

**377. The Dependence of Optical Rotatory Power on Chemical Constitution. Part XXXVIII. (–)-1-Chloro-3-phenoxypropan-2-ol and (–)-Glycide Phenyl Ether.**

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The hydrogen phthalate of (–)-1-chloro-3-phenoxypropan-2-ol is an intermediate in the preparation of (–)-glycide phenyl ether. The (–)-alcohol was prepared to check the optical purity of the ether. Rotatory powers of the (–)-alcohol and its hydrogen phthalate are recorded.

The rotatory dispersions of the homogeneous (–)-glycide phenyl ether, between 6708 and 3180 Å., and of solutions in a variety of solvents, in the visible spectrum, are recorded. Drude equations cannot be derived solely from the experimental results, but a number of two-term equations and one of three terms for the homogeneous ether, and a three-term equation (but none with two terms) for the solution in ethyl ether can be calculated for assumed characteristic wave-lengths which are in part derived from the absorption spectrum.

The rotatory powers and dispersion characteristics of the ether are very sensitive to changes of temperature or of solvent: increase of temperature, and dissolution in ethereal solvents, result in the lowest rotatory power. The rotatory dispersion is most complex in ethereal solutions. It is suggested that these observations can be explained by assuming molecular association in the homogeneous substance, which is lessened by increase of temperature or dissolution in ether.

1-CHLORO-3-PHENOXYPROPAN-2-OL was prepared as described by Boyd and Marle (*J.*, 1910, **97**, 1788) and converted into the hydrogen phthalate by the usual method. The (–)-ester was obtained by recrystallisation of its brucine salt. Hydrolysis of the (–)-ester with potassium

hydroxide yields (–)-glycide phenyl ether,  $\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\overset{\text{O}}{\text{C}}\text{H}\cdot\text{CH}_2$ , which on treatment with hydrochloric acid yields (–)-1-chloro-3-phenoxypropan-2-ol; the (–)-(hydrogen phthalate) prepared from this alcohol has the same rotatory power as that from which the ether was prepared, indicating that no racemisation occurs at any of the stages of preparation.

Table I summarises the absorption spectrum of glycide phenyl ether,  $\text{CH}_2\cdot\overset{\text{O}}{\text{C}}\text{H}\cdot\text{CH}_2\cdot\text{OPh}$ , which is dominated by the absorption of the phenyl chromophore, and shows the usual effects of substitution on the absorption spectrum of benzene, *viz.*, some loss of vibrational fine structure, displacement to longer wave-lengths, and an increase in intensity of the long-wave band.

TABLE I.

*The ultra-violet absorption spectrum of glycide phenyl ether.*

(1) *In mixed octanes.*

$\lambda_{\text{max.}}$ , Å. ....	2770	2705	2650	2195
$\epsilon_{\text{max.}}$ .....	1520	1740	1230	7480

(2) *Homogeneous.* No selective absorption down to 2940 Å. For a layer of 0.10 cm. the optical density rises smoothly from 0.05 at 3100 Å. to 0.78 at 2940 Å., corresponding to a molar extinction coefficient of about 0.5, *i.e.*, of the same order as in octane solution at this wave-length.

TABLE II.

*Specific rotatory powers of (–)-glycide phenyl ether, homogeneous.*

<i>t</i> , 18.5°; <i>l</i> , 0.5 :														
$\lambda$ .	6708.	6438.	6107.	5893.	5780.	5461.	5086.	4800.	4678.	4358.				
$[\alpha]$ , obs. ...	18.5°	20.2°	22.9°	24.9°	25.5°	28.2°	32.9°	37.2°	38.6°	45.6°				
$[\alpha]$ , calc. ...	18.1°	—	—	—	—	28.2°	—	—	—	46.5°				
<i>t</i> , 18°; <i>l</i> , 0.25 :														
$\lambda$ .	4707.	4647.	4630.	4602.	4556.	4528.	4476.	4461.	4415.	4383.	4337.	4285.	4260.	4202.
$[\alpha]$ , obs.	38.9°	39.1°	39.6°	40.4°	41.3°	42.2°	43.1°	44.0°	44.9°	45.8°	46.7°	47.6°	48.5°	49.4°
<i>t</i> , 18.5°; <i>l</i> , 0.05 :														
$\lambda$ .	4346.	4088.	3873.	3603.	3485.	3394.	3292.	3180.						
$[\alpha]$ , obs. ....	46.8°	52.3°	57.7°	68.2°	73.7°	78.9°	84.4°	89.7°						
$[\alpha]$ , calc. ....	—	—	—	71.3°	—	—	84.4°	87.0°						

