STUDIES IN THE WADDEN INVERSION WITH
SPECIAL REFERENCE TO THE EFFECT OF A
PHENYL GROUP ATTACHED TO THE ASYMMETRIC
CARBON ATOM

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STUDIES IN THE GALVIN INVERSION
WITH SPECIAL REFERENCE TO THE EFFECT
OF A PHENYL GROUP ATTACHED TO
THE ASYMMETRIC CARBON ATOM.

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February, 1932.
P. Walden, in 1895 when studying the action of reagents on dextrorotatory chlorosuccinic acid, found that strong bases, like potassium hydroxide, gave a laevorotatory malic acid, whereas if weak bases such as silver oxide were used, a dextrorotatory malic acid was obtained.

The change of sign of rotation which occurs in passing from dextro-chlorosuccinic acid to laevo-malic acid does not necessarily indicate the occurrence of a change of configuration, since a great number of reactions are known, in which, although the links of the asymmetric carbon atom are not disturbed, the compound obtained has the opposite sign of rotation to that of the parent substance. The above and similar types of reactions are usually referred to as Walden Inversion reactions.

The discovery of the Walden Inversion is of
great importance because it concerns not only optical activity but the mechanism of substitution in general.

In the usual type of reactions studied, the occurrence of a Walden Inversion is only revealed after two displacement reactions have occurred. For example, in the scheme given above, one of the malic acids has the same configuration as the chlorosuccinic acid from which it was made, whilst the other has the opposite configuration, but it is not possible to decide which of these two acids has the same configuration as dechlorosuccinic acid. Compounds containing a phenyl group directly attached to the asymmetric carbon atom react quite differently from those which are purely aliphatic in character. Thus McKenzie and Clough (J.C.S., 1913, 103, 887), obtained chlorides of opposite sign by the interaction of thienyl chloride and of phosphorus trichloride with 1-phenylmethylcarbinol.
The Walden inversion has so far been investigated in the following types of reactions:

\[
\begin{align*}
R\ R\ R\ C\ OH & \xrightarrow{\text{Cl}_2,\ \text{HCl},\ \text{SOCl}_2,\ \text{etc.}} R\ R\ R\ C\ X \\
1\ 2\ 3 & \rightarrow 1\ 2\ 3 \\
R\ R\ R\ X & \xrightarrow{\text{AgO, H}_2\text{O, KOH}} R\ R\ R\ C\ OH \\
1\ 2\ 3 & \rightarrow 1\ 2\ 3 \\
R\ R\ R\ C\ NH & \xrightarrow{\text{NOCl}} R\ R\ R\ C\ OH \\
1\ 2\ 3 & \rightarrow 1\ 2\ 3 \\
R\ R\ R\ C\ NH & \xrightarrow{\text{NOBr, NOCl}} R\ R\ R\ C\ X \\
1\ 2\ 3 & \rightarrow 1\ 2\ 3 \\
R\ R\ R\ C\ X & \xrightarrow{\text{NH}_3} R\ R\ R\ C\ NH \\
1\ 2\ 3 & \rightarrow 1\ 2\ 3
\end{align*}
\]

Many hypotheses have been put forward with regard to the mechanism of the Walden inversion. Walden (Ber., 1896, 22, 133; 1897, 30, 3148; Walden and Lutz, Ber., on the ground that 1897, 30, 2795) suggested that strong bases probably act in the ionised state, whereas the weak bases are likely to form additive compounds leading to an inversion of configuration. Walden, therefore, concluded that the mode of action of potassium hydroxide represented normal replacement of a group without change of configuration, and the mode of action of silver oxide, an abnormal reaction with change of configuration.

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This view has not been supported by the results of the experiments of Fischer (Annalen, 1911, 301, 132) and of McKenzie (J.C.S., 1906, 811) as shown by the following scheme, in which the results of certain displacements are different from those predicted by Walden's hypothesis.

\[
\begin{align*}
\text{d-alanine} & \xrightarrow{\text{H}^+} \text{d-\(\delta\)-bromopropionic acid} & \xrightarrow{\text{Ag}^+, \text{CO}} & \text{1-lactic acid} \\
\text{NO}_2\text{Br} & \text{NO}_2\text{Br} & \text{CH}_2 & \\
\text{1-\(\delta\)-bromopropionic acid} & \xrightarrow{\text{H}^+, \text{CO}^2} & \text{d-alanine} & \text{d-lactic acid}
\end{align*}
\]

Hypotheses Put Forward to Explain the Walden Inversion.

The general ideas underlying the other important hypotheses of the Walden Inversion are that the reactants form an intermediate compound, and that the entering group separates from this intermediate compound, and rejoins on the opposite side of the molecule, to that occupied by the group to be displaced.

Armstrong (J.C.S., 1896, 69, 1599,) was the first to postulate the formation of an intermediate compound.

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Fischer (Annalen, 1911, 391, 132) and Werner (Ber., 1911, 44, 83) introduced the idea of the substituent group entering on the opposite side of the molecule; Fischer refers to the existence of the entering group in an ionized form.

These views were elaborated by Cadorer (Chem. Zeit., 1910, 34, 1004; 1912, 35, 1327), who explained the formation of intermediate compounds as being due to residual affinity, and pointed out the necessity for the entering group to take up its position before the replaced group leaves, in order to preserve the asymmetry of the molecule, whether or not an inversion occurs.

Büchner (Annalen, 1912, 308, 330), who recognised the process of substitution as involving an exchange of ions, postulated the free existence of the asymmetric group as an ion, called a "witterion", which was assumed to retain its asymmetry, although the central carbon atom was covalently attached to three other groups.
McKenzie and Clough (J.C.S., 1913, 103, 687) showed that several of Billam's conclusions could not be supported experimentally, and expressed the view that the "Swittemord" had its configuration stabilised by the presence of its electric charge. More recently McKenzie, Roger and Wills (J.C.S., 1927, 779), have brought forward experimental evidence which they consider supports this view. On the other hand, Kenyon, Lipscombe, and Phillips (J.C.S., 1930, 415), and Kenyon and Phillips (J.C.S., 1930, 1676), have brought forward evidence to prove that the free existence of a positively charged carbonium ion, in an optically active condition, is not possible.

Lowry (Deuxieme Conseil de Chimie Solvay, 1925, 40) after consideration of evidence derived from the X-ray analysis of the crystal structure of calcite (Bragg, Proc. Roy. Soc., 1914, A, 99, 496), and basic beryllium acetate (Bragg and Morgan, ibid., 1923, A, 104, 437) concluded that the group to be displaced ionised, and the carbonium cation adopted a planar configuration. The entering group was considered to approach the molecule from the opposite side to that occupied by the ionised group. Lowry pointed out the similarity between the resulting structure and that of the HF ion.
On the other hand, Kenyon and Phillips concluded that the planar configuration was more likely to lead to complete racemisation, than to an optically active product of either sign.

Previous to 1923, hypotheses for the explanation of the mechanism of the Walden inversion were incomplete in scope, and limited in application, for two reasons:

(a) The rigid theory of the quadrivalence of the carbon atom, and the lack of understanding of the mechanism of valency, made it impossible to formulate a comprehensive theory of the Walden inversion.

(b) The difficulty of determining the relative configuration of the product, and its parent compound, as distinct from their signs of rotation, made it impossible to say definitely in which reactions a Walden inversion had occurred.

The development of the electronic theory of valency has given a new insight into the mechanism of the reactions of carbon compounds. The carbon atom may now be considered to form linkages by :-

\[
\begin{array}{c}
-+\
\end{array}
\begin{array}{c}
\text{F} \\
\text{H} \\
\text{F}
\end{array}
\begin{array}{c}
\text{X} \\
\text{R}
\end{array}
\begin{array}{c}
\text{R} \\
\text{OH} \\
\text{Y}
\end{array}
\begin{array}{c}
\text{R} \\
\text{2}
\end{array}
\]
(a) **Covalence** formed by sharing of electrons supplied equally by the combining atoms.

(b) **Electrovalence** when one atom donates an electron to the other, acquiring thereby a positive charge, and giving the accepting atom a negative charge.

(c) **Semicovalence** double bonds, or a double bond, each consisting of one electro- and one covalency.

A few elements are considered to form single electron linkages in certain circumstances. The hypotheses of the Walden inversion have been modified to utilise the electronic theory of valency by Kenyon and Phillips (J. Faraday Soc., 1930, 25, 451) who consider that in a substitution reaction, either:—

(a) The entering group exists in solution as an anion, and attaches itself to the opposite side of the asymmetric carbon atom, while the carbonium radicle separates as a cation, and the union of the cation, and the union takes place with inversion of configuration.

(b) The carbonium radicle separates as an anion, in which case a product of the same configuration is produced.
This theory depends on the view that the carbononium kation with only 6 electrons is optically labile and will invert its configuration when an entering group is attracted to the other side of the molecule. In the absence of such an entering group, the unstable configuration may remain (Konyon and Phillips, J.C.S., 1930, 1675).

Further the theory is based on the view that a carbononium ion having a complete octet of electrons is optically stable. This is supported by the experiments of Marvel and Noyes (J.A.C.S., 1930, 43, 2259), and Chiles and Noyes (ibid., 1932, 44, 1798) who isolated and resolved ethyl disaccharate; and Kuhn and Albrecht (Ber., 1927, 60, 1297), who prepared sodium aci-β-nitrobutane in an optically active form.

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CO}_2\text{Et} & \quad \text{Et} \\
\uparrow & \\
\text{C} & \quad \text{H} \quad \text{N} \\
\text{C}_2\text{H}_5 & \quad \text{Et}
\end{align*}
\]
The Relative Configuration of Optically Active Compounds.

The value of experimental results in Walden inversion reactions has been greatly reduced by the difficulty experienced in ascertaining the configuration of the product obtained from a substitution reaction.

The methods, at present available, for the determination of the relative configurations of optically active compounds, with one centre of asymmetry, are:-

(a) The physico-chemical method of Clough (J.C.S., 1918, 113, 533) utilised by Friesenborg and Braun (Ber., 55, 1339) and others, which is based on the hypothesis that the rotatory powers of similarly constituted compounds possessing the same configuration, are influenced in a similar manner by changes in external conditions, and by the introduction of the same substituent into a given radicle attached to the asymmetric carbon atom. This method was hampered by lack of criteria, by which to decide whether any two given compounds were similarly constituted.
(b) The method of Phillips (J.C.S. 1923, 123, 44), Houssia, Kenyon and Phillips, J.C.S., 1929, 1700) who showed that $p$-toluenesulphonic and $p$-toluenesulphinic esters of optically active compounds could be made from optically active materials in a manner that insured that no change of configuration occurred. These esters gave derivatives of the carbonium radicle by a series of reactions which were similar in type; and, as the relative configuration of one such compound and the parent compound was known from the method of preparation, then that of the others could be deduced.

(c) A proposed method is based on the observation that the physical properties of a compound RX depends on the polarity of the substituent group X. Applying this to optical activity Rule (J.C.S., 1924, 125, 1121; ibid 1929, 2564; Trans Faraday Soc., 1930, 24, 321) has shown that the magnitude of rotation of a series of compounds RX falls in the order of the polarity of $X$, so that if the position of any group is known, with respect to a table of substituent groups in increasing order of polarity, then its sign of rotation, and approximate rotatory power may be deduced.!
The Scope of the Present Research.

The present research was carried out in order to bring further experimental evidence to bear on the question of the influence of an adjacent phenyl group on the configuration of a product obtained from a substitution reaction.

It has been found that when the halogenation of 1-phenylmethylcarbinol is carried out in the presence of pyridine, with thionyl chloride, with the chlorides and oxychloride of phosphorus, and, in the absence of pyridine, with the chlorides of phosphorus, the product obtained is α-β-chloroethylbenzene; while with phosphorus oxychloride, in the absence of pyridine, almost complete racemisation occurs. These results may be compared with the production of α-β-chloroethylbenzene when thionyl chloride was used in the absence of pyridine.

By the method of Phillips using the p-toluensulphonic ester of 1-phenylmethylcarbinol, the configuration of the chloro-derivative of phenylmethylcarbinol has been established. The conclusion reached has been confirmed by a consideration of the rotatory power of derivatives of 1-phenylmethylcarbinol when arranged in order of increasing polarity.
of the substituent groups. Investigation of the reactions of phenylmethylcarbonyl \textit{p}-toluenesulphonate showed that unlike aliphatic \textit{p}-toluenesulphonates, it resembled the corresponding sulphonate/behave in its reagents, and it has been found to give a new type of inversion reaction.

The electronic theory of valency has been extended to explain the reactions of optically active compounds containing an adjacent phenyl group, and also the part played by the phenyl group in these reactions.

The occurrence of racemisation in substitution reactions has been studied, and an explanation of the phenomenon is suggested.
THE HALOGENATION OF OPTICALLY ACTIVE PHENYL METHYL CARBINOL

IN THE PRESENCE AND ABSENCE OF PYRIDINE, BY THIONYL CHLORIDE AND THE CHLORIDES AND OXYCHLORIDE OF PHOSPHORUS.

In the presence and also in the absence of pyridine, the action of thionyl chloride on optically active aliphatic hydroxy compounds (e.g., ethyl d-lactate, Frankland and Garner, J.C.S., 1914, 108, 1191; 1-β-ethyl alcohol, Levine and Kisekta, J. Biol. Chem., 1924, 59, 49; McKenzie and Tisdale, ibid., 1924, 62, 351) is accompanied by a change in the sign of rotation.

\[
\text{CH}_3 \text{CH} (\text{OH}) \text{CO} \text{Et} + \text{SOCl}_2 \rightarrow \text{CH}_3 \text{C(\text{Cl})COEt}
\]

The action of phosphorus pentachloride on ethyl d-lactate (Purdie and Williamson, J.C.S., 1924, 2620) also leads to a change of sign of rotation.

Towards compounds containing a phenyl group directly attached to the asymmetric carbon atom, the behaviour of phosphorus trichloride and phosphorus pentachloride is similar to their behaviour towards the purely aliphatic compounds. On the other hand, the behaviour
of thionyl chloride towards the semi-aromatic compounds differs from that of the chlorides of phosphorus, and also from its own behaviour towards aliphatic compounds, since with the semi-aromatic compounds (e.g., ethyl \( {\text{I}} \)-mandelate, McKenzie and Clough, J.C.S., 1910, 27, 2564; McKenzie and Barrow, J.C.S., 1911, 29, 1910), it yields products with the same sign of rotation.

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

It has been shown, however, that in the presence of pyridine and other bases, the action of thionyl chloride on ethyl \( {\text{I}} \)-mandelate leads to a result similar to that obtained when phosphorus pentachloride is used (Kenyon, Lipscomb and Phillips, J.C.S., 1930, 415). The halogenation of \( {\text{I}} \)-phenylmethylcarbinol has now been studied from this standpoint, since the substantiation and extension of this observation, by the investigation of the combined action of thionyl chloride and tertiary bases on other compounds containing an \( {\alpha} \)-phenyl group,
is obviously desirable. It is also of interest to determine the influence (if any) of tertiary bases on the sign of rotation of the products obtained, using the chlorides and the oxychloride of phosphorus.

The results of the investigation, together with the sign and magnitude of the rotation of the product, are given in Table 1.
### TABLE 1.

**The Specific Rotatory Powers of α-Chloroethylbenzene**

obtained by the Halogenation of 1-Phenylmethylecarbinol.*

<table>
<thead>
<tr>
<th>Halogenating Agent</th>
<th>Tertiary Base</th>
<th>Specific Rotary Power of 1-alcohol</th>
<th>Specific Rotary Power of α-chloroethylbenzene</th>
<th>Observer</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOCl₂, 2.5 mols.</td>
<td>none</td>
<td>-31.7</td>
<td>-33.3</td>
<td>McC. and C.</td>
</tr>
<tr>
<td>SOCl₂, 2.0 mols.</td>
<td>Pyridine, 1 mol.</td>
<td>49.8</td>
<td>+17.3</td>
<td>Taylor.</td>
</tr>
<tr>
<td>SOCl₂, 2.0 mols.</td>
<td>Pyridine, 2 mols.</td>
<td>49.8</td>
<td>+36.3</td>
<td>Taylor.</td>
</tr>
<tr>
<td>SOCl₂, 2.0 mols.</td>
<td>Quinoline, 2 mols.</td>
<td>43.7</td>
<td>+16.1</td>
<td>Taylor.</td>
</tr>
<tr>
<td>HCl</td>
<td>none</td>
<td>51.3</td>
<td>+6.9</td>
<td>P. and K.</td>
</tr>
<tr>
<td>PCl₃, 3.5 mols.</td>
<td>none</td>
<td>51.7</td>
<td>+10.1</td>
<td>McC. and C.</td>
</tr>
<tr>
<td>PCl₃, 2.0 mols. K₂CO₃</td>
<td>51.7</td>
<td>+19.0</td>
<td>Taylor.</td>
<td></td>
</tr>
<tr>
<td>PCl₃, 2.0 mols.</td>
<td>Pyridine, 1 mol.</td>
<td>49.8</td>
<td>+64.1</td>
<td>Taylor.</td>
</tr>
<tr>
<td>PCl₃, 2.5 mols.</td>
<td>none</td>
<td>33.9</td>
<td>+0.3</td>
<td>Taylor.</td>
</tr>
<tr>
<td>PCl₃, 2.0 mols.</td>
<td>Pyridine, 1 mol.</td>
<td>52.1</td>
<td>+12.6</td>
<td>Taylor.</td>
</tr>
<tr>
<td>PCl₅, 2.0 mols.</td>
<td>none</td>
<td>43.7</td>
<td>+4.5</td>
<td>Taylor.</td>
</tr>
<tr>
<td>PCl₅, 2.0 mols.</td>
<td>Pyridine, 1 mol.</td>
<td>43.8</td>
<td>+10.4</td>
<td>Taylor.</td>
</tr>
</tbody>
</table>

*Throughout the theoretical portion of this thesis it is assumed that only 1-phenylmethylecarbinol was used. Actually some of these experiments were performed using the α-alcohol.*
For purposes of comparison the sign and magnitude of rotation of the \( \alpha \)-chloroethylbenzene obtained by the action of hydrogen chloride (Pickard and Kenyon, J.C.S., 1911, 22, 45) and of thionyl chloride and phosphorus trichloride (Hodgson and Clough, J.C.S., 1913, 123, 687) on \( \alpha \)-phenylmethylcarbinol have been incorporated in this table; the specific rotatory powers (\( [\alpha]_D \)) of the products obtained by these authors having been calculated from the recorded values, by aid of the dispersion ratio, \( [\alpha]_D \), and \( [\alpha]_583 \), which has been determined for this purpose.

