

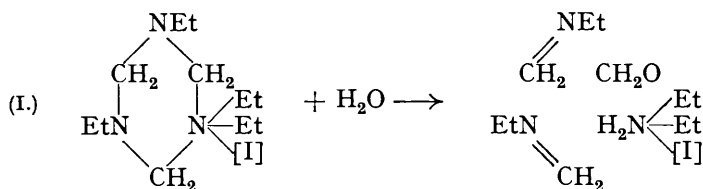
245. The Cyclic Methyleneamines. Hydrolysis of Quaternary Compounds. Preparation of Aliphatic Secondary Amines. Part I.

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The quaternary compounds formed from triethyltrimethylenetriamine ($\text{CH}_2 : \text{NEt}$)₃ with methyl iodide and ethyl iodide are hydrolysed by water. The product in the presence of alkali gives a tetra-alkylmethylenediamine together with cyclic methyleneamines. It is possible to separate these by distillation, and from the former to prepare the corresponding secondary amine. The method is being further explored with a view to its general application.

EINHORN and PRETTNER (*Ber.*, 1902, **35**, 2942; *Annalen*, 1904, **334**, 220) showed that the quaternary compounds obtained by the union of methyl iodide with triethyl- and trimethyl-trimethylenetriamine, when crystallised from cold alcoholic solution, gave hydriodides of the original cyclic bases; they further observed that isomeric hydriodides resulted on crystallisation from hot alcohol. As a preliminary to the examination of these isomers, it was decided to investigate the breakdown products of the quaternary compounds in aqueous solution.

Triethyltrimethylenetriamine ethiodide (I) in aqueous solution is decomposed into formaldehyde and triethyltrimethylenetriamine hydriodide, whereas in acid solution it decomposes to give a mixture of the salts of diethylamine and ethylamine. It thus seemed probable that the quaternary compound is hydrolysed as follows:



and in acid solution the methylene compounds would further react, $\text{NEt}:\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_2\text{Et} + \text{CH}_2\text{O}$, so that salts of both the mono- and the di-ethylamine would be formed.

In aqueous solution alone some of the triamine would be generated: $3\text{NEt}:\text{CH}_2 \rightarrow (\text{NEt}:\text{CH}_2)_3$, with subsequent separation of the hydriodide. Consequently, addition of alkali should result, not only in the regeneration of this base, but in the formation of tetra-alkylmethylenediamine: $2\text{NHR}_2 + \text{CH}_2\text{O} \rightarrow \text{CH}_2(\text{NR}_2)_2 + \text{H}_2\text{O}$. In order to confirm this, triethyltrimethylenetriamine methiodide was hydrolysed in this way, and the mixture of bases, when separated and fractionated, gave as final products *s.*-dimethyl-diethylmethylenediamine, $\text{CH}_2(\text{NMeEt})_2$, and the original base.

The formation of these quaternary compounds with subsequent hydrolysis by water appears similar to the hydrolysis of the quaternary compounds formed from the condensation product of benzaldehyde with hydrazine, which was used by Thiele (*Annalen*, 1910, **376**, 244) to prepare methylhydrazine. In this connection it is noteworthy that the Schiff bases form unstable quaternary compounds hydrolysing to alkyylanilines (Decker and Becker, *ibid.*, 1913, **395**, 362). *s.*-Dimethyldiethylmethylenediamine, like the cyclic methyleneamines, decomposed slowly in moist air with liberation of formaldehyde. It is much less soluble in water than triethyltrimethylenetriamine but dissolves readily in hydrochloric acid. By warming this solution gently, formaldehyde is evolved. From the aqueous residue on further evaporation, the nitroso-derivative of methylethylamine was prepared in good yield.

The yield of methiodide being 85–90% of the theoretical, that of tetra-alkylmethylenediamine was about 75%. The yield of recovered triethyltrimethylenetriamine is also in the region of 75%. Further quantities can be recovered from the alkaline residues. There is considerable loss of cyclic base if it is not completely dried before distillation: resinification appears to take place.

EXPERIMENTAL.

Triethyltrimethylenetriamine Ethiodide.—To 1 mol. of the base, prepared from ethylamine and 40% formaldehyde (J., 1931, 1490) and carefully dried over barium oxide and redistilled immediately before use, 3 mols. of ethyl iodide, dried and redistilled, were added. The mixture, set aside for several hours, gradually deposited needles of the ethiodide. The mother-liquor was drained off, and the ethiodide rapidly dried between absorbent sheets; it melted at 95–100° (decomp.) (Found: I, 38.5. Calc. for $C_{11}H_{26}N_3I$: I, 38.8%). The mother-liquor slowly deposited a further small crop after a few hours. Slight decomposition takes place in moist air.

Decomposition with water. The ethiodide dissolves slowly in water when added a little at a time, and when exposed to the air, triethyltrimethylenetriamine hydriodide is deposited, m. p. and mixed m. p. 124° (Einhorn and Prettnner gave m. p. 121°). Formaldehyde was evolved and a smell of the base was evident, but no other product was detected.

