378. *Reactions of Nitroparaffins. Part II. The Reaction of 2-Nitropropane with Formaldehyde and Ammonia.*

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2-Nitropropane with formaldehyde in the presence of ammonia yields a secondary amine, di-(2-nitro*iso*butyl)amine (I; R = H), also obtained in a purer form when 2-nitropropane reacts with formaldehyde and sodium cyanide. When, in the former mixture, ammonia was replaced by methylamine the *N*-methyl derivative of (I) was produced. Formaldehyde, 2-nitropropane, and *cyclo*hexylamine give N-cyclo*hexyl-2-nitro*iso*butylamine*.

IT has been shown (Hirst, Jones, Minahan, Ochynski, Thomas, and Urbanski, *J.*, 1947, 924) that 1-nitropropane reacts with formaldehyde and ammonia yielding polymeric substances. 2-Nitropropane reacts with ammonia and formaldehyde in an analogous manner, but does not yield compounds of high molecular weight; instead, di-(2-nitro*iso*butyl)amine (I; R = H) is produced (cf. Senkus, *J. Amer. Chem. Soc.*, 1946, **68**, 11).

$$NO_2\cdot CHMe_2 + 2CH_2O + NH_3 \longrightarrow (NO_2\cdot CMe_2\cdot CH_2)_2NR \quad (I.)$$

The same substance is formed in better yield if the ammonia is replaced by sodium cyanide, probably as a result of the reactions :

$$CH_2O + NaCN + H_2O \longrightarrow OH{\cdot}CH_2{\cdot}CN + NaOH$$
$$OH{\cdot}CH_2{\cdot}CN + NaOH + H_2O \longrightarrow OH{\cdot}CH_2{\cdot}CO_2Na + NH_3$$

If sodium cyanide is replaced by potassium cyanide, the yield is reduced.

If the ammonia is replaced by methylamine or *cyclo*hexylamine, the product is, respectively, (I; $R = CH_3$) or *N-cyclo*hexyl-2-nitro*iso*butylamine. All these condensations are similar to those encountered in the Mannich reaction.

EXPERIMENTAL.

Di-(2-*nitro*iso*butyl*)*amine*.—2-Nitropropane (0·2 mol., 17·8 g.) was mixed with 40% formaldehyde (0·4 mol., 30 c.c.) and 28% ammonia (0·2 mol., 12 c.c.). A spontaneous reaction occurred with evolution of heat, and an oily layer separated. After *ca.* 30 minutes the reaction subsided, and the solution was then boiled for an hour. The oil was separated from the cooled solution and purified by washing it with water. It partly crystallised when kept. *Di-*(2-*nitro*iso*butyl*)*amine* (I; R = H), isolated on a tile (yield, 2·4 g.), was recrystallised from alcohol and water; it formed white plates, m. p. 35° [Found : C, 44·1; H, 8·1; N, 19·5; *M* (Rast), 213. $C_8H_{17}O_4N_3$ requires C, 43·8; H, 7·8; N, 19·2%; *M*, 219], soluble in most organic solvents but insoluble in water.

(I; R = H) was prepared in better yield by mixing 2-nitropropane (17·8 g.) with 40% formaldehyde (100 c.c.) and a solution of sodium cyanide (16 g.) in water (50 c.c.). A spontaneous reaction ensued, the temperature increasing by *ca.* 50°. After *ca.* 15 minutes the reaction subsided, and the solution was then boiled for a further 45 minutes. An oily product (7·1 g.) had separated, which solidified on the addition of cold water (150 c.c.). Recrystallised from aqueous alcohol, it had m. p. 35°, undepressed on admixture with the previous sample (Found : N, 19·4%).

The amine (5 g.) was dissolved in hot (*ca.* 100°) 50% sulphuric acid (27 g.); the *hydrogen sulphate* which separated on cooling, crystallised from acetic acid as needles, m. p. 170° (decomp.) (4·1 g.) (Found : C, 29·9; H, 6·5; N, 13·0; S, 9·8. $C_8H_{17}O_4N_3,H_2SO_4$ requires C, 30·3; H, 6·5; N, 13·2; S, 10·1%). It can also be prepared by using 10% sulphuric acid. It is sparingly soluble in cold, but readily soluble in hot water, alcohol, acetone, or acetic acid, and insoluble in ether, benzene, or chloroform.