It can be seen from Table 1 that, as in the previous experiments with ethyl \( \beta \)-mandelate, the presence of either pyridine or quinoline causes a reversal in the sign of rotation of the \( \alpha \)-chloroethylbenzene obtained, when thionyl chloride is employed as the halogenating agent. Further the larger the proportion of pyridine employed, within limits, the greater the magnitude of rotation of the resulting \( \alpha \)-chloroethylbenzene. Where the chlorides of phosphorus were employed, the \( \alpha \)-chloroethylbenzene obtained, had the opposite sign of rotation to the original alcohol, and further, the presence of pyridine caused the magnitude of the rotation of the product to increase.
When phosphorus oxychloride was employed alone, the resulting α-chloroethylbenzene was almost optically inactive, but in the presence of pyridine, it had a moderately large rotatory power of the opposite sign to that of the alcohol.

When potassium carbonate was added to the reacting mixture of phosphorus trichloride and 1-phenylmethylearbinol, the sign and magnitude of the rotation of the product was identical with that obtained by Mc.Kenzie and Clough (loc.cit.) using phosphorus trichloride alone. On reaction of phosphorus trichloride and pyridine with 1-phenylmethylearbinol \([\alpha]_{\text{D}}^2 +64^\circ\) the α-chloroethylbenzene obtained had \([\alpha]_{\text{D}}^2 +64^\circ\). This is significant in view of Mc. Kenzie and Clough's (loc. cit.) observation that, when the reaction between the 1-alcohol and thionyl chloride was carefully controlled, the α-chloroethylbenzene obtained under varying conditions, always possessed a specific rotatory power of \([\alpha]_{\text{D}}^2 -63^\circ\). This constancy in the rotatory power was advanced as a reason for concluding that halogenation occurred without any appreciable racemisation. It therefore follows that
the α-chloroethylbenzene obtained by the reaction of phosphorus trichloride and pyridine, is also optically pure and that one of these reactions is an example of inversion without the occurrence of any racemisation.

\[
\begin{align*}
\text{Ph} & \quad \text{H} \\
\text{Me} & \quad \text{Cl} \\
\text{Ph} & \quad \text{H} \\
\text{Me} \quad \text{OH} \\
\end{align*}
\]

\[
\left[\alpha\right] + 64.1 \quad 1-
\]

\[
\left[\alpha\right] - 63.3
\]

The effect of variation of the conditions governing the halogenation reactions on the yields of the products obtained are given in tables VII and IX.

It will be seen from table VII that the reaction between phosphorus pentachloride and phenylmethylcarbinol was successfully carried out by two distinct methods, each giving a 70% yield. This is in contrast to the observations of Mc.Kenzie and Clough (loc.cit), who were unable to isolate any α-chloroethylbenzene when using phosphorus pentachloride. When used in conjunction with pyridine, the chlorides and oxychloride of phosphorus give a greater yield of the desired chloride. This result is in agreement with the larger yield of methyl α-di-chlorophenyl acetate obtained by the combined action of phosphorus oxychloride and pyridine on methyl
and with the observation of Boyd and Laidham (J. C.S. 1928, 315) that the diaryloxypyropyl chlorides are not formed from the corresponding alcohols in the presence of phosphorus oxychloride alone, but only when pyridine is present.

The presence of potassium carbonate in the reaction with phosphorus trichloride lowered the yield of \( \alpha \)-chloroethylbenzene to 20%, which is much lower than that obtained in the other halogenation reactions investigated although McKeemie and Clough, unfortunately, do not give the yield obtained when phosphorus trichloride was used alone.

In table IX, the reactions carried out with phosphorus oxychloride are summarised; it was found that the halogenation reaction did not proceed at temperatures below 50°C, but that once started, the reaction raised the temperature of the reactants to much higher temperatures, when styrene and a polymeride of styrene were obtained. It was therefore, found necessary to keep the reactants between the temperature range of 10°- 20° C, and this was done by using a large excess of an inert solvent, ether, and allowing 24-48 hours for the reaction to reach completion. A 60% yield of \( \alpha \)-chloroethylbenzene was
thus obtained, together with a 23\% yield
of \( \alpha^\prime \)-diphenyldiethylether. The ether had the same
sign of rotation as the alcohol used. When the
d-alcohol \( [\alpha]_D^{25} + 7 (1=0.25) \) was employed the
\( \alpha^\prime \)-diphenyldiethylether obtained had \( \alpha = +20^\circ \)
(1=0.25). This would correspond to a calculated
specific rotatory power of \( \alpha = +190 (1=1.0) \) for the ether
when the optically pure alcohol is employed.

The need for careful temperature control,
possibly accounts for the failure of Boyd and Jadhas
(loc. cit.) to obtain the diaryloxypropyl chlorides
from the corresponding alcohols by the use of phosphorus
oxychloride alone and the low yield of \( \alpha \)-chlorophenyl-
acetate obtained by Wagner - Jaureg (loc. cit).

Higher boiling products were obtained from the
reaction of phosphorus oxychloride with phenylmethyl
carbinol, which were shown to contain phosphorus.
Attempts were made to isolate these compounds in a pure
state, since, it was thought that, their further study
might give valuable information as to the chemical
constitution of the intermediate compounds produced in
halogenation reactions. They could not, however, be
induced to crystallise, and their distillation at
pressures well below 0.1 mm. was attended by

-22-
decomposition. The distillates obtained were free from phosphorus, and consisted almost entirely of styrene and its polymers.

According to the views of Kenyon and Phillips (Trans. Faraday Soc., 1930, 26, 451), the reaction of thionyl chloride with 1-β-octanol occurs with inversion of configuration; while from its reaction with 1-phenylmethylcarbinol the chloride is produced without the occurrence of a change in configuration. From this view, it would follow that, the halogenation of phenylmethylcarbinol by the chlorides and the oxychloride of phosphorus, in the presence, or in the absence of pyridine, and by thionyl chloride in the presence of pyridine, is attended by an inversion of configuration. This is in direct agreement with the explanation of the mechanism of the halogenation of ethyl 1-mandelate, given by Kenyon, Lipscomb, and Phillips (loc. cit.)

In order to substantiate this hypothesis, and in order to draw definite conclusions as to the mechanism of the replacement of hydroxyl by chlorine, it is necessary to determine the relative configurations of

-23-
phenylmethylearbitrol and α-chloroethylbenzene. This has been carried out by the p-toluene sulphonate method of Phillips, and is described in the following section.
THE REACTIONS OF 1-PHENYLPROPIONYL

1-P-TOLUENSULFONIUM AND 1-P-TOLUESULFONIUM.

The Preparation and General Reactions of Aromatic Sulphinic Esters.

Esters of the aromatic sulphinic acids have been prepared by the interaction of the sodium salts of the acids with the chloroformates of the alcohols (Otto and Bossing, Ber., 1885, 19, 2439; 1886, 19, 1224). Phillips (J.C.S., 1923, 2552) prepared p-toluenesulphinic esters by the reaction of p-toluenesulphonyl chloride on the alcohols. The method was successfully applied to the preparation of the p-toluene sulphinates of phenylmethylcarbinol, by Kenyon and Phillips (J.C.S., 1930, 1076). The esters have also been prepared by displacement of the ethoxy group of ethyl p-toluenesulphinate, by warming that ester with the alcohol, under reduced pressure (Phillips loc. cit.), or by warming the ethyl ester with the alcohol in the presence of a suitable solvent, which is distilled off carrying water, formed in the reaction, with it (Houssia, Kenyon, and Phillips J.C.S., 1923, 1700).
The esters are usually obtained as viscous oils, which can be distilled under reduced pressure in some instances, but usually decompose, *within the occurrence of side reactions.* Isomerisation to the corresponding sulphone may take place on standing, and conversion to the corresponding *p*-toluenesulphonic ester is effected by oxidising agents. Phillips (loc. cit.) failed to obtain any sign of reaction between the *p*-toluenesulphonates of aliphatic alcohols and metallic salts. It has long been known that halogen react with *p*-toluenesulphinic acid according to the equation:-

\[
\text{C}_6\text{H}_5\text{SO}_3\text{H} + \text{X} \rightarrow \text{C}_6\text{H}_5\text{SO}_3\text{X} + \text{HX}
\]

Houssia Kenyon and Phillips (loc. cit.) found that analogous reactions take place when esters of *p*-toluenesulphinic acid are used. This was made the basis of a method for determining the relative configurations of laevorotatory \(\beta\)-octyl alcohol and laevorotatory \(\beta\)-chloro-octane.

The preparation of the *p*-toluenesulphinic ester of 1-\(\beta\)-octanol may be represented as follows:-

\[
\text{C}_6\text{H}_5\text{C} \quad \text{H} \quad \text{C}_6\text{H}_5\text{C} \quad \text{H}
\]

\[
\text{C}_6\text{H}_5 \quad \text{CH}_2 + \text{Cl} \quad \text{SO}_3\text{H} \quad \text{C}_6\text{H}_5 \quad \text{SO}_3\text{C}_6\text{H}_5
\]

-26-
It can be assumed that, reaction occurs without disturbing the valency bonds of the asymmetric carbon atom, and the resulting \( p \)-toluenesulphinate will, therefore, have the \( \delta \)-configuration. When the \( p \)-toluenesulphinate of the \( \delta \)-octyl alcohol is treated with (a) chlorine, (b) hypochlorous acid, the products obtained are-(a) the chloro-derivative of the alcohol, and (b) the alcohol.

These two reactions are closely similar in \( \delta \)-configuration type, the hydroxyl \( \delta \)-ion acting in an identical manner with the chlorine \( \delta \)-ion; thus the chloride, and the alcohol formed, may be assumed to have the same configuration, \( \delta \)-\( \delta \)-1a.

Since when the \( \delta \)-sulphinate is used, the secondary octyl alcohol recovered is dextrorotatory, the reactions take place with inversion of configuration, and the \( \delta \)-octyl chloride formed which is dextrorotatory, has therefore the \( \delta \)-configuration.
The Reaction of 1-3-Octylcarbinol With (a) Chlorine
(b) Hypochlorous Acid.
The Reactions of 1-Phenylmethylcarbonyl p-Toluene sulphonate.

The p-toluene sulphinic ester of 1-phenylmethylcarbinol was prepared by the reaction of p-toluene sulphinyl chloride with the 1-alcohol. Owing to its unstable nature, it was not distilled, and even on standing at room temperature, it was slowly converted to the corresponding sulphone.

The ester was found to react with acetic acid to give phenylmethylcarbonyl acetate. The ester did not react with boiling ethyl alcohol, but in the presence of lithium chloride, 1-phenyli diethyl ether was formed. At first, it was thought that the products arose from quantities of the p-toluene sulphonate produced intermediately by oxidation of the sulphinic ester; but identical results were obtained when the reactions were carried out in an atmosphere of nitrogen. These results are in marked contrast to those obtained from the reactions of the sulphinic esters, so far investigated, none of which have a phenyl group attached to the central carbon atom.

Although the sulphonyl group, attached to the
phenylmethylcarbinyl radicle, can be readily replaced in the presence of lithium chloride, it resists replacement by other groups. For example, only traces of \( \alpha \)-phenyldiethyl ether were obtained by the action of sodium ethoxide on the \( p \)-toluenesulphinic ester, while an attempt to obtain \( \alpha \)-phenylethylamine, by the action of concentrated aqueous ammonia on the sulphinic acid in a sealed tube, at 100°C, failed to give any appreciable yield of the desired amine. The reactions carried out with the \( p \)-toluenesulphinic ester are tabulated in table II. The specific rotatory powers of the ether and acetate obtained, are given; and the specific rotatory power of the ether, formed by the reaction of the potassium derivative of \( l \)-phenylmethylcarbinol and ethyl bromide, is also given for comparative purposes. Since the latter reaction does not involve a change of the valency bonds of the asymmetric carbon atom, the product may be considered to have the same configuration as the \( l \)-alcohol, and to be optically pure.
TABLE II

The Reactions attempted with 1-phenylmethylecarbinyl p-Toluenesulphonate.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Product</th>
<th>Rotatory Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl alcohol, lithium chloride, (N₂)</td>
<td>( \alpha )-phenyldiethyl ether</td>
<td>-16.5</td>
</tr>
<tr>
<td>Ethyl alcohol, lithium chloride, air.</td>
<td>( \alpha )-phenyldiethylether</td>
<td>-11.2</td>
</tr>
<tr>
<td>Potassium 1-phenylmethyl-( \alpha )-phenyldiethyl carbinoxide, ethyl bromide, ether.</td>
<td>( \alpha )-phenyldiethyl ether</td>
<td>-88.8</td>
</tr>
<tr>
<td>1-( \alpha )-chloroethylbenzene, ethyl alcohol.</td>
<td>( \alpha )-phenyldiethyl ether</td>
<td>+13.5</td>
</tr>
<tr>
<td>Acetic acid (N₂)</td>
<td>phenylmethylcarbinyl acetate</td>
<td>0</td>
</tr>
<tr>
<td>Ethyl alcohol.</td>
<td>no reaction</td>
<td>-</td>
</tr>
<tr>
<td>Sodium ethoxide.</td>
<td>( \alpha )-phenyldiethyl ether (trace)</td>
<td>-</td>
</tr>
<tr>
<td>Aqueous ammonia.</td>
<td>no reaction</td>
<td>-</td>
</tr>
</tbody>
</table>
The ether obtained from the 1-sulphinate had a negative sign of rotation when air was excluded, and also when air was bubbled through the reaction mixture. In this case, the specific rotatory power of the ether was less than when air was not employed. Since 1-α-chloroethylbenzene, when warmed with ethyl alcohol, gives dextrorotatory α-phenyldiethyl ether (Phillips and Kenyon J.C.S., 1930, 1676), the former reactions may be explained on the assumption that, lithium chloride reacts with the sulphinate to give α-chloroethylbenzene with a reversal of sign of rotation, and that the α-chloroethylbenzene formed, is changed to α-phenyldiethyl ether by reaction with the ethyl alcohol, thus undergoing a second reversal of sign of rotation. The ether would therefore have the same sign of rotation as the parent alcohol. When air is bubbled through the reactants, it is probable that, besides the reaction described above, some 1-sulphinate oxydises to the 1-sulphonate and this reacts directly with ethyl alcohol, to give the dextrorotatory ether, which would lower the sign of rotation of the laevo ether, formed through the intermediate formation of the chloride.

The phenylmethylcarbinyl acetate, formed by
the reaction of the 1-sulphinate and acetic acid, was optically inactive.

The courses of the reactions are given diagrammatically on p. 45a.

The Preparation and Properties of p-Toluene sulphonie esters.

The p-toluene sulphonylic esters of various alcohols have been prepared by the direct action of p-toluene sulphonylic chloride, or ethyl p-toluene sulphonate, on the alcohol, (Ferns and Lapworth J.C.S., 1912, 101, 273, and Phillips loc. cit) or on the potassium derivative of the alcohol (Frye and Paterson J.C.S., 1906, 32, 332).

Where direct preparation is not possible, as in the case of the β-ethyl ester, the sulphonie ester is firstly prepared by reaction of the p-toluene sulphinyl chloride and the alcohol, and is then oxidised by potassium permanganate to the corresponding p-toluene sulphonate. These reactions are considered to take place without disturbing the valency bonds of
the asymmetric carbon atom, and the resulting sulphonate has therefore, the same configuration as the parent alcohol.

Ferns and Lapworth have shown that the sulphonic esters undergo many reactions, in which they resemble halide esters, rather than those of carboxylic acids; this is true of the reactions with alkalies, alkoxides, metallic salts, aliphatic alcohols, amines and Grignard reagents. Thus, for example, ethyl alcohol reacts with a sulphonic ester to give the corresponding ethyl ether, but, with a carboxylic ester, the alcohol is liberated and the ethyl ester of the carboxylic acid is formed. With metallic salts, the sulphonic ester reacts to give the ester of the alcohol and the acid radicle, together with the metallic sulphonate; whereas the carboxylic ester is without action on metallic salts.

\[
\begin{align*}
R-O-SO_2\text{C}_7\text{H}_8 \quad &\quad RO\quad CO\quad CH_3 \\
^{\text{EtO}}|H\quad &\quad ^{\text{H}}|OEt \\
^{\text{CH}_3\text{COO}}|E\quad &\quad ^{\text{OEt}} \\
^{\text{RO\quad } E\text{T} + \text{CH}_3\text{COOR}}\quad &\quad ^{\text{ROH} + \text{CH}_3\text{COOEt}}.
\end{align*}
\]
The essential difference in the behaviour of the two types of compounds is, that the division of the sulphonate molecule takes place between the carbon and the oxygen atoms, leaving the link between oxygen and sulphur intact. The division of the carboxylic ester takes place between the oxygen and the carbon atom of the carbonyl group, and the oxygen remains attached to the alkylating radicle. It will be noted that the valency bonds of the \( \alpha \)-carbon atom will remain intact in the case of the carboxylic ester, but one of them will be disturbed in the sulphonate ester.

The difference may be ascribed to the positive charge in the sulphur atom, which attracts electrons from the oxygen, which, in turn, attracts the covalent linkage electrons by which it is joined to the central carbon atom. The movement of electrons is illustrated diagramatically by the use of an arrow, instead of the usual valency bond.

The oxygen, once having attracted the electrons to itself, tends to separate from the carbon atom, retaining a negative charge, and leaving the carbon with a positive charge.

The movement of electrons is shown in the diagram.

In the reactions of carboxylic esters, the
A Comparison Between Carboxylic and Sulphonic Esters.

The movement of electrons is shown as follows:

[Chemical structures and reactions]

---

---
oxygen shows a tendency to break from the carboxyl carbon atom, and to retain its attachment to the central carbon atom.

The reaction of the \( p \)-toluenesulphonates of secondary alcohols with metallic salts to yield esters was applied to the study of optically active secondary alcohols by Phillips (J.C.S., 1925, 44), who found that \( \alpha \)-benzylmethylearbyl \( p \)-toluenesulphonate, on reaction with potassium acetate, \( \alpha \)-acetooacetate, gave the corresponding ester with the \( \alpha \)-configuration.

Similar results were obtained, using the \( p \)-toluenesulphonates of ethyl \( \alpha \)-lactate (Kaneyo, Phillips, and Turley, J.C.S., 1925, 127, 393), of \( \alpha \)-menthol and \( \alpha \)-octanol (Phillips, ibid. p. 2566), and of the \( \alpha \)- and \( \beta \)-methylcyclohexanols (Gough, Hunter, and Kenyon, J.C.S., 1932, 2062).

Kaneyo, Phillips, and Turley (loc. cit.) also found that, the dextroretatory \( p \)-toluenesulphonate of ethyl lactate gave levorotatory \( \alpha \)-halogenated propionic acids by interaction with alkali halides and Grignard reagents; and moreover showed that, as in the case of acyl derivatives, the formation of these halogen derivatives was attended by a Walden inversion.

Meusss, Kenyon, and Phillips (J.C.S., 1929, 1700) applied this method to the determination of the
configuration of \(1\beta\)-octanol, \(1\beta\)-Octyl

\(1\beta\)-toluenesulphonate was prepared by oxidation of the

\(1\beta\)-toluenesulphinate with potassium permanganate.

