355. *Studies on Nitroamines. Part V. Some Properties of Hydroxymethyl- and Aminomethyl-nitroamines.*

By ALEX. H. LAMBERTON, C. LINDLEY, P. G. OWSTON, and J. C. SPEAKMAN.

In Parts III and IV of this series, the production of a number of compounds of types (I) and (II) has been reported. Their mode of formation and chemical individuality is now considered, the following conclusions being drawn : (*a*) in aqueous solution, hydroxymethylnitroamines (I) react predominantly as mixtures of formaldehyde and the nitroamine, but they have greater stability in mineral acid; (*b*) compounds of type (I) are not precursors of type (II); reaction probably proceeds by decomposition of type (I), followed by formation of the hydroxymethyl amine ($NR'_2{\cdot}CH_2{\cdot}OH$), and union thereof with the nitroamine; (*c*) aminomethylnitroamines (II) decompose, on (or after) dissolution in water, to formaldehyde and salts of the nitroamine anion with the amino-cation. In alkaline solution substances of type (II) yield the nitroamine anion and an equilibrium mixture of amine, formaldehyde, and hydroxymethylamine, whilst in mineral acid they are stabilised, possibly by formation of the cation $NO_2{\cdot}NR{\cdot}CH_2{\cdot}\overset{\oplus}{N}HR'_2$.

AT an early stage in the progress of the work detailed in Parts III and IV of this series it became apparent that parallel consideration should be given to the mechanism of formation and to the stability of compounds of types (I) and (II). The results of this work are best discussed and interpreted in terms of the reversible reactions (*A*), (*B*), and (*C*).

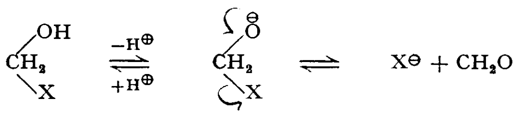
$$\underset{\text{(I.)}}{NO_2{\cdot}NR{\cdot}CH_2{\cdot}OH} \qquad\qquad \underset{\text{(II.)}}{NO_2{\cdot}NR{\cdot}CH_2{\cdot}NR'_2}$$

$$(A)\quad NHR{\cdot}NO_2 + CH_2O \rightleftharpoons NO_2{\cdot}NR{\cdot}CH_2{\cdot}OH$$

$$(B)\quad NHR'_2 + CH_2O \rightleftharpoons NR'_2{\cdot}CH_2{\cdot}OH$$

$$(C)\quad NHR{\cdot}NO_2 + CH_2O + NHR'_2 \rightleftharpoons NO_2{\cdot}NR{\cdot}CH_2{\cdot}NR'_2$$

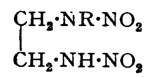
(*D*)



$$\mathrm{CH_2(OH)X} \underset{+H^{\oplus}}{\overset{-H^{\oplus}}{\rightleftharpoons}} \mathrm{CH_2(O^{\ominus})X} \rightleftharpoons X^{\ominus} + CH_2O$$

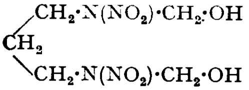
Reaction A.—The formal analogy between cyanohydrins (see Lapworth *et al.*, *J.*, 1930, 448; 1931, 1387) and hydroxymethylnitroamines is illustrated in equation *D* ($X = {\cdot}NR{\cdot}NO_2$ or CN). The nitroamine ion is, however, relatively more stable than the cyanide ion (the K_a

values for hydrogen cyanide and methylnitroamine are 5×10^{-10} and 5×10^{-7}, respectively), and it has been found that, unlike hydrogen cyanide which reacts with cotarnine to give a ψ-cyanide, methylnitroamine and nitrourethane yield cotarninium salts in the form of water-soluble gums (curves II*a*, II*b*, Fig. 2). It would therefore be expected that the equilibrium in equation *A* would lie more to the left than in the case of the formation of cyanohydrins. In fact, aqueous solutions of the compounds (III; R = CH_2·OH) and (IV) can be accurately



$$\begin{array}{l} CH_2\cdot NR\cdot NO_2 \\ | \\ CH_2\cdot NH\cdot NO_2 \end{array}$$

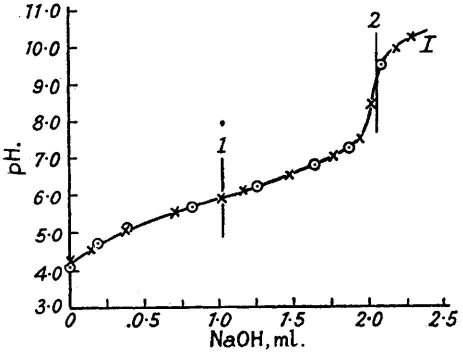
(III.)



