valuable discussions and continuing interest and to Professor Charles D. Hurd of Northwestern University for his helpful suggestions and advice. The author is also indebted to Dr. Shiro Satoh for n.m.r. studies. Thanks are given to Mr. Tadashi Ikegami for his assistance in the experimental work.

β,β-Dinitroalkylamines and -nitramines, and Related Compounds[1]

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The condensation of 2,2-dinitroalkanols with ammonia, aliphatic amines, and aromatic amines has been investigated, the conditions for the preparation of the 2,2-dinitroalkylamines have been determined, and the formed amines have been nitrated. The properties of the compounds are described and it is shown that the condensation reaction can be reversed by certain weak Lewis bases. The nitration products are more stable toward such bases.

Mannich condensations of 1,1-dinitroparaffins with formaldehyde and amines can be carried out by heating the components in a polar medium or by condensing 2,2-dinitro alcohols with ammonia or amines to give various substituted 2,2-dinitroalkylamines.[2]

In the present investigation the condensation reaction with 2,2-dinitropropanol (I) has been carried out with a series of primary and secondary amines. The

$$\underset{\mathrm{I}}{\mathrm{MeC(NO_2)_2CH_2OH}}$$

conditions for the reaction are highly specific for each case, by-products appear as contaminants, and the purification of the products is often rendered difficult by the formation of mixed crystals between product and starting material. In the case of aliphatic primary amines, the condensation product II can be isolated as a crystalline nitrate III or as the corresponding nitramine IV if it is not possible to purify II. The ease of dehydration of the nitrates III differs depending on the

$$\underset{\mathrm{II}}{\mathrm{RNHCH_2C(NO_2)_2Me}} \qquad \underset{\mathrm{III}}{\mathrm{R\overset{+}{N}H_2CH_2C(NO_2)_2MeNO_3^-}}$$

$$\underset{\mathrm{IV}}{\mathrm{RN(NO_2)CH_2C(NO_2)_2Me}}$$

nature of R. For R = small alkyl 100% nitric acid does not bring about the conversion to IV without an additional dehydrating agent such as acetic anhydride.[3] Amines II with R containing functional groups are usually nitrated with 100% nitric acid directly to nitramines IV and the corresponding nitrates III are then obtained only by using a stoichiometric amount of nitric acid in an inert solvent.

The condensation reaction with 2,2-dinitropropanol works equally well with unsaturated amines (*e.g.*, allylamine), diamines, amino alcohols, and hydrazine derivatives.

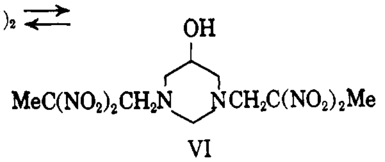
When a primary amine is used in the reaction with 2,2-dinitropropanol, a single 2,2-dinitropropyl group is usually introduced, an exception being the alkaline condensation with glycine.[4,5] Other electron-withdrawing substituents inactivate amino groups; thus, amides, urethans, and ureas do not react with I under the conditions investigated. While I fails to condense with guanidine under the usual conditions, it can be made to react with aminoguanidine bicarbonate. The product, however, is not the expected amine but the aminoguanidine salt of 1,1-dinitroethane. It is evident that in this case I has undergone a reversal of the Henry reaction under the influence of the amine to give 1,1-dinitroethane and formaldehyde. The final product in all these reactions is probably determined to some extent by the relative solubilities of the products and the basicities of the amines. Another example of an abnormal reaction is the condensation of I with 1,3-diamino-2-propanol. The formed 2,2,10,10-tetranitro-4,8-diaza-6-undecanol (V) disproportionates in the aqueous reaction mixture and the resultant oil gives a formaldehyde condensation product VI on cooling or seeding and the 1,1-dinitroethane salt VII on crystallization from methanol. The following equilibria are postulated for

$$\underset{\mathrm{V}}{\mathrm{MeC(NO_2)_2CH_2NHCH_2CH(OH)CH_2NHCH_2C(NO_2)_2Me}}$$

$$\mathrm{V + H_2O \rightleftharpoons I + \underset{VIIA}{H_2NCH_2CH(OH)CH_2NHCH_2C(NO_2)_2Me}}$$

$$\mathrm{I + H_2O \rightleftharpoons MeCH(NO_2)_2 + CH_2(OH)_2}$$

$\mathrm{+\ V\ CH_2(OH)_2} \rightleftharpoons$



$\mathrm{+\ H_2O}$

VI

$$\mathrm{VIIA + MeCH(NO_2)_2 \rightleftharpoons}$$

$$\underset{\mathrm{VII}}{\mathrm{Me\overset{-}{C}(NO_2)_2\overset{+}{N}H_3CH_2CH(OH)CH_2NHCH_2C(NO_2)_2Me}}$$

V in aqueous solution. If the condensation of I with 1,3-diamino-2-propanol is carried out in the presence of 1 mole of aqueous formaldehyde, VI is obtained in excellent yield as the only product. The structure of VI is based on analyses, infrared absorption spectra, and reactions.

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission and presented before the Division of Organic Chemistry at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[2] P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **64**, 19 (1964).

[3] A summary of the extensive work by Wright and others on this subject is given by A. H. Lamberton, *Quart. Rev.* (London), **5**, 75 (1951).

[4] H. Feuer, G. B. Bachmann, and W. May, *J. Am. Chem. Soc.*, **76**, 5124 (1954).

[5] M. B. Frankel and K. Klager, *ibid.*, **79**, 2953 (1957).

Dinitropropylamines with other nitratable groups can be nitrated simultaneously in several positions. Thus the amines derived from ethanolamine,[6] 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-(hydroxymethyl)-1,3-propanediol, and 1,3-diamino-2-propanol[7] yield crystalline nitrate esters, *e.g.*, VIII and IX. The nitration product from crude V

$$\mathrm{MeC(NO_2)_2CH_2N(NO_2)CMe(CH_2ONO_2)_2}$$

VIII

$$\mathrm{MeC(NO_2)_2CH_2N(NO_2)C(CH_2ONO_2)_3}$$

IX

has been separated by fractional crystallization into two nitrates, the expected nitrate X[7] and a new nitrate XI. Nitration of XI under more drastic conditions gives X. Based on these relationships, the following structures are assigned to X and XI. When VI is

$$\mathrm{MeC(NO_2)_2CH_2N(NO_2)CH_2CH(ONO_2)CH_2N(NO_2)CH_2C(NO_2)_2Me}$$

X

$$\mathrm{MeC(NO_2)_2CH_2N(CH_2ONO_2)CH_2CH(ONO_2)CH_2N(NO_2)CH_2C(NO_2)_2Me}$$

XI

nitrated with 100% nitric acid and concentrated sulfuric acid at 70°, it is directly converted to X in an over-all yield of 78–81% (from dinitropropanol).