Table II gives the specific rotatory powers of homogeneous (–)-glycide phenyl ether in visible and ultra-violet light, down to the limit of transmission. The plot of  $1/\alpha - \lambda^2$  is a

straight line, except for the three points below  $\lambda$  3300 Å. One-term Drude equations can be calculated from a variety of pairs of points in the dispersion ( $\alpha$ - $\lambda$ ) curve, but the resulting  $\lambda_0$ 's vary somewhat widely, and if points lying within less than 300 Å. of each other on the wave-length scale are used for the calculation, the  $\lambda_0$  values pass through a minimum as the wave-lengths of the points used pass along the wave-length scale, suggesting that there is an inflection in the  $\alpha$ - $\lambda$  plot. It therefore appears that a two-term equation would be required to fit the observed results satisfactorily. We have not been able to calculate a two-term equation from any four points read from a smooth curve drawn through  $\alpha$ - $\lambda$ . We have, however, been able to derive several equations which fit tolerably well the observed results, by assuming values of  $\lambda_1$  and  $\lambda_2$  and calculating  $k_1$  and  $k_2$  from two of the observed points. Calculated values of  $[\alpha]_\lambda$  from one such equation,

$$[\alpha]_\lambda = \frac{0.763}{\lambda^2 - 0.0795} - \frac{8.415}{\lambda^2 - 0.0324}$$

are given in Table II. All the equations so derived are consistent with the idea that one of the absorption bands of the phenyl chromophore, and one in the experimentally inaccessible region below 1900 Å., are optically active. A three-term equation

$$[\alpha]_\lambda = \frac{-1.334784}{\lambda^2 - 0.0795} + \frac{2.047924}{\lambda^2 - 0.0729} - \frac{8.772339}{\lambda^2 - 0.0169}$$

has also been fitted to the results. This was derived by starting with the 2770 and 2650 Å. maxima in the absorption spectrum as characteristic frequencies for the first two terms, and 1300 Å. for the third term. The first two frequencies were then increased, in accordance with the frequently observed relation  $\lambda_0 - \lambda_{\max.} \sim 100$  Å. (Lowry, "Optical Rotatory Power," London, 1935, pp. 145, 146) until an equation to fit the observed results was obtained:  $\lambda_1$  and  $\lambda_2$  in the equation given above correspond to characteristic frequencies of 2830 and 2700 Å. This procedure has a practical justification in that the calculation of the three-term equation involves the use of an additional experimental observation, and so results in a somewhat better fit to the observations. There cannot be any physical significance in the separation, in the dispersion equation, of two terms with characteristic frequencies which are fine-structure (vibrational) maxima in the absorption band of a single electronic excitation process: the first two terms of this equation must be regarded as arising from difficulties in computation and as together covering the contribution to the rotatory power from anisotropy in the phenyl chromophore.

Table III gives the rotatory dispersion of (–)-glycide phenyl ether in ethyl ether solution. We have not been able by any method to derive a one- or two-term equation to fit these results. A three-term equation

$$[\alpha]_\lambda = \frac{40.122936}{\lambda^2 - 0.0795} + \frac{50.901337}{\lambda^2 - 0.729} - \frac{14.482839}{\lambda^2 - 0.0169}$$

can be derived by assuming the same three wave-lengths as above, and this fits a smooth curve of  $\alpha$ - $\lambda$  within the scatter of the observed points.

