XXII.—*The Action of Ethylene Dibromide on Xylidine and ψ -Cumidine.*

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AMONG the reactions announced by Hofmann in his classical researches on amines is that between ethylene dibromide and aniline whereby important bases are formed each of which has been fruitful as leading to subsequent discovery. Of these, two are especially notable, namely, diphenylethylenediamine and diphenyldiethylenediamine. The latter is now called diphenylpiperazine, a name suggested by Merz and Mason (*Ber.*, 1887, 20, 267), which shows in a happy manner its relation to other heterohexacyclic compounds. The following experiments were undertaken with the object of applying this reaction to the production of the related xylil and cumyl bases, and of obtaining from them derivatives homologous with those which Mills has described (*Trans.*, 1900, 77, 1020). We have also endeavoured to extend this reaction with the view of preparing methylenediamine derivatives and have succeeded in obtaining a series of well crystallisable methylene compounds. The study of these as well as their behaviour with phenylcarbimide we propose to continue.

Dixylylethylenediamine, $C_2H_4(NH \cdot C_6H_3Me_2)_2$.

Pure xylidine of commerce (b. p. 212°) which consists chiefly of the unsymmetrical meta-isomeride was employed. Four mols. of the base were brought together with 1 mol. of ethylene dibromide in presence of sufficient sodium carbonate to neutralise the hydrogen bromide set free. In order to moderate the reaction, the base was mixed with the sodium carbonate in a flask fitted with a reflux condenser and the ethylene dibromide gradually added through the latter. The reaction was completed by heating in an oil-bath for three hours at 145 — 150° , the mass being frequently shaken. The contents of the flask were shaken into cold water, which removed the sodium salts and left a soft, resinous mass. This was washed with cold rectified spirit and afterwards extracted with the hot solvent. From this solution on cooling, white feathery crystals separated; after recrystallising three times from absolute alcohol they melted at 74 — 75° . On analysis:

0.2094 gave 0.6186 CO_2 and 0.1710 H_2O . C = 80.56; H = 9.06.

$C_{18}H_{24}N_2$ requires C = 80.59; H = 8.95 per cent.

Dixylylethylenediamine nitrate, $C_2H_4(NH \cdot C_6H_3Me_2)_2 \cdot 2HNO_3$, was prepared by adding dilute nitric acid to an alcoholic solution of the

base. Rise of temperature was prevented by surrounding the vessel containing the solution with cold water. On standing, small colourless needles were deposited which, after washing with water, melted at 165° . These were recrystallised from dilute alcohol and then melted at 166° . On analysis:

0.3982 gave 47.6 c.c. moist nitrogen at 13° and 747.5 mm. $N = 13.91$.

$C_{18}H_{24}N_2 \cdot 2HNO_3$ requires $N = 14.21$ per cent.

Dixylylethylenediamine Platinichloride, $C_2H_4(NH \cdot C_6H_3Me_2)_2 \cdot H_2PtCl_6$, separates as bright yellow, glistening crystals when a solution of platinic chloride in alcohol is added to an alcoholic solution of the base. The salt was dried at 130° , and, on analysis:

0.0542 gave 0.0157 Pt. $Pt = 28.96$.

$C_{18}H_{24}N_2 \cdot H_2PtCl_6$ requires $Pt = 28.79$ per cent.

Dixylylethylenediamine Mercurichloride, $C_2H_4(NH \cdot C_6H_3Me_2)_2 \cdot HgCl_2$, is deposited as pale yellow, well-formed crystals by allowing a mixture of alcoholic solutions of the base and mercuric chloride, in molecular proportion, to stand for 24 hours; it may be recrystallised from dilute alcohol. The melting point is not definite, but is reached at about 118° . On analysis, 34.3 per cent. of Hg was obtained, whilst the formula requires 37.1 per cent. There can be no doubt, however, that the formula given is the correct one, for it is very difficult to obtain these mercurichlorides without admixture of either mercuric chloride or the base.

Tetranitrodixylylethylenediamine, $C_2H_4[NH \cdot C_6H(NO_2)_2Me_2]_2$, was obtained by treating a solution of the base in glacial acetic acid with an excess of concentrated nitric acid. On warming, a brisk reaction commenced, which, for its completion, required the application of heat. Pale yellow crystals made their appearance, increasing in quantity as the liquid cooled. The crystals were collected and washed, first with acetic acid and then with water. After drying, they melted at 220° . On analysis:

0.3542 gave 57.2 c.c. moist nitrogen at 12° and 752.5 mm. $N = 18.98$.

$C_{18}H_{20}O_8N_6$ requires $N = 18.75$ per cent.

After the separation of the tetranitro-derivative, the solution, on addition of water, deposited a small quantity of an orange-red, semi-plastic mass, which became crystalline and melted at $52-53^{\circ}$. There was not sufficient of the substance to enable a further study to be made of it, but from the analogous experience of Mills (Trans., 1900, 77, 1021), in the case of ethylenediphenyldiamine there can be no doubt that this compound is an isomeric *tetranitro*-derivative.

An attempt was next made to prepare a dinitro-derivative. In the

first experiment, the base was dissolved in cold concentrated nitric acid, and when the reaction was complete the resulting liquid was thrown into cold water. An orange powder was precipitated, which melted sharply at 191—192°. On analysis:

0.1723 gave 26.6 c.c. moist nitrogen at 16° and 750 mm. $N = 17.9$.

$C_{18}H_{21}O_6N_5$ requires $N = 17.37$ per cent.

This substance, therefore, may be a *trinitrodixylylethylenediamine*.

