The *N*-Nitroxymethyl Derivatives of 1,3-Dinitroperhydro-1,3,5-triazine, Piperidine, and Succinimide

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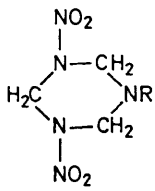
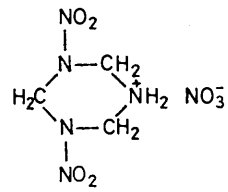
N-Nitroxymethylpiperidine and *N*-nitroxymethylsuccinimide have been prepared and their reactions with nucleophiles and nitric acid under various conditions have been compared. Their relative reactivities have been explained in terms of the degree of carbonium ionic character of the methylenic carbon atom attached to the nitroxy-group. 1,3-Dinitro-5-nitroxymethylperhydro-1,3,5-triazine has eluded preparation from either (*a*) the *N*-acetoxymethyl analogue with nitric acid in acetonitrile or (*b*) the *N*-chloromethyl analogue with silver nitrate also in acetonitrile. In case (*a*) an interaction with the solvent is explained and in case (*b*) the formation of the bicyclic nitramine 1,5-bis-(3,5-dinitroperhydro-1,3,5-triazin-1-yl)-2,4-dinitro-2,4-diazapentane has been proved.

1,3-DINITRO-5-NITROXYMETHYLPERHYDRO-1,3,5-TRIAZINE (I) has been postulated [1] as a reaction intermediate in the low-temperature conversion of hexamine by means of nitric acid into 1,3,5-trinitroperhydro-1,3,5-triazine (III) (RDX). Evidence was obtained by treating the gummy product formed by addition of diethyl ether to the reacting system with ethanol; the ethyl ether (VII)



(I) R = $CH_2 \cdot O \cdot NO_2$ (VIII) R = $CH_2 \cdot OMe$
(II) R = $CH_2 \cdot O \cdot NO$ (IX) R = $CH_2 \cdot OAc$
(III) R = NO_2 (X) R = $CH_2 \cdot O \cdot CO \cdot CF_3$
(IV) R = NO (XI) R = H
(V) R = CH_2Cl (XII) R = $CH_2 \cdot OH$
(VI) R = CH_2Br (XIII) R = CHO
(VII) R = $CH_2 \cdot OEt$ (XIV) R = $CH_2 \cdot \overset{+}{N} \equiv CMe$ NO_3^-



(XV)

$RCH_2 \cdot N(NO_2) \cdot CH_2 \cdot N(NO_2) \cdot CH_2 \cdot N(NO_2) \cdot CH_2 \cdot O \cdot NO_2$
(XVI) R = OAc
(XVII) R = $O \cdot NO_2$

was isolated. Bell and Dunstan [2] have found that 1-acetoxymethyl-3,5-dinitroperhydro-1,3,5-triazine (IX) is unreactive towards simple alcohols but that in the presence of a cold nitration mixture the corresponding ethers are formed, which suggests the intervention of the species (I), particularly since on adding acetic anhydride in place of the alcohols nitroxy-terminated linear nitramines (XVI) and (XVII) are formed. However the rate of formation of RDX from hexamine was observed [3] to be greater than that from the acetate (IX), so it was concluded that different intermediates were present in the two nitrolyses. The interest in the nitroxymethyl group [if (I) is a reaction intermediate] lies (*a*) in the mechanism of the final step of the RDX synthesis, *i.e.* requiring conversion of $>N \cdot CH_2 \cdot O \cdot NO_2$ into $>N \cdot NO_2$, and (*b*) in the preceding fission of $>N-CH_2-$ originating from hexamine leading to the formation of species (I).

Reed [4] has reported the synthesis of compound (I) from the trifluoroacetate (X) and cold nitric acid, but efforts to repeat his work both here and elsewhere [2] have failed. In addition, no success has been achieved by using salts such as nitronium tetrafluoroborate in organic solvents.[5]

The *N*-nitroxymethyl derivatives of piperidine and succinimide provide electronically suitable model systems; the electron availability on the NH system being greater in the former and less in the latter than in the case of 1,3-dinitroperhydro-1,3,5-triazine. 1,3-Dinitroperhydro-1,3,5-triazine (XI) is only known as its salts, most commonly the nitrate (XV) (PCX). Attempts to prepare the free amine result in rapid hydrolysis to form methylenedinitramine, formaldehyde, and ammonia.[6] Hydroxymethyl derivatives of piperidine [7] and succinimide [8] have both been prepared, the latter being the more stable, but the corresponding 1-hydroxymethyl-3,5-dinitroperhydro-1,3,5-triazine (XII) has not been obtained.[9] However alkoxymethyl,[8,10,11] and halogenomethyl [1,12,13] derivatives have been prepared in all three cases. Generally the stability of these compounds, *e.g.* under aqueous conditions, increases in the order piperidine, 1,3-dinitroperhydro-1,3,5-triazine, succinimide derivatives.

