CCLXXXVIII.—*The Preparation of the Optically Active Phenylmethylcarbinols.*

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SOME years ago, Pickard and Kenyon (J., 1911, **99**, 45) obtained *d*-phenylmethylcarbinol by the fractional crystallisation of the brucine salt of its acid succinic ester, but were unable to prepare the corresponding *l*-alcohol. *l*-Phenylmethylcarbinol was prepared by the crystallisation of the brucine salt of its acid phthalic ester by Ott (*Ber.*, 1928, **61**, 2139), but it was not optically pure, since its rotatory power, $[\alpha]_{5893}^{19^\circ} - 40{\cdot}95^\circ$, was less than that, $[\alpha]_{5893}^{20^\circ} + 42{\cdot}86^\circ$, of the product obtained by Pickard and Kenyon. As considerable quantities of the optically pure alcohol were required for another investigation, further attempts have been made to prepare the pure *d*- and *l*-varieties of this alcohol, which are herein described.

The results of the experiments show that by the crystallisation of the brucine salt of the hydrogen phthalic ester of phenylmethylcarbinol it is possible to prepare the *l*-alcohol rapidly and in reasonably large quantities. The *d*-alcohol can be obtained only in small quantity by the method now described, but it is suggested that an alternative procedure is available for the preparation of this isomeride in large quantities from the mother-liquors containing the more soluble brucine salt. By the recovery of the hydrogen phthalic ester and treatment with carbon disulphide, its rotatory power may be considerably enhanced. This procedure yields a hydrogen phthalic ester of fairly high rotatory power in good quantity. The *d* + *dl*-alcohol obtained by the hydrolysis of this ester may be used as the starting point in the preparation of optically pure *d*-alcohol by the succinate method of Pickard and Kenyon (*loc. cit.*).

EXPERIMENTAL.

Phenylmethylcarbinol was obtained in 76% yield by the interaction of magnesium methyl bromide and 70% of the theoretical quantity of benzaldehyde (Marshall, J., 1915, **107**, 509). The magnesium methyl bromide was prepared by passing methyl bromide vapour (1 mol.) into ether, covering magnesium (1 mol.). The carbinol obtained was converted into its acid phthalic ester by heating it with a solution of phthalic anhydride (1 mol.) in dry pyridine (1 mol.) on the steam-bath for 2 hours. The *dl*-phenylmethylcarbinyl hydrogen phthalate separated from acetic acid or benzene in leaflets, m. p. 108°; yield, 85% (0·2594 g., dissolved in alcohol, required for neutralisation 9·7 c.c. of *N*/10-sodium hydroxide. Calc., 9·6 c.c.). The brucine salt of the hydrogen phthalic ester crystallised readily from acetone. The brucine salts of the two isomerides differed only slightly in solubility in cold acetone, but showed a mark difference in hot acetone. The brucine salt was therefore treated with hot acetone insufficient in amount to dissolve it completely, the hot solution filtered, and the undissolved salt washed with successive portions of boiling acetone. After this operation had been repeated 8—10 times, the sparingly soluble brucine salt remaining, m. p. 152° (decomp.), had $[\alpha]_{5461}^{17^\circ}$ − 45·7° in acetone ($c = 5{\cdot}100$, $l = 2$) and $[\alpha]_{5461}^{18^\circ}$ − 47·7° in chloroform ($c = 5{\cdot}085$, $l = 2$). On decomposition, this brucine salt yielded the hydrogen phthalic ester as an oil, which had $\alpha_{5461}^{15^\circ}$ −3·51° ($l = 0{\cdot}25$) in the homogeneous state. After several months, the oil set to a mass of needles which had m. p. 81—82° and $[\alpha]_{5461}^{20^\circ}$ + 39·8° in ethyl alcohol ($c = 5{\cdot}1220$, $l = 2$), $[\alpha]_{5461}^{20^\circ}$ − 59·7° in carbon disulphide ($c = 8{\cdot}4800$, $l = 2$), and $[\alpha]_{5461}^{20^\circ}$ + 1·23° in chloroform ($c = 6{\cdot}5100$, $l = 2$).