The nitrate X melts with evolution of nitrogen oxides at 160° to give a colorless solid which has been identified as an equimolar mixture of 2,2,4,8,10,10-hexanitro-4,8-diaza-6-undecanone (XII) and the corresponding secondary alcohol XIII. In the absence of detectable amounts of other products the pyrolysis reaction can be written as follows. The new ketone XII can be pre-

$$\underset{\mathrm{X}}{\mathrm{2R_2CHONO_2}} \xrightarrow{\Delta} \mathrm{2NO_2 + 2R_2CHO\cdot} \longrightarrow \underset{\mathrm{XII}}{\mathrm{R_2C{=}O}} + \underset{\mathrm{XIII}}{\mathrm{R_2CHOH}}$$

$$\mathrm{R = MeC(NO_2)_2CH_2N(NO_2)CH_2}$$

pared in high yields by oxidation of XIII. It is extraordinarily reactive toward bases. Nitrite ion is instantly eliminated when XII is treated with dilute sodium hydroxide or aliphatic amines or even when it is warmed with dimethylformamide. Since secondary nitramines do not normally exhibit such sensitivity, this behavior is ascribed to the activating effect of the carbonyl group.

The condensation product from glycine ethyl ester has been nitrated to ethyl 3,5,5-trinitro-3-azahexanoate (XIV) which gives the known 3,5,5-trinitro-3-azahexanoic acid (XV)[8] on hydrolysis. The yield in the hydrolysis step is dependent on the reaction conditions since XV is sensitive to acid and base. Esterification of the corresponding acid chloride XVI with I and pyridine[9] has given the 2,2-dinitropropyl ester XVII.

$$\mathrm{XVI + I} \xrightarrow{\text{pyridine}} \underset{\mathrm{XVII}}{\mathrm{MeC(NO_2)_2CH_2N(NO_2)CH_2COOCH_2C(NO_2)_2Me}}$$

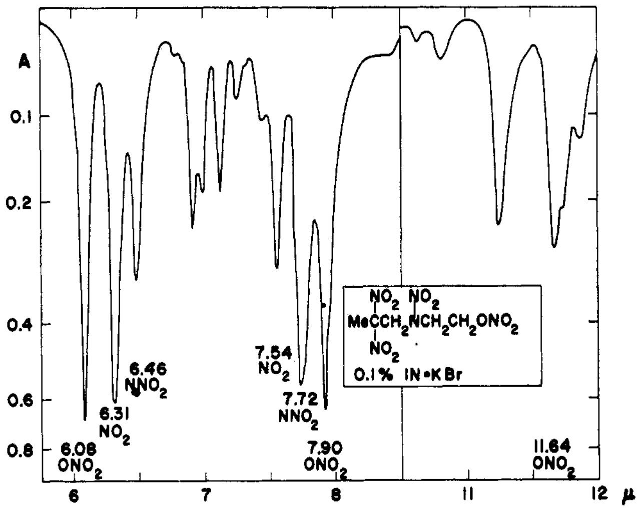
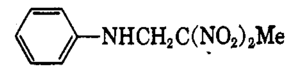
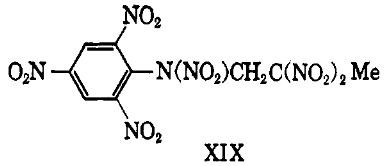


Figure 1.—Infrared absorption spectrum of 3,5,5-trinitro-3-azahexyl nitrate.

Primary aromatic amines can be condensed with 2,2-dinitropropanol provided that they do not contain too many electron-withdrawing substituents. *m*-Nitroaniline and the *para* isomer have been condensed in this fashion but the reaction is slow, while 2,4-dinitroaniline and picramide are recovered under the same conditions. The three phenylenediamines react readily with I in polar media, as does 1,3,5-triaminobenzene, but the products are difficult to purify. Only N,N′-bis(2,2-dinitropropyl)-*o*-phenylenediamine and the *para* isomer have been obtained analytically pure. Aryldinitropropylamines with reactive aromatic rings will give nitroaryldinitropropylnitramines on nitration. Thus, N-(2,2-dinitropropyl)aniline (XVIII) is nitrated to N-(2,2-dinitropropyl)-N,2,4,6-tetranitroaniline (XIX), an analog of tetryl.

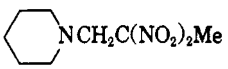


XVIII

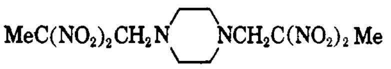


XIX

Secondary amines such as diethylamine, pyrrolidine, piperidine, and piperazine react readily to give the N-(2,2-dinitropropyl)amines. Only the reaction with ethylenimine is abnormal, inasmuch as the product is not cyclic but polymeric. Weakly electron-withdrawing substituents, as in diethyl iminodiacetate, do not prevent the reaction. Dinitropropyldialkylamines (open chain or cyclic), *e.g.*, XX and XXI, yield crystalline nitrates with nitric acid in dichloromethane.



XX



XXI

A striking characteristic of the dinitropropylamines is that they are colored, varying from pale yellow to deep orange. Moreover, this color varies as a function of the basicity of the amino nitrogen. Thus, bis(2,2-dinitropropyl)amine is very weakly colored while XVIII is

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[6] M. H. Gold, C. R. Vanneman, K. Klager, G. B. Linden, and M. B. Frankel, *J. Org. Chem.*, **26**, 4729 (1961).

[7] K. Baum and W. T. Maurice, *ibid.*, **27**, 2231 (1962).

[8] M. B. Frankel and K. Klager, *ibid.*, **23**, 1813 (1958).

[9] L. W. Kissinger, T. M. Benziger, H. E. Ungnade, and R. K. Rohwer, *ibid.*, **28**, 2491 (1963).

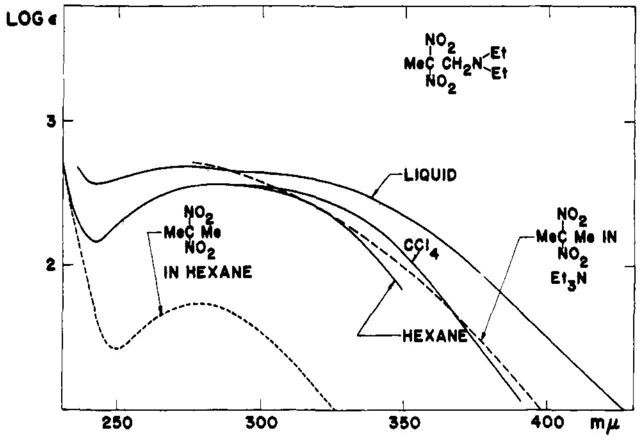


Figure 2.—Ultraviolet absorption spectra of diethyl-2,2-dinitropropylamine (———) and 2,2-dinitropropane (– – – –).

orange. The nitrate salts and nitramines, on the other hand, are all colorless. The origin of the color has been investigated by means of absorption spectra.

The dinitropropyl amines have essentially normal NO_2 stretching bands, the secondary amines have normal (weak) NH stretching bands, and the hydroxyl bands in the alcohols are comparable in wave lengths and intensities with those in analogous alcohols without nitro groups if weak interactions are neglected. The nitration of the compounds to nitramines causes shifts of nearby stretching bands to shorter wave lengths, as might be expected with the introduction of a strongly electron-attracting group. Nitro, nitramino, and nitrato bands usually are separated sufficiently so that it is possible to make definite assignments, as in the case of 3,5,5-trinitro-3-azahexyl nitrate (Figure 1). In compounds where nitro and nitramino *as*-stretching bands are close together, the *sym*-stretching bands assume greater importance for diagnostic purposes since they are usually quite strong and remain well separated.

