

172. *The Reaction of 1-Nitropropane with Formaldehyde and Ammonia.*

By E. L. HIRST, J. K. N. JONES, (MRS.) S. MINAHAN, F. W. OCHYNSKI, A. T. THOMAS, and T. URBANSKI.

Products of both high and low molecular weight are formed by the interaction of 1-nitropropane, formaldehyde, and ammonia. The reaction is shown to be essentially one of the type described by Mannich, in which the nitropropane provides the necessary active hydrogen atom. Amongst the products are ring compounds of the 1:3-tetrahydro-oxazine and 1-oxa-3-azacyclooctane type.

CONSIDERABLE interest has been shown recently in the chemistry of the nitro-paraffins (see, for example, Johnson and Degenry, *J. Amer. Chem. Soc.*, 1939, **61**, 3194; Spring and Degenry, *ibid.*, 1942, **64**, 1063; Senkus, *ibid.*, 1946, **68**, 11; Johnson, *ibid.*, pp. 12, 14) and it is opportune to summarise work carried out during the past few years, but hitherto withheld from publication by reason of war-time secrecy regulations. One of the authors has previously shown that the large-scale preparation of nitro-paraffins was practicable (Urbanski, *Rocz. Chem.*, 1936, **16**, 466; 1937, **17**, 161; *Compt. rend.*, 1936, **203**, 620; 1937, **204**, 870) and has indicated their use for the production of combustible resins (Urbanski, B.P. Appln. 7681, 5th June, 1942; U.S.P. Appln. 488,456, 25th May, 1943). These resinous materials were made by the interaction of nitropropane, formaldehyde, and ammonia, and it was therefore of interest to investigate the nature of the reactions responsible for their formation. The present paper records some of the results obtained in a study of reactions which had not at that time been reported in the literature, despite the interest displayed by earlier workers (*e.g.*, Henry; Mousset; Duden, Bock, and Reid; Cerf de Mauny; Zief and Mason) in the condensation of formaldehyde, nitro-paraffins, and amines. The resins obtained from 1-nitropropane, formaldehyde, and ammonia are basic. The precise nature of the portion of high molecular weight is still uncertain, but the types of linkage are indicated by the structures of the accompanying materials of low molecular weight and by the nature of the decomposition products of the resinous materials.

The first stage in the series of reactions is the formation of 2-nitrobutanol (I) and 2-nitro-2-ethylpropane-1:3-diol (II). Since ammonia is present, together with formaldehyde, hexamethylenetetramine is also produced and this yields with (II) a molecular *complex*. When warmed in water this complex gives a resin similar to those obtained by the interaction of the three components. The mechanism of the reaction appears to resemble that of the Mannich reaction. From (II) and ammonia a *base* (III) is produced, and this then reacts with formaldehyde, giving the *N*-hydroxymethyl derivative (IV), which on cyclisation gives the *oxazine* (V). No evidence for the formation of *N*-methyl derivatives was obtained. Since only one of the hydrogen atoms in (V) can react with formaldehyde it follows that (V) cannot yield a polymer on further condensation, and its production in reactions designed to lead to resin formation is to be avoided. Under appropriate conditions, however, there may be as much as 30% of (V) present in the crude resin. It is an oil which can be separated by distillation or by precipitation of the crystalline *hydrochloride*, and yields with methyl iodide a crystalline *methiodide* (VI). The corresponding hydroxide decomposes when heated yielding nitrobutene and other decomposition products.

