out as above to give 2.670 g. (0.13 mole, 74 or 93% based on unrecovered starting material) of oil, n^{25}_D 1.5564.

Infrared analysis[39] carried out as above showed 98.8% of cyclopentyl *p*-methoxyphenyl and 1.2% of 2-*p*-methoxyphenylcyclohexanone.

Starting material (*cis*-III) recovered from the acid extracts amounted to 0.680 g. (0.0031 mole, 18%).

Reaction of *cis*-I with Silver Oxide.—*cis*-I (3.10 g., 0.015 mole) in 200 ml. of hexane was heated under reflux with stirring with 8 g. of freshly prepared and thoroughly washed silver oxide for 96 hours. The hot mixture was filtered to remove silver salts and concentrated under vacuum under nitrogen at room temperature to leave 2.51 g. of yellow oil.

Microanalysis showed 2.06 ± 0.05% chlorine (Found: Cl, 2.14, 2.06, 1.98). Assuming that all the chlorine is present as *cis*- (or *trans*)-I this corresponds to 0.318 g. of chlorohydrin (I) (9.8% of starting material or 12.4% of the oil).

The infrared spectrum[39] in carbon tetrachloride showed hydroxyl absorption and carbonyl absorptions at 1715 and 1677 cm.$^{-1}$ corresponding to 2-phenylcyclohexanone and cyclopentyl phenyl ketone, respectively. A solution of 88.5 mg./ml. was prepared and the percentage transmission at 1350 and 1122 cm.$^{-1}$ used to obtain the concentrations of cyclopentyl phenyl ketone and 2-phenylcyclohexanone.

Reaction of *cis*-I with 3% ethanolic silver nitrate for 108 hours and analysis as above gave 70 wt. % of oil, which chlorine analysis indicated contained 12% of I. The infrared spectrum[39] showed three carbonyl bands at 1677, 1715 and 1727 cm.$^{-1}$ corresponding to the two ketones above and 1-phenylcyclopentanecarboxaldehyde. In addition there was nitrate ester absorption at 1560 cm.$^{-1}$ and a test for nitrogen was positive. Repetition of this rearrangement with added calcium carbonate to neutralize the acid formed eliminated the band at 1727 cm.$^{-1}$. These rearrangement conditions were not examined further.

Reaction with Nitrous Acid of *trans*-II.—*trans*-II (6.00 g., 0.031 mole) in 420 ml. of 50% aqueous acetic acid was treated with 6 g. (0.87 mole) of sodium nitrite under the conditions used with the *cis* isomer above. In this case the neutral fraction was extracted into ether, the evaporation of which left 4.53 g. of solid. The infrared spectrum[39] of this solid showed bands for hydroxyl (3571 and 3484 cm.$^{-1}$) and carbonyl (1721, 1677 cm.$^{-1}$). Nitrogen was shown to be present. The mixture was heated under reflux for 1.5 hours with 30 ml. of 10% sodium hydroxide and 20 ml. of ethanol. Extraction with pentane gave 1.43 g. of solid. The infrared spectrum[39] of this solid had no carbonyl at 1723 cm.$^{-1}$ but had intense hydroxyl bands and also carbonyl bands at 1715 and 1677 cm.$^{-1}$ characteristic of 2-phenylcyclohexanone and cyclopentyl phenyl ketone, respectively. Further extraction of the saponification mixture with ether gave 3.21 g. of liquid which crystallized slowly to give 1.96 g. (33%) of solid. Comparison of the infrared spectrum[39] with that of an authentic sample indicated it to be a mixture of phenylcyclohexanediols.

Reaction of 1-Phenylcyclohexene Oxide (III) with Nitrous Acid in Aqueous Acetic Acid.—The reaction of III (5.0 g. 0.029 mole) with 7.3 g. (0.10 mole) of sodium nitrite in 190 ml. of water containing 100 ml. of glacial acetic acid was carried out as described above for the rearrangement of *trans*-II. The reaction mixture was extracted with chloroform and ether. Trituration of the product obtained after evaporation of the solvents with pentane left 2.49 g. of solid, m.p. 62–89°, which had an infrared spectrum characteristic of the phenylcyclohexanediols.