Electron spin resonance measurements for one representative compound (XXI) show that there are no free radicals in the pure compound.[10]

The yellow color in 2,2-dinitropropylamines is similar in secondary and tertiary amino compounds, as are the ultraviolet absorption spectra; *i.e.*, the presence or absence of an N–H bond is not essential for color nor for the abnormal absorption spectra which have been reported for other β-nitramines.[11] We have now observed abnormal spectral behavior of more than one type for 2,2-dinitropropyl amines. In hexane the low-intensity (n → π*) transition of the *gem*-dinitro group[12] of dinitropropylamines has a greatly increased intensity, similar in magnitude to the spectrum of a *gem*-dinitro compound in a tertiary amine (Figure 2).[13] Solvents like carbon tetrachloride give a slight red shift and may therefore act as abnormal solvents also in this case.[12] Both of these solvents, however, give spectra which are comparable with that of the pure liquid and Beer's law is obeyed. One may assume therefore that the compounds remain intact in such solvents. The color is due to the enhanced and broadened absorption of the dinitro group.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF DINITROPROPYLAMINES

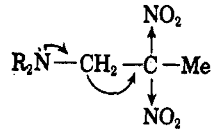
Amine	Solvent	λ_{max_1}, mμ	ε	λ_{max_2}, mμ	ε[a]	% ion
Et_2NR[b]	0.1 *N* HCl	275	45	...	...	0
	C_6H_{14}	280	370	...	...	0
	CCl_4	280[c]	364	...	...	0
	MeOH	...	...	377	14,400	82
	95% EtOH	...	...	377.5	16,100	92
	H_2O	...	...	380	13,100[d]	75[d]
	0.1 *N* NaOH	...	...	380	17,600	100
$(CH_2)_5NR$ (XX)	0.1 *N* HCl	sh 270	67	...	...	0
	C_6H_{14}	268	396	...	...	0
	CCl_4	270	414	...	...	0
	MeOH	...	...	376.5	12,000	58
	95% EtOH	...	...	377	13,800	79
	H_2O	...	...	379	15,150	86
	0.1 *N* NaOH	...	...	380	17,500	100
Nitrate	MeCN	281	74	...	...	0
HNR_2	0.1 *N* HCl	270	152	...	...	0
	MeCN	sh 248	830	...	...	0
	95% EtOH	sh 250	880	378	280[e]	1.6[e]

[a] After 60 min. at 25°. [b] R = $MeC(NO_2)_2CH_2$. [c] 270–300 mμ. [d] The slow rate of hydrolysis in this case is due to the small solubility of the compound in water. [e] The absorptivity of the 0.00075 *M* solution increased to 560 (3.2% ion) after 195 min. at 25°.

In weak Lewis bases such as alcohol and water, three different types of 2,2-dinitropropylamines give time-dependent spectra and the solvolysis reaction is the faster the stronger the basic character of the amino nitrogen (Table I). The spectral findings include the formation of a new band at 377–379 mμ, which in 0.1 *N* sodium hydroxide has a molar absorptivity of 17,500, identical with the value for 1,1-dinitroethane in this solvent. In the case of XX the cleavage reaction has been carried out also on a preparative scale and the salt of 1,1-dinitroethane has been isolated and identified by infrared spectra. It is apparent therefore that water and alcohols can bring about a reversal of the Mannich reaction.

Salts of 2,2-dinitropropylamines in nonaqueous solutions or the amines in aqueous acids give spectra which obey Beer's law and which are similar to those of the *gem*-dinitro compounds (Table I, Figure 3). It appears, therefore, that the abnormal spectral behavior in the 2,2-dinitroalkylamines can be traced to the unshared electron pair of the amino nitrogen.

The described phenomena are believed to be due largely to the strong inductive effect of the amino nitrogen which is transmitted through the methylene group. Evidence for such inductive effects has been obtained



$$R_2\ddot{N}-CH_2-\underset{\underset{NO_2}{\downarrow}}{\overset{\overset{NO_2}{\uparrow}}{C}}-Me$$

from a study of 1,1-dinitroalkane salts and from n.m.r. spectra.[14]

Several other 2-substituted 2,2-dinitroalkanols have been converted to amines by the convenient procedure with ammonium acetate.[5] 2-Bromo-, 2-chloro-, and 2-nitro-substituted bis(2,2-dinitroethyl)amines have been obtained in this way in good yield and high purity. In the case of 2,2,2-trinitroethanol an excess of am-

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[10] The authors are indebted to Dr. W. F. Forbes, The University of Waterloo, for the e.s.r. spectrum.

[11] T. Urbanski, *Tetrahedron*, **6**, 1 (1959), and cited references.

[12] H. E. Ungnade and L. W. Kissinger, *J. Org. Chem.*, **22**, 1088 (1957).

[13] H. E. Ungnade, E. D. Loughran, and L. W. Kissinger, *J. Phys. Chem.*, **64**, 1410 (1960).

[14] M. J. Kamlet and D. J. Glover, *J. Org. Chem.*, **27**, 537 (1962); W. H. Stefaniak, T. Urbanski, and M. Witanowski, *J. Am. Chem. Soc.*, **86**, 554 (1964).

monium acetate causes cleavage to nitroform. The formed amines have been converted to the known crystalline nitramines, $[XC(NO_2)_2CH_2]_2NNO_2$.

Experimental[15]

Alkyl-2,2-dinitropropylamines.—Simple primary alkylamines could be condensed with 2,2-dinitropropanol in good yields in concentrated aqueous solution. It was essential, however, that the amine was added last or that the alcohol was kept in excess during the addition. In the case of volatile amines, a mixture of the amine hydrochloride and 2,2-dinitropropanol was stirred while 1 molar equiv. of base was added; *e.g.*, to alkylamine hydrochloride (0.1 mole) and 2,2-dinitropropanol (0.1 mole) in 4 ml. of water was added dropwise with stirring a solution of sodium hydroxide (0.1 mole) in 20 ml. of water. The mixture was stirred 0.5 hr. and extracted with ether or dichloromethane. Evaporation of the dried solutions gave alkyl-2,2-dinitropropylamines in 68–100% yield ($\lambda_{NO_2}^{liq}$ 6.36–6.38, 7.53 μ). Since these amines were difficult to purify they were usually not isolated but converted directly to the crystalline nitrates.

A slight excess of 70% nitric acid was added to ether solutions (methyl and ethylamine) or 1 molar equiv. of 100% nitric acid to dichloromethane solutions (butylamine) of the crude amines. The nitrates were filtered with suction, and dried to give the following yields (R, %): Me, 44; Et, 66; Bu, 95. For the preparation of nitramines the nitrates were sufficiently pure; for analysis they were crystallized from acetonitrile. 2,2-Dinitro-4-azapentane nitrate melted at 120–121° and had $\lambda_{NO_2}^{KBr}$ 6.32, 7.55 μ; $\lambda_{NO_3^-}^{KBr}$ 7.24 μ.

Anal. Calcd. for $C_4H_{10}N_4O_7$: C, 21.25; H, 4.46; N, 24.78. Found: C, 21.63, 21.78; H, 5.42, 4.98; N, 24.55, 24.39.