[1] K. W. Dunning and W. J. Dunning, *J. Chem. Soc.*, 1950, (*a*) 2920, (*b*) 2925.
[2] J. A. Bell and I. Dunstan, *J. Chem. Soc.* (*C*), 1969, 1556.
[3] J. A. Bell and I. Dunstan, *J. Chem. Soc.*, (*C*), 1969, 1559.
[4] R. Reed, *J. Org. Chem.*, 1958, **23**, 975.
[5] J. A. Bell and I. Dunstan, personal communication.
[6] A. H. Lamberton, *Quart. Rev.*, 1951, 75.
[7] R. G. Kostyanovskii and O. A. Pan'shin, *Izvest. Akad. Nauk S.S.S.R., Otdel, khim, Nauk*, 1963, 182 (*Chem. Abs.*, 1963, **58**, 12,507f).
[8] E. Cherbuliez and G. Sulzer, *Helv. Chim. Acta*, 1925, **8**, 567.
[9] G. F. Wright in 'The Chemistry of the Nitro and Nitroso Groups,' ed. H. Fever, Interscience, New York, 1969, p. 657.
[10] G. M. Robinson and R. Robinson, *J. Chem. Soc.*, 1923, **123**, 532.
[11] C. M. McLeod and G. M. Robinson, *J. Chem. Soc.*, 1921, **119**, 1470.
[12] H. Böhme and H. Ellenberg, *Chem. Ber.*, 1959, **92**, 2976.
[13] L. W. Kissinger and H. E. Ungrade, *J. Org. Chem.*, 1958, **23**, 818.

RESULTS AND DISCUSSION

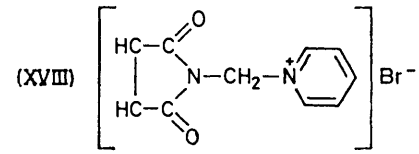
N-Nitroxymethylpiperidine.— *N*-Ethoxymethylpiperidine, prepared from piperidine by a Mannich condensation was converted with anhydrous hydrogen iodide into *N*-iodomethylpiperidine. Treating the latter in dichloromethane with silver nitrate gave an almost quantitative precipitate of silver iodide. The yellow oil remaining after removing the solvent and purification by column chromatography slowly yielded a hygroscopic solid whose i.r. spectrum indicated the presence of an ionic nitrate salt. Owing to handling problems *N*-nitroxymethylpiperidine was not treated with nitric acid to investigate its possible conversion to *N*-nitropiperidine. However when *N*-acetoxymethylpiperidine or *N*-n-butoxymethylpiperidine was treated with anhydrous nitric acid in carbon tetrachloride only *N*-nitroxymethylpiperidine could be isolated. When a mixture of nitric acid and acetic anhydride was used, the acetoxy-compound gave both *N*-nitro- and *N*-nitroso-piperidine. Some *N*-acetylpiperidine was formed in addition but the reaction did not go to completion. *N*-n-Butoxymethylpiperidine gave only a trace of *N*-nitropiperidine and the other reaction products included n-butyl acetate, n-butyl nitrate, and n-butoxymethyl acetate. The formation of the last of these was only suggested from elemental and i.r. analyses and not confirmed by synthesis. *N*-Acetylpiperidine and *N*-acetoxymethylpiperidine may also have been present. Direct *N*-nitrosation of *N*-n-butoxymethyl piperidine was achieved with dinitrogen tetroxide in carbon tetrachloride.

N-Nitroxymethylpiperidine is unstable: it is easily hydrolysed and undergoes nucleophilic displacement readily, *e.g.* with sodium ethoxide. The reactivity of the *N*-(substituted methyl)piperidine derivatives will depend on the nature of the substituent in addition to the electron availability on the nitrogen atom. With poor leaving groups, *e.g.* AcO^- or Bu^nO^-, nitric acid probably assists by protonation prior to bonding of the nitrate ion to the methylenic carbon atom to form the nitroxymethyl product, which is found in both cases. With the more powerful *N*-nitrating system, *e.g.* a mixture of nitric acid and acetic anhydride, direct electrophilic attack upon the ring nitrogen atom is a competing reaction and accounts for the formation of *N*-nitropiperidine from both the *N*-acetoxy- and the *N*-n-butoxymethyl derivative.

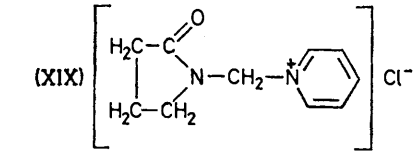
N-Nitroxymethylsuccinimide.—*N*-Bromomethylsuccinimide was converted into the nitroxymethyl compound with silver nitrate in acetonitrile.[14] The product was a stable white crystalline solid, unreactive towards water. No reaction was detected with nitric acid, even in a mixture with concentrated sulphuric acid.

As expected, no reaction was observed between *N*-acetoxymethylsuccinimide and (i) nitric acid under anhydrous conditions in carbon tetrachloride, (ii) nitric acid in concentrated aqueous solution, or (iii) dinitrogen tetroxide. However, *N*-bromomethylsuccinimide reacted immediately with pyridine in acetonitrile solution to give *N*-(succinimidomethyl)pyridinium bromide (XVIII). N.m.r. evidence supported the identification

(XVIII)



(XIX)



of the analogous but very hygroscopic pyridinium compound (XIX) formed from *N*-chloromethyl-2-pyrrolidone but no reaction was detected with *N*-iodomethylpiperidine.

