THE INVESTIGATION OF THE WALDEN INVERSION AND
ALLIED SUBJECTS USING \( \alpha-\beta \)-BUTANOL

AND ITS p-TOLUENESULPHONIC AND
p-TOLUENESULPHONIC ESTERS.

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Although the study of organic chemistry is largely concerned with substitution reactions of most diverse types, agreement has not yet been reached with regard to the nature of the processes by which this replacement of one radical by another in a molecule is brought about. When it is remembered, however, that substitution is intimately associated with valency, the reason for these controversies becomes apparent, since no hypothesis has suffered more changes under the stress of prolonged investigations than that of valency.

During the first half of the 19th century, although nothing was known as to the exact nature of valency, that is to say, of the power which enables the atom of carbon, for example, to hold in stable union four atoms of hydrogen or of chlorine, but which will not permit the atom of hydrogen or of chlorine to do the same thing as regards carbon, yet a fundamental idea of valency was gradually developing.

In spite of this lack of a definite idea of valency, numerous theories of substitution were put forward. Inorganic chemists, following Berzelius, postulated the existence of a polar type of chemical affinity whereby unlike elements were held together by polar forces which were probably electrical in character. On the other hand, organic chemists, as the
result of Dumas' experiments on the substitution of "electronegative" chlorine for "electropositive" hydrogen, postulated a non-polar type of affinity in which carbon could be linked to either hydrogen or chlorine by a non-polar valency. Like elements, therefore, would also be linked together by a non-polar valency, e.g., hydrogen to hydrogen, or chlorine to chlorine. Nothing in itself the symmetry of molecules and elements. The first real advance came with the recognition by Frankland in 1852 that every atom is inherently endowed with a specific combining power, varying within certain limits, by which it is able to unite with a definite number of atoms of other elements. Following directly from this came the hypotheses of Kekule andCouper concerning the mode of combination of carbon and the development of a theory of chemical structure, which effected a fusion of the older theories which had so long divided the opinions of chemists. Valency, at first merely an arithmetical property of atoms, now became a geometrical property, and for the first time the atom was invested with forces emanating from it in definite directions, instead of being regarded as a mere lump of matter. From this time studies of the constitution of organic compounds took on a new form, and great numbers of compounds, hitherto unthought of, were prepared because theory indicated their existence. No clear conception of the mechanisms of the reactions occurring could be obtained, however, since the theory of valency was developed solely from compounds of simple
and definite composition to the exclusion of all those that
were variable and complex, and hence proved increasingly
inadequate when used to explain the complex phenomena of
chemistry. It was regarded as impossible.

The next great advance came in 1874 when van't Hoff, and
and independently Le Bel, by combining the results of Pasteur's
work on the relation between the asymmetry of molecules and
optical activity with Kekulé's idea of the tetrahedral,
arrangement of the four groups attached to a quadrivalent
hydrogen atom, put forward their brilliant conception of
asymmetry and thus opened up the field of stereochemistry,
and which it was to prove of considerable value in the elucidation
of the mechanism of substitution reactions. According
to this conception, a molecule can be considered to be a
stable system of material points and the four valencies of
the central carbon atom, which are equal to one another, are
directed towards the four corners of a circumscribed tetra-
hedron. If the four affinities of the carbon atom are
satisfied by four different univalent groups, two, and not more
than two, tetrahedra are obtained, of which one is the mirror
image of the other and cannot be superposed on it.

During the replacement of one of the groups attached to
the asymmetric carbon atom by a new group, it was therefore
assumed that either a compound of the same configuration as
the original compound would be formed if the new group
preferentially took up the position of the extruded group,
or else that the entering group would take up any position
without preference, in which case there would be formed 50%
of one enantiomorph and 50% of the other, resulting in an
optically inactive product. It was regarded as impossible
to convert an optically active compound into its enantiomorphous
form without previously racemising it and then resolving the
furnishing of the latter into dextrorotatory or laevorotatory acid
racing compound.

In 1895, however, Walden, who was then investigating the
optically active modifications of halogen substituted succinic
acids, was led to the wholly unexpected conclusion that in
certain reactions, not only was an optically active product
obtained, but the new compound possessed the same configura-
tion as the mirror image of the parent compound. Thus, Walden
obtained from dextromalic acid by means of phosphorus penta-
chloride a laevochlorosuccinic acid which gave laevomalic acid
when silver oxide was used to effect the replacement of
chlorine by the hydroxyl radical, but dextromalic acid when
potassium hydroxide was used for this purpose:

\[
\begin{align*}
\text{COOH} & \quad \text{COOH} \\
\text{H}_2\text{C}-\text{CH} \quad \text{PCl}_5 & \quad \text{H}_2\text{C}-\text{Cl}.
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{COOH} & \quad \text{CH}_2\text{COOH} \\
\text{KOH} & \quad \text{COOH} \\
\text{CH}_2\text{COOH} & \quad \text{CH}_2\text{COOH}
\end{align*}
\]
From the above, it is obvious that since a malic acid opposite in configuration to the original malic acid was obtained, during one of the substitution reactions an inversion has occurred, but irrespectively of whether or not a configurative change occurs in the transformation of dextromalic acid into laevosuccinic acid, in one or other of the transformations of the latter into dextromalic or laevomalic acid respectively, a rearrangement of the groups attached to the asymmetric carbon atom must occur by some process which does not consist in the simple replacement of the group without simultaneous disturbance of the bonds. This may involve either the migration of one of the remaining groups to the bond left vacant by the group displaced, or the inversion of the molecule as a whole. In the case of optically active compounds, by following the change in sign of optical power. As pointed out above, the discovery of the case inversion opens an era in organic chemistry with regard to the mechanism of the theory of substitution in general.

According to van't Hoff's hypothesis, the groups attached to the carbon atom in space are fixed and do not readily interchange positions, so that the second alternative appears the more likely.
Numerous cases of the substitution of a group directly attached to an asymmetric carbon atom were subsequently studied, and it was demonstrated that Walden inversions probably occur in the following transformations:

\[
\begin{align*}
R_1R_2R_3\cdot CH & \xrightarrow{\text{HCl, HCl.}} \xrightarrow{\text{SbCl}_3 \text{ etc.}} R_1R_2R_3\cdot Cl \cdot (\text{Br.}) \\
R_1R_2R_3\cdot Cl \cdot (\text{Br.}) & \xrightarrow{\text{AcOH, H}_2\text{O}} \xrightarrow{\text{HCl etc.}} R_1R_2R_3\cdot Cl \\
R_1R_2R_3\cdot Cl \cdot (\text{Br.}) & \xrightarrow{\text{NH}_3} \xrightarrow{\text{HCl etc.}} R_1R_2R_3\cdot NH_3 \\
R_1R_2R_3\cdot NH_3 & \xrightarrow{\text{HCl etc.}} \xrightarrow{\text{H}_2\text{O}} R_1R_2R_3\cdot Cl \\
R_1R_2R_3\cdot NH_3 & \xrightarrow{\text{HCl (Br.)}} \xrightarrow{\text{HCl etc.}} R_1R_2R_3\cdot Cl \cdot (\text{Br.})
\end{align*}
\]

It was also realised that similar rearrangements must occur in reactions with symmetrical compounds, though here the changes could not be detected, as in the case of optically active compounds, by following the changes in sign of rotatory power. As Frankland said in 1873, the discovery of the Walden inversion marks an epoch in our views with regard to the mechanism of the process of substitution in general.

The importance of this phenomenon of optical inversion led not only to a large amount of experimental work, but also to much speculation, and from 1895 until the formulation of the electronic theory of valency the mystery of the Walden inversion deepened with each addition made to the list of reactions during which it could be shown to occur, while the literature of the subject became a catalogue of apparently unconnected and often conflicting facts. The fundamental difficulty was
Since no direct evidence was available for the absence of a means of ascertaining whether a change in the sign of rotation during any given reaction indicated a change in configuration, and whether identity of sign of rotation in the case of two different compounds corresponded to identity of configuration. Many instances are known where a reversal of sign occurs although substitution takes place remote from the asymmetric carbon atom. Thus, amyl alcohol, when heated with halogen and other acids, yields derivatives and acid esters of opposite sign. In this case there can be no question of the occurrence of a Walden inversion, since the hydroxyl group displaced is not attached to the asymmetric carbon atom. Moreover, the sign of rotation of a compound may change from solvent to solvent. For example, α-β-cetyl acetate is dextrorotatory in ethyl alcohol but laevorotatory in carbon disulphide solution. Many attempts were therefore made to deduce the occurrence or non-occurrence of inversions from considerations of the probable mechanisms of the reactions which occurred, but such attempts were hampered by a strict adherence to the theory of van't Hoff, that the four valencies of the carbon atom were fixed, equal in value and indivisible. The theory of residual affinity was therefore developed and abnormal phenomena were then explained as being caused by the mutual influence of unsaturated atoms in the molecular complex, or to illustrate the formation of possible intermediate additive products during a reaction. Werner, Fischer and others formulated possible reaction mechanisms along these
lines, in which the attraction of a saturated carbon atom for groups not actually attached by the four valencies of the carbon, or the attachment of the attracted group to one of the four substituent groups was considered to be the initial stage of a reaction. These explanations appear defective when critically examined and moreover do not allow of the prediction of a change of configuration in uninvestigated cases. Thus, Fischer had observed the formation of additive compounds when nitrosyl bromide acted upon either alanine or aspartic acid, and this led him to regard the initial stage in the action of a reagent as an additive process. For example, by utilising the residual affinity of the asymmetric carbon atom, ammonia may dissociate and attach itself in the manner indicated by the dotted lines:

![Diagram](attachment://diagram.png)

When hydrogen bromide is subsequently removed the amino group may either take the place of the bromine atom - "normal reaction" - or there may be a rearrangement, in which one of the other groups steps in, with change of configuration - "abnormal reaction" - or both reactions may occur simultaneously resulting in more or less complete racemisation.

 cadamer suggested a mechanism for the action of metallic
hydroxides on halogen acids and also emphasized the necessity
for assuming the formation of intermediate compounds in order to
maintain continuous asymmetry during the process of substitution.
During the simple replacement of one group by another the
asymmetric carbon atom would be attached, momentarily at least,
to only three groups, and this would lead immediately to the
production of a symmetrical system since the three groups would
fall into the same plane as the asymmetric carbon atom. Addition
of the new group would therefore result in the formation of a
racemic product.

Olah also discussed the possibility of substitution
occurring with or without change of configuration. On
his views, the action of a cation (e.g., Ag⁺) or, for example,
chlorosuccinic acid is supposed to lead to change of configuration,
whilst the action of an anion (e.g., CH⁻) is not
attended by such a change. Thus:

\[ \text{Cl}^- + \text{Ag}^+ \rightarrow \text{AgCl} \]

Inversion of configuration.

\[ \text{HO} \rightarrow \text{Cl}^- + \text{H}^+ \]
When optical inversion occurs, the chlorine is gradually withdrawn from the sphere of attraction of the carbon by the silver cation. The three residual groups, by their momentum, overshoot the equilibrium point which brings them into the region where the propagation of optical activity was regarded same plane as the carbon atom, and hence the region opposite to the chlorine becomes vacant for the attachment of the second halogen atom. In the other hand, hydration of the anion OH.

Walden arrived at a similar conclusion and argued that because of many of halogen ions and large change of entropy the reaction with strong alkalis, which are largely ionised, would probably be one of direct displacement. The reaction with silver oxide would occur with inversion and could be accounted for by the formation of an additive compound with the chloro-compound followed by the elimination of the metallic chloride.

Billmann also based his speculations on the assumption that the hydroxyl anion of potassium hydroxide and the silver salt ion and silver hydroxide respectively, in aqueous solution, would the active constituents of these ions. He argued that the transformation of two bases, but whilst Cadamer and Walden concluded that silver ions probably led to hydrolysis with change of configuration, Billmann arrived at the opposite conclusion. Thus Billmann supposed that the transformation of silver α-bromopropionate into α-hydroxypropionate in aqueous solution was caused by the silver ion; that the reaction with silver ions with the halogen of the anion silver oxide or silver nitrate would probably be decomposition.
In this example preservation of optical activity was regarded as probably due to the presence of a positive charge at the central carbon atom. On the other hand, hydroxylation of the potassium salt was regarded as a slow reaction which was effected by means of hydroxyl ions and led to change of configuration:

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

Biilmann further attempted to apply his views of the mechanism of the Walden inversion to the action of nitrous acid and nitrosyl bromide, respectively, on amino-acids and their esters. He assumed that the transformation:

\[\text{amino-acid} \xrightarrow{\text{HNO}_2} \text{hydroxy acid},\]

occurred without change of configuration owing to the rapid and straightforward action of nitrous acid on amino-acids. For similar reasons he assumed that nitrosyl bromide would also react with amino-acids without change of configuration. On the other hand, Biilmann suggested that the action of nitrosyl bromide on esters of amino-acids would probably be accompanied by configurative change. He based this reasoning on the formation of nitrosyl bromide in the reaction:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH} & \quad \text{CH} \\
\text{CO}_2 & \quad \text{CO}_2 \\
\end{align*}
\]
by configurative change. He bases his reasoning on the formation of diazo-acetic ester by the action of nitrous acid on amino-acetic ester, configurative change occur in the case of the ester as of the acid. In nitrosyl bromide, an empirical identity was found. Each of these reactions will always equally easy which indicates that, in the case of the ester of an amino-acid, the diazo-group can come into connexion with the asymmetric carbon atom itself. If the diazo-ester were actually formed, however, complete racemisation would result, since the asymmetry of the carbon atom is lost, thus \( \text{CH}_2=\text{CH}_2 \text{COOEt} \rightarrow \text{CH}_2 \text{CH}_2 \text{COOEt} + \text{H}_2\text{O} \). If it be assumed that in the reaction between nitrosyl bromide and esters of amino-acids the halogen attaches itself to the carbon asymmetric carbon atom at the point where the diazo-group, if formed, would do so, then the reaction would be accompanied by a change of configuration.

By comparing the reactions

- d-alanine \( \text{NOBr} \rightarrow 1-\alpha\)-bromopropionic acid
- d-alanine ester \( \text{NOBr} \rightarrow d-\alpha\)-bromopropionic ester,

he concluded that since nitrosyl bromide acts upon alanine ester to produce bromopropionic acid without change of sign, that inversion is less liable to occur with an ester than...
with an acid and therefore that the first reaction proceeds with inversion.

Does the configurative change occur in the case of the acids or of the esters? Obviously, any empirical regularity which exists with one hypothesis would also be equally consistent with the opposite hypothesis. As Frankland said in 1813, "there does not exist at the present time any criterion whereby the relations between the configuration of an optically active compound and that of a derivative can be decisively ascertained." Reactions suggest that inversions occur whenever the indecisive nature of the explanations put forward by the above workers is largely due to the fact that the reactions which they discussed were not known to occur definitely with inversion. In 1923, however, it was shown that the \( \rho \)-toluenesulphonic ester of \( \sigma \)-benzylmethylcarbinol reacts with salts of carboxylic acids with inversion and, more recently, this type of reaction has been proved to be attended without exception by an inversion. The work described in this thesis is mainly concerned with an attempt to obtain evidence as to whether an inversion occurs during other reactions of \( \rho \)-toluenesulphonates.
cyanide, potassium thiocyanate, etc., are also attended by inversion. The method adopted in the present work is based on the investigations of Rule, who has shown that the magnitude of the rotatory powers of compounds containing a common optically active radical is dependent on the polarity of the substituent group. The β-buty1 derivatives obtained by the interaction of d-β-buty1 p-toluenesulphonate with these salts have been examined from this standpoint. No reactions occurred in b. The application of the electronic theory to the consideration of these reactions suggests that inversions occur whenever the p-toluenesulphonyl radical is replaced by an anion, and it is concluded that the reactions of d-β-buty1 p-toluenesulphonate with other salts besides those of carboxylic acids are attended by inversion and yield a series of derivatives of the l-alcohol. On the other hand, evidence has been obtained that when this d-sulphonate reacts with primary and secondary amines, no inversion occurs, whilst the reactions with anhydrous acids result in complete racemisation. As far as possible, experimentally, these conclusions have been substantiated by a study of the reactions of d-β-buty1 p-toluenesulphonate.

In this reaction complete substitution of a group attached to the organic side carbon atom does not occur, the intramolecular hydrogen atom of the hydroxyl group alone being displaced, and it is justified, therefore, to assume that the movement occurs without change in configuration.
In this reaction complete substitution of a group attached to the asymmetric carbon atom does not occur, the hydrogen atom of the hydroxyl group alone being displaced, and it is justifiable, therefore, to assume that the conversion occurs without change in configuration.
When refluxed in alcoholic solution with potassium benzoate, \( d \)-benzylmethylcarbinyl \( \beta \)-toluenesulphonate yielded a laevorotatory benzylmethylcarbinyl acetate. A Walden inversion must be involved in this change since a dextro-rotatory acetate is obtained by the action of acetic anhydride on \( d \)-benzylmethylcarbinol.

In addition, it can be assumed that in general, it can be assumed that in general, it can be assumed that

\[
\text{C}_6\text{H}_5\text{CH}_2\text{OH} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{H} \quad \text{(First without change)}
\]

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad 0.30\text{C}_7\text{H}_7
\]

\[
\text{Ag}_2\text{O} \quad \text{K}_2\text{CO}_3\text{CH}_3
\]

\[
\text{C}_6\text{H}_5\text{CH}_2\text{H} \quad \text{C}_6\text{H}_5\text{CH}_2\text{H} \quad 0.30\text{CH}_3
\]

\[
\text{CH}_3 \quad 0.30\text{CH}_3 \quad \text{CH}_3 \quad \text{H} \quad \text{(Second without change)}
\]

Similar inversion reactions have since been realised with the \( \beta \)-toluenesulphonic esters of \( d \)-\( \beta \)-octanol and \( l \)-menthol (Phillips, J.C.S., 1925, 133, 2363), ethyl \( d \)-lactate (Kenton, Phillips and Turley, ibid., 1925, 135, 300), and the \( \alpha \)- and \( \beta \)-cyclohexanols (Cough, Hunter and Kenton, ibid., 1926, 2032). The reaction between the alkali salts of carboxylic acids and \( \beta \)-toluenesulphonic esters is, therefore, a general inversion reaction.

Similar results have been obtained in the present investigation of the reactions of \( d \)-\( \beta \)-butyl \( \beta \)-toluenesulphonate. The sulphonic ester could not be prepared satisfactorily by the action of \( \beta \)-toluenesulphonyl chloride on the alcohol, and was therefore prepared by the oxidation of the sulphonic ester.
The $\delta$-\(\beta\)-butyl \(\eta\)-toluenesulphinic acid used in this investigation was prepared by the direct action of \(\eta\)-toluenesulphinyl chloride on $\delta$-$\beta$-butanol ($\alpha^{100} + 13.33^\circ$) using pyridine or 5% potassium carbonate to remove the hydrogen chloride formed during the reaction. Since the four bonds of the asymmetric carbon atom presumably remain undisturbed, it can be assumed that the \(\eta\)-toluenesulphinic acid is produced without change of configuration. If freshly prepared, the acid distilled readily at very low pressures and was obtained as a colourless liquid with $n^D_{130} 1.5353$ and $\gamma^D_{5461} +9.48^\circ$. This sulphinic acid, on oxidation with potassium permanganate in neutral solution, yielded $\delta$-$\beta$-butyl \(\eta\)-toluenesulphone, which could be distilled at low pressures, but showed a marked tendency to decompose. On distillation it was obtained as a colourless liquid with $n^D_{130} 1.5030$ and $\gamma^D_{5461} +13.20^\circ$.

When heated under reflux with an alcoholic solution of potassium acetate, the $\delta$-sulphone yielded a laevorotatory $\beta$-butyl
acetate $\alpha = 20.19^\circ$ which must have been produced with inversion of configuration since, when the $\alpha$-alcohol is treated with acetic anhydride, a dextrorotatory acetate with $\alpha = 30.17^\circ$ (Pickard and Kenyon, J.C.S., 183, 630) is obtained. Similarly, the interaction of $\beta$-butyl $p$-toluenesulphonate and potassium benzoate in ethyl alcoholic solution yields $1\beta$-butyl benzoate $\alpha = -44.03^\circ$, whereas $\alpha$-butanol with benzoyl chloride gives $\alpha$-butyl benzoate with $\alpha = +40.59^\circ$.

Whilst methods are thus available by which it can be proved that $\alpha$-butyl $p$-toluenesulphonate reacts with salts of carboxylic acids with inversion, it is more difficult to obtain evidence for the occurrence of inversion when this sulphonate reacts with salts of other acids, because the derivatives obtained cannot be prepared directly from the alcohol without disturbing the bonds of the asymmetric carbon atom. Noussa, Kenyon and Phillips (J. 1939, 1700) have, however, suggested that since all the reactions of $p$-toluenesulphonic esters with salts involve the replacement of the $p$-toluenesulphonyl group by an anion, they are all reactions closely similar in type, and if one occurs with inversion they will all occur with inversion. Since $\alpha$-butyl $p$-toluenesulphonate yields a laevorotatory acetate and laevorotatory bromide and iodide when refluxed respectively with potassium acetate, ethyl magnesium bromide and potassium iodide, on this assumption, laevorotatory $\beta$-bromo- and $\beta$-iodo-butanes
have the same configuration as \( \text{1-\( \beta \)-butanol} \).

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} & \quad 0.30\text{C}_2H_5 \\
\text{C} & \quad 1.00 & \quad \text{I} \\
\text{C}_2H_5 & \quad 2.78 \\
\text{I} & \quad 3.00
\end{align*}
\]

The assumption that \( \text{d-\( \beta \)-butyl \( p \)-toluene sulphinate} \) reacts with ethyl magnesium bromide and with potassium iodide with inversion.

This assumption receives support from the results of other
workers who have approached the problem of the relative configurations of hydroxy compounds and their halogen derivatives from an entirely different standpoint. Recently, Mr. Shackleton has shown in these laboratories that laevorotatory halogen derivatives are produced by the action of thionyl chloride and the chlorides and oxychlorides of phosphorus on \( d-\beta \)-butanol, so that if the laevorotatory \( \beta \)-halogen butanes have the same configuration as \( d-\beta \)-butanol, as the results of the sulphonate and sulphinate reactions suggest, then the interaction of the above reagents with aliphatic secondary alcohols is attended by inversion. Some workers (Harker, Freudentberg and Levens) have obtained evidence that the laevorotatory hydroxy acids have the same configuration as the laevorotatory chloro-acids, and since the halogenating agents enumerated above convert the laevorotatory hydroxy acids into dextrorotatory chloro-acids, they have concluded that the halogenations occur with inversion.

The method used by these workers was a purely physical one which was put forward by Clough in 1916, and is based on the assumption that the rotatory powers of compounds of similar configuration are in general influenced similarly by changes in external conditions, (solvent, dissolved salts, temperature, etc.) and also by the introduction of the same substituent into a given radical attached to the asymmetric carbon atom. In order to find out how closely allied in constitution the
compounds must be before the hypothesis breaks down. Clough compared the rotatory powers of the naturally occurring α-hydroxy acids, dextro-malic, dextro-tartaric, lactic and lactic-glycemic and their esters, under widely different experimental conditions and found that the rotatory powers altered in a regular manner with similar changes in experimental conditions. These acids, as the result of much ingenious synthetrical work on the part of Fischer (Ber., 22, 1877), Freudenberg (Ber., 1914, 47, 3037; 1923, 55, 1339; 1923, 56, 126, 368; 1924, 57, 1547; 1925, 58, 1733, 2359; 1930, 60, 455; 1922, 55, 1404), and Wohl (Ber., 1917, 50, 455; 1922, 55, 1404), have been proved to possess the same configuration as dextro-tartaric acid which, in turn, can be derived from d-glucose.

The rotatory powers of dextro-malic and their esters with water:

\[
\text{C} \quad \text{H}_2 \text{O}
\]

\[
\text{C} \quad \text{H}_2 \text{C} \text{O} \text{H}
\]

\[
\text{H} \text{C} \text{O} \text{H}
\]

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

\[
\text{CH}_2 \text{OH}
\]

These naturally occurring α-amino acids and their esters altered in a regular manner with similar changes in experimental conditions with Clough's hypothesis. These acids have been proved to possess the same configuration since they can
be interconnected by reactions which do not affect the groups attached to the asymmetric carbon atom. The amino acids and the chloro acids exist in racemic and optically active forms.

**α-Amino-Acids.**

Optically active amino acids exist in racemic and optically active forms. The COOH end of amino acids in solution is the COOH end of amino acids in solution. The COOH end of amino acids in solution is the COOH end of amino acids in solution. The COOH end of amino acids in solution is the COOH end of amino acids in solution.

Assuming the validity of Clough's hypothesis, Clough, and later Karver and Freudenberg, and Kuhn, compared the rotatory powers of chloro-acids and their esters with those of the hydroxy acids and their esters, and the rotatory powers of amino and hydroxy acids with those of chloro-acids. As a result, it is now generally agreed that the naturally occurring α-hydroxy acids are enantiomorphously related to the naturally occurring α-amino-acids and have the same configuration as the corresponding dextrorotatory α-chloroacids. These conclusions are supported by modern views of polarity which suggest that since hydroxyl and chloro groups are of the same order of polarity their influence on rotatory power should be similar.

Recently, Kuhn has described an ingenious method, based on Clough's hypothesis, for detecting the occurrence of α-
inversion, in which the physical properties of the optically inactive modifications of tartaric, dichlorosuccinic and chloromalic acids are compared. Dichloromalic esters should be Tartaric and dichlorosuccinic acids exist in racemic and meso-forms which differ in melting point, crystalline form, etc. The existence of the meso-form depends on the fact that the two halves of each molecule of these acids contain the same three groups. In chloromalic acid, however, the form corresponding to the meso-form can exist in two optically active forms which combine to give a molecular racemic compound. Hence there are two racemic or dl-chloromalic acids.

