CCCII.—*A Simplified Method for the Resolution of Methyl*-n-*hexylcarbinol.*

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SOME years ago a method of resolving *sec.*-octyl alcohol (methyl-*n*-hexylcarbinol) into its optically active forms was described by Pickard and Kenyon (T., 1907, **91**, 2058) which may be briefly described as follows : The alcohol is converted into its hydrogen phthalic ester by heating with phthalic anhydride and this in turn is converted into its brucine salt, which is fractionally crystallised from acetone until constant rotation is reached. By this means, the optically pure, dextrorotatory form of the hydrogen phthalic ester is obtained and this on hydrolysis yields the optically pure dextro-alcohol. The more soluble portions of the brucine salt are decomposed, when a hydrogen phthalic ester of fairly high lævo-rotation is obtained; this is combined with cinchonidine, and the cinchonidine salt crystallised from acetone until optical purity is reached. In this way, the optically pure lævo-alcohol is obtained.

This method of resolving *sec.*-octyl alcohol works quite smoothly and gives good results, but it suffers from two drawbacks which become considerable when relatively large amounts of material are employed; in the first place, the solubility in acetone of the brucine salt of *d*-*sec.*-octyl hydrogen phthalate is very much less than that of the corresponding *dl*- or *l*-compound, and although this has the great advantage of giving a very sharp separation of the *d*- and the *l*-isomerides, yet it has the inevitable drawback from the practical point of view of requiring the employment of large volumes of acetone, this having proved itself by far the most useful of the commoner solvents for this purpose. The second drawback arises from a cause of an opposite character; the solubility of the cinchonidine salt of *l*-*sec.*-octyl hydrogen phthalate is not considerably less than that of the *dl*-form, and consequently the separation of the optically pure *l*-form of the hydrogen phthalate requires a larger number of crystallisations of the cinchonidine salt, and the proportion obtained is also much less than is the case with the brucine salt.

As fairly large quantities of the optically pure forms of *sec.*-octyl alcohol were required in the course of some work, experiments were initiated with the view of increasing the convenience and, if possible, the efficiency of the method outlined above, and the following results have been obtained.

It has been found that the optically active modifications of *sec.*-octyl hydrogen phthalate are much less soluble in acetic acid than the inactive modification, and that, in consequence, the crystallisation of a partly resolved sample rapidly gives the optically pure form of *sec.*-octyl hydrogen phthalate.

The procedure can perhaps be most concisely described by giving the details of an actual experiment, and this is done in the experimental portion of this paper. It will be seen that the employment of large volumes of acetone is avoided and the use of cinchonidine dispensed with altogether. In addition, the actual labour involved is probably only about one-tenth of that required by the original method, and the saving of time correspondingly great.

As the conversion of *sec.*-octyl alcohol into its hydrogen phthalic ester and its regeneration from this by hydrolysis are both almost quantitative reactions, it will be seen that the optically active *sec.*-octyl alcohols become substances which are readily available in considerable amounts.

EXPERIMENTAL.

To a warm solution of *sec.*-octyl hydrogen phthalate (278 grams) in acetone (600 c.c.) is added brucine (394 grams), and the mixture warmed until solution is complete. After cooling, the crystals of brucine salt (A) are filtered off, pressed, and washed in the funnel with acetone (250 c.c.) to remove adhering mother-liquor. The combined filtrate and washings are concentrated to about half bulk and poured into dilute hydrochloric acid, when the hydrogen phthalic ester separates as an oil which quickly sets to a crystalline mass. It is filtered off, washed with cold water, and spread on porous plate. It is not necessary to dry the product, but if this is done, it is found that its weight is approximately one-half of that of the hydrogen phthalate originally taken, and that it has the rotation in 5 per cent. solution in absolute alcohol of $[\alpha]_{5461}$ − 47°.

The crystals A are dissolved in the minimum amount of hot ethyl alcohol and decomposed by pouring the solution into dilute hydrochloric acid. The weight of hydrogen phthalic ester obtained is about half of that originally taken and its rotation is about $[\alpha]_{5461} + 47°$.

These two lots of partly active *sec.*-octyl hydrogen phthalate are now separately crystallised twice from acetic acid (about twice their weight of 90 per cent. acetic acid being required for solution in each case), when they are obtained in an optically pure condition and possess the rotations $[\alpha]_{5461} - 58{\cdot}5°$ and $[\alpha]_{5461} + 58{\cdot}3°$, respectively.

The amount of pure product obtained in each case was, respectively, 99 grams and 96 grams, corresponding to a yield of 70 per cent. of that theoretically possible.

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