ABSTRACT OF THESIS.

"STUDIES IN THE OPTICAL PROPERTIES OF CARBON AND SULPHUR COMPOUNDS. THE RESOLUTION OF MIXED SULPHOXIDES AND SULPHILIMINES."

submitted to the

UNIVERSITY OF LONDON

for the degree of

DOCTOR OF PHILOSOPHY

by

JOSEPH HOLLOWAY, B.Sc., (Lond), A.I.C.

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The application of the electronic theory of valency to chemical problems has shed a new light on many hitherto obscure problems and has provided the inspiration for several epoch-making researches.

In particular, Lowry, in 1923, from theoretical considerations based on the above theory, introduced the conception of "mixed" or "semipolar" double bonds. The possible existence of semipolar double bonds, revealed by the application of the electronic theory of valency, has been confirmed experimentally by two unique methods. On the one hand, Sugden, in 1925, after determining the parachors of a number of compounds containing a double bond, showed that substances, which could be represented on theoretical grounds as possessing a semipolar double bond, gave values lower than those calculated for an ordinary double covalency. On the other hand, Phillips, in the same year, detected a new kind of optical activity in a series of sulphinates of the type \(\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO} \cdot \text{OR}\).

The present thesis is concerned with further research on this new type of optical activity. For instance, it is now shown that mixed sulphoxides, which, according to the older formulation \(\text{\text{K}}\cdot\text{K} \cdot \text{S} = 0\), could not be suspected of existing in enantiomorphously related forms, are capable of being resolved into their optically active forms. Furthermore, a mixed sulphilimine, \(\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{N} = \text{S} \cdot \text{C}_2\text{H}_5 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}\), an example of the new type of quadrivalent sulphur compound discovered by Raper, has been shown to exist in enantiomorphously related forms. It is pointed out
The most recent development of the theories discussed in the thesis is the question as to the mode of attachment of two univalent atoms or groups when they replace the divalent element or group attached to a quadrivalent sulphur atom by a semipolar double bond. Experimental evidence is not yet sufficiently great to determine whether the component covalency and electrovalency of the semipolar double bond are utilised separately or whether the univalent atoms or groups become attached to the sulphur atom by identical valencies each equal in value to half a semipolar double bond, in other words, by a semipolar single bond. Enough data, are, however, available to give verisimilitude to the idea of the semipolar single bond and to stimulate further research along these lines.
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September, 1927.
carried out at Battersea Polytechnic under the supervision of Dr. J. Kenyon, F.I.C., to whom, and to Dr. H. Phillips, F.I.C., the author wishes to express his thanks for their help and advice.
## PART I. The Preparation and Optical Properties of Organic Sulphur Compounds

### A. Historical Account

- \[ \text{Theoretical} \quad \text{Practical} \]

### B. Application of Newer Electronic Theories of Valency:

1. The Structure of the Atom
2. The Semi-Polar Double Bond
3. The Parachor

- \[ \text{Theoretical} \quad \text{Practical} \]

### C. The Preparation and Resolution of m-Carboxyphenylethyl sulphone

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PART II. The Preparation and At tempted Resolution of Methyl-n-propylphenylmethane.

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The experimental portion of this thesis is concerned mainly with:

(a) the preparation and resolution of organic sulphur compounds into their optically active forms in order to substantiate experimentally deductions made from the modern electronic theories of valency as to the constitution of such compounds.

(b) the preparation and attempted resolution of an asymmetric hydrocarbon.

Although the ultimate physical cause of optical activity is only vaguely understood, a study of the optical properties of organic compounds may shed much light on the structure of molecules. The history of the theory of valency since 1870 shows that new ideas on valency are universally accepted when they lead to the discovery of a new type of optical activity.

A brief account of the earlier work on optical activity will serve to show that investigations into the phenomena of optical activity gave rise to the theory of the tetrahedral arrangement of the carbon valency bonds in space.

Biot, the pioneer worker in optical activity
and solutions to be due to the arrangement of the atoms within the molecules. In 1844, Mitscherlich, examined tartaric and para-tartaric (racemic) acids, and found that, although chemically they were identical, ordinary tartaric acid was dextro-rotatory whilst the para-tartaric acid was optically inactive. About ten years later, Pasteur succeeded in resolving racemic acid into its two optically active components by the fractional crystallisation of sodium ammonium racemate and subsequent mechanical separation of the two types of crystal produced, and found that the aqueous solution of one form rotated the plane of polarisation to the right (d) and the other to the left (l). He also discovered that, in the presence of a mould (penicillium glaucum) and a phosphate, a partial separation could be effected since the mould preferentially destroyed the d-form. In 1862, Pasteur elaborated a third method of separation. He combined an optically active base with the racemic acid and separated the salts thus obtained by fractional crystallisation. Thus, using d-cinchonine Pasteur obtained a mixture of d-cinchonine d-tartrate and d-cinchonine l-tartrate, from a saturated solution of which the latter salt readily crystallised. The alkaloid was then removed from the d-cinchonine l-tartrate leaving the optically active acid. In 1870, Wislicenus resolved lactic acid into its optically active components and both he and Pasteur concluded that as the optical isomers were chemically identical, the cause of the optical activity must be due to a
substance to be optically active it must possess an asymmetric carbon atom, which could be considered to be situated at the centre of a tetrahedron with its four valencies directed towards the four corners and attached to four dissimilar elements or groups of elements. This arrangement could give rise to two forms which are related as is an object to its mirror image, e.g. the two forms of lactic acid may be represented as

\[
\begin{align*}
&\text{H}_3C \quad \text{CH}_3 \\
&\text{HO} \quad \text{OH} \\
&\text{CO}_2\text{H} \quad \text{HO}_2\text{C}
\end{align*}
\]

one of which rotates the plane of polarisation to the right and the other to the left. It was thought, at first, that the asymmetric carbon atom must be joined to two other carbon atoms but in 1914 Pope and Read resolved into its optically active forms by combining it with brucine and strychnine.

Owing to the resolution of 1-methyl-cyclohexylidene-L-acetic acid by Perkin, Pope and Wallach in 1906 it is now considered more accurate to ascribe the observed optical activity as being due to the enantiomorphic structure of the optically active molecule, i.e. the molecule possesses a structure which is non-super-
there is no carbon atom which can be called asymmetric.

Barker and Marsh (J., 1913, 102, 838) gave as the complete conditions for geometrical enantiomorphism:

(a) no plane of symmetry in the molecule.

(b) " centre " " " " "

(c) " alternating axis of symmetry in the molecule.

SIMPLE AND COMPLEX DISPERSION.

Biot, in the first half of the last century, divided optically active substances into the following two classes.

(a) Those in which the magnitude of the rotation of the different simple rays was reciprocal to the square of the wave length.

(b) Those which did not obey the inverse square law, e.g. tartaric acid, the rotatory power of the active forms of which increased in certain parts of the spectrum with increasing wave length.

Many attempts have been made to obtain a dispersion equation to represent accurately the behaviour of optically active substances over as wide a range of the spectrum as could be observed. The best, so far, is that of Drude, who deduced mathematically, in 1898, the equation

\[ \alpha = \sum \frac{k_0}{\lambda^2 - \lambda_0^2} \]
corresponding to the frequency at which the substance is absorbing energy.

There is one term in this equation for each asymmetric centre. If the optical rotatory power of a substance for light of any wave-length can be expressed by a Drude equation of one term, the substance is said to show simple rotatory dispersive power; should two or more terms be required to predict accurately the rotatory power of a substance for light of any desired wave length the substance is said to exhibit complex rotatory dispersion. (Lowry and Dickson, Trans. Faraday Soc., 1914, 10, 96.)

A rough practical method of deciding whether the dispersion of a substance is simple or complex consists in determining the rotatory power for light of several different wave-lengths and plotting a graph showing the relationship between $\frac{1}{\lambda}$ and $\lambda^2$. If a straight line can be drawn through the points obtained the dispersive power of the substance is probably simple. This method, however, is not sufficiently accurate to detect the small deviations which often occur. If a straight line is indicated the conclusion should always be confirmed by a determination of the values of $k_o$ and $\lambda_o$ from any two of the rotatory powers observed; the values of the constants may then be substituted in the Drude equation, from which the rotatory powers for all the other wave lengths can be calculated. If these agree closely with the observed values it may be concluded that the substance exhibits simple rotatory dispersion.
The researches of Pope and his pupils along these lines will now be considered.
A. Historical Account.

B. Application of the newer electronic theories of valency.

A. THE WORK OF POPE, PEACHEY, and SMILES.

Attention has already been drawn to the fact that a compound containing an asymmetric carbon atom C, a, b, c, d, may exist in two optically active isomeric forms. The researches of Pope and others in the early part of the century have proved that compounds containing other quadrivalent atoms such as sulphur, selenium and tin attached to four different univalent radicals also exist in optically active isomeric forms.

Sulphur compounds (Pope and Peachey, J., 1900, 77, 1072.)

The sulphur compounds selected were derivatives of methylethylthetine bromide

\[
\begin{align*}
\text{CH}_3 & \quad \text{S} & \quad \text{CH}_2 \cdot \text{CO}_2\text{H} \\
\text{C}_2\text{H}_5 & & \text{Br}
\end{align*}
\]

which were resolved into their optically active components by means of camphorsulphonic acid. The sparingly soluble a-camphorsulphonate melted at 118° - 120° and had a molecular rotation \([M]_D + 68°\). The rotation for the camphorsulphonate ion was +51.7° and this gave a rotation of +16.3° for the thentine ion.

The corresponding platinichloride (S.\text{Me.Et.Cl.} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_2, \text{Pt.Cl}_4 had a molecular rotation of +30.2°. The formula

\[
\begin{align*}
\text{CH}_3 & \quad \text{S} & \quad \text{CH}_2 \cdot \text{CO}_2\text{H} \\
\text{C}_2\text{H}_5 & & \text{Br}
\end{align*}
\]

was given to methylethylthetine bromide and the authors concluded that the asymmetry of their compounds was
equal value.

\[ R_1 > c < R_3 \]
\[ R_2 > c < R_4 \]

Selenium compounds of analogous composition were resolved by Pope and Neville (J., 1902, 81, 1052) and formulated in a similar manner to the sulphur compounds.

Smiles (J., 1900, 77, 1174) obtained methyl-ethylyphenylacetyl sulphine bromide (from methylethyl-sulphide and bromoacetophenone) 

\[ \text{Me} > S < \text{CH}_2\text{CO.C}_6\text{H}_5 \]
\[ \text{Et} > S < \text{Br} \]

in optically active modifications by a similar process. Smiles adopted Pope's view concerning the optical activity of the sulphines.

Werner ("Lehrbuch der Stereochemie", 1904, p. 317) put forward the idea that the fourth valency of the quadrivalent sulphur atom in the thetines and sulphines was different from the other three. He drew a sharp distinction between the optical activity of quadrivalent carbon and that of quadrivalent sulphur and suggested that in the latter case the sulphur atom and three dissimilar atoms or groups were situated at the corners of a tetrahedron and that the fourth atom or group was coordinated with the sulphur atom.

One of the objects of this thesis is to substantiate experimentally those theoretical views which have been advanced, namely, that when an atom of quadrivalent sulphur is united to three elements or groups of elements, three valency bonds of quadrivalent sulphur are equivalent and are directed along the edges
The modern conceptions of the structure of the atom, and the electronic theories of valency to which they have given rise.

B. APPLICATION OF THE NEWER ELECTRONIC THEORIES OF VALENCE.

(1) The Structure of the Atom. According to modern views a neutral atom is composed of a central nucleus with a positive charge equal to \( N \), the atomic number, around which a group of \( N \) electrons is situated.

In 1916, Lewis and Kossel, independently, developed the idea that the electrons of the inert gases are arranged in an exceedingly stable way and that the chemical properties of other atoms are explained by their desire to attain this stable arrangement by the giving or taking up of electrons. It is assumed that this can occur in two ways:—either by the complete transference of one or more electrons from one atom to another, when the resulting charged atoms or ions are held together by the electrostatic attraction of their charges (ionised or polar links, electrovalencies); or by the sharing of electrons between two atoms, two shared electrons forming a link (non-polar links, co-valencies). In the majority of compounds stability is attained when this re-distribution gives each atom an outer group of eight (less often two or eighteen) electrons. Thus:

Helium (atomic number 2) has 2 electrons in its outer shell.

Neon ( 10) = 2 + 8
Argon ( 18) = 2 + 8 + 8
Krypton ( 36) = 2 + 8 + 18 + 8
There are seven periods in the periodic classification:

1. H, He.
2. Li to F, Ne. Eight elements with a regular progression of properties from metallic to non-metallic and ending with an inert gas.
3. Na to Cl, A. Similar.
4. K to Br, Kr. 18 elements.
5. Rb to I, X. 18 "
6. Cs to Em. 32 "
7. 5 radioactive elements.

This thesis is chiefly concerned with groups (2) and (3).

In group (2) Li to F, Ne.

Li (atomic number 3) has 2 + 1 electrons.

Be (4) 2 + 2
B (5) 2 + 3
C (6) 2 + 4
N (7) 2 + 5
O (8) 2 + 6
F (9) 2 + 7
Ne (10) 2 + 8

In the case of a carbon compound

the electronic configuration of the molecule is quite easily deduced. The neutral carbon atom possesses four valency electrons in its outer shell and it is able to give one of these to be shared with one from each of the four monovalent groups with which it unites. In this
These considerations of valency from the standpoint of the electronic theory can also be applied to compounds of carbon in which the central atom is attached to three groups one of which is united by a double bond. The formulation of ketones of the type $R_1 > C = 0$ is as follows: four co-valency bonds are produced by the sharing of duplets of electrons and the oxygen is united to the carbon by two covalency bonds.

The electrons of the members of the sulphur group are arranged as follows:

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8</td>
<td>(2) 6</td>
</tr>
<tr>
<td>S</td>
<td>16</td>
<td>(2) (8) 6</td>
</tr>
<tr>
<td>Se</td>
<td>34</td>
<td>(2) (8) (18) 6</td>
</tr>
<tr>
<td>Te</td>
<td>52</td>
<td>(2) (8) (18) (18) 6</td>
</tr>
<tr>
<td>Cr.</td>
<td>24</td>
<td>(2) (8) (8 + 5) 1</td>
</tr>
</tbody>
</table>

It will be seen that in the case of oxygen, sulphur, selenium and tellurium there are six valency electrons in the outer shell, the inner shell (or shells) being complete.

According to Sidgwick, chromium has six electrons which may be used for valency purposes, but some of them may be drawn into the preceding group which
the octet by transference or sharing. Thus:

\[ \text{S} \quad \rightarrow \quad (2) \quad (8) \quad (8) \quad \text{(argon number)} \]

\[ \text{H} - \text{S} - \text{H} = (2) \quad (8) \quad (4, \underline{4}) \quad \text{(shared electrons underlined)} \]

If chromium behaved in the same way we should get

\[ \text{Cr} - \quad - \quad (2) \quad (8) \quad (8) \quad (8) \]

\[ \text{R} - \text{Cr} - \text{R} = (2) \quad (6) \quad (8) \quad (4, \underline{4}) \]

These are both impossible, because the unshared electrons still in the fourth group would be drawn into the third and the stability of the octet would thus be destroyed.

