107. *Hofmann's Ethylene Bases. Synthesis of ββ'-Diaminodiethylamine and of ββ'-Diaminodiethylmethylamine.*

By Frederick G. Mann.

The interaction of ethylene dichloride and dibromide with ammonia was investigated by Hofmann (*Proc. Roy. Soc.*, 1860, **10**, 224, 619; 1862, **11**, 413, 424; *Ber.*, 1870, **3**, 762; 1871, **4**, 666; 1890, **23**, 3297, 3711), who isolated ethylenediamine as the chief product and a number of aliphatic and cyclic polyamines as by-products. Although these polyamines have been comparatively neglected since Hofmann's work, they are of interest for three reasons. (1) The isolation of many of them has never been repeated; Fargher (J., 1920, **117**, 1351), using, like Hofmann, large quantities of the reactants, isolated only two. (2) They are of value for the elucidation of certain stereochemical problems, of which the following paper is an illustration. (3) If freely available, they would probably prove of great biochemical interest, as they contain the lower homologues of the naturally occurring spermine and spermidine, which have been shown by Dudley, Rosenheim, and Starling (*Biochem. J.*, 1926, **20**, 1082; 1927, **21**, 97) to be *NN'*-bis-γ-aminopropylbutylenediamine, $C_4H_8(NH{\cdot}C_3H_6{\cdot}NH_2)_2$, and *N*-γ-aminopropylbutylenediamine, $NH_2{\cdot}C_4H_8{\cdot}NH{\cdot}C_3H_6{\cdot}NH_2$, respectively.

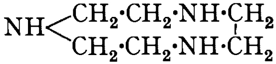
Attempts have therefore now been made to identify these polyamines as decisively as Hofmann's description of their properties and derivatives allows, and then to synthesise certain of the lower members by methods which would produce them easily and in good yield.

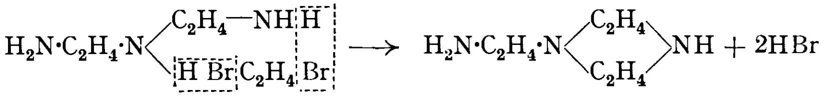
Hofmann showed that a complete fractionation of the amines obtained by the interaction of ethylene dibromide and ammonia gave the following compounds, some of which were obtained pure, and all of which were characterised as salts with the binary halogen acids or with chloroplatinic or chloroauric acid.

(A) Ethylenediamine, $C_2H_6N_2$, b. p. 117—121°.

(B) "Diethylenediamine," $C_4H_{10}N_2$, b. p. 145—146°. This was shown by Majert and Schmidt (*Ber.*, 1890, **23**, 3718) to be identical with piperazine, with the "ethylenimin" or "diethylenedi-imin" of Ladenberg (*Ber.*, 1888, **21**, 758; 1890, **23**, 3740), and with the "spermin" of Schreiner (*Annalen*, 1878, **194**, 68).

(C) "Diethylenetriamine," $C_4H_{13}N_3$, b. p. 208°. Fargher (*loc. cit.*) found this base to be the chief by-product in the preparation of ethylenediamine, and prepared a number of its derivatives: the properties of the latter show that the base is identical with the ββ'-diaminodiethylamine, $NH(C_2H_4{\cdot}NH_2)_2$, whose synthesis is now described. Hofmann notes that this and the following triamine differ from the diamines in not giving stable hydrates.

(D) "Triethylenetriamine," $C_6H_{15}N_3$, b. p. 216°. Meyer and Jacobsen [" Lehrbuch der Organischen Chemie," 1913, I (2), 246] assign the improbable nine-membered symmetric ring structure  $NH<\begin{smallmatrix}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2\\CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2\end{smallmatrix}$ to this base. Hofmann showed, however, that the base on neutralisation with hydrochloric acid gave a dihydrochloride, $C_6H_{15}N_3,2HCl$, which, when recrystallised from concentrated hydrochloric acid, formed a trihydrochloride, $C_6H_{15}N_3,3HCl$: the latter, however, when dissolved in water underwent partial hydrolysis, giving a strongly acidic solution from which the dihydrochloride could be recovered. It has been shown by Mann and Pope (*Proc. Roy. Soc.*, 1925, *A*, **109**, 444) that a tertiary amine group, when associated with β-primary amine groups, may be almost neutral. For example, ββ'β''-triaminotriethylamine gives a stable trihydrochloride, $N(C_2H_4{\cdot}NH_2,HCl)_3$: crystallisation from concentrated hydrochloric acid gives a tetrahydrochloride, but the fourth molecule of acid is lost even on exposure to air. It is highly probable, therefore, that Hofmann's compound is β-aminoethylpiperazine, formed by the action of ethylene dibromide on the amine (C) :

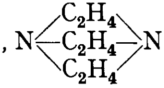
(C.)  (D.)

$$H_2N{\cdot}C_2H_4{\cdot}N<\begin{smallmatrix}C_2H_4—NH\,H\\H\,Br\,C_2H_4\,Br\end{smallmatrix} \longrightarrow H_2N{\cdot}C_2H_4{\cdot}N<\begin{smallmatrix}C_2H_4\\C_2H_4\end{smallmatrix}>NH + 2HBr$$

(E) " Triethylenetetramine," $C_6H_{18}N_4$, b. p. 266—267°. Hofmann obtained this compound also by the condensation of ethylene dibromide with an excess of ethylenediamine, and thus showed it to be *NN'*-bis-β-aminoethylethylenediamine : it is the only polyamine that Hofmann thus synthesised directly.

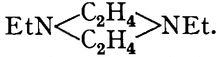
$$C_2H_4Br_2 + 2NH_2{\cdot}C_2H_4{\cdot}NH_2 = C_2H_4(NH{\cdot}C_2H_4{\cdot}NH_2)_2 + 2HBr.$$

Although Fargher (*loc. cit.*) isolated the triamine (C) and the tetramine (E) in moderate quantity and described a number of their derivatives, he was unable to detect the presence of piperazine (B) or its derivative (D). He was, however, in accordance with the directions of Kraut, Rhoussopoulos, and Meyer (*Annalen*, 1882, **212**, 251) for the preparation of ethylenediamine, using a large excess of aqueous ammonia (17—20 mols.), and it would appear, therefore, that the cyclic piperazine derivatives are formed only under Hofmann's conditions, a small excess of alcoholic ammonia (3—4 mols.) being employed.

A further claim by Hofmann (*Proc. Roy. Soc.*, 1859, **9**, 153) to have isolated triethylenediamine,  $N\begin{smallmatrix}C_2H_4\\C_2H_4\\C_2H_4\end{smallmatrix}N$, was not substantiated, Harries (*Annalen*, 1897, **294**, 350) stating that this base was actually hexaethylenetetramine or bis-(*NN'*-ethylene)bispiperazine,  $C_2H_4<\begin{smallmatrix}N{:}C_4H_8{:}N\\N{:}C_4H_8{:}N\end{smallmatrix}>C_2H_4$.

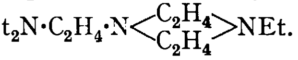
Various higher homologues of these amines were also obtained by Hofmann (*Proc. Roy. Soc.*, 1862, **11**, 420). Thus the interaction of ethylene dibromide with ethylamine gave :—

(F) " Ethylene-diethyldiamine," $C_6H_{16}N_2$, or *NN'*-diethylethylenediamine, $EtNH{\cdot}C_2H_4{\cdot}NHEt$.

(G) " Diethylene-diethyldiamine," $C_8H_{18}N_2$, or 1 : 4-diethylpiperazine,  $EtN<\begin{smallmatrix}C_2H_4\\C_2H_4\end{smallmatrix}>NEt$.

(H) " Diethylene-triethyltriamine," $C_{10}H_{25}N_3$, or ββ'-bisethylaminotriethylamine, $(EtNH{\cdot}C_2H_4)_2NEt$.

Finally, since the ethylamine used was admittedly impure, and contained ammonia and probably diethylamine, two further bases were obtained :—

(I) " Triethylene-triethyltriamine," $C_{12}H_{27}N_3$. Salts of this amine with the binary halogen acids proved so soluble in water that Hofmann's identification was based on the platinichloride and aurichloride : this compound is probably the triethyl derivative of (D), *i.e.*, 1-β-diethylaminoethyl-4-ethylpiperazine,  $Et_2N{\cdot}C_2H_4{\cdot}N<\begin{smallmatrix}C_2H_4\\C_2H_4\end{smallmatrix}>NEt$.

(J) " Diethylene-diethyltriamine," $C_8H_{21}N_3$. The formation of this compound was due to the ammonia present, and the amine may be ββ'-bisethylaminodiethylamine,

$$(EtNH{\cdot}C_2H_4)_2NH,$$

or *N*-β-aminoethyl-*NN'*-diethylethylenediamine, $EtNH{\cdot}C_2H_4{\cdot}NEt{\cdot}C_2H_4{\cdot}NH_2$. Hofmann notes, however, that the amine normally forms a dihydriodide, and that an unstable trihydriodide is obtained only by crystallisation from a large excess of acid. This behaviour (as in the amine D) indicates a tertiary amine-group, and the unsymmetrical formula is therefore probably correct. Moreover, a characteristic property of this triamine was the marked insolubility of its hydrochloride in aqueous alcohol. It has now been found that this property is shared by the trihydrochloride of ββ'-diaminodiethylmethylamine, $(H_2N{\cdot}C_2H_4)_2NMe$, but not by that of ββ'-diaminodiethylamine (C), thus providing further evidence for the presence of a tertiary amine group.

Further higher homologues, such as *NNN'N'*-tetraethylethylenediamine,

$$Et_2N{\cdot}C_2H_4{\cdot}NEt_2,$$

were obtained by the interaction of ethylene dibromide and diethylamine (*loc. cit.*, p. 425). Since the latter was impure, and the products moreover were isolated as quaternary ammonium salts, their accurate identification is impossible.

Hofmann's first triamine, ββ'-diaminodiethylamine, has now been synthesised from the corresponding dihydroxy-derivative, $NH(C_2H_4{\cdot}OH)_2$, very pure supplies of which are available commercially as " diethanolamine." The latter was converted by interaction with thionyl chloride into *ββ'-dichlorodiethylamine hydrochloride*, $(C_2H_4Cl)_2NH,HCl$, following directions (p. 464) kindly supplied by Dr. H. McCombie and Mr. D. Purdie, and attempts were then made to condense the dichloro-compound with potassium phthalimide to give *ββ'-diphthalimidodiethylamine*, $(C_6H_4{:}C_2O_2{:}N{\cdot}C_2H_4)_2NH$. Considerable difficulties were at first experienced at this stage, owing chiefly to the instability of the free dichlorodiethylamine base,* which decomposed violently on attempted distillation under reduced pressure, and changed to a solid even at room temperature during 12 hours. The benzoyl derivative was useless for the condensation owing to its curiously unstable nature : even on recrystallisation from rectified spirit it underwent hydrolysis to *dichlorodiethylamine benzoate*, $C_6H_5{\cdot}CO_2H,NH(C_2H_4Cl)_2$. The diphthalimido-compound was finally prepared by liberating the crude dichlorodiethylamine from the hydrochloride with alkali, and, when dried, warming it directly with potassium phthalimide.

The diphthalimidodiethylamine, when heated with hydrochloric acid, underwent rapid hydrolysis and ββ'-diaminodiethylamine trihydrochloride, $(HCl,H_2N{\cdot}C_2H_4)_2NH,HCl$, was obtained. This crude product requires recrystallisation in order to remove traces of ammonium chloride and piperazine dihydrochloride (p. 470) formed by ring closure during the process of hydrolysis and subsequent evaporation. There is no doubt that this base is identical with the " diethylenetriamine " of Hofmann and Fargher : its platinichloride, $2(H_2N{\cdot}C_2H_4)_2NH,3H_2PtCl_6$, decomposes rapidly on attempted recrystallisation from hot water, as Hofmann (*loc. cit.*, 1862, **11**, 407) describes, and its tripicrate has the same m. p. as that given by Fargher.

During the investigation recorded in the following paper, the need arose for a similar triamine containing a central tertiary amine group, and for this purpose *ββ'-diaminodiethylmethylamine* has also been synthesised. A suspension of diphthalimidodiethylamine in boiling acetone was smoothly methylated with methyl iodide and silver oxide, giving *ββ'-diphthalimidodiethylmethylamine*, $(C_6H_4{:}C_2O_2{:}N{\cdot}C_2H_4)_2NMe$, which also underwent a rapid hydrolysis with hydrochloric acid to give *diaminodiethylmethylamine trihydrochloride* $(HCl,H_2N{\cdot}C_2H_4)_2NMe,HCl$. This trihydrochloride differs markedly from the above non-methylated hydrochloride in being far less soluble in aqueous alcohol : it is therefore best recrystallised from hydrochloric acid containing only a few drops of alcohol, whereas diaminodiethylamine trihydrochloride requires 80% alcohol saturated with hydrogen chloride for this purpose. The constitution of this methylated triamine is placed beyond doubt by the above synthesis. It has been confirmed, however, by treatment of the triamine in sodium hydroxide solution with an excess of benzenesulphonyl chloride,

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* A study of the general chemistry of this amine by the above authors will appear later.

followed by precipitation with hydrochloric acid : *bis(benzenesulphonamidoethyl)methylamine monohydrochloride,* $(C_6H_5{\cdot}SO_2{\cdot}NH{\cdot}C_2H_4)_2NMe,HCl$, was thus obtained, proving that methylation has provided a central tertiary amine group.

EXPERIMENTAL.

ββ'-*Dichlorodiethylamine Hydrochloride.*—Thionyl chloride (130 c.c.), dissolved in chloroform (130 c.c.), is added to a solution of diethanolamine (50 g.) in chloroform (150 c.c.), at first cautiously and then more rapidly, during about 10 minutes. Without delay the mixture is boiled vigorously and occasionally shaken until a clear solution is formed (about 20 minutes); within a few minutes thereafter, considerable crystallisation rapidly occurs. The flask is at once chilled by immersion in ice-water, and after thus standing for one hour, the semi-solid product is filtered off, washed thrice with chloroform and then with ether, and dried. ββ'-*Dichlorodiethylamine hydrochloride* is thus obtained as white crystals (50 g. or 59%) : cautious addition of ether to the original filtrate gives a second less pure crop (*ca.* 15 g. or 18%)." The first crop is sufficiently pure for direct use in the following synthesis, but may be obtained analytically pure by recrystallisation from acetone containing a small quantity of alcohol, as white leaflets, m. p. 216—217°, freely soluble in water and alcohol, but only slightly soluble in acetone (Found : C, 27·2; H, 5·6; N, 7·7; Cl, 59·5. $C_4H_9NCl_2,HCl$ requires C, 26·9; H, 5·7; N, 7·85; Cl, 59·6%).

When the hydrochloride (4·0 g.), dissolved in water (30 c.c.), was treated in turn with ice (40 g.), benzoyl chloride (3·0 c.c.), and 10% sodium hydroxide solution (30 c.c.) and vigorously shaken, the benzoyl compound rapidly separated in small lumps. These were washed with sodium hydroxide solution and with water, dried, and recrystallised thrice from rectified spirit. The initial recrystallisation was very slow, the others much more rapid. The fine white crystals, m. p. 135—136°, obtained proved to be *dichlorodiethylamine benzoate* (Found : C, 50·0; H, 5·6; N, 5·4; Cl, 26·95. $C_{11}H_{15}O_2NCl_2$ requires C, 50·0; H, 5·7; N, 5·3; Cl, 26·9%). The identification of this compound as a benzoate rather than a benzamido-derivative was confirmed by adding it with stirring to cold sodium hydroxide solution : it then readily gave oily drops, presumably of free dichlorodiethylamine, which slowly dissolved if the aqueous solution was in considerable excess. Since the original crude product did not behave in this way, the hydrolysis of the original benzoyl derivative to the benzoate must have occurred during the recrystallisation.

A solution of diethanolamine in acetic acid (5 vols.) was saturated with dry hydrogen chloride at 0° and then heated in a sealed tube at 100° for 8 hours. On evaporation an oil was obtained which solidified on cooling and then, thrice recrystallised from alcohol, gave only ββ'-*diacetoxydiethylamine hydrochloride,* $(AcO{\cdot}C_2H_4)_2NH,HCl$, as white crystals, m. p. 147—149° (Found : N, 6·15; Cl, 15·9. $C_8H_{16}O_4NCl$ requires N, 6·2; Cl, 15·7%).

ββ'-*Dibromodiethylamine Hydrobromide,* $(C_2H_4Br)_2NH,HBr$.—A mixture of diethanolamine (1 vol.) and acetic anhydride (5 vols.) was boiled under reflux for 1½ hours. Fractional distillation under atmospheric pressure removed the excess of anhydride and then under reduced pressure gave *aceto*-ββ'-*diacetoxydiethylamide* $(AcO{\cdot}C_2H_4)_2NAc$, as a colourless liquid, b. p. 212—214°/23·5 mm. (Found : C, 51·0, 51·0; H, 7·5, 7·4; N, 6·15; *M*, cryoscopically in 2·787% benzene solution, 231; in 5·419%, 250; in 8·009%, 268. $C_{10}H_{17}O_5N$ requires C, 51·9; H, 7·4; N, 6·1%; *M*, 231. In spite of the consistently low carbon values, the nitrogen content shows decisively that this compound is the triacetyl, and not the diacetyl, derivative). The triacetyl compound (5 g.), dissolved in acetic acid (50 g.) which had previously been saturated at 0° with dry hydrogen bromide, was heated in a sealed tube for 5 hours at 170°. The product was evaporated on a sand-bath to small bulk, mixed with a small quantity of concentrated hydrobromic acid and some animal charcoal, evaporated again to small bulk, filtered, and chilled. The crystals which separated were recrystallised from alcohol, a second crop being obtained by dilution of the alcoholic filtrate with ether. Dibromodiethylamine hydrobromide was thus obtained in colourless crystals, m. p. 203—205° (Found : Br, 76·6. Calc. : Br, 76·9%). Although this preparation of the hydrobromide is a great advance on that of Gabriel and Eschenbach (*Ber.*, 1897, **30**, 810), it offers no advantages over the hydrochloride for the synthesis of the triamine.

ββ'-*Diphthalimidodiethylamine.*—Powdered ββ'-dichlorodiethylamine hydrochloride (40·0 g.) and 20% potassium hydroxide solution (64·0 c.c.; 1 mol.) were added in turn to ice (20 g.). The free amine, which rapidly separated, was extracted and dried (potassium carbonate) in ether (*ca.* 30 c.c.), and recovered under reduced pressure at room temperature, a fine stream of dry carbon dioxide-free air being passed through the liquid to facilitate the removal of the ether (yield, 25·6 g. or 80%). The oily dichlorodiethylamine was thoroughly mixed with powdered potassium phthalimide (2 mols.; 67 g.), pressed into a compact mass in a conical flask, and heated. At about 145°, a vigorous reaction set in : the flask was removed from the bath and the contents were well stirred for a few minutes to prevent overheating. Heating at 145—150° was then continued for 1 hour, the product usually forming a solid mass within 20 minutes. The cold product was powdered, thoroughly washed with water, dried (yield, 61·5 g.), and repeatedly crystallised from much boiling alcohol, ββ'-*diphthalimidodiethylamine* being obtained as colourless crystals, m. p. 178—180° (Found : C, 66·2; H, 4·7; N, 11·3. $C_{20}H_{17}O_4N_3$ requires C, 66·1; H, 4·7; N, 11·6%).

ββ'-*Diaminodiethylamine Trihydrochloride.*—A mixture of the diphthalimidodiethylamine (30 g.) and dilute hydrochloric acid (300 c.c.; 1 : 1 by vol.) was boiled under reflux for 2 hours, a clear solution being obtained even before boiling started. The product was chilled, the phthalic acid separated, and the solution evaporated to small bulk on the water-bath and finally to dryness in a desiccator. The solid product was triturated with absolute alcohol, filtered, washed with alcohol and ether, and dried. The trihydrochloride obtained contained traces of ammonium chloride and piperazine hydrochloride formed by ring closure, but was sufficiently pure for most synthetic purposes. It could be purified by recrystallisation from 80% alcohol saturated with hydrogen chloride, a second crop being obtained by dilution of the filtrate with ether (Found : Cl, 49·8; N, 19·5. Calc. : Cl, 50·1; N, 19·75%). The trihydrochloride melts at 228—230° to a semi-solid product which does not liquefy completely below 280° : it is possible that partial transformation into piperazine dihydrochloride occurs at the lower temperature, a process that Hofmann (*Ber.*, 1890, **23**, 3724) found to occur readily on dry distillation. Fargher (*loc. cit.*) gives m. p. 233° for the trihydrochloride.

The platinichloride was prepared by adding a solution of the trihydrochloride (1 g.) in water (10 c.c.) to one of chloroplatinic acid (30 c.c.; 4 mols.) containing 6·7% of platinum. The crystals which rapidly separated were washed with ice-cold water and dried over calcium chloride (Found : C, 6·9; H, 2·4; Pt, 40·8. Calc. for $C_8H_{32}N_6Cl_{18}Pt_3$: C, 6·7; H, 2·25; Pt, 40·8%). The deep orange crystals were unaffected when heated to 280°, but attempted recrystallisation from hot water rapidly caused conversion into other more soluble platinum compounds.

The tripicrate, obtained as a fine yellow precipitate on addition of the trihydrochloride to an excess of sodium picrate solution, had m. p. 210—212° (decomp.) with preliminary softening : Fargher gives m. p. 212°. Analysis indicated, however, that it was a stable *dihydrate*, which was unchanged after two recrystallisations from much boiling alcohol (Found : C, 32·0; H, 3·4; N, 20·0. $C_4H_{13}N_3,3C_6H_3O_7N_3,2H_2O$ requires C, 32·0; H, 3·2; N, 20·3%).

ββ'-*Diphthalimidodiethylmethylamine.*—Freshly prepared silver oxide (4·2 g.) and methyl iodide (2·5 c.c.; 2 mols.) were added in turn to a suspension of finely powdered diphthalimidodiethylamine (8 g.) in hot acetone (500 c.c.), and the whole boiled under reflux for 3 hours. The solution was then filtered, and the acetone removed by distillation; the residue, on cooling, gave a brittle solid, which was powdered and extracted with a small quantity of boiling alcohol. The extract deposited colourless crystals of ββ'-*diphthalimidodiethylmethylamine*, m. p. 124—126° after recrystallisation from alcohol (Found : C, 66·6; H, 5·1; N, 10·9. $C_{21}H_{19}O_4N_3$ requires C, 66·8; H, 5·1; N, 11·1%). The methylated compound is markedly more soluble in most liquids than the original diphthalimido-compound.

