XI.—*The Rearrangement of the Alkylanilines.*

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WHEN an alkylaniline is heated in a sealed tube with hydrogen chloride (Hofmann and Martius, *Ber.*, 1871, 4, 742) or certain metal chlorides (Reilly and Hickinbottom, J., 1920, **117**, 103) migration of the alkyl group from nitrogen to the nucleus occurs. This change has been regarded by Reilly and Hickinbottom as a true isomerisation and by Beckmann and Correns (*Ber.*, 1922, 55, 852; compare also Howard and Derrick, *J. Amer. Chem. Soc.*, 1924, 46, 166) as consequent to dissociation of alkyl halide from the alkylaniline hydrochloride.

If the latter assumption is correct, the formation of *p*-aminoalkylbenzene should be diminished or prevented under conditions which favour the removal of alkyl halide. It is necessary to select the conditions so that side reactions may be either detected or eliminated.

The behaviour of ethylaniline and butylaniline on heating in presence of metal chlorides in open tubes has been examined. If the rearrangement is due to the intermediate formation of alkyl chloride, either through the presence of traces of water (compare Chapman, J., 1925, **127**, 2818),

$$\begin{aligned}2NHR{\cdot}C_6H_5 + CdCl_2 + H_2O &\longrightarrow 2RCl + 2C_6H_5{\cdot}NH_2 + CdO\\ &\longrightarrow 2R{\cdot}C_6H_4{\cdot}NH_2 + CdCl_2 + H_2O,\end{aligned}$$

or by exchange of halogen from metal to alkyl group, the product should contain a high proportion of aniline and a considerable quantity of metal or metal oxide. It is assumed that the reaction between the benzene nucleus and alkyl halide is not accelerated by metal chlorides. This assumption is supported by the observation that aluminium chloride or zinc chloride has no appreciable effect on the rearrangement of methylaniline hydrochloride (Beckmann and Correns, *loc. cit.*).

Butylaniline and ethylaniline, when heated in open tubes with the chloride of cobalt, cadmium, or manganese at 220—290°, gave *p*-aminobutyl- and *p*-aminoethyl-benzene, respectively. No alkyl chloride was detected during the reaction, and the yield of aniline was negligible. The rearrangement proceeded readily even when precautions were taken to exclude traces of moisture. When zinc chloride was used as a promoter, the principal product was *p*-aminoalkylbenzene; small quantities of aniline and more complex primary amines were also present.

To refute still further the view that the reaction may proceed according to the scheme given above, the behaviour of the alkylaniline hydrochlorides on being heated in open tubes was compared with that of the free secondary amines in presence of metal chlorides under similar conditions. Ethylaniline hydrochloride, heated at 220—290° in open tubes, gave chiefly aniline, but also a small quantity of another primary amine. Dry butylaniline hydrochloride under similar conditions yielded *p*-amino-*n*-butylbenzene. The presence of small quantities of volatile impurities in the hydrochloride resulted in the production of aniline and *n*-butyl chloride.

The isomerisation of alkylanilines may be effected also by heating them in open tubes with metal salts other than chlorides.

EXPERIMENTAL.

In most of the experiments the amine hydrochloride or the mixture of amine and metallic salt was heated to the required temperature in a long, vertical test-tube. The volatile products could be collected when desired.

The secondary amines were carefully freed from traces of primary and tertiary amines.

Rearrangement of Alkylanilines in Presence of Metal Chlorides.

(a) *Formation of* p-*Aminoethylbenzene from Ethylaniline.*—(1) *In presence of cobalt chloride.* Dry ethylaniline (15 g.) and anhydrous cobalt chloride (7 g.), heated at 240—270° for 12 hours in a tube fitted with phosphoric oxide guard-tubes, yielded a solid, bluish-green mass of *p*-aminoethylbenzene cobaltochloride mixed with a small quantity of unchanged secondary amine. The pure cobaltochloride separated from methyl alcohol as a bright blue, crystalline mass.

In other experiments the ethylaniline was dried over fused potassium hydroxide or phosphoric oxide and distilled on to anhydrous cobalt chloride in an apparatus open to the air only through a train of phosphoric oxide tubes. The rearrangement under these conditions proceeded readily.

When cobalt chloride was used as a promoter a varying quantity of a grey, magnetic powder remained when the reaction product was dissolved in methyl alcohol (Found: Co, 96·8%. Found in the powder from another experiment in which the materials had not been dried: Co, 93·0%).