The pentane extract gave 1.63 g. of solid which infrared analysis indicated was cyclohexanediol acetate (1721 cm.$^{-1}$) and a nitrite ester band at 1560 cm.$^{-1}$. Saponification with 10% sodium hydroxide in ethanol gave a solid with no infrared absorption[39] at 1721 cm.$^{-1}$ and a weak band for 2-phenylcyclohexanone at 1715 cm.$^{-1}$.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE METCALF LABORATORIES, BROWN UNIVERSITY]

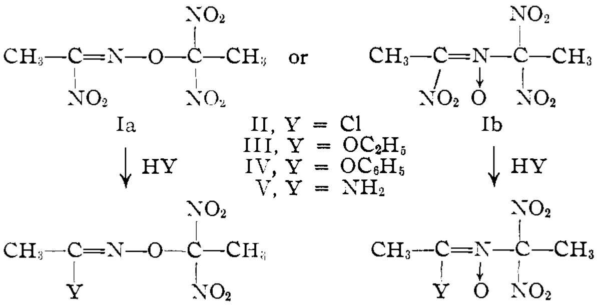
Reaction of 1,1-Dinitroethane with its Salts[1]

BY JOHN S. BELEW, CHARLES E. GRABIEL AND LEALLYN B. CLAPP

RECEIVED MARCH 12, 1954

Reaction of 1,1-dinitroethane with certain amine (and ethylenimine) salts of 1,1-dinitroethane resulted in a trinitro compound identified as 2,5,5-trinitro-3-aza-4-oxa-2-hexene (or 2,4,4-trinitro-3-aza-2-pentene 3-oxide) (I). Assignment of these structures was made on the basis of reactions, degradations and infrared spectra.

During the course of trying to open the ethylenimine ring with a variety of nucleophilic agents, mononitroparaffins have been used and found only to catalyze polymerization of the imine. However, when 2,2-dimethylethylenimine was allowed to react with 1,1-dinitroethane, an acid[2] of strength comparable to propionic, a salt was formed. With a second molecule of 1,1-dinitroethane, the salt reacted to give a white crystalline compound which on the basis of reactions, degradations, and infrared spectra has been assigned the alternate structures, 2,5,5-trinitro-3-aza-4-oxa-2-hexene, (Ia) and 2,4,4-trinitro-3-aza-2-pentene 3-oxide, (Ib).



$$CH_3-\underset{NO_2}{C}=N-O-\overset{NO_2}{\underset{NO_2}{C}}-CH_3 \quad \text{or} \quad CH_3-\underset{NO_2}{C}=\underset{\overset{\downarrow}{O}}{N}-\overset{NO_2}{\underset{NO_2}{C}}-CH_3$$

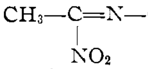
Ia Ib

$$\downarrow HY \qquad \downarrow HY$$

II, Y = Cl
III, Y = OC_2H_5
IV, Y = OC_6H_5
V, Y = NH_2

$$CH_3-\underset{Y}{C}=N-O-\overset{NO_2}{\underset{NO_2}{C}}-CH_3 \qquad CH_3-\underset{Y}{C}=\underset{\overset{\downarrow}{O}}{N}-\overset{NO_2}{\underset{NO_2}{C}}-CH_3$$

IIa-Va IIb-Vb

On the basis of these structures one may reasonably account for the replacement of one nitro group on carbon 2 by chlorine (II) in a reaction with alcoholic hydrogen chloride, by ethoxy (III) or phenoxy (IV) groups with the appropriate base, or by an amine group (V) with aqueous ammonia. Replacement of a nitro group by chlorine is reminiscent of a comparable displacement in a nitrolic acid,[3] and suggests the presence of the structure  $CH_3-\underset{NO_2}{C}=N-O-$ in Ia.

Alternately, 4-nitropyridine oxide is a vinylog of the nitrone structure Ib; since 4-nitropyridine oxide undergoes displacement of the nitro group by

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[1] Presented at the Symposium on Oxides of Nitrogen, sponsored by the Office of Ordnance Research, at Chicago, Ill., September 3–4, 1953. This work was supported by Office of Ordnance Research Contract DA-19-020-ORD-592 with Brown University.

[2] H. W. Jacobson, Ph.D. Thesis, Purdue University, 1942.

[3] A. Werner and H. Buss, *Ber.*, **28**, 1280 (1895); M. Z. Jowitschitsch, *ibid.*, **39**, 786 (1906).

negative ions such as chloride,[4] it is not unreasonable to expect the nitrone to behave similarly. Both the trinitro (I) and the chloro (II) compounds will react with aqueous ammonia to yield the 2-amino product V. Cyclohexylamine and other amines also behave in like manner toward I and II to yield products related to V but quite unstable. When the reaction with cyclohexylamine and compound II was allowed to proceed vigorously, a small amount of N-cyclohexylacetamide was sublimed away from the impure product, evidence that the acetyl group is latent in the skeletal structure.