(IV.)

and directly titrated with sodium hydroxide, using phenolphthalein as indicator (Part III). Furthermore, it has now been shown that the formaldehyde of both (III; R = CH_2·OH) and (IV) can be determined accurately in cold water by means of iodine and alkali, whilst a dilute aqueous solution of (III; R = CH_2·OH) is indistinguishable, on potentiometric titration, from a mixture of formaldehyde and ethylenedinitroamine (curve 1, Fig. 1).

Fig. 1.

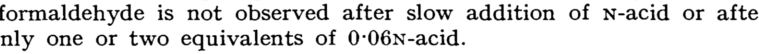


I {○ *Ethylenedinitroamine.*
 {× *Compound (III;* R = CH_2·OH).
— *Also in presence of* 1 *equiv. excess of formaldehyde.*

In contrast to the stability of cyanohydrins in acid solution, the decomposition of hydroxymethylnitroamines (equation *D*; X = NR·NO_2) appears to be only partly suppressed, presumably on account of the greater stability of the nitroamine ion. When aqueous solutions of (III; R = CH_2·OH) or (IV) were acidified and treated with Brady's reagent (2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid), quantitative precipitation of the formaldehyde derivative occurred, but, if the solid compounds were dissolved in 2N-hydrochloric acid instead of water, the yield of hydrazone precipitated under the same conditions fell to 50% and 60%, respectively.

It would be too sweeping, however, to conclude that in neutral or alkaline solutions the interaction of formaldehyde and nitroamines may always be disregarded (Myers and Wright, "Nitrolysis of Hexamine, Part IV," *Canadian J. Res.*, in the press). Further, Chute, Downing, McKay, Myers, and Wright (*ibid.*, Part I) have drawn attention to the stabilisation of nitroamine by formaldehyde, and we have found that, in the presence of formaldehyde, nitroamine can be titrated with sodium hydroxide to a moderately stable end-point, whilst, conversely, the formaldehyde is shielded to some extent from precipitation as the 2 : 4-dinitrophenylhydrazone.

Reaction B.—The reversibility of this reaction is generally accepted. Potentiometric measurements now reported show that the decrease in basicity observed after the addition of formaldehyde to morpholine solutions may be accounted for quantitatively in terms of the following scheme :

(*E*)  (*F*)

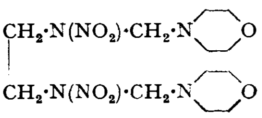
When solutions of morpholine hydrochloride and formaldehyde are mixed and treated with Brady's reagent, the hydrazone is at once precipitated; if, however, formaldehyde is allowed to react first with morpholine base, hydroxymethylmorpholine is produced and, after rapid addition of a large excess of acid, the precipitation of the hydrazone is delayed and scanty. This retention of formaldehyde is not observed after slow addition of N-acid or after the rapid addition of only one or two equivalents of 0·06N-acid.

These results may be satisfactorily correlated. Morpholine hydrochloride does not react with formaldehyde, the carbonyl group having presumably no affinity for the morpholinium ion. Morpholine does react and, on rapid acidification, salts of both morpholine and hydroxymethylmorpholine are formed; the hydroxymethylmorpholine salt may be relatively stable in acid solution (cf. Robinson and Robinson, *J.*, 1932, 532, who comment on the stability of $\mathrm{BuO{\cdot}CH_2{\cdot}\overset{\oplus}{N}R_3}$ in contrast to $\mathrm{BuO{\cdot}CH_2{\cdot}NR_2}$). On slow acidification, the stronger base (morpholine) engages the limited amount of acid, equilibrium E is disturbed, and formaldehyde is freed.