2,2-Dinitro-4-azahexane nitrate melted at 111–112° and had $\lambda_{NO_2}^{KBr}$ 6.32, 7.61 μ; $\lambda_{NO_3^-}^{KBr}$ 7.24 μ.

Anal. Calcd. for $C_5H_{12}N_4O_7$: C, 25.01; H, 5.03; N, 23.33. Found: C, 24.81, 25.20; H, 5.32, 5.24; N, 23.27.

2,2-Dinitro-4-azaoctane nitrate melted at 127–128° and had $\lambda_{NO_2}^{KBr}$ 6.30, 7.62 μ; $\lambda_{NO_3^-}^{KBr}$ 7.23 μ.

Anal. Calcd. for $C_7H_{16}N_4O_7$: C, 31.35; H, 6.01; N, 20.89. Found: C, 31.35; H, 6.13; N, 20.16.

The nitramines were prepared as follows. The crystalline nitrate (0.05 mole) was added with stirring to a solution of acetic anhydride (45 ml.), 100% nitric acid (7 ml.), and 3 drops of concentrated hydrochloric acid, contained in an ice bath. The mixture was warmed cautiously to 54° and cooled to 20° during 0.5 hr. It was poured on ice and filtered with suction. The methyl and ethyl compounds were crystallized to constant melting point from ethanol or benzene–hexane.

2,2,4-Trinitro-4-azapentane, 79% yield, melted at 66–67°; $\lambda_{NO_2}^{KBr}$ 6.34, 7.56 μ; $\lambda_{NNO_2}^{KBr}$ 6.55, 7.82 μ.

Anal. Calcd. for $C_4H_8N_4O_6$: C, 23.08; H, 3.87; N, 26.92. Found: C, 23.34, 23.81; H, 4.56, 4.17; N, 26.56, 26.89.

2,2,4-Trinitro-4-azahexane, m.p. 82–83°, was obtained in 93% yield and had $\lambda_{NO_2}^{KBr}$ 6.34, 7.53 μ; $\lambda_{NNO_2}^{KBr}$ 6.52, 7.86 μ. Its melting point remained unchanged when the sample was chromatographed on acid-washed alumina from benzene solution.

Anal. Calcd. for $C_5H_{10}N_4O_6$: C, 27.03; H, 4.54; N, 25.23. Found: C, 27.43, 26.97; H, 4.70, 4.79; N, 25.41.

2,2,4-Trinitro-4-azaoctane was liquid at 25° and was extracted with dichloromethane. The residual oil from the extract (91%) could be chromatographed on acid-washed alumina from benzene solution or crystallized from benzene–petroleum ether below 0° to give colorless needles: m.p. 23–24°; $\lambda_{NO_2}^{KBr}$ 6.34, 7.56 μ; $\lambda_{NNO_2}^{KBr}$ 6.46, 7.84 μ.

Anal. Calcd. for $C_7H_{14}N_4O_6$: C, 33.62; H, 5.64; N, 22.41. Found: C, 33.70, 33.80; H, 5.83, 5.53; N, 22.68, 22.30.

Dinitroethane, Aminoguanidinium Salt.—Carbon dioxide was evolved when a mixture of 2,2-dinitropropanol (1.50 g., 0.01 mole) and aminoguanidine bicarbonate (1.36 g., 0.01 mole) was heated on a steam bath for 10 min. A yellow solid (0.12 g.) crystallized on cooling of the mixture to 0°. This was identical with authentic material from 1,1-dinitroethane and aminoguanidine bicarbonate: m.p. 115° dec. (from ethanol); $\lambda_{C=N}^{KBr}$ 6.01 s μ; $\lambda_{\bar{C}(NO_2)_2}^{KBr}$ 6.76 m, 7.53 m, 8.10 s, 9.00 s μ.

Anal. Calcd. for $C_3H_{10}N_6O_4$: C, 18.56; H, 5.19; N, 43.30. Found: C, 18.39, 18.59; H, 6.10, 5.65; N, 43.51, 43.49.

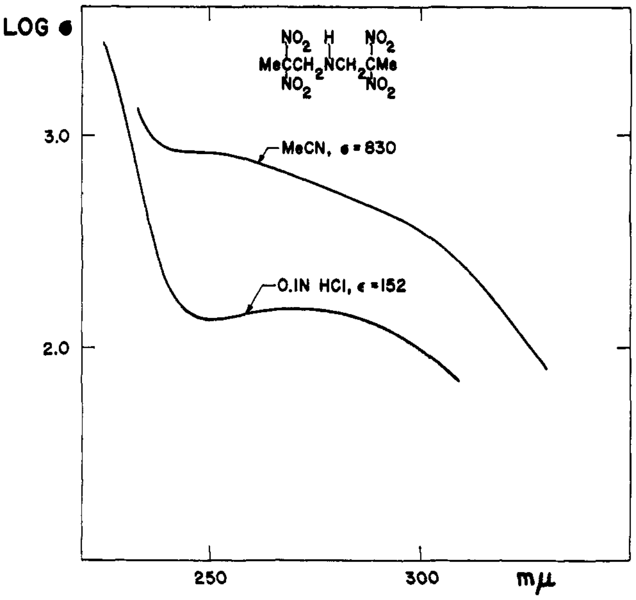

Figure 3.—Ultraviolet absorption spectra of bis(2,2-dinitropropyl)amine.

3,5,5-Trinitro-3-azahexyl nitrate was obtained in 75% yield from 5,5-dinitro-3-azahexanol[6] (λ_{OH}^{liq} 2.97 μ; $\lambda_{NO_2}^{liq}$ 6.36, 7.53 μ) by nitration with 100% nitric acid at 60°. It melted at 116.5–118.5° (lit. m.p. 108–111°,[6,16] 117–118°[17]) and had $\lambda_{NO_2}^{KBr}$ 6.31, 7.54 μ; $\lambda_{NO_3}^{KBr}$ 6.08, 7.90, 11.64 μ; $\lambda_{NNO_2}^{KBr}$ 6.46, 7.72 μ (Figure 1).

Anal. Calcd. for $C_5H_9N_5O_9$: C, 21.21; H, 3.21; N, 24.73. Found: C, 21.16; H, 3.83; N, 24.45.

2-(Hydroxymethyl)-2-methyl-5,5-dinitro-3-azahexanol, from 2-amino-2-methyl-1,3-propanediol and 2,2-dinitropropanol (yield 67%), melted at 89–90° (from 1,2-dichloroethane) and had $\lambda_{NO_2}^{KBr}$ 6.36, 7.50 μ.

Anal. Calcd. for $C_7H_{15}N_3O_6$: C, 35.45; H, 6.38; N, 17.72. Found: C, 35.38, 35.02; H, 6.61, 6.37; N, 17.15.

On nitration with excess 100% nitric acid at 60° it was converted in 69% yield to 2-(2,2-dinitropropylnitramino)-2-methyl-1,3-propanediol dinitrate (VIII): m.p. 77–78° (from benzene–petroleum ether); $\lambda_{NO_2}^{KBr}$ 6.34, 7.57 μ; $\lambda_{NO_3}^{KBr}$ 6.07, 7.84, 11.74 μ; $\lambda_{NNO_2}^{KBr}$ 6.43, 7.74 μ.