The \(p\)-toluenesulphonic ester of the \(1\)-alcohol was

converted, by the action of (a) lithium chloride into

the chloro-derivative, and (b), by potassium acetate,

into the acetate.

These reactions were considered to be closely

similar in type, because it can be assumed that the

negative chloride and acetate ions act in an identical

manner, and, therefore, the acetate and the chloride

produced, were considered to have the same configuration.

The preparation of the dextrorotatory acetate,

from the \(d\)-alcohol and acetic anhydride, gives the sign

of rotation of the \(d\)-acetate; since this reaction does not

involve the replacement of any groups attached to the

asymmetric carbon atom.

Since the relative configurations of the alcohol

and acetate are known, and, since the dextrorotary

chloride and acetate have the same configuration; it

follows that the dextrorotatory \(\beta\)-chloro-octane has the

same configuration as the \(d\)-alcohol.
The Reaction of 1-β-Octyl p-toluenesulphonate with

(a) Lithium Chloride and (b) Potassium Acetate.

1-sulphonate

dextro-β-chloro-cotane
dextro-β-octyl acetate

Preparation of d-Octyl Acetate.
This conclusion is the same as that reached from a consideration of the reactions of 1-β-octyl p-toluenesulphinate with chlorine and hypochlorous acid. The fact that two independent methods lead to the same conclusion, increases the probability that each is correct.

The Reactions of 1-Phenylmethylcarbinyl p-Toluenesulphonate.

The methods of Roussia, Kenyon, and Phillips (loc.cit), for determining the relative configurations of alcohols and their halides, has not so far been extended to compounds having a phenyl group attached to the asymmetric carbon atom. The relative configurations of these alcohols and their halides are of especial interest, in view of the anomalous results obtained by their interaction with thionyl chloride.

In this research, the configuration of the chloro-derivative of 1-phenylmethylcarbinol is determined by a study of the reaction of 1-phenylmethylcarbinyl p-toluenesulphonate with various reagents.

The preparation of the p-toluenesulphonate of
phenylmethylcarbinol has presented considerable
difficulty; unsuccessful attempts having been made
in these laboratories over the space of several
years. The reaction of p-toluensulphenyl chloride
on the alcohol, and on its potassium derivative, had
failed to give any appreciable quantities of the sulphonyl
ester, and it was decided, therefore, to concentrate
on the attempted oxidation of the p-toluensulphinate
to the corresponding sulphonate.

The oxidation of the sulphinic acid by aqueous
potassium permanganate, gave a quantity of acetophenone
owing to oxidation of the phenylmethylcarbinyl radicle.
The attempted oxidation by means of hydrogen peroxide
was unsuccessful, owing to the occurrence of hydrolysis,
giving phenylmethylcarbinol.

The sulphinic acid, in benzene solution, was oxidised
to some extent by air; the oxidation however, was very
slow and large quantities of α-phenylthiolethiophene were
formed. A summary of the air oxidation reactions is
given in table X, p. 16a.

The oxidation was finally, successfully carried
out by means of hyperol, using a hygroscopic solvent, such as, ethyl alcohol, acetic acid, or, acetic anhydride. The use of these solvents probably accounts for the success of the method, since experience has shown that, the sulphinate and sulphonate are both readily hydrolysed by water. It was therefore impossible to purify the sulphonate by washing, so that direct distillation of the ester was attempted; but, even at pressures below one millimeter, decomposition occurred, with evolution of sulphur dioxide and subsequent sharing. Owing to its instability towards heat, and its high reactivity, the oxidation of the sulphinate to sulphonate, and the reaction of the sulphonate, were effected in one operation.

The series of reactions carried out in this manner, with the sulphonate are tabulated in table III. The "reactants" column, refers to the materials, including hyperol, added to the original p-toluenesulphinate, the oxidation and substitution reactions occurring together.

The preparation of the ethyl ether, p-butyl ether, and the acetate, having the same configuration as the l-alcohol, is also included in the table. The ethers were made by the interaction of potassium
1-phenylmethyl carbinolide with the alkyl bromide. This method of preparation did not involve any change in the valency bonds of the asymmetric carbon atom.
**TABLE III**

The Reactions of 1-Phenylethylcarbinyl p-Toluenesulphonate.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Product</th>
<th>Rotatory power of Product, $\alpha_{N/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl alcohol, hyperol, 1-lithium chloride, 1-sulphinate</td>
<td>$\alpha$-Phenyldiethyl ether</td>
<td>-3</td>
</tr>
<tr>
<td>Ethyl alcohol, hyperol, 1-sulphinate</td>
<td>$\alpha$-Phenyldiethyl ether</td>
<td>+18</td>
</tr>
<tr>
<td>[Potassium 1-phenylmethyl-$\alpha$-phenylidithyl carbinol, ethyl bromide]</td>
<td>Phenylethylcarbinyl acetate</td>
<td>-69.8</td>
</tr>
<tr>
<td>[Acetic acid, hyperol, 1-sulphinate]</td>
<td>Phenylethylcarbinyl acetate</td>
<td>+11</td>
</tr>
<tr>
<td>Acetic anhydride, 1-phenylethylcarbinol</td>
<td>Phenylethylcarbinyl acetate</td>
<td>-94.2</td>
</tr>
<tr>
<td>n-Butyl alcohol, hyperol, 1-sulphinate</td>
<td>$\alpha$-phenylethyl n-butyl ether</td>
<td>+20</td>
</tr>
<tr>
<td>[Potassium 1-phenylmethyl-$\alpha$-phenylethyl n-butyl carbinol, n-butyl bromide]</td>
<td>-76.3</td>
<td></td>
</tr>
<tr>
<td>Acetic anhydride, hyperol, lithium chloride, 1-sulphate</td>
<td>(1) $\alpha$-chloroethyl benzene</td>
<td>+1.03</td>
</tr>
<tr>
<td>(1) phenylmethyl carbinyl acetate</td>
<td>+1.4</td>
<td></td>
</tr>
<tr>
<td>Acetic anhydride, hyperol, 1-$\alpha$-chloroethylbenzene</td>
<td>1-$\alpha$-chloroethyl benzene</td>
<td>-41</td>
</tr>
</tbody>
</table>
From the table, it will be seen that, unlike the corresponding sulphinic ester, the 1-sulphonate reacts with ethyl alcohol alone, to give d-phenyl(diethyl) ether having $\alpha 5461+18$. Then lithium chloride is added to the reactants the d-phenyl(diethyl) ether obtained has $\alpha 5461 - 8$. This rotatory power is lower than that obtained by the reaction of ethyl alcohol and lithium chloride on the 1-sulphinate, viz $\alpha 5461 - 16.5$. The reaction is explained on the assumption that two chains of reactions occur simultaneously. 1-Phenylmethylcarbiny1 p-toluene sulphinic ester is expelled to the sulphonate, which reacts, partly, with ethyl alcohol with inversion of configuration to give d-d-phenyl(diethyl) ether, and partly with lithium chloride to give d-d-chloroethylbenzene, which by further reaction with ethyl alcohol gives the 1-ether.

The mixture of d- and 1- ether has the resulting rotatory power of $\alpha 5461 - 8 (l=1.0)$.

The action of acetic acid on the 1-sulphonate gives an optically active acetate, in contrast to the inactive product obtained when the 1-sulphinic ester is employed. The dextro-rotatory acetate obtained has $\alpha 5461 + 11 (l=1.0)$. Since the acetate, obtained by reaction of the 1-alcohol and acetic anhydride, is levorotatory, it can be concluded that the formation of
the dextrorotatory acetate, from the 1-\(n\)-toluene sulphonate ester, is attended by inversion of configuration.

The \(n\)-butyl ether is formed by the action of \(n\)-butyl alcohol on the 1-sulphonate with inversion of configuration, since the rotatory power of the ether is \(\alpha 5461 + 20\ (1=1.0)\), while the 1-ether, formed by the action of the potassium derivative of the 1-alcohol on \(n\)-butyl bromide has \(\alpha 5461 - 76.8\ (1=1.0)\).

When the 1-\(n\)-toluene sulphonate is treated with acetic anhydride and lithium chloride, water being also present from the hyperol used in oxidising the sulphonate, \(d\)-phenylmethylecarbinyl acetate, \(\alpha 5461 + 1.4\ (1=1.0)\), and dextrorotatory \(d\)-chloroethylbenzene, \(\alpha 5461 + 1.06\ (1=1.0)\) are obtained.

The reaction of 1-\(d\)-chloroethylbenzene, acetic anhydride, and hyperol was attempted, but the recovery of 1-\(d\)-chloroethylbenzene, with only a slight diminution in rotatory power, is proof that the \(d\)-acetate was formed by the action of acetic anhydride (or acetic acid) on the 1-sulphonate, and not by interaction of acetic anhydride with the dextrorotatory \(d\)-chloroethylbenzene.

The configurations of laevorotatory \(d\)-phenylethyl \(n\)-butyl ether, \(d\)-phenylidithyl ether and phenylmethylecarbinyl acetate. By reference to tables II and III, it will be seen that the laevorotatory ethyl and \(n\)-butyl ethers.
and the acetate of phenylmethylcarbinol, have been prepared by methods which did not involve the rearrangement of the valency bonds attached to the asymmetric carbon atom. These products must, therefore, have the same configuration as the \( \alpha \)-alcohol.

The Relative Configurations of Phenylmethylcarbinol and \( \alpha \)-Chloroethylbenzene.

The reaction of lithium chloride, and of acetic anhydride with \( \alpha \)-phenylmethylcarbinyl \( \beta \)-toluenesulphinate may be represented as shown in the diagram.

\[
\begin{align*}
\text{L} & \quad \text{Ph} \quad \text{C}^\text{H}^\text{H}^\text{O} \quad \text{C}^\text{H}^\text{H}^\text{S} - \text{C}^\text{H}^\text{H}^\text{H} \\
\text{d} & \quad \text{Li} \quad \text{Ce} \quad \text{C}^\text{H}^\text{H}^\text{O} \quad \text{C}^\text{H}^\text{H}^\text{S} - \text{C}^\text{H}^\text{H}^\text{H}
\end{align*}
\]

It has been proved that dextro-rotatory phenylmethylcarbinyl acetate has the same configuration as the \( \alpha \)-alcohol and it is therefore evident, that the acetate is formed with inversion of configuration. Since the reaction can be considered to consist in the
replacement of the sulphinate group by acetate ions and since chloride ions probably replace the sulphinate group in an analogous manner, it is concluded that the $\alpha$-chloroethylbenzene is formed by the same mechanism as the acetate; i.e. with inversion of configuration, and hence dextrorotatory $\alpha$-chloroethylbenzene has the same configuration as the dextrorotatory acetate, and, therefore, the same configuration as the $d$-alcohol.
The reactions of the L-sulphinate and the L-sulphonate may be represented by the following schemes:

(I)

\[ \text{Ph} - \text{H} - \overset{\text{Air, hyperol}}{\longrightarrow} \text{Ph} - \overset{\text{EtO}}{\text{O}} - \overset{\text{Me}}{\text{O}} - \overset{\text{C}_7\text{H}_7}{\text{S}} \quad (1) \text{-sulphinate} \]

\[ \text{Cl} - \overset{\text{LiCl}}{\text{Me}} - \overset{\text{EtO}}{\text{O}} - \overset{\text{Me}}{\text{O}} - \overset{\text{C}_7\text{H}_7}{\text{S}} \quad (1)\text{-sulphonate} \]

\[ \text{Ph} - \overset{\text{C}_7\text{H}_7}{\text{Me}} - \overset{\text{Ethyl alcohol}}{\text{H}} \]

\[ \text{Cl} - \overset{\text{LiCl}}{\text{Me}} - \overset{\text{Ethyl alcohol}}{\text{H}} \]

(II)

\[ \text{Ph} - \overset{\text{O}}{\overset{\text{Me}}{\text{O}}} - \overset{\text{H}}{\overset{\text{H}}{\text{H}}} - \overset{\text{Butyl alcohol}}{\text{O}} - \overset{\text{Ph}}{\text{O}} - \overset{\text{C}_2\text{H}_5\text{C}_7\text{H}_7}{\text{O}} - \overset{\text{Me}}{\text{O}} \]

\[ \text{Me} - \overset{\text{O}}{\overset{\text{Me}}{\text{O}}} - \overset{\text{H}}{\overset{\text{H}}{\text{H}}} - \overset{\text{Butyl alcohol}}{\text{O}} - \overset{\text{Me}}{\text{O}} \]
(III)

Ph
\[ \begin{array}{c}
\text{C} \\
\text{Me} \\
\downarrow
\end{array} \]
\[ \text{H} \]
\[ \text{Ph} \]
\[ \text{O} \]
\[ \text{S} \]
\[ \text{O} \]
\[ \text{MeCO}_{2}\text{Me} \]
Acetic acid

Ph
\[ \begin{array}{c}
\text{C} \\
\text{Me} \\
\downarrow
\end{array} \]
\[ \text{H} \]
\[ \text{Ph} \]
\[ \text{O} \]
\[ \text{S} \]
\[ \text{O} \]
\[ \text{MeCO}_{2}\text{Me} \]
Acetic acid
THE DETERMINATION OF THE RELATIVE CONFIGURATIONS OF
PHENYL-METHYLCARBINYL DERIVATIVES BY AN INDEPENDENT METHOD.

It has been realized that the physical properties of a compound $R\cdot X$, where $X$ is an alkyl or aryl radical, are dependent on the polarity of $X$. For example, if the derivatives $Ph\cdot X$ and $H\cdot X$ are arranged according to the polarity of $X$, a regular increase in their $M.p.'s$ and $b.p.'s$ through the positive series, and a decrease through the negative series, is observed. Further, if the mono-substituted benzenes are arranged according to the proportions of $o$-, $p$-, and $m$-, disubstituted derivatives which they yield, it is found that with the order of groups as given below, the negative groups lead to $o$- and $p$- substitution, and the positive groups lead to $m$-substitution.

_Benzene substitution._

\begin{align*}
\text{OH, F, Cl, I, Br, CH}_3, \text{H, CO}_2\text{H, NO}_2
\end{align*}

_Specific inductive capacities._

\begin{align*}
\text{OH, Cl, Br, I, CO}_2\text{H, CHO, COCH}_3, \text{CH, NO}_2
\end{align*}
Influence on dissociation constants of monosubstituted acetic or benzoic acids.

Cl, Br, I, OMe, OH, NeH, CO₂H, CN, NO₂

M.p.'s, and b.p.'s of derivatives PhX and HX.

OH, NE₂, SH, Br, Cl, CHO, NO₂, SO₃H.

It will be seen, that similar orders of arrangement are obtained by consideration of, the specific inductive capacities, the influence on the dissociation constants of weak acids, and the rise of m.p.'s and b.p.'s of mono-substituted benzenes. These fall through the negative series, and rise through the positive series.

Euler (loc.cit.) has shown, that a similar order can be established, from a consideration of the effect of the groups on optical activity. Derivatives of β-ocetyl and β-aryl alcohols are arranged in table IV in increasing order of positive rotatory power, which is also the order of increasing polarity of the substituents.
TABLE IV.

The Molecular Rotation of Derivatives of d-Octyl and d-Aryl Alcohols.

<table>
<thead>
<tr>
<th>Derivative</th>
<th>Molecular Rotation $[\eta]_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = \text{d-Octyl}$</td>
<td>$\text{d-Aryl}$</td>
</tr>
<tr>
<td>R.OH</td>
<td>$+11.99$</td>
</tr>
<tr>
<td>R.OCH$_3$</td>
<td>$+12.5$</td>
</tr>
<tr>
<td>R.O.CO.CH$_3$</td>
<td>$+13.0$</td>
</tr>
<tr>
<td>R.O.CO.CH$_2$.Cl</td>
<td>$+17.3$</td>
</tr>
<tr>
<td>R.BF$_3$</td>
<td>$+53.1$</td>
</tr>
<tr>
<td>R.O.CO.C$_6$H$_4$.Me (g-)</td>
<td>$+63.1$</td>
</tr>
<tr>
<td>R.O.CO.C$_6$H$_5$.</td>
<td>$+73$</td>
</tr>
<tr>
<td>R.O.CO.C$_6$H$_4$.Me (p-)</td>
<td>$+103$</td>
</tr>
</tbody>
</table>
The effect of each substituent group on the rotatory power of a compound depends on the formation of a dipole, due to the fact that, the centre of negative electrical charge in the molecule does not necessarily coincide with the centre of positive electrical charge.

Sir J.J. Thomson (Phil. Mag., 46, 427) considered that the electronegative groups or atoms were those that needed an electron to complete the octet. (CH₂, CH₃, Cl.) and the electro positive groups those that after completing the octet, had an extra electron (NH₂, CO₂H, NH₃, Cl). The doublet may be due to the electrons of an electro-vaIency, or of a covalency, being attracted out of position, by the influence of any of the various groups in the molecule.

Although the doublet must, of necessity, consist of equal positive and negative charges, the group is labelled according to the charge borne by the atom nearest the centre of the molecule; thus, \( \text{NH}_3\text{Cl} \) is "a positive" group, although the sum of the charges on NH₃ and Cl is zero. \( \text{NH}_2 \) forms a linkage as a negative group; this is a covalent linkage in which the magnitude of the dipole would depend on the arrangement of the electrons \( \text{C} - \text{NH}_2 \), tending towards an electrovalency.
The polarity of a group is affected by various factors: (a) The solvent may influence the ionization of the group.

E.g. The specific rotatory powers of 1-phenylmethylcarbinyl hydrogen phthalate in carbon disulphide, chloroform, and ethyl alcohol are tabulated.

**TABLE V.**

The specific rotatory powers of 1-phenylmethylcarbinyl hydrogen phthalate in various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\left[\alpha\right]_D^{461}$ 1-phenylmethylcarbinyl hydrogen phthalate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CS}_2$</td>
<td>$-59.7$</td>
</tr>
<tr>
<td>$\text{CHCl}_3$</td>
<td>$+1.23$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{OH}$</td>
<td>$+39.3$</td>
</tr>
</tbody>
</table>

(b) The nature of the various other groups forming the molecule, i.e. whether electron attracting or repelling.

An example of the effect of introduction of a phenyl group into the molecule was discovered by Mc.Keenzie and Ween (J.C.S., 1910, 97, 473), who found that 1-benzoquinone on treatment with phenyl magnesium iodide gave
a dextrorotatory glycol, although the valency bonds
attached to the asymmetric carbon atom were not
disturbed during the reaction.

\[
\begin{align*}
\text{Ph} & \quad \text{CH}_2\text{OH} \quad \text{CO} \quad \text{Ph} \quad \overset{\text{PhHCl}}{\xrightarrow{\text{D} = 112.6}} \quad \text{Ph} \quad \text{CH}_2\text{OH} \quad \text{Cl} \quad \overset{\text{Ph}_2}{\xrightarrow{\text{D} = 221.3}} \\
\end{align*}
\]

The observations, on the effect of the polarity
of a substituent group, on the rotatory power of a
compound have been applied to the determination of the
configuration of dextrorotatory \(\alpha\)-chloroethylbenzene, in
order to confirm the conclusions reached from the
results of the reactions of the \(p\)-toluene-sulphonic esters.

