CCCXXXIX.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXXII. The Resolution of Phenylbenzylcarbinol.*

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IN view of the marked alterations in rotatory power and rotatory dispersion which are effected when an aromatic nucleus is introduced into the molecule of an aliphatic secondary alcohol (compare *inter alia*, Part XXV, J., 1925, **127**, 1094), it seemed desirable to study the effect of the introduction of two aromatic nuclei into the molecule of an aliphatic secondary alcohol.

With this object in view, the optically active modifications of phenylbenzylcarbinol have been prepared and their optical properties examined. The noteworthy results of this investigation are as follows : The effect of temperature on the rotatory power of the alcohol is very marked (Table I), there being a ten-fold increase on cooling from 125° to 20°, and the specific rotatory power of this alcohol at 20° is the largest yet recorded for a secondary alcohol; at the same time the rotatory dispersion ratio $\alpha_{4358}/\alpha_{5461}$ changes from 2·57 at 125° to 1·79 at 20°. The effect of solvents on the rotatory power is also very pronounced (Table II), the value of $[\alpha]_{5461}^{25°}$ changing from $-11{\cdot}0°$ in pyridine solution to $+64{\cdot}1°$ in ethyl-alcoholic solution, whilst in benzene solution the rotatory dispersion is anomalous. When the values of the specific rotatory powers of the alcohol in the homogeneous state are plotted against the squares of the wave-lengths of light used, the resulting curve is non-linear.

The acetate of *l*-phenylbenzylcarbinol, which is dextrorotatory, increases in rotatory power with rise of temperature, the values being given in Table III.

Phenylbenzylcarbinol has already been obtained in an optically active condition by Levene (*J. Biol. Chem.*, 1925, **65**, 507) by the method herein described, but the rotatory power obtained ($[\alpha]_D^{20°}$ $+ 18{\cdot}54°$) indicates that the resolution was incomplete.

EXPERIMENTAL.

Phenylbenzylcarbinol was prepared by adding an ethereal solution of benzaldehyde (96 g.) to a vigorously stirred and ice-cold ethereal solution of benzyl magnesium chloride, prepared from 126 g. of benzyl chloride, and working up the product in the usual way. The crude carbinol (m. p. 61°) was purified by crystallisation from light petroleum containing 5% of benzene, being thus obtained as white needles, m. p. 67°, b. p. 177°/15 mm.; yield 154 g., 78%.

Phenylbenzylcarbinyl hydrogen phthalate, prepared by heating a mixture of the carbinol (120 g.) and phthalic anhydride (90 g., previously crystallised from dry chloroform to remove traces of phthalic acid) at 120° for 24 hours and working up the product in the usual manner, was obtained (192 g., 91%), after crystallisation from a mixture of ether and light petroleum, in small needles, m. p. 131° (Found, by titration with NaOH: *M*, 347. Calc.: *M*, 346).

d-*Phenylbenzylcarbinyl Hydrogen Phthalate.*—Quinine (110 g.) was dissolved in a hot solution of *dl*-phenylbenzylcarbinyl hydrogen phthalate (100 g.) in acetone (200 c.c.), and the resulting *d*A,*l*B salt, which separated on standing, was removed by filtration and recrystallised four times from 1½ times its weight of ethyl alcohol, the rotatory power of the *d*-phenylbenzylcarbinyl hydrogen phthalate obtained from it by decomposition having then become constant. The pure *quinine* salt forms soft, silky needles, m. p. 205° (decomp.), which are too insoluble in cold solvents to allow of its rotatory power being determined; it was dissolved in the minimum amount of hot alcohol and the solution poured into a slight excess of dilute hydrochloric acid; the precipitated *d*-hydrogen phthalic ester, after washing and drying, was crystallised from acetic acid (40 c.c. of 90%) and subsequently from ether–light petroleum, being obtained as fine needles, m. p. 131°; yield 31 g., a further 7 g. being obtained by working up the mother-liquors: $[\alpha]_{D}^{25^\circ}$ $+32{\cdot}75^\circ$, $[\alpha]_{5461}^{25^\circ}$ $+38{\cdot}75^\circ$ ($c = 5{\cdot}0$, in ethyl alcohol, 99%).

l-*Phenylbenzylcarbinyl Hydrogen Phthalate.*—The partially active *l*-hydrogen phthalic ester (50 g.; $[\alpha]_{5461}^{25^\circ}$ $-30{\cdot}7^\circ$ in alcohol), obtained by the decomposition of the more soluble fractions of the quinine salt, was dissolved in methyl alcohol (150 c.c.) and the hot solution mixed with cinchonine (42·5 g.). The *l*A,*d*B salt, which separated from the solution on standing, after four recrystallisations from methyl alcohol containing 10% of acetone reached constancy of m. p., 110°, and of rotatory power, $[\alpha]_{5461}^{25^\circ}$ $+82{\cdot}3^\circ$ ($c = 4{\cdot}90$ in ethyl alcohol). The pure *cinchonine* salt was dissolved in hot alcohol and decomposition effected as described above. The recrystallised *l*-phenylbenzylcarbinyl hydrogen phthalate has m. p. 131° and $[\alpha]_{5461}^{25^\circ}$ $-38{\cdot}80^\circ$ ($c = 5{\cdot}00$ in ethyl alcohol); yield 31 g.