Decomposition with hydrochloric acid. An aqueous solution of the ethiodide (5 g.) was acidified with hydrochloric acid and evaporated to a syrup on the water-bath. Formaldehyde was copiously evolved, and the last traces of it were removed by heating in an air-oven at 70° for several hours. Benzenesulphonyl chloride was added in slight excess, followed by excess sodium hydroxide solution. Vigorous shaking afforded a white residue of benzenesulphon-diethylamide, 2.5 g., m. p. and mixed m. p. 42° on recrystallisation. The filtrate, acidified with hydrochloric acid, gave an oil which gradually solidified on standing and was identified as benzenesulphonethylamide (m. p. and mixed m. p.).

Methiodide of the base. The dry, freshly distilled base (60 c.c.) was dissolved in dry ether (40 c.c.), and a solution of methyl iodide (30 c.c.) in dry ether (30 c.c.) slowly added with shaking. Separation of the methiodide began at once. After 4 hours, the mass was almost solid. A portion removed and dried in absorbent sheets had m. p. 98–100° (Einhorn and Prettnner gave 97°).

Hydrolysis of the methiodide. An excess of water was added to the mass. This dissolved slowly, forming hard lumps at first. On complete solution, the ethereal layer was removed and freed from base by washing with hydrochloric acid. The washings were added to the aqueous layer, which was now treated with excess potassium hydroxide. The mixed bases separated as an oil, and after 48 hours' standing, they were extracted with ether and dried over barium oxide.

Separation of the bases. On distillation of the ether, a little amine also passed over. Some methylethylamine was recovered from the distillate by evaporation with hydrochloric acid and conversion into the nitrosoamine. When the ether had passed over, the temperature rose slowly to 80°, and a few c.c. of liquid (apparently ethyl isocyanide) then distilled. At 105° distillation recommenced, with slight discoloration of the liquid. Two fractions were collected: (a) b. p. 105–135°, (b) b. p. 185–210°, the latter with a slight yellow tinge. These were refractionated, (b) eventually giving triethyltrimethylenetriamine, b. p. 205–208°, as main product, and (a) affording a basic liquid, b. p. 128–133°. Further small amounts of the cyclic base could be recovered from the alkaline residues by steam distillation, evaporation of the distillate to small bulk after acidifying, and subsequent addition of formaldehyde followed by excess alkali.

s.-Dimethyldiethylmethylenediamine, b. p. 131°, d_4^{18} 0.7888, was obtained from fraction (a) (Found: C, 64.5; H, 13.9; N, 21.7; V.D., 60. $C_7H_{18}N_2$ requires C, 64.6; H, 13.8; N, 21.5%; V.D., 65). It is slightly hydrolysed in moist air, giving formaldehyde.

Nitrosomethylethylamine.—The foregoing diamine (14 c.c.) was acidified with concentrated hydrochloric acid and evaporated to a syrup on the water-bath. Formaldehyde was copiously evolved, and the last traces were driven off in an air-oven at 80°. Water (12.5 c.c.) was added, the liquid transferred to a distillation flask, and sodium nitrite (21 g. in 12.5 c.c. of hot water) slowly added. The distillate obtained by rapid heating of the mixture was redistilled with a little dilute sulphuric acid, and the nitrosoamine separated from the resultant aqueous solution by addition of excess potassium carbonate. Dehydrated over anhydrous potassium carbonate, it distilled as a pale yellow liquid with a characteristic nitrosoamine odour; b. p. 163°/747 mm., d_4^{18} 0.9448 (Found: C, 40.9; H, 9.1; N, 31.7. Calc. for $C_3H_8ON_2$: C, 40.9; H, 9.09; N, 31.8%).

Methylethylamine.—The nitrosoamine (9.5 g.) was refluxed with excess concentrated hydrochloric acid for 5 hours. Evaporation on the water-bath removed the excess acid, and the hydrochloride of the base separated as a waxy solid, m. p. 124–125° (Found: Cl, 37.0. Calc. for $C_3H_{10}NCl$: Cl, 37.2%). To the solid hydrochloride in a distillation flask, cooled in ice-

salt and fitted with a condenser and ice-cooled receiver, a concentrated solution of potassium hydroxide was added slowly from a tap-funnel. The mixture was distilled, and the distillate redistilled over solid potassium hydroxide to give methylethylamine, b. p. 35—38° (5 g.). When a slight excess of this base was added to a saturated solution of 2 : 4-dinitrochlorobenzene in alcohol, the solution turned deep orange, and after 2 hours, on shaking, 2 : 4-dinitrophenylmethylethylamine separated in orange needles. Recrystallised from alcohol, it melted sharply at 55° (Found : C, 47.9; H, 4.9; N, 18.7. $C_9H_{11}O_4N_3$ requires C, 48.0; H, 4.8; N, 18.7%).

Methylethylamine in aqueous solution was shaken with a slight excess of *p*-toluenesulphonyl chloride in the presence of sodium hydroxide. The oil separating was washed alternately with sodium hydroxide and hydrochloric acid and then warmed with alcoholic soda. On removal of the alcohol, the oil was extracted with ether, and distilled; b. p. 210°/50 mm. (Found : N, 6.7. Calc. for $C_{10}H_{15}O_2NS$: N, 6.6%); the thick oil could not be induced to crystallise.

It is hoped to examine the quaternary compounds of other trialkyltrimethylenetriamines with a view to test the general applicability of the method.

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