For the purposes of this determination, the
substituent groups are arranged in the following order
of increasing electro positive polarity:

- \(\text{CO}_2\text{CH}_3\), \(\text{OC}_4\text{H}_4\text{OT}, \text{Cl}, \text{OH}, \text{NH}_2\) negative.
- \(\text{COOH}, \text{NH}_3\text{Cl}, \text{CO}_2\text{C}_6\text{H}_4\text{COOH}\) positive.

The arrangement is based on the order of
increasing polarity obtained as deduced from a considera-
tion of (a) the influence on the dissociation constants

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of mono-substituted acetic and benzole acids; (b).
The rotatory powers of d-β-octyl, and (c) d-aryl derivatives.

Table VI gives the values for these properties, on which the arrangements of the groups is based.
TABLE VI.

Molecular Rotatory Powers of 1-\(\beta\)-octyl and \(d\)-aryl Derivatives.

<table>
<thead>
<tr>
<th>Group</th>
<th>(k) for substituted derivative</th>
<th>(d)-(\beta)-octyl derivative</th>
<th>(d)-aryl derivative</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3)</td>
<td>-</td>
<td>+11.75</td>
<td>-</td>
</tr>
<tr>
<td>(\text{CH}_4)</td>
<td>-</td>
<td>+13.2</td>
<td>-</td>
</tr>
<tr>
<td>(\text{CH}_2\text{H}_5)</td>
<td>(23 \times 10^{-5})</td>
<td>+13.9</td>
<td>-</td>
</tr>
<tr>
<td>negative</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>(155 \times 10^{-5})</td>
<td>+48.0</td>
<td>-</td>
</tr>
<tr>
<td>CH</td>
<td>(15 \times 10^{-5})</td>
<td>+12.67</td>
<td>-5.2</td>
</tr>
<tr>
<td>(\text{NH}_2)</td>
<td>(1.3 \times 10^{-5})</td>
<td>-</td>
<td>-5.2</td>
</tr>
<tr>
<td>COOH</td>
<td>-</td>
<td>-</td>
<td>+10.5</td>
</tr>
<tr>
<td>positive</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{NH}_3) Cl</td>
<td>-</td>
<td>+43</td>
<td>-</td>
</tr>
<tr>
<td>(\text{COOCH}_2\text{H}_4\text{COOH})</td>
<td>-</td>
<td>+21</td>
<td>-</td>
</tr>
</tbody>
</table>

References to Table VI:
1. Pickard and Kenyon, J.C.S., 1911. 4. J. Kenyon
and Mc. Nicol, J.C.S., 1923, 10. 5. Koussa, Phillips and
Kenyon, J.C.S., 1929, 1700. 7. Calc. from Phillips, J.C.S.,
1930, 331.
The molecular rotations of derivatives of 
\( d \)-phenylmethylecarbinol are given in table VII.
# TABLE VII.

The Molecular Rotations of Derivatives of 3-Phenylmethylcarbinol.

<table>
<thead>
<tr>
<th>Substituent Group</th>
<th>Molecular Rotation Ethyl Alcohol Solution</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 CO ( \text{CH}_2 ) CO.H</td>
<td>( [\theta]_D +200.1 )</td>
<td>1</td>
</tr>
<tr>
<td>0. CO. C.H</td>
<td>+196.6</td>
<td>2</td>
</tr>
<tr>
<td>0. CO.CH</td>
<td>+96</td>
<td>3</td>
</tr>
<tr>
<td>0. C.H</td>
<td>94.5</td>
<td>4</td>
</tr>
<tr>
<td>0. C.H</td>
<td>35.1</td>
<td>5</td>
</tr>
<tr>
<td>negative</td>
<td>Cl</td>
<td>59.1</td>
</tr>
<tr>
<td>CH</td>
<td>42.0</td>
<td>7</td>
</tr>
<tr>
<td>NH(_2)</td>
<td>38.1</td>
<td>8</td>
</tr>
<tr>
<td>positive</td>
<td>NH(_3) Cl</td>
<td>7.9</td>
</tr>
<tr>
<td>0.C. C.H.COO</td>
<td>-39.6</td>
<td>10</td>
</tr>
</tbody>
</table>

References to Table VII:
1.2.3.4.5.6.7. Taylor. 8. Markwald and Meth. Ber., 1906, 38.
2907. 9. Pointet. loc. cit.
From a study of the table, the values for the molecular rotations will be seen to fall into a decreasing series. It will be noticed that dextrorotatory \( \delta \)-chloroethylbenzene fits into the series of \( \delta \)-derivatives, whereas the laevorotatory compound would be completely out of place. This affords confirmatory evidence of the previous conclusion that the configuration of laevorotatory \( \delta \)-chloroethylbenzene is the same as that of \( 1 \)-phenylmethylcarbinol.

The \( p \)-toluenesulphonic ester however, does not hold the same position in the table for phenylmethyl carbirnyl derivatives as it holds for those of secondary \( \beta \)-octyl. The probable effect of the aromatic radicle, which, conceivably, reverses the polarity of the sulphinate group, will be discussed in the section to be devoted to the influence of a constituent phenyl group on the properties of a compound.
THE MECHANISM OF THE HALOGENATION OF 1-PHENYLMETHYLECARBINOL.

In the previous sections of this work (p. 44, p. 56), \( \alpha \)-chloroethylbenzene has been shown to have the same configuration as the corresponding alcohol having the same sign of rotation. It is now possible, from a consideration of the optical rotatory power of \( \alpha \)-chloroethylbenzene, to arrive at a definite conclusion as to its configuration, when prepared by any of the previously described halogenation reactions performed with 1-phenylmethylcarbinol.

From such considerations it follows that, the halogenation of phenylmethylcarbinol by the chlorides of phosphorus, in the presence or absence of pyridine, and by phosphorus oxychloride and thionyl chloride, in the presence of pyridine, is attended by an inversion of configuration; while halogenation takes place without the occurrence of a change in configuration, when thionyl chloride alone is employed.

This latter result, which is in contrast to that obtained by the interaction of thionyl chloride and
1-β-octanol, is explained by an extension of the hypothesis of Kenyon and Phillips (loc. cit.). While thionyl chloride, on interaction with 1-β-octanol, forms a complex which fulfills the essential conditions necessary for a Walden inversion to occur, in that (a) the entering chlorine atom is liberated as an anion, and (b) the asymmetric radicle separates as a positively charged ion, it is evident that these conditions are not fulfilled in the case of 1-phenylmethylicarbinal. The formation of 1-α-chloroethylbenzene from 1-phenylmethylcarbinol, may be explained by assuming that the chlorine enters the reaction as a kation, and that the asymmetric radicle separates as an anion. Since the asymmetric carbon atom retains a complete octet of electrons, the configuration of the radicle is rigidly fixed, and the 1-chloride results.

The course of the reaction depends on the relative electron retaining capacities of the sulphinoxy group, and of the asymmetric radicle. In the case of phenylmethylcarbinal chlorosulphinate, the adjacent phenyl group is electron absorbing and causes the asymmetric carbon atom to retain electrons, and thus separate with a negative charge.

In view of the high rotatory power of the 1-α-chloroethylbenzene obtained, [α]5461 - 62.3, it
The Reaction of 1-β-D-Glucosyl and Thiacyl Chloride

\[
\begin{align*}
\text{C}_6\text{H}_{13} & \quad \text{H} \\
\text{C}_3 & \quad \text{O, H, Cl} \quad \text{Me, O, + Cl} \\
\text{H} & \quad \text{O, } \quad \text{H} \\
\text{C}_3 & \quad \text{O, } \quad \text{O} \\
\text{H} & \quad \text{O} \\
\text{C}_3 & \quad \text{O} \\
\text{H} & \quad \text{O} \\
\text{C}_3 & \quad \text{O} \\
\end{align*}
\]

The Reaction of 1-phenylmethylcarbinol and Thiacyl Chloride

\[
\begin{align*}
\text{Ph} & \quad \text{H} \\
\text{Me} & \quad \text{O, S, Cl} \\
\text{Ph} & \quad \text{H} \\
\text{Me} & \quad \text{O, S, Cl} \\
\text{Ph} & \quad \text{H} \\
\text{Me} & \quad \text{O, S, Cl} \\
\text{Ph} & \quad \text{H} \\
\end{align*}
\]
is considered by McKenzie and Clough (J.C.S.1913, 597),
that the reaction probably occurs with complete absence
of racemisation, and may be considered to follow completely
the course given in diagram II.

With thionylchloride and pyridine (or other tertiary base).

When pyridine is present, an intermediate
pyridinium complex (III) is formed from the chlorosulphinate
(IV). The formation of the pyridinium complex assists
the sulphinoxy group to attract electrons, and thus cause
the asymmetric carbonium radicle to separate as a cation.
It also induces the formation of a chlorine anion, which
can enter the molecule from the opposite side resulting
in the formation of the chloride, with an inversion of
configuration.

The d+dl-α-chloroethylbenzene, obtained as the
final product of the reaction, is considered to be formed
by the decomposition of the chlorosulphinate IV and its
pyridinium complex III. The relative proportions of the
two intermediates is influenced by the amount of pyridine
present in solution. Thus, when one molecule is used,
the d+dl chloride formed has \( \Delta_{5461+17.3} \), and when two
molecules are used, the pyridinium complex is formed
in larger quantities and the chloride then has \( \Delta_{5461+36.3} \). This result supports the

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The Reaction of 1-Phenylmethylcarbinol with
Thiophenyl Chloride and Pyridine.

\[
\begin{align*}
\text{Ph} & \quad \text{H} & \quad \text{Cl} \\
\text{Me} & \quad \text{O} & \quad \text{+} & \quad \text{Cl} \\
& \quad \text{I} & \\
\text{Ph} & \quad \text{H} & \quad \text{Cl} & \quad \text{C}_9\text{H}_5\text{N} \quad \text{O} & \quad \text{Me} \\
& \quad \text{I} & \quad \text{(IV)} & \quad \text{Cl} & \quad \text{(III)} \\
\text{Ph} & \quad \text{H} & \quad \text{Cl} & \quad \text{Me} & \quad \text{C}_9\text{H}_5\text{N} \\
& \quad \text{I} & \\
\end{align*}
\]
assumption that the $d$-chloride arises from decomposition of the pyridinium complex, and that the chlorosulphinate on decomposition leads to the formation of $l$-or $dl$-chloride.

With phosphorus trichloride in the absence of pyridine.

The possible intermediate compounds, with their mode of decomposition are set out in the accompanying schemes.

The final product obtained, when phosphorus trichloride alone is used, has $[\alpha]3461 + 10.4, l=1d$ and is thus a mixture of the $d$-and $dl$-chlorides.

The formation of the $d$-chloride is explained by the transitory existence of the intermediate compound (V), which, being ionized can give a chloride ion. This latter is free to take up its position on the opposite side of the asymmetric molecule, and cause an inversion of configuration. The production of considerable quantity of the $dl$-chloride is explained by the two alternative un-ionized intermediates VI and VII, either, or both of which may be considered to be in equilibrium with the ionized compound. These both decompose to give an asymmetric carbonium cation and a chloride ion, but since the chloride ion is not
The Reaction of 1-Phenylmethylcarbinol With Phosphorus Trichloride in the Absence of pyridine.
liberated until the complex itself splits up, the asymmetric radicle is able to attain the equilibrium condition, having equal proportions of the \( \alpha \) - and \( \beta \) -configurations. On combination with the chloride ion, the \( \alpha\beta \)-chloride is obtained, and mixing with the \( \alpha \)-chloride, gives the \( \alpha\beta \)-product.

With phosphorus trichloride in the presence of pyridine.

The reaction can be explained by the formation of a pyridinium complex, VIII, which is ionized and is therefore accompanied by a chloride ion.

Only one molecular proportion of pyridine was present in the reaction, and it is possible that a proportion of this entered into combination with the hydrochloric acid liberated in the reaction. It is therefore unlikely that all the asymmetric complex enters into combination with the pyridine. The chloride may thus arise from the same intermediate complexes as were formed when pyridine was not present.

When, however, any of these phosphorus complexes decompose in the presence of pyridine, chlorine anions
The reaction of 1-phenylmethylcarbinol with phosphorus trichloride in the presence of pyridine.

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

(VIII)

With phosphorus pentachloride.
from the pyridine hydrochloride, are present in solution, before the intermediate compound begins to decompose. The essential conditions necessary for an inversion to occur are therefore attained, and the resulting, probably optically pure, d-chloride has $[\alpha]_D^{25}+64.1$.

With Phosphorus pentachloride.

The low rotatory power of the product obtained $[\alpha]_D^{25}+4.54$ may be explained by assuming the formation of an ionized complex $X$, which has a free chlorine atom, and gives the d-$q$-chloroethylbenzene on decomposition and also the simultaneous formation of an unionized complex $X$, which gives the d$_1$-chloride by a similar method of decomposition, as described in the case of phosphorus trichloride.

With Phosphorus pentachloride and pyridine.

Since only one molecular proportion of pyridine was used this would be expected to be mostly employed in combination with the liberated hydrochloric acid.

The intermediate compounds formed were the same as those assumed to be formed when pyridine was not employed.
The Reaction of 1-Chloroethylcarbinol with Phosphorus Pentachloride and Pyridine.
Since the chloride formed has a specific 
rotatory power of \( [\alpha]_D^{546} + 10.4 \), it is evident that 
(a) a large proportion of the unionized intermediate com-

pound present, decomposes to give the asymmetric 
carbonium kation, which racemizes before a chlorine 
anion is able to take up its position to ensure 
inversion of configuration, so that the resulting product 
is the \( \text{dL}- \) chloride; and (b), a quantity of a pyridinium 
complex XI is formed which gives the \( \text{dL}- \) chloride on 
decomposition. The final product is therefore 
\( \text{d+dl-dL-} \) chloroethylbenzene.

With phosphorus oxychloride.

The almost optically inactive \( \text{dL-} \) chloroethylbenzene 
obtained, together with the isolation of appreciable 
quantities of the levorotatory \( \text{dL-diphenyldithylether} \)
having \( [\alpha]_D^{546} \) may be explained by the formation of an 
unionized intermediate compound XII. (a) This decomposes 
to give a positively charged carbonium ion. These 

cations racemize yielding the \( \text{dL-} \) chloride, when they 
combine with the chlorine anions liberated during 
decomposition of the intermediate compound. (b) 
The intermediate decomposes in the presence of
The Formation of \( \alpha\)-Diphenylmethyl Ether.
negative phenylmethylcarbinol basic ions XIII. These latter combine with the racemised phenylmethylcarbinyl carbonium cations, giving the 1l-di-dieher.

It will be noticed that the formation of the phenylmethylcarbinol ion does not involve the disturbance of any of the valency bonds of the asymmetric carbon atom, the radicle must, therefore, form the ether still retaining the l-configuration. Now if decomposition of the phosphorus oxychloride intermediate compound leads to inversion of the configuration of the carbonium radical, then the ether formed would be internally compensated and would exhibit no optical activity. The relatively high value obtained for the rotatory power of the ether makes it probable that the carbonium ion does racemise, so that the final product consists of equal proportions of the 1l and the di-dieher.

The formation of the internally compensated diether in the manner described may account for the results obtained by Konyon and Phillips (J.C.S., 1933, 1676), who obtained 1l-di-dieher having $\chi^\circ = 0.50^\circ$ (l=0.25) from the 1-alcohol by gentle boiling, under reflux, with aqueous hydrochloric acid.

With phosphorus oxychloride and pyridine,

The production of di-chloroethylbromone having
δ, SICL + 12.0 may be accounted by the following scheme:
The characteristic effect of the phenyl group, on the reactions of radicles to which it is attached, has been noticed by several workers. Mc. Kenzie and Clough (loc. cit.), and Frankland (J.C.S., 1913, 103, 733) noted its anomalous effect on the halogenation reactions of thionyl chloride.

Fors and Lapworth (J.C.S., 1912, 101, 273) have shown, that the phenyl group has a marked influence on the reactions of sulphonnic esters, which are thereby rendered more reactive. They ascribe this effect to "depression of the unsaturated character of the sulphur atom, to which the nucleus is directly attached".

Rule (J. Faraday Soc., 1933, 321) has observed the progressive alterations in the rotatory power of compounds made by the introduction of successive phenyl groups into the molecule (see also Mc. Kenzie and Tren's results p. 50).

The influence of a phenyl group, attached to the central carbon atom, on the properties of a molecule, is revealed by three widely differing series of
$\delta_{5.61+1.6}$ may be accounted by the following scheme:
(1) Its effect on the configuration of the product of a substitution reaction.

The reaction of thiophenyl chloride with phenylmethyloxetinol may be explained by decomposition of the chlorosulphinate formed immediately, in the following manner:

\[
\begin{align*}
\text{Ph} & \quad \text{H} \quad \text{Cl} \\
\text{Me} & \quad \text{o} \quad \text{S} \quad \text{O} \\
\text{Ph} & \quad \text{H} \quad + \quad \text{Cl} \\
\text{Me} & \quad \text{o} \quad \text{S} \quad \text{O}
\end{align*}
\]

In the diagram, covalent linkages are represented by single lines, these linkages having arrows denote that the two shared electrons are attracted towards one of the atoms, as indicated by the arrow. Since the phenyl group is electron absorbing, the asymmetric carbon atom will be left with a slight positive charge and will in turn attract electrons from the contiguous oxygen atom, which in turn attracts electrons from the sulphur atom. This atom then has one unit positive charge, plus an extra positive charge. It therefore tends to absorb the
two electrons forming the covalency between chlorine
and itself, thus neutralizing its own charge, but
causing the chlorine atom to acquire a positive
charge, and tend to separate as a kation.

The electron movement is shown more clearly
in the diagram.

The same tendency is observed in the linkage
between the asymmetric carbon atom and the oxygen
atom, the covalency electrons are already attracted
to the carbon atom, and it is therefore easy for the
link to break with the carbon retaining the two electrons
an an anion, as in the accompanying scheme.

The sulphur dioxide molecule is liberated,
including the oxygen atom previously attached to the
carbon atom. The oxygen, initially, has a positive
charge but, by sharing two more electrons with sulphur,
the electronic octet of the oxygen is reformed, a
double covalency between oxygen and sulphur is
established, and the positive charge is now attached to
the sulphur atom, giving the normally accepted formula
for sulphur dioxide.