Compound I was unaffected by vigorous acid oxidation, for example, with chromic acid in glacial acetic acid, hot nitric acid, or hot sulfuric acid and gave an unsatisfactory Kuhn–Roth determination because it sublimed away from the chromic acid–sulfuric acid reagent. Alkaline degradations were more informative. Aqueous potassium hydroxide liberated 1.7 moles of acetic acid from the trinitro compound I, accompanied by small amounts of ammonia (0.09 mole) and hydroxylamine (0.03 mole) while sodium ethoxide allowed a quantitative determination of the nitro groups as nitrite ion (2.98 moles). Finally, a Kuhn–Roth determination on 2-amino-5,5-dinitro-3-aza-4-oxa-2-hexene (or 2-amino-4,4-dinitro-3-aza-2-pentene 3-oxide) gave 1.9 moles of acetic acid. These degradation studies on the trinitro compound I and its amino derivative V indicate the presence of three nitro groups, two terminal methyl groups, and two latent acetyl groups in the skeleton of compound I.

Catalytic reductions on the trinitro compound I with Adams catalyst resulted in a disappointing hydrogen uptake: 7.4 moles in ethanol and 5.2 moles in glacial acetic acid. An abundance of ammonia was produced in the reductions, obscuring the presence of other products and the method was abandoned as a means of structure determination.

The infrared spectrum of 2,5,5-trinitro-3-aza-4-oxa-2-hexene (or 2,4,4-trinitro-3-aza-2-pentene 3-oxide) (Fig. 1) reveals the presence of both a mononitro group at 6.4 μ and a *gem*-dinitro group at 6.3 μ in the anti-symmetric stretching region and at 7.45 and 7.55 μ, respectively, in the symmetric stretching region. These values are in agreement with published data[5] on mononitro compounds and with other *gem*-dinitro compounds.[6] The infrared spectra of the trinitro (I), chloro (II) and ethoxy (III) compounds differ appreciably only in the 6-μ region. A band of medium intensity at 6.15 μ in the chloro compound (II, Fig. 1) and a strong band at 6.07 μ in the ethoxy (III) and at 6.05 μ in the phenoxy (IV) do not appear in the spectra of the trinitro compound (I). These bands lie in the region assigned to C=N vibrations.[7] The fact that the position of this C=N absorption band shifts in these three derivatives is further corroboration that the groups Y have replaced the mononitro group when they are formed from compound I. The C=N absorption band in the trinitro compound is too weak to be observed as is the case with acetonitrolic acid, $CH_3—C(NO_2)=NOH$.[8]

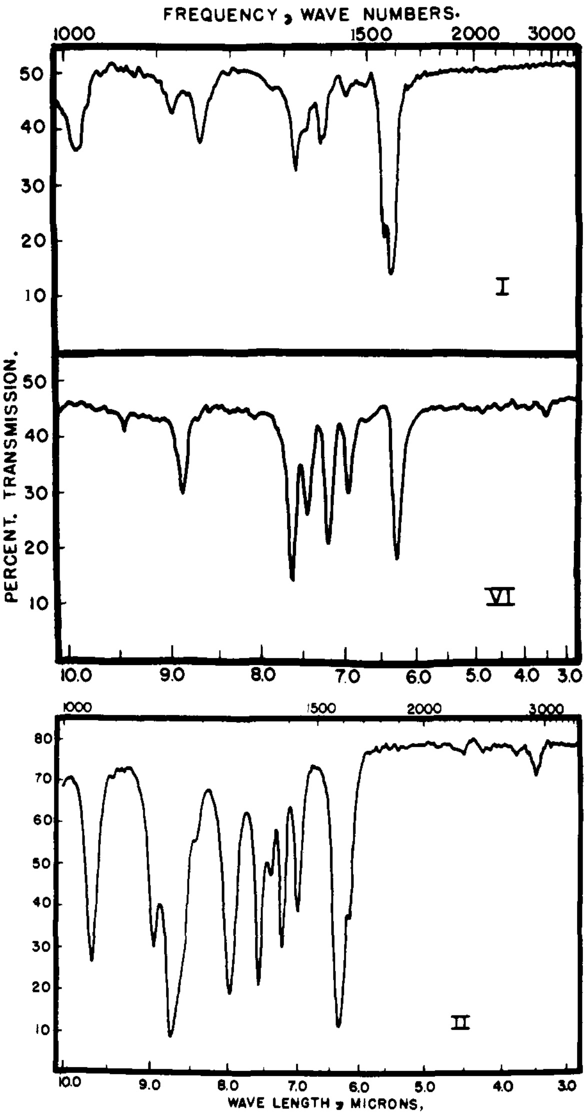

Fig. 1.—Infrared spectra of 2,5,5-trinitro-3-aza-4-oxa-2-hexene, (or 2,4,4-trinitro-3-aza-2-pentene 3-oxide) (I) (0.013 *M* solution in chloroform); 2,2,3,3-tetranitrobutane (VI) (in carbon tetrachloride solution); and 2-chloro-5,5-dinitro-3-aza-4-oxa-2-hexene (or 2-chloro-4,4-dinitro-3-aza-2-pentene 3-oxide). (II) (in carbon tetrachloride solution).