It is evident that the stability of *N*-(substituted methyl) derivatives, including complexes with pyridine, is determined by the degree of carbonium ionic character sustained by the methylenic carbon atom. In the case of succinimide the strongly electron-withdrawing influence of the two carbonyl groups and the quaternary nature of the nitrogen atom effectively prevent carbonium ion formation. Further consequences of the reduction of the electron availability on the nitrogen atom are (*a*) to reduce its susceptibility to electrophilic attack and (*b*) to allow nucleophilic attack by an S_N2 type mechanism at the methylenic carbon atom.

1,3-*Dinitro*-5-*nitroxymethylperhydro*-1,3,5-*triazine* (I).—The interpretation of the strongly contrasted stabilities of *N*-nitroxymethyl-piperidine and -succinimide suggests an intermediate stability for compound (I). Although there exists some uncertainty about the isolation of compound (I), the analogues (V)—(IX) have been prepared. Preliminary investigations showed a measurable interaction between nitric acid and compound (IX) in acetonitrile at room temperature at concentrations of 0·1 and 0·004M, respectively. RDX (III) was isolated and a simple conversion of the acetate was indicated by the presence of an isosbestic point at 238 nm, but the final spectrum in each case did not correspond to 100% conversion to RDX, although RDX was unaffected by nitric acid under similar conditions. First-order kinetics were observed and the order of the reaction with respect to nitric acid was found to be *ca.* 0·5.

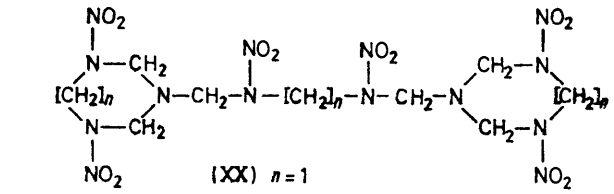
Solutions in acetonitrile of the *N*-halogenomethyl compounds (V) and (VI) underwent a slow change which could be followed by u.v. spectroscopy. In both cases the changing spectra had isosbestic points at 238 nm and the rates of change were of the same order as in the reaction of the 1-acetoxymethyl substrate (IX) ($1·02 \times 10^{-4}$M) with nitric acid ($1·2 \times 10^{-2}$M). A similar rate of change was evident when the variation of conductivity with time of the 1-chloromethyl compound

[14] A. F. Ferris, K. W. McLean, I. G. Marks, and W. D. Emmons, *J. Amer. Chem. Soc.*, 1953, **75**, 4078.

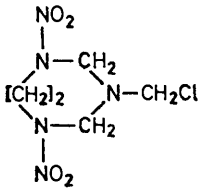
was followed in acetonitrile. With perchloric acid (4×10^{-5}M) and the same concentration of 1-acetoxymethyl-3,5-dinitroperhydro-1,3,5-triazine as before, the rate of change of the u.v. absorption was found again to be similar. The mean rate constant from alternative methods of determination was $(4{\cdot}85 \pm 0{\cdot}50) \times 10^3$ min^{-1} The first-order constants, although approximate, are so close to each other as to suggest that they represent the same rate-determining step. In acetonitrile solution ionisation of the halogenomethyl compounds is possible, since both provide a good leaving group (halide ion). Although no spectral change was observed when the 1-acetoxymethyl compound was dissolved in acetonitrile alone, the addition of nitric or perchloric acid may enhance any dissociation by protonation. The ionisation steps might be slow and rate-determining but could not be expected to proceed to completion. To account for the almost quantitative changes that occur, solvent intervention seems likely to be the dominant factor, giving an adduct such as (XIV). Interaction of this type has been observed [15] in the reaction of α-phenylethyl chloride with silver fluoroborate in acetonitrile. A high yield of *N*-α-phenylethylacetamide was obtained when the reaction mixture was added to water.

The observed fractional order in nitric acid may be due to its involvement in protonation and hydrogen bonding with the solvent and the product as well as with the acetate substrate. The interaction to give the adduct (XIV) with acetonitrile does not preclude the formation in part of the 1-nitroxymethyl compound (I), but all attempts to isolate the latter were unsuccessful. Concentration of the solution resulted in RDX formation, which may proceed by rearrangement of compound (I) with elimination of formaldehyde. The suggestion that species (I) is an intermediate in the conversion of (IX) into RDX cannot be confirmed or rejected. The demonstration that 1-methoxymethyl and similar derivatives may be isolated by addition of methanol or the appropriate nucleophilic reagent to the system may equally well be attributed to the presence of protonated (IX), or the carbonium ion derived from it by the elimination of acetic acid, or compound (I) or an ion pair or solvated ion pair derived from (I).