TABLE III.

*Specific rotatory powers of (–)-glycide phenyl ester in diethyl ether solution.*

<i>t</i> , 19.6°; <i>c</i> , 10.32; <i>l</i> , 1.0 above, and 0.5 below $\lambda$ 4000.									
$\lambda$ .	6438.	5893.	5780.	5461.	5086.	4800.	4358.	3998.	3983.
$[\alpha]$ .....	7.2°	8.3°	8.7°	9.6°	10.5°	11.1°	12.3°	13.0°	14.5°
$\lambda$ .	3937.	3907.	3843.	3813.	3756.	3680.	3545.		
$[\alpha]$ .....	16.0°	17.4°	18.95°	23.3°	24.8°	30.6°	38.0°		

Table IV gives the rotatory powers of (–)-glycide phenyl ether in a variety of solvents, in the visible spectrum. The variations are greater than can be accounted for by variations in the refractive indices of the solutions since the rotivities ( $\Omega = 3[\alpha]/(n^2 + 2)$ ; Beckman and Cohen, *J. Chem. Physics*, 1936, 4, 784; 1938, 6, 163) vary over almost as wide a range as the specific rotatory powers.

Table V gives the rotatory power of homogeneous (–)-glycide phenyl ether, at temperatures from 25° to 174°. The effect of increase in temperature on the rotatory power is exceptionally great. In di-*n*-butyl ether solution (Table IV) the temperature effect is even greater, and the characteristics of anomalous rotatory dispersion, *i.e.*, inflection, maximum, and change of sign of rotation, are evident, moving towards longer wave-lengths as the temperature is increased;

the first two are apparent in the red and the blue region of the spectrum at 41°, at 80° they have disappeared and the third is evident in the green.

TABLE IV.  
*Specific rotatory powers of (–)-glycide phenyl ether in various solvents.*

Solvent.	l.	c.	Temp.	Wave-length, A.										[α] <sub>4358</sub>		Ω <sub>D</sub> .
				6708.	6438.	6104.	5893.	5780.	5461.	5086.	4800.	4358.	4358.	5461.		
Carbon di- sulphide	0.5	15.0	17°	—	18.8°	—	22.7°	—	27.7°	32.3°	37.1°	47.1°	1.70	1.70	14.8	
Pyridine	1.0	5.2	16	17.9°	19.2	21.7°	22.6	24.6°	27.3	31.7	34.6	43.6	1.60	15.8		
Benzene	1.0	10.3	21	16.6	18.3	20.3	21.9	23.0	25.7	30.1	34.3	42.4	1.65	15.5		
Methyl alcohol	0.5	10.0	17	—	16.7	—	20.3	21.6	24.3	26.2	30.2	35.4	1.49	15.9		
Nitro- methane	1.0	9.2	20	12.7	14.4	15.8	17.7	18.6	20.6	23.3	25.6	30.1	1.48	13.5		
Acetone	0.5	9.4	19	—	12.3	—	16.2	17.9	19.7	23.6	25.9	27.8	1.41	12.5		
„	0.5	36.0	17	—	15.1	—	—	20.5	24.0	27.1	29.4	34.8	1.45	—		
Ethyl alcohol	1.0	8.1	18	10.3	11.5	13.1	14.1	14.5	16.4	19.1	20.7	24.9	1.52	10.9		
n-Propyl chloride	1.0	12.9	19	9.6	10.1	11.1	12.0	13.1	14.3	15.4	16.4	19.8	1.37	9.1		
Diethyl ether	0.5	18.4	17	—	—	—	11.6	11.9	14.4	14.6	—	19.2	1.33	8.9		
„	1.0	13.0	20	—	7.2	—	8.3	8.7	9.6	10.5	11.1	12.2	1.27	6.4		
„	1.0	13.0	17	—	7.9	—	9.1	9.5	10.5	11.6	12.4	13.6	1.30	7.0		
Di-n-propyl ether	1.0	9.6	19	—	7.8	—	9.6	10.1	11.4	11.9	12.8	14.9	1.30	—		
Diisopropyl ether	1.0	10.0	21	—	6.6	—	8.3	8.4	9.1	10.0	10.6	11.0	1.26	—		
1 : 4-Dioxan	1.0	9.1	20	—	6.7	—	8.2	9.0	10.0	10.8	11.8	13.5	1.35	6.1		
„	0.5	32.0	17	—	—	—	—	—	16.4	—	—	25.0	1.52	—		
Di-n-amyl ether	1.0	11.2	21	—	5.9	—	8.1	8.5	9.5	10.0	—	11.0	1.16	—		
Di-n-butyl ether	1.0	9.4	22	—	5.3	—	—	6.9	7.6	7.8	—	8.4	1.15	—		

