NEW APPROACHES TO THE SYNTHESIS OF
CARBENES AND BENZYNES

BY

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STATEMENT

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

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Signed [Signature]

(M. P. Serridge)
ABSTRACT

The elimination of stable molecules from o-disubstituted benzenes to give benzyne is reviewed, and the synthesis and reactions of new potential benzyne precursors are described.

Benzenetrimethylammonium-2-carboxylate, benzenedimethylsulphonium-2-carboxylate, benzenediazonium-2-sulphonate, the tosylate of salicylic acid, o-sulphobenzoic anhydride and 2-phenyl-1,3-benzoxazin-4-one were prepared. The pyrolysis and photolysis of these o-benzobetaines and cyclic o-disubstituted benzenes were studied under a variety of conditions in the presence and absence of benzyne traps (particularly tetracyclone). In no case was benzyne detected, the main reactions being rearrangement of the betaine or the loss of one stable molecule followed by reaction of the resultant zwitterion.

The desulphurisation of catechol thionocarbonate, another potential route to benzyne, gave the trimer 3-benzodioxolidene benzo-1,4-dioxan-2-one catechol ketal. However, deoxygenation of the analogous 4,5-diphenylidioxolen-2-one gave stilbene through the intermediacy of diphenylacetylene.

Arising from the above use of tetracyclone, its deoxygenation by phosphines and phosphites was
studied. With triphenylphosphine the novel octaphenylfulvalene was formed but tributylphosphine gave tetraphenylcyclopentadiene, thus providing a useful route to this compound. The reaction of tetracyclone and phosphites resulted in the formation of various phosphates, phosphonates and reduction products of tetracyclone; these reactions are discussed and rationalised.

Independent syntheses of octaphenylfulvalene through the intermediacy of tetraphenylcarbenacyclopentadiene from 1-diazo- and 1,1-dibromo-2,3,4,5-tetraphenylcyclopentadiene were also studied. However, hydrogen abstraction or bond insertion by the carbene, rather than its dimerisation, were observed.

Unsuccessful attempts to generate tetraphenylbenzyne are also reported.

Mechanisms are proposed for all the new reactions.
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INTRODUCTION
Elimination of Stable Molecules from \( \alpha \)-Disubstituted Benzene.

\( \beta \)-Eliminations are reactions in which two atoms or groups situated on adjacent carbon atoms are removed with the formation of a new multiple linkage. Thus, in the case of the \( \alpha \)-disubstituted benzene compound (I) the elimination of \( X \) and \( Y \) leads to the formation of benzyne (II).

\[
\begin{align*}
\text{(I)} & \quad \xrightarrow{\text{elimination}} \quad \text{(II)} \\
& \quad \xrightarrow{X + Y} \\
& \quad \xrightarrow{\text{formation of benzyne}}
\end{align*}
\]

(In the above scheme and also in subsequent representations the nature of the charges on \( X \) and \( Y \) are omitted as general cases are being considered.)

The elimination of \( X \) and \( Y \) can proceed by three principal mechanisms:

1. The El mechanism.

One bond (e.g. the C-X bond) is broken first, leading to the formation of a carbonium ion intermediate which undergoes rupture of the C-Y bond to form benzyne.

\[
\begin{align*}
\text{(I)} & \quad \xrightarrow{-X} \quad \text{(II)} \\
& \quad \xrightarrow{-Y} \\
& \quad \xrightarrow{\text{formation of benzyne}}
\end{align*}
\]

2. The Elcb mechanism.
One bond (e.g. the C-Y bond) is broken first, so that the reaction proceeds through an intermediate carbanion.

\[
\begin{align*}
\text{benzene} & \quad \xrightarrow{\gamma} \quad \\text{carbanion} \quad \xrightarrow{x} \quad \text{benzene} \\
\end{align*}
\]

(I)

3. The E2 mechanism.

The elimination of X and Y and the formation of the bond between the adjacent carbon atoms occur simultaneously.

\[
\begin{align*}
\text{benzene} & \quad \xrightarrow{\gamma} \quad \\text{carbanion} \quad \xrightarrow{x} \quad \text{benzene} \\
\end{align*}
\]

(I)

The three elimination mechanisms differ in the order of the breaking of the C-X and C-Y bonds. The mechanism by which a particular β-elimination occurs depends on the relative strengths of the C-X and C-Y bonds and the stability of the transition state. α-Benzobetaines are compounds of the type (III) and interest has been shown recently in these compounds where X and Y are stable molecules. The overall reaction leading to benzyne may be represented as:

\[
\begin{align*}
\text{benzene} & \quad \xrightarrow{\gamma} \quad \text{benzene} + X + Y \\
\end{align*}
\]

(III)
This reaction is favoured by the elimination of two neutral, stable molecules and also by the fact that benzyne itself is a stable, albeit a very reactive, intermediate.

The earliest known example of (III) was made by Hantzsch and Davidson who diazotised anthranilic acid to obtain benzenediazonium-2-carboxylate (IV).

In aqueous solution (IV) was found to lose nitrogen slowly to form salicylic acid in good yield. Thus, the C-N bond is first broken leaving a positive charge on the carbon atom of the benzene ring as in the E1 mechanism. However, the intermediate also carries a negative charge and is thus a zwitterion which, instead of losing a molecule of carbon dioxide, reacts with water to produce salicylic acid.
When (IV) was heated in benzene or in toluene both nitrogen and carbon dioxide were lost and polymeric products resulted. However, decomposition in furan yielded 1,4-dihydronaphthalene-1,4-endoxide (V) (55%) and decomposition in benzene in the presence of anthracene gave tryptycene (VI) (30%).

Diazotisation of anthranilic acid in aprotic media has been used to generate benzyne without actually isolating the inner salt.

The thermal decomposition of (IV) has been studied extensively. Substituted anthranilic acids have been used to ascertain the intermediacy of benzyne in these reactions. For example, when 4-ido- and 5-iodobenzenediazonium carboxylates were decomposed in the presence of benzoic acid, the ratio of the two isomeric products was the same in each case. Deviation of the meta:para ratio from 1:1 was interpreted in terms of the effect of the iodine atom. This and further reactions (where iodine was replaced by...
5.
fluorine and by a nitro group) showed that the thermal
de decomposition of (IV) proceeded by way of an intermediate
having benzyne type symmetry.

\[
\begin{align*}
\text{N}_2^+ & \quad \text{I} \\
\text{CO}_2^- & \quad \text{I} \\
\text{I} & \quad \text{I}
\end{align*}
\]

Competitive Diels Alder reactions employing
cyclohexadiene and furan as traps for the reactive
intermediate variously generated from (IV), from 1,2,3-
benzothiadiazole-1,1-dioxide, and from o-fluorobromobenzene
with lithium amalgam, magnesium, and lithium magnesium
amalgam in the presence of magnesium bromide were performed.
The constancy of the ratio of products from these reactions
supported the conclusion that they all proceed through the
same intermediate which is benzyne or benzyne solvated with
tetrahydrofuran \(^9\). However, in its reactions with 2-pyridones
(IV) gave products differing markedly from those obtained
using chlorobenzene and sodamide as the benzyne precursor \(^10\).
Thus, when 1-methyl-2-pyridone was allowed to react with
diazotised anthranilic acid the adduct (VII) (10%) was
obtained, whereas the product obtained using chlorobenzene
and sodamide was 1-methyl-3-phenyl-2-pyridone (VIII).

\[ \text{(VII)} \]
\[ \text{(VIII)} \]

In the course of these experiments acridone (IX) was isolated as a byproduct of the reaction involving (IV) and its formation was thought to result from attack of benzyne on anthranilic acid.

\[ \text{(IX)} \]

Tetrachlorobenzyne has been identified as an intermediate in the thermal decomposition of 3,4,5,6-tetrachlorobenzenediazonium-2-carboxylate.\(^\text{11}\)

The photolytic decomposition of (IV) has led to evidence for the existence of gaseous benzyne from the coincident results of time resolved optical and mass spectrometry.\(^\text{12-14}\) The decay of the transient absorption spectrum attributed to benzyne was accompanied by increasing intensity of the biphenylene spectrum. Observation of the decomposition of (IV) in a time of flight mass spectrometer showed, initially, peaks at \( m/z = 28,44 \) and 76 corresponding to nitrogen, carbon dioxide and benzyne respectively. The decay of the 76 peak was matched by the rise of the peak at 152 corresponding to
biphenylene (X). The reaction was thus assumed to be of the form:

\[ \text{(IV)} \rightarrow \text{biphenylene} + \text{N}_2 + \text{CO}_2 \]

Yaroslavsky proposed a two step decomposition corresponding to a formal El mechanism, the first step being loss of nitrogen with the formation of the intermediate (XI):

\[ \text{(IV)} \rightarrow \text{intermediate (XI)} \]

Thus, reactions with isocyanides gave phthalimides:

\[ \text{(XI)} + \text{C} \equiv \text{N} \rightarrow \text{phthalimide} \]

In 1960 the preparation of the betaine diphenyliodonium—
2-carboxylate (XII) was reported\textsuperscript{16}. The procedure was modified by Le Goff\textsuperscript{17} who showed that thermal decomposition of (XII) yielded benzyne which was trapped with tetraphenyl-cyclopentadienone (tetracyclone) and with anthracene.

\[
\begin{align*}
\text{(XII)} & \rightarrow \text{Biphenylene} \\
& \rightarrow \text{Iodobenzene}
\end{align*}
\]

Flash pyrolysis of solid (XII) at 325° yielded biphenylene and iodobenzene\textsuperscript{17}. However, it was found that under conditions which were too mild for decomposition (XII) rearranged thermally to phenyl 2-iodobenzoate (XIII) (5\%)\textsuperscript{18}.

\[
\begin{align*}
\text{(XII)} & \rightarrow \text{(XIII)}
\end{align*}
\]

When (XII) was decomposed in the absence of a benzyne trap, xanthone (XIV) and 3,4-benzocoumarin (XV) were obtained. Their formation was postulated via the \(\beta\)-lactone intermediate proposed by Yaroslavsky for the decomposition of (IV)\textsuperscript{18}. 
Therefore, the decomposition of (XII) to form benzyne proceeds by an El mechanism.

When the phenyl group of (XII) carried an electron withdrawing substituent rearrangement to the ester occurred, as was to be expected, rather than formation of benzyne. Correspondingly, electron donating substituents did not repress benzyne formation.

Fieser used the betaines (IV) and (XII) as benzyne precursors in a series of reactions in which he demonstrated the transient existence of the hitherto unknown isobenzofuran.

Aprotic diazotisation of o-aminophenylboric acid (XVI) led to the generation of benzyne and its trapping with anthracene.
The aminocarbinol (XVII) was diazotised and the diazonium salt allowed to decompose at room temperature. Isolation of the 2,4-dinitrophenylhydrazone of p-methoxyacetophenone (0.3%) indicated the possible generation of benzyne.

Quaternisation of methyl N,N-dimethylanthranilate and subsequent hydrolysis yielded the betaine (XVIII).
Willstätter and Kahn\textsuperscript{23} reported the rearrangement of (XVIII) on melting to methyl \(N,N\)-dimethyl anthranilate. An exactly similar rearrangement had been observed in the case of the \textit{meta}-isomer\textsuperscript{24}. However, rearrangement of (XVIII) was accompanied by loss of carbon dioxide in a side reaction to give dimethyl aniline. Owing to difficulty encountered in drying the betaine it was not known whether this reaction involved water.

Reactions analogous to the elimination of two stable molecules from an \(o\)-benzobetaine are the fragmentations of molecules consisting of benzene with an \textit{ortho}-fused ring system. Wittig diazotised aniline-2-sulphinic acid to give the sulphinate analogue of (IV), 1,2,3-benzothiadiazole-1,1-dioxide (XIX)\textsuperscript{25}.

The product (XIX) was given a cyclic structure rather than that of the betaine on the basis of its solubility in non-polar solvents, the insensitivity of its rate of decomposition to structural and environmental factors, and
also its reduction by zinc and acetic acid to 1,2,3-benzothiadiazoline-1,1-dioxide (XX).

Mild thermolysis of (XIX) led to the generation of benzyne which was identified by its adducts with furan, cyclopentadiene, anthracene, α-pyrone, 2,5-diphenyl-3,4-benzofuran and phenyl azide.

The attempted formation of biphenylene from dibenzothiaza-cycloheptatriene-dioxide (XXI) was unsuccessful. At 700° dibenzothiophene-1,1-dioxide (XXII) was formed (10%)<sup>28</sup>.

\[
\text{XXI} \xrightarrow{700°} \text{XXII}
\]

Fields obtained dibenzofuran from pyrolysis of (XXII) by rearrangement to the sulphinate ester (XXIII) followed by loss of sulphur monoxide.<sup>28</sup>

\[
\text{XXII} \rightarrow \text{XXIII}
\]

The mass spectrum of (XXII) showed that the behaviour on electron impact closely followed that on pyrolysis.

Wittig obtained evidence of benzyne generation by photolysis and pyrolysis of phthaloyl peroxide (XXIV)<sup>27</sup>. Photolysis in the presence of tetracyclone yielded 1,2,3,4-tetraphenylnaphthalene (7.4%) and pyrolysis at 600° yielded
biphenylene (27%). However, no products were obtained which suggested a stepwise loss of carbon dioxide.

Evidence for a stepwise loss of stable molecules from an ortho-fused ring system was obtained by Brown and Solly, who pyrolysed indanetrione (XXV) at 500–800°C and obtained benzocyclobutenedione (XXVI), anthraquinone (XXVII), fluorenone (XXVIII) and phenanthrenequinone (XXIX) together with biphenylene and triphenylene. They suggested the following scheme:
These schemes closely parallel the stepwise loss of carbon monoxide which occurs in the mass spectral fragmentation of the indanetione molecular ion.

The mass spectrum of phthalic anhydride showed an ion of $m/e = 76$ which corresponded with benzyne ($C_6H_4$). Fields and Meyerson$^{30}$ pyrolysed phthalic anhydride in benzene at 690°. The reaction products consisted of biphenyl (85%) and naphthalene (15%). This, together with mass spectral evidence of fluorenone as a minor product suggested that the reaction proceeded by a stepwise loss of carbon dioxide and carbon monoxide.
When the pyrolysis was carried out in o-, m- and in p-dichlorobenzene the ratios of the products showed a strong preference of benzyne for 1,4- over 1,2- addition. In general the competing reactions follow the scheme:

The generality of the generation of arynes by pyrolysis of anhydrides was shown by Fields and Meyerson who pyrolysed nine aromatic and two heterocyclic anhydrides in admixture with pyridine. However, tetrachlorophthalic anhydride gave low yields of products derived from tetrachlorobenzyne and tetrabromophthalic anhydride gave no products attributable
to tetrabromobenzene.

Pyrolysis of tetrachlorophthalic anhydride in the vapour phase gave hexachlorobenzene and octachloro-
biphenylene. On the other hand, tetrabromophthalic anhydride gave only hexabromobenzene and none of the perhalogenated biphenylene.33
1. Benzene and other aromatic solvents, methylene chloride and ether were purified by refluxing over and distilling from calcium hydride. Aromatic solvents and methylene chloride were stored over molecular sieves (type 5A) and ether over sodium wire. Petrol refers to petroleum spirit b.p. 40-60°.

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

3. Column chromatography was performed using basic alumina (Spence type H), neutral alumina (Woelm) or silica gel (B.D.H. or Hopkin & Williams M.F.C.). Chromatographic fractions containing insignificant amounts of material are not recorded.