A compound described as 2,2,3,3-tetranitrobutane by Miller and Hunt[9] has a melting point (119–120°) near that of the trinitro compound (I) (121.2–121.6°). Synthesis of 2,2,3,3-tetranitrobutane (m.p. 162.2–163.0°) from dimethylglyoxime by the general nitration method of Farago and Roberson[10] and by the addition of nitrogen dioxide to 2,3-dinitro-2-butene[6] proved that the compound reported by Miller and Hunt was not a tetranitrobutane.

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[4] H. J. den Hertog and W. P. Combé, *Rec. trav. chim.*, **70**, 581 (1951).

[5] D. C. Smith, C. Y. Pan and J. R. Nielsen, *J. Chem. Phys.*, **18**, 706 (1950).

[6] C. E. Grabiel, D. E. Bisgrove and L. B. Clapp, THIS JOURNAL, in press.

[7] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, Chapter 3.

[8] C. E. Grabiel, Ph.D. Thesis, Brown University, 1954.

[9] A. J. Miller and H. Hunt, *J. Phys. Chem.*, **49**, 20 (1945).

[10] J. Farago and E. B. Roberson, Atlantic City Meeting of the American Chemical Society, Sept., 1952, Abstracts, p. 41M.

Repetition of Miller's[11] preparation by the electrolytic reduction of the sodium salt of 1,1-dinitroethane[12a] or more simply by the acidification[12b] of the potassium salt of 1,1-dinitroethane to a *p*H of about 5 gave a product identical with 2,5,5-trinitro-3-aza-4-oxa-2-hexene (or 2,4,4-trinitro-3-aza-2-pentene 3-oxide).

The infrared spectra of the trinitro compound (I) and 2,2,3,3-tetranitrobutane (VI) (Fig. 1) are remarkably similar. Terminal methyl groups are probable in both structures from the absorption bands at 3.47 and 6.99 μ, but the spectrum of the tetranitrobutane does not show the absorption band of a mononitro compound at 6.4 μ in addition to the peak for the *gem*-dinitro group at 6.3 μ which the trinitro compound (I) does exhibit. The structure of 2,2,3,3-tetranitrobutane[6] itself was corroborated by catalytic reduction to 2,3-diaminobutane.

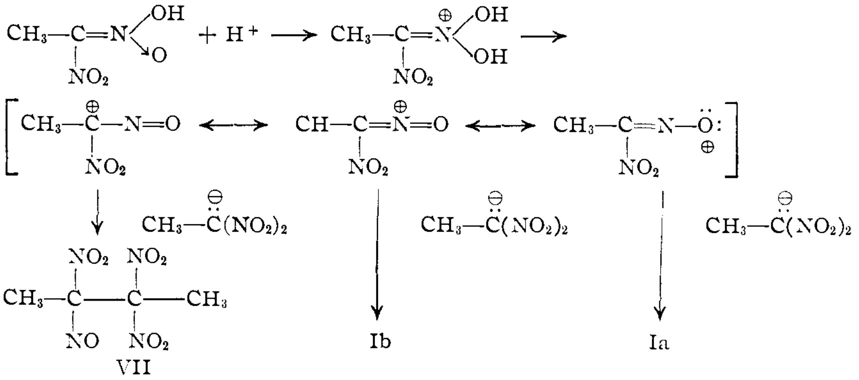
Finally, maximal intensity measurements in the infrared on the anti-symmetric stretching bands of the nitro group made it a certainty that compound I contained only three nitro groups and that two of them were in a *gem*-relationship. The maxima are of the order of 400–550 per nitro group per centimeter.[13]

Molecular weight determinations[14] by the ebullioscopic method in benzene (220, 223) and from X-ray diffraction data (211) are compatible with a molecular weight of 222 for the trinitro compound, $C_4H_6N_4O_7$ (I).

