CCXXIX.—*Studies in the Naphthalene Series. Part I. The Methylation of α-Naphthylamine.*

By BASKER GOKHLÉ and FREDERICK ALFRED MASON.

THE importance of dimethylaniline in the chemistry and technology of dyes is well known, particularly for the production of malachite green, methyl violet 2B, colours of the triarylmethane, oxazine, and thiazine series, auramine O, and rhodamine.

As little or no use has been made in the colour industry of the analogous dimethyl-α-naphthylamine, the present investigation was undertaken to examine its method of preparation and possible uses in the production of dyes.

Dimethyl-α-naphthylamine was prepared first by Landshoff (*Ber.*, 1878, **11**, 638) by alkylating α-naphthylamine by means of methyl iodide and later by Hantzsch (*Ber.*, 1880, **13**, 2053) by heating α-naphthylamine hydrochloride and methyl alcohol under pressure at 180°. Although the latter method gave good yields in glass tubes, for the preparation of larger quantities it appeared to involve the use of an enamelled autoclave, which was not at the time available.

The alkylation has now been effected by means of α-naphthylamine sulphate and methyl alcohol in a steel autoclave. The walls of the autoclave were not attacked and some iron nails left in the vessel were later recovered with no loss in weight. The final yield of base amounted to 61% of the theoretical, but the product was contaminated by about 26% of α-naphthol, formed rather unexpectedly by hydrolysis of the dimethylamino-group, which is thus much less firmly attached to the naphthalene nucleus than it is to the benzene nucleus in dimethylaniline; and this is corroborated by the fact that *p*-nitrosodimethyl-α-naphthylamine is unstable whereas *p*-nitrosodimethylaniline is quite stable.

Small quantities (20—50 g.) of the base are conveniently prepared, in 70% yield, by the methylation of α-naphthylamine by means of methyl sulphate in an alkaline solution. Rodionow and Voedensky (*Compt. rend.*, 1929, **190**, 117), using methyl *p*-toluenesulphonate as an alkylating agent (compare D.R.-P. 112177), obtained a 90% yield of dimethyl-α-naphthylamine.

EXPERIMENTAL.

Preparation of Dimethyl-α-naphthylamine.—(1) *By Hantzsch's method.* α-Naphthylamine hydrochloride (15 g.) and dried methyl alcohol (15 c.c.) were heated for 8 hours at 180° in a sealed tube: 11 g. of the dimethyl derivative were obtained, b. p. 272—274°/

760 mm. Later the same process was carried out in an ordinary steel autoclave containing a loosely fitting porcelain liner : the best result was obtained on heating together well-dried α-naphthylamine hydrochloride (200 g.) and methyl alcohol (200 c.c.) at 180°/33 atms. for 8 hours. The product, freed from primary and secondary bases by means of acetic anhydride and fractionation, gave 158 g. of the tertiary base (yield, 80%).

(2) *By means of sulphuric acid and methyl alcohol.* Powdered and well-dried α-naphthylamine sulphate (100 g.) and methyl alcohol (100 c.c.) were heated in an autoclave at 180° for 8 hours. The liquid product after cooling was heated to drive off the excess of methyl alcohol, poured into water, just made alkaline with ammonia, and isolated and dried (with potassium carbonate) in ether : on distillation it gave α-naphthol as a colourless liquid up to about 160°/20 mm. ; above 160°, the product was chiefly dimethyl-α-naphthylamine. After further separation, there were obtained α-naphthol (13 g.) and dimethyl-α-naphthylamine (48 g.). The yield of tertiary base under different conditions varied from 30% to 65% of the theoretical.

(3) *By means of methyl sulphate.* Well-powdered α-naphthylamine (28·6 g. ; 1/5 g.-mol.) was stirred into water (150 c.c.), cooled in a freezing mixture, and sodium hydroxide (36 g., as 150 c.c. of 24% solution) and methyl sulphate (50 g.) were then added simultaneously during 2 hours, the mixture being kept just alkaline. After a further 4 hours' stirring, the liquid was nearly neutralised with hydrochloric acid, acetic anhydride (8 c.c.) added to acetylate any secondary base, and the product made alkaline with sodium hydroxide. The oil produced was extracted with ether and fractionated (yield, 24·8 g. ; 70·2%).

Attempts to improve the yield by increasing the proportion of methyl sulphate were unsuccessful.

COLLEGE OF TECHNOLOGY, MANCHESTER. [*Received, May 28th,* 1930.]