This must obviously happen so long as any unshared valency electrons remain to the chromium. A real analogy between chromium and sulphur will only be found when all the six valency electrons are shared. This happens in the case of sulphur, with sulphuric acid in the anion of which the sulphur has completed its octet by taking up two electrons from the hydrogen atoms and shares all these eight electrons with four oxygen atoms.

\[ \begin{array}{c}
: \underline{0} : \\
: & : \underline{0} : S : \underline{0} : \\
: 0 : & : \\
: \underline{0} : \\
\end{array} \]

so that the whole octet of the sulphur is shared. The chromium analogue to this is quite stable, being in fact the chromate ion

\[ \begin{array}{c}
: \underline{0} : \\
: & : \underline{0} : \text{Cr} : \underline{0} : \\
: 0 : & : \\
: \underline{0} : \\
\end{array} \]

The chromium here has increased its twenty-four original electrons to twenty-six, of which eight are shared, giving (2) (8) (8) (8) leaving no unshared electrons in
e.g. Chromous ion \( \text{Cr}^{3+} \) 22 = (2) (3) (12).
Chromic ion \( \text{Cr}^{6+} \) 21 = (2) (8) (11).

from \( \text{Cr} 24 \), where the work of removing these electrons is of the same order as the energy of chemical reactions. No analogous cations can be formed by sulphur, because, there, all the valency electrons must remain in the outer group and if this is less than eight it is very unstable.

The readiness with which the organic sulphides are oxidised and the ease with which they yield addition compounds was "explained" according to the older theories of valency by the readiness with which the sulphur passes from the di- to the tetra- or hexavalent state; for example:

\[
\begin{array}{c}
R_1 \\
R_2
\end{array}
\xrightarrow{\text{s + Br}_2} 
\begin{array}{c}
R_1 \\
R_2
\end{array}
\xrightarrow{\text{Br}}
\begin{array}{c}
R_1 \\
R_2
\end{array}
\xrightarrow{\text{S}}
\begin{array}{c}
R_1 \\
R_2
\end{array}
\xleftarrow{\text{Br}}
\begin{array}{c}
R_1 \\
R_2
\end{array}

The sulphoxides are:

\[
\begin{array}{c}
R_1 \\
R_2
\end{array}
\xrightarrow{\text{s = 0}}
\begin{array}{c}
R_1 \\
R_2
\end{array}
\xleftarrow{\text{s = 0}}
\begin{array}{c}
R_1 \\
R_2
\end{array}
\]

the sulphones are:

\[
\begin{array}{c}
R_1 \\
R_2
\end{array}
\xrightarrow{\text{o = 0}}
\begin{array}{c}
R_1 \\
R_2
\end{array}
\xleftarrow{\text{o = 0}}
\begin{array}{c}
R_1 \\
R_2
\end{array}
\]

(2) The Semi-polar Double Bond.

According to the older theories of valency the ketones and sulphoxides were formulated in a similar manner:

\[
\begin{array}{c}
R_1 \\
R_2
\end{array}
\xrightarrow{\text{c = 0}}
\begin{array}{c}
R_1 \\
R_2
\end{array}
\xleftarrow{\text{s = 0}}
\begin{array}{c}
R_1 \\
R_2
\end{array}
\]

The application of the electronic theory suggests that the two classes of compounds may be structurally dissimilar and predictions based on the electronic formulation of
electrons in its outermost shell and the configuration of an organic sulphide may be deduced in a similar manner to that of the carbon compound (page //).

\[ \begin{array}{c}
  R_1 \\
  \cdot \\
  \cdot \\
  \cdot \\
  R_2 \cdot S \cdot \\
  \cdot \\
  \cdot \\
  \cdot \\
 \end{array} \]

It is evident that if the sulphur atom is united to two monovalent groups \( R_1 \) and \( R_2 \) it is already in possession of its full complement of electrons. If an attempt be made to formulate a compound containing a quadrivalent sulphur atom on the same lines as the ketone (see page //) the sulphur atom is left with a surplus of electrons (ten instead of eight) as shown below.

\[ \begin{array}{c}
  R_1 \cdot \\
  \cdot \\
  \cdot \\
  \cdot \\
  R_2 \cdot S \cdot \cdot \\
  \cdot \\
  \cdot \\
  \cdot \\
 \end{array} \]

It is therefore necessary to conclude that, when a sulphur atom is united to two monovalent elements or groups \( R_1 \) and \( R_2 \) by co-valencies (as in organic sulphides) and has a complete octet of electrons, any further union effected with other elements must be accomplished without the addition of more electrons to the valency shell of the sulphur atom. This can be done if the sulphur atom contributes both electrons to the duplet by which the atoms are joined, thus

\[ \begin{array}{c}
  R_1 \cdot \\
  \cdot \\
  \cdot \\
  \cdot \\
  R_2 \cdot S \cdot \cdot \\
  \cdot \\
  \cdot \\
  \cdot \\
 \end{array} \]
charged and that the sulphur atom, which has virtually lost an electron or a half share of two electrons, will be positively charged. (The electron with a circle round it in the formula represents the sulphur electron which virtually becomes an oxygen electron). A double bond is present, but it consists of one covalency and one electrovalency and is termed a "semipolar" double bond. The linking common in carbon compounds which consists of two covalencies is called a non-polar double bond. This has been shown to exist in ketones. It is obvious, therefore, that sulphoxides cannot have the ketonic structure \[ R_1 \rightleftharpoons S \rightarrow R_2 \]. This deduction is amply substantiated experimentally as the sulphoxides do not show any of the characteristic properties of ketones. For example:—

(a) they do not condense with hydroxylamine or with phenylhydrazine.

(b) they cannot be reduced to compounds analogous to secondary alcohols.

(c) they are basic; many sulphoxides give crystalline addition compounds with nitric acid.

A third type of double bond occurs in ionisable compounds such as calcium sulphide, in which the atoms are united by two electrovalency bonds. In this compound the calcium atom gives up the two electrons in its outer shell to complete the octet of the sulphur atom which in the neutral condition has only six valency electrons in its outermost valency shell. By so doing the calcium gains two positive charges and imparts two negative
The possible existence of semipolar double bonds, revealed by the application of the electronic theories of valency, has been confirmed experimentally by two unique methods. The first method depends upon Sugden's correlation of chemical constitution with density and surface tension. The second method arises from the deduction that if a compound of quadrivalent sulphur, such as a mixed sulphoxide, contains a semipolar double bond, then it does not possess a plane of symmetry and should therefore exist in enantiomorphously related forms.

(3) The Parachor and the Electronic Theory of Valency.

Sugden (J., 1925, 125, 1177) by a modification of Macleod's relation \[ \gamma = c (D - d)^4 \]
where \( \gamma \) = surface tension.

" \( D \) = density of liquid) at one

" \( d \) = " vapour) temperature

has obtained the expression

\[ P = \frac{M}{(D - d)} \gamma^\frac{1}{4} \]

where \( M \) = molecular weight, and \( \frac{M}{(D - d)} \) corresponds to the molecular volume at low temperatures, when \( d \) is small. Hence a comparison of \( P \) for different substances is a comparison of molecular volumes at temperatures at which the liquids have the same surface tension. The constant \( P \) has been named the "parachor" by Sugden, and it is a function which can be calculated with certainty for a compound of given composition, without being affected to any marked extent by the physical conditions under which the measurements are made. A single constant
evaluated was the effect of a double bond, which was found to add 23.2 units to the molecular parachor. The type of double linking to which this applied was that between carbon and carbon as in ethylene, and carbon and oxygen, as in ketones. A number of compounds of sulphur were investigated (J., 1925, 127, 1525) and several anomalous cases were found in which the presence of a double bond between the sulphur and oxygen atoms appeared to have little effect on the parachor. The accumulated data provided definite experimental evidence of the existence of two kinds of double bonds, one common in carbon compounds which caused an increase in the parachor of 23.2 units, and another present in derivatives of the oxyacids of sulphur, which lowered the molecular parachor by 1.6 units e.g. thionyl chloride, sulphuryl chloride, ethyl ethanesulphonate, dimethylsulphate and diethylsulphate. The electronic formulae of these sulphur compounds indicates the presence of one or more semi-polar double bonds and the effect of this type of linking on the parachor is readily understood when it is remembered that this constant is a measure of molecular volume. The semi-polar double bond consists of a covalency with a super-imposed electrovalency; its effect should therefore be that of a single bond, which is taken as zero, and the effect of the electrostatic attraction between two charged atoms, which should cause a contraction in volume. It is significant that most of the substances quoted gave a negative value (mean - 1.6) for the parachor of a semi-polar double bond.
Convincing experimental evidence as to the true nature of the double bond between sulphur and oxygen in these compounds was provided by Phillips (J., 1925, 127, 2552) who succeeded in preparing n-alkyl esters of p-toluenesulphinic acid in an optically active condition.

A determination of the parachor of ethyl-p-toluenesulphinate showed that the bond between the sulphur and the sulphonyl oxygen could be considered to be semipolar. If these sulphinic esters are formulated according to the older theories of valency as $R\cdot S(\cdot O) C_7 H_7$ it is difficult to see why they should exist in enantiomorphously related forms. If, however, they are represented according to the electronic theory of valency as,

$$\begin{align*}
\text{S}^+ & \quad \text{or} \quad \text{S}^- \\
\text{R}_1 & \quad \text{R}_1
\end{align*}$$

in which the crosses and dots have the same significance as before, it will be seen that if the three covalencies exerted by the sulphur atom are not coplanar then these esters should exist in enantiomorphously related forms.

From the chemical behaviour of sulphonylides and also by analogy with sulphinic esters it might be deduced that sulphonylides should also exist in enantiomorphously related forms. It will now be shown that sulphonylides of the type $R_1 \quad R_2$ can be resolved into their optically active components. It might be mentioned that this resolution was commenced at the same time as the resolution of $d1 - m -$ carboxyphenyl methyl.
C. THE PREPARATION AND RESOLUTION OF \( m \)-CARBOXYPHENYL ETHYL SULPHOXIDE.

\( \text{dl-}m \)-Carboxyphenyl ethyl sulphotoxide was prepared by the oxidation with 2N nitric acid of the corresponding sulphide, obtained by the ethylation of \( m \)-thiobenzoic acid with ethyl-p-toluenesulphonate.

Its brucine salt, after recrystallisation first from acetone and then from ethyl alcohol until no further increase in rotatory power occurred, had \( \left[ \alpha \right]_{5461}^{25}^{\circ} + 70^{\circ} \) in chloroform solution. This salt gave on decomposition with aqueous sodium hydroxide \( \text{dl-}m \)-carboxyphenyl ethyl sulphotoxide with \( \left[ \alpha \right]_{5461}^{25}^{\circ} + 235^{\circ} \) in chloroform solution. The more soluble brucine salt was recovered from the mother liquors from the \( \text{L.B.} \text{L.A} \) salt and on decomposition gave a sulphoxide with \( \left[ \alpha \right]_{5461}^{25}^{\circ} - 39^{\circ} \). Portions of this, were combined with quinine, morphine, strychnine, cinchonidine, cinchonine and phenylethylamine but no effective separation of the \( \text{d-} \) and \( \text{l-} \) forms of the sulphoxide was obtained.

The quinidine salt, however, after recrystallisation first from acetone and then from benzene, containing a little ethyl alcohol, until no further increase in rotatory power occurred had \( \left[ \alpha \right]_{5461}^{25}^{\circ} + 102^{\circ} \) in chloroform solution and gave on decomposition with aqueous sodium hydroxide \( \text{l-}m \)-carboxyphenyl ethyl sulphotoxide with \( \left[ \alpha \right]_{5461}^{25}^{\circ} - 232^{\circ} \) in chloroform solution.

The satisfactory agreement between the specific rotatory powers of the two enantiomorphs indicates that both were obtained optically pure.

The specific rotatory powers of the optically pure sulphotoxide are given in Table I.
SPECIFIC ROTATORY POWERS OF 1-m-CARBOXYPHENYL ETHYL
SULPHOXIDE in various solvents at 25° C. \( \alpha = g. \) of
sulphoxide in 100 c.c. solution, \( \lambda = 2. \)

\[ \alpha = 0.02 c [\alpha] \lambda \]

<table>
<thead>
<tr>
<th>Solvents</th>
<th>( c )</th>
<th>( \lambda 6708 )</th>
<th>( \lambda 5893 )</th>
<th>( \lambda 5790 )</th>
<th>( \lambda 5461 )</th>
<th>( \lambda 4358 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl alcohol</td>
<td>2.7500</td>
<td>+126°</td>
<td>+165°</td>
<td>+171°</td>
<td>+202°</td>
<td>+418°</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.2250</td>
<td>150°</td>
<td>202°</td>
<td>211°</td>
<td>236°</td>
<td>445°</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>4.0985</td>
<td>217°</td>
<td>255°</td>
<td>260°</td>
<td>287°</td>
<td>465°</td>
</tr>
<tr>
<td>Pyridine</td>
<td>1.5750</td>
<td>167°</td>
<td>238°</td>
<td>251°</td>
<td>282°</td>
<td>460°</td>
</tr>
<tr>
<td>Potassium Salt in water)</td>
<td>1.2650</td>
<td>113°</td>
<td>153°</td>
<td>160°</td>
<td>180°</td>
<td>355°</td>
</tr>
</tbody>
</table>

SPECIFIC ROTATORY POWERS OF 1-m-CARBOXYPHENYL ETHYL
SULPHOXIDE in Chloroform at 25° C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( c )</th>
<th>( \lambda 5790 )</th>
<th>( \lambda 5461 )</th>
<th>( \lambda 4358 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>3.8150</td>
<td>-207°</td>
<td>-232°</td>
<td>-440°</td>
</tr>
</tbody>
</table>

D. THE PREPARATION AND ATTEMPTED RESOLUTION OF dl-1-
DIMETHYLAMINO-4'-METHYLDIPHENYL SULPHOXIDE.

dl-4-Dimethylamino-4'-methyldiphenyl sulphoxide, m.p. 198°, was prepared by heating together p-toluene-
sulphinic acid and dimethylaniline according to the
method described by Hinsberg (Ber., 1903, 36, 108) for
the preparation of 4-aminodiphenyl sulphoxide.

Attempts to resolve dl-4-dimethylamino-4'-
methyldiphenyl sulphoxide by recrystallisation of the
salts it formed with d-camphorsulphonic acid or d-
Harrison, Kenyon, and Phillips (loc. cit.), however, succeeded in resolving the much more stable \textit{dl-}L-\textit{amino-}L'-\textit{methyl}di\textit{phenyl sul}phoxide.

E. THE CHEMICAL AND PHYSICAL PROPERTIES OF THE OPTICALLY ACTIVE SULPHOXIDES.

The \textit{dl}-sulphoxide is a racemic compound with physical properties widely different from those of the optically active enantiomorphs. For example, the optically active forms are very soluble in chloroform, water, acetone, ethyl alcohol, methyl alcohol, benzene etc., but the \textit{dl}-sulphoxide is only moderately soluble in water and benzene. All three forms are insoluble in ordinary ether or in petroleum ether. It has been found impossible, owing to their great solubility, to crystallise the active forms from any solvent.

The melting point of the optically active form is over 30° lower than that of the \textit{dl}-sulphoxide.

