CXXII.—*The Preparation of Secondary Alkylarylamines and their Purification.*

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The isolation of the pure secondary amine from the products of interaction of an alkyl halide and a primary arylamine can be economically and conveniently accomplished by the following process. The alkyl bromide is heated with an excess (usually $2\frac{1}{2}$—4 mols.) of the primary aromatic amine. The tendency for the alkyl halide to yield tertiary amine is thus repressed and the product consists almost entirely of the secondary amine and the excess of the primary amine combined with the hydrogen bromide liberated in the reaction. The separation of the primary and secondary amines is effected by Morgan's method (E.P. 102,834, 1916) depending on the formation of sparingly soluble additive compounds of zinc chloride and aniline or its homologues of the general formula $B_2,ZnCl_2$. The alkylanilines do not form compounds with zinc chloride in the presence of water (compare Reilly and Hickinbottom, J., 1920, **117**, 127).

It has now been found that the excess of aniline or *m*-xylidine can be completely precipitated by the addition of a 50% solution of zinc chloride to the mixture of amines liberated from the product of the reaction between the primary amine and the alkyl halide; the uncombined secondary amine is isolated by draining the precipitated zincichloride and extracting with light petroleum. The yield of secondary amines thus obtained from *n*-propyl, *iso*propyl, and *n*-butyl bromides was upwards of 70% of the theoretical, calculated on the weight of the alkyl halide; frequently it was of the order of 75—85%. Further purification to remove small quantities of tertiary amines consisted in converting the crude secondary amine into its hydrobromide and crystallising this from alcohol (for *n*-butylaniline hydrobromide, benzene is a better solvent). Another method, also employed for ethyl-, *n*-propyl-, and *iso*propyl-anilines, was to prepare the acetyl derivative, which after distillation and crystallisation yielded the pure secondary amine on hydrolysis.

The yield of *iso*butylaniline obtained by the method now described was always small (30—40%). This is due, in part at least, to the presence of *tert*.-butyl bromide in the *iso*butyl bromide. According to Michael, Scharf, and Voigt (*J. Amer. Chem. Soc.*, 1916, **38**, 653) this is a normal impurity in *iso*butyl bromide, and one very difficult to remove. It does not, however, affect the purity of the *iso*butylaniline, as the tertiary bromide yields butylene when warmed with aniline (compare Nef, *Annalen*, 1899, **309**, 164 .

EXPERIMENTAL.

n-*Propylaniline*.—Aniline (230 g.; 2½ mols.) was heated with *n*-propyl bromide (1 mol.) under reflux in a boiling water-bath for 5 hours, the product was rendered alkaline, and the amines were separated and treated with a solution of 150 g. of zinc chloride in 150 g. of water. The mixture, when cooled and stirred, was rapidly converted into a thick paste which, after 12 hours, was drained on a large Buchner funnel, washed with cold water, pressed to remove as much as possible of the water, and extracted several times with boiling light petroleum. The extracts were combined, washed with water and with dilute aqueous ammonia, and dried over potassium carbonate. Removal of the solvent left *n*-propylaniline, which was obtained almost pure after two distillations: yield, 94·5 g. (70%); b. p. 218—222°. A further quantity (10 g.), collected between 222° and 230°, contained an appreciable amount of the tertiary amine.

A very convenient method of preparing aceto-*n*-propylanilide consisted in distilling equal weights of the secondary amine and acetic anhydride: the distillate collected between 240° and 265° and once crystallised from light petroleum was pure aceto-*n*-propylanilide, m. p. 48—49°.

*iso*Propylaniline, b. p. 206—208° (yield, 73%), was prepared in the same way from aniline and *iso*propyl bromide and freed from traces of tertiary amine by conversion into its acetyl derivative, m. p. 42°, and subsequent hydrolysis.

n-*Butylaniline.*—Aniline (130 g.) and *n*-butyl bromide (70 g.), heated in a boiling water-bath for 3 hours, gave, after removal of the excess of aniline by Morgan's method, approximately pure *n*-butylaniline (57 g.; yield, 75%). After purification through the hydrobromide, the amine had b. p. 235—235·5°/744 mm. (yield, 38 g.; 50%). A further quantity was obtained by fractional crystallisation of the mother-liquor of the hydrobromide.

iso*Butylaniline.*—*iso*Butyl bromide (prepared by heating *iso*butyl alcohol with concentrated hydrobromic acid: it contained some *tert.*-butyl bromide) (120 g.) was heated with aniline (2½ mols.) in a boiling water-bath for 2 hours, and the excess of aniline subsequently removed as described above. The crude *iso*butylaniline gave the following fractions on distillation: 225°, 9 g.; 225—227°, 26 g.; 227—231°, 20 g.

Pure *iso*butylaniline was obtained by converting the crude product into hydrobromide by the addition of concentrated hydrobromic acid, crystallising the salt from absolute alcohol, and decomposing it with aqueous sodium hydroxide. The amine was characterised by its p-*toluenesulphonyl* derivative, which crystallised from alcohol in slender prismatic needles, m. p. 122—123° (Found: N, 4·7. $C_{17}H_{21}O_2NS$ requires N, 4·6%).

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