The alcohol, b. p. 93°/14 mm., obtained from the hydrogen phthalic ester by hydrolysis had $\alpha_{5461}^{18^\circ}$ — 13·27°, $\alpha_{5893}^{20^\circ}$ — 10·94°, and $\alpha_{4358}^{20^\circ}$ — 28·06° (all $l = 0{\cdot}25$).

By this procedure the *l*-alcohol may be obtained fairly rapidly in good yield, in comparatively few operations : *e.g.*, from 1·3 mols. of *dl*-phenylmethylcarbinyl hydrogen phthalate there was obtained 0·27 mol. of *l*-alcohol of maximum activity.

d-*Phenylmethylcarbinol*.—The mother-liquors from the less soluble brucine salt were concentrated and seeded with a crystal of the brucine salt of *d*-phenylmethylcarbinyl hydrogen phthalate. The crop of crystals obtained, after crystallising four times from acetone, had m. p. 85° and yielded a hydrogen phthalic ester with $[\alpha]_{5461}^{20^\circ}$ — 28° in ethyl-alcoholic solution. On further crystallisation (6—8 times) from acetone, there was obtained a small quantity of the brucine salt with m. p. 107° (decomp.), $[\alpha]_{5461}^{22^\circ}$ — 29·7° in ethyl alcohol ($c = 5{\cdot}0500$, $l = 2$). The hydrogen phthalic ester obtained from this salt solidified to a white crystalline mass, m. p. 81—82°, which had $[\alpha]_{5461}^{24^\circ}$ — 40·7° in ethyl alcohol ($c = 3{\cdot}010$, $l = 2$).

Some difficulty was experienced with these crystallisations, since the salt in the first stages was easily soluble in acetone, and in the later stages tended to crystallise in either of two forms, depending on the temperature. If allowed to crystallise over-night at room temperature, the salt was produced in hard masses, m. p. 107°, whereas if it was cooled in ice and crystallised rapidly, light powdery crystals were formed containing acetone of crystallisation, m. p. 100—101° (decomp.). 1 G., kept in an air-oven at 90° until its weight was constant (3 hours), lost 0·079 g., *i.e.*, 7·9%, corresponding to 1 mol. of acetone of crystallisation.

Further portions of the fully active brucine salt could be obtained by decomposing the first mother-liquors from the crystallisations, which yielded the hydrogen phthalic ester as an oil. The activity of this could be easily and rapidly increased by treatment with dry carbon disulphide, in which the *dl*-ester is practically insoluble and the *d*- (or *l*-) ester is easily soluble. Thus, 25 g. of *l* + *dl*-ester ($[\alpha]_{5461}^{18^\circ}$ — 9·2° in ethyl alcohol), treated with 500 c.c. of carbon disulphide, deposited about 15 g. of the *dl*-ester, and from the mother-liquor, approx. 10 g. of *l* + *dl*-ester were obtained as an oil, with $[\alpha]_{5461}^{18^\circ}$ — 23·7° in ethyl alcohol. This ester, on conversion into brucine salt and recrystallisation as described, was obtained with maximum activity.

On hydrolysis of the hydrogen phthalic ester ($[\alpha]_{5461}^{24^\circ}$ — 40·7°) *d*-phenylmethylcarbinol was obtained, b. p. 98—99°/20 mm., with, $\alpha_{5461}^{19^\circ}$ + 13·02° and $\alpha_{5893}^{19^\circ}$ + 10·87° ($l = 0{\cdot}25$), whence $[\alpha]_{5461}^{19^\circ}$ + 51·36° and $[\alpha]_{5893}^{19^\circ}$ + 42·88°.

It is interesting to compare some of these data with those derived from the closely similar methyl-*n*-hexyl- and methyl-*cyclo*hexyl-carbinols.

	Methylcarbinol.		
	n-Hexyl.	*cyclo*Hexyl.	Phenyl.
d-Alcohol (homog.), $[\alpha]_{5461}^{20^\circ}$	$+10{\cdot}39^\circ$	$+\ 7{\cdot}23^\circ$	$+51{\cdot}36^\circ$
d-Hydrogen phthalic ester in ethyl alcohol ($c = 5$), $[\alpha]_{5461}^{20^\circ}$	$+58{\cdot}5$	$+66{\cdot}8$	$-40{\cdot}7$
M. p. of *dl*-ester	55	140	108
M. p. of *d*- or *l*-ester	75	75	81—82

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