The asymmetric complex contained in the optically active sulphoxides is destroyed by oxidation; the sulphones thus produced being optically inactive. In the same way optically active ethyl-\textit{p}-toluene sulphinate gave optically inactive ethyl-\textit{p}-toluenesulphonate (Phillips, J., 1925, 127, 2552).

Phillips also showed that the asymmetric sulphinic ester molecule possessed a certain mobility, since \textit{p}-toluenesulphinic esters of \textit{L}-\textit{a}-octanol and of \textit{L}-menthol, which contain the \textit{p}-toluene sulphinoxy radicle in an optically active state, exhibit marked mutarotation.
intervals. Consequently, methyl p-toluenesulphinate was prepared by the action of p-toluenesulphynil chloride on methyl alcohol, potassium carbonate or pyridine being used to remove the hydrochloric acid formed. Sufficient determinations were taken to show that mutation actually occurred, but, unfortunately, the investigation had to be abandoned as the experimenter suffered severe physical inconvenience from the physiological effects of the sulphinic esters.

Solutions of the optically active sulphoxides, on the other hand, show no signs of mutarotation even after standing for several months, so it would appear that in these compounds the bond between the sulphur atom and the sulphoxy oxygen atom is perfectly stable.

With reference to the figures given in Table I, if $\chi$ is plotted against $\chi^2$ for the optically active sulphoxide in various solvents, curves are obtained showing:

(i) that the rotatory dispersion is generally complex.

(ii) that the influence of one solvent compared with that of another is not very great.

The complex dispersion is probably due to the benzene nucleus in these compounds and to the influence of solvents owing to the presence of the semipolar double bond.

The fact that 2-m-carboxyphenyl ethyl sulphoxide has a low rotation in water in the form of its potassium salt seems to support the contention of Rule (J., 1927, 54) that the polarity of substituent groups affects the rotatory power of an optically active substance. In this case, the positive carboxyl group in I

\[
\begin{align*}
\text{I} & \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\
\text{II} & \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5
\end{align*}
\]
atom of the sulphonyl group is shown by the change of rotatory power. The effect is even more marked in the case of 1,4'-amino-4'-methylidiphenyl sulfoxide, which undergoes a reversal of sign when the amino group is converted into a positive ammonium ion by means of hydrochloric acid.

The resolution of mixed sulfoxides into their optically active forms confirms the views previously expressed, that the double bond between the oxygen atom and the sulphur atom is not an ordinary double bond. According to the electronic theory of valency the constitution of these compounds is more accurately represented by formulae such as I or II,

\[
\begin{align*}
&I \quad \text{ or } \quad II \\
&\begin{array}{c}
R_1 \\
S^+ \quad \circ \quad \text{or} \quad \circ \quad \text{or} \\
R_2 \\
\end{array}
\end{align*}
\]

in which the valency electrons of the sulphur atom are represented by crosses. The electrons contributed by the other elements or groups attached to the sulphur atom are represented by dots. As there are only six electrons in the outer shell of the neutral oxygen atom the sulphur atom contributes both electrons to form the covalency by which the two atoms are united:

\[
\begin{align*}
&\begin{array}{c}
R_1 \\
\times S x \quad + \quad \circ \\
R_2 \\
\end{array}
\end{align*}
\]

The molecular asymmetry of sulphinic esters and sulfoxides thus appears to be associated with a sulphur atom which
corners of which lie the three dissimilar groups.

There thus appears to be little doubt that a quadrivalent sulphur atom, when attached to three groups or atoms, exerts three covalencies and one electrovalency.

It is of particular interest to consider whether quadrivalent sulphur maintains this same type of valency when in combination with four univalent atoms or groups. In other words, is the semipolar double bond, with which it unites with a divalent element such as oxygen, split up into its component covalency and electrovalency each of which is employed to effect a union with two univalent atoms or groups, or do these atoms or groups become united to the sulphur atom by identical valencies each equal in value to half a semi-polar double bond?

Such a question has recently acquired added interest since Sugden (J., 1927, 1173) has stated that although the rule of eight can be supported by much experimental evidence there are certain cases in which ordinary single valency linkages are neither covalencies nor electrovalencies. He determined the parachors of phosphorus and antimony pentachlorides and found that his results supported the hypothesis put forward by Prideaux (Chem. and Ind., 1923, l2, 672) that two of the chlorine
exist as ions. This type of linkage was called by Sugden a "semi-polar single bond". In phosphorus pentachloride the phosphorus atom acquires a positive charge and the two chlorine atoms share one negative charge.

This conception obviously has a bearing on the constitution of compounds of quadrivalent sulphur containing four univalent atoms or groups attached to the sulphur atom. Thus it is possible that the constitution of $d$-methylethylthetine $d$-camphorsulphonate of Pope and Peachey (J., 1900, 77, 1072) may not be as indicated in I, but rather as in II.

$$\begin{align*}
&\left[ \begin{array}{c}
\text{CH}_2\text{CO}_2\text{H} \\
\text{C}_2\text{H}_5\text{S} \\
\text{CH}_3
\end{array} \right] + \\
&\begin{array}{c}
\text{C}_2\text{H}_5\text{S} \\
\text{CH}_3
\end{array}
\end{align*}$$

II.

In I the semipolar double bond, present in sulphinic esters and sulphones, is utilised for the attachment of the acetic acid residue by a covalency and the camphor-sulphonyloxoxy ion by an electrovalency. In II, however, this semipolar double bond is represented as being split into two semipolar single bonds each of which is employed to attach a group directly to the sulphur atom.

Either of the above formulae would explain the observed enantiomorphism of the camphorsulphonate. It might be objected that $d$-methylethylthetine $d$-camphor-
by other ions in aqueous solution without loss of rotatory power. It may, however, be possible that a camphorsulphonoxy radical united to a sulphur atom by a semipolar single valency would be readily replaceable. Indeed, should there be any truth in such a formulation, it is possible that each semipolar single valency is associated with one of the two lone pairs of electrons which the original sulphide sulphur atom contained. Thus in the valency shell of the sulphur atom there still remains two unattached electrons which, acting as points of attack, may constitute a source of weakness under the action of reagents. Furthermore, in aqueous solution, the camphorsulphonate may exist as an equilibrium mixture of the type

\[
\begin{align*}
\text{C}_2\text{H}_5 & \quad \text{CH}_2 \cdot \text{COOH} \quad + \quad \text{H} \cdot \text{OH} \\
\text{CH}_3 & \quad \text{O} \cdot \text{SO}_2 \text{C}_10\text{H}_{15}^0 \\
\text{C}_2\text{H}_5 & \quad \text{CH}_2 \cdot \text{COOH} \\
\text{CH}_3 & \quad \text{OH} \\
\end{align*}
\]

which would readily explain the supposed ionising power of the camphorsulphonoxy group.

From this standpoint the constitution of the dihalogen compounds of organic sulphides are of particular interest. It would appear that the two following formulae might now be suggested as representing the
It is evident, on the assumption that the presence of semipolar single linkages in IV leads, as in the case of the camphorsulphonate mentioned above, to the sulphur atom possessing a tetrahedral environment, that such mixed dibromides could not be obtained optically active. Should, however, formula (III) more accurately represent their constitution then such compounds might be expected to exist in enantiomorphously related forms.

The attempted resolution of such compounds presents some experimental difficulties. Thus, it has been found that m-carboxyphenyl ethyl sulphide dibromide reacts readily with alkaloids, such as brucine, and loses bromine. Attempts were therefore made to prepare this dibromide in an optically active condition from the corresponding optically active sulphoxide. Although this sulphoxide was brought into contact with dry hydrogen bromide under various conditions the dibromide was invariably obtained optically inactive. It is, of course, possible that during the replacement of the oxygen atom of the sulphoxide racemisation occurred, and therefore the optical inactivity of the dibromide obtained cannot be taken as proving conclusively that such a compound cannot exist in an optically active condition. Nevertheless, it is remarkable that Phillips (loc. cit) was able to prepare optically active sulphinic esters by alkyloxy interchange without the occurrence of complete racemisation and was thus able to prove that the disruption of the linkage between the oxygen atom of the
aqueous solutions of hydrobromic acid has been studied.
then dissolved in N. hydrobromic acid the rotatory power
of d-carboxyphenyl ethyl sulfoxide remained practically
unchanged for a considerable period as can be seen from
the values quoted in Table II.

In 3N. hydrobromic acid, however, the sulfoxide
gradually racemised, as can be seen from the values quoted
in Table III.

<table>
<thead>
<tr>
<th>TABLE II</th>
</tr>
</thead>
</table>

| SPECIFIC ROTATORY POWERS OF d-m-CARBOXYPHENYL ETHYL |
| SULFOXIDE IN 1.1 N HYDROBROMIC ACID SOLUTION AT 25° C |
| c = 1.5280 g., l = 2, α = 0.02. c [α]_λ |
| t = time in hours. |

<table>
<thead>
<tr>
<th>t</th>
<th>λ5790</th>
<th>λ5461</th>
<th>λ4358</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>114°</td>
<td>157°</td>
<td>317°</td>
</tr>
<tr>
<td>1.8</td>
<td>138°</td>
<td>151°</td>
<td>312°</td>
</tr>
<tr>
<td>7.2</td>
<td>138°</td>
<td>151°</td>
<td>313°</td>
</tr>
<tr>
<td>14.4</td>
<td>138°</td>
<td>153°</td>
<td>313°</td>
</tr>
<tr>
<td>31.2</td>
<td>139°</td>
<td>154°</td>
<td>314°</td>
</tr>
<tr>
<td>62.8</td>
<td>136°</td>
<td>146°</td>
<td>312°</td>
</tr>
<tr>
<td>81.6</td>
<td>131°</td>
<td>140°</td>
<td>311°</td>
</tr>
<tr>
<td>108.4</td>
<td>130°</td>
<td>139°</td>
<td>308°</td>
</tr>
<tr>
<td>158.8</td>
<td>121°</td>
<td>136°</td>
<td>262°</td>
</tr>
</tbody>
</table>

28
SPECIFIC ROTATORY POWERS OF γ-m-CARBOXYPHENYLETHYL SULPHOXIDE in 3.3 N Hydrobromic Acid Solution at 25° C.

\[ c = 1.4400 \text{ g.}, \quad \lambda = 2, \quad \alpha = 0.02, \quad \gamma (\alpha) \lambda \]

\[ t = \text{time in hours}. \]

<table>
<thead>
<tr>
<th>t (hours)</th>
<th>( \lambda_{5790} )</th>
<th>( \lambda_{5461} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>144°</td>
<td>160°</td>
</tr>
<tr>
<td>48</td>
<td>121°</td>
<td>135°</td>
</tr>
<tr>
<td>72</td>
<td>115°</td>
<td>120°</td>
</tr>
<tr>
<td>114</td>
<td>95°</td>
<td>107°</td>
</tr>
<tr>
<td>312</td>
<td>71°</td>
<td>80°</td>
</tr>
<tr>
<td>480</td>
<td>45°</td>
<td>51°</td>
</tr>
<tr>
<td>648</td>
<td>27°</td>
<td>31°</td>
</tr>
<tr>
<td>816</td>
<td>22°</td>
<td>25°</td>
</tr>
<tr>
<td>1084</td>
<td>14°</td>
<td>16°</td>
</tr>
<tr>
<td>1588</td>
<td>0°</td>
<td>0°</td>
</tr>
</tbody>
</table>

Again, owing to the possible occurrence of racemisation during the replacement of the sulphoxyl oxygen atom by other atoms or groups these experiments do not provide any conclusive evidence. However, they are not inconsistent with the view that in N. hydrobromic acid solution the sulphone may exist in the form of an addition compound which may have the constitution

\[ \text{COOH} \]

\[ \text{S} \]

\[ \text{Et} \]

\[ \text{Br} \]
thereby losing its enantiomorphous configuration. This is probably a reversible reaction.

That the bromine atoms of m-carboxyphenyl ethyl sulphide dibromide are but loosely linked to the sulphur atom is evident from the readiness with which the dibromide reverts to the sulphide. The change occurs rapidly when the dibromide is subjected to the action of dilute alkalies, and may even occur when it is exposed to the air.

From the considerations and experimental work described above it is obvious that no formula can yet be advanced which can be conclusively stated to represent accurately the constitution of compounds of quadrivalent sulphur containing four groups or atoms united to the sulphur atom.
to the valency of sulphur developed in this thesis was obtained from the preparation and resolution of m-carboxyphenylethylsulphine-p-toluenesulphonylimine.

Chloramine-T, the parent substance of the sulphilimines, was prepared by the action of sodium hypochlorite on p-toluenesulphonamide (Dakin, Cohen, Daufresne, and Kenyon, Proc. Roy. Soc., 1916, B., 81, 236) and was given the formula \( C_6H_4.CH_2.SO. (ONa) : N.Cl \). Raper prepared the sulphilimines by condensing chloramine-T with dialkyI sulphides. Mann and Pope (J., 1922, 121, 1052) formulated these compounds as \( C_6H_4.CH_2.SO_2.N:S.X.Y.(I) \) and pointed out that "the sulphilimines might be expected to exist in enantiomorphously related forms owing to the operation of a trihedral disposition of the three valency directions of the doubly linked nitrogen atom." They suggested that the space arrangement in the sulphilimines was similar to that existing in cyclohexylene-dithiocarbonate-2-pyridylhydrazone (II) which was resolved by Mills and Schindler (J., 1923, 123, 316).

Before proceeding to a discussion of the views of Mann and Pope and to the alternative hypothesis put forward in this thesis, it will be necessary to review briefly the work of Mills and his collaborators with regard to the configuration of the doubly-linked tervalent nitrogen atom.

The resolution by Mills and his collaborators of compounds containing the grouping \( \{C = N - \) into optically active forms confirms the view, first expressed by Hantzsch and Werner, that when a tervalent nitrogen
formula for the oxime of cyclo-hexylene-carboxylic acid resolved by Mills and Bain (J., 1910, 27, 1866) would contain a plane of symmetry and would not be resolvable

\[
\text{HO}_2\text{C.CH}_2\text{CH}_2\text{C} = \text{N.OH}. \quad \text{(III)}
\]

It is obvious on stereochemical grounds that the carboxyl group and the hydrogen atom attached to the carbon atom marked with an asterisk are not in the same plane as the rest of the molecule. The group

\[
\text{CO}_2\text{H.CH}_2\text{CH}_2\text{C} = \text{N} - \text{CH}_2\text{CH}_2
\]

possesses a plane of symmetry but the fact that the oxime can be resolved into its enantiomorphously related forms proves that the hydroxyl groups must be situated outside this plane. Providing, however, that the hydroxyl group is not situated in the plane of symmetry this does not preclude the possibility that the carbon and nitrogen atoms and the hydroxyl group may be in the same plane.

In order to avoid the possibility that a mobile hydrogen atom might migrate and give rise to an ordinary asymmetric carbon atom, Mills and Schindler (J., 1923, 163, 316) prepared the pyridylhydrazone of cyclohexylene-dithiocarbonate (II). As this compound was resolved into its enantiomorphously related forms it was stated that there could be no doubt that the nitrogen atom is the centre of asymmetry. The cyclohexylene ring may be assumed to occupy a plane inclined at an angle to that
common to both rings are in a third plane. If one considers the group

\[
\begin{align*}
\text{C} & \text{= N -} \\
\text{CH}_2 & \quad \text{CH} - S \\
\text{CH}_2 & \quad \text{CH} - S
\end{align*}
\]

it is obvious that there is a plane of symmetry. The resolution of the pyridylhydrazone of cyclohexylendithiocarbonate into its enantiomorphous forms proves that the NH·Py· group cannot lie in this plane of symmetry, but it is to be noted that it does not prove that the NH·Py· group is not in the same plane as the >C = N - group.

