250. *Walden Inversion Reactions of* d-*β-Butyl,* d-*β-Octyl, and* d-*Benzylmethylcarbinyl* p-*Toluenesulphonates.*

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THE Walden inversion which occurs when *p*-toluenesulphonic esters of *d* *-secondary alcohols react with salts of carboxylic acids (X = O·CO·R)

$$d\text{-RO}\cdot\text{SO}_2\text{C}_7\text{H}_7 + \overset{+}{\text{M}}\overset{-}{\text{X}} = l\text{-RX} + \overset{+}{\text{M}}\overset{-}{\text{O}}\cdot\text{SO}_2\text{C}_7\text{H}_7$$

can be detected because, by the use of the appropriate acid chloride, *d*-RX can be prepared directly from *d*-ROH, a reaction in which the oxygen atom immediately attached to the asymmetric radical R is not disturbed. This method of detecting the inversion is not available when X does not contain an oxygen atom through which it becomes linked to R; in these cases, other methods must therefore be used to decide whether or not the replacement of the *p*-toluenesulphonoxy-group occurs with inversion.

Rule (J., 1924, **125**, 1121; *Trans. Faraday Soc.*, 1930, **26**, 321) has shown that, as the positive character of the substituent X increases, the magnitude of rotation of the derivatives, RX, either increases or decreases in a regular manner. This finding can be used to determine whether a series of derivatives are of the same configuration, because only when this is so will their rotatory powers alter in a regular manner. Series of derivatives have now been prepared from three *d*-*p*-toluenesulphonic esters, and, applying the above criterion, it has been found that, although the sulphonic esters react with salts with inversion, yet their reaction under certain conditions with ammonia and primary and secondary amines may proceed without inversion.

β-*Butyl Derivatives* (with R. B. SHACKLETON).—d-(+)β-*Butyl* p-*toluenesulphonate* was prepared by oxidation of the corresponding d-p-*toluenesulphinic* ester, obtained from *d*-(+)β-butanol and *p*-toluenesulphinyl chloride. (—)β-Butyl acetate, benzoate, iodide, *thiocyanate*, and *selenocyanate* were each prepared by heating the *d*-sulphonate with an ethyl-alcoholic solution of the appropriate sodium or potassium salt; (—)β-butyl cyanide was prepared in a similar manner in acetone solution. The small quantity of the (—)cyanide thus obtained was hydrolysed to (—)methylethylacetic acid, and since it can be assumed that the valency bonds of the asymmetric carbon atom were not disturbed during the hydrolysis, it follows that (—)methylethylacetic acid has the same configuration as (—)β-butyl cyanide. Further supplies of the (—)acid were obtained by the resolution of the *dl*-acid (Marckwald, *Ber.*, 1896, **29**, 53; 1899, **32**, 1089), and were converted into the corresponding (—)acid chloride, (—)ethyl ester, and (—)amide. When the last was dehydrated, it yielded the (—)cyanide of the same configuration.

(—)β-*Butyl disulphide* and (+)*diselenide* were obtained respectively by hydrolysis of the (—)thiocyanate and the (+)selenocyanate. The (—)disulphide was reduced to the (—)*thiol*, and the (—)thiocyanate was oxidised to (+)β-*butanesulphonic acid*. From their method of preparation, it can be concluded that the (—)mercaptan, (+)sulphonic acid and the (—)thiocyanate are configuratively similar.

(—)β-*Butyl ethyl*, n-*butyl*, and *phenyl ethers* were prepared by heating the *d*-sulphonate, in the presence of potassium carbonate, with the appropriate alcohol or with phenol.

The *d*-sulphonate condensed readily with pyridine, giving pyridinium (—)β-butyl *p*-toluenesulphonate. Excellent yields of (—)N-β-*butylpiperidine* and (—)N-β-*butyl*-p-*toluidine* were obtained by the interaction of the *d*-sulphonate with the required base. The constitution of the former derivative was established by a comparison of the properties of its picrate and its platinichloride with those of (—)*N*-β-butylpiperidine produced by the condensation of (—)β-butylamine with pentamethylene dibromide, a method of preparation which proves that (—)β-butylpiperidine has the same configuration as (—)β-butylamine. Confirmatory evidence that *p*-toluenesulphonic esters yield *N*-substituted derivatives is afforded by the identity of the m. p.'s of the picrates and the

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* The sign *d*- and *l*- are used to denote configurations; (—) and (+) signify lævo- and dextrorotation respectively. It is assumed throughout that all the (+) alcohols used possess the *d*-configuration.

platinichlorides of the piperidyl derivative obtained from *n*-butyl *p*-toluenesulphonate with those of similar salts of *N*-*n*-butylpiperidine produced by the condensation of *n*-butylamine with pentamethylene dibromide.

By the action of aqueous ammonia on the *d*-sulphonate, (—)β-butylamine was obtained in small yield and isolated as its hydrochloride. The rotatory power of the hydrochloride being very small (Thomé, *Ber.*, 1903, **36**, 582), the amine was converted into its benzoyl derivative, which has a high rotation (Pope and Gibson, J., 1912, **101**, 1702).

d-β-Butyl *p*-toluenesulphonate reacted with Grignard reagents in a manner similar to that with which it reacted with salts. Whereas, however, it gave (—)β-butylbenzene when treated with phenylmagnesium bromide, (—)β-butyl bromide was the main product when ethylmagnesium bromide was used. This agrees with the experience of Gilman and Beaber (*J. Amer. Chem. Soc.*, 1925, **51**, 518), who found that when R in RMgX is of low molecular weight, as in propyl- and *n*-butyl-magnesium bromides, the yield of hydrocarbon obtained by the action of RMgX on a *p*-toluenesulphonic ester is low; but that when R is of high molecular weight, as in lauryl- and phenyl-magnesium bromides, good yields are obtained. Ethyl α-*p*-toluenesulphonoxypropionate would appear to be an exception to this rule, since it yields the α-bromo-derivative with both ethyl- and phenylmagnesium bromides (Kenyon, Phillips, and Turley, J., 1925, **127**, 399). (—)β-Butyl bromide was also prepared by the action of bromine on *d*-β-butyl *p*-toluenesulphinate in chloroform solution. *p*-Toluenesulphonyl bromide was the other product of the reaction which, there are reasons to believe (Houssa, Kenyon, and Phillips, J., 1929, 1705), occurs with inversion. Houssa and Phillips (J., 1932, 108) have shown that a change of sign of rotation occurs when β-octanol is converted into β-octyl chloride by the usual reagents. In order to ascertain whether a similar change occurs during the conversion of (—)β-butanol into β-butyl bromide, the bromide has been prepared from this alcohol by a variety of methods with the results summarised in Table I. As in the similar series of experiments with β-octanol, a change of sign of rotation occurred in all the reactions.

TABLE I.

The rotatory powers of the (+)β-*butyl bromides obtained from* (—)β-*butanol* ($[\alpha]_{5461}^{20^\circ}$ — 7·09°; 1 *mol.*) *by the action of various reagents.*

Reagent.	Solvent.	$\alpha_{5461}^{t^\circ}$ (*l*, 0·5).	$n_D^{t^\circ}$ of β-butyl bromide.	Yield, %.
HBr gas in excess at 0°	none	6·14°/15°	1·442/15°	39·0
HBr gas in excess at 60°	none	7·52/16	1·437/12	10·8
HBr aq. + $ZnBr_2$ (0·3 mol.)	none	4·50/18	1·440/21	32·0
HBr aq. (*d* 1·7) in excess	H_2O	1·00/19	1·424/21	21·6
HBr + H_2SO_4 (2 : 1) in excess	H_2O	3·60/15	1·439/16	52·0
KBr (1 mol.) + H_2SO_4 (1 mol.)	none	0·00	1·424/18	18·6
PBr_3 (1 mol.)	Et_2O	8·02/19	1·434/19	29·0
PBr_3 (1 mol.) + $ZnBr_2$ (0·3 mol.)	none	2·04/16	1·437/17	39·5
PBr_3 (1 mol.) + C_5H_5N (2 mols.)	none	1·36/18	1·420/17	5·5
PBr_5 (1 mol.)	Et_2O	8·72/14	1·439/18	16·2
PBr_5 (1 mol.) + $ZnBr_2$ (0·3 mol.)	none	7·04/17	1·438/17	21·6
PBr_5 (1 mol.) + C_5H_5N (2 mols.)	none	8·28/16	1·439/17	7·6
$SOBr_2$ (1 mol.)	none	7·02/18	1·425/18	41·3
$SOBr_2$ (1 mol.) + C_5H_5N (2 mols.)	none	3·00/21	1·426/21	14·7

A change of sign took place also when *d*-(+)β-*butyl chloroformate* was decomposed by heating it in the presence of pyridine, (—)β-butyl chloride being obtained. (+)β-Butyl chloride, however, was produced when the *d*-chloroformate was heated alone or in the presence of either magnesium or mercuric chlorides. Complete racemisation ensued when the *d*-chloroformate underwent decomposition in the presence of zinc chloride. Experiment showed that (+)β-butyl chloride racemises when heated with zinc chloride, thus affording a probable explanation of the optical inactivity of the β-butyl chloride produced from the *d*-chloroformate in the presence of this reagent. So far as the influence of pyridine on its mode of decomposition is concerned, *d*-β-butyl chloroformate behaves similarly to the *d*-β-octyl ester (Houssa and Phillips, J., 1929, 2510, and *loc. cit.*).

β-*Octyl Derivatives* (with Miss Doris E. Kahn and Frederick H. Yorston).—These derivatives were prepared from the *d*-*p*-toluenesulphonic ester (Phillips, J., 1925, **125**, 2565) by methods similar to those by which the β-butyl derivatives were prepared, with the following exceptions: (—)β-*octylthiol* was prepared by heating the *d*-sulphonate with an ethyl-alcoholic solution of sodium hydrogen sulphide: *phenyl* (—)β-*octyl sulphide*, by using an ethyl-alcoholic solution of sodium phenyl sulphide; (—)β-octyl chloride, by using an ethyl-alcoholic solution of lithium chloride; (—)β-*octyl methyl* and *ethyl sulphides* were prepared from the (—)thiol by using methyl and ethyl sulphate respectively. The specific rotatory powers of (—)β-octylthiol and (—)β-octyl methyl and ethyl sulphides were determined over a wide range of temperature (— 70° to + 100°) for light of seven different wave-lengths. When $1/\alpha$ is plotted against λ^2, the points fall on a straight line, indicating that, under the experimental conditions, none of the three compounds exhibits complex rotatory dispersion. These determinations were made to ascertain whether optically active thio-ethers would show the complex rotatory dispersion exhibited by the simple aliphatic oxygen ethers of (+)γ-nonanol (Kenyon and Barnes, J., 1924, **125**, 1395).