d- *and* l-*Phenylbenzylcarbinols.*—The free carbinols were obtained by gently boiling for 15 minutes the respective hydrogen phthalic esters with a slight excess of dilute aqueous sodium hydroxide. The liberated alcohols were extracted with ether and subsequently crystallised from ether–light petroleum; they each have m. p. 67°. Their rotatory powers are given in Table I.

l-*Phenylbenzylcarbinyl acetate* (l-αβ-*diphenylethyl acetate*), prepared by the slow addition of acetyl chloride (3 g.) to a solution of *l*-phenylbenzylcarbinol (6 g.) in dry pyridine (15 c.c.), was obtained as a colourless oil (6·3 g.), b. p. 182°/15 mm. (Found, by hydrolysis with alcoholic potassium hydroxide: *M*, 241. $C_{16}H_{16}O_2$ requires *M*, 240); $[\alpha]_{5461}^{17^\circ}$ + 28·00°.

TABLE I.

Specific rotatory powers of *d*-phenylbenzylcarbinol in the homogeneous state at different temperatures.

	$[\alpha]_\lambda^{t^\circ}$.					
t.	4358.	5461.	5780.	5893.	6708.	$\frac{\alpha_{4358}}{\alpha_{5461}}$.
125°	+16·70°	+ 6·51°	+ 5·22°	+ 5·03°	+ 3·41°	2·569
115	20·59	8·68	7·21	6·70	4·98	2·373
100	28·65	12·92	11·18	10·30	7·42	2·217
90	35·00	16·57	14·38	13·39	10·32	2·112
80	41·61	20·40	17·68	16·80	12·85	2·039
70	51·00	25·40	22·12	20·64	16·06	2·007
60	61·90	31·82	27·88	26·11	20·20	1·945
By extrapolation :						
20	120·2	67·1	—	—	—	1·79

TABLE II.

(*a*) Specific rotatory powers of *d*-phenylbenzylcarbinol in various solvents ($c = 5·00$).

	$[\alpha]_\lambda^{25^\circ}$.					
Solvent.	4358.	5461.	5780.	5893.	6708.	$\frac{\alpha_{4358}}{\alpha_{5461}}$.
Pyridine	− 14·15°	−11·00°	−10·20°	− 9·81°	− 8·45°	1·28
Chloroform	− 12·02	− 9·71	− 9·10	− 8·50	− 7·65	1·24
Carbon disulphide	− 9·00	− 8·15	− 7·50	− 7·20	− 6·45	1·11
Benzene	− 0·20	− 3·00	− 3·00	− 3·00	− 3·00	0·07
Carbon tetrachloride	+ 6·90	+ 1·0	+ 0·6	+ 0·5	+ 0·2	6·9
Acetone	+ 44·63	+22·10	+19·1	+17·8	+13·7	2·19
Ethyl alcohol ...	+120·8	+64·09	+55·3	+52·8	+38·7	1·88
Ethyl alcohol (*l*-carbinol)	—	−64·04				
Ethyl alcohol (at 17°)	+126·8	+65·4	+57·2	—	—	1·93

(*b*) Specific rotatory powers of *d*-phenylbenzylcarbinyl hydrogen phthalate in various solvents ($c = 5·00$).

Acetone	+32·8°	+14·71°	+12·50°	+12·01°	+11·00°	—
Benzene	− 9·71	− 9·1	− 9·0	− 8·9	− 7·7	—
Chloroform	− 5·3	− 5·1	− 4·7	− 4·6	− 4·3	—
Ethyl alcohol ...	+38·75	—	—	+32·75	—	—
Ethyl alcohol (*l*-ester)	−38·80	—	—	—	—	—

TABLE III.

Specific rotatory powers of the acetate of *l*-phenylbenzylcarbinol in the homogeneous state at different temperatures.

	$[\alpha]_{\lambda}^{t^{\circ}}$.					
t.	4358.	5461.	5780.	5893.	6708.	$\frac{\alpha_{4358}}{\alpha_{5461}}$.
130°	+78·18°	+43·81°	+38·46°	+36·86°	+27·82°	1·784
120	76·54	43·09	37·92	36·18	26·66	1·776
110	74·94	42·02	37·26	35·38	26·31	1·776
90	70·98	40·33	35·62	34·49	25·25	1·760
80	66·43	38·06	33·22	31·81	23·85	1·745
50	59·75	35·15	30·28	29·00	22·02	1·698
30	52·24	31·09	27·07	25·65	19·61	1·680
17	47·12	28·00	24·52	23·51	17·69	1·682

The specific rotatory power of this ester determined at 17° was found to be unchanged after the above data had been obtained. A portion of the ester was hydrolysed and the resulting carbinol possessed a rotatory power identical with that of the carbinol from which the ester was prepared. It is thus evident that no racemisation had taken place during either the esterification or the subsequent heating of the ester.

Determination of Densities.—

d-Phenylbenzylcarbinol: $d_4^{t^{\circ}}$ = 1·0358 at 70°, 1·0251 at 86°, 1·0210 at 92°, 1·0152 at 100°, 1·0095 at 110°, 1·0031 at 120°.

l-Phenylbenzylcarbinyl acetate: $d_4^{t^{\circ}}$ = 1·0831 at 17°, 1·0723 at 30°, 1·0552 at 50°, 1·0380 at 70°, 1·0214 at 90°, 1·0041 at 110°, 0·9958 at 120°, 0·9870 at 130°.

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