48. *The Separation of β-Picoline, γ-Picoline, and 2 : 6-Lutidine from their Mixture.*

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These three bases have been separated as β- and γ-picoline oxalates (from alcohol) and 2 : 6-lutidine monomercurichloride (from water) in satisfactory yields.

The methods available for the preparation of β-picoline, γ-picoline, and 2 : 6-lutidine from the " β-picoline " fraction of coal tar bases (b. p. 140—145°) mostly depend on the crystallisation of complex salts; the crystallisation of dimercurichlorides and/or zincichlorides from alcohol is normally employed (*e.g.*, Flaschner, J., 1909, **95**, 669; Constam and White, *Amer. Chem. J.*, 1903, **29**, 4; Meisenheimer, *Annalen*, 1920, **420**, 192, 197; Heap, Jones, and Speakman, *J. Amer. Chem. Soc.*, 1921, **43**, 1936). 2 : 6-Lutidine has, however, been separated as hydrobromide (Marcuse and Wolfenstein, *Ber.*, 1899, **32**, 2526) and as the hydrochloride *via* the ferrocyanide (Koenigs and Happe, *Ber.*, 1903, **36**, 2907). In the absence of β-picoline, γ-picoline may be obtained by removal of the 2 : 6-lutidine with benzaldehyde and zinc chloride (Bailey and McElvain, *J. Amer. Chem. Soc.*, 1930, **52**, 1633). All these methods, except the last, which is of limited application, are very laborious and uneconomical.

An expeditious method of separation, giving satisfactory yields, has now been worked out. The bases are converted into oxalates and these are crystallised from alcohol; 2 : 6-lutidine remains in the initial mother-liquor and is subsequently separated as the monomercurichloride (Garrett and Smythe, J., 1902, **81**, 454) from dilute hydrochloric acid. γ-Picoline oxalate (m. p. 137—138°) is readily obtained and contains base and acid in the ratio of 4 : 5; β-picoline oxalate (m. p. 119—121°), with a ratio of base to acid of 2 : 3, separates from the mother-liquor somewhat less readily. The rather less satisfactory separation of the β-picoline oxalate is probably due to some esterification of the oxalic acid, as the mother-liquor on repeated evaporation (under reduced pressure) becomes syrupy.

EXPERIMENTAL.

" β-Picoline " was obtained from crude pyridine bases (b. p. 90—155°) supplied by the South Eastern Tar Distillers Ltd. of Tonbridge. These were fractionated through a Vigreux column (1 m. × 2 cm.) until further fractionation no longer changed the size of the fractions; from 1 gallon there were obtained 1900 c.c. of pyridine, b. p. 115—116°, 600 c.c. of α-picoline, b. p. 128—129°, 850 c.c. of " β-picoline," b. p. 142—144°, 550 c.c. of 2 : 4-lutidine, b. p. 155—156°, 400 c.c. of residue, b. p. above 170°, together with about 100 c.c. of total intermediate fractions.

β- and γ-Picoline.—100 C.c. of the " β-picoline " fraction were warmed to 80°, 110 g. of commercial anhydrous oxalic acid added during 10 minutes, and 150 c.c. of boiling absolute alcohol then stirred in. The crystalline mass deposited on cooling was washed with a little alcohol, the filtrate and washing being reserved for the preparation of 2 : 6-lutidine. The precipitated oxalates were twice crystallised from absolute alcohol (solid added to boiling alcohol) without filtration; a third crystallisation, the hot solution being filtered (pump), afforded γ-picoline oxalate in large colourless plates of constant m. p. 137—138°. Evaporation of the mother-liquors under diminished pressure gave a mixture of β- and γ-picoline oxalates, which was further crystallised. From the more concentrated mother-liquors pure β-picoline oxalate separated in small colourless prisms, m. p. 119—121° (constant) after recrystallisation from alcohol. Several evaporations caused the mother-liquors to become too syrupy to deposit further crystals; from these the bases were recovered (see below) and returned for oxalate separation. The use of hydrated oxalic acid, treatment of batches larger than 100 g. at a time, and heating solutions for more than the minimum time necessary, seriously diminished the yields. Both oxalates were very readily soluble in cold water and somewhat soluble in cold alcohol, γ-picoline oxalate being the less soluble.

The bases were obtained from the oxalates by solution in the minimum quantity of water and distillation with an excess of 50% potassium hydroxide solution; the distillate was dehydrated with solid potassium hydroxide and distilled. β-Picoline boiled at 144·0°/760 mm. (corr.), and γ-picoline at 144·6°/760 mm. (corr.). Recovery of the bases was 95—97% of the theoretical with 100 g. batches of oxalate.

The constant-boiling mixtures of the bases and water had the following boiling points: β-picoline and water, b. p. 96·8°/760 mm. (corr.), and γ-picoline and water, b. p. 97·2°/760 mm. (corr.).

Recovery of bases from oxalate mother-liquors was effected by distilling off as much alcohol as possible under diminished pressure, diluting the residue with an equal volume of dilute hydrochloric acid, and distilling off the rest of the alcohol under diminished pressure. The residue was cautiously basified with 30% sodium hydroxide solution, and the base separated by steam-distillation. The distillate was fractionated through a 50 cm. Vigreux column; the constant-boiling mixture of bases with water was separated easily from the excess of water and dehydrated with potassium hydroxide, and the bases distilled.

Identification and Analysis of Oxalates.—The base, prepared from its oxalate, was converted into (*a*) the dimercurichloride, (*b*) the picrate, and (*c*) the corresponding acid by oxidation with calcium permanganate: these derivatives were identified by their m. p. Analysis was accomplished by distilling 5 g. of the oxalate with 10 c.c. of water and 12 c.c. of 50% potassium hydroxide solution and determining the base in the distillate by titration with N-sulphuric acid with ferric chloride as indicator, and the oxalate in the still residue after acidification by titration with potassium permanganate.

The oxalate, m. p. 119—121°, gave a dimercurichloride, m. p. 147°, picrate, m. p. 148—149°, and acid by oxidation, m. p. 234° agreeing with those recorded in the literature for the derivatives of β-picoline (Found: base : acid = 2 : 3).

The oxalate, m. p. 137—138°, gave a dimercurichloride, m. p. 129—130°, picrate, m. p. 165°, and acid by oxidation, m. p. 315°, agreeing with those recorded in the literature for the derivatives of γ-picoline (Found: base : acid = 4 : 5).

2 : 6-*Lutidine.*—This was separated from the initial mother-liquors from the preparation of the oxalates. The recovered constant-boiling mixture with water was used without dehydration; 200 c.c. of this were mixed with 100 c.c. of concentrated hydrochloric acid and 150 c.c. of water and added to a solution of 200 g. of mercuric chloride in 1 l. of boiling water. On cooling, 2 : 6-lutidine monomercurichloride separated; after recrystallisation from water containing 2% of its volume of concentrated hydrochloric acid, it melted at 187—188°. Further quantities were obtained by concentrating the mother-liquors and recrystallising the products. The base was obtained by steam-distillation with an excess of 30% sodium hydroxide solution; the constant-boiling mixture [b. p. 95·6°/760 mm. (corr.)] was separated by fractionation and dehydrated with potassium hydroxide, and the base distilled, b. p. 144·4°/760 mm. (corr.).

Recovery of bases from the mercurichloride mother-liquors was effected by evaporating these to a small bulk, decomposing the salts cautiously with excess of 30% sodium hydroxide, and steam-distilling and isolating the bases as in the case of 2 : 6-lutidine. The recovered bases were returned for oxalate separation.

From 700 c.c. of the " β-picoline " fraction there were obtained 158 g. of γ-picoline, 71 g. of β-picoline, 267 g. of 2 : 6-lutidine, and 100 g. of recovered bases (mostly β-picoline).

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