4. Infrared (i.r.) spectra were recorded in the range 4000-650 cm.\(^{-1}\) on a Perkin Elmer 237 spectrophotometer. Solid samples were run as nujol mulls and liquids as thin films, both between rock salt plates. The absorption peaks of new compounds were corrected using polystyrene as reference.
5. Ultraviolet (u.v.) spectra were recorded in the range 200-450 m\(\mu\) on a Unicam SP800 spectrophotometer. Absolute ethanol was used as solvent.

6. Proton magnetic resonance (p.m.r.) spectra were recorded on a Perkin Elmer R 10 60 Mc/s or a Varian A60 instrument. Deuteriochloroform and carbon tetrachloride were used as solvents with tetramethysilane as the internal reference.

7. Mass spectra were recorded on an Associated Electrical Industries M.S.9 spectrometer.

8. Gas liquid chromatography (G.L.C.) was performed on a Perkin Elmer F11 gas chromatograph with nitrogen carrier gas and a flame ionisation detector. A Honeywell recorder fitted with a disc integrator was used.

9. Melting point (m.p.) determinations were carried out in an electrically heated block apparatus, using corrected thermometers, the sample being contained in a capillary tube.

10. Where possible, compounds were characterised by comparison of their melting points and mixed melting points (m.m.p.) and i.r. spectra with those of authentic specimens.

11. Photolyses were carried out using a Hanovia 500 watt medium pressure lamp.
EXPERIMENTAL
19.

EXPERIMENTAL SECTION I

o-BENZORETAILNES

1. PREPARATION AND REACTIONS OF BENZENETRIMETHYLAMMONIUM-2-CARBOXYLATE.

(i) N-Methylanthranilic Acid.

Anthranilic acid (50 g., 0.37 mol) in an equivalent amount of aqueous sodium hydroxide solution (14.6 g. in 200 ml.) was cooled in ice. Dimethyl sulphate (34.5 ml., 0.37 mol.) was added with stirring over 0.25 hr. Stirring was continued for a further 0.5 hr. The separated N-methylanthranilic acid was removed by filtration, washed with water and dried (43.7 g., 79.3%), m.p. 157-163°, (lit. m.p. 175-182°).

(ii) Methyl N-Methylanthranilic acid.

N-Methylanthranilic acid (40 g., 0.25 mol.) was refluxed in dry methanol with concentrated sulphuric acid (10 ml.) for 100 hr. The solvent was removed and an ethereal solution of the residue was washed with aqueous sodium carbonate and then with water. The ethereal solution was dried and evaporated leaving the ester as a brown, viscous liquid (31.8 g., 73%).
(iii) **Methyl N,N-Dimethylantranilate.**

The ester (31.8 g., 0.18 mol.) was stirred with an excess of iodomethane (50 ml.) for 24 hr. The precipitated hydriodide (5.0 g.) was removed by filtration. More of the hydriodide was collected over a period of 200 hr. The hydriodide was obtained as a pale yellow solid (41.0 g., 96%), m.p. 153-155° (lit. m.p. 163° after crystallisation).

The hydriodide (20.5 g, 0.09 mol.) was dissolved in an excess of aqueous potassium hydroxide solution and a brown oil separated. The mixture was extracted with ether and the ethereal solution was dried and evaporated to give methyl N,N-dimethylantranilate as a light brown liquid (12.0 g., 97%).

(iv) **Benzenetrimethylammonium-2-carboxylate.**

The above ester (12.0 g., 0.07 mol.) was treated with iodomethane as in (iii). After 200 hr. the methiodide was obtained in quantitative yield as a pale yellow solid, m.p. 147-150° (lit. m.p. 153°).

The methiodide (10.0 g., 0.05 mol.) was stirred with an aqueous suspension of freshly prepared silver oxide. The mixture was filtered and the filtrate evaporated to dryness. The betaine was obtained as a white solid (5.6 g., 98%). Crystallisation from ethanol gave colourless crystals, m.p. 226-227° (lit. m.p. 227°).

The overall yield based on anthranilic acid was 39%.
(Found: C, 64.9; H, 7.3; N, 7.3. Calc. for C₁₀H₁₃NO₂: C, 67.0; H, 7.3; N, 7.8%) A satisfactory analysis could not be obtained.

m/e at 70 e.v. 179, 164, 148, 132, 118, 105, 104, 91, 77, 57, 44; at 16 e.v. 179, 164, 148, 132.

ν max. 1590 (broad), 1062, 1048, 945, 938, 850, 808, 790, 762, 732, 710 cm⁻¹

**Pyrolysis of the Betaine.**

(i) The betaine was heated at 100°/0.1 mm. Methyl N,N-dimethylantranilinate (87%) was obtained.

(ii) Benzenetrimethylammonium-2-carboxylate (0.25 g., 1.4 mmol.) was heated with zinc powder (3.0 g.). White fumes were evolved but no effect was observed on moist universal pH paper. Heating was continued until a brown liquid was observed to reflux in the reaction vessel. The mixture was cooled and extracted several times with ether to give methyl N,N-dimethylantranilinate (0.2 g., 80%), (shown by comparison of i.r. spectra).

(iii) The above experiment was repeated in the presence of tetraphenylcyclopentadienone (tetracyclone). T.L.C. showed the complete absence of 1,2,3,4-tetraphenyl-naphthalene.

**Photolysis of the Betaine.**

A solution of the betaine (0.5 g., 2.8 mmol.)
in dimethylformamide (80 ml.) was irradiated in a pyrex vessel for 2 hr. under nitrogen. The solution was poured into water (400 ml.), acidified and extracted with ether. The ethereal solution gave benzoic acid (320 mg., 93%), m.p. and m.m.p. 120-121°. During the photolysis no trimethylamine could be detected by passing the reaction gases (carried by the stream of nitrogen) through an aqueous solution of picric acid.

This experiment was repeated but without the irradiation. The betaine was recovered and no benzoic acid was found.
Two methods were used in the preparation of this betaine:

1. From S-Methylthiosalicylic Acid.

S-Methylthiosalicylic acid was prepared from thiosalicylic acid and dimethyl sulphate in alkaline solution. 34

S-Methylthiosalicylic acid (1.68 g., 0.01 mol.) was stirred in dimethyl sulphate (50 ml.) at 100° for 24 hr. The dark brown solution was poured into ether (400 ml.) with vigorous stirring and a pale brown gum separated. The ether was decanted and the residual gum was washed several times with ether and then stirred with an aqueous suspension of freshly prepared silver oxide. The mixture was filtered and the filtrate evaporated to dryness. The residue was extracted with hot ethanol which on cooling gave benzenedimethylsulphonium-2-carboxylate as clusters of colourless needles (0.6 g., 33%), m.p. 164-165°.

(Found: C, 58.4; H, 5.1. C₉H₁₀O₂S requires: C, 59.3; H, 5.5%) A satisfactory analysis could not be obtained.

m/e at 70 e.v. 182, 151, 122, 121, 85, 77, 71; at 14 e.v. 182, 167, 151, 150, 122.

ν_max. 1595, 1570, 1240 (broad), 1063, 1015, 848, 765, 720 cm⁻¹
(ii) From Methyl S-Methylthiosalicylate.

Thiosalicylic acid (4.0 g., 0.025 mol.) in dry ether (100 ml.) was shaken with a solution of diazomethane (3.0 g., 0.07 mol.) in dry ether (50 ml.). After frothing had subsided the solution was evaporated to dryness and the pale yellow residue was crystallised from petrol-ether to give pale yellow needles of methyl S-methylthiosalicylate (3.9 g., 82.5%), m.p. 64-66°, (lit. m.p. 66-67°). When S-methylthiosalicylic acid (8.0 g., 0.05 mol.) was treated with diazomethane (3.0 g., 0.07 mol.) as above, methyl S-methylthiosalicylate was obtained (4.1 g., 47.3%), m.p. 65-66°. An attempt to prepare the ester from dimethyl sulphate and thiosalicylic acid in aqueous sodium hydroxide was unsuccessful and the acid was quantitatively recovered.

Methyl S-methylthiosalicylate (1.82 g., 1 mmol.) was stirred for 2 hr. in dimethyl sulphate (25 ml.) and then the solution was poured into ether (250 ml.) A light brown gum separated. The ether was decanted and the gum was washed repeatedly with ether and stirred with an aqueous suspension of freshly prepared silver oxide at 60°. The mixture was filtered and the filtrate evaporated to dryness. The residue was extracted with hot ethanol, the solution charcoaled, filtered and cooled to give the betaine as colourless needles (1.2 g., 66%), m.p. and m.m.p. 163-164°.
**Attempted Formation of the Betaine.**

When S-methylthiosalicylic acid was heated to reflux in an excess of iodomethane, it was recovered almost quantitatively. Similarly, it was unaffected by stoichiometric amounts of dimethyl sulphate on refluxing in methanol, ethanol, nitromethane or dimethylsulphoxide (the last two producing considerable amounts of intractable tars).

Methyl S-methylthiosalicylate was also found to be unaffected by iodomethane.

**Pyrolysis of the Betaine.**

(i) The betaine (0.9 g., 5 mmol.) was heated under reflux in dry dimethylformamide for 12 hr. under nitrogen. The solution was filtered leaving an amorphous grey powder (38 mg.), m.p. > 300°. The filtrate was poured into a large excess of water and the mixture was extracted with ether. The ethereal solution gave methyl S-methylthiosalicylate (266 mg., 29%), m.p. and m.m.p. 64-66°. The aqueous layer was acidified with dilute hydrochloric acid and again extracted with ether to give a trace of S-methylthiosalicylic acid.

(ii) The betaine (1.82 g., 0.01 mol.) and tetracyclone (3.86 g., 0.01 mol.) were heated under reflux for 24 hr. in dry diethyl digol. The solution was poured into an excess of water and the mixture was extracted with ether.
The ethereal extract was chromatographed on neutral alumina. Elution with petrol-ether (10:1) gave methyl S-methylthiosalicylate (660 mg., 32%); petrol-ether (4:1) gave tetracyclone (3.6 g., 95%).

(iii) The betaine was pyrolysed at 300°. Much charring occurred and after cooling extraction with ether left intractable tars. The ethereal solution gave methyl S-methylthiosalicylate (6%). When the betaine was pyrolysed at 350°/0.3 mm. the ester was again obtained (15%). This experiment was repeated with an intimate mixture of the betaine and sodium chloride. Methyl S-methylthiosalicylate was obtained by ether extraction of the cooled mixture (27%).

**Photolysis of the Betaine.**

The betaine (0.4 g., 22 mmol.) was irradiated in dry dimethylformamide for 3 hr. under nitrogen. Traces of a silver mirror were observed on the surfaces of the reaction vessel and the solution darkened. The solution was poured into water and acidified. Ether extraction gave S-methylthiosalicylic acid (33 mg., 8%), m.p. 150-154°, m.m.p. 156-158°.

When the photolysis was carried out over 15 hr. the solution became black. It was filtered leaving a black amorphous solid (35 mg.), m.p. > 300°. The filtrate was worked up as above but no identifiable products were obtained.
3. PREPARATION AND REACTIONS OF BENZENEDIAZONIUM-2-SULPHONATE.

(i) As described by Hurtley and Smiles\textsuperscript{36}, a cooled solution of sodium nitrite (4.0 g.) was slowly added to a mixture of aniline-2-sulphonic acid (10 g., 0.07 mol.) and crushed ice (10 g.) cooled in an ice-salt bath, the temperature of the mixture being kept below 5°. Concentrated hydrochloric acid (65 ml.) was added dropwise and the mixture was stirred vigorously. The solid diazonium compound was removed by filtration and washed with ethanol and dry ether. It was obtained as an off-white crystalline solid (4.2 g., 40%), m.p. 121-122° (dec.). Slow heating caused it to soften and darken at 121° followed by rapid decomposition over 140°.

(ii) Aniline-2-sulphonic acid (1.5 g., 9 mmol.) was stirred in ethanol (25 ml.) at 0°. Concentrated hydrochloric acid (1.4 ml., 14 mmol.) was added dropwise followed by the dropwise addition of amyl nitrite (1.2 ml.) at 0° with vigorous stirring. After 2 hr. the mixture was filtered and the solid diazonium compound (1.35 g., 84%) washed with ethanol and dry ether.

Pyrolysis of Benzenediazonium-2-sulphonate.

(i) Benzenediazonium-2-sulphonate (0.5 g.) was refluxed in water (20 ml.) for 1 hr. The solution became yellow.
The water was removed on the rotary evaporator, leaving a brown solid (320 mg.) m.p. > 300°. This compound gave a purple colour with aqueous ferric chloride solution. It failed to give any reaction with bromine water.

(ii) Benzenediazonium-2-sulphonate (0.9 g., 5 mmol.) and tetracyclone (1.9 g., 5 mmol.) were refluxed in diethyl digol (40 ml.) over night. The solution was poured into water (200 ml.) and extracted with ether. The ethereal extract showed the complete absence of 1,2,3,4-tetraphenylnaphthalene on T.L.C.

Photolysis of Benzenediazonium-2-sulphonate.

The betaine (0.5 g.) in water (50 ml.) was irradiated for 5 hr. under nitrogen. The water was removed by distillation leaving a brown solid (374 mg.) identical to that obtained above.
4. **ATTEMPTED PREPARATIONS OF o-(4-PYRIDOXY)BENZOIC ACID.**

(i) **From Methyl Salicylate and 4-Chloropyridine.**

Methyl salicylate was distilled and added dropwise to a solution of sodium in dry methanol. The white sodium salt was precipitated, filtered and dried under reduced pressure.

Commercial 4-chloropyridine hydrochloride was dissolved in water and the solution was made strongly alkaline with aqueous potassium hydroxide solution. The liberated 4-chloropyridine was extracted with ether, dried, the ether evaporated and the residue distilled, b.p. 19-21°/0.5 mm.

The sodium salt of methyl salicylate (8.8 g., 0.05 mol.), 4-chloropyridine (5.6 g., 0.05 mol.) and freshly prepared activated copper powder (0.1 g.), were heated at 180-190° for 1 hr., care being taken to exclude moisture. After cooling, the mixture was extracted first with ether and then with water. The aqueous extract was extracted with ether and the combined ethereal solutions were dried and evaporated. The residue (2.6 g.) was fractionally distilled. Tars and a trace of salicylic acid were obtained.

Experiments were also performed with the potassium salt of salicylaldehyde and 4-chloropyridine without success.
(ii) **From Methyl Salicylate and Pyridyl-4-pyridinium Dichloride.**

Dry pyridyl-4-pyridinium dichloride (10 g., 44 mmol.), the dry sodium salt of methyl salicylate (8.8 g., 50 mmol.) and methyl salicylate (360 mmol.) were heated on a steam bath for 1 hr., and then at 170-180° for 3 hr. The mixture was cooled and extracted with ether. The ether was evaporated and methyl salicylate (36 ml., 75%) was removed by distillation. The residue was an intractable tar. The ether insoluble material proved inseparable by distillation. Ethanol extraction left a dark brown intractable residue (2.7 g.) m.p. > 300°. The ethanolic extract was chromatographed on silica and salicylic acid (1.5 g.) was obtained, m.p. and m.m.p. 159-160°.