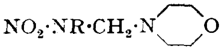
Reaction C.—It was pointed out by Lapworth *et al.* (*loc. cit.*) that the electron-restraining properties of the nitrile group should inhibit the removal of the hydroxyl ion from cyanohydrins, and thus (*a*) prevent the preparation of derivatives of malononitrile by the action of cyanide ions on cyanohydrins and (*b*) entail an indirect formation of α-amino-nitriles from cyanohydrins and secondary bases. Similarly, hydroxymethylnitroamines (type I) may resist elimination of the hydroxyl ion. The failure of many workers to prepare cyclonite from nitroamine and formaldehyde (private communications) is thus comprehensible, and the reactions which occur when a preformed hydroxymethylnitroamine (I) is treated with a secondary base very possibly involve decomposition to nitroamine and formaldehyde (equation A), formation of the aminomethyl alcohol (equation B), and condensation of the nitroamine and aminomethyl alcohol by process (G). Myers and Wright ("Nitrolysis of Hexamine, Part IV," *loc. cit.*), however, favour the direct condensation of hydroxymethylnitroamine and base.

$$(G)\quad \mathrm{NHR{\cdot}NO_2 + HO{\cdot}CH_2{\cdot}NR'_2 \longrightarrow NO_2{\cdot}NR{\cdot}CH_2{\cdot}NR'_2 + H_2O}$$

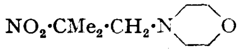
It is difficult to decide this point experimentally, but compound (V) appears to be precipitated more rapidly when, in place of separate addition, a preformed mixture of morpholine and formaldehyde is added to an aqueous solution of the morpholine salt of ethylenedinitroamine.



(V.)



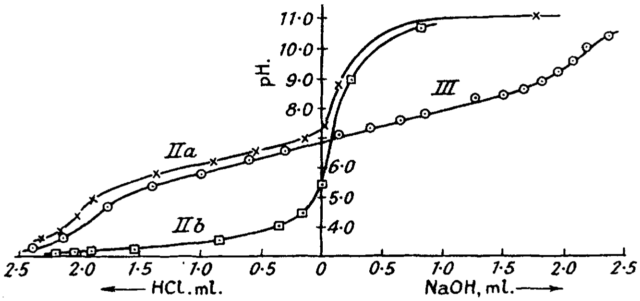
(VI.)



(VII.)

Compounds (III; R = morpholinomethyl) and (V) (Part III), morpholinomethylmethylnitroamine (VI; R = Me), and the aminomethylnitroamines (VI; R = $\mathrm{CO_2Et}$ or $\mathrm{CO{\cdot}NH_2}$) are

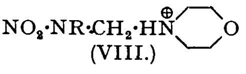
Fig. 2.



IIa. Methylnitroamine + cotarnine (1 : 1).
IIb. Nitrourethane + cotarnine (1 : 1).
III. Compound V.

water-soluble in varying degree, but very sparingly soluble in ether or benzene. They can be titrated directly with sodium hydroxide, using thymolphthalein as indicator, and, with the single exception of compound (VI; R = $\mathrm{CO{\cdot}NH_2}$), the methylene groups can be accurately determined as formaldehyde by iodine in cold alkaline solution. By contrast, 4-2′-nitro*iso*butylmorpholine (VII), since prepared independently by Johnson (*J. Amer. Chem. Soc.*, 1946, **68**, 13), was found to be a typically covalent compound, insoluble in water, easily soluble in ether and benzene, and not titratable with alkali.

