STUDIES IN THE WALDEN INVERSION.

A. THE RELATIVE CONFIGURATION OF ETHYL D-LACTATE AND DEXTROROTATORY ETHYL o-CHLOROPROPIONATE.

B. THE MOLECULAR DISSYMMETRY OF SULPHINATES, CHLOROSULPHINATES, AND MIXED SULPHITES.

A THESIS

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ABSTRACT

of THESIS to be submitted
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STUDIES IN THE VAlID INVERSION.

A. The Relative Configuration of Ethyl d-lactate and Dextrorotatory Ethyl o-chloropropionate.

B. The Molecular Dissymmetry of p-Toluene sulphonates, Sulphonites, and Chlorosulphonates.

An experimental study has been made of the interactions of (a) phosphorus pentachloride, (b) phosphorus pentabromide, and (c) thionyl chloride on optically active ethyl lactate in the presence of tertiary bases.

Optically active ethyl d-g-toluene sulphonoxypropionate has been prepared and its interactions with chlorine, bromine, and hypochlorous acid are described.

Ethyl d-g-chlorosulphonoxypropionate has been prepared and its decomposition in the presence and absence of pyridine is described.

The above interactions and also the interaction of optically active ethyl d-g-toluene sulphonoxypropionate and certain alkaline metal salts are discussed from the point of view of the Walden inversion. The definite form-
ulation of the probable mechanism of these interactions is attempted, and it is concluded that ethyl \(d^+(\cdot)-\)lactate is configuratively related to dextrorotatory ethyl \(\alpha\)-chloropropionate.

The asymmetry of the sulphur atom in ethyl \(\alpha\)-\(p\)-toluenesulphonylpropionate, ethyl \(\alpha\)-chlorosulphonylpropionate, and ethyl lactyl \(\alpha\)-amyl sulphite is discussed, and the results of the fractional distillation of these compounds are given.
The work described in this thesis was carried out at Patterson Polytechnic under the general supervision of Dr. J. Kenyon, and Dr. H. Phillips, whom the author sincerely thanks for their interest and advice.
I. From a consideration of the sign of rotatory power of the chloride and other halogen derivatives obtained by the interaction of ethyl $\text{d}-\text{G}-\text{toluene-sulphonic acid}$ propionate with the alkali salts of the halogen acids and with potassium thiocyanate and potassium selenocyanide. ---------------pages 1-16.

II. From a consideration of the sign of rotatory power of the chloride, bromide, and ethyl lactate obtained by the interaction of ethyl $\text{d}-\text{G}-\text{toluene-sulphonic acid}$ propionate with chlorine, bromine, and hypochlorous acid. ---------------pages 17-25.

III. From a consideration of the sign of rotatory power of the chloride and bromide obtained by the interaction of ethyl $\text{d}-\text{lactate}$ with the pentachloride and the pentabromide of phosphorus in the presence of tertiary bases. ---------------pages 26-33.

IV. From a consideration of the sign of rotatory power of the chloride obtained by the decomposition of ethyl $\text{d}-\text{G}-\text{chlorosulphonic acid}$ propionate in the presence and in the absence of tertiary bases. ---------------pages 34-43.
V. From a consideration of the influence of the polarity of the substituents on the magnitude of
the sign of rotation of ethyl d-lactyl derivatives.

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lactate in the presence of tertiary bases, ----- 97-99.
The preparation and reactions of ethyl d-g-chloro-
sulphonypropionate, ----------------------- 99-107.
The preparation of zinei sulphites, \( 105-119 \).

The determination of paraohor, \( 120-133 \).
The isomeric lactic acids offered the first authentic case in which the observed number of isomeric substances exceeded the structural possibilities. As a result of his very searching experiments on the lactic acids, Wieland was able to welcome and sponsor, with great enthusiasm, the conception of the asymmetric carbon atom put forward by van't Hoff and Le Bel.

According to van't Hoff, there proceeds from the carbon atom in the compound CR, an unknown force, which tends to drive the four groups attached to it as far away from each other as possible, thus causing a tetrahedral orientation. If all the groups are dissimilar, an irregular tetrahedron will result, and concomitantly, second order symmetry will disappear, and such an arrangement will exist as object and its non-supersposable mirror image.

When for instance the hydroxyl group of an optically active α-hydroxy-acid is replaced by a chlorine atom, it does not follow necessarily that the entering atom will take up the position vacated by the retiring group. That a rearrangement may take place was demonstrated for the first time by Walden (Ber., 1896, 22, 133) who succeeded in realising the following optical cycle:
In an optical cycle it can be seen that an inversion of configuration has taken place after two substitution reactions have occurred. Owing to the fact that a change in the sign of rotation does not necessarily indicate a change in configuration, the problem arises, during which of the two reactions does the inversion occur?

There are two main lines of approach to the solution of this problem:

1. the determination of the relative configuration of the parent compound and its derivative by a scrutiny of evidence obtained by various physico-chemical methods, and

2. the diagnosis of a change of configuration or of a non-inversion from a consideration of the mechanism of the chemical reaction involved.

The great importance of the phenomenon of the Caien inversion has been recognized by many prominent chemists, and has led to much brilliant experimental work and to much
speculation as to the mechanism of the process. Fischer (Her., 1906, 32, 2694) considered that 'this discovery is the most surprising observation in the field of optically active substances since the fundamental investigations of Pasteur'. Frankland in 1913, devoted his presidential address to the Chemical Society entirely to a remarkably complete and inspiring review of the experiments, which had been carried out on the salicin inversion up to that time, and of the theories involved.
THE RELATIVE CONFIGURATIONS OF ETHYL D-LACTATE AND IDENTICAL ETHER ETHYL D-SULPHOXYACETATE.

I. From a Consideration of the Sign of Rotatory Power of the Chloride and other Halogen Derivatives obtained by the interaction of Ethyl d-α-p-Toluene-sulphonyloxy-propanoate with the Alkali Salts of the Halogen Acids and with Potassium Thiocyanate and Potassium Selenocyanide.

1. Earlier attempts to describe the mechanism of the Wadon inversion.

Many attempts have been made to throw light on the relative configuration of a parent molecule and its substitution product by a consideration of the possible mechanisms of the reaction involved. With the increase in knowledge of organic reactions, the conviction has gained ground that addition precedes substitution. To account for the existence of such intermediate addition compounds, investigators have postulated the existence of special valency or affinity forces.

Fischer (Annalen, 1911, 321, 132) suggested that the substituent became loosely attached to the reactant molecule before the retiring group left; so that when the latter did issue, the substituent could either take its place
without inversion, or could take the place of one of the other groups which moved into the position vacated by the retiring group, and thus cause the substitution to occur with inversion. But conditions of attachment must be fulfilled for the one or the other rearrangement to take place, Fischer could not state.

Saying more attention to the spatial position of the attached substituent, Bamber (2, 1911, 6, 631) gave a more logical indication of the necessary conditions for an inversion to occur. He considered that if the substituent became attached to any of the three faces, ABC, ABC, DBC, contiguous to the retiring group X, in the tetrahedral molecule, then the replacement will take place without configurative change; whilst if attachment occurs at the opposite face, ABC, then inversion will occur. But here the reference is merely shifted. What is it that determines whether the attachment will take place at the opposite or at a contiguous face?

Cadam (Chem. Zeit., 1910, 52, 1094; 1912, 52, 1327) emphasized the necessity for assuming the formation of intermediate complexes in order to preserve continuous asymmetry; for he considered that if only three groups were left attached to the asymmetric carbon atom, these groups would swing into the same plane with the carbon atom and give rise to racemisation. He suggested that the replacement of chlorine by the hydroxyl group occurred in the
following way. The oxygen atom of the hydroxyl group be-
came loosely attached to both the chlorine and the carbon
atoms,

```
\begin{align*}
\text{a} & \equiv \text{Cl} \\
\text{c} & \equiv \text{O} \\
\text{b} & \equiv \text{H}
\end{align*}
```

then the attachment between the carbon and the oxygen atoms
gradually became stronger, whilst that between the chlorine
and the carbon atoms became weaker and weaker until com-
plete severance occurred. Such a process would not in-
volve a configurative change. On the other hand it consid-
ered that silver oxide caused an inversion in the following
way:

```
\begin{align*}
\text{a} & \equiv \text{Cl} \\
\text{c} & \equiv \text{O} \\
\text{b} & \equiv \text{H}
\end{align*}
```

Here the chlorine was gradually withdrawn from the sphere
of attraction of the carbon atom by the silver cation and
meanwhile the other three groups tended to set in a plane
so leaving the opposite region free for the attachment of
the hydroxyl group. It is now suggested that this view of
the mechanism of the inversion would be more complete if
it were definitely stated that the attachment of the hyd-
roxyl group took place before the chlorine atom became
completely severed from the carbon atom. Piilson(Ammelen,
1911, 112, 155) however, attributed the results obtained
XIII. Hydroxylation of a chlorocompound by silver oxide and potassium hydroxides to the difference in the solubility of the resulting metallic halides. He contended that the silver ion would remove the chlorine atom rapidly and therefore without inversion, whilst the potassium ion would react more slowly and give rise to inversion; conclusions which are at variance with those of Cadman.

Penyon and Phillips have now given definite formulation to the intermediate complexes which are assumed to occur during substitution reactions of interest in the valdon inversion. Furthermore they have developed a comprehensive theory of the mechanism of the inversion, with the result that the occurrence of an inversion can be inferred with a high degree of probability (Trans. Faraday Soc., 1932, 28, 415).

The p-toluene-sulphonate reaction as a means of correlating the configurations of ehe acute 3-lactate and ehe acute 4-chloromacronate.

In 1935, Phillips (C.12) has begun to apply the properties of the optically active esters of p-toluene-sulphonic acid to the study of the valdon inversion. He showed that the p-toluene-sulphonate of a-tamylplastylactonol reacts in alcoholic solution with potassium acetate to form a levorotatory tamylplastylactonyl acetate, the rotatory power of which indicates that an inversion of configuration to the extent of 50° has taken place.
(1922, 122; 39) applied this method to the study of the configurative changes which occur during the interaction of the p-toluene sulphonate of ethyl d-lactate with potassium acetate, benzoate, phenylacetate, and also with the alkali salts of the halogen acids.

Ethyl d-p-toluene sulphonoxypropionate was prepared by the interaction of ethyl d-lactate and p-toluene sulphonyl chloride in the presence of pyridine. It is assumed that in this reaction no configurative change occurs, because the reaction involves merely the replacement of the hydrogen of the hydroxyl group, a process which is not likely to disturb the valencies of the asymmetric carbon atom.

\[ \text{CH}_2CH=CHCH=CH}_2 \quad \text{CH}_2CH=CHCH=CH}_2 \]

For a similar reason it may be assumed that benzyli chloride also reacts with ethyl d-lactate without a configurative change, (II). Now this latter reaction produces levorotatory ethyl d-benzoxyloxypropionate, which has \( [\alpha]_D^{20} = -29.6^\circ \). On the other hand, the sulphonate of ethyl d-lactate given with potassium benzoate, dextrorotatory ethyl d-benzoxyloxypropionate, which has \( [\alpha]_D^{20} = 30.56^\circ \). In the premises given, it must be concluded that a salient inversion has occurred during the production of the benzyli derivative from the sulphonate.
These changes are represented in the following diagram.

\[ \text{CH}_3 - C - 
\text{CH} \quad \text{CH}_3 - C - 
\text{CH} \quad \text{CH}_3 - C - 
\text{CH} \quad \text{CH}_3 - C - 
\]

\[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

\[ \text{[a]}^20 - 11.6^\circ \quad \text{[a]}^20 + 45.6^\circ \]

\[ \text{CH}_3 - C - 
\text{CH} \quad \text{CH}_3 - C - 
\text{CH} \quad \text{CH}_3 - C - 
\text{CH} \quad \text{CH}_3 - C - 
\]

\[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

\[ \text{[a]}^20 - 21.8^\circ \quad \text{[a]}^20 + 31.5^\circ \]

in the same way, ethyl \( \gamma \)-phenylacetoxypropanate and ethyl \( \gamma \)-acetoxypropanate were obtained from the same sulphonate and had rotary powers (see table I, p. 128) opposite in sign but almost equal in magnitude to those of the derivatives obtained by direct acylation.

Similar inversion reactions have been realized with the \( \gamma \)-toluencesulphonates of \( \beta \)-\( \beta \)-octanol and \( \beta \)-menthol (Phillips, J., 1945, 1, 525, 255), and the \( \gamma \)- and \( \beta \)-methylcyclohexanols (C., u., n., n., and n., J., 1945, 1, 525, 255) and the regularity of the results obtained is evidence of the inherent soundness of this method of studying the inversion.
When the sulphonate of ethyl $d$-lactate was refluxed with the alkali salts of the halogen acids in alcoholic solution, the halogen derivatives obtained had rotatory powers opposite in sign to the rotatory power of the parent sulphonate. Assuming that the levorotatory ethyl $g$-chloropropionate is produced from the dextrorotatory sulphonate by the same general mechanism which produces the ethyl $g$-acetoxypropionate with inversion, it may be concluded therefore, that the chloride also is produced with inversion and should be designated ethyl $d$-($-$)$g$-chloropropionate.

Ethyl $d$-($-$)$g$-thiocyanopropionate and ethyl $g$-($-$)$g$-selenocyanopropionate have now been prepared by the interaction of the corresponding potassium salts and the sulphonate of ethyl $l$-lactate. In both cases the product has a rotatory power of the same sign as that of the sulphonate and hence as that of the ethyl $l$-lactate from which the sulphonate was made. Nevertheless, it may be concluded that in these cases too a full inversion has occurred, and that levorotatory $g$-thiocyanopropionate and ethyl $g$-selenocyanopropionate are configuratively related to ethyl $g$-lactate.

It is now suggested that these conclusions may be supported by the following experiments. When dextrorotatory ethyl $g$-chloropropionate is refluxed with potassium acetate in alcoholic solution, one should obtain levorotatory ethyl $g$-acetoxypropionate, as proposed by Gorer, Phillips, and Walker. $\text{[Ref]}$. It is legitimate to assume that a
similar course of reaction will be followed when the mace
chloride is refluxed with potassium bromide, potassium thiocyanate, and potassium selenocyanide respectively, and that
the products obtained will be configuratively related to
each other. The production, then, of levorotatory ethyl α-
tromopropionate, dextrorotatory ethyl α-thiocyan- and α-
selenocyanoglycinate will support the evidence obtained
from the sulphonate reaction.

(iii) The mechanism of the sulphonate reaction.

In terms of the electronic theory of valency, the structure of ethyl α-p-toluene sulphonic glycolate may be repre-
sented thus,

\[
\begin{array}{c}
\text{CH}_3 \\
\text{C}_2 \text{H}_5
\end{array}
\xrightarrow{\text{H}}
\xrightarrow{\text{O}}
\xrightarrow{\text{O}}
\xrightarrow{\text{C}_2 \text{H}_5}
\xrightarrow{\text{CH}_3}
\]

It contains a sulphur atom covalently linked to a p-tolyl
group, to an oxygen atom (which is covalently linked to the
aromatic carbon atom) and linked to two oxygen atoms by
means of semipolar bonds. Now in the sulphonate reaction
with potassium benzoate, it is suggested that the potassium
cation becomes attached to the two negatively charged oxygen
atoms and weakens the oxygen-asymmetric carbon link. As the
sulphonic group leaves, the other groups begin to swing to
the opposite configuration. But it will be noticed that the
retiring group is preponderantly positive and so will most
likely take with it the binding electrons between the oxygen and the asymmetric carbon atom. The positive charge which tends to be left on the asymmetric carbon atom will orientate the benzene union into a position favourable for attachment to the opposite side of the molecule just as the rettating group leaves. This process will give rise to an inversion.

It is highly probable that lithium chloride will react with the same type of mechanism; it will be merely a matter of substituting a chloride ion for a benzate ion.

The same general mechanism can be formulated for the reactions between the sulphonate of ethyl 2-lactate and all the
alkali salts mentioned in the foregoing discussion.

There are two features of this reaction which must be emphasized. These are:

1. the group about to retire has become preponderantly positive, and thus tends to leave behind a carbonium cation by taking with it the oxygen-carbon binding electrons, and

2. the entering group exists as an anion.

It is suggested that these are the essential conditions for the occurrence of a Walden inversion. All those reactions in which the retiring group becomes preponderantly positive whilst the entering group exists as an anion are accompanied by an inversion. The inversion is due to the production and instability of a tri-cova lent carbonium cation. If the special mechanism, which enables the entering group to take up its position just as the retiring group leaves, be absent, then the carbonium cation will be liberated and, owing to the oscillation of the three groups, will give rise to a racemised product.

The instability of the carbonium cation might be inferred from the fact that it contains only six electrons in its valency orbits. Its instability, however, has been demonstrated by Kenyon and Phillips (J. Amer. Chem. Soc., 1933, 55/6) who showed that when 2-methyl-1-naphthylcarbonylethyl sulphone sulphonate isomersise, an optically inactive sulphone is produced, probably by the reactions represented in the follow-
The fact that the carbonium group joins on to the sulphur atom, indicates that the former does not separate as a neutral group. If then, in the course of a substitution reaction, the carbonium cation separates, it is just as likely to give one form as the other when it combines with the union and so will lead to complete racemisation. In this connection it is of interest to consider the views of Mörner on the mechanism of the inversion reaction.

(iv) The hypothesis of Mörner.

Mörner (43, 1926, 2457; 1929, 1502; 1930, 2017) assumes that when in an optically active molecule one of the radicals splits off, the three remaining radicals linked to the asymmetric carbon atom oscillate between two configurations, each of which, by the addition of a new radical, will produce only one of the two possible optical antipodes. He assumes, further, that the fraction of the reaction product which retains its original configuration is proportion-
al to the probability that the oscillating molecule reacts with the entering ion Y while still in the original configuration; this probability will increase with the length of time of oscillation and with the speed of the reaction between the oscillating molecule and Y. After making simplifying assumptions, Årdam obtains the relationship;

\[ n = k C F \quad \text{where} \]

\[ n = \text{the fraction of the reaction product which retains its original configuration,} \]

\[ C = \text{the mean concentration of the entering radical,} \]

\[ F = \text{the kinetic activity factor of Brönsted, and} \]

\[ k = \text{a constant.} \]

It will be seen from this equation that the form of reaction product which increases in amount with increasing concentration of the entering radical in solution has the same configuration as the original substance.

To test this equation, Årdam used the reaction between levo-bromosuccinic acid and potassium xanthogenate, of which data had been obtained by Sölsberg (Den. 1926, 52, 125; Sven. Kem. Tidskr., 1927, 39, 1). He found that the values of \( n \), calculated from his equation, agreed fairly well with the percentages of dextro-xanthogenosuccinic acid found by Sölsberg. He concludes from this that levo-bromosuccinic acid
i-configure
tively related to \( \beta \)-methylacetoacetonic acid.
The agreement between the calculated and observed values
for the interaction of \( \beta \)-bromocetonic acid and potassium
hydrosulphide was not by any means as good.

Now an examination of the reaction used by Byrdon
reveals some ground for criticism. He formulates the reaction as:

\[
\text{CH}_3\text{COCH} = \text{CH} = \text{COCH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{COCH} = \text{CH} = \text{COCH}_3 + \text{Br}_2
\]

Firstly, why does the bromine at a become detached as an
anion and leave behind a carbonium cation? It seems likely
that the potassium cation in the solution becomes attached
to the bromine atom, thus making it preponderantly positive;
it leaves the molecule, takes with it the binding electron,
and produces momentarily the carbonium cation. Meanwhile,
as the process of reorientation is going on, the group be-
gins to swing over, facilitating the orientation of the
xanthogene anion at the opposite side of the molecule. This
process would produce only one of the two possible isomers,
that which is produced by inversion.