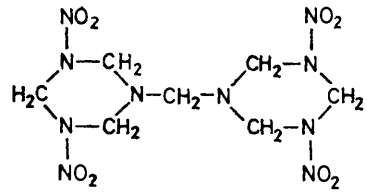
Reaction of 1-*Chloromethyl*-3,5-*dinitroperhydro*-1,3,5-*triazine* (V) *with Silver Nitrate.*—Treatment of the *N*-chloromethyl compound with silver nitrate in acetonitrile led to rapid, almost quantitative precipitation of silver chloride. A similar result was obtained with the bromo-analogue. Concentration of the mother liquors caused a product to separate in high yield, together with a smaller amount of RDX. This product was convertible into RDX in high yield by nitric acid, indicative of the presence of the 1,3-dinitroperhydrotriazine system. Attempts to determine the molecular weight by cryoscopic and ebullioscopic methods and vapour phase osmometry all failed to give reproducible results but there were indications of a molecule containing between two and three RDX units. A partial *X*-ray crystallographic analysis on a single crystal carried out by J. R. C. Duke (E.R.D.E, Waltham Abbey) indicated a molecular weight of 514 (±2) based upon the most probable case of four molecules per unit cell (although the quality of the crystals precluded a determination of the symmetry of the unit cell with certainty). This information, together with mass spectrometric and n.m.r. data, indicated that the product was 1,5-bis-(3,5-dinitroperhydro-1,3,5-triazin-1-yl)-2,4-dinitro-2,4-diazapentane (XX), with structure similar to that of the



(XX) $n = 1$
(XXI) $n = 2$



(XXII)



(XXIII)

product (XXI) previously synthesised [16] from ethylenedinitramine, formaldehyde, and ammonia. The similarity suggested that the latter bicyclic nitramine (XXI) should be formed on treatment of 3-chloromethyl-1,5-dinitroperhydro-1,3,5-triazepine (XXII) with silver nitrate in acetonitrile. This was found to be the case. If compound (I) is formed initially from compound (V) and silver nitrate, and goes on either to form the bicyclic nitramine (XX) or to eliminate formaldehyde to give RDX then the nitroso-analogue (IV) of RDX should be formed when silver nitrite is used in place of silver nitrate. This nitroso-derivative (IV) was in fact formed in high yield with the evolution of formaldehyde. Kornblum [17] has suggested that nitrite esters are formed at the expense of nitroalkanes if the transition state in a nucleophilic substitution with silver nitrite has more carbonium ion character. One would expect the nitrite ester (II) to be formed to the greater extent here and thus to eliminate formaldehyde in a manner comparable to the nitrate ester (Scheme 1).

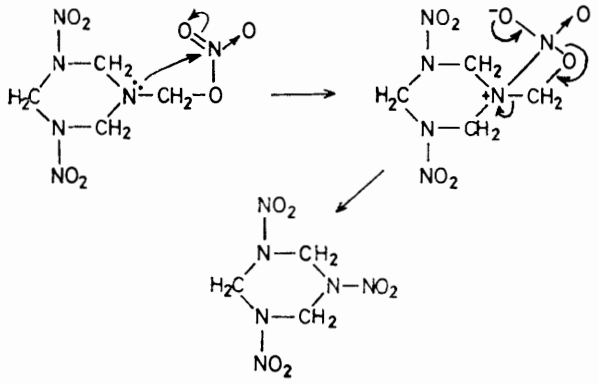
The reaction of silver nitrate with the 1-chloromethyl compound was carried out at various dilutions; in each case cold methanol was added to the filtrate after removing the silver chloride, and the 1-methoxymethyl ether (VIII) was found to be produced in greater yields from the more dilute solutions. Thus the nitrate ester

[15] N. Kornblum and D. H. Hardies, *J. Amer. Chem. Soc.*, 1966, **88**, 1707.

[16] J. A. Bell and I. Dunstan, *J. Chem. Soc.* (*C*), 1966, 862.

[17] N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. Chem. Soc.*, 1955, **77**, 6269.

may be present in the high dilution reactions but formation of the bicyclic nitramine is favoured by the relatively high concentrations necessary for a termolecular combination; one mechanistic possibility is