When the sodium salt of methyl salicylate and pyridyl-4-pyridinium dichloride were stirred in dimethylsulphoxide for 24 hr. at room temperature, 3 hr. at 100° or 5 hr. at reflux, only intractable tars were recovered. Similar results were obtained from reactions involving the potassium salt of salicylaldehyde.
Salicylaldehyde (12.2 g., 0.1 mol.) in dry pyridine (100 ml.) was cooled to 0° and toluene p-sulphonyl chloride (tosyl chloride) (21 g., 0.11 mol.) was added. The mixture was stirred for 2 hr. in the cold and was then poured into water (500 ml.). A white solid separated. The mother liquor was decanted and the residual solid was taken up in ether. The solution was washed several times with water, dried and evaporated leaving a gum which on trituration with petrol gave the tosylate of salicylaldehyde (11.2 g., 40%), m.p. 37-38° (lit.® m.p. 39-60°). This tosylate was mixed with an equivalent amount of freshly prepared silver oxide in aqueous sodium hydroxide (4 equivalents). The mixture was warmed at 60° for 0.25 hr., filtered and the residue washed with warm water. The combined filtrate and washings were acidified and extracted with ether. The ethereal solution was washed with water, dried and evaporated to give the tosylate of salicylic acid (3.0 g., 43%), m.p. 139-161° (lit.® m.p. 134-136°). Crystallisation from ether gave colourless leaflets, m.p. 163-164°.

(Found: C, 57.5; H, 4.1; S, 10.9. Calc. for C₁₄H₁₂O₆S: C, 56.9; H, 4.1; S, 10.9%) Equivalent weight by titration against N/10 sodium hydroxide = 300. Calculated for
Hydrolysis with hot concentrated potassium hydroxide solution gave salicylic acid (86%); an ethereal solution of diazomethane gave the tosylate of methyl salicylate, m.p. 81-83°, m.m.p. 82-84°, (lit.\(^3\) m.p. 85-87°).

Methyl salicylate and tosyl chloride were reacted as above to give the tosylate of methyl salicylate, (9.4%), m.p. 83-84°. This tosylate was shaken for 48 hr. with N/10 sodium hydroxide solution (1 equivalent). The mixture was filtered leaving the tosylate of methyl salicylate (90%), and the filtrate was acidified and extracted with ether. The ethereal solution gave the tosylate of salicylic acid (6.3%), m.p. 152-158°, m.m.p. 158-160°. The tosylate of methyl salicylate was also converted to the tosylate of the acid (12%) by refluxing with sodium iodide (1 equivalent) in dimethylsulphoxide.

Salicylic acid (13.8 g., 0.1 mol.) and tosyl chloride (19.1 g., 0.1 mol.) were stirred for 12 hr. in pyridine (100 ml.) at 0-5°. The solution was poured into water and the white precipitate was filtered and dried. Crystallisation from chloroform gave disalicylde as colourless platelets (2.0 g., 14%), m.p. 206-208°.

(Found: C, 69.3; H, 3.3; M.W. 240. Calc. for \(C_{14}H_8O_4\):
C_{70.0}; H, 3.3; M.W. 240)

The aqueous solution was acidified and extracted with ether to give the tosylate of salicylic acid as an off-white solid (300 mg., 1%), m.p. 147-154°, m.m.p. 152-156°.

Pyrolysis of the Sodium Salt.

The tosylate of salicylic acid in an ethanol-water mixture was neutralised with N/10 sodium hydroxide solution. The solution was evaporated to dryness leaving the sodium salt (i.r.) as a colourless amorphous solid. The sodium salt (1.0 g., 3 mmol.) was heated at 350°/0.3 mm. A sublimate formed which was found to be disalicylilde (300 mg., 50%), m.p. 201-204°, m.m.p. 204-205°. An amorphous residue was also obtained (340 mg.), m.p. > 300°, and this was not examined further.

When the sodium salt was heated under reflux in diethyl digol in the presence of tetracyclone, no 1,2,3,4-tetraphenylnaphthalene was observed on T.L.C.

Photolysis of the Sodium Salt.

The sodium salt (0.5 g., 1.5 mmol.) in dry dimethylformamide (75 ml.) was irradiated for 6 hr. in an atmosphere of nitrogen. The solution was poured into water (400 ml.) and extracted with ether. The ethereal solution gave a dark brown gum (140 mg.). This was chromatographed on neutral alumina. No identifiable
products were obtained. Photolyses over longer periods of time gave similar results.
SECTION II

o-SULPHOBENZOIC ANHYDRIDE

Saccharin (o-sulphobenzoic imide) was mixed with water and concentrated hydrochloric acid and heated under reflux to form ammonium o-sulphobenzoate (88%, lit. 90%). By warming with thionyl chloride in benzene this was converted into o-sulphobenzoic anhydride (79.3%, lit. 64-66%), m.p. 124-126°, (lit. m.p. 126-127°).

m/e at 70 e.v. 184, 120, 104, 92, 76, 64, 44, 50; at 14 e.v. 184, 120.

ν max. 1838, 1818, 1590, 1360, 1200 (broad), 1058, 1018, 980, 850, 800, 780, 755, 745, 694, 665 cm⁻¹

At 200°/0.3 mm. the anhydride sublimed unchanged. At normal pressures it was distilled without decomposition at 320°.

The anhydride (1.0 g.) in dry acetonitrile was irradiated under nitrogen for 3 hr. The solvent was removed and the residue extracted with chloroform. The chloroform solution was shaken with aqueous sodium hydroxide solution which on acidification and ether extraction gave benzoic acid (18 mg., 4%), m.p. 114-117°, m.m.p. 119-121°.
Experiments with Chlorotris(triphenylphosphine) Rhodium I.

Rhodium trichloride (1.0 g.) and triphenylphosphine (6.0 g.) in absolute ethanol (150 ml.) were heated under reflux for 20 hr. Red crystals of the rhodium complex deposited and were filtered from the hot solution, (3.3 g., 73%).

(i) Reaction with o-Sulphobenzoic Anhydride.

The rhodium complex (50 mg., 0.05 mmol.) and o-sulphobenzoic anhydride (360 mg., 2 mmol.) were heated at 260° for 0.25 hr. The evolution of sulphur dioxide was ascertained by potassium dichromate paper. The mixture was cooled and extracted with ether. The ethereal solution was extracted with aqueous sodium carbonate solution which on acidification and further ether extraction gave benzoic acid (27 mg., 12%). The remaining ethereal solution was chromatographed on silica. Ether-methanol (50:1) gave triphenylphosphine oxide (7 mg., 50% theoretical for the elimination of one molecule of triphenylphosphine). When the above reaction was carried out at 220°, no sulphur dioxide was evolved but a small amount of a rhodium complex was isolated which gave off sulphur dioxide on heating. The rhodium complexes isolated in the above experiments all showed the characteristic triphenylphosphine type spectrum in the region 1600-650 cm. and also showed a sharp peak at 2040 or 2060 cm. Reaction of the rhodium complex in benzene with
sulphur dioxide gave a yellow solid which showed no peaks at 2040 or 2060 cm\(^{-1}\). The complexes were not investigated further.

(ii) Reaction with Diphenylcyclopropenone.

Diphenylcyclopropenone was made by the method described by Breslow.\(^2\) Dibenzyl ketone was brominated in glacial acetic acid to give \(\alpha,\alpha'-\)dibromodibenzyl ketone, (90%). This was dissolved in methylene chloride and added to a methylene chloride solution of triethylamine. The diphenylcyclopropenone was isolated as its bisulphate which gave diphenylcyclopropenone as slightly pink needles (20%), m.p. 118-120°, (lit\(^2\) m.p. 119-120°).

(a) Diphenylcyclopropenone (103 mg., 0.5 mmol.) and the rhodium complex (462 mg., 0.5 mmol.) were shaken at room temperature for 2 hr. in benzene. T.L.C. showed the complete absence of diphenylcyclopropenone. The solvent was removed and the residue chromatographed on silica. Elution with ether gave cis-1,2-diphenlacrylic acid, (24 mg., 25%), m.p. 168-171°, m.m.p. 173-175°.

(b) Diphenylcyclopropenone (103 mg., 0.5 mmol.) and the rhodium complex (462 mg., 0.5 mmol.) in dry benzene were refluxed for 8 hr. The products were chromatographed on silica. Petrol-benzene (20:1) gave diphenylacetylene (tolan) (63 mg., 70%) m.p. and m.m.p. 60-62°; benzene gave a rhodium complex (51 mg.), m.p. 210-213°; ether gave triphenylphosphine oxide (147 mg.), m.p. and m.m.p.
154-156°C. The rhodium complex, probably a rhodium-carbonyl complex (i.r. showed a strong, sharp peak at 1965 cm.⁻¹), was not investigated further.

(c) Diphenylcyclopropenone (103 mg, 0.5 mmol.) and chlorocarbonylbis(triphenylphosphine) iridium (390 mg, 0.5 mmol.) were refluxed in benzene for 8 hr. Chromatography gave tolan (38 mg, 44%) and diphenylcyclopropenone (54 mg, 53%) together with unidentified iridium complexes.

2-PHENYL-3,1-BENZOXAZIN-4-ONE

N-Benzoylanthranilic acid was prepared by the method of Steiger. This acid (11.2 g, 0.05 mol.) and acetic anhydride (20.4 g, 0.2 mol.) were refluxed for 1 hr. Acetic anhydride (15 ml) was then collected by fractional distillation below 139°C through an electrically heated column. The remaining solvent was removed under reduced pressure. On cooling the residue in the flask solidified. Crystallisation from ethyl acetate-hexane gave pale buff needles of 2-phenyl-3,1-benoxazinin-4-one, (9.4 g, 85%), m.p. 123-124°C, (lit. m.p. 123-124°C).
m/e 223, 179, 146, 105, 77, 76.

νmax. 1760, 1600, 1570, 1310, 1257, 1060, 1035, 1024, 1008, 760, 680 cm.⁻¹

This benoxazizinone was found to be stable to
distillation at normal pressures, sublimation at 300°/0.3 mm. and irradiation in furan for 12 hr. under nitrogen.
SECTION III

CYCLIC THIONOCARBONATES AND CARBONATES

1. CATECHOL THIONOCARBONATE

The method of Autenreith and Hefner was used to prepare catechol thionocarbonate. Thiophosgene was added dropwise to a vigorously stirred solution of catechol in a large excess of aqueous sodium carbonate. The mixture was stirred for 18 hr. and then filtered. The violet residue was washed with cold water and dried, (47%), m.p. 151-153°. Sublimation gave pale yellow needles, m.p. 154-155°, (lit. m.p. 154°).

(Found: C, 55.3; H, 2.7; S, 21.4. Calc. for C₇H₆O₆S:
C, 55.3; H, 2.6; S, 21.0%)

$\gamma_{\text{max}}$ 1352, 1295, 1255, 1235, 1215, 1120, 1050, 1010, 985, 948, 900, 825, 757 cm⁻¹

Desulphurisation of Catechol Thionocarbonate.

Catechol thionocarbonate (570 mg., 3 mmol.) in an excess of triethyl phosphite (15 ml.) was heated under reflux in an atmosphere of nitrogen for 4 hr. The triethyl phosphite was distilled, b.p. 94°/12 mm., and the residue was triturated with petrol to give a yellow solid (94 mg.), m.p. 169-174°. Crystallisation from
ether-methanol (10:1) gave colourless needles of 3-benzo-
dioxolidene benzo-1,4-dioxan-2-one catechol ketal, m.p. 177-178°.
(Found: C, 69.9; H, 3.6. C_{21}H_{12}O_6 requires: C, 70.0; 
H, 3.4%) 
m/e 360, 283, 269, 268, 252, 240 (base peak), 212, 196, 
161, 151, 121. 
\( \lambda_{\text{max.}} \) 1757, 1600, 1352, 1285, 1220, 1070, 996, 975, 935, 
738 cm\(^{-1}\) 
\( \lambda_{\text{max.}} \) 220 (log \( \varepsilon \) 4.14); 279 (3.94).

When the reaction was carried out in the presence of cyclohexene, after removal of the solvent, T.L.C. showed the residual mixture to be the same as in its absence.

**Attempted Desulphurisations of Catechol Thionocarbonate.**

(i) Catechol thionocarbonate was heated with an excess of triphenylphosphine for periods of 1 hr. to 3 hr. at temperatures of 150° to 250° under nitrogen. In all these experiments chromatographic work up on neutral alumina gave triphenylphosphine oxide and trace amounts of triphenylphosphine sulphide. No other products were obtained.

(ii) Catechol thionocarbonate was recovered unchanged after being heated at 200° in an intimate mixture with zinc dust. Similarly, Raney nickel in dry refluxing
benzene produced no reaction.

(iii) A benzene solution of catechol thionocarbonate was irradiated for 12 hr. under nitrogen. The solvent was removed and the residue found to be catechol thionocarbonate, (98%), m.p. and m.m.p. 152-153°.

Attempted Desulphurisation of Catechol Thionocarbonate in the presence of Tetracyclone.

Catechol thionocarbonate (250 mg., 1.7 mmol.), tetracyclone (1.0 g., 25 mmol.) and triphenylphosphine (1.0 g., 37 mmol.) were heated under reflux in 1,2,4-trichlorobenzene (40 ml.) for 1 hr. in an atmosphere of nitrogen. The solvent was distilled, b.p. 90°/8 mm. and the mixture was chromatographed on neutral alumina.

Elution with petrol-benzene (4:1) gave triphenylphosphine (320 mg., 32%); petrol-benzene (1:1) gave a yellow crystalline solid (177 mg.), m.p. 288-294°. Sublimation gave colourless crystals, m.p. 321-323°, thought to be octaphenylfulvalene.

(Found: C, 94.1; H, 5.6; M.W. determined cryoscopically 793. Ce8H40 requires: C, 94.5; H, 5.5% M.W. 736)
m/e approx. 735.

ν max. 1600, 1070, 1030, 760, 750, 705 cm.⁻¹
λ max. 235, 255, 310, 367 μ
Petrol-benzene (1:4) gave tetracyclone, (840 mg., 84%) and ether-methanol (10:1) gave triphenylphosphine oxide, (45%).
Phosgene (11 g., 0.11 mol.) was added to benzoin (21.2 g., 0.1 mol.) stirred in dry toluene at 0-5°. Then 2,6-lutidine (14 ml.) in dry toluene (30 ml.) was added dropwise over 0.5 hr. The mixture was stirred at 0-5° for a further 2 hr. and then left over night. The dark red-brown mixture was filtered and the residue was washed with cold water in which nearly all of it dissolved. The aqueous washings were shaken with the toluene filtrate and then discarded. The toluene solution was washed with more water, dilute hydrochloric acid and finally with water, dried and evaporated. The liquid residue was fractionally distilled. 4,5-Diphenyldioxolen-2-one distilled as a pale yellow liquid, b.p. 176°/1.5 mm., which on cooling in a carbon dioxide-acetone bath gave a yellow solid (17.0 g.). Crystallisation from hexane (200 ml.) gave colourless plates (14.2 g., 59%), m.p. 74.5-76°, (lit. m.p. 74-76°).

$\nu_{\text{max.}}$ 1815, 1235, 1205, 1064, 1025, 948, 758, 691 cm$^{-1}$

**Deoxygenation of 4,5-Diphenyldioxolen-2-one.**

A solution of 4,5-diphenyldioxolen-2-one (2.0 g., 0.08 mol.) in tributylphosphine (10 ml.) was heated at reflux under nitrogen for 12 hr. The tributylphosphine was removed by distillation, b.p. 94-96°/0.1 mm. and
the residue chromatographed on neutral alumina. Elution with petrol-ether (20:1) gave a mixture of hydrocarbons (150 mg.), the bulk of which was shown by G.L.C. to be trans-stilbene. No cis-stilbene was observed. Elution with petrol-ether (7:1) gave desoxybenzoin (400 mg., 25%), m.p. and m.m.p. 58-60°; petrol-ether (1:1) gave a white solid (300 mg.), m.p. 74-77°. Crystallisation gave colourless platelets of 2,3-diphenyl-5-propyl-1,4-dioxadiene, (13.6%).