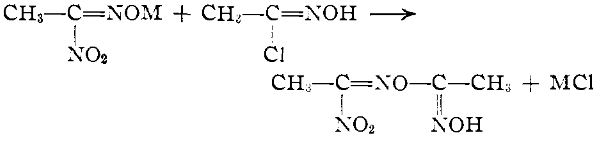
The authors prefer the oximino ether structure (Ia) for the following reasons. The trinitro compound cannot be converted to a desoxy compound by treatment with phosphorus pentachloride, a reaction characteristic of nitrones.[15] Furthermore, if the compound has any of the basic properties of a nitrone,[15] one might expect to titrate it against a strong acid[16] such as perchloric in glacial acetic acid[17] as a solvent. This titration, however, indicated no salt formation with the trinitro compound.

The authors had relegated structure Ib to a less important role in the structure of the trinitro compound but a referee persuaded us that it should be given equal prominence with Ia since: (1) the nitrone structure should be more resistant to oxidation and perhaps to acid hydrolysis than the oximino ether structure, (2) the displacement reactions with chloride, ethoxide and phenoxide ions and with ammonia can be as well accommodated with nitropyridine oxide chemistry as with nitrolic ester (or nitroöximino ether) chemistry, and (3) a mechanism for formation of the nitrone has more attraction than any we have been able to write for the nitrolic ester.

The grouping —C=N—O—C(NO_2)$_2$— or —C=N(O)—C(NO_2)$_2$— appears to be a new function and there is no precedent in the literature for a path of formation nor for a second synthesis. Of the following paths, the most reasonable one leads to 2-nitroso-2,3,3-trinitrobutane (VII), but this structure is untenable in light of the chemistry of the compound as described previously. Formation of Ib, however, is more reasonable than formation of (Ia) in view of the less likely canonical contributing intermediate with an oxygen bearing a positive charge. Alternatively, the reaction may be pictured as a displacement of a hydroxy group on the aci form of 1,1-dinitroethane by dinitrocarbanion, $CH_3\overset{\ominus}{\ddot{C}}(NO_2)_2$. This leads to the same structures VII, Ib and Ia and does not aid in rationality. It seems premature to speak of a mechanism.



Attempts to synthesize the trinitro compound by other paths failed. Attempts were made on the basis of trying to prepare O- and N-ethers of oximes. Not unexpectedly, neither the silver nor the sodium salt of acetonitrolic acid would remove any halogen from 1-chloro-1,1-dinitroethane in acetonitrile or acetone. In another attempt at synthesis, sodium (or silver) acetonitrolate was treated with acethydroxamyl chloride with the expectation of getting



$$CH_3-\underset{NO_2}{\underset{|}{C}}=NOM + CH_3-\underset{Cl}{\underset{|}{C}}=NOH \longrightarrow CH_3-\underset{NO_2}{\underset{|}{C}}=NO-\underset{NOH}{\underset{\|}{C}}-CH_3 + MCl$$

VIII

the oximino compound VIII. The intention was then to nitrate this product to obtain the trinitro compound, (I). However, the intermediate was not obtained.

Acknowledgment.—Early in our work we had the benefit of discussions with W. C. Lothrop and G. R. Handrick and were apprised of the experimental work on a similar problem of C. R. Morgan, T. U. Hall and C. W. Sauer, all of Arthur D. Little,

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[11] A. J. Miller, Ph.D. Thesis, Purdue University, 1943.

[12] (a) A sample supplied by Arthur D. Little, Inc., gave no depression in a mixed melting point with our own preparations. (b) Experiments at Arthur D. Little, Inc., have produced yields of 25–40% by this method; private communications.

[13] J. F. Brown, Jr., "Infrared Spectroscopy of Nitro Compounds," paper presented at the Symposium on Oxides of Nitrogen, sponsored by the Office of Ordnance Research, Chicago, Ill., Sept. 3–4, 1953. The authors are grateful to Dr. Brown for suggesting this measurement and for information from his paper before presentation.

[14] Arthur D. Little, Inc., private communication.

[15] L. I. Smith, *Chem. Revs.*, **23**, 222, 238 (1938).

[16] This possible difference in properties expected of the two structures was pointed out to us by Dr. G. F. Wright, University of Toronto.

[17] J. S. Fritz, *Anal. Chem.*, **22**, 1028 (1950).

Inc., Cambridge, Massachusetts. Dr. Sauer first suggested the structure of compound Ia.

Experimental[18]

2,5,5-Trinitro-3-aza-4-oxa-2-hexene (I).—The ammonium salt[19] of 1,1-dinitroethane[20] was prepared by the following modification of Hantzsch's method. Twenty grams (0.166 mole) of 1,1-dinitroethane was dissolved in 25 ml. of ethanol and cooled in an ice-bath to 5°. Concentrated ammonium hydroxide was added dropwise with stirring until the solution was basic to litmus. Ether (40 ml.) was added and the mixture was allowed to stand 45 minutes in the ice-bath. The yellow salt was collected and dried in a vacuum desiccator; yield 18.9 g., 85%, m.p. 90–93° dec. The salt could not be recrystallized but could be stored in the refrigerator for a week without appreciable decomposition.