Anal. Calcd. for $C_7H_{12}N_6O_{12}$: C, 22.59; H, 3.25; N, 22.59. Found: C, 23.21, 23.05; H, 3.65, 3.62; N, 22.47.

2,2-Bis(hydroxymethyl)-5,5-dinitro-3-azahexanol, prepared similarly from 2-amino-2-(hydroxymethyl)-1,3-propanediol, was not obtained pure. A product melting at 76–78° (from isopropyl alcohol–petroleum ether) was sufficiently pure for nitration but samples melting as high as 82–83° did not give satisfactory analyses. Nitration with excess 100% nitric acid at 60° gave 75–78% of 2,2-bis(hydroxymethyl)-3,5,5-trinitro-3-azahexanol trinitrate (IX): m.p. 66–67° (from benzene–petroleum ether); $\lambda_{NO_2}^{KBr}$ 6.31, 7.71 μ; $\lambda_{NO_3}^{KBr}$ 6.01, 7.94, 12.54 μ; $\lambda_{NNO_2}^{KBr}$ 6.40, 7.84 μ.

Anal. Calcd. for $C_7H_{11}N_7O_{15}$: C, 19.41; H, 2.56; N, 22.64. Found: C, 19.99; H, 3.73; N, 22.00.

2,2,10,10-Tetranitro-4,8-diaza-6-undecanol (V) was obtained as a viscous oil with $\lambda_{NO_2}^{liq}$ 6.38, 7.54 μ from concentrated solutions of I and 1,3-diamino-2-propanol in yields of 66–76%. Crystallization of the crude V from methanol gave a 5% yield of fine yellow prisms of 1,1-dinitroethane, 6,6-dinitro-2-hydroxy-4-azaheptylammonium salt (VII): m.p. 114.5° dec.; $\lambda_{\bar{C}(NO_2)_2}^{KBr}$ 6.74, 8.10, 9.00 μ.

Anal. Calcd. for $C_8H_{18}N_6O_9$: C, 28.06; H, 5.30; N, 24.55. Found: C, 27.78; H, 5.63; N, 24.86.

When the crude V was crystallized from isopropyl alcohol or from benzene–petroleum ether, a colorless solid separated in 40% yield which melted at 80–81° and was identified as the hexahydropyrimidine VI.

1,3-Bis(2,2-dinitropropyl)-5-hydroxyhexahydropyrimidine (VI).—To a mixture of I (9.0 g., 0.06 mole) and 1,3-diamino-2-pro-

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[15] Microanalyses were by M. Naranjo and thin layer chromatography was by S. Yasuda. All temperatures are corrected.

[16] M. B. Frankel and G. B. Linden, U. S. Patent 2,934,558 (April 26, 1960).

[17] M. B. Frankel, *J. Org. Chem.*, **27**, 331 (1962).

panol (2.7 g., 0.03 mole) in 10 ml. of water was added formalin (2.43 ml., 0.03 mole) as soon as the oily product precipitated. The mixture was shaken at 25° for 10 min.; the crystallized oil was filtered with suction and dried to give 10.0–10.44 g. (92–95%) of crude VI, m.p. 75°. The pure alcohol was obtained by recrystallization from benzene–petroleum ether and melted at 80–81°; $\lambda_{\mathrm{OH}}^{\mathrm{C_6H_6}}$ 2.80 μ (ϵ 91), compared with $\lambda_{\mathrm{OH}}^{\mathrm{C_6H_6}}$ 2.79 μ (ϵ 75) for cyclohexanol; $\lambda_{\mathrm{NO_2}}^{\mathrm{KBr}}$ 6.38, 7.53 μ; VI-d_1, $\lambda_{\mathrm{OD}}^{\mathrm{C_6H_6}}$ 3.79 μ.

Anal. Calcd. for $C_{10}H_{19}N_6O_9$: C, 32.78; H, 4.95; N, 22.95. Found: C, 32.88; H, 5.18; N, 22.96.

Acetate.—To a solution of VI (1.46 g., 0.004 mole) in 10 ml. of dichloromethane was added pyridine (0.32 g., 0.004 mole) and then acetyl chloride (0.32 g., 0.004 mole) and the mixture was refluxed for 4 hr. The solution was washed with 5 ml. of water, dried over sodium sulfate, and evaporated to give 1.48 g. (91%) of yellow oily acetate. After purification by column and thin layer chromatography on silica gel, the pale yellow prisms melted at 110–111°. The acetate could be crystallized from benzene–petroleum ether and had $\lambda_{\mathrm{max}}^{\mathrm{KBr}}$ 5.75, 6.39, 7.59, and 8.06 μ.

Anal. Calcd. for $C_{12}H_{20}N_6O_{10}$: C, 35.29; H, 4.94; N, 20.59. Found: C, 35.30; H, 5.43; N, 20.36.

2,2,4,8,10,10-Hexanitro-4,8-diaza-6-undecyl Nitrate (X).—Nitration of crude V with 100% nitric acid and acetic anhydride[7] gave a 69% yield of crude nitrate which on digestion with 1,2-dichloroethane and water furnished pure X, m.p. 160° dec., in 20% yield.

Anal. Calcd. for $C_9H_{15}N_9O_{15}$: C, 22.09; H, 3.09; N, 25.77. Found: C, 21.72; H, 3.41; N, 25.39.

The dichloroethane-soluble product was freed from solvent and recrystallized twice from warm benzene. Colorless aggregates of XI crystallized on cooling and were filtered and dried, yield 5%, m.p. 101–102°.

Anal. Calcd. for $C_{10}H_{17}N_9O_6$: C, 23.12; H, 3.20; N, 24.28. Found: C, 23.22; H, 3.66; N, 24.44.

When XI was nitrated with a mixture of equal volumes of 100% nitric acid and concentrated sulfuric acid at 70°, it was converted to X in 95% yield.

The diamine VI furnished a crystalline dinitrate, m.p. 117° dec., $\lambda_{\mathrm{NO_3^-}}^{\mathrm{KBr}}$ 7.24 μ, with 2 molar equiv. of 100% nitric acid in ether or acetic anhydride or with excess nitric acid without solvent at 0°.

Anal. Calcd. for $C_{10}H_{20}N_8O_{15}$: C, 24.39; H, 4.10; N, 22.76. Found: C, 24.63, 24.11; H, 4.68, 4.50; N, 23.30.

Prolonged nitration of VI with 100% nitric acid and acetic anhydride at 0–20° gave XI containing a little acetate, and direct nitration of VI with 100% nitric acid and concentrated sulfuric acid at 70° gave nearly pure X in 80% yield.

When X was heated in a wax bath beyond 160°, the sample exploded at 168°. Maintaining the sample temperature at 160° caused evolution of nitrogen oxides and formation of a colorless solid, m.p. 175° dec., in 93% yield.

Anal. Calcd. for $C_9H_{14}N_8O_{13} \cdot C_9H_{16}N_8O_{13}$: C, 24.39; H, 3.41; N, 25.29. Found: C, 24.30; H, 3.77; N, 25.18.

The product was in all respects identical with an equimolar mixture of XII and XIII; in particular the infrared spectra were superimposable.

