XLIX.—*The Action of Ethylene Dibromide on Monomethylaniline.*

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THE action of ethylene dibromide on monomethylaniline was investigated by one of us in 1906, in order to prepare diphenyldimethylethylenediamine, $NMePh\cdot CH_2\cdot CH_2\cdot NMePh$, with the view of examining compounds containing two asymmetric nitrogen atoms.

A mixture of the two in the proportion of one gram-molecule of ethylene dibromide to two gram-molecules of monomethylaniline was heated on a water-bath under a reflux condenser for several days. The viscous mass thus obtained was treated with potassium hydroxide, and the oil which separated was dried and distilled under diminished pressure.

An oil which distilled at about 100°/12 mm. appeared to be monomethylaniline, then at 230—235° a solid distilled, which, when crystallised from alcohol, ether or light petroleum, separated in lustrous plates melting at 163°:

0·1800 gave 0·5295 CO_2 and 0·1285 H_2O. C = 80·2; H = 7·93.
0·1533 „ 16·3 c.c. N_2 at 18° and 736 mm. N = 12·0.
$C_{16}H_{20}N_2$ requires C = 80·0; H = 8·33; N = 11·7 per cent.

Molecular-weight determinations by the cryoscopic method in benzene gave results in sufficiently close agreement with the expected value, 240.

The compound did not appear to be well suited to the purpose in hand, and in February, 1907, a paper by Fröhlich appeared (*Ber.*, 1907, **40**, 763), in which a compound prepared by the action of four gram-molecules of monomethylaniline on one of ethylene dibromide at 60—70°, was described as "NN′-dimethyläthylendianilin." This base crystallised in prisms melting at 47°, and on analysis gave:

C = 79·77; H = 8·58; C = 79·80; H = 8·49; N = 11·56, 11·76,

results also satisfactory for the supposed compound.

Previous to this (*Ber.*, 1898, **31**, 3256), Bischoff stated that he had obtained a compound by the action of ethylene dibromide on monomethylaniline (proportions not given) which crystallised in plates melting at 165°. In Fröhlich's paper this discrepancy is dismissed in a footnote to the effect that it was an error.*

The subject seemed worthy of further investigation, but the pressure of other work prevented this until recently.

On examining the reaction between ethylene dibromide and monomethylaniline in different proportions at different temperatures, it was found that up to 100° the result was independent of the temperature, and depended only on the relative proportions of the two substances present.

When two gram-molecules of monomethylaniline and one of ethylene dibromide were used, the compound melting at 163° was always obtained, but the yield was in every case poor (50 grams of monomethylaniline gave only about 5 grams of the pure compound).

When five gram-molecules of base to one of ethylene dibromide were taken, the prisms described by Fröhlich as melting at 47° were produced, and the yield was fairly good (35 grams of base yielded about 10 grams of the pure compound).

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* (*Loc. cit.*) "Vergl. diese Berichte **31**, 3256 (1898). Die Angabe eines Schmp. 165° muss auf einem Irrtum beruhen."

The method of preparation used in both cases was the same as that described above, but in the later work the vacuum distillation was omitted. The bases liberated by alkali were distilled until a temperature of about 200° was reached, and the residue was extracted with alcohol or light petroleum The compounds separated from these solutions on keeping. At least four days' heating under a reflux condenser on a water-bath is advisable if a good yield is desired.

Molecular-weight determinations in benzene solution by the cryoscopic method gave the following results:

Compound, m. p. 47°:

0·2012, in 20·96 benzene, gave $\Delta t = -0{\cdot}214$. M.W. = 236.

Compound, m. p. 163°:

0·3535, in 17·69 benzene, gave $\Delta t = -0{\cdot}440$. M.W. = 237.

$NMePh{\cdot}CH_2{\cdot}CH_2{\cdot}NMePh$ requires M.W. = 240.

Nothing therefore which had hitherto been done could give any clue to the nature of the difference between the compounds.

Properties of the substance melting at 47°.—Crystalline needles, fairly soluble in alcohol, ether, light petroleum, or benzene. The base is very soluble in hydrochloric acid, from which needles of a hydrochloride could be crystallised with some difficulty. Gravimetric synthesis and analysis of this gave results corresponding with a dihydrochloride:

0 5011 gave 0·6626 hydrochloride. Ratio, hydrochloride/substance = 1·32 : 1.

0·4183 gave 0·3665 AgCl. Cl = 21·7.

The monohydrochloride requires above ratio = 1·15 : 1. Cl = 12·8 per cent.

The dihydrochloride requires above ratio = 1·30 : 1. Cl = 22·6 per cent.

(It was found to be difficult to purify this compound, owing to its great solubility.)

The solution of the base in hydrochloric acid gives, with platinic chloride, a precipitate of very small, orange needles, which decompose on heating.

The base combines with methyl iodide in the cold to give a crystalline compound fairly soluble in alcohol, from which it separates in prisms melting at 163°:

0·1712 required 9·05 c.c. $N/20$-$AgNO_3$. I = 33·6.

$NMePh{\cdot}CH_2{\cdot}CH_2{\cdot}NMePh,MeI$ requires I = 33·2 per cent.

On heating the base with methyl iodide in a sealed tube at 100°, the resulting compound was practically insoluble in alcohol, and separated from hot water in prisms melting at 219°:

0·1537 required 11·65 c.c. $N/20$-$AgNO_3$. I = 48·3.

$NMePh{\cdot}CH_2{\cdot}CH_2{\cdot}NMePh,2MeI$ requires I = 48·46 per cent.