Ammonium 1-nitroethanenitronate (4.5 g.) was allowed to stand one day at room temperature with an equivalent (3.9 g.) of 1,1-dinitroethane. Trituration with 95% ethanol gave 1.48 g. (19%) of a nearly white crystalline compound, m.p. 116–121°. Recrystallization from ethanol, followed by sublimation at 70° (0.5 mm.) gave an analytical sample of 2,5,5-trinitro-3-aza-4-oxa-2-hexene, m.p. 121.2–121.6°. Infrared spectrum (0.013 *M* solution in chloroform, μ): 6.30 (strong), 7.55 (medium), *gem*-dinitro; 6.41 (strong), 7.45 (medium), nitro.

Anal. Calcd. for $C_4H_6N_4O_7$: C, 21.63; H, 2.72; N, 25.23. Found: C, 22.19, 21.96; H, 3.09, 2.99; N, 24.67, 25.61, 25.08.

Salts similar to ammonium 1-nitroethanenitronate but not further characterized were prepared from various amines and 1,1-dinitroethane in yields of 85–90%. These salts were used to prepare compound I by the method just described, with the following yields: cyclohexylammonium, 36%; 2,2-dimethylethylenimmonium, 39%; 2-ethylethylenimmonium, 29%; piperidinium, 24%; diethylammonium, 24%. The last three did not give consistent results.

It is probably unwise to use more than 5 g. of any one salt in a preparation. Once, using 18.9 g. of the ammonium salt of 1,1-dinitroethane with an equivalent amount of 1,1-dinitroethane (16.5 g.) a violent exothermic reaction ensued from which only carbon and ammonium nitrate were isolable.

Larger quantities of 2,5,5-trinitro-3-aza-4-oxa-2-hexene were safely prepared in aqueous solution from the potassium salt of 1,1-dinitroethane.[12b] The *p*H of a solution of 24 g. (0.20 mole) of 1,1-dinitroethane in water was adjusted to 5.2, the equivalence point,[8] by addition of dilute potassium hydroxide solution. After standing at room temperature for eight days, the yellow crystals were collected and recrystallized from ethanol; yield 3.2 g. (14%), m.p. 119–121°; mixed m.p. with the sample prepared from an organic salt, no depression.

2-Chloro-5,5-dinitro-3-aza-4-oxa-2-hexene (II).—Four grams of 2,5,5-trinitro-3-aza-4-oxa-2-hexene (I) was dissolved in 50 ml. of absolute ethanol and saturated with anhydrous hydrogen chloride. The solution was refluxed one-half hour and then reduced to half the original volume in a stream of dry air. After cooling to 60°, water was added to precipitate the white crystalline chloro compound; yield 2.23 g. (58%), m.p. 66–70°. Recrystallization from dilute ethanol raised the m.p. to 70–71°, but satisfactory analytical data could not be obtained on the compound when it was prepared by this method.

The analytical sample was prepared in the following way: to 20 ml. of 20% hydrochloric acid, 1.92 g. (0.01 mole) of 2-amino-5,5-dinitro-3-aza-4-oxa-2-hexene (V) was added and the mixture was allowed to stand for 24 hours at room temperature. Colorless needles formed which upon filtration and drying amounted to 0.27 g. (13%), m.p. 68–70°. Recrystallization from dilute ethanol raised the m.p. to 70.5–71.0°. A mixed m.p. of samples prepared by the two methods gave no depression. Infrared spectrum (0.013 *M* solution in chloroform, μ): 6.11 (medium), C=N; 6.30 (strong) 7.52 (medium), *gem*-dinitro. The spectrum shown in Fig. 1 was taken in carbon tetrachloride for comparison with the spectrum of compound VI.

Anal. Calcd. for $C_4H_6ClN_3O_5$: C, 22.71; H, 2.86; Cl, 16.76; N, 19.86. Found: C, 23.10; H, 3.18; Cl, 17.01, 16.91; N, 19.91.