Benzylmethylcarbinyl Derivatives (with Nicholas E. Cochinaras).—Unlike the corresponding β-butyl and β-octyl esters, *d*-benzylmethylcarbinyl *p*-toluenesulphonate can be prepared by the direct interaction of the *d*-alcohol and *p*-toluenesulphonyl chloride (Phillips, J., 1923, **123**, 44). The series of derivatives was prepared from the *d*-sulphonate by using similar methods to those used in the preparation of the other series of derivatives, except that (—)α-chloro-β-phenylpropane was prepared by the interaction of the *d*-sulphonate with (*a*) ethylmagnesium chloride in ether and (*b*) lithium chloride in ethyl alcohol. (—)α-Cyano-β-phenylpropane was obtained by the interaction of the *d*-sulphonate with potassium cyanide in acetonitrile as well as in ethyl alcohol. The (—)β-phenyl-*n*-propylthiol was prepared from (—)α-thiocyano-β-phenylpropane. (—)α-Ethoxy-β-phenylpropane has been prepared by the interaction of the *d*-sulphonate with ethyl alcohol containing potassium carbonate and also with sodium ethoxide (Phillips, *loc. cit.*). (—)α-Phenoxy-β-phenylpropane was prepared by the interaction of the *d*-sulphonate with sodium phenoxide in ethyl-alcoholic solution.

The Relative Configurations of the Derivatives.

In Table II the derivatives are arranged in order of the increasing positive character of the substituent groups. This order has been decided mainly from the values of the dipole moments of similarly constituted compounds, but partly from the directive influence of the groups on aromatic substitution and their influence on the dissociation constants of the monosubstituted acetic acids in which they are present as substituents. The sulphonic acids have been placed among the feebly positive groups to make allowance for the compensating effects which the negative ends of the dipoles associated with the sulphonyl oxygen atoms exert on the dipole between the asymmetric carbon atom and the sulphur atom (Rule, *loc. cit.*).

The rotatory powers of the derivatives obtained from the three *d*-sulphonic esters were determined for light of three wave-lengths and in ethyl-alcoholic solution in order to guard against drawing erroneous conclusions from rotation data distorted by dispersion effects. The reactions of *p*-toluenesulphonic esters are attended by unknown amounts of racemisation, and for this reason, where the magnitude of the rotatory power of the optically pure derivative is known, it has been substituted for that of the derivative obtained from the *p*-toluenesulphonic ester. This is not possible in every case, and consequently the rotatory powers do not show a regular gradation in magnitude.

The precise order in which the groups are placed is not a crucial matter. The main questions to be settled are whether the rotations of the *l*-series increase or decrease in (—)rotatory power as the groups become more positive, and, if each series contains (+)rotatory as well as (—)rotatory members, at what point in each series the rotatory powers of the derivatives change in sign.

The most conclusive evidence as to the trend of the rotatory powers in each series is

TABLE II.

Specific rotatory powers, $[\alpha]_{5461}$, *of the methyl-*R*-carbinyl derivatives.*

(*a*) Homogeneous; (*b*) in solution (EtOH, unless otherwise stated; *c*, 5); (*c*) sign of rotatory power of *l*-derivative.

	R = C_2H_5.			R = *n*-C_6H_{13}.			R = $C_6H_5\cdot CH_2$.		
	(*a*).	(*b*).	(*c*).	(*a*).	(*b*).	(*c*).	(*a*).	(*b*).	(*c*).
$-N\cdot C_5H_{10}$	−63·5°	− 6·7°	(+)	−18·9°	− 6·5°	(+)	−19·0°	−13·5°	(−)
$-NH\cdot C_6H_4Me$	−45·0	−40·8	(+)	− 5·1	− 9·0	(+)	−16·4	−40·4	(+)
$-NH\cdot COPh$	—	−18·8 [1]	(+)	—	—		—	—	
$-NH_2$	− 2·3	− 0·4	(+)	—	—			+ 8·6	(+)
$-SO_2\cdot O$	—	+ 1·6 [2]	(+)	—	+200 [2]	(+)	—	—	
$-SO_2\cdot OH$	+ 3·0	+ 0·9 [3]	(+)	—	+164 [3]	(+)	—	—	
$-NH\cdot C_6H_4Me$	—	− 4·7 [4]	(+)	—	+14·7 [5]	(−)	—	−13·4 [5]	(+)
$-NH_3$	—	+ 0·4 [6]	(−)	—	—			−49·5 [7]	(−)
$-NHC_5H_{10}$	—	+ 1·8 [8]	(−)	—	+22·7 [9]	(−)	—	−20·1 [10]	(−)
$-CO\cdot O-$	—	− 9·0 [11]	(−)	—	—		—	− 8·6	(−)
$-C_6H_5$	−33·2 [12]	−18·7	(−)	—	—		—	—	
$-OC_4H_9$	−27·6	−21·4	(−)	—	—				
$-OC_2H_5$	−23·7	−19·6	(−)	−20·3 [13]	−17·7 [13]	(−)	−25·7 [14]	−24·4 [14]	(−)
$-OC_6H_5$	−28·5	−22·6	(−)	−22·6	−19·6	(−)	−73·8	−52·0	(−)
$-SCH_3$	—	—		−15·6	—	(−)	—	—	
$-SH$	−28·3	− 5·4	(−)	−36·4	—	(−)	−15·6	−16·2	(−)
$-SC_6H_5$	—	—		−13·8	− 2·0	(−)	−12·6	−29·3	(−)
$-SC_2H_5$	—	—		−19·0	—	(−)	—	—	
$-OH$	−16·4	−18·0	(−)	−11·6	−11·2	(−)	−31·9	−19·4	(−)
$-CO\cdot OH$	−14·5	−14·4	(−)	—	—		−24·8	−25·4	(−)
$-CO\cdot OC_2H_5$	− 6·0	− 8·4	(−)	—	—		−32·6	−36·3	(−)
$-O\cdot CO\cdot CH_3$	−25·4 [15]	−30·5 [15]	(−)	− 8·0	− 4·2	(−)	− 7·5	− 9·5	(−)
$-O\cdot COPh$	−46·6 [16]	−48·0 [16]	(−)	−39·7	−47·4	(−)	−78·8	−86·9	(−)
$-I$	− 2·6	− 3·2	(−)	—	—		—	—	
$-Cl$	—	—		−31·0	—	(−)	−24·9	−16·2	(−
$-Br$	−17·7	−19·0	(−)	−31·6	−34·3	(−)	− 8·1	− 6·7	(−)
$-COCl$	− 5·3	−14·4 [17]	(−)	—	—		−24·9	−22·5 [17]	(−)
$-CN$	− 9·2	− 9·3	(−)	—	—		−25·1	—	(−)
$-CO\cdot NH_2$	—	− 5·2	(−)	—	—		—	−62·9	(−)
$-SeCN$	−13·9	−13·7	(−)	—	—		—	—	
$-SCN$	−44·9	−29·6	(−)	−86·3	−79·9	(−)	−134·8	−120·3	(−)

[1] *c*, 0·906. [2] Na salt in water. [3] In water. [4] In 0·477*N*-HCl. [5] In glacial HOAc. [6] In *N*-HCl. [7] In 2*N*-HCl. [8] In *N*-HCl. [9] In 6*N*-HCl. [10] In 0·53*N*-HCl. [11] In water, as Na salt. [12] Harrison, Kenyon, and Shepherd, J., 1926, 662. [13] Phillips, J., 1925, **127**, 2587. [14] Phillips, J., 1923, **123**, 23. [15] Pickard and Kenyon, J., 1914, **105**, 830. [16] Kenyon and Pickard, J., 1915, **107**, 115. [17] In C_6H_6.

provided by the rotations of the benzoates. The (—)alcohols when treated with benzoyl chloride yield the configuratively similar *l*-benzoates. These esters all have higher (—)rotations than the corresponding alcohols. Kenyon and Pickard (*loc. cit.*) have shown that the benzoates of β-hexanol and β-undecanol also have higher (—)rotations than the corresponding (—)alcohols. Since the benzoyloxy-group is more positive than the hydroxyl group, the higher (—)rotations of the benzoates indicate that as the positive character of the substituents in the series increases the (—)rotation increases. Further, when the (—)alcohols are converted into their potassio-derivatives and the negative character of the hydroxyl group is thereby increased, their (—)rotations decrease, in agreement with the conclusion drawn from the rotatory powers of the *l*-benzoates. In addition, it is known that the ethoxy- and *n*-butoxy-derivatives of each *l*-series are lævorotatory, because these again can be prepared from the *l*-(—)alcohol by methods unlikely to lead to configurative change. Each *l*-series is known to contain (+) as well as (—) members, because Pickard, Kenyon, and Hunter (J., **1923**, **123**, 1) have shown that these three (—)alcohols yield (+)formates with formic acid, and from each of these esters the original alcohol can be recovered by hydrolysis unchanged in either sign or magnitude of rotatory power, indicating that the (+)formates have the same configuration as the (—)alcohols. Lastly, from the present investigation it is known that the thiols of the β-butyl and β-octyl series when oxidised yield (+)sulphonic acids, and there is not much likelihood that these oxidations are accompanied by inversion because the bonds of the asymmetric carbon atoms presumably remain undisturbed (Levene and Mikeska, *J. Biol. Chem.*, 1924, **59**, 473).

If the (—)rotatory powers of these *l*-series increase as the positive character of the substituent increases, and each series contains (+)rotatory as well as (—)rotatory members, then further deductions can be made concerning the rotatory powers of the amines and acids belonging to each series of derivatives. Rule (J., 1927, 54) has pointed out that the conversion of amino- and substituted amino-groups into the cationic state should cause the rotatory powers of amines and their derivatives to approach in magnitude those of the derivatives containing more positive substituents, whilst the conversion, by salt formation, of the carboxylic and sulphonic acid groupings into the anionic state should cause their rotatory powers to approach those of the derivatives containing more negative substituents. On this hypothesis, the (—)rotations of the amino- and substituted amino-derivatives of each *l*-series should increase [or their (+)rotations decrease] in hydrochloric acid solution, whilst the (—)rotations of the carboxylic and sulphonic acids should decrease [or their (+)rotations increase] when they are converted into salts. Similarly, the (—)rotations of the salts of the mercaptans should be lower than those of the mercaptans themselves.

Consideration of the numerical values of $[\alpha]_{5461}$ of the derivatives in the homogeneous state and also in ethyl-alcoholic solution at ordinary temperatures (Table II), as well as of other rotation data recorded in the experimental section, shows that the lævorotatory powers of the derivatives obtained by the action of salts, Grignard reagents, alcohols, pyridine, and phenol on the *d*-sulphonates fall into line with the lævorotatory powers of the esters and ethers which are known to be members of the *l*-series. The *d*-sulphonates thus appear to react with these reagents with inversion.

The stereochemical nature of the reaction between the *d*-sulphonates and ammonia and secondary amines is, however, much less definite. In the β-butyl series, for example, the piperidino-, *p*-toluidino-, and benzamido-derivatives obtained from the *d*-sulphonate all have relatively large (—)rotations which become smaller when these bases are dissolved in hydrochloric acid. If these derivatives were produced with inversion and are members of the *l*-series, this is the reverse of what would have been expected from Rule's findings (*loc. cit.*). It is possible, therefore, that these derivatives have been produced without inversion and are members of the *d*-series. Thus, if, as in column (*c*) referring to the β-butyl derivatives, the sign of rotation of the *l*-series of these derivatives is entered in accordance with this view, it will be seen that the rotatory powers of the derivatives as far as the *p*-toluidino-compound are dextrorotatory, whilst the remainder become increasingly lævorotatory as the positive nature of the substituent increases. Further, in agreement with Rule's finding (*loc. cit.*), the (—)rotation of these bases increases [they change from (+) to (—)] in acid solution when the nitrogen-containing group becomes cationic.

