CCXXV.—*The Relative Configurations of* d-β-*Octanol and its Dextrorotatory Halides. The Interconversion of the Optically Active β-Octanols by a New Method.*

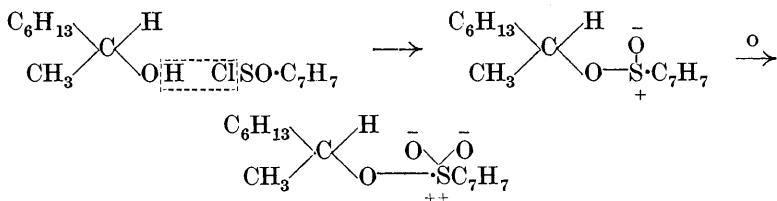By ARMAND JOSEPH HENRI HOUSSA, JOSEPH KENYON, and HENRY PHILLIPS.

ON treatment with hydrogen chloride, bromide or iodide (Pickard and Kenyon, J., 1911, **99**, 45), or thionyl chloride or bromide (Levene and Mikeska, *J. Biol. Chem.*, 1924, **59**, 45; McKenzie and Tudhope, *ibid.*, 1924, **62**, 551) *d*-β-octanol yields lævorotatory halides. The configurational relationship of these halides to the parent *d*-alcohol is still unsettled, and hence it has not yet been decided whether their formation, by means of the reagents enumerated above, is attended by a Walden inversion. The reason for this is that sign of rotation and configuration do not go hand in hand. For example, di-*d*-β-octyl sulphite is lævorotatory (Hunter, J., 1924, **125**, 1391), although by its mode of preparation it must be considered to have the same configuration as *d*-β-octanol.*

By the aid of two chemical methods, which could apparently be utilised to determine the relative configurations of any optically active secondary alcohol and its halides, evidence has now been obtained that *d*-β-octanol has the same configuration as the dextro-rotatory β-halogenated octanes. The principle underlying both methods is the conversion of a derivative of the optically active alcohol into (*a*) the alcohol or a carboxylic ester of the alcohol, (*b*) a halide, by closely similar reactions. The assumption is made that since the alcohol (or ester) and the halide are produced under

---

* Dextrorotatory β-octanol is referred to as *d*-β-octanol. Derivatives of this alcohol having the same configuration are considered to have a *d*-configuration.

similar experimental conditions, by reactions of the same type, they have the same configuration. Further, if the configuration of the derivative used, relative to that of the optically active alcohol, is known, then, should a Walden inversion occur, it can be detected.

In the reactions to be discussed this is possible, since the derivatives of d-β-octanol used—the p-toluenesulphonyl and dl-p-toluenesulphinyl derivatives—can be prepared by the following methods which ensure that these esters have a d-configuration. The sulphinic ester is prepared by the interaction of dl-p-toluenesulphinyl chloride and d-β-octanol in the presence of pyridine (Phillips, J., 1925, **127**, 2565) :

$$\begin{array}{c} \mathrm{C_6H_{13}} \\ \diagdown \\ \mathrm{CH_3} \end{array}\!\!\!\! \mathrm{C} \begin{array}{c} \diagup \mathrm{H} \\ \diagdown \mathrm{O\overset{\cdot\cdot}{H}\ \ \overset{\cdot\cdot}{Cl}SO\cdot C_7H_7} \end{array} \longrightarrow \begin{array}{c} \mathrm{C_6H_{13}} \\ \diagdown \\ \mathrm{CH_3} \end{array}\!\!\!\! \mathrm{C} \begin{array}{c} \diagup \mathrm{H} \\ \diagdown \mathrm{O{-}\overset{\bar{O}}{\underset{+}{S}}\!\cdot\!C_7H_7} \end{array} \overset{o}{\longrightarrow}$$

$$\begin{array}{c} \mathrm{C_6H_{13}} \\ \diagdown \\ \mathrm{CH_3} \end{array}\!\!\!\! \mathrm{C} \begin{array}{c} \diagup \mathrm{H} \\ \diagdown \mathrm{O{-}\!\!\!-\!\!\!-\!\!\overset{\bar{O}\ \ \bar{O}}{\underset{++}{\cdot SC_7H_7}}} \end{array}$$