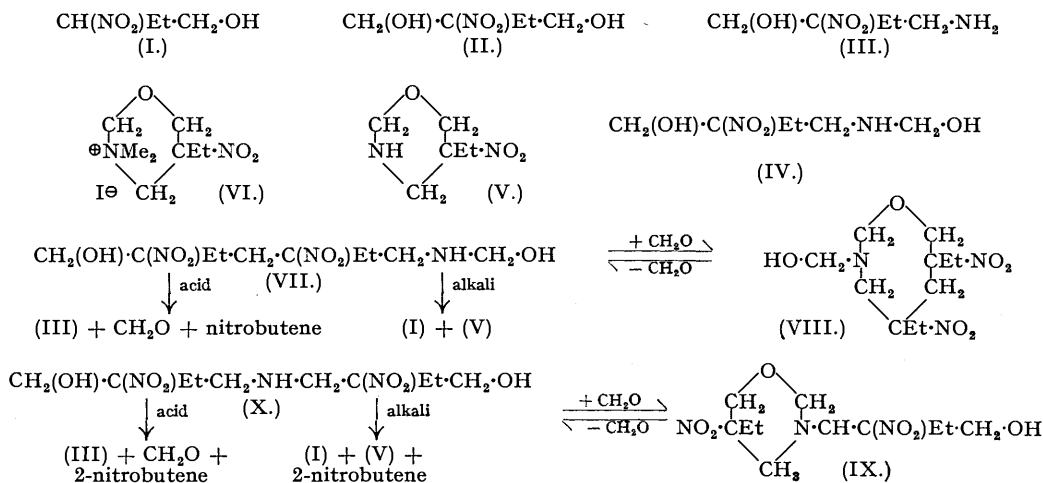
If the reaction between nitropropane, formaldehyde, and ammonia was interrupted shortly after the nitropropane had dissolved, an oily product was precipitated on cooling. It crystallised slowly, and either (VIII) or (X) was formed according to the conditions of the reaction, (VIII) being found when 1 mol. of ammonia was used per mol. of nitropropane, and (X) when 0.5 mol. of ammonia was used. (VIII) lost formaldehyde on being warmed with concentrated hydrochloric acid and gave the crystalline *hydrochloride* of (VII), and when the latter was warmed with formaldehyde it passed back into (VIII). The hydrochloride of (VII) gave a *picrate*; with sodium nitrite it gave an oily nitroso-compound which was reconverted into (VII) on being heated with concentrated hydrochloric acid, the presence of an imino-group being thus proved. The hydrochloride of (VII) when boiled in aqueous solution decomposed with the formation of the *hydrochloride* of (III), 2-nitrobutene, and formaldehyde. With aqueous sodium hydrogen carbonate it gave the crystalline base (VII) which decomposed on distillation in a vacuum giving (V) and (I). The formation of (VII) and (VIII) can be represented as an example of the Mannich reaction, and the formulæ suggested for these substances serve to explain their mode of origin and their chemical properties.

The *base* (IX) gives a series of reactions similar to those of (VIII). It dissolves in cold

concentrated hydrochloric acid giving a *hydrochloride* which hydrolyses in water, regenerating (IX). If (IX) is heated with dilute hydrochloric acid, 1 mol. of formaldehyde is eliminated and the *hydrochloride* of the secondary base (X) is formed. The hydrochloride of (X) when heated with aqueous formaldehyde regenerates the tertiary base (IX). The hydrochloride of (X) gave a well-defined *picrate* and an oily nitroso-compound which regenerated the hydrochloride of (X) when heated with concentrated hydrochloric acid, indicating the presence of an imino-group. The hydrochloride of (X) on treatment with aqueous sodium carbonate gave the corresponding crystalline base which decomposed when boiled with water or on distillation under reduced pressure with formation of (I), 2-nitrobutene, and (V). The hydrochloride of (X), on prolonged boiling with water, gave ammonium chloride, formaldehyde, 2-nitrobutene, and the hydrochloride of (III). The formation of (IX) and (X) and their chemical properties can most easily be explained by the mechanism shown in the accompanying scheme.

Substance (V) can be obtained from the resin by distillation under reduced pressure or by the action of hydrochloric acid, as well as by the decomposition of the bases (VII) and (X). It forms a picrate and hydrochloride and an oily nitroso-derivative. The hydrochloride when boiled with water eliminates 1 mol. of formaldehyde with formation of the hydrochloride of (III). This reaction is reversible, the hydrochloride of (III) regenerating the hydrochloride of (V) on crystallisation from propyl alcohol containing formaldehyde.