In the β-octyl series, the rotatory powers of the piperidino- and *p*-toluidino-derivatives are also in agreement with the view that these derivatives have the same configuration as the *d*-sulphonate. Both these bases have relatively large (—)rotations, which become relatively large (+)rotations when the bases are dissolved in hydrochloric and acetic acids respectively (the hydrochloride of the *p*-toluidino-derivative is sparingly soluble in water). These rotation data would agree closely with those of the members of the *l*-series if the signs of rotation of the substances in the homogeneous state and in acid solution were reversed. Unfortunately, β-octylamine could not be isolated from the products of the interaction, under various experimental conditions, of the *d*-sulphonate with ammonia, so that further evidence bearing on the stereochemistry of the interaction of *d*-β-octyl *p*-toluenesulphonate with amines could not be obtained.

In the benzylmethylcarbinyl series, the evidence for the non-occurrence of an inversion during the formation of the amino- and substituted amino-derivatives is not so definite. *p*-Toluidine again appears to have reacted with the sulphonate without inversion, since the *p*-toluidino-derivative obtained is less lævorotatory in hydrochloric acid solution than in the homogeneous state. (+)α-Phenyl-β-propylamine and its (—)piperidyl derivative, produced from this *d*-sulphonate by the action of ammonia and piperidine respectively, are, however, more lævorotatory in acid solution, suggesting that they have arisen with inversion.

From the evidence afforded by the methods of comparison employed, it would appear that the three *d*-sulphonates investigated react with salts, Grignard reagents, pyridine, and phenol with inversion. With ammonia and piperidine, the *d*-β-butyl and *d*-β-octyl *p*-toluenesulphonates may react without inversion. With *p*-toluidine all three sulphonates react without inversion, but the results suggest that *d*-benzylmethylcarbinyl *p*-toluenesulphonate reacts with ammonia and piperidine with inversion.

EXPERIMENTAL.

β-*Butyl Derivatives.*

The *d* *-β-butanol required was prepared by Pickard and Kenyon's method (J., 1911, **99**, 45). In the homogeneous state it had $[\alpha]^{20^\circ}_{5893}$ + 13·83°, $[\alpha]^{20^\circ}_{4359}$ + 27·23°; in ethyl alcohol (*c*, 4·992) $[\alpha]^{20^\circ}_{5893}$ + 11·00°, $[\alpha]^{20^\circ}_{4359}$ + 29·17°; in ether (*c*, 5·000) $[\alpha]^{20^\circ}_{4893}$ + 18·20°, $[\alpha]^{20^\circ}_{5461}$ + 21·00°, $[\alpha]^{20^\circ}_{4359}$ + 39·00°; as the potassium salt in ether (*c*, 5·384) $[\alpha]^{20^\circ}_{5893}$ + 10·96°, $[\alpha]^{20^\circ}_{5461}$ + 14·00°, $[\alpha]^{20^\circ}_{4359}$ + 22·10°.

d-β-*Butyl* p-*toluenesulphinate* was prepared by the gradual addition of *p*-toluenesulphinyl chloride (30 g.) (Hilditch, J., 1910, **97**, 2585) to a solution of *d*-β-butanol (13 g.) in pyridine (15 g.) cooled in a freezing mixture. After 12 hrs., water was added, the separated oil extracted with ether and washed with water, hydrochloric acid, sodium carbonate, and finally with water. When distilled, the dried extract gave *d*-β-butyl *p*-toluenesulphinate, b. p. 98—100° $<$ 0·1 mm. (Found: C, 62·2; H, 7·6. $C_{11}H_{16}O_2S$ requires C, 62·3; H, 7·6%). It had $d^{13^\circ}_{4^\circ}$ 1·085, $d^{25^\circ}_{4^\circ}$ 1·066, $n^{25^\circ}_{D}$ 1·5252, $[\alpha]^{13^\circ}_{5893}$ + 7·37°, $[\alpha]^{13^\circ}_{5461}$ + 8·46°, $[\alpha]^{13^\circ}_{4359}$ + 14·08° in the homogeneous state; $[\alpha]^{13^\circ}_{5893}$ + 6·07°, $[\alpha]^{13^\circ}_{5461}$ + 7·08°, $[\alpha]^{13^\circ}_{4359}$ + 15·77° in ethyl alcohol (*c*, 4·946). It is probable that the rotatory powers recorded are those of *d*-β-butyl *dl*-*p*-toluenesulphinate, because the method of preparation employed does not favour the separation of the ester into its optical isomerides (Phillips, *loc. cit.*).

(+)β-Butanol was recovered without loss of rotatory power by heating its *p*-toluenesulphinic ester with each of the following reagents: (*a*) anhydrous formic acid, a complex reaction occurring; (*b*) glacial acetic acid, a mixture of the alcohol and its acetate being formed; (*c*) piperidine, *p*-toluenesulphinpiperidide, m. p. 131—132° (Found: N, 6·0. Calc.: N, 6·3%), being formed; (*d*) *p*-toluidine, an unstable compound, m. p. 265°, being produced, which decomposes in hot ethyl alcohol. The interaction of the *l*-sulphinate and benzoquinone on the steam-bath gave 3 : 6-dihydroxyphenyl-*p*-tolylsulphone, m. p. 212° (Found: C, 58·8; H, 4·7. Calc.: C, 59·1; H, 4·6%).

d-β-*Butyl* p-*Toluenesulphonate*.—Water was added, to incipient cloudiness, to a solution of the *d*-sulphinate (40 g.) in acetone (100 c.c.). After addition of magnesium sulphate (20 g.), the well stirred solution was slowly mixed with finely powdered potassium permanganate (20 g.), and kept cold by addition of ice. Ice and water were added before passage of sulphur dioxide, and the decolorised solution was extracted with ether. When completely free from acid by-products, the sulphonate distilled, b. p. 95° $<$ 0·1 mm.; but it decomposed at 100° when acids were present. Less decomposition occurred when the ester was distilled in the presence of a small quantity of freshly ignited potassium carbonate (Found: C, 58·0; H, 7·0. $C_{11}H_{16}O_3S$ requires C, 57·9; H, 7·0%). d-β-*Butyl* p-*toluenesulphonate* had $d^{20^\circ}_{4^\circ}$ 1·146, $n^{13^\circ}_{D}$ 1·5080, $[\alpha]^{20^\circ}_{5893}$ + 11·10°, $[\alpha]^{20^\circ}_{5461}$ + 12·98°, $[\alpha]^{20^\circ}_{4359}$ + 12·98° in the homogeneous state and $[\alpha]^{20^\circ}_{5893}$ + 5·80°, $[\alpha]^{20^\circ}_{5461}$ + 7·00°, $[\alpha]^{20^\circ}_{4359}$ + 11·80° in ethyl alcohol (*c*, 5·000).

When the ester was prepared by the action of *p*-toluenesulphonyl chloride on the alcohol in the presence of pyridine or on the potassium derivative of the alcohol in ether, the yield was smaller than that given by the above method.

(−)N-β-*Butylpiperidine*.—(a) *From the* d-*sulphonate*. The *d*-sulphonate (11 g.) and piperidine (8 g.) were warmed together on the steam-bath for 2 hrs., and the resulting mixture made alkaline and extracted with ether. From the dried (potassium carbonate) ethereal extract (−)N-β-*butylpiperidine*, b. p. 75—76°/25 mm. (5 g.) was obtained (Found: C, 76·6; H, 13·3. $C_9H_{19}N$ requires C, 76·6; H, 13·5%). It had $d^{25^\circ}_{4^\circ}$ 0·835, $n^{21^\circ}_{D}$ 1·4486, $[\alpha]^{25^\circ}_{5893}$ − 54·59°, $[\alpha]^{25^\circ}_{4359}$ − 99·60° in the homogeneous state and $[\alpha]^{24^\circ}_{5893}$ − 5·9°, $[\alpha]^{24^\circ}_{4359}$ − 9·1° in ethyl alcohol (*c*, 5·000). The hydrochloride, long needles, after recrystallisation from acetone, had $[\alpha]^{16^\circ}_{5893}$ + 1·40°, $[\alpha]^{16^\circ}_{4359}$

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* *d*- and *l*- denote optically pure dextro- and lævo-rotatory compounds; the partly active compounds are given the prefixes (+) and (−) respectively.

$+$ 4·4° in N-hydrochloric acid (c, 5·000) and $[\alpha]^{23^\circ}_{5893}$ $+$ 0·96°, $[\alpha]^{23^\circ}_{5461}$ $+$ 1·24°, $[\alpha]^{23^\circ}_{4359}$ $+$ 3·03° in water (c, 4·420).

(b) *From* β-*butylamine.* Pentamethylene bromide (2·7 g.) was heated under reflux with ($-$)β-butylamine (2·6 g., $[\alpha]^{15^\circ}_{5461}$ $-$ 4·61°) in ether (10 c.c.) for 12 hrs. More ether was then added together with dilute sodium hydroxide. From the dried ethereal extract ($-$)N-β-butylpiperidine, b. p. 78—80°/23 mm. (1 g.), was isolated (Found: C, 76·0; H, 13·2%). It had $n_D^{16\cdot2^\circ}$ 1·4513, $[\alpha]^{15^\circ}_{5461}$ $-$ 4·59° (l, 0·25), and gave a platinichloride, m. p. and mixed m. p. 197—198°.

dl-N-β-*Butylpiperidine*, b. p. 70°/21 mm., $n_D^{21\cdot2^\circ}$ 1·4484, was prepared from (a) the *dl*-sulphonate, (b) *dl*-β-butyl iodide. The m. p.'s and mixed m. p.'s of the platinichlorides of the two piperidides obtained were 197°: the m. p.'s and mixed m. p.'s of the corresponding picrates were 100°.

($-$)β-*Butyl*-p-*toluidine*.—The *d*-sulphonate (6 g.) and *p*-toluidine (5 g.) were warmed on a steam-bath for 6 hrs. and the resulting mixture made alkaline and extracted with ether. From the dried extract ($-$)β-*butyl*-p-*toluidine*, b. p. 136—138°/25 mm. (1 g.), was obtained (Found: C, 81·3; H, 10·5. $C_{11}H_{17}N$ requires C, 81·0; H, 10·4%). It had $d_{4^\circ}^{21^\circ}$ 0·916, $n_D^{18\cdot3^\circ}$ 1·5272, $[\alpha]^{21^\circ}_{5893}$ $-$ 37·45°, $[\alpha]^{21^\circ}_{4359}$ $-$ 86·18° in the homogeneous state, $[\alpha]^{21^\circ}_{5893}$ $-$ 35·74°, $[\alpha]^{21^\circ}_{4359}$ $-$ 77·96° in ethyl alcohol (c, 5·310; l, 1), and $[\alpha]^{21^\circ}_{5893}$ $-$ 3·0°, $[\alpha]^{21^\circ}_{4359}$ $-$ 8·16° in 0·477N-hydrochloric acid (c, 5·740).