2-Ethoxy-5,5-dinitro-3-aza-4-oxa-2-hexene (III).—To a solution of 0.50 g. (0.0024 mole) of 2-chloro-5,5-dinitro-3-aza-4-oxa-2-hexene (II) in 20 ml. of absolute ethanol was added 10 ml. of absolute ethanol in which was dissolved 0.08 g. (0.0035 mole) of sodium. After standing 24 hours at 15°, sodium chloride and sodium nitrite were removed by filtration and 50 ml. of water was added; long white needles formed overnight at 15° and were collected and dried, yield 80 mg. (16%), m.p. 93–95°. The analytical sample was prepared by sublimation at 70° (0.5 mm.), m.p. 94.8–95.3°. Infrared spectrum (1% carbon tetrachloride solution, μ): 6.07 (strong), C=N; 6.25 (medium), 7.53 (strong), *gem*-dinitro.

Anal. Calcd. for $C_6H_{11}N_3O_6$: C, 32.58; H, 5.01; N, 19.00. Found: C, 31.97; H, 5.14; N, 18.65.

2-Phenoxy-5,5-dinitro-3-aza-4-oxa-2-hexene (IV).—To a solution of 0.64 g. (0.0031 mole) of 2-chloro-5,5-dinitro-3-aza-4-oxa-2-hexene (II) in 17 ml. of phenol at 50° was added 0.40 g. (0.0031 mole) of potassium phenoxide.[21] After five days at room temperature, the reaction mixture was poured into 50 ml. of ice-cold 15% sodium hydroxide. The precipitate was collected and dried in a vacuum desiccator. Sublimation at 40° (0.5 mm.) yielded 0.25 g. of unreacted starting material. The temperature was raised and the residue sublimed at 70° (0.5 mm.), yield 0.10 g. (12%), m.p. 94–96°. Recrystallization from dilute ethanol, followed by sublimation at 90° (0.5 mm.) gave an analytically pure sample of 2-phenoxy-5,5-dinitro-3-aza-4-oxa-2-hexene, m.p. 97.4–98.0°. Infrared spectrum (1% carbon tetrachloride solution, μ): 6.05 (strong), C=N; 6.27 (medium), 7.51 (medium), *gem*-dinitro; 6.72 (medium), phenyl.

Anal. Calcd. for $C_{10}H_{11}N_3O_6$: C, 44.61; H, 4.12; N, 15.61. Found: C, 44.95, 44.89; H, 4.59, 4.61; N, 15.62.

2-Amino-5,5-dinitro-3-aza-4-oxa-2-hexene (V).—Concentrated ammonium hydroxide (10 ml.) was allowed to stand over 1.00 g. of 2,5,5-trinitro-3-aza-4-oxa-2-hexene (I) for 24 hours at room temperature. The crystalline plates characteristic of the trinitro compound were transformed into white needles. The product was collected, washed with water, and dried quickly in a vacuum desiccator. Recrystallization from benzene–heptane gave 0.72 g. (83%) of a pure product, m.p. 95–97° dec. The compound was necessarily analyzed on the day it was prepared.

Anal. Calcd. for $C_4H_8N_4O_5$: C, 25.00; H, 4.20; N, 29.16. Found: C, 25.03; H, 4.39; N, 29.03.

2-Cyclohexylamino-5,5-dinitro-3-aza-4-oxa-2-hexene (IX).—Cyclohexylamine reacted with either 2-chloro-5,5-dinitro-3-aza-4-oxa-2-hexene (II) or the trinitro compound I in a manner analogous to that with ammonia. The yield with aqueous cyclohexylamine and the chloro compound II was 93% when the reaction was carried out at room temperature over a 24-hour period; m.p. 82–84° dec. The reaction was allowed to proceed without cooling in one experiment and the product, m.p. 75–82°, was purified by sublimation. Beyond the cyclohexylamine product (m.p. 82–83°) in the sublimation tube a second substance collected which was recrystallized from benzene–heptane (m.p. 104–105°). This was proved to be N-cyclohexylacetamide, m.p. 104–105°, by taking a mixed m.p. with an authentic sample. Isolation of N-cyclohexylacetamide indicates that the acetyl group is latent in the original chloro compound (II) and hence also in the trinitro compound (I). Infrared spectrum (Nujol mull, μ): 3.00 (weak), 6.40 (strong), N—H; 6.10 (medium), C=N; 6.30 (strong), 7.52 (medium) *gem*-dinitro.

Degradations of 2,5,5-Trinitro-3-aza-4-oxa-2-hexene (I). a. With Aqueous Potassium Hydroxide.—Preliminary alkaline hydrolysis of the trinitro compound I followed by acidification and ether extraction permitted the identification of acetic acid in the ether extract by conversion to the *p*-nitrobenzyl ester, m.p. 77–79°. The m.p. was not depressed by mixed m.p. with an authentic sample.