During this interaction, only the hydrogen atom of the hydroxyl group is replaced and the valencies of the asymmetric carbon atom can be assumed to remain undisturbed. Similarly, it is very improbable that these valencies will be disturbed during the oxidation of the sulphinic ester to the sulphonic ester, since this change only involves the addition of an oxygen atom to the sulphur atom. The d-β-octyl dl-p-toluenesulphinate and p-toluenesulphonate prepared from d-β-octanol by these methods have therefore a d-configuration. They are both dextrorotatory.
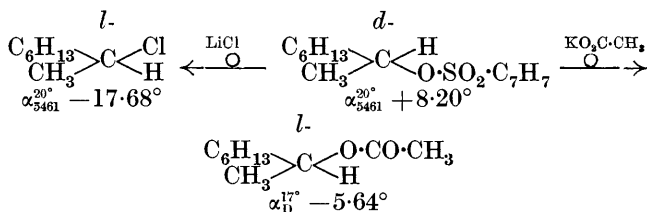
Method 1. *The Conversion of* d-β-*Octyl* p-*Toluenesulphonate into* l-β-*Octyl Acetate and Lævorotatory* β-*Chloro-octane.*—When heated under reflux with alcoholic solutions of potassium acetate and potassium benzoate, d-β-octyl p-toluenesulphonate yields β-octyl acetate and β-octyl benzoate which are both lævorotatory (Phillips, *loc. cit.*, p. 2565). It can be concluded that a Walden inversion occurs during the preparation of these esters, since d-β-octanol gives a dextrorotatory acetate on treatment with acetic anhydride (Pickard and Kenyon, J., 1914, **105**, 830) and a dextrorotatory benzoate with benzoyl chloride and pyridine (Kenyon and Pickard, J., 1915, **107**, 121).

The regularity with which the p-toluenesulphonates of optically active secondary alcohols yield esters of opposite configuration with salts of carboxylic acids is very striking. It was demonstrated for the first time with d-benzylmethylcarbinyl p-toluenesulphonate (Phillips, J., 1923, **123**, 44), and the p-toluenesulphonates of ethyl d-lactate (Kenyon, Phillips, and Turley, J., 1925, **127**, 399), of

l-menthol (Phillips, *loc. cit.*, p. 2566), and of the α- and β-methyl-*cyclo*hexanols (Gough, Hunter, and Kenyon, J., 1926, 2052) have since been shown to react in a similar manner.

Kenyon, Phillips, and Turley (*loc. cit.*) also found that the dextro-rotatory *p*-toluenesulphonate of ethyl lactate gave lævorotatory α-halogenated propionates with alkali halides and Grignard reagents and suggested that, as in the case of the acyl derivatives, the formation of these halogen derivatives was attended by a Walden inversion.

It has now been found that *d*-β-octyl *p*-toluenesulphonate * reacts in alcoholic solution with lithium chloride to form a lævorotatory β-chloro-octane and hence this sulphonic ester (as indicated in the scheme below) can be converted into a lævorotatory acetate and chloride by reactions of the same type.

$$l\text{-} \qquad\qquad\qquad d\text{-}$$

$$\underset{\alpha_{5461}^{20°}\ -17·68°}{\underset{CH_3}{C_6H_{13}}{>}C{<}^{Cl}_{H}} \xleftarrow[\ \ \underset{O}{\ }\ \ ]{LiCl} \underset{\alpha_{5461}^{20°}\ +8·20°}{\underset{CH_3}{C_6H_{13}}{>}C{<}^{H}_{O·SO_2·C_7H_7}} \xrightarrow[\ \ \underset{O}{\ }\ \ ]{KO_2C·CH_3}$$

$$l\text{-}$$

$$\underset{\alpha_D^{17°}\ -5·64°}{\underset{CH_3}{C_6H_{13}}{>}C{<}^{O·CO·CH_3}_{H}}$$
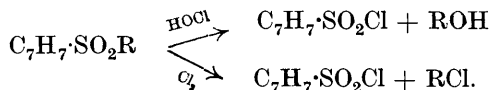
Apart from the unsaturated nature of the acetate ion, as opposed to the saturated nature of the chlorine ion, there is no obvious reason why the reaction of the ester with lithium chloride should follow a different course from that which it follows with potassium acetate. This being so, it can be concluded that the lævorotatory β-chloro-octane is formed with inversion of configuration and therefore has the same configuration as *l*-β-octanol.

Method 2. The Conversion of d-β-*Octyl* dl-p-*Toluenesulphinate into* l-β-*Octanol and Lævorotatory* β-*Chloro-octane.*—It has long been known (Otto, *Annalen*, 1867, **141**, 372; Otto and Trager, *Ber.*, 1891, **24**, 485) that *p*-toluenesulphinic acid reacts with halogens according to the equation
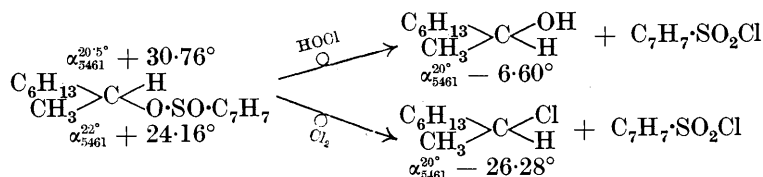
$$C_7H_7·SO_2H + X_2 = C_7H_7·SO_2X + HX.$$
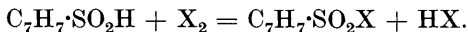
Analogous reactions have now been found to take place when *p*-toluenesulphinic esters are treated with aqueous solutions of (*a*) hypochlorous acid, (*b*) chlorine :

$$C_7H_7·SO_2R \underset{Cl_2}{\overset{HOCl}{\rightleftarrows}} \begin{array}{l} C_7H_7·SO_2Cl + ROH \\ C_7H_7·SO_2Cl + RCl. \end{array}$$