The base (III), which was unstable even at room temperature, is a primary amine, since it gives nitrogen with aqueous sodium nitrite. The action is, however, complex since the initial gentle evolution of nitrogen was followed by a violent reaction in which nitrous oxide, as well as nitrogen, was evolved and a greenish water-insoluble oil was produced.



EXPERIMENTAL.

Additive Compound [(C₅H₁₁O₄N)₃,C₆H₁₂N₄] of 2-Nitro-2-ethylpropane-1 : 3-diol and Hexamethylenetetramine.—1-Nitropropane (1 mol., 89 g.) was added to a cold mixture of 40% formaldehyde (3 mols., 225 c.c.) and 33% ammonia (1 mol., 59 c.c.). The mixture was stirred at room temperature until the nitropropane disappeared (12–15 hours). After some time the aqueous solution was separated from an oily precipitate (containing 2-nitrobutanol). The addition of sodium chloride to the aqueous solution salted out an oil, which solidified in fine needles (100 g.). It was the additive compound of 2-nitro-2-ethylpropane-1 : 3-diol (3 mols.) and hexamethylenetetramine (1 mol.); white needles from chloroform, m. p. 117°. The additive compound is very readily soluble in water, soluble in alcohol, very slightly soluble in ether. It gave hexamethylenetetramine picrate, m. p. 179°, with picric acid, and hexamethylenetetramine hydrochloride with hydrochloric acid. It was dissociated in solution. For example, ebulliometric determination in chloroform gave *M*, 158 [calc. for hexamethylenetetramine, 140; for 2-nitro-2-ethylpropane-1 : 3-diol, 149. (C₅H₁₁O₄N)₃,C₆H₁₂N₄ requires *M*, 587]. When heated it was converted into a resin.

Another method for the preparation of the additive compound consisted in mixing concentrated aqueous solutions of 2-nitro-2-ethylpropane-1 : 3-diol (4.47 g.) with hexamethylenetetramine (1.40 g.). The crystalline additive product (4.2 g.) was precipitated on standing [Found : CH₂O, determined by the 2 : 4-dinitrophenylformhydrazone method, 30.5. (C₅H₁₁O₄N)₃,C₆H₁₂N₄ requires CH₂O, 30.8%].

Resin A.—1-Nitropropane (1 mol., 89 g.) was heated with 40% formaldehyde (3 mols., 225 c.c.) and 33% ammonia (1 mol., 59 c.c.) with stirring at 90–95° for 15–30 minutes. The reaction was then stopped by rapid cooling (pouring on ice). An oily layer containing nitro-olefins was separated

by decantation. The liquor was reheated and the temperature maintained at 90—95° for 8 hours with efficient stirring.

The resin formed a separate phase which was isolated by decantation. It was washed with hot water and dried in a partial vacuum. By evaporation of the liquor an additional quantity was obtained (yield, 110—125 g.).

Resin B.—2-Nitro-2-ethylpropane-1 : 3-diol (1 mol., 149 g.) was mixed with 40% formaldehyde (1 mol., 75 c.c.) and 33% ammonia ($\frac{1}{2}$ mol., 295 c.c.). The temperature was kept between 90° and 95° for 10 hours with stirring. The oily product was precipitated and, after cooling, was separated from the liquor, washed, and dried in partial vacuum (yield, 110 g.). The resin was a colourless and odourless viscid liquid.

Isolation of (V) from resins A and B. Fractionation of the resin under reduced pressure gave two fractions: (a) b. p. 140° (bath temp.)/0.01 mm., n_D^{20} 1.4720; (b) b. p. 160—180° (bath temp.)/0.01 mm., n_D^{20} 1.4880. Both fractions with methyl iodide gave a derivative, m. p. 218° (decomp.), identical with the methiodide of 5-nitro-3-methyl-5-ethyltetrahydro-1 : 3-oxazine (VI) described below. The liquid air trap of the distillation apparatus contained 2-nitrobutene and a blue nitroso-derivative of unknown constitution.