Oxidation of the mixture (0.25 g.) in acetic acid (10 ml.) with excess chromic oxide (0.20 g.) gave 0.18 g. (72%) of colorless ketone XII, m.p. 175° dec., which was identical with authentic material.

2,2,4,8,10,10-Hexanitro-4,8-diaza-6-undecanol (XIII).—The nitrate X was converted to XIII by modifications of the procedures used previously.[7] Thus, the acetolysis of X (3.0 g.) with acetic anhydride (24 ml.) and concentrated sulfuric acid (2.4 ml.) at 80° was complete in 13 min. The mixture was poured on ice and the product was filtered with suction, washed, and dried to give 2.95 g. (98%) acetate, m.p. 155.5–156.5° (from 1,2-dichloroethane). A mixture of acetate (4.00 g., 0.008 mole), methanol (160 ml.), and concentrated hydrochloric acid (8 ml.) was refluxed 48 hr. Evaporation of the reaction mixture under reduced pressure gave 3.26 g. (89%) of alcohol XIII, m.p. 169–170° after crystallization from ethanol or methanol.

2,2,4,8,10,10-Hexanitro-4,8-diaza-6-undecanone (XII).—Crude alcohol (XIII) (2.66 g., 0.006 mole) was added slowly with stirring to a solution of chromic oxide (0.60 g., 0.006 mole) in acetic acid (20 ml.). The mixture was stirred 1 hr. at 60–80° and diluted with stirring with 100 ml. of water. The precipitated ketone was washed with water and dried, giving 2.46 g. (93%) of XII which melted at 175° dec. after crystallization from acetonitrile (approximate solubility 4 g. per 100 ml.). For infrared spectra see Table II.

TABLE II

INFRARED ABSORPTION BANDS[a]

Compd.	*as*- NO_2	*s*- NO_2	*as*- NNO_2	*s*- NNO_2	Other
V	6.38	7.54	..	..	OH, 2.83
VI	6.38	7.53	..	..	OH, 2.82
VI acetate	6.39	7.59	..	..	C=O, 5.75, C-O, 8.06
VI dinitrate	6.32	7.55	..	..	NH, 3.01, NO_3^-, 7.24
X	6.36	7.54	6.46	7.86	NO_3, 6.04, 7.76, 11.69 11.79
XI	6.34	7.54	6.46	7.86	NO_3, 6.02, 7.75, 11.5
XII	6.36	7.54	6.46	7.85	C=O, 5.71
XIII	6.36	7.54	6.47	7.88	OH, 2.88
XIII acetate	6.34	7.54	6.48	7.81	C=O, 5.72, C-O, 8.11

[a] Compound V as liquid film, all others in potassium bromide; values are given in μ.

Anal. Calcd. for $C_9H_{14}N_8O_{13}$: C, 24.43; H, 3.19; N, 25.34. Found: C, 24.86; H, 3.58; N, 25.25.

1,2-Bis(2,2-dinitropropyl)-1-methylhydrazine.—The condensation of methylhydrazine with 2,2-dinitropropanol in aqueous solution at 60° gave a 63% yield of product: m.p. 93–94° (from isopropyl alcohol); $\lambda_{\mathrm{NO_2}}^{\mathrm{KBr}}$ 6.31, 6.38, 7.51 μ.

Anal. Calcd. for $C_7H_{14}N_6O_8$: C, 27.10; H, 4.55; N, 27.09. Found: C, 26.95, 27.22; H, 5.13, 4.98; N, 26.47.

1,1-Dimethyl-2-(2,2-dinitropropyl)hydrazine was obtained from the analogous condensation with 1,1-dimethylhydrazine in 93% yield as an unstable yellow oil: b.p. 50° (0.03 mm.); $n^{25}\mathrm{D}$ 1.4580; $\lambda_{\mathrm{NO_2}}$ 6.36, 7.54 μ.

Anal. Calcd. for $C_5H_{12}N_4O_4$: C, 31.25; H, 6.29. Found: C, 31.71; H, 6.84.

Ethyl 3,5,5-Trinitro-3-azahexanoate (XIV). The condensation of glycine hydrochloride ethyl ester with dinitropropanol and sodium acetate in water gave an 81–85% yield of oily ester ($\lambda_{\mathrm{NO_2}}^{\mathrm{liq}}$ 6.36, 7.52 μ; $\lambda_{\mathrm{C=O}}^{\mathrm{liq}}$ 5.72 μ; $\lambda_{\mathrm{C-O}}^{\mathrm{liq}}$ 8.28 μ) which was directly nitrated with 100% nitric acid at 60° to give 83–84% of crystalline ethyl 3,5,5-trinitro-3-azahexanoate: m.p. 88–89° (from carbon tetrachloride); $\lambda_{\mathrm{NO_2}}^{\mathrm{KBr}}$ 6.34, 7.54 μ; $\lambda_{\mathrm{C=O}}^{\mathrm{KBr}}$ 5.73 μ; $\lambda_{\mathrm{C-O}}^{\mathrm{KBr}}$ 8.21 μ; $\lambda_{\mathrm{NNO_2}}^{\mathrm{KBr}}$ 6.43, 7.81 μ.

Anal. Calcd. for $C_7H_{12}N_4O_8$: C, 30.01; H, 4.31. Found: C, 29.31; H, 4.77.

3,5,5-Trinitro-3-azahexanoic Acid (XV).—The hydrolysis of the ethyl ester was examined under various conditions. Refluxing with concentrated hydrochloric acid for 18 hr. gave only an 18% yield of the desired acid. The ester was largely unchanged in concentrated sulfuric acid at 25° or in boiling dilute base. It was destroyed in boiling alcoholic base and dilute alcoholic hydrochloric acid. Only a boiling (92° at 580 mm.) 50% by volume solution of 36% hydrochloric acid in formic acid produced the organic acid at a rate appreciably faster than the rate of destruction. The acid XV was obtained in yields of 42, 74 and 83–100% after 2 hr., 1 hr., and 0.5 hr., respectively, and melted at 139–140°[8] ($\lambda_{\mathrm{NO_2}}^{\mathrm{KBr}}$ 6.30, 7.54 μ; $\lambda_{\mathrm{C=O}}^{\mathrm{KBr}}$ 5.81 μ; $\lambda_{\mathrm{NNO_2}}^{\mathrm{KBr}}$ 6.42, 7.82 μ). The reaction with thionyl chloride gave a nearly quantitative yield of acid chloride XVI[8]: m.p. 90–91° (from carbon tetrachloride); $\lambda_{\mathrm{NO_2}}^{\mathrm{KBr}}$ 6.31, 7.63 μ; $\lambda_{\mathrm{C=O}}^{\mathrm{KBr}}$ 5.51μ; $\lambda_{\mathrm{NNO_2}}^{\mathrm{KBr}}$ 6.39, 7.88 μ.

2,2-Dinitropropyl 3,5,5-trinitro-3-azahexanoate (XVII), from the pyridine-catalyzed esterification of XVI and I,[9] melted at 120–121°; $\lambda_{\mathrm{NO_2}}^{\mathrm{KBr}}$ 6.31, 6.36, 7.55 μ; $\lambda_{\mathrm{C=O}}^{\mathrm{KBr}}$ 5.63 μ; $\lambda_{\mathrm{C-O}}^{\mathrm{KBr}}$ 8.27 μ.