When pyridine is employed, the formation of
a pyridinium chloride can be assumed in which the
nitrogen and sulphur atoms bear positive charges.
The Position of Electrons During the Decomposition
of Phenylethylammonium \( \alpha \)-Toluene sulphirate.

Original 6 Electrons (6) = = = = = = = =
Original CI Electrons (7) = = = = = = = =
Original S Electrons (9) = = = = = = = =
Electrons Attached to Other Groups — — —

or

\[ O + \rightarrow O \]
These atoms, therefore, attract the electrons from the oxygen atom, which, in turn, attracts them from the asymmetric carbon atom. The asymmetric carbon atom thus loses these electrons, in spite of the feeble counter attraction due to the phenyl group.

\[
\begin{align*}
\text{Ph} & \quad \text{C} \quad \text{H} \\
\text{Me} & \quad \text{Cl} \\
\text{Me} & \quad \text{O} \quad \text{Cl} \\
\text{Ph} & \quad \text{S}^+ \quad \text{H}^+ \\
\text{Me} & \quad \text{Cl} \\
\end{align*}
\]

The covalently linked asymmetric carbon atom has, therefore, a small positive charge, while the shared electrons, linking it to oxygen, are attracted to the oxygen atom; so that, on rupture of the bond, the carbonium radicle has a positive charge, and the oxygen a negative charge.

When Phosphorus trichloride, or pentachloride is used, the phosphorus complex is itself sufficiently electron attracting to counteract the attraction of the adjacent phenyl group.

In the case of the interaction of aliphatic alcohols with thionyl chloride, e.g., 1-\(\beta\)-octanol, there is no electron attracting group in the asymmetric radicle, and the electronic attraction is towards the sulphur, and thence towards the chlorine atom.
The Decomposition of the Phenylmethylearanyl-
Sulfoisoxo-Dipyridinium Complex.

The Decomposition of the Phosphonium Complexes.
The Decomposition of 1-\beta-Octanol Chlorosulphinate
(II) The influence of the phenyl group on the stability of the valency bonds of a central carbon atom.

The weakness of the linkages of a carbon atom, when one of them is attached to a phenyl group has been long recognised.

Thus benzyl halides are more reactive than the corresponding aliphatic derivative. Strauss and Hussey (Ber., 1909, 42, 3100) have also found, that the reactivity of the halogen in benzyl chloride is greatly increased by successive replacement of the hydrogen by phenyl groups; while triphenylmethylichloride, in suitable solvents, is a strong electrolyte.

The extreme case is triphenylmethyl, where the fourth linkage is so weak that it breaks down altogether. Also, in this research, it has been observed that the p-toluenesulphonic ester of phenylmethylcarbinol is more highly reactive than corresponding aliphatic derivatives.

The presence of the phenyl group also affords an explanation of the difference between the reaction of phenylmethylcarbinyl p-toluenesulphinate, and the p-toluenesulphinic esters of purely aliphatic alcohols, when rupture of the C-O-S linkages occurs between
carbon and oxygen under certain conditions, in the case of phenylmethylcarbinyl derivatives; but always between oxygen and sulphur, in reactions of the aliphatic esters.

With phenylmethylcarbinyl $p$-toluenesulphinate, although the attraction of electrons from the central carbon atom, due to the single positive charge on the sulphur atom, is insufficient in itself to cause the C-O link to rupture, and while the double positive charge, borne by the sulphur atom of sulphonio esters, is sufficient to have this effect (see p 34); attraction of the phenyl group for electrons may also cause the break to occur with a $p$-toluenesulphinic ester in the presence of certain reagents, e.g. lithium chloride and acetic acid.

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

The weakness of the carbon atom linkage, as shown by the increased reactivity of phenylmethylcarbinyl $p$-toluenesulphonate, is again explained by the electron attracting properties of the phenyl group.

-72-
With semi-aromatic compounds, the effect of the sulphonic group, in causing a rupture of the C=O linkage, is accentuated by the tendency for electrons to flow, from the carbon atom, towards the phenyl group.

The existence of $\text{C}_6\text{H}_{5}$phenylmethyl may be explained as follows:

Instead of making up its octet of electrons the carbon atom would have one free electron only, making seven in all.

The attraction of the covalent linkage electrons by the phenyl groups, robs the carbon atom of its full share of the negative charge due to these electrons, thus allowing the carbon atom to maintain its free electron and acquire a slight positive charge. The half positive charge thus acquired may be considered to stabilise the configuration of the carbon atom with only seven electrons, in the same way that a configuration of six electrons may be stabilised by a complete positive charge, as in the carbonium cation.

The carbon atom thus forms weak electro-valencies with the phenyl group in addition to the generally accepted co-valencies.
Its effect on the polarity of other substituent groups.

It was pointed out in a previous section (p 56) from a consideration of the rotatory powers of p-toluene sulphonic esters, that the p-toluene sulphonic group acted as an electro positive group in combination with the s-ethyl radical, but in combination with the phenylmethylcarbinyi radical, it behaved as an electro negative group. The electron attracting properties of the phenyl group may again provide an explanation to the phenomena.

\[
\begin{align*}
\text{Ph} & \quad \text{H} & \quad \text{C}_6\text{H}_3 & \quad \text{H} \\
\text{Me} & \quad \text{O} & \quad \text{S} & \quad \text{C}_7\text{H}_7 & \quad \text{Me}
\end{align*}
\]

The weakness of the C-O linkage in phenylmethylcarbinyi p-toluene sulphinate, and its tendency to ionize to a positive carbonium radicle as in its isomerisation to the sulphone, is in complete agreement with the proposed polar representation of the linkage C-O, which may be considered to be intermediate the electro and coevalencies. However, in the purely aliphatic compounds, when the carbonium radicle is neutral, the effect of the positive sulphur atom is predominant, and by its tendency to attract electrons from the oxygen atom, it reduces its own positive charge and causes the oxygen to acquire a
slight positive charge $\delta^+_{\text{S}}$ so that the
sulphinoxy group behaves as an electro positive grouping.
The occurrence of the phenomenon of racemisation has been observed, to a greater or lesser degree, in a wide variety of reactions of optically active compounds.

Thus, although the \( \alpha \)-chloroethylbenzene, obtained by the interaction of phosphorus trichloride and pyridine, on the 1-alcohol, had \( [\alpha] \_5481 + 64 \), that obtained by the use of phosphorus trichloride alone had \( [\alpha] \_5481 + 10 \), and with phosphorus oxychloride, inactive \( \alpha \)-chloroethylbenzene was obtained. In the latter two reactions, partial and complete racemisation respectively occurred.

By an extension of the hypothesis used to explain Walden inversion reactions, it is seen that racemisation may occur in the following ways:

1. The carbonium radicals may separate as kations, and the entering anions separate simultaneously with, and not previous to, the decomposition of the intermediate compounds. Since the anions are not in position on the opposite sides of the molecules, when the carbonium ions separate, these latter attain, or partially attain, an equilibrium mixture of the \( \alpha \) and 1-forms, and, on combination with the anions, the \( \alpha 1 \)-product is obtained; thus undergoing complete or
The Isomerisation of 1-Phenylmethylcarbinyl p-Toluenesulphonate to the α-Phenylethylsulphone.
partial racemisation. The isomerisation of 1-phenylmethylcarbiny1 p-toluenesulphonate to the corresponding sulphone (Kenyon and Phillips, J.C.S., 1933, 1676) is an example. In this case the entering group, the sulphinyl radical, is only liberated simultaneously with the formation of the phenylmethylcarbonium ion.

Even if the anions are liberated before the positive carbonium ions are formed, they may not necessarily all take up positions on the opposite sides of the molecules, and so cause a complete inversion of configuration, but they may allow a proportion of the carbonium radicals to racemise before formation of the final product.

(11) Racemisation may possibly be considered to occur when the intermediate compound ionises in both of two ways (a) to give a carbonium kation and an entering group as an anion, resulting in formation of the final product with the opposite configuration; and (b) to give a carbonium anion with a positively charged entering group, resulting in the formation of a final product with the same configuration as the parent compound. The mixture of the two enantiomorphs gives a partially racemised product, its sign and magnitude of rotation depending on the relative
The possible formation of β-1-Dibenzylbutane.

and Cl-α-Chloroethylbenzene.
proportions of (a) and (b) formed.

The absence of evidence of side reactions, in several reactions where racemisation takes place, is proof that the two types of ionisation do not occur simultaneously. For example, the interaction of phenylmethyl carbinol and phosphorus trichloride would give α-chloroethylbenzene, \( \beta \)-\( \gamma \)-diphenylbutane and chlorine; whereas in practice, only the α-chloroethylbenzene is recovered.

(iii) When the carbonium radicles separate as anions, partial racemisation may take place through migration of the hydrogen atom directly attached to the asymmetric carbon atom:

\[
\begin{align*}
\text{R}_1 & \quad \text{H} \\
\text{C} & \\
\text{R}_2 & \quad \text{C}
\end{align*}
\]

\[
\begin{align*}
\text{R}_1 & \quad \text{H} \\
\text{C} & \\
\text{R}_2 & \quad \text{C}
\end{align*}
\]

It will be noticed that the compounds isolated, having an asymmetric carbonium anion, from which the stability of the terevalent carbon atom is deduced, have relatively immobile groups attached to the asymmetric carbon atom (see p. 9) whereas, in many reactions of optically active compounds, the asymmetric carbon atom is directly attached to a hydrogen atom.

The mobility of the hydrogen atom would account for the occurrence of racemisation in reactions, in which
a change in configuration does not occur. But in view of the fact that some reactions have been investigated, in which there has not been a change in configuration, and in which the degree of racemisation has been shown to be very small, it is unlikely that this type of racemisation occurs to a notable degree.

If the isolation of a product without the occurrence of a Walden inversion, may be explained on the assumption that the carbonium radicle separates as an anion, and that the asymmetric carbon atom, having its complete octet of electrons, is optically stable; then in this case neither inversion of configuration nor racemisation is considered to take place.

It is however considered that the occurrence of racemisation, in reactions of optically active compounds, is, in general, due to the formation of an intermediate compound which, on decomposition, liberates a positive carbonium ion which racemises before an entering group, in the form of an anion, can take up its position on the opposite side of the molecule to that held by the displaced group.
EXPERIMENTAL.

The Preparation and Resolution of
Phenylmethylcarbinol.

_d_-Phenylmethylcarbinol was prepared by Pickard and Kenyon (J.C.S., 1911, 99, 45) by the fractional crystallisation of the _l_-brucine salt of the hydrogen succinio ester. Ott (Ber., 1923, 51, 2089) obtained the _l_-alcohol by crystallisation of the _l_-brucine salt of the solid phthalic ester, but it was not critically pure having \([\alpha]_D^2 = 40.95^\circ\) as compared with \([\alpha]_D^2 = 43.95^\circ\) obtained by Pickard and Kenyon.

_d_-Phenylmethylcarbinol was obtained by the interaction of magnesium methyl bromide and 90% of the theoretical quantity of benzaldehyde (Marshall, J.C.S., 1915, 107, 509). The magnesium methyl bromide was prepared by passing methyl bromide vapour (3 mols.) into a mixture of dry ether and magnesium (3 mols.).

After decomposition of the magnesium compound, washing and distillation of the ethereal solution, the _d_-phenylmethylcarbinol was obtained in 75% yield.
The phenylmethylcarbinol obtained was converted into the acid phthalic ester by heating it on the steam bath for two hours with phthalic anhydride (1.1 molar), and pyridine (1.1 molar). The crude hydrogen phthalate was poured into dilute hydrochloric acid to neutralise the pyridine; the hydrogen phthalate was extracted with ether, and the ether solution extracted with sodium carbonate solution from which the sodium salt of the hydrogen phthalate was obtained, while any unchanged alcohol remained in ether solution. On decomposition of the sodium salt with dilute acid, the acid phthalate was precipitated, filtered, dried, dissolved in dry chloroform, and filtered to remove free phthalic acid. Finally, pure dl-phenylmethylcarvinyl hydrogen phthalate was obtained by evaporation of the chloroform.

Preparation of l-Phenylmethylcarbinol.

Optically active phenylmethylcarbinol was prepared by resolving the l- brucine salt of dl-phenylmethylcarvinyl hydrogen phthalate by fractional crystallisation from hot acetone.
The brucine salt (1000 g.) dissolved in 1½ litres of acetone, was crystallised in the cold. The crop of crystals were mixed with 250 c.c. acetone, filtered and washed with successive portions (100 c.c.) of hot acetone until a melting point of 152°C was reached. At this point, a small quantity of the salt was decomposed into phenylmethylcarbaryl hydrogen phthalate and its specific rotatory power taken. The dextrorotatory \(-\)-phenylmethylcarbaryl hydrogen phthalate had a specific rotatory power of \(\alpha_{\text{D}}\) \(= +3.9\) \(\text{mdeg} \) \(\text{per} \ %.\text{M.}\) alcohol \(+33.1\) \%. On standing three or four days, the crystalline form in \(\%\) \(\text{M.}\) was obtained. The mother liquor was concentrated, poured into dilute hydrochloric acid, and extracted with ether. The ether solution was washed and dried, and the ether distilled off to give partially active phenylmethylcarbaryl hydrogen phthalate. The partially active hydrogen phthalate, dissolved in an equal quantity of pure carbon disulphide, was seeded with a crystal of the inactive hydrogen phthalate, and was allowed to stand for twenty four hours. The \(\text{dl-}\) phthalate crystallised out leaving a mother liquor of active material having a higher
rotary power. This operation was repeated until a rhthalate of specific rotary power $\alpha_{0.61} = 35$ was obtained. On recrystallisation to the brucine salt, and after recrystallisation from acetone a further three times, the fully active brucine salt of the laevorotatory hydrogen rhthalate was obtained. From 1000 grams of brucine salt, 250 grams of active brucine salt giving the $d$-alcohol and 100 grams corresponding to the $d$-alcohol were obtained. A considerable quantity of the regenerator was used in the experiments as partially active material, while the material of low activity was added to the next batch of brucine salt for resolution. Laevorotatory phenylmethylcarbinol, fully active $\alpha_{0.61} = 13.23$ ($l = 0.25$), was obtained from the dextrorotatory phenylmethylcarbinyl hydrogen rhthalate by steam distillation, after addition of the theoretical quantity of caustic soda. The distillate was extracted with methylene chloride, washed and dried over potassium carbonate. On distillation, the $l$-alcohol b.p. $94^\circ$ /$82$ mm., $100^\circ$ /$20$ mm., and $105^\circ$ /$25$ mm., having $d$ $20^d$ 1.5235, and $\alpha_{0.61} = 13.23, \alpha_{546} = 10.61$ ($l = 0.25$), was obtained. In ethyl alcohol solution, $l$-phenylmethylcarbinol had $[\alpha]_{546} = -34.8$ ($\alpha = 12.25$).
THE INTERACTION OF PHENYLARYLCARBONYL WITH
HALOGENATING AGENTS.

\( \alpha \)-Chloroethylbenzene.

\( \alpha \)-Chloroethylbenzene was prepared by the action of thionyl chloride on the \( \alpha \)-alcohol after the method of McVennie & Clough (J.C.S., 1940, 27, 2564). The \( \alpha \)-chloroethylbenzene was separated from the thionyl chloride-alcohol mixture by extraction with methylene chloride, washing with dilute acid, water and sodium carbonate, drying over potassium carbonate, evacuation of the solvent, and distillation in vacuo. It was further purified by repeated fractionation at 15 mm. pressure. The product finally had b.p. 73°/15mm. (Found: Cl, 25.2. Calc. Cl, 25.2.) 

\( \alpha \)-Chloroethylbenzene has \( \alpha \) D 1.5280, \( \beta \) D 1.5289, \( \beta \) D 1.5264, \( \beta \) D 1.5253 and \( \beta \) D 1.5230. The purity of the products obtained in subsequent experiments was judged by comparing their refractive indices with these values, which are given in graphical form in fig. 1.
The Variation of the Refractive Index of α-chloroethylbenzene with Temperature.
(1). With Thiocetyl Chloride in the Presence of
Pyridine.

Preliminary experiments with the al-alcohol.

In order to find the most favourable conditions
for the reactions the following series were carried
out with al-alcohol:

(1). Thiocetyl chloride (4.8g. 1 mol.) was added,
slowly and with agitation to a mixture of the alcohol
(4.8g. 1 mol.) and pyridine (3.2g. 1 mol.) and cooled
in ice. The mixture was then warmed for 1 hour on
the water-bath; on cooling, it was extracted with
methylene chloride and washed successively with water,
dilute hydrochloric acid, water, sodium carbonate,
water and finally dried over potassium carbonate.
After distilling off the solvent the dl-α-chloromethyl-
benzene was distilled in vacuo giving, after four
distillations 2.5g. of the chloro-compound having
b.n. 73°/13mm., nD 1.5541, and 0.5g. of unchanged
alcohol.

(11). Thiocetyl chloride (7.2g. 3 mol.) was added to
a mixture of 4.8g. (3 mol.) pyridine and 2.44m.
(1 mol.) of dl-phénylméthylcarbinol using the same
experimental procedure as previously described.
<table>
<thead>
<tr>
<th>Reagent</th>
<th>Mols to 1 mol. alcohol</th>
<th>Tertiary base</th>
<th>Method employed</th>
<th>Yield</th>
<th>N%</th>
<th>D%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOCl₂</td>
<td>1 mol.</td>
<td>1 mol (pyr)</td>
<td>Add SOCl₂ to mixture</td>
<td>50%</td>
<td>1.531</td>
<td></td>
</tr>
<tr>
<td>SOCl₂</td>
<td>3 mols.</td>
<td>3 mols (pyr)</td>
<td>ditto</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOCl₂</td>
<td>1 mol.</td>
<td>2 mols (pyr)</td>
<td>ditto</td>
<td>35%</td>
<td>1.531</td>
<td></td>
</tr>
<tr>
<td>SOCl₂</td>
<td>2 mols.</td>
<td>2 mols (pyr)</td>
<td>ditto</td>
<td>65%</td>
<td>1.531</td>
<td></td>
</tr>
<tr>
<td>SOCl₂</td>
<td>2 mol.</td>
<td>1 mol (pyr)</td>
<td>ditto</td>
<td>90%</td>
<td>1.531</td>
<td></td>
</tr>
<tr>
<td>SOCl₂</td>
<td>2 mol. (2 mols)</td>
<td>(pyr)</td>
<td>Add mixture to SOCl₂</td>
<td>33%</td>
<td>1.527</td>
<td></td>
</tr>
<tr>
<td>SOCl₂</td>
<td>2 mols.</td>
<td>2 mols (quin)</td>
<td>Add mixture to SOCl₂</td>
<td>50-85%</td>
<td>1.525</td>
<td></td>
</tr>
<tr>
<td>SOCl₂</td>
<td>2 mols.</td>
<td>1 mol. (quin)</td>
<td>ditto</td>
<td>70%</td>
<td>1.525</td>
<td></td>
</tr>
<tr>
<td>PCl₅</td>
<td>2 mols.</td>
<td>(quin)</td>
<td>Add alcohol to PCl₅</td>
<td>70%</td>
<td>1.525</td>
<td></td>
</tr>
<tr>
<td>PCl₅</td>
<td>2 mols.</td>
<td></td>
<td>Add alcohol to PCl₅ in boiling ether</td>
<td>70%</td>
<td>1.522</td>
<td></td>
</tr>
<tr>
<td>PCl₅</td>
<td>2 mols.</td>
<td>1 mol. (pyr)</td>
<td>Add mixture to PCl₅</td>
<td>70%</td>
<td>1.525</td>
<td></td>
</tr>
<tr>
<td>PCl₃</td>
<td>2 mols.</td>
<td>1 mol. (pyr)</td>
<td>Add mixture to PCl₃</td>
<td>65%</td>
<td>1.529</td>
<td></td>
</tr>
<tr>
<td>PCl₃</td>
<td>2 mols.</td>
<td>1 mol. (pyr)</td>
<td>Add PCl₃ to mixture</td>
<td>60%</td>
<td>1.522</td>
<td></td>
</tr>
<tr>
<td>PCl₃</td>
<td>2 mols (2 mols K₂CO₃)</td>
<td>Add alcohol to PCl₃ and PCl₃ in ether</td>
<td>20%</td>
<td>1.523</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
"Mixture" = phenylmethylocarbino + tertiary base. Unless otherwise stated, reactants were cooled in a freezing mixture and finally warmed for \( \frac{3}{4} \) hour on completion of reaction.
The quantity of \( \text{dl-\(\alpha\)-chloroethylbenzene} \) obtained was negligible. The main product consisted of 0.5 g of a viscous oil which was not further investigated.