* To avoid confusion, in the theoretical portions of this paper it is assumed that *d*-β-octanol and its derivatives were always studied. Actually in many of the experiments *l*-β-octanol and its derivatives were used.

These reactions thus provide a means of converting the sulphinic ester of an optically active alcohol into the parent alcohol and its chloride by reactions of the same type.

In the scheme below are recorded the experimental results obtained with d-β-octyl dl-p-toluenesulphinate.

$$\begin{array}{c} \alpha_{5461}^{20\cdot5^{\circ}} + 30\cdot76^{\circ} \\ \underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_{13}}}{>}}\mathrm{C}\underset{\mathrm{O\cdot SO\cdot C_7H_7}}{\overset{\mathrm{H}}{<}} \\ \alpha_{5461}^{22^{\circ}} + 24\cdot16^{\circ} \end{array} \xrightarrow[\underset{Cl_2}{\overset{HOCl}{}}]{} \begin{array}{l} \underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_{13}}}{>}}\mathrm{C}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{<}} + \mathrm{C_7H_7\cdot SO_2Cl} \\ \alpha_{5461}^{20^{\circ}} - 6\cdot60^{\circ} \\ \\ \underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_{13}}}{>}}\mathrm{C}\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{<}} + \mathrm{C_7H_7\cdot SO_2Cl} \\ \alpha_{5461}^{20^{\circ}} - 26\cdot28^{\circ} \end{array}$$

The formation of l-β-octanol by the interaction of this sulphinic ester and hypochlorous acid proves conclusively that a Walden inversion has taken place, since d-β-octyl dl-p-toluenesulphinate has the same configuration as d-β-octanol. It can be concluded, therefore, that the production of lævorotatory β-chloro-octane by the interaction of the sulphinic ester with chlorine is also attended by a Walden inversion and hence that d-β-octanol has the same configuration as dextrorotatory β-chloro-octane. This is the conclusion also reached from a consideration of the results given by the sulphonate method. The fact that two widely different experimental methods lead to the same conclusion increases considerably the inherent probability that it is correct.

The conversion of d-β-octanol into l-β-octanol by the action of hypochlorous acid on d-β-octyl dl-p-toluenesulphinate adds a new method to those already available by means of which optically active secondary alcohols may be interconverted. The older methods are the sulphonate method of Phillips (loc. cit.) and the method of McKenzie and Clough (J., 1913, **103**, 687) which is applicable when a phenyl group is directly attached to the asymmetric atom.

A comparison of the action of halogens and of hypochlorous acid on d-β-octyl d-p-toluenesulphinate and l-β-octyl l-p-toluenesulphinate has not yet been made. The experiments now recorded were made on a d-β-octyl ester prepared by the method most likely to yield the compound owing none of its optical activity to the p-toluenesulphinoxy-radical. The results obtained have not therefore been influenced by the presence of an asymmetric sulphur atom in the sulphinic ester molecule.

It is unlikely that the action of halogens on d-β-octyl dl-p-toluenesulphonate is greatly modified by variations in experimental conditions, since in chloroform solution chlorine and bromine give rise to halides which are also lævorotatory. The rotatory power

(α^{t}_{5893}) of the β-chloro-octane thus prepared, and the rotatory powers of other β-chloro-octanes prepared during the course of this investigation and also by other workers using different methods, are recorded in Table I.

TABLE I.

Authors.	Method of preparation of d-β-chloro-octane.	Observed rotatory power of d-β-chloro-octane obtained ($a_{5\,893}$).	
P. and K.	HCl on l-alcohol.	$+17 \cdot 6°$	$t = 17°$
McK. and T.	SOCl₂ on l-alcohol. In presence of pyridine.	$+29 \cdot 19$	20
L. and M. ⎫ H., K., and P. ⎭	SOCl₂ on l-alcohol.	$+26 \cdot 7$	
,,	In absence of pyridine.	$+31 \cdot 0$	15
,,	LiCl on l-sulphonic ester.	$+14 \cdot 9$	20
,,	Cl₂ + water on l-sulphinic ester.	$+22 \cdot 2$	20
,,	Cl₂ + chloroform on l-sulphinic ester.	$+11 \cdot 6$	20

The reaction between l-β-octanol and thionyl chloride in the absence of pyridine has been studied and from the value of the rotatory power of the β-chloro-octane obtained ($\alpha^{20°}_{5983} + 31 \cdot 0°$) it can be seen that the presence of pyridine does not influence the magnitude of the rotatory power of the resulting β-chloro-octane. The rotatory powers of this compound prepared by the methods now described are somewhat low. The cause of this loss of rotatory power is unknown, but it may be associated with the fact that octylene is a by-product of both reactions.

