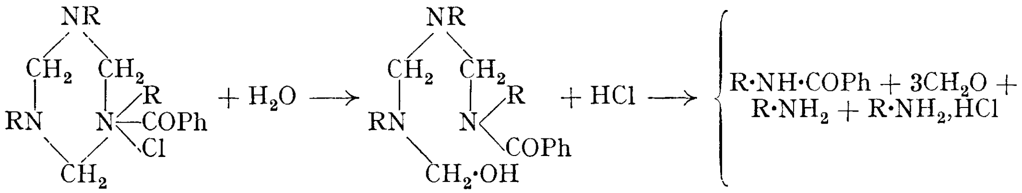
194. *The Action of Benzoyl Chloride and of Hydrogen Sulphide on Cyclic Methyleneamines.*

By JOHN GRAYMORE.

BENZOYL chloride added to aqueous solutions of the bases produced gluey masses which gradually decomposed, giving formaldehyde and benzoalkylamides in practically theoretical yields according to the equation

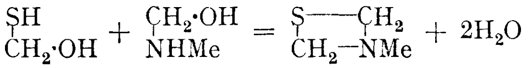
$$2(R{\cdot}N{:}CH_2)_3 + 3Ph{\cdot}COCl + 6H_2O = 3R{\cdot}NH{\cdot}COPh + 3R{\cdot}NH_2,HCl + 6CH_2O$$

The anhydrous bases in dry ether yielded with benzoyl chloride immediate precipitates of additive compounds, $(R{\cdot}N{:}CH_2)_3,Ph{\cdot}COCl$. These are unstable in moist air and decompose readily in water, liberating formaldehyde and the amide of the primary base. Probably the additive compound first reacts with water as pyridine acid chlorides do with alkali, and hydrolysis ensues :



An aqueous solution of trimethyltrimethylenetriamine at 0° saturated with hydrogen sulphide slowly evolved methylamine and subsequently gave the substance C_3H_7NS, m. p. and mixed m. p. 138°, obtained by Le Fèvre from methylamine, formaldehyde, and hydrogen sulphide (J., 1932, 1142). At the ordinary and at higher temperatures methylamine was evolved rapidly and the final product was methylthioformaldin (Wohl, *Ber.*, 1886, **19**, 2345).

Hydrogen sulphide and trimethyltrimethylenetriamine in dry ether gave a *hydrosulphide*, $(Me{\cdot}N{:}CH_2)_3,H_2S$. This salt decomposed rapidly in moist air; in aqueous solution methylamine was evolved and methylthioformaldin was ultimately deposited. These results indicate hydrolysis of the base in the presence of hydrogen sulphide as a first stage to give $Me{\cdot}NH{\cdot}CH_2{\cdot}OH$, followed by reaction with hydrogen sulphide : $Me{\cdot}NH{\cdot}CH_2{\cdot}OH + H_2S = Me{\cdot}NH_2 + SH{\cdot}CH_2{\cdot}OH$. Condensation would then take place as suggested by Le Fèvre :



$$\begin{array}{l}SH\\ CH_2{\cdot}OH\end{array} + \begin{array}{l}CH_2{\cdot}OH\\ NHMe\end{array} = \begin{array}{l}S\text{——}CH_2\\ CH_2\text{—}NMe\end{array} + 2H_2O$$

EXPERIMENTAL.

Tris-β-phenylethyltrimethylenetriamine.—β-Phenylethylamine hydrochloride (1 mol.) was dissolved in a small quantity of water, and a 40% solution of formaldehyde (1 mol.) added, followed by an excess of sodium hydroxide a little at a time with shaking. Much heat was developed, a gelatinous mass separating. The reaction was completed by gentle warming and vigorous shaking, the *base* separating as a clear liquid. It was extracted with ether, dried over barium oxide, and obtained, on distillation, as a pale yellow oil with a peculiar odour, b. p. 255° [Found : C, 81·1; H, 8·2; N, 10·5; *M*, in benzene, 380. $(C_8H_9N{:}CH_2)_3$ requires C, 81·2; H, 8·3; N, 10·5%; *M*, 399]. The hydrochloride, precipitated by dry hydrogen chloride from ethereal solution, decomposed readily in air or on warming, giving formaldehyde and β-phenylethylamine hydrochloride.