Hahn therefore argued that the physical properties of the racemic chloromalic acid which was configuratively similar to the racemic tartaric and racemic dichlorosuccinic acids would be more nearly intermediate between those of the racemic dihydroxy and dichlorosuccinic acids than between those of the racemic di-chloromalic, racemic di-chloromalic, meso-dihydroxy and dichlorosuccinic acids. Similarly, the physical properties of the dl-chloromalic acid with the meso configuration would be more nearly intermediate between those of the meso-dihydroxy and meso-dichlorosuccinic acids than between those of the racemic varieties. Hence by a comparison of the physical properties of the optically inactive acids, racemic dichloromalic and racemic dichloromalic, the configurations of the two dl-chloromalic acids were determined. The method used to detect the occurrence or non-occurrence of a Walden inversion can be illustrated by the interaction of
methyl \textit{meso}dl-chloromalate with thionyl chloride in the presence of pyridine. If substitution proceeds without inversion two molecules of \textit{meso}-dichlorosuccinic ester should be obtained from each double molecule of the \textit{meso}-dl-chloromalate, but if inversion occurs the product should be racemic methyl dichlorosuccinate. Actually the racemic methyl \textit{meso}-dichlorosuccinate was obtained, so that it can be concluded that the substitution of the hydroxyl group of \textit{meso}-dl-chloromalate by the chlorogroup using thionyl chloride is accompanied by inversion of configuration.

\begin{align*}
\text{racemic dl-chloromalate} & & \text{meso dl-chloromalate} \\
\text{H} - \text{C} - \text{Cl} & & \text{H} - \text{C} - \text{Cl} \\
\text{H} - \text{C} - \text{Cl} & & \text{H} - \text{C} - \text{Cl}
\end{align*}

\begin{align*}
\text{meso dichlorosuccinate} & & \text{racemic dichlorosuccinate} \\
\text{H} - \text{C} - \text{Cl} & & \text{H} - \text{C} - \text{Cl} \\
\text{H} - \text{C} - \text{Cl} & & \text{H} - \text{C} - \text{Cl}
\end{align*}

Similarly, the configurations of the optically active chloromalic acids, which can be derived from dextromalic acid by replacing one of the hydrogen atoms of the \textit{CH}_2 group by
chlorine, can be correlated with those of dextro-tartaric and dextrochlorosuccinic acid on the one hand and with those of meso-tartaric and meso-dichlorosuccinic acids on the other. When these conclusions are applied to the action of phosphorus pentachloroide on dextro-malic acid, it can be deduced that the reaction proceeds with inversion, laevorotatory chlorosuccinic acid being obtained.

Hahn therefore concludes that the action of either thionyl chloride or phosphorus pentachloride on a hydroxy acid compound is attended by inversion. Hence, a hydroxy compound has the same configuration as the corresponding halide with the same sign of optical rotatory power, which again confirms the conclusions previously drawn, that sulphonates react with salts of halogen acids with inversions.

The rotation of a salt in a chloroform solution depends only on the optical rotatory power of the salt's parent. Kolbe's found that the specific rotation of a base such as quinine varies only between $-9$ and $+9$ when dissolved separately in hydrochloric, nitric, sulphuric, phosphoric, hydroxy, nitric and hydroxy acids, while A. H. Laidlaw found that the rotatory power of the hydrocyanate, nitro, phosphoric, and succinylultrahydrocyanate between the values 0.3 and 29.7. Similarly, the rotation rotation of a salt formed from an optically active base and an optically active salt will be the sum of the rotatory rotations possessed by the optically active aqueous and organic when they are separated with optically inactive aqueous.

In addition to attempts to determine the relative configurations of similarly constituted derivatives from a study of their optical rotatory powers, other attempts were made to ascertain configurational relationships from a study of the manner in which the rotatory power changed with variation of the groups attached to the asymmetric carbon atom. Research in this direction commenced soon after the establishment of van't Hoff's principle of asymmetry. Among electrolytes, very simple relations were found to exist, which are readily explained by the Arrhenius theory of electrolytic dissociation. Thus, the limiting rotation of a salt in dilute aqueous solution depends only on the optical rotatory power of the active radical. Oudemans found that the specific rotation of a base such as quinine varied only between -272° and -320° when dissolved respectively in hydrochloric, nitric, sulphuric, phosphoric, perchloric, formic, acetic and oxalic acids, whilst H. H. Landolt found that the rotatory powers of the monolithium, sodium, potassium and ammonium salts of tartaric acid lie between the values 27.5° and 28.5°. Similarly, the molecular rotation of a salt formed from an optically active base and an optically active acid will be the sum of the molecular rotations possessed by the optically active cation and anion when they are combined with optically inactive ions.
with non-electrolytes, less obvious relations exist, but
an attempt to connect the magnitude of the rotation with the
dimensions of the radicals composing the asymmetric molecule was
made in 1890 by A. Crum Brown (Proc. Roy. Soc. Edin., 1890, 17, 161) and independently by P. A. Guyo (Compt. rend., 1890, 119, 714). It is assumed that, as the rotatory power is due
to the difference between the four groups around the asymmetric
carbon atom, so its magnitude may correspond to the magnitude
of this difference. Thus, if \( K_1, K_2, K_3, K_4 \), represent the
value of some common property of each group, an expression
\((K_1-K_2)(K_1-K_3)(K_1-K_4)(K_2-K_3)(K_2-K_4)(K_3-K_4)\) would be related
to the magnitude of the rotatory power. This expression has a
value zero when two of the groups are equal, and changes its
sign while retaining its value when the positions of two of the
groups are interchanged. The chief difficulty lies in the
choice of a suitable property. If weight is chosen, the
objection arises that compounds such as, for example, methyl
acetylmandelate \( \text{CH}_3\text{CO} \text{Mand} \), containing groups of equal weight
but of different structure, often show considerable rotatory
power. This suggests that before reasonable conclusions can be
drawn, the distances of the centres of gravity of the four
groups from the centre of gravity of the molecule must be known.
van't Hoff considered that other properties, such as dielectric
constant, might be tested along the lines put forward by Crum
Brown and Guye. This suggestion is of special interest from
the point of view of modern polarity theories. Eventually,
the theory of Crum Brown and Guye had to be abandoned, as apart
With non-electrolytes, less obvious relations exist, but an attempt to connect the magnitude of the rotation with the dimensions of the radicals composing the asymmetric molecule was made in 1889 by A. Crum Brown (Proc. Roy. Soc. Edin., 1890, 17, 161) and independently by R. A. Guye (Compt. rend., 1890, 110, 714). It is assumed that, as the rotatory power is due to the difference between the four groups around the asymmetric carbon atom, so its magnitude may correspond to the magnitude of this difference. Thus, if \( K_1, K_2, K_3, K_4 \), represent the value of some common property of each group, an expression

\[
(K_1-K_2) (K_1-K_3) (K_1-K_4) (K_2-K_3) (K_2-K_4) (K_3-K_4)
\]

would be related to the magnitude of the rotatory power. This expression has a value zero when two of the groups are equal, and changes its sign while retaining its value when the positions of two of the groups are interchanged. The chief difficulty lies in the choice of a suitable property. If weight is chosen, the objection arises that compounds such as, for example, methyl acetylmandelate \( 146^\circ \), containing groups of equal weight but of different structure, often show considerable rotatory power. This suggests that before reasonable conclusions can be drawn, the distances of the centres of gravity of the four groups from the centre of gravity of the molecule must be known. Van't Hoff considered that other properties, such as dielectric constant, might be tested along the lines put forward by Crum Brown and Guye. This suggestion is of special interest from the point of view of modern polarity theories. Eventually, the theory of Crum Brown and Guye had to be abandoned, as apart
from the influence of external conditions such as solvent, temperature, concentration, wave length, etc., on rotatory power, many other factors of a constitutional character, such as double and triple bonds, the presence of closed rings, lactonic and anhydride bonds, structural isomerism, optical superposition, were also found to influence the rotatory power.

No definite progress was made until 1907, when Betti began a series of investigations in which he tried to correlate the influence of substituents on rotatory power with their influence on other properties. The most complete results were obtained using a series of Schiff's bases (Formula I) obtained by condensing β-naphtholphenyl-aminomethane (Formula II) with benzaldehyde and substituted benzaldehydes. A series containing the double bond was found to fall in a similar order. Thus, by measuring the absorption of specific gravity, rotatory power, benzaldehyde and substituted benzaldehydes containing the phenyl group are found to fall in a similar order. Thus:

\[
\begin{align*}
\text{I} & \quad \text{C}_6\text{H}_5\text{C}-\text{NH}_2 \\
\text{II} & \quad \text{C}_6\text{H}_5\text{C} = \text{H}_2\text{N} \quad \text{C}_6\text{H}_5\text{C} \quad \text{C}_6\text{H}_5\text{C} \quad \text{C}_6\text{H}_5\text{C}
\end{align*}
\]

As a measure of the "chemical masses" of the substituents, Betti used the dissociation constants of the acids derived from the aldehydes employed. The molecular rotatory powers of the compounds in benzene solution varied from \(-931^o\) to \(+937^o\), and when arranged in order of magnitude gave a series which agreed very closely with that representing the dissociation constants of the acids. Thus, for monosubstituted ortho-compounds, the influence of substituents on rotatory power and dissociation constants was studied.
on the dissociation constant respectively is:

\[ \sqrt{K} = \text{NO}_2 < \text{Cl} < \text{OH} < \text{H} < \text{OCH}_3 \]

The agreement in the para-series is closer than in the ortho-series where there are probably disturbances caused by the direct space effect of the substituent group. The relative influences of these substituents on other properties of compounds containing them have also been shown to fall in a similar order. Thus, by measuring the velocities of Friedel Crafts' reactions between \( p \)-bromobenzensulphonyl chloride and various \( p \)-substituted benzenes, Olivier obtained the series:

\[ \text{CH}_3 > \text{H} > \text{Br} > \text{Cl} > \text{NO}_2 \]

The series \( \text{CH}_3 > \text{H} > \text{I} > \text{Br} > \text{Cl} > \text{CO}_2\text{H} > \text{NO}_2 \) was obtained by the same author from a comparison of the rates of hydrolysis of \( p \)-substituted benzyl chlorides. Similar series have been obtained by measurements of the dissociation constants of acids and bases (Flursheim, J.C.S., 1909, 93, 713) and of the rate of hydrolysis of esters of substituted benzoic acids (Kellar, Zeit. Phys. Chem., 1907, 24, 221) Robinson, (Ann. Rev. Chem. Soc., 1922, 93) has called it a general polar series and the
radicals comprising it, polar groups.

Until recent years, chemists were very slow to admit that there were two kinds of chemical affinity. The majority of organic chemists followed Kohlrausch in representing all the bonds between atoms as non-polar, whilst others, such as Fry, adopted the suggestion made by Thomson and Ramsay that a polar valency was a Faraday tube of force passing from a positive charge in one atom to a negative charge in another, and assumed that all valencies were of the polar type. The vast increase in the knowledge of the structure of the atom during the last twenty years, however, enabled Thomson, Rutherford, Bohr, Langmuir and others to produce atomic models which indicated a relation between atomic structure and valency and so led to the development of the electronic theory of valency.

According to the electronic theory of valency, the elements owe their valency to a powerful but mysterious force which urges them to build up groups of 2, 8, 18 and 32 electrons. This force appears to be identical with "chemical affinity" known to generations of chemists, since it is this which determines chemical combination between atoms. The building up of the stable groups of electrons, which in the case of the elements from carbon to calcium are usually octets, can be done in three ways, and three corresponding types of valency are recognised:

(1) Electrovalencies, which are polar or ionisable linkages between oppositely charged ions of a salt formed by the passing
of one or more electrons completely from one atom to the
other. Molecules containing such dipoles would, when placed in an
electrostatic field, tend to align themselves with their dipoles
(2) Covalence, which are formed by the more or less equal
sharers of the electrons by both the atoms concerned in the
case, the exact lengths would give a measure of the dipole
strength in a corrected form density and molecular weights of the
(3) The semi-polar double bond, postulated by Lowry and
substance. W. L. and P. (J., 1924, 162, 210) calculated
Sidgwick, in which one atom supplies both electrons constituting
a group of molecules having common oxygen atoms or groups of the
the link. The existence of such a link is supported by
kinds XIX and XX, where X is a radicle containing, and
measurements of paraarons and dielectric constants. Further
found that in these cases to increase the binding capacity of
evidence is also available in the case of sulphones, &c.,
both types of molecule, the substances fall into the class
which have been resolved into their rotating isomers by Harrison,
E. G. (1924, J., 162, 210), and by Mesbah together with the
example of Kenyon and Phillips (J., 1926, 2079), and which owe their
asymmetry to the presence of a semi-polar double bond.

Where the test for retrograde change is simple of course
A rigid distinction cannot be drawn between non-polar
molecules and those classified on a much smaller basis by the list of
compounds containing only covalent linkages and polar compounds
a theory of dielectrics due to Pocke, (Ann. Chem. 33. 1891), containing ionised linkages, and the existence of intermediate
91. Pocke's Verhage, Leningr., 1890). It is not necessarily
stages is indicated by the comparison of solubility, volatility,
apparent, that the double bond of a semi-polar compound, hydrogen
and dielectric constants of compounds. The covalent link is
in a molecule of the atom of the molecule in question, since most
now regarded as an extreme case of the ionised link, since most
of the double bonds of a molecule can be defined as the charge
covalent links possess dipole moments. The introduction of
an is the one role of the group substituted by the distance between
a polar group into a hydrocarbon molecule causes an unequal
the polar group denuded by the molecules of the dipole moment,
sharers of the electrons of the link, which are attracted more
strongly by one of the component parts of the molecule, this
part thus acquiring a "small negative charge while the other be
acquires an equal positive charge. Such a dipole varies in its
strength and orientation with the nature of the substituent, and
it was suggested by J. J. Thomson (Phil. Mag. 1923, 46, 497) that molecules containing such dipoles would, when placed in an electrostatic field, tend to orient themselves with their dipoles opposing the field, so that measurements of dielectric constants for long wave lengths would give a measure of the dipole strength if corrected for density and molecular weight of the substance. Rule and Paterson (J.C.S. 1924, 125, 2155) calculated a number of molecular inductive capacities for compounds of the types $C_2H_7X$ and $C_3H_5X$, where $X$ is a variable substituent, and found that in their power to increase the inductive capacity of both types of compounds, the substituents fell into the order: $NO_2 > CN > Cl > Br > CH_3 > H$, thus providing another example of a polar series.

Within the last few years, the whole theory of polar molecules has been placed on a much sounder basis by the aid of a theory of dielectrics due to Debye (Physikal. Zeit. 1912, 13, 97; Polare Molekeln. Leipzig 1929). It is now generally accepted that the dipole moment of a monosubstituted hydrocarbon is a true index of the polarity of the substituent atom or group. The dipole moment of a molecule may be defined as the charge on any one pole of the dipole multiplied by the distance between the poles. Debye developed his theory in the following manner:

When polar molecules are placed in an electrostatic field, there are two main effects: (1) an equilibrium will be set up between the tendency for the molecules to orientate themselves in opposition to the field and the tendency for them to be oriented
equally, in all directions as the result of thermal agitation. At equilibrium, a certain number of molecules, depending on their polarity, will be opposing the field. (2) There will be an appreciable distortion of the molecules due to the external field, the electrons being attracted towards the positive side of the field and the protons towards the negative side. This will lead to an induced polarisation of the molecules distinct from the permanent polarisation due to the presence of polar groups.

The dielectric constant is a measure of the total change in the field strength due to the presence of the molecules, i.e. a measure of the combined effects of orientation and distortion. According to Debye, the electric moment or total polarisation $P$ per gram molecule is given by

$$ P = \varepsilon  \frac{N}{d} (\varepsilon - 2)^{-1} $$

$$ = P_D + \mu $$

where $\varepsilon$ is the dielectric constant, $N$ the molecular weight, and $d$ the density of the substance. $\mu$ cannot be evaluated directly but both $P$ and $P_D$ are amenable to measurement. By using an alternating field of sufficient frequency, the molecules do not have time to set themselves parallel to the field and the dielectric constant then obtained is a measure of the distortion effect $P_D$. The Lorentz - Lorentz equation

$$ P_D = \frac{N}{n^2 \varepsilon D} - \frac{1}{n^2 \varepsilon D} = P_D + P_a $$
gives the value of the distortion term where \( n_p \) is the refractive index for infrared radiation which is used in order to take into account both electronic and atomic distortions. The atomic distortion \( P_A \) is usually small compared with the electronic distortion \( P_e \) which can be obtained by using visible light, since the refraction index for visible light depends only on the latter term.

\[
F_e = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{N}{d}
\]

The next general equation needed from their work is

By making the appropriate measurements, Debye was able to give a value to \( P_\mu \), the permanent polarisation of the molecule. A consideration of the conditions limiting the orientation of dipole forces in a steady field then enabled Debye to arrive at the following relationship between \( P_\mu \) and the dipole moment \( \mu \) of the molecule,

\[
P_\mu = \frac{N}{9 \, K \, T \, \mu^2} \text{ for various simple diatomic molecules with the same dipole moment} \]

where \( N \) is Avogadro's number, \( K \) is the gas constant for a single molecule, and \( T \) is the absolute temperature. Two effects can be distinguished in this connexion, namely, dipole association and thermal agitation. Polar molecules exert forces on each other when close together as in a liquid or highly compressed gas, and therefore tend to arrange themselves to minimise their external fields. This will apparently change their dipole moments, and in order to ensure that the measurements of
dielectric constants are made when each molecule is separated from its neighbours, so that dipole association cannot take place, measurements are made in the vapour state or in dilute solution in a non-polar solvent such as benzene or hexane.\(^4\)

These methods have been used by Höjendahl, (Thesis, Copenhagen, 1928), L'Arrêta (Leipsicenum Vertrico, 1929), C. P. Smyth (Chem. Rev. 1930, 543), J. Williams (Chem. Rev. 1929, 509), and many other investigators who have determined the dipole moments of a large number of compounds.

The most general conclusion reached from their results is that the dipole moments of monosubstituted hydrocarbons are to a great extent characteristic of the substituent which gives rise to the dipole and are not influenced by the nature of the hydrocarbon radical. Thus nitroparaffins and aromatic nitro-compounds have almost identical dipole moments. Höjendahl points out that the dipole moments of homologues are practically identical, while Bejer shows that various simple aliphatic alcohols have the same dipole moment. It can therefore be concluded that the electron shift which constitutes a dipole takes place only in the immediate neighbourhood of the substituent group, and since the measurements of dipole moments places the substituents in the series,

\[
\text{NO}_2 > \text{CH} > \text{CHO} > \text{Halogenes} > \text{OCO}_2 > \text{O} > \text{CH}_3 > N(\text{CH}_3)_2 > \text{NH}_2
\]

the general polar series can be seen to represent a gradual transition from groups which attract electrons strongly to groups which repel electrons.
Such a theory affords a ready explanation of the regularities noted in connexion with reaction velocity and rates of hydrolysis, and especially in connexion with Betti's investigations. These have recently been extended by Rule (Trans. Faraday Soc., 1930 25, 323) to the 1-methyl and 1-octyl esters of monosubstituted acetic acids $X.CH_3.COOCH_2.H_2O$ and $X.CH_2.COOCH_2.H_17$, and a striking parallelism has been shown to exist between series representing dipole moments, optical rotatory powers and dissociation constants of the parent acids.

| Homogeneous Esters of Monosubstituted Acetic Acids, $X.CH_2.COOH$. |
|---|---|---|---|
| $x$ | $\mu$ | $K_0$ of acid. | $\eta$ M/D $\nu$ | $\eta$ M/D $\nu$ |
| N(CH$_3$)$_2$ | 1.3 × 10$-10$ | -158.9 | - |
| H. | 1.8 × 10$-5$ | -157.3 | -11.8 |
| CH$_3$ | 1.4 | -150.2 | -13.9 |
| COOH | 130 | -160.2 | - |
| CO$_2$H | 22 | -160.6 | - |
| OC$_2$H$_5$ | 33 | -165 | -13.3 |
| CH$_3$ | 15 | -165 (at 94°C) | - |
| NH | -1.7 | -169 | -23.3 |
| Br. | -1.3 | -171 | -17.9 |
| Cl. | -1.3 | -174 | - |
| CN. | -3.3 | - | - |

Rule has therefore put forward the hypothesis that, assuming the validity of the theory of polarity, the magnitude of the optical rotatory power of an asymmetric compound is dependent on the magnitude and arrangement of the dipoles within
the molecule. Betti, on the other hand, suggests that optical rotatory power depends on the dipole moment of the molecule as a whole. (Trans. Faraday Soc. 1930, 26, 357).

According to Rule's hypothesis, optical rotatory power is dependent on the polarity of the substituent group, positive and negative groups influencing the rotation of the parent compound in opposite senses and the rotatory power varies in opposite directions in accordance with the polar series. Hence, if the derivatives of the parent compound are arranged in order of increasing optical rotation, those having the increasing order of optical rotation, this order is also that of the increasing positive polarity of the substituents. Furthermore, all the members of this series of derivatives would possess the same configuration.
A COMPARISON OF THE ROTATORY POWERS OF THE 

BUTYL DERIVATIVES PREPARED FROM $d^{-}$-BUTYL $p$-TOLUENESUL-

PHONATE AND $p$-TOLUENESULPHONATE

In each case the reaction mixture was poured into water and then it has been proved that the $p$-touluenesulphonie esters of secondary alcohols react with salts of carboxylic acids with inversion of configuration. These esters also react with other salts besides those of carboxylic acids, and on the assumption that such reactions are attended by inversion it should be possible to obtain from the $p$-touluenesulphonate of, for example, $d$-dextro- or $d$-alcohol, a service of derivatives of the laevo- or $l$-alcohol. In accordance to Bude's tertial hypotenosis, the rotatory powers of these derivatives should vary in a regular manner, when they are arranged according to the increase in the positive character of their substituent groups. It is obvious that a derivative possessing the same configuration as the $d$-dextro- or $d$-alcohol would not find an appropriate place in such a series. If, therefore, a derivative prepared from the $d$-$p$-touluenesulphonie ester does not fall into place amongst the laevo- or $l$-derivatives, it can be concluded that its formation is not accompanied by a supposed Walden inversion with phenol, in each case in the presence of water. In the present work, $d$-butyl acetate, benzoate, iodide, cyanide, thiocyanate and selenocyanate were prepared from $d$-$d$-butyl $p$-touluenesulphonate by refluxing it with alcohol
or acetone solutions of the appropriate salts, when reactions occurred according to the general equation:

\[ C_4H_9C\text{SO}_4^+ + \text{MX} \rightarrow C_4H_9\text{X} + \text{M} \cdot \text{SO}_4\cdot C\text{H}_2 \]

In each case the reaction mixture was poured into water and then extracted with ether in the usual way. The ether was distilled off through a fractionating column and the residual liquid fractionated carefully since the comparatively low boiling points of some of the \( \beta \)-butyl derivatives did not permit of their ready separation from ether and ethyl alcohol. In this manner the \( \beta \)-butyl esters enumerated above were obtained and were all found to be laevorotatory.

\( \beta \)-butyl thiocyanate and selenocyanate were each obtained in good yield, and were used as the sources of other compounds. For example, by refluxing these esters with alcoholic potassium hydroxide, \( \beta \)-butyl disulphide and \( \beta \)-butyl diselenide were obtained respectively. The disulphide was then reduced to the mercaptan and the thiocyanate oxidised to the sulphonic acid. Since these derivatives were obtained from the thiocyanate without disturbing the four bonds of the asymmetric carbon atom, they all have the same configuration.

The interaction of the \( \beta \)-sulphonate with \( \beta \)-butyl alcohol, ethyl alcohol and with phenol, in each case in the presence of potassium carbonate, proceeded smoothly and yielded laevorotatory \( \beta \)-butyl \( \beta \)-butyl ether, \( \beta \)-butyl ethyl ether, and \( \beta \)-butyl phenyl ether respectively.
Owing to the extremely small yield of -butyl cyanide obtained by the interaction of the sulphonate with potassium cyanide, the acid chloride, amide and ethyl ester were prepared from methylethyl acetic acid which was resolved by means of brucine using the method of Markwald (Ber., 1896, 29, 53).

An interesting point arises on considering the reactions of sulphonates with Grignard reagents. α-β-Butyl p-toluenesulphonate reacts with Grignard reagents in a manner similar to that with which it reacts with salts.

\[
\begin{align*}
(1) \quad & \text{C}_4\text{H}_9\cdot\text{O} \cdot \text{SO}_2\cdot\text{C}_7\text{H}_7 + \text{R} \cdot \text{Mg} \cdot \text{X} = \text{C}_4\text{H}_9\cdot\text{R} + \text{Mg} \cdot \text{O} \cdot \text{SO}_2\cdot\text{C}_7\text{H}_7 \\
(2) \quad & \text{C}_4\text{H}_9\cdot\text{O} \cdot \text{SO}_2\cdot\text{C}_7\text{H}_7 + \text{R} \cdot \text{Mg} \cdot \text{X} = \text{C}_4\text{H}_9\cdot\text{X} + \text{Mg} \cdot \text{O} \cdot \text{SO}_2\cdot\text{C}_7\text{H}_7
\end{align*}
\]

Whereas, however, it yields β-butylbenzene when treated with phenylmagnesium bromide, as in equation (i), β-butyl bromide is obtained when it is treated with ethylmagnesium bromide, as in equation (ii). The formation of hydrocarbons by the interaction of p-toluenesulphonates and Grignard reagents has been noted by other workers. For example, by the interaction of magnesium phenylbromide and ethyl p-toluenesulphonate (Ferns and Lapworth, J.C.S., 1912, 101, 273) and β-chloroethyl p-toluenesulphonate (Gilman and Beaber, J. Amer. Chem. Soc., 1923, 45, 239), ethylbenzene and β-chloroethylbenzene, respectively, were obtained in small yield. From an extensive study of the reaction between sulphonates and Grignard reagents, Gilman and Beaber (ibid, 1925, 518) have concluded that where the Grignard reagent RMgX contains an R group of low molecular
weight, as in propyl magnesium and butyl magnesium bromides, the yield of aliphatic hydrocarbon is low. Where the R group is large, as in lauryl magnesium bromide, good yields of hydrocarbon are obtained, and this also occurs with arylmagnesium halides, such as phenyl magnesium bromide and alkyl p-toluenesulphonates. The formation of a halogen derivative was noticed in the interaction of the p-toluenesulphonyl derivative of optically active ethyl lactate and phenylmagnesium bromide, which gave, not the expected α-phenylpropionic ester, but α-bromopropionic ester in good yield and having a high rotatory power. (Kenyon, Phillips and Turley, J.C.S., 1925, 399). Reactions of this sulphonyl ester with ethyl magnesium bromide and magnesium ethyl iodide also yielded the corresponding halogen derivatives of ethyl lactate. The formation of both halogen derivatives and hydrocarbons in these reactions indicates that the R and X groups in Grignard reagents are similarly linked and that the linkage is probably similar to that between potassium and the acetate radical in potassium acetate.