In the interaction of d-β-octyl dl-p-toluenesulphinate with halogens and hypochlorous acid, octylene is formed in appreciable quantities. Its formation accounts for the presence of octane dihalides amongst the products of this interaction and possibly also for the presence of small quantities of other by-products which have not been identified. Since both chlorine and hypochlorous acid are oxidising agents, it was thought possible that some of the products obtained may have been derived from d-β-octyl p-toluenesulphonate produced by the oxidation of the sulphinic ester. It was found, however, that both chlorine and hypochlorous acid are without action on the sulphonic ester under the experimental conditions employed.

From the standpoint of the Walden inversion, these reactions of sulphinic esters are of particular interest. Investigations of the optical properties of p-toluenesulphinic esters (Phillips, loc. cit.) have provided experimental evidence that the constitution of the p-toluenesulphinoxy-radical can be indicated by a formula such as (I) and it is therefore probable that with, for example, chlorine, d-β-octyl dl-p-toluenesulphinate would combine to form an intermediate complex in which the sulphur atom is quadrivalent (II). It is this intermediate complex which dissociates to give β-chloro-

octane and p-toluenesulphonyl chloride. It is possible that inter-mediate complexes of analogous constitution are formed during the
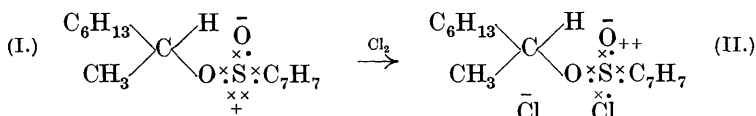
other reactions leading to the formation of β-chloro-octane. For example, the intermediate complexes formed during the interaction of hydrogen chloride and of β-octanol and of lithium chloride and β-octyl p-toluenesulphonate could be formulated as in (III) and (IV).
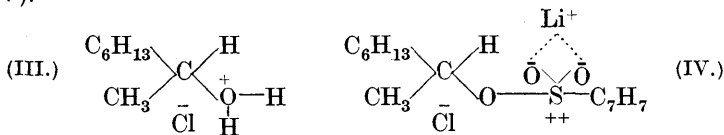
These formulæ suggest that the linkage between the negative radical and the asymmetric carbon atom is weakened by the con-version of the negative radical into a group which carries an excess positive charge. When this positive group leaves the complex as a neutral compound, it takes away two electrons from the octet of the asymmetric carbon atom. It is possible that the Walden inversion occurs during this process, $i.e.$, prior to the addition of the chlorine ion to the carbonium ion. On the other hand, the addition of the chlorine ion to the asymmetric carbon atom may occur simultan-eously with the withdrawal of the positive group, but on the opposite side of the asymmetric complex, as suggested by Gadamer (*Chem.-Ztg.*, 1912, **36**, 1327) and Lowry (Deuxième Conseil de Chemie Solvay, 1925, 40).

A Review of Previous Work bearing on the Relative Configurations of
d-β-*Octanol and its Dextrorotatory Halides.*

The conclusion that d-β-octanol and its dextrorotatory halides have the same configuration agrees with that drawn by Pickard and Kenyon (*loc. cit.*) from the fact that the rotatory powers of dextrorotatory β-bromo-octane fitted the characteristic diagram of d-β-octanol and its derivatives, but did not fit the characteristic diagram of l-β-octanol and its derivatives. Levene and Mikeska (*loc. cit.*; see also Levene, *Chem. Reviews*, 1925, **2**, 205), however, have put forward the view that d-β-octanol has the same con-figuration as the lævorotatory halides, basing this conclusion on the following observations. The change $C_8H_{17} \cdot OH \longrightarrow C_8H_{17}Br$ is accompanied by a change of sign of rotation, as is also the change

