

457. The Resolution of Methylisobutylcarbinol.

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Dextrorotatory methylisobutylcarbinol, in an optically pure form and in good yield, can be conveniently obtained from the commercially available (\pm)-carbinol.

IN order to increase the relatively small number of organic compounds of simple structure which can be conveniently prepared in an optically pure condition in amounts suitable for experimental investigations, we have examined the resolution of methylisobutylcarbinol (4-methylpentan-2-ol) which has recently become commercially available at low cost.

The resolution of this alcohol was described by Pickard and Kenyon (*J.*, 1911, **99**, 45), but as the description of procedure is far too brief we have given it with the added necessary details in the experimental section of this communication.

Two crystallisations of the brucine salt of methylisobutylcarbiny hydrogen phthalate are sufficient to yield the optically pure (+)-carbinol, but we were unable, as were Pickard and Kenyon (*loc. cit.*), to prepare a second alkaloidal salt of this ester, which would effect the separation of optically pure (–)-methylisobutylcarbinol.

Since Pickard and Kenyon (*loc. cit.*) found that fractional crystallisation of the brucine and the cinchonidine salt of the hydrogen succinate yielded respectively the (–)- and the (+)-carbinol, the rotatory powers of which were equal in magnitude and almost identical with that of the (+)-carbinol prepared by the method herein described, it seems highly probable that optical purity has been attained.

Observed Rotatory Powers of (+)-Methylisobutylcarbinol for Various Wave-lengths
(l , 2.00; t , 19.5°).

λ , A.	6438	5893	5461	5086	4800	4678	4358	4078
α	+28.29°	+34.22°	+40.27°	+46.77°	+52.97°	+56.12°	+65.48°	+76.3°

The values of λ^2 , plotted against $1/\alpha$, lie on a straight line.

It is interesting to record that a specimen of (–)-methylisobutylcarbinol which had $[\alpha]_{5893}^{17}$ –20.80° when prepared in 1909 had $[\alpha]_{5893}^{17}$ –19.54° after being kept in a stoppered bottle for 40 years.

EXPERIMENTAL.

Commercial methylisobutylcarbinol was dried (K_2CO_3) and distilled through a 6-inch column; it distilled almost completely at 130.5–131°.

(\pm)-Methylisobutylcarbiny Hydrogen Phthalate.—A mixture of the alcohol (112 g.), phthalic anhydride (163 g.), and pyridine (88 g.) was heated on the steam-bath until it became homogeneous. Next day the resultant oil was dissolved in acetone (300 c.c.) and mixed with dilute hydrochloric acid (140 c.c. of concentrated acid plus 140 c.c. of ice and water), the whole being well stirred. The solution was then diluted with ice and water (3–4 l.) until the oily hydrogen phthalate was completely precipitated. The mixture was set aside for 2 days with occasional stirring, during which time the aqueous layer was twice decanted and replaced by water to which hydrochloric acid (10 c.c.) had been added. The solidified acid ester was dissolved in aqueous sodium carbonate, and the solution extracted with ether to remove a little unesterified carbinol. The aqueous layer was acidified with hydrochloric acid, and the liberated acid ester extracted with ether. The ethereal extract was washed 12 times with dilute hydrochloric acid to ensure complete removal of pyridine.

Evaporation of the dried ethereal solution yielded (\pm)-methylisobutylcarbiny hydrogen phthalate (255 g., 93%) as an oil which readily set to a hard crystalline mass when inoculated. A "seed" was obtained by placing a little of the oil, contained in a vacuum desiccator, in a refrigerator overnight. It melts at 43–44° and is too soluble in the usual solvents for convenient recrystallisation. Unless the method of purification, outlined above, is followed, the compound will not crystallise.

(+)-Methylisobutylcarbiny Hydrogen Phthalate.—Brucine (466 g. of the tetrahydrate) was added quickly to a hot solution of the (\pm)-ester (250 g.) in acetone (3.1 l.). On cooling, a crop (*A*) of crystalline brucine salt readily separated. This after one recrystallisation from acetone yielded crop (*B*) (191 g.) of optically pure brucine salt of (+)-methylisobutylcarbiny hydrogen phthalate, m. p. 167–168°. By concentration of the mother-liquor from crop (*B*) and recrystallisation of the salt which separated, a further 36 g. of pure brucine salt were obtained.

The brucine salt (226 g.) was decomposed by adding it to a mechanically stirred mixture of acetone (350 c.c.), water (200 c.c.), and concentrated hydrochloric acid (55 c.c.). The resultant product was diluted with water (3 l.), whereupon the brucine hydrochloride dissolved and the acid ester separated as an oil. This (83.5 g., 67%) was removed by means of ether and crystallised rapidly when inoculated with the (\pm)-ester; it had m. p. 44.5–46°, was too soluble for recrystallisation, and had $[\alpha]_{5893}^{20}$ +51.01° and $[\alpha]_{5461}^{20}$ +61.72° (c , 5.000; l , 2 in chloroform).

(+)-Methylisobutylcarbinol.—A current of steam was passed through a solution of the (+)-acid ester (82.4 g.) and potassium hydroxide (46 g.) in water (200 c.c.). The steam distillate yielded (+)-methylisobutylcarbinol (28.1 g.), b. p. 63–64°/45 mm., $d_4^{19.5}$ 0.8075, $\alpha_{5893}^{19.5}$ +34.22° (l , 2).

(–)-Methylisobutylcarbinol. The filtrate left after removal of crop (*A*) of the brucine salt was

concentrated to *ca.* 700 c.c. and mixed with concentrated hydrochloric acid (80 c.c.) and ice-water (160 c.c.), and the product, after dilution with water (3 l.), extracted with ether. The resultant hydrogen phthalate (140.5 g.) had $[\alpha]_{5893}^{19.5} -31.2^\circ$ in chloroform and, when hydrolysed with potassium hydroxide (79 g.), yielded the partly resolved carbinol (45.7 g.), b. p. 64—65°/45 mm., $\alpha_{5893}^{19.5} -20.95^\circ$ (*l*, *2*).

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