(Found: C, 82.5; H, 6.7. C₁₈H₁₈O₂ requires: C, 82.0; H, 6.5% M.W. 278)

m/e 278, 260, 245, 233, 205, 173, 143, 139, 115, 105, 91, 77, 58.

ν max. 1735, 1640, 1262, 1200, 1124, 1108, 1000, 980, 967, 951, 693 cm⁻¹

τ 2.77 (multiplet, 10 H); τ 3.83 (singlet, 1 H), τ 7.48 (triplet, 2 H, J=7.5 c.p.s.); τ 8.3 (quartet, 2 H, J=8 c.p.s.); τ 9.02 (triplet, 3 H, J=7 c.p.s.).

λ max. 216 (logε 3.02); 261 (logε 4.09).

**Attempted Deoxygenations of 4,5-Diphenyldioxolen-2-one.**

A solution of 4,5-diphenyldioxolen-2-one was refluxed under nitrogen in trimethyl phosphite for 3 hr. The phosphite was distilled leaving unchanged starting material. Similarly, 4,5-diphenyldioxolen-2-one was heated at 200° under nitrogen with an excess of triphenyl-
phosphine without reaction.

Reaction of Diphenylacetylene with Tributylphosphine.

Diphenylacetylene (tolan) (2.0 g.) was refluxed in tributylphosphine (15 ml.) under nitrogen for 12 hr. The solution became dark brown. The tributylphosphine was distilled, b.p. 96°/0.1 mm., and the residue was chromatographed on silica. Elution with petrol-ether mixtures gave a mixture of compounds which were not separated further by chromatography on neutral alumina. G.L.C. showed the presence of a small amount of stilbenes in the ratio trans:cis = 5:1. No tolan was recovered from the reaction, nor was the presence of tolan detected by G.L.C.
SECTION IV

REACTIONS OF TETRACYCLONE WITH PHOSPHINES AND PHOSPHITES

1. TETRACYCLONE AND TRIPHENYLPHOSPHINE

Tetracyclone (4.0 g., 0.1 mol.) and triphenylphosphine (4.0 g., 0.15 mol.) were heated under reflux in 1,2,4-trichlorobenzene (50 ml.) for 3 hr. in an atmosphere of nitrogen. The solvent was distilled, b.p. 46°/2.4 mm., and the residue was stirred with ether and filtered. The filtrate was chromatographed on neutral alumina. Elution with petrol-ether (10:1) gave colourless crystals, (386 mg.), m.p. 321-323°, thought to be octaphenylfulvalene. This compound was identical to that obtained from the reaction involving catechol thionocarbonate, tetracyclone and triphenylphosphine.

2. TETRACYCLONE AND TRIMETHYL PHOSPHITE

(1) Tetracyclone (1.9 g., 5 mmol.) was heated under reflux in trimethyl phosphite (25 ml.) for 3 hr. under nitrogen. The solution was allowed to cool and the trimethyl phosphite was removed on the rotary evaporator, leaving a yellow mixture which was chromatographed on neutral alumina. Elution with petrol-ether (10:1) gave
2,3,4,5-tetraphenylcyclopentenone (230 mg., 12%), m.p. 158-160°, m.m.p. 160-161°. Ether gave dimethyl 2,3,4,5-tetraphenylcyclopentadienyl phosphate (450 mg., 18%), m.p. 170-172°. Crystallisation from ether-petrol (1:1) gave colourless needles, m.p. 174.5-175.5°.

(Found: C, 75.3; H, 5.5; P, 6.2% M.W. 494. C₃₁H₂₇O₄P requires: C, 75.3; H, 5.5; P, 6.3% M.W. 494)

m/e 494, 370, 291, 265, 178, 109.

λ_max. 1608, 1280, 1038, 980, 930, 918, 855, 795, 768, 743, 705, 692 cm⁻¹

τ2.5-3.1 (multiplet, 20 H); τ4.9 (doublet, J=5 c.p.s., 1 H); τ6.75 (doublet, 3 H, J=1.5 c.p.s.); τ6.95 (doublet, 3 H, J=1.5 c.p.s.)

λ_max. 245 (logε 4.23); 331 (logε 4.15).

(ii) Tetracyclone (1.9 g., 5 mmol.) was stirred in trimethyl phosphite (25 ml.) under nitrogen for 24 hr. at room temperature. The solution gradually changed from purple to pale yellow. The solvent was removed on the rotary evaporator and the residue taken up in ether. The clear ethereal solution deposited dimethyl 2,3,4,5-tetraphenylcyclopentadienyl phosphate (665 mg., 27%) as colourless needles, m.p. and m.m.p. 172-174°.

(iii) Tetracyclone (1.9 g., 5 mmol.) was heated in trimethyl phosphite (25 ml.) under nitrogen until refluxing commenced, at which point the purple colour of the solution faded. The solution was cooled and the
trimethyl phosphite removed. The residue was chromatographed on neutral alumina. Elution with ether gave dimethyl 2,3,4,5-tetraphenylcyclopentadienyl phosphate (177 mg., 7%), m.p. 171-172°, m.m.p. 173-174°. No other identifiable products were obtained.

(iv) 2,3,4,5-Tetraphenylcyclopentenone was heated under reflux for 24 hr. in trimethyl phosphite under nitrogen. The phosphite was removed and the residue taken up in ether. Concentration of the solution gave colourless needles of the starting material (80%). The filtrate was chromatographed on neutral alumina but no products were obtained. Similarly, no reaction was observed at room temperature.

3. TETRACYCLONE AND TRIETHYL PHOSPHITE

(1) Tetracyclone (1.9 g., 5 mmol.) was heated under reflux in triethyl phosphite (25 ml.) under nitrogen for 3 hr. The triethyl phosphite was distilled, b.p. 65°/20 mm., and the residue was chromatographed on neutral alumina. Elution with ether gave diethyl 2,3,4,5-tetraphenylcyclopentadienyl phosphate (175 mg., 7%), m.p. 166-167°. Crystallisation from petrol-ether (1:1) gave colourless needles, m.p. 167-168°.

(Found: C, 75.6; H, 5.9; P, 5.9% M.W. 522. C₃₂H₃₆O₄P requires: C, 75.8; H, 5.9; P, 5.9% M.W. 522)
m/e 522, 370, 221, 99, 81, 67, 58.

$\nu_{\text{max.}}$ 1632, 1600, 1290, 1275, 1055, 1032, 977, 900, 790, 774, 700, cm.$^{-1}$

$\tau$2.4-3.1 (multiplet, 20 H); $\tau$4.9 (doublet, 1 H, $J=4$ c.p.s.);

$\tau$6.3-6.75 (multiplet, 4 H); $\tau$9.1 (triplet, 6 H, $J=7$ c.p.s.)

$\lambda_{\text{max.}}$ 248 (log $\varepsilon$ 3.26); 331 (log $\varepsilon$ 3.14).

(ii) Tetracyclone (1.9 g., 5 mmol.) was stirred in triethyl phosphite (25 ml.) until the purple colour of the tetracyclone had disappeared (3 hr.). The solvent was distilled, b.p. 65-70$^\circ$/20 mm., and the residue was chromatographed on silica. Elution with petrol-ether (3:1) gave 2,3,4,5-tetraphenylcyclopentenone, (450 mg., 24%), m.p. and m.m.p. 162-163$^\circ$; petrol-ether (1:1) gave diethyl 2,3,4,5-tetraphenylcyclopentadienyl phosphate, (620 mg., 25%), m.p. and m.m.p. 167-168$^\circ$.

(iii) The above experiment was repeated in a flask sealed with a serum cap. Analysis of the mixture after 24 hr. by G.L.C. showed the complete absence of ethylene and acetaldehyde; this was confirmed by comparison with an authentic mixture. An unidentified peak with a very low retention time was observed.

4. TETRACYCLONE AND DIMETHYL PHOSPHITE

(i) Tetracyclone (1.9 g., 5 mmol.) was heated under reflux in dimethyl phosphite (25 ml.) under nitrogen
for 3 hr. The phosphite was distilled, b.p. 70-75°/15 mm. and ether added to the residue. Tetraphenylcyclopentadiene separated as an off-white solid (520 mg., 28%), m.p. 174-178°. Crystallisation from ether gave colourless needles, m.p. and m.m.p. 184-185°, (lit.* 180°).

The ethereal filtrate was chromatographed on neutral alumina. Elution with petrol–ether (1:1) gave more tetraphenylcyclopentadiene (180 mg., 9%).

m/e 370; calculated M.W. 370.

\[ \nu_{\text{max.}} 1600, 790, 755, 700, 692 \text{ cm}^{-1} \]

\[ \tau_{2.8} \text{ (multiplet, 20 H); } \tau_{5.97} \text{ (singlet, 2 H).} \]

(ii) Tetracyclone (1.9 g., 5 mmol.) was heated under reflux in dimethyl phosphite (25 ml.) under nitrogen until the purple colour had disappeared, (0.25 hr.). The dimethyl phosphite was removed, b.p. 72°/15 mm., and the residue was chromatographed on neutral alumina. Elution with petrol–ether (3:1) gave 2,3,4,5- tetraphenylcyclopentenone (225 mg., 12%), m.p. and m.m.p. 159-161°. Ether gave 4-dimethoxyphosphinyl-2,3,4,5- tetraphenylcyclopent-2-enone, (556 mg., 22%), m.p. 217-218°.

(Found: C, 74.6; H, 5.5; P, 7.0. C_{31}H_{27}O_4P requires: C, 75.2; H, 5.5; P, 6.3% M.W. 494)

m/e 494, 478, 444, 382, 365, 355, 290, 279, 239, 200, 191, 178, 77.

\[ \nu_{\text{max.}} 1700, 1605, 1354, 1265, 1160, 1053, 1030, 950, \]

...
892, 830, 805, 758, 715, 702 cm$^{-1}$

\( \tau 2.5-3.3 \) (multiplet, 20 H); \( \tau 5.2 \) (doublet, 1 H);

\( \tau 6.4 \) (doublet, 3 H, \( J=4.2 \) c.p.s.); \( \tau 6.8 \) (doublet, 3 H, \( J=4 \) c.p.s.).

\( \lambda_{\text{max}} \) 222 (log \( E \) 3.47); 300 (log \( E \) 4.10).

(iii) When tetracyclone was stirred with dimethyl phosphite under nitrogen at room temperature, there was no decolorisation after 96 hr.

(iv) 2,3,4,5-Tetraphenylcyclopentenone (300 mg., 0.75 mmol.) was refluxed in dimethyl phosphite (25 ml.) under nitrogen for 3 hr. The phosphite was distilled, b.p. 70°/15 mm., and the residue chromatographed on silica. Elution with petrol-ether (3:1) gave tetraphenylcyclopentadiene (70 mg., 23%), m.p. and m.m.p. 184-185°. Petrol-ether (1:1) gave 2,3,4,5-tetraphenylcyclopentadiene, (66 mg., 22%), m.p. and m.m.p. 160-161°.

(v) A solution of diethyl 2,3,4,5-tetraphenylcyclopentadienyl phosphate (250 mg., 0.5 mmol.) in dimethyl phosphite (10 ml.) was refluxed under nitrogen for 3 hr. The dimethyl phosphite was distilled, b.p. 65°/12 mm., and the residue chromatographed on silica. Petrol-ether (3:1) gave 2,3,4,5-tetraphenylcyclopentenone (112 mg., 58%), m.p. and m.m.p. 162-163°. None of the starting phosphate was recovered.
Tetracyclone (1.9 g., 5 mmol.) was refluxed in tributylphosphine (25 ml.) under nitrogen for 24 hr. The phosphine was distilled, b.p. 90-95°/3 mm., and the residue washed with ether. A colourless solid, tetr phenylcyclopentadiene, separated, (1.06 g., 60%), m.p. and m.m.p. 183-184°.

Reduction products of tetracyclone.
(i) Tetracyclone (1.0 g., 2.5 mmol.) was heated at 270-280° with zinc dust (2.0 g.) for 1 hr. After cooling the mixture was extracted with a large volume of ether, filtered and the filtrate chromatographed on neutral alumina. Petrol-benzene (5:1) gave tetraphenylcyclopentadiene (50 mg., 5%) as colourless needles, m.p. 181-182°, (lit. 47 m.p. 180°).
(ii) Tetracyclone (2.0 g., 5 mmol.) was heated under reflux in glacial acetic acid (500 ml.) and zinc dust (5.0 g.) was added. When decolorisation was complete the solution was decanted and cooled. The mixture was filtered leaving a residue of 2,3,4,5-tetraphenylcyclopentadienyl-ol acetic acid solvate. 47 The filtrate was evaporated and the residue washed with ether and filtered leaving 2,3,4,5-tetraphenylcyclopentenone (1.25 g., 63%), m.p. 161-163°, (lit. 47 m.p. 162-163°).
SECTION V

DERIVATIVES OF TETRAPHENYLCYCLOPENTADIENE

1. 1-DIAZ-2,3,4,5-TETRAPHENYLCYCLOPENTADIENE

(i) Tosyl hydrazine (1.17 g., 5 mmol.) was dissolved in dry dioxan (40 ml.) and the solution was refluxed under nitrogen. Concentrated sulphuric acid (2 ml.) was added, followed by dropwise addition of tetracyclone (1.9 g., 5 mmol.) in dry dioxan (50 ml.) over 0.25 hr. The mixture was heated under reflux for 2.5 hr., cooled and poured into water (500 ml.). The mixture was filtered and the residue chromatographed on basic alumina. Elution with petrol-ether (20:1) gave 1-diazo-2,3,4,5-tetraphenylcyclopentadiene (497 mg., 26%) as clusters of orange-red needles, m.p. 139-141°, (lit.* m.p. 142-143°). Crystallisation from petrol-ether (5:1) gave orange-red needles, m.p. 146.5-147.5° (dec.). However, prolonged boiling caused decomposition.

When equivalent amounts of tosyl hydrazine and tetracyclone were refluxed in ethanol or in benzene the tetracyclone was quantitatively recovered. Equivalent amounts of tosyl hydrazine and tetracyclone were refluxed in a minimum volume of glacial acetic acid for 0.25 hr. The solution was cooled and filtered leaving a
residue of tetracyclone (81%). The filtrate was evaporated and the residue extracted with ether to give 2,3,4,5-tetraphenylcyclopentenone (18%), m.p. and m.m.p. 159-160°.

**Photolysis**

1-Diazo-2,3,4,5-tetraphenylcyclopentadiene (250 mg., 0.64 mmol.) in dry benzene (25 ml.) was irradiated under nitrogen at room temperature for 6 hr. The benzene was distilled and the residue was chromatographed on neutral alumina. Mixtures of gums were eluted showing a great number of spots on T.L.C. A trace of a crude solid (m.p. ~130°) was obtained by trituration with petrol. The mass spectrum of this solid had a mass peak at 446, suggesting it was pentaphenylcyclopentadiene. (lit\(^\text{m.p.} 258-259°\))

Various photolyses of the diazo- compound in benzene were performed but T.L.C. of the resulting mixtures indicated that reproducible results were not being obtained.

**Pyrolysis**

(i) 1-Diazo-2,3,4,5-tetraphenylcyclopentadiene (250 mg., 0.64 mmol.) in dry tetralin (5 ml.) was refluxed under nitrogen for 2 hr. After cooling, the mixture was chromatographed on silica. A mixture of unidentified tars was obtained. These were not investigated further.
(ii) 1-Diazo-2,3,4,5-tetraphenylcyclopentadiene (1.0 g., 2.5 mmol.) was refluxed in dry carbon tetrachloride (50 ml.) in air for 48 hr. T.L.C. of the mixture after 3 hr., 20 hr. and 48 hr. showed a gradual increase in the concentration of tetracyclone. No spots other than that corresponding to the starting material were observed. The solvent was removed and the mixture chromatographed on basic alumina. Elution with petrol-ether (10:1) gave tetracyclone (291 mg., 30%), m.p. and m.m.p. 222-224°.