($+$)β-*Butylamine*.—By the recrystallisation of *dl*-β-butylamine hydrogen tartrate from water, *l*-β-butylamine *d*-hydrogen tartrate was obtained, from which ($-$)β-butylamine, $[\alpha]^{15^\circ}_{5461}$ $-$ 4·61°, was isolated. From one of the mother-liquors, ($+$)β-butylamine was liberated, possessing the following rotatory powers: $[\alpha]^{15^\circ}_{5893}$ $+$ 2·03°, $[\alpha]^{15^\circ}_{4359}$ $+$ 3·40° in the homogeneous state; $[\alpha]^{15^\circ}_{5893}$ $+$ 0·22°, $[\alpha]^{15^\circ}_{4359}$ $+$ 1·80° in ethyl alcohol (c, 4·960); $[\alpha]^{15^\circ}_{5893}$ $+$ 1·27°, $[\alpha]^{15^\circ}_{5461}$ $+$ 1·47°, $[\alpha]^{15^\circ}_{4359}$ $+$ 2·25° in water (c, 5·100); $[\alpha]^{15^\circ}_{5893}$ $-$ 0·30°, $[\alpha]^{15^\circ}_{4359}$ $-$ 1·60° in N-hydrochloric acid (c, 5·006).

($+$)*Benzo*-β-*butylamide*.—(a) This was prepared from β-butylamine by Pope and Gibson's method (J., 1912, **101**, 1706) from *d*-β-butylamine *l*-α-bromocamphor-π-sulphonate; needles, m. p. 92°; $[\alpha]^{20^\circ}_{5461}$ $+$ 37·1°, $[\alpha]^{20^\circ}_{5893}$ $+$ 30·7° in ethyl alcohol (c, 1·0026).

(b) *From the* d-*sulphonate*. The *d*-sulphonate (30 g.) and ammonia (12 g.; d 0·88) were heated together in a sealed tube at 100° for 10 hrs. The contents, rendered strongly alkaline, were distilled in steam into dilute hydrochloric acid. The dry residue, obtained by evaporation of the acid distillate, was extracted with acetone, β-butylamine hydrochloride being obtained. This gave no measurable rotation in water (c, 0·72). It was converted into ($-$)*benzo*-β-*butylamide*, which was recrystallised twice from alcohol (Found: C, 74·5; H, 8·5. $C_{11}H_{15}ON$ requires C, 74·6; H, 8·5%). Before recrystallisation it had $[\alpha]^{19^\circ}_{5461}$ $-$ 35·1° in ethyl alcohol (c, 1·112), and after recrystallisation m. p. 88—89°, $[\alpha]^{17^\circ}_{5893}$ $-$ 14·35°, $[\alpha]^{17^\circ}_{4359}$ $-$ 32·01° (c, 0·906). The *d*-sulphonate did not react with sodium benzamide in ethyl-alcoholic solution. It was without action also on *p*-toluenesulphonamide in ethyl alcohol containing potassium carbonate, on potassium phthalimide in either ethyl-alcoholic or acetone solution, and on phthalimide itself in ethyl-alcoholic solution.

($-$)β-*Butyl Thiocyanate*.—The *d*-sulphonate (40 g.) and potassium thiocyanate (24 g.) in ethyl alcohol (50 c.c.) were heated under reflux for 12 hrs. The *thiocyanate*, isolated in the usual manner (Found: C, 51·4; H, 7·8. C_5H_9NS requires C, 52·2; H, 7·8%), had $d_{4^\circ}^{22^\circ}$ 0·960, $n_D^{19\cdot5^\circ}$ 1·4621, $[\alpha]^{22^\circ}_{5893}$ $-$ 44·64°, $[\alpha]^{22^\circ}_{4359}$ $-$ 74·80° in the homogeneous state; $[\alpha]^{20^\circ}_{5893}$ $-$ 24·98°, $[\alpha]^{20^\circ}_{4359}$ $-$ 50·36° in ethyl alcohol (c, 5·003).

($-$)β-*Butyl Disulphide*.—The ($-$)thiocyanate (8 g., $[\alpha]^{22^\circ}_{5893}$ $-$ 44·64°) was heated under reflux with potassium hydroxide (6 g.) in ethyl alcohol (100 c.c.) for 12 hrs. The resulting *disulphide* (5 g.) (Found: C, 53·9; H, 10·0. $C_8H_{18}S_2$ requires C, 53·9; H, 10·2%) had b. p. 95—97°/14 mm., $d_{4^\circ}^{14^\circ}$ 0·942, $n_D^{18\cdot5^\circ}$ 1·5031; $[\alpha]^{14^\circ}_{5893}$ $-$ 93·55°, $[\alpha]^{14^\circ}_{5461}$ $-$ 111·25°, $[\alpha]^{14^\circ}_{4359}$ $-$ 196·9° in the homogeneous state, and $[\alpha]^{16^\circ}_{5893}$ $-$ 84·23°, $[\alpha]^{16^\circ}_{5461}$ $-$ 95·31°, $[\alpha]^{16^\circ}_{4359}$ $-$ 178·24° in ethyl alcohol (c, 5·010).

($-$)β-*Butylthiol*.—($-$)β-Butyl disulphide (4 g., $[\alpha]^{14^\circ}_{5461}$ $-$ 26·45°, l 0·25) in acetic acid (30 c.c.) was reduced with tin (5 g.) and concentrated hydrochloric acid (10 c.c.), the ($-$)*thiol* (0·8 g.), b. p. 83—85°, being obtained (Found: C, 54·3; H, 10·6. $C_4H_{10}S$ requires C, 53·3; H, 11·1%). It had $d_{4^\circ}^{17^\circ}$ 0·830, $[\alpha]^{17^\circ}_{5893}$ $-$ 17·35°, $[\alpha]^{17^\circ}_{4359}$ $-$ 49·00° in the homogeneous state; $[\alpha]^{17^\circ}_{5893}$ $-$ 2·60°, $[\alpha]^{17^\circ}_{4359}$ $-$ 13·6° in ethyl alcohol (c, 5·000); $[\alpha]^{17^\circ}_{5893}$ $-$ 1·80°, $[\alpha]^{17^\circ}_{4359}$ $-$ 10·20° as the potassio-derivative in ethyl alcohol (c, 5·000).

($+$)β-*Butanesulphonic Acid*.—The ($-$)thiocyanate (2 g., $[\alpha]^{20^\circ}_{5893}$ $-$ 44·64°) in nitric acid (20 c.c., 60%) was warmed on the steam-bath for 24 hrs., the non-volatile residue from the resulting solution being evaporated to dryness several times with water. The residual viscous liquid had b. p. 125° <0·1 mm. (Found: C, 33·5; H, 7·4. $C_4H_{10}O_3S$ requires C, 34·7; H, 7·3%). It had $d^{25^\circ}_{4^\circ}$ 1·227, $n^{19\cdot7^\circ}_{D}$ 1·4365; $[\alpha]^{25^\circ}_{5893}$ + 2·32° in the homogeneous state; $[\alpha]^{25^\circ}_{5893}$ + 0·92°, $[\alpha]^{25^\circ}_{5461}$ + 1·85°, $[\alpha]^{25^\circ}_{4359}$ + 4·61° in ethyl alcohol (*c*, 5·421); $[\alpha]^{25^\circ}_{5893}$ + 0·75°, $[\alpha]^{25^\circ}_{5461}$ + 0·94°, $[\alpha]^{25^\circ}_{4359}$ + 3·39° in water (*c*, 5·308); and as a sodium salt, $[\alpha]^{25^\circ}_{5893}$ + 1·14°, $[\alpha]^{25^\circ}_{4359}$ + 5·69° in water (*c*, 6·153).

(−)β-*Butyl Selenocyanate.*—The *d*-sulphonate (11 g.) and potassium selenocyanate (8 g.) were heated under reflux for 12 hrs. with ethyl alcohol (30 c.c.); the *selenocyanate*, a somewhat viscous, yellow liquid, b. p. 83—84°/16 mm., with a penetrating nauseous odour, was isolated (Found: C, 37·5; H, 5·7. C_5H_9NSe requires C, 37·0; H, 5·6%). It had $d^{20^\circ}_{4^\circ}$ 1·445, $n^{19^\circ}_{D}$ 1·4965, $[\alpha]^{20^\circ}_{5893}$ − 11·34° in the homogeneous state; $[\alpha]^{20^\circ}_{5893}$ − 12·10°, $[\alpha]^{20^\circ}_{4359}$ − 24·60° in ethyl alcohol (*c*, 5·040). During this preparation no selenium was precipitated, but in a further experiment, using (−)sulphonate prepared from (−)β-butanol ($[\alpha]^{17^\circ}_{5461}$ − 4·6°, $l = 1$), selenium was precipitated, and much less racemisation occurred, since the (+)selenocyanate obtained had $[\alpha]^{12^\circ}_{5461}$ + 13·15°.

(+)β-*Butyl diselenide*, b. p. 130°/16 mm., was prepared by heating the (+)selenocyanate (2·5 g., $[\alpha]^{12^\circ}_{5461}$ + 13·15°) with potassium hydroxide (2 g.) in ethyl alcohol (20 c.c.) for 12 hrs. (Found: C, 35·4; H, 6·5. $C_8H_{18}Se_2$ requires C, 35·3; H, 6·6%). It had $n^{20^\circ}_{D}$ 1·5357, $[\alpha]^{20^\circ}_{5461}$ + 8·09° (*l*, 0·25).

(−)β-*Butyl Acetate.*—(a) *Using potassium acetate in ethyl alcohol.* The (+)sulphonate (10 g.) from (+)β-butanol ($[\alpha]^{20^\circ}_{5461}$ + 12·66°, $l = 1$) was heated under reflux with potassium acetate (12 g.) in ethyl alcohol (25 c.c.) for 12 hrs. (−)β-Butyl acetate (0·8 g.), b. p. 116—117°, $d^{19^\circ}_{4^\circ}$ 0·873, $n^{18^\circ}_{D}$ 1·3899 (Pickard and Kenyon, J., 1914, **105**, 830, record $d^{15\cdot5^\circ}_{4^\circ}$ 0·8758, $n^{20^\circ}_{D}$ 1·387), and some ethyl β-butyl ether were produced. The acetate had $[\alpha]^{19^\circ}_{5461}$ − 20·19° in the homogeneous state and $[\alpha]^{19^\circ}_{5461}$ − 18·86° in ethyl alcohol (*c*, 5·046). In a similar manner from (−)β-butyl *p*-toluenesulphonate, prepared from (−)β-butanol, $[\alpha]^{20^\circ}_{5461}$ − 9·52° (*l*, 2), (+)β-butyl acetate, $[\alpha]^{18^\circ}_{5461}$ + 10·52°, was obtained.

(b) *Using acetic acid.* The (−)sulphonate [7 g., from (−)β-butanol, $[\alpha]^{18^\circ}_{5461}$ − 9·2°, $l = 2$] was heated in glacial acetic acid (50 c.c.) on a steam-bath for 12 hrs. The (+)β-butyl acetate produced had b. p. 109—114°, $n^{18^\circ}_{D}$ 1·3890, $[\alpha]^{18^\circ}_{5461}$ + 2·5° (*l*, 0·25).

(−)*Ethyl* β-*Butyl Ether.*—The *d*-sulphonate (15 g.) in ethyl alcohol (10 c.c.) was heated with potassium carbonate (5 g.) on a steam-bath for 24 hrs.; water was added, and the required *ether* isolated by extraction with ether and purified by heating with phthalic anhydride and by distillation from sodium (Found: C, 68·4; H, 13·4. $C_6H_{14}O$ requires C, 70·6; H, 13·8%). It had b. p. 82—83°, $d^{20^\circ}_{4^\circ}$ 0·745, $[\alpha]^{20^\circ}_{5893}$ − 21·31°, $[\alpha]^{20^\circ}_{4359}$ − 41·04° in the homogeneous state; $[\alpha]^{12^\circ}_{5893}$ − 18·80°, $[\alpha]^{12^\circ}_{4359}$ − 37·00° in ethyl alcohol (*c*, 2·814).