Action of Benzoyl Chloride on Trimethyltrimethylenetriamine.—The freshly distilled triamine (1 mol.) was dissolved in dry ether and treated with a solution of benzoyl chloride (1 mol.) in dry ether, added a little at a time. Heat was developed, a heavy white solid separating. The supernatant liquor was quickly decanted and the additive *compound* was washed rapidly several times with dry ether and dried in a vacuum over calcium oxide; attempts to crystallise it from chloroform usually resulted in decomposition [Found : Cl, 13·1. $(C_2H_5N)_3,C_6H_5{\cdot}COCl$ requires Cl, 13·2%].

Hydrolysis. 5 G. of the above solid were added to a small quantity of water. Formaldehyde was liberated, the smell of the base became apparent, and an oil separated, which crystallised after several days and, after recrystallisation from ether, had m. p. and mixed m. p. (with benzomethylamide) 78—80°. Hydrochloric acid was added to the residual liquor, the excess of formaldehyde removed by boiling, and the methylamine hydrochloride recovered by evaporation and purification in the usual way.

Triethyltrimethylenetriamine–Benzoyl Chloride.—This separated as a white solid, soluble in chloroform, when the base (1 mol.) in dry ether was mixed with benzoyl chloride. It was purified and dried as described above [Found: Cl, 11·2. $(C_3H_7N)_3,C_6H_5\cdot COCl$ requires Cl, 11·4%]. Hydrolysis with a small quantity of water gave benzoethylamide, m. p. (after recrystallisation from water) and mixed m. p. 67°.

Action of Benzoyl Chloride on Tris-β-phenylethyltrimethylenetriamine.—The base appeared to yield with benzoyl chloride a similar additive compound as a gelatinous mass. On hydrolysis with water a sticky solid was obtained with evolution of formaldehyde. The former was extracted with ether and a little hydrochloric acid. The ethereal layer on drying over sodium sulphate deposited crystals of benzo-β-phenylethylamide, m. p. and mixed m. p. 110°. β-Phenylethylamine hydrochloride was recovered on evaporation and crystallisation of the aqueous acid layer.

Action of Dry Hydrogen Sulphide on Anhydrous Trimethyltrimethylenetriamine.—The base (10 g.), distilled over barium oxide and dissolved in anhydrous ether, was saturated with dry hydrogen sulphide (over phosphoric oxide) at 0°. After 48 hours, the ether was rapidly removed from the long needle-like crystals of the *hydrosulphide* and this was dried in a vacuum over anhydrous sodium sulphate [Found: S, 19·6. $(CH_3\cdot N\dot{:}CH_2)_3,H_2S$ requires S, 19·6%]. It dissolved readily in hydrochloric acid with liberation of hydrogen sulphide. Addition of excess of caustic soda to the solution precipitated methylthioformaldin (mixed m. p. 65°).

Preparation of Methylthioformaldin.—A solution of methylamine hydrochloride (20 g.) in 100 c.c. of water was treated with 40% formaldehyde (80 g.) and cooled, and sodium hydroxide (13 g.), dissolved in a small quantity of water, was added slowly with cooling. After 2 hours the solution was saturated with hydrogen sulphide and kept. The first crop of crystals was then removed, and the solution again saturated with hydrogen sulphide. This treatment was repeated until there was no further deposition (yield, 32 g.). *Methylthioformaldin hydrobromide* formed monoclinic crystals from water, m. p. 170° (Found: Br, 36·9. $C_4H_9NS_2,HBr$ requires Br, 37·0%).

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[*Received, March 2nd,* 1935.]