332. *Polyamines. Part II. The Preparation of ββ'-Diaminodiethylamine and* NN'-*Bis-(β-aminoethyl)ethylenediamine.*

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BY the action of ethylenediamine upon *p*-toluenesulphon-β-chloroethylamide (Peacock and Dutta, J., 1934, 1303) in alcoholic solution, *N*-(β-*p*-toluenesulphonamidoethyl)ethylenediamine (I), $C_7H_7\cdot SO_2\cdot NH\cdot C_2H_4\cdot NH\cdot C_2H_4\cdot NH_2$, and NN'-*bis*-(β-p-*toluenesulphonamidoethyl*)*ethylenediamine* (II), $(C_7H_7\cdot SO_2\cdot NH\cdot C_2H_4\cdot NH)_2C_2H_4$, are slowly formed. From (I), by hydrolysis with concentrated hydrochloric acid in a sealed tube or with boiling 60% sulphuric acid, ββ'-diaminodiethylamine was obtained (Hofmann, *Proc. Roy. Soc.*, 1862, **11**, 413; *Ber.*, 1890, **23**, 3711; Fargher, J., 1920, **117**, 1353; Mann, J., 1934, 461). Mann's method (*loc. cit.*) is the best for the preparation of this base. From (II), by hydrolysis, *NN'*-bis-(β-aminoethyl)ethylenediamine (III), $(NH_2\cdot C_2H_4\cdot NH)_2C_2H_4$ (Hofmann, *locc. cit.*), was prepared. The substance (II) was also obtained by the prolonged action of *p*-toluenesulphon-β-chloroethylamide on (I), and (I) and (II) were produced when a solution of sodium ethoxide in alcohol was slowly added to a boiling solution of ethylenediamine dihydrochloride and *p*-toluenesulphon-β-chloroethylamide (cf. Moore, Boyle, and Thorn, J., 1929, 39).

The present results with ethylenediamine afford further evidence of the resistance to hydrolysis of the chlorine atom in *p*-toluenesulphon-β-chloroethylamide (Peacock and Dutta, *loc. cit.*). It can therefore be used under conditions where the use of phthalo-β-bromoethylimide would be unlikely to be successful (Ristenpart, *Ber.*, 1896, **29**, 2526).

By the action of concentrated aqueous ammonia upon ββ'-dibromodiethylamine hydrobromide (Peacock and Dutta, *loc. cit.*), piperazine and ββ'-diaminodiethylamine were formed.

The base (I) in alcoholic solution readily formed sparingly soluble co-ordination compounds with copper sulphate and with nickel sulphate. The base (III) gave with copper sulphate a very soluble co-ordination compound, and with potassium chloroplatinite a sparingly soluble compound which seemed to be the chloroplatinite of the co-ordination complex. These co-ordination compounds are under examination.

EXPERIMENTAL.

The Action of Ethylenediamine on p-*Toluenesulphon*-β-*chloroethylamide*.—The amide (117 g.; ½ mol.) was dissolved in rectified spirit (225 c.c.), and ethylenediamine (60 g.; 1 mol.) added. Next day the mixture was boiled under reflux for 11 hours; a crystalline precipitate consisting mainly of ethylenediamine dihydrochloride separated. The alcohol was distilled off, and the residue acidified with concentrated hydrochloric acid and extracted with cold water (A). The viscous residue was extracted with boiling water (B). The final residue has not yet been identified. The solution (A) was evaporated to dryness, and the residue extracted with boiling rectified spirit, which left ethylenediamine dihydrochloride undissolved. The alcoholic solution on concentration and cooling deposited N-(β-p-*toluenesulphonamidoethyl*)*ethylenediamine dihydrochloride* (87 g.), m. p. 182° after recrystallisation from aqueous alcohol and hydrochloric acid (Found: Cl, 21·4. $C_{11}H_{19}O_2N_3S,2HCl$ requires Cl, 21·5%). The free base (I) was soluble in sodium hydroxide solution. By the action of *p*-toluenesulphonyl chloride and sodium hydroxide the tri-*p*-toluenesulphonyl derivative of ββ'-diaminodiethylamine was formed, m. p. (from glacial acetic acid) 170°, unaltered by admixture with the compound prepared by Peacock and Dutta (*loc. cit.*).

The solution (B) was cooled and hydrochloric acid added; NN'-*bis*-(β-p-*toluenesulphonamidoethyl*)*ethylenediamine dihydrochloride* (16 g.) separated in colourless plates, m. p. 246°, sparingly soluble in cold water and in ethyl alcohol, less soluble in dilute hydrochloric acid (Found: Cl, 13·1. $C_{20}H_{30}O_4N_4S_2,2HCl$ requires Cl, 13·4%). The free *base* (II) from this dihydrochloride melted at 160° (Found : N, 11·95. $C_{20}H_{30}O_4N_4S_2$ requires N, 12·3%).