(−)β-*Butyl* n-*butyl ether*, b. p. 130—131°, was prepared in a similar manner from the *d*-sulphonate (15 g.), potassium carbonate (5 g.), and *n*-butanol (6 g.) (Found: C, 73·6; H, 13·7. $C_8H_{18}O$ requires C, 73·8; H, 13·8%). It (2 g.) had $d^{15^\circ}_{4^\circ}$ 0·769, $n^{17\cdot5^\circ}_{D}$ 1·3972; $[\alpha]^{15^\circ}_{5893}$ − 23·42°, $[\alpha]^{15^\circ}_{4359}$ − 44·45° in the homogeneous state; $[\alpha]^{15^\circ}_{5893}$ − 21·65, $[\alpha]^{15^\circ}_{4359}$ − 41·70° in ethyl alcohol (*c*, 5·034).

(−)*Phenyl* β-*butyl ether*, b. p. 92—93°/20 mm., was prepared in a similar manner from the *d*-sulphonate (15 g.), potassium carbonate (5 g.), and phenol (30 g.) (Found: C, 79·8; H, 9·3. $C_{10}H_{14}O$ requires C, 80; H, 9·3%). It (5 g.) had $d^{18^\circ}_{4^\circ}$ 0·935, $n^{18\cdot5^\circ}_{D}$ 1·4873; $[\alpha]^{18^\circ}_{5893}$ − 16·47°, $[\alpha]^{18^\circ}_{4359}$ − 54·93° in the homogeneous state; $[\alpha]^{18^\circ}_{5893}$ − 20·81°, $[\alpha]^{18^\circ}_{4359}$ − 42·01° in ethyl alcohol (*c*, 5·020).

d-β-*Butyl Chloroformate.*—*d*-β-Butanol (10 g.) and quinoline (17·2 g.) in ether (40 c.c.) were run slowly into a stirred ice-cold solution of carbonyl chloride (14 g.) in ether (30 c.c.). After 12 hrs. at room temperature, the mixture was washed with dilute hydrochloric acid and dried (sodium sulphate), d-β-*butyl chloroformate* (14·4 g.), b. p. 24—25°/13 mm., being obtained (Found: Cl, 25·9. $C_5H_9O_2Cl$ requires Cl, 26·1%). It had $n^{19^\circ}_{D}$ 1·4093, $[\alpha]^{19^\circ}_{5461}$ + 19·18° (*l*, 0·5).

(−)β-*Bromobutane.*—(a) *From the* d-*sulphonate.* To an ice-cold solution of ethylmagnesium bromide in ether (50 c.c.), prepared from ethyl bromide (5 g.) and magnesium (0·9 g.), was added slowly an ethereal solution of the *d*-sulphonate (10 g.). After the initial vigorous reaction had ceased, the mixture was heated under reflux for 1 hr., and subsequently decomposed with ice and hydrochloric acid. The (−)β-bromobutane (2·5 g.), b. p. 90—91°, had $d^{25^\circ}_{4^\circ}$ 1·251, $n^{19\cdot5^\circ}_{D}$ 1·4359; $[\alpha]^{25^\circ}_{5893}$ − 12·24°, $[\alpha]^{25^\circ}_{4359}$ − 27·92° in the homogeneous state; $[\alpha]^{23^\circ}_{5893}$ − 17·02°, $[\alpha]^{23^\circ}_{4359}$ − 34·36° in ethyl alcohol (*c*, 5·054).

(b) *From the* d-*sulphinate.* Bromine (8 g.) in light petroleum (40 c.c.) was added to a solution of the *d*-sulphinate (10 g.) in the same solvent (40 c.c.). *p*-Toluenesulphonyl bromide,

m. p. and mixed m. p. 95—97°, crystallised from the solution, from which (–)β-bromobutane (3·5 g.), b. p. 85—87°, was isolated. It had $n_D^{18^\circ}$ 1·4337 and $[\alpha]_{5461}^{17^\circ}$ – 2·60°.

(–)β-*Iodobutane*.—(*a*) The *d*-sulphonate (15 g.) and potassium iodide (9 g.) in a mixture of acetone (50 c.c.) and ethyl alcohol (5 c.c.) were heated under reflux for 12 hrs. The (–)β-iodobutane, b. p. 121—122°, isolated had $d_{4^\circ}^{20^\circ}$ 1·585, $n_D^{19^\circ}$ 1·4945; $[\alpha]_{5893}^{20^\circ}$ – 2·14°, $[\alpha]_{4359}^{20^\circ}$ – 5·26° in the homogeneous state; $[\alpha]_{5893}^{20^\circ}$ – 2·99°, $[\alpha]_{4359}^{20^\circ}$ – 5·78° in ethyl alcohol (*c*, 5·02). (*b*) (–)β-Butanol ($[\alpha]_{5461}^{24^\circ}$ – 5·17°, *l* = 1) cooled in a freezing mixture was saturated with hydrogen iodide; the β-iodobutane produced had $[\alpha]_{5461}^{24^\circ}$ + 10·95°.

(–)*Methylethylacetic Acid*.—After the *d*-sulphonate (25 g.) and potassium cyanide (15 g.) in a mixture of acetone (50 c.c.) and ethyl alcohol (5 c.c.) had been heated under reflux for 80 hrs., the mixture was distilled in steam. The distillate contained small quantities of β-butyl cyanide, methylethylacetamide and methylethylacetic acid. They were collected in ether and heated under reflux with dilute potassium hydroxide. The methylethylacetic acid (0·1001 G. required 0·0393 g. NaOH for neutralisation. Calc.: 0·0392 g.) isolated had $[\alpha]_{5461}^{25^\circ}$ – 6·00° in water (*c*, 2·002). Attempts to prepare β-butyl cyanide from the sulphonate and silver cyanide in either acetone or ethyl alcohol or from mixtures of potassium and silver cyanides in acetone were unsuccessful.

(+)*Methylethylacetic Acid*.—The *dl*-acid (Kahlbaum) was partly resolved by means of brucine (Marckwald, *Ber.*, 1896, **29**, 53) and the *d* + *dl*-acid obtained ($[\alpha]_{5461}^{20^\circ}$ + 5·30°, *l* = 1) was further separated by crystallisation of its silver salt from water (Marckwald, *Ber.*, 1899, **32**, 1092). It had $d_{4^\circ}^{20^\circ}$ 0·934, $n_D^{21\cdot2^\circ}$ 1·4044; $[\alpha]_{5893}^{20^\circ}$ + 12·29°, $[\alpha]_{4359}^{20^\circ}$ + 24·93° in the homogeneous state; $[\alpha]_{5893}^{24^\circ}$ + 12·17°, $[\alpha]_{4359}^{24^\circ}$ + 22·15° in ethyl alcohol (*c*, 5·012); $[\alpha]_{5893}^{20^\circ}$ + 4·05°, $[\alpha]_{5461}^{20^\circ}$ + 7·86°, $[\alpha]_{4359}^{20^\circ}$ + 15·24° in benzene (*c*, 5·190); $[\alpha]_{5893}^{26^\circ}$ + 15·58°, $[\alpha]_{5461}^{26^\circ}$ + 21·57°, $[\alpha]_{4359}^{26^\circ}$ + 39·77° in water (*c*, 2·503); as sodium salt $[\alpha]_{5893}^{24^\circ}$ + 6·75°, $[\alpha]_{4359}^{24^\circ}$ + 10·2° in water (*c*, 6·070).

(+)Ethyl methylethylacetate, b. p. 130°, prepared from methylethylacetic acid (5 g., $[\alpha]_{5461}^{20^\circ}$ + 5·68°) had $d_{4^\circ}^{26^\circ}$ 0·860, $n_D^{23\cdot5^\circ}$ 1·3957, $[\alpha]_{5893}^{26^\circ}$ + 5·16°, $[\alpha]_{4359}^{26^\circ}$ + 11·34° in the homogeneous state; $[\alpha]_{5893}^{26^\circ}$ + 4·20°, $[\alpha]_{4359}^{26^\circ}$ + 13·80° in ethyl alcohol (*c*, 5·000); $[\alpha]_{5893}^{26^\circ}$ + 3·40°, $[\alpha]_{5461}^{26^\circ}$ + 6·00°, $[\alpha]_{4359}^{26^\circ}$ + 11·20° in benzene (*c*, 5·000).

(+)*Methylethylacetyl chloride*, b. p. 119—120°, was prepared by the action of thionyl chloride (15 g.) on the (+)acid (12 g., $[\alpha]_{5461}^{20^\circ}$ + 5·68°) (Found: C, 47·4; H, 7·5. C_5H_9OCl requires C, 47·8; H, 7·5%). It had $d_{4^\circ}^{24^\circ}$ 0·990, $n_D^{17\cdot5^\circ}$ 1·4177; $[\alpha]_{5893}^{24^\circ}$ + 4·51°, $[\alpha]_{4359}^{24^\circ}$ + 9·41° in the homogeneous state; $[\alpha]_{5893}^{24^\circ}$ + 12·23°, $[\alpha]_{4359}^{24^\circ}$ + 24·26° in benzene (*c*, 5·070).

(+)*Acetomethylethylamide*, long needles, m. p. 156°, was obtained by the action of ammonium carbonate on a solution of the (+)acid chloride (5 g., $[\alpha]_{5461}^{24^\circ}$ + 5·25°) in ether (Found: C, 59·5; H, 10·8. $C_5H_{11}ON$ requires C, 59·4; H, 10·9%). It had $[\alpha]_{5893}^{18^\circ}$ + 3·39°, $[\alpha]_{4359}^{18^\circ}$ + 7·39° in ethyl alcohol (*c*, 5·008); $[\alpha]_{5893}^{18^\circ}$ + 18·05°, $[\alpha]_{5461}^{18^\circ}$ + 24·07°, $[\alpha]_{4359}^{18^\circ}$ + 59·72° in benzene (*c*, 2·326).

(+)β-*Butyl cyanide*, b. p. 125—126°, was obtained by the action of phosphoric oxide (10 g.) on (+)acetomethylethylamide (3 g.) described above (Found: C, 71·4; H, 10·5. C_5H_9N requires C, 72·2; H, 10·9%). It had $d_{4^\circ}^{20^\circ}$ 0·786, $n_D^{22\cdot5^\circ}$ 1·3875; $[\alpha]_{5893}^{20^\circ}$ + 7·58°, $[\alpha]_{4359}^{20^\circ}$ + 15·52° in the homogeneous state; $[\alpha]_{5893}^{20^\circ}$ + 5·24°, $[\alpha]_{4359}^{20^\circ}$ + 16·92° in ethyl alcohol (*c*, 4·196); $[\alpha]_{5461}^{19^\circ}$ + 11·9° in benzene (*c*, 4·38).