(iii). Thiochryl chloride (4.8 g, 2 mols.) was added to a mixture of 3.2 g (2 mols.) pyridine and 2.44 g (1 mol.) of \( \text{dl-phenylmethylcarbinol} \) using the same experimental methods. The \( \alpha\)-chloroethylbenzene (1.7 g) obtained had \( \beta \) 1.5412.

(iv). Thiochryl chloride (2.49 g, 1 mol.) was added to a mixture of the alcohol (2.44 g, 1 mol.) and pyridine (3.2 g, 2 mols.). The \( \text{dl-\(\alpha\)-chlooroethylbenzene} \) (1 g) isolated had \( \beta \) 1.5818.

(v). Thiochryl chloride (4.8 g, 2 mols.) was added to a mixture of \( \text{dl-phenylmethylcarbinol} \) (2.44 g) (1 mol.) and pyridine (1.8 g, 1 mol.). The \( \alpha\)-chloroethylbenzene (2.3 g) obtained had \( \beta \) 1.5281.

(v'). A mixture of 2.44 g (1 mol.), of the \( \text{dl-alcohol} \), and 3.2 g (2 mols.) of pyridine was added to 4.8 g (2 mols.) of thiochryl chloride, cooled in ice, using the same experimental procedure as used in the previous experiments. \( \alpha\)-Chloroethylbenzene (1.1 g) having \( \beta \) 1.5276 was obtained.

The various reagents used, and the yields obtained are tabulated in Table IV.
Using Optically Active Pheny lmethylcarbinol

1. Using one molecular proportion of pyridine. Thiophyl chloride (4.78 g.; 2 mols.) was added slowly to an agitated solution of the 1-alcohol (2.44 g.; 1 mol.), 

\[ \alpha_{\lambda 4} = 12.6 \] (1 = 0.25) in pyridine (1.52 g.; 1 mol.).

The resulting mixture was cooled in ice and salt. The resulting mixture was maintained at 50° for about 30 minutes, and then poured into water, from which the \( \alpha \)-chloroethylbenzene was extracted with methylene chloride. The methylene chloride extract was washed successively with dilute hydrochloric acid, dilute aqueous sodium carbonate and water, and dried over potassium carbonate. The \( \alpha \)-chloroethylbenzene (2.3 g.), b.p. 70°/10mm., obtained, after evaporation of the solvent, was repeatedly fractionally distilled until it had \( \alpha \) 1.5282. It then had \( \alpha_{\lambda 6} = 4.7 \) (1 = 0.25).

2. Using two molecular proportions of pyridine. The reaction was carried out as described above except that 3.15 g. of pyridine was used. The \( \alpha \)-chloroethylbenzene (1.3 g.) obtained, had \( n \) 1.5272 and 

\[ \alpha_{\lambda 6} = 9.98 \] (1 = 0.25).

3. Using three molecular proportions of pyridine. Very small yields of \( \alpha \)-chloroethylbenzene were obtained.
probably owing to the combination of the \( \alpha \)-chloroethylbenzene produced with the excess of pyridine.

with Thionyl Chloride in the presence of Quinoline.

Preliminary experiments using the \( \text{dl} \)-alcohol.

(a). Using two molecular proportions of quinoline, 5.13 g. quinoline and 2.44 g. (1 mol.) of the \( \text{dl} \)-alcohol were added to 4.76 g. (2 mol.) of thionyl chloride using the experimental procedure described above. \( \alpha \)-chloroethylbenzene (2.4 g.) was obtained having \( n_\text{D} 1.5288 \)

(b). Using one molecular proportion of quinoline, 1.4 g. only, \( \alpha \)-chloroethylbenzene was obtained.

Using optically active Phenyethylalcohol.

The \( \text{dl} \)-alcohol 2.44 g.; \( \alpha \)\( \text{N} \)/44.28 (I=1.0), thionyl chloride (4.76 g.; 2 mol.) and quinoline (5.13 g.; 2 mol.) were employed and the reaction was carried out as described above in (a). The \( \beta \)-\( \alpha \)-chloroethylbenzene (2.3 g.), b.p. 91°/21 mm., had \( \alpha \)\( \text{N} \)/44.28 = 4.3 (I=0.25).

(II). Phosphorus Trichloride, in the presence of Pyridine.

Preliminary experiment using the \( \text{dl} \)-alcohol.

A mixture of 2.44 g. (1 mol.) of the \( \text{dl} \)-alcohol and 1.8 g. (1 mol.) of pyridine was added slowly to
5.5g. (2 mols.) of phosphorus trichloride, cooled in 
an ice-salt mixture. The reactants were well shaken 
between each addition of the alcohol and after warming 
at 50°C for about 30 minutes, the α-chloroethylbenzene 
was extracted and purified as described above. The 
yield obtained was 2.0g. having n D 1.5298.

Using the same quantities as before, the experiment 
was repeated with the sole difference that the phos-
phorus trichloride was added to the alcohol-pyridine 
mixture. The α-chloroethylbenzene obtained (1.8g.) 
had n D 1.5298.

Using Optically Active Phenyldimethylcarbinol.

In the presence of Pyridine. A solution of the 
1-alcohol (2.44g.; 1 mol; α <sub>4</sub> = 12.8 (l=0.25)) in 
pyridine (1.58g.; 1 mol) was added slowly to phos-
phorus trichloride (5.5g.; 2 mols.) cooled in an 
ice-salt mixture. The reactants were well shaken 
between each addition of the alcohol, and after warming 
at 50°C for 30 minutes the α-chloroethylbenzene was ex-
tracted and purified as described above. The final 
product (2.0g.) b.p. 81°/31°, had n D 1.5290 and
In the presence of Potassium Carbonate. The 1-alcohol [2.44g; \(\alpha_{546} = 13.1 \text{ (1}=0.25\)] in ether (10cc.) was added slowly and with constant shaking to an ice-cold mixture of phosphorus trichloride (5.5g; 2 mols.) and anhydrous potassium carbonate (5.5g; 2 mols.) in ether (10cc.). The excess of phosphorus trichloride and the ether were removed under diminished pressure, and the residue was extracted with ether. From this ethereal extract \(\alpha\)-\(\alpha\)-chloro-ethylbenzene (0.5g.), b.p. 92°/25mm., with \(\alpha_{546} + 2.5\) (1=0.25) was obtained together with a higher boiling product which was optically inactive.

Phosphorus pentachloride.

In the absence of pyridine. McKenzie & Clough (10, cit.) were unable to isolate any definite product from the direct action of phosphorus pentachloride on phenylethylcarbinol. The methods outlined below gave \(\alpha\)-chloroethylbenzene in 70% yield (1). The alcohol (2.44g.) was added to ice-cold phosphorus pentachloride (5.5g.; 2 mols.). At the end of the
initial vigorous reaction, the mixture was warmed on a steam bath and then kept at room temperature for 30 minutes. The product was dissolved in methylene chloride and the solution obtained was washed with water and dried. From this solution α-chloroethylbenzene (2.0 g.) was obtained, b.p. 81°/21 mm.

(ii) The alcohol (4.88 g.; 1 mol.) dissolved in dry ether (15 cc.) was added to a solution of phosphorus pentachloride (2 mol.) in boiling ether (50 cc.). The ethereal solution was heated under reflux for 15 minutes, washed successively with water and dilute sodium carbonate solution, and dried with potassium carbonate. After evaporation of the ether α-chloroethylbenzene (4 g.) was obtained, b.p. 88°/27 mm.,

In the presence of Pyridine. A solution of the alcohol (2.44 g.; 1 mol.) in pyridine (1.8 g.; 1 mol.) was added to the phosphorus pentachloride (8.5 g.; 2 mol.) cooled in an ice-salt mixture. After warming at 50° for 30 minutes, the chloroethylbenzene (2.0 g.) was extracted in the usual manner; b.p. 78°/13 mm.,

[Page Number: 34]
Using Optically Active Phenylmethylamine.  

(a). In the absence of pyridine. Experiment (i). was repeated using the d-alcohol having $\alpha_{5}^{V}=+44.28$ (1=1.0). The $\alpha$-chloroethylbenzene obtained was levorotatory, having $\beta_{D}^{12}=1.5283$, and $\alpha_{5}^{V}=-1.271$ (1=0.25).  

(b). In the presence of pyridine. A solution of the l-alcohol (2.44g.; 1 mol., $\alpha_{5}^{V}=12.8$ (1=0.25)) in pyridine (1.58 g.; 1 mol.) was added to the phosphorus pentachloride (8.3 g.; 2 mols.) cooled in an ice-salt mixture. After warming at 50° for 30 minutes the $\alpha$-chloroethylbenzene (2.05g.) was extracted in the usual manner: b.p. 73°/12 mm. $\beta_{D}^{12}=1.5283$, $\alpha_{5}^{V}+2.73$ (1=0.25).  

Phosphorus oxychloride.  

(a). In the presence of pyridine. The d-alcohol (2.44g.; 1 mol. $\alpha_{5}^{V}=+6.52$ (1=0.25)) dissolved in pyridine (1.58g.; 1 mol.) was added with constant agitation to phosphorus oxychloride (6.2g.; 2 mols.). After extraction in the usual manner, $\alpha$-chloroethylbenzene (1.9g.), b.p. 83°/25 mm. $\beta_{D}^{12}=1.5313$, $\alpha_{5}^{V}=-95$.  


— 2.58 (1=0.25), was obtained. In a further experiment using the \( \alpha \)-alkanol \( (3.4g; \ \alpha_{548} = 13.23 \) \( (1=0.25) \) \( \alpha \)-chloroethylbenzene \( (2.0g) \), b.p. 99°/95mm., \( n^2^5 = 1.5259, \ \alpha_{548} + 3.21 (1=0.25) \), was obtained.

(b). In the absence of pyridine.

Preliminary experiments with the \( \alpha \)-alkanol:

(i). Phosphorus oxychloride \( (8.2g, 2 \text{ mole}) \) was added slowly to the alcohol \( (3.4g, 1 \text{ mole}) \) cooled in ice. On warming slightly, a violent action occurred and hydrochloric acid was evolved. The mixture was then left on the water bath for 30 minutes. After extraction and washing in the usual manner, a gumy undistillable residue was obtained, which failed to crystallise after extraction with alcohol, ether, or benzene.

(ii). Phosphorus oxychloride \( (8.2g, 2 \text{ mole}) \) was added slowly to \( 2.4g (1 \text{ mole}) \) of phenylethylcarbinol. Care was taken to ensure that the reaction had finished before making any further addition. The mixture was refluxed for 30 minutes and then transferred to a distillation flask, without preliminary washing. A black, undistillable, tarry product was obtained.
(iv). Phosphorus oxychloride (3.7g.; 1 mol.) was added to 2.4g. (1 mol.) of the alcohol in boiling carbon tetrachloride solution, and the mixture was refluxed for 30 minutes. After washing the product and evaporation of the solvent, the residue gave on distillation: (a) small quantities of styrene, b.p. 90°/40mm. (b) metastyrene, b.p. 105°/1mm. (Found: C, 92.0; H, 7.8. Calc. C, 92.2; H, 7.7%).

(v). Phosphorus oxychloride (2.79; 0.8 mol.) was dissolved in 20ccs. of ether, and 2.4ccs. (1 mol.) of α-phenylmethylcarbinol was added slowly to the boiling solution, and distillation continued for 30 minutes. After extraction in the usual manner, an oil (1.7ccs.) b.p. 87°/20mm. having φ 1.5310 was obtained.

It consisted of phenylmethylcarbinol containing a small quantity of α-chloroethylbenzene.

(vi). Phenylmethylcarbinol (4.8g.; 1 mol.) was added to a solution of 7.4g. (1 mol.) of phosphorus oxychloride in boiling carbon tetrachloride, and the mixture was refluxed for 30 minutes. After washing and evaporation of the carbon tetrachloride, an oil was obtained, containing a small quantity of α(α'-diphenyldiethyl)-ether, b.p. 83°/1mm., 105°/18mm.; having φ 1.5454.

(Found: C, 84.2; H, 7.8. Calc. C, 85.0; H, 7.9%).
The main portion of the product proved to be metastyrene b.n. 185°/1mm.

(vii). The alcohol (2.4g.; 1 mol.) was added to a solution of 2.7g. (0.8 mol.) phosphorus oxychloride in boiling carbon tetrachloride, the mixture was refluxed for 30 minutes. The product, after washing gave on distillation, α-chlorostyrylbenzene (0.3cc.) b.n. 88°/15mm. and metastyrene, b.n. 170°/1mm.

(ix). Phosphorus oxychloride (14.8g.; 1 mol.), was dissolved in carbon tetrachloride (150ccs.) and 9.8g. (1 mol.), of phenylmethylcarbinol added to the boiling mixture. After refluxing for 30 minutes, washing and evaporation of the solvent, α,α'-diphenyl-diethylether b.n. 80°/1mm. (0.5cc.), and metastyrene (5.0g.) b.n. 170°–200°/1mm., were obtained.

(xii). Phenylmethylcarbinol (4.8g.; 1 mol.), and phosphorus oxychloride (7.4ccs.; 1 mol.), were refluxed for one hour with 50ccs. of ether. A soda lime tube was connected to the end of the reflux condenser to absorb hydrochloric acid vapour, and to prevent moisture diffusing into the reaction flask. After the extraction and washing had been carried out following the usual procedure, an oil was obtained which on distillation gave (a) styrene, b.n. 60–72°/27mm. (b) α-chlorostyrylbenzene, b.n. 72–98°/27mm.
(c). phenylmethylcarbinol b.p. 100° / 20 mm. (d). metastyrene b.p. 180° / 1 mm.

(xiii) Phosphorus oxychloride (11g., 0.5 mols.), was added to 4.8g. of the α-alcohol in cold ether solution. The mixture was allowed to stand for 48 hours, was explained, and then dried in the usual manner. On repeated fractionation impure α-chloroethylbenzene was isolated b.p. 72° / 10 mm. (Found: Cl. 21%. Theoretical for α-chloroethylbenzene, 25.2%). The fraction therefore contained 84% α-chloroethylbenzene.

(xvi). Phosphorus oxychloride was redistilled and was allowed to stand for two days in a desiccator with beakers containing respectively, potassium hydroxide, and phosphorus pentachloride. The last traces of hydrochloric acid were thus removed from solution in the oxychloride. The ether used was distilled from phosphorus pentachloride and finally stood over sodium.

Pure phosphorus oxychloride (50g.; 3 mols.), was added to 20g. (1 mol.) of α-phenylmethylcarbinol in 150 cc. of ether and stood at room temperature for 48 hours. After extraction with ether, washing, drying, and evaporation of the solvent, α-chloroethylbenzene (12g.) b.p. 80° / 20 mm., having n D 2.5°.
1.5295 and α'-diphenyldistylethene (5g.) b.p. 105°/1 atm.,
138°/16 mm., d. 1.005 and having nD 1.5422.
(Round: 0, 946; 1, 7.8; Calc. C, 65.0; H, 7.9%).
The α'-diphenyldistylethene gave no sign of decomposition
when heated to 135° (a), alone (b), with the residue
from the distillation (c), with the phosphoric acid.
The residue was proved to contain phosphorus. The
experiment failed to give either styrene or unchanged
phenylmethylcarbinol.

Using Optically Active Phenylmethylcarbinol.

In the presence of pyridine, with α-phenylmethyl-
carbinol having α5401 = 7.10 (1=0.25) using the same
proportions and procedure as in (xvi.), above,
α-chlorostyrylbenzene was isolated having nD 1.5295
α5401 = 0.15 (1=0.25). Round: C1, 24.8%; calc.,
25.2%. The α'-diphenyl-distylethyl ether obtained had
nD 1.5454 and α5401 = 26.30 (1=0.2%).

In a second experiment, using di-ether醇 α5401 = 6.55
(1=0.25), α-chlorostyrylbenzene b.p. 73°/15 mm.,
was obtained, and was optically inactive.
A summary of the reactions carried out with α-
phenylmethylcarbinol is given in Table VIII, showing
the yields of ω-chlorostyrylbenzene obtained by varying the experimental conditions. The experiments carried out with optically active phenylenecarbinol are tabulated in Table I. (p. 17) and include the results obtained in the phosphorus oxychloride reactions.

The experimental results of the interaction of dl-phenylethylcarbinol with phosphorus oxychloride under various experimental conditions are tabulated in Table IX.
TABLE IX.