(iii) The diazo-compound (250 mg., 0.64 mmol.) in dry toluene was refluxed for 12 hr. The toluene was removed on the rotary evaporator and the residue was chromatographed on neutral alumina. Elution with petrol-ether (20:1) gave 1-benzyl-2,3,4,5-tetraphenylcyclopentadiene (33 mg., 18%), m.p. 179-181°, m.m.p. with tetraphenylcyclopentadiene depressed.

(Found: C, 93.7; H, 6.1; M.W. 460. C₃₆H₂₈ requires:
C, 93.8; H, 6.1% M.W. 460)

ν_max. 1600, complex pattern of bands 1150-1000, 760, 690 cm⁻¹

It showed a red coloration in concentrated sulphuric acid and the solution fluoresced red under u.v. light.

Elution with petrol-ether (10:1) gave tetraphenylcyclopentadiene (67 mg., 28%) m.p. 166-171°, m.m.p. 179-181°. The i.r. spectrum was identical to that of an authentic sample.
2. 1,1-DIBROMO-2,3,4,5-TETRA PHENYL CYCLOPENTADIENE

(i) Tetraphenylcyclopentadiene (2.2 g., 6 mmol.) was stirred in carbon disulphide (70 ml.) and bromine (12 mmol.) in carbon disulphide was added dropwise over 1 hr. The mixture was stirred over night and the 1,1-dibromo-2,3,4,5-tetraphenylcyclopentadiene filtered from the reaction mixture as a yellow solid, (2.6 g., 80%), m.p. 148-150°. Crystallisation from petrol-ether (3:1) gave yellow crystals, m.p. 154-156° (lit. m.p. 157°).

(ii) Tolan (10 g., 51 mmol.) in ether (25 ml.) was shaken with lithium shavings (1.2 g.) under nitrogen. After an induction period of 5-10 min. the mixture became dark red. Shaking was continued for 2 hr. and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene \(^{51}\) was precipitated as an orange powder. Carbon tetrabromide (3.75 g., 11.25 mmol.) in ether (50 ml.) was added to the suspension and the mixture was refluxed for 0.5 hr. The mixture was filtered and the filtrate chromatographed on silica. Elution with petrol-ether (20:1) gave a mixture of two compounds. This was washed with hot ethanol. Filtration left a residue of 1,1-dibromo-2,3,4,5-tetraphenylcyclopentadiene (1.9 g., 32% on carbon tetrabromide) which crystallised from ether-petrol (1:1) as pale yellow plates, m.p. 153-154°, m.m.p. 154-155°. The ethanolic filtrate was reduced to dryness leaving a pale yellow
solid which was dissolved in ether, the solution charcoaled, filtered and the volume reduced. Tetraphenylbutadiene was obtained as colourless needles (2.2 g., 12% on tolan) m.p. 181-182°, (lit. m.p. 182.5-183°).

A solution of the dibromo-compound (1.25 g., 2 mmol.) in dimethoxysthane-water (10:1, 50 ml.) was cooled to -60° in a chloroform-liquid nitrogen slush bath. Freshly prepared cuprous bromide (0.6 g., 4 mmol.) was added and the mixture was stirred vigorously and allowed to warm up. At -30° the colour began to change from yellow to purple. When the temperature had risen to 0° the mixture was filtered. The residue was dissolved in ether, the ethereal solution washed with water, dried and evaporated. The residue was chromatographed on silica. Elution with petrol-ether (50:1) gave 1,1-dibromo-2,3,4,5-tetraphenylycyclopentadiene (580 mg., 46.4% recovery) m.p. 151-154°, m.m.p. 154-155°. Petrol-ether (20:1) gave tetracyclone (280 mg., 36%), m.p. and m.m.p. 219-221°.

1,1-Dibromo-2,3,4,5-tetraphenylycyclopentadiene was treated with zinc and with copper in refluxing benzene, and also with sodium iodide in acetone. In each material reaction the starting was quantitatively recovered.
SECTION VI

ATTEMPTED PREPARATIONS OF TETRAPHENYLANTHRANILIC ACID

(i) Tetr phenylphthalic Anhydride.

Tetr phenylphthalic anhydride was prepared by Grummitt’s method from tetracyclone and maleic anhydride in refluxing bromobenzene. The anhydride was obtained as a colourless solid (85%, lit. 87-89%), m.p. 296–300°, (lit. m.p. 289–290°).

(ii) Tetr phenylphthalimide.

Tetr phenylphthalic anhydride (20 g.) was heated to 350° and dry gaseous ammonia was passed through the melt for 1 hr. After cooling, the pale yellow solid was broken up and extracted with hot methanol. The solution was charcoaled, filtered and evaporated. Tetr phenylphthalimide was obtained as a pale yellow solid (17.5 g., 88%), m.p. 300-310°. Crystallisation from ethanol raised the m.p. to 327-329° and a sample sublimed for analysis had m.p. 333-334°.

(Found: C, 85.0; H, 4.5; N, 2.8% M.W. 451. C₂₅H₂₁NO₂ requires: C, 85.5; H, 4.6; N, 3.1% M.W. 451)

ν max. 3160, 3045, 1757, 1704, 1400, 1350, 1100, 1068, 1050, 1015, 782, 740, 725, 718, 690 cm⁻¹

τ 2.75–3.3 (multiplet, 24 H); τ 7.87 (singlet, 1 H).
The anhydride was recovered (94%) from attempted reactions with concentrated ammonia in ethanol.

**Attempted Hofmann Degradation of the Imide.**

(a) Tetraphenylphthalimide (4.5 g., 0.01 mol.) was added to a mixture of aqueous sodium hydroxide (0.12 mol.) and bromine (0.01 mol.) at 0°. The mixture was heated at 80° for 3 hr., cooled and filtered. The residue was tetraphenylphthalimide (4.42 g., 98%).

(b) Tetraphenylphthalimide (1.12 g., 2.5 mmol.) and sodium (0.23 g., 0.01 g. atom) in methanol (150 ml.) was cooled to 0° and bromine (0.4 g., 2.5 mmol.) was added dropwise with vigorous stirring. The mixture was stirred for 3 hr. and then a small amount of sodium metabisulphite was added to destroy excess of hypobromite. The solution was refluxed for 3 hr. The methanol was distilled and the residue extracted with ether. The ethereal solution was washed with water, dried and evaporated to give tetraphenylphthalic acid (950 mg., 86%), m.p. 294-296°. The acid was identified by sublimation at 200°/0.1 mm. which gave tetraphenylphthalic anhydride (92%), m.p. and m.m.p. 295-298°. Also the i.r. spectrum was identical to that of an authentic specimen.

(c) The above experiment was carried out as far as
stirring for 3 hr. The solvent was then removed and the residue extracted with ether to give tetraphenylphthalic acid (92%). When the bromine was omitted the imide was recovered (80%).

(d) The imide (2.25 g., 5 mmol.) and potassium hydroxide (0.3 g., 5 mmol.) in methanol (250 ml.) was cooled to 0° and bromine (0.8 g., 5 mmol.) was added dropwise. The mixture was stirred over night and then filtered leaving tetraphenylphthalimide (620 mg., 28% recovery). The filtrate was evaporated and the residue extracted with ether to give tetraphenylphthalic acid (1.6 g., 71%).

(iii) Tetraphenylphthalic Acid.

Tetraphenylphthalic anhydride (0.9 g., 2 mmol.) and sodium hydroxide (4 equivalents) were refluxed in ethylene glycol (50 ml.) for 4 hr. The solution was poured into water (400 ml.), acidified and extracted with ether. The ethereal solution was dried and the volume reduced giving colourless crystals of tetraphenylphthalic acid (340 mg., 30%), m.p. 290-292°, (lit.* m.p. 287°). Evaporation to dryness gave a further yield of the acid (460 mg., total yield 90%)

Attempted Oxidative Decarboxylation of Tetraphenylphthalic Acid.

Tetraphenylphthalic acid and a 6 fold excess
of lead tetraacetate were refluxed in dry acetonitrile containing a trace of pyridine under nitrogen. The solvent was removed and the residue extracted with ether. The ethereal solution gave only tetraphenylphthalic acid (95%).

Attempted Schmidt Reaction.

Tetraphenylphthalic acid (4.7 g., 0.01 mol.) and concentrated sulphuric acid (20 ml.) in dioxan (50 ml.) were warmed to 40-50°. Sodium azide (0.012 mol.) was added and the mixture stirred for 4 hr. The mixture was poured on to ice and filtered. The residue was extracted with ether, washed with water, dried and evaporated to give tetraphenylphthalic anhydride (2.8 g., 58%), m.p. and m.m.p. 293-295°. Reactions with tetraphenylphthalic anhydride, fuming sulphuric acid and sodium azide failed to give any tetraphenylanthranilic acid.
DISCUSSION OF RESULTS
SECTION I

o-BENZOBETAINES

The generation of benzyne under moderate laboratory conditions from easily obtainable, stable precursors has long been desirable. The o-benzobetaines and related compounds described in this thesis were prepared with a view to just such a preparation of benzyne. In the general case, decomposition of (I) would give benzyne if $X$ left with, and $Y$ left without the bonding electrons; and if decomposition is faster than any reaction between $X$ and $Y$.

$$\begin{align*}
\text{benzenediazonium-2-carboxylate}^2-10 & \quad \text{(II)} \\
\text{diphenyliodonium-2-carboxylate} & \quad \text{(III)}
\end{align*}$$

Consequently its reactions are limited to those involving

On the other hand, diphenyliodonium-2-carboxylate (III) requires flash pyrolysis or, in solution, temperatures of the order of 160° before decomposition occurs.
thermally stable compounds.

\[
\begin{align*}
\text{phenyl} & \quad \text{CO}_2^- \quad \rightarrow \quad \text{benzyne} + \text{PhI} + \text{CO}_2 \\
(\text{III})
\end{align*}
\]

When o-aminophenylboronic acid (IV) was diazotised, the diazonium salt decomposed under conditions similar to those used in the decomposition of (II) to give benzyne.\(^21\) However, the usefulness of this method is limited by the instability of the diazonium compound and also by the difficulty of preparing (IV).

\[
\begin{align*}
\text{B(OH)}_2^- \quad \text{NH}_2 \quad \rightarrow \quad \text{PhBH} \quad \rightarrow \quad \text{benzyne} + \text{B(OH)}_2OR + \text{N}_2 \\
(\text{IV}) \quad \text{R=isoamyl or H}
\end{align*}
\]


Benzenetrimeethylammonium-2-carboxylate (V) could be expected to decompose to benzyne by loss of carbon dioxide and trimethylamine, both very stable molecules. In principle, this desired fragmentation is very similar to the decomposition of (II), requiring decarboxylation and the separation of trimethylamine, a good leaving group.\(^55\)

\[
\begin{align*}
\text{PhB} \quad \text{NH}_3^+ \quad \text{CO}_2^- \quad \rightarrow \quad \text{benzyne} + \text{Me}_3\text{N} + \text{CO}_2 \\
(\text{V})
\end{align*}
\]
The betaine (V) was prepared by the method of Willstatter and Kahn according to the scheme:

\[
\begin{align*}
\text{NH}_{\text{Me}} & \quad \text{CO}_2\text{H} \\
& \rightarrow \\
\text{NH}_{\text{Me}} & \quad \text{CO}_2\text{Me} \\
& \rightarrow \\
\text{NMe}_3 & \quad \text{I}^- \\
& \leftarrow
\end{align*}
\]

(V)

The preparation of the starting material, \( N \)-methylantranilic acid, was attempted by the methylation of amines described by Ullman.\(^{56}\) Dimethyl sulphate was added to an ethereal solution of anthranilic acid. However, the conversion to \( N \)-methylantranilic acid occurred in less than 0.5% yield, the starting material being recovered in almost quantitative amounts. (This is not reported in the experimental section.)

The stages in the synthesis of (V) which involved iodomethane were found to proceed to completion only if the product was removed at intervals by filtration. This indicates that the reaction reaches an equilibrium. The hydrolysis of the methiodide to the betaine was carried out with freshly prepared moist silver oxide, a very mild hydrolysing agent which acts effectively as silver hydroxide.
The infra-red spectrum of the betaine showed no hydroxyl peak and the mass spectrum had the highest mass peak at 179 showing that the betaine was not hydrated. The fragmentation pattern indicated an initial loss of methyl to give an ion of mass 164 (base peak); no peak was observed at 76 corresponding to benzyne.

Pyrolysis of (V) gave only methyl N,N-dimethyl-anthranilate. Willstatter and Kahn\textsuperscript{23} had reported the formation of this ester and also of dimethylaniline, the yield of which increased with the amount of moisture present. However, our pyrolyses gave no dimethylaniline and no reaction was observed when the betaine was refluxed in water. Rearrangement of the betaine is presumably due to the nucleophilic character of the carboxylate anion and its enforced proximity to the trimethylammonium ion. Indeed, the geometry is highly favourable for intramolecular nucleophilic attack by the carboxylate ion on a methyl group, displacing the dimethylaniline group in a cyclic 6-membered transition state.
Unfortunately, this rearrangement occurs to the exclusion of benzyne formation as is shown by the failure of the pyrolyses to produce any 1,2,3,4-tetraphenynaphthalene in the presence of tetracyclone.

Willstatter and Kahn also reported the isomerisation of the para-isomer. The stereochemistry of this compound precludes direct interaction between the carboxylate and the trimethylammonium ions of the same molecule. Therefore, this reaction must be intermolecular. The rearrangement of (V) could also be intermolecular although, as noted above, the proximity of the groups on the ortho-positions of the benzene ring would strongly favour an intramolecular mechanism.

An analogous reaction occurs when α-betaine (VI) is heated to form methyl dimethylammoniumacetate. In this case the isomerisation begins at 135°; between 135° and 293° the betaine is stable and the ester is the labile form; above 293° the betaine does not exist. Surprisingly, this isomerisation is said not to occur in the case of the β- and γ-betaines.

\[ \text{Me}_3\text{NCH}_2\text{CO}_2 \rightleftharpoons \text{NMe}_2\text{CH}_2\text{CO}_2\text{Me} \]

(VI)
The photolysis of benzenetrimethylammonium-2-carboxylate (V) in dry dimethylformamide produced an almost quantitative yield of benzoic acid. Thus, trimethylamine has been lost but reduction has also occurred. Direct loss of trimethylamine would leave the zwitterion (VII) but this is an unlikely intermediate since no products derived from its tautomeric form (VIII) were observed and no disalicylide was obtained.

\[
\text{(V) \rightarrow } \text{C}^+\text{O}_2^- \xleftarrow{} \text{(VII) \rightarrow } \text{H}_2\text{O} \text{ (VIII)}
\]

When the photolysis was conducted in aqueous solution no reaction was observed. Therefore, the dimethylformamide must be participating in the reaction to form benzoic acid. Formamide is known to dissociate to give hydrogen radicals on irradiation\(^5\) and similarly, hydrogen radicals are involved in the peroxide initiated addition of dimethylformamide to cis-cis-1,5-cyclooctadiene\(^5\)\(^9\). Thus, dimethylformamide is probably the source of hydrogen required to reduce a transient intermediate to benzoic acid. Trimethylamine is known to be decomposed on irradiation\(^6\)\(^0\). This would explain the
failure to trap trimethylamine with picric acid during the photolysis of (V). Also, if the trimethylamine, instead of being lost completely, remains associated with the intermediate in the form of an ylid, it would not be observed during the irradiation and the benzoic acid would only be liberated on subsequent acidification.