(–)β-*Butylbenzene*.—The *d*-sulphonate (10 g.) was added to an ice-cold solution of phenylmagnesium bromide in ether (50 c.c.), prepared from magnesium (2 g.) and bromobenzene (13 g.). (–)β-Butylbenzene (1·5 g.), b. p. 70—76°/60 mm., $n_D^{19^\circ}$ 1·5044 (Harrison, Kenyon, and Shepherd, J., 1926, 662, record $n_D^{25^\circ}$ 1·4883, $d_{4^\circ}^{23^\circ}$ 0·8609), some benzene, and also diphenyl (m. p. and mixed m. p. 70°) were obtained. The (–)β-butylbenzene had $[\alpha]_{5893}^{23^\circ}$ – 17·88°, $[\alpha]_{5461}^{23^\circ}$ – 21·65°, $[\alpha]_{4359}^{23^\circ}$ – 39·50° in the homogeneous state; $[\alpha]_{5893}^{23^\circ}$ – 16·35°, $[\alpha]_{4359}^{23^\circ}$ – 34·89° in ethyl alcohol (*c*, 5·016).

(–)β-*Butyl Benzoate*.—(a) *Using potassium benzoate*. The (+)sulphonate (10 g.) and potassium benzoate (7 g.) in ethyl alcohol (35 c.c.) were heated under reflux for 12 hrs. The (–)β-butyl benzoate (1·2 g.), b. p. 98—99°/13 mm., had $d_{4^\circ}^{17^\circ}$ 1·002, $n_D^{22^\circ}$ 1·5005; $[\alpha]_{5461}^{17^\circ}$ – 44·09° (Kenyon and Pickard, J., 1915, **107**, 121, record $n_D^{20^\circ}$ 1·4930). (+)β-Butyl benzoate (1·5 g.), $n_D^{23\cdot5^\circ}$ 1·5007, $[\alpha]_{5461}^{18^\circ}$ + 5·16°, was obtained in a similar manner from the (–)sulphonate [10 g., from (–)β-butanol, $[\alpha]_{5461}^{18^\circ}$ – 2·96°, *l* = 0·5].

(b) *Using benzoic acid*. The (–)sulphonate [20 g., from (–)β-butanol, $[\alpha]_{5461}^{23^\circ}$ – 5·84°] and benzoic acid (32 g.) were heated together on the steam-bath for 24 hrs. *dl*-β-Butyl benzoate (7·5 g.), b. p. 115—117°/20 mm., $n_D^{21\cdot3^\circ}$ 1·4933, was produced. It (2·2 g.) was also recovered from a mixture of (+)benzoate (5 g., $[\alpha]_{5461}^{21^\circ}$ + 5·20°), benzoic acid (3·4 g.), and *p*-toluenesulphonic acid (5 g.) which had been heated on a steam-bath for 24 hrs.

(+)β-Butyl benzoate, unchanged in rotation (1·8 g.), was recovered from a mixture of the (+)benzoate (2 g., $[\alpha]^{20^\circ}_{5461}$ + 2·69°, l = 0·25) and benzoic acid (2 g.) which had been heated in a similar manner. When the benzoic acid was replaced by *p*-toluenesulphonic acid, the β-butyl benzoate decomposed.

β-*Octyl Series.*

d-β-Octanol (Kenyon, J., 1922, **121**, 2540) has $[\alpha]^{20^\circ}_{5893}$ + 9·48°, $[\alpha]^{20^\circ}_{4359}$ + 22·40° in ethyl alcohol (*c*, 4·992); $[\alpha]^{20^\circ}_{5461}$ + 18·07° in ether (*c*, 5·110); $[\alpha]^{20^\circ}_{5461}$ — 40·72° as the potassio-derivative in ether (*c*, 6·461).

(—)N-β-*Octylpiperidine.*—A mixture of the *d*-sulphonate [11·5 g., from (+)β-octanol, $[\alpha]^{20^\circ}_{5461}$ + 9·47°, l = 1] and piperidine (7·5 g.) was warmed on a steam-bath for 24 hrs. Dilute sodium hydroxide was added, and the oil extracted with ether and dried (potassium carbonate). After removal of the ether, the residual liquid separated into two layers, the lower being unchanged sulphonate. When distilled, the upper layer gave two main fractions, (i) b. p. 65—125°/13 mm. (1 g.), which was chiefly β-octanol, (ii) b. p. 125—128°/13 mm. (5 g.), which was (—)β-*octylpiperidine.* When redistilled, b. p. 125—126°/13 mm. (Found: C, 79·1; H, 13·2. $C_{13}H_{27}N$ requires C, 79·2; H, 13·7%), it had $d^{18^\circ}_{4^\circ}$ 0·820, $n^{16^\circ}_{D}$ 1·4288; $[\alpha]^{18^\circ}_{5893}$ — 16·76°, $[\alpha]^{18^\circ}_{4359}$ — 29·25° in the homogeneous state; $[\alpha]^{19^\circ}_{5893}$ — 5·76°, $[\alpha]^{19^\circ}_{4359}$ — 12·01° in ethyl alcohol (*c*, 5·090); $[\alpha]^{18^\circ}_{5893}$ + 18·18°, $[\alpha]^{18^\circ}_{4359}$ + 39·40° in 6*N*-hydrochloric acid (*c*, 5·228).

(—)N-β-*Octyl*-p-*toluidine.*—The *d*-sulphonate (11 g.) and *p*-toluidine (8·6 g.) were heated together on a steam-bath for 24 hrs., and the product when distilled gave some β-octanol and *p*-toluidine, followed by (—)N-β-*octyl*-p-*toluidine*, which was redistilled, b. p. 163—164°/15 mm. (Found: C, 81·3; H, 11·4. $C_{15}H_{25}N$ requires C, 82·2; H, 11·4%). It was insoluble in both dilute and concentrated hydrochloric acid; it had $d^{21^\circ}_{4^\circ}$ 0·782, and $n^{15\cdot5^\circ}_{D}$ 1·5122; $[\alpha]^{21^\circ}_{5893}$ — 12·05°, $[\alpha]^{21^\circ}_{4359}$ — 33·26° in the homogeneous state; $[\alpha]^{19^\circ}_{5893}$ — 8·16°, $[\alpha]^{19^\circ}_{4359}$ — 20·05° in ethyl alcohol (*c*, 4·858); $[\alpha]^{19^\circ}_{5893}$ + 11·20° in glacial acetic acid (*c*, 5·092).

(—)β-*Octyl Thiocyanate.*—A solution of the *d*-sulphonate (10 g.) and potassium thiocyanate (16 g.) in ethyl alcohol (20 c.c.) was heated under reflux for 24 hrs., and worked up in the usual manner; there was obtained (—)β-*octyl thiocyanate* (4 g.), b. p. 119—120°/15 mm. (Found: C, 62·9; H, 9·9. $C_9H_{17}NS$ requires C, 63·1; H, 10·0%). It had $d^{20^\circ}_{4^\circ}$ 0·795, $n^{17^\circ}_{D}$ 1·4651; $[\alpha]^{20^\circ}_{5893}$ — 71·41°, $[\alpha]^{20^\circ}_{4359}$ — 149·5° in the homogeneous state; $[\alpha]^{20^\circ}_{5893}$ — 64·68°, $[\alpha]^{20^\circ}_{4359}$ — 140·0° in ethyl alcohol (*c*, 5·010).

(—)β-*Octylthiol.*—The solution obtained by dissolving potassium (14 g.) in ethyl alcohol (100 c.c.) was saturated with hydrogen sulphide, mixed with the *d*-sulphonate (40 g.), and heated under reflux for 7 hrs. The filtered mixture was poured into water, and the oily products extracted with ether. On distillation three fractions were obtained: (i) b. p. 55—75°/15 mm. (1 g.), mainly ethyl β-octyl ether; (ii) b. p. 75—95°/15 mm. (8 g.), mainly β-octylthiol; (iii) b. p. 90—105°/15 mm. (1 g.), leaving a higher-boiling residue (iv) (4 g.). Refractionation gave (—)β-*octylthiol,* b. p. 78—80°/22 mm. in a current of hydrogen (Found: C, 65·6; H, 12·0. $C_8H_{18}S$ requires C, 65·8; H, 12·3%). On warming an ethyl-alcoholic solution of the (—)thiol with mercuric oxide, (—)β-octyl mercurio-mercaptide was obtained, m. p. 43° (decomp.) (after recrystallisation from ethyl alcohol containing ether, in which it had $[\alpha]_{5461}$ — *ca.* 58°). An ethyl-alcoholic solution of (—)β-octylthiol neutralised with the calculated amount of *N*-sodium hydroxide had $[\alpha]_{5461}$ — 9·0°. Fraction (iv) was twice redistilled and obtained with b. p. 135°/2 mm., $d^{25^\circ}_{4^\circ}$ 0·8382. It was probably (—)di-β-octyl sulphide and had $[\alpha]_{5780}$ — 30·45°, $[\alpha]_{5461}$ — 35·82°, and $[\alpha]_{4359}$ — 58·2° (l, 1).

(—)*Methyl* β-*Octyl Sulphide.*—(—)β-Octylthiol (4·5 g.) was added to sodium hydroxide (15 c.c., 2*N*), and the mixture dissolved in the minimum amount of methyl alcohol. Methyl sulphate (3·9 g.) was added slowly, and the solution maintained at 80° for 2 hrs.; the separated oily layer was dried in ether over potassium carbonate. Distillation gave (—)*methyl* β-*octyl sulphide,* b. p. 90—91°/18 mm. (Found: C, 67·2; H, 12·3. $C_9H_{20}S$ requires C, 67·5; H, 12·5%).

(—)*Ethyl* β-*Octyl Sulphide.*—No reaction occurred when either β-octyl chloride or the *p*-toluenesulphonate was heated under reflux with an ethereal suspension of potassium hydrogen sulphide. Heated under reflux for 24 hrs. with an ethyl-alcoholic solution of potassium hydrogen sulphide, the *d*-sulphonate reacted readily, and two volatile products were isolated: (i), b. p. 47—85°/13 mm., mainly octylene; (ii), b. p. 85—95°/13 mm., mainly (—)*ethyl* β-*octyl sulphide.* When redistilled, (ii) had b. p. 99—100°/17 mm. (Found: C, 69·0; H, 12·6. $C_{10}H_{22}S$ requires C, 69·0; H, 12·6%).

Details of the rotations of the last three compounds are given in the following table.