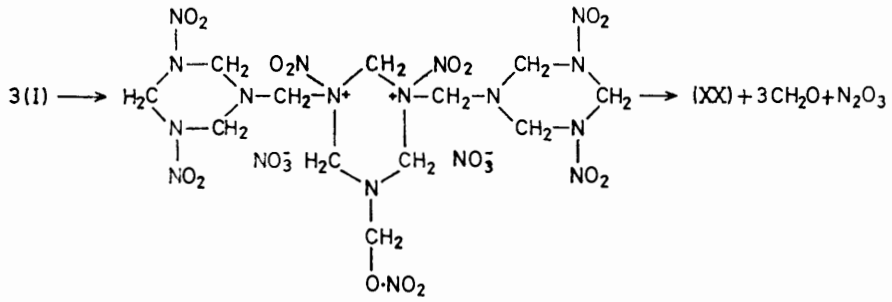


SCHEME 1

shown in Scheme 2. Even at high dilutions the yield of RDX could not be significantly increased, possibly owing to solvent interaction of acetonitrile with the nitrate ester (I) of the same type as observed between the solvent and 1-chloromethyl-3,5-dinitroperhydro-1,3,5-triazine. Although the 1-chloromethyl compound is not recoverable from acetonitrile solutions after a prolonged period, no bicyclic nitramine could be detected as a product of the reaction. Thus an essential step in the formation of the bicyclic nitramine (XX) appears to be a nucleophilic attack in a ring-opening process which appears not so likely with the chloride ion, *i.e.* the latter is less nucleophilic than the nitrate ion in acetonitrile. A more powerful nucleophile should therefore facilitate the bicyclic nitramine formation; this prediction was confirmed by use of silver trifluoroacetate. Immediate precipitation of silver chloride occurred and the 1-chloromethyl compound (V) was converted in 82% yield into compound (XX). Repetition with silver bromate produced only 7% of compound (XX), the main product being 3,5-dinitroperhydro-1,3,5-triazine-1-carbaldehyde (XIII). The bromate would be expected to have a low nucleophilicity but simple comparison was not possible owing to oxidation of the methylene side chain.

The use of silver trifluoroacetate suggested the possibility of synthesising 1,3-dinitro-5-trifluoroacetoxymethylperhydro-1,3,5-triazine (X) [claimed by Reed to be an intermediate in his synthesis of (I)] by carrying out the reaction with the 1-chloromethyl compound (V) in a less polar solvent, such as 1,2-dimethoxyethane. The reaction however produced 1,1′-methylenebis-3,5-dinitroperhydro-1,3,5-triazine (XXIII) in high yield, together with trifluoroacetic anhydride.

These studies show that the *N*-nitroxymethyl compound (I) resembles its piperidine analogue (in its instability and high reactivity) much more closely than it resembles the corresponding succinimide derivative. The electrons on the substituted nitrogen atom are well able to stabilise the carbonium ion formed from dissociative cleavage of a nitrate group but not as well as in the piperidine analogue. In addition, nucleophilic attack at the methylenic carbon atom is easier than in the piperidine analogue. The isolation of compound (I) is rendered even more difficult by its readiness to form the bicyclic nitramine or to eliminate a molecule of formaldehyde and form RDX.



SCHEME 2

EXPERIMENTAL

Materials.—Anhydrous nitric acid, dinitrogen tetroxide, and their solutions in carbon tetrachloride were prepared and standardised as described previously.[18] Acetronitrile (B.D.H. Laboratory Reagent) was purified according to the method of Kevill.[19] Silver nitrate (B.D.H.) and *N*-nitrosopiperidine (Eastman Organic Chemicals) were used as supplied.

The following materials were prepared according to standard methods: *N*-ethoxymethylpiperidine,[11] *N*-butoxymethylpiperidine,[10] *N*-nitropiperidine,[20] *N*-bromomethylsuccinimide,[13] *N*-acetoxymethylsuccinimide,[8] *N*-nitrosuccinimide,[21] *N*-chloromethyl-2-pyrrolidone,[22] and 1-chloromethyl-,[1a] 1-bromomethyl-,[1b] 1-ethoxymethyl-,[1a] 1-methoxymethyl-,[1a] and 1-acetoxymethyl-3,5-dinitroperhydro-1,3,5-triazine.[23] The reported preparation of

[18] T. G. Bonner, R. A. Hancock, G. Yousif, and F. R. Rolle, *J. Chem. Soc.* (*B*), 1969, 1237.
[19] D. N. Kevill and R. F. Shutoff, *J. Chem. Soc.* (*B*), 1969, 366.
[20] W. D. Emmons, *J. Amer. Chem. Soc.*, 1954, **76**, 3468.
[21] H. F. Kauffmann and A. Burger, *J. Org. Chem.*, 1954, **19**, 1662.
[22] M. F. Shostakovskii and F. Sidel'Kovskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 892.
[23] W. J. Chute, A. F. McKay, R. H. Meen, G. S. Myers, and G. F. Wright, *Canad. J. Res.*, 1949, **27B**, 503.

N-iodomethylpiperidine [12] was modified to include a final recrystallisation in the absence of atmospheric moisture.

N-Acetoxymethylpiperidine [24] was purified by repeated vacuum distillations to remove traces of *N*-acetylpiperidine. The product distilled at 50° and 1 mmHg and showed n_D^{19} 1·4503 (lit.,[24] n_D^{21} 1·4497).

1-Chloromethyl-2-pyrrolidone [22] was purified by vacuum distillation; the fraction boiling at 80° and 1 mmHg was collected. The product, which was previously reported as a liquid, slowly crystallised to give a hygroscopic solid, m.p. 36—42° (Found: Cl, 26·6. Calc. for C_5H_8ClNO: Cl, 26·55%).

N-*Nitroxymethylpiperidine*.—To a solution of *N*-iodomethylpiperidine (22·3 g, 0·1 mol) in dry dichloromethane (140 ml) was added silver nitrate (33·5 g, 0·2 mol), and the solution was kept cool in an ice-bath with intermittent shaking for 2 h. The precipitated silver iodide was separated, washed free of silver nitrate, dried, and shown to correspond to 93% of the available iodide. The residue was chromatographed on cellulose with dry methanol as eluant to yield a yellow viscous liquid which crystallised slowly to give a hygroscopic product, $\nu_{max.}$ 1360s and 1610w cm^{-1}. Attempted distillation under vacuum resulted in violent decomposition with the apparent formation of *N*-nitropiperidine.