ββ'-*Diaminodiethylmethylamine Trihydrochloride.*—A mixture of the above diphthalimido-compound (25 g.), concentrated hydrochloric acid (140 c.c.), and water (60 c.c.) was boiled under reflux for 2 hours, the clear solution chilled, the phthalic acid separated, and the filtrate evaporated on the water-bath to small bulk; the almost solid mass obtained on cooling and stirring was redissolved in hot concentrated hydrochloric acid, which on cooling deposited only a very small quantity of the above trihydrochloride and phthalic acid. The cold filtered solution was treated with alcohol drop by drop : the fine emulsion which first separated was rapidly converted on stirring into a fine crystalline precipitate, and the more copious addition of alcohol then precipitated the remainder of the trihydrochloride in almost theoretical yield. The *trihydrochloride* was washed with alcohol and ether and dried (Found : C, 26·6; H, 8·0; N, 18·3; Cl, 46·7. $C_5H_{15}N_3,3HCl$ requires C, 26·5; H, 8·0; N, 18·5; Cl, 46·95%). Being very soluble in water and in hydrochloric acid but almost insoluble in alcohol, it was best recrystallised from concentrated hydrochloric acid containing a few drops of alcohol; on slow cooling, it separated in colourless leaflets, m. p. 239° (decomp.).

The *platinichloride*, $2(H_2N{\cdot}C_2H_4)_2NMe,3H_2PtCl_6$, prepared in the usual way, formed deep orange-coloured crystals of the *hexahydrate* (Found : Pt, 37·3. $C_{10}H_{48}O_6N_6Cl_{18}Pt_3$ requires Pt, 37·2%), which, however, rapidly lost water of crystallisation even when confined over calcium chloride (Found for the anhydrous material: C, 8·3; H, 2·5; N, 5·6; Pt, 39·8. $C_{10}H_{36}N_6Cl_{18}Pt_3$ requires C, 8·2; H, 2·5; N, 5·7; Pt, 40·0%). This platinichloride is far more stable than that of diaminodiethylamine and may be recrystallised from hot water without change.

The *trioxalate*, $(H_2N\cdot C_2H_4)_2NMe,3C_2H_2O_4,H_2O$, which is one of the most characteristic salts of the base, separated rapidly when cold concentrated aqueous solutions of the trihydrochloride and of oxalic acid were mixed. It is only moderately soluble in cold water, and separates from hot water in colourless crystals, m. p. 205° (decomp.) (Found : C, 32·75; H, 5·6; N, 10·2. $C_{11}H_{23}O_{13}N_3$ requires C, 32·6; H, 5·7; N, 10·4%).

The *tripicrate*, $(H_2N\cdot C_2H_4)_2NMe,3C_6H_2(NO_2)_3\cdot OH$, was obtained by adding an aqueous solution of the trihydrochloride cautiously to one containing an excess of sodium picrate. It is freely soluble in acetone, but only slightly soluble in boiling water or alcohol. Two recrystallisations from alcohol gave the pure tripicrate as a bright yellow, crystalline powder, m. p. 203—205° (decomp.) : it is unstable when exposed to light, developing a reddish-orange colour (Found : N, 20·9. $C_{23}H_{24}O_{21}N_{12}$ requires N, 20·9%).

Bis(benzenesulphonamidoethyl)methylamine Monohydrochloride.—Benzenesulphonyl chloride (2·5 c.c.; 3 mols.) was added to a solution of the trihydrochloride (1·5 g.) in 10% sodium hydroxide solution (50 c.c.), and the mixture shaken for 2 hours. When the clear solution was acidified with hydrochloric acid, a fine emulsion separated. On standing over-night, the emulsion coagulated and solidified, and a further crop of needles also appeared. The solid product was collected and twice recrystallised from alcohol, the above *monohydrochloride* being obtained as colourless crystals, m. p. 163—164°, freely soluble in cold water but almost insoluble in cold absolute alcohol (Found : C, 47·3; H, 5·5; Cl, 8·2. $C_{17}H_{24}O_4N_3ClS_2$ requires C, 47·05; H, 5·6; Cl, 8·2%).

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