The specific rotatory powers $[\alpha]^{t^\circ}_{\lambda}$ of (—)β-octylthiol and methyl and ethyl β-octyl sulphides in the homogeneous state.

t.	$d^{t^\circ}_{4^\circ}$.	λ 6708.	λ 6104.	λ 5780.	λ 5461.	λ 4602.	λ 4358.	λ 4078.
				(—)β-Octylthiol.				
—78°	0·911	—	—	39·4	44·7	—	76·2	—
0	0·849	24·1	29·5	33·5	38·3	57·2	65·2	78·6
25	0·830	22·9	28·2	32·0	36·4	53·7	62·0	—
97	0·773	—	—	28·1	32·2	—	55·2	66·0
				(—)Methyl β-octyl sulphide.				
—78	0·921	—	—	18·4	20·9	—	33·7	—
0	0·855	—	—	14·7	16·6	—	26·7	—
27	0·834	—	—	13·9	15·6	—	25·2	—
97	0·780	—	—	12·3	13·8	—	21·9	—
				(—)Ethyl β-octyl sulphide.				
—30	0·878	—	—	22·0	24·5	—	39·7	—
0	0·854	13·6	16·6	18·6	21·1	30·4	34·2	40·1
25	0·835	—	—	16·8	19·0	—	30·9	36·1
98	0·782	9·8	12·2	13·5	15·2	21·8	24·7	—

(+)β-*Octanesulphonic Acid.*—(—)β-Octyl thiocyanate (4 g., $[\alpha]^{20^\circ}_{5461}$ — 149·5°) was heated on a steam-bath with nitric acid (15 c.c.) and water (2 c.c.) until a clear solution was obtained. After dilution with water, the solution was evaporated to small bulk, diluted again with water, and neutralised with barium carbonate. When the clear solution was concentrated, the barium salt crystallised; it was recrystallised twice from water, giving platelets, unmolten at 320°. The *acid* (0·0400 g. required 0·0082 g. NaOH. Calc. : 0·0083 g.) had $[\alpha]^{20^\circ}_{5893}$ 156·7°, $[\alpha]^{20^\circ}_{4359}$ + 276·2° in water (*c*, 1·34); its sodium salt had $[\alpha]^{20^\circ}_{5893}$ + 134·7°, $[\alpha]^{20^\circ}_{4359}$ + 404° in water (*c*, 0·0872).

(—)*Phenyl* β-*Octyl Ether.*—The *d*-sulphonate (14 g.), phenol (24 g.), and potassium carbonate (14 g.) were heated together on a steam-bath, and the portion of the product insoluble in sodium hydroxide was collected in ether, dried, and distilled. The main fraction, *phenyl* (—)β-*octyl ether*, b. p. 130—150°/20 mm., was redistilled, b. p. 144—145°/20 mm. (Found : C, 81·4; H, 10·8. $C_{14}H_{22}O$ requires C, 81·5; H, 10·7%). It had $d^{23^\circ}_{4^\circ}$ 0·904, $n^{19^\circ}_{D}$ 1·4878; $[\alpha]^{23^\circ}_{5893}$ — 18·54°, $[\alpha]^{23^\circ}_{4359}$ — 39·85° in the homogeneous state; $[\alpha]^{26^\circ}_{5893}$ — 15·00°, $[\alpha]^{26^\circ}_{4359}$ — 29·40° in ethyl alcohol (*c*, 5·000).

(+)*Phenyl* β-*octyl sulphide*, b. p. 178°/20 mm. (Found : C, 75·7; H, 9·7. $C_{14}H_{22}S$ requires C, 75·7; H, 9·9%), prepared by the interaction of the *l*-sulphonate (14 g.) and an ethyl-alcoholic solution of sodium thiophenoxide (19 g.), had $d^{17^\circ}_{4^\circ}$ 0·944, $n^{18^\circ}_{D}$ 1·5256, $[\alpha]^{17^\circ}_{5893}$ + 11·31°, $[\alpha]^{17^\circ}_{4359}$ + 22·38° in the homogeneous state; $[\alpha]^{17^\circ}_{5893}$ + 0·99°, $[\alpha]^{17^\circ}_{4359}$ + 3·98° in ethyl alcohol (*c*, 5·004).

(—)β-*Bromo-octane.*—The *d*-sulphonate (9 g.), dissolved in ether, was added slowly to an ice-cold Grignard reagent prepared from bromobenzene (8 g.) and magnesium (1·2 g.). After 12 hrs., the mixture was warmed on a steam-bath for 1 hr., cooled, and poured on ice. By fractional distillation of the products, (—)β-bromo-octane (2 g.), b. p. 78—79°/18 mm., was obtained with $d^{20^\circ}_{4^\circ}$ 1·086, $n^{21^\circ}_{D}$ 1·4521, $[\alpha]^{20^\circ}_{5893}$ — 26·52°, $[\alpha]^{20^\circ}_{4359}$ — 53·05° in the homogeneous state; $[\alpha]^{20^\circ}_{5893}$ — 29·8°, $[\alpha]^{20^\circ}_{4359}$ — 59·4° in ethyl alcohol (*c*, 4·902); a small quantity of diphenyl (m. p. and mixed m. p. 70°) was isolated, as well as a liquid optically inactive product, b. p. 100—101°/18 mm.

Benzylmethylcarbinyl Series.

The *d*-benzylmethylcarbinol was prepared as described by Pickard and Kenyon (*loc. cit.*) and Phillips (*loc. cit.*). It has now been found that the concentrated mother-liquors from which the less soluble *l*-brucine *d*-benzylmethylcarbinyl phthalate has been removed deposit the *l*-A, *l*-B salt. This is sparingly soluble in cold but very soluble in hot acetone, and after 5 or 6 recrystallisations is obtained optically pure.

	Brucine salt.	Benzylmethylcarbinyl hydrogen phthalate.	Benzylmethylcarbinol.
d-	Glistening needles, m. p. 153°; $[a]_{5893}$ —4·98° (*c*, 5; *l* = 2 in $CHCl_3$)	(oil) $[a]_{5893}$ +44·5°, $[a]_{5461}$ +53·0° (*c*, 5·0; *l* = 2 in $CHCl_3$)	$a^{16^\circ}_{5461}$ +8·17° (*l*, 0·25)
l-	Soft, feathery needles, m. p. 83°; $[a]^{16^\circ}_{5893}$ —16·33°, $[a]^{16^\circ}_{5461}$ —22·31°, $[a]^{16^\circ}_{4359}$ —51·99° (*c*, 5·020; *l* = 1 in $CHCl_3$)	(oil) $[a]_{5893}$ —44·7°, $[a]_{5461}$ —53·2°	$a^{14^\circ}_{5893}$ —6·82°, $a^{14^\circ}_{5461}$ —8·08°, $a^{14^\circ}_{435}$ —15·3° (*l*, 0·25)

d-Benzylmethylcarbinyl hydrogen phthalate had $[\alpha]^{24^\circ}_{5893}$ + 43·11°, $[\alpha]^{24^\circ}_{5461}$ + 51·81°, $[\alpha]^{24^\circ}_{4359}$ + 98·47° in ethyl alcohol (*c*, 5·636); $[\alpha]^{26^\circ}_{5893}$ + 45·25°, $[\alpha]^{26^\circ}_{5461}$ + 80·63°, $[\alpha]^{26^\circ}_{4359}$ + 151·8° as the sodium salt in water (*c*, 5·356). The *l*-benzylmethylcarbinol had $\alpha^{25^\circ}_{5893}$ − 13·85° (*l*, 0·5) in the homogeneous state and $[\alpha]^{25^\circ}_{5893}$ − 20·20°, $[\alpha]^{25^\circ}_{4359}$ − 45·60° in ether (*c*, 5·044; *l*, 1); $[\alpha]^{25^\circ}_{5893}$ − 27·70° as potassio-salt in ether (*c*, for alcohol 4·948).

(−)β-*Piperidino-α-phenylpropane.*—The *d*-sulphonate (5 g.) and piperidine (6 g.) were heated together on a steam-bath for 12 hrs., and the resulting product made alkaline and extracted with ether. From the dried (sodium sulphate) ethereal extract, (−)β-*piperidino-α-phenylpropane*, b. p. 142—143°/11 mm., was obtained (Found: C, 83·1; H, 10·2. $C_{14}H_{21}N$ requires C, 82·8; H, 10·3%). It had $d^{19^\circ}_{4^\circ}$ 0·962, $n^{25^\circ}_{\mathrm{D}}$ 1·5244, and $[\alpha]^{19^\circ}_{5893}$ − 16·63°, $[\alpha]^{19^\circ}_{4358}$ − 35·15° in the homogeneous state; $[\alpha]^{21^\circ}_{5893}$ − 11·84°, $[\alpha]^{21^\circ}_{4359}$ − 22·07° in ethyl alcohol (*c*, 4·984; *l*, 1); $[\alpha]^{21^\circ}_{5893}$ − 16·89°, $[\alpha]^{21^\circ}_{4359}$ − 30·97° in 0·53*N*-hydrochloric acid (*c*, 5·036).

(−)β-p-*Toluidino-α-phenylpropane.*—The *d*-sulphonate (5·8 g.) and *p*-toluidine (8·6 g.) were heated on a steam-bath for 3 hrs. The (−)β-p-*toluidino-α-phenylpropane*, b. p. 183—184°/11 mm. (Found: C, 85·3; H, 8·3. $C_{16}H_{19}N$ requires C, 85·3; H, 8·4%), had $d^{19^\circ}_{4^\circ}$ 1·013, $n^{22^\circ}_{\mathrm{D}}$ 1·5709, with $[\alpha]^{19^\circ}_{5893}$ − 12·60°, $[\alpha]^{19^\circ}_{4359}$ − 41·02° in the homogeneous state; $[\alpha]^{19^\circ}_{5893}$ − 33·08°, $[\alpha]^{19^\circ}_{4359}$ − 93·08° in ethyl alcohol (*c*, 5·200; *l*, 1); $[\alpha]^{22^\circ}_{5893}$ − 12·77°, $[\alpha]^{22^\circ}_{4358}$ − 25·17° in glacial acetic acid (*c*, 5·128; *l*, 1). It was insoluble in hydrochloric acid, but a clear solution obtained by adding 5 c.c. of an ethyl-alcoholic solution of the amine to 5 c.c. of 0·53*N*-hydrochloric acid had $[\alpha]^{22^\circ}_{5893}$ − 12·77°, $[\alpha]^{22^\circ}_{4359}$ − 25·17° (*c*, 2·564).

(+)β-*Amino-α-phenylpropane.*—The *d*-sulphonate (8 g.) was heated for 6 hrs. in a sealed tube with ethyl alcohol (10 c.c.) saturated with ammonia. The contents of the tube were then poured into dilute hydrochloric acid, and the solution extracted with ether. The aqueous acid layer was made alkaline; the liberated (+)β-*amino-α-phenylpropane* had b. p. 102°/16 mm. (Found: C, 79·3; H, 9·6. $C_9H_{13}N$ requires C, 80·0; H, 9·6%). It had $d^{19^\circ}_{4^\circ}$ 0·941, $n^{20^\circ}_{\mathrm{D}}$ 1·4704, $[\alpha]_{5893}$ + 1·40°, $[\alpha]_{5780}$ + 1·61° in the homogeneous state; $[\alpha]_{5780}$ − 45·1°, $[\alpha]_{4359}$ − 86·6° in 2·0*N*-hydrochloric acid (*c*, 2·828).

(−)β-*Thiocyano-α-phenylpropane*, b. p. 158°/16 mm., was prepared by heating the *d*-sulphonate (15 g., 1 mol.) with potassium thiocyanate (15 g., 1 mol.) in ethyl alcohol (40 c.c.) for 7 hrs. (Found: C, 67·9; H, 6·3. $C_{10}H_{11}NS$ requires C, 67·9; H, 6·2%). It had $d^{20^\circ}_{4^\circ}$ 1·072, $n^{26\cdot5^\circ}_{\mathrm{D}}$ 1·5495; $[\alpha]_{5893}$ − 116·02° in the homogeneous state; $[\alpha]_{5893}$ − 118·5° in ethyl alcohol (*c*, 1·020)

(−)β-*Phenyl*iso*propyl disulphide*, b. p. 144°/0·1 mm. (Found: C, 71·2; H, 7·4. $C_{18}H_{22}S_2$ requires C, 71·5; H, 7·3%), obtained by heating the above thiocyanate with ethyl alcohol containing potassium hydroxide (1·5 g.) for 5 hrs., had $d^{20^\circ}_{4^\circ}$ 1·072, $n^{24\cdot5^\circ}_{\mathrm{D}}$ 1·5794 and $[\alpha]_{5461}$ − 10·0° (*l*, 0·25).