Anal. Calcd. for $C_8H_{12}N_6O_{12}$: C, 25.02, H, 3.15; N, 21.88. Found: C, 25.34, 25.19; H, 3.87, 3.69; N, 21.39.

N-(2,2-Dinitropropyl)aniline (XVIII).—A 93% yield of crude amine was obtained by heating equimolar mixtures of aniline and 2,2-dinitropropanol 1 hr. on a steam bath. The orange oil was dried by taking up in dichloromethane and separating the water. The solvent was removed and the oil, dissolved in benzene, adsorbed on acid-washed alumina. The yellow benzene eluate was concentrated and crystallized after addition of petroleum ether. The orange-yellow plates melted at 56–57°; $\lambda_{\mathrm{NH}}^{\mathrm{KBr}}$ 2.90 μ; $\lambda_{\mathrm{NO_2}}^{\mathrm{KBr}}$ 6.36, 7.55 μ.

Anal. Calcd. for $C_9H_{11}N_3O_4$: C, 48.00; H, 4.92; N, 18.66. Found: C, 48.22, 48.33; H, 5.05, 5.18; N, 18.17, 18.34.

A crystalline nitrate was formed when 100% nitric acid was added to a solution of the amine (0.005 mole) in 5 ml. dichloromethane at 25°. It had $\lambda_{\mathrm{NO_2}}^{\mathrm{KBr}}$ 6.35, 7.54 μ and $\lambda_{\mathrm{NO_3^-}}^{\mathrm{KBr}}$ 7.23 μ and dissociated into the starting materials when redissolved in dichloromethane. When nitrated with 100% nitric and concentrated sulfuric acid N-(2,2-dinitropropyl)aniline was converted to N-

(2,2-dinitropropyl)-N-2,4,6-tetranitroaniline (XIX), m.p. 130° dec. (from ethanol), in 47% yield: $\lambda^{\text{KBr}}_{\text{NO}_2}$ 6.31, sh 6.38, 6.44, 7.48, sh 7.58, 7.78 μ.

Anal. Calcd. for $C_9H_7N_7O_{12}$: C, 26.68; H, 1.74; N, 24.20. Found: C, 27.00; H, 1.97; N, 23.73.

N-(2,2-Dinitropropyl)-*m*-nitroaniline.—*m*-Nitroaniline was condensed with 2,2-dinitropropanol (2 moles) by heating with 1 mole of glacial acetic acid on a steam bath for 5 hr. The crude solid (83%) contained *m*-nitroaniline and was purified by adsorption on acid-washed aluminum oxide from benzene solution. The light yellow benzene eluates contained crystalline amine which was recrystallized from benzene–petroleum ether: m.p. 90–91°; yield 35%; $\lambda^{\text{KBr}}_{\text{NH}}$ 2.96 μ; $\lambda^{\text{KBr}}_{\text{NO}_2}$ 6.35, 6.55, 7.54, 7.42 μ.

Anal. Calcd. for $C_9H_{10}N_4O_6$: C, 40.00; H, 3.73; N, 20.74. Found: C, 39.97; H, 3.96; N, 20.54.

The crystalline nitrate had $\lambda^{\text{KBr}}_{\text{NO}_3^-}$ 7.25 μ; $\lambda^{\text{KBr}}_{\text{NO}_2}$ 6.36, 6.53, 7.44, 7.93 μ.

N-(2,2-Dinitropropyl)-*p*-nitroaniline.—The analogous condensation with *p*-nitroaniline gave a 15% yield of crude solid which was crystallized from 95% ethanol to give yellow needles: m.p. 179–180°; $\lambda^{\text{KBr}}_{\text{NH}}$ 3.01 μ; $\lambda^{\text{KBr}}_{\text{NO}_2}$ 6.36, 6.65, 7.64, 7.56 μ.

Anal. Calcd. for $C_9H_{10}N_4O_6$: C, 40.00; H, 3.73; N, 20.74. Found: C, 40.07, 40.15; H, 4.00, 4.01; N, 20.54.

o-Nitroaniline, 2,4-dinitroaniline, and 2,4,6-trinitroaniline failed to condense with 2,2-dinitropropanol under the conditions tried.

All three phenylenediamines condensed readily with 2,2-dinitropropanol but the products from the *meta* isomer and also from 1,3,5-triaminobenzene were very insoluble and sensitive to air and could not be purified.

N,N′-Bis(2,2-dinitropropyl)-*o*-phenylenediamine.—The condensation of *o*-phenylenediamine without solvent at 93° gave a yellow oil which solidified. It was purified by adsorption on acid-washed alumina from benzene solution and crystallized in yellow needles (37%): m.p. 92–93° (from benzene–petroleum ether); $\lambda^{\text{KBr}}_{\text{NH}}$ 3.03 μ; $\lambda^{\text{KBr}}_{\text{NO}_2}$ 6.40, 7.52 μ; λ_{max} 240 mμ (log ε 3.96), 292 mμ (log ε 3.46) in hexane containing 2% dioxane.

Anal. Calcd. for $C_{12}H_{16}N_6O_8$: C, 38.72; H, 4.33; N, 22.59. Found: C, 38.79; H, 4.52; N, 22.42.

N,N′-Bis(2,2-dinitropropyl)-*p*-phenylenediamine.—The analogous condensation with the *para* isomer gave an orange solid which was purified by chromatographing a 1:1 acetone–benzene solution on acid-washed alumina and melted at 129° dec. (from acetone–benzene): yield 56%; $\lambda^{\text{KBr}}_{\text{NH}}$ 2.93 μ; $\lambda^{\text{KBr}}_{\text{NO}_2}$ 6.34, 6.40, 7.50 μ; $\lambda^{\text{MeCN}}_{\text{max}}$ 252 mμ (log ε 4.22), 320 mμ (log ε 3.42).

Anal. Calcd. for $C_{12}H_{16}N_6O_8$: C, 38.72; H, 4.33; N, 22.59. Found: C, 38.82; H, 4.58; N, 22.42.

N-(2,2-Dinitropropyl)piperidine (XX).—Mixing the components without solvent gave a 91% yield of oil which crystallized and melted at 47–48° (from hexane), $\lambda^{\text{KBr}}_{\text{NO}_2^-}$ 6.35, 7.53 μ.

Anal. Calcd. for $C_8H_{15}N_3O_4$: C, 44.24; H, 6.96; N, 19.35. Found: C, 44.66; H, 7.42; N, 18.93.

The nitrate was prepared in dichloromethane and crystallized after concentrating the solution to a small volume: yield 64%; m.p. 91° dec.; $\lambda^{\text{KBr}}_{\text{NO}_2}$ 6.29, 7.67 μ; $\lambda^{\text{KBr}}_{\text{NO}_3^-}$ 7.25 μ.

Anal. Calcd. for $C_8H_{16}N_4O_7$: C, 34.29; H, 5.75; N, 19.95. Found: C, 34.28; H, 5.94; N, 19.45.

