4',5'-hexamethylbibenzyl and bromo-2,4,5,2',4',5'-hexamethylbibenzyl obtained in the different solvent systems are shown in Table 10.

Table 10

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Durene</th>
<th>Bibenzyl</th>
<th>Bromobibenzyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>19</td>
<td>5.9</td>
<td>7.0</td>
</tr>
<tr>
<td>Dioxan</td>
<td>24</td>
<td>1.7</td>
<td>8.5</td>
</tr>
<tr>
<td>DME</td>
<td>15</td>
<td>2.7</td>
<td>12.8</td>
</tr>
<tr>
<td>50:50 THF/DME</td>
<td>21</td>
<td>2.9</td>
<td>10.2</td>
</tr>
</tbody>
</table>

From Table 10 it can be seen that the different solvents lead to some variation in the amounts of the products obtained. The higher-boiling solvent, dioxan, gave an increase in yield of durene and corresponding decrease in yield of hexamethylbibenzyl, whereas dimethoxyethane gave a slight increase in yield of bromohexamethylbibenzyl and corresponding decrease in yield of hexamethylbibenzyl, compared to those obtained in tetrahydrofuran. The yields of the three
Scheme 19
products obtained using the mixture of dimethoxyethane and tetrahydrofuran are in close agreement with those obtained by Hall in the reaction of bromodurene with potassium t-butoxide in the autoclave (Table 11).

Table 11
Reaction of Bromodurene with Potassium t-butoxide at 220°

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (m/100m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durene</td>
<td>24.6</td>
</tr>
<tr>
<td>Bibenzyl</td>
<td>2.7</td>
</tr>
<tr>
<td>Bromobibenzyl</td>
<td>10.7</td>
</tr>
</tbody>
</table>

The similarity between the yields of products obtained using the "complex base" system and those obtained by Hall suggests the same mechanism to apply in both cases. The "complex base" reaction in tetrahydrofuran, which was carried out for seven days, gave two further products. The mass spectra of the latter two compounds suggested them to be 2-(2,4,5-trimethylbenzyl)-tetrahydrofuran (265) and the isomer 3-(2,4,5-trimethylbenzyl)-tetrahydrofuran (266). Both of these compounds showed a molecular ion of m/e 204, one with base peak at m/e 71 showing loss of a fragment of mass 133.

The formation of the substituted tetrahydrofurans (265 and 266) provides evidence for a radical mechanism involving the trimethylbenzyl radical (267) which may react with the solvent. This is in agreement with the radical mechanism postulated by Hall, involving formation of the carbene intermediate (155) (Scheme 19).
Scheme 20
Since Robertson obtained results which contradicted Hall's evidence against an alternative mechanism (Scheme 20) involving nucleophilic displacement of bromine, the test for this evidence was reinvestigated. The nucleophilic displacement mechanism (Scheme 20) involves formation of the bromotrimethylbenzyl bromide (160) which would be expected to react with potassium t-butoxide to give the aryl t-butyl ether (163).

A mixture of isomeric bromotrimethylbenzyl bromides was added to the reaction of bromodurene and "complex base" in
tetrahydrofuran and the reaction mixture was examined for the presence of the corresponding t-butyl ethers. Two new peaks were obtained on examination by g.l.c. coupled with high-resolution mass spectrometry and identified as 2-bromo-3,4,6-trimethylbenzyl t-butyl ether (163) and 3-bromo-2,4,5-trimethylbenzyl t-butyl ether (164) by their mass spectra, which were identical to those obtained by Hall.

The formation of these t-butyl ethers confirms the result obtained by Hall and substantiates evidence against Scheme 20. Hall found that the yields of durene were approximately the same from reactions in both the presence and absence of the added bromotrimethylbenzyl bromides and that the yields of hexamethylbiphenyl and bromohexamethylbiphenyl were less in the reaction in the presence of the added bromides. In the "complex base" system the yields of all the products were found to have decreased, durene in particular, in the reaction in the presence of the added bromides compared to the
yields obtained in their absence. This is not surprising, however, since the base may be used in the formation of ethers in preference to the dehydrobromination of bromodurene.

Conclusions

The products obtained from thermal decompositions of sodium 2-bromophenoxides can be rationalised by a mechanism involving formation of a 1,2-ketocarbene intermediate and subsequent nucleophilic attack at the electron-deficient centre of the ketocarbene. Good evidence is obtained for the exclusion of benzoxirene intermediates in these decompositions but more experimental evidence is required to confirm the intermediacy of benzothiirenes in the thermal decomposition of sodium 2-bromothiophenoxides. The formation of thianthrene, cleanly, by thermal decomposition of sodium 2-bromothiophenoxide and the formation of diaryl ethers and diaryl sulphides in the presence of added sodium phenoxides and thiophenoxides, respectively, may be of synthetic value.

Experiments involving the reaction of bromodurene with "complex base" gave results consistent with those obtained by Hall\(^90\) and confirm the evidence against a mechanism involving the bromotrimethylbenzyl anion as an intermediate.
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