Isolation of (IX) by steam distillation of the resin A or B. The resin *A* or *B* (9.3 g.) was distilled in steam giving an oil (6 g.) which was mainly the base (V), since with methyl iodide it gave the crystalline methiodide (VI). The aqueous distillate was extracted with ether and then with benzene, and the combined extracts were dried (Na_2SO_4) and evaporated to a syrup (4 g.) under reduced pressure. The syrup crystallised on standing and, after tiling and recrystallising from benzene, 5-nitro-5-ethyl-3-(2-nitro-2-hydroxymethylbutyl)tetrahydro-1 : 3-oxazine (IX), m. p. 101°, was isolated (Found: C, 45.4; H, 7.2; N, 13.9. $\text{C}_{11}\text{H}_{21}\text{O}_6\text{N}_3$ requires C, 45.4; H, 7.2; N, 14.4%).

Preparation of the Bases (VIII) and (IX).—1-Nitropropane (1 mol., 89 g.) was mixed with 40% formaldehyde (3 mols., 225 c.c.) and 33% ammonia (1 mol., 59 c.c.) and heated with stirring during 1½ hours at 90—95°. The hot solution was then poured into ice-water. The oily precipitate crystallised on standing (after ca. 2 weeks), yielding crystals of 5 : 7-dinitro-3-hydroxymethyl-5 : 7-diethyl-1-oxa-3-azacyclooctane (VIII). Recrystallised from ether and then from chloroform or from benzene-light petroleum, it gave white needles, m. p. 97° (yield, 15—20 g.). It was soluble in hot water, cold ether, alcohol, acetone, and benzene, insoluble in light petroleum. It was less soluble in chloroform than (IX). Mixed with (IX) it gave considerable depression of m. p. (70—73°) [Found: C, 45.3; H, 7.0; M (ebulliometrically in benzene), 280. $\text{C}_{11}\text{H}_{21}\text{O}_6\text{N}_3$ requires C, 45.4; H, 7.2%; M, 291].

The base (VIII) gave with cold concentrated hydrochloric acid the hydrochloride, m. p. 174° (Found: C, 40.1; H, 6.7; N, 12.1; Cl, 10.9. $\text{C}_{11}\text{H}_{21}\text{O}_6\text{N}_3\cdot\text{HCl}$ requires C, 40.3; H, 6.5; N, 12.8; Cl, 10.8%). This hydrochloride hydrolysed in cold water yielding the free base (VIII). On being warmed with concentrated hydrochloric acid the hydrochloride lost one molecule of formaldehyde and was converted into the hydrochloride of hydroxymethyl-2 : 4-dinitro-4-hydroxymethyl-2-ethylhexylamine (VII), m. p. 179° (Found: CH_2O , 10.9. Loss of 1 mol. of CH_2O requires 10.3%). It depressed the m. p. of the hydrochloride of (VIII). This hydrochloride of (VII) was insoluble in ether, benzene, and chloroform, readily soluble in water and hot alcohol, sparingly soluble in cold alcohol. It recrystallised from alcohol in the form of small plates, m. p. 179° (decomp.) (Found: C, 38.4; H, 7.1; N, 12.4; Cl, 11.2. $\text{C}_{10}\text{H}_{21}\text{O}_6\text{N}_3\cdot\text{HCl}$ requires C, 38.0; H, 6.7; N, 13.3; Cl, 11.3%). On being heated with concentrated aqueous formaldehyde it gave an oil, which was extracted with ether; the dried extracts were evaporated in partial vacuum to a syrup, which crystallised slowly. After standing the crystals were triturated with ether and filtered. Recrystallisation from benzene gave the pure base (VIII), m. p. and mixed m. p. 97°. The hydrochloride of (VII) reacted with sodium nitrite and gave an oily nitroso-derivative soluble in ether. The latter regenerated the hydrochloride of (VII) on treatment with concentrated alcoholic hydrogen chloride.

The hydrochloride of (VII) was dissolved in alcohol and aqueous picric acid was added. The pale yellow picrate of (VII) was precipitated, m. p. 154° (Found: C, 38.2; H, 4.8; N, 16.4. $\text{C}_{10}\text{H}_{24}\text{O}_{13}\text{N}_6$ requires C, 37.8; H, 4.7; N, 16.5%). The picrate was unstable and could not be recrystallised from water.