(2) *In presence of zinc chloride.* Ethylaniline (40 g.) was heated with half its weight of fused zinc chloride in a long-necked flask at 210° for 8 hours and finally for 2 hours at 260°. The product, triturated with an aqueous solution of zinc chloride and freed from the uncombined amine by washing with ether, yielded the primary amines as zincichlorides. Distillation of the free primary amines, followed by fractional crystallisation of the sulphates, furnished

pure *p*-aminoethylbenzene sulphate (14 g.) and a further quantity contaminated with aniline sulphate. There was a residue of amines of higher molecular weight.

p-Aminoethylbenzene was identified in the form of its acetyl derivative—slender needles from water, m. p. 95° (Beilstein and Kuhlberg, *Annalen*, 1870, **156**, 208)—and its sulphate (Found : H_2SO_4, 28·4. Calc. : H_2SO_4, 28·8%). Replacement of the amino-group by chlorine and oxidation of the chlorohydrocarbon by alkaline permanganate yielded *p*-chlorobenzoic acid.

(b) *Formation of* p-*Amino*-n-*butylbenzene from* n-*Butylaniline.*—(1) *In presence of cobalt chloride.* A mixture of *n*-butylaniline and cobalt chloride, maintained at 230—240° for 15 hours, gave a product consisting of *p*-amino-*n*-butylbenzene and some unchanged secondary amine. No butyl chloride was detected.

(2) *In presence of zinc chloride.* Butylaniline (35 g.) and zinc chloride (19 g.), heated at 220—230° for 11 hours, yielded *p*-amino-*n*-butylbenzene (18 g.), impure aniline (1·8 g.), primary amines of higher molecular weight (4·5 g.), and secondary amines (8 g.).

(3) *In presence of manganese chloride.* The product after 15 hours' heating at 240—250° contained approximately 30% of *p*-amino-*n*-butylbenzene. No appreciable quantity of other primary amines was present.

(4) *In presence of cadmium chloride.* Dry butylaniline and anhydrous cadmium chloride, heated at 190° for 4 hours and then at 250—290° for 14 hours, gave *p*-amino-*n*-butylbenzene cadmichloride, some secondary amine, and a trace of a tertiary amine.

p-Amino-*n*-butylbenzene was isolated from the reaction mixture usually through its insoluble zincichloride, and was freed from other primary amines by fractional crystallisation of its sulphate. It was identified by comparison of its benzenesulphonyl derivative, m. p. 78°, and acetyl derivative with authentic specimens.

Behaviour of Alkylaniline Hydrochlorides on Heating.

Ethylaniline Hydrochloride.—The dry hydrochloride, heated in an open tube at 200—220° for 15 hours, gave a pale yellow, soft, crystalline mass (Found : Cl, 15·7%) consisting of a mixture of primary and secondary amines with a small quantity of diethylaniline. The primary amines comprised aniline (80% was isolated in a pure state), and another amine not definitely identified. In many other experiments, the principal product was aniline, although the temperature and duration of heating were varied considerably.

Butylaniline Hydrochloride.—No butyl chloride was obtained when the dry hydrochloride was heated at 230—235° for 18 hours. The product was *p*-amino-*n*-butylbenzene and a small quantity of aniline.

The presence of free hydrogen chloride or of benzene in the hydrochloride led to the isolation of *n*-butyl chloride (6·2 c.c. from 23 g. of hydrochloride in one experiment); the residual amines contained chiefly aniline, some *n*-butylaniline, and another primary amine in small quantity.

Rearrangement of Alkylanilines in Presence of Sulphates and Phosphates.

Silver Sulphate.—Ethylaniline (6 g.) and silver sulphate (2 g.), maintained at 200—230° for 16 hours, gave a dark brown, viscous mass having the odour of hydrogen sulphide and containing embedded in it a cake of silver sulphide with some silver sulphate (Found : Ag, 89·3; S, 6·4%). Extraction with alcohol, evaporation of the alcoholic solution with dilute hydrochloric acid, and filtration to remove tarry material yielded a solution from which *p*-aminoethylbenzene was isolated through its zincichloride and sulphate. Other primary amines, more complex than *p*-aminoethylbenzene, were also present, but were not isolated in a pure state.

Butylaniline, heated with silver sulphate under similar conditions, yielded *p*-amino-*n*-butylbenzene. A considerable proportion of more complex and amorphous products was present. The yield of pure sulphate was usually 0·2 g. from 5 g. of secondary amine. Prolonged heating reduced the yield of primary amine.

Anhydrous copper sulphate, heated with *n*-butylaniline at 200—250°, gave a dense black tar from which a primary amine was isolated as a sparingly soluble sulphate, but the yield was so small that the reaction was not further examined.

Copper Phosphate.—Ethylaniline (5 g.), heated with copper phosphate (2 g.) at 250° for 14 hours, yielded *p*-aminoethylbenzene, metallic copper (Cu, 98·6%), and metaphosphoric acid.

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