10. *The Cyclic Methyleneimines. Part III. Hydrolysis of Quaternary Compounds. Preparation of Secondary Amines.*

By John Graymore.

Hydrolysis of the products formed by the action of benzyl chloride on certain cyclic methyleneimines yielded a mixture of a secondary and a tertiary amine. With trimethyltrimethylenetriamine the quaternary compound *dibenzyldimethylammonium chloride* was obtained in addition. Ethyl bromide combines slowly with triethyltrimethylenetriamine. Allyl iodide reacts readily; acid hydrolysis of its addition product gave ethylallylamine and ethylamine.

In previous work (Blundell and Graymore, J., 1939, 1787) it was shown that certain cyclic methyleneimines formed quaternary derivatives with alkyl iodides, but no reaction could be observed with alkyl chlorides.

The present communication deals with the action of benzyl chloride, ethyl bromide, and allyl iodide on the bases. Addition of benzyl chloride took place readily, but the subsequent hydrolysis was attended by unexpected results in that with both the bases used it produced a tertiary amine in addition to the expected secondary amine. Further, trimethyltrimethylenetriamine also gave a good yield of *dibenzyldimethylammonium chloride*. The latter was isolated in the form of its *mercuric chloride* addition compound.

The addition product obtained from the methyl base with benzyl chloride separated in crystalline form. Analytical results on the product (washed free from the excess of benzyl chloride) indicated that it was a mixture. Hydrolysed by acid, it gave a mixture of the hydrochlorides of methylamine, benzylmethylamine, and benzyldimethylamine with dibenzyldimethylamine chloride. The formation of the amines could readily be accounted for by hydrolysis of the normal quaternary derivatives of the cyclic methyleneimine, but the appearance of a quaternary ammonium chloride amongst the products of hydrolysis suggested an addition of a further molecule of benzyl chloride, preceded by opening of the ring.

Attempts to separate the constituents of the addition products have failed, so the course of the reaction is still obscure.

Addition of allyl iodide to triethyltrimethylenetriamine took place rapidly. Acid hydrolysis of the product yielded ethylamine, ethylallylamine, and formaldehyde.

Combination of ethyl bromide with triethyltrimethylenetriamine and hydrolysis of the product follow the normal course; the yield is very small.

EXPERIMENTAL.

The analyses, due in the main to Drs. Weiler and Strauss, are micro-analyses.

Action of Benzyl Chloride on NN′N″-*Trimethyltrimethylenetriamine*.—To the base (30 g.), dried, redistilled, and cooled in ice–salt, benzyl chloride (29 g.) was gradually added. After 1 day a portion of the white crystalline product was washed with dry ether, and the ether removed in a vacuum, giving a mixture, m. p. 115—117° (Found: N, 15·7; Cl, 17·4. Calc. for $C_6H_{15}N_3,C_7H_7Cl$: N, 16·4; Cl, 13·9%. Calc. for $C_6H_{15}N_3,2C_7H_7Cl$: N, 11·0; Cl, 18·6%).

Hydrolysis of the addition product. A solution of the remainder of the product in hydrochloric acid was separated from unchanged chloride, steam-distilled to remove formaldehyde, and evaporated on the water-bath to incipient crystallisation. After rapid cooling, the crystals were removed and washed with warm chloroform, and the undissolved methylamine hydrochloride filtered off. The original mother-liquor, evaporated further, was thus gradually separated into a chloroform solution and a residue of methylamine hydrochloride (30 g.), m. p. and mixed m. p. 226°. The final residues did not crystallise but dissolved wholly in warm chloroform. The combined chloroform extracts on evaporation gave a thick syrup which did not crystallise. A solution of this in water was boiled to remove traces of chloroform and rendered alkaline with caustic soda. Ether then extracted a base (9 c.c.), b. p. 194—200°, which was shown to contain benzylmethylamine by formation of 2 : 4-dinitrobenzylmethylaniline, m. p. and mixed m. p. 141—142°. The remainder of the base was shaken with *p*-toluenesulphonyl chloride in alkali to remove the benzylmethylamine. The residual base was distilled into hydrochloric acid; the solution was evaporated to small bulk, and caustic soda added. The oil separating was isolated by means of ether and converted into benzyldimethylamine picrate, m. p. 94—95° (Found: N, 15·4. Calc. for $C_9H_{13}N,C_6H_3O_7N_3$: N, 15·4%).