The hydrochloride of (VII) (1.45 g.) was dissolved in water, and sodium hydrogen carbonate and ether were added. The syrupy base (1.33 g.) was isolated on evaporation of the solvent. The base (VII) (1.33 g.) on distillation under reduced pressure gave a fraction (0.74 g.), n_D^{20} 1.4670, b. p. 140° (bath temp.)/0.01 mm., and a still residue (0.35 g.). The volatile fraction consisted of the base (V) and 2-nitrobutanol. These were separated by dissolving the base in the calculated quantity of hydrochloric acid. The 2-nitrobutanol (I) was then extracted with ether. The base (V) was characterised by its hydrochloride, m. p. 203° (decomp.), and picrate, m. p. 153°, not depressed on admixture with an authentic specimen.

The hydrochloride of (VII) (888 mg.) was dissolved in water and the solution boiled. Decomposition occurred and formaldehyde and 2-nitrobutene distilled. The aqueous solution remaining in the flask was evaporated to dryness under reduced pressure and the residue (516 mg.) was triturated with acetone and filtered. The residue (68 mg.) was ammonium chloride. The acetone solution was evaporated to a syrup and triturated with ether; the hydrochloride of the base (III), m. p. 126° (see below), then crystallised. The aqueous distillate contained formaldehyde (Found: 9%; 1 mol. requires 9.5%) and 2-nitrobutene (characteristic odour, absorption of bromine, polymerises with alkali).

Preparation of (IX).—2-Nitro-2-ethylpropane-1 : 3-diol (1 mol., 149 g.) was heated with 40% formaldehyde (1 mol., 75 c.c.) and 33% ammonia ($\frac{1}{2}$ mol., 26 c.c.) at 95—96° for ca. 1½ hours. The product (IX) was isolated by pouring into ice-water. It recrystallised from ether, chloroform, or benzene-light petroleum in long needles, m. p. 101°. Yield, 50 g. [Found: C, 45.6; H, 7.0; N, 14.5; M (ebulliometrically in benzene), 285. Calc. for $\text{C}_{11}\text{H}_{21}\text{O}_6\text{N}_3$: C, 45.4; H, 7.2; N, 14.4%; M, 291].

A simple method of isolating the base (IX) from the resin *B* consisted in dissolving the resin in cold hydrochloric acid. The solution was poured on ice. The resinous substance precipitated was extracted

with ether, the extracts were dried and the ether was evaporated. The residue solidified into crystals of (IX), m. p. and mixed m. p. 98°.

The base (IX) reacted with cold concentrated hydrochloric acid, yielding the *hydrochloride*, m. p. 156° (Found: C, 40.4; H, 6.8; N, 12.6; Cl, 10.6. $C_{11}H_{21}O_6N_3 \cdot HCl$ requires C, 40.3; H, 6.5; N, 12.8; Cl, 10.8%). The same product was obtained by passing hydrogen chloride through a solution of the base (IX) in chloroform or carbon tetrachloride. It is insoluble in ether or chloroform, soluble in alcohol. On dissolving in water it hydrolyses giving the free base (IX), m. p. 101° (Found: C, 45.1; H, 7.3; N, 13.3%).

Hydrochloride of (X).—The base (IX) or its hydrochloride, when heated with concentrated hydrochloric acid, lost a molecule of formaldehyde and was converted into the hydrochloride of bis-2-nitro-2-hydroxymethylbutylamine (X) (Found: CH_2O , 10.3. Loss of one mol. of CH_2O requires 10.3%). The *hydrochloride* separated in plates or needles from absolute alcohol, m. p. 186° (Found: C, 38.0; H, 6.8; N, 12.7; Cl, 11.2. $C_{10}H_{19}O_6N_3 \cdot HCl$ requires C, 38.0; H, 6.7; N, 13.3; Cl, 11.3%). On warming an aqueous solution of the hydrochloride with formaldehyde solution (40%) an oil separated and was extracted with ether. The extract was dried (Na_2SO_4) and the ether removed; the base (IX) then crystallised. M. p. and mixed m. p. [with base (IX)] 99°.

The hydrochloride reacted with sodium nitrite solution giving the nitroso-derivative which separated as an oil. It was extracted with ether and the dried extracts were evaporated under reduced pressure. Concentrated hydrochloric acid reconverted it into the parent hydrochloride of (X), m. p. and mixed m. p. 186°.

Isolation of the Base (X).—The hydrochloride of (X) was dissolved in a minimum amount of water, and ether and excess of sodium hydrogen carbonate solution were added. The ethereal layer was separated and the aqueous solution extracted twice with ether. The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure to a syrup, which crystallised on trituration with a little ether. The *compound* separated in a good yield as a white crystalline solid, and was recrystallised from ether-light petroleum, m. p. 54° [Found: C, 43.1; H, 7.5; (OH), 11.8. $C_{10}H_{19}O_4N_3(OH)_2$ requires C, 42.9; H, 7.5; (OH), 11.3%]. The *picrate*, after recrystallisation from water, had m. p. 148° (Found: C, 37.8; H, 5.1; N, 16.7. $C_{16}H_{24}O_{13}N_6$ requires C, 37.8; H, 4.7; N, 16.5%).

On boiling an aqueous solution of the base (X) two molecules of formaldehyde were liberated (Found: CH_2O , 19%. Two mols. of CH_2O require 21.5%). On distillation under reduced pressure, the base (X) (1.4 g.) gave a fraction (0.9 g.), b. p. 140° (bath temp.)/0.01 mm., n_D^{20} 1.4665, containing basic material, and a still residue (unchanged material). With alcoholic hydrogen chloride the distillate gave the crystalline hydrochloride (V), m. p. 202°. Titration with dilute hydrochloric acid showed that some of the distillate was neutral and not soluble in acid. After neutralisation the solution was therefore extracted with ether and the extracts were distilled under reduced pressure giving a fraction (0.3 g.), b. p. 120° (bath temp.)/0.01 mm., n_D^{20} 1.4438. This was 2-nitrobutanol, n_D^{20} 1.4430.

The hydrochloride of (X) (385 mg.) was dissolved in water and heated at 93° for 12 hours. The solution was then evaporated under reduced pressure and the residue (202 mg.) was triturated with acetone. The insoluble material (18 mg.) was identified as ammonium chloride. The acetone solution on evaporation gave a crystalline solid, m. p. 126°. This was the hydrochloride of (III). The aqueous distillate was extracted with ether and the formaldehyde estimated in the aqueous solution (Found: CH_2O , 7. One mol. requires 9.3%). The ethereal extract on evaporation left an oil (10 mg.) which had the reactions of 2-nitrobutene. On heating the hydrochloride of (X) with sodium hydroxide solution and then adding acid and distilling, two molecules of formaldehyde were eliminated (Found: CH_2O , 18.0. 2 mols. of CH_2O require 19.0%).

Action of Concentrated Hydrochloric Acid on Resin A.—(a) The resin dissolved in concentrated hydrochloric acid with evolution of heat. The solution was then evaporated under reduced pressure to a syrup. On standing, crystals separated. They were fractionated into hydrochlorides of (V), (VII), (X), and (IV) by the differences of their solubilities in alcohol and ether. The hydrochloride of (V) is less soluble than that of (X), which in turn is less soluble than that of (VII). The most soluble is the hydrochloride of (IV). The yields varied, (IV) being obtained in the greatest proportion (up to 30% by weight of the resin). (VII) was not obtained from Resin B.

(b) The resin was dissolved in chloroform (or alcohol) and hydrogen chloride bubbled through the solution. The gas was strongly absorbed, the colour of the solution changed from light yellow to deep orange, heat was evolved, and an evolution of formaldehyde occurred. At first a thick emulsion appeared, which then crystallised. The crystals were separated and washed with chloroform and ether. Hydrogen chloride was again passed through the filtrate and a second crop of crystals was formed and separated. This was repeated several times and finally several fractions were collected, representing the hydrochlorides of the four bases mentioned above. Yield, 80 g. from 100 g. of Resin A.