On comparing the sulphilimine (I) with (II) and (III), and even assuming that the >S = N- group in I is similar from a stereochemical point of view to the >C = N- group in (II) and (III), it is not obvious why the sulphilimine molecule should be asymmetric. The presence of the cyclohexylene ring inclined at an angle to the plane of the >C = N- group in (II) may be a necessary factor in producing the phenomenon of optical
would not be resolvable into optical forms, but like the simple oximes might exist in cis- and trans- forms. Further, in (III) the carboxyl group and the hydrogen atom attached to the carbon atom in the para-position to the carbon atom joined to the oximino-group are not in the same plane as the hydroaromatic nucleus. Mann and Pope, however, prepared and examined d- and L-
camphorylidinemethylethylsulphine-p-toluenesulphonylimine.

\[ \text{C}_{10}\text{H}_{14}\text{O} : \text{CH} \cdot \text{S} \cdot \text{Et} \cdot \text{Me} : \text{N} \cdot \text{SO}_{2} \cdot \text{C}_{6}\text{H}_{4} \cdot \text{Me}. \]

and stated that neither of these compounds furnished any indication of stereoisomerism of the type d-C, d-S, and d-C - L-S and that, therefore, they proposed to investigate other methods for realising this type of isomerism.

Now, as a working hypothesis, let it be supposed that the centre of "expected" optical activity is the sulphur atom, which, by analogy with that of the sulphinic esters and mixed sulphonylides, may be considered to be positively charged and occupying the apex of a tetrahedron at the other three corners of which lie the groups X and Y and the p-toluenesulphonimido group, the nitrogen atom of which bears a negative charge. The formula of a sulphilimine could then be written \( \text{C}_{6}\text{H}_{4} \cdot \text{Me} \cdot \text{SO}_{2} \cdot \text{N} \cdot \text{S} \cdot \text{X} \cdot \text{Y} \).

As in the case of the sulphonylides, it will be necessary to examine the preparation of the sulphilimines from the standpoint of the electronic theory of valency in order to see how the above formulation is derived.
If, however, the views of Lowry, Phillips and Sugden, which have been developed in this thesis, are applied the reaction can be represented thus:

\[
\text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{NH}_2 + \text{Na} \cdot \text{OCl} = \text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{N} - \text{Cl} + \text{H}_2\text{O}
\]

In this formula for chloramine-T, the sulphur atom is surrounded by its normal octet of electrons, whilst the nitrogen atom is linked by two covalencies and an electrovalency. This linkage is not affected whether the sodium ion is attracted to the nitrogen atom, or to either of the negatively charged oxygen atoms.

The second stage in the preparation of sulphilimines is the condensation of chloramine-T with alkyl sulphides. Since the experiment is conducted in aqueous alcoholic solution it is conceivable that the sodium and chlorine atoms separate as ions forming a solution of sodium chloride and leaving the radicle

\[
\text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{N} = \text{O}
\]

containing a nitrogen atom with six electrons in its outer shell. It will be recalled that when a dialkyl sulphide takes up an atom of oxygen to form a sulphoxide, the sulphur atom contributes both electrons to form the co-
One of these virtually acts as an oxygen electron, the sulphur atom becomes positively charged and the oxygen atom negatively charged. The two atoms thus become united by a semi-polar double bond.

The nitrogen atom of the radicle $\text{Me}_6\text{H}_4\text{SO}_2\text{N}$ resembles an oxygen atom in having six electrons, so that the reaction between the radicle and the dialkyl sulphide might proceed according to the following equation:

$$\text{Me}_6\text{H}_4\text{SO}_2\text{N} + \text{R}_1\text{S} = \text{Me}_6\text{H}_4\text{SO}_2\text{N} + \text{R}_1\text{S}$$

Here again the sulphur atom contributes both electrons to form the covalency which unites the sulphur and nitrogen atoms. At the same time the sulphur atom becomes positively charged, the nitrogen atom acquires a negative charge, thus forming an electrovalency which, together with the covalency, constitutes a semi-polar double bond.

Since $\text{dl}-\text{m}$-carboxyphenylethyl sulphoxide was resolved into its optically active forms there appeared to be no reason, if the above arguments are valid, why the corresponding sulphilimine should not also be capable of existing in enantiomorphously related forms. $\text{dl}-\text{m}$-Carboxyphenylethylsulphine-$\text{p}$-toluenesulphonylimine was, therefore, prepared by the condensation of chloramine $\text{T}$ with $\text{m}$-carboxyphenylethylsulphide.
from acetone changed rapidly in rotatory power and when optically pure the $\text{L}$. $\text{B}$. $\text{L}$. $\text{A}$. salt had $[\alpha]_{5461}^{25^\circ} = 157^\circ$
in ethyl alcoholic solution. On decomposition of this salt with dilute hydrochloric acid the $\text{L}$-$\text{m}$-carboxyphenyl-ethylsulphine-$\text{p}$-toluenesulphonylimine was obtained with $[\alpha]_{5461}^{25^\circ} = 373^\circ$ in ethyl alcoholic solution. The more soluble brucin salt was recovered from the mother liquors from the crystallisation of the $\text{L}$. $\text{B}$. $\text{L}$. $\text{A}$. salt and on decomposition gave a sulphilimine with $[\alpha]_{5461}^{25^\circ} + 242.6^\circ$.

This was combined with cinchonidine and the salt obtained was repeatedly crystallised from alcohol till its rotatory power remained unchanged on further recrystallisation. It then had $[\alpha]_{5461}^{25^\circ} + 50^\circ$ in ethyl alcoholic solution and on decomposition gave $\text{L}$-$\text{m}$-carboxyphenylethylsulphine-$\text{p}$-toluenesulphonylimine with $[\alpha]_{5461}^{25^\circ} + 364^\circ$ in ethyl alcoholic solution. This result showed that cinchonidine was not a suitable alkaloid for obtaining the dextro-rotatory sulphilimine. Therefore, $\text{d} + \text{dl}$-sulphilimine having $[\alpha]_{5461}^{25^\circ} + 270^\circ$ in ethyl alcoholic solution was combined with strychnine and the strychnine salt obtained was repeatedly crystallised from alcohol until its rotatory power remained unchanged on further recrystallisation. It then had $[\alpha]_{5461}^{25^\circ} + 152^\circ$ in ethyl alcoholic solution and on decomposition gave $\text{d}$-$\text{m}$-carboxyphenylethylsulphine-$\text{p}$-toluenesulphonylimine with $[\alpha]_{5461}^{25^\circ} + 373^\circ$ in ethyl alcoholic solution. The satisfactory agreement between the specific rotatory powers of the two enantiomorphs indicates that both were obtained optically pure. It is interesting to
The specific rotatory powers of the optically pure sulphilimine in various solvents are given in Table IV.

### Table IV.

**Specific Rotatory Powers of:**

1. **(I)** l-m-Carboxyphenylethylsulphine-p-toluensulphonylimine in various solvents at 25° C.
2. **(ii)** d-m-Carboxyphenylethylsulphine-p-toluensulphonylimine in alcohol at 25° C.
3. **(iii)** Strychnine salt of the d-Sulphilimine in alcohol at 25° C.
4. **(iv)** (a) Sodium salt of the l-Sulphilimine in water at 25° C.
   (b) Sodium salt of the l-Sulphilimine an equimolecular quantity of sodium borate in water at 25° C.

\[
\alpha = \frac{g}{2} \text{ } \alpha = \frac{c}{2} \text{ } \alpha = \frac{\lambda}{2} \text{ } \alpha = \frac{\lambda}{2} \text{ } \alpha = \frac{\lambda}{2} \text{ } \alpha = \frac{\lambda}{2} \text{ } \alpha = \frac{\lambda}{2} \text{ } \alpha = \frac{\lambda}{2} \text{ } \alpha = \frac{\lambda}{2} \text{ } \alpha = \frac{\lambda}{2} \text{ } \alpha = \frac{\lambda}{2} \text{ } \alpha = \frac{\lambda}{2} \]

<table>
<thead>
<tr>
<th>Solvents</th>
<th>c</th>
<th>(\lambda_{6708})</th>
<th>(\lambda_{5893})</th>
<th>(\lambda_{5790})</th>
<th>(\lambda_{5461})</th>
<th>(\lambda_{4359})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) Ethyl Alcohol</td>
<td>2.7725</td>
<td>(-226^\circ)</td>
<td>(-308^\circ)</td>
<td>(-324^\circ)</td>
<td>(-373^\circ)</td>
<td>(-690^\circ)</td>
</tr>
<tr>
<td>Pyridine</td>
<td>2.5695</td>
<td>(-200^\circ)</td>
<td>(-290^\circ)</td>
<td>(-307^\circ)</td>
<td>(-344^\circ)</td>
<td>(-670^\circ)</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>0.8980</td>
<td>(-213^\circ)</td>
<td>(-286^\circ)</td>
<td>(-307^\circ)</td>
<td>(-343^\circ)</td>
<td>(-640^\circ)</td>
</tr>
<tr>
<td>Glacial Acetic Acid</td>
<td>1.9165</td>
<td>(-233^\circ)</td>
<td>(-280^\circ)</td>
<td>(-306^\circ)</td>
<td>(-334^\circ)</td>
<td>(-643^\circ)</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.2315</td>
<td>(-243^\circ)</td>
<td>(-300^\circ)</td>
<td>(-322^\circ)</td>
<td>(-365^\circ)</td>
<td>(-678^\circ)</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.6380</td>
<td>-</td>
<td>-</td>
<td>(-305^\circ)</td>
<td>(-345^\circ)</td>
<td>(-642^\circ)</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.5600</td>
<td>(-204^\circ)</td>
<td>(-272^\circ)</td>
<td>(-286^\circ)</td>
<td>(-330^\circ)</td>
<td>(-621^\circ)</td>
</tr>
<tr>
<td>(II) Ethyl Alcohol</td>
<td>2.3425</td>
<td>-</td>
<td>-</td>
<td>+323^\circ</td>
<td>+373^\circ</td>
<td>+689^\circ</td>
</tr>
<tr>
<td>(III) Ethyl Alcohol</td>
<td>2.3915</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+152^\circ</td>
<td>-</td>
</tr>
<tr>
<td>(IV) (a) Water</td>
<td>1.7950</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-318^\circ</td>
<td>-363^\circ</td>
</tr>
<tr>
<td>(b) Water</td>
<td>1.7550</td>
<td>-</td>
<td>-</td>
<td>-232^\circ</td>
<td>-367^\circ</td>
<td>-666^\circ</td>
</tr>
</tbody>
</table>
the latter substance would influence the rotatory power of the sulphilime in the same manner that it enhances the rotatory power of solutions of tartaric acid. Thus it is conceivable that a molecule of the borate might become coordinated with a molecule of the sulphilime

\[
\begin{align*}
H & \quad \text{C}_6\text{H}_4\cdot\text{COONa}.
\text{HO} & \quad \text{B}
\text{H} & \quad \text{C}_2\text{H}_5
\end{align*}
\]

The results showed that the rotatory power was not enhanced by the addition of sodium borate.
plotted against $\frac{1}{\alpha}$ for solutions of

(a) $d$-m-Carboxyphenyl Ethyl (b) $l$-m-Carboxyphenylethyl-sulphine-
Sulphoxide in $P$-toluenesulphonylimine in

I. Water (Potassium Salt)
II. Methyl Alcohol
III. Chloroform
IV. Ethyl Alcohol
V. Pyridine
VI. Chloroform
VII. Ethyl Acetate
VIII. Ethyl Alcohol
contrast to the wide divergence between the physical properties of the optically active and optically inactive sulfoxides and sulphinates. Hence, \textit{dl-m-carboxyphenylethylsulphine-\textit{p}-toluenesulphonylimine} is probably a mixture of the two enantiomorphs and not a racemic compound.

\textit{dl-m-Carboxyphenylethylsulphine-\textit{p}-toluenesulphonylimine} was converted by the action of concentrated hydrochloric acid into a mixture of \textit{p}-toluenesulphonamide, \textit{m}-carboxyphenylethylsulphoxide and sulphide; whilst the sulphonamide and \textit{m}-carboxyphenylethylsulphone were the sole products of the action of hydrogen peroxide.

With reference to the figures given in Table IV, if $\frac{1}{\lambda}$ is plotted against $\chi^2$ for the active sulphilimine in various solvents and curves are drawn then the table and curves show that the specific rotatory powers of the optically active \textit{m}-carboxyphenylethylsulphine-\textit{p}-toluenesulphonylimine is but slightly influenced by solvents, with the possible exception of glacial acetic acid. Under the experimental conditions employed the sulphilimine exhibits simple rotatory dispersion in ethyl alcohol since a straight line is obtained when $\frac{1}{\lambda}$ for this compound is plotted against $\chi^2$. If the value of $\chi$ for $\lambda_{5461}$ is calculated from those of $\lambda_{6708}$ and $\lambda_{5893}$ by applying the "one-term" Drude Equation the result (372.3) is practically identical to the observed value (372.8). The calculated value of $\lambda_0$ for the sulphilimine is 2547.

The specific rotatory power of the sulphilimine in solvents remains unchanged on standing for several
A comparison of the curves of the sulphoxides and the sulphilimines shows that dispersion is less complex in corresponding solvents in the sulphilimines than in the sulphoxides.

It will be remembered that d-m-carboxyphenyl-ethylysulphoxide has a lower rotation in the form of its potassium salt and that L-4-amino-4'-methyl-diphenyl-sulphoxide suffers a reversal of sign of rotation in hydrochloric acid solution, in agreement with Rule's views. The sulphilimine, on the other hand, is practically uninfluenced by solution in sodium hydroxide solution nor is the rotation enhanced by the addition of boric acid. It is also interesting to note that in the case of the chloroform solution, dilution lowers the magnitude of rotation.

To Prove the Absence of Water in the Sulphilimine Molecule

It was considered important that the optically active sulphilimine should be examined to prove conclusively that it did not contain a molecule of water. Under ordinary circumstances this fact would escape detection since the substance was dried in a vacuum prior to analysis and after its rotatory power had been determined. Thus the possibility existed that the optically active sulphilimine had the constitution

\[
\text{GOOH} \quad \begin{array}{ccc}
\text{H} & \quad \text{H}
\end{array}
\text{S} \quad \text{N} \quad \text{SO}_2 \cdot \text{C}_7\text{H}_7
\]

whilst after drying in vacuo, when a molecule of water was
it might remain united by two semi-polar single valencies.

\[
\text{COOH} \quad \begin{array}{c}
\text{Et} \\
\text{N}_2\text{SO}_2 \cdot \text{C}_7\text{H}_7
\end{array}
\]

Consequently, \(\lambda\)-sulphilimine (0.3874 g.) was heated at 98.5\(^\circ\) C and 16 m.m. pressure for seven hours. There was a very small initial loss due probably to moisture previously absorbed from the air but the weight remained constant (0.3870 g.) for 4 hours. The product was divided into two portions one of which (0.2589 g.) was analysed showing that it had the empirical formula

\(\text{C}_{16}\text{H}_{17}\text{O}_4\text{NS}_2\) corresponding to \(m\)-carboxyphenylethylsulphine-\(p\)-toluenesulphonylimine.