Ω<sub>D</sub> homogeneous = 16.9. Dispersion ratio, homogeneous = 1.62.

TABLE V.  
*The effect of temperature on the specific rotatory power of homogeneous (–)-glycide phenyl ether (l, 0.5).*

Temp.	Specific rotatory powers at λ (A.).						[α] <sub>4358</sub>		α <sub>D</sub> .
	6438.	5780.	5461.	5086.	4800.	4358.	[α] <sub>5461</sub>		
25.5°	19.5°	24.9°	26.8°	31.3°	35.3°	43.6°	1.62	1.106	
42.8	16.7	20.8	23.5	27.0	—	37.2	1.58	1.093	
61.0	14.1	17.8	19.8	22.8	26.0	31.3	1.58	1.079	
80.0	11.8	15.0	16.7	19.6	21.8	26.0	1.55	1.064	
98.0	10.4	12.7	14.3	16.4	18.4	21.8	1.53	1.051	
141	—	7.9	8.3	—	—	11.9	1.42	1.018	
174	—	5.3	5.5	—	—	6.8	1.24	0.993	

In secondary carbinols with simple rotatory dispersion (Pickard and Kenyon, *J.*, 1911, **99**, 45; 1912, **101**, 620; 1913, **103**, 1923), and in camphor (Gore and Lowry, *Proc. Roy. Soc., A*, 1932, **135**, 22), an increase in temperature of 100° decreases the rotatory power by some 20%, and in (–)-menthol, the effect is even less (Pickard and Kenyon, *J.*, 1915, **107**, 35). In substances which do not undergo a change in molecular configuration with increase of temperature, a decrease in rotatory power of this magnitude is to be expected, on account of the decrease in refractive index, which appears in the numerator of the quantum-mechanical expression for rotatory power (Born and Jordan, "Elementare Quantenmechanik," 1930, p. 250) and on account of increased freedom of rotation about single bonds (Kauzmann, Walter, and Eyring, *Chem. Reviews*, 1940, **26**, 377). In compounds with rigid ring structures, the latter effect will not operate, as indicated by (–)-menthol. The powerful effect of temperature on the rotatory power of (–)-glycide phenyl ether may therefore be an indication that a change in the molecular species occurs on increase of temperature. Such a change is also the most likely cause of the wide variation in rotatory powers in different solvents. This variation does not appear to be

an effect of the electrostatic field of the solvent in the optically active molecule, since it apparently is not related to the dielectric constant of the solvent. It is not likely to be caused by combination of the solvent with the solute (which could alter the rotatory power by forming a new species of optically active substance, *i.e.*, imparting anisotropy to a previously optically inactive absorption band) because such combination would be lessened by increase in temperature, and so the dispersion should become more like that of the homogeneous substance on raising the temperature of the solution, whereas the dispersion in *n*-butyl ether solution at various temperatures (Table VI) indicates that the contrary is the case. It is also not caused by a large shift in the position of the long-wave band of the optically active ether in solution; solvents modify the fine structure of absorption bands, but do not cause a shift such as would account for their effects on the rotatory dispersion of glycide phenyl ether.

TABLE VI.