$C_8H_{17}\cdot SH \longrightarrow C_8H_{17}\cdot SO_3H$.   Since no change in configuration can be assumed to occur during the oxidation of the thiol group, it is assumed that the reversal in sign of rotation is due to the change in polarity of the group attached to the asymmetric carbon atom. Levene and Mikeska state that since the change in polarity $^-OH \longrightarrow\ ^-Br$ is similar to the change $^-SH \longrightarrow\ ^-SO_3H$, it can be inferred that the reversal in sign of rotation is due to this change in polarity and not to any configurative change of the molecule. Rule (J., 1924, **125**, 1121) has shown that such changes in the polarity of groups attached to an asymmetric carbon atom do undoubtedly influence the magnitude of the optical rotation of the compound. It is, however, difficult to conceive on what theoretical grounds Levene and Mikeska conclude that the change $^-OH \longrightarrow\ ^-Br$ is commensurate with the change $^-SH \longrightarrow\ ^-SO_2\cdot OH$.   In recent years the relative polarities of groups have received considerable attention.   It has been shown that the polarities of groups can be determined by various methods, including the orienting influence which they exert on aromatic substitution, their influence on the specific inductive capacities of compounds, such as EtX and PhX, and by their influence on the dissociation constants of substituted acetic (or benzoic) acids.   Francis, Andrews, and Johnson (*J. Amer. Chem. Soc.*, 1926, **48**, 1624) have also pointed out that if a series of monosubstituted benzenes, PhX, is arranged in accordance with Holleman's series for diminishing *op*-orienting power, the m. p.'s and b. p.'s fall through the *op*-series and rise through the *m*-series, and a similar relation exists for the compounds of the type HX.   If, now, the group ^-SH be inserted in this series, its position being fixed by the b. p. ($-61°$; Steele and Bagster, J., 1910, **97**, 2607) and m. p. ($-82°$; Bagster, J., 1911, **99**, 1222) of hydrogen sulphide, the following series is obtained :
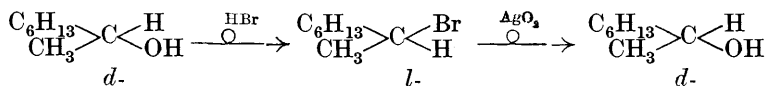
Negative, *op*-orienting.	Positive, *m*-orienting
OH, NH₂, SH, Br, Cl, CH₃, H.	CHO, NO₂, SO₃H, CO₂H.

From a consideration of this series it can be concluded that OH is more negative than SH, which is more negative than Br or Cl.   On the other hand, the SO_3H group is a positive group and hence the change SH $\longrightarrow$ SO₃H is, from the point of view of polarity, a far greater change than that of OH $\longrightarrow$ Br.

It is possible to question not only the validity of the assumption of Levene and Mikeska, but also their experimental technique.   The rotatory power of the β-octyl mercaptan was determined in the homogeneous state, whereas that of the acid was determined in solution.   It is well known, however, that both the magnitude and the sign of rotation of an optically active compound are dependent on the experimental conditions under which it is examined.   For

example, d-β-octyl acetate has $[M]_D + 11·7°$ in the homogeneous state and $[M]_D - 15·4°$ in solution in carbon disulphide (Pickard and Kenyon, *loc. cit.*).

In these circumstances it is justifiable to maintain the conclusion that d-β-octanol has the same configuration as its dextrorotatory halides. It then follows that during the changes

$$\underset{d\text{-}}{\overset{C_6H_{13}}{\underset{CH_3}{>}}C<\overset{H}{\underset{OH}{}}} \xrightarrow[\underset{}{O}]{HBr} \underset{l\text{-}}{\overset{C_6H_{13}}{\underset{CH_3}{>}}C<\overset{Br}{\underset{H}{}}} \xrightarrow[\underset{}{O}]{Ag_2O_3} \underset{d\text{-}}{\overset{C_6H_{13}}{\underset{CH_3}{>}}C<\overset{H}{\underset{OH}{}}}$$

realised by Pickard and Kenyon (*Ber.*, 1912, **45**, 1592), from which the d-β-octanol was recovered with little loss of rotatory power, two complete inversions of the configuration of the asymmetric molecule occurred, and therefore the change $C_8H_{17}Br \longrightarrow C_8H_{17}·OH$ is also accompanied by a Walden inversion. Evidence is thus forthcoming that many reactions take place with inversion of configuration and this appears to necessitate a changed attitude towards the Walden inversion. It is suggested that, far from being a comparatively rare phenomenon, it occurs whenever a group attached to an asymmetric carbon atom is replaced, unless a phenyl group is directly linked to the asymmetric carbon atom or a carboxyl group is present in the molecule. These disturbing factors may, however, lead to the occurrence of two inversions during the replacement. Whether this is actually the explanation of these exceptions will be the subject of future communications.

EXPERIMENTAL.