The interaction of α-β-dibutyl p-toluenesulphonate with pyridine proceeded very readily according to the equation:

\[ \text{CH}_3\text{H}_2\text{N} + \text{C}_2\text{H}_5\text{O} \rightarrow \text{CH}_3\text{H}_2\text{N} \rightarrow \text{C}_2\text{H}_5\text{N} - \text{C}_2\text{H}_5 \text{H} \text{O} \]

After purification and drying over phosphorus pentoxide in a vacuum desiccator, N-β-butyly pyridinium p-toluenesulphonate was obtained as a white crystalline solid, m.p.50°. With
platinic chloride it yielded a salt \((\text{C}_5\text{H}_3\text{N} \cdot \text{C}_4\text{H}_9)_2 \text{PtCl}_6\)
m.p. 263° which was practically inactive in aqueous solution.

The reaction of the sulphonate with ammonia was carried out in a scaled tube in which the ester and the requisite amount of 0.500 ammonia were heated together. The butylamine produced was isolated as the hydrochloride, but owing to its extremely small rotatory power \((-201.15°\) for the hydrochloride of the fully active 1-β-butylamine, (More, 1965, 36, 587), it was converted into the benzoate by the Schotten Baumann reaction, since this derivative has a relatively high optical rotation (Pope and Gibson, J.C.S., 1913, Vol. 11, 1703). The rotatory power of the benzoate so obtained is given in Table I.

The reactions of the sulphonate with piperidine and with p-toluidine proceeded with great ease, and the products were easily separated by fractional distillation.

The interaction of optically inactive α-β-toluene-sulphonate
\[ \text{C}_4\text{H}_9\text{O} \cdot 3\text{O}_2 \cdot \gamma \gamma + \text{C}_6\text{H}_5\text{NH} \cdot \text{HCl} = \text{C}_4\text{H}_9\text{O} \cdot 2\text{O}_2 \cdot \gamma \gamma + \text{C}_6\text{H}_5\text{NH} \cdot \text{HCl} \]
\[ \text{C}_4\text{H}_9\text{O} \cdot 3\text{O}_2 \cdot \gamma \gamma + \text{C}_6\text{H}_5\text{NH} \cdot \text{HCl} = \text{C}_4\text{H}_9\text{O} \cdot 3\text{O}_2 \cdot \gamma \gamma + \text{C}_6\text{H}_5\text{NH} \cdot \text{HCl} \]

The interaction of piperidine and β-butyl p-toluene-sulphonate may proceed in one of two ways, since the addition of the β-butyl radical to the nitrogen atom may be followed by either (1) elimination of the hydrogen atom attached to the nitrogen atom, with the sulphonyo radical as p-toluene-sulphonic acid, resulting in the formation of N-β-butyl piperidine:-
or (2) elimination of the hydrogen atom attached to an adjacent carbon atom, followed by the migration of the β-buty1 radical to this carbon atom, and the formation of α-β-buty1 piperidine.

The interaction of optically inactive α-buty1 p-toluenesulphonate and piperidine was shown to yield N-β-buty1 piperidine by synthesising this compound from β-buty1 aniline and pentamethylenedibromide. The picrates of the compounds obtained from these two reactions possessed identical melting points and mixed melting points, and similar phenomena were observed with the platinic salts. Similarly a comparison of these derivatives with the picrate and platinic salt respectively of the compound obtained by the interaction of optically inactive β-buty1 iodide and piperidine showed that this product was also N-β-buty1 piperidine.
It was further shown that the piperidine derivative and the β-butyamine obtained from d-β-butyl p-toluene sulphonate possessed the same relative configuration, since by refluxing an ethereal solution of laevorotatory β-butyamine with penta-

methylenedibromide, N-β-butyl piperidine was obtained with the same sign of rotatory power.

Since this reaction is unlikely to be attended by inversion, it follows that laevorotatory β-butyamine and laevorotatory N-β-butyl piperidine possess the same configuration.

These conclusions have been substantiated by the results obtained from reactions between piperidine and n-butyl p-
toluene sulphonate and n-butyl iodide respectively. The products obtained were identical, since the picrates and platinic salts respectively had identical melting points and mixed melting points. Moreover, the interaction of n-
butyl bromide and piperidine has been shown to yield a piperidine derivative identical with that obtained from n-
butyramine and pentamethylenedibromide. (J. v. Braun, Ber.,
40, 3330; 42, 2641)

It can therefore be concluded that the N-alkyl piperidine derivative is usually obtained when alkyl p-toluene sulphonates and alkyl halides react with piperidine.
In Table I the derivatives obtained from d-β-buty1
p-toluene sulphonate by the reactions outlined above have been
arranged in increasing order of the positive character of the
substituent groups. In this Table the specific rotatory
powers of the derivatives in the homogeneous state and in
solutions of the same concentration in ethyl alcohol are
recorded for light of three wave lengths. In some instances
the rotatory powers in other solvents are recorded. Since,
however, the optical rotatory power of a compound is dependent
on many factors, both known and unknown, and the reactions by
which the β-buty1 derivatives are prepared are accompanied by
recrystallization, in many cases to unknown degrees, it will be
seen that there is not a close parallelism between the series
representing the magnitude of the rotatory powers and that
representing the polarities of the substituent groups. The
determination of the occurrence of a Walden inversion, there-
fore, is largely dependent on the sign of rotatory power of
the product obtained, although in Table II the full rotatory
powers are given where possible. From Table II it can be seen
that there is a general tendency for increased positive
polarity of the substituent group to produce an increased
negative rotation, not only for the substance in the homogeneous
state but also in solution. Thus, there is a steady increase
in negative rotatory power from the alcohol through the
halogen derivatives, acetyl derivative, valeric acid, acid
chloride and ethyl ester, butyl benzoate, cyanide, benzoic
 derivative to the thio-cyanate corresponding to an increase in
positive polarity of the substituent group.

The position of 1-β-buty1 sulphanic acid among the
inorganic series of derivatives appears to be anomalous,
since this compound has a deuterotation. It is obtained by
oxidising 1-β-buty1 thioeyanate, a reaction which is unlikely
to be attended by inversion since the four bonds attached to
the asymmetric carbon atom are not disturbed. It is probable
that the decrease in negative rotation observed on passing
from either the thioeyanate or the mercaptan to the sulphonie
acid is caused by the partial neutralisation of the effect of
the positively charged sulphur atom by the contrary influence
of the more distant negatively charged oxygen atom. Although
in the case of the β-buty1 derivatives, this leads to a reversal
of sign, Levene and Niiyama record two instances where the
mercaptan and the corresponding sulphinic acid possess the
same sign of rotation — namely, the derivatives of methyl-
naphthyl carbonyl and p-pikloxyphenyl carbonyl.

This compensating effect of the negative end of the
dipole has been illustrated in the case of the aromatic
sulphonic acids, where it is found that nitration of the free
acid containing three equivalent negatively charged oxygen
atoms yields 14% of the μ-nitro compound, while nitration of
the sulphonic ester containing only two negatively charged
oxygen atoms — a decrease in the compensating negative charge
by 2/3 — yields 32% of the μ-nitro derivative.
Levone and Niseiha have attempted to establish configurational relationships between hydroxy and halogen derivatives by comparing their rotatory powers with those of the thiols and sulphonic acids. For example, the substitution of the hydroxyl group of dextrorotatory $\beta$-octyl alcohol by bromine leads to the formation of a levorotatory bromide. The change $\text{C}_8\text{H}_7\text{SH} \rightarrow \text{C}_8\text{H}_7\text{SO}_2\text{H}$ is also accompanied by a change of sign. Similar relationships exist amongst the analogous derivatives of other alcohols such as methylthethyl carbinol, isobutylmethy carbinol and benzylphenyl carbinol. Since no change in configuration can be assumed to occur during the oxidation of the thiol group, the reversal in sign of rotation accompanying this change must be due to the change in polarity of the group attached to the asymmetric carbon atom. Levone and Niseiha therefore argued that since the difference in polarity between the $-\text{OH}$ and $\text{Cl}$ groups is qualitatively similar to that between the $-\text{SH}$ and $-\text{SO}_2\text{Cl}$ groups, the reversal in sign of rotation is due to this change in polarity and not to any configurative change in the molecule. Hence, it is concluded that in the series of alcohols investigated the alcohols are configurationally related to the halides which rotate in the opposite direction and enantiomorphously related to the halides rotating in the same direction.
It is possible to determine the relative polarities of groups by many methods, some of which were mentioned in the previous chapter. An additional method is based on the observation of Francis, Andrews and Johnson (J. Amer. Chem. Soc., 1923, 45, 1624), who pointed out that if a series of monosubstituted benzenes, PhX, is arranged in accordance with the Holloman's series for diminishing \( \pi \)-orienting power, the n.p.'s and b.p.'s fall through the \( \pi \)-series and rise through the \( n \)-series, and a similar relation exists for the compounds of the type IX. From a consideration of the n.p. \((-32^\circ)\); Bagster, J., 1911, 22, 1222) and the b.p. \((-31^\circ)\); Steele and Bagster, J., 1910, 27, 2007) of hydrogen sulphide, the position of the \(-\text{SH}\) group can be ascertained, and the following series is then obtained (Chou, Kenyon and Phillips, J. 1929, 1705): -CH\(_2\)-, negative, \( \pi \)-orienting; \( \text{H} \), positive, \( \pi \)-orienting.

\[ \text{Cl, } \text{Br, } \text{I, NO}_2, \text{SO}_2 \text{H, CCl}_3, \text{H} \]

It can be seen that the change in polarity from \(-\text{OH}\) to \(-\text{Br}\) (both negative groups) is much less than that between \(-\text{SH}\) (negative group) and \(-\text{SO}_2\text{OH}\) (positive group).

Further, since the \(-\text{SH}, -\text{OH}\) and \(-\text{Cl}\) groups have polarities of the same order of magnitude, their influence on rotatory power should be similar. The dextroretortatory alcohol and dextroretortatory halide are therefore configurationally related. Moreover, Levene's conclusions are not supported by the results
obtained by Clough, Harper, Freudenborg and Hahn in connexion with the configurations of hydroxy compounds and their halogen derivatives. Since optical rotatory power varies markedly with the polarity of the substituent group, Rule has pointed out that similar changes should occur when one of these substituents acquires an electric charge by ionisation. In the case of a simple aliphatic carboxylic acid ionisation will lead to the formation of a negatively charged carboxyl radical in place of the neutral group, and rotatory power will therefore alter in the direction of the rotatory powers of the other more negative substituents and may even be accompanied by a change in sign. Thus, lactic, glyoxylic and methanesuccinic acids all suffer a reversal of sign when converted into their sodium salts. 1-Methylethylacetic acid with $\alpha = -8.47^\circ$ in water forms a sodium salt with $\alpha = 2.01^\circ$ in water; 1-ethyl sulphonie acid with $\alpha = 0.34^\circ$ in water gives a sodium salt with $\alpha = 1.03^\circ$ in water; 1-ethyl hydrogen phthalate with $\alpha = 47.80^\circ$ in ethyl alcohol gives a sodium salt with $\alpha = 31.95^\circ$ in ethyl alcohol. Similar changes were observed in the ionisation of methylglycol $\alpha = 22.00^\circ$ in ether to $\alpha = 14.80^\circ$ for the potassium salt in ether, and methylglycolacetan with $\alpha = 3.46^\circ$ in ethyl alcohol to the potassium salt with $\alpha = 4.00^\circ$ in ethyl alcohol. In each case increased ionisation and therefore increased negative polarity of the substituent group produces a decreased negative rotation, and so fits into the table of laevor-
derivatives in accordance with Rule's hypothesis.

Similarly the conversion of a negative amino group into
the positive -\( ^{\dagger} \)NH group in acid solution - a process involving
the addition of a proton - will cause the rotatory power to
change in the direction of that of the more positive sub-
stituents and in this case involves a reversal of sign. Thus,
\( \beta \)-butylamine with \( \alpha = 15^\circ \) in water has \( \alpha = 15^\circ \) in 0.4\% in
H-hydrochloric acid; \( \beta \)-butyl piperidine with
\( \alpha = 39^\circ + 0.7^\circ \) in ethyl alcohol has \( \alpha = 39^\circ + 1.3^\circ \) in H-
hydrochloric acid and \( \beta \)-butyl p-toluidine with
\( \alpha = 43^\circ + 44.33^\circ \) has \( \alpha = 43^\circ + 4.72^\circ \) in 0.477 \( \% \). hydrochloric
acid. Ionisation, in each case, causes an increase in negative
rotatory power corresponding to the increased positive
polarity of the substituent group, and these derivatives there-
fore fit into the table of the laevio-series of Derivatives.
Hence it follows that the dextro-rotatory amines have the same
configuration as the laevio-rotatory alcohol. The amino-
derivatives obtained from the \( \beta \)-\( \beta \)-butyl \( \beta \)-toluenesulphonate,
however, were laevio-rotatory both in the homogeneous state and
in ethyl alcoholic solution, but were dextro-rotatory in
hydrochloric acid solution, thus showing an increased positive
rotation when converted into the hydrochloride. Hence, the
amine derivatives obtained from the \( \beta \)-sulphonate fit into the
series of derivatives of the dextro- or \( \beta \)-alcohol and not into
that of the laevio-alcohol. It is therefore concluded that
\( \beta \)-\( \beta \)-butyl \( \beta \)-toluenesulphonate, in reactions with primary and
secondary amine, yields the corresponding \( \beta \)-butyl derivative without change of configuration.

Further evidence to substantiate these conclusions was sought in a study of the reactions of \( \beta \)-butyl \( p \)-toluenesulphinate. \( p \)-Toluenesulphonic esters have certain interesting reactions which they share in common with \( p \)-toluenesulphonic acid. Thus, when shaken with aqueous solution of hypochlorous acid, \( p \)-toluenesulphonic acid is converted into \( p \)-toluenesulphonyl chloride and water. A similar reaction occurs between \( p \)-toluenesulphonic acid and halogens, for example, with bromine, \( p \)-toluenesulphonyl bromide and hydrobromic acid are formed.

\[
\text{CH}_3\text{C}_6\text{H}_4\text{SOOH} + H\text{OCl} = \text{CH}_3\text{C}_6\text{H}_4\text{SOOCl} + H_2\text{O}
\]

\[
\text{CH}_3\text{C}_6\text{H}_4\text{SOOH} + Br_2 = \text{CH}_3\text{C}_6\text{H}_4\text{SOOBr} + HBr
\]

Similar reactions are undergone by the \( p \)-toluenesulphonic esters. Thus, with hypochlorous acid, \( p \)-toluenesulphonyl chloride is produced and the alcohol is liberated, and with bromine, \( p \)-toluenesulphonyl bromide and the alkyl bromide. The alcohol and the bromide obtained by these reactions possess the opposite sign of rotatory power to that of the original alcohol.

\( p \)-Toluenesulphonic acid was also found to react with cyanogen bromide, \( p \)-toluenesulphonyl bromide and hydrocyanic acid being produced. The interaction of cyanogen bromide with \( \beta \)-butyl \( p \)-toluenesulphinate should by a similar reaction yield \( \beta \)-butyl cyanide and \( p \)-toluenesulphonyl bromide. Actually, the products isolated from this interaction were ammonium \( p \)-toluene-sulphonate, a yellow liquid which analysis showed was probably
p-tolylisothiocyanate, and a solid m.p. 113°C, which crystallised in prisms, gave an analysis corresponding to the p-toluenesulphonyl derivative of ethylmethacrylate and was optically inactive. Presumably, owing to the presence of water, hydrolysis of the original products occurred with formation of ammonia, methylethylacetamide, which reacted with the p-toluenesulphonyl bromide, and p-toluenesulphonic acid arising from a side reaction. p-Toluenesulphonic acid also condenses readily with benzoquinone to form 3:1 dihydroxyphenyl p-tolyl sulphone (Hinsberg, Ber., 1894, 27, 3359).

\[
\begin{align*}
\text{OH} & \quad \text{HO} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7 \quad \text{OH} \\
\text{O} & \quad \text{O} + \quad \text{HO} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7 \\
\end{align*}
\]

A small quantity of this compound was isolated from the black tar which resulted on warming β-butyl p-toluenesulphonate with benzoquinone, the butyl radical having been eliminated as butylene.

With anhydrous formic and acetic acids p-toluenesulphinic acid yields di-p-tolyl disulphoxide. A small quantity of this compound was isolated from the reactions of d-β-butyl p-toluenesulphonate with anhydrous formic and acetic acids, and β-butyl formate and acetate of the same sign of optical rotatory power as the original alcohol and with no diminution in magnitude of rotatory power were obtained respectively.

The interaction of d-β-butyl p-toluenesulphonate with primary and secondary amines also yielded β-butanol of the
same sign and magnitude of rotatory power as the original alcohol.

The results of these experiments demonstrate clearly the great difference which exists between the reactions of \( \text{n-toluene-sulphinic} \) and \( \text{p-toluene-sulphonic} \) esters, the sulphinic esters showing a tendency to react at the O-S linkage to a much more marked extent than the sulphonic esters. Then, however, the sulphonic esters react with compounds which link up with the sulphur atom of the \( \text{n-toluene-sulphonic} \) group, e.g., bromine and benzoquinone,

\[
\begin{align*}
\text{RC} = \text{O} & \quad \text{RC} = \text{OSO}_{2}\text{C}_{6}\text{H}_{5} \\
\downarrow & \quad \downarrow
\end{align*}
\]

the alkyl radical is detached and the reaction then simulates the type of reaction undergone by the sulphonic esters.
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>SPECIFIC GRAVITY</th>
<th>HOMOGENEOUS $[\alpha]_t^0$</th>
<th>SOLUTION $[\alpha]_t^0$</th>
<th>CONCENTRATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_4\text{H}_9\text{NC}_2\text{H}_5$</td>
<td>25 0.840</td>
<td>-54.59°</td>
<td>-9.10°</td>
<td>5.000 N.HCl</td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9\text{NC}_2\text{H}_5\text{CH}_3$</td>
<td>21 0.916</td>
<td>-63.53°</td>
<td>-18.76°</td>
<td>5.310 EtOH</td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9\text{NH}$</td>
<td>15 0.729</td>
<td>-99.60°</td>
<td>-32.01°</td>
<td>4.960 EtOH</td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9\text{NHCOCH}_3$</td>
<td>17 0.824</td>
<td>-63.53°</td>
<td>-32.01°</td>
<td>4.960 EtOH</td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9\text{NHCOCH}_3$</td>
<td>24</td>
<td>-99.60°</td>
<td>-32.01°</td>
<td>4.960 EtOH</td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9\text{SH}$</td>
<td>17 0.830</td>
<td>-63.53°</td>
<td>-32.01°</td>
<td>4.960 EtOH</td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9\text{CC}_2\text{H}_5$</td>
<td>20 0.745</td>
<td>-23.72°</td>
<td>-23.72°</td>
<td>4.960 EtOH</td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9\text{CC}_2\text{H}_5$</td>
<td>16 0.868</td>
<td>-41.04</td>
<td>-41.04</td>
<td>4.960 EtOH</td>
</tr>
</tbody>
</table>

**Table 1:** Specific rotation powers of $\beta$-butyl derivatives prepared from $\alpha$-$\beta$-butyl p-toluenesulphonate.
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>CONCENTRATION</th>
<th>SOLVENT</th>
<th>SPECIFIC GRAVITY</th>
<th>&quot;&quot;</th>
<th>0.6808</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>18 0.925</td>
<td>20 1.098</td>
<td>13 1.085</td>
<td>+2.22</td>
<td>2.27</td>
</tr>
<tr>
<td>H₄C₉H</td>
<td>15 0.973</td>
<td>19 1.078</td>
<td>17 1.002</td>
<td>3.00</td>
<td>1.28</td>
</tr>
<tr>
<td>H₄C₉H₂O₄</td>
<td>25 1.227</td>
<td>20 0.934</td>
<td>20 0.934</td>
<td>4.82</td>
<td>5.93</td>
</tr>
<tr>
<td>C₄H₉C₉H</td>
<td>20 0.925</td>
<td>20 1.098</td>
<td>13 1.085</td>
<td>+2.22</td>
<td>2.27</td>
</tr>
<tr>
<td>C₄H₉OC₆H</td>
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<td>20 0.934</td>
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<td>5.93</td>
</tr>
<tr>
<td>C₄H₉C₉H</td>
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<td>20 1.098</td>
<td>13 1.085</td>
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<td>2.27</td>
</tr>
<tr>
<td>C₄H₉OC₆H</td>
<td>25 1.227</td>
<td>20 0.934</td>
<td>20 0.934</td>
<td>4.82</td>
<td>5.93</td>
</tr>
<tr>
<td>C₄H₉OC₆H₂</td>
<td>15 0.973</td>
<td>19 1.078</td>
<td>17 1.002</td>
<td>3.00</td>
<td>1.28</td>
</tr>
<tr>
<td>H₄C₉H₂O₄</td>
<td>25 1.227</td>
<td>20 0.934</td>
<td>20 0.934</td>
<td>4.82</td>
<td>5.93</td>
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<td>25 1.227</td>
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<td>20 0.934</td>
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<td>SOLUTION $\alpha_{t^0}$</td>
<td>CONCENTRATION</td>
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<td>$C_4H_9NC_5H_{10}$</td>
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<td>Logan, J.C.S.</td>
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<td>-1.18°</td>
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<td>$C_4H_9NC_5H_8$</td>
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<td>-1.18°</td>
<td>5.000</td>
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<tr>
<td>Pope and Gibson, J.C.S.</td>
<td>$C_4H_9SH$</td>
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<td>Concentration</td>
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<td>Pickard and Kenyon, J.C.S.</td>
<td>C$_4$H$_9$COCH$_3$</td>
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<td>-30.17</td>
<td>-30.45</td>
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<td>Pickard and Kenyon, J.C.S., 1915, 129.</td>
<td>C$_4$H$_9$SO$_2$C$_7$H$_7$</td>
<td>20</td>
<td>-12.98</td>
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<td>Marckwald, Ber., 29, 53.</td>
<td>C$_4$H$_9$COCH</td>
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<td>-31.11</td>
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<td>Harrison, Kenyon and Shepherd, J.C.S., 1926, 658.</td>
<td>C$_4$H$_9$C$_6$H$_5$</td>
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<td>5.000</td>
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<td>-34.43</td>
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By recognising the existence of both polar and non-polar types of valency and the tendency for atoms to form stable groups of electrons by means of one or more types of valency linkage, the electronic theory of valency enables a much clearer view to be obtained of the mechanism of substitution reactions, and it can now be seen that the older theories assumed a number of fundamental postulates for which there was no justification. Thus, the existence of complex intermediate compounds as were suggested by Werner, Fischer and others can now be seen to be impossible, since the addition of another atom or group to a carbon atom already covalently linked to four other groups and therefore possessing a complete shared octet of electrons, would cause an increase to ten electrons in the valency shell, which is contrary to the octet rule.

Moreover, on the electronic theory of valency, when the mechanism of substitution reactions is now discussed, it is necessary to know whether the group to be displaced separates from the adjacent carbon atom (1) as an anion, (2) as a cation, or (3) as a neutral molecule, leaving respectively a carbonium cation, an anion or a neutral molecule. Further, since in each case the carbon atom is momentarily attached to only
three groups, the stability of such carbonium ions and the
conditions under which they will retain their asymmetry must
be considered. In addition, the nature of the entering group
must be known, whether it takes part in the reaction as an
ion, a cation or as a neutral molecule.