Potentiometric titrations have been carried out with sodium hydroxide and hydrochloric acid on dilute solutions of compound (V). The pH–neutralisation curve obtained (curve III, Fig. 2) resembles that of a salt of a weak acid and a weak base, and indicates that decomposition follows (or accompanies) dissolution in water. The positive ion (or ions), studied during titration with sodium hydroxide, behaves as an effectively stronger acid than the morpholinium ion (*i.e.*, morpholine appears to have been converted into an effectively weaker base), its apparent strength varies during the course of the titration, and the results can be interpreted in terms of equations (*E*) and (*F*). The aminomethylnitroamines are therefore assumed to be effectively decomposed in aqueous solution by reversal of equation (*G*), followed by equilibration of the aminomethyl alcohol according to equations (*E*) and (*F*); and compounds (III; R = morpholinomethyl) and (V) then yield more than 80% of their formaldehyde on treatment with Brady's reagent. If, however, these solids are dissolved in 2N-hydrochloric acid, no hydrazone is precipitated in 5 hours, and only 10—20% of the theoretical amount separates in 24 hours. This retention of formaldehyde in strongly acid solution might be due to the formation of the stable cation of hydroxymethylmorpholine (see discussion of reaction *B*), or to the formation, without rupture, of the stable cation (VIII).



(VIII.)

A decision between these alternatives was made by cryoscopic determinations of molecular weight in N-hydrochloric acid. The freezing point of hydrochloric acid is lower than that of water, on account of the ions which the solution contains. If some soluble material is now added, the total number of dissolved particles is normally increased; a further depression of the freezing point is thus produced, from which the molecular weight of the added compound could be calculated. However, if an aminomethylnitroamine is added, it may react as a simple amine and combine with the protons in the solution to yield ammonium cations (VIII); the total number of dissolved particles will not then be augmented. If no other reaction occurs and salt formation is complete, no further depression of the freezing point is to be expected and the molecular weight of the added aminomethylnitroamine would apparently be infinite. Formation of the cation of hydroxymethylmorpholine would also take up protons, but at the same time molecules of the nitroamine ($NHR{\cdot}NO_2$) would be set free, and a corresponding depression of the freezing point might be expected.

On account of greater solubility in water, morpholinomethylmethylnitroamine (VI; R = Me) was used; towards Brady's reagent it behaved in the same way as the compounds (III; R = morpholinomethyl) and (V). In water, the apparent molecular weight was one third of the formula weight, the decomposition of these substances in accordance with equation (*C*) being thus confirmed; but the high apparent molecular weight in acid suggested that the compound existed mainly as the cation (VIII).

EXPERIMENTAL.

Potentiometric Titrations.—These were carried out at 20° using the glass electrode; 0·06M-titrant was run in to 0·001—0·003M-solutions of the substance investigated, and formaldehyde was used as 0·05M-solution of pH 6—7. The pH-scale was standardised by the method of Hitchcock and Taylor (*J. Amer. Chem. Soc.*, 1937, **59**, 1812), and pH values are reliable to within 0·02 unit. Details and the methods of calculating the dissociation constant have been described elsewhere (*J.*, 1940, 855).

The addition of ½, 1, 2, etc. equivalents (calculated) of titrant is marked in Figs. 1, 2, and 3 by short vertical lines.

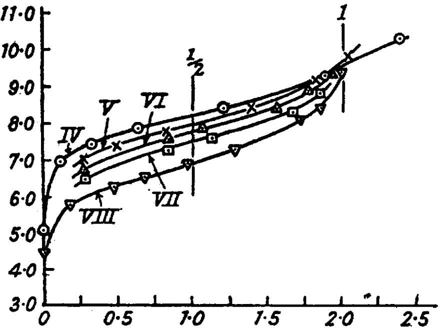


FIG. 3.

IV.	*Morpholine hydrochloride alone.*		
V.	,,	,,	+½ *mole formaldehyde.*
VI.	,,	,,	+1 ,, ,,
VII.	,,	,,	+2 *moles* ,,
VIII.	,,	,,	+7 ,, ,,