2. Benzenedimethylsulphonium-2-carboxylate.

The sulphur analogue of (V) is benzenedimethylsulphonium-2-carboxylate (IX). Decomposition of (IX) might give benzyne and the stable molecules carbon dioxide and dimethylsulphide, another good leaving group.\

\[ \text{C}_6\text{H}_5\text{SMe}_2 - \text{CO}_2 \rightarrow \text{C}_6\text{H}_5 + \text{SMe}_2 + \text{CO}_2 \]

(IX)

Sulphonium compounds are less readily formed and less stable than the corresponding ammonium compounds. This was found to be the case with (IX) which could not be prepared by a synthesis analogous to that of benzene-trimethylammonium-2-carboxylate (V). The preparation of (IX) required methylation of S-methylthiosalicylic acid. Alkyl thioethers are easily methylated at room temperatures by iodomethane, but methylation of aryl thioethers requires the use of dimethyl sulphate, often at elevated temperatures. The following preparations of ortho-
substituted sulphonium salts are described in the literature. S-Methyl-2-nitrophenol was warmed on a water bath with an excess of dimethyl sulphate for 48 hr. to give o-nitrophenyl dimethylsulphonium methyl sulphate which was converted to the iodide by warming with an aqueous solution of potassium iodide:

\[
\text{S-Me-
\text{NO}_2 + \text{Me}_2\text{SO}_4 \rightarrow \text{O-N-Me-
\text{Me}_2\text{SO}}_4 \rightarrow \text{O-N-Me-
\text{Me}_2\text{I}}.
\]

Similarly, Kehrmann and Sava heated o-methoxy-thioanisole with dimethyl sulphate at 100° to obtain o-methoxyphenyl dimethylsulphonium methyl sulphate. This was converted to the iodide as above and then to the hydroxide.

\[
\text{S-Me-
\text{Ome} \rightarrow \text{O-Me-
\text{Me}_2\text{SO}}_4 \rightarrow \text{O-Me-
\text{Me}_2\text{I}}.
\]

By analogy with the above schemes, S-methyl-thiosalicylic acid was heated at 100° with dimethyl sulphate. The resultant o-dimethylsulphonium benzoic acid methyl sulphate \((X)\), \(R = \text{H}\), was stirred with a suspension of freshly prepared silver oxide to give \((\text{IX})\).
The betaine (IX) was also prepared by an exactly similar method from dimethyl sulphate and methyl S-methylthiosalicylate.

\[
\begin{align*}
\text{R} = H \text{ or Me} \\
\text{The harsh methylating conditions are required because of the greater electronegativity of sulphur than nitrogen, with the consequence that sulphur is less ready than nitrogen to share its lone pair of electrons. It was found that both S-methiosalicylic acid and methyl S-methylthiosalicylate were unreactive towards iodomethane, even at reflux, and towards dimethyl sulphate at room temperatures or at elevated temperatures in a solvent such as ethanol.}
\end{align*}
\]

Kucsman and Krenmer reported the preparation of methyl S-methylthiosalicylate by reaction of dimethyl sulphate and thiosalicylic acid but we tried to repeat this reaction without success. The ester was prepared by reaction of diazomethane with thiosalicylic acid and also with S-methylthiosalicylic acid.

Mass spectral fragmentation of the betaine (IX) showed initial loss of methyl but no peak was
observed at 76 corresponding to benzyne. The pyrolyses of (IX) paralleled those of the trimethylammonium betaine (V). The only identified product was methyl 8-methyl-thiosalicylate, presumably formed by intramolecular nucleophilic attack of the carboxylate anion on a methyl group of the sulphonium cation.

Alternatively, the reaction could proceed through initial hydrogen abstraction from a methyl group, formation of a 5-membered cyclic intermediate and a 1,3-shift of a methyl group with subsequent reopening of the 5-membered ring to give the ester.

The above mechanism is analogous to the thermal rearrangement of dimethyl(2-acetyl-4-methyl-phenyl)sulphonium hydroxide (XII) to 3-methoxy-3,5-p-methyl-2,3-dihydro-
thianaphthene (XIII) observed by Krollpfeiffer.\textsuperscript{64}

However, the rearrangement of the betaine (IX) by this mechanism proceeds through a sulphonium ylid (XI) which is ideally situated for direct methylation of the neighbouring carboxylic acid group without involving the formation and rupture of a carbon-carbon bond.

The photolysis of (IX) in dimethylformamide gave S-methylthiosalicylic acid in small yield. Aryl sulphonium salts have a strong tendency to dissociate into their components. For example, methyl p-cresyl sulphide can be methylated with dimethyl sulphate but on heating the sulphonium salt decomposes into its components.\textsuperscript{65}

Hence, the S-methylthiosalicylic acid could
result from a reaction involving an ionic impurity of the type MX.

\[
(IX) + MX \rightarrow \text{reaction products}
\]

A trace of a silver mirror was observed on the surfaces of the reaction vessel after the photolysis indicating the presence of a small amount of complexed silver ion which could participate in the above reaction \((M = Ag)\). Friedman \(^6\) has reported complexing of silver ion with benzenediazonium-2-carboxylate and shown that the products of decomposition depend on the concentration of silver ion.


By analogy with benzenediazonium-2-carboxylate (II), the betaine benzenediazonium-2-sulphonate (XIV) would seem to be a potential benzyne precursor. Benzyne could be formed by loss of nitrogen and sulphur trioxide:

\[
(XIV)
\]

Initially we prepared (XIV) by the method described by Hurtley and Smiles \(^6\) who diazotised aniline-
2-sulphonic acid at 0° using sodium nitrite and hydrochloric acid. We found the reaction to proceed in fairly low yield and the amount of (XIV) obtained decreased markedly with small rises in temperature above 5°. Therefore, aprotic diazotisation of aniline-2-sulphonic acid was employed. By this method the yield of the betaine was 84% i.e. twice the best yield obtained by the conventional diazotisation procedure. The physical properties of the two products were identical, showing that the product of the Hurtley and Smiles method was the zwitterion and not the diazonium chloride.

Compound (XIV) was found to lose nitrogen very readily but under no conditions could we effect the loss of sulphur trioxide. An aqueous solution of (XIV) was neutral in the cold but on refluxing, nitrogen was evolved and the resultant solution was shown to be phenolic. However, on removal of the solvent the residue was found to be polymeric and was not the expected phenol-2-sulphonic acid. The product of photolysis of the betaine was also polymeric having the same i.r. spectrum as the product obtained above. The decomposition of (XIV) in diethyl digol produced no 1,2,3,4-tetraphenylnaphthalene in the presence of tetracyclone indicating the complete absence of benzyne formation. Presumably the intermediate zwitterion produced by loss of nitrogen from (XIV) is able to react with either the solvent or with another
zwitterion before cleavage of the carbon-sulphur bond occurs.

4. \( \varphi \text{-}(4\text{-Pyridoxy})\text{benzoic Acid.} \)

The reactions with 4-chloropyridine and with pyridyl-4-pyridinium dichloride with methyl salicylate or salicylaldehyde were performed in an attempt to prepare \( \varphi \text{-}(4\text{-pyridoxy})\text{benzoic acid} \) (XV). In the event of obtaining (XV) it was proposed to react it with iodomethane to obtain the methylpyridinium iodide (XVI) which on treatment with an aqueous suspension of silver oxide would lose the elements of hydriodic acid to form the betaine (XVII).

\[
\begin{align*}
\text{(XV)} \quad \overset{\text{MeI}}{\rightarrow} \quad \text{(XVI)} \\
\text{(XVII)}
\end{align*}
\]

It was then intended to conduct pyrolytic and photolytic experiments with the betaine (XVII) to effect the formation of benzyne. The \( \text{N}\text{-methylpyridone} \) should be an excellent leaving group and intramolecular reactions should be much less likely than with the ammonium and
73. Sulphonium betaines already discussed.

\[ \text{(XVII)} \]

Aryl pyridyl ethers are a well authenticated class of compounds prepared by reacting a phenol with a halopyridine. However, very few o-substituted pyridyl ethers have been prepared. In the case of the 2-pyridyl ethers (XVIII), compounds are known where \( R = \text{p-C}_6\text{H}_4\text{OMe} \), \( \text{o-C}_6\text{H}_4\text{NO}_2 \), \( \text{p-C}_6\text{H}_4\text{CO}_2\text{Me} \) and \( \text{o-C}_6\text{H}_4\text{CO}_2\text{H} \). 

\[ \text{(XVIII)} \]

To prepare (XVIII) \( R = \text{o-C}_6\text{H}_4\text{CO}_2\text{Me} \) the sodium salt of methyl salicylate was heated with an equivalent amount of 2-bromopyridine and a catalytic amount of copper powder at 180-190° for 1 hr. The pyridyl ether was obtained in 52% yield. Saponification with alcoholic potassium hydroxide solution gave the acid \( R = \text{o-C}_6\text{H}_4\text{CO}_2\text{H} \). In some attempts to prepare 2-pyridyl ethers the copper powder was omitted and the reactants were heated to 210-220° without reaction.

Two \( \text{o-(4-pyridoxy)aryl ethers} \) are described in the literature. \( \text{o-(4-Pyridoxy)toluene} \) (XIX) was prepared by Renshaw and Conn who heated pyridyl-4-pyridinium
dichloride, o-cresol and the sodium salt of o-cresol on a water bath for 1 hr. and at reflux for 5 hr.

Kato and Hamaguchi obtained compound (XX) by heating the silver salt of methyl salicylate with 2,6-dimethyl-4-chloropyridine for 1 hr. at 140° and 1 hr. at 180°. However, the yield of (XX) is merely reported as low and no physical details are given; no picrate was obtained.

Basically, our attempts to prepare (XV) were based on the methods described above. Reactions were attempted between the sodium salt of methyl salicylate or the potassium salt of salicylaldehyde and 4-chloropyridine and between the above salts and pyridyl-4-pyridinium dichloride for a variety of reaction times and temperatures. However, no 4-pyridyl ethers were obtained. We can only conclude that either no reaction is taking place or the ether, once formed, is rapidly decomposed. However, no evidence to support the latter conclusion was obtained apart from intractable tars and polymeric products.
5. The Tosylate of Salicylic Acid.

The toluene-\(p\)-sulphonate (tosylate) anion is known to be a good leaving group in elimination reactions.\(^5\) Consequently, the anion of the tosylate of salicylic acid (XXI) might be expected to decompose according to the scheme:

\[
\begin{align*}
&\text{XXI} \\
&\text{tosylate of salicylic acid}
\end{align*}
\]

(The anion (XXI) is not an \(o\)-benzobetaine but is included here because of its similarity to that class of compounds.)

The method of preparation of the tosylate of salicylic acid reported in the literature was oxidation of the tosylate of \(o\)-cresol with manganese dioxide and sulphuric acid.\(^6\) However, we chose to make the tosylate of salicylaldehyde and employed the very mild oxidant silver oxide to convert this to the acid. The tosylate of salicylaldehyde (XXII) was made by a modification of Tipson's general method.\(^7\) The salicylaldehyde was treated with tosyl chloride in dry pyridine at 0\(^\circ\). Dry pyridine was used because of the ease of hydrolysis of tosyl chloride. The latter was added in one batch and vigorous stirring ensured that the temperature did not rise significantly.
The relatively low yield of (XXII) can be ascribed to various factors. There is the possibility of reaction between (XXII) and salicylaldehyde to form an ether (XXIII).

Also (XXII) can react with pyridine to form a quaternary salt (XXIV), and with pyridine hydrochloride to form o-chlorobenzaldehyde (XXV).

Tipson\textsuperscript{71} states that formation of the ether (XXIII) is decreased by conducting the reaction at room
temperature and further lowering the temperature to 0° decreases the formation of the quaternary salt (XXIV). We found that the yield of the tosylate was markedly decreased when the reaction was carried out at higher temperatures.

The conversion of (XXII) to the tosylate of the acid (XXVI) went in 45% yield. Presumably, the conversion was accompanied by hydrolysis of the tosylates to salicylaldehyde, salicylic acid and toluene-\(p\)-sulphonic acid.

The preparation of (XXVII) was also attempted by hydrolysis of the tosylate of methyl salicylate (XXVII) which was prepared by the method used to prepare the tosylate of salicylaldehyde. However, the conversion was achieved in very low yield because extremely mild conditions had to be employed to effect hydrolysis without removing the tosyl group.

![Chemical structure diagrams](image)

Direct reaction between tosyl chloride and salicylic acid was unsuccessful; the major product was disalicylaldehyde.

The tosylate (XXVI) was converted to its sodium salt and this was pyrolysed at 350°/0.3 mm. The product of the pyrolysis was shown to be disalicylaldehyde. Thus, the
tosyl group has been eliminated and the zwitterion has dimerized, or intermolecular displacement has occurred. The latter reaction is more likely in view of the absence of the products usually obtained from the tautomeric form of the zwitterion.

Again no benzyne products were observed in the above pyrolysis or when the sodium salt was refluxed in diethyl digol in the presence of tetracyclone.
The compound p-sulphobenzoic anhydride (I) was prepared by the method of Clarke and Dreger from ammonium p-sulphobenzoate and thionyl chloride.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{SO}_3\text{NH}_4 & + \text{SO}_2 \\
\text{CO}_2\text{H} & \quad \rightarrow \\
\text{SO}_3 & + \text{NH}_4\text{CO}_2 + \text{SO}_2 \\
& + \text{H}_2\text{O}
\end{align*}
\]

The anhydride is very sensitive to hydrolysis to the free acid and so it was very important to ensure that it was kept dry.

Compound (I) is analogous to an o-benzobetaine in that fragmentation by loss of the stable molecules sulphur dioxide and carbon dioxide could lead to the formation of benzyne. However, the anhydride proved stable to heating to 200°/0.3 mm. at which point it sublimed unchanged. Similarly, it was stable at reflux at 320°. Photolysis in dry acetonitrile gave a small yield of benzoic acid (2%); no benzyne products were obtained.

During the course of this investigation Fields and Meyerson reported the pyrolysis of a mixture of (I) and benzene at 690° in a Vycor tube with a contact time of 18 seconds. The formation of benzyne was suggested by the isolation of naphthalene, phenylnaphthalene and
biphenyl. However, no biphenylene was detected.

\[ \text{(I)} \]

Meyerson and Fields \(^{72}\) also report the appearance of a peak at 76 in the mass spectral fragmentation of (I) at 70 e.v. which is in agreement with our observations. We also observed the fragmentation at 14 e.v. and established that the primary process in the fragmentation is loss of sulphur dioxide rather than sulphur trioxide or carbon dioxide. At 70 e.v. and at 14 e.v. no peak was observed at 140 corresponding to loss of carbon dioxide and at 14 e.v. no peak was observed at 104 corresponding to loss of sulphur trioxide. At 70 e.v. the mass spectral fragmentation can be represented as:

Brown \(^{72}\) also pyrolysed (I) at 730 ± 20°/0.05 ± 0.02 mm. for 1 hour and obtained biphenylene in 5.5% yield.
Therefore, pyrolytic conditions more vigorous than ours are required to effect fragmentation of (I).