Adding an excess of hydrogen chloride in alcohol to the amine (3 g.) in ether (30 c.c.) gave an immediate crystalline precipitate of the *hydrochloride* (1·2 g.), m. p. 178° (decomp.) (from acetic acid) (Found : N, 16·0; Cl, 13·8. $C_8H_{17}O_4N_3,HCl$ requires N, 16·0; Cl, 13·9%), also obtained by dissolving the amine in hot aqueous 10% hydrochloric acid.

The amine hydrochloride (1 g.) was dissolved in cold water (20 c.c.) and a 20% solution of sodium nitrite was added. The white precipitate formed was dissolved in ether, washed with 10% sodium carbonate and then with water, and dried (Na_2SO_4). Evaporation left the *nitroso*-compound, which crystallised from ether in needles, m. p. 128° (0·8 g.) (Found: C, 39·3; H, 6·9; N, 22·8. $C_8H_{16}O_5N_4$ requires C, 39·6; H, 6·45; N, 22·6%). It gives a positive Liebermann reaction, and is almost insoluble in water but readily soluble in ether. It dissolved slowly in boiling hydrochloric acid to yield the hydrochloride of (I; R = H) which separated on cooling, m. p. and mixed m. p. 176°. The *N*-nitroso-compound was recovered unchanged after treatment with 10% sodium hydroxide.

N-*Methyldi-*(2-*nitro*iso*butyl*) *amine*.—2-Nitropropane (6 g.), paraformaldehyde (2 g.), a 30% solution of methylamine (3 c.c.), and water (25 c.c.) were mixed, warmed at 60° for 3 hours, and cooled. The mixture was extracted with ether. Evaporation gave a syrup (7 g.), which was distilled under reduced pressure. Fraction 1 (b.p. 80°/0·02 mm.) crystallised partly when kept; after draining on a tile, 2-nitro*iso*butyl alcohol m. p. 79°, was obtained (Found : C, 40·1; H, 7·4; N, 11·8. Calc. for $C_4H_9O_3N$: C, 40·3; H, 7·6; N, 11·8%). Fractions II (b. p. 90°/0·02 mm.) and III (b. p. 110°/0·02 mm.) did not crystallise; with hydrochloric acid they formed N-*methyldi-*(2-*nitro*iso*butyl*)*amine hydrochloride*, m. p. 166° (decomp.) (Found: C, 40·2; H, 7·2; N, 15·6; Cl, 13·3. $C_9H_{19}O_4N_3,HCl$ requires C, 40·1; H, 7·4; N, 15·6; Cl, 13·2%).

Keeping the syrupy tertiary amine in methyl iodide gave the crystalline *methiodide* which, when recrystallised from alcohol–ether, had m. p. 169° (Found : C, 32·1; H, 5·9; N, 12·3; I, 36·6. $C_{10}H_{22}O_4N_3I$ requires C, 32·0; H, 5·9; N, 11·2; I, 33·9%).

N-cyclo*Hexyl-*2-*nitro*iso*butylamine Hydrochloride*.—2-Nitropropane (3 g.) was warmed with paraformaldehyde (1 g.), *cyclo*hexylamine (1 g.), and water (50 c.c.) at 60° for 1 hour. The product was isolated by extraction with ether. The resultant syrup yielded, with concentrated hydrochloric acid, crystalline N-cyclo*hexyl-*2-*nitro*iso*butylamine hydrochloride*. Recrystallised from aqueous alcohol, this had m. p. 201° (Found : C, 50·8; H, 9·1; N, 11·4; Cl, 14·6. $C_{10}H_{20}O_2N_2,HCl$ requires C, 50·7; H, 8·9; N, 11·8; Cl, 15·0%).

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