In a second experiment, an alcoholic solution of the base was heated to boiling with concentrated nitric acid. The solution was thrown into an excess of water, when brownish-yellow crystals separated which melted at 152—154°. On analysis:

0.1598 gave 18.3 c.c. moist nitrogen at 13° and 767 mm. $N = 13.43$.

$C_{18}H_{23}O_2N_3$ requires $N = 13.41$ per cent.

The dinitro-compound sought was not obtained, as the derivative just described has a composition corresponding to that of a *mononitrodixylylethylenediamine*, $C_6H_3Me_2 \cdot NH \cdot C_2H_4 \cdot NH \cdot C_6H_2Me_2 \cdot NO_2$.

Dixylylpiperazine, $C_6H_3Me_2 \cdot N \cdot (C_2H_4)_2 \cdot N \cdot C_6H_3Me_2$.

This base was produced by using no alkali, but a larger proportion of ethylene dibromide, than in the preparation of the diamine. The reaction is more violent, and it is necessary to add the dibromide carefully in small quantities. Gentle warming is required to start the reaction, which is completed by heating for 2 hours in an oil-bath at 150°. The piperazine, after repeated recrystallisation from absolute alcohol, was obtained in shining, white leaflets which melted at 151°. On analysis:

0.2374 gave 0.7113 CO_2 and 0.1997 H_2O . $C = 81.72$; $H = 9.34$.

0.2802 „ 0.8401 CO_2 „ 0.2335 H_2O . $C = 81.77$; $H = 9.25$.

$C_{20}H_{26}N_2$ requires $C = 81.63$; $H = 8.84$ per cent.

Di-ψ-cumylethylenediamine, $C_2H_4(NH \cdot C_6H_2Me_3)_2$.

The ψ-cumidine employed melted at 67°. The proportion of base to ethylene dibromide, and the method followed generally, were the same as described for the homologous xylyl compound, save that the recrystallisation was effected from benzene. A variation of this method, in which no sodium carbonate was used, but the mass, after washing with rectified spirit, was treated with potassium hydroxide solution before recrystallisation from benzene, gave a good yield. The diamine recrystallised twice from benzene was obtained in the form of brilliant, colourless needles melting at 168°. These dissolve

readily in benzene, but only slightly in hot alcohol or ether. On analysis :

0.2550 gave 0.7556 CO_2 and 0.2190 H_2O . $\text{C} = 80.81$; $\text{H} = 9.52$.

$\text{C}_{20}\text{H}_{28}\text{N}_2$ requires $\text{C} = 81.08$; $\text{H} = 9.45$ per cent.

Di- ψ -cumylethylenediamine Nitrate, $\text{C}_2\text{H}_4(\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_3)_2\cdot 2\text{HNO}_3$, was obtained in the same manner as described above for the corresponding xylol salt. It consists of colourless needles melting at 154° . On analysis :

0.2074 gave 22.4 c.c. moist nitrogen at 17° and 755 mm. $\text{N} = 12.5$.

$\text{C}_{20}\text{H}_{30}\text{O}_6\text{N}_4$ requires $\text{N} = 13.2$ per cent.

Di- ψ -cumylethylenediamine Platinichloride,

was prepared as in the case of the corresponding xylol compound, and precipitated as a buff-coloured powder. On analysis :

0.3451 gave 0.0939 Pt. $\text{Pt} = 27.49$.

$\text{C}_{20}\text{H}_{28}\text{N}_2\cdot\text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 27.64$ per cent.

Di- ψ -cumylethylenediamine Mercurichloride,

corresponds in method of preparation to its xylol homologue. The crystals were a little darker in colour and melted at 150° . The analysis also gave a lower percentage of mercury than that calculated from the formula. Found $\text{Hg} = 33.2$; required $\text{Hg} = 35.2$ per cent.

Dinitrodi- ψ -cumylethylenediamine, $\text{C}_2\text{H}_4(\text{NH}\cdot\text{C}_6\text{HMe}_3\cdot\text{NO}_2)_2$.—It is remarkable that, working in exactly the same manner as for the preparation of the tetranitrodixylethylenediamine, we obtained with the cumyl base, not a tetranitro-, but a dinitro-derivative. The product melted at 97 — 98° , and was precipitated as a pale yellow powder. On analysis :

0.1694 gave 20.5 c.c. moist nitrogen at 16° and 753.5 mm. $\text{N} = 14.0$.

$\text{C}_{20}\text{H}_{26}\text{O}_4\text{N}_4$ requires $\text{N} = 14.5$ per cent.

An isomeride obtained by dissolving the base in concentrated nitric acid with application of heat, gave, on throwing the liquid into water, a compound melting at 49 — 50° . On analysis :

0.2069 gave 26 c.c. moist nitrogen at 18° and 769.6 mm. $\text{N} = 14.43$.

$\text{C}_{20}\text{H}_{26}\text{O}_4\text{N}_4$ requires $\text{N} = 14.5$ per cent.

Di- ψ -cumylpiperazine, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{N}:(\text{C}_2\text{H}_4)_2:\text{N}\cdot\text{C}_6\text{H}_2\text{Me}_3$.

ψ -Cumidine (2 mols.) was mixed with ethylene dibromide (1 mol.), and heated in a closed tube at 200° for 3 hours. The contents were treated with boiling water and the residue dissolved in

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hot rectified spirit; from the solution, on cooling, crystals were deposited which melted at 148—150°. Recrystallisation from ether gave large, brilliant needles which had the same melting point. They were readily soluble in chloroform, but less so in light petroleum. On analysis:

0.2338 gave 0.6984 CO_2 and 0.1954 H_2O . $\text{C} = 81.4$; $\text{H} = 9.28$.

$\text{C}_{22}\text{H}_{30}\text{N}_2$ requires $\text{C} = 81.91$. $\text{H} = 9.25$ per cent.

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