The rhodium complex (II) is known to abstract carbon monoxide from aldehydes and sulphur dioxide from sulphonyl chlorides. Therefore, the experiments with chlorotris(triphenylphosphine) rhodium I (II) were carried out with the intention of removing sulphur dioxide from o-sulphobenzoic anhydride (I) to form an intermediate which would spontaneously lose carbon dioxide to form benzyne.

\[
\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl} + \text{RCHO} \rightarrow \text{Rh}(\text{Ph}_3\text{P})_2\text{COCl} + \text{RH} + \text{Ph}_3\text{P}
\]

(II)

\[
2\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl} + \text{RSO}_2\text{Cl} \rightarrow \text{Cl}(-\text{RhSO}_2\text{Rh}) \text{Ph}_3\text{P}\text{Cl}
\]

(II) + \text{RCl} + 4\text{Ph}_3\text{P}

The catalytic desulphonylation of sulphonyl chlorides proceeds smoothly at 235°, this being the temperature at which the sulphur dioxide bridged complex loses sulphur dioxide. When the rhodium complex (II) was heated with (I) at 220°, no sulphur dioxide was evolved but a rhodium complex containing sulphur dioxide was isolated; at 260° sulphur dioxide was evolved and benzoic acid was isolated. Thus, extraction of sulphur dioxide from (I) is occurring but the intermediate is then being reduced to benzoic acid before decarboxylation can occur.
Triphenylphosphine was isolated from the reaction but it is known that the rhodium complex (II) loses a molecule of triphenylphosphine on heating in vacuo or on refluxing in toluene or xylene.\textsuperscript{76}

Although (II) has been widely used in decarbonylations, desulphonylations, hydrogenations and carbonylations,\textsuperscript{74-78} it has not been used in the formation of an olefinic or acetylenic linkage. Thus, in spite of the failure of desulphonylation of (I) to give benzyne, reactions were performed with the rhodium complex and diphenylcyclopropenone (III) in the hope of decarbonylating it to form tolan (IV).

Diphenylcyclopropenone (III) was prepared by Breslow's method.\textsuperscript{42}

Diphenylcyclopropenone decomposes on heating above its melting point. Breslow\textsuperscript{42} reports that at 160° for 14 hours it decarbonylates to give an 80% yield of tolan; at 190° the decarbonylation is much more rapid.
but at 145-150° after 36 hours only 20% tolan is formed with a 40% yield of a dimer of diphenylcyclopropenone. When the ketone (III) was shaken with the rhodium complex (II) in benzene for 2 hours a 25% yield of cis-1,2-diphenylacrylic acid (V) was obtained. No tolan was found and no starting material was recovered. (Cis-1,2-diphenylacrylic acid can be obtained by hydrolysis of (III) by ethanolic sodium hydroxide and an authentic specimen was prepared by this method.) The acid (V) is possibly an artefact formed in work up of the reaction, although on this reasoning one would expect some recovery of starting material.

When the reactants were refluxed in dry benzene decarbonylation proceeded smoothly and tolan was formed in good yield.

A similar decarbonylation of (III) was observed when it was refluxed in benzene with chlorocarbonyl-bis(triphenylphosphine) iridium, although in lower yield. Tolan was formed in 44% yield and (III) was recovered in 53% yield. Thus, the decarbonylation with the iridium complex is probably less complicated than that with the
rhodium complex and the yield of tolan based on unrecovered starting material was 91.5%. However, when o-sulphobenzoic anhydride and the iridium complex were refluxed in benzene no desulphonylation occurred.

The decarbonylation of diphenylcyclopropenone probably proceeded through an intermediate solvated complex which reacts with (III) to give a complex molecule which loses carbon monoxide and then liberates tolan. Tsuji and Ohno have proposed this type of mechanism for the decarbonylation of aldehydes.

\[
\text{Rh(BPh}_3\text{)}_2\text{Cl} + \text{S} \quad \rightarrow \quad \text{Rh(BPh}_3\text{)}_2\text{SCl} + \text{Ph}_3\text{P}
\]

(III)

\[
\text{CO} + \text{Rh(BPh}_3\text{)}_2\text{SCl} \quad \leftarrow \quad \text{Rh(BPh}_3\text{)}_2\text{S(III)Cl}
\]

+ \text{PhC}≡\text{CPh}

\[(S = \text{solvent, in this case benzene.})\]
2-PHENYL-3,1-BENZOXAZIN-4-ONE

The compound 2-phenyl-3,1-benzoxazin-4-one (VI) was prepared by the method of Zentmeyer and Wagner as a potential benzyne precursor.

\[
\text{NH}_2 \quad \text{CO}_2\text{Na} \quad + \quad \text{NaOH} + \text{PhCOCl} \quad \rightarrow \quad \text{NHCOPh} + \text{NaCl} + \text{H}_2\text{O}
\]

\[
\text{(VI)} \quad \xrightarrow{\text{HCl}} \quad \text{Ac}_2\text{O} \quad \rightarrow \quad \text{NHCOPh} \quad \xrightarrow{\text{CO}_2 + \text{PhCEN}}
\]

The desired fragmentation was the breaking of the heterocyclic ring and the elimination of carbon dioxide and benzonitrile.

However, (VI) was subjected to irradiation and pyrolysis without any decomposition being observed. Mass spectral fragmentation showed the base peak to be the parent ion (223); a large peak was observed at 179 corresponding to loss of carbon dioxide and a large peak at 105 \((\text{C}_6\text{H}_4\text{CO}^+)\). No peak corresponding to the loss of
benzonitrile was observed. However, a relatively small peak was observed at 76 corresponding to benzyne.
The attempted generation of benzyne from catechol thionocarbonate (I) was initially prompted by Corey's stereospecific olefin synthesis from 1,2-diols. The 1,2-diol was converted into the thionocarbonate by treatment with thiocarbonyldiimidazole or by successive treatment in dry tetrahydrofuran solution with n-butyl lithium, carbon disulphide and iodomethane. The thionocarbonate was desulphurised with refluxing trialkyl phosphites to give the olefin:

\[
\overset{O}{C} - C\overset{O}{C} \xrightarrow{\text{thiocarbonyldiimidazole}} \overset{O}{C} = C\overset{(RO)_3P}{\xrightarrow{\text{triaalkyl phosphite}}} \overset{O}{C} = C + CO_2 + (RO)_3PS
\]

Thus, (I) prepared from catechol and thiophosgene, could by analogy give benzyne on treatment with a trialkyl phosphite.

Prior to Corey's work, Keough and Grayson.
had deoxygenated cyclic carbonate esters to obtain the corresponding olefin. Ethylene carbonate reacted with triphenylphosphine at 130-200° under nitrogen.

\[
\begin{align*}
\text{CH}_2\text{-O}\text{C}=\text{O} + \text{Ph}_3\text{P} &\rightarrow \text{CH}_2\text{=CH}_2 + \text{CO}_2 + \text{Ph}_3\text{PO} \\
\end{align*}
\]

Phenylethylene carbonate required the presence of copper powder catalyst before reaction commenced. Use of a more basic phosphine (e.g. tributylphosphine) favoured olefin formation. However, ethylene carbonate was unaffected by refluxing triethyl- or triphenyl phosphite.

During our investigation of the reaction between catechol thionocarbonate and trialkyl phosphites, both Corey\(^{82,83}\) and Hull\(^{84}\) published results of their work on the same reactions. Corey at first suggested,\(^{79}\) without giving any evidence, that the product of the reaction was a cyclopropane derivative (II). However, Hull\(^{84}\) proposed structure (III) for the product of the reaction.
This structure was based on the i.r. spectrum which showed a strong, sharp peak at 1756 cm\(^{-1}\) (the trioxygenated olefinic group) and on the following experimental evidence: hydrogenation gave compound (IV), tetracyanoethylene gave (V) and hydrolysis gave (VI), (VII), catechol and methylene dioxybenzene.

Corey then supported Hull's structure largely on mass spectral data.

Haines prepared the thionocarbonates of 1,2-5,6-di-O-isopropylidene-D-mannitol and benzyl 2-O-benzyl-\(\beta\)-L-arabinopyranoside and successfully reacted them with trimethyl phosphite to obtain the olefinic carbohydrates.

Our preparation of catechol thionocarbonate was essentially that described by Autenreith and Hefner. However, instead of purifying the product by repeated crystallisations from ethanol it was found more convenient
to sublime the crude solid under reduced pressure. The thionocarbonate was obtained as pale yellow needles (92% from the crude reaction product).

**Reaction of Catechol Thionocarbonate with Triethyl Phosphite.**

The following mechanisms are possible for the generation of benzyne in this reaction:

(i) Attack of the phosphite on sulphur with subsequent formation of a carbene which could give benzyne by loss of a molecule of carbon dioxide.

\[
\text{O} = \text{S} + (\text{EtO})_3\text{P} \rightarrow \text{O} \quad \text{C} \quad \text{Et} \quad \text{Et} \quad (\text{EtO})_3\text{P} = \text{S} \\
\text{(I)}
\]

(ii) Attack of the phosphite on the carbon atom of the thionocarbonyl group with formation of a 6-membered cyclic intermediate which decomposes to give benzyne.
The formation of the product (III) can be explained by mechanism (i) if the intermediate carbene is too stable to eliminate carbon dioxide. Dimerisation of the carbene would occur and the carbene could then attack an ether oxygen of the dimer.

This postulate is supported by the fact that no benzyne products were ever observed. Also reaction of phthalic anhydride with triethyl phosphite produces the dimer.
In this case the carbene is stabilised by resonance. The carbene obtained from catechol thionocarbonate can be stabilised similarly.

However, the occurrence of a free carbene is unlikely in view of the failure to trap it by reaction in the presence of cyclohexene and by no observation of a phosphonate derived from reaction of the carbene with triethyl phosphite or traces of the secondary diethyl phosphite.

We suggest the following mechanism which does
not involve a free carbene: attack of the phosphite on (I) giving rise to a phosphorus ylid which reacts with another molecule of (I) to give the dimer; reaction then occurs with a further molecule of (I) to give (III).

\[(I) + (\text{EtO})_3\text{P} \rightarrow \text{Phenyl-S-P(\text{EtO})_3} \]

\[\text{Phenyl-S-P(\text{EtO})_3} \rightarrow \text{Phenyl-P(\text{EtO})_3+EtO}_3\text{PS} \]

It is reported that in the reaction of the trithio-
carbonate (VIII) with trimethyl phosphite, the dimer (IX) can be isolated.\(^{87}\)

\[ \text{(VIII)} \quad 2 \text{S} + 3 \text{(MeO)}_3\text{P} \rightarrow \text{(IX)} \quad \text{+ 2(MeO)}_2\text{S} \]

**Attempted Desulphurisations of Catechol Thionocarbonate.**

The reactions of catechol thionocarbonate (I) with triphenylphosphine produced small amounts of triphenylphosphine sulphide but no trace of a desulphurised product. The sulphide is probably formed by reaction of the triphenylphosphine with traces of sulphur in the starting material. The attempted desulphurisation of (I) with Raney nickel was unsuccessful, probably as a result of insufficient activity of the nickel. Benn and May\(^{88}\) heated a benzene solution of (I) and a tenfold weight of Raney nickel under reflux for 4 hours. Fractional distillation and G.L.C. analysis showed the products to be methylenedioxybenzene, catechol and a compound which they suggested to be the dimer (X).

\[ \text{(X)} \]

Catechol thionocarbonate was irradiated on the premise that C=S compounds with \(\pi - \pi^*\) transitions at
about 250 mµ appear to lose sulphur readily on irradiation. Schmidt and Kabitzke irradiated 0-ethylthioacetate (XI) with light of wavelength 254 mµ at 40° in the absence of solvent to obtain 2,3-dioethoxy-2-butene (XII). They proposed the following scheme and actually isolated (XIII) from the reaction. However, we observed no reaction on irradiation of catechol thionocarbonate.

As desulphurisation of catechol thionocarbonate failed to result in benzyne, we decided to investigate the analogous reaction to give a stable, acyclic acetylene. Therefore, 4,5-diphenyldioxolen-2-one (XIV) was prepared with the intention of deoxygenating it to form tolan. The compound (XIV) was prepared by Pfeiffer's method from phosgene and benzoin in the presence of a tertiary base. The reaction proceeds in two stages. Initial mixing of benzoin and phosgene results in the formation of the chloroformic ester (XV) with elimination of hydrogen chloride. The base is then added and a second molecule of hydrogen chloride is eliminated to form (XIV).
The second reaction is a base catalysed enolis- 
ation of the ketone with nucleophilic displacement of the 
chlorine by the enolate anion.

When reaction was attempted between thiophosgene 
and benzoin under similar conditions, the benzoin was 
quantitatively recovered. The mixing of benzoin and 
thiophosgene was carried out in a variety of solvents 
at elevated temperatures without any reaction being 
observed. This is presumably due to the much lower 
reactivity of thiophosgene compared to phosgene.³⁰ 

If (XIV) could be deoxygenated, then drawing 
the analogy with the formation of ethylene from ethylene 
carbonate,³¹ we could expect to obtain tolan (XVI). 
This reaction is intermediate between the formation of 
a stable double bond in the olefin syntheses and the 
attempted formation of a formal strained aromatic triple 
band in the generation of benzyne. No cyclic carbonates 
or thionocarbonates have been reported as precursors 
in acetylene syntheses.
4,5-Diphenyldioxolen-2-one was unattacked by trialkyl phosphites at reflux or by triphenylphosphine at elevated temperatures. This is in agreement with the results of Keough and Grayson. However, these workers reported that deoxygenation of cyclic carbonates to form olefins was favoured by use of tributylphosphine. Therefore, we refluxed (XIV) in tributylphosphine in the hope of obtaining tolan according to the scheme:

\[
\text{(XIV)} \quad \text{PhC} = \text{C-Ph} + \text{Bu}_3\text{P} \rightarrow \quad \text{(XVI)} \quad \text{Ph-C} = \text{C-Ph} + \text{Bu}_3\text{PO} \quad \downarrow
\]

However, no tolan was observed; trans-stilbene was produced. When tolan was heated under reflux in tributylphosphine, analysis by G.L.C. showed the presence of a mixture of hydrocarbons among which were trans and cis-stilbene in the ratio 5:1. Thus the trans-stilbene obtained above could have resulted from reduction of tolan by impurities (e.g. secondary phosphines) in the tributylphosphine. No tolan was present in the reaction products showing that it would not survive the reaction between (XIV) and tributylphosphine.

\[
\text{Ph-C} = \text{C-Ph} + \text{Bu}_3\text{P} \rightarrow \quad \text{Ph} = \text{Ph} + \quad \text{Ph} = \text{Ph} \quad \downarrow
\]

5 : 1
The reaction between (XIV) and tributylphosphine also resulted in the formation of desoxybenzoin (XVII). Attack of the phosphine at an olefinic carbon atom followed by loss of carbon dioxide and reaction of the resultant ylid with water would give rise to (XVII). Tolan could also be obtained by this scheme since the intermediate ylid could undergo an internal Wittig reaction.

\[
\text{Ph} = \text{C} = \text{C} = \text{Ph} + \text{Bu}_3\text{PO} \rightarrow \text{Ph} - \text{C} = \text{C} - \text{Ph} + \text{CO}_2 + \text{Bu}_3\text{PO}
\]

(XVII)

The formation of the 2,3-diphenyl-5-propyl-1,4-dioxadiene (XVIII) from (XIV) and tributyl phosphine proceeds by a mechanism which at the present moment is unknown. However, its formation can be rationalised
by the following scheme: nucleophilic attack of the phosphorus on the oxygen of the carbonyl group followed by hydrogen abstraction to give the ylid (XIX) which could react with a molecule of (XIV) to form the epoxide (XX). This compound would be rapidly deoxygenated by tributylphosphine \(^9\) and the product (XVIII) would result from coincident or subsequent rearrangement.

\[
(XIV) + Bu_3P \rightarrow (XIX) \quad \text{downward arrow}
\]

\[
\begin{align*}
(XIV) & \quad \text{downward arrow}

\quad (XIX)

\quad (XX) & \quad \text{downward arrow}

\quad (XVIII)
\end{align*}
\]
This work was carried out as a result of the observation that catechol thionocarbonate, tetracyclone, and triphenylphosphine in refluxing 1,2,4-trichlorobenzene gave rise to a hydrocarbon, m.p. 323-325°, the hitherto unknown octaphenylfulvalene or octaphenylnaphthalene. The reaction was repeated without the catechol thionocarbonate and it was found that the hydrocarbon was formed by attack of the phosphine on tetracyclone (I). The u.v. spectrum of the hydrocarbon is not at all similar to that of heavily substituted naphthalenes such as tetraphenyl naphthalene or 6-methyl-1,2,3,4-tetraphenylnaphthalene, and in fact shows extended conjugation suggesting that the compound is the fulvalene (II).