The correspondence of curve VI, Fig. 3, at pH > 7·5, with curve III, Fig. 2, shows that any interaction between morpholine and formaldehyde is probably the same in both cases. The curves (Fig. 3) show that formaldehyde renders morpholine an effectively weaker base, but, in agreement with the greater slopes of curves V, VI, VII, and VIII, as compared with IV, the apparent dissociation constant varies during the titration. The effect of formaldehyde on morpholine is progressive and does not cease with the addition of 1 mole of formaldehyde, and it is concluded that the interaction of formaldehyde with morpholine does not go to completion. Further investigation was made by titrating a solution containing morpholine and its hydrochloride with formaldehyde. The results confirmed those shown in Fig. 3, but it was found that 4-hydroxymethylmorpholine was not produced instantaneously; pH values became constant only 2—5 minutes after each addition of sodium hydroxide or formaldehyde. More exact data were therefore obtained by making up solutions (containing known amounts of morpholine, its hydrochloride, and formaldehyde) separately, and measuring the pH values at leisure. Results are shown in Table I, in which a, b, and f are, respectively, the molar concentrations of morpholine hydrochloride, sodium hydroxide, and formaldehyde; $[H^+]$ and $[OH^-]$ were calculated from the pH by the relations, $pH = -\log_{10} [H^+]f_1$ and $[H^+] \times [OH^-] = 0{\cdot}68 \times 10^{-14}$, f_1 being the activity coefficient for a univalent ion calculated by the Debye–Hückel limiting law.

The results can be accounted for in terms of the equations E and F. Neglecting activity effects (these experiments were carried out at constant ionic strength), these equilibria lead to the relation

$$K_i = K_a . A\{F/[H^+] + A(1 + [H^+]/K_a)(K_a/[H^+]^2)\}(B - K_aA/[H^+]),$$

where K_i = the instability constant (equation E) of hydroxymethylmorpholine, K_a = the acidity constant (equation F) of the morpholinium ion (which may be estimated from the data represented by Curve IV, Fig. 3, as $2{\cdot}8 \times 10^{-9}$), $A = a - b + [OH^-]$, $B = b - [OH^-]$, and $F = f - a$.

TABLE I.

	$a = 0{\cdot}00342$.							
	$b = 0{\cdot}00141$.				$b = 0{\cdot}00204$.			
f	0·00000	0·00169	0·00346	0·00678	0·00000	0·00345	0·00684	0·01360
$10^8 \times [H^+]$	0·414	0·865	1·50	2·80	0·194	0·656	1·26	2·34
$10^6 \times [OH^-]$	0·0175	0·85	0·49	0·26	0·038	0·011	0·59	0·29
$10^3 \times K_i$	—	0·80	0·89	0·92	—	0·82	0·90	0·97

Calculated values of K_i are constant within experimental error, thus indicating that the above data are consistent with equations E and F.

The reactions occurring during the titrations shown in Fig. 3 were proved reversible. Morpholine hydrochloride and formaldehyde (1 : 1) were titrated with sodium hydroxide to pH 10·5 as in Curve VI; no deviation from the curve was observed on back-titration with acid. Reversibility on rapid (but mild) acidification was also found by adding, to a similar solution of morpholine hydrochloride and formaldehyde, sodium hydroxide to pH 10, followed at once by hydrochloric acid to pH 2; subsequently, the titration curve with sodium hydroxide, when the pH value exceeded 5·5, did not differ appreciably from Curve VI.

Estimation of Potential Formaldehyde.—The formaldehyde derived from 0·05—0·1 g. of material was determined by six methods; the results of three of these are given in Table II.

Method A (direct Romijn titration). The material was dissolved in water, and the formaldehyde determined by treatment with an excess of iodine and of sodium hydroxide.

Method B. The material was dissolved in water (20 ml.) and, after eighteen hours, 10N-hydrochloric acid (5 ml.) and 2 : 4-dinitrophenylhydrazine (50 ml. of a saturated solution in 2N-hydrochloric acid) were added. After five hours at 0° the hydrazone was collected and weighed.

Method C. The material was dissolved in 2N-hydrochloric acid (25 ml.); after 18 hours, Brady's reagent was added and the hydrazone collected as described in method *B*.

TABLE II.