**Found:** C, 54.8; H, 4.8; N, 3.9; S, 18.0;

\(\text{C}_{16}\text{H}_{17}\text{O}_4\text{NS}_2\) requires C, 54.7; H, 4.8; N, 4.0; S, 18.2%.

The second portion (0.1276 g.) had \([\alpha]_{5780}^{25^\circ} = 305^\circ; \quad [\alpha]_{4359}^{25^\circ} = 64^\circ2^\circ\) in chloroform solution, \((\lambda = 2; \quad \epsilon = 0.6580\)), showing that the rotatory power was unchanged. This establishes almost beyond a doubt that the molecule of the optically active \(m\)-carboxyphenylethylsulphine-\(p\)-toluenesulphonylimine does not contain a molecule of water and that it does possess a semipolar double bond.
Complex Rotatory Dispersion.

Lowry and others have suggested that substances exhibiting complex rotatory dispersion may contain two components with different rotatory powers and that an additional optically active centre may arise from labile intramolecular valency changes. Such labile valency changes have long been postulated as the underlying causes of the complex rotatory dispersion of the esters derived from the optically active secondary alcohols and the n-aliphatic carboxylic acids. Two isodynamic forms were written

\[ \text{R} \not\rightarrow \not\rightarrow 0 \quad \Rightarrow \quad \not\rightarrow \not\rightarrow 0 \]

They had different signs of rotation and different rotatory dispersive powers but their rotatory dispersion curves could be reproduced by Drude equations containing two terms of opposite signs. The following alternative formulation, based on the views already expressed in this thesis, appears to indicate more fittingly that an additional centre of asymmetry may be present, e.g. 1-β-octyl acetate could be written

\[
\begin{align*}
1 \cdot \text{C}_6\text{H}_{13}-\text{CH}^+ & \quad \text{C}_6\text{H}_{13}-\text{CH} \quad \text{C}_6\text{H}_{13}-\text{CH}^+ \quad \text{C}_6\text{H}_{13}-\text{CH}^+ \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 \\
\text{d. } & \quad \not\rightarrow \quad 0 = \not\rightarrow \quad 0 \quad \not\rightarrow \quad + \not\rightarrow \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

The presence of an unsaturated linking, however, does not necessarily give rise to complex dispersion since Kenyon and Snellgrove (J., 1925, 127, 1169) have shown that secondary alcohols containing a vinyl group exhibit simple

44
by Kenyon and Hewitt (J., 1925, 127, 1094) who showed that secondary alcohols containing a phenyl group are complex, while aliphatic secondary alcohols are usually simple (Pickard and Kenyon J., 1911, 29, 45, et seq.)

In view of the complicated nature of the problem it was decided to prepare and resolve a series of hydrocarbons having regard to the following considerations:

(1) they should be of simple constitution and contain only one asymmetric centre.

(ii) the optical properties of the members of a series should be compared.

The series \( \text{C}_6\text{H}_5\cdot(\text{CH}_2)\cdot\text{CH} \cdot\text{R} \) was chosen and the first member \( \text{dl-sec.-butylbenzene} \ (\text{C}_6\text{H}_5\cdot\text{CH} \cdot\text{CH}_2\cdot\text{C}_2\text{H}_5) \) was prepared and resolved by Harrison, Kenyon and Shepherd (J., 1926, 658). Since this hydrocarbon could not be resolved by direct combination with an optically active substance, the hydrocarbon was nitrated and concerted into \( \text{dl-p-amino-sec.-butylbenzene} \) by reduction. This amine was resolved by means of \( \text{d-tartaric acid} \) yielding \( \text{d-p-amino-sec.-butylbenzene} \) having

\[ [\alpha]^{20\circ}_{5461} + 40.98^\circ \text{ and } [\alpha]^{20\circ}_{5893} + 33.86^\circ. \]

The \( \text{d-p-amino-sec.-butylbenzene} \) was diazotised and the corresponding diazonium chloride obtained was reduced in aqueous solution to the required \( \text{d-sec.-butylbenzene} \) having b.p. 172° and \[ [\alpha]^{20\circ}_{5461} + 33.15^\circ. \]

An examination of the rotatory powers for light of other wave-lengths showed that the hydrocarbon exhibited complex rotatory dispersion. These results appear to support the view that the benzene nucleus, which may be considered
phenylmethane was prepared by the reduction of $\beta$-phenyl-
$\beta$-amylene $\text{C}_6\text{H}_5 \xrightarrow{\text{CH}_2} \text{C} = \text{CH.C}_2\text{H}_5$

obtained by the distillation of methyl-$n$-propyl-phenyl-
carbinol. The hydrocarbon was nitrated and converted
into the $\text{dl}$-$n$-amino-derivative by reduction. The yields
obtained were very small and it was not found possible
to resolve the amine into its optically active components.
The Preparation of m-Chlorosulphonylbenzoic Acid
(b) by means of Brucine

The Preparation of m-Thiolbenzoic Acid

The Preparation of m-Ethylthiolbenzoic Acid

The Resolution of m-Carboxyphenylethyl Sulphoxide
(a) by means of Brucine
(b) by means of Quinidin.

The Preparation of m-Carboxyphenylethylsulphide Dibromide.

The Preparation of dl-m-Carboxyphenylethylsulphine-p-toluenesulphonylimine

The Resolution of dl-m-Carboxyphenylethylsulphine-p-toluenesulphonylimine
(a) by means of Brucine
(b) by means of Cinchonidine and Strychnine.

The Preparation of p-Toluene sulphinic Acid

The Preparation of p-Toluene sulphinyl Chloride

The Preparation of Methyl-p-toluenesulphinate

The Preparation of l-Dimethylamino-l'-methyl-diphenyl Sulphoxide.

The Preparation of Methyl-n-propylphenyl Carbinol
(b) by means of Pheny1-β-Amylene.

The Preparation of Methyl-n-propyl-phenyl-methane.

The Preparation of Methyl-n-propyl-p-nitrophenvl-methane.
**Stage I.**

m-Chlorosulphonylbenzoic Acid (Smiles and Stewart, J., 1921, 119, 1792).

![Chemical Structure](image)

Benzoic acid (300 g.) was added to chlorosulphonic acid (144.5 g.) and the mixture was heated at 125° for 1½ hours. The cooled liquid was carefully poured on to a large quantity of crushed ice, when the m-chlorosulphonylbenzoic acid separated as a creamy white solid. It was broken up under water, filtered, washed, dried, and recrystallised from hot benzene. It then had m.p. 174° C and weighed 387 g. **Yield 83%.**

**Stage 2.**

Reduction of m-Chlorosulphonylbenzoic acid to m-Thiolbenzoic Acid.

![Chemical Structure](image)

To a solution of m-chlorosulphonylbenzoic acid (80 g.) in warm glacial acetic acid (300 c.c.) heated on a steam bath, zinc dust, together with sufficient hydrochloric acid to maintain a vigorous reaction, was added in small quantities at a time over a period of 1½ hours. A white substance separated, which re-dissolved near the end of the reaction, leaving a slightly turbid solution. After 6 or 7 hours the solution was filtered through glass wool.
had m.p. 145° - 147° C and weighed 66 g. Yield 80%.

It was found that when m-chlorosulphonylbenzoic acid was reduced in this manner, a hard white solid was occasionally precipitated during the course of the reaction, which could not be made to dissolve by prolonged heating. It was isolated and identified as m-dithiolbenzoic acid as follows:

(a) It had m.p. 245°.

(b) A portion was dissolved in caustic soda solution, hydrochloric acid was added and the precipitate obtained removed by filtration. It was found that the filtrate contained no zinc and that the m.p. of the precipitate was 245°.

(c) Some m-dithiolbenzoic acid was prepared by the method of Smiles and Stewart (loc. cit.) and a mixed melting point was taken. The result (245°) confirmed the view that the white substance was the disulphide.

(d) The substance was dissolved in excess of caustic soda solution and two molecular proportions of dimethyl sulphate were added. The mixture was shaken for one hour and then filtered. The filtrate was acidified with hydrochloric acid and the precipitate obtained was filtered, dried, recrystallised from alcohol and then had m.p. 129° - 130°, and was proved to be m-methylthiolbenzoic acid by direct comparison with an authentic specimen of that substance.
these conditions by \textit{m}-dithiolbenzoic acid.

(f) It was converted into \textit{m}-thiolbenzoic acid by heating on a steam-bath with caustic soda solution and either (i) zinc dust or (ii) glucose until the precipitate obtained by adding hydrochloric acid to a portion of the reaction mixture was completely soluble in alcohol. The \textit{m}-thiolbenzoic acid was precipitated by means of hydrochloric acid, washed with cold water and filtered. When recrystallised from aqueous alcohol it had m.p. 146° - 147°.

Since \textit{m}-dithiolbenzoic acid can be reduced in acetic acid solution by means of zinc, its precipitation during the course of several of the reductions suggests that, under the experimental conditions employed, it forms an intermediate stage in the reduction of \textit{m}-chlorosulphonylbenzoic acid, rather than that it arises through atmospheric oxidation of the thiol acid.

\textbf{Stage 3.}

\textbf{The Preparation of \textit{m}-Ethylthiolbenzoic Acid.}

This compound is not described in the literature and several attempts were made to ethylate \textit{m}-thiolbenzoic acid before a successful procedure was found. These are briefly described below:-

\textbf{Method A.} (unsuccessful).

To a solution of \textit{m}-thiolbenzoic acid (30.8 g.) dissolved in alcohol (100 c.c.) a solution of sodium (4.6 g.) in ethyl alcohol (100 c.c.) was added. Ethyl bromide (21 g.)
poured into dilute caustic soda. The insoluble portion was extracted with ether and the ether removed from the aqueous portion by the passage of air. The aqueous portion was then acidified with concentrated hydrochloric acid and the crystalline precipitate obtained was filtered off. After recrystallising from alcohol until no further change in its m.p. was produced it had m.p. 99° - 100° and weighed 20 g.

**Analysis.**

(a) 0.5066 g. substance required 17.1 c.c. 0.1158 N potassium hydroxide for complete neutralisation; 0.4844 g. required 16.6 c.c. Molecular weight 255.7; 254.6. Calculated for m-ethylthiobenzoic acid 182. The product was not further investigated.

**Method B.** (unsuccessful).

When potassium ethyl sulphate was used as the ethylating agent the acid was recovered unchanged.

**Method C.** (successful).

m-Thiolbenzoic acid (78 g.) dissolved in 10% aqueous sodium hydroxide (1000 c.c.), was mixed with a solution of ethyl m-toluenesulphonate (200 g.) in ethyl alcohol (500 c.c.) and the whole heated under reflux on a steam bath for 6-8 hours. The action was complete when no precipitate appeared on pouring a portion of the reaction mixture into water. The liquid was then filtered and the m-ethylthiobenzoic acid precipitated from it by the addition of concentrated hydrochloric acid. It was washed with cold water and recrystallised twice from aqueous alcohol.
Molecular weight 181. Calculated for m-ethylthiolbenzoic acid \( \text{C}_{9}\text{H}_{10}\text{SO}_{3} \), 182.

\[ \text{Stage 4.} \]

The Oxidation of m-ETHYLTHIOLBENZOIC ACID

to dl-m-Carboxyphenyl ethyl sulphone.

The oxidation of m-ethylthiolbenzoic acid to the corresponding sulphone presented some difficulty and several reagents were tried before a satisfactory result was obtained. A brief account of these experiments is given below:

(1) m-Ethylthiolbenzoic acid (32 g.) was dissolved in a solution of potassium carbonate (37 g.) in water (250 c.c.). Hydrogen peroxide (Merck's Perhydrol) (28 g.) was added very slowly with continuous stirring. The temperature was not allowed to rise above 60° C. The addition of hydrogen peroxide required about ten minutes. The solution was cooled, filtered, and made just acid with concentrated hydrochloric acid. The precipitate of white glistening plates was washed with water and after drying had m.p. 162° - 164°. 0.2680 g. required for complete neutralisation 11.00 c.c. of 0.1158 N. potassium hydroxide. Molecular weight 210. Calculated for m-carboxyphenyl ethyl sulphone \( \text{C}_{9}\text{H}_{10}\text{SO}_{4} \) 214. Calculated for m-carboxyphenyl ethyl sulphone \( \text{C}_{9}\text{H}_{10}\text{SO}_{4} \) 214.

(2) m-Ethylthiolbenzoic acid (18 g.) was dissolved in acetone (50 c.c.) and hydrogen peroxide (Merck's perhydrol) (16 g.) was added slowly with shaking and the whole was cooled in ice. The acetone was then removed by distillation, the residue mixed with concentrated hydrochloric
probably \(m\)-carboxyphenyl ethyl sulphone with traces of the required \(m\)-carboxyphenyl ethyl sulphoxide.

(3) \(m\)-Ethylthiobenzolic acid (7 g.) was dissolved in chloroform (100 c.c.) and bromine (6 g.) was added; caustic soda solution was then added until, after acidifying with hydrochloric acid, a substance m.p. 85° was obtained. It was found to contain bromine.

In a second experiment \(m\)-ethylthiobenzolic acid (9 g.) was dissolved in carbon bisulphide (100 c.c.) and bromine (13 g.) was added, when red crystals of the dibromide separated, having m.p. 100° - 102°. On addition of hydrochloric acid to a solution of this substance in sodium hydroxide, a white powder m.p. 80° - 90° was obtained. It contained no bromine.

(4) Attempts, using sodium hypochlorite and hypobromite were also unsuccessful.

(5) \(m\)-Ethylthiobenzolic acid (12.5 g.) was dissolved in turpentine (300 c.c.) and air was passed through the solution for 2½ hours. The oil was washed with potassium carbonate solution which was then extracted with ether. The ether remaining in the aqueous portion was removed by a current of air. This alkaline solution was acidified and gave a very small precipitate. The turpentine was distilled in a current of steam, but nothing was obtained but a brown mass.

(6) The most satisfactory method of oxidation was as follows:-
ethylthiolbenzoic acid had dissolved. The solution was then cooled, filtered, and extracted with chloroform. The chloroform solution was dried by means of calcium chloride and the chloroform was removed by distillation. The residual sulfoxide was crystallised either from benzene or from a mixture of chloroform and petroleum ether and then had m.p. 104° - 106° and weighed 52 g. Yield 60%.

**Analysis.**

Found: C 54.5; H, 51.1; S, 16.2. C_{9}H_{10}SO_{3} requires C, 54.5; H, 5.0; S, 16.1%. 0.5020 g. required for complete neutralisation 21.8 c.c. 0.1158 N. potassium hydroxide. Molecular weight is 198.8. Calculated for m-carboxyphenyl ethyl sulfoxide (C_{9}H_{10}SO_{3}), 198.

---

dl-m-Carboxyphenyl ethyl sulfoxide was found to be moderately soluble in hot water, more easily soluble in warm alcohol, acetone or chloroform and fairly soluble in warm benzene and cold chloroform and cold alcohol. It was practically insoluble in ether or petroleum ether.