Reaction with sodium ethoxide. A solution of sodium ethoxide (0·03 mol) in ethanol (13 ml) was added slowly and with stirring to a cooled (5—10°) solution of *N*-nitroxymethylpiperidine (5·4 g, 0·03 mol) in dry ethanol (20 ml). When addition was complete the white solid which had precipitated was separated, dried, recrystallised from water, and shown to be sodium nitrate (1·6 g). The solvent was removed from the ethanolic solution which remained, leaving a colourless liquid (2·1 g) which was purified by distillation at atmospheric pressure (b.p. 170—174°) and identified (i.r. spectrum) as 1-ethoxymethylpiperidine (lit.,[11] b.p. 176°).

N-*Nitroxymethylsuccinimide*.—Silver nitrate (18·0 g, 0·11 mol) dissolved in acetonitrile (30 ml) was added dropwise with stirring to a cooled (10°) solution of *N*-bromomethylsuccinimide (19·0 g, 0·1 mol) in the same solvent (30 ml). The silver bromide which formed was filtered off, washed with acetonitrile, and dried (yield 18·1 g, corresponding to 96% uptake of bromide). On removal of the solvent a solid remained which was recrystallised from ethanol to give N-*nitroxymethylsuccinimide* as white non-hygroscopic needles, m.p. 109—111° (10 g, 59%) (Found: C, 34·4; H, 3·6; N, 16·2. $C_5N_6N_2O_5$ requires C, 34·5; H, 3·5; N, 16·1%), $\nu_{max.}$ 1640 (O–NO_2) and 1720 cm^{-1} (C=O). The substance gave a positive result in a nitrate test with diphenylamine and sulphuric acid.

Nitration of Piperidine and Succinimide Derivatives.—N-*Acetoxymethylpiperidine*. (a) *Anhydrous nitric acid in carbon tetrachloride*. A solution of anhydrous nitric acid (1·5 g, 0·024 mol) in carbon tetrachloride (50 ml) was added slowly to a stirred and cooled (5—10°) solution of *N*-acetoxymethylpiperidine (3·0 g, 0·019 mol) in the same solvent (20 ml). The insoluble yellow oil which formed was separated, washed several times with carbon tetrachloride, and shown by t.l.c. (cellulose plates; methanol) to contain mostly *N*-nitroxymethylpiperidine.

(b) *Nitric acid and acetic anhydride*. The reagent was prepared by adding concentrated nitric acid (2·7 g, 0·043 mol) dropwise to cooled (−10°) and stirred acetic anhydride (11 g, 0·11 mol) and then stored at −80°. To a solution of acetyl nitrate (3·5 g, 0·033 mol) at 5°, *N*-acetoxymethylpiperidine (2 g, 0·013 mol) was added slowly and with stirring. The solution was allowed to warm slowly to 50°; a reaction then commenced which was controlled by occasional cooling. When the reaction was complete the solution was poured on ice (5 g) and extracted with dichloromethane (3 × 5 ml); the extract was washed with water (3 × 5 ml), dried, and evaporated to yield a yellow liquid which t.l.c. [silica gel; isopentane–1,2-dichloroethane–methanol (85 : 13 : 2 v/v/v)] showed to contain both *N*-nitro- and *N*-nitroso-piperidine, together with some *N*-acetylpiperidine and some unchanged starting material.

N-*Butoxymethylpiperidine*. (a) *Nitric acid in carbon tetrachloride*. Anhydrous nitric acid (5 ml, 0·116 mol) in carbon tetrachloride (50 ml) was added dropwise to a cooled (10°) stirred solution of *N*-butoxymethylpiperidine in the same solvent (50 ml). An insoluble yellow oil was formed. Solvent and nitric acid were removed by distillation at 30° and 15 mmHg. T.l.c. showed that the product consisted mostly of *N*-nitroxymethylpiperidine, with a trace of *N*-nitropiperidine.

(b) *Nitric acid and acetic anhydride*. To a cooled (0°) stirred solution of *N*-butoxymethylpiperidine (8·66 g, 0·05 mol) in carbon tetrachloride (25 ml), acetyl nitrate (53 g, 0·051 mol) was added at 0°. The solution was then allowed to warm to 20° during 12 h. Solvent was removed by distillation under reduced pressure (30° at 15 mmHg) and a second fraction was collected at 40° and 2 mmHg. The volatile products were analysed by g.l.c. (Apiezon K on Celite; nitrogen as carrier gas; column temperature 80°). Four products were separated, two of which had retention times corresponding to n-butyl acetate and n-butyl nitrate. A third component, separated on a preparative scale with a Pye Automatic Preparative Chromatograph at a temperature of 118°, was presumed to be n-butoxymethyl acetate (Found: C, 57·4; H, 9·7. Calc. for $C_7H_{14}O_3$: C, 57·5; H, 9·75%), $\nu_{max.}$ 1725 (ester CO), and 1360 (O–C–O), and 1230s cm^{-1} (acetate). The fourth component was obtained in extremely small quantity and was not identified. The involatile residue was analysed by t.l.c. and shown to be mostly *N*-nitroxymethylpiperidine.

