

**175.** *The Reduction Products of Certain Cyclic Methylenamines. Part II.*

By JOHN GRAYMORE.

THE method employed for the preparation of secondary amines (J., 1931, 1490) has been extended to other cyclic methylenamines. In all the cases examined, the condensation  $3R \cdot NH_2 + 3CH_2O = (R \cdot N : CH_2)_3 + 3H_2O$  proceeds normally to give a practically theoretical yield of the cyclic base. These bases are stable in neutral or alkaline solution, but readily decompose in the presence of acid, rapidly on warming, evolving formaldehyde and giving the corresponding salt of the original primary amine used. They all form urates soluble in water, but the solubility of these is not so great as

in the previous cases studied. The bases form oily additive products with bromine and iodine, the investigation of which is not yet complete.

Reduction with zinc dust and hydrochloric acid proceeds smoothly, the secondary alkylmethyamines being the main product,



#### EXPERIMENTAL.

*Triisobutyltrimethylenetriamine*.—20 G. of freshly distilled *isobutylamine* (b. p. 68°), well cooled, were added gradually with shaking to an ice-cold solution of formaldehyde (21 g. of 40%). Immediate separation of an oily *base* took place. Caustic soda was added to complete the separation and the base was removed and finally dehydrated over barium oxide. It distilled from barium oxide as a colourless liquid, b. p. 255°, having the characteristic odour of these compounds;  $d^{18}_4$  0.8220 [Found: C, 70.6; H, 12.9; *M*, ebullioscopic in benzene, 254.  $(C_4H_9 \cdot N \cdot CH_2)_3$  requires C, 70.6; H, 12.9%; *M*, 255].

The *picrate* crystallised from alcohol in squat prisms, m. p. 107° [Found: C, 52.1; H, 7.4.  $(C_4H_9 \cdot N \cdot CH_2)_3 \cdot C_6H_3O_7N_3$  requires C, 52.1; H, 7.4%]. It decomposed in boiling water, evolving formaldehyde; *isobutylamine picrate*, m. p. 148°, was isolated from the solution.

The *oxalate*, precipitated by the base from a concentrated alcoholic solution of oxalic acid, crystallised from aqueous alcohol in pearly plates, m. p. 165° [Found: C, 59.1; H, 10.1.  $(C_4H_9 \cdot N \cdot CH_2)_3 \cdot H_2C_2O_4$  requires C, 59.1; H, 10.1%].

*Reduction*. The freshly distilled base (20 g.) was dissolved in well-cooled dilute hydrochloric acid, and zinc dust (20 g.) added. Hydrochloric acid (110 g.,  $d$  1.16, diluted to 1 in 3) was added slowly with cooling. After 15 minutes, the mixture was very gradually heated to boiling (2 hours). Ebullition was maintained until any trace of formaldehyde perceptible had disappeared. The mixture of amines was distilled from excess of caustic soda into hydrochloric acid. *Methylisobutylamine* was isolated from this solution in the form of its nitroso-derivative, b. p. 185–186° (Stoermer and von Lepel, *Ber.*, 1896, **29**, 2110), converted into the hydrochloride, m. p. 177°, by heating with alcoholic hydrogen chloride, and regenerated therefrom (12 g.), b. p. 76–78°.

The *picrate* crystallised from alcohol in yellow needles, m. p. 103° (Found: C, 41.7; H, 5.0.  $C_5H_{13}N \cdot C_6H_3O_7N_3$  requires C, 41.8; H, 5.1%).

The *hydrobromide*, prepared by adding a slight excess of the base to hydrobromic acid and evaporating the solution in a vacuum,

crystallised from water in needles, m. p.  $203^{\circ}$  (Found: Br, 47.6.  $C_5H_{13}N \cdot HBr$  requires Br, 47.6%).

2 : 4-Dinitromethylisobutylaniline crystallised quickly from a warm solution of 2 : 4-dinitrochlorobenzene in alcohol on addition of a slight excess of methylisobutylamine; m. p.  $92-93^{\circ}$  after recrystallisation from hot alcohol (Found: C, 52.1; H, 5.9.  $C_{11}H_{15}O_4N_3$  requires C, 52.2; H, 5.9%).