	% Formaldehyde found by methods			
Compounds.	*A*.	*B*.	*C*.	Calc. % of formaldehyde.
N-Hydroxymethylethylenedinitroamine (III; $R = CH_2{\cdot}OH$)	16·2 16·5	16·1	7·8	16·7
NN'-Dihydroxymethyltrimethylenedinitroamine (IV)	26·2 26·6	26·2	17·5	26·8
N-Morpholinomethylethylenedinitroamine (III; R = morpholinomethyl)	12·3 12·4	11·6	nil	12·0
NN'-Dimorpholinomethylethylenedinitroamine (V)	17·2 17·3	14·6	nil	17·2

Notes on alternative methods tested. Preliminary boiling under reflux (20 minutes) with water, followed by a Romijn determination, gave satisfactory results similar to those of method *A*. Distillation of formaldehyde from dilute sulphuric acid was unsatisfactory; blank determinations using ethylenedinitroamine showed that acetaldehyde (identified by formation of iodoform and of the 2 : 4-dinitrophenylhydrazone) was produced. Attempts to determine the formaldehyde by the use of sodium hydrogen sulphite were unsuccessful.

Interaction of Nitroamine and Formaldehyde.—Nitroamine (28—37 mg. of theoretical equiv. 62; "Inorg. Syntheses," Vol. I, 468) was dissolved in water (10 ml.) and at once titrated (during 1, 2, or 3½ minutes) with sodium hydroxide, to thymolphthalein. Equivalents of 65, 68, and 71, respectively were obtained. Dissolution in 0·2M-formaldehyde (10 ml.) and titration during 2 minutes gave equivalents of 64, 65, and 65. The stabilising effect of the formaldehyde was marked at the end-point of the titrations, when the alkaline solutions were set aside, and the extent of the nitroamine decomposition measured by back-titration with standard acid. For example, in water alone 38% of the titrated acidity had disappeared in about 35 seconds, and 97% in 6 minutes, whilst keeping in formaldehyde for the same periods led to losses of only 1% and 56%, respectively.

Nitroamine was also observed to shield formaldehyde from precipitation as the 2 : 4-dinitrophenylhydrazone. Aliquots (10 ml.) of a standard solution of formaldehyde [formaldehyde content; 9·3, 9·2 mg. (iodometrically), and 9·5 mg. (Brady)] were added to nitroamine (10—12 mg., freshly dissolved in 10 ml. of water), and the resultant mixtures titrated with sodium hydroxide. After the end-point had been attained, the solutions were re-acidified (with 5 ml. of concentrated hydrochloric acid) either immediately or after standing for a time (25 minutes) known to suffice for the destruction of nitroamine in the presence of formaldehyde. By precipitation with Brady's reagent, the formaldehyde found was 9·4 or 9·5 mg. after destruction of the nitroamine, but only 6·8 or 7·0 mg. after retention of the nitroamine by immediate acidification.

Action of Morpholine on Formaldehyde.—An equilibrium mixture of morpholine and formaldehyde was prepared from standard solutions of 0·06M-morpholine hydrochloride (5 ml.), 0·05M-formaldehyde (5 ml.), and 0·095M-sodium hydroxide (3 ml.). On rapid acidification with hydrochloric acid (30 or more equivalents of at least 1M-acid) and treatment with Brady's reagent, precipitation of the hydrazone commenced only after 10 minutes, and was slight even after 24 hours. If, as an intermediate treatment, hydrochloric acid was added slowly (2 equivalents in 35 minutes) or the mixture was set aside with one or two equivalents of acid, precipitation commenced after 15—35 seconds under comparable final conditions of acidity.

N-*Morpholinomethylmethylnitroamine* (VI; R = Me).—38% Formaldehyde (0·5 ml.) and morpholine (0·5 ml.) were added to methylnitroamine (0·4 g.), and the mixture cooled to 0°. The *morpholinomethyl* compound (0·55 g.), which rapidly separated as rhombic prisms, m. p. 84—86°, was collected and washed with ice-water (2 ml.), alcohol, and ether [Found : C, 41·1; H, 7·6; CH_2O (direct Romijn titration), 17·5, 16·8; equiv., 178. $C_6H_{13}O_3N_3$ requires C, 41·4; H, 7·5; CH_2O, 17·1%; equiv., 175].