(c) *Dinitrogen tetroxide in carbon tetrachloride*. Nitrogen dioxide was passed *via* a phosphorus pentoxide drying tower into a solution of *N*-butoxymethylpiperidine (3·0 g, 0·017 mol) in carbon tetrachloride (30 ml) at 20° until the solution became saturated. The solution was stirred for 48 h then evaporated. A yellow oil remained which was distilled and collected at 48° and 4 mmHg; t.l.c. showed it to be *N*-nitrosopiperidine (1·43 g, 70%).

N-*Acetoxymethyl- and* N-*nitroxymethyl-succinimide*. (a) *Aqueous 70% nitric acid*. The substrates [*N*-acetoxymethylsuccinimide (0·5 g, 0·003 mol), *N*-nitroxymethylsuccinimide (1·0 g, 0·0057 mol)] were added to 70% nitric acid (10 ml) at room temperature. Starting material was recovered in the case of *N*-acetoxymethylsuccinimide by extraction of the solution after 30 min with dichloromethane (3 × 10 ml), washing with water (3 × 5 ml), drying ($MgSO_4$), and evaporation, and in the case of *N*-nitroxymethylsuccinimide by removal of nitric acid and water under vacuum.

(b) *Nitric acid–sulphuric acid*. Concentrated (70%) nitric acid (2 ml) was added to cooled (0°) concentrated sulphuric acid (3 ml). *N*-Nitroxymethylsuccinimide (0·25

[24] H. Boehme, H. S. Bohm, E. Köhler, and J. Roehr, *Annalen*, 1963, **664**, 130.

g, 0·001 mol) was then added slowly with stirring. After 2 h the solution was poured into iced water (30 ml) and the starting material was recovered by extraction with dichloromethane.

Reactions of Piperidine, Succinimide, and 2-Pyrrolidone Derivatives with Pyridine.—*N-Bromomethylsuccinimide.* Pyridine (2·0 ml, 0·026 mol) was added slowly to a cooled (5°) stirred solution of *N*-bromomethylsuccinimide (4·9 g, 0·025 mol) in acetonitrile (40 ml). The white solid which separated was removed and recrystallised from aqueous ethanol to give N-(*succinimidomethyl*)*pyridinium bromide* as white needles, m.p. 270—275° (decomp.) (Found: C, 44·3; H, 4·1; Br, 29·5; N, 10·3; ionic Br^- 29·3. $C_{10}H_{11}BrN_2O_2$ requires C, 44·4; H, 4·2; Br, 29·3; N, 10·2%); τ (CD_3·CN) 1·5 (5H, m), 3·8 (2H, s), and 7·2 (4H, s).

N-Chloromethyl-2-pyrrolidone. Pyridine (3·9 ml, 0·053 mol) in acetonitrile (10 ml) was added slowly to a stirred solution of *N*-chloromethyl-2-pyrrolidone (6·03 g, 0·053 mol) in acetonitrile (30 ml), the temperature being maintained below 15°. After 20 min the solvent was removed, leaving a white solid which was washed with carbon tetrachloride and filtered off in the absence of moisture; m.p. 140—165° (decomp.); τ (CD_3·NO_2) 1·5 (5H, m), 3·8 (2H, s), 6·5 (2H, t), and 7·7 (4H, m).

Reactions of 1-Acetoxymethyl-3,5-dinitroperhydro-1,3,5-triazine with Nitric Acid and Perchloric Acid in Acetonitrile.—*Nitric acid.* Standardised anhydrous nitric acid solutions in acetonitrile at 25·0° were added to the acetate in acetonitrile at 25·0°. Part of each reaction solution was then transferred to a constant temperature (25·0°) cell (1 cm; silica) and the spectrum (200—300 nm) was recorded at intervals for *ca.* 30 h. A solution of nitric acid of the same concentration was used as reference. Rate constants were determined by measurement of the optical density at 228 nm (Δ_t) and determining the slope of the plot of ln ($\Delta_\infty - \Delta_t$) against time (t).

Perchloric acid. Perchloric acid solutions were prepared by diluting a 0·1N-solution of perchloric acid in glacial acetic acid. Kinetic runs were carried out in the same manner as those involving nitric acid.

Interaction of 1-Chloromethyl-3,5-dinitroperhydro-1,3,5-triazine with Acetonitrile.—Change in u.v. spectrum. A 0·0001M-solution of the chloromethyl compound in acetonitrile was made up at 25·0° and the change in spectrum was observed during 30 h. Measurement of the rate of change of optical density at 228 nm was used to determine the first-order rate constant for the reaction.

Conductivity measurements. The recrystallised chloromethyl compound (0·0023 g) was dissolved in acetonitrile (100 ml) at 25·0°. The conductivity change of the solution was recorded (MEL conductivity bridge; platinum electrode dip-type cell). The conductivity of pure acetonitrile was recorded at the same temperature and the first-order rate constant for the conductivity change was determined.