Secondly, Byrdon contends that the three groups attached
to the free carbonium cation oscillate and thus cause vary-
ing amounts of the two forms to be produced depending upon
the concentration. Renzon and Phillips have shown however
that if the carbonium cation is formed in the absence of
the special mechanism which leads to an inversion, then the
product will be completely reversed.
Thirdly, the variation of the rotatory power of the product with concentration may not be due to the mechanism postulated by Wyrsch, but to the interference by the ionised carboxyl group.

![Chemical Diagram]

That compounds containing a free carboxyl group are prone to behave in a complicated manner is also indicated by the apparently conflicting experimental results obtained when halogeno-acids were hydroxylated and amino-acids and esters are deaminated (compare Senyon and Phillips, loc.cit.).

(vi) An examination of the carbonate reaction from the standpoint of Wyrsch's hypothesis.

An examination of Table I., p. 16, will reveal the fact that the acetyl-, phenylacetyl-, and the benzoyl-derivatives are formed from the ethyl 4-toluenesulphonxypropanate by a complete or almost complete inversion. In other words there is an insignificant amount of racemisation, but the halogeno-derivatives are formed with a very large amount of
reacination. To too, with the γ-thiocyanato- and the γ-
selecnocyanato-derivatives, there are indications that these
may not be optically pure. It is interesting to consider
a probable cause of this difference.

The experiments on the interaction of ethyl 1-γ-
toluenesulphonylhydroxypropionate and potassium thiocyanate lead
to the view that concentration is influencing the magnitude
of the potatory power of the product. As the concentration
of the potassium thiocyanate was diminished, the magnitude
of the levorotatory power increased. This indicates, on
Jörmum's theory, that the levorotatory form of ethyl γ-
thiocyanato-propionate has the opposite configuration to that
of the sulphonate from which it is formed. That is, it is
formed by inversion. This conclusion is that reached also
on the basis of the general theory of Kenyon and Phillips.
There, Jörmum contends that the different amounts of the
1- and 2-forms produced in the reaction are due to the
same process—the combination of the union with the carbo-
nium cation when the latter is in either of the two con-
figurations—the ratio of the amounts of the two forms
depending upon the concentration of the union. Kenyon and
Phillips consider that the production of both forms in
different amounts is due to two entirely distinct processes.

These are:

1. the mechanism which leads to a complete inversion, α;
2. the complete severance of the carbonium cation which
then yield equal amounts of the 6- and 1-forms, i.e.
give rise to a completely racemised product.

The occurrence of a partly racemised product simply means
that these two processes are going on side by side; and
that the rotatory power of the product is due to that form
which has been produced by inversion.

Now the experimental conditions may influence the magni-
itude of the rotatory power of the product, by causing the
processes 1 and 2 to be followed to different extents. In
the experiments of Kenyon Phillips and Turley (loc. cit.) the
concentrations of the alkali salts were high in all cases;
so that it would seem that the nature of the anion was just
as significant as the concentration. Suppose that in the
sulphonate reaction, using equimolecular proportions of
reactants, all the molecules form the complex,

\[ \text{process which would lead to inversion. Excess of } R \cdot X \]

i.e., excess of cations as well as anions—for they would be
introduced together—may influence some of the above complex
molecules in two ways;

1, the anions may speed up the removal of the preponder-

antly positive group, and so liberate a free carbonium
cation, the anion not having had time to take up its
proper position for attachment to the opposite side, 
the cations may hinder the proper attachment of the 
union at the opposite side as the preponderantly 
positive group leaves, and so assist in the formation 
of a free carbonium cation.

(vii) Conclusion.

From a consideration of the reaction which occurs 
when ethyl \( \beta \)-\( \beta \)-toluene-sulphoneoxypropionate is re-
fluxed with lithium chloride, it may be concluded that 
ethyl \( \beta \)-\( \beta \)-lactate has the same configuration as ethyl 
\( \beta \)-\( \beta \)-chloro-propionate.
**Table I**

A comparison of the optical losses of the products obtained from the p-toluenesulphonate of Ethyl d-lactate.

<table>
<thead>
<tr>
<th>Derivative</th>
<th>Prepared by</th>
<th>Otherwise</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-toluene-sulphonate</td>
<td>prepared</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acetyl</th>
<th>$\alpha^D_{20^o} -24.87^\circ$</th>
<th>$\alpha^D_{20^o} +27.0$</th>
<th>96%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylacetox</td>
<td>$\alpha^D_{20^o} -23.69^\circ$</td>
<td>$\alpha^D_{20^o} +21.2^\circ$</td>
<td>99% ; ;</td>
</tr>
<tr>
<td>$\alpha$-Chloro-</td>
<td>$\alpha^D_{20^o} -1.51^\circ$</td>
<td>$\alpha^D_{20^o} -0.4^\circ$</td>
<td>largely</td>
</tr>
<tr>
<td>$\alpha$-bromo-</td>
<td>$\alpha^D_{20^o} -1.51^\circ$</td>
<td>$\alpha^D_{20^o} -0.4^\circ$</td>
<td>largely</td>
</tr>
<tr>
<td>$\alpha$-iodo-</td>
<td>$\alpha^D_{20^o} -0.4^\circ$</td>
<td>$\alpha^D_{20^o} -0.4^\circ$</td>
<td>largely</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Benzoyl</th>
<th>$\alpha^D_{20^o} +13.65^\circ$</th>
<th>$\alpha^D_{20^o} -13.7^\circ$</th>
<th>100% inv'n</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-thiocyanate</td>
<td>$\alpha^D_{20^o} +7.51^\circ$</td>
<td>$\alpha^D_{20^o} +7.51^\circ$</td>
<td>Same sign</td>
</tr>
<tr>
<td>$\alpha$-selenocyanate</td>
<td>$\alpha^D_{20^o} +0.85^\circ$</td>
<td>$\alpha^D_{20^o} +0.85^\circ$</td>
<td>Sulphonate.</td>
</tr>
</tbody>
</table>

Actually the last two compounds were obtained as the levorotatory forms from the levo-rotatory sulphonate.
II. From a consideration of the sign of optical rotation of the Chloride, Bromide, and Ethyl Lactate obtained by the interaction of Ethyl d-α-β-Toluenesulphonyloxypropionate with Chlorine, Bromine, and Hypochlorous Acid.

(1) The configurations of the p-toluenesulphonate and the p-toluenesulphonate of ethyl d-lactate.

Ethyl d-α-β-p-toluenesulphonyloxypropionate can be prepared by the interaction of ethyl d-α-β-lactate and p-toluenesulphonylchloride in the presence of pyridine. It is a colourless, highly reflecting oil which can be distilled only at the vacuum of the discharge tube, about 0.1 mm.

During its preparation it is highly probable that the bond between the asymmetric carbon atom and the oxygen of the hydroxyl group is undisturbed, and so the resulting sulphinate will have the same configuration as the parent ethyl d-(+)-lactate.

\[
\text{CH}_3 \quad \text{O} \\
\text{H} - \text{C} - \text{O} \quad \text{Et} \\
\text{OEt} \quad \text{Lactate} \\
\text{CH}_3 \quad \text{O} \\
\text{H} - \text{C} - \text{O} \quad \text{Et} \\
\text{OEt} \quad \text{Lactate}
\]

'd' (+)
Now since the \( p \)-toluenesulphonate of ethyl \( \delta \)-lactate is formed by a similar mechanism, it is legitimate to conclude that the sulphinate and the sulphonate have the same configuration. This conclusion is supported very strongly by the fact that when the \( p \)-toluenesulphonate of ethyl \( \delta \)-lactate is oxidised to the corresponding sulphonate, the latter has the same sign and practically the same magnitude of rotatory power as that of the \( p \)-toluenesulphonate obtained directly from ethyl \( \delta \)-lactate by means of \( p \)-toluenesulphonyl chloride. This relationship may be indicated as follows:

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{COOEt} & \xrightarrow{\text{pyridine}} \text{CH}_2\text{CH}_2\text{SO_3Et} \\
\end{align*}
\]

Since the oxidation involves merely the donation, by the sulphur atom, of two electrons to form a semipolar link with
the additional oxygen atom, the linkages of the asymmetric carbon atom are presumably left undisturbed.

(11) The mechanism of the interaction of hypochlorous acid and the p-toluenesulphinate of ethyl d-lactate.

When ethyl d-(+)-γ-p-toluenesulphinoxy-propionate reacts with hypochlorous acid in aqueous solution, ethyl l-lactate is produced. Therefore the product must have been formed by inversion. This reaction too, can be formulated in terms of the general theory of Kenyon and Phillips.

The asymmetric nature of the p-toluenesulphinoxy group has been demonstrated by Phillips (J., 1925, 127, 2564) so that the electronic make-up of the sulphur atom in ethyl d-γ-p-toluenesulphinoxy-propionate is presumably as follows:

\[
\begin{align*}
\text{CH} & \quad \text{O} \\
3 & \\
\text{H} & \quad \text{S} \quad \text{O} \quad \text{S} \\
\text{C} \quad \text{Et} & \\
2 &
\end{align*}
\]

It seems likely that the interaction of this sulphinate with hypochlorous acid proceeds by the addition of a positive chlorine ion to the sulphur atom, whilst the hydroxyl negative ion takes up a favourable position for attachment to the carbonyl cation as the retiring group leaves.
in this reaction, the retarding group becomes preponderantly positive, and as it leaves, it takes with it the C–C binding electrons and thus causes the asymmetric carbon atom to become positively charged. As the retarding group is in the process of leaving, the three primary groups begin to swing into a plane with the carbon; but the positive charge on the latter orientates the hydroxyl union as is shown in the diagram. Just as the sulphonic group leaves, the hydroxyl group becomes attached. The whole process has taken place with a hindered inversion.

(iii) The mechanism of the interaction of chlorine with the p-toluenesulphonate of ethyl g-lactate.

Then ethyl g-(+)-g-p-toluenesulphinoxypropionate reacts with chlorine water, ethyl-g-chloropropionate possessing a high levorotation is produced. The mechanism suggested for this reaction is that the chlorine molecule exists
in dynamic equilibrium with a pair of chlorine ions, one being an anion the other a cation, and that the cation becomes covalently linked to the sulphur atom of the sulphinate thus, making the group containing this sulphur atom preponderantly positive, causes it to proceed to leave behind it a carbonium cation which orients the chlorine anion as shown in the diagram.

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

Since levorotatory ethyl \(\text{d}-\text{chloropropionate} \) and ethyl \(\text{l}-\text{lactate} \) are produced from the same sulphinate by reactions which appear to be strictly analogous, it follows that the first two substances are configuratively related.

It is interesting to notice that consistently high values for the rotatory power of the chloride were obtained by this reaction, with bromine in chloroform solution, ethyl \(\text{d}(-)\)-\(\text{p}\)-toluenesulphinoxypropionate have a highly levo-

rotatory ethyl \(\text{d}-\text{tromopropionate} \).
Similar reactions have been carried out on the \( l-\beta \)-octyl esters of \( p \)-toluenesulphonic and \( p \)-toluenesulphinic acids by Housea, Kenyon and Phillips, (\textit{J.}, 1922, 1706) and the results obtained by these investigators are similar to those obtained in the present investigation.

Attempts were made to prepare ethyl \( L-\beta \)-thioglycero- 

\[ + \] 

\[ \text{production} \] 

\[ \text{of the thiochemical derivative of the thiocyanate by using the appropriate solvent, but the choice of solvent is essentially restricted by the conditions necessary for the production of the desired product.} \]
preparation of the thiocyanogen, \((\text{SCN})_2\).

Fruitless attempts were made to prepare ethyl \(\alpha\)-selenocyanopropionate by refluxing the sulphinate with cyanogen triselenide, \((\text{CN})_3\) Se, in chloroform solution.

There appears to be a close analogy between the halogen radicals on the one hand and the thio- and selenocyanogen radicals on the other (Birkenbach and Hellermann, Ber., 1925, 59, 766, 2377; Challenger, Peters, and Halevey, J., 1926, 1648). Birkenbach and Hellermann refer to thiocyanogen and selenocyanogen as the 'pseudo halogens' and have actually isolated selenocyanogen(\(\text{SeCN})_2\). Although nascent selenocyanogen can be prepared (Haußmann and Högler, Ber., 1926, 59, 179) it is more convenient to prepare and use the cyanogen triselenide, and since Challenger, Peters, and Halevey (loc. cit.) have shown that this substance undergoes many of the reactions which might be expected of selenocyanogen, the triselenide was used in the experiments with ethyl \(\alpha\)-p-toluenesulphinoxypropionate. In view of the above considerations it is surprising that the \(\beta\)-toluenesulphinate of ethyl \(\alpha\)-lactate which reacts so readily with chlorine to give ethyl \(\alpha\)-chloropropionate does not appear to react in an analogous manner with thiocyanogen and selenocyanogen. It is probable that favourable experimental conditions were not secured in the experiments to which reference is now being made.
III. From a consideration of the *sign of rotation*

toec of the chloride and bromide obtained by the
interaction of ethyl *d*-lactate with the pentachlor-
ide and pentabromide of phosphorus in the presence
of tertiary bases.

(1) The mechanism of the interaction of ethyl *d*-lactate and phosphorus pentachloride in the presence
of pyridine and other tertiary bases.

In 1895 Walden (Proc., 21, 1267) obtained dextrorotat-
tory ethyl *g*-chloropropanate, \([\alpha]_p^{12} = +12.86^\circ\), by the action
of phosphorus pentachloride on sarcosolic acid followed
by the addition of ethyl alcohol. He also obtained dextro-
rotatory ethyl *g*-bromopropanate, \([\alpha]_p^{12} = +7.46^\circ\), by the
action of phosphorus pentabromide on 'ethyl *d*-lactate' (from sarcosolic acid). The yields of these products were
poor and it will be seen that the rotatory powers were
decomparatively low.

Walden (loc. cit., 1895, 214) obtained ethyl *g*-chloro-
propanate, \([\alpha]_p^{5} = +47.66^\circ\), by the action of phosphoric
pentachloride on lactic acid, followed by the addition of
ethyl alcohol. He found the action of phosphorus pentabrom-
-
ide on lactic acid to be very vigorous, giving only a small yield of partly racemised ethyl \( \alpha \)-bromo-\( \beta \)-propanoate, \([\alpha]_D \) +20.5°. Ethyl \( \alpha \)-lactate in chloroform when added to the pentabromide gave ethyl \( \alpha \)-bromo-\( \beta \)-propanoate having \([\alpha]_D \) -43.5°.

The interaction of phosphorus pentachloride and of phosphorus pentabromide and ethyl \( \alpha \)-lactate in the presence of the tertiary bases, puridine, quinoline, and iminquinoline, has now been studied. Ethyl \( \gamma \)-chloropropanoate and ethyl \( \gamma \)-bromo-\( \beta \)-propanoate having high dextrorotatory powers were obtained, see table II. In every reaction the rotatory power of the product are opposite in sign to that of the ethyl lactate used; and had also a uniformly high value. It seems from this that the tertiary base ensures the formation of the complex which leads to an inversion.

With phosphorus pentachloride alone the following intermediate compound is probably formed,

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

whilst with pyridine this complex undergoes a further change to

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

whilst with guanidine this complex undergoes a further change to
In both complexes I and II the retarding group becomes positive, whilst the entering group exists as an anion in the vicinity of the asymmetric carbon atom. The second complex II however contains the retarding group in a preponderantly positive state and so facilitates the occurrence of an inversion, by ensuring that the removal of the bonding electrons of the asymmetric carbon atom and the oxygen is conducted in a regular manner, whilst the chlorine anion can approach the positively charged carbonium ion as the other three groups begin to swing over. The tertiary base displaces as a chlorine anion, a chlorine atom which is covalently linked to the phosphorus atom; and, by reason of the linkage which the base forms with the phosphorus atom, creates an additional positive centre in the group about to leave the molecule. As these seem to be the essential conditions for the occurrence of a sudden inversion, it may be concluded that ethyl d-l-malate is configuratively related to dextrorotatory ethyl α-chloropropionate and dextrorotatory ethyl α- bromopropionate.
(11) The interaction of ethyl 6-Lactate and phosphorus pentachloride considered from the standpoint of
Wurtz's hypothesis.

Wurtz (loc. cit.) contends that the replacement of the
hydroxyl group by chlorine through the agency of phosphorus
pentachloride or thionyl chloride is not the same type of
reaction as that involving the replacement of the hydroxyl
group by means of halogen ions. He does not allow that the
reaction with phosphorus pentachloride involves the pro-
duction of ions at all. He contends that when the phos-
phorus pentachloride reacts with a hydroxy compound, addition
or proximity of the pentachloride molecule causes the re-
moval of the hydroxyl group. Further, he contends that the
entering radical must, at the moment of the splitting of
the active molecule, always be very nearly at the same dis-
tance from the vacant place at the asymmetric carbon atom and
consequently the entering radical will always take very
nearly the same time in occupying the place. This distance
referred to will depend upon the nature of the reacting
molecules, but will be independent of the concentrations.
In what phase of the oscillation, replacement occurs, will
depend upon the structure of the molecules and upon the
period of oscillation. Wurtz concludes that, as these
quantities have constant values, only either the one or the
other form of the reaction product will result. It is im-
important to notice that in Södén's opinion only one form of the reaction product will be produced, and this may be of the inverted or the original configuration according to the structure and size of the reacting molecules and to the time of oscillation. Accidental influences such as casual shocks from the surrounding molecules of the solvent may cause a little racemisation; but if this latter occurs in a greater degree, then it is due to secondary influences not directly connected with the 'double decomposition'.

These conclusions are in the main not in agreement with the views of Kenyon and Phillips.

Firstly, whilst admitting that addition precedes the scission, he gives no indication of the cause or nature of such addition; whereas Kenyon and Phillips give definite formulation to the addition compounds which most likely arise.

Secondly, Kenyon and Phillips contend that with the exception of the particular case where a phenyl group is attached to the asymmetric carbon atom (compare Kenyon, Lipson, and Phillips, J., 1930, 415; Kenyon, Phillips, and Taylor, J., 1931, 352), the interaction of a hydroxy compound with such reagents as phosphorus pentachloride and thionyl chloride always proceeds either by the special mechanism which leads to inversion, or, through the liberation of the unstable carbonium cation, gives a completely racemised product.
As far as the optical purity of the product of this type of reaction is concerned, Hückel's postulate that the product should be practically optically pure is in agreement with the results of the experiments which have now been carried out. An examination of Table II reveals the remarkable regularity of the results obtained by the use of phosphorus pentachloride and pentatremoxide and of thionyl chloride in the presence of tertiary bases. There seems little doubt but that these values are approaching very closely to the values for the optically pure compounds.

It would seem, then, that if an inversion has accompanied the production of the ethyl g-chloropropionate and ethyl g-bromopropionate, it has taken place to the extent of practically a hundred per cent. The optical rotatory power of the ethyl g-chloropropionate obtained in these experiments, contrasts very clearly with the value of the rotatory power of the same compound obtained by the interaction of ethyl g-g-toluene-sulphonoxypropionate and lithium chloride. This again raises the question of the effect of the concentration of the reactants. It is evident that the tertiary base is much more effective in increasing the positive nature of the retiring group than is an alkali ion. This has the effect of ensuring that the reaction proceeds only in one way—by that mechanism leading to an inversion.

On these grounds it may be concluded that dextro-
rotary ethyl α-chloropropionate is configuratively re-
lated to ethyl d-(+)-lactate.

That the halogenation of hydroxy compounds by phos-
phorus pentachloride takes place with inversion was the
tentative conclusion reached by Frankland (J., 1913, 103, 713)
on the grounds of the regularity with which this reagent
causes a change in the sign of rotation when it converts a
hydroxy compound into its halogen derivative.