It has been shown that if in reaction

\[ a \overset{+}{\equiv} b - C - X \]

\[ a - b - C - \overset{+}{X} \]

\[ a - b - C - \overset{+}{X} \]

with formation of hydrogen radicals and an active hydrogen
\[ a - b - C - \overset{+}{X} \]

A considerable amount of evidence is available that the
rupture of a molecule as depicted in reaction (3), where the
radical and the group each retain the electron they originally
contributed to the covalent linkage, is only a thermal or a
photochemical effect. For example, the molecular weight of
iodine obtained by vapour pressure measurements at 600° cor-
responds with the formula \( I_2 \), and becomes smaller as the tempera-
ture is further raised until at 1500° it reaches half the
initial value. This vapour does not act as a gaseous conduc-
tor on applying a voltage, indicating that the iodine molecule
has been completely split up into neutral iodine radicals, each
with seven valency electrons as in (a), and not into ions as
in (b).

\[ 2 \overset{+}{I} \overset{-}{\equiv} 2 \overset{+}{I} \]

and a side reaction then occurs:

\[ \overset{+}{I} \overset{-}{\equiv} 2 \overset{+}{I} \]

(b)
The chlorine molecule breaks up in a similar way into neutral radicals under the influence of light. An unsuccessful attempt was made by Bodenstein in 1914 to detect the formation of chlorine ions during the photochemical reaction between hydrogen and chlorine. It has been shown that this reaction depends on the absorption of light by chlorine, but it does not follow Einstein's law of photochemical equivalence, since it has a quantum yield of $10^6$. It is therefore assumed that a chain reaction occurs, one quantum of light causing the rupture of one molecule of chlorine into two active, neutral radicals, each of which in turn breaks up a hydrogen molecule with formation of hydrogen chloride and an active hydrogen radical which then reacts with another chlorine molecule, thus:

\[
\begin{align*}
\text{Cl}_2 & \quad = \quad \text{Cl} + \text{Cl} \\
\text{Cl} + \text{H}_2 & \quad = \quad \text{ClH} + \text{H} \\
\text{H} + \text{Cl}_2 & \quad = \quad \text{HCl} + \text{Cl} \\
i.e. \quad \text{Cl} + \text{H}_2 + \text{Cl}_2 & \quad = \quad 2\text{HCl} + \text{Cl}.
\end{align*}
\]

Polanyi has recently shown that the reaction between hydrogen and chlorine can be initiated not only by light, but also by vapourising a small quantity of sodium vapour into the mixture of the unreacted gases. The neutral sodium atom attacks a chlorine molecule thus:

\[
\text{Na} + \text{Cl}_2 \quad = \quad \text{NaCl} + \text{Cl}
\]

and a chain reaction then commences, hydrogen chloride being formed.
Spectroscopical evidence has also been obtained by 
Laving and Dewar, that water vapour at 1000° contains 
neutral hydrogen and hydroxyl radicals, and by Baker, that 
the flames produced by the combustion of ammonia in oxygen 
and hydrogen in nitrous oxide contain neutral OH and N\textsubscript{2}O 
radicals.

Experimental evidence for the decomposition of organic 
compounds into free radicals by heat has been presented by 
Pénet, who showed that the vapour of lead tetraethyl 
Pb(O\textsubscript{2}Et\textsubscript{4}), when mixed with an inert gas and passed through a 
heated tube, decomposed with the formation of free ethyl 
radicals, since the decomposed gas would remove lead mirrors 
from a colder part of the tube to form lead tetraethyl once 
more. This work has recently been extended by Rice, Johnston 
and Evering (J. Amer. Chem. Soc., 54, 1932), who show that a 
condensable gas such as steam or carbon dioxide may be sub-
stituted for the permanent gas in the decomposition of lead 
tetraethyl, and that a great variety of organic compounds, 
when heated in the range 600-1000° decompose into free radicals 
so that by removing the products rapidly from the furnace the 
free radicals formed can be combined with many different 
metals. For example, acetone was found to give only methyl 
groups, and propane gives 20% of methyl and 20% of ethyl 
groups. Other works almost be obtained, however, since the 

The rupture of a molecule in a polar field, such as that 
produced by the presence of an ionic reagent, results in the
formation of ions, since the two electrons of the covalent link will be attracted towards one part of the molecule by the positive ion originally present in the system. For example, the reaction between chlorine and potassium hydroxide in aqueous solution may be represented thus:

\[ \text{RO} \quad \text{Cl} \quad \text{Cl} + \quad \text{K} \]

The chlorine atom possesses a surplus of electrons and is present as \( \text{RO} \quad \text{Cl} \quad \text{Cl} + \quad \text{K} \) since aqueous containing this.

The majority of reactions are most easily explained by assuming that the reacting molecules separate into positive and negative ions in this way.

The possible reactions which involve the transformation of the optically active radical into either a cation or an anion now remain to be considered. It is sometimes possible to decide which type of change occurs by a consideration of the nature of the reagent containing the entering group.

Thus, in the bromination of an alcohol by means of hydrobromic acid the bromine atom, in accordance with its general behaviour, probably reacts as an anion. The hydroxyl group of the alcohol must therefore be removed as an anion, leaving a positively charged carbonium cation which will then link up with the bromine anion:

\[ \text{HCO} \quad \text{CH} \quad \text{H} + \quad \text{Br}^- \]

Such evidence cannot always be obtained, however, since the entering group is often present covalently linked as, for example, the chlorine in phosphorus trichloride or in thionyl
chloride. In these cases the chloride finally obtained is probably formed from the decomposition of intermediate products such as CH₃OPCl₂ and CH₃0.3021. It is therefore necessary to consider whether carbonium cations and anions are stable and could give rise to optically active products when liberated during substitution reactions.

The carbonium anion possesses a complete octet of electrons and is relatively stable since compounds containing this structure have been isolated in optically active forms, e.g.,

(1) the sodium salt of anti-β-nitrobutane (Kuhn and Albrecht, Ber., 1937, 60 (2), 1837) and (2) the diazo ester (Jarrel and Noyes, J. Amer. Chem. Soc., 1929, 51, 2350; Chiles and Noyes, ibid., 1929), lithium butyl (3) probably possesses a similar structure. 1925 (4) (5) (6) 1925, 1926 (7)

(1) \[
\begin{align*}
\text{Et} & \quad \bigcirc \quad \text{N} \quad \bigcirc \quad \text{Na} \\
\text{Et} & \quad \bigcirc \quad \text{C} \quad \bigcirc
\end{align*}
\]
Sodium anti-β-nitrobutane

A carbonium anion is therefore sufficiently stable to exist free and could combine with a positively charged atom with an incomplete octet of electrons to form a compound of the same configuration.
The remaining possibility, type (1), in which the asymmetric carbon atom loses the two electrons of the bond link with the group removed, has now to be considered. There is a considerable amount of evidence to show that carbonium cations are not optically stable in the free state, but tend to pass into an equilibrium mixture of the dextro- and laevo-forms.

\[ \text{a} \xrightarrow{\text{d}} \text{c} \xleftarrow{\text{b}} \text{a} \]

This radical has been shown to occur in positive rays (J. J. Thomson, "The Electron in Chemistry", 1933), in triphenyl-methane compounds, and its existence is postulated in the activated forms of carboxylic acids and esters (Bragg and Morgan, Proc. Roy. Soc., 104. (a) 437; Lowry and Cutler, J. 1935. 127. 609; Phillips, J. 1935. 125. 2563).

and the radical \( \text{C}^+ \) has been suggested as a unit in crystals of calcite as the result of X-ray analyses. This evidence indicates that while a carbonium cation cannot be considered to exist as an individual chemical molecule, it may exist momentarily in the free state. Optically active compounds containing a carbonium cation have not been isolated in the free state, probably because the carbon atom possesses only six electrons, with the result that the radical oscillates between...
the d- and l- forms. The analogous sulphur compounds such as sulphinates, sulphotides and sulphilimines have been isolated in optically active forms and their structural stability is probably due to the fact that the central sulphur atom possesses a complete octet of electrons.

The optical instability of carbonium cations is demonstrated in striking fashion by the isomerisation of d-phenylmethylcarbinyl p-toluenesulphinate to form optically inactive p-tolylα-phenylethyl sulphone. This isomerisation probably proceeds by the preliminary separation of the optically active phenylmethylcarbinyl radicals as cations, followed by their union with the sulphur atoms of the p-toluenesulphin- oxy ions through the lone pairs of electrons of the sulphur atoms.

\[
\begin{align*}
\text{C}_6\text{H}_5 & \to \text{C} \to \text{S}^+ - \text{C}_7\text{H}_7 & \text{C}_6\text{H}_5 & \to \text{C} \to \text{S}^+ - \text{C}_7\text{H}_7 \\
\text{CH}_3 & & \text{CH}_3 & \\
\text{Optically active.} & & \\
\text{C}_6\text{H}_5 & \to \text{C} \to \text{S}^+ - \text{C}_7\text{H}_7 & \text{C}_6\text{H}_5 & \to \text{C} \to \text{S}^+ - \text{C}_7\text{H}_7 \\
\text{CH}_3 & & \text{CH}_3 & \\
\text{Optically inactive} & & 
\end{align*}
\]

It is probable, therefore, that racemisation of the phenylmethylcarbinyl ion occurs before combination with the sulphur atom takes place. The racemisation which occurs during this
isomerisation is not due to the chemical instability of the sulphone or of the phenylmethacrylonitrile ion, since α-tolyl \( \alpha \)-phenylethyl sulphone can be prepared in an optically active state by the action of \( \alpha \)-chloroethylbenzene on sodium α-toluenesulphonate in alcoholic solution:

\[
\begin{align*}
\text{C}_6\text{H}_5 \quad & \quad \text{C} - \text{Cl} + \text{Na} \quad \text{C}_6\text{H}_5
g & \quad \quad \uparrow \quad \quad \downarrow
g & \quad \quad \text{C} - \text{H} \quad \quad \text{C}_6\text{H}_5
\end{align*}
\]

In this reaction, the chloro-group is probably removed as an anion and thereby causes the asymmetric carbon atom to become a cation. In spite of the conversion of the optically active radicals into cations an optically active sulphone is produced.

Further, the complex rotatory dispersion of compounds containing ketonic groups can be explained (Lowry and Cutler, 1925; Phillips, 1935) by the presence of an additional centre of asymmetry produced by the activation of the ketonic group. For example, \( 1-\beta \)-cetyl acetate may be written as an equilibrium mixture of the three forms:

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

The conclusion can therefore be drawn that only one type of substitution reaction, that in which carbonium cations are
produced, will lead to inversion. The idea that in substitution reactions attended by inversion, the entering group is attracted to the opposite side of the molecule to that occupied by the group to be displaced, although suggested by many early investigators of the problem, is only sanctioned by modern ideas of valency and polarity.

In order to explain the mechanisms of many reactions both in inorganic and in organic chemistry, the existence of intermediate compounds is postulated. Ebert (Naturwissenschaften, 13, 631, (1925)) for example, has shown that when ethyl alcohol and hydrochloric acid are mixed, the molar polarisation obtained is higher than that of either of the components, which is explicable on the assumption that a compound is formed between them. From molar polarisation data it appears that like molecules can become associated in several ways, the stability of the orientation of one molecule relative to another depending partly on the shape of the molecules, since this determines the minimum distance to which the polar parts of a molecule may approach, partly upon the presence or absence of dipoles, and partly upon the sizes and locations of the dipoles and the directions of their axes. The extent and even the type of orientation may vary with the temperature and the distance apart of the molecules. The two most common ways in which association can take place may be illustrated diagrammatically as follows:— (Cryst. Chem. Rev, 1929, 6, 549)
The dipole moment of a complex such as (1) would be more than twice that of a single molecule, while the dipole moment of two molecules associated in the same manner as in (2) would be zero. Rule and Neilson have produced evidence that dipole association is operative among the rotations they have observed.

The action of hydrochloric acid on methyl alcohol may be represented as the association of two dipoles as in (1).

Thus:—In any case, if the chlorine acid acid be expressed as

\[ \text{CH}_3\text{OH} + \text{H}^+ \rightarrow \text{CH}_3\text{O}^+ + \cdot \text{H} \]

the association of the hydrochloric reaction will occur.

Compound formation then occurs by the donation of two electrons by the hydroxyl oxygen to the hydrogen ion of the hydrochloric acid molecule, the neutral water molecule is then eliminated, two electrons being withdrawn from the octet of the carbon atom in the process, and thereby a system is left which will give rise to an inversion of configuration.

\[ \text{Cl} \rightarrow \text{H}^+ \text{O} \rightarrow \text{Cl} \rightarrow \text{H}^+ - \text{O} - \text{H} \rightarrow \text{Cl} \rightarrow \text{H}^+ + \text{O}^{-} + \text{H}_2\text{O} \]

But, if dipole association occurs as in (2), then the action of hydrogen chloride would lead to the production of a halide of the same configuration, since on removal of water from the molecular complex, the chlorine anion would take the place of the hydroxyl group.
This method, however, is not a probable one, as in the majority of cases special considerations and forces of electrical repulsion would not permit of the near approach of the chlorine anion to the carbon tetrahedron on the same side as the hydroxyl group and, moreover, it is not supported by Ebert's observation.

In any case, if the chlorine anion fails to connect up successfully with the carbonium cation at the same moment as the hydrogen proton, racemisation will occur.

\[
\begin{align*}
\text{In this connexion the isomerisation of dextrorotatory phenylmethylcarbinyl dl-\(p\)-toluene-sulphinate to optically inactive p-tolyl \(\alpha\)-phenylethyl sulphone, and the formation of an optically active sulphone by the interaction of sodium \(p\)-toluene-sulphinate and \(\alpha\)-chloroethylbenzene is of interest.}
\end{align*}
\]
In the former case the phenylmethylcarbinyl cations separate from the \( \text{n-toluene} \) sulphonyl oxygen ions and recombine giving an optically inactive sulphone, whereas in the latter case, where they separate from chlorine ions in the presence of \( \text{n-toluene} \) sulphonyl oxygen ions, an optically active sulphone is produced. Inversion, therefore, can take place only in the presence of negative ions. In their absence racemisation occurs.

It is probable that dipole association precedes the interaction of Grignard reagents with sulphonates. Since a Grignard reagent contains two dipoles association may occur in two ways. For example, the association of ethyl magnesium bromide and \( \beta \)-butyl \( \text{n-toluene} \) sulphonate may be represented either by:

\[
\begin{align*}
\text{C}_2\text{H}_5\text{MgBr} & \quad \text{C}_4\text{H}_9\text{O}^+\text{SO}_2\text{C}_7\text{H}_7 & \quad \text{C}_2\text{H}_5\text{MgBr} & \quad \text{----- (a)} \\
\text{Br}^-\text{MgC}_2\text{H}_5 & \quad \text{C}_4\text{H}_9\text{O}^+\text{SO}_2\text{C}_7\text{H}_7 & \quad \text{Br}^-\text{MgC}_2\text{H}_5 & \quad \text{----- (b)}
\end{align*}
\]

Owing to the strong electrostatic attraction between magnesium and the ethyl and bromine anions respectively, association will occur to reduce the force of attraction between the bromine ion and butyl ion, or between the ethyl ion and butyl ion to a minimum. Both size of ion and charge will be operative, and, in general, it may be said that association will occur so that \( \frac{e_o}{r^4} \) is a minimum, where \( e \) is the charge on the butyl ion and \( e' \) that on the adjacent radical of the Grignard reagent, and \( r \) is the distance between them.

When the dipole of the molecule is in the opposite
direction to that described above, i.e., where the positive end is away from the carbon atom. Now \( \text{H} \to \text{C} - \text{X} \) now remains to be considered. This may lead to the approach of positive ions to the opposite face of the molecule so that occupied by the group X, but in this case, combination can only occur after the loss of X as a positively charged group and the migration of the positive substituent to the other side of the molecule.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} \to \text{C} \quad \rightarrow \quad \text{H} \to \text{C} - \text{X}
\end{align*}
\]

Obviously reactions of this type will not be attended by inversion. The nature of this reaction will be discussed more fully in the next section.

For example, the action of thioacetyl and carbonyl chlorides on alkyl mercaptans, sulfur mercaptocarboxylates of the sulfanilic acid configuration in the crinoid estate is produced. Similarly, the action of sulfur chlorides on \( \text{C} \text{H}_2 \text{C} - \text{SH} \) and \( \text{C} \text{H}_2 \text{C} - \text{SH} \) lead to the formation of chlorides of the same configuration as the original alcohols. In each reaction the chloride is produced by the decomposition of an intermediate acid chloride in which the chlorine is still covalently linked, e.g.,

\[
\begin{align*}
\text{C}_6\text{H}_5 \text{Cl} - \text{H} & \quad \text{C}_6\text{H}_5 \text{Cl} - \text{CH}_3 \\
\text{C}_6\text{H}_5 \text{Cl} & \quad \text{C}_6\text{H}_5 \text{Cl} - \text{CH}_3 \\
\text{C}_6\text{H}_5 \text{Cl} & \quad \text{C}_6\text{H}_5 \text{Cl} - \text{CH}_3
\end{align*}
\]

\( \beta \)-Substitution with sulfanilic anhydride, \( \beta \)-formate.
Modern theories of valency provide a reasonable explanation of the mechanism of reactions which occur with inversion, but the route followed by reactions which occur without inversion is obscure. One generalisation is possible, however, namely, that when reactions of compounds which do not contain carboxyl groups are unattended by inversion the entering group is covalently linked in the final phase of the reaction. For example, by the action of thienyl and carbonyl chlorides on ethyl-1-mandelate, ethyl phenylchloroacetate of the same configuration is produced. On the other hand, reaction of ethyl-1-mandelate with a mixture of electrons and electron acceptors produces a product of the same configuration as the original ester is produced. Similarly, the action of carbonyl chloride on d-β-3-octanol and d-β-butanol also leads to the formation of chlorides of the same configuration as the original alcohols. In each reaction the chlorine is produced by the decomposition of an intermediate acid chloride in which the chlorine is still covalently linked, e.g.,

\[ CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \]

Phenylmethylchlorosulphinate

\[ PH_3 \quad CH_3 \quad CCl_3 \]

Phenylmethylchloroformate

\[ C_6H_5 \quad CH_3 \quad C_6H_5 \quad CH_3 \]

β-Butylchlorocarbonate
Hence when, for example, the chlorosulphinic ester decomposes, it is conceivable that it might decompose in either of two ways, as shown below:

\[
\text{C}_6\text{H}_5 + \text{Et} \rightarrow \text{C}_6\text{Et} + \text{SO}_2 + \text{Cl}^+ \quad (1)
\]

\[
\text{H} - \text{C} - \text{SO}_2 - \text{Cl} \quad (2)
\]

The elimination of the neutral \(\text{SO}_2\) molecule will result either in the formation of a carbonium anion containing the asymmetric carbon atom with a complete octet of electrons and a chlorine ion with a sextet of electrons and therefore positively charged (1), or alternatively a chlorine anion with a complete octet of electrons and a carbonium cation with an incomplete octet of electrons (2). The first mode of decomposition has all the features of a substitution reaction which occurs without configurative changes. It gives rise to a radical containing the asymmetric carbon atom in the anionic state, which can form the centre of a stable radical capable of retaining its configuration unchanged and, moreover, able to combine with a cation — such as the chlorine cation — giving rise to a molecule with the same configuration. If the decomposition of the complex occurs under conditions which...
compel the chlorine atom to separate as an anion, then the
intermediate chlorosulphinate group in the reverse reaction must proceed with inversion of configuration, since
rotatory power of chlorosulphinate is present to prevent
the chlorine ion is then attracted towards the opposite side
of the molecule to that occupied by the group to be displaced,
and when replacement occurs links up with the carbonium cation
with inversion. This condition was realised by Kanyon,
Lipson the pHillips (J.C.S., 1836, 410) who found that
dextrorotatory ethylphenylchloroacetate results if ethyl
\( 1 \)-mandelyl chlorosulphinate decomposes in the presence of
pyridine, in which case it can be assumed that a new complex
is formed which contains the entering group as an anion. On
these views the decomposition of ethyl \( 1 \)-mandelyl chloro-
sulphinate in the presence and absence of pyridine can be
formulated thus:-

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CHO} & \rightarrow \text{C}_6\text{H}_5\text{CO}^- + \text{Cl}^+ \\
\text{H} - \text{C} - \text{O} & \rightarrow \text{H} - \text{C} - \text{O}^- + \text{N}\cdot\text{C}_5\text{H}_5^+ \\
\text{pyridine} & \rightarrow \\
\text{C}_6\text{H}_5\text{CHO} & \rightarrow \text{C}_6\text{H}_5\text{CO}^- + \text{Cl}^+ \\
\end{align*}
\]

\( 1 \)-Mandellic acid, the intermediate phase in the
interaction of ethyl \( 1 \)-mandelyl and carbonyl chloride,
behaves in a similar manner to the corresponding chlorosul-
finate mentioned in the previous in a certain case, sul-
phinate. It decomposes on heating to give carbon dioxide and
laevorotatory ethylphenylchloroacetate but yields the dextro-
rotatory ester if decomposed in the presence of pyridine
(Kenyony, Liposcomb and Phillips, J.C.S. 1931, 2375).

\[
\begin{align*}
\text{C}_6\text{H}_5\text{C}^\text{H} & \xrightarrow{\text{Heat}} \text{EtO}_2\text{C}^\text{Cl} \\
\text{C}_6\text{H}_5\text{C}^\text{H} & \xrightarrow{\text{Heat} + \text{Pyridine}} \text{EtO}_2\text{C}^\text{Cl}
\end{align*}
\]

Similar results have been obtained by Houssia and Phillips
(J.C.S., 1932, 108) with \text{d}-octyl chloroformate and by
Mr. Shackleton in these laboratories with \text{d}-butyl chloro-
formate. These esters decompose on heating to yield chlorides
of the same configuration as the original alcohol and with
only a small loss of rotatory power; when decomposed in the
presence of pyridine a chloride of the opposite configuration
is obtained without any pronounced racemisation.

These results are also in agreement with the alternative
hypothesis that the intermediate complex decomposes as in
(2) with formation of a carbonium cation. It can be seen
from a space model of the intermediate complex that the chlorine
atom lies very close to the asymmetric carbon atom, and it is
therefore conceivable that combination of the carbonium cation
with the chlorine anion might occur before racemisation takes
place. Further, when chlorosulphinates and chloroformates
are decomposed in the presence of a tertiary base, the
entering chloro-group is no longer covalently linked but exists as a free chlorine anion. Hence these reactions proceed with inversion in the same way as all other reactions where the entering group is present as an anion. On the other hand, although the isomerisation of phenyl methylearbinyl m-toluene-sulphinate is similar to the decomposition of these chlorsulphinates and chloroformates in that there are no ions present in the system, yet this isomerisation results in the formation of an optically inactive sulphone. It was concluded that the phenylmethylearbinyl radical separates from the m-toluene-sulphonyloxy group as a cation and then recombines with it, but that racemisation occurs owing to the absence of negative ions which could link up with the optically active radical. On this evidence it is difficult to understand why, if the asymmetric radical in chlorsulphinates and chloroformates separates as a carbonium cation, the chloride is formed with practically no racemisation.

It is conceivable that sulphonates might also react with certain compounds without inversion provided that those compounds could become covalently linked. The reactions of sulphonates with salts in dissociating solvents occurs in the presence of negative ions, dipole association takes place and the reaction proceeds with inversion of configuration. It may be possible, however, to form an intermediate complex where the entering group is covalently linked by causing the sulphonate to react with compounds containing hydrogen, not
in the ionised state, but covalently linked to another atom such as oxygen or nitrogen. These reactions are made possible by the peculiar nature of hydrogen.

For many years the position of hydrogen in the Periodic Table was a continual source of controversy since hydrogen could be regarded as a lower homologue either of the univalent metals or of the univalent halogens. With the development of the electronic theory of valency, however, the relationships between hydrogen and the other univalent elements became much clearer. As Lowry pointed out in 1923 (Chem. and Ind. Reviews, 1923, Vol I. 43) hydrogen is unique in that it can attain a stable configuration either with no electrons, as in the hydrogen ion $H^+$, or with two electrons, as in the hydrogen molecule $H:H$. The hydrogen ion is distinguished by mobility and freedom to wander from one electrovalent bond to another, while the hydrogen radical remains irreversibly attached to one duplet of the eight electrons making up the octet of the other atom. In the case of hydrogen, there can be a progressive change from one type of valency to the other.

Pauling considers that the hydrogen bond in crystal structures is ionic, i.e., the hydrogen atom may lose its electron to atoms of large electron affinity such as fluorine, oxygen and possibly nitrogen, and become a small positive ion. This ion has a co-ordination number of two and can therefore form such groups as $\text{H}^+\cdot\text{F}^-$ or $\text{H}^+\cdot\text{O}^-$. In anhydrous acids and acids salts it can therefore be assumed
that the hydrogen exists as a positive ion, and is attached by a covalent link in all other compounds.

The limiting conditions which decide whether polar or non-polar compounds are formed have been discussed by Fajans. If two ions of opposite sign approach closely to one another, each will cause a disturbance of the other's electrons when the distance between them is sufficiently small, and if the distance is great enough the electrons will be diverted into new orbits associated with both electrons and thus will produce a covalent linkage. Such a change will depend on the attraction of the positive ions for electrons and the firmness with which these electrons are held by the negative ion. In the case of the positive ion the formation of covalencies is favoured by a high charge and small size since the intensity of the external field falls off as the diameter of the ion increases. Similar considerations can be applied to the negative ion, since increasing charge and increasing size both tend towards a looser binding of the external electrons and so favour the formation of covalencies. Thus, the tendency towards the formation of non-polar compounds increases on passing from fluorine to iodine where there is an increase in size, and from iodine through selenium to arsenic where there is an increase in charge. The conditions favouring the production of polar or non-polar compounds when two ions approach each other can therefore be summarised as follows.
Hydrogen bromide to hydrogen iodide. This is also the order

<table>
<thead>
<tr>
<th>Polar compounds</th>
<th>Non-polar compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low charge</td>
<td>High charge</td>
</tr>
<tr>
<td>Positive ion large</td>
<td>Positive ion small</td>
</tr>
<tr>
<td>Negative ion small</td>
<td>Negative ion large</td>
</tr>
</tbody>
</table>

Thus, hydrogen chloride will react with an alkali only in

Smith gives the following values for the dipole moments

of halogens and their derivatives \( \textit{J. Amer. Chem. Soc.}, 1930; \)

\[ 52, (3), 2227 \]—Similarly, hydrogen chloride cannot be regarded

as a reducing agent. Chlorine bromine and iodine, while

\[ X_2 \text{gas} \text{calc.} \quad 0.13 \text{g vanishing} \quad 0.65 \text{at} \]

\[ X \text{liq.} \quad \text{Calc.} \quad 1.07 \text{dipole} \quad 0.52 \text{calc.} \quad 0.65 \text{calc.} \]

\[ X \text{gas} \quad \text{Calc.} \quad 1.03 \text{dipole} \quad 0.79 \text{calc.} \quad 0.65 \text{calc.} \]

\[ C_2H_2X_2 \text{for} n=2 \text{.}3 \text{.} \]

Smyth has shown that the moment of the hydrogen

chloride molecule is greatly decreased by the shift of its

electron charge with the position in the Periodic Table.