*Tri-n-butyltrimethylenetriamine*.—This was prepared from *n*-butylamine (20 g.) and 40% formaldehyde (21 g.) in the cold. The oily base, dried over barium oxide for 2 days, had b. p.  $285^{\circ}$  and  $d^{17}_{40}$  0.8550 [Found: C, 70.6; H, 12.9; *M*, ebullioscopic in benzene, 248.  $(C_4H_9 \cdot N \cdot CH_2)_3$  requires C, 70.6; H, 12.9%; *M*, 255].

The *picrate* was obtained from alcoholic solution as a syrup which crystallised after several days, and was recrystallised from aqueous alcohol, forming needles, m. p.  $75-76^{\circ}$ , slightly soluble in water. It decomposed when heated with water, evolving formaldehyde [Found: C, 52.0; H, 7.4.  $(C_4H_9 \cdot N \cdot CH_2)_3 \cdot C_6H_3O_7N_3$  requires C, 52.1; H, 7.4%].

The *hydrochloride*, obtained as a feathery mass from the base and hydrogen chloride in benzene, was extremely deliquescent [Found: Cl, 12.2.  $(C_4H_9 \cdot N \cdot CH_2)_3 \cdot HCl$  requires Cl, 12.2%].

*Reduction*. This was done, and the methyl-*n*-butylamine isolated, as in the case of the isobutyl compound. The *nitrosoamine* was a yellow oil, b. p.  $198^{\circ}$  (Found: C, 51.6; H, 10.35.  $C_5H_{12}ON_2$  requires C, 51.7; H, 10.35%), and the hydrochloride formed somewhat deliquescent needles, m. p.  $170^{\circ}$  (Found: Cl, 28.7. Calc. for  $C_5H_{13}N \cdot HCl$ : Cl, 28.7%). The recovered base (12–13 g.) had  $90-91^{\circ}$ .

*Methyl-n-butylamine picrate* was prepared in alcoholic solution and crystallised in needles, m. p.  $110-111^{\circ}$ , slightly soluble in water (Found: C, 41.8; H, 5.05.  $C_5H_{13}N \cdot C_6H_3O_7N_3$  requires C, 41.8; H, 5.1%).

*Triisoamyltrimethylenetriamine*.—*iso*Amylamine (20 g.) readily condensed with formaldehyde (18 g. of 40% solution) on gradual admixture with much cooling and shaking. Heat was evolved and the cyclic base separated immediately. It was purified as in the previous cases and obtained as a rather unpleasant-smelling oil, b. p.  $299-300^{\circ}$ ,  $d^{18}_{40}$  0.8250, insoluble in water but soluble in alcohol and ether [Found: C, 72.7; H, 13.1; *M*, ebullioscopic, 294 (mean).  $(C_5H_{11} \cdot N \cdot CH_2)_3$  requires C, 72.7; H, 13.1%; *M*, 297].

The *oxalate*, precipitated from a concentrated alcoholic solution of oxalic acid, crystallised from aqueous alcohol in light leaflets, m. p.  $115^{\circ}$ , sparingly soluble in cold water [Found: C, 62.0; H, 10.6.  $(C_5H_{11} \cdot N \cdot CH_2)_3 \cdot H_2C_2O_4$  requires C, 62.0; H, 10.6%]. It decom-

posed in hot aqueous solution, giving off formaldehyde; *isoamylamine* oxalate, m. p.  $165^{\circ}$ , was isolated from the residual liquor.

The *picrate* separated from alcoholic solution as a syrup and crystallised from acetone, cooled in a freezing mixture, in tufts of needles, m. p.  $75^{\circ}$  (indistinct), soluble in water and alcohol [Found : C, 54.7; H, 7.9.  $(C_5H_{11}\cdot N\cdot CH_2)_3\cdot C_6H_3O_7N_3$  requires C, 54.75; H, 8.0%].

The *hydrochloride*, obtained from benzene solution, was so deliquescent that its m. p. could not readily be determined [Found : Cl, 10.6.  $(C_5H_{11}\cdot N\cdot CH_2)_3\cdot HCl$  requires Cl, 10.6%].