More recently, Kuhn and Wagner-Jauregg (Ber., 1928,
61, 481) have proposed a method for the elucidation of the
configuration of optically active substances which does not
depend on the comparison of optical activities. From a study
of the conversion of L-(−)-malic acid into d-(−)-chloro-
succinic acid by the action of phosphorus pentachloride,
these investigators conclude that an inversion occurs when
a hydroxy group is replaced by a chlorine atom during
halogenation by means of phosphorus pentachloride.
<table>
<thead>
<tr>
<th>TABLE II</th>
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<tbody>
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<td><strong>The Rotatory Forces of the Halogen Derivatives of Ethyl $d$-lactate prepared during the present investigation.</strong></td>
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<tr>
<td><strong>Ethyl $a$-Chlorocrotonate.</strong></td>
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<td>HCl on ethyl $d$-lactate + pyridine</td>
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<td>SOCl$_2$</td>
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<td>Chlorosulphinate + pyridine</td>
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<td>Heat on chlorosulphinate</td>
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<tr>
<td>p-Toluencesulphinate + Chlorine</td>
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<tr>
<td><strong>Ethyl $a$-Bromocrotonate</strong></td>
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<td>HBr on ethyl $d$-lactate + pyridine</td>
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<tr>
<td>p-Toluencesulphinate + bromine</td>
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<td>Ethyl $a$-chlorocrotonate prepared by saller, [oub]</td>
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<td>; $a$-bromo</td>
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IV. From a Consideration of the Sign of Rotatory Power of the Chloride obtained by the Decomposition of Ethyl α-Chlorosulphonylpropionate in the Presence and in the Absence of Pyridine.

(1) The mechanism of the decomposition of ethyl α-(+)-α-chlorosulphonylpropionate.

Frankland and Garner (3, 1914, 105, 1191) investigated the action of thionyl chloride on partially active ethyl lactate (α + 2.5°; l=1) in the absence of pyridine, and isolated the intermediate ethyl α-chlorosulphonylpropionate having α + 77.62°; l=1. They found that when this compound was heated with pyridine hydrochloride at 80° for six hours, sulphur dioxide was evolved and ethyl α-chloroacrylate (α -3.32°; l=1) was isolated. This last product, on heating with pyridine hydrochloride for 19 hours at 105°, entirely lost its activity.

Ethyl α-α-chlorosulphonylpropionate (α 16° +83.00; l=0.25; [α] 16° 5790 ) has now been prepared by the action of thionyl chloride in excess on ethyl d-lactate.

It is a colourless liquid which fumes in moist air, is
fairly stable to heat, but can be distilled only at the low pressure of the water tap vacuum pump. Since this reaction involves merely the replacement of the hydrogen of the hydroxyl group in ethyl $\delta$-lactate, it may be assumed as before that the linkages of the asymmetric carbon atom are undisturbed.

The chlorosulphonate will therefore have the same configuration as ethyl $\delta$-(+)lactate. When this chlorosulphonate is treated with pyridine in ethereal solution, a red oil gradually separates, leaving in solution ethyl $\delta$-chlorosulphonate which has a very high leucorotatory power ($\alpha^\circ = 21.7^\circ ; l=1$). It seems likely, that in this reaction, the pyridine displaces the chlorine atom of the chlorosulphonate as an anion. The sulphur group then becomes preponderantly positive and begins to leave the molecule, taking with it the binding electrons of the oxygen-asymmetric carbon atom, and thus tending to leave behind an unstable carbonium cation. Meanwhile, the other three groups begin to swing round, and the positive charge which begins to develop on the asymmetric carbon atom, orients the
chlorine anion so that this can become attached as soon as the retarding group leaves the molecule.

\[
\begin{align*}
\text{CH}_3\text{O} & \quad \text{CO Et} \\
H-C-O-S-Cl & + \text{Cl-} \\
\text{CO Et} & \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{O} & \quad \text{CO Et} \\
H-C-O-S-N^+ & + \text{Cl-} \\
\text{CO Et} & \\
\end{align*}
\]

'd' (+)

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

From a consideration of this mechanism it may be concluded that a Walden inversion has occurred, and that dextrorotatory ethyl \(\alpha\)-chloropropionate is configuratively related to ethyl \(\alpha\)-(-)-lactate.

Thus when the dextrorotatory chlorosulphinate was distilled at ordinary pressure, sulphur dioxide and a little hydrogen chloride were evolved and levo-rotatory ethyl \(\alpha\)-chloropropionate was isolated. It should be noted
that the rotatory power of the product of this reaction
is small, \( \alpha = -2.2; I = 0.5 \). This reaction probably involves
the splitting off of a chlorine anion which leaves behind
it a positively charged sulphur group. The sulphur group
then proceeds to leave the molecule, taking with it the
binding electrons between the asymmetric carbon atom and the
oxygen atom and tending thereby to produce a carboxonium
cation. Meanwhile the chlorine anion becomes suitably
orientated for attachment at the opposite side of the mole-
cule when the sulphur group finally retires.

\[
\begin{align*}
\text{CH}_3 & \quad \text{O}^- \\
\text{R} - \text{C} - \text{O} - \text{Et} - \text{Cl} & \quad \text{Cl}^- \\
\text{CO Et} & \quad 'd' (+) \\
& \quad \text{CO Et}
\end{align*}
\]

\[
\begin{align*}
\text{H} \text{CH}_3 & \quad \text{O}^- \\
\text{R} - \text{C} - \text{O} - \text{Et} - \text{Cl} & \quad \text{Cl}^- \\
\text{CO Et} & \quad 'l' (-) \\
& \quad \text{CO Et}
\end{align*}
\]

This is essentially the inversion mechanism, and supports
the conclusion previously drawn concerning the relative
configuration of ethyl \( d-(+) \)-lactate and its chloro-
derivative.

The low rotatory power of the product of the above
reaction indicates that considerable racemisation has taken
place. At the high temperature used to cause the decompos-
iton, it may happen that with some of the molecules the
positive group leaves too rapidly for the chlorine anion to become properly orientated for attachment to the positively charged carbon atom just as the positive group leaves. Consequently, carbonium cations are liberated and these add to the chlorine anions to form both configurations of the chloride in equal amounts. The rotatory power of the product then is due to that form which has been produced by inversion.

There is only one other recorded example of an optically active chlorosulphonate; this is amylechlorosulphonate prepared by Mc Kenzie and Clough (J., 1943, 103, 633). But Kenyon and Phillips (loc. cit.) postulate the intermediate formation of a chlorosulphonate whenever thionyl chloride reacts with a hydroxy compound. This intermediate compound, on decomposing by the mechanism described above, will give rise to a Walden inversion. In this connection, it is important to point out that there is one factor which may alter the course of the decomposition. If a phenyl group be attached to the asymmetric carbon atom, the electron attracting properties of the former may cause the latter to retain the C--O binding electrons and give rise to a stable carbocation anion.

\[
\begin{align*}
&\text{CH}_3\text{C}(-\text{Cl})\text{Cl} \quad \text{CH}_3\text{C}(-\text{Cl})\text{Cl} \\
&\text{EtCOO} \quad \text{EtCOO}
\end{align*}
\]
The stable carbonium ion attaches itself to the chlorine cation without inversion. Pyridine however, reverses the sign of rotation of the ethylphenylchlorocarbonate obtained from ethyl 1-mandelate, (Penyon, Lipscomb, and Phillips, J., 1939, 415). It is evident that the pyridine overcomes the effect of the phenyl group, and causes the retiring group to become sufficiently positive to enable it to take with it the bonding electrons between the oxygen and the asymmetric carbon atom, thus leaving behind the unstable carbonium cation which reacts with inversion as previously described.

(11) The interaction of ethyl 1-(−)-chlorosulphinoylpropionate with hydroxy compounds in the presence of pyridine.

When a mixture of n-amy alcohol and pyridine in ether is treated with ethyl 1-(−)-chlorosulphinoylpropionate a precipitate of pyridine hydrochloride is immediately formed, and a highly levorotatory ethyl lactylamyl sulphite is obtained from the ethereal solution. If ethyl L-lactate be substituted for the n-amy alcohol, then di-ethyl-lactyl sulphite is produced. The reaction follows a regular course.
giving rise to remarkably little by-product.

Two important observations may be made about these experiments.

1. A chlorosulphinate would immediately give a sulphite with a hydroxy compound in the presence of pyridine.

2. It may be possible to demonstrate the formation of the intermediate chlorosulphinate, in those cases in which it is too unstable to be isolated, by adding a mixture of an alcohol and pyridine and isolating the sulphite formed.

(iii) The interaction of ethyl d-lactate and thionyl chloride in the presence of tertiary bases.

The use of pyridine in conjunction with thionyl chloride was first described by Sarrzeus (Compt. rend., 1911, 152, 1514, 1601). When thionyl chloride is added to ethyl d-lactate in the presence of pyridine, quinoline and 1,2-quinolinol, levorotatory ethyl g-chloropropanoate of a uniformly high rotatory power is produced. On the basis of the theory of Kenyon and Phillips, the chlorosulphinate is first formed and this then decomposes by passing through the pyridine intermediate complex as already described. They contend (Kenyon Lipscomb and Phillips, loc. cit.) that the pyridine will actually assist in the production of the chlorosulphinate. This view, so far as it is applied to the chlorination of ethyl d-lactate, is now controverted. If the
chlorosulphinate were formed during the reaction, one would expect that a considerable quantity of di-ethyl-lactyl sulphite would be formed during the addition of thionyl chloride to a mixture of ethyl lactate and pyridine. This however is not in accord with the experimental results.

The evidence would indicate that in the presence of pyridine the intermediate chlorosulphinate is not formed. Then pyridine and ethyl lactate are mixed, a considerable amount of heat is evolved; a phenomenon which seems to indicate that chemical combination has taken place between these substances by a mechanism which may be represented thus:

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_3 \\
\text{H} & \quad \text{C} - \text{O} - \text{H} \quad + \quad \text{N}\left(\right) \\
\text{C}_2\text{H}_3\text{OH} & \quad \text{C}_2\text{H}_5\text{NH}^+ \quad \text{Cl}^{-}
\end{align*}
\]

The hydrogen of the hydroxyl group probably becomes co-ordinated with the nitrogen of the pyridine molecule. There is very strong evidence that the hydrogen of a hydroxyl group can by co-ordination acquire a valency of four (compare Sidgwick, *The Electronic Theory of Valency*, p. p. 73, 117, 147). The thionyl chloride may then react with this co-ordinated complex in the following way:
It is postulated that the sulphur atom of thionyl chloride loses a chlorine atom as an anion, becomes positively charged and co-ordinates with the oxygen atom of the hydroxyl group. This process has the effect of making the 'pyridine-hydroxyl' group preponderantly positive. Again we have the same general conditions for inversion; the preponderantly positive group on retirement tends to leave behind a carbocation which proceeds to orientate the chlorine anion suitably for attachment by inversion.
(iv) The constitution of the red oil formed when ethyl α-β-chlorosulphinoxypropionate is treated with pyridine in ethereal solution.

When ethyl α-chlorosulphinoxypropionate and pyridine are mixed together in ether, an ether insoluble red oil slowly separates, leaving an ethereal solution which contains a highly levorotatory ethyl α-chloropropionate, and, from the amounts of ionized chlorine and sulphur dioxide the ethereal solution yields, unchanged chlorosulphinate. The oil is completely soluble in water, giving rise to chlorine ions and sulphur dioxide, and yielding a picrate which is not pyridine picrate. No residue was obtained on removing the ether from the ethereal extract of the aqueous solution of the red oil.

The analysis of the picrate obtained (m.p. 93°, C. 16.9; H, 3.9) shows that the number of carbon atoms present is equal to the number of hydrogen atoms. The formula must therefore be C H as regards these two atoms. The base present in the red oil may be a reduction product of pyridine or may be some condensation product of pyridine and part of the lactic acid molecule. It is apparent that the constitution of the oil is worthy of further investigation.
THE RELATIVE CONFIGURATION OF ETHYL D-LACTATE
AND DEXTRANOLY ETHYL D-LACTATE.

V. SOME CONSIDERATION OF THE INFLUENCE OF THE
POLARITY OF THE SUBSTITUENTS ON THE MAGNITUDE AND
THE SIGN OF ROTATION OF ETHYL D-LACTATE DERIVATIVES.

(1) THE RELATIONSHIP BETWEEN THE ELECTRICAL POLARITY
AND ROTATORY POWER.

If the centres of gravity of the electronic and
nuclear charges in a molecule do not coincide, a permanent electric dipole will be produced. Højendahl, Fryth, Williams, ERRERA, and others have investigated compounds containing such dipoles with the result that definite dipole contributions may be assigned to individual groups. These groups may be arranged in a series representing a gradual transition from strongly electropositive - negative end of the pole towards the parent molecule, to strongly electronegative - positive end towards the parent molecule.

Recent investigations into the electronic structure
of matter lead to the view that molecular dissymmetry may depend upon the disposition and configuration of the combining electrons or the atoms themselves, rather than upon the arrangement of the atoms in the molecule. It seems likely therefore that the electric moment of the active
molecule will have some definite effect on the magnitude of the rotatory power; and that a definite alteration in the polarity of one of the groups will cause a definite change in rotatory power. A comprehensive investigation into the effect of the polarity of a substituent on the optical rotatory power of a compound is being carried out by Hulse and his co-workers (Trans. Faraday Soc., 1930, 32).

Now it follows that if changes in the polarity of substituents cause analogous changes in the magnitude of the rotatory power, then the derivatives, obtained from an optically active parent compound, when arranged in the order of their polarities should give a smooth series of rotatory powers, if the derivatives are configuratively related. There are two hindrances to the application of this method:

1. the order of the groups in accordance with their polarities, as determined by different methods, is not always the same, and

2. partial racemisation may throw the rotatory powers of the derivatives out of a smooth series.

Nevertheless, as data are accumulated, this method may prove to be a valuable corroborative test of relative configuration.
(11) An examination of the series of derivatives of ethyl d(+)-lactate.

Table III of the document contains a list of the compounds prepared during the course of this investigation. It will be seen that the dextro-rotatory power of the members of this series decreases from the acetate through the bromide, chloride, hydroxy compound to the benzoate. This is also roughly the order of increasing positive polarity of the groups, COOC₂H₅, Br, Cl, OH, COOC₆H₅, and indicates that the derivatives forming this series are configuratively related.

Certain investigations (see references at the end of this section) lead to the conclusion that the hydroxyl group is more positive than the bromine group; but there is definite evidence that the benzoyle group is much more positive than either of these so that the dextro-rotatory bromide and the hydroxy compound fit in better with the series containing the levorotatory benzoyle and thiocyno derivatives, than would the levorotatory bromide and hydroxy compound.

It may be accepted (Robinson J., 1926, ) that the p-toluene sulphonyl group is less positive than the benzoyle group. The dextro-rotatory p-toluene sulphonate of ethyl d-lactate is therefore more correctly placed in the series given than would be its enantiomer. So too with
the thiocyanato and selenocyanato derivatives: experiment shows (Herckenrath and Zeilermann, Ber., 1925, 58, 736) that these groups should be placed towards the positive end of the polarity series. The levo-rotatory thiocyanopropionate is therefore much better placed in the given rotatory power series than would be its dextrorotatory isomer. The selenocyanato derivative should be more levo-rotatory that the thiocyanato derivative; but probably the ethyl $\alpha$-selenocyanopropionate obtained from the $\alpha$-toluenesulphonate was partly racemised. Nevertheless, the dextrorotatory isomer would be still more discordant if it were inserted instead.

(iii) Conclusions.

Considering then, that experiments on the determination of relative polarities lead to the view that the lactate group is more negative than the CH, Cl, Br, groups, which are themselves situated towards the negative end of the series, whilst the benzoyl and thiocyanato groups are definitely situated well over to the positive end, it may be concluded that dextrorotatory ethyl $\alpha$-chloropropionate belongs to the same series as ethyl $\alpha$-lactate and is therefore configuratively related to the latter.

Support of this conclusion is forthcoming from the experiments of Patterson and Lawson (J., 1923, 2042) on the relative configuration of the derivatives of $\text{methyl } \beta$-($\text{--}$)-lactate. In these experiments, dispersion effects were used
as a criterion of relative configuration. Table IV shows that the order of increasing dextrorotation of the acetate hydroxy compound and the benzoate is similar to the order of increasing positive polarity of the CH, COCH, CH, C H CO groups.

This tendency is also maintained in the series given in table V.

<table>
<thead>
<tr>
<th>Table V</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Intactory Lovers of Derivatives of Ethyl d-Lactate which are supposed to have the same configuration.</td>
<td></td>
</tr>
<tr>
<td>R-C=O-C-Cl</td>
<td>α</td>
</tr>
<tr>
<td>R-C=O-He</td>
<td>90.1</td>
</tr>
<tr>
<td>R-C=O-COC H</td>
<td>74</td>
</tr>
<tr>
<td>R-C=O-Et</td>
<td>79.7</td>
</tr>
<tr>
<td>R-C=O-COC H</td>
<td>56</td>
</tr>
<tr>
<td>R-C=O-C H</td>
<td>53.4</td>
</tr>
<tr>
<td>R-C=O-CH</td>
<td>3</td>
</tr>
<tr>
<td>R=Br</td>
<td>43.5</td>
</tr>
<tr>
<td>R=OCOC H C H</td>
<td>41.4</td>
</tr>
<tr>
<td>R=Cl</td>
<td>31</td>
</tr>
<tr>
<td>R=NH</td>
<td>11.26</td>
</tr>
<tr>
<td>R=NH</td>
<td>11.2</td>
</tr>
<tr>
<td>R=OCN</td>
<td>-1.7</td>
</tr>
<tr>
<td>R=SCH</td>
<td>-45</td>
</tr>
<tr>
<td>R=CCOC H</td>
<td>-27.2</td>
</tr>
</tbody>
</table>
### TABLE 11

The rotatory powers of ketone 1-isocetate and its derivatives which are supposed to have the same configuration.

<table>
<thead>
<tr>
<th></th>
<th>( \alpha )</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H-OCOCH</td>
<td>5730</td>
<td>236.7°</td>
</tr>
<tr>
<td>H-CH3</td>
<td></td>
<td>93.6</td>
</tr>
<tr>
<td>H-OCOOCH</td>
<td></td>
<td>54.6</td>
</tr>
<tr>
<td>H-OCOOCH Cl</td>
<td></td>
<td>49.1</td>
</tr>
<tr>
<td>H-OCOOCH2Cl</td>
<td></td>
<td>34.2</td>
</tr>
<tr>
<td>H-OCOOCl</td>
<td></td>
<td>22.81</td>
</tr>
<tr>
<td>H-CH</td>
<td></td>
<td>8.22</td>
</tr>
<tr>
<td>H-OCOC H</td>
<td></td>
<td>21.1</td>
</tr>
<tr>
<td>H-OCO C H (NO)</td>
<td></td>
<td>51.3</td>
</tr>
</tbody>
</table>

### TABLE 14

The rotatory powers of d-amp alcohol and its derivatives supposed to be formed without change in configuration.

<table>
<thead>
<tr>
<th></th>
<th>( \alpha_0 )</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H-CH</td>
<td></td>
<td>5.2°</td>
</tr>
<tr>
<td>H-CH3</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>H-OCOOCH2</td>
<td></td>
<td>3.2</td>
</tr>
<tr>
<td>H-OCOOCl</td>
<td></td>
<td>4.9</td>
</tr>
<tr>
<td>H-OCOOCH2Cl</td>
<td></td>
<td>5.1</td>
</tr>
<tr>
<td>H-Fr</td>
<td></td>
<td>9.5</td>
</tr>
<tr>
<td>H-OCOC H</td>
<td></td>
<td>9.5</td>
</tr>
</tbody>
</table>
The Selection of a Series of Substituent Groups.

of interest in the present investigation, arranged according to their probable polarities, so as to represent a gradual transition from electronegative to strongly electropositive groups.

From the study of dipole moments, Williams infers that the following groups are arranged in the order of increasing positive polarity:

\[ \text{Cl} \quad \text{Br} \quad \text{Cl} \quad \text{CH} \]

Flurscheim (Mem. Manchester Phil. Soc., 1929, 61, 111) studied the influence of substituents on the dissociation constants of substituted acetic and benzoic acids, and from his conclusions it may be inferred that the groups Cl, Br, and CO are situated distinctly towards the positive end of the polarity series.

By the measurements of the decomposition potentials of the corresponding potassium salts in aqueous solution, Berckenbach and Fellermann (loc. cit.) show that the thio-cyano and the selenocyano groups should be placed well over to the positive end of the polarity series, whilst the Cl and the Br groups should be placed towards the negative end.

\[ \text{F} \quad \text{Cl} \quad \text{Br} \quad \text{SCH} \quad \text{SeCH} \]
The OEt and OCH₃ groups are negative groups. Their relative directing power has been examined by Robinson (J. 1925, 193).

The position of the sulphonyl group may be inferred from the work of Robinson (loc. cit.) who nitrated the various derivatives of E₂S₅₇₅ and estimated the proportions of o-, m-, and p- isomerides formed in each case.

Ingold (J. 1926, 2440) has studied the directing influence of the groups H.H, R.NH, R.NH₂, R.NR₂, by nitrating compounds of this type and determining the proportions of the ortho, meta, and para derivatives formed in each case. He found that on nitrating E₂NE₃, the proportion of the meta derivative was 85%, whilst Kollman and de Bruyn (loc. trav. Chem. 1919, 12, 79) found that 46% of the meta derivative was formed when E₂NO₂ was nitrated.

From these considerations the following series may be deduced.

\[
\begin{array}{cccccc}
\text{NH} & \text{CH} & \text{NO} & \text{NE} \\
2 & 2 & 2 & 3 \\
\end{array}
\]

Since it has been shown that benzoic acid is a stronger acid than acetic acid, it may be inferred that the acetoxy group is a negative group whilst the benzoyloxy group tends to act as a positive group.

From such considerations as these the following series is adopted as representing a gradual transition from
electro-negative groups to strongly electro-positive groups.

\[
\begin{array}{c}
\text{H, CH}_3, \text{CN, OCN, Br, Cl, OH,} \\
\text{OH, COC CH}_2 \text{, CN, OCN, Br, Cl, OH,}
\end{array}
\]
The Molecular Dissymmetry of Sulfimates
Chlorosulfimates and Mixed Sulfimates.

(1) **The probable cause of the high rotatory power of ethyl d(+)-α-chlorosulphinoxypropionate.**

From table III it will be seen that the ethyl d-g-chlorosulphinoxypropionate prepared by the interaction of ethyl d-lactate and thiocynl chloride has an unusually high rotatory power. This is seen clearly by a comparison of the magnitudes of the rotatory powers of the ethyl d-lactyl derivatives containing the grouping

$$\text{CH (CHOROR) CO C H,}$$

where $R = \text{Cl}$

<table>
<thead>
<tr>
<th>$R$</th>
<th>$\alpha$</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>+532°</td>
<td>1</td>
</tr>
<tr>
<td>CH(C(O)CO Et</td>
<td>+138.4°</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>$\text{H}$</td>
<td>+53.3°</td>
<td></td>
</tr>
</tbody>
</table>

Now it can be seen from table III that, in general, the rotatory powers of ethyl d-lactyl derivatives decrease in magnitude as the positive nature of the substituent increases. But the chlorine group (Cl) is more positive than either the asyl (CC H ) or the ethyl lactyl

$$\text{(CH CH(O)CO Et) group ; and yet the rotatory power of}$$
the chlorosulphinate, CH$_3$CH(C6H5COCl) CO Et, is much higher than that of either ethyl $\text{d}$-lactyl $\text{p}$-amyl sulphite or ethyl $\text{d}$-dilactyl sulphite. Furthermore, it is unusual for an organic substance of a simple structure, of which the rotatory power depends solely on the presence of one asymmetric carbon atom, to have a rotatory power as high as 332°.

There is, however, a possible additional source of the rotatory power of ethyl $\text{d}$-glycerol sulphinate. By the preparation of $\text{p}$-alkyl esters of $\text{p}$-toluenesulphinic acid in an optically active condition, Phillips (J., 1929, 127, 2252) has shown that a sulphur atom attached to three dissimilar groups can give rise to an asymmetric molecule. Phillips concluded that the classical formula assigned to sulphinic esters, CH$_3$C=O(\text{S})OR, inadequately expresses their structure.

In the basis of the electronic theory of valency, the sulphur atom has six electrons in the valency orbits.

"It can form a di-covalent compound by sharing two of its electrons with two other groups and so complete its octet in the following way:

\[ \text{R}^1 \text{S}^+ \text{R}^1 \]

If the octet be considered as the maximum for sulphur, the only way in which it can form further attachments is
by donating electrons to other groups and becoming positively charged. In other words, it may combine with other groups or atoms by forming semipolar linkages (compare Lowry, Trans. Faraday Soc., 1923, 19, 285). The structure of ethyl p-toluenesulphonate should therefore be represented thus:

\[
\begin{align*}
\text{O Et} & \quad \text{O Et} & \quad \text{O Et} \\
\text{S} & \quad \text{S} & \quad \text{S} \\
\text{C H} & \quad \text{C H} & \quad \text{C H} \\
77 & \quad 77 & \quad 77
\end{align*}
\]

Experimental evidence for the postulated existence of a semipolar link between the sulphur and the sulphonyl-oxygen atoms has been obtained by the determination of the parahor of compounds containing this group. The parahor (Fugden J., 1924, 125, 1177; ibid., 1925, 127, 1525, 1668, 2517) provides evidence of the existence of two kinds of double bond. The parahors of such compounds as ethylene and acetone, in which the double bond consists of four shared electrons, indicate that this 'non-polar' type of double bond contributes +23 units to the value of the molecular parahor. On the other hand, an examination of the parahors of such compounds as diethyl sulphite, thionyl chloride and phosphorus oxychloride, which on the basis of the electronic theory of valency should be formulated:

\[
\begin{align*}
\text{EtO} & \quad \text{Cl} & \quad \text{Cl} \\
\text{R} & \quad \text{R} & \quad \frac{1}{2}
\end{align*}
\]
shows that an increment of 23 units is not contributed by this type of bond. This semipolar type of bond actually contributes a decrement of about -1.6 units to the parac-chor of the molecule in which it occurs.

Sugden (compare Hillips, loc.cit.) has determined the paracbor of ethyl \textit{p}-toluenesulphonate. The observed value, 410.3, agrees very closely with the paracbor of 410.7 cal-culated on the assumption that the bond between the sulphur atom and the sulphonoyl oxygen atom is semipolar. If the bond in this compound were a non-polar double bond, the calculated paracbor would then be 435.5.

The spatial disposition of the sulphur atom in such sulphonates may be represented by the structure:

\[
\begin{array}{c}
R' \\
\text{S} \\
R
\end{array}
\]

in which the sulphur atom and other groups occupy the apices of a tetra-}

hedron.

Similar centres of asymmetry as that which exists in ethyl \textit{p}-toluenesulphonate have been shown to exist in mixed sulphonates and sulphilamines by Tennyson, Clark, Harri-
sen, and Hillips (J., 1926, 2973; 1927, 183) who resolved the following compounds into their enantiomers:

\[
\begin{align*}
\alpha & = 25^\circ \\
\beta & = 423^\circ \\
\gamma & = 127^\circ \\
\delta & = 124^\circ
\end{align*}
\]
From the above results it can be concluded therefore that chlorosulphonates and mixed sulphites will probably have the constitution:

\[ R-\text{O}^\ominus \text{Cl} \quad \text{and} \quad R-\delta^\ominus \text{O}^\ominus \text{Cl} \]

and that the sulphur atoms of chlorosulphonates and unsymmetrical sulphites will be asymmetric.

The chlorosulphonate obtained by the action of thionyl chloride on ethyl \( \delta \)-lactate may not be an equimolecular mixture of the two probable forms, ethyl \( \delta \)-lactyl \( \delta \)-chlorosulphonate and ethyl \( \delta \)-lactyl \( \delta \)-chlorosulphonate, but may contain an excess of one of these isomers. Now the paragraph of thionyl chloride, 17h.5, reveals the probable presence of a semipolar link in this molecule, so that the sulphur, chlorine and oxygen atoms may be so disposed in space that they occupy the corners of a tetrahedron:

\[ \begin{array}{c}
\text{Cl} \\
a \\
\text{S} \\
\text{Cl} \\
b \\
\text{O} \\
\end{array} \]

Such a molecule is of course symmetrical and cannot exist in enantiomorphous forms, but it is important in the present discussion to distinguish between the two chlorine atoms: for if Cl(a) were replaced by the ethyl \( \delta \)-lactyl group the resulting molecule may be ethyl \( \delta \)-lactyl \( \delta \)(sae)-chlorosulphonate, whilst if Cl(b) were replaced by the ethyl \( \delta \)-lactyl group, ethyl \( \delta \)-lactyl \( \delta \)-chlorosulphonate may
It will be seen that the structures represented by (I) and (II) are not enantiomorphously related and so the molecules which these diagrams represent may not be formed with equal velocities. The thionyl chloride may, under the influence of the asymmetric centre in ethyl d-lactate, react in a preferential way, giving more of the one form than of the other. Indeed, it was noted that from the standpoint of asymmetric synthesis, the interaction of thionyl chloride is in some respects unique.

A probable intermediate stage in this reaction would conceivably be the formation of the complex:
The complex (III) probably results through the process involving first the co-ordination of the hydroxyl hydrogen atom of the ethyl \(\delta\)-lactate molecule with one of the chlorine atoms of the thiocarbonyl chloride molecule. This co-ordination may then cause the OR group to become negatively charged and to split off as an anion. The positive charge on the sulphur atom then orients the -OR anion so that the sulphur atom can become attached to this anion as the positively charged \(\text{HCl}^+\) group leaves the molecule. Now it will be seen that the optically active ethyl \(\delta\)-lactate can co-ordinate with either of the two similarly linked chlorine atoms: in so doing it will cause the sulphur atom to become asymmetric, and will decide the configuration of the chlorosulphenoxy radical produced. Under these circumstances it is conceivable that the reaction might occur so that only one isomer was produced. Such an occurrence has of course never been detected during studies of asymmetric synthesis involving the production of an asymmetric carbon atom; but amongst
those studies it is difficult to find an example in which
the production of a new asymmetric centre would appear to
be so closely under the control of the existing optically
active group. Usually the existing optically active group
is separated from the carbon atom which is to be made asym-
metric, as in the reduction of 1-sentyl pyruvate (Mc

\[
\text{reduction} \\
\text{CH}_3 \text{CO}_2\text{C}_6\text{H}_5 \xrightarrow{-} \text{CH}_3 \text{CO}_2\text{C}_6\text{H}_4 \text{CH}_3
\]

Cohen and Shiosuma (J., 1921, 112, 1816) obtained an active
phenylethocetic acid (\( \alpha_D = -10^\circ \) in alcohol solution).
by the action of thionyl chloride on the racemic mandelic
ester of \( \beta \)-senthol. The result obtained in this exper-
iment may in some way be due to the production of an asym-
metric sulphur atom in the intermediate chlorosulphinate,
the formation of which is postulated by Kenyon, Lipacomb,
and Phillips (J., 1930, 415).

If the interaction of thionyl chloride and ethyl \( \beta \)-
lactate is attended by a complete asymmetric synthesis,
so that only one isomer is produced, then the high rotat-
ory power of the chlorosulphinate obtained would be account-
ed for; since many of the optically active sulphur compounds
of this type which have been resolved, have high rotary
powers.
Evidence of the optical purity of ethyl d-
\text{-}d$\text{-}$chlorosulphinoxypropionate.

For the reasons which have been stated in the fore-
going section, attempts have been made to obtain evidence
as to the optical purity of ethyl d-$d$-chlorosulphinoxy-
propionate.

Phillips (loc. cit.) has shown that d-$d$-octyl-d$_2$-p-
toluene sulphinate is readily separated into its isomers by
careful fractional distillation. In a similar way, ethyl
d-$d$-d$_2$-p-toluene sulphinoxypropionate has now been partly
separated into its isomers by a slow fractional distillation
at low pressure. From table $\overline{V_{19}}$, it is evident that
the differences in the values of the rotatory powers of
the fractions collected is due to the separation of the
two forms of the sulphinate, ethyl l-$d$-d$_2$-p-toluene sulph-
inoxypropionate and ethyl l-$d$-d$_2$-p-toluene sulphinoxypropion-
ate. For instance in table $\overline{V_{19}}$ (iv), although the refract-
ive indices of the fractions are practically the same and
the temperature of the distillation remains almost constant,
it will be seen that the rotatory powers of the first and
last fractions are no different as $\alpha$ = $7.13^\circ$ and
$\alpha$ = $19.67^\circ$ for $l = 0.25$. The occurrence of these two forms
of the sulphinate are presumably due to the presence of an
asymmetric sulphur atom in the sulphinate portion of the
Evidence of the separation of the isomers of ethyl 1-lactyl n-amyl sulphite by fractional distillation has now been obtained. An examination of Table VII shows that the rotatory powers of the fractions collected differ very widely, although the refractive indices and the sulphur content of the fractions remain practically the same. For instance, in the record of the last distillation on p. 115 it will be seen that whereas the first fraction has a rotatory power of $\alpha = -15.12^\circ; l=2.5$, the last fraction has a rotatory power of $\alpha = -48.31^\circ; l=3.5$, but the refractive indices of these two fractions differ only by three units in the fourth decimal place, and the determined sulphur content in practically the same for the first as for the last fraction. It seems from these distillation experiments that the ethyl 1-lactyl n-amyl sulphite prepared by the interaction of ethyl 1-q-chlorosulphinoxypropionate and n-amyl alcohol in the presence of pyridine, is a mixture of

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \quad \text{H} \\
\text{H-C-C-C-C-C H} & \quad \text{and} \\
\text{CO H} & \quad \text{2} \quad \text{5} \quad \text{11} \quad \text{5} \quad \text{11}
\end{align*}
\]

'1' '1' 'd'
Furthermore, it seems to be adequately demonstrated that isomers of this nature can be separated by careful slow fractional distillation.

From the foregoing results then, it is reasonable to suppose that if the chlorosulphinate from ethyl d-lactate is a mixture of the d-lactyl d-chlorosulphinate and d-lactyl l-chlorosulphinate, these would be separable by fractional distillation. An examination of table VIII will reveal the fact that there were no indications that the chlorosulphinate could be separated into fractions having distinctly different rotatory powers. Considering the chemical nature of the chlorosulphinate, the boiling points, refractive indices and rotatory powers of the various fractions were remarkably constant. From the high value of the rotatory power of this compound, it might be expected that if both forms were present and were separable by distillation, obvious indications of such a separation would reveal themselves as relatively large differences in the values of the rotatory powers of the fractions.

It would seem then, from these experiments, that the ethyl d-d-chlorosulphanoxypropionate prepared by the interaction of ethyl d-lactate and vinyl chloride may be optically pure and consist of only one of the two possible isomers:

\[
\begin{align*}
\text{R} & : -\text{O} \quad \text{R} : -\text{O} \\
\text{Cl} & : -\text{Cl} \\
\text{C} & : -\text{C}1
\end{align*}
\]
In order to obtain further evidence as to the optical purity of ethyl D-α-chlorosulphinoxypropionate, ethyl-lactyl n-asyl sulphite was prepared by two methods. In the actual experiment, ethyl l-lactate was used so that in the following discussion this form is referred to.

1. If the chlorosulphinate of ethyl l-lactate consists of the one form only, then when it reacts with n-asyl alcohol it may give but one form of ethyl l-lactyl n-asyl sulphite:

$$\text{CH}_3 - \text{CH}_2 - \text{C} - \text{O} - \text{CH}_2 - \text{COEt} \quad \text{CH}_3 - \text{CH}_2 - \text{C} - \text{O} - \text{CH}_2 - \text{COEt}$$

2. Whilst thionyl chloride, under the influence of the asymmetric centre in ethyl l-lactate, may give, by a complete asymmetric synthesis, only one of the chlorosulphinate; it will give the two probable forms of n-asyl chlorosulphinate when it reacts with n-asyl alcohol, for the latter does not contain an asymmetric centre. The di-n-asyl chlorosulphinate so produced should give by its interaction with ethyl l-lactate the two probable forms of ethyl l-lactyl
If the foregoing is a correct statement of the case, then one would expect the magnitude of the rotary power of the sulphite prepared by method (1.) to be widely different from the magnitude of the rotary power of the sulphite prepared by method (2.). This was not found to be so. The rotary powers of the two specimens of ethyl 1-lactyl \( n \)-amyl sulphite prepared by the two methods, 1 and 2, were practically the same: the ethyl 1-lactyl \( n \)-amyl sulphite prepared from ethyl 1-\( \alpha \)-chlorosulphinoxy-propanate and \( n \)-amyl alcohol had \( \alpha = -35.14^\circ; l=0.5 \), whilst the sulphite prepared from \( n \)-amyl chlorosulphinate and ethyl 1-lactate had \( \alpha = -37.15^\circ; l=0.5 \). Furthermore, the sulphite obtained from ethyl 1-\( \alpha \)-chlorosulphinoxy-propanate (method 1), \( \alpha = -33.14; l=0.5 \), on careful distillation gave fractions which had different rotary powers but practically the same refractive index and sulphur content, compare table VII. The same phenomena were observed when the sulphite prepared from \( n \)-amyl chlorosulphinate (method 2) was carefully distilled. These results seem to indicate that both preparations,
that obtained by method 1, and that obtained by method 2, are mixtures of the two forms of the sulphite, ethyl L-lactyl \( \alpha \)-amyl \( \alpha \)-sulphite and ethyl L-lactyl \( \alpha \)-amyl L-sulphite.

It may not be concluded that because the sulphite prepared from ethyl \( \alpha \)-chlorosulphinoxypropionate (method 1) appeared to be a mixture of the two forms of the sulphite, then the original ethyl \( \alpha \)-chlorosulphinoxypropionate was a mixture of the two probable forms of the chlorosulphinate; for it may be that the two forms of sulphite arise owing to the occurrence of racemisation during the reaction. The interaction between the ethyl \( \alpha \)-chlorosulphinoxypropionate and \( \alpha \)-amyl alcohol involves the replacement of the chlorine atom which is directly attached to the sulphur atom, the asymmetry of which is probable. Although it is conceivable that under these circumstances racemisation may occur, it cannot be inferred that it has taken place; and so the results obtained from the preparation of ethyl L-lactyl \( \alpha \)-amyl sulphite by the methods 1 and 2, may not be considered as evidence as to the optical purity of ethyl \( \alpha \)-chlorosulphinoxypropionate prepared by the interaction of thionyl chloride on ethyl L-lactate.

(iii) The mechanism of the production of ethyl L-lactyl \( \alpha \)-amyl sulphite.
The preparation of ethyl 1-lactyl p-aryl sulphite by the interaction of ethyl 1-g-chlorosulphinoxypropionate with p-aryl alcohol did not proceed smoothly. A mixture of substances was obtained which distilled over a wide range of temperature. By a long series of fractional distillations the presence in this mixture of di-p-aryl sulphite, ethyl 1-lactyl p-aryl sulphite and ethyl di-1-lactyl sulphite was revealed, but the isolation of these substances in a pure state in this way would prove to be a very tedious process. Evidence of their presence was obtained by comparing the respective fractions with the pure substances prepared by different methods.

Then ethyl 1-g-chlorosulphinoxypropionate is treated with p-aryl alcohol, hydrogen chloride is evolved, and this last substance may cause secondary reactions to take place in such a way as to give rise to the three sulphites mentioned above. It is suggested that the p-aryl alcohol first coordinates with the chlorine atom of the chlorosulphinate, and then the aryl group separates as an anion leaving the Cl-H group positively charged. This latter group then leaves the sulphur atom, taking with it the C-Cl bonding electrons and thus developing an additional positive charge on the sulphur atom. Meanwhile the aryl-oxy anion becomes orientated by the positive charge on the sulphur atom, so that it joins onto the latter as the Cl-H.
group leaves:

\[
\begin{align*}
&\text{CH}_3 \quad \text{C}^- \\
&\downarrow \quad \uparrow \quad \uparrow \\
&\text{H} \quad \text{CH}_3-\text{O} \quad \text{Cl} \quad \text{H} \\
&\text{CO CO}_2 \text{H} \quad 5 \quad 11
\end{align*}
\]

\[
\begin{align*}
&\text{CH}_3 \quad \text{C}^- \\
&\downarrow \quad \uparrow \quad \uparrow \\
&\text{H} \quad \text{CH}_3-\text{O} \quad \text{Cl} \quad \text{H} \\
&\text{CO CO}_2 \text{H} \quad 5 \quad 11
\end{align*}
\]

To account for the production of both ethyl di-lactyl sulphite and di-n-amyl sulphite, it may be assumed that the chlorine ion from the hydrogen chloride molecule begins to form an attachment with the positively charged sulphur atom of the ethyl lactyl n-amyl sulphite and causes the ethyl lactyl group to leave the sulphur atom as an anion:

\[
\begin{align*}
&\text{CH}_3 \quad \text{C}^- \\
&\downarrow \quad \uparrow \quad \uparrow \\
&\text{H} \quad \text{CH}_3-\text{O} \quad \text{Cl}_2 \quad \text{H} \\
&\text{CO CO}_2 \text{H} \quad 5 \quad 11
\end{align*}
\]

This ethyl lactyl anion can then form ethyl di-lactyl sulphite by competing with the asyloxy anion for the
lactyl sulphinooxy cation, \( \text{III} \). The aryl chlorosulphinate, \( \text{VII} \), can then react with the aryl alcohol to form di-aryl sulphite.

Since pyridine had proved to be such a valuable reagent in experiments involving the use of thiocetyl chloride, ethyl lactyl chlorosulphinate, \( p \)-toluenesulphonic and sulphinic chlorides, it was thought that possibly it would facilitate the formation of mixed sulphites by removing the hydrogen chloride which was liberated. The experiments which were then carried out with pyridine showed that this reagent has a remarkable influence on the course of the reaction, resulting in a good yield of ethyl lactyl \( p \)-aryl sulphite almost entirely free from by-products. It is suggested that when the pyridine is mixed with \( p \)-aryl alcohol in petrol-ether solution, the following changes take place:

\[
\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{pyridine}} \text{CH}_2\text{CH}_2\text{Cl} \text{Na}^+ \text{CH}_3\text{CN} \]

when the chlorosulphinate is added to this complex, the pyridinium ion co-ordinates with the chlorine atom of the chlorosulphinate and forms the complex:

\[
\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{pyridine}} \text{Cl}^+\text{Na}^-\text{CH}_3\text{CN} \]

which then decomposes by a process involving the retirement of \(-\text{Cl}\text{H}:\text{NC}_5\text{H}_4^+\) as pyrid-
ine hydrochloride whilst the allyloxy union joins on to the sulphur atom. The pyridine removes the R-Cl group in a regular manner from the sphere of the reaction, a process facilitated by the insolubility of pyridine hydrochloride in petroleum ether.

That pyridine facilitates the formation of mixed sulphotes was observed independently by Voss and Planke (Annalen, 1931, 487, 253), who showed that if pyridine were omitted in the preparation of ethyl methyl sulphite, a mixture of di-methylsulphite, di-ethylsulphite, and methyl ethyl sulphite ensued.

(iv) **The attempts to resolve n-allyl di-chlorosulphinates.**

Attempts were made to demonstrate the presence of an asymmetric centre in the chlorosulphinates by the resolution of n-allyl chlorosulphinates. The method adopted for this purpose depends upon the difference in reaction velocity which may be induced by an asymmetric environment. If an optically active compound B reacts with the two forms of an optically compound A and A', it does not follow that the velocities will be equal in the two cases. Though the affinity constants m will be equal, there will in general be a difference in reaction velocities, because the products formed are not mirror images.

Then the product obtained by mixing two molecular equivalents of n-allyl chlorosulphinates with one molec-
ular equivalent of ethyl 1-dl-lactate was distilled, a small quantity of n-amyl chlorosulphinate having a small levorotation was obtained. By-products were produced during this reaction as has already been explained, and so the yield of the chlorosulphinate was small.

With l-menthol in the absence of pyridine a fraction was obtained which boiled over a range of temperature including the boiling point of pure n-amyl chlorosulphinate, but had a strong mentholic odour, darkened rapidly and had a comparatively high rotatory power, $\alpha _p +12.6^\circ; l=0.5$.

From the mixture obtained by first treating n-amyl chlorosulphinate with l-menthol in the presence of pyridine then adding ethyl alcohol and pyridine, a small quantity of feebly levorotatory ethyl n-amyl sulphite was obtained. (v) The paraphors of ethyl n-chlorosulphinomethylate n-amyl chlorosulphinate, and ethyl-lactyl n-amyl sulphite.

It has been pointed out, p. 55, that the paraphor of a compound may reveal which bond — a non-polar or a semi-polar double bond — is present in the molecule. In order to throw further light on the electronic environment of the sulphur atom in each of the three compounds mentioned above, their paraphors were determined. The details of the calculation and the experimental technique involved are discussed fully in the experimental
The observed paracch for ethyl \( \gamma \)-chloroaliphosphoxy-propionate was found to be 330.5 (mean), which is almost identical with the sum of the atomic paracchors, 330.4, for the structure \( \text{CH} \{\text{CO} \text{Cl}) \text{CO} \text{C} \text{Ol} \}, \) ignoring the bond 
\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\end{array}
\]
between the sulphur atom and the sulphonyl-oxygen atom. If this bond were a double bond then the calculated paracchor would become 403.4. The observed paracch for ethyl \( \gamma \)-chloro-propionate, using the same apparatus and technique, was found to be 291.7. The paracchor increment caused by the \( (-\text{O-S-O}-) \) group is therefore 58.8, a value which is almost identical with the mere sum of the atomic paracchors for the oxygen atoms and one sulphur atom, 58.2. From this it may be concluded that the measurements of the paracchor indicate the presence of a semipolar bond, associated with the sulphur atom, in ethyl \( \gamma \)-chloroaliphosphoxy-propionate.

The observed paracch for \( \gamma \)-methyl chlorosulphinate, 535.4, is very nearly equal to the sum of the atomic paracchors for this compound, 534.6. The observed paracch 556.7 for ethyl-lactyl \( \gamma \)-methyl sulphite is in accord with the sum of the atomic paracchors, 555.2. It may be concluded that these compounds also contain a semipolar link.
CONCLUSION

In this Thesis it is suggested that the mechanism of the substitution of the hydroxyl group of ethyl \(\beta\)-lactate by a chlorine atom, through the agency of either phosphorus pentachloride or thionyl chloride in the absence or presence of tertiary bases, always involves the formation and subsequent decomposition of intermediate compounds. Such compounds have been given definite formulation in terms of the electronic theory of valency; and their probable mode of decomposition has been definitely indicated. These intermediate compounds have two fundamental features in common:

1. they all give levorotatory ethyl \(\alpha\)-chloropropionate;
2. the retiring group, being preponderantly positive, takes away the binding electrons and proceeds to expose a carbonium cation, which then orientates the entering anion suitably for attachment at the opposite side of the molecule as the other three groups begin to oscillate.

It is contended that this mechanism leads to a Sieden inversion. Pyridine may facilitate such an inversion by increasing the positive nature of the retiring group.

It is also suggested that during the decomposition of the \(p\)-toluenesulphonate of ethyl \(\beta\)-lactate by means of lithium chloride, and during the decomposition of the \(p\)-toluenesulphinate of ethyl \(\beta\)-lactate by means of chlorine
similarly constituted intermediate compounds form. The probable formulation of these compounds has also been given. It is pointed out that these intermediate compounds have also the fundamental features mentioned in 1, and 2, and so it is contended that they too decompose by that mechanism which leads to inversion.

On these grounds it is concluded that ethyl \( \alpha \)-lactate has the same configuration as dextrorotatory ethyl \( \alpha \)-chloro-propionate.

This conclusion is in harmony with the views of Kuhn (loc. cit.) and of Freudenberg and Lux (Ber., 1928, 61, 1083). The latter investigators, reviewing the results afforded by optical and chemical methods of determining the configurations of active compounds, indicate that \( \alpha \)-hydroxy acids and \( \alpha \)-halogen acids of the same configuration almost universally suffer similar changes in rotation under the influence of the same substituents provided that the use of solvents is avoided and all dipolar and associating groups (carboxyl, hydroxyl, amino,) are masked, (compare Clough, J., 1918, 113, 526). They conclude that dextrorotatory \( \alpha \)-halogeno acids are configuratively related to the dextrorotatory \( \alpha \)-hydroxy acids.

By the fractional distillation of octyl \( \alpha \)-toluene-sulphinate, ethyl \( \alpha \)-\( \gamma \)-toluene-sulphinoxypropionate, and ethyl-\( \gamma \)-actyl \( \alpha \)-amyl sulphite, evidence is obtained that
these compounds may be separated into isomers due to the asymmetric nature of the sulphur atom they contain.

There is evidence that n-amyl chlorosulphinate can be obtained in an optically active condition. The para-chords of ethyl γ-chlorosulphinooxypropionate and n-amyl chlorosulphinate indicate the presence in these compounds of a semipolar link.

It may be concluded that the chlorosulphinate group, \( \text{R} --- \text{SOCl} \), contains a semipolar link and has an asymmetric environment.

Of the two experimental methods which were tried to produce evidence as to the optical purity of ethyl γ-chlorosulphinooxy propionate, one - the fractional distillation method - gave a positive result, whilst the other - the preparation of ethyl-lactyl n-amyl sulphite in two ways - gave a negative result. The optical purity of this chlorosulphinate then, must be left an open question.
EXPERIMENTAL

The Resolution and Esterification of Lactic Acid.

Purdie and Walker (J., 1892, 64, 754) attempted the resolution of lactic acid by means of the strychnine salt; and although definite signs of resolution were observed, the process was slow and unsatisfactory.

Purdie (J., 1893, 63, 1143) found that when a supersaturated solution of zinc ammonium lactate was inoculated with a seed of either the 'l' or the 'd' salt, a partly active salt was deposited. This is an example of the tendency pointed out by Gernon (Compt. rend., 1866, 63, 543), of a supersaturated solution of an optically inactive compound to deposit the excess solute in one form only when suitably seeded, even when the racemoid is the stable phase.

Most of the ethyl l-lactate which was used in the present investigation was made from l-lactic acid obtained from inactive zinc ammonium lactate by following the instructions of Purdie and Walker (J., 1895, 67, 616).

Four litres of a hot supersaturated solution containing two litres of lactic acid, previously rendered alkaline with ammonia, and 1120 g. of zinc lactate, were filtered through glass wool and poured into two
large glass globes (arc lamp covers) and cooled rapidly. Leavo-rotatory seeds of the fully active zinc ammonium lactate were then stirred in carefully, and after 14 hours, the liquor was filtered from the heavy sludge which had formed. The filtrate was then heated with more zinc lactate and treated as before, except that the dextrorotatory zinc ammonium salt was used as the seed. By seeding alternately with the one form and then the other, nine crops were obtained, each weighing about 250 g. and having \( \alpha^\circ_{D} 1.41 \); \( l=2 \), for 1.51 g. in 20 cc of dilute ammonia solution (50 cc of concentrated ammonia solution and 100 cc of water). The impure zinc ammonium lactate was recrystallised five times from ammonia solution until the specific rotatory power reached the value of \( \alpha^\circ_{D} -13.10 \); \( c = 3 \), compare \( \alpha^\circ_{D} +10.0^\circ \), Wood and scarf (J., 1923, 124, 600).

Very little use seems to have been made of this method. Henderson and Prentice (J., 1902, 81, 653) reported that although they found the method tedious, it gave excellent results when the requisite precautions were observed.

Jungfleisch (Compt. rend., 1904, 134, 56) resolved lactic acid by the use of quinine, but does not give exact data of the yields. The morphine method discovered by Irvine (J., 1906, 82, 939) was improved by
Patterson and Forsyth (J., 131, 103, 2363) who, using a principle first applied by Pope and Peachey (J., 132, 73, 1896), added only half the molecular quantity of morphine to the solution of lactic acid which had been treated with a half the molecular quantity of caustic soda. In this way practically the whole of the morphine is deposited as the sparingly soluble salt of $d$(-) lactic acid. Two careful recrystallizations of this salt from water are sufficient to give an optically pure morphine $d$-lactate, having $\alpha_D = 71.3^\circ, c=5$.

Most of the ethyl $d$-lactate used in the present investigation was obtained from $d$-lactic acid which had been prepared from inactive lactic acid by this method.

It sometimes happens that commercial lactic acid is partly active, and this has significance in the resolution process, for, in the Kurdie method, it decides which seed should be added first, whilst in the morphine method it decides the proportions of morphine and caustic soda which should be used for a maximum yield of the morphine salt. Furthermore, if the activity of the commercial specimen of lactic acid is considerable, as indeed it sometimes is, then the best way of obtaining optically pure lactic acid is to take advantage of the greater solubility of the active zinc lactate over that of the racemate (Patterson and Forsyth, loc. cit.).
The following methods have been used to esterify optically active lactic acid.

1. By the silver salt method, Walker (J., 1895, 67, 914) obtained ethyl α-lactate having \( [\alpha]_D^{19} +10.5^\circ \).

2. By the action of sulphuric acid and ethyl alcohol on optically active zink ammonium lactate, Burdie and Williamson obtained ethyl β-lactate having \( [\alpha]_D^{19} -18.05^\circ \) (J., 1896, 64, 818).

3. By refluxing the sodium α-lactate, obtained by decomposing the morphine salt, with ethyl \( p \)-toluenesulphonate, Kenyon, Phillips, and Turley (loc. cit) obtained ethyl α-lactate having \( [\alpha]_D^{19} +11.29^\circ \).

It is now accepted that the value obtained by Walker is too high; his product was most likely contaminated by the highly rotating ethyl α-ethoxypropionate.

In the present investigation it was found convenient to acidify the ammonium salt solution, obtained by decomposing the morphine salt, with sulphuric acid and to extract the lactic acid in a continuous extraction apparatus using ether as the solvent. The lactic acid obtained from the dried ether extract was mixed with twice the theoretical quantity of ethyl alcohol and double this volume of dry benzene, a half a cc. of concentrated sulphuric acid being also added to catalyse the reaction. The mixture was heated on an oil bath kept at
96° for 5 hours, during which time, the ternary mixture of ethyl alcohol, benzene and water distilled slowly through an eight bulb fractionating column. Then the distillation of the water ceased, the process was stopped; and after neutralising the sulphuric acid with calcium carbonate, the product was distilled. Ethyl d-lactate was obtained having b.p. 34-56°/17mm., n° 1.4156, α°D +5.70°; l=0.5.

The Interaction between Ethyl 1-α-p-Toluenesulphonoxypyrroprionate and Potassium Thiocyanate.

Ethyl 1-dl-α-p-toluenesulphonylpropionate (13.6g. α°D=37.7; l=1) was refluxed in alcohol solution with potassium thiocyanate (8g.) for six hours. The product was mixed with ether and filtered from the potassium p-toluenesulphonate which separated during the reaction. From the ether extract, ethyl α-thiocyanopropionate was obtained having b.p. 116-118°/13mm., α°D = -0.08°; l=1, n° 1.4650, and weighing 12g.

Found: C, 45.3; H, 5.55; CH₂CH(CH₃)COOC₂H₅ requires: C, 45.28; H, 5.66%.

The ethyl α-thiocyanopropionate obtained by using the same p-toluenesulphonate (10.86g) and potassium thiocyanate (4.88g.) in 40cc of alcohol had b.p. 119-120°/
From fully active sulphonate (α \(^{20^\circ}\) -27.5\(^{\circ}\); l=0.5, 5893)

8.16 g. and potassium thiocyanate (4 g.) in 50 cc of alcohol, ethyl α-thiocyanopropionate was obtained having b.p. 112\(^{\circ}\)/20 mm., α \(^{20^\circ}\) -7.5\(^{\circ}\); l=0.5, n 1.4657.

Pound : C, 45.2; H, 5.7%.

**The Interaction between Ethyl 1-α-p-Toluenesulphonyloxynopropionate and Potassium Selenocyanide.**

Potassium selenocyanide (6 g.) was dissolved in 50 cc of alcohol (93%) and refluxed with ethyl 1-α-p-toluene-sulphonyloxynopropionate (α \(^{20^\circ}\) -27.5\(^{\circ}\); l=0.5, 10 g.).

A red colouration developed immediately and a thick mass of potassium p-toluenesulphonate was thrown down during the first five minutes. After refluxing for six hours, the product was treated with a large bulk of water (300 cc) and extracted with ether. The residue remaining after the removal of the dry ether was heated to 90\(^{\circ}\) at 15 mm., and then distilled on the 'lyvac' pump. Ethyl α-selenocyanopropionate was obtained having b.p. 91 mm. 63-64\(^{\circ}\), α \(^{17.5^\circ}\) -0.89; l= α - 0.91, α \(^{17.5^\circ}\) -1.38, n 1.4905.
The selenium content was estimated by weighing the elementary selenium which was precipitated by sulphur-dioxide, after first decomposing the compound with nitric acid in a sealed tube as in the estimation of sulphur by the Carus method.

Found: Se, 35.0.  CH$_3$SCOCOOCC$_2$ requires: Se, 35.3.

The ethyl $\beta$-$\gamma$-toluenesulphonate used in the experiments, which have been described in the foregoing, was made by the interaction of ethyl $\beta$-lactate and $\gamma$-toluenesulphonic chloride in the presence of pyridine as described by Kenyon, Phillips, and Turley (loc. cit.).

The potassium selenocyanide used was made by the interaction of elementary selenium and potassium cyanide (Muthmann & Schröder, Ber., 1900, 35, 1765).

The Preparation and Reactions of Ethyl $\beta$-$\gamma$-$\delta$-$\epsilon$-Toluenesulphinocyanonate.

(1) The preparation of the $\delta$-toluenesulphinate.

$\delta$-Toluenesulphonic acid was precipitated from a hot filtered solution of sodium $\gamma$-toluenesulphinonate by the addition of hydrochloric acid. The crystals were filtered, washed and pressed, and then desiccated over calcium chloride in a vacuum desiccator for two weeks.
the calcium chloride being renewed from time to time.

In the meantime, commercially purified thionyl chloride was distilled successively from quinoline, linseed oil, and beeswax (Meyer and Schlegel, Monatsh., 1915, 24, 562). The final product was water white and had b.p. 78°. All the thionyl chloride used in this investigation was so purified.

The final product was water white and had b.p. 78°. All the thionyl chloride used in this investigation was so purified.

p-Toluenesulphinyl chloride was made when required by the method of Hilditch and Smiles (Proc., 1908, 14, 4113; Hilditch, J., 1910, 27, 2935). Thionyl chloride (43 g., 1.1 mol.) was dissolved in an equal volume of dry ether. To this solution the dried sulphinic acid (52 g.) was added slowly with constant agitation. When all the acid had dissolved, the mixture was warmed very gently until all the hydrogen chloride ceased to be evolved. The ether and excess thionyl chloride were then removed in a vacuum at ordinary temperature, and the oily residue was dissolved in petroleum ether. This solution was filtered from a small quantity of white solid which separated and then subjected to a vacuum at ordinary temperature for a day. The p-toluenesulphinyl chloride remained as a pale yellow oil.

The p-toluenesulphinyl chloride (35 g.) was then added slowly with vigorous stirring to a mixture of ethyl d-lactate (α° +11.5°; l=1, 25 g.) and dry pyridine(1:1 5893
mol.) cooled in a freezing mixture. After 12 hours, water was added and the ether extract of the resulting liquid was washed well with water, dilute hydrochloric acid, water, and finally dried over potassium carbonate. The residue obtained on removing the ether was heated to 100° at 15 mm., and then distilled on the 'hyvac' pump. Ethyl \( \alpha \)-\( \alpha \)-p-toluene sulphinoxy propionate was obtained having b.p. 110°/0.1 mm., oil bath temperature 133-134° C.,

\[
\begin{align*}
\alpha &= +12.41^\circ, \\
\beta &= +14.83^\circ, \\
\gamma &= +24.2^\circ; \\
\lambda &= 0.25, \\
\mu &= 4359.
\end{align*}
\]

\( n D = 1.5199 \). This specimen was re-distilled twice, a large middle fraction being collected during each distillation. The final specimen of ethyl \( \alpha \)-\( \alpha \)-p-toluene sulphinoxy propionate had

\[
\begin{align*}
\alpha &= +13.38^\circ, \\
\beta &= +15.77^\circ, \\
\gamma &= +26.81^\circ; \\
\lambda &= 0.25, \\
\mu &= 4359.
\end{align*}
\]

\( n D = 1.5197, d = 1.163, d = 1.131. \) Yield: 60%. 1.0376 g. of this specimen required 16.1 cc of \( \frac{1}{2} \) alcoholic potash solution for hydrolysis. Mol. weight found: 257.7, calculated: 256.

The following specimens of the sulphinate were prepared in the same way;
(i) from ethyl d-lactate $\alpha^\circ/\rho = +11.3^\circ$; $l = 0.25$.

(ii) $l-$; $\alpha = -13.24^\circ$.

(iii) $l-$d-1$-$; $\alpha = -8.55^\circ$.

(ii) The oxidation of ethyl d-\(\alpha\)-\(\beta\)-toluenesulphinoxypropionate to the corresponding sulphonate.

Ethyl $d$-(\(\alpha\)-\(\beta\)-toluenesulphinoxypropionate (2.56 g., $\alpha^\circ/\rho = +13.35^\circ$; $l = 0.25$) was mixed with acetone (25 cc.) and magnesium sulphate (0.63 g.) dissolved in 4 cc. of water. To this mixture was added slowly with vigorous stirring potassium permanganate (0.63 g.), when permanently coloured with permanganate, the mixture was treated with water, decolorised with sulphur dioxide, and extracted with ether. Ethyl $d$-(\(\alpha\)-\(\beta\)-toluenesulphinoxypropionate was obtained from the dried ether extract; it had b.p. 135$^\circ/0.1$ mm., $n^\rho 1.5005$, $\alpha^\circ/\rho = +13.95^\circ$.

$\alpha = 18.5^\circ + 15.89^\circ$; $l = 0.25$. This rotatory power compares favourably with that of the ethyl $d$-(\(\alpha\)-\(\beta\)-toluenesulphinoxypropionate, $\alpha = 21^\circ + 32.2^\circ$; $l = 0.5$, $n^\rho 16.5^\circ$.

1.5011, prepared from $p$-toluenesulphonyl chloride by
Kersten, Phillips, and Turley (loc. cit.).

0.352 g. of the sulphonate required 31.15 cc of N/2 caustic potash solution for hydrolysis. Molecular wt found: 273.0, calculated: 272.

(iii) The interaction of chlorine water and ethyl d-(+)-α-p-toluenesulphonylpropionate.

Ethyl d-(+)-α-p-toluenesulphonylpropionate (5.12 g., α = +13.35°; l=0.25) was added slowly with vigorous shaking to the required volume of chlorine water made by passing purified chlorine into ice cold water. Heat was evolved, and after being shaken for an hour, the liquid was cooled in a freezing mixture. The crystalline p-toluenesulphonyl chloride which separated was filtered, washed with petroleum ether and recrystallised from this solvent. It had m.p. 70°, and gave an amide with ammonium carbonate having m.p. 137°.

The ethyl α-chloropropionate obtained from the dried petroleum ether extract of the reaction liquor, had b.p. 46°/13 mm., α = +5.25°; l=0.25, n = 1.44169.

On re-distillation under ordinary pressure the specimen had b.p. 143-144°/756 mm., α = -5.27°, α = -4.63°; l=0.25.
The interaction of bromine and ethyl d-(+)-
\(\alpha\)-p-toluene-sulphonyloxypropionate.

Bromine (4.8 g. in 20 cc of chloroform) was added slowly to ethyl d-(+)-\(\alpha\)-p-toluene-sulphonyloxypropionate (7.68 g., \(\alpha\)° +13.35; \(l=0.25\)) in 25 cc of chloroform.

At the end of eight days practically complete decolorisation had taken place. The solvent was drawn off in a vacuum at ordinary temperature, the residue was diluted with petroleum ether and cooled in a freezing mixture. The \(\alpha\)-toluene-sulphonyl bromide (6.5 g.) which separated as a mushy crystalline mass gave an amide with ammonium carbonate having m.p. 137°.

The ethyl \(\alpha\)-bromopropionate obtained from the ether solution had b.p. 55-58°/15 mm., 156-157°/760 mm.,

\[
\begin{align*}
\alpha & = 55°, \\
\beta & = 57°, \\
\alpha & = 16°, \\
\beta & = 16°.
\end{align*}
\]

Found: Br 44.32; C 57.90.

CH\(\text{ClBrCOCOC} \text{H}_2\) requires: Br, 44.24.

From a specimen of 1-dl-\(\alpha\)-toluene-sulphinate, ethyl \(\alpha\)-bromopropionate was obtained by the same method. It had

\[
\begin{align*}
\alpha & = 57°, \\
\beta & = 5.95°; l=0.5.
\end{align*}
\]
The interaction of hypochlorous acid and ethyl d-(-)-α-p-toluenesulphinoxypropionate.

Ethyl d-(-)-α-p-toluenesulphinoxypropionate (10.24 g., α = 65°; l=1) was shaken vigorously with the requisite quantity of hypochlorous acid solution (Organic Syntheses, 5, 31) until a blue colour was persistently given to starch-iodide paper. The liquor was cooled in a freezing mixture, and the p-toluenesulphonyl chloride which separated as a crystalline mass was filtered, washed and recrystallised from petroleum ether. It gave an amide with ammonium carbonate having m.p. 137°, the chloride itself having m.p. 70° and weighing 4.9 g.

The petroleum ether extract of the reaction liquid gave after drying a liquid which distilled at 45-56°/14 mm, and had nD 1.4177, αD -5.31°; l=0.5.

After nine distillations through a column two homogeneous liquids were obtained. These were ethyl α-chloropropionate which had b.p. 42°/14 mm, nD 1.4166, α 16° -9.10°; l=0.5, found: Cl, 25.68; calc. Cl, 26.01; and ethyl l-(-)-lactate which had b.p. 45-51°/14 mm, α 16° -4.78°; l=0.5, nD 1.4155, found: molecular weight by hydrolysis, D 417.6, calc. 418.
(vi) An attempt to prepare ethyl α-thiocyanopropionate by the interaction of thiocyanogen and ethyl 1-α-p-toluene sulphonylpropionate.

A solution of thiocyanogen in glacial acetic acid was prepared by the method of Kaufmann (Analyst, 1926, 51, 157) and standardised by adding a measured volume of the solution to potassium iodide solution and titrating the liberated iodine with sodium thiosulphate solution. Ethyl 1-α-p-toluene sulphonylpropionate (10 g., α = 21.5°; l = 0.5) was slowly added to this solution of thiocyanogen (100 cc), drops of the reaction liquid being removed from time to time for testing with starch-iodide paper. When all the sulphinate had been added the resulting liquid no longer gave a blue colour with the paper. Water was added, and the aqueous liquid was extracted with petroleum ether. After being washed well with water, dilute sodium carbonate solution and water, the ethereal extract was dried over anhydrous sodium sulphate. The residue remaining on the removal of the ether was small (4.0 g.) and decomposed when attempts were made to distil it under a pressure of 14 mm.

(vii) An attempt to prepare ethyl α-selenocyanopropionate by the interaction of triseleno cyanogen and ethyl 1-α-p-toluene sulphonylpropionate.

To prepare triseleno cyanogen (Peters, private com-
A dilute mixture of chlorine and moist air was passed over the surface of a 20% solution of potassium selenocyanide (see p. 62) in water kept cool by a freezing mixture of ice and salt. A red precipitate formed, which, after the concentration of the chlorine in the moist air had been gradually increased over the period of an hour, turned yellow. This yellow precipitate was filtered, dried, and recrystallised from chloroform, m.p. 134.°

Trisceleno cyanogen (14 g.) was dissolved in chloroform and refluxed with ethyl 1-g-p-toluenesulphinoxypropionate (10g. α -21.9°; l=0.5) for several days. The yellow colour due to the seleno-cyanogen persisted and a small amount of selenium was deposited. On working up the liquid in the usual way, a residue was obtained which decomposed when an attempt was made to distil it on the 'hyvac' pump, 0.1 mm.
The Separation of the Isomers of Ethyl 1-α-β-dl-Toluene-
sulphinoxypropionate by Distillation.

The ethyl 1-α-β-dl-toluene-sulphinoxypropionate obtained as described on page 83 had after two preliminary
distillations α = -15.72; l = 0.25. This specimen was then
distilled very slowly on the 'hyvac' pump at 0.1 mm. The
temperature of the distillation rose from 110° to 112°
whilst the fractions were being collected.

(i) The first fractionation gave:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>α</th>
<th>l</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>-8.75°; l = 0.25, 20°</td>
<td>5461</td>
<td>1.5170</td>
</tr>
<tr>
<td>F2</td>
<td>-9.57°</td>
<td></td>
<td>1.5156</td>
</tr>
<tr>
<td>F3</td>
<td>-12.75°</td>
<td></td>
<td>1.5192</td>
</tr>
<tr>
<td>F4</td>
<td>-19.21°</td>
<td></td>
<td>1.5198</td>
</tr>
</tbody>
</table>

(ii) Each of these fractions was separated into two
fractions.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>α</th>
<th>l</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF1</td>
<td>-3.00°; l = 0.25, 20°</td>
<td>5461</td>
<td>1.5165</td>
</tr>
<tr>
<td>BF1</td>
<td>-11.41°</td>
<td></td>
<td>1.5189</td>
</tr>
<tr>
<td></td>
<td>20°</td>
<td></td>
<td>20°</td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>AP2</td>
<td>α</td>
<td>54.61</td>
<td>n</td>
</tr>
<tr>
<td>BF2</td>
<td>-12.79°</td>
<td>1.5191</td>
<td></td>
</tr>
<tr>
<td>AP3</td>
<td>-7.75°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BF3</td>
<td>-15.31°</td>
<td>1.5197</td>
<td></td>
</tr>
<tr>
<td>AP4</td>
<td>-17.10°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BF4</td>
<td>-22.85°</td>
<td>1.5200</td>
<td></td>
</tr>
</tbody>
</table>

(iii) AP2 and AP3 were mixed and distilled:

A; -3.16°; 1.5179  
B; -10.51°; 1.5193  

(iv) BF1, BF2, BF3 and AP4 were mixed and distilled:

C; -7.13°; 1.5195  
D; -12.34°; 1.5198  
E; -12.67°; 1.5199  

Fraction B, found: C; 56.03; H; 5.93; S; 12.59%  
Fraction C, found: C; 55.5; H; 5.76; S; 12.94%  
Calculated for CH$_2$CH(=O)C$_6$H$_5$: C; 56.2; H; 6.25; S; 12.5%
A different specimen of ethyl l-γ-<i>p</i>-dl-toluencesulphinoxypropionate (α<sup>16°</sup> = -15.7; l=0.25) was distilled six times, a large middle fraction being collected each time until the refractive index remained practically constant. The final specimen had α<sup>16°</sup> = -15.7; l=0.25, 17°

n 1.5198. This was now distilled very slowly over a period of four hours and the following fractions were collected.

<table>
<thead>
<tr>
<th>l=0.25</th>
<th>19°</th>
<th>19°</th>
<th>19°</th>
<th>19.5°</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5799</td>
<td>5461</td>
<td>4305</td>
<td></td>
</tr>
</tbody>
</table>

F1:  -2.97°  -3.24°  -3.75°  1.5198
F2:  -11.75° -13.34° -22.75° 1.5199
F3:  -18.13° -20.68°  —    1.5200

It will be seen that the fractions vary considerably in rotatory power although the refractive index remains practically constant. The variation in rotatory power is presumably due to the separation of the isomers of ethyl l-γ-<i>p</i>-dl-toluencesulphinoxypropionate.

(i) With phosphorus pentachloride and pyridine.

A mixture of ethyl L-(−)-lactate (α = −11.15°; λ=1, 11.8 g., 1 mol.) and pyridine (7.3 g., 1 mol.) was added slowly to phosphorus pentachloride (40.3 g., 2 mol.) with vigorous stirring and intense cooling. The final mixture was heated at 50–60° for an hour, and then slowly added to iced water. The oil which separated was extracted treated with ether and from the dried ether extract ethyl α-chloropropionate was obtained having b.p. 41-42°/13 mm., b.p. 144°/761 mm., α° 20.9°; λ=1, n° 1.4163, 879°  

$$d_4 = 1.0725.$$ Found: Cl, 23.86, calculated: Cl, 26.9.

(ii) With phosphorus pentachloride and quinoline.

A mixture of ethyl L-(−)-lactate (α = −11.15°; λ=1, 5.9 g., 1 mol.) and quinoline (6.45 g., 1 mol.) was added to phosphorus pentachloride (20.4 g., 2 mol.) as described under (i). The ethyl α-chloropropionate obtained had b.p. 143-144°/761 mm., α° 20.98°; λ=1, n° 1.4168, 879°.
and weighed 3.8 g. Found: Cl, 25.9, calculated: Cl, 26.0%.

(iv) with phosphorus pentachloride and isoquinoline.

Ethyl α-chloropropionate was obtained from the same quantity of reagents as in (ii), but using isoquinoline instead of quinoline. It had b.p. 143-144°/761 mm., weighed 3.85 g., and had α + 20.50°; d = 1, n D 1.4167.

Found: Cl, 25.9; calculated: Cl, 26.0%.

(iv) with phosphorus pentachloride and potassium carbonate.

Phosphorus pentachloride was added to dry ether (20.4 g., 2 moles in 40 cc.) and well shaken to break up the crystalline conglomerates. Potassium carbonate (13.4 g., 2 moles) was then added and to the resulting mixture ethyl-β-lactate (5.9 g., 1 mol., α = 11.15°; d = 1) was slowly added with vigorous shaking and cooling. The product was poured into iced water and extracted with ether. From the dried ether extract, ethyl α-chloropropionate was obtained having b.p. 143-144°/760 mm., α = 20.56°; d = 1, n D 1.4165.

Found: Cl, 25.61; calculated: Cl, 26.0%. Yield: 3.7 g.
(v) With phosphorus pentabromide and pyridine.

Ethyl L-lactate ($\alpha = -11.15^\circ$, $\lambda = 1$, 3.54 g., 1 mol.) was mixed with pyridine (4.64 g., 2 mols) and added slowly with stirring and cooling to phosphorus pentabromide (12.33 g., 1 mol.) just covered with dry benzene. A vigorous reaction occurred and the mass became pasty. After standing at ordinary temperature for three hours, the mass was mixed carefully with iced water, and the oil which separated was extracted with ether. From the dried ether extract, ethyl $\alpha$-bromopropionate was obtained having b.p. 55-57$^\circ$ /15 mm., $\alpha^{17^\circ} = 22.05^\circ$, $\lambda = 3.5$, $n^D_{1.4458}$, $d_4^1 = 1.3872$, and weighing 2.0 g.

(vi) With phosphorus pentabromide and quinoline.

Ethyl $\alpha$-bromopropionate was obtained by using quinoline (2.0 g., 1 mol.) and the same quantities of ethyl L-lactate and phosphorus pentabromide as in (v). It had b.p. 55-55$^\circ$ /15 mm., $\alpha^{17^\circ} = 21.92^\circ$, $\lambda = 0.5$, $d_4^1 = 1.3875$, $n^D_{1.4458}$, and weighed 2.1 g.

(vii) With phosphorus pentabromide and isoquinoline.

Using the same quantities of reagents as in (vi)
ethyl d-tromopropionate was obtained having b.p. 36-37 / 17°  17°  11°  16°  15°  
17 mm., α 17°  -22.06°, l=0.5, d 16.8°, n 1.3573, ρ 1.4456., 
and weighing 1.85 g.
Found: Br, 44.32 %. CH₂CBrCOOC₂H requires: Br, 44.21.
3  3

The Interaction of Thionyl Chloride and Ethyl d-
Lactate in the Presence of Tertiary Bases.

(1) In the presence of Pyridine.

Ethyl d-lactate (4.72 g., α 16° D) was mixed 
with pyridine (3.16 g.) and cooled well in a freezing mix-
ture. Thionyl chloride (4.75 g.) was then added very slowly 
with shaking and cooling. Towards the middle of this oper-
ation the mass became almost solid but changed to a gummy 
consistency on the further addition of the reagent. After 
being allowed to warm to the room temperature, the mixture 
was heated at 60° for an hour and then poured into iced 
water. The dried ether extract of this liquid gave on dis-
tillation ethyl d-chloropropionate which had b.p. 45°/19mm., 
17°  17°  17°  17°  17°  
19.56°  -22.06°, α -23.38°, d -44.8°, l=1, 
5893  5790  4561  4359
20°  15°  5
n 1.4166, d 1.3353, and weighed 3.8 g.
(ii) In the presence of quinoline.

The same procedure and quantities of ethyl $\beta$-lactate and thionyl chloride as in (i) were used. In the presence of quinoline (5.36 g.) ethyl $\gamma$-chloropropionate was obtained having b.p. 40.5°/13m.

\[ \begin{align*}
\alpha & = -15.36, \quad \beta = -23.61, \quad \gamma = -25.00, \quad \delta = 44.01; \\
\alpha & = 5833, \quad \beta = 5720, \quad \gamma = 5461, \quad \delta = 4359.
\end{align*} \]

1st, $\alpha = 1.4165$, $\beta = 1.0354$, and weighing 3.9 g.

Yield: 0.1, 25.9, calculated: 0.1, 26.3.

(iii) In the presence of isoquinoline.

Using the same quantities of reagents and procedure as in (ii) ethyl $\gamma$-chloropropionate was obtained having

\[ \begin{align*}
\text{b.p.} & = 40.5°/13m., \quad \alpha = 17°, \quad \beta = -20.13, \quad \gamma = -22.51, \quad \delta = 1.4167; \\
\alpha & = 5833, \quad \beta = 5720, \quad \gamma = 5461, \quad \delta = 4359.
\end{align*} \]

$\beta = 1.0355$, and weighing 3.1 g.
The preparation and reactions of ethyl d-(+)
α-chlorosulphinoxypropionate.

(i) The preparation of ethyl d-(+) α-chlorosulphinoxy-
propionate.

Ethyl d-(+) lactate (14.5 g; α +11.5°; l = 1) was slowly
added to thionyl chloride (22 g, excess) with agitation
and cooling (Frankland and Garner, J, 1914, 105,
1101). Heat was evolved and there was a copious evolut-
ion of hydrogen chloride. After being heated on a water
bath for two hours, the product was heated at 90° at a
pressure of 15 mm. For two hours and then distilled on the
'thvac' pump. A long necked flask was used having a long
side tube surrounded by a condenser packed with ice. The
entire bulk distilled at 45-45°/0.1 mm. Ethyl d-α-chloro-
prophinoxypropionate was thus obtained having

16° α +83.85°, α +75.05°, α +172.4°; l = 0.25, n 1.4533;
5790 54.64 4.359

16°

13°

1.2019

Frankland and Garner (loc. cit) obtained by the same
method ethyl d-dl-α-chlorosulphinoxypropionate having

16° α +77.62°; l = 1, from ethyl d-dl-lactate (α + 2.5°; l = 1).

The density and refractive index were not stated.
The fractional distillation of ethyl d-α-chlorosulphinoxypropionate.

If the sulphur atom in ethyl d-α-chlorosulphinoxypropionate is asymmetric, this compound as prepared by the method described in (1) may be a mixture of the two isomers, ethyl d-α-dichlorosulphinoxypropionate and ethyl d-α-l-chlorosulphinoxypropionate. With the purpose of effecting the separation of these isomers, ethyl d-α-chlorosulphinoxypropionate (α = +53.0°; λ = 0.36), prepared and distilled as described in (1), was very slowly distilled into fractions the rotatory powers and refractive indices of which were determined.

Table VIII (p. 106) is a record of the data obtained from this distillation. It will be seen from this table that there is very little change in rotatory power as the distillation progresses.

The action of water on ethyl d-α-chlorosulphinoxypropionate.

Ethyl d-α-chlorosulphinoxypropionate (α = +82.0°; λ = 0.36) was shaken with water for five minutes, and then the resulting liquid was extracted with ether. The ethereal extract was washed well with water and dilute sodium carbonate solution, and finally dried over anhydrous sodium sulphate. The ethyl d-lactate which
was obtained from the ethereal extract had b.p. 45°/12 mm., α\(^{16\circ}\) +11.02; l=1, n\(^{15\circ}\) 1.4155, and weighed 2 g.

The rotatory power of the ethyl d-lactate from which the ethyl d-chlorosulphinoxypropionate was made had α\(^{16\circ}\) +11.5°; l=1; so that it will be seen that very little racemisation has occurred during these reactions.

(iv) The action of heat on ethyl d-α-chlorosulphinoxypropionate.

Ethyl d-α-chlorosulphinoxypropionate (α\(^{16\circ}\) +63.94; l=0.25, 15 g.) was distilled slowly through a column at ordinary pressure. Sulphur dioxide and a little hydrogen chloride were evolved. The distillate weighed 10.91 g. and had α\(^{16\circ}\) +6.2°; l=0.5. For the complete loss of sulphur dioxide, 15 g. of the chlorosulphinate should lose 4.8 g. in weight. The distillate was dissolved in ether, washed with water, dilute sodium carbonate solution, water, and finally dried over potassium carbonate. The ethyl d-chloro- propionate obtained from the ethereal extract had b.p. 143-145°/156 mm., α\(^{16\circ}\) -2.2°; l=0.5, n\(^{17\circ}\) 1.4168, and weighed 7.95 g.

(v) The interaction between pyridine and ethyl d-α- chlorosulphinoxypropionate in ethereal solution.
Pyridine (15.0 g., 1 mol.) was added slowly with cooling to ethyl d-\(\text{dichlorosulfoxipropionate (40 g., 1 mol.) in 50cc of dry ether. A small white precipitate (0.41 g.) formed immediately and from this the solution was filtered. The filtrate was allowed to stand in a stoppered flask for two days and during this time a pale yellow oil separated. The oil darkened to a red colour, settled on the bottom of the flask, and left a clear supernatent ethereal layer. By decantation the ethereal layer was transferred to a stoppered measuring cylinder, and made up to 100 cc. by ether washings from the red oil. The flask was then placed on the pump for an hour to remove adherent solvent. The oil frothed somewhat, probably due to the evolution of sulphur dioxide, and finally weighed 20 g.

A weighed sample of the oil (1.130 g.) was steam distilled from phosphoric acid. The liberated sulphur dioxide decolorised 71.1 cc of C.0072 N iodine solution.

Found: 80.152.

2.759 g. of the oil was dissolved in water and the resulting solution was made up to 100 cc. 20 Cc portions of this solution were titrated by the Volhard method for the estimation of chloride ion. 23.66 Cc of \(\text{F/10 silver nitrate}\)
nitrate were required: Cl, 14.43.

10 cc of the ethereal solution were shaken with caustic soda solution in a stoppered flask, and after the removal of the ether, the sulphur dioxide was estimated by distillation from phosphoric acid into iodine solution. Found: 106 cc of the ethereal solution would require 102 cc of 0.0472 N iodine solution. The solution therefore contains 3.46% Cl.

10 cc of the ethereal solution were shaken with dilute sodium carbonate solution, and then titrated by the Volhard method. Found: Cl (ionised), 1.766 g.

50 cc of the ethereal solution were washed with water hydrochloric acid, water, and dried over potassium carbonate. After the removal of the ether, 5.435 g. of residue remained; this gave, on distillation,

| P | b.p. 46-52° /757 mm. | 0.675 E. |
| 1 | ; 142-148° | 4.03 E. |
| 2 | ; about 270° | 0.55 g. |
| 3 | Tarry residue | 0.26 E. |

P had d₄⁵° = 10.81; l=0.5. On redistillation it had d₄⁵° = 10.87; l=0.5. Calculated for ethyl α-chloropropionoate: Cl, 28.5.

The aqueous washings from the preceding experiment were treated with a saturated solution of picric acid in
... alcohol had m.p. 165° and melted at the same temperature when mixed with pyridine picrate.

The oil was entirely soluble in water, giving an optically inactive solution the ethereal extract of which gave no residue on the removal of the ether. On steam distilling the oil from caustic soda, no basic substances were evolved. For the standard sulphuric acid into which the distillate was passed did not alter in strength. It was not found possible to estimated the nitrogen by the Fehdahl method.

6 g. of the oil were dissolved in alcohol and treated with a saturated solution of picric acid. Yellow crystals, 4.5 g., were obtained having m.p. 55°. On recrystallisation from acetone fine specimens of large crystals were obtained m.p. 55°. Found: C, 46.9; H, 3.9%.

**Results of Analyses.**

<table>
<thead>
<tr>
<th>Composition</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ether solution contains Cl,</td>
<td>1.726</td>
</tr>
<tr>
<td>; Cl(organic),</td>
<td>2.265</td>
</tr>
<tr>
<td>Oil contains Cl</td>
<td>2.686</td>
</tr>
<tr>
<td>White precipitate contains Cl</td>
<td>0.190</td>
</tr>
<tr>
<td></td>
<td>6.227</td>
</tr>
</tbody>
</table>

Weight of chlorine in 40 g. of ethyl d-chlorosulphinoxypropionate 7.99 g.
Ethereal solution contains $\text{Cl}_2$ $3.40$ g.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>Oil</td>
<td>Oil</td>
</tr>
<tr>
<td>$3.20$</td>
<td>$3.20$</td>
<td>$3.20$</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>$7.20$</td>
<td>$7.20$</td>
</tr>
</tbody>
</table>

Weight of $\text{Cl}_2$ in $40$ g. of Ethyl $\gamma$-chlorosulphinoxypropionate $12.32$ g.

The deficit of sulphur dioxide is probably due to the mechanical loss in the pump during the removal of the adherent solvent and to the reduction of the pyridine, which apparently takes place.

It will be noticed that the Cl and $\text{SO}_2$ in the ethereal solution are present almost in the same proportions as they exist in ethyl $\gamma$-chlorosulphinoxypropionate. It may be concluded from this that the ethereal solution does contain unchanged chlorosulphinate.

Since the oil contains ionisable chlorine, it seems possible that it may contain part of the lactic acid molecule condensed with the pyridine or with some reduction product of the pyridine. The formation of such a condensation product may account for the absence in the oil of a steam volatile base.
### Table VIII

**The Fractional Distillation of Ethyl d-α-Chlorosulphonic Acid**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>L.P.</th>
<th>α (16°)</th>
<th>α (16°)</th>
<th>α (16°)</th>
<th>n (19°)</th>
<th>b.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 m.</td>
<td>5709</td>
<td>5661</td>
<td>4333</td>
<td>D</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>43-44°</td>
<td>83.30°</td>
<td>94.95°</td>
<td>172.36°</td>
<td>1.4583</td>
<td>-</td>
</tr>
<tr>
<td>F2</td>
<td>83.91</td>
<td>95.11</td>
<td>170.41</td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>F3</td>
<td>82.90</td>
<td>95.16</td>
<td>172.11</td>
<td>15.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F4</td>
<td>82.11</td>
<td>94.16</td>
<td>163.36</td>
<td>1.4584</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

F2 and F3 were then mixed and re-distilled.

<table>
<thead>
<tr>
<th></th>
<th>L.P.</th>
<th>α (32.75°)</th>
<th>α (35.95°)</th>
<th>α (170.76°)</th>
<th>α (1.4583)</th>
<th>15.83</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>83.46</td>
<td>95.96</td>
<td>172.99</td>
<td>1.4583</td>
<td>-</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>83.46</td>
<td>95.96</td>
<td>172.99</td>
<td>1.4583</td>
<td>-</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>83.46</td>
<td>95.96</td>
<td>172.99</td>
<td>1.4583</td>
<td>-</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>82.97</td>
<td>95.16</td>
<td>170.95</td>
<td></td>
<td>15.34</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

After standing two weeks in a stoppered bottle,

A. had +32.06° +35.95° +170.19

C. 82.76° 94.71° 169.46
<table>
<thead>
<tr>
<th>Fr.</th>
<th>Temp.</th>
<th>a</th>
<th>α</th>
<th>β</th>
<th>n</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>1.5</td>
<td>33.5</td>
<td>-113.42</td>
<td>139.8</td>
<td>1.45830</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>139.86</td>
<td>1.45834</td>
<td></td>
</tr>
<tr>
<td>F3</td>
<td>114.61</td>
<td>131.87</td>
<td>;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F4</td>
<td>114.61</td>
<td>131.87</td>
<td>;</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(a) n-Amylchlorosulphinate.

n-Amyl alcohol (12.6g.) was added slowly to thionyl chloride (30g., excess) with cooling and vigorous shaking. After the mixture had stood two hours in a desiccator, the excess thionyl chloride was removed on the pump at ordinary temperature, and the product was distilled at as low a temperature as possible. By shaking vigorously during the early part of the distillation, bumping and decomposition was avoided, and a yield of 80% was achieved.

The n-amylchlorosulphinate obtained, after re-distillation until the refractive index remained constant, had

\[ \frac{n}{D} = 1.45654, \text{ b.p. } 71.5-71.75/13\text{mm.}, \text{ d} \text{ b} 1.1253. \]

0.4821G. of this substance, after being heated with alcoholic potash in a sealed tube for 3 hours and then acidified with acetic acid, decolorised 56.4cc of N/10 iodine solution; calculated : 56.55cc.

0.5111G. similarly treated required by the Volhard method 30cc N/10 silver nitrate solution; calc. 29.97cc.

(b) Ethyl lactyl n-amyl sulphite.

(1) Using ethyl ß-chlorosulphinoxypropionate alone.

Ethyl ß-di-α-chlorosulphinoxypropionate (10g., α
-110.7°; λ=0.5) was carefully added to n-amyl alcohol (4.4g.), with cooling and shaking. Heat was evolved and hydrogen
chloride was given off. After being heated at 90° for two hours to complete the reaction, the amber coloured product was heated at 110° at 15mm. and then distilled on the \textit{h-y-v-a-c} pump. Table $\text{\textit{II}}$ contains the data of the distillation.

The sulphur content of these fractions was estimated by decomposing the sulphite with potassium dichromate and hydrochloric acid, and weighing as barium sulphate.

(11) \textit{In petroleum ether solution.}

The reaction was carried out in petroleum ether solution, but still a product was obtained from which it was found impossible to isolate which could be distilled without change in refractive index and rotatory power.

(11) \textit{From n-amyl chlorosulphinate.}

n-amyl chlorosulphinate (8.5g. in 10cc of dry petroleum ether) was added to ethyl 1-di lactate (a$_p$ 7.91°; l=1) (5.9g., in 25cc of petroleum ether). The product obtained as described under (1) had bp. 130-150°/14mm, n$_D$ 1.43572, $\alpha$ $-23.99^\circ$, $\alpha$ $-27.16^\circ$, $\alpha$ $-46.04^\circ$; l=0.5.

Table $\text{\textit{II}}$ contains the data of the fractional distillation of this product.

(iv) \textit{From ethyl l-gl-x-chlorosulphinoxypropionate and pyridine.}

Ethyl l-$\alpha$-cholorosulphinoxypropionate (a $-83.21^\circ$ ; $\alpha$ 5720

l=0.25, 10g.) was added slowly to a mixture of n-amyl alcohol (4.4g.) and pyridine (3.95g.) in 20cc of petroleum
ether. A white precipitate of pyridine hydrochloride was immediately thrown down. This was filtered rapidly through a sintered glass funnel and weighed. Found: 5.81g.; calc. 5.73g.

The filtrate was treated with water, and the ether extract of the resulting liquor, after being dried over potassium carbonate, gave on distillation ethyl L-lactyl \( \eta \)-amyl sulphite having b.p. 140-142\(^\circ\)/13mm., \( \alpha^\circ_0 \) 39.14; \( D = 0.5 \), and weighing 12g. Found: 12.57. CH(CH(\( \eta \)-O-C H \(_2\) ) CO C H \(_2\) requires: 8, 12; 7, 25 11

Table VII contains the data of the fractionation of this product.

(v) From \( \eta \)-amylchlorosulphinic acid and pyridine.

\( \eta \)-Amylchlorosulphinic acid (2.42g.) was added to ethyl L-lactate (\( \alpha^\circ_0 -11.26 \); \( D = 1, 1.5g \)) mixed with petroleum ether and pyridine. Pyridine hydrochloride was precipitated as before and weighed 1.46g. Water was added to the petroleum ether solution and the ether extract of the resulting liquor was washed and dried in the usual way. The ether extract yielded on distillation ethyl L-lactyl \( \eta \)-amyl sulphite having b.p. 140-142\(^\circ\)/13mm., \( \alpha^\circ_0 \) 14.377, \( \alpha^\circ_0 \) 37.15. Found: 8, 12.5.

The white precipitate obtained in these experiments was analysed in the following way. A weighed sample was
treated with caustic soda and steam distilled. The pyridine which distilled was collected in water and titrated with standard sulphuric acid using ferric chloride as indicator. The residue in the distillation flask was acidified with nitric acid and titrated by the Volhard method for the estimation of chloride ion.

(vi) n-Butyl sulphite

Thionyl chloride (4.96g) (1 mol) was slowly added to n-butyl alcohol (7.04g, 2 mol) with cooling and vigorous shaking. After standing overnight in a desiccator, the product was warmed at 50 for two hours and then distilled.

The n-butyl sulphite obtained had b.p. 127.5° /12mm, and weighed 5.5g. Found: C, 14.31, (C H ) 58 requires: C, 14.45, d₄ 0.9822; d₄0 0.9933.

(vii) Ethyl di-d-lactyl sulphite

Ethyl d-lactate (α +11.6; β =1, 2 mol, 11.6g) was mixed

with thionyl chloride (6g, 1 mol) slowly with cooling. After standing for an hour the product was warmed at 70° for an hour and then distilled. The ethyl di-d-lactyl sulphite obtained had b.p. 111-112° / 0.1mm., oil bath 120-125°,

α +15.60, α +56.14, α +95.8; β =0.25, n 1.4402, 13°

57.90 54.61 43.59

and weighed 12.4g. Re-distillation on the water top pump gave a distillate having b.p. 161°/14mm.

TABLE VII

Fractional distillations of the products obtained in the preparation of ethyl-ethyl n-aryl sulfonate.

(1) Using ethyl α-chloroalkylphenoxyacrylate and n-aryl alcohol without pyridine.

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th></th>
<th>E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.p.</td>
<td>70-80°/0.1 mm.</td>
<td>7.6 g.</td>
<td>80-96°/0.1 mm.</td>
</tr>
<tr>
<td>α</td>
<td>-23.5°; l = 0.5</td>
<td></td>
<td>α</td>
</tr>
<tr>
<td>D</td>
<td>15°</td>
<td></td>
<td>D</td>
</tr>
<tr>
<td>n</td>
<td>1.4367</td>
<td></td>
<td>n</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>1</th>
<th>2</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.p.</td>
<td>70-77°</td>
<td>77-92°</td>
<td>75-77°</td>
<td>-20°</td>
<td>over 90°</td>
</tr>
<tr>
<td>α</td>
<td>-17.3°</td>
<td>-25.1°</td>
<td>-10.5°</td>
<td>-11.1°</td>
<td>-23.6°</td>
</tr>
<tr>
<td>D</td>
<td>15°</td>
<td></td>
<td>D</td>
<td>15°</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>1.4365</td>
<td>n</td>
<td>1.4374</td>
<td>n</td>
<td>1.4379</td>
</tr>
</tbody>
</table>

Found: α 12.81°.
TABLE VII  Cont.

(11) Using the reagents as in (11) but in petroleum ether.

<table>
<thead>
<tr>
<th>F1</th>
<th>F2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>b.p.</td>
<td>96/0.1</td>
</tr>
<tr>
<td></td>
<td>over 96°</td>
</tr>
<tr>
<td>a</td>
<td>-21.4°</td>
</tr>
<tr>
<td>D</td>
<td>1.4350</td>
</tr>
<tr>
<td></td>
<td>1.4375</td>
</tr>
<tr>
<td>n 19.5°</td>
<td>1.4365</td>
</tr>
<tr>
<td></td>
<td>1.4375</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>F1</th>
<th>221</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.p.</td>
<td>130-132°/14mm.</td>
</tr>
<tr>
<td></td>
<td>140-145°</td>
</tr>
<tr>
<td>a 16°</td>
<td>-14.07° ; l=0.5</td>
</tr>
<tr>
<td></td>
<td>-24.15°</td>
</tr>
<tr>
<td>n 15°</td>
<td>1.4350</td>
</tr>
<tr>
<td></td>
<td>1.4372</td>
</tr>
<tr>
<td>Found:</td>
<td>9.42.93 %</td>
</tr>
<tr>
<td></td>
<td>9. 12.71 %</td>
</tr>
<tr>
<td>Column 1</td>
<td>Column 2</td>
</tr>
<tr>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td><strong>(111)</strong> Using n-amyl chlorosulphonate and ethyl lactate in petroleum ether but without pyridine.</td>
<td></td>
</tr>
<tr>
<td>B.p. 130-150°/14mm., α 15° 16° 16°</td>
<td>5770</td>
</tr>
<tr>
<td>B.p. 130-134°/12mm.</td>
<td>134-140° (4.0E)</td>
</tr>
<tr>
<td>α</td>
<td>-16.2°</td>
</tr>
<tr>
<td>nD</td>
<td>1.4359</td>
</tr>
<tr>
<td>Column 1</td>
<td>Column 2</td>
</tr>
<tr>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>152</td>
<td>252</td>
</tr>
<tr>
<td>B.p. 141-148°</td>
<td>149-154°</td>
</tr>
<tr>
<td>α</td>
<td>-11.5°</td>
</tr>
<tr>
<td>nD</td>
<td>1.43522</td>
</tr>
<tr>
<td>Viscosity, 12.94</td>
<td>12.83</td>
</tr>
</tbody>
</table>
(iv) Using ethyl α-chlorosulphonic acidate and 1-naphthol alcohol in the presence of pyridine.

\[ \text{b.p. } 140-142^\circ /13 \text{mm.}, \quad \alpha_d \text{ } -39.14^\circ; \quad l=0.5 \]

<table>
<thead>
<tr>
<th></th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.p.</td>
<td>137°/13mm.</td>
<td>139°</td>
<td>142°</td>
</tr>
<tr>
<td>α</td>
<td>-18.81°</td>
<td>-24.31°</td>
<td>-45.1°</td>
</tr>
<tr>
<td>n</td>
<td>1.4375</td>
<td>1.4376</td>
<td>1.4376</td>
</tr>
<tr>
<td>l</td>
<td></td>
<td></td>
<td>1.4376</td>
</tr>
</tbody>
</table>

Pounds: 3. 12.85 12.61 12.75

<table>
<thead>
<tr>
<th></th>
<th>19(3)</th>
<th>29(3)</th>
<th>39(3)</th>
<th>49(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.p.</td>
<td>140-145°</td>
<td>144-145°</td>
<td>144-145°</td>
<td>144-146°</td>
</tr>
<tr>
<td>α</td>
<td>-15.12° (l=0.5)-30.32°</td>
<td>-35.75°</td>
<td>-43.31°</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>1.4373</td>
<td>1.4374</td>
<td>1.4374</td>
<td>1.4376</td>
</tr>
<tr>
<td>l</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Pounds: 3. 12.81 12.85 12.77 12.72
(c) The resolution of n-amyliclosulphinate.

(i) By ethyl-4-lactate

Ethyl 4-lactate (13.18 g., $d_2^0 = 1.16^0$) was added slowly with cooling to n-amyliclosulphinate (37.53 g., 2 mols). After standing overnight in a desiccator the product was distilled. The temperature rose steadily from 55 to 85° and then to 150°. The fraction boiling between 55-85° had $\alpha = -6.40^0$; $l = 0.5$, and was re-distilled into the following fractions:

<table>
<thead>
<tr>
<th>bp.</th>
<th>n</th>
<th>$\alpha$  \ 17°</th>
<th>$l$ in 0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>55-70°</td>
<td>1.4492</td>
<td>-0.74°</td>
<td></td>
</tr>
<tr>
<td>70-73.5</td>
<td>1.4535</td>
<td>-1.23</td>
<td></td>
</tr>
<tr>
<td>73-77</td>
<td>1.4552</td>
<td>-3.04</td>
<td></td>
</tr>
<tr>
<td>over 77</td>
<td>1.4432</td>
<td>-13.65</td>
<td></td>
</tr>
</tbody>
</table>

For fraction bp. 70-73.5° found: $\alpha = 13.5$; Cl, 20.6°.

CH Cl requires: $\alpha = 13.7$; Cl, 20.8°.

(ii) By l-menthol.

n-amyliclosulphinate (10.5 g., 2 mols) was treated with l-menthol (4.8 g., 1 mol.) in petroleum ether solution. Hydrogen chloride was evolved. After the removal of the ether on the pump at ordinary temperature, the product was distilled. The distillation commenced about 65° and continued.
whilst the temperature rose steadily, thus giving rise to the same phenomenon as was observed in the preparation of mixed sulphites in the absence of pyridine. The fraction distilling between 60-80°/14 mm. had $\alpha^{16\circ} + 12.6^\circ; l=0.5$.

It had a mentholic odour and rapidly turned black. When this fraction was re-distilled it gave rise to the following fractions:

<table>
<thead>
<tr>
<th>Fraction: b.p. 60-80°/14 mm.</th>
<th>$\alpha^{16\circ} + 12.6^\circ; l=0.5$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>b.p. 60-70°</td>
<td>b.p. 70-80°</td>
</tr>
<tr>
<td>$\alpha^{16\circ} + 20.6^\circ$</td>
<td>$\alpha^{16\circ} + 4.2^\circ$</td>
</tr>
<tr>
<td>D</td>
<td>D</td>
</tr>
</tbody>
</table>

b.p. 60-65°

$\alpha^{16\circ} + 20.9^\circ$

b.p. 65-70°

$\alpha^{16\circ}$ too small in amount to determine.

n. 1.4502

$\text{These results seem to indicate that the main fraction collected (b.p. 60-80°) is a mixture of some mentholic compound having a high dextrorotatory power and } _{\text{p}}\text{-amyl chlorosulphinate having either a levorotatory power or a small dextrorotatory power.}$

The liquid left in the flask after distilling the fraction (b.p. 60-80°) was distilled on the 'hyvac' pump,
but the liquid distilled continuously over the wide
temperature range of 60-160°/0.1mm., and was not further
examined. It was presumably a mixture of n-amy1 l-menthyl
sulphite and di-l-menthyl sulphite.

(iii) By 1-menthol in the presence of pyridine.

l-Menthol (15.6g., 1 mol.) was mixed with pyridine
(7.9g.) in petroleum ether, and added to n-amy1chlorosulph-
inato (34.4g., 2 mol.) also in petroleum ether. The ether
solution was filtered from the precipitate of pyridine hyd-
rochloride which immediately formed, and added to a mix-
ture of ethyl alcohol (4.6g., 1 mol.) and pyridine (7.9g.).
After filtering the ether solution from the pyridine hyd-
rochloride which again formed, the former was washed,
dried and distilled. Two almost homogeneous fractions were
obtained showing that the pyridine simplifies the course of
the reaction and hinders the formation of by-products.

Table K contains the record of the fractional dis-
tillation of the product obtained in the experiment.

ethyl n-amy1 sulphite was obtained having b.p. 105°/14 mm.,
α = -1.4°, 1=9.5. Found: C 32.13; C H O N 30 requires:
32.0%. 

n-amy1 l-menthyl sulphite was obtained having b.p. 93.5°/
0.1mm., α = 17.3°, 1=9.5, n^2 1.4636. d_2 0.9926.
Found: C 21.95; C H O N requires: 22.0%.
| TABLE Ix |

Distillation of the product obtained in the preparation of optically active ethyl \( n \)-amyl sulphite.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>1F2</th>
<th>2F2</th>
<th>3F2</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P.</td>
<td>103°/14mm</td>
<td>70-73°/0.1mm</td>
<td></td>
</tr>
<tr>
<td>( \alpha ) (16°)</td>
<td>( D ) = -1.4, ( l = 0.5, 5)( E )</td>
<td>( D ) = -8.12°; ( l = 0.5, 23)°</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction</th>
<th>1-3F2</th>
<th>2÷3F2</th>
<th>3-3F2</th>
<th>4-3F2</th>
<th>5-3F2</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P.</td>
<td>90.5°</td>
<td>20.5°</td>
<td>20.5°</td>
<td>20.5°</td>
<td>90.5°/0.1mm</td>
</tr>
<tr>
<td>( \alpha ) (16°)</td>
<td>( 5461 ) = -14.52°</td>
<td>-16.70°</td>
<td>-17.10°</td>
<td>-17.00°</td>
<td>-16.8°</td>
</tr>
<tr>
<td>( n ) (16°)</td>
<td>1.4535</td>
<td>1.4535</td>
<td>1.4636</td>
<td>1.4636</td>
<td>1.4636</td>
</tr>
</tbody>
</table>
(a) **The calculation of the parachor from the experimental data.**

Since the large internal pressure of a liquid is bound to affect the molecular volume; and since the theories of the liquid state all lead to the conclusion that surface tension and internal pressure are closely related, it seems to be reasonable to assume that the effect of internal pressure can be allowed for by using the results of surface tension measurements. Secleod (Trans. Faraday Soc., 1923, 19, 38) showed that the following simple relationship existed between the surface tension and density of a liquid,

\[ y = C (\rho - d) \]

where \( \rho \) and \( d \) are the densities of the liquid and its vapour respectively,

\( y \) is the surface tension of the liquid,

\( C \) is a constant which does not vary with the temperature of the given liquid until a temperature within about 30° of the critical temperature is reached.

Sugden (J., 1924, 125, 1165) developed the definition of the 'parachor' from this relationship.
From \( y = C \left( D - d \right)^{\frac{4}{7}} \) it follows that

\[
C^{\frac{1}{7}} = \frac{y^{\frac{1}{7}}}{D - d} = \frac{y_{1}^{\frac{1}{7}}}{D_{1} - d_{1}},
\]

and if \( y_{1} \) be suitably chosen, then \( d_{1} \) is very small compared with \( D_{1} \) and may be neglected. Multiplying through by the molecular weight, \( M \), the following expression is obtained:

\[
\frac{M}{D_{1}} = \frac{1}{y_{1}^{\frac{1}{7}}} \cdot \frac{M}{D - d} = \frac{1}{y_{1}^{\frac{1}{7}}} \cdot \frac{M}{C^{\frac{1}{7}}},
\]

and making

\[
y_{1} = 1 \quad \frac{M}{D_{1}} = \frac{M}{D - d} = \frac{1}{y_{1}^{\frac{1}{7}}} \quad \text{results.}
\]

\( M / D_{1} \) is the molecular volume at unit surface tension, and is termed by Sugden, the 'parachor'. Representing this quantity by \([P]\) the final expression used in calculating the parachor is obtained.

\[
[P] = \frac{M}{D - d} \quad y_{1}^{\frac{1}{7}}
\]

The determination of the parachor then simply involves the determination of the density and surface tension of a compound of known molecular weight.

(b) The determination of the densities.

The apparatus used in the determination of the densities
of the liquids under investigation consisted of a graduated dilatometer which was suspended vertically in a frame fitted to a two litre beaker containing water which was mechanically stirred. Figs 1 and II illustrate the shape of the dilatometer and its setting, whilst figs 3 and 4 show how the dilatometer was filled, emptied and dried.

The dilatometer was thoroughly cleaned with a hot mixture of chromic and nitric acids, rinsed with freshly distilled water and dried by means of a stream of dry filtered air. It was calibrated by means of clean mercury and freshly distilled water for different temperatures and for different marks on the scale. All weighings were corrected for buoyancy. The temperatures were determined by N.P.L. standard thermometers. The method was found to be an excellent one for routine density determinations of organic liquids at different temperatures. The results are accurate to about 3 units in the fourth decimal place.

(c) The determination of surface tension.

The surface tensions of the liquids under investigation were determined first by the method of the maximum bubble pressure described by Sugden (J., 1924, 125, 27), and checked for two of the liquids by the method of the double capillary rise described also by Sugden (J., 1921,
The apparatus used in the determination of the surface tension by the maximum bubble pressure method was essentially the same as that described by Sugden and need not be detailed here. After being cleaned and dried in the usual way, the apparatus was calibrated by the observations on the pressure differences produced by benzene in the bubbler, and the constant for the instrument was then calculated in the following way:

The surface tension is given by the expression \( \gamma = A P \phi \)

where
- \( \gamma \) = the surface tension of the liquid,
- \( A \) = the constant of the instrument,
- \( P \) = the pressure difference in dynes, i.e. the difference in gauge reading for the large and small tubes, multiplied by \( \phi \) (961) and the density of the liquid used in the manometer, in this experiment, alcohol.
- \( \phi \) = a correction factor = \( 1 + 0.09 \frac{r}{D} \)

where
- \( r \) = the radius of the larger tube = 0.1325 cm.
- \( D \) = the density of the liquid in the bubbler, i.e. the liquid of which the surface tension is required.

\( g = 981 \text{ cm. per sec. per sec.} \)
With benzene in the bubbler, the pressure for the fine tube was 7.75 cm whilst that for the large tube was 6.675 cm. The difference in pressure therefore was 7.075 cm of alcohol. From this the pressure in dynes was calculated.

Adopting the value of 29.953 dynes per cm. for the surface tension of benzene at 12.5° and the value of 0.8870 g. per cc. for the density of this liquid at the same temperature, the constant (A) of the instrument was calculated and found to be 0.00523. With the other liquids successively in the bubbler, the pressure differences were observed and from the data so obtained and from the known value of (A), the surface tensions were calculated. Table X contains the record of the surface tensions and densities of the liquids at different temperatures together with the parachor calculated from these data.

It was considered advisable to determine the surface tension of ethyl α-chlorosulphinoxypropionate and n-amyl chlorosulphinate by a second method, and for this purpose the method of double capillary rise was adopted.

The general theory of the rise of liquids in tubes of any diameter is discussed by Sugden (loc. cit.) who uses the following equation for the calculation of surface tensions.

\[ 2y \left( \frac{1}{b_1} - \frac{1}{b_2} \right) = \pi g (D - d) \]
where

\[ \gamma \]

is the surface tension of the liquid,

\[ H \]

is the vertical distance between the lowest points of the meniscuses in the two vertical capillary tubes of radii \( r_1 \) and \( r_2 \).

\( b_1 \) and \( b_2 \) are the radii of curvature at these lowest points.

\( D \) and \( d \) are the densities of the liquid and its vapour.

By a method of successive approximations, using a table supplied by Sugden (loc. cit.), the values of \( b_1 \) and \( b_2 \) were obtained in terms of \( r_1 \) and \( r_2 \). For this purpose the following expression was used:

\[ a = \frac{H}{1/b_1 - 1/b_2} \]

the final values of \( a \) used are given in table .

Table \( X \) is a record of the dimensions of the tubes and of the experimental results obtained. It will be noticed that the values for the surface tension obtained by the two methods are in good agreement.
Bent to prevent dirt from rubber from fouling capillary.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.
The Record of the Surface Tensions, Densities, and Parachors.

### (i) Methyl d-α-chlorosulphinoxypropionate

<table>
<thead>
<tr>
<th>$d_{4}^{°}$</th>
<th>$t_{2}^{°}$</th>
<th>$y$</th>
<th>$t_{2}^{°}$</th>
<th>Thence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2821</td>
<td>12.6°</td>
<td>35.35</td>
<td>11.0°</td>
<td>$d_{4}^{°} = 1.2977 - $</td>
</tr>
<tr>
<td>1.2697</td>
<td>22.6°</td>
<td>32.38</td>
<td>32.0</td>
<td>0.001237t.</td>
</tr>
<tr>
<td>1.2567</td>
<td>32.7°</td>
<td>30.51</td>
<td>45.2</td>
<td>$y = 36.91 - $</td>
</tr>
<tr>
<td>1.2461</td>
<td>41.7°</td>
<td></td>
<td></td>
<td>0.1416 t.</td>
</tr>
</tbody>
</table>

Parachor calculated from $\frac{y^{2/3}}{d_4} = \left[ \frac{P}{d_4} \right]^{14°} = 380.8$

$\left[ \frac{P}{d_4} \right]^{32°} = 380.3$

Sum of the atomic parachors for CH CH(CH(OCCI)) COOH --------------- 380.4

### (ii) n-Amyl chlorosulphinate

<table>
<thead>
<tr>
<th>$d_{4}^{°}$</th>
<th>$t_{2}^{°}$</th>
<th>$y$</th>
<th>$t_{2}^{°}$</th>
<th>Thence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0952</td>
<td>10.8°</td>
<td>29.92</td>
<td>14°</td>
<td>$d_{4}^{°} = 1.1383 - $</td>
</tr>
<tr>
<td>1.1260</td>
<td>23.0°</td>
<td>28.30</td>
<td>25.8</td>
<td>0.00113t.</td>
</tr>
<tr>
<td>1.1038</td>
<td>33.5°</td>
<td>27.45</td>
<td>40.8</td>
<td>$y = 31.21 - $</td>
</tr>
<tr>
<td>1.0932</td>
<td>40.0°</td>
<td></td>
<td></td>
<td>0.0322 t.</td>
</tr>
<tr>
<td>TABLE X Cont.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parachor calculated from $\frac{1}{2} \times \rho = [\rho]^{14} = 354.4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sum of the atomic parachors for</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C II UCHCl ----- ----- ----- ----- = 354.6</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>5 11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(iii) Ethyl-lactyl n-amyl sulfonate.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>(t)</td>
<td>(t)</td>
<td>(t)</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0301</td>
<td>5.9</td>
<td>32.6</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>1.0662</td>
<td>20.0</td>
<td>30.35</td>
<td>59.0</td>
<td></td>
</tr>
<tr>
<td>1.0505</td>
<td>36.4</td>
<td>75.37</td>
<td>79.4</td>
<td></td>
</tr>
<tr>
<td>1.0373</td>
<td>50.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parachor calculated from $\frac{1}{2} \times \rho = [\rho]^{7.8} = 558.6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sum of the atomic parachors for</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH CHOOC, O C II ----- ----- ----- ----- = 558.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(iv) Ethyl α-chloropropionate.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>7.9</td>
<td>15.1</td>
<td>32.7</td>
<td>45.0</td>
</tr>
<tr>
<td>d</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0040</td>
<td>1.0354</td>
<td>1.0640</td>
<td>1.0932</td>
<td></td>
</tr>
<tr>
<td>y = 39.27 at 5.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parachor calculated from $\frac{1}{2} \times \rho = [\rho]^{5.1} = 291.7$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sum of the atomic parachors for</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH CHCl COOC II = 292.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE XI.

Record of Data obtained in the Determination of Surface Tension by the Method of Double Capillary Rise.

(i) Ethyl o-chlorocinnamidate.

H = 2.255 cm. at 25°, a = 0.05356, D = 1.2668.

\[ \theta = 25^\circ \]

whence \( y = 33.29 \). By bubble pressure, \( y = 33.37 \).

H = 2.165 cm. at 37°, a = 0.05137, D = 1.2520.

\[ \theta = 37^\circ \]

whence \( y = 31.66 \). By bubble pressure, \( y = 31.68 \).

(ii) n-Butyl chloroacetic acid.

H = 2.325 cm. at 6.6°, a = 0.05533, D = 1.1329.

\[ \theta = 6.6^\circ \]

whence \( y = 30.69 \). By bubble pressure, \( y = 30.68 \).

H = 2.26 cm. at 16.4°, a = 0.05417, D = 1.1230.

\[ \theta = 16.4^\circ \]

whence \( y = 29.75 \). By bubble pressure, \( y = 29.70 \).

H = 2.21 cm. at 24.1°, a = 0.05225, D = 1.1111.

\[ \theta = 24.1^\circ \]

whence \( y = 28.66 \). By bubble pressure, \( y = 28.70 \).

\[ r = 0.01755 \text{ cm.} \quad r = 0.0685 \text{ cm.} \quad y \text{ is expressed in dynes per cm.} \]
The Hammet Constants used in the Calculation of the Sum of the Atomic Charges:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>17.1</td>
</tr>
<tr>
<td>C</td>
<td>4.5</td>
</tr>
<tr>
<td>O</td>
<td>20.0</td>
</tr>
<tr>
<td>(Ether) O</td>
<td>60.0</td>
</tr>
<tr>
<td>S</td>
<td>54.3</td>
</tr>
<tr>
<td>Cl</td>
<td>48.2</td>
</tr>
</tbody>
</table>

Double bond = 23.2

Semi polar
bond = 1.6 (about)

---

END
ABSTRACT

of THESIS to be submitted
for the DEGREE of DOCTOR of PHILOSOPHY in CHEMISTRY
in the University of London by N. Gerrand, M.Sc., A.I.C.

STUDIES IN THE PENDEN INVERSION.

A.

The Relative Configuration of Ethyl d-lactate
and Dextrorotatory Ethyl d-chloropropionate.

B.

The Molecular Dismmetry of p-Toluene-sulphine-
ates, Sulphites, and Chlorosulphinates.

An experimental study has been made of the inter-
actions of (a) phosphorus pentachloride, (b) phosphorus
pentabromide, and (c) thionyl chloride on optically ac-
tive ethyl lactate in the presence of tertiary bases.

Optically active ethyl d-p-toluene-sulphinoxypropionate has been prepared and its interactions with
chlorine, bromine, and hypochlorous acid are described.

Ethyl d-d-chlorosulphinoxypropionate has been
prepared and its decomposition in the presence and ab-
sence of pyridine is described.

The above interactions and also the interaction
of optically active ethyl d-p-toluene-sulphonoxypropionate
and certain alkaline metal salts are discussed from the
point of view of the Penden inversion. The definite fora-