*The effect of temperature on the specific rotatory power of (–)-glycide phenyl ether in n-butyl ether solution (c, 9.4; l, 1.0).*

Temp.	Specific rotatory powers at $\lambda$ (A.).					$[\alpha]_{4358}$ $[\alpha]_{5461}$
	6438.	5780.	5461.	5086.	4358.	
22°	–5.3°	–6.9°	–7.6°	–7.7°	–8.4°	1.105
41	–3.2	–3.8	–4.3	–5.3	–4.1	0.953
81	–2.4	–1.1	–	–	+1.9	—
96	–1.3	–0.7	+0.3	–	+3.2	11.8

TABLE VII.

*Specific rotatory powers of phenyl (–)-sec.-butyl ether in the homogeneous state and in solution in various solvents.*

Solvent.	l.	c.	t.	$\lambda$ , A.							$[\alpha]_{4358}$ $[\alpha]_{5461}$	
				6438.	5893.	5780.	5461.	5086.	4800.	4678.		4358.
None (homogeneous)	0.25	—	18°	29.3°	36.0°	37.7°	42.1°	51.0°	59.4°	62.3°	74.9°	1.78
Diethyl ether .....	1.0	9.1	19	28.3	34.2	36.2	41.2	50.1	57.2	61.0	73.9	1.78
(±)-Propylene oxide	1.0	5.1	16	28.2	35.5	38.4	43.4	50.7	—	—	77.4	1.78

Aliphatic ethers of octan-2-ol (Kenyon and McNicol, *J.*, 1923, **123**, 14) and of benzylmethylcarbinol (Phillips, *J.*, 1923, **123**, 22) have simple rotatory dispersions in the visible spectrum, and their rotatory powers are much less sensitive than those of glycide phenyl ether to change in temperature or solvent, being reduced by not more than 50% by a 100° increase of temperature. The rotatory powers of the *n*-alkyl ethers of nonan-3-ol (which exhibits complex rotatory dispersion in the visible spectrum, Kenyon and Barnes, *J.*, 1924, **125**, 1395), undergo a similar reduction on increase of temperature. It therefore appears that the extreme sensitivity to temperature changes which is shown in the rotatory power of glycide phenyl ether is not a general characteristic of optically active ethers; and sensitivity to solvent changes is not a characteristic of phenyl ethers in particular, since the results in Table VII indicate that the rotatory power of phenyl *sec.*-butyl ether is comparatively insensitive to changes in solvent. It therefore appears that these sensitivities in glycide phenyl ether are connected with the presence of the ethylene oxide groups. They may be due to some form of molecular association at ordinary temperature in the homogeneous substance, which is lessened by increase of temperature or by dissolution in ethereal solvents. At ordinary temperatures the rotatory power of the homogeneous ether is controlled by optically active absorption bands at about 2700–2800 and 1300 A., the 1300-A. band being dominant in the visible region. At elevated temperatures or in ethereal solutions, the association is lessened, resulting in a relative increase in the contribution of the phenyl chromophore (*i.e.*, the term at about 2700–2800 A.) to the rotatory power, so that the dispersion becomes more complex. This increase is indicated by comparison of the two three-term equations given above: dissolution in ethyl ether increases  $k_1$  and  $k_2$  (associated with the phenyl chromophore) more than  $k_3$  (associated with the high-frequency chromophore). The dispersion of the homogeneous ether becomes more complex at elevated temperatures, as shown by the decrease in dispersion ratios to 1.24 at 174° (Table V), and the combined effect of dissolution in an ethereal solvent and increase in temperature is even more pronounced (Table VI). These suggestions imply that the association involves the ethylene oxide ring, and that the oxygen atom of ethereal solvents can displace the association.

The rotatory power of phenylbenzylcarbinol (Gerrard and Kenyon, *J.*, 1928, 2564) is as

sensitive as that of glycide phenyl ether to increase of temperature or to solvent effects, which suggests that a similar discussion, involving association through the hydroxyl group, may be applicable to the structure of the carbinol.

EXPERIMENTAL.