Reaction of 1-Chloromethyl-3,5-dinitroperhydro-1,3,5-triazine with Silver Salts.—Silver nitrate in acetonitrile. To a cooled (10°), stirred solution of the chloromethyl compound (2·0 g, 0·009 mol) in acetonitrile (10 ml), a solution of silver nitrate (1·6 g, 0·009 mol) in acetonitrile (5 ml) was added slowly. The silver chloride immediately precipitated was filtered off. From the filtrate a white solid gradually crystallised (0·63 g, 42%) which recrystallised from nitromethane to give 1,5-*bis*-(3,5-*dinitroperhydro*-1,3,5-*triazin*-1-*yl*)-2,4-*dinitro*-2,4-*diazapentane* (XX), m.p. 127—128° (Found: C, 21·05; H, 3·55; N, 38·0. $C_9H_{18}N_{14}O_8$ requires C, 21·0; H, 3·5; N, 38·3%), mol. wt. (single crystal *X*-ray) 514 ± 2, τ (CD_3·NO_2) 3·97br (6H) and 4·94br (12H). The solvent was removed from the filtrate and the colourless oil slowly crystallised (yield 0·17 g, 8·1%). The crystals were washed with chloroform, dried, and shown to be RDX (III) (m.p. 202—204°). The yield of the bicyclic nitramine could be increased by removing the solvent immediately after removal of silver chloride and allowing the remaining oil to crystallise.

When reaction solutions were added to cold (0°) dry methanol after the removal of silver chloride, 1 methoxymethyl-3,5-dinitroperhydro-1,3,5-triazine could be separated.

Silver nitrite in acetonitrile. Silver nitrite (0·87 g, 0·005 mol) in acetonitrile (5 ml) was added slowly to a stirred, cooled solution of the chloromethyl compound (1·3 g, 0·005 mol) in the same solvent (10 ml). After the liberation of formaldehyde, the precipitated silver chloride (95·5%) was filtered off and the filtrate was evaporated to leave a pale yellow solid (0·8 g, 73%). Recrystallisation from ethanol afforded yellow needles of 1,3-dinitro-5-nitrosoperhydro-1,3,5-triazine (Found: C, 17·45; H, 2·85; N, 40·6. Calc. for $C_3H_6N_6O_5$: C, 17·5; H, 2·95; N, 40·75%), τ (CD_3·NO_2) 3·7 (2H, s), 3·9 (2H, s), and 4·3 (2H, s).

Silver bromate in acetonitrile. Silver bromate (1·0 g, 0·005 mol) in acetonitrile (5 ml) was added slowly to a stirred, cooled (15°) solution of the chloromethyl compound (1·0 g, 0·0044 mol) in acetonitrile (10 ml). Silver chloride was precipitated and filtered off (0·63 g, 88%); bromine was also evolved. The filtrate was cooled to 0° and a white crystalline solid formed (0·47 g, 52%) which yielded 3,5-*dinitroperhydro*-1,3,5-*triazine*-1-*carbaldehyde* (XIII), m.p. 184—185° (from acetonitrile) (Found: C, 22·1; H, 3·45; N, 32·55. $C_4H_7N_5O_5$ requires C, 23·4; H, 3·4; N, 34·2%), τ (CD_3·CN) 1·9 (1H, s), 3·9 (2H, s), 4·4 (2H, s), and 4·6 (2H, s).

Dry ether (10 ml) was added to the filtrate, giving the bicyclic nitramine (XX) (0·05 g, 7%), m.p. 128°.

Silver trifluoroacetate in acetonitrile. Silver trifluoroacetate (1·0 g, 0·0045 mol) in acetonitrile (15 ml) was added slowly to a stirred solution of the chloromethyl compound (1·0 g, 0·0044 mol) in the same solvent (15 ml) maintained at room temperature. The precipitated silver chloride was removed (0·57 g, 91%) and the filtrate was evaporated to give the bicyclic nitramine (XX) (0·64 g, 82%).

Reaction of 3-Chloromethyl-1,5-dinitroperhydro-1,3,5-triazepine (XXII) *with Silver Nitrate.*—To a solution of the perhydrotriazepine (XXII) (3·43 g, 0·014 mol) in acetonitrile (30 ml) at 20° was added a solution of silver nitrate (2·3 g, 0·014 mol) in the same solvent (20 ml), slowly and with stirring. The precipitated silver chloride was removed (1·6 g, 82%) and the filtrate was evaporated to give 1,6-bis-(1,5-dinitroperhydro-1,3,5-triazepin-3-yl)-2,5-dinitro-2,5-diazahexane (XXI), m.p. 204—205° (from dimethylformamide–benzene) [lit.,[16] 205·7° (decomp.)] (Found: C, 25·85; H, 4·4; N, 35·5. Calc. for $C_{12}H_{24}N_{14}O_{12}$: C, 25·9; H, 4·3; N, 35·25%), τ [$(CD_3)_2SO$] 4·84br (12H) and 5·83br (12H). The structure was confirmed by hydrolysis as described by Dunstan.[16]

We thank the Procurement Executive of the Ministry of Defence for support.

[2/129 *Received*, 21*st January*, 1972]