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[18] In the experimental part only the preferred structure of the trinitro compound (Ia) and its derivatives (IIa–Va) is given. Melting points reported to tenths of a degree are corrected. Analyses by S. M. Nagy, Microchemical Laboratory, M.I.T., Cambridge, Massachusetts.

[19] A. Hantzsch and F. E. Dollfus, *Ber.*, **35**, 257 (1902).

[20] H. Shechter and L. Zeldin, THIS JOURNAL, **73**, 1276 (1951).

[21] A. N. Meldrum and M. M. Patel, *J. Indian Chem. Soc.*, **5**, 92 (1928).

Acetic acid also was identified in an alkaline hydrolysis by means of Duclaux constants.[22]

Quantitative hydrolysis of 1.000 g. (0.00450 mole) of the trinitro compound I with 3% potassium hydroxide followed by acidification and distillation indicated that 0.00748 mole (1.66 equivalents) of acetic acid was liberated in the degradation.

The amount of volatile amine liberated in a similar alkaline hydrolysis was found to be 0.12 equivalent, of which 0.09 mole proved to be ammonia and 0.03 mole to be hydroxylamine, identified as cyclohexanone oxime. While this is not enough hydroxylamine to be satisfying as proof of the =N—O— linkage in compound I, still it is some evidence, for neither 1,1-dinitroethane nor sodium nitrite under the same conditions yielded any hydroxylamine.

b. **With Sodium Ethoxide.**—The nitro groups in 2,5,5-trinitro-3-aza-4-oxa-2-hexene (I) were removed quantitatively by sodium ethoxide as nitrite ion. One millimole (0.222 g.) of the trinitro compound I was added to a solution of 0.12 g. (0.0051 mole) of sodium in 30 ml. of absolute ethanol. The reaction mixture was heated five minutes on the steam-bath and the nitrite ion was determined by evolution of nitrogen with sulfamic acid[23]; volume of nitrogen (S.T.P.), 67.0 ml. (2.98 equivalents).

From 2-chloro-5,5-dinitro-3-aza-4-oxa-2-hexene (II), 1.98 equivalents of nitrite ion were removed by the same method. Other *gem*-dinitro compounds, however, did not give quantitative results, pointing up the contention that the nitro groups in I and II are not isolated *gem*-dinitro functions. The method, then, is not a general one for determination of nitro groups in aliphatic compounds as is shown by the following results. The number given after the name of the compound is the number of equivalents of nitrite ion removed by the method just described, the reaction time being as long as four hours for 2-nitropropane: 1,1-dinitropropane,[24] 0.00; 2-nitropropane, 0.52; 2-nitroso-2-nitropropane,[2] 1.38; 2,2-dinitropropane,[2] 1.6; 2,2,3,3-tetranitrobutane,[6] 2.8; 3,3,4,4-tetranitrohexane,[6] 2.2.

c. **Kuhn–Roth Determination.**—It was not possible to carry out a Kuhn–Roth determination of terminal methyl groups on the trinitro (I) and the chloro (II) compounds because they sublimed out of the reaction mixture. However, 2-amino-5,5-dinitro-3-aza-4-oxa-2-hexene (V) reacted smoothly in the modified procedure of Barthel and LaForge[25] to give 1.91 molar equivalents of acetic acid which is satisfactory evidence of *two* terminal methyl groups in the amino derivative. By implication, since a rearrangement is unlikely, the trinitro compound I also has two terminal methyl groups.

Attempted Reactions of 2,5,5-Trinitro-3-aza-4-oxa-2-hexene (I) with Phosphorus Pentachloride.—One gram of 2,5,5-trinitro-3-aza-4-oxa-2-hexene was refluxed in 50 ml. of benzene with 1 g. of phosphorus pentachloride for 17 hours. The trinitro compound I was recovered quantitatively from the reaction mixture. Likewise, after the same reactants had been kept in the molten state (no solvent) for five hours, 100% of the trinitro compound was recovered.

Titration of 2,5,5-Trinitro-3-aza-4-oxa-2-hexene (I) with Perchloric Acid.—The trinitro compound I was titrated in glacial acetic acid[17] with standard perchloric acid[26] using a Beckman model H2 *p*H meter with a glass electrode and a reference electrode of silver–silver chloride. The titration curve of 2,5,5-trinitro-3-aza-4-oxa-2-hexene (I) showed no break, indicating no tendency to form a salt with the perchloric acid.

Infrared Spectra.—Infrared spectra were measured in a double beam recording spectrometer, a modified[27] Perkin-Elmer model 12B with a sodium chloride prism. For solution spectra, matched cells were used, made of sodium chloride plates separated by a 1-mm. Teflon spacer sealed with Perfluