

## 7. *The Cyclic Methyleneimines. Part IV. Hydrolysis of Quaternary Compounds. Preparation of Secondary Amines.*

By JOHN GRAYMORE.

Two products have been obtained by the action of a dry ethereal solution of benzenesulphonyl chloride on *NN'N''*-trimethyltrimethylenetriamine, also in dry ether. One has been identified as *methylaminobismethylenebenzenesulphonmethylamide*. The other, an unstable substance, has been shown to be a halogen derivative of a formaldehyde-methylamine condensation product.

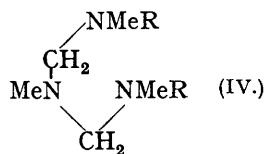
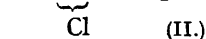
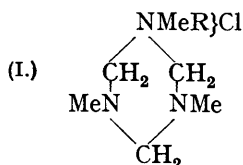
*p*-Toluenesulphonyl chloride under similar conditions has also given the latter product. *Methylenebis-p-toluenesulphonmethylamide* and *p*-toluenesulphonmethylamide have also been obtained in this reaction.

FURTHER evidence is now recounted in support of the suggestion (Part III; J., 1941, 39) that addition of alkyl halides to the cyclic methyleneimines is followed by opening of the methyleneimino-ring.

When benzenesulphonyl chloride was added to *NN'N''*-trimethyltrimethylenetriamine in dry ethereal solution, a crystalline product separated. On hydrolysis in acid solution, this substance gave methylamine and formaldehyde as sole products. The crystals were extremely unstable in moist air and could not be dried in a vacuum without decomposition, so accurate analytical results were difficult to obtain.

When allowed to evaporate in the open or in contact with water, the ethereal solution remaining gave an excellent yield of *bis(benzenesulphonmethylamidomethyl)methylamine* (IV; R = Ph·SO<sub>2</sub>). Although there is, as yet, no direct experimental evidence, it seems probable that the base first adds benzenesulphonyl chloride (I; R = Ph·SO<sub>2</sub>). In this connection it may be noted that addition compounds of hexamethylenetetramine with acid chlorides, *e.g.*, (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>·C<sub>6</sub>H<sub>5</sub>·COCl, have been reported (Hartung, *J. pr. Chem.*, 1892, 46, 1). Addition of a further molecule of benzenesulphonyl chloride would give a diquaternary ammonium compound, which by loss of methylene dichloride could pass into *bis(benzenesulphonmethylamidomethyl)methylamine* (IV). However, this would not explain the formation of the second product, since methylene dichloride has no action on trimethyltrimethylenetriamine.

It is suggested that the addition of benzenesulphonyl chloride is followed by opening of the ring, giving (II; R = Ph·SO<sub>2</sub>). Interaction of the latter with trimethyltrimethylenetriamine or methylenemethylamine would result in the formation of *bis(benzenesulphonmethylamidomethyl)methylamine* (IV) and *methylenebisdimethylidimethylenediamine chloride* (III). The analytical data suggested the separation of the latter in a form containing 4 mols. of formaldehyde. This is not improbable, since trimethyltrimethylenetriamine, as usually prepared, contains appreciable quantities of formaldehyde.



*p*-Toluenesulphonyl chloride, added to trimethyltrimethylenetriamine in dry ether, gave an unstable crystalline compound, the properties of which are identical with those of the compound obtained with benzenesulphonyl chloride. Evaporation of the ethereal solution, however, gave a syrup from which

*p*-toluenesulphonmethylamide and *methylenebis-p-toluenesulphonmethylamide*,  $\text{CH}_2(\text{NMe}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7)_2$ , were separated. These probably result from the breakdown of a compound of type (IV). Bis(benzenesulphonmethylamidomethyl)methylamine readily decomposed in acid or alkaline solution to give formaldehyde, methylamine, and benzenesulphonmethylamide.

Attempts to prepare sulphonilamides of type (IV) have so far met with little success.