Preparation of Esters of p-*Toluenesulphinic Acid by Frankland and Aston's Method.—Ethyl* dl-p-*toluenesulphinate.* The method devised by Frankland and Aston for the preparation of ethyl tartrate was more convenient and gave better yields of ethyl *dl-p*-toluenesulphinate than the methods described by Phillips (*loc. cit.*). Moist ethyl alcohol was continuously distilled from a solution of anhydrous *p*-toluenesulphinic acid (65 g.) in ethyl alcohol (200 c.c.) into the " drying " flask containing freshly ignited potassium carbonate (100 g.) and ethyl alcohol (200 c.c.). From this drying flask the alcohol was continuously returned by distillation to the " reaction " flask containing the alcoholic solution of the acid. A steady interchange of ethyl alcohol was maintained between the two flasks for 4—5 hours. The contents of the reaction flask were then poured into water and the ethyl *dl-p*-toluenesulphinate which separated was extracted with ether. The ethyl *dl-p*-toluenesulphinate (63 g.) isolated from the dry ethereal extract had b. p. 75—76°/<0·1 mm. and $n_D^{26°}$ 1·5309. If, during the preparation, the " reaction " flask

was heated too strongly (above 125°) or for longer than 5 hours, the ester obtained was contaminated with di-p-tolyl disulphoxide.

Methyl p-toluenesulphinate (27 g.), b. p. 82—85°/<0·1 mm., $n_D^{20°}$ 1·5436, was prepared by a similar method from p-toluenesulphinic acid (100 g.) and methyl alcohol.

l-β-Octyl dl-p-toluenesulphinate (10 g.), $n_D^{20°}$ 1·5038, $\alpha_{5461}^{20°}$ −28·2° ($l = 1·0$), was prepared by this method, the reaction mixture of l-β-octanol (10 g.) and p-toluenesulphinic acid (20 g.) being diluted with benzene, which during distillation carried the water formed in the reaction flask into the drying flask. The method, however, proved unsuitable for the preparation of the large quantities of l-β-octyl dl-p-toluenesulphinate required for this research. This ester was therefore prepared by heating together equimolecular quantities of l-β-octanol and ethyl dl-p-toluenesulphinate as described by Phillips (*loc. cit.*), where it was shown that this method caused no inversion or loss of rotatory power of the optically active β-octyl radical, and gave an ester of the same configuration as that given by p-toluenesulphinyl chloride.

The Interaction of Optically Active β-*Octyl* dl-p-*Toluenesulphinate with Chlorine, Bromine and Hypochlorous Acid.*—(a) *With chlorine in chloroform solution.* A slow stream of dry chlorine was passed for 1·5 hours into a solution of l-β-octyl dl-p-toluenesulphinate (15 g.) [$\alpha_{5461}^{26°}$ −28·18° ($l = 1·0$), $n_D^{25°}$ 1·5054] in chloroform (65 c.c.), and after 6 days the solution was distilled in a current of steam, and the distillate extracted with chloroform. The product obtained from the dried extract, on fractional distillation, gave fraction I, b. p. 65—75°/20 mm., which contained chlorine and had $\alpha_{5461}^{25°}$ +13·6° ($l = 1·0$), $n_D^{25°}$ 1·4606; fraction II, b. p. 80—105°/20 mm. (mainly 100°/20 mm.), which contained chlorine and had $\alpha_{5461}^{25°}$ +15·2° ($l=1·0$), $n_D^{25°}$ 1·4563; fraction III, b. p. 110—125°/20 mm. (mainly 125°/20 mm.), which contained a little sulphur besides chlorine and had $\alpha_{5461}^{25°}$ +15·32° ($l = 1·0$), $n_D^{25°}$ 1·4662; and fraction IV, b. p. 130—145°/20 mm., which contained more than a trace of sulphur besides chlorine and had $\alpha_{5461}^{25°}$ +10·56° ($l = 1·0$), $n_D^{25°}$ 1·4869.

Fraction I was d-β-chloro-octane containing some dichloro-octane. The higher-boiling fractions (II, III, and IV) consisted of more highly chlorinated β-chloro-octanes, as they were similar to the products obtained in experiments described below.

Action of chlorine on octylene. Hydrogen chloride was evolved when chlorine (4·8 g.) was passed into a solution of octylene (6 g.) in carbon tetrachloride (15 c.c.). The solution was freed from chlorine and hydrogen chloride, the solvent removed, and the product systematically fractionated. The largest fraction obtained, fraction I, which was dichloro-octane, had b. p. 90—115°/21 mm., $n_D^{25°}$

1·4509 : more highly chlorinated products made up fraction II, b. p. 115—135°/22 mm., $n_D^{25°}$ 1·4691, and fraction III, b. p. 135—155°/22 mm., $n_D^{25°}$ 1·4820. This experiment was repeated, except that only sufficient chlorine (3·8 g.) was passed into a solution of octylene (5·6 g.) in carbon tetrachloride to convert the octylene completely into dichloro-octane. Side reactions again occurred, however, and in addition to dichloro-octane, b. p. 93—95°/22 mm., $n_D^{25°}$ 1·4507 (6·5 g.), a higher-boiling fraction was obtained, b. p. 95—120°/22 mm., $n_D^{25°}$ 1·4606.