The *hydrochloride of 5-nitro-5-ethyltetrahydro-1:3-oxazine (V)* was isolated in the form of white crystals, insoluble in ether, benzene, and chloroform, readily soluble in water and alcohol, m. p. 203° (decomp.) (Found: C, 36.8; H, 6.5; N, 13.9; Cl, 17.9. $C_6H_{12}O_3N_2 \cdot HCl$ requires C, 36.7; H, 6.6; N, 14.2; Cl, 18.1%). Sodium nitrite converted it into an oily, pale yellow nitroso-derivative, soluble in hot water, insoluble in cold water, and volatile with steam. It was not decomposed on boiling with water. It distilled under reduced pressure, b. p. 130° (bath temp.)/0.01 mm., n_D^{20} 1.5000. The free base (V) was prepared from the hydrochloride (2.15 g.) by the action of sodium hydrogen carbonate and extraction with ether. Yield, 1.8 g. It is an oily liquid insoluble in water, n_D^{20} 1.4873 [Found: C, 45.4; H, 7.5; M (Rast), 162. $C_6H_{12}O_3N_2$ requires C, 45.1; H, 7.5%; M, 160]. The hydrochloride with aqueous picric acid gave a pale yellow *picrate*, m. p. 156° (Found: C, 36.8; H, 4.0; N, 18.0. $C_{12}H_{18}O_{10}N_4$ requires C, 37.0; H, 3.8; N, 18.0%).

Preparation of (VI).—The base (V) (2 g.) by the action of methyl iodide gave the crystalline *methyl iodide (VI)*, m. p. 218° (decomp.). Yield, 1.5 g. It can also be prepared directly from the resin. The resin (3.028 g.) was dissolved in methyl iodide and the solution warmed. After 12 hours the crystals, which had separated, were triturated with acetone, filtered off, and dried. Yield, 0.7 g. It was recrystallised from methyl alcohol; m. p. 218° (decomp.) (Found: C, 30.6; H, 5.3; N, 8.4; I, 39.7;

NO_2 , 15.4. $\text{C}_8\text{H}_{11}\text{O}_3\text{N}_2\text{I}$ requires C, 30.4; H, 5.4; N, 8.9; I, 40.2; NO_2 , 14.6%). With picric acid it gave the corresponding *picrate*, m. p. 210°, after recrystallisation from water (Found: C, 40.4; H, 4.5; N, 16.8. $\text{C}_{14}\text{H}_{19}\text{O}_{10}\text{N}_5$ requires C, 40.4; H, 4.1; N, 16.8%).

An aqueous suspension of silver oxide (10 g.) converted the methiodide (1.775 g.) into the hydroxide of (VI) (1.2 g.) which, on distillation, decomposed violently, giving various liquid and gaseous products. The distillate was strongly alkaline and had a pronounced odour resembling that of methylamine. Addition of picric acid to a solution of the gaseous products absorbed in dilute hydrochloric acid gave a pale yellow picrate soluble in water and alcohol and almost insoluble in dilute hydrochloric acid; m. p. 156°. It was identified (by mixed m. p.) as dimethylamine picrate. The liquid distillate contained an aldehyde or ketone, which formed a 2:4-*dinitrophenylhydrazone*, m. p. 166° (Found: C, 49.8; H, 4.2; N, 21.6. $\text{C}_{11}\text{H}_{14}\text{O}_4\text{N}_4$ requires C, 49.6; H, 5.3; N, 21.1%), and a base, which, with methyl iodide, gave a derivative, m. p. >300°.

Decomposition of the Hydrochloride of (V).—When the hydrochloride of (V) was boiled with water, formaldehyde (1 mol.) was evolved (Found: CH_2O , 14.1. 1 mol. of CH_2O requires 15.2%). On evaporation of the aqueous solution, the *hydrochloride* of 2-nitro-2-hydroxymethylbutylamine (III) remained. It is a crystalline solid, very soluble in alcohol, acetone, and water, sparingly soluble in ether, m. p. 126°, and is the final product of decomposition of the more complex bases (VIII), (X), (V), and (VII). No crystalline picrate or methiodide could be prepared. It was recrystallised from propyl alcohol; m. p. 126° (Found: C, 32.6; H, 7.0; N, 14.1; Cl, 19.5. $\text{C}_6\text{H}_{12}\text{O}_3\text{N}_2\cdot\text{HCl}$ requires C, 32.7; H, 6.8; N, 15.2; Cl, 19.3%).