The *urate* was a white amorphous powder only slightly soluble in water. It decomposed at a high temperature without melting. Boiled with water, it decomposed, evolving formaldehyde [Found : C, 59.3; H, 9.0.  $(C_5H_{11}\cdot N\cdot CH_2)_3\cdot C_5H_4O_3N_4$  requires C, 59.35; H, 9.0%].

*Reduction.* This was done as in the previous cases and gave 10 g. of methyl*isoamylamine*, b. p.  $108^{\circ}$ , isolated through the *nitrosoamine*, b. p.  $204-205^{\circ}$  (Found : C, 55.4.  $C_6H_{14}ON_2$  requires C, 55.3%), and the crystalline hydrochloride, m. p.  $178^{\circ}$ .

*Methylisoamylamine hydrobromide* crystallised from an aqueous solution of the components in needles, m. p.  $183^{\circ}$ , soluble in alcohol and water (Found : Br, 44.0.  $C_6H_{15}N\cdot HBr$  requires Br, 44.0%).

*Tribenzyltrimethylenetriamine.*—This was prepared from 20 g. of benzylamine and 18 g. of 40% formaldehyde solution in a freezing mixture, separation of the treacly *base* being completed by addition of caustic soda. The base was extracted and dried (48 hours over barium oxide) in ether, distilled above  $200^{\circ}$ , and again dried over barium oxide; on redistillation it had b. p.  $240^{\circ}$  and  $d_{15}^{25}$  1.05 (yield, 80%). It is insoluble in water but soluble in alcohol, ether, and benzene [Found : C, 80.6; H, 7.5; *M*, ebullioscopic in benzene, 352 (mean).  $(C_6H_5\cdot CH_2\cdot N\cdot CH_2)_3$  requires C, 80.6; H, 7.6%; *M*, 357].

The *oxalate*, precipitated from alcoholic solution and recrystallised from aqueous alcohol, formed plates, m. p.  $135^{\circ}$  (decomp.) [Found : C, 69.8; H, 6.5.  $(C_6H_5\cdot CH_2\cdot N\cdot CH_2)_3\cdot H_2C_2O_4$  requires C, 69.8; H, 6.5%]. Its aqueous solution evolved formaldehyde when boiled, and benzylamine oxalate, m. p.  $201^{\circ}$ , was isolated from the residual liquor.

*Reduction.* 20 G. of tribenzyltrimethylenetriamine were dissolved in cold dilute hydrochloric acid, 30 g. of zinc dust added, followed gradually by 420 c.c. of dilute hydrochloric acid (1 : 3). Reduction was carried out as before and the mixed amines were collected in hydrochloric acid. The hydrochlorides obtained from the solution were dissolved in water and shaken with benzenesulphonyl chloride and sodium hydroxide, an excess of the latter being finally added,

and the mixture warmed to dissolve the sulphonamide of the primary amine. The insoluble benzenesulphonbenzylmethanamide crystallised from acetone in tiny hard granules, m. p.  $130^{\circ}$ , soluble in alcohol (Found : C, 64.4; H, 5.7. Calc. : C, 64.3; H, 5.75%). From the filtrate, benzenesulphonbenzylamine, m. p.  $88^{\circ}$ , was obtained by precipitation with hydrochloric acid and recrystallisation from acetone (Found : C, 63.1; H, 5.3. Calc. : C, 63.2; H, 5.3%).

*p*-Toluenesulphonbenzylmethanamide crystallised from acetone in squat prisms, m. p.  $92^{\circ}$  (Found : C, 65.4; H, 6.1.  $C_{15}H_{17}O_2NS$  requires C, 65.45; H, 6.15%).

2 : 4-Dinitromethylbenzylaniline separated slowly in long yellow needles from an alcoholic solution of 2 : 4-dinitrochlorobenzene containing a slight excess of benzylmethanamine; m. p.  $140^{\circ}$  after recrystallisation from alcohol (Found : C, 58.5; H, 4.5.  $C_{14}H_{13}O_4N_3$  requires C, 58.5; H, 4.5%).

The method is being extended to other primary aliphatic and aromatic amines.

STOCKPORT COLLEGE.

[Received, February 22nd, 1932.]

---