#### EXPERIMENTAL.

*Action of Benzenesulphonyl Chloride on NN'N''-Trimethyltrimethylenetriamine.*—Benzenesulphonyl chloride (5 c.c.) in dry ether was mixed with a dry ethereal solution of the base (5 c.c.) and kept for 2 days. The white crystalline *product* (III), m. p. 118—120° (decomp.), was removed and washed quickly with dry ether (Found: C, 42.4; H, 8.0; N, 14.9, 15.5; Cl, 17.7, 18.4.  $\text{C}_9\text{H}_{22}\text{N}_4\text{Cl}_2\cdot 4\text{CH}_2\text{O}$  requires C, 41.4; H, 8.0; N, 14.9; Cl, 18.8%). It was readily soluble in chloroform, and could be reprecipitated by ether. It decomposed readily in moist air, giving formaldehyde. When dried in a vacuum at the ordinary temperature, it lost weight and an odour resembling that of methyl isocyanide developed. When its solution in hydrochloric acid was steam-distilled to remove formaldehyde, evaporated to dryness, and extracted with chloroform, it yielded methylamine hydrochloride, m. p. and mixed m. p. 225°. On distillation of its aqueous solution formaldehyde was copiously evolved. The aqueous distillate, evaporated with hydrochloric acid, gave formaldehyde and methylamine hydrochloride; the latter was identified by means of its derivative with 2:4-dinitrochlorobenzene.

The ethereal solution, left to evaporate spontaneously, slowly deposited needle-like crystals. After being washed with water and small quantities of ether, *bis(benzenesulphonmethylamidomethyl)methylamine* was recrystallised from chloroform-ether, forming needles, m. p. 122—123°, insoluble in water and slightly soluble in ether (Found: C, 51.6; H, 5.8; S, 16.0.  $\text{C}_{17}\text{H}_{23}\text{O}_4\text{N}_3\text{S}_2$  requires C, 51.4; H, 5.8; S, 16.1%). The substance dissolved readily in cold hydrochloric acid, but decomposed, giving formaldehyde, in boiling acid solution. Distilled from sodium hydroxide, it decomposed slowly, giving a distillate in which formaldehyde and methylamine were easily detected. When acidified, the residual liquor gave benzenesulphonmethylamide as an oil which slowly solidified, m. p. 29—30° (Found: N, 8.0. Calc. for  $\text{C}_7\text{H}_9\text{O}_2\text{NS}$ : N, 8.2%).

*p-Toluenesulphonyl Chloride and the Base.*—Trimethyltrimethylenetriamine (5 g.) in dry ether was mixed with a solution of *p*-toluenesulphonyl chloride (6 g.) in dry ether. The solution developed an immediate turbidity and after several days deposited a crystalline substance, m. p. 118—122°, which exhibited the properties of the *product* (III) above (Found: N, 15.2. Calc. for  $\text{C}_9\text{H}_{22}\text{N}_4\text{Cl}_2\cdot 4\text{CH}_2\text{O}$ : N, 14.9%).

The syrupy liquid left on spontaneous evaporation of the residual ethereal solution in air was treated with cold dilute hydrochloric acid to remove any residual base. The crystalline solid remaining was collected, extracted with cold sodium hydroxide solution, and then warmed gently with sodium hydroxide solution until the smell of *p*-toluenesulphonyl chloride was not apparent. The residual *methylenebis-p-toluenesulphonmethylamide* crystallised from ether in cubes (0.7 g.), m. p. 117—118° (Found: C, 53.6; H, 5.5; S, 17.1.  $\text{C}_{17}\text{H}_{22}\text{O}_4\text{N}_2\text{S}_2$  requires C, 53.4; H, 5.75; S, 16.8%). When boiled with dilute acid, it decomposed, giving formaldehyde and *p*-toluenesulphonmethylamide (m. p. and mixed m. p.). The sodium hydroxide extracts, on acidification, gave *p*-toluenesulphonmethylamide (m. p. and mixed m. p.).

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