The outer electrons under the attraction of the positive charge of

the atom in which it is already exerted. It is well

the hydrogen nucleus and that these electrons are more rigidly

bound than these in the iodine atom. Greater ease of dis-

may be reduced by vanishing and 0.59 atm.

placement of the electrons makes possible greater decrease in

the molecule as the result of attraction by the hydrogen nuclei.

Greater in less than iodine, 0.65 than in 0.59, and in 0.52 so that the moment decreases from hydrogen chloride through
hydrogen bromide to hydrogen iodide. This is also the order in the corresponding organic halogen derivatives. The reactivity of the halogen acids in halogenation and reducing reactions is in the reverse order of their moments. Thus, hydrogen chloride will react with an alcohol only in the presence of dehydrating agents, hydrogen bromide will react in the cold, whereas hydrogen iodide reacts very readily in the cold. Similarly, hydrogen chloride cannot be regarded as a reducing agent, hydrogen bromide is a weak one, while hydrogen iodide is a strong reducing agent.

On Fajans's theory, the hydrogen ion, owing to its minute size, should coordinate with extreme ease, and indeed it is doubtful how far an unsolvated ion can exist in an associated solvent. Thus the effect of mixing hydrogen chloride with water is merely to enable the hydrogen ion to coordinate with a water molecule, so that the ionised acid is really an ionised oxonium salt.

\[ \text{HCl} + \text{H}_2 \text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+ \]

The power of a hydrogen atom to act as acceptor varies to a marked degree with the position in the Periodic Table of the atom to which it is already combined. It is well known that the hydrogen in C-H cannot act as acceptor, in N-H it does so reluctantly and in O-H and F-H very readily. In the same way the coordinating power of hydrogen is much greater in I-H than in F-H, in S-H than in S-Cl, and in F-H^+ the value again rises. In Cl-H and Br-H, the coordinates are...
...then in Cl-X, i.e., its coordinating power in X-H increases as X changes from an earlier to a later group in the first period, or within a given group from the second period to the first. In other words, its coordinating power increases as the moment of X-H in which hydrogen is always positive increases. This is to be expected, since if the formation of a coordinate link consists in the hydrogen taking a share in a pair of unshared electrons of another atom, it will do so the more readily the smaller the positive charge of this atom.

This variation in the coordinating power of hydrogen provides a possible explanation of the reactions of β-buty1 p-toluenesulphonate with anhydrous acids and with primary and secondary amines, and also possibly a general explanation of the reactions of sulphonates with salts in alcoholic solutions.

It can now be seen that the interaction of a sulphonate with a primary or secondary amine or with an anhydrous carboxylic acid may proceed by the coordination of the hydrogen atoms of these compounds with the oxygen atom of the ester linkage, thus:

\[ \text{R} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7 \cdot \text{O} \cdot \text{H} \rightarrow \text{R} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7 \cdot \text{H} \cdot \text{NR} \]

It is significant that these reactions either proceed without inversion or result in complete racemisation. The possibilities again arise, as with the chlorosulphinates and...
chloformates, that the asymmetric radical will separate either as a cation or as an anion, and similar considerations can be applied. If a carbonium anion is formed, then the complex must decompose so that the coordinating hydrogen atom must take with it the two electrons with which it forms a covalent link with the nitrogen atom of the amine or with the oxygen atom of the carboxylic group.

\[
\begin{align*}
 & \begin{array}{c}
 \text{CH}_3 \text{C}_2 \text{H}_5 \text{O}^+ \text{SO}_2 \text{C}_7 \text{H}_7 \\
 \text{H}^+ \\
 \end{array} \\
 & \begin{array}{c}
 \text{CH}_3 \text{C}_2 \text{H}_5 \text{O}^+ \text{SO}_2 \text{C}_7 \text{H}_7 \\
 \text{H}^+ \\
 \end{array}
\end{align*}
\]

No reactions are known in which hydrogen attached to nitrogen or to oxygen can be removed as a negative ion. Even in the reactions of halogens attached to nitrogen, as in the chloramines and cyanogen halides, where the halogen has presumably a stronger electron affinity than the nitrogen atom, the halogen usually reacts as a positive ion and leaves a negatively charged nitrogen atom.

\[
\begin{align*}
 & \begin{array}{c}
 \text{H}_2 \text{C} \text{N}^+ \text{Br}^- + \text{NO}_2 \text{SO}_2 \text{C}_7 \text{H}_7 \\
 \rightarrow \text{HCON} + \text{NO}_2 \text{SO}_2 \text{C}_7 \text{H}_7 \text{Br}^- \\
 \end{array}
\end{align*}
\]

Moreover, the interaction of piperidine and an alkyl p-toluenesulphonate also yields, besides the alkyl piperidine, a small quantity of the alcohol unchanged in sign and
nitrogen atom during the course of the free radical reaction the magnitude of rotatory power, as well as the p-toluenesulphonate has diminished in intensity, even more so than the p-phenyl derivative of piperidine, indicating that the hydrogen in the reaction occurs at the nitrogen atom in piperidine, and has again been removed as a positive ion leaving a negatively charged nitrogen atom.

\[
\begin{align*}
R* \text{S}^- & \xrightarrow{\text{O}} S* \text{C}_7\text{H}_7 \\
\text{R*} & \text{S}^- \xrightarrow{\text{O}} S* \text{C}_7\text{H}_7 \rightarrow \text{RCH} + \text{C}_5\text{H}_10 \text{H}_3\text{SO}_2\text{C}_7\text{H}_7
\end{align*}
\]

This reaction is similar to the alcoholysis which occurs to some extent in the interaction of a sulphonate and an alcohol.

\[
\begin{align*}
\text{R*} & \text{S}^- \xrightarrow{\text{O}} S* \text{C}_7\text{H}_7 \\
\text{R*} & \text{S}^- \xrightarrow{\text{O}} S* \text{C}_7\text{H}_7 \rightarrow \text{RCH} + \text{EtCO}_2\text{C}_7\text{H}_7
\end{align*}
\]

On the other hand, if the asymmetric radical separates as a cation, then the complex must decompose so that the nitrogen atom of the amine and the ester oxygen atom of the carboxylic acid become anionic and the coordinating hydrogen atom separates as a cation.

\[
\begin{align*}
\text{H} & \text{S}^+ \xrightarrow{\text{O}} \text{C}_2\text{H}_5 \text{S}^- \text{C}_7\text{H}_7 \\
\text{H} & \text{S}^+ \xrightarrow{\text{O}} \text{C}_2\text{H}_5 \text{S}^- \text{C}_7\text{H}_7
\end{align*}
\]

From a space model of the intermediate complex formed from the sulphonate and piperidine, it appeared that the
nitrogen atom, during one phase of its free rotation round the single bond linking it to hydrogen, came exceedingly close to the asymmetric carbon atom, and it is possible, therefore, that the reaction may proceed via the formation of a carbonium cation and yet not be attended by racemisation such as occurred in the isomerisation of phenylmethylcarbiny1 p-toluenesulphonates. A radical has been eliminated as butylene. 

A few examples are known where the nitrogen atom separates as a neutral radical, but nevertheless it readily picks up two electrons and thus acquires a negative charge. For example, chloramine-T will dissociate to give a neutral p-toluenesulphonimido-radical, which acts as a radical acceptor as a cation which then combines with the tonic acid.

\[
\begin{align*}
\text{C}_7\text{H}_5\text{N}^- + \text{H}_2\text{O} &\rightarrow \text{C}_7\text{H}_5\text{N}^+ + \text{H}_2\text{O} \\
\text{C}_7\text{H}_5\text{N}^+ + \text{Cl}^- &\rightarrow \text{C}_7\text{H}_5\text{Cl}^- + \text{N}^+ \\
\end{align*}
\]

The nitrogen atom can then complete its octet at the expense of one of the two lone pairs of electrons present in the valency shell of the sulphur atom of a thioether, with the formation of a semi-polar double bond. Of racemisation, the \(\beta\)-butyl \(\beta\)-butyl p-toluenesulphonate finally obtained optically inactive.

\[
\begin{align*}
\text{C}_7\text{H}_5\text{N}^- + \text{S}^2^- &\rightarrow \text{C}_7\text{H}_5\text{N}^+ + \text{S}^2^- \\
\text{C}_7\text{H}_5\text{N}^+ + \text{S}^2^- &\rightarrow \text{C}_7\text{H}_5\text{S}^- + \text{N}^+ \\
\end{align*}
\]

The interaction of \(\beta\)-butyl p-toluenesulphonate with anhydrous carboxylic acids, however, yielded \(\beta\)-butyl esters which were optically inactive. For example, \(\beta\)-butyl p-toluenesulphonate with the above radicals.
toluenesulphonate reacted with benzoic acid and gave an optically inactive β-buty1 benzoate. When an optically active
β-buty1 benzoate was warmed with an equimolecular proportion of p-toluenesulphonic acid the solution darkened rapidly and
benzoic acid separated in long needles. No β-buty1 benzoate
was isolated from the reaction mixture and, presumably, the
β-buty1 radical had been eliminated as butylene. Optically
active β-buty1 benzoate heated in a similar way with an equi-
molecular proportion of benzoic acid was recovered with its
rotatory power unchanged. It can therefore be concluded that
when excess benzoic acid reacts with d-β-buty1 p-toluenesul-
phonate the optically active radical separates as a cation
which then combines with the benzoate ion:
\[
\text{C}_7\text{H}_7^+\text{SO}_2\text{O}_2\text{C}_4\text{H}_9^+ + \text{O}_2\text{CO}_2\text{H} = \text{C}_4\text{H}_9^+\text{O}_2\text{CO}_2\text{C}_6\text{H}_5^- + \text{H}_3\text{SO}_2\text{C}_7\text{H}_7.
\]
The β-buty1 benzoate thus formed is then acted on by the sul-
phonic acid, the butyl radical again separating as a cation
which is partly lost as butylene and partly reconverted into the
benzoate by the excess benzoic acid present. Since each re-
action is accompanied by a certain amount of racemisation, the
β-buty1 benzoate finally obtained is optically inactive.

The interaction of d-β-buty1 p-toluenesulphonate with anhydrous formic acid also yielded an optically inactive product,
in this case β-buty1 formate.

It is conceivable that the reactions of p-toluenesulphonates
with salts in alcoholic solution proceed via the coordination of
a hydrogen ion with the ester molecule. Free hydrogen ions
would readily be produced in the system by the interaction of the sulphonate with ethyl alcohol. If the reacting salt is soluble in ethyl alcohol, then free acid ions will also be present. In effect, the solution will be a dilute solution of the free acid with the acid present in the dissociated state. Association with the sulphonic ester molecule will then occur, and on coordination of the hydrogen ion and subsequent removal of the sulphonyoxy group, the $\beta$-butyl ester will be produced with inversion of configuration. The velocity of such a reaction will therefore depend to a large extent on the dissociation constant of the acid.

This suggestion provides an explanation of the marked differences in the rates of interaction of $\beta$-butyl $p$-toluenesulphonate with metallic salts noticed. The reactions with potassium thiocyanate and selenocyanate proceeded very readily, the flask being filled with a solid mass of white crystals of potassium $p$-toluenesulphonate after heating the mixture for about thirty minutes on a water bath. The product was in each case obtained in very good yield and only a small quantity of $\beta$-butyl ethyl ether was obtained as a byproduct. The reaction with potassium iodide also proceeded with great ease. Potassium acetate and benzoate reacted rather less readily, a gelatinous mass which was first formed giving place to a crystalline precipitate on continued boiling. The esters were obtained in good yield but a larger quantity of $\beta$-butyl-ethyl ether was obtained. On the other hand, practically no
reaction occurred with potassium cyanide and potassium phthalimide. Further, while ethyl and n-butyl alcohols and phenol reacted readily with the sulphonate, phthalimide, benzamide and p-toluencesulphonamide did not react under the conditions tried. From the purely qualitative results of these experiments it appears that reactions between sulphonates and metallic salts in ethyl alcohol solution depend on the strength of the acid from which the salt is derived, although it is undoubtedly influenced by the solubilities of the salts in the solvent. Table III gives the dissociation constants of some of these acids:

<table>
<thead>
<tr>
<th>Acid</th>
<th>$K_{250}$</th>
<th>Rate of reaction approx.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSCN, HCl, HBr</td>
<td>Strong acids</td>
<td>React very readily</td>
</tr>
<tr>
<td>Acetic</td>
<td>$120,000 \times 10^{-10}$</td>
<td>React less readily</td>
</tr>
<tr>
<td>Benzoic</td>
<td>$60,000,000 \times 10^{-10}$</td>
<td>Practically no reaction</td>
</tr>
<tr>
<td>HCN</td>
<td>$15 \times 10^{-10}$</td>
<td>Reacts readily - probably owing to high concentration</td>
</tr>
<tr>
<td>Phenol</td>
<td>$1.3 \times 10^{-10}$</td>
<td></td>
</tr>
</tbody>
</table>

It appears that when the hydrogen ion concentration falls below a certain limit, little or no reaction occurs. Below this limit the hydrogen is covalently linked as in the amines and alcohols and reaction proceeds readily by coordination of the hydrogen atom with the sulphonate as before. In these reactions there is a high concentration of potential hydrogen ions.
Two general conclusions can be drawn from this work. Reactions which proceed with inversion take place in the presence of free anions and hydrogen cations (a), while reactions which proceed without inversion are possibly the result of the decomposition of the complex produced by the coordination of the two compounds by means of a hydrogen atom which is covalently linked to one of them, (b).

\[
(a) \quad \begin{array}{c}
\text{A} \\
\text{B}
\end{array} \begin{array}{c}
\text{C} \\
\text{D}
\end{array} - \text{X} + \text{H} \rightarrow \begin{array}{c}
\text{A} \\
\text{B}
\end{array} \begin{array}{c}
\text{C} \\
\text{D}
\end{array} - \text{X} + \begin{array}{c}
\text{A} \\
\text{B}
\end{array} + \text{H}
\]

\text{inversion.}

\[
(b) \quad \begin{array}{c}
\text{A} \\
\text{B}
\end{array} \begin{array}{c}
\text{C} \\
\text{D}
\end{array} - \text{X} \quad \begin{array}{c}
\text{A} \\
\text{B}
\end{array} \begin{array}{c}
\text{C} \\
\text{D}
\end{array} - \text{NR} + \text{H}
\]

\text{no inversion.}

Commercial secondary butyl alcohol was dried over successive quantities of freshly fused potassium carbonate and was then carefully fractionated, the liquid boiling at 97-99°C being collected separately and then used for subsequent experiments.

Resolution of methylethylcarbinol.

β-Butyl hydrogen phthalate was prepared by the method described by Pickard and Kenyon (J.C.S., 1911, 99, 45.), with a few slight modifications. Equimolecular proportions of β-butanol (500 g.) and phthalic anhydride (1000 g.) were heated under reflux on a boiling water bath for about 48 hours. The oily product was then poured into four litres of water and stirred vigorously by means of a mechanical stirrer. After fifteen minutes, a quantity of crushed ice was added and the stirring continued until the hydrogen phthalate solidified. The hydrogen phthalate was thus obtained as a coarse white powder which was removed by filtration, washed with water and spread on porous plates to dry. It then had m.p. 55°, and m.p. 55-57° after recrystallisation from a small quantity of methylene chloride. The acid phthalate m.p. 55° was found to be sufficiently pure for resolution by means of brucine.

β-Butyl hydrogen phthalate (2 mols.) was dissolved in acetone (2 litres) and heated to boiling on a water bath.
Anhydrous brucine (2 mols) was then added in small quantities and the mixture shaken. It was then heated under reflux for about one hour and left to cool overnight. The first crop of crystals obtained was recrystallised eight times from methyl alcohol and then gave optically pure d-β-butyl hydrogen phthalate.

After working up the mother liquors, a total yield of 35 grams of fully active hydrogen phthalate was obtained m.p. 46-47°.

From the resolution of 740 grms. of β-butyl hydrogen phthalate, 219 grms. of optically pure hydrogen phthalate were obtained with $\alpha$-20$^\circ$ = 39.60°, $\alpha$-20$^\circ$ = 47.50°, $\alpha$-20$^\circ$ = 56.70° in ethylalcohol solution (C = 5.000). The sodium salt of d-β-butyl hydrogen phthalate was prepared by neutralising the acid ester with sodium carbonate solution, evaporating to dryness and extracting the residue with hot alcohol. On standing, the alcoholic solution deposited long needle shaped crystals with $\alpha$-20$^\circ$ = 30.41°, $\alpha$-20$^\circ$ = 51.95°, $\alpha$-20$^\circ$ = 56.70° in ethyl alcohol solution (C = 5.020).

d-β-Butanol was obtained by warming 219 grms. of d-β-butyl hydrogen phthalate with a concentrated solution of sodium hydroxide (100 gr. NaOH in 200 cc. water) and then removing the free alcohol by means of a current of steam. The aqueous distillate was salted out with potassium carbonate, and the alcohol separated. Any remaining alcohol was extracted from the aqueous solution with ether, the etheral extract added to the first quantity of alcohol and the whole dried over successive small quantities of fused potassium carbonate and finally over calcium chloride.

At 15 cc. decomposition was observed, but at
fused barium oxide. $\beta$-Butanol forms a constant boiling mixture with ether at 84° C and with water at 94° C. From this experiment, 59 grms. of $\alpha / \beta$-butanol were obtained b.p. 99-100°, $d_{20}^0 0.803$, $n_{20}^0 1.3954$. The following values for the optical rotatory power under various conditions were observed:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Homogeneous Solution</th>
<th>Ethanol Solution</th>
<th>Ether Solution</th>
<th>Potassium Salt in Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°</td>
<td>$\alpha = 0.5$</td>
<td>$\alpha = 4.92$</td>
<td>$\alpha = 5.000$</td>
<td>$\alpha = 5.534$</td>
</tr>
<tr>
<td>5.59</td>
<td>+ 0.75°</td>
<td>+ 1.05</td>
<td>+ 0.75</td>
<td></td>
</tr>
<tr>
<td>6.61</td>
<td>+ 0.90</td>
<td>+ 1.05</td>
<td>+ 0.75</td>
<td></td>
</tr>
<tr>
<td>11.00</td>
<td>+ 1.49</td>
<td>+ 1.85</td>
<td>+ 1.19</td>
<td></td>
</tr>
</tbody>
</table>

The residual mother liquors from the resolution were concentrated and decomposed and the partially active laevorotatory phthalate extracted. In this manner, $\alpha / \beta$-butanol (116 g.) with $\alpha = 5461 - 4.76° (l = 1)$ was obtained from $\alpha / \beta$-butyl hydrogen phthalate (538 g.) with $\alpha = 78° - 17.0°$.

**Preparation of $\beta$-Butyl p-Toluenesulphonate.** Method I. Finely powdered p-toluenesulphonyl chloride (19 g.) was added in small quantities to a solution containing $\beta$-butanol (7.4 g.) and pyridine (9 g.) cooled in a freezing mixture, and shaken vigorously. A thick white precipitate separated and was left for 12 hours. Water was then added and the oily layer which separated was extracted with ether. The ethereal extract was washed with dilute hydrochloric acid, water and dried with potassium carbonate. After removal of the ether, the residue was distilled. At 15 mm, decomposition soon occurred, but at
0.1 mm. a few drops of a colourless distillate were obtained before decomposition occurred. This distillate solidified after standing a few minutes and was soluble in dilute sodium carbonate solution, and therefore probably consisted chiefly of \( p \)-toluenesulphonic acid. It was concluded that the \( \beta \)-butyl \( p \)-toluenesulphonate formed contained impurities which caused the ester to decompose when distilled.

Method II. \( \beta \)-Butanol (1 mol.) was refluxed with \( p \)-toluenesulphonyl chloride in dry ethereal solution in the presence of potassium carbonate for 3 hours. After removing most of the ether, \( p \)-toluenesulphonyl chloride m.p. 63° separated. No reaction appeared to have taken place.

Method III. Potassium shot (4 g.) was covered with dry ether in a flask fitted with a reflux condenser, and \( \beta \)-butanol (3 g.) was added slowly. When the potassium had completely dissolved, \( p \)-toluenesulphonyl chloride (19 g.) was added in small quantities at a time in a finely ground condition. A vigorous reaction occurred. After standing for 12 hours, carbon dioxide was passed through the mixture and water was then added. The ethereal extract was washed and dried over fused potassium carbonate. On removing the ether, an attempt was made to distil the residue in a high vacuum, but decomposition set in before any distillate was obtained. It was concluded that the \( p \)-toluenesulphonic ester obtained by this method was too impure to distil without decomposition.

Method IV. \( \beta \)-Butyl \( p \)-toluenesulphonate was prepared by the oxidation of \( \beta \)-butyl \( p \)-toluenesulphinate.
Preparation of $p$-toluenesulphinyl chloride.

Method 1. $p$-Toluenesulphinyl chloride (11 g.) in ether (10 cc.)

Preparation of $p$-toluenesulphinyl chloride.

$p$-Toluenesulphinic acid was prepared by acidifying an aqueous solution of sodium $p$-toluenesulphinate (supplied by Messrs. Boots) with hydrochloric or dilute sulphuric acid. $p$-Toluenesulphinyl chloride was prepared when required by Hilditch and Smiles' method (Ber., 1903, 41, 4113; Hilditch, J. 1910, 27, 2535.) Thionyl chloride (1 - 1 mols.) (which had been distilled over quinoline, linseed oil and beeswax and was water-white in appearance) was dissolved in an equal volume of dry ether and $p$-toluenesulphinic acid (1 mol.) was added gradually with shaking. When all the acid had dissolved, the mixture was warmed gently, until gases were no longer evolved. The ether and excess thionyl chloride were then removed in a vacuum at the ordinary temperature, and the oily residue was dissolved in light petroleum. The solution was then filtered from the small quantity of white solid which was precipitated and then subjected to a vacuum at ordinary temperature for at least six hours.

$p$-Toluenesulphinyl chloride then remained as a clear yellow oil.
Preparation of \( \beta \)-Butyl \( \beta \)-toluene sulphonate.

Method I. \( \beta \)-Toluene sulphonphnyl chloride (34 g.) in ether (10 cc.) was added to a mixture of \( \beta \)-butanol (10 g.) in ether (50 cc.) containing anhydrous potassium carbonate (13 g.). A gentle effervescence of carbon dioxide took place which lasted several hours. After 24 hours, water was added and the ethereal layer was separated, washed with water and dried over potassium carbonate. After removal of the ether, the residually yellowish oil was distilled in a high vacuum. Although considerable darkening occurred, \( \beta \)-butyl \( \beta \)-toluene sulphonate was obtained as a colourless liquid (24 g.), b.p. 33-35\(^\circ\) and \( n_d^\circ 1.5250 \). The residual dark tar would not distil at a higher temperature and deposited crystals on cooling.

Method II. \( \beta \)-Butyl \( \beta \)-toluene sulphonate was also prepared by gradually adding \( \beta \)-toluene sulphonphnyl chloride (30 g.) to a solution of \( \beta \)-butanol (13 g.) in pyridine (15 g.) cooled in a freezing mixture. After 12 hours, water was added and the oil which separated was extracted with ether. The ethereal extract was thoroughly washed with water, dilute hydrochloric acid, water, dilute sodium carbonate solution and water, and was then dried over potassium carbonate. The ether was removed and the residue distilled in a high vacuum. \( \beta \)-Butyl \( \beta \)-toluene sulphonate (25 g.) was obtained \( n_d^\circ 1.5255 \).

The \( \beta \)-butyl \( \beta \)-toluene sulphonate obtained in each experiment was mixed and redistilled, and then had \( n_D^\circ 1.5252, d_4^\circ 1.085, d_4^{30\circ} 1.066 \). Found: C, 62.8\%, H, 7.6\%; \( C_{11}H_{16}O_2S \) requires
d-β-Dutyl p-toluenesulphinate prepared by the interaction of d-β-butanol (α 10° 6.63°; 1 = 0.5) and p-toluenesulphinyl chloride in the presence of pyridine, had \( \frac{d}{d^0} \) 13° + 7.27°, in the homogeneous state, and \( \frac{d}{d^0} \) 13° + 14.93° (1 = 0.5) in the ethanolic solution, (ε = 4.345; 25°C). d-β-Dutyl p-toluenesulphonate was prepared from the sulphide ester by oxidation in neutral solution. d-β-Dutyl p-toluenesulphinate \( \frac{d}{d^0} \) 13° + 3.46°, (40 g.) was dissolved in acetone (100 cc.); water was added to produce incipient cloudiness and magnesium sulphate (20 g.) was dissolved in the solution. The mixture was stirred vigorously while finely powdered potassium permanganate (20 g.) was added slowly, a little ice being added if too much heat was developed. The solution, now permanently coloured, was diluted with ice and water and sulphur dioxide was passed in until the manganese mud just dissolved. The solution was then extracted with ether and washed with water and dilute sodium carbonate solution and finally dried over potassium carbonate. On removal of the ether, a colourless oily residue (39 g.) was obtained. A small quantity (2 g.) was then distilled in a high vacuum, and gave a colourless distillate b.p. 05°, before decomposition occurred. It was found that the presence of a small quantity of fused potassium carbonate in the distillation flask enabled the ester to be distilled with little or no decomposition. On redistillation
the d-\(\beta\)-butyl p-toluenesulphonate had \(n_D^{15^\circ} 1.5080\), \(d_4^{20^\circ} 1.146\), and \(\alpha_{5896}^{20^\circ} -11.10^\circ\), \(\alpha_{5461}^{20^\circ} 12.93^\circ\), \(\alpha_{4359}^{20^\circ} +21.16^\circ\) in the homogeneous state (1 = 0.5) and \(\alpha_{5896}^{20^\circ} + 5.00^\circ\), \(\alpha_{5461}^{20^\circ} + 7.00^\circ\) \(\alpha_{4359}^{20^\circ} + 11.00^\circ\) (1 = 1) in ethyl alcohol solution (1 = 5.000). Found: C, 53.0%; H, 7.0%; \(C_{11}H_{16}O_3S\) requires C, 57.9%; H, 7.0%.

Acetate in Ethyl-alcoholic Solution.

\(d-\beta\)-Butyl p-toluenesulphonate (10 g.) prepared from \(d-\beta\)-butanol with \(\alpha_{5461}^{20^\circ} -12.86^\circ\) (1 = 1) was added to absolute ethyl alcohol (25 cc.) containing fused potassium acetate (12 g.) and heated under reflux for 12 hours. A thick gelatinous mass was first formed, but on continued heating, this gradually disappeared and gave place to a crystalline precipitate. The reaction mixture was then cooled, poured into water and the oil which separated, extracted with ether. The ethereal extract was washed with water and dried over potassium carbonate. The ether was distilled off through a fractionating column, and on fractionating the residue, two main portions were obtained. (1) b.p. 78-82\({^\circ}\), which was a mixture of ethyl alcohol and \(\beta\)-butylethylether. (2) b.p. 113-117\({^\circ}\), (0.3 g.). On re-distillation, fraction (2) boiled at 116-117\({^\circ}\) and had \(n_D^{15^\circ} 1.3339\), \(d_4^{20^\circ} 0.3734\), (cf. Pickard and Kenyon J.C.S., 1915, 129) and 
\(\alpha_{5396}^{19^\circ} -16.36^\circ\), \(\alpha_{5461}^{19^\circ} -20.19^\circ\), \(\alpha_{4359}^{19^\circ} -33.29^\circ\) homogeneous, (1 = 0.23) and \(\alpha_{5396}^{19^\circ} -15.41^\circ\), \(\alpha_{5461}^{19^\circ} -19.36^\circ\), \(\alpha_{4359}^{19^\circ} -30.82^\circ\)
in ethyl alcohol solution ($c = 5.046$). Considerable decomposition occurred during the first distillation owing to the presence of unchanged $p$-toluenesulphonic ester.

1 + dl-$\beta$-Butyl $p$-toluenesulphonate prepared from 1 + dl-$\beta$-butanol ($\alpha_{5461}^{20^\circ} 9.52^\circ; 1 = 2$), when treated with potassium acetate in ethyl alcoholic solution in a similar way, yielded $\text{dl} + \text{dl-} \beta$-butyl acetate with $\alpha_{5461}^{18^\circ} 10.52^\circ$.

Reaction between d-$\beta$-Butyl $p$-toluenesulphonate and Potassium Benzoate in Ethyl-alcoholic Solution.

d-$\beta$-Butyl $p$-toluenesulphonate (10 g.) prepared from d-$\beta$-butanol ($\alpha_{3461}^{20^\circ} 12.66^\circ; 1 = 1$), was heated under reflux with potassium benzoate (7 g.) in absolute ethyl alcohol (35 cc.) for 12 hours. The product was isolated as described above.

On distillation, two fractions were obtained, (1) (1 g.) b.p. 78-82° which was crude $\beta$-butyl ethyl ether. (2) (1.2 g.) b.p. 93-100°/13 mm. from which, by refractionation, 1-$\beta$-butyl benzoate was obtained with b.p. 98-99°/13 mm. $n_D^{22°} 1.5005$, $d_{17}^{17°} 1.002$.

(cf. Pickard and Kenyon, J.C.S., 1915, 129) and $\alpha_{5396}^{17°} - 33.48^\circ$, $\alpha_{5461}^{17°} - 44.09^\circ$, $\alpha_{4333}^{17°} - 73.45^\circ$ homogeneous, (1 = 0.25) and $\alpha_{5896}^{18°} - 27.50^\circ$, $\alpha_{5396}^{18°} - 45.31^\circ$, $\alpha_{5461}^{18°} - 75.65^\circ$ in absolute ethyl alcohol ($c = 5.010$).

The $\text{dl} + \text{dl-} \beta$-butyl benzoate (1.5 g.) obtained in a similar way from 1-$\beta$-butyl $p$-toluenesulphonate (10 g.) prepared from 1 + dl-$\beta$-butanol ($\alpha_{5461}^{18°} - 2.36^\circ; 1 = 0.5$) had $\alpha_{5461}^{18°} + 5.16^\circ$, $n_D^{25.5°} 1.5007$. 
Reaction between $\beta$-dButyl $\beta$-Toluenesulphonate and Potassium Thiocyanate in Ethyl Alcoholic Solution

$\beta$-d-Butyl $\beta$-Toluenesulphonate (45 g.) prepared from $\beta$-d-Butanol (19° C, 11.99; 101) and potassium thiocyanate (24 g.) in absolute alcohol (30 cc.) were heated under reflux for 12 hours. Within about 30 minutes, the mixture set to a solid mass which broke up on continued heating. The product was poured into water and extracted with ether in the usual way. On distillation, three fractions were obtained. F (1) (1 cc.) b.p. 73-82°, F (2) (3.5 g.) b.p. 57-58°/10 mm. On refluxing this portion, 1-$\beta$-Butyl thiocyanate was obtained b.p. 59-61°/17 mm, nD 1.4951, d25 0.980 and had $\alpha$ 556° 44.54°, $\alpha$ 5461, 44.91°, $\alpha$ 4553 - 74.30° (1 = 0.5) homogeneous, and $\alpha$ 5286 - 24.59°, $\alpha$ 4356 - 22.59°, $\alpha$ 4351 - 50.36° in ethyl alcohol solution, (c = 0.003). Found, C 51.4%, H 7.76%. $C_6H_5NS$ requires C, 52.2%; H, 7.82%. F (3). The brown oily residue remaining after F (2) was removed was distilled in a high vacuum, and gave a viscous yellow oil (3 cc.) b.p. 120°-150°/0.1 mm. This partly solidified on cooling. On addition of light petroleum, a white solid separated which had mp. 25°. It recrystallised from aqueous ethyl alcohol in long needles mp. 75-75° and contained sulphur. Found: C, 60.4%, H, 5.2%. $C_6H_5S_2O_2$ requires C, 60.4%; H, 5.0%, and was therefore, di-$\beta$-tolyl disulphoxide. The portion soluble in light petroleum was redistilled at 1 mm. and yielded two fractions. F (1) b.p. 105-150°. F (2) b.p. 150-160°. The higher fraction
solidified completely on standing, the lower fraction partly solidified and also contained a small quantity of a yellow oil. On recrystallising the solid from aqueous ethyl alcohol, it was obtained in colourless plates mp. 45°. Found: C, 67.9%; H, 5.6, S, 26.0%. $\text{C}_{14}\text{H}_{14}\text{S}_2$ requires C, 63.3%; H, 5.7, S, 26.0% and was therefore di-$\text{p}$-tolyldisulphide.

Di-$\text{p}$-tolyldisulphoxide is probably formed to a small extent during the distillation of the sulphinic ester and is reduced to the disulphide when sulphur dioxide is passed through the mixture after oxidation with potassium permanganate.

$\text{d} + \text{dl-}\beta$-Butyl thiocyanate prepared in a similar way by the interaction of potassium thiocyanate and $\text{l} + \text{dl-}\beta$-butyl p-toluenesulphonate obtained from $\text{l-}\beta$-butanol ($\alpha^{20}_\text{D} 9.52$; $\text{l} - \text{2}$) had $\alpha^{190}_\text{D} = 5.76^\circ$, ($\text{l} - 0.25$) $n^{14.50}_\text{D}$ 1.4642.

Preparation of $\text{l-}\beta$-Butyl Disulphide.

$\text{l-}\beta$-Butyl thiocyanate (9 g.) ($\sqrt{\alpha^{22}_\text{D}} = 44.91^\circ$) was refluxed with a solution of potassium hydroxide (6 g.) in ethyl alcohol (100 cc.) for 12 hours. It was then poured into water, extracted with ether and the ethereal extract washed with water and dried over anhydrous potassium carbonate. After removing the ether, the residue was distilled and yielded two fractions: F(1) 1 g. b.p. 45-95°/14 mm. F(2) (5 g.) b.p. 95-97°/14 mm. Fraction (1) was redistilled, and the higher boiling portion added to F(2). F(2) on redistillation had b.p. 97-99°/14 mm., $n^{13.0}_D$ 1.5051, $d^{14.0}_2$ 0.942 and $\sqrt{\alpha^{14}_5396} = 93.85^\circ$. 
$\alpha_{D}^{20^\circ} = 111.23^\circ$, $\alpha_{D}^{25^\circ} = 196.99^\circ$ homogeneous, and $\alpha_{D}^{16^\circ} = 84.83^\circ$

$\alpha_{D}^{13^\circ} = 95.31^\circ$, $\alpha_{D}^{18^\circ} = 178.24^\circ$ in ethyl alcohol solution

($\epsilon = 5.010$) Found: C, 53.9, H, 10.0; $C_{6}H_{10}S_{2}$ requires C, 53.9; H, 10.2%.

A similar (5 g.) was dissolved in glacial acetic acid (100 cc.) and $d$-$\beta$-butyl disulphide prepared from $d$-$\beta$-butyl thiocyanate $\alpha_{D}^{13^\circ} = 5.76^\circ$; $\epsilon = 0.257$ by a similar method, had $\alpha_{D}^{20^\circ} = 9.52^\circ$; ($\epsilon = 0.25$).

Preparation of 1-$\beta$-Butyl Sulphonic Acid.

1-$\beta$-Butyl thiocyanate ($\alpha_{D}^{20^\circ} = 44.91^\circ$) (2 g.) was heated under reflux with nitric acid (20 cc. of 60% HNO$_3$) on a boiling water-bath for about 24 hours, when a clear solution was obtained. It was diluted with water and evaporated on a water bath, fresh quantities of water being added repeatedly until all the nitric acid had been removed. A pale yellow viscous liquid was obtained which boiled at 125$^\circ$ at 0.1 mm. and had $n_{D}^{20^\circ} = 1.4365$, $\alpha_{D}^{25^\circ} = 1.22^\circ$. Found: C, 33.5; H, 4.1%.

$C_{6}H_{10}O_{3}$ requires C, 34.5; H, 7.2%. The following values for the optical rotatory power under various conditions were:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\alpha_{D}^{20^\circ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$+0.02$</td>
<td>$+0.85$</td>
</tr>
<tr>
<td>$+0.04$</td>
<td>$+3.80$</td>
</tr>
<tr>
<td>$+0.73$</td>
<td>$+0.94$</td>
</tr>
<tr>
<td>$+1.64$</td>
<td>$+3.59$</td>
</tr>
</tbody>
</table>

A solution containing 5 g. of the acid in 4 cc. of alcohol was converted into the sodium salt.

$\alpha_{D}^{13^\circ} = 5.421$ in $\text{HCl}, C = 5.302$ for acid.

$\alpha_{D}^{13^\circ} = 6.153$ for sodium salt.
Preparation of 1-β-Butyl mercaptan.

1-β-Butyl mercaptan was prepared by the reduction of 1-β-Butyl disulphide $\left(\alpha_{12\text{°}} = 23.45\text{°}; \lambda = 0.25\right)$. Method I.

β-Butyl disulphide (4 g.) was dissolved in glacial acetic acid (30 cc.) and concentrated hydrochloric acid (10 cc.) added. Granulated tin (5 g.) was then added and the mixture heated gently under reflux on a water bath. Owing to its relatively low boiling point some of the mercaptan was carried out of the flask by the hydrogen generated. When the reaction was complete the mixture was poured into water and extracted with β-ether. The etheral extract was washed with water, dilute sodium carbonate solution and water, and dried over anhydrous sodium sulphate. The etheral extract was then fractionated and a small quantity of 1-β-butyl mercaptan (0.3 g.), b.p., 83-85°C. was obtained. This had $\lambda_{17\text{°}} 0.830\text{°}, \lambda_{5686} 17.35\text{°}$.

[Further analysis data is presented here, including values and comparisons with expected values.]

C H S requires C 53.5, H 11.1%. Method II. To 1-β-Butyl disulphide (5 g.) in amyl alcohol (100 g.), sodium (4 g.) was added in small quantities. The product was then extracted six times with water and with dilute sodium hydroxide solution. The aqueous extract was shaken with methylene chloride to remove any amyl alcohol and then cooled in a freezing mixture. After
acidifying with ice-cold hydrochloric acid the solution was
extracted with methylene chloride, and the methylene chloride
extract dried over anhydrous sodium sulphate. On distilla-
tion a small quantity of mercaptan was obtained, but it could
not be separated by distillation from the amyl alcohol
present.

The Reaction between d-β-Dutyl p-toluenesulphonate and Potas-
sium Selenocyanate in Ethyl-alcoholic Solution.

d-β-Dutyl p-toluenesulphonate (11 g.) prepared from d-β-
butanol (α 20° 5° 34.1; 1 = 1) and potassium selenocyanate
(8 g.) in absolute alcohol (50 cc.) were heated under reflux
for 12 hours on a boiling water bath. A solid mass of white
crystals filled the flask in about 20 minutes. The product
was then poured into water and extracted with ether in the
usual manner. On distillation two fractions were obtained.

F. (1) b.p. 65-70°/15 mm. F. (2) b.p. 73-82°/15 mm. On re-
fractionation the higher boiling portion, 1-β-butyl selenocy-
anate was finally obtained as a yellow, somewhat viscous
liquid with a penetrating and nauseous odour (2.5 g.) b.p.
83-94°/15 mm. nD 1.4965, d° 1.445 and α 20° 5° 5836 = 11.54°,
C° 20° - 12.23°, C° 5° 5431 - 13.89°. (The violet line was
absent); in the homogeneous state (1 = 0.25) and α 20° 5° 5836 = 12.10°,
C° 5° 5431 - 13.69°, C° 20° - 24.60° in ethyl alcoholic solu-
tion (g = 5.040). Found: C, 37.5%; H, 5.7%; C₄H₈SeS requires
C, 37.04; H, 5.6%. This reaction was attended by considerable
reacnon since $\text{d} + \text{t1-} \beta$-butyl selenocyanate prepared by a similar method from 1-\(\text{d1-} \beta\)-butyl p-toluenesulphonate obtained from 1-\(\text{d1-} \beta\)-butanol ($\alpha^{17\circ}_{5461} = 4.6\circ; l = 1$) had $\alpha^{12\circ}_{5461} + 13.15\circ$. During this preparation the white solid first formed turned dark green and then brown, a fine grey deposit of selenium being finally formed.

Preparation of $\text{d-} \beta$-Butyl Diselenide:

$\text{d-} \beta$-Butyl selenocyanate $\alpha^{12\circ}_{5461} + 13.15\circ$ (8.5 g.) was refluxed with potassium hydroxide (2 g.) in ethyl alcohol (20 cc.) for 12 hours, and the product was then poured into water and extracted with ether in the usual way. On distillation, $\text{d-} \beta$-butyl diselenide (1.5 g.) was obtained, b.p. 130$\circ$ / 10 mm., $n_D 1.5337$ and $\alpha^{20\circ}_{5461} 8.92\circ$ ($l = 0.23$). Found: C, 33.4; H, 3.5% (C H Se) required C, 33.3; H, 3.6%.

Attempts were made to prepare $\beta$-butyl species by the Reaction between $\text{d-} \beta$-Butyl p-Toluenesulphonate and Potassium Cyanide in Acetone and Ethyl Alcohol Solution with a mixture of selenocyanate and potassium cyanide $\alpha^{20\circ}_{5461} + 12.93\circ$ (25 g.) and potassium cyanide (15 g.) were heated in a mixture of acetone (50 cc.) and ethyl alcohol (5 cc.) for 30 hours under reflux. An ethyl alcohol solution alone resulted in a black tar. The mixture was then steam distilled in order to separate the product as completely as possible from uncharged sulphonate, the distillate extracted with ether and the ethereal extract dried over anhydrous sodium sulphate. After removing the
ether, the residual liquid was distilled and yielded three fractions:—
(1) b.p. 70-100° (1 g.) (2) b.p. 100-130° (1 g.)
(3) b.p. 130-162° (0.5 g.) Fractions (2) and (3) were acid
to litmus and as these could not be separated into pure sub-
stances by further fractionation they were mixed and then
hydrolysed with aqueous potassium hydroxide. When hydroly-
sis was complete, the mixture was evaporated to dryness, the
residue dissolved in a small quantity of water and made acid to
Congo Red with 60% sulphuric acid. The mixture was then
extracted with ether and the ethereal extract washed with water
and dried over anhydrous sodium sulphate. On distillation,
methylethyl acetic acid (0.1 g.) was obtained. (0.1001 g.
required 0.03923 g. NaOH for neutralisation using phenolphthalein
as indicator; theory, 0.03922 g. The aqueous solution of the
acid had \( \frac{\rho}{\rho} = 3.461 \)
Attempts were made to prepare β-butyl cyanide by the
interaction of the sulphonate with silver cyanide in acetone
solution and in ethyl alcoholic solution, and with a mixture of
potassium and silver cyanides in varying proportions in acetone
solution, but no reaction appeared to take place.

Resolution of Methylethylacetic Acid.

Optically inactive methylethylacetic acid (prepared by
Kahlbaum) was resolved by means of the brucine salt according
to the method described by Raskwald (Ber., 22, 53.). The
optical activity of the partially active acid obtained was...
further increased by recrystallising the silver salt from water.

Rarckwald, Ber., 32, 1902. Methylmethylacetic acid (27 g.)
\( \alpha^20^\circ = 6.30^\circ, \lambda = 1 \) was dissolved in water (2 litres), freshly
precipitated silver oxide (65 g.) was added and the mixture
boiled under reflux for one hour. The liquid was filtered
while hot through a hot funnel and left to crystallise. Silver
valerate (29 g.) separated in white plates and was removed by
filtration. About 4 gms. of this crop was acidified with
dilute hydrochloric acid, the supernatant liquid decanted and
the free valeric acid extracted with ether and dried over sodium
sulphate. A 90% yield of acid was obtained on distillation
with optical rotatory power \( \alpha^20^\circ = 3.43^\circ, \lambda = 1 \). Successive
recrystallisations of this crop yielded acids with \( \alpha^20^\circ = 10.53^\circ, \)
\( \alpha^20^\circ = 12.52^\circ \) and \( \alpha^20^\circ = 13.52^\circ, \alpha^20^\circ = 14.54^\circ, \lambda = 1 \)
respectively. As this last crop was reduced to 4 g. further
purification was not attempted. On concentrating the mother
liquor from the first crop, 23 g. of silver valerate, which
yielded an acid with \( \alpha^20^\circ = 3.50^\circ \), was obtained. Further
concentration of the mother liquor yielded 10 g. of salt with
an acid of rotation \( \alpha^20^\circ = 2.05^\circ, \lambda = 1 \), b.p. 70-75/25 mm,
\( n_2^1^\circ = 1.4044, d_2^0^0 \) 0.934.

The following values of the optical rotatory power of
methylmethylacetic acid were made:

\[
\lambda = 3395, \quad \lambda = 3481, \quad \lambda = 4335 \quad \text{Concentration.}
\]
\[
\alpha^20^\circ = +12.20^\circ + 14.47^\circ + 24.93^\circ \quad \text{homogeneous, } \lambda = 0.25
\]
\[
\alpha^24^0 = +12.17^\circ + 14.36^\circ + 22.15^\circ \quad \text{EtOH, } C = 5.012
\]
Preparation of Ethyl Valerate.

Ethyl valerate was prepared by refluxing methyl ethylacetic acid $\alpha_{20} = 5.33^\circ$ (5 g.) with absolute ethyl alcohol (10 g.) and concentrated sulphuric acid (0.5 g.) for 6 hours. The product was then poured into water and extracted with ether. The ethereal extract was washed with water, dilute sodium carbonate solution, water, and then dried over anhydrous potassium carbonate. On distillation, the ethyl ester was obtained, b.p. 130°C, $n_{D}^{20} = 1.3967$, $d_{20}^{o} = 0.860$, and $\alpha_{D}^{20} = 5.13^\circ$.

$$\alpha_{D461}^{20} + 6.70^\circ$$, $\alpha_{D533}^{20} + 11.34^\circ$ homogeneous (1 = 0.25) and $\alpha_{D5461}^{20} = 6.40^\circ$, $\alpha_{D533}^{20} = 11.29^\circ$ in benzene solution ($\alpha = 5.000$) and $\alpha_{D5461}^{20} = 4.20^\circ$, $\alpha_{D533}^{20} = 8.40^\circ$, $\alpha_{D533}^{20} = 13.80^\circ$ in absolute ethyl alcohol solution ($\alpha = 5.000$).

Preparation of Methyl Ethylacetetyl Chloride.

Methyl ethylacetetyl acid (12 g.) $\alpha_{D461}^{20} = 5.63^\circ$ was mixed with freshly distilled thionyl chloride (15 g.) and allowed to stand for 12 hours in a flask fitted with a soda lime absorption apparatus. The mixture was then fractionated, the pure acid
chloride being obtained finally with b.p. 119-120°C, 
\[ \text{D}^2_0 1.4177, \text{d}^2_4 0.990 \text{ and } \left[ \alpha \right]_{D}^{24} + 4.51^\circ, \left[ \alpha \right]_{D}^{24} + 5.25^\circ, \]
\[ \left[ \alpha \right]_{D}^{24} + 9.41 \text{ homogeneous } (1 = 0.5) \text{ and } \left[ \alpha \right]_{D}^{24} + 12.33^\circ, \]
\[ \left[ \alpha \right]_{D}^{24} + 14.39^\circ, \left[ \alpha \right]_{D}^{24} + 21.9^\circ \text{ in benzene solution } (c = 3.07) \]
Found, C, 47.4; H, 7.5%; \( \text{C}_3\text{H}_5\text{OC}_2\text{H}_5 \) requires C, 47.8;
H, 7.5%.

Preparation of Methylthylacetonamide.

1. Methylthylacetyl chloride (5 g.) \( \left[ \alpha \right]_{D}^{24} - 5.25^\circ \), was
added slowly to powdered ammonium carbonate covered with dry
ether in a flask. The ether layer was then decanted and the
solid residue extracted twice with hot ether. The ethereal
solution was then concentrated, light petroleum added and the
amide left to crystallise. The amide was obtained in long
needle-shaped crystals (3.3 g.) m.p. and had
\[ \left[ \alpha \right]_{D}^{24} + 3.39^\circ, \left[ \alpha \right]_{D}^{24} + 5.19^\circ, \left[ \alpha \right]_{D}^{24} + 7.59^\circ \text{ in absolute}
\text{ethyl alcohol } (c = 0.003) \text{ and } \left[ \alpha \right]_{D}^{24} + 13.0^\circ, \left[ \alpha \right]_{D}^{24} + 24.07^\circ, \]
\[ \left[ \alpha \right]_{D}^{24} + 59.72^\circ \text{ in benzene } (c = 2.323). \]
Found C, 59.5°, H 10.8%; \( \text{C}_5\text{H}_{11}\text{ON} \) requires C 59.4;
H, 10.9%.

Preparation of d-\( \beta \)-Butyl Cyanide.

Methylthyl acetonide (3 g.) and phosphorus pentoxide
(10 g.) were mixed in a distilling flask and heated in an oil
bath. The cyanide distilled over between 110° and 115°C, and
was then fractionated, the portion boiling at 128-9°C being
collected separately. This had \( \text{D}^2_0 1.3375, \text{d}^2_4 0.738, \)
and \( \alpha_{\text{D}}^{20^\circ} + 7.58^\circ, \alpha_{\text{D}}^{20^\circ} + 9.19^\circ, \alpha_{\text{D}}^{20^\circ} + 16.52^\circ \) homogenous \((l = 0.25), \) and \( \alpha_{\text{D}}^{20^\circ} + 5.34^\circ, \alpha_{\text{D}}^{20^\circ} + 2.30^\circ, \alpha_{\text{D}}^{20^\circ} + 13.32^\circ \) in ethyl alcohol solution \((C = 4.195)\) and \( \alpha_{\text{D}}^{20^\circ} + 6.17^\circ, \alpha_{\text{D}}^{19^\circ} + 11.19^\circ \) and \( \alpha_{\text{D}}^{19^\circ} + 13.45^\circ \) in benzene \((C = 4.320)\). Found C, 71.4; H, 10.3; C\(_5\)H\(_5\)N required C, 72.2; H, 10.8.

Reaction between \( d\)-\( p\)-Toluene sulphonic acid and Grignard reagent-

Reagents-

To the ice-cold reagent prepared from ethyl bromide \((5 \text{ g})\), magnesium \((0.9 \text{ g})\) and ether \((50 \text{ cc})\), the dextrorotatory sulphonic acid \((10 \text{ g})\) prepared from \( d\)-\( \beta\)-Butanol \((\alpha_{\text{D}}^{20^\circ} + 13.23^\circ; l = 1)\) in ether \((50 \text{ cc})\) was slowly added, a vigorous reaction occurring after being heated under reflux for one hour, the mixture was poured on to ice and dilute hydrochloric acid was added. The ethereal solution was washed first with water and then with dilute sodium carbonate solution. After drying with anhydrous potassium carbonate, the ethereal solution was fractionated and yielded \( 1\)-\( \beta\)-Butyl bromide \((2.5 \text{ g})\) b.p. 90-91\(^\circ\), \( n_D^{19.5^\circ} 1.4339, d_4^{20^\circ} 1.281, \) which had \( \alpha_{\text{D}}^{25^\circ} - 18.24^\circ, \alpha_{\text{D}}^{25^\circ} - 17.62^\circ, \alpha_{\text{D}}^{25^\circ} - 27.92^\circ \) \((l = 0.25)\) homogenous, and \( \alpha_{\text{D}}^{25^\circ} - 17.02^\circ, \alpha_{\text{D}}^{25^\circ} - 12.90^\circ, \alpha_{\text{D}}^{25^\circ} - 34.66^\circ \) in ethyl alcohol solution \((C = 5.054)\). \( \alpha_{\text{D}}^{25^\circ} + 12.56^\circ \) was titrated with potassium iodide \((3 \text{ g})\) in solution \((50 \text{ cc})\) containing ethyl alcohol \((5 \text{ cc})\) for 12 hours. Water was then
(2) With Phenyl Magnesium Bromide.

The procedure described above was closely followed. d-\(\beta\)-Butyl \(p\)-toluenesulphonate (10 g.) was added to the ice-cold Grignard reagent prepared from magnesium (2 g.) bromobenzene (13 g.) and ether (50 cc.). On distilling the product, several fractions were obtained. (1) (3 cc.) b.p. 76°-87° which could not be separated by further fractionation and consisted chiefly of benzene. (2) (1.5 g.) b.p. 70-76°/60 mm. On redistillation 1-\(\beta\)-butyl benzene was obtained, b.p. 75-78°/60 mm. (1 g.)

\[ n_D^1 = 1.5044 \text{ and } \sqrt{\chi^{225}}^2 = 17.39^0, \sqrt{\chi^{5461}}^2 = 12.35^0, \sqrt{\chi^{250}}^2 = 32.50^0 \]

(1 = 0.25) homogeneous, and \(\sqrt{\chi^{225}}^2 = 16.35^0, \sqrt{\chi^{250}}^2 = 13.24^0, \sqrt{\chi^{5461}}^2 = 34.28^0 \) in absolute ethyl alcohol (\( c = 5.015 \)).

(cf. Harrison, Kenyon and Shepherd, J.C.S. 1933, 653).

(1 g.)

A colourless liquid which solidified readily on cooling, b.p. 216-220°/60 mm. On recrystallisation from methyl alcohol this had m.p. 70°; mixed m.p. with diphenyl was also 70°.

d + dl-\(\beta\)-Butyl benzene obtained in a similar way from 1 + dl-\(\beta\)-butanol (\(\alpha^{20} = 4.72^0; \text{I} = 1 \)) had \( n_D^2 = 1.4369 \text{ and } \sqrt{\chi^{225}}^2 = 8.69^0 \)

(1 = 0.25).

Reaction between d-\(\beta\)-Butyl \(p\)-Toluenesulphonate and Potassium Iodide in Acetone - Ethyl alcoholic Solution.

\(\beta\)-Butyl \(p\)-toluenesulphonate (15 g.) (\(\sqrt{\chi^{20}}^2 = 12.98^0 \)) was refluxed with potassium iodide (9 g.) in acetone (50 cc.) containing ethyl alcohol (5 cc.) for 12 hours. Water was then
added and the mixture extracted with ether in the usual manner.

On fractionating the product, 1-β-iodobutane was obtained b.p. 121-122°C, nD 1.4343, d20 1.533, with \( \alpha^{20} = 2.14^\circ \), \( \alpha_{D}^{20} = 2.59^\circ \), \( \alpha_{D}^{5451} = 5.26^\circ \) homogeneous (\( I = 0.23 \)) and
\( \alpha_{D}^{20} = 2.99^\circ \), \( \alpha_{D}^{5451} = 3.19^\circ \), \( \alpha_{D}^{4358} = 3.73^\circ \) in ethyl alcohol solution. (\( I = 5.01^\circ \)). This reaction was attended by considerable racemisation, since 1+dl-β-iodobutane prepared by saturating 1+dl-β-butanol (α\( _{D}^{24} = 5.17^\circ \); \( I = 1 \), cooled in a freezing mixture, with hydrogen iodide had \( \alpha_{D}^{24} = 10.95^\circ \).

**Reaction between β-Butyl ρ-Toluenesulphonate and Silver Nitrite.**

(a) *In Ethyl Alcoholic Solution.* After removing the water,

β-Butyl ρ-toluenesulphonate (10 g.) and silver nitrite (10 g.) were heated together in ethyl alcoholic solution for 48 hours. The solid product was then removed by filtration and the alcoholic solution was diluted with water and extracted with ether in the usual way. On distillation, crude β-butyl ethyl ether was obtained, but no nitro-compound was isolated.

(b) *In Acetone Solution.* A similar experiment was performed using acetone as a solvent. The solid product was removed by filtration and the aqueous acetone solution was extracted with ether. A small quantity of the sulphonic ester was recovered but no evidence was obtained that β-nitrobutane had been formed.
Reaction between $1 + dl\beta$-Butyl $p$-Toluene-sulphonate and Potassium Pthalimide.

(1) In Ethyl Alcohol Solution. $1 + dl\beta$-Butyl $p$-Toluene-sulphonate (19 g.; $\alpha^{17}\degree C = 4.20\degree$; $l = 1$) and potassium pthalimide (20 g.) were heated in absolute ethyl alcohol solution (20 cc.) for 40 hours. The mixture was then steam distilled to remove alcohol and any $\beta$-butyl ethyl ether formed, and the non-volatile portion extracted with ether. The ethereal extract was washed with water and dried over potassium carbonate. After removing the ether, a pale yellow oil (0.2 g.) b.p. 103\degree C/0.1 mm., was obtained which had $\alpha^{546}\degree = 1.5\degree$ ($l = 0.25$). The substance contained sulphur but no nitrogen. Owing to the very small quantity obtained, this substance was not investigated further.

(2) In Acetone Solution. $1 + dl\beta$-Butyl $p$-Toluene-sulphonate (10 g.; $\alpha^{17}\degree C = 4.20\degree$; $l = 1$) and potassium pthalimide (7 g.) were heated together in acetone solution for 60 hours. The mixture was then steam distilled and the residue extracted with chloroform, and the extract washed and dried over sodium sulphate. On removal of the chloroform, a yellow crystalline solid, m.p. 181\degree was obtained, which on re-crystallisation from aqueous alcohol
had n.p. 233° alone and when mixed with phthalimide.
No evidence was obtained from these reactions with
potassium phthalimide that N-β-butyl phthalimide had
been formed.

Reaction between β-Butyl p-Toluene sulphonate and
Phthalimide.

β-Butyl p-toluenesulphonate (12 g.) and phthalimide
(7.5 g.) were mixed and heated on a boiling water bath
for 60 hours. The mixture became brownish-purple
in colour, but a yellow precipitate was obtained on
adding water. The precipitate was removed by
filtration and dried, and then had n.p. 233°. After
recrystallisation from aqueous alcohol it had n.p.
233° alone and when mixed with phthalimide. It was
concluded that no reaction had taken place.
Reaction between \( \delta \- \beta \)-Butyl \( \delta \)-Toluene sulphonate and Ethyl Alcohol in the Presence of Potassium Carbonate.

\( \delta \- \beta \)-Butyl \( \delta \)-Toluene sulphonate (15 g.) prepared from \( \delta \- \beta \)-butanol (\( \alpha \) \( \delta \)-20° + 13.20°) was heated with absolute ethyl alcohol (10 cc.) and anhydrous potassium carbonate (5 g.) for 24 hours on a boiling water bath. After adding water the mixture was extracted with ether and the etheral extract was washed repeatedly with water and finally dried over potassium carbonate. The ether was then removed through a fractionating column and the residue heated with phthalic anhydride (50 g.) for 24 hours on a water bath. Dilute sodium carbonate solution was then added and the solution extracted with ether in the usual way. The residue obtained after removing the ether was allowed to stand over sodium for two days and was then distilled over a fresh quantity of sodium. Two fractions were obtained P(1) b.p. 75°-80° (1.5 g.) P(2) b.p. 80°-80° (0.5 g.). On redistillation \( \delta \- \beta \)-butyl ethyl ether was obtained b.p. 82-83° (0.5 g.) and had \( \delta \) 20° 0.745, and \( \alpha \) \( \delta \)-20° - 21.31°, \( \alpha \) \( \delta \)-20° - 23.72°, \( \alpha \) \( \delta \)-50° - 41.02°, homogeneous (\( \alpha \) = 0.35) and \( \alpha \) \( \delta \)-50° - 18.10°, \( \alpha \) \( \delta \)-100° - 19.00°, \( \alpha \) \( \delta \)-100° - 57.00° in ethyl alcohol solution (\( \alpha \) = 2.514). Found: C, 63.4%; H, 7.4%; \( \delta \) \( \delta \)-14° requires C, 70.3%; H, 13.8%. Owing to the closeness of the boiling points of ethyl alcohol and \( \beta \)-butyl ethyl ether, great difficulty was experienced in obtaining the ether free from alcohol. A trace of alcohol was still present even after treating the mixture successively with phthalic anhydride and sodium.
A similar procedure was followed. d-β-Butyl p-toluene sulphonate (15 g.) prepared from d-β-butanol
\( (\gamma_{20}^{20.0} + 13.22^\circ) \) was heated with n-butanol (6 g.) and potassium carbonate (5 g.) for 24 hours on a boiling water bath. The crude ether obtained was heated with phthalic anhydride (30 g.) as before and, after it had been recovered, it was allowed to stand over sodium for three days and was finally distilled from a fresh quantity of sodium. 1-β-Butyl-n-butyl ether (2 g.) was obtained, b.p. 130-131°. \( n_D^{17.5} 1.3972, d_4^{15} 0.769 \) with
\[ \begin{align*} &\frac{\gamma_{15}^{15.0} - 23.42^\circ, \gamma_{5461}^{15.0} - 27.57^\circ, \gamma_{4358}^{15.0} - 44.45^\circ, \text{homogeneous}}{5696} \\ &\left( \gamma = 0.25 \right) \text{ and } \gamma_{5896}^{15.0} - 21.65^\circ, \gamma_{5461}^{15.0} - 21.43^\circ, \gamma_{4358}^{15.0} - 41.70^\circ \text{ in ethyl alcohol solution, } (\gamma = 5.034). \end{align*} \]
Found: C, 73.6; H, 13.7%; \( C_8H_{18}O \) requires C, 73.8; H, 13.8%.

d-β-Butyl p-toluene sulphonate (15 g.) \( (\gamma_{5461}^{20.0} + 12.98^\circ) \) and phenol (30 g.) were heated together in the presence of anhydrous potassium carbonate (5 g.) for 24 hours on a boiling water bath. An excess of a concentrated sodium hydroxide solution was added and the mixture distilled in a current of steam. The distillate was extracted with ether, the ethereal extract washed with dilute sodium hydroxide solution and water...
and then dried over potassium carbonate. Two fractions were obtained on distilling the liquid remaining after the ether had been removed. Fl. (5 g.) b.p. 68-70°/20 mm. F2. (about 5 drops) b.p. 116-126°/20 mm.; this was phenetole. Fraction (1) was redistilled and then had b.p. 92-93°/20 mm., m^5.8° 1.4374, d^4° 0.798 and [α]^18° - 15.97°, [α]^19° 5461 - 22.54°, [α]^20° 4388 - 54.33°, homogeneous, (L = 0.25) and [α]^18° 5466 - 23.61°, [α]^19° 5461 - 22.54°, [α]^20° 4388 - 12.61° in ethyl alcohol solution (c = 5.02°).

Reaction between Sodium Benzanide and 1,1-dl-β-Butyl n-Toluene-sulphonate.

(a) Sodium benzanide was prepared by adding a solution of sodium ethoxide containing sodium (2 g.) in absolute alcohol (20 c.c.) to a concentrated solution of benzanide (10 g.) in alcohol. After refluxing the mixture for 30 minutes the excess alcohol was removed and the solid sodium benzanide was then heated for 50 hours on a boiling water bath with 1-β-butyl n-toluene-sulphonate (10 g.; [α]^20° 5461 - 5.30°). The mass was stirred up from time to time, and a strong odour of almonds, possibly due to the formation of benzonitrile, was noticed. Water was then added to the product and the mixture extracted with ether. The ethereal extract was washed twice with sodium hydroxide solution, then with water, and finally dried over potassium carbonate. The ether was then removed and the residue dissolved in aqueous alcohol. A small quantity (0.05 g.) of a colourless solid m.p. 202° which crystallised in plates was
first obtained. This solid contained nitrogen but no sulphur and was possibly the dibenzoyl derivative of \( \beta \)-butylaniline. 

\( \text{C}_8\text{H}_8(\text{C}_6\text{H}_5\text{N}_2)_2 \). On diluting the mother liquor with water and allowing to stand for several days, \( \beta \)-butylaniline benzate crystallised out in long needles m.p. 106\(^\circ\)C. A solution in ethyl alcohol \( (\rho = 1.10, \eta = 1) \) was optically inactive.

(b) Benzamide \( (5 \ g.) \) was dissolved in absolute ethyl alcohol \( (50 \ c.c.) \) in a flask fitted with a reflux condenser, and sodium \( (1 \ g.) \) was added. When the sodium had dissolved \( \beta \)-butyl \( \rho \)-toluene sulphonate \( (10 \ g.) \) was added, and the mixture heated on a water bath for 2 hours, when a copious precipitate of sodium \( \rho \)-toluene sulphonate was obtained. The mixture was then cooled, poured into water and extracted with ether and the etheral extract washed and then dried over anhydrous sodium sulphate. The ether was then removed and on redistillation yielded a fraction b.p. 78\(^\circ\)-84\(^\circ\)C, which was probably a mixture of ethyl alcohol and \( \beta \)-butyl ethyl ether. The solid residue had m.p. 137\(^\circ\)C, and on recrystallisation from hot water had m.p. 130\(^\circ\)C. It was therefore benzamide. No benzoyl derivative of \( \beta \)-butylaniline was isolated.

Reaction between \( \text{l} + \text{dl-} \beta \)-butyl \( \rho \)-toluene sulphonate and \( \rho \)-toluene sulphonamide in the Presence of Potassium Carbonate.

To \( \text{l} + \text{dl-} \beta \)-butyl \( \rho \)-toluene sulphonate \( (7 \ g.; \text{b.p. 143\(^\circ\)}\)\), \( \rho \)-toluene sulphonamide \( (11 \ g.) \) and potassium carbonate \( (9 \ g.) \) were mixed in benzene \( (50 \ c.c.) \), (the benzene had been distilled
over phosphorus pentoxide) and heated on a boiling water bath for 48 hours. The potassium carbonate was filtered off and the benzene removed. Considerable decomposition of the unchanged β-buty1 p-toluenesulphonate occurred. On recrystallizing the solid residue twice from ether and light petroleum it had m.p. 137° alone and when mixed with p-toluenesulphonamide, no evidence was obtained that the p-toluenesulphonyl derivative of β-buty1amine had been formed.

Reaction between Ethyl p-Toluenesulphonate and Chloramine-T.

Ethyl p-toluenesulphonate (10 g.) and chloramine-T (12 g.) were mixed and heated on a boiling water bath for 12 hours. Chlorine was evolved. Water was then added and the mixture extracted with ether. The ether extract was washed with water and dried over anhydrous sodium sulphate, then filtered and dried over potassium carbonate. The addition of potassium carbonate caused an intense blue colour which changed rapidly to dark brown. The original yellow colour of the solution reappeared on adding dilute hydrochloric acid. After the ether had been removed, the brown residue was distilled in a high vacuum, two fractions being obtained. F1. (3 g.), b.p. 134°-140°C. F2. (2 g.), b.p. 150-160°. On redistillation F2 gave a colourless
viscous liquid b.p. 157-160° which solidified on cooling to a white solid m.p. 29°C. On recrystallisation from a mixture of isopropyl ether and light petroleum, it had m.p. 54-60°, and after two further recrystallisations, m.p. 63°. The mixed m.p. with ethyl p-toluenesulphonamide was also 63°. Hence, the interaction of ethyl p-toluenesulphonate and chloramine-T yields ethyl p-toluenesulphonamide.

Reaction between β-Butyl p-toluenesulphonate and Chloramine-T.

β-Butyl p-toluenesulphonate (10 g.) and chloramine-T (12 g.) were mixed and heated on a boiling water bath for 12 hours. After a short time, a strong aldehydic odour was noticed but no chlorine appeared to be evolved. Water was then added and the solid which separated was extracted with ether in the usual way. After part of the ether had been removed, the solution was left to crystallise. The crystals obtained had m.p. 120° alone and when mixed with p-toluenesulphonamide. No evidence was obtained that the p-toluenesulphonyl derivative of β-butylamine had been formed. Presumably, hydrolysis of the sulphonate and of chloramine-T occurred with formation of p-toluenesulphonamide, β-butanol and hypochlorous acid, the water necessary for these reactions to take place being provided by the water of crystallisation of chloramine-T. The β-butanol was then oxidised to aldehyde by the hypochlorous acid.
\[
\begin{align*}
\text{EtOH} + \text{H}_2\text{O} \rightarrow & \quad \text{H}_2\text{O} + \text{EtOH} \\
\text{C}_4\text{H}_6\text{COH} + \text{HCl} \rightarrow & \quad \text{C}_3\text{H}_6\text{CHO} + \text{H}_2\text{O} + \text{HCl}
\end{align*}
\]

**Reaction between β-Butyl p-Toluene sulphonate and Ammonia.**

1. **In Ethyl Alcoholic Solution.**
   
   (a) Absolute ethyl alcohol (100 c.c.) saturated with dry ammonia was added to β-butyl p-toluene sulphonate (10 g.) and left in a desiccator for three days. Hydrochloric acid was then added and the solution extracted with ether. The aqueous extract was then evaporated to dryness and the solid residue distilled over solid potassium hydroxide. About 1 cc. of β-butylamine was obtained.

   (b) Alcoholic ammonia (15 c.c.) and β-butyl p-toluene sulphonate (3 g.) were heated together in a sealed tube at 100°C. The solid product obtained was dissolved in water, acidified with hydrochloric acid and extracted with ether as before. The solid residue, obtained on evaporating the aqueous extract to dryness, did not yield any β-butylamine when distilled with solid potassium hydroxide.

2. **Using 0.250 Ammonia.**

   Three sealed tubes, each containing d-β-butyl p-toluene sulphonate (10 g.), prepared from d-β-butanol (d_10^o = 1.018) and 0.250 ammonia (4 g.) were heated at 100°C for 10 hours. A brown oil formed at the top of a colourless lower layer containing large crystalline plates. The contents of the tubes were steam distilled with sodium hydroxide and the distillate
collected in dilute hydrochloric acid. The hydrochloric acid solution was then evaporated to dryness on a water bath, concentrated hydrochloric acid being added from time to time in order to prevent loss by hydrolysis. The \( \beta \)-butylamine hydrochloride and ammonium chloride were separated by extracting the dry mixture in a Soxhlet extractor with dry acetone in which the amine hydrochloride is soluble but ammonium chloride insoluble. After removing the acetone from the extract obtained the residual brown tar was triturated with dry ether, when a white solid separated. This solid was removed by filtration and recrystallised from a small quantity of acetone, long, colourless needles of \( \beta \)-butylamine hydrochloride being obtained. A solution of the hydrochloride in water \( (\alpha = 0.721) \) was optically inactive in a 2 dm. tube. The hydrochloride was then converted into \( \beta \)-butylamine benzoate by the Schotten Baumann reaction. The product then had \( [\alpha]_D^{19^\circ} - 35.1^\circ \) in ethyl alcohol solution \( (\alpha = 1.113) \), and after two recrystallisations from aqueous alcohol it was obtained with m.p. \( 83-89^\circ \mathrm{C} \) and \( [\alpha]_D^{17^\circ} - 14.35^\circ, [\alpha]_D^{17^\circ} - 18.7^\circ, [\alpha]_D^{17^\circ} - 33.01^\circ \).

Found: C, 74.5; H, 6.5%; \( \text{C}_{11} \text{H}_{15} \text{ON} \) requires C 74.6; H, 6.5%.

After standing the mixture for 10 minutes it was left to Reaction between \( \text{d-}\beta \)-Butyl p-Toluenesulphonate and Piperidine.

\( \text{d-}\beta \)-Butyl p-Toluenesulphonate \((11 \text{ g.}) \) prepared from \( \text{d-}\beta \)-butanol \( (\alpha_{5461}^{19^\circ} + 13.26^\circ) \) and piperidine \( (3 \text{ g.}) \) were mixed and warmed on a water bath for two hours. On cooling, large colourless plates separated. After adding dilute sodium
hydroxide solution the mixture was extracted with ether, and
the ethereal extract washed with water and dried with potassium
carbonate. After removal of the ether and excess piperidine
by distillation, N-α-β-butyl piperidine (5 g.) was obtained,
b.p. 73-76°/25 mm. On redistillation this had b.p.75-8°/25 mm.,
H2 1.4486, d2 0.835 and \( \alpha_5^{25°} = 54.59°, \alpha_4^{25°} = 63.53°, \)
\( \alpha_4^{25°} - 99.60° (1 = 0.25) \) homogeneous, and \( \alpha_4^{24°} = 5.9°, \)
\( \alpha_4^{24°} - 5.7°, \alpha_4^{24°} - 9.1° \) in ethyl alcohol solution \( \alpha = 5.00° \)
Found: C, 76.6; H, 13.3%. C9H19N requires C, 76.6; H, 13.5%.
The hydrochloride was prepared by mixing N-β-butyl piperidine
(1 g.) and concentrated hydrochloric acid (2 g.) and evaporating
to dryness on a water bath. The solid residue was then re-
crystallised from acetone and was obtained in long needles.
N-β-butyl piperidine hydrochloride had \( \alpha_3^{16°} + 1.40°, \)
\( \alpha_4^{16°} 1.80°, \alpha_4^{16°} + 4.4° \) in N-hydrochloric acid solution
\( \alpha = 5.000 \) and \( \alpha_4^{25°} + 0.96°, \alpha_4^{25°} + 1.24, \alpha_4^{25°} + 3.03 \)
in water \( \alpha = 4.420 \).

The platinic salt was prepared by mixing platinic chloride
(0.48 g.) and hydrochloric acid (0.3 g.of 35% acid), and adding
the solution to N-β-butyl piperidine (0.2 g.) in ethyl alcohol.
After warming the mixture for 15 minutes it was left to

crystallise. The orange-coloured solid obtained was recrystallised
from ethyl alcohol, when long needles separated,
m.p. 195°C, with decomposition. The salt was optically inactive
in aqueous solution.
Reaction between Piperidine and (a) Optically Inactive β-Butyl
Toluene-4-sulphonate. The procedure described above for the
optically active sulphonate was followed exactly. The optically
inactive N-β-butyl piperidine yielded a platinic salt
m.p. 107°C, and a picrate m.p. 93-100°C.

(b) Optically Inactive β-Butyl Iodide. β-Butyl iodide
(6 g.) and piperidine (6 g.) were mixed. On warming for a few
minutes a white crystalline solid separated. Excess of sodium
hydroxide solution was then added and the mixture extracted
with ether in the usual manner. N-β-Butyl piperidine (4 g.)
b.p. 70°C/21 mm., and nD 31.20° 1,4434 was obtained. Platinic salt,
m.p. 137°C, and mixed m.p. with platinic salt of (a) 107°C.

Piperidine, m.p. 100°C, and mixed m.p. with picrate of (a) 100°C.

(c) n-Butyl p-Toluene-4-sulphonate. The procedure described
above for the optically active β-butyl n-toluene-4-sulphonate was
closely followed. N-n-butyl piperidine b.p. 60-70°C/26 mm.
was obtained. Platinic salt m.p. 179°C. Picrate m.p. 132°C.

(d) n-Butyl Bromide. The procedure described above for
β-butyl iodide was followed. N-n-butyl piperidine b.p. 70°C/20 mm.
was obtained, Platinic salt m.p. 179°C, and mixed m.p. with
platinic salt from (c) 179°C. Picrate, m.p. 132°C and mixed
m.p. with picrate of (c) 132°C.

Reaction between 4-β-Butyl p-Toluene-4-sulphonate and Pyridine.

4-β-Butyl p-toluene-4-sulphonate (6 g.) prepared from 4-β-
butanol ($\alpha^{23} \text{D} = 12.35$) was warmed with pyridine (2 g.) for six hours on a boiling water bath, when a pale yellow viscous liquid was obtained. The product was dissolved in water and extracted with ether to remove any unchanged sulphonate. The aqueous portion was concentrated on a water bath and then heated to 100$^\circ$ in a high vacuum (0.1 mm.) for about one hour. It was finally allowed to stand in a vacuum desiccator over phosphorous pentoxide, and after a few days it solidified completely. The solid had m.p.50$^\circ$ and was very soluble in water and in ethyl alcohol. $\text{N-}$-$\beta$-$\text{Butyl pyridinium p-toluenesulphonate}$ had $\alpha^{24}$ $\text{D} = 1.16$, $\alpha^{24}$ $\text{D} = 1.18$, $\alpha^{24}$ $\text{D} = 1.53$ in absolute ethyl alcohol solution ($\alpha = 8.470$) and $\alpha^{24}$ $\text{D} = 1.24$, $\alpha^{24}$ $\text{D} = 1.25$, $\alpha^{24}$ $\text{D} = 1.58$ in aqueous solution. The platinic salt $\left[\text{H}_5\text{N}\cdot\text{C}_4\text{H}_9\cdot\text{J}_2\cdot\text{PtCl}_6\right]$ had m.p. 203$^\circ$ on recrystallisation from aqueous alcohol, and was optically inactive in aqueous solution.

The picrate was prepared by mixing the warm alcoholic solutions of the pyridinium salt and picric acid in the requisite proportions. On cooling, long yellow needles separated the picrate was recrystallised from ethyl alcohol. On cooling, long yellow needles separated which on recrystallisation from ethyl alcohol had m.p.163$^\circ$.

The mixed m.p. with pyridine picrate was also 163$^\circ$ and it was concluded that the salt obtained from $\beta$-$\text{butyl pyridinium p-toluenesulphonate}$ and picric acid was pyridine picrate. Small quantities with elution, after eluting for 24 hours...

Reaction between $\alpha$-$\beta$-$\text{Butyl p-Toluenesulphonate}$ and $\text{p-Toluidine}$.