**The Resolution of dl-m-Carboxyphenyl ethyl sulfoxide.**

(a) By means of Brucine.

dl-m-Carboxyphenyl ethyl sulfoxide (51 g.) and brucine (100 g.) were dissolved in hot acetone and the crystalline material - rosettes of fine needles m.p. 98° - 100° - which separated on cooling, was removed by filtration. The filtrate was concentrated to quarter bulk and the
the brucine salt, from which it is evident that acetone is unsuitable for effecting the complete separation of the d-A, d-B, and l-A, l-B salts.

The salt was therefore dissolved in hot ethyl alcohol (120 c.c.) and the crop of crystals obtained on cooling the solution (about 50 g. of m.p. 105° - 115°) was filtered off. The filtrate was concentrated when a further crop of crystals (about 10 g.) separated on standing. The brucine salt separated in large transparent rhombs which, after desiccation, melted at 125° - 126° with decomposition. The course of the fractional crystallisation and the results obtained are best shown in the following chart. All determinations of the rotatory powers of the sulphoxide and of the brucine salt to ascertain the course of the resolution were made in chloroform solution at 20° C (c = 2.5; l = 2.).
Sodium hydroxide solution (60 c.c.) was added, the brucine precipitated was filtered off, and the remainder extracted with chloroform. The filtrate was acidified with hydrochloric acid and the sulphoxide liberated was extracted with chloroform (5 times). The chloroform solution was dried by means of calcium chloride and the chloroform removed by distillation. The sulphoxide remaining was crystallised from benzene (100 c.c.) and weighed 32 g. 

\[
\alpha = 39^\circ
\]
(2) dl-\textit{m}-Carboxyphenyl ethyl sulphoxide (27.5 g.)

+ Brucine (55 g.) dissolved in ethyl alcohol (50 c.c.).

\[ [\alpha]_{\text{D}}^{5461} = 68.5^\circ \]

\[ m.p. 125^\circ - 126^\circ \]

\[ [\alpha]_{\text{D}}^{5461} = 55^\circ \]

\[ \text{Filtrate, yielded } 10.5 \text{ g.} \]

\[ m.p. 100^\circ - 102^\circ \]

\[ [\alpha]_{\text{D}}^{5461} = 158^\circ \]

\[ (l = 2; c = 2.1450), \]

after drying for three days.
were dissolved in water and a dilute solution of sodium hydroxide added. The precipitated brucine was removed by filtration, whilst that remaining in the solution was removed by extracting three times with chloroform. The filtrate containing the sodium salt of the \( \text{d-sulphoxide} \) was then acidified with hydrochloric acid and the sulphoxide liberated was extracted five times with chloroform. The product obtained on the removal of the chloroform by distillation was thoroughly dried and had m.p. 71° and weighed 6 g. Yield 60%.

It had \( \left[ \alpha \right]_{5461}^{25^\circ} + 236^\circ \left( l = 2; c = 2.2500 \right) \) in chloroform solution.

The specific rotatory powers of \( \text{d-\( m \)-carboxyphenyl ethyl sulfoxide} \) in various solvents at 25° C are given in Table I, pages 19 and 20.

**THE RESOLUTION OF \( \text{d1-\( m \)-CARBOXYPHENYLETHYL SULPHOXIDE} \) (contd.)**

**THE RESOLUTION OF \( \text{d1-\( m \)-CARBOXYPHENYLETHYL SULPHOXIDE} \) (contd.)**

(b) An attempt by means of strychnine.

(1) \( \text{l + d1-\( m \)-Carboxyphenyl ethyl sulfoxide} \) \( \left[ \alpha \right]_{5461}^{25^\circ} = 68.5^\circ \)

(\( \alpha^2 \text{ fil.} \)) (12.8 g.) and strychnine (22 g.) were dissolved in a hot mixture of methyl alcohol and acetone (60 c.c.) and the crystals obtained on cooling were filtered off. The course of the fractional crystallisation is shown on the accompanying chart VI (1).

(11) A mixture of \( \text{d1-\( m \)-carboxyphenylethylsulphoxide} \) (38.7 g.) and strychnine (60 g.) was treated in a similar manner and the results are also shown on the chart (VI (2)).
filter Chart V: 1\(^{-1}\) 5461\(^{-1}\) - 38.7 g. and strychnine (22 g.) dissolved in methyl alcohol and acetone (60 c.c.).

<table>
<thead>
<tr>
<th>A</th>
<th>Filtrate, yielded sulphoxide (4.4 g.)</th>
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<tbody>
<tr>
<td>m.p. 190° - 195°</td>
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<tr>
<th>B</th>
<th>Filtrate, yielded sulphoxide (1.8 g.)</th>
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</thead>
<tbody>
<tr>
<td>m.p. 195° - 196°</td>
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<tr>
<th>C</th>
<th>Filtrate, yielded sulphoxide (1.0 g.)</th>
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<tbody>
<tr>
<td>m.p. 195° - 197°</td>
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<tr>
<th>D</th>
<th>Filtrate, yielded sulphoxide (0.7 g.)</th>
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<tbody>
<tr>
<td>m.p. 195° - 197°</td>
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<tr>
<th>E</th>
<th>Filtrate, yielded sulphoxide (0.4 g.)</th>
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<tr>
<td>m.p. 195° - 197°</td>
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<th>F</th>
<th>Filtrate, yielded sulphoxide (0.95 g.)</th>
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<tr>
<td>m.p. 195° - 197°</td>
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<tr>
<th>G</th>
<th>Filtrate, yielded sulphoxide (0.6 g.)</th>
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<tbody>
<tr>
<td>m.p. 195° - 197°</td>
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(2) dl-Sulphoxide (38.7 g.) + Strychnine (60 g.) dissolved in methyl alcohol and acetone (250 c.c.)

<table>
<thead>
<tr>
<th>A'</th>
<th>Filtrate, yielded sulphoxide (12.8 g.)</th>
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<tr>
<td>m.p. 193° - 194°</td>
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</table>

<table>
<thead>
<tr>
<th>B'</th>
<th>Filtrate, yielded sulphoxide (3.9 g.)</th>
</tr>
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<tbody>
<tr>
<td>m.p. 197°</td>
<td></td>
</tr>
</tbody>
</table>

(\(\alpha\))
\[ \alpha \]_{5461}^{20^\circ} + 3^\circ 
\]
\[ \alpha \]_{5461}^{20^\circ} + 11^\circ 
\]
\[ \alpha \]_{5461}^{20^\circ} + 119^\circ 
\]

On decomposition in the usual manner \( K \) gave sulphoxide (0.4 g.) with
\[ \alpha \]_{5461}^{20^\circ} + 146^\circ \text{ in chloroform.} 

\( l = 2; \quad c = 2.0 \).
alkaloid for effecting the resolution of dl-m-carboxyphenyl ethyl sulfoxide.

(c) An Attempt by means of cinchonidine. A mixture of m-carboxyphenyl ethyl sulfoxide (13.6 g.) \([\alpha]_{5461}^{20^\circ} = 61.4^\circ\) and cinchonidine (18.5 g.) was dissolved in hot acetone, but no crystals were formed on cooling. The acetone was removed by distillation and the cinchonidine salt remaining was dissolved in warm benzene. The crop of crystals obtained on cooling was filtered off. The course of the fractional crystallisation and the results obtained are shown on the following chart. All determinations of the rotatory powers of the sulfoxide and of the cinchonidine salt to ascertain the course of the resolution were made in chloroform solution at 20° C \(C = 1.25; \Gamma = 2.0\).
1 + dl-m-Carboxyphenyl ethyl sulphoxide (13.6 g.)

\[ \alpha \]_5461^{20} = 64.4° + Cinchonidine (18.5 g.)

dissolved in benzene (100 c.c.).

\[ \alpha \]_5461^{20} = 177°

m.p. 195° - 197°

Filtrate, left to deposit more crystals.

B (2.5 g.) Filtrate

m.p. 198°

[\alpha]_5461^{20} = 91°

Filtrate, yield sulphoxide (4.0 g.) with

[\alpha]_5461^{20} = 125°

B' filtrate

C (1.5 g.)

m.p. 198°

[\alpha]_5461^{20} = 73°

Filtrate yielded sulphoxide (0.3 g.) with

[\alpha]_5461^{20} = 108°

On decomposition in the usual manner gave sulphoxide (0.5 g.) with

[\alpha]_5461^{20} = +8°

\( l = 2; \quad \sigma = 2.50 \).

From the above results it is clear that cinchonidine is not a suitable alkaloid for effecting a separation of \( \alpha \)- and \( l \)-m-carboxyphenyl ethyl sulphoxides.
ethyl sulphoxide from $\text{L-al} - \text{m} - \text{carboxyphenylethyl}$
sulphoxide by taking advantage of the fact that the $\text{L}$-
sulphoxide is much more soluble in benzene than the $\text{Dl}$-
sulphoxide. The results are shown in Chart VIII.
1 + dl-m-Carboxyphenyl ethyl sulphone therefore (52 g.) with
\( [\alpha]_{5461}^{200} = 45^\circ \) in chloroform, from the more
soluble brucine salt, dissolved
in benzene (80 c.c.).

\[ A \ (32 \text{ g.}) \]
\[ \left[\alpha\right]_{5461}^{200} = 39^\circ \text{ in chloroform} \]
\( (l = 2; \ c = 1.25) \)

\[ B \ (26 \text{ g.}) \]
\[ \text{Filt.} \]
\[ m.p. 100^\circ \]
\[ \left[\alpha\right]_{5461}^{200} = 30^\circ \]

\[ C \ (21 \text{ g.}) \]
\[ \text{Filt.} \]
\[ \left[\alpha\right]_{5461}^{200} = 23.8^\circ \]

\[ D \ (16 \text{ g.}) \]
\[ \text{Filt.} \]
\[ 20^\circ - 4^\circ \]
\[ 5461 \]

\[ E \ (12 \text{ g.}) \]
\[ \text{Filt.} \]

Inactive in
chloroform.

\[ A' \text{ Filt.} \]
A sample was
evaporated to
dryness and dried
in vacuo. It
gave sulphone
with
\[ \left[\alpha\right]_{5461}^{200} = 77^\circ \]
in chloroform.

\[ A^2 \ (6.3 \text{ g.}) \]
\[ \left[\alpha\right]_{5461}^{200} = 4^\circ \]
Evaporated to
half bulk.

\[ A^3 \ (1.35 \text{ g.}) \]
\[ \text{Filt.} \]
Inactive in
chloroform.
Evaporated to
dryness, dried
in vacuo. It
gave sulphoxide
(0.5 g.) with
\[ \left[\alpha\right]_{5461}^{200} = 170^\circ \]
in chloroform.

The residue from the \( A^3 \) filtrate would not crystallise
further from benzene.
Phenylethylamine (2.0 g.) was dissolved in water (100 c.c.) and evaporated to small bulk. As no crystals separated the water was removed in vacuo and the salt was dissolved in alcohol. On addition of acetone the salt was precipitated and filtered off. It was dried in a vacuum desiccator and had \([\alpha]_{20}^{20} = 18^\circ\) in alcohol \((l = 2; c = 1.25)\) and weighed 2.1 g. Unfortunately the salt proved to be very hygroscopic so that further work along these lines was abandoned.

(f) By means of quinine, morphine and cinchonine. No crystalline salt of dl-m-carboxyphenyl ethyl sulfoxide with morphine, quinine or cinchonine, could be obtained from any solvent.

The Resolution of dl-m-Carboxyphenyl ethyl sulfoxide (contd.)

(g) By means of quinidine. A mixture of dl-m-carboxyphenyl ethyl sulfoxide (15 g.) and quinidine (25 g.) was dissolved in hot acetone (150 c.c.) but no crystals formed on cooling. Most of the acetone was removed by distillation and the residue was dissolved in hot benzene (150 c.c.). The crystals of the quinidine salt (about 6 g.) obtained on cooling the solution were filtered off; the filtrate was concentrated to half bulk and allowed to stand, when a further crop of crystals (about 14 g.) separated. The crystals were recrystallised from benzene to which a few drops of alcohol had been added. The course of the fractional crystallisation and the results obtained are shown in the following chart:
dl-m-Carboxyphenyl ethyl sulfoxide (15 g.) + quinidine (25 g.) in benzene (150 c.c.)

\[ \alpha \]$_{5461}^{20^\circ}$ + 130° in chloroform.

(1 = 2; \( \beta = 1.25 \)).

Filtrate. Sample decomposed. Sulphoxide obtained (1 g.) with \( \alpha \)$_{5461}^{20^\circ}$ + 30° in chloroform.

(1 = 2; \( \beta = 1.25 \)).

The remainder was concentrated and allowed to stand.

\[ \alpha \]$_{5461}^{20^\circ}$ - 30°

m.p. 194°

\[ \alpha \]$_{5461}^{20^\circ}$ + 119°

6 (2 g.)

Filtrate. Decomposed. Sulphoxide obtained (0.34 g. with [\( \alpha \]$_{5461}^{20^\circ}$ - 30°

m.p. 196°

\[ \alpha \]$_{5461}^{20^\circ}$ + 121°

m.p. 198° - 199°

\[ \alpha \]$_{5461}^{20^\circ}$ + 106°

B (4.5 g.)

Filtrate.

m.p. 188°

\[ \alpha \]$_{5461}^{20^\circ}$ + 123°

m.p. 198° - 199°

\[ \alpha \]$_{5461}^{20^\circ}$ + 103°

D (1 g.)

Filtrate.

m.p. 198° - 199°

\[ \alpha \]$_{5461}^{20^\circ}$ + 102°

m.p. 198° - 199°

\[ \alpha \]$_{5461}^{20^\circ}$ + 102°

Decomposed.

Sulphoxide obtained (0.765 g.) Dried in vacuum for 3 days.

[\( \alpha \]$_{5461}^{25^\circ}$ - 232°; [\( \alpha \]$_{5790}^{25^\circ}$ - 207°; [\( \alpha \]$_{5461}^{25^\circ}$ - 440°]
(I) \( m \)-Carboxyphenyl ethyl sulphide dibromide was prepared by the action of dry hydrogen bromide on \( \alpha + \text{dl}-m \)-carboxyphenyl ethyl sulfoxide \( \left[ \alpha \right]_{5461}^{20^\circ} = 140^\circ \) in dry chloroform solution. The yellowish red crystals which separated had m.p. 102\(^\circ\); 0.5 g. made up to 20 c.c. either with alcohol or acetone gave solutions which were inactive.

(II) Dry hydrobromic acid was passed into a chloroform solution of \( \alpha - m \)-carboxyphenyl ethyl sulfoxide \( \left[ \alpha \right]_{5461}^{25^\circ} = 236^\circ \) phosphorus pentoxide being added to remove the water formed during the reaction. The \( m \)-carboxyphenyl ethyl sulphide dibromide thus formed had m.p. 97\(^\circ\); 0.5 g. made up to 20 c.c. with alcohol gave a solution which was inactive in a 2 d.m. tube to light of \( \lambda_{5461} \).

(III) \( m \)-Carboxyphenyl ethyl sulphide dibromide was also prepared by the direct action of bromine on ethylthiobenzolic acid dissolved in carbon bisulphide. It had m.p. 102\(^\circ\).