N-*Morpholinomethylnitrourethane* (VI; R = CO_2Et).—Morpholine (1 ml.) was added with water-cooling to nitrourethane (1·3 g.) in water (2 ml.). The salt solution was filtered, and 38% formaldehyde (1 ml.) added; after 30 minutes, scratching induced crystallisation of the *monohydrate*. The solid was collected, washed with ice-water, acetone, and ether, and air-dried at room temperature; prisms (1·5 g.), m. p. 85—86°, were obtained [Found : C, 38·5; H, 6·8; CH_2O (by direct Romijn titration), 11·6; equiv., 250, 249. $C_8H_{15}O_5N_3,H_2O$ requires C, 38·2; H, 6·8; CH_2O, 11·9%; equiv., 251]. The product, which was easily soluble in water or alcohol, moderately in hot chloroform or ethyl acetate, and insoluble in ether or benzene, crystallised from ethyl acetate, but the hot solution had an odour of formaldehyde, and the crystallised material was no purer than that precipitated directly from water. Formaldehyde was also eliminated on heating the substance or drying it in a vacuum-desiccator. The *morpholine* salt of nitrourethane, prepared for comparison by admixture, with cooling, of morpholine (0·1 ml.) and nitrourethane (0·13 g.), crystallised from ethyl acetate (5 ml.) in needles (0·2 g.), m. p. 75° (decomp.), which were easily soluble in water, soluble in alcohol or chloroform, and insoluble in ether or cold ethyl acetate (Found : C, 38·0; H, 7·0. $C_7H_{15}O_5N_3$ requires C, 38·0; H, 6·8%).

Morpholinomethylnitrourea (VI; R = $CO{\cdot}NH_2$).—The method described for *N*-morpholinomethylnitrourethane, but with the substitution of nitrourea (1 g. in 4 ml. of water) for the aqueous solution of nitrourethane, yielded the *morpholinomethyl* compound as prisms (1·5 g.), m. p. 120° (decomp.), slightly soluble in water, but insoluble in alcohol or ether (Found : C, 35·6; H, 5·9%; equiv., 204. $C_6H_{12}O_4N_4$ requires C, 35·3; H, 5·9%; equiv., 204). Determination of formaldehyde by the direct Romijn titration gave low and variable results; it appears that in this case the liberation of formaldehyde and its reaction with iodine do not proceed smoothly to completion in alkaline solution, the best figures (13·7, 13·9%; cf. theoretical 14·7%) being obtained when the aqueous solutions were kept for 35 and 50 minutes, respectively, before proceeding with the determination. Attempts to form the morpholine salt of nitrourea by mixing the anhydrous constituents resulted in immediate decomposition, and evaporation, *in vacuo*, of an aqueous solution of the salt yielded morpholine-4-carboxyamide (Knorr, *Annalen*, 1898, **301**, 8; for the course of reaction see Davis and Blanchard, *J. Amer. Chem. Soc.*, 1929, **51**, 1790).

4-2′-*Nitro*iso*butylmorpholine* (VII).—2-Nitropropane (9 ml.), morpholine (10 ml.), 38% formaldehyde (10 ml.), and 10N-sodium hydroxide (0·2 ml.) were warmed to 30°, and sufficient alcohol was added to give a homogeneous solution. After 15 hours at 30° the mixture was acidified, diluted with water (20 ml.), and extracted with ether. The extract was washed with sodium hydrogen carbonate, dried, and distilled. 4-2′-Nitro*iso*butylmorpholine (8·5 g.), b. p. 106—108°/2 mm., crystallised from ligroin (b. p. 60—80°) in stout prisms or cubes, m. p. 46—48° (Found : C, 51·0; H, 8·4; N, 14·9. Calc. for $C_8H_{16}O_3N_2$: C, 51·0; H, 8·6; N, 14·9%), soluble in organic solvents, but insoluble in water; the solution in aqueous alcohol could not be titrated with alkali. Johnson (*J. Amer. Chem. Soc.*, 1946, **68**, 13) has since reported m. p. 43°, b. p. 90—91°/0·5 mm.

Apparent Molecular Weight of N-*Morpholinomethylmethylnitroamine.*—Concentration in water, 3·98, 5·47, 5·92 g./l. : apparent *M*, 57, 64, and 62, respectively.

Concentration in 0·967N-hydrochloric acid, 6·32, 9·48, 9·66, 20·24 g./l. : apparent *M*, 500, 470, 530, and 800, respectively.

THE UNIVERSITY, SHEFFIELD, 10.

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