(b) *With chlorine water.* d-β-Octyl dl-p-toluenesulphinate (48 g.) [$\alpha_{5461}^{22°}$ +24·16° ($l = 1·0$), $n_D^{25°}$ 1·5071], prepared from l-β-octanol [$\alpha_{5461}^{22°}$ +9·46° ($l = 1·0$)], was shaken with a solution of chlorine (11·55 g.; 0·91 mol.) in water (1750 c.c.). This solution of chlorine was prepared by passing the gas into water at 0° and was used immediately its concentration had been determined. The chlorine was at once absorbed and p-toluenesulphonyl chloride crystallised from the mixture, which was subsequently distilled in steam. The distillate was extracted with ether, and the product obtained from the dried extract systematically fractionated. After the removal of a small quantity of octylene, three fractions were isolated : Fraction I (7 g.), b. p. 72—74°/27 mm., $n_D^{20°}$ 1·4271, $\alpha_{5461}^{20°}$ −25·56° ($l = 1·0$), which was mainly l-β-chloro-octane; fraction II, b. p. 75—95°/27 mm.; and fraction III, b. p. 95—110°/27 mm. The l-β-chloro-octane (fraction I) was redistilled and was finally obtained having b. p. 68—69°/22 mm., $n_D^{20°}$ 1·4271, and $\alpha_{5461}^{20°}$ −26·28° ($l = 1·0$). Fractions II and III were again distilled and separated into fraction (a), b. p. 69—90°/22 mm., $n_D^{25°}$ 1·4286, $\alpha_{5461}^{20°}$ −16·64° ($l = 1·0$); fraction (b), b. p. 90—105°/22 mm., $n_D^{25°}$ 1·4451, $\alpha_{5461}^{20°}$ −0·81° ($l = 1·0$); and fraction (c), b. p. 105—120°/22 mm., $n_D^{25°}$ 1·4547, $\alpha_{5461}^{20°}$ −4·84° ($l =1·0$). These fractions were too small for further investigation.

(c) *With bromine in chloroform solution.* Bromine (9 g.) in chloroform (50 c.c.) was added to a solution of l-β-octyl dl-p-toluenesulphinate (15 g.) in chloroform (15 c.c.) at 0°. The product obtained, after removal of the dry, bromine-free chloroform, was separated by distillation into two fractions : fraction I (7·5 g.), b. p. 75—80°/20 mm.; fraction II (2·7 g.), b. p. 110—115°/ 20 mm. Fraction I was d-β-bromo-octane and after repeated distillation was finally obtained with b. p. 76—77°/18 mm., $\alpha_{5461}^{20°}$ +24·6° ($l = 1·0$), $n_D^{25°}$ 1·4398. Fraction II, dibromo-octane, was obtained on redistillation with b. p. 114—116°/20 mm., $n_D^{25°}$ 1·4925, and $\alpha_{5461}^{20°}$ +2·16° ($l = 1·0$) (Found : Br, 58·5. Calc. for $C_8H_{16}Br_2$: Br, 58·9%).

Action of bromine on octylene. Bromine (7·7 g.) in chloroform (10 c.c.) was added to a solution of octylene (5·4 g.) in chloroform

(15 c.c.) maintained at 0°. The product isolated consisted entirely of dibromo-octane, b. p. 114—116°/20 mm. and $n_D^{25°}$ 1·4935.

(d) *With hypochlorous acid.* d-β-Octyl dl-p-toluenesulphinate (43 g.) [$\alpha_{5461}^{20·5°}$ +30·76° ($l=1·0$), $n_D^{26°}$ 1·5054], prepared from d-β-octanol [$\alpha_{5461}^{23°}$ +9·63°], was shaken with a solution of hypochlorous acid (9·44 g.; 1·12 mols.) in water (200 c.c.). This solution of hypochlorous acid was prepared by the method described in " Organic Syntheses," Vol. V, p. 31, and its concentration determined immediately before use. After the ester had been shaken with the acid for 45 minutes, the emulsion obtained was cooled in ice ; p-toluenesulphonyl chloride (9 g.), m. p. 70°, then crystallised. The filtered solution was distilled in steam for 20 minutes. The non-volatile residue was extracted with ether : it consisted of d-β-octyl p-toluenesulphonate (10 g.) and had $\alpha_{5461}^{20°}$ +7·64° ($l = 1·0$) and $n_D^{21°}$ 1·4871.