\( m \)-Carboxyphenyl ethyl sulphide dibromide formed yellowish red crystals having m.p. 102\(^\circ\) which were soluble in most organic solvents. Unlike the corresponding sulphide and sulfoxide, the dibromide was soluble in ether.

A series of experiments with \( m \)-carboxyphenyl ethyl sulphide dibromide were conducted over a period of two months to show that this substance lost bromine to the air.
dissolved in excess of 2 N. sodium hydroxide solution was heated on a steam bath for half an hour. After cooling, excess of 2 N. nitric acid was added and the \( m \)-carboxyphenyl-ethyl sulphide (0.24 g.) m.p. 100°, which was precipitated, was removed by filtration. The bromine in the filtrate was estimated by Volhard's method.

Found: Br., 45.0%.

\( \text{C}_9\text{H}_10\text{SO}_2\text{Br}_2 \) requires 46.8%.

(b) \( m \)-Carboxyphenyl ethyl sulphide dibromide (0.2730 g.) dissolved in ethyl alcohol (20 c.c.) was heated under reflux on a steam bath and sodium (2.5 g.) was added at intervals for half an hour. The solution was boiled for one hour, cooled, diluted with water (20 c.c.) and the alcohol distilled off. After cooling, excess of 2 N. nitric acid was added and the bromine was determined by Volhard's method (Stepanow, \textit{Ber.}, 1906, 39, 14056). No precipitate of \( m \)-carboxyphenyl ethyl sulphide was obtained but a strong odour of mercaptan was noticeable.

Found: Br., 45.3%.

\( \text{C}_9\text{H}_10\text{SO}_2\text{Br}_2 \) requires Br. 46.8%.

The method of Stepanow may be used to estimate the halogen in a halogenated nucleus; but it is not probable that bromine would be removed from a brominated nucleus under the experimental conditions employed in (1) (a). Hence as the result of experiments (1) (a) and (b) agree, it must be concluded that the bromine atoms are attached to the sulphur atom.

Similar experiments were performed at intervals
(a) Found: Br, 37.9 %.
(b) " Br, 38.1 %.

(3) 14 days later:
(a) Found: Br, 28.0 %.
(b) " Br, 28.2 %.

(4) 3 weeks later:
(a) Found: Br, 17.2 %.
(b) " Br, 17.5 %.

(5) 2 weeks later:
(a) Found: Br, 15.3 %.
(b) " Br, 15.6 %.

Finally, a sample was left in a small flask covered with a filter paper. The bromine evolved destroyed the filter paper, moist air entered and the substance lost its red colour and became hygroscopic.

dl-\textit{m}-Carboxyphenylethylsulphine-\textit{p}-toluenesulphonylimine.

To a solution of \textit{m}-methylthiolbenzoic acid (110 g.) in warm alcohol (550 c.c.) made just alkaline by the addition of 3 N. sodium hydroxide, chloramine-T (197 g; 1.1 mols.) in warm water (550 c.c.) was added and the mixture heated on a steam bath for two hours. Dilute hydrochloric acid was added to the resulting solution after cooling and \textit{dl}-\textit{m}-carboxyphenylethylsulphine-\textit{p}-toluenesulphonylimine then separated, m.p. 114.7°.

Yield 100 g. (50%).

By recrystallisation from aqueous ethyl alcohol it was obtained as small needles m.p. 114.9°.

(Found: C, 54.8; H, 4.8; N, 3.9; S, 18.0; C_{16}H_{17}O_{4}NS_{2} requires C, 54.7; H, 4.8; N, 4.0; S, 18.2%).
The Resolution of dl-m-Carboxyphenylsulphine-p-toluene-Sulphonylimine.

(a) By means of brucine.

To dl-m-carboxyphenylethylsulphine-p-toluene-sulphonylimine (45 g.) in acetone (150 c.c.) and a little ethyl alcohol, brucine (55 g.) was added, and the mixture was warmed until a solution was complete. After cooling, the brucine salt (m.p. 160° - 161°) which crystallised was removed by filtration and recrystallised from four successive quantities (about 150 c.c. in each case) of acetone and alcohol until constancy of rotatory power was reached. The course of the crystallisation is shown in the accompanying chart. dl-Brucine dl-m-carboxyphenylethylsulphine-p-toluene-sulphonylimine had m.p. 161° and 

\[ [\alpha]_{D}^{20} = 157°; \quad [\alpha]_{D}^{20} = 287° \]  in ethyl alcohol.

(\( l = 2; \quad \alpha = 1.106 \)).

The optically pure salt, dissolved in warm ethyl alcohol, was added to dilute hydrochloric acid. After 18 hours, the dl-m-carboxyphenylethylsulphine-p-toluene-sulphonylimine had separated completely. It crystallised from aqueous alcohol in prismatic needles, m.p. 149° - 150°. Its specific rotatory powers in various solvents is recorded in Table II (p. 19). All determinations of the rotatory powers of the sulphilimine and of the brucine salt to ascertain the course of the resolution were made in ethyl alcoholic solution at 20° (\( c = 2.5; \quad l = 2 \)).
(1) dl-Phenylamino-\(\text{C}_{4} \text{H}_{2} \text{Se} \) sulfide + Brucine (20 g.) dissolved in acetone (50 c.c.) containing a little ethyl alcohol.

\[\begin{align*}
\text{A} & \quad \text{Filtrate (60 c.c.)} \\
& \quad \text{Sulphilimine obtained (6.8 g.), m.p. 114^\circ - 119^\circ, with } [\alpha]_{5461}^{20\circ} + 24^\circ \\
& \quad \text{Dissolved in alcohol and acetone.}
\end{align*}\]

\[\begin{align*}
\text{B} & \quad \text{Filtrate (100 c.c.)} \\
& \quad \text{Sulphilimine obtained (2.2 g.), m.p. 114^\circ - 119^\circ, with } [\alpha]_{5461}^{20\circ} + 122^\circ \\
& \quad \text{Dissolved in alcohol alone.}
\end{align*}\]

\[\begin{align*}
\text{C} & \quad \text{Filtrate (60 c.c.)} \\
& \quad \text{Sulphilimine obtained (0.6 g.), m.p. 114^\circ - 119^\circ, with } [\alpha]_{5461}^{20\circ} + 1.2^\circ \\
& \quad \text{m.p. 159^\circ}
\end{align*}\]

\[\begin{align*}
\text{D} & \quad (11.0 \text{ g.}) \\
& \quad \text{Filtrate (60 c.c.)} \\
& \quad \text{Sulphilimine obtained (11 g. with } [\alpha]_{5461}^{20\circ} + 279^\circ \\
& \quad \text{m.p. 161^\circ} \\
& \quad \text{[\alpha]_{5461}^{20\circ} - 157^\circ}
\end{align*}\]

Decomposed and yielded sulphilimine (3.7 g.), m.p. 114^\circ - 115^\circ,

\[\begin{align*}
& \quad [\alpha]_{5461}^{25\circ} - 368^\circ \text{ in ethyl alcohol,} \\
& \quad (\alpha = 2; \ \beta = 2.5425)
\end{align*}\]

(2) dl-m-Carboxyphenylethylsulphine-p-toluesulphonylimine (29.5 g.) + Brucine (33 g.) dissolved in acetone containing a little ethyl alcohol.

\[\begin{align*}
\text{A} & \quad \text{Filtrate (100 c.c.)} \\
& \quad \text{Sulphilimine obtained (11 g. with } [\alpha]_{5461}^{20\circ} + 279^\circ \\
& \quad \text{m.p. 160^\circ}
\end{align*}\]

\[\begin{align*}
\text{B} & \quad \text{Filtrate (80 c.c.)} \\
& \quad \text{Sulphilimine obtained (4.6 g. with } [\alpha]_{5461}^{20\circ} + 237^\circ \\
& \quad \text{m.p. 161^\circ}
\end{align*}\]
Filtrate (50 c.c.)
Sulphilimine obtained
(1.5 g.) with $[\alpha]^20^\circ_{\text{5461}} + 19^\circ$

\(\bullet\) Filterate

\(\bullet\) Sulphilimine obtained
(0.8 g.), inactive in ethyl alcohol.

\(\bullet\) Filterate

\(\bullet\) Sulphilimine obtained
(1 g.), inactive in ethyl alcohol.

\(\bullet\) Filterate

\(\bullet\) Sulphilimine obtained
(8 g.), m.p. 161°, with
$[\alpha]^20^\circ_{\text{5461}} - 157^\circ$ in ethyl alcohol.

\(\bullet\) Filterate

\(\bullet\) Sulphilimine obtained
(8 g.), m.p. 161°, with
$[\alpha]^25^\circ_{\text{5461}} - 372.8^\circ$ in ethyl alcohol.

\(\bullet\) Filterate

\(\bullet\) Sulphilimine obtained
(8 g.), m.p. 161°, with
$[\alpha]^20^\circ_{\text{5461}} + 100^\circ$

\(\bullet\) Filterate

\(\bullet\) Sulphilimine obtained
(8 g.), m.p. 161°, with
$[\alpha]^25^\circ_{\text{5461}} - 372.8^\circ$ in ethyl alcohol.

\(\bullet\) Filterate

\(\bullet\) Sulphilimine obtained
(8 g.), m.p. 161°, with
$[\alpha]^20^\circ_{\text{5461}} + 100^\circ$

\(\bullet\) Filterate

\(\bullet\) Sulphilimine obtained
(8 g.), m.p. 161°, with
$[\alpha]^25^\circ_{\text{5461}} - 372.8^\circ$ in ethyl alcohol.
crystallisation of the brucine salt of \( \text{d-}[\text{m-carboxyphenyl-ethylsulphine-}p\text{-toluenesulphonylimine} \) (A and A' filtrates) was added to dilute hydrochloric acid, and the acetone removed by the passage of air. The \( \text{d+}[\text{m-carboxyphenyl-ethylsulphine-}p\text{-toluenesulphonylimine} (17.8 \text{ g. with} \ [\alpha]_{5461}^{200} + 2\frac{1}{2}.6^\circ \text{ in ethyl alcohol}) \) which was precipitated was dissolved in ethyl alcohol (500 c.c.) and to the warm solution obtained, cinchonidine (14.9 g.) was added. After standing overnight, the cinchonidine salt, m.p. 173^\circ - 174^\circ, was removed by filtration and repeatedly crystallised from the minimum of ethyl alcohol (about 100 c.c.) until its rotatory power remained unchanged on further recrystallisation. The 1-cinchonidine \( \text{d-m-carboxyphenylethylsulphine-}p\text{-toluenesulphonylimine} \) thus obtained had m.p. 198^\circ - 199^\circ and \([\alpha]_{5461}^{200} + 50^\circ \) in chloroform solution (\( \alpha = 1.050; \ 1 = 2 \)). On decomposition as previously described it gave \( \text{d+}[\text{m-carboxyphenylethyl-}p\text{-toluenesulphonylimine} \) m.p. 149^\circ - 150^\circ \([\alpha]_{5461}^{200} + 364^\circ \) in ethyl alcohol (\( \alpha = 2; \ 1 = 2.0700 \)).

To the \( \text{d+}[\text{m-carboxyphenylethylsulphine-}p\text{-toluenesulphonylimine} (5.2 \text{ g.}) \) in alcohol (20 c.c.), strychnine (5.0 g.) was added and the mixture was warmed until solution was complete. After cooling, the strychnine salt (m.p. 165^\circ) which crystallised, was removed and recrystallised from alcohol until its rotatory power remained unchanged on further recrystallisation. The 1-strychnine \( \text{d-m-carboxyphenylethylsulphine-}p\text{-toluenesulphonylimine} \) thus obtained had m.p. 174^\circ and \([\alpha]_{5461}^{200} + 152^\circ \) in ethyl
\[ [\alpha]^{25} +323^\circ, \quad [\alpha]^{25} +373^\circ, \quad [\alpha]^{25} +689^\circ \] in ethyl alcohol \((\alpha = 2.3425; \ \beta = 2)\).

All determinations of the rotatory powers of the sulphilimine and of the cinchonidine salts to ascertain the course of the resolution were made in ethyl alcoholic solution at 20\(^\circ\) C \((\alpha = 2.5; \ \beta = 2)\).
(1) Sulphonylimine (2 g.), m.p. 173° - 174°. Sulphonylimine obtained from toluenesulphonylimine (17.8 g.), $[\alpha]_{D}^{133} + 2^{2} 2^{0}$, dissolved in ethyl alcohol.

- **A**
  - m.p. 173° - 174°
  - Filtrate (160 c.c.)
  - Sulphonylimine obtained (9 g.), m.p. 145°, with $[\alpha]_{D}^{133} + 166^{0}$

- **B**
  - m.p. 198° - 199°
  - Filtrate (200 c.c.)
  - Sulphilimine obtained (5.5 g.), m.p. 145°, with $[\alpha]_{D}^{133} + 175^{0}$

- **C**
  - m.p. 198° - 199°
  - Filtrate (200 c.c.)
  - Sulphilimine obtained (0.6 g.)

- **D**
  - m.p. 198° - 199°
  - Filtrate
  - Sulphilimine obtained (1.3 g.), m.p. 147°, with $[\alpha]_{D}^{133} + 230^{0}$

- **E**
  - m.p. 198° - 199°
  - Filtrate
  - Sulphilimine obtained (1.9 g.), m.p. 148°, with $[\alpha]_{D}^{133} + 293^{0}$

- **F**
  - m.p. 198° - 199°
  - Filtrate
  - Sulphilimine obtained (1.4 g.), m.p. 148° - 149°, with $[\alpha]_{D}^{133} + 304^{0}$

- **G**
  - m.p. 198° - 199°
  - Filtrate
  - Sulphilimine obtained (0.8 g.), m.p. 149°, with $[\alpha]_{D}^{133} + 322^{0}$

- **H**
  - m.p. 198° - 199°
  - Filtrate
  - Sulphilimine obtained (0.7 g.), m.p. 149° - 150°, with $[\alpha]_{D}^{133} + 349^{0}$

- **K**
  - m.p. 198° - 199°
  - Filtrate
On decomposition it gave
sulphilimine (1 g.), m.p.
149° - 150°, with
\[ \alpha \]^{+200}_{5461} + 364° in ethyl
alcohol (\( l = 2; \ c = 2.070 \)).