Dibenzyldimethylammonium chloride. The liquor remaining after the ethereal extraction was made acid, and an excess of mercuric chloride solution added, giving a copious white precipitate, which crystallised from hot water in long needles, m. p. 167—168° (Found: C, 36·3; H, 3·6; Cl, 20·4; N, 2·7; Hg, 37·95. $C_{16}H_{20}NCl,HgCl_2$ requires C, 36·0; H, 3·6; Cl, 20·0; N, 2·6; Hg, 37·6%).

A solution of the product in hot water was freed from mercury by means of hydrogen sulphide, evaporated to small bulk, and then allowed to evaporate spontaneously. After some days large crystals were obtained. These were dissolved in acetone and shaken with anhydrous sodium carbonate (to remove the acid which persisted on recrystallisation from water); on evaporation of the acetone a liquid was obtained which crystallised in white plates, m. p. 85—90° (indistinct) (Found: Cl, 13·6. $C_{16}H_{20}NCl$ requires Cl, 13·6%).

Action of Benzyl Chloride on NN′N″-*Triethyltrimethylenetriamine*.—To the base (1 mol.), freshly distilled from barium oxide, benzyl chloride (1 mol.) was added slowly. Crystals separated at first, but gave place to a toffee-like mass. A solution of this in hydrochloric acid was filtered from the unchanged chloride, steam-distilled to remove formaldehyde, evaporated to small bulk on the water-bath, and repeatedly extracted with ether after addition of caustic soda in excess. The ethereal layer, dried over barium oxide and distilled from a water-bath into hydrochloric acid, gave a residual oil and ethylamine hydrochloride (in the distillate). The residual oil had b. p. 194—200° (mainly 199—200°); dissolved in dry benzene, it was converted into a mixture of picrates (m. p. 80—110°). The picrates were separated by fractional crystallisation from hot alcohol, giving benzylmethylethylamine picrate, m. p. 113—114° (Found: N, 14·8. Calc. for $C_{10}H_{15}N,C_6H_3O_7N_3$: N, 14·8%), and *benzylethylamine picrate*, m. p. 122—123° (Found: C, 49·6; H, 4·6; N, 15·2. $C_9H_{13}N,C_6H_3O_7N_3$ requires C, 49·45; H, 4·4; N, 15·4%).

NN'N''-*Trimethyltrimethylenetriamine dichloride* was obtained by passing dry chlorine into the base in chloroform until a yellow colour began to develop. The dichloride was slowly deposited in short white needles after addition of ethyl acetate; m. p. 128—130° (decomp.) (Found: N, 20·7. $C_6H_{15}N_3Cl_2$ requires N, 21·0%). It decomposed in moist air, giving off formaldehyde.

Action of Allyl Iodide on Triethyltrimethylenetriamine.—To the base (9 g.), dissolved in dry ether (20 c.c.), allyl iodide (10 g.) was added. Separation of the addition product in white needles commenced at once. After 24 hours the mixture was treated with excess of hydrochloric acid, ether and unchanged allyl iodide separated, and the acid layer steam-distilled to remove formaldehyde. Evaporation to dryness was followed by extraction of the bases with ether after their liberation by concentrated sodium hydroxide solution. The ethereal solution was dried over barium oxide and distilled from a water-bath, the ethylamine being finally recovered as the hydrochloride (8 g.). Ethylallylamine (3 c.c.), b. p. 78—80°, was distilled after removal of the ether (Found: N, 16·5. Calc. for $C_5H_{11}N$: N, 16·5%).

Ethylallylamine picrate separated from a benzene solution of picric acid on addition of the base. Recrystallised from hot alcohol, it formed pale yellow rhomboids, m. p. 102° (Found: C, 42·5; H, 4·5; N, 17·7. $C_{11}H_{14}O_7N_4$ requires C, 42·4; H, 4·5; N, 17·8%).

Action of Ethyl Bromide on Triethyltrimethylenetriamine.—Ethyl bromide (10 c.c.) was added to the base (15 c.c.) in dry ether; the product, which separated slowly in white needles, was washed with dry ether and dried in a vacuum, giving a quaternary *compound*, m. p. 112—114° (decomp.), in 10% yield (Found: Br, 28·8. $C_{11}H_{26}N_3Br$ requires Br, 28·5%). On hydrolysis with hydrochloric acid and steam-distillation this gave ethylamine and diethylamine, identified by the derivatives formed with *p*-toluenesulphonyl chloride.

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