The Reactions of Phosphorus Oxychloride and Phenylmethylenecarbinal.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Solvent</th>
<th>Mols. POCl₃</th>
<th>Temp. of reaction</th>
<th>time of reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-</td>
<td>2</td>
<td>uncontrolled</td>
<td>½ hour</td>
<td>gum</td>
</tr>
<tr>
<td>II</td>
<td>-</td>
<td>2</td>
<td>50°C</td>
<td>½ hour</td>
<td>tarry mass undistillable</td>
</tr>
<tr>
<td>IV</td>
<td>CCl₄</td>
<td>2</td>
<td>50</td>
<td>½ hour</td>
<td>styrene, metastyrene, α-β-β-dichlorostyrenes, phenylmethylenecarbinal</td>
</tr>
<tr>
<td>V</td>
<td>Ether</td>
<td>0.8</td>
<td>50</td>
<td>½ hour</td>
<td>α-β-dichlorostyrenes, phenylmethylenecarbinal</td>
</tr>
<tr>
<td>VI</td>
<td>CCl₄</td>
<td>2</td>
<td>50</td>
<td>½ hour</td>
<td>styrene, metastyrene, α-β-diphenyldiethyl ether</td>
</tr>
<tr>
<td>VII</td>
<td>CCl₄</td>
<td>0.8</td>
<td>50</td>
<td>½ hour</td>
<td>metastyrene, styrene, phenylmethylenecarbinal</td>
</tr>
<tr>
<td>IX</td>
<td>CCl₄</td>
<td>1</td>
<td>50</td>
<td>½ hour</td>
<td>metastyrene, α-β-diphenyldiethyl ether</td>
</tr>
<tr>
<td>XII</td>
<td>CCl₄</td>
<td>1</td>
<td>50</td>
<td>1 hour</td>
<td>styrene, metastyrene, phenylmethylenecarbinal, α-β-chloroethylbenzene (trace)</td>
</tr>
<tr>
<td>XIII</td>
<td>Ether</td>
<td>3</td>
<td>20</td>
<td>48 hours</td>
<td>α-β-chloroethylbenzene, styrene (trace), α-β-diphenyldiethyl ether</td>
</tr>
<tr>
<td>XVI</td>
<td>Ether</td>
<td>3</td>
<td>20</td>
<td>48 hours</td>
<td>α-β-chloroethylbenzene (50%) α-β-diphenyldiethyl ether (25%)</td>
</tr>
</tbody>
</table>
THE OXYDATION OF \textit{PHENYLACETYL}IMID. \textit{p-}
TOLYIENESULPHUINATE AND THE REACTION OF
\textit{PHENYL acetyl}IMID. \textit{p-}TOLYIENESULPHUINATE
AND \textit{p-}TOLYIENESULPHUINATE.

THE Preparation of \textit{dil-}Phenylmethylglycidyl \textit{p-}
Toluene sulphinic acid.

Peters of \textit{p-}toluene sulphinic acid may be prepared
by direct action of the alcohol with distillation
off, or water formed (Houssea, Kenyon and Phillips,
J.C.S., 1925, 1700); or by the interaction of the
acid chloride with the alcohol (Phillips, J.C.S.,
1925, 3565).

\textit{p-}Toluene sulphinic acid may be prepared by reducing
recrystallised \textit{p-}toluene sulphotryl chloride by a strong
solution of sodium sulphite (Blawstrand, Ber., 1870,
2, 965) and purified by recrystallising its sodium
salt from water. The acid, obtained by decomposition
of the pure sodium salt, was partly dried on a porous
plate and then completely dried by desiccation over calcium chloride in a vacuum.

\( p \)-toulenesulphiryl chloride was prepared by gradual addition of the acid (1 mol.) to a solution of thioryl chloride (1.1 mol.) in an equal volume of dry ether; the thioryl chloride was purified as previously described. When all the acid had dissolved, the mixture was warmed very gently until evolution of hydrogen chloride and sulphur dioxide ceased. The ether and excess thioryl chloride were removed by evacuation at room temperature. The oily residue was dissolved in petroleum ether and filtered from the small quantity of white solid usually precipitated; it was then subjected to a vacuum overnight at room temperatures, after which the \( p \)-toulenesulphiryl chloride was obtained as a yellow oil. The method is due to Hilditch and Smiles (Beryl, 1908, 41, 4113; Hilditch, J.C.S., 1910, 97, 5585).

Phenylmethylcarbinyl \( p \)-toulenesulphinate was prepared from the acid chloride by the method of Kervyn and Phillips (J.C.S., 1930, 1678). \( p \)-Toulenesulphiryl chloride (12.4g.) was added slowly to an ice-cold solution of \( p \)-phenylmethylcarbinol (8.5g.) in pyridine (6.2g.). The resulting mixture was triturated with ether (25cc.) in order to facilitate the reaction.
more ether was then added, and the ethereal solution washed with dilute hydrochloric acid, and then repeatedly with aqueous potassium carbonate. The ether was removed from the dried extract, partly by distillation at ordinary temperatures, and subsequently at 15°C. The dl-phenylmethylcarbinol p-toluene-sulphinate was thus obtained as a colourless viscous liquid, which was freed from traces of dl-phenylmethylcarbinol by gently heating it at less than 0.1 mm; yield 95% of theory. (Found, C, 12.5. O 15. 0. 2. 2 requires 12.3%).

The Reaction of dl-Phenylmethylcarbinol p-Toluene-sulphinate with Oxidising Agents.

(1). Using potassium permanganate. Potassium permanganate (20g.) and potassium sulphate (20g.) were ground to a fine powder and added slowly to a solution of phenylmethylcarbinol p-toluene sulphotimine (14g.) in acetone (50cc.). The mixture was sealed by a stream of cold water.

After all the permanganate had been added, sulphur dioxide was bubbled through the solution to dissolve the precipitated manganese dioxide. A quarter of the acetone was distilled off; the remaining solution
was poured into water, extracted with ether, washed with water and dried. The product gave on distillation d-l-phenylmethylcinnamyl, b.p. 93°/1 mm., acetophenone, b.p. 95°/1 mm. and a residue of d-l-phenyl-ketoleuconic acid, together with a product which commenced to decompose at 110°C., and failed to crystallise from the common solvents. This product was probably the d-l-phenylmethylcinnamyl-p-toluenesulphonate.

Hydroperoxide:

(1) Peroxydrol (50%, 88% N₂O₃) was added to the d-l-culbinate (10g.) in 1000cc. of acetone. After removal of the acetone, a sudden darkening of the residue was noticed. On distillation, small quantities of d-l-phenylmethylcinnamyl were obtained b.p. 95°/1 mm. Acetophenone (5g.) b.p. 95-100°/1 mm. R 22 1.5220.

The residue, containing d-l-phenylmethylethanesulphonic acid, failed to crystallise from alcohol, acetone, or petroleum.

(11) Using peracetic acid, to a solution of the d-l-culbinic ester (9.5g.) in 1000cc. of absolute alcohol hyperval (5g.) was added with constant shaking. After

-10°
extraction with methylene chloride, the products obtained were, \( \alpha \)-pheryl-diesthylether, b.p. 73°C/15mm., n\( \rho \) 1.4971; and \( \alpha \)-pheryl-methylecarbinol, b.p. 95°C/15mm.

The residue may have contained some pheryl-methylcarbinyl \( \beta \)-toluenesulphonate, but consisted mainly of \( \alpha \)-pheryl-ethyl-sulphide and \( \beta \)-toluenesulphonic acid. The usual solvents failed to give a satisfactory resolution of this mixture.

(iv). Using hydrogen peroxide. Peroxydol (60cc. of 30%, 1 mol. \( \text{H}_2\text{O}_2 \)) was added slowly to pheryl-methylcarbinyl \( \beta \)-toluenesulphonate in 40cc. of absolute alcohol. The mixture was concentrated by distilling off the greater part of the alcohol. The concentrated alcoholic solution was divided into three portions.

(a). One portion was refluxed for 24 hours with dry lithium chloride, extracted with methylene chloride, dried and distilled. A small quantity of \( \alpha \)-pheryl-diesthylether, b.p. 78°C/15mm. was obtained.

(b) and (c). The remaining portions of the alcoholic solution were refluxed with potassium acetate and potassium thiocyanate respectively. The yield of volatile product was, in each case, too small for identification, the main production in each case being \( \alpha \)-pheryl-ethyl-sulphide.

The sulphonlic ester appears to be a very reactive.
compound which readily reacts with ethyl alcohol and water giving rise to 2-phenylethanol, which is oxidised to acetophenone.

The Reaction of dl-Phenylmethylcarbinyl n-Toluene sulphinic acid with Metallic Salts.

(i). With lithium chloride in ethyl alcohol solution

Lithium chloride (15g.) was added to the sulphinic ester (10g.) dissolved in 40 c.c. of absolute alcohol. After refluxing for 24 hours, the mixture was extracted, washed and distilled. The products isolated were:

- styrene, b.p. 83°/15mm., α-phenylethyl ether, b.p. 78°/14mm., nD 1.50 containing some α-chloroethylbenzene;
- 2-phenylethanol, b.p. 85°/15mm., nD 1.5076; ethyl n-toluene sulphinic acid b.p. 140°/15mm., 74°/1mm., nD 1.5380. An undistillable residue was obtained consisting of a mixture of n-tolyl-α-phenylethylsulphone and some unchanged sulphinic ester.

(ii). With potassium carbonate in ethyl alcohol solution

The sulphinic ester was prepared as described on p. 104. Ethyl alcohol was obtained in a high state of purity by distilling 93° ethyl alcohol from calcium. Potassium carbonate was freshly ignited for use in the experiment.
A mixture (10g.) of the sulphinic ester, ethyl alcohol (40ccs.) and potassium carbonate (25g.) was refluxed on a waterbath for 24 hours. The top of the reflux condenser was connected to a calcium chloride drying tube. The alcohol was distilled off through a fractionating column; the residue was extracted with methylene chloride, washed and dried. It gave on distillation a very small quantity of \( \text{ethyl} \rightarrow \text{ethyl} \) and \( \text{m-tolyl} \rightarrow \alpha \)-phenyl-diesthyl ether, together with a residue of \( \text{m-tolyl} \rightarrow \alpha \)-pheryl-ethyl-sulphone.

(iii). With lithium chloride and potassium carbonate in ethyl alcohol. The reagents were purified as described previously, the lithium chloride was fused to remove moisture.

A mixture of \( \text{p-sulphinic ester} \) (10g, 1 mols.), 40ccs. ethyl alcohol (50 mols.), and potassium carbonate (25g.; 5 mols.) was refluxed for 48 hours. The excess ethyl alcohol was removed by distillation, the residue was extracted with methylene chloride, washed, dried, and distilled after removal of the solvent. The main products were \( \alpha \rightarrow \) phenyl-diesthylether (30-40°) b.p. 73°/14mm., \( \beta \rightarrow \beta \) 1.4071, and phenylethylcarbinol (60-70°) b.p. 91°/14mm., \( \eta \rightarrow \beta \) 1.5240. A very small residue only of the sulphone was obtained. The complete
absence of \( \alpha \)-chloroethylbenzene leads to the conclusion that the presence of some water causes hydrolysis of the \( \pi \)-toluenesulphinate to give phenylmethylether-nol and that any chloro-compound formed reacts with ethyl alcohol to give \( \alpha \)-phenylethylether.

(iv). With lithium chloride in acetone-tile solution.
The \( \alpha \)-sulphuric ester (10g., 1 mol.), acetone-tile (40 ccs.) and (8g., 5 mols.), lithium chloride were refluxed on a water bath for 48 hours. After extraction, washing and distillation, \( \alpha \)-chloroethylbenzene (1cc.) obtained with phenylethylether-nol, b.p. 90°/25mm. having \( n^\alpha \) 1.5280 was obtained. A small quantity of ethyl \( \pi \)-toluenesulphinate was also obtained, b.p. 76°/1mm.

(vi.) With \( \pi \)-butyl alcohol and potassium carbonate.
Ten ccs. of the \( \pi \)-toluenesulphuric ester were dissolved in 50 ccs. of \( \pi \)-butyl alcohol and 25g. (5 mols.) of potassium carbonate were added. The mixture was refluxed on an oil bath for 48 hours. On addition of methylene chloride, potassium \( \pi \)-toluene sulphinate separated out as a white solid. After filtration, the butyl alcohol was distilled off through a column. The residue was re-extracted and washed. Distillation of the product gave a few drops of an oil b.p. 100°/15mm., \( n^\alpha \) 1.5214, which was probably \( \alpha \)-pherylethyl \( \pi \)-butyl ether.

-110-
Ph. Me. CH.OC₄H₉: A large residue of \( \text{-} \text{toly} \text{1} \alpha \)-phenylethylsulphone was obtained. In a further experiment the distillate (0.8ccs.) was heated with phthalic anhydride for 24 hours, to remove any free butyl alcohol and phenylethylcarbinol, it was then allowed to stand over aqueous sodium carbonate for 24 hours.

After extraction and washing in the usual manner, the \( \text{r} \)-butyl ether (0.3ccs.) b.p. 110°/25mm., was obtained.

(vi). With potassium thiocyanate in acetonitrile solution. Potassium thiocyanate (15g.) of-phenylmethylearbinyl \( \text{r} \)-toluene sulphinate (8g.) and 40ccs. of acetonitrile were refluxed for 48 hours. Potassium \( \text{r} \)-toluene sulphinate crystallised from the solution.

After extraction, washing, drying and evaporation of the solvent the product was distilled at 1mm. pressure, giving phenylethylcarbinol admixed with a little phenylethylthiocyanate b.p. 50°/1mm. (0.4ccs.). The residue of \( \text{r} \)-toly1 \( \alpha \)-phenylethylsulphone, on further heating, commenced to distil at 130° 0/1mm. and solidified in the condenser.

(vii). With potassium acetate in acetonitrile solution. Potassium acetate (30g.) \( \text{r} \)-toluene sulphonic ester (10g.) and 30ccs. of acetonitrile were refluxed for 48 hours and treated as in the previous experiments.
The product consisted mainly of p-tolyl-α-phenylethyl-
sulphone together with some uncharged p-toluene-
sulphonic ester.

(1). With aqueous ammonia. p-Tolyl sulphinic
ester (15 g., 1 mol.) and concentrated aqueous ammonia
(20 ccs., 1 mol.) were heated at 110°C in a sealed tube
for 5 hours. On opening the tube, the product was
extracted with ether, and washed with hydrochloric
acid. The hydrochloric acid extract was neutralised
with sodium carbonate and any amine extracted by a
further treatment with ether. After washing, drying,
and evaporation of the ether, a small viscous residue
(0.2 g.) was obtained, indicating a negligible pro-
duction of phenylethylamine.

(2). With glacial acetic acid. Ten grams of the
acetyl-
sulphonic ester were mixed with 40 ccs. of acetic
acid which had been dried by freezing and remelting
alternately three times. After 12 hours standing,
the mixture was heated for a further 12 hours, the re-
action being carried in an atmosphere of nitrogen.
The mixture was allowed to stand over an excess
sodium carbonate for 24 hours, extracted, washed and
the solvent removed by distillation. The remaining
oil, on distillation, gave phenylmethylcarbinyl acetate
(3g.) b.p. 105°/15mm. having n D 1.5025. Found, 73.21; H, 7.38. Theory requires C, 73.17; H,
7.32. A small residue of α-phenylethylsulphone was also obtained.

(xf). With sodium ethoxide. To the solution obtained by dissolving sodium (3g.) absolute alcohol, was added
the α-sulphinic ester (10g.); the mixture was allowed to stand for 12 hours and finally warmed for 12 hours
extracted, washed, dried and the solvent evaporated.
On distillation, phenylmethylocininal (2-3g.) was obtained. Although some α-phenyl diethyl ether was
produced the yield was too small to allow conclusive identification.

The Oxidation of Phenylmethylocininal α-Toluene-
sulphinate by Air.

(1). With ethyl alcohol and potassium carbonate in
an oxidising atmosphere. The α-toluene sulphinic
ester (10g.) ethyl alcohol (40c.c.) freshly distilled
from metallic calcium, and 25g. potassium carbonate
were mixed in a 250cc. conical flask fitted with a re-
flux condenser, and a bent glass tube reaching to within
1/2in. from the bottom of the flask. The top of the
reflux condenser was connected through a calcium chloride tube to the suction pump while the end of the glass tube was connected to the outlet of a Dresser bottle containing more dry ethyl alcohol. The mixture was refluxed for 48 hours, while at the same time, a stream of air was drawn through the mixture. The air was dried by passage through sulphuric acid and then saturated with alcohol vapour from the Dresser bottle, so that evaporation of the alcohol from the reaction flask was avoided. On extraction of the residue, phenylmethylcarbinol (500 g.), contaminated with a little \( \alpha \)-pheryl-disthylether, was obtained.

b.p. 98°/20mm.

(ii). In an inert atmosphere. A parallel experiment was carried out in a similar apparatus using a stream of dry nitrogen instead of air. Phenylmethylcarbinol (500 g.) and a small quantity of \( \alpha \)-pheryl-disthylether was obtained.

(iii). With lithium chloride and ethyl alcohol in an oxidising atmosphere. A further experiment was carried out in a similar apparatus using lithium chloride and ethyl alcohol; a stream of dried air was drawn through the solution. \( \alpha \)-Pheryl-disthylether was obtained in 60% yield; it had b.p. 78°/14mm., and \( \eta \) D 1.4975. Found C, 79.3; H, 9.3; C, \( \text{H} \) 14.
requires: C. 30.0, H., 3.3. A residue of \( \alpha \)-phenylethylsulphione was also obtained.

(iv). With lithium chloride and ethyl alcohol
in an inert atmosphere. The preceding experiment was repeated in a stream of nitrogen; \( \alpha \)-phenylmethylether was obtained in 60% yield, \( \beta \)-toluene 79°/14mm.
and \( \beta \)-1.4375, together with a quantity of \( \alpha \)-phenylethylsulphione. When the time of reaction was shortened,
a small yield of \( \alpha \)-chloromethylbenzene was obtained.

The Oxidation of \( \alpha \)-Phenylethylarachinal \( \beta \)-Toluene Sulphinate Controlled by Titrations.

(1). With Air. A train of Deschall bottles contain-
taining (1): sulphuric acid to dry the incoming air
(2): benzene to saturate the air with benzene vapour
and (3): a solution of \( \beta \)-toluenesulphuric ester (SOa)
in 100cc. benzene. The outlet of the third bottle
was connected through calcium chloride tubes to the
water suction pump. A second train was also arranged,
differing from the first only in that 10g. of dry
potassium carbonate were added to the \( \beta \)-toluysul-
phonic ester solution.

Two reactions were expected to proceed simultaneously

(a), the oxidation of the \( \beta \)-toluene sulphinate to the
corresponding \( p \)-toluene-sulphinate, and (b) the conversion of phenylmethylcarbaryl \( p \)-toluene-sulphinate to the \( \alpha \)-phenethylthyl-sulphone. The progress of the isomerisation (b) was followed by hydrolysis of a sample of the reacting mixture in a known excess of alcoholic potash, and titration of the unused potash with standard acid. From the amounts of potassium hydroxide used, the total phenylmethylcarbaryl \( p \)-toluene sulphinate plus \( p \)-toluene-sulphonate was calculated. Since the sulphone is not hydrolysed by alcoholic potash, the potash required for hydrolysis, subtracted from the potash required by the original solution, represents the quantity of sulphone produced. The amount of oxidation was determined by titration of samples with a standard solution of perbenzoic acid, using starch-iodide paper as an indicator. It was discovered however that the oxidation of the \( p \)-toluene sulphinate by perbenzoic acid proceeded so slowly that the end of the titration was indefinite, and a further group of experiments were carried out using the bromide-bromate method of titration.