The usual reaction between a ketone and a phosphine or a phosphite involves donation of electrons by phosphorus to the electronegative carbon atom of the carbonyl function. However, the electronegativity of this carbon atom in (I) is markedly decreased by delocalisation into the cyclopentadiene ring producing a flow of electrons away from the oxygen.
Thus the oxygen is the electronegative centre and the phosphorus can donate electrons to this atom with the formation of a quasi-phosphonium ion. This ion can then react with another molecule of tetracyclone to form an epoxide (III) which could, in turn, be reduced to the fulvalene (II) by an excess of phosphine or phosphite. Compound (II) could also be formed by deoxygenation of (I) followed by dimerisation of the resulting carbene.

However, when reactions were performed between (I) and phosphites, no trace of the fulvalene (II) was
obtained. Instead the dialkyl 2,3,4,5-tetraphenylcyclopentadienyl phosphate was obtained presumably by further reaction of the quasi-phosphonium ion. The formation of the diethyl cyclopentadienyl phosphate (IV) could result from intramolecular hydrogen abstraction from the β-carbon atom of an ethoxy group with the formation of ethylene; or abstraction from the α-carbon atom with the formation of ethylene or acetaldehyde.

![Chemical structure diagrams]

However, no ethylene or acetaldehyde was observed by G.L.C. of the reaction mixture and comparison of the chromatogram so obtained with one obtained from a mixture of acetaldehyde and ethylene in ethanol. Thus, the reaction does not proceed by the above pathways. This conclusion is supported by the fact that the reaction between (I) and trimethyl phosphite gives the methyl homologue of (IV).
In this case, intramolecular hydrogen abstraction would lead to the unlikely expulsion of methylene or to formaldehyde.

\[ \text{(I) } + (\text{OEt})_3\text{P} \]

An alternative mechanism involves dealkylation of the intermediate by phosphite and presumably this is the most likely pathway.

\[ \text{(IV)} \]

These reactions between tetracyclone and trialkyl phosphites are similar to those reported between phthalic anhydride and trialkyl phosphites,\textsuperscript{66} which give comparable phosphate esters. However, in the latter case biphthalyl, analogous to our desired fulvalene, was the major product.
After our work was completed, Borowitz and Anschel reported the reactions between triethyl phosphate and fluorenone. At room temperature they obtained 2,2,2-triethoxy-4,5-bis-diphenylene-1,3,2-dioxaphospholane (V); at 150-180° they obtained 9-diphenylene phenanthrone (VI) and the fused ring fulvalene bifluorenylidene (VII).

The reactions we performed with tetracyclone and trialkyl phosphites formed 2,3,4,5-tetraphenylcyclopentenone (VIII) in varying yields. The mechanism is unknown but tetracyclone and related cyclopentadienes are reduced with great ease.

An independent synthesis of (IV) (R = Me) was attempted by reaction between tetracyclone (I) and dimethyl phosphate. Unfortunately (IV) was not formed and the products of the reaction were (VIII) and 4-dimethoxyphosphinyl-2,3,4,5-tetraphenylcyclopent-2-enone (IX). Prolonged refluxing of (I) with dimethyl phosphate gave tetraphenylcyclopentadiene (X) as the
main product. This compound was also formed by heating (VIII) under reflux in dimethyl phosphite.

Thus, the formation of (VIII) in reactions between (I) and trialkyl phosphites could result from the presence of a small amount of a dialkyl phosphite. This conclusion is supported by the formation of (VIII) by heating diethyl-2,3,4,5-tetraphenylcyclopentadienyl phosphate (IV) under reflux in dimethyl phosphite.

Borowitz and Anschel obtained the fulvalene (VII) by prolonged refluxing of fluorenone in tributylphosphine. However, prior to their report we investigated the reaction of tetracyclone (I) with refluxing tributylphosphine. No fulvalene was obtained, the major reaction product being tetraphenylcyclopentadiene (X). This reaction constitutes a very useful synthetic route to the interesting diene (X) which is very tedious to prepare otherwise. Presumably deoxygenation of (I) followed by hydrogen abstraction by the carbene is involved.
However, further investigation of this reaction is necessary before a mechanism can be assigned with certainty.
The compounds 1-diazotetraphenylcyclopentadiene (I) and 1,1-dibromo-2,3,4,5-tetraphenylcyclopentadiene (III) were synthesised as proposed precursors to the formation of tetraphenylcarbenacyclopentadiene in the hope that it would in turn form the previously discussed octaphenylfulvalene.

Tetracyclone does not show reactions characteristic of a normal ketone because of delocalisation into the cyclopentadiene ring.

Only two carbonyl derivatives were known previously, the 4-nitro- and the 2,4-dinitrophenylhydrazones and these were obtained only under vigorous conditions. By analogy we prepared the tosyl hydrazone of tetracyclone by reaction between tosyl hydrazine and tetracyclone in refluxing dioxan containing concentrated sulphuric acid. The tosyl hydrazone was not isolated but was decomposed by chromatography to give (I).

After this work was complete Lloyd and Wasson employed the same procedure for the preparation of the tosyl hydrazone but they isolated it and decomposed it.
in good yield to (I). An attempt to follow their isolation procedure was found unsatisfactory and was abandoned as a preparative route.

Previous syntheses of (I) and other diazo-cyclopentadienes involved reaction of toluene p-sulphonyl azide with the cyclopentadiene in the presence of an amine or with the lithium salt of the cyclopentadiene. However, the synthesis of (I) by these methods required tetraphenylcyclopentadiene, the preparation of which was tedious until the novel reaction between tetracyclone and tributylphosphine had been discovered (p. 107).

Evidence for the formation of the carbene from (I) can be found in the formation of tetraphenylcyclopentadienyldiene-pyran and -thiins.
Both photolyses and pyrolyses were carried out with (I) in various solvents. Photolysis in benzene led to a trace of pentaphenylcyclopentadiene formed by insertion of the carbene in the C-H bond of benzene. However, repetition of this experiment produced a variable number of products as observed on T.L.C. but none of the supposed octaphenylfulvalene. Pyrolysis of (I) in toluene also resulted in insertion in a C-H bond of the methyl group to give 1-benzyl-2,3,4,5-tetraphenylcyclopentadiene. Insertion in this much more reactive C-H bond gave much more product than in the benzene case.

Tetraphenylcyclopentadiene was also obtained, presumably by hydrogen abstraction by the carbene. Traces of other products, thought to be hydrocarbons, may have been reduction products of tetraphenylcyclopentadiene derivatives as these are known to undergo partial reduction of the cyclopentadiene ring. Pyrolysis of (I) in
refluxing carbon tetrachloride in air gave tetracyclone. Mixtures of unidentified decomposition products were also obtained. The tetracyclone could have been formed by reaction of the carbene with the oxygen of the air. No fulvalenes were obtained.

When Lloyd and Wasson pyrolysed (I) in boiling mesitylene, they obtained tetraphenylocyclopentene.\(^4\) Pauson and Williams decomposed 1-diazo-2,3,5-triphenylcyclopentadiene but obtained no fulvalene or other tractable product.\(^9\) It would seem that steric factors prevent fulvalene formation as decomposition of 1-diazo-2,3,4-triphenylcyclopentadiene in ethanol led to the formation of the hexaphenylfulvalene.\(^9\)

\[
\text{\begin{tikzpicture}
\end{tikzpicture}}
\]

The compound 1,1-dibromo-2,3,4,5-tetraphenylocyclopentadiene was first prepared by the method of Braye, Hubel and Caplier.\(^5\) 1,4-Dilithiotetraphenylobutadiene (II) was obtained from tolan and lithium
shavings by the method of Smith and Hoehn.\textsuperscript{54} Reaction of (II) with carbon tetrabromide gave 1,1-dibromo-2,3,4,5-tetraphenylocyclopentadiene (III), together with 1,2,3,4-tetraphenylbutadiene.

\[
\text{PhC≡CPh} + 2\text{Li} \rightarrow \text{PhC≡CPh} \quad \text{(II)}
\]

\[
\text{AlBr}_3 + \text{PhC≡CPh} \rightarrow \text{PhC≡CPh} \quad \text{(III)}
\]

The conversion of (II) into (III) is a general reaction for the formation of heterocyclic cyclopentadienes.\textsuperscript{50}

\[
(\text{II}) + \text{RnX(Hal)}_2 \rightarrow \text{PhC\textsubscript{2}X-Rn} + 2\text{LiHal}
\]

\[
X = \text{P, As, Sb}
\]

The reaction of (II) with cuprous bromide was prompted by the reaction of hexabromocyclopentadiene (IV) under similar conditions. Kwitowski and West\textsuperscript{99} obtained perbromofulvalene (V) as dark blue crystals. They showed that the two cyclopentadienyl rings are twisted out of plane by steric hindrance between the 2,5- and the 2',5'-
bromine atoms and the dihedral angle at the central C-C bond is 41°. A similar distortion from planarity would be expected in octaphenylfulvalene. It should be noted that 2,2',3,3',5,5'-hexaphenylfulvalene is unknown. The 1,1-dihydro- derivatives of the above two fulvalenes have been prepared\textsuperscript{97,98} and presumably owe their stability to the lack of steric hindrance between adjacent phenyl groups due to the increased distance between the central carbon atoms and their tetrahedral geometry.

When (III) was treated with cuprous bromide below 0° no octaphenylfulvalene was obtained. However, reaction did take place with the formation of tetracyclone. No evidence of carbene initiated products was found. It should be noted that commercial cuprous bromide did not react with (III) and so cuprous bromide freshly prepared from cupric bromide and sodium sulphite was used.

\(\alpha\)-Eliminations of halogen from gem-dihalo-compounds is widely known. However, when McBee treated hexachlorocyclopentadiene (VI) with cuprous chloride he obtained perchloro-9,10-dihydrofulvalene (VII).\textsuperscript{100} McBee pyrolysed (VII) and obtained a compound m.p. 345-347° to which he ascribed the perchlorofulvalene structure. Mark\textsuperscript{101} subsequently obtained the perchlorofulvalene as dark blue crystals by the action of esters of trivalent phosphorus on (VII) and he showed the compound m.p. 345-347° to be \(\text{C}_{15}\text{Cl}_{12}\) and most probably a tetracyclic chlorocarbon.
Gas phase dechlorination of (VI) has resulted in the formation of the perchlorofulvalene and perchloronaphthalene\textsuperscript{102}. Compound (VII) was shown to be an intermediate in the fulvalene formation but this was not confirmed in the case of the naphthalene. Also no attempt was made to convert the fulvalene to the naphthalene pyrolytically.

Pauson and Williams\textsuperscript{98} carried out debrominations on several dibromocyclopentadienes. They found that 1,1-dibromo-2,3,4-triphenylcyclopentadiene (VIII) was debrominated by zinc or copper in boiling benzene to give the fulvalene (IX). However, zinc in ethanol gave the triphenylcyclopentadiene (X).
When 1,1-dibromo-2,3,5-triphenylcyclopentadiene (XI) was treated with zinc in refluxing benzene Pauson and Williams obtained a product which they thought to be 1,1-dibromo-1,1-dihydro-hexaphenylfulvalene (XII). When they attempted to debrominate (III) similarly they obtained intractable tars. In contrast to this we failed to obtain any reaction when (III) was treated with zinc or copper in refluxing benzene or with sodium iodide in acetone.
Tetraphenylantranilic acid was desired as a precursor to tetraphenylbenzyne. Diazotisation of the acid would give tetraphenylbenzenediazonium-2-carboxylate which by analogy with benzenediazonium-2-carboxylate would decompose to give nitrogen, carbon dioxide and tetraphenylbenzyne. It was intended to conduct the decomposition in the presence of tetracyclone to obtain octaphenylnaphthalene.

Tetraphenylphthalimide (I) was prepared with a view to converting it to tetraphenylantranilic acid by way of a Hofmann degradation. Its preparation was analogous to the preparation of phthalimide from phthalic anhydride and involved passage of ammonia gas into molten tetraphenylphthalic anhydride (II); milder conditions failed.

\[
\begin{align*}
&\text{(II)} \quad \text{+ \text{NH}_3} \quad \text{\rightarrow} \quad \text{(I)} \\
&\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array}
\end{align*}
\]

Attempts to convert (I) into the corresponding anthranilic acid were unsuccessful. The reaction failed in aqueous solution because of the insolubility of (I). In methanol (I) was hydrolysed to tetraphenylphthalic acid.
(III) by bromine and sodium even at 0°. However, no hydrolysis was observed when the bromine was omitted. This suggests that bromination of (I) is taking place followed by ring opening. However, instead of rearrangement then occurring, hydrolysis took place.

\[(I) + Br_2 \rightarrow (III)\]

Aromatic amides and bromoamides are particularly susceptible to this hydrolysis. Hauser and Renfrow report that the rearrangement to the amine is accelerated more than hydrolysis by raising the temperature. Thus our reaction conditions (0° for 3 hours followed by heating) probably enhanced the hydrolysis to the diacid. In fact this hydrolysis occurred to the exclusion of rearrangement as shown by the almost quantitative yields of (III).

The acid (III) was prepared by hydrolysis of (II) and was used in an attempted oxidative decarboxylation by lead tetraacetate. Grob, Ohta and Weiss report that the rearrangement to the amine is accelerated more than hydrolysis by raising the temperature. Thus our reaction conditions (0° for 3 hours followed by heating) probably enhanced the hydrolysis to the diacid. In fact this hydrolysis occurred to the exclusion of rearrangement as shown by the almost quantitative yields of (III).
obtained olefins from aliphatic 1,2-dicarboxylic acids by use of lead tetraacetate. Moore and Arzoumanian applied this reaction to phthalic acid but obtained only phthalic anhydride and benzoic acid as pure compounds. We observed complete lack of reaction between (III) and lead tetraacetate, presumably due to steric hindrance.

An attempted Schmidt reaction with (III) produced only (II) by dehydration by the concentrated sulphuric acid. The anhydride (II) was unaffected by sodium azide and concentrated sulphuric acid. Some reaction appeared to be taking place with sodium azide and fuming sulphuric but no products were isolated. These observations are in agreement with the failure of highly substituted or hindered aromatic dibasic acids such as tetrachlorophthalic acid and naphthalic acid to undergo the Schmidt reaction. However, tetrachloro- and tetrabromophthalimides undergo the Hofmann degradation in very high yield. This would indicate that the failure of tetraphenylphthalimide to undergo the reaction is not simply due to steric factors but is a result of a very large difference in the rates of hydrolysis and rearrangement.
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