1-Chloro-3-phenoxypropan-2-ol.—From phenol (376 g.), epichlorohydrin (370 g.), sodium hydroxide (2 g.), and water (20 c.c.), 364 g. of the redistilled alcohol, b. p. 134—136°/6 mm., were obtained, together with a few g. of glycerol *aa'*-diphenyl ether, m. p. 80° (Boyd and Marle, *J.*, 1909, **95**, 1807, give m. p. 80°) (Found : C, 73.4; H, 6.4. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>3</sub> : C, 73.7; H, 6.6%).

1-Chloro-3-phenoxypropan-2-ol (270 g.) was added to a warm solution of phthalic anhydride (222 g.) in pyridine (132 g.). After 10 days at room temperature the mixture was dissolved in acetone and poured into cold dilute hydrochloric acid. The precipitated inactive *hydrogen phthalate* was filtered off, dissolved in ether, extracted with sodium hydrogen carbonate solution, precipitated with hydrochloric acid, dissolved in ether, dried (CaCl<sub>2</sub>), and precipitated (436 g.) from the concentrated solution by addition of light petroleum. On recrystallisation from ether—light petroleum the ester was obtained as colourless plates, m. p. 97—98° (Found, by titration with 0.1N-sodium hydroxide : equiv., 335. C<sub>17</sub>H<sub>15</sub>O<sub>5</sub>Cl requires equiv., 334.5). If the reaction mixture is dissolved in toluene, instead of in acetone as above, the ester crystallises with m. p. 97° when the solution is poured into hydrochloric acid.

Dry brucine (788 g.) was dissolved in a solution of the hydrogen phthalate (669 g.) in dry ethyl acetate. The brucine salt (m. p. 108—110°) which crystallised during 2 weeks was recrystallised 4 times from ethyl acetate and then 5 times from acetone (brucine hydrogen phthalate was filtered off from each solution); the final (tenth) crop weighed 44 g. The ninth and the tenth crops yielded hydrogen phthalate with the same rotatory power ( $[\alpha]_D^{25}$  —12.2° in ethyl ether), suggesting that the resolution was complete.

Ice-cold hydrochloric acid was poured into a mixture of the brucine salt of the above (—)(hydrogen phthalate) and acetone. The (—)-ester separated and was extracted with ether; the solution was washed with dilute hydrochloric acid, and extracted with sodium hydrogen carbonate solution, from which the (—)(hydrogen phthalate) was precipitated by addition of hydrochloric acid. The ester was extracted with ether, washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). On removal of the ether under reduced pressure, the (—)-ester remained as an uncrystallisable viscous liquid. Rotatory powers are in the Table. From a concentrated solution, in ether, of the hydrogen phthalate obtained from brucine salt which had been only twice recrystallised, ester of low rotatory power ( $[\alpha]_D^{25}$  —6.0° in ether) crystallised, leaving in solution, ester with  $[\alpha]_D^{25}$  —10.5° (*i.e.*, 85% of the maximum rotatory power).

*Specific rotatory powers of (—)-1-chloro-3-phenoxy-2-propyl hydrogen phthalate (1 = 2).*

Solvent.	c.	Temp.	λ, A.							$[\alpha]_{4358}^{25}$ $[\alpha]_{5461}^{25}$
			6438.	5893.	5780.	5461.	5086.	4800.	4358.	
Ethyl ether .....	9.6	17°	—10.0°	—12.2°	—13.3°	—15.2°	—17.7°	—21.8°	—28.7°	1.89
Carbon disulphide .....	11.7	18	1.7	2.2	2.3	2.7	4.4	—	5.5	2.04
Acetone .....	11.8	18	5.2	6.6	7.2	8.1	9.9	11.3	15.4	1.90
Chloroform .....	13.2	19	4.1	4.8	4.9	5.8	7.7	—	9.9	1.70
Pyridine .....	11.4	20	0.48	0.53	—	0.75	—	—	—	—
Benzene .....	11.6	17	—	1.1	—	—	—	—	—	—

(—)-Glycide Phenyl Ether.—The levorotatory hydrogen phthalate was hydrolysed to glycide phenyl ether by steam-distillation of 5-g. portions from 12.5N-potassium hydroxide (5 c.c.); with weaker alkali the hydrolysis was incomplete, and with larger proportions of 12.5N-alkali larger proportions of undistillable by-products were obtained. The distillate was extracted with ether; the extract was dried and, after removal of the ether, (—)-glycide phenyl ether was distilled; it had b. p. 133°/23 mm.,  $n_D^{17}$  1.5310,  $d_4^{25}$  1.106,  $d_4^{100}$  1.049 (2.0 g. from 10 g. of the hydrogen phthalate) (Found : C, 71.95; H, 6.7. Calc. for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub> : C, 72.0; H, 6.7%). Rotatory powers are given in the following paper. (±)-Glycide phenyl ether has been described by Boyd and Marle (*J.*, 1908, **93**, 838) and Rider and Hill (*J. Amer. Chem. Soc.*, 1930, **52**, 1521).

(—)-1-Chloro-3-phenoxypropan-2-ol.—(—)-Glycide phenyl ether (6.5 g.) was shaken for 30 minutes with concentrated hydrochloric acid (6 c.c.) in cold water (6 c.c.). An ethereal extract from the mixture was washed 3 times with aqueous sodium hydroxide (0.1 mol.), then with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. (—)-1-Chloro-3-phenoxypropan-2-ol (7 g. from 15 g. of the ether) was obtained on distillation of the residue, with b. p. 143—5°/20 mm.,  $n_D^{19}$  1.5378. (—)-Glycide phenyl ether,  $[\alpha]_D^{17}$  —24.4°, gives (—)-1-chloro-3-phenoxypropan-2-ol of  $[\alpha]_D^{19}$  —2.1°, and the alcohol yields, by the method described above, (—)(hydrogen phthalate) with the same rotatory power as the phthalate from which the ether was prepared.

Phenyl (+)-*sec.*-butyl ether was prepared from (+)-*sec.*-butyl alcohol with  $[\alpha]_{5893}^{17}$  +10.9°. The alcohol (5 g.) was saturated with dry hydrogen bromide, heated under reflux for 1 hour, washed with concentrated sulphuric acid to remove butenes and with sodium hydrogen carbonate solution, and dissolved in ether. The solution was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The residue of *sec.*-butyl bromide (3 g.) distilled at 80—86°. It was heated for 12 hours with freshly prepared sodium phenoxide (2.75 g.) for 12 hours; the mixture was then extracted with ether, the extract was washed with 3N-sodium hydroxide, dried (CaCl<sub>2</sub>), and concentrated. Phenyl *sec.*-butyl ether (0.85 g.) distilled from the residue, with b. p. 75—76°/10 mm.,  $n_D^{18}$  1.4978,  $d_4^{18}$  0.9350,  $[\alpha]_D^{18}$  +28.34°. Sprung and Wallis (*J. Amer. Chem. Soc.*, 1934, **56**, 1715) give b. p. 84—85°/14 mm.,  $n_D^{25}$  1.4926,  $[\alpha]_D^{25}$  +30.02°. Since the *sec.*-butyl alcohol was not optically pure the rotatory powers of the ether given in Table VII have been multiplied by 13.87/10.9, to bring them to the values for ether prepared from optically pure alcohol; these values,

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however, cannot be regarded as the rotatory powers of optically pure ether, as there was probably some racemisation during the preparation of the bromide.

Rotivities  $\Omega$  were calculated from  $\Omega = 3[\alpha]/(n^2 + 2)$ , by using the weighted means of refractive indices of solvents and solute.

The absorption spectrum was determined by Dr. G. H. Beaven using a Beckman photo-electric quartz spectrophotometer and hot-cathode hydrogen discharge. Thanks are expressed to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries Limited for grants, and to Professor R. G. W. Norrish, F.R.S., who kindly put at our disposal the ultra-violet polarimeter.

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