The compound melting at 47° was heated in a current of dry hydrogen chloride to 205—210°, when methyl chloride was evolved and a solid residue obtained, which, when extracted with water and treated with sodium hydroxide, yielded a crystalline precipitate soluble in alcohol and ether; after recrystallisation this melted at 65°, and corresponded in every respect with diphenylethylenediamine,

$$NHPh\cdot CH_2\cdot CH_2\cdot NHPh,$$

prepared by Hofmann (*Proc. Roy. Soc.*, 1859, **9**, 388; compare also Morley, *Ber.*, 1879, **12**, 1794, and Bischoff, *Ber.*, 1889, **22**, 1783). It therefore appears that the compound melting at 47°, resulting from the action of methylaniline (4 mols.) on ethylene dibromide (2 mols.), is diphenyldimethylethylenediamine, $NMePh\cdot CH_2\cdot CH_2\cdot NMePh$.

This was confirmed by preparing the compound melting at 47° from diphenylethylenediamine by the action of methyl iodide at 100°.

It still remains to determine the constitution and mode of formation of the compound melting at 163°.

Properties of the compound melting at 163°.—The compound is sparingly soluble in all solvents, being very much less soluble than the compound melting at 47°. It is sparingly soluble in hydrochloric acid on boiling, and from the solution short, lustrous prisms of the hydrochloride readily separate on cooling:

0·5052 gave 0·6641 hydrochloride. Ratio, hydrochloride/substance = 1·31 : 1.

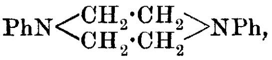
0·3478 gave 0·3242 AgCl. Cl = 23·0.

A platinichloride was obtained as a fine brown, crystalline precipitate.

With methyl iodide the same product was obtained either at the ordinary temperature (analysis I) or at 100° (analysis II); this was fairly soluble in alcohol, from which it separated in plates melting at 183°:

I. 0·2744 gave 0·1680 AgI. I = 33·1.
II. 0·1821 „ 0·1113 AgI. I = 33·1.

It appeared on consideration that the properties of this substance closely resembled those of diphenylpiperazine,



$$PhN\Big\langle\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\Big\rangle NPh,$$

prepared by Hofmann (*loc. cit.*) by the action of excess of ethylene dibromide on aniline. We therefore prepared diphenylpiperazine in this way, and found it to be identical in all respects with the compound melting at 163°, and obtained from monomethylaniline. The melting points of the two compounds and that of a mixture of the two in any proportions were identical. The analytical results previously obtained (pp. 417, 418):

$$C = 80\cdot 2;\ H = 7\cdot 93;\ N = 12\cdot 0;\ M.W. = 237$$

are in close agreement with those required by $C_{16}H_{18}N_2$, namely, C = 80.7; H = 7·63; N = 11·8 per cent. M.W. = 238.

The dihydrochloride requires Cl = 22·8 per cent. (Found, Cl = 23·0), and the methyl iodide compound requires I = 33·4 per cent. (Found, I = 33·1). Another analysis gave the following result:

0·2510 gave 0·7390 CO_2 and 0·1710 H_2O. C = 80·3; H = 7·57.

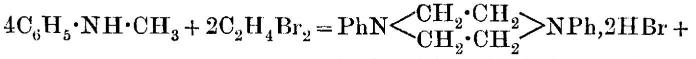
Since the compositions of diphenylpiperazine and diphenyldimethylethylenediamine differ only by two atoms of hydrogen, in such large molecules analytical results do not distinguish between them effectively.

The formation of diphenylpiperazine from monomethylaniline and ethylene dibromide would involve the elimination of the methyl groups from the former probably as methyl bromide. If methyl bromide could actually be detected among the products of the reaction, the mechanism of the process would be clear. However, there is present in the mixture a secondary base, methylaniline, which would probably react immediately with methyl bromide, giving a tertiary base. If, therefore, we could detect dimethylaniline in the oil distilling between 180° and 210°/760 mm., it would be very probable that methyl bromide had been removed from one molecule of methylaniline and had reacted with another molecule of the same base.

It was actually found that the oil boiling at about 190° consisted almost entirely of dimethylaniline, as proved by the preparation from it of nitrosodimethylaniline, by its reaction with methyl iodide, and by the absence of any action with acetyl chloride.

It was then shown that the methyl bromide was removed by direct interaction of ethylene dibromide and diphenyldimethylethylenediamine (m. p. 47°), since diphenylpiperazine was obtained when these were heated together at 100° for some days.

The above facts show that the reaction between two molecules of monomethylaniline and one of ethylene dibromide is to be represented by the equation:



$$4C_6H_5{\cdot}NH{\cdot}CH_3 + 2C_2H_4Br_2 = PhN\left<\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{matrix}\right>NPh,2HBr + 2C_6H_5{\cdot}N(CH_3)_2\,HBr$$

Diphenylpiperazine hydrobromide.

Dimethylaniline hydrobromide.

and is to be added to the number of abnormal reactions which have been observed to take place between alkylhalides and secondary and tertiary bases. This reaction, however, differs from other abnormal reactions in that a methyl group is actually displaced, whereas in other cases it is the methyl group which has been found to displace other alkyl groups.

Summary.

It has been shown that by the interaction of four gram-molecules of monomethylaniline and one of ethylene dibromide, diphenyldimethylethylenediamine, NMePh·CH_2·CH_2·NMePh, and monomethylaniline hydrobromide are formed, whereas by the interaction of two gram-molecules of monomethylaniline with one of ethylene dibromide, diphenylpiperazine and dimethylaniline hydrobromide are formed.

The hydrochlorides of both bases and the quaternary compounds formed by both bases with methyl iodide are described.

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