$\alpha$-$\beta$-$\text{Butyl p-toluenesulphonate}$ (6 g.) prepared from $\alpha$-$\beta$-
butanol \( \alpha _{5461}^{20} = 12.96^\circ ; 1 = 1 \) and p-toluidine (5 g.) were warmed on a water bath for 6 hours. The solid product was dissolved in caustic soda solution, extracted with ether, and the ethereal solution washed with water and dried over potassium carbonate. After removal of the ether, the residue was distilled under reduced pressure, when two main fractions were obtained. F.(1) b.p. 110-130\^\circ /25 \text{ mm.}, which solidified on cooling and was chiefly p-toluidine. F.(2) b.p. 133-4^\circ /25 \text{ mm.}

On redistillation, N-\( \beta \)-butyl p-toluidine (1 g.), b.p. 135-6^\circ /25 mm. was obtained, and had \( n^D_{5896}^{18.30} = 1.5272 \), \( d_6^{21} = 0.916 \) and \( \alpha _{5461}^{21} = 37.45^\circ \), \( \alpha _{5461}^{21} = 44.93^\circ \), \( \alpha _{4358}^{21} = 86.18^\circ \), homogeneous, \( l = 0.25 \), \( \alpha _{5896}^{21} = 35.74^\circ \), \( \alpha _{5461}^{21} = 40.94^\circ \), \( \alpha _{4358}^{21} = 77.96^\circ \), in ethyl alcohol solution \( c = 5.310 \) and \( \alpha _{5896}^{21} = 3.00^\circ \), \( \alpha _{5461}^{21} = 4.72^\circ \), \( \alpha _{4358}^{21} = 8.16^\circ \) in 0.477 N. HCl \( c = 5.740 \).

**Preparation of \( \beta \)-Butylamine.**

(1) **Preparation of Methylethylketoxime.** Methylethyl ketone was carefully fractionated and the portion boiling 79-81\^\circ was collected separately. Solutions of hydroxylamine hydrochloride (69 g. in 100 c.c. water) and sodium hydroxide (40 g. in 100 c.c. water) were mixed, and methylethyl ketone (80 g.) was added in small quantities with shaking. After standing for 24 hours all smell of hydroxylamine had gone and a pale yellow oil had separated at the top of the liquid in the flask. The oxime was extracted with ether, washed with water and dried over anhydrous
sodium sulphate. After removing the ether, methylethylketoxime was obtained b.p.153°/750 mm. or 80-82°/30 mm.

(i) **Reduction of Methylethylketoxime.** Methylethylketoxime (61 g.) was dissolved in 99% ethyl alcohol (1 litre) in a 3-necked flask fitted with two double surface condensers in series. Sodium (65 g.) was added in small lumps through one of the side necks. When the reaction became less vigorous the flask was heated on a water bath, aqueous alcohol and finally water being added from time to time. The butylamine was then removed in a current of steam and absorbed in dilute hydrochloric acid. The acid solution was evaporated to dryness, a little aqueous copper or lead nitrate added. It was therefore concentrated hydrochloric acid being added to prevent loss by hydrolysis. It was found that the best method of obtaining the free base was to distil the solid hydrochloride (60 g.) (33-73 g.) was distilled with a concentrated solution of aqueous potassium hydroxide, and after the aqueous layer which separated was removed, was finally distilled over solid potassium hydroxide. The distillate was then allowed to stand over solid potassium hydroxide, and after the aqueous layer which separated was removed, was finally distilled over solid potassium hydroxide. The free base was obtained. 

(ii) **Resolution of β-Butylamine.** A solution of silver bromo camphorsulphonate (30 g.) was added to β-Butylamine hydrochloride (8 g.) in water (10 cc.) and the mixture was heated to boiling. After crystallization the solution was cooled and the crystals filtered off. The mother liquors were washed with cold water and dried. The product was then recrystallized from absolute alcohol. The residue of the mother liquors was allowed to stand over potassium hydroxide, and after the aqueous layer which separated was removed, was finally distilled over solid potassium hydroxide. The free base was obtained, b.p. 67-69°. An attempt to extract the amine from the alkaline solution of the hydrochloride by means of ether in a continuous extractor was unsuccessful owing to the low boiling point and high solubility of the amine.
in water (10 cc.) and then filtered. The filtrate was evaporated to a syrup and was then left in a vacuum desiccator for 48 hours. When it had become as solid as possible it was dissolved in anhydrous ethyl acetate. The bromcamphorsulphonate could not be made to crystallise, and this method was abandoned.

(b) \( \beta \)-Butylamine (24 g.) was added to \( d \)-tartaric acid (50 g.) dissolved in a small quantity of water and left to crystallise. Repeated recrystallisation from 90% ethyl alcohol of the crop thus obtained caused irregular variations in the rotatory power of the tartrate probably owing to hydrolysis and loss of \( \beta \)-butylamine and the presence of increasing amounts of free tartaric acid. It was therefore necessary to recover the amine from the salt and determine the rotatory power of the free base. \( \beta \)-Butylamine hydrogen tartrate (8 g.) was distilled with a concentrated solution of sodium hydroxide (5 g.), the distillate dried over solid potassium hydroxide and finally fractionated over solid potassium hydroxide. \( \beta \)-Butylamine (1.5 g.) b.p. 88° was obtained. After removal of two crops of \( \beta \)-butylamine hydrogen tartrate, the mother liquor was concentrated and then decomposed. \( 1- \beta \)-Butylamine (2.6 g.) with \( [\alpha]_{5461}^{15} = 4.61° (c = 0.25) \) was obtained. Other samples of \( \beta \)-butylamine were obtained with \( [\alpha]_{5461}^{15} = -2.0°, [\alpha]_{5461}^{15} = -1.2°, [\alpha]_{5461}^{15} = 3.7° \). The following specific rotations of \( d-\beta \)-butylamine under various conditions were observed:-

\[ \alpha \]
Preparation of N-1/β-Butyl Piperidine by the Interaction of Pentamethylene Bromide and 1/β-Butylamine.

Pentamethylene bromide (2.7 g.) (prepared by the method described in Organic Syntheses (Vol. IX)) in dry ether (5 cc.) was added to 1/β-butylamine (2.3 g.; χ = 0.25) in dry ether (5 cc.) and the mixture was refluxed for 12 hours, when there was a heavy crystalline deposit in the flask. The product was then dissolved in caustic soda solution, extracted with ether, and the ethereal extract washed with water and dried with potassium carbonate. On removal of the ether, the residue was distilled under reduced pressure, two fractions being obtained. F(1) b.p. 90-80°/23 mm. F(2) b.p. 93-97°/23 mm. This was unchanged pentamethylene bromide. Fraction (1), on redistillation, yielded N-1/β-butyl piperidine (1 g.) b.p. 78-80°/23 mm., nD 1.4515 and χ 0.25.

Formation C, 76.0; H, 13.2; CgH19N requires C, 76.6; H, 13.5%.

The platinic salt had m.p. 197-198°, and mixed m.p. with platinic salt obtained from product of the interaction of d-β-butyl p-toluenesulphonate and piperidine was also 197-198°.
Reaction between 1 + dl-\(\beta\)-Butyl p-Toluene sulphonate and Benzoic Acid.

1 + dl-\(\beta\)-Butyl p-toluene sulphonate (\(\alpha_{5461}^{23^\circ} = -5.84^\circ; 1 = 1\)) (20 g.) and benzoic acid (32 g.) which had been dried for four days over phosphorus pentoxide in a vacuum desiccator were mixed and heated in a boiling water bath for 24 hours. A homogeneous solution was formed which rapidly darkened. Excess sodium carbonate solution was then added and the ester removed by a current of steam. The distillate was extracted with ether and the ethereal extract dried over potassium carbonate. After removing the ether, the residual ester was distilled in vacuo. \(\beta\)-Butyl benzoate (7.5 g.) was obtained, b.p. 115-117\(\circ\)/20 mm. n\(D\) = 1.4933 and was optically inactive in a 1 dm. tube (Theoretical yield 15.6 g.).

Reaction between 1 + dl-\(\beta\)-Butyl Benzoate, Benzoic Acid and p-Toluene sulphonic Acid.

1 + dl-\(\beta\)-Butyl benzoate (\(\alpha_{5461}^{21^\circ} = -5.20^\circ; 1 = 1\)) (5 g.), anhydrous benzoic acid (3.4 g.) and p-toluene sulphonic acid (5 g.) were mixed and heated on a boiling water bath for 12 hours. The \(\beta\)-butyl benzoate was isolated as described above. On distillation \(\beta\)-butyl benzoate (2.2 g.) was obtained and was optically inactive.

Reaction between 1 + dl-\(\beta\)-Butyl Benzoate and Benzoic Acid.
was warmed with anhydrous benzoic acid (2.0 g.) for 24 hours on a boiling water bath. The liquid was then poured into dilute sodium carbonate solution and extracted with ether in the usual way. On distillation, \( d+dl-\beta \)-butyl benzoate (1.3 g.) was obtained with \( \alpha^\circ \text{Ba} = 70^\circ + 2.70^\circ \) (i = 0.33).

Reaction between \( d+dl-\beta \)-Butyl Benzoate and \( \alpha \)-Toluene sulphoninic Acid.

\( d+dl-\beta \)-Butyl benzoate (2 g.) \( (\alpha^\circ \text{Ba} = 70^\circ + 2.69^\circ) \) and \( \alpha \)-toluene sulphoninic acid (2 g.) were mixed and heated together on a boiling water bath for 24 hours. Long crystals of benzoic acid filled the flask and a brown tarry liquid remained. On adding water sodium carbonate solution and extracting with ether in the usual way, no \( \beta \)-butyl benzoate was isolated. It was concluded that the \( \beta \)-butyl radical had been lost as butylene:

\[
\text{C}_6\text{H}_5\text{COOC}_6\text{H}_5 + \text{C}_7\text{H}_7\text{SO}_3\text{CH} = \text{C}_6\text{H}_5\text{COCH} + \text{C}_6\text{H}_5\text{COCH} + \text{C}_7\text{H}_7\text{SO}_3\text{CH}.
\]

Reaction between \( 1-dl-\beta \)-Butyl \( \alpha \)-Toluene sulphoninate and Anhydrous Formic Acid.

Anhydrous formic acid was prepared by Naguesne's method (Bull. Soc. Chim. 1923, 1841; 59, 662; Pickard, Kenyon and Hunter, J.C.S. 1933, 128, 9). Commercial (90%) formic acid was mixed with enough pure (99%) sulphuric acid to form the monohydrate \( \text{H}_2\text{SO}_4\cdot\text{H}_2\text{O} \) with all the water present. The mixture was then distilled under reduced pressure, the formic acid being collected in a receiver cooled in ice water, where it solidified.
The temperature throughout was kept below 70°C, in order to reduce the dehydrogenation of the formic acid to a minimum.

\[1 + \text{dl-}\beta\text{-Butyl } p\text{-toluenesulphonate (10 g.) prepared from } 1 - \beta\text{-butanol } \text{to } 105\text{°C} - 108.5\text{°C} \text{ and anhydrous formic acid (30 g.) were refluxed for 6 hours on a boiling water bath. A black liquid was obtained in about ten minutes. The product was then steam distilled and the distillate extracted with ether. The ethereal extract was washed with dilute sodium carbonate solution and water and then dried with potassium carbonate.}

On fractionating the residue left after removing the other, \(\beta\text{-butyl formate was obtained (0.5 g.) b.p. 65 - 68\text{°C}, n_D 1.3920, and was optically inactive in a 0.35 dm. tube.}

The non-volatile residue from the steam distillation formed a blue solution which gave a dark green syrupy liquid which solidified on slow evaporation. This was soluble in alcohol and acetone but insoluble in ether, benzene and carbon tetrachloride. On adding carbon tetrachloride to a solution of the substance in acetone, a dark green precipitate formed which was removed by filtration. On recrystallisation from ethyl alcohol and isopropyl ether, a minute quantity of a dark green solid was obtained.

\[\text{Glacial acetic acid}.

Commercial glacial acetic acid was cooled in ice and the supernatant liquid decanted from the solidified acid. \[1 + \text{dl-}\beta\text{-Butyl } p\text{-toluenesulphonate (7 g.) prepared from } 1 - \beta\text{-butanol}

(α$\text{D}^\circ = 9.3^\circ$; $l = 2$) and glacial acetic acid (50 cc.) were
heated for 12 hours on a boiling water bath. The black tarry
product was then steam distilled and the distillate extracted
with ether. After washing the etheral extract with dilute
sodium carbonate solution and water, and drying with potassium
carbonate, the ether was removed and the residue fractionated
$\alpha + \beta$-butyl acetate b.p.100-114$^\circ$ was obtained which on redistillation had b.p.112.114$^\circ$, $n\text{D}^\circ 1.3830$ and $\alpha$ in $\text{D}^\circ 10^\circ + 3.3^\circ$.

This reaction is attended by considerable racemisation since
the ether prepared by the interaction of $\alpha + \beta$-butyl n-
toluene sulphonate, prepared from $\alpha + \beta$-butanol ($\alpha$ $\text{D}^\circ = 9.52^\circ$;
$l = 2$), and potassium acetate in ethyl alcoholic solution, had
$\alpha$ in $\text{D}^\circ 10^\circ + 10.3^\circ$. It is probable that the glacial acetic acid
used still contained a trace of water which prevented complete
racemisation occurring, such as took place with benzoic and
formic acids. The ether was distilled in vacuo, washed
since acetic acid solution and water and then dried with

Reactions of $\beta$-Butyl n-Toluenesulphonate.

Interaction of $\alpha + \beta$-Butyl n-Toluenesulphonate and Bromine in

Petroleum Ether Solution.

Bromine (3 g.) in light petroleum (40 cc.) was added to a
solution of $\alpha + \beta$-butyl n-toluenesulphonate (10 g.) in light
petroleum (40 cc.) and the mixture allowed to stand for 48 hours.

A crystalline precipitate (3 g.) of n-toluenesulphonyl bromide
was obtained, which, on recrystallisation from ether and light
from $\alpha + \beta$-butanol ($\alpha$ $\text{D}^\circ = 4.53^\circ$; $l = 1$) and aqueous bromide.
petroleum, had m.p. 95-97°. The supernatant liquid was
decanted, washed with dilute sodium hydroxide solution and water
and dried with anhydrous potassium carbonate. On removing the
light petroleum and fractionating the residue, two fractions
were obtained F.1. (2 g.) b.p. 63-65°, F2. (3.5 g.) b.p. 85-97°.
On repeated fractionation the second fraction yielded 1- β-buty1
bromide, b.p. 92-93°, nD20 1.4387 and [α]D17° = 2.80°,
[α]D17 = 5.15.

Cyanogen bromide was prepared by adding potassium cyanide
solution to a mixture of bromine and water cooled in a freezing
mixture, according to the method described in Organic Syntheses
(Vol XI, p. 30). p-Toluencesulphinic acid (9 g.) and cyanogen
bromide (6 g.) were mixed and warmed gently on a water bath.
A vigorous reaction occurred with copious evolution of hydrogen
cyanide. The product was dissolved in ether, washed with
water, dried over sodium sulphate, and crystallised from dilute
sodium hydroxide solution and water and then dried with
anhydrous potassium carbonate. On removal of part of the ether
anhydrous sodium sulphate and addition of light petroleum to the residue, p-toluencesul-
phinic acid crystallised out, and had m.p. 95-97°. An ether solution in a beaker was carefully
inactivated in a b. d. tube. Found: C, 55.0; H, 7.6; N,
0.8.

Reaction between 1-β-Butyl p-toluesulphinate and
Cyanogen Bromide.

1-β-Butyl p-toluesulphinate (20 g.) prepared
from 1-β-Butanol (α19° = 4.03°; 1 = 1) and cyanogen bromide.
(10 g.) were heated together in a sealed tube at 100°C for 14 hours. On cooling, the tube contained a brown liquid, a quantity of long colourless needles (0.5 g.) and there was a strong mustard oil odour. A similar experiment with L-β-butyl p-toluenesulphinate (10.6 g.), cyanogen bromide (5.3 g.) and water (0.5 g.) increased the amount of solid product to 3.4 g. The crystals were filtered off, washed with benzene and re-crystallised from a mixture of methyl alcohol and isopropyl ether, when long needles were obtained which melted above 300°C. They contained sulphur and nitrogen, evolved ammonia with sodium hydroxide solution and were very soluble in water, methyl and ethyl alcohols, but were insoluble in ether, acetone and benzene, and were optically inactive. Found: C, 43.3; H, 5.5; S, 16.4.

C₂H₅SO₂CONH₂ requires C 44.4, H, 5.8, S, 16.9%. The solid product was therefore ammonium p-toluenesulphonate.

The liquid portion of the reaction mixture was steam distilled. After several days long, colourless needles m.p.108° separated from the non-volatile portion, together with a considerable quantity of tar. On recrystallisation from hot water, the crystalline solid had m.p.118° and contained nitrogen and sulphur. An ethyl alcoholic solution (c = 2.26) was optically inactive in a 1 dm. tube. Found: C, 56.0, H, 7.0; C₄H₇SO₂CONH₂ requires C, 56.5, H, 6.7%. The substance was probably the p-toluenesulphonyl derivative of methylethyl-acetamide. The distillate was extracted with ether, washed with dilute
sodium hydroxide solution, water, and dried with anhydrous calcium chloride. The ether was then removed and the residue fractionated, two chief fractions being obtained. F. (1) b.p. 65-69°/30 mm. F. (2) b.p. 110-120°/30 mm. F. (1) was too small to allow of further purification, but it contained nitrogen and had \( \alpha_{546}^0 = 0.14^\circ (l = 0.25) \), and possibly contained \( /- \)-butyl cyanide. F. (2) b.p. 119°/26 mm. containing nitrogen and sulphur, which was optically inactive was obtained.

The mixture was then boiled with water, and heated with potassium carbonate. A concentrated solution of potassium cyanide was obtained, containing any \( /- \)-tolyl thiocyanate. The whole of the

It was therefore \( /- \)-tolyl-isothiocyanate. The whole of the

The mixture was then poured into water and extracted with ether. The etheral extract was washed with water and dried with potassium carbonate. The \( /- \)-tolyl disulphide was obtained, indicating that fraction (2) did not contain it. A concentrated solution of potassium cyanide was obtained, containing any \( /- \)-tolyl thio-cyanate.

Interaction of 1 + \( /- \)-Butyl \( /- \)-Toluene sulphinate and Cyanamide.

Cyanamide was prepared by passing dry ammonia gas into a dry ethereal solution of cyanogen bromide cooled in ice until precipitated and having no further reaction occurred. The precipitate of ammonium bromide was removed by filtration and the ethereal solution was concentrated by warming gently on a water bath. The residual
oily liquid was left in a vacuum desiccator over fused calcium chloride for three days, when solidification occurred.

1+dl-β-Butyl p-toluenesulphinate (10 g.) and cyanamide (2 g.) were mixed and heated on a gently boiling water bath for six hours. A thick precipitate formed which was removed by filtration. This substance was insoluble in all the usual organic solvents but was sparingly soluble in hot water from which it was recrystallised. It was obtained as a pale yellow amorphous powder. Found: C, 32.6; H, 4.3%. Nitrogen was present. The substance was probably a polymer of cyanamide. The p-toluenesulphinic ester was recovered unchanged, and it was therefore concluded that polymerisation of the cyanamide by heat occurred before reaction with the p-toluenesulphinic ester could take place.

Interaction of 1+dl-β-Butyl p-Toluenesulphinate and Cyanogen.

1+dl-β-Butyl p-toluenesulphinate (10 g.) was added to a solution of copper sulphate (25 g.) in water (300 c.c.) in a stoppered bottle. A concentrated solution of potassium cyanide (26 g.) was added quickly, the stopper replaced and the bottle shaken for two hours on a mechanical shaker. The mixture was then extracted with ether in the usual way. On distillation no β-butyl cyanide was isolated, and it was concluded that the p-toluenesulphinic had not reacted with the cyanogen.
Interaction of \(1+\text{dl}-\beta\)-Butyl \(p\)-Toluene-sulphinate and Thiocyanogen.

Powdered lead thiocyanate (32 g.) was placed in a large stoppered bottle and covered with dry ether (250 cc.). A solution of bromine (4.5 cc.) in ether (200 cc.) was added slowly. \(1+\text{dl}-\beta\)-Butyl \(p\)-toluene-sulphinate (10 g.) was then added and the mixture shaken on a mechanical shaker for two hours. A large quantity of an orange-coloured product separated and was removed by filtration. This substance was insoluble in hot water, but lead bromide was obtained when the hot aqueous extract was filtered. This substance was probably a polymer of thiocyanogen. The ethereal extract was not found to contain any \(\beta\)-butyl thiocyanate. It was concluded that the thiocyanogen polymerised before reaction with the \(p\)-toluene-sulphinic ester took place. A pale yellow crystalline solid precipitated was obtained, but decomposed on heating.

Interaction of \(1+\text{dl}-\beta\)-Butyl \(p\)-Toluene-sulphinate and Piperididine

\(1+\text{dl}-\beta\)-Butyl \(p\)-toluene-sulphinate (8 g.) prepared from \(1-\beta\)-butanol (\(\alpha_{D}^{18}=4.23\)) and piperidine (3.5 g.) were mixed and heated on a water bath for 36 hours, when a viscous, brown liquid was obtained. This was distilled at 60 mm./pressure and any volatile products were collected in a receiver cooled in a freezing mixture. The residue solidified on cooling to a dark brown mass and after three recrystallisations from acetone had m.p. 131-132°C. It contained nitrogen and sulphur and was \(\beta\)-Butyl \(p\)-toluene-sulphinate prepared from \(1+\text{dl}-\beta\)-methyl.
(α<sup>1</sup>)<sup>13</sup>C - 3.11 (1:1) was poured on a water bath with gradual
optically inactive in acetone solution. Found: N, 6.0%.
A compound is almost colorless and is almost insoluble in cold acetone solution (α<sup>1</sup>)<sup>13</sup>C -
3.11 requires N, 6.3%. The compound is therefore p-
toulene sulphonamide and is almost insoluble in the
acetone solution.
The distillate was extracted with ether and the ethereal extract
then dried with potassium carbonate. On distillation, 1-<i>dl</i>-<i>β</i>-butanol was
obtained (86°-20°, with α<sup>19</sup>°<sup>0</sup> = 4.26°; (1 = 1).

Interaction of 1-<i>dl</i>-<i>β</i>-Butyl p-Toluenesulphonate and p-Toluidine

1-<i>dl</i>-<i>β</i>-Butyl p-toluenesulphonate (5.3 g.) prepared from
1-<i>β</i>-butanol (α<sup>19</sup>°<sup>0</sup> = 4.23°) and p-toluidine (2.7 g.) were
mixed and heated on a boiling water bath for 12 hours. The
mixture solidified on cooling. Light petroleum (40°-60°) was
then added and the mixture filtered. A pale yellow crystal-
line solid m.p. 235° was obtained, but decomposed on attempting
/Butanol (α<sup>17</sup>°<sup>0</sup> = 1.04; (1 = 0.33).

Reaction between 1-<i>dl</i>-<i>β</i>-Butyl p-toluenesulphonate and Glacial
Acetic Acid.

Commercial glacial acetic acid was cooled in ice and water
and the liquid portion then decanted from the solid acid. 1-<i>dl</i>-<i>β</i>-Butyl p-toluenesulphonate prepared from 1-<i>dl</i>-<i>β</i>-butanol
(α\(^{10}\)\(^0\) - 4.14\(^0\); \(1 = 1\)) was warmed on a water bath with glacial acetic acid (25 cc.) containing acetic anhydride (5 cc.) for 6 hours. The black tarry product was then steam distilled, the distillate was extracted with ether and the ethereal extract distilled. The tarry product was added to water washed with dilute sodium carbonate solution and water, and then dried over anhydrous potassium carbonate. On removing the solvent the distillate was distilled to remove any mixture of ether and distilling the residue, two fractions were obtained.

F.(1) b.p. 80-100\(^0\); F.(2) b.p. 100-110\(^0\). Repeated fractions of F.(1) gave a liquid b.p. 95\(^0\)-100\(^0\), chiefly at 98\(^0\), which was 2-β-butanol, α\(^{15}\)\(^0\) - 4.00\(^0\); \(1 = 1\). Repeated fractions of F.(2) yielded β-butyl acetate (1.59 b.p. 113-113\(^0\), 0.5386); the ethereal washings were again filtered, and which had n\(^{17.5}\)\(^0\) 1.5965, and \(\alpha\(^{17}\)\(^0\) - 6.04\(^0\).

Anhydrous Formic Acid.

\(1+\alpha\)-β-butyln-toluene sulphinate (15 g.) prepared from \(1+\alpha\)-β-butanol (α\(^{18}\)\(^0\) - 4.14\(^0\)) was heated with anhydrous formic acid prepared by Daquinie's method (10 cc.) for 6 hours on a boiling water bath. The black tarry product was steam distilled and the distillate extracted with ether as before.

After removing the ether the residual liquid was refluxed with a small quantity of alcoholic potassium hydroxide (2 cc. of 5\% solution) for 6 hours. The liquid was then poured into water and extracted with ether in the usual way. On dis-tillation, 1-β-butanol (0.3 g.) was obtained with α\(^{18}\)\(^0\) - 4.11\(^0\) (\(1 = 1\)).
Interaction of \(1+dl-\beta\)-Butyl \(p\)-Toluene sulphinate and Quinone.

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1+dl-\beta\)-Butyl \(p\)-toluene sulphinate (10 g.) prepared from \(1+dl-\beta\)-butanol \(\times_{54.1}^{12.0} = 4.14^0; l = 1\) was added to quinone (6 g.) and the mixture warmed gently for 6 hours. The resulting black tar was steam distilled to remove any unchanged quinone, and the residual tar was extracted four times with boiling water. On cooling the aqueous extract, a yellow precipitate separated (1.6 g.). This was removed by filtration, dissolved in ethyl alcohol and boiled with animal charcoal for about 30 minutes. The mixture was again filtered, and after adding sufficient water to the filtrate to produce incipient cloudiness the solution was left to crystallise. The yellow crystalline precipitate obtained was again recrystallised from aqueous alcohol, when yellow prisms were obtained, m.p. 212°C, which were optically inactive in ethyl alcohol and in acetone solution. Found: C, 55.3; H, 4.7. \(C_{13}H_{12}O_3\) requires C, 52.6; H, 4.6. The compound was therefore 3:6 dihydroxyphenyl \(p\)-tolyl sulphone.