The steam distillate was extracted with ether, and the product systematically fractionated, three main fractions being obtained : fraction I (2·6 g.), b. p. 35—40°/22 mm., which rapidly decolorised bromine water and consisted of octylene ; fraction II (0·8 g.), b. p. 68—72°/22 mm., which after redistillation had $n_D^{22°}$ 1·4255 and $\alpha_{5461}^{20°}$ −24·36° ($l = 1·0$) and was l-β-chloro-octane ; and fraction III (5·6 g.), b. p. 82—86°/22 mm., which was l-β-octanol and had $\alpha_{5461}^{20°}$ −7·0° ($l = 1·0$). This l-β-octanol was further purified by redistillation. It was obtained with $n_D^{21°}$ 1·4273, $\alpha_{5461}^{20°}$ −6·44° ($l = 1·0$), and was now pure, since on further distillation it (2 g.) had $n_D^{21°}$ 1·4270 and $\alpha_{5461}^{20°}$ −6·60° ($l = 1·0$).

This experiment was repeated with d-β-octyl dl-p-toluenesulphinate (20 g.) [$\alpha_{5461}^{20°}$ +26·53° ($l = 1·0$), $n_D^{20°}$ 1·5086] and a solution of hypochlorous acid (4 g.; 1·02 mols.) in water (132 c.c.). The products obtained were similar, being (a) impure octylene, b. p. up to 40°/17 mm., $n_D^{19°}$ 1·4148, (b) l-β-chloro-octane, b. p. 56—63°/16 mm., $n_D^{19°}$ 1·4255, $\alpha_{5461}^{19°}$ −12·4° ($l = 1·0$), and (c) l-β-octanol, b. p. 77—83°/15 mm., $n_D^{18°}$ 1·4300, $\alpha_{5461}^{19°}$ −7·28° ($l = 1·0$).

In order to prove that the products described above did not arise from β-octyl p-toluenesulphonate, into which it was possible that the sulphinic ester might have been converted by the hypochlorous acid, d-β-octyl p-toluenesulphonate (10 g.) was treated in an identical manner with 66 c.c. of the same hypochlorous acid solution. After shaking, the mixture was distilled in steam. No volatile products were obtained.

Similarly, in order to prove that the products did not arise by the interaction of β-octanol and hypochlorous acid (the β-octanol arising owing to hydrolysis of the sulphinic ester under the conditions of the experiment), d-β-octanol (10 g.) was shaken with 66 c.c. of a solution of hypochlorous acid. The mixture was distilled in steam, and the

alcohol isolated with ether. It had undergone some change, since it could be separated by distillation into two fractions : fraction I, b. p. 60—72°/17 mm., $\alpha_{5461}^{20°}$ +3·32° ($l = 1·0$), $n_D^{17°}$ 1·4194, and fraction II, b. p. 75—83°/17 mm., $\alpha_{5461}^{20°}$ +7·08° ($l = 1·0$), $n_D^{17°}$ 1·4260. This result is consistent with the view that the d-β-octanol was either partly oxidised to the corresponding ketone and/or partly converted into l-β-chloro-octane. The amount of reaction which occurred was, however, small and the nature of the products obtained clearly proves that in the experiment in which d-β-octyl dl-p-toluenesulphinate was used the l-β-chloro-octane and l-β-octanol produced were derived from the interaction of the sulphinic ester with hypochlorous acid.

The Interaction of d-β-*Octyl* p-*Toluenesulphonate and Lithium Chloride.*—d-β-Octyl p-toluenesulphonate (13 g.) [$\alpha_{5461}^{20°}$ + 8·20° ($l = 1·0$), $n_D^{20°}$ 1·4940], prepared from d-β-octyl dl-p-toluenesulphinate by oxidation with potassium permanganate (Phillips, *loc. cit.*, p. 2586), was heated under reflux for 30 hours with a solution of lithium chloride (6·5 g.) in ethyl alcohol (50 c.c.). The reaction mixture was poured into water and the oily product which separated was isolated with ether. It consisted almost entirely of l-β-chloro-octane which, after repeated distillation was obtained (2·5 g.) with b. p. 70°/26 mm., $\alpha_{5461}^{20°}$ −17·68° ($l = 1·0$), and $n_D^{20°}$ 1·4262.

Interaction of d-β-*Octanol and Thionyl Chloride.*—d-β-Octanol (10 g.) [$\alpha_{5461}^{23°}$ +9·63° ($l = 1·0$)], dissolved in three volumes of light petroleum, was slowly added to a solution of freshly distilled thionyl chloride (30 g.) in an equal volume of light petroleum maintained at 0°. After removal of the light petroleum in a vacuum at the ordinary temperature the residue was repeatedly distilled; it then gave l-β-chloro-octane, b. p. 68°/22 mm., $n_D^{20°}$ 1·4267, $\alpha_{5461}^{20°}$ −36·68°, $\alpha_{5893}^{20°}$ −31·0° ($l = 1·0$).