The hydrochloride of (III) (1 g.) reacted with the calculated quantity of sodium nitrite dissolved in water (5 c.c.). A colourless gas was evolved, briskly at first and then more slowly; the solution became slightly milky and heat was evolved. Total volume of gas at N.T.P., 145 c.c. (Found: N_2 , 67.6; NO , 1.8; N_2O , 24.1; CO_2 , 5.5; CO , 1.0%). This reaction occurred, if only 0.25 mol. of sodium nitrite was added. Addition of urea failed to prevent the second part of the reaction from occurring, once nitrogen had been evolved. The yellow-green oil which separated had an odour resembling that of diazomethane. The oil (0.43 g.) was extracted with ether and distilled under reduced pressure. Much decomposition occurred and a yellow acidic oil (0.1 g.) passed over, n_D^{18} 1.4700, b. p. 140° (bath temp.)/0.01 mm. (Found: C, 45.6; H, 7.4; N, 8.9%). Formaldehyde was liberated on boiling the hydrochloride of (III) with sodium hydroxide (Found: CH_2O , 11. One mol. requires CH_2O , 16.2%).

The oily base (III) was obtained by ethereal extraction of a solution of the hydrochloride made alkaline. Evaporation of dried extracts under reduced pressure gave a syrup which evolved ammonia on standing with formation of crystals. The crystals were basic, m. p. 98° depressed on admixture with (VIII) or (IX) (Found: C, 39.1; H, 7.1; N, 13.1. $\text{C}_8\text{H}_{12}\text{O}_3\text{N}_2$ requires C, 40.4; H, 7.7; N, 13.5%). This crystalline substance gave no test for primary or secondary nitro-groups. It was insoluble in ether. It gave ammonia with alkalis, whilst with concentrated alcoholic hydrogen chloride it gave formaldehyde and the hydrochloride of (III), m. p. 126°.

A sample of the mother liquor, after removal of the crystalline derivative, m. p. 98°, gave with concentrated hydrochloric acid a mixture of the hydrochloride of (V), m. p. 203° (decomp.), and the hydrochloride of (III), m. p. 126°. After removal of the base (III) by ether extraction, the mother liquors, on heating, gave an oily base with a piperidine-like odour. This was extracted with ether and the dried extracts were evaporated. The strongly alkaline oil (10% yield calculated on the weight of hydrochloride) was distilled under reduced pressure; b. p. 160°/16 mm., n_D^{23} 1.4862 (Found: C, 46.8; H, 8.1; N, 20.4. $\text{C}_{10}\text{H}_{20}\text{O}_4\text{N}_4$ requires C, 46.2; H, 7.7; N, 21.6%). The oil gave no crystalline picrate or methiodide. The oily methiodide contained 34.8% of iodine.

Characteristic Reaction for Bases (VIII) and (IX) and their Derivatives (VII) and (X).—The substance [(VIII), (IX), (VII), or (X)] was shaken with bromine dissolved in carbon tetrachloride; alcohol was added to produce a clear solution followed by the addition of alcoholic potassium hydroxide. The solution lost its bromine colour and became pink-red. The addition of a drop of acid deepened the colour but excess changed it to yellow. Addition of potassium hydroxide brought back the red colour. The base (V), its methiodide (VI), and the base (III) did not give this reaction.

Our thanks are due to Professor J. E. Lennard-Jones, F.R.S., Chief Scientific Officer, Ministry of Supply, for permission to publish this paper.

ARMAMENT RESEARCH DEPARTMENT, ROYAL ARSENAL, WOOLWICH.
THE UNIVERSITY, BRISTOL.

[Received, October 4th, 1946.]