Optically Active α-(2-Naphthyl)-ethylamine as Resolving Base

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The number of bases available for optical resolution of racemic acids is rather restricted. To be suitable for this purpose, a base must be optically active, chemically stable and not too expensive. In addition, its salts must have good crystallisation properties. About ten commercially available natural alkaloids fulfil these conditions. A few synthetic bases, *e. g.* α-phenylethylamine and α-phenyl*iso*propylamine [1] (benzedrine), for which both antipodes are available, have also been used with good success. In recent years, quaternary alkaloid salts [2] and *iso*thiuronium salts [3] have been recommended, especially for weak acids. The purpose of this paper is to draw attention to α-(1-naphthyl)-ethylamine and α-(2-naphthyl)-ethylamine, especially to the latter compound.

The synthesis and resolution of these bases were first described by Samuelsson in 1923 [4]. The preparation of the methyl naphthyl ketones used as starting materials was, however, very tedious in those days and to our knowledge the amines have not found practical use for stereochemical purposes. For some years the ketones have been commercially available and the optically active bases are now as easily accessible as the active phenylethylamines. The salts of the 2-naphthyl derivative especially crystallise very readily and we have found this base suitable for the resolution of several acids, *e. g.* terpenylic acid and α-(2-thianaphthenyl)-propionic acid. For the resolution of the latter acid, ten different bases were tried but only α-(2-naphthyl)-ethylamine yielded the levorotatory acid [5]. In the case of terpenylic acid, this amine had far better resolving power than any other base tried [6].

The resolution of the racemic α-(2-naphthyl)-ethylamine was carried out according to the method of Samuelsson. We have found, however, that a slight modification in the amount of solvent is advisable to ensure the best resolution. A brief description is given here; for details the original paper of Samuelsson should be consulted.

Experimental. Racemic α-(2-naphthyl)-ethylamine was prepared according to Organic Reactions [7].

Resolution. A mixture of 128.4 g (0.075 mole) of the racemic amine and 112.6 g (0.075 mole) of tartaric acid is dissolved in 5.0 l of hot water. After standing at room temperature over-night, the crystals are filtered off. This procedure gives about 120 g salt of the (+)-amine. The base is liberated with dilute sodium hydroxide and taken up in ether. The ether solution is transferred to a 5-l beaker and 95 ml (0.19 mole) of 2 M sulphuric acid is added with vigorous stirring. The salt obtained is recrystallised twice from the necessary amount of boiling water, yielding the sulphate of the pure (+)-amine with the composition $(C_{12}H_{13}N)_2 \cdot H_2SO_4 \cdot 2H_2O$ and the m. p. 261—263°.

From the mother liquor after the first crystallisation of the tartrate the partially resolved (—)-amine is liberated and treated in the same way.

The yield of each antipode is 50—60 % of the theoretical.

The amines are best stored as sulphates. The free bases have the m. p. 53° and $[\alpha]_D = \pm 19°$ (in ethanol solution).

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