Similar results were obtained when a solution of sodium (0·92 g.) in alcohol (10 c.c.) was added during 10 hours to a boiling solution of *p*-toluenesulphon-β-chloroethylamide (4·66 g.) and ethylenediamine dihydrochloride (2·66 g.) in alcohol (10 c.c.) and water (5 c.c.).

The dihydrochloride of (I) was heated with 5 parts by weight of concentrated hydrochloric acid in a sealed tube at 160° or with 4 parts of 66% sulphuric acid under reflux at 160—170° for 7—9 hours. In each case the product was made strongly alkaline and steam-distilled from an oil-bath at 160—170°. The ββ'-diaminodiethylamine in the distillate was neutralised with hydrochloric acid and evaporated to dryness. The hydrochloride obtained by the sulphuric acid hydrolysis crystallised with some difficulty.

NN'-*Bis*-(β-*aminoethyl*)*ethylenediamine* (III).—The di-*p*-toluenesulphonyl derivative (II) (13·2 g.) was heated for 8 hours in an oil-bath at 160—170° with concentrated sulphuric acid (30 g.) and water (15 g.). The product was made strongly alkaline with sodium hydroxide and steam-distilled from an oil-bath at 170—190°. The base was neutralised with hydrochloric acid and evaporated to dryness; the *tetrahydrochloride* (8·0 g.) after crystallisation from ethyl alcohol and hydrochloric acid had m. p. 266—270° (Found : Cl, 48·5. $C_6H_{18}N_4,4HCl$ requires Cl, 48·6%). The tetrabenzoyl compound, crystallised from boiling ethyl alcohol (sparingly soluble), melted at 230° (Hofmann, *loc. cit.*, gives 228—229°).

The base (I) reacted very slowly in boiling alcoholic solution with *p*-toluenesulphon-β-chloroethylamide; after 12 hours, reaction had taken place only to the extent of about 10%.

Co-ordination Compounds.—An alcoholic solution of the base (I) was prepared by adding a solution of the calculated amount of sodium in alcohol to an alcoholic solution of the dihydrochloride of (I) and filtering off the sodium chloride. Copper sulphate solution with excess of this solution at once formed a light violet *precipitate*, insoluble in cold water and sparingly soluble in boiling water {Found : N, 11·75. $[(C_{11}H_{19}O_2N_3S)_2Cu(H_2O)_2]SO_4$ requires N, 11·8%}. Calcium bromide, similarly treated, gave a product very soluble in water, which on evaporation gave no crystalline substance (cf. Peacock, J., 1913, **103**, 672). Nickel sulphate solution, similarly treated, gave a violet-blue solution which after a few minutes deposited a violet precipitate. This substance was sparingly soluble in water and appeared to be a mixture.

An alcoholic solution of (III) was similarly prepared and added to copper sulphate solution; on evaporation, very hygroscopic, dark blue crystals were obtained. An aqueous solution of the tetrahydrochloride of (III) and the calculated amount of sodium hydroxide was added to a hot aqueous solution of potassium chloroplatinite; after a few minutes a flesh-coloured crystalline precipitate formed, which was soluble in boiling water to a colourless solution and crystallised again on cooling. A similar product was obtained by adding sodium hydroxide to a solution of the tetrahydrochloride of (III) mixed with potassium chloroplatinite. This *substance* may be $[Pt(C_6H_{14}N_4)]PtCl_4$ (Found : N, 8·0. $C_6H_{14}N_4Cl_4Pt_2$ requires N, 8·3%). Potassium chloropalladite behaved similarly, but the palladous compound seemed more soluble.

The Action of Ammonia on ββ′-Dibromodiethylamine Hydrobromide.—The hydrobromide (Peacock and Dutta, *loc. cit.*) (35 g.) was heated with 6*N*-alcoholic ammonia (500 c.c.) for 8 hours in an autoclave at 100°. The alcohol was distilled, the residue evaporated to dryness, excess of sodium hydroxide added, and the bases distilled from an oil-bath at (1) 130°, (2) 130—180°, (3) 180—190°. Each product was acidified with hydrochloric acid and evaporated to dryness. The product from (3) was converted into *p*-toluenesulphonyl derivatives, which were treated with aqueous sodium hydroxide. From the alkaline solution, hydrochloric acid precipitated a substance, which after recrystallisation melted at 170° alone or mixed with the tri-*p*-toluenesulphonyl derivative of ββ′-diaminodiethylamine (Peacock and Dutta, *loc. cit.*). The product insoluble in sodium hydroxide, m. p. 285—286° after crystallisation from glacial acetic acid, was the di-*p*-toluenesulphonyl derivative of piperazine (Peacock and Dutta, *loc. cit.*); it was also obtained from fractions (1) and (2).

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