(2) Strychnine (5.0 g.) + d + dl-Sulphilimine (5.2 g.), \[ \alpha \]^{+200}_{5461} + 270°,
dissolved in ethyl alcohol, (20 c.c.):

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<tbody>
<tr>
<td>A</td>
<td>Filtrate</td>
</tr>
<tr>
<td>m.p. 165°</td>
<td>Sulphilimine obtained from first three filtrates (0.27 g.), m.p. 145°, [ \alpha ]^{+200}_{5461} + 74°</td>
</tr>
<tr>
<td>B</td>
<td>Filtrate</td>
</tr>
<tr>
<td>m.p. 173°</td>
<td></td>
</tr>
<tr>
<td>C</td>
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</tr>
<tr>
<td>m.p. 176°</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Filtrate</td>
</tr>
<tr>
<td>m.p. 174°</td>
<td>Sulphilimine obtained (0.2 g.) with [ \alpha ]^{+200}_{5461} + 89°</td>
</tr>
<tr>
<td>E</td>
<td>Filtrate</td>
</tr>
<tr>
<td></td>
<td>Sulphilimine obtained (0.13 g.) with [ \alpha ]^{+200}_{5461} + 158°</td>
</tr>
<tr>
<td>F</td>
<td>Filtrate</td>
</tr>
<tr>
<td></td>
<td>Sulphilimine obtained (0.11 g.) with [ \alpha ]^{+200}_{5461} + 231°</td>
</tr>
<tr>
<td>G</td>
<td>Filtrate</td>
</tr>
<tr>
<td>m.p. 174°</td>
<td>Sulphilimine obtained (0.10 g.) with [ \alpha ]^{+200}_{5461} + 281°</td>
</tr>
<tr>
<td>H</td>
<td>Filtrate</td>
</tr>
<tr>
<td></td>
<td>Sulphilimine obtained (0.06 g.) with [ \alpha ]^{+200}_{5461} + 324°</td>
</tr>
<tr>
<td>K</td>
<td>Filtrate</td>
</tr>
</tbody>
</table>
Sulphilimine obtained (0.07 g.) with \([\alpha]_{20}^{5461} + 300^\circ\)

Filtrate
Sulphilimine obtained (0.09 g.) with \([\alpha]_{20}^{5461} + 340^\circ\)

in ethyl alcohol.

\(\frac{1}{2} = 2; \quad \alpha = 0.9566\)

On decomposition, \(M\) gave \(d\)-sulphilimine (0.53 g.), m.p. 150° - 151°, with

\([\alpha]_{25}^{5461} + 373^\circ\) in ethyl alcohol.

\(\frac{1}{2} = 2; \quad \alpha = 2.3425\).
A mixture of the dl-sulphilimine (6 g.) with concentrated hydrochloric acid (18 c.c.) on a steam bath for five minutes was neutralised by sodium carbonate and the p-toluenesulphonamide (2.5 g., m.p. 138°) precipitated, removed by filtration. The filtrate was acidified and the m-ethylthiolbenzoic acid (1.0 g., m.p. 99°) liberated was removed by filtration and recrystallised from aqueous alcohol. The m-carboxyphenylethylsulphoxide remaining in the solution was extracted five times with chloroform and the chloroform removed by distillation. The sulphoxide had m.p. 102° - 104° and weighed 1.0 gm. 0.5 g. made up to 20 c.c. in chloroform was inactive in a two decimetre tube in light of wave length λ 5461. The total yield of hydrolytic products was 75%.

**THE INTERACTION OF dl-m-CARBOXYPHENYLETHYSULPHINE-p-TOLUENESULPHONYLMINE AND HYDROGEN PEROXIDE.**

A mixture of the dl-sulphilimine (1/2 g.) and hydrogen peroxide (Merck's Perhydrol) (35 c.c.) was heated on a steam bath with occasional shaking, and gave a clear solution in fifteen minutes. The crystalline material (3 g. m.p. indefinite) which separated on cooling, was crystallised from a small bulk of ethyl alcohol, glistening leaflets (1.5 g.) of m-carboxyphenylethylsulphone (m.p. 162° - 164°) being obtained. After dilution the filtrate yielded a second crop of crystals (0.5 g.) which proved to be p-toluenesulphonamide, m.p. 138°.
p-Toluenesulphonyl chloride (300 g.) was added to a solution of crystalline sodium sulphite (860 g.) in water (1500 c.c.) and the mixture was stirred for 14 hours, during which time it was maintained alkaline by the addition of a strong solution of caustic soda. When the reduction was complete crystals of the sodium salt of p-toluenesulphinic acid separated and were filtered off and recrystallised from water. The filtrate from the first filtration was acidified, the acid filtered off and converted into the sodium salt, which was recrystallised.

The total yield of sodium p-toluenesulphinate was 176 g.

The acid was obtained, as required, from the aqueous solution of the sodium salt by the addition to it of hydrochloric acid. It was partly dried on a porous plate and completely dried by being left in a vacuum desiccator containing calcium chloride for a few days.

The Preparation of p-toluenesulphinyl chloride (Ber., 1908, 41, 443; Hilditch, J., 1910, 27, 2565).

Pure thionyl chloride (43 g.) was dissolved in dry ether (50 c.c.) and finely powdered dry p-toluenesulphinic acid (52 g.) was added gradually with shaking. When all the acid had dissolved, the mixture was carefully warmed on a water-bath till there was no further evolution of gas and until the warm mixture remained warm after

The thionyl chloride was water-white in appearance, having been distilled successively from quinoline, linseed oil and beeswax (Meyer and Schlegel, Monatsch., 1913, 31, 569).
was dissolved in light petroleum. The solution thus obtained was filtered from the small quantity of white solid which separated and subjected to a vacuum at ordinary temperature for five or six hours to remove the petroleum and any residual thionyl chloride. The p-toluenesulphinyl chloride remained as a yellow oil. One sample was blue, changing to green on the addition of ether.

The Preparation of Methyl-p-toluenesulphinate.

p-Toluenesulphinyl chloride (172 g.) in ether *(100 c.c.) was added to a mixture of methyl alcohol (32 g.) and ether (300 c.c.) covering freshly desiccated and finely ground potassium carbonate (207 g.). Carbon dioxide was evolved and the reactants were allowed to remain in contact, with intermittent stirring, for 6 days. Water was then added, the mixture stirred, and the ethereal layer separated, repeatedly washed with water and finally dried over potassium carbonate. The ethereal extract was decanted on to anhydrous sodium sulphate and filtered. On the removal of ether, the crude methyl p-toluenesulphinate (50 g.) was obtained, which when distilled, using a mercury vapour pump, gave a colourless distillate (40 g.) and left a black tarry residue. The colourless distillate was redistilled at 12 mm. and gave a product with b.p. 130.5° - 131.5°/12 mm. which had $\eta_{D}^{25°} = 1.5405$.

* A Fleuss pump, backing a Langmuir mercury-vapour pump, was used to obtain a pressure less than 0.1 mm. A discharge tube was used as a rough gauge.
Experiment on the changes in density and refractive index of methyl-p-toluene sulphinate.

One batch of pure methyl-p-toluene sulphinate was distilled on 9/4/25 and three fractions A, B, C collected (See Table XII).

A second batch was distilled at the same pressure, on 14/4/25 and three fractions A', B' and C' collected, at the same temperature.

It was proposed to determine the changes, if any, in the refractive index and density of the above specimens over a period of several months. The results, as far as they were determined, are shown on the accompanying chart.

Unfortunately, severe attacks of dermatitis resulted from the handling of methyl-p-toluene sulphinate, even though the experimenter was wearing rubber gloves. Consequently, work on this substance had to be abandoned.
### Batch I

<table>
<thead>
<tr>
<th>Date</th>
<th>Refractive Index $n^\circ_D$</th>
<th>Remarks</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/4/25</td>
<td>1.5405</td>
<td>B.p. 130.5° - 131.5°/12 mm. First distillation product.</td>
<td>1.1520</td>
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<tr>
<td>9/4/25</td>
<td>A. 1.5408</td>
<td>Second distillation product 1</td>
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</tr>
<tr>
<td></td>
<td>B. 1.5394</td>
<td>fractions.</td>
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</tr>
<tr>
<td></td>
<td>C. 1.5381</td>
<td>b.p. 11/12 mm.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A. 1.5408</td>
<td>127° - 129°.</td>
<td>1.1511</td>
</tr>
<tr>
<td></td>
<td>B. 1.5394</td>
<td>129° - 130°.</td>
<td>1.1523</td>
</tr>
<tr>
<td></td>
<td>C. 1.5381</td>
<td>130° - 132°.</td>
<td>1.1525</td>
</tr>
<tr>
<td>23/4/25</td>
<td>A. 1.5397</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B. 1.5404</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C. 1.5381</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20/5/25</td>
<td>A. 1.5390</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B. 1.5383</td>
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</tr>
<tr>
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<td>C. 1.5382</td>
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<td>A. 1.5386</td>
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</tr>
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<td>B. 1.5381</td>
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</tr>
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<td>C. 1.5374</td>
<td></td>
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</tr>
<tr>
<td>16/6/25</td>
<td>A. 1.5342</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>B. 1.5342</td>
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</tr>
<tr>
<td></td>
<td>C. 1.5342</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Date</td>
<td>Refractive Index n&lt;sub&gt;25&lt;/sub&gt;D</td>
<td>Remarks</td>
<td>Density</td>
</tr>
<tr>
<td>------------</td>
<td>----------------------------------</td>
<td>-----------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>14/4/25</td>
<td>1.5403</td>
<td>First distillation product kept 6 days.</td>
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</tr>
<tr>
<td>7 p.m.</td>
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<td>Second distillation 3 fractions. B.p. 11/mm.</td>
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<tr>
<td>14/4/25</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>A' 1.5408</td>
<td>127° - 129°</td>
<td>1.1511</td>
</tr>
<tr>
<td></td>
<td>B' 1.5394</td>
<td>129° - 130°</td>
<td>1.1523</td>
</tr>
<tr>
<td></td>
<td>C' 1.5381</td>
<td>130° - 132°</td>
<td>1.1525</td>
</tr>
<tr>
<td>16/4/25</td>
<td>A' 1.5406</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B' 1.5404</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C' 1.5381</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23/4/25</td>
<td>A' 1.5406</td>
<td></td>
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<tr>
<td></td>
<td>B' 1.5405</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>C' 1.5380</td>
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<td></td>
</tr>
<tr>
<td>20/5/25</td>
<td>A' 1.5397</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>B' 1.5397</td>
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</tr>
<tr>
<td></td>
<td>C' 1.5381</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27/5/25</td>
<td>A' 1.5397</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B' 1.5400</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C' 1.5394</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
and dimethylaniline (1375 g.) was heated on a steam bath for eight hours. The product was then distilled in a current of steam to remove the excess dimethylaniline. The mixture remaining in the flask was made alkaline with sodium hydroxide, warmed, and filtered. The crude insoluble product thus obtained was dissolved in hydrochloric acid and the solid impurities were removed by filtration. On addition of sodium hydroxide a blue solid was precipitated which was difficult to purify. Attempts to prepare and purify the oxalate, tartrate, hydrochloride, and sulphate were unsuccessful. The most satisfactory method was found to be as follows:

The substance (150 g.) and N. hydrochloric acid (300 c.c.) were ground together in a large mortar, made up to 500 c.c. with additional acid and warmed gently. The insoluble impurities were removed by filtration and sodium hydroxide was added to the filtrate until it was alkaline. The precipitate obtained was filtered off and crystallised first from acetone, which removed most of its blue colour, and then from alcohol 4-Dimethylamino-4'-methyldiphenyl sulphoxide was then finally obtained as very pale blue crystals, m.p. 195° - 198°.

Yield 125 g. Found: N, 5.4; C15H17-ONS requires N, 5.4%.

It was found impossible to obtain a crystalline salt of 4-Dimethylamino-4'-methyldiphenyl sulphoxide either with a-camphorsulphonic acid or with a-tartaric acid, although numerous solvents were employed.
Stage 1.

**n-Propyl Bromide.**

Sulphur dioxide was passed into a mixture of crushed ice (1075 g.) and bromine (1000 g.) until all the bromine had dissolved. **n-Propyl alcohol (650 g.) was added to this solution and then concentrated sulphuric acid (1000 g.) was poured in gradually with shaking; the whole being kept cooled by crushed ice, applied externally.** The product was heated under reflux on a steam-bath for two hours and the upper layer of **n-propyl bromide distilled off directly from an oil bath into a receiver containing ice-cold water.** The bromide was then separated from the water, washed (a) with water (b) twice with concentrated sulphuric acid (c) twice with sodium carbonate solution (d) with water, and finally dried over calcium chloride. The crude product was distilled and the fraction boiling at 70° - 73° was collected. **Yield 780 g.**

**Stage 2.**

**Methyl-n-propylphenylcarbinol.**

**n-Propyl bromide (130 g.) was run from a tap funnel on to magnesium turnings (24 g.) covered with ether, in a flask cooled by crushed ice, applied externally. Iodine (a trace) was added to start the reaction and the mixture was shaken continuously. When the magnesium had dissolved, acetophenone (120 g.) and an equal volume of ether were added and the mixture was cooled and shaken continuously. The product was decomposed by means of ice-water, and methyl-n-propylphenylcarbinol finally
The methyl-n-propylphenyl carbinol decomposed at its boiling point, 216° at ordinary pressure, yielding β-phenyl-β-amylene having b.p. 89° - 90°/16 mm. and 199°/760 mm.

Stage 1.

The Reduction of β-Phenyl-β-amylene.

The unsaturated hydrocarbon (120 g.) and ethyl alcohol (1200 c.c.) were placed in a three litre flask fitted with a reflux condenser. Clean sodium (120 g.) was added gradually, the reaction developing sufficient heat to keep the mixture boiling. When the reaction was complete the product was cooled, water was added, about 5 c.c. at a time, with shaking and the whole was poured into dilute acetic acid (6.5%). On diluting to seven litres the saturated hydrocarbon separated as an oil on the surface. It was removed, the aqueous layer extracted three times with benzene and the extracts added to the hydrocarbon. The combined extracts were washed with water to remove alcohol, dried over calcium chloride and the benzene removed by distillation. The crude product remaining was fractionally distilled, the fraction distilling between 190° and 193° being pure methyl-n-propyl-phenyl-methane. The absence of the unsaturated hydrocarbon was proved by testing with (a) bromine, (b) potassium permanganate.

Stage 5.

The Nitration of Methyl-n-propyl-phenylmethane.

To dl-methyl-n-propyl-phenylmethane (70 g.) a
was gradually added with constant stirring during two and a half hours, the temperature being kept between 20° and 30° by means of ice-cold water. The mixture was stirred for one and a half hours after all the acid mixture had been added; the product was diluted with water and cooled, when the nitro-compound was extracted with ether. The ethereal solution was washed (1) with water; (2) with sodium carbonate solution; (3) with water 3 times, and finally dried over calcium chloride. The product obtained on removal of the ether by distillation was fractionally distilled under reduced pressure and gave an oil, b.p. 120° - 150°/17 mm., which, after it had been filtered and cooled, in an ice-salt mixture, set to a yellow solid m.p. 156° - 158°. Yield 40.8.

Stage 6.

The Reduction of Methyl-n-propyl-p-nitrophenyl-Methane.

The p-nitrocompound (40 g.) was reduced by means of tin (55 g.) and concentrated hydrochloric acid (1400 c.c.) at the temperature of the steam-bath. The undissolved tin was filtered off, caustic soda (100 g.) in aqueous solution was added and the whole was subjected to distillation in a current of steam. The steam distillate was extracted with ether and the crude product, after the removal of the ether, was dissolved in a hot solution of oxalic acid (10 g.) and water (500 c.c.). On cooling a crystalline precipitate of methyl-n-propyl-p-aminophenyl methane, m.p. 159° - 160°, separated. This was added to a solution of caustic soda and the liberated amine extracted with ether. The oil obtained after the removal of the ether was fractionally distilled and gave methyl-n-
propyl-\(\alpha\)-aminophenyl-methane, b.p. 255°. Yield 7.0 g.

All attempts to resolve this amine by fractional crystallisation of the salts it formed with either d-tartaric acid or with d-camphorsulphonic acid were unsuccessful.