(−)β-*Cyano-α-phenylpropane*, b. p. 117°/17 mm., was prepared by heating the *d*-sulphonate (15 g.) in acetonitrile (20 c.c.) containing water (1·5 c.c.) and sodium cyanide (7·5 g.) under reflux for 30 hrs. (Found: C, 82·1; H, 8·2. $C_{10}H_{11}N$ requires C, 82·8; H, 7·6%). It had $d^{19^\circ}_{4^\circ}$ 0·980, $n^{26^\circ}_{\mathrm{D}}$ 1·5098; $[\alpha]_{5893}$ − 20·6° in the homogeneous state; $[\alpha]_{5893}$ − 15·50° in ethyl alcohol (*c*, 0·5154).

(−)β-Phenyl-α-methylpropionic acid was obtained by hydrolysing the (−)cyanopropane (2·5 g., $[\alpha]_{5461}$ − 5·6°, $l = 0{\cdot}25$) in aqueous ethyl alcohol containing sodium hydroxide (0·87 g.). It had b. p. 162°/16 mm. (Kipping and Hunter, J., 1903, **83**, 1005, give b. p. 160°/12 mm.), $n^{23\cdot5^\circ}_{\mathrm{D}}$ 1·5009; $[\alpha]_{5461}$ − 0·35° (*l*, 0·25); its sodium salt had $[\alpha]_{5461}$ − 8·63° in water (*c*, 1·448).

(+)β-*Phenyl-α-methylpropionic acid.* The *dl*-acid was resolved according to the method of Pickard and Yates (J., 1909, **95**, 1019). It had $d^{24^\circ}_{4^\circ}$ 1·062, $n^{24^\circ}_{\mathrm{D}}$ 1·5008; $[\alpha]^{24^\circ}_{5893}$ + 20·36°, $[\alpha]^{24^\circ}_{4359}$ + 45·38° in the homogeneous state; $[\alpha]^{21^\circ}_{5893}$ + 17·87°, $[\alpha]^{21^\circ}_{4359}$ + 44·49° in ethyl alcohol (*c*, 5·034); $[\alpha]^{23^\circ}_{5893}$ + 40·68°, $[\alpha]^{23^\circ}_{4358}$ + 89·97° as the sodium salt in water (*c*, for acid, 5·114). The (−)methyl ester, b. p. 105°/16 mm., obtained by heating (−)β-cyano-α-phenylpropane ($[\alpha]_{5461}$ − 25·1°) in methyl alcohol containing sulphuric acid, had $[\alpha]_{5461}$ − 8·02° (*l*, 0·25) in the homogeneous state and $[\alpha]_{5461}$ − 28·2° in ethyl alcohol (*c*, 0·1768); and the (+)ethyl ester, b. p. 116°/15 mm., prepared from (+)β-phenyl-α-methylpropionyl chloride (1 g., $[\alpha]^{23^\circ}_{5461}$ + 24·94°), and ethyl alcohol (3 c.c.), had $d^{18^\circ}_{4^\circ}$ 0·866, $n^{16^\circ}_{\mathrm{D}}$ 1·4911; $[\alpha]^{18^\circ}_{5893}$ + 26·93°, $[\alpha]^{18^\circ}_{4359}$ + 58·18° in the homogeneous state; $[\alpha]^{21^\circ}_{5893}$ + 29·17°, $[\alpha]^{21^\circ}_{4359}$ + 66·88° in ethyl alcohol (*c*, 5·036).

(−)α-*Phenyl-β-propylthiol*, b. p. 105—110°/16 mm. (Found: C, 71·1; H, 8·1; S, 21·0. $C_9H_{12}S$ requires C, 71·1; H, 7·9; S, 21·0%), obtained by reducing the disulphide (4 g.) in glacial acetic acid solution with tin (6 g.), had $d^{19^\circ}_{4^\circ}$ 0·999, $n^{20^\circ}_{\mathrm{D}}$ 1·5312; $[\alpha]_{5893}$ − 15·3° in the homogeneous state; $[\alpha]_{5893}$ − 15·1° in ethyl alcohol (*c*, 1·399).

(−)Phenyl α-phenyl-β-propyl ether, b. p. 156°/10 mm., was prepared by the interaction of the *d*-sulphonate (5·8 g.) and an ethyl-alcoholic solution (25 c.c.) of sodium phenoxide (9·3 g.). It had $d_{4^\circ}^{20^\circ}$ 1·029, $n_D^{20^\circ}$ 1·5571 (Phillips, J., 1923, **123**, 44, gives $n_D^{20^\circ}$ 1·5573), $[\alpha]_{5893}^{20^\circ}$ − 61·49°, $[\alpha]_{4359}^{20^\circ}$ − 135·8° in the homogeneous state; $[\alpha]_{5893}^{20^\circ}$ − 45·24°, $[\alpha]_{4359}^{20^\circ}$ − 92·85° in ethyl alcohol (*c*, 5·042).

(−)*Phenyl α-phenyl-β-propyl sulphide*, b. p. 177—178°/11 mm. (Found : C, 79·3; H, 7·0. $C_{15}H_{16}S$ requires C, 79·0; H, 7·0%), was prepared by the interaction of the *d*-sulphonate (5·8 g.) and an ethyl-alcoholic solution of sodium thiophenoxide (9·6 g.).. It had $d_{4^\circ}^{19^\circ}$ 1·070, $n_D^{25\cdot5^\circ}$ 1·5952; $[\alpha]_{5893}^{19^\circ}$ − 38·66°, $[\alpha]_{4358}^{19^\circ}$ − 91·36° in the homogeneous state; $[\alpha]_{5893}^{19^\circ}$ − 24·68°, $[\alpha]_{4359}^{19^\circ}$ − 58·33° in ethyl alcohol (*c*, 5·024).

Interaction of the d-*Sulphonate with Phenylmagnesium Bromide*.—The *d*-sulphonate was added slowly to the ice-cold Grignard reagent prepared from bromobenzene (8 g.) and magnesium (1·1 g.). After 12 hrs., the mixture was warmed on a steam-bath for 1 hr., cooled, and decomposed with ice and acetic acid. By fractional distillation of the products, (−)α-phenyl-β-propyl bromide (1·5 g.), b. p. 113°/12 mm., was obtained. It had $d_{4^\circ}^{14^\circ}$ 1·373, $n_D^{14^\circ}$ 1·5492; $[\alpha]_{5893}^{14^\circ}$ − 24·10°, $[\alpha]_{4359}^{14^\circ}$ − 53·26° in the homogeneous state; $[\alpha]_{5893}^{14^\circ}$ − 22·96°, $[\alpha]_{4358}^{14^\circ}$ − 49·75° in ethyl alcohol (*c*, 4·964). Another experiment, in which an excess of Grignard reagent was used, yielded a small quantity of impure (−)α-methyldibenzyl, b. p. 165°/20 mm.

β-*Chloro-α-phenylpropane*.—(a) *By means of lithium chloride*. The *d*-sulphonate (9 g., 1 mol.), lithium chloride (3·9 g., 3 mols.), and ethyl alcohol (15 c.c.) were heated under reflux for 8 hrs. The only products obtained when the mixture was added to water were (i) an unsaturated hydrocarbon and benzylmethylcarbinyl ethyl ether, b. p. 63—83°/17 mm., (ii) b. p. 90—100°/17 mm. Fraction (ii), redistilled, b. p. 94°/17 mm., gave (−)β-*chloro-α-phenylpropane* (Found : Cl, 22·5. $C_9H_{11}Cl$ requires Cl, 22·9%), $d_{4^\circ}^{19^\circ}$ 1·038, $n_D^{22^\circ}$ 1·5198, $[\alpha]_{5780}$ − 5·65° (*l*, 0·25).

(b) *By means of ethylmagnesium chloride*. The (−)sulphonate (5 g., $[\alpha]_{5461}$ − 16·3° in benzene) in ether (50 c.c.) was added to a solution of ethylmagnesium chloride (magnesium, 0·43 g.; 1 mol.); the mixture was heated under reflux for 1 hr., then decomposed with ice and hydrochloric acid. The (+)β-chloro-α-phenylpropane obtained (yield almost theoretical) had b. p. 94°/17 mm., $n_D^{22^\circ}$ 1·5198; $[\alpha]_{4359}$ + 21·2° in the homogeneous state; $[\alpha]_{4359}$ + 17·0° in ethyl alcohol (*c*, 1·171; *l*, 2).

(+)β-*Bromo-α-phenylpropane*, b. p. 121°/17 mm., was prepared as in (*a*) above, but from (−)sulphonate (10 g., $[\alpha]_{5461}$ − 11·7° in benzene), sodium bromide (10·5 g.), and ethyl alcohol (15 c.c.) (Found : Br, 39·8. $C_9H_{11}Br$ requires Br, 39·9%). It had $d_{4^\circ}^{19^\circ}$ 1·263, $n_D^{20\cdot5^\circ}$ 1·5385; $[\alpha]_{5893}$ + 5·9° in the homogeneous state; $[\alpha]_{5893}$ + 6·1° in ethyl alcohol (*c*, 1·015; *l*, 2).

(+)β-Phenyl-α-methylpropionyl chloride, b. p. 123°/16 mm., prepared by the action of thionyl chloride (4 g.) on the (+)acid (4 g., $[\alpha]_{5461}^{24^\circ}$ + 24·78°), had $d_{4^\circ}^{23^\circ}$ 1·100, $n_D^{21^\circ}$ 1·5191; $[\alpha]_{5893}^{23^\circ}$ + 19·96°, $[\alpha]_{4359}^{23^\circ}$ + 48·08° in the homogeneous state; $[\alpha]_{5893}^{23^\circ}$ + 17·03°, $[\alpha]_{4359}^{23^\circ}$ + 45·21° in benzene (*c*, 5·112).

(+)β-*Phenyl-α-methylpropionamide*, m. p. 113—114°, obtained by the action of ammonium carbonate (3 g.) on the (+)acid chloride (1 g., $[\alpha]_{5461}^{23^\circ}$ + 24·94°) in ether (10 c.c.), had $[\alpha]_{5893}^{18^\circ}$ + 53·07°, $[\alpha]_{4359}^{18^\circ}$ + 118·7° in ethyl alcohol (*c*, 2·544).

Di-(*α-benzylethyl*) *Sulphide*.—The (−)sulphonate (12 g., $[\alpha]_{5780}$ − 23·49° in benzene) was heated under reflux for 10 hrs. in ethyl alcohol (15 c.c.) containing sodium sulphide (29·5 g.; cryst.). The main product was *di-*(*α-benzylethyl*) *sulphide*, b. p. 209°/16 mm. (Found: S, 12·0. $C_{18}H_{22}S$ requires S, 11·9%). It had $d_{4^\circ}^{20^\circ}$ 1·072, $n_D^{24\cdot5^\circ}$ 1·5794; $[\alpha]_{5780}$ + 4·25°, $[\alpha]_{5461}$ + 4·9° (*l*, 0·25).

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