(ii). Two Dreschel bottles were charged with a solution of phenylmethylcarbaryl \( p \)-toluene-sulphinate made up to 50ccs with benzene. To one was also added 10g. of potassium carbonate. Air was drawn
## Table X.

The Oxidation of Phenylmethylcarbinyl p-Toluenesulphonate

by Air.

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>With Potassium Carbonate</th>
<th>Without Potassium Carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%ages of original</td>
<td>%ages of original</td>
</tr>
<tr>
<td></td>
<td>Sulphate</td>
<td>Sulphate</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>60%</td>
<td>20%</td>
</tr>
<tr>
<td>12</td>
<td>55%</td>
<td>42.5%</td>
</tr>
<tr>
<td>24</td>
<td>55%</td>
<td>35%</td>
</tr>
<tr>
<td>72</td>
<td>45%</td>
<td>33.5%</td>
</tr>
<tr>
<td>26</td>
<td>40%</td>
<td>33.5%</td>
</tr>
</tbody>
</table>
through each bottle with the same arrangement as in the previous experiment. The progress of the reaction was followed by (a) hydrolysis with alcoholic potash as before and (b) oxidation of the unchanged sulphinate by the bromide-bromate method.

In this method a slight excess of an \( \frac{7}{10} \) solution of potassium bromate was added to a 5cc. sample of the reacting mixture. Two cc. each of concentrated solutions of hydrochloric acid, and potassium bromide were added and the mixture was shaken for one minute. Potassium iodide solution was then added carefully and shaken to liberate iodine in place of free bromine. The excess iodine was titrated with \( \frac{7}{10} \) sodium thiosulphate solution. The results of this series of experiments are given in Table X.

The results show that (a) some oxidations of phenylmethylcarbaryl \( p \)-toluenesulphinate in the presence of air does occur. (b) Isomerisation of the \( p \)-toluene sulphonate to the corresponding \( p \)-tolyll-sulphone takes place (c). The presence of potassium carbonate tends to inhibit the isomerisation reaction.
and therefore increases the yield of phenylethylcarbinyl 
\( \text{p-} \) -toluenesulphonate obtained. (d) Oxidation 
comes to a standstill when 40\% of sulphonate has 
oxidised to the sulphonate.

(iii). The air-treated \( \text{dL-} \) -phenylethylcarbinyl 
\( \text{p-} \) -toluenesulphonate, containing no potassium carbonate 
was filtered from precipitated sulphone and was evap-
orated in vacuo to remove the greater portion of the 
benzene (a) one half was refluxed with lithium chloride 
and acetonitrile as described previously. A yield 
of less than 5\% of \( \alpha \)-chloroethylbenzene was 
obtained (b). A further quantity of the aerated 
\( \text{p-} \) -toluenesulphonate was treated with petroleum ether, 
in an attempt to crystallise the \( \text{p-} \) -toluenesulphonic 
ester formed, but without achieving any measure 
of success.

(iv). Oxidation by hydrogen peroxide. Hydrogen
peroxide (1 mol. 1.4 ccs. of 30%) was added to a solution of the p-toluene sulphinate (10 ccs.) in ether. Titrations of equal samples of (a) the hyperol in ether solution before addition of the p-toluene sulphinate (b) immediately after addition of the p-toluene sulphinate, and (c) 24 hours after addition of the p-toluene sulphinate, showed no change in the concentration of hydrogen peroxide, indicating that oxidation had not taken place. The method used was to add standard potassium iodide to a sample of known volume, to acidify, and to titrate the liberated iodine with standard thiosulphate. It was shown, by experiment, that free iodine was without action on the phenylmethyleareryl p-toluene sulphinate. Titration with acid, after hydrolysis in alcoholic potash, showed the extent of isomerisation to be 20%.

(v) Oxidation by perhydrol in presence of acetic acid. The above experiment was repeated in acetic acid solution in place of ether. Titrations with potassium iodide and sodium thiosulphate showed that the oxidation proceeded very rapidly when once started and continued to completion. The resulting acetic acid solution was poured into sodium carbonate solution, extracted with methylene chloride, and, after washing and evaporation, gave pure phenylmethyleareryl
acetate (1m.) which was found by analysis to contain 90% of the acetate, the remainder being phenylmethylcarbinol.

The Oxidation of Phenylmethylcarbinol \( \text{p}-\text{toluene} \) sulphonate by Pyrocol in the Presence of Various Reagents.

(i) With lithium chloride in acetonitrile solution.
Pyrocol (free parhydrate; 10g., 1 mol.) was added slowly to a mixture of the \( \text{p}-\text{toluene} \) sulphonate, (15g., 1 mol.) potassium carbonate (20g.), and lithium chloride (10g.). After standing for 12 hours, and the mixture was warmed for a further hour

the product obtained after distillation of the solvent and acetonitrile, contained a trace of \( \alpha \)-chloroethylbenzene, but consisted mostly of a gummy mass. Formed partly by the participation of acetonitrile in the reaction.

(ii) With potassium carbonate in ethyl alcohol solution.
Pyrocol (10g.) the sulphinic ester (15g.), potassium carbonate (30g.) and 50cc. of ethyl alcohol were mixed, allowed to stand for 12 hours, and refluxed for another 12 hours.

On extraction and separation of the products \( \alpha \)-phenyl-diethyl ether (3g.) was isolated, having b.p.
30°/20mm. and n \( \frac{n}{d} \) 1.4673.

(iv). With glacial acetic acid. Hypercol was dried by pressing out on a porous plate, and standing in a desiccator over phosphorus pentoxide overnight. Glacial acetic acid was obtained in a pure state by freezing a laboratory sample, pouring off the liquid, thawing and refreezing altogether three times.

Hypercol (10g.) and benzylecarbimyl \( \mu \)-toluene sulphonate (15g.) were dissolved in 50cc. of glacial acetic acid, and allowed to stand for 12 hours. The mixture was poured gradually into sodium carbonate solution, extracted with methylene chloride, washed and dried. On distillation, benzylecarbimyl acetic acid (4g.) was obtained, b.p. 105°/25mm., n \( \frac{n}{d} \) 1.5038, d\(_{20} \) 0.950.

(v). With potassium carbonate and lithium chloride, in ethyl alcohol solution. The reagents used were \( \mu \)-toluene sulphonate (15g.); potassium carbonate (25g.); hypercol (10g.); lithium chloride (20g.); ethyl alcohol (50cc.). The alcohol was dried by distillation from metallic calcium, the lithium chloride by fusion, and the potassium carbonate by heating to redness in a silica dish.

After mixing, the reactants were allowed to stand
12 hours, then refluxed for 12 hours, the joints in the apparatus being luted with paraffin wax and the top of the reflux condenser fitted with a calcium chloride tube, to exclude moisture. After pouring into water, extracting, washing and drying in the usual manner, the following fractions were obtained.

(i). A mixture of \( \alpha \)-chlorostyrylbenzene and \( \alpha \)-phenylethyl ether, b.p. 78-93°/25mm., (ii).
\( \alpha \)-phenylethyl ether, b.p. 85-93°/25mm., (iii).

Butyl methyldiacetone, b.p. \( 92-105°/25mm. \), with (iv) a small residue of \( \alpha \)-phenylethyl sulphide.

(v). With butyl alcohol and potassium carbonate.

Biphenol (10g.), phenylmethyldiacetone potassium sulphate (15g.) and potassium carbonate (20g.) were mixed in 50ccs. of butyl alcohol, stood for 12 hours, and finally heated on a water bath for 12 hours. After extraction with methylene chloride, washing and drying, the methylene chloride was distilled off, and the butyl alcohol distilled from an oil bath, using a fractionating column.

The residual oil was distilled under reduced pressure giving an oil (5-6g.) 90°/21mm. and only a small residue. The distillate was heated overnight with phthalic anhydride to free the butyl ether obtained from phenylmethyldiacetone and butyl alcohol, the
former having a boiling point close to that of the
butyl ether. The resulting mixture was poured
into sodium carbonate solution and left for 24
hours. The n-buty1 ether was extracted, dried
and distilled, in the usual manner. n-Buty1 α-phenyl-
ethyl ether (40g.) was obtained, b.p. 103°/20mm., p
1.4960. Found: C., 81.1 %, 81.9 %; H., 11.0 %
requires: C., 81.0 %; H., 10.1 %.

(ix). With magnesium ethyl chloroide (Grignard's
reagent). Pyrenol (10g.), the α-sulphuric acid
ester (10g.) were mixed in 100cc. of dry ether and was
allowed to stand for 24 hours. Magnesium ethyl-
chloride solution was made by dissolving magnesium
(2g.) in an ether solution of ethylchloroide.

The ethereal solution of the sulphonic acid ester was
added slowly to the well-cooled Grignard reagent,
when a vigorous reaction occurred. After standing
the mixture overnight, the ethereal solution was
mixed with ice, separated, washed with dilute hydro-
chloric acid, water and sodium carbonate, and dried.
On distillation in vacuo, an oil containing phenyl-
methylquinolone was obtained, b.p. 103°/20mm., this was
heated with phthalic anhydride for 24 hours and was
left over sodium carbonate for a further 24 hours.
The final product (3g.) free from phenylethylcarbinol had, b.p. 115/21mm. and was shown by analysis to be a mixture; the constituents were not identified.

No appreciable quantity of α-chloroethylbenzene was obtained.

(2.) With lithium chloride and potassium carbonate in ethyl alcohol solution. Hypereol (10g.) the α-sulphinic ester (15g.) lithium chloride (25g.) and potassium carbonate (25g.) were mixed in 50cc. of absolute alcohol, freshly distilled from calcium metal. After standing in the cold for three hours, the alcohol was evaporated under reduced pressure, 100cc. dry ether was then added, and the mixture was refluxed for 12 hours; then extracted, and treated in the usual manner.

On distillation in vacuo α-phenyldisethyl ether (2g.) b.p. 86°/30mm. and having δ 22 D 1.6974 was obtained α-phenylethylsulphone and some impure sulphonic ester was also obtained.

(3.) With lithium chloride and potassium carbonate in absence of a solvent. The hypereol (10g.) α-sulphinic ester (15g.) lithium chloride (25g.), and potassium carbonate (25g.) were mixed without employment of solvent. After standing for 12 hours, the
mixture was warmed for a further 12 hours, extracted, washed and distilled.

On attempted distillation in vacuo, a residue of $p$-chloro-$\alpha$-phenylethylsulphone and the $p$-toluenesulphonic ester was obtained.

(xi) With lithium chloride and potassium carbonate in acetonitrile solution.

The previous experiment (xi) was repeated with the difference that acetonitrile, freshly distilled from phosphorus pentoxide, was added to the mixture, after it had already been warmed for 12 hours without solvent, in order to oxidise the sulphonic ester before the acetonitrile was added. After heating under reflux for 12 hours the acetonitrile was distilled off, and the residue was extracted with ether, washed, dried and distilled. The product consisted of $\alpha$-phenylethylsulphone and the $p$-toluenesulphonic ester of phenylmethylcarbinol, but contained no appreciable quantity of $\alpha$-chloroethylbenzene.
THE REACTIONS OF OPTICALLY ACTIVE PHENYLACETYL-
CAPRINYL-\(\alpha\)-TOLUENE SULPHONATE.

The preparation of 1-phenylmethylcarbimyl \(\alpha\)-toluene sulphinate. Using \(\text{1-alkali}\) \(\alpha\)-toluene and adopting the procedure of page 104 the \(\text{1-}\)toluene sulphonic ester obtained had \(\alpha\) \(\text{54e}^2\) - 18.3 (1=0.25). It also had \([\alpha]_D = -73.4 \text{ (c=0.32)}\) in ethyl alcohol solution whence \([\alpha]_D = -130.6\).

The Reactions of the \(\text{1-Sulphonic Ester in the Abosence of Dimetal.}

(1). With acetic acid in an inert atmoosphere.

The same procedure was adopted as used for the experiment on the \(\text{dl-}\)material, including passage of nitrogen through the reactants. The phenylmethyl-
carbimyl acetate obtained had b.p. \(105^\circ/15\text{mm.}\) and \(n^\circ = 1.5064\), and was optically inactive.

(2). With ethyl alcohol and lithium chloride, in an inert atmosphere. Using the experimental procedure of page 113 passing nitrogen into the reaction mixture, the \(\alpha\)-phenylacetyethyl ether obtained had b.p. \(80^\circ/15\text{mm.} \quad n^\circ = 1.4973\), and \(\alpha\) \(\text{54e}^2 = -3.28 \text{ (1=0.25)}\).
(iii). With lithium chloride and ethyl alcohol
in a stream of air. The procedure adopted was the
same as in experiment (iii) page 114, using \( \alpha \)-sul-
phiric ester prepared from the \( \beta \)-alcohol \( \alpha_{5481}^\circ = 13.15^\circ \)
\((l=0.25)\). The \( \alpha \)-bromide ester obtained had b.p.
79°/14mm. \( n_D^\circ = 1.4676 \), and \( \alpha_{5481}^\circ = 2.8^\circ \)
\((l=0.25)\).

The Reactions of the \( \beta \)-Sulphiric Ester in the Presence
of Epinephrine.

(i). With ethyl alcohol. Using the procedure of
experiment (ii) page 119 the \( \beta \)-sulphirinate from the \( \beta \-
alcohol \( \alpha_{5481}^\circ = -13.15^\circ \) \((l=0.25)\); the \( \alpha \)-bromide ester obtained had b.p. 80°/15mm., \( n_D^\circ = 1.4979 \) and
\( \alpha_{5481}^\circ = 4.50 \) \((l=0.25)\).

By the reaction of the potassium derivative of the
\( \beta \)-alcohol on ethyl bromide (Kerpy and Phillips, loc.
cit.) levor-\( \alpha \)-bromide ester is obtained having
\( \alpha_{5431}^\circ = 23.8^\circ \) \((l=0.25)\). It also has \( \lambda_{5930}^\circ = -33.9^\circ \)
in ethyl alcohol \((c=0.4)\) whence \([M]_D = -95.4^\circ \).

(ii). With lithium chloride and ethyl alcohol.
Using \( \beta \)-sulphirinate obtained from the \( \beta \)-alcohol \( \alpha \)
\( 5481^\circ = 13.15 \) \((l=0.25)\), and adopting the procedure
of experiment (v), page 120, the levor-\( \alpha \)-bromide ester-
ether obtained had b.p. 79°/14 mm., \( n_0^2 \) 1.4975 and
\( \alpha_{548}^1 = 2.0 \) (1 = 0.25).

(iv). With acetic acid. Using \( L \)-sulphinic acid from the \( L \)-alcohol \( \alpha_{548}^1 = 13.15 \) (1 = 0.25) and adopting the procedure of experiment (iv) page 120 the dextro-handed, dextrorotatory phenylmethyl carbinyl acetate obtained had b.p. 108°/15 mm., \( n_0^2 \) 1.5017 and \( \alpha_{548}^1 = 7.75 \) (1 = 0.25).

(iv1). The preparation of \( L \)-phenylmethylcarbinyl acetate. The \( L \)-alcohol \( \alpha_{548}^1 = 13.15 \) (1 = 0.25) (3g.) and acetic anhydride (3g.) were mixed and warmed for two hours. The mixture was poured into sodium carbonate, extracted with isopropyl ether, washed dried and the solvent removed by distillation. The product was fractionated under diminished pressure.

The \( L \)-acetate obtained had b.p. 102°/18 mm., \( n_0^2 \) 1.5048 and \( \alpha_{548}^1 = 23.55 \) (1 = 0.25) (35%).

(4v). With \( n \)-butyl alcohol. Using \( L \)-sulphinic acid obtained from the \( L \)-alcohol \( \alpha_{548}^1 = 13.15 \) (1 = 0.25) and adopting the procedure of experiment (vi). page 121, dextrorotatory phenylmethyl \( n \)-butyl ether was obtained with b.p. 102°/23 mm., \( n_0^2 \) 1.4061 and
having \( \alpha_{548}^{1+} + 4.11 \). (I = 0.25). (xii). The preparation of 1-\( \alpha \)-phenylethyl \( n \)-butyl ether. Powdered potassium (1.6 g) was dissolved in 1-phenylmethylcarbinol (5 g, \( \alpha_{548}^{1+} - 13.15 \) (I = 0.25)) and dissolved in 50 cc. of ether. To the mixture \( n \)-butyl bromide (4 g) was added slowly and the mixture finally warmed gently for 1 hour. On extraction, and distillation, \( n \)-butyl ether was obtained having b.p. 100°/20 mm. This impure product was heated overnight with phthalic anhydride and allowed to stand for a further 24 hours over sodium carbonate solution, and again extracted and distilled. The \( n \)-butyl ether finally obtained had: b.p. 100°/21 mm., \( \alpha_{548}^{1+} 1.4958 \) and \( \alpha_{548}^{1+} - 13.2 \), \( \alpha \) 53.8 in ethyl alcohol solution (c = 7.2); whence \( \beta \) 94.5.

(v). With lithium chloride in acetic anhydride solution. The 1-sulphonate prepared from the 1-alcohol having \( \alpha_{548}^{1+} - 13.15 \) (I = 0.25). The method of experiment (xi) page 124a, was used to carry out the reaction, with the sole difference that the mixture was warmed for 4 hours instead of 12 as used with the diester. The products obtained were:

(a) dextro-\( \alpha \)-chloroethylbenzene b.p. 75°/15 mm.
n D 1.5307 α \text{D}_{5461} + 0.37 (l = 0.25) (b) dextro-phenyl-
methylcarbaryl acetate b.p. 105 °/15 mm., n \text{D}_{20} 1.5042;
it had \text{D}_{5461} + 0.35 (l = 0.25).

(vii). The attempted reaction of L-α-chloroethyl-
benzene acetic anhydride and hymal.

In order to show that the acetic obtained in experiment
(vi) was obtained from the sulfinate and not by reaction
with the L-chloroethylbenzene, which had previously
arisen by the reaction of lithium chloride on the sul-
finate, the following experiment was carried out:-
L-α-chloroethylbenzene (5g.) α \text{D}_{5461} = 4.3 (l = 0.25)
were mixed with hymal (1g.) and acetic anhydride
(30cc.). after standing for 8 hours the reactants were
warmed for a further 4 hours extracted, and allowed
to stand for 24 hours over sodium carbonate solution.
The mixture was extracted, washed and dried, the
solvent evaporated and the resulting oil was fraction-
ally distilled under reduced pressure. The final pro-
duct gave L-α-chloroethylbenzene (2.5g) b.p. 76 °/1mm
having \text{D}_{5461} = 3.7 (l = 0.25); a trace phylmethyl-
carbaryl acetate was produced but was not sufficient
to isolate in a state of purity.
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