The corresponding condensation with trinitroethanol gave a 47% yield of N-(2,2,2-trinitroethyl)piperidine, b.p. 90° (0.02 mm.) from a molecular still, $n^{25}\text{D}$ 1.4819, $\lambda^{\text{liq}}_{\text{NO}_2}$ 6.27, 7.67 μ.

Anal. Calcd. for $C_7H_{12}N_4O_6$: C, 33.87; H, 4.87; N, 22.57. Found: C, 33.73; H, 5.68; N, 21.97.

N-(2,2-Dinitropropyl)pyrrolidine, 84% yield, boiled at 50° (0.02 mm.), $n^{25}\text{D}$ 1.4712, $\lambda^{\text{liq}}_{\text{NO}_2}$ 6.36, 7.54 μ.

Anal. Calcd. for $C_7H_{13}N_3O_4$: C, 41.38; H, 6.45; N, 20.68. Found: C, 41.26; H, 6.69; N, 20.58.

N,N′-Bis(2,2-dinitropropyl)piperazine (XXI) was obtained by condensing amine and dinitropropanol in aqueous ethanol. The crude solid (91%) was crystallized from acetonitrile as yellow needles, m.p. 159° dec., with $\lambda^{\text{KBr}}_{\text{NO}_2}$ 6.36, 7.51, 7.60 μ.

Anal. Calcd. for $C_{10}H_{18}N_6O_8$: C, 34.29; H, 5.18; N, 24.00. Found: C, 34.30; H, 5.40; N, 24.06.

The dinitrate crystallized from dichloromethane: m.p. 90–91° dec.; $\lambda^{\text{KB}}_{\text{NO}_2}$ 6.25, 6.35, 7.50, 7.59 μ.

Anal. Calcd. for $C_{10}H_{20}N_8O_{14}$: N, 23.53. Found: N, 23.27.

Diethyl(2,2-dinitropropyl)amine, obtained in 99% yield by condensing I and diethylamine at 50°, boiled at 55° (0.02 mm.), $n^{25}\text{D}$ 1.4515, $d^{25}{}_{25}$ 1.11, $\lambda^{\text{liq}}_{\text{NO}_2}$ 6.36, 7.53 μ.

Anal. Calcd. for $C_7H_{15}N_3O_4$: C, 40.97; H, 7.37; N, 20.44. Found: C, 41.11; H, 7.57; N, 20.64.

Bis(2-chloro-2,2-dinitroethyl)nitramine.—When a mixture of 2-chloro-2,2-dinitroethanol (3.07 g., 0.018 mole), ammonium acetate (3.0 g., 0.039 mole), and water (5 ml.) was warmed for 30 min. at 60° an oil precipitated. This was extracted with six 5-ml. portions of dichloromethane, dried, and evaporated leaving 2.71 g. (93.5%) of oily bis(2-chloro-2,2-dinitroethyl)amine. The crude amine was dissolved with stirring in 15 ml. of ice-cold 100% nitric acid. Then the mixture was warmed to 60° for 30 min. It was poured on ice, filtered with suction, washed with water, and dried. The dry solid (2.13 g., 69%) was crystallized from benzene containing a little petroleum ether and melted at 145.5–146.5° (lit.[18] m.p. 146–147°).

The nitramine reacted with sodium iodide in anhydrous methanol to give only a small amount (24%) of the disodium salt with $\lambda^{\text{KBr}}_{\text{max}}$ 6.75, 8.13, and 8.87 μ.

Bis(2-bromo-2,2-dinitroethyl)nitramine.—The analogous condensation with 2-bromo-2,2-dinitroethanol gave 97% of crude bis(2-bromo-2,2-dinitroethyl)amine which furnished 55% of nitramine on nitration: m.p. 160° dec. (lit.[18] m.p. 165–167°).

Anal. Calcd. for $C_4H_4Br_2N_6O_{10}$: C, 10.54; H, 0.88; Br, 35.05; N, 18.44. Found: C, 10.88; H, 2.02; Br, 35.55; N, 17.95.

Bis(trinitroethyl)nitramine.—Stirring a mixture of trinitroethanol (0.01 mole) and ammonium acetate (0.02 mole) in 2 ml. of water 0.5 hr. at 60° gave a clear yellow solution. After extraction with dichloromethane the aqueous layer deposited 0.22 g. of yellow prisms which gave an infrared spectrum identical with authentic ammonium nitroform, prepared from nitroform and anhydrous ammonia in dichloromethane. The pure salt had infrared bands in potassium bromide at 3.11 m (N–H), 6.50 m, 6.80 m, 7.15 m, 7.93 s, 8.66 s, 11.55 m, 12.68 m, and 13.58 m μ.

Bis(trinitroethyl)amine was obtained by adding ammonium acetate (0.19 g., 0.0025 mole) to a solution of trinitroethanol (0.905 g., 0.005 mole) in 1 ml. of water. The solution became homogeneous on stirring at 25° and after a few seconds an oil separated which solidified on cooling to 5°. The solid amine, which was filtered with suction, washed with water, and dried, weighed 0.38 g. An additional amount was obtained by extracting the filtrates with dichloromethane, giving a total of 0.72 g. (84%). The amine has been described previously.[19] When nitrated with 4 ml. of 100% nitric acid at 55°, the crude amine gave 0.10 g. of the known[19b,20] nitramine, m.p. 90–91° (from carbon tetrachloride), and 0.30 g. of unchanged starting material. No attempt was made to determine the optimum conditions for the nitration.

Bis(2,2-dinitropropyl)nitramine.—Nitration of the known amine[5] with 100% nitric acid at 60° gave an 84% yield of nitramine, m.p. 188.5° dec., lit.[21] m.p. 187–189°.

The infrared absorption bands of these amine and nitramine compounds appear in Table III.

Absorption Spectra.—Infrared absorption spectra were determined with a Perkin-Elmer Model 21 spectrophotometer except for solution spectra which were obtained with the Perkin-Elmer Model 421 spectrophotometer. Ultraviolet spectra were determined with a Cary Model 14 spectrophotometer at 25°.

TABLE III

INFRARED ABSORPTION BANDS OF BIS(2-X-2,2-DINITROETHYL)AMINES AND -NITRAMINES[a]

X	Compd.	λ_{NH}	$\lambda_{as\text{-NO}_2}$	$\lambda_{s\text{-NO}_2}$	$\lambda_{as\text{-NNO}_2}$	$\lambda_{s\text{-NNO}_2}$
Cl	Amine	2.95 m	6.29 s	7.65 m	...	...
Cl	Nitramine	...	6.27 s	7.66 m	6.37 m	7.86 m
Br	Amine	2.95 m	6.29 s	7.68 m	...	...
Br	Nitramine	...	6.27 s	7.67 s	6.35 m	7.86 m
NO_2	Amine	2.97 m	6.26 s	7.69 m	...	...
NO_2	Nitramine	...	6.21 s	7.71 m	6.32 m	7.81 m
Me	Amine[b]	2.95 m	6.35 s	7.51 m	...	...
Me	Nitramine	...	6.31 s	7.54 m	6.41 m	7.85 s

[a] Solids in KBr, liquids as capillary films; values are given in μ. [b] Ultraviolet absorption in 0.1 *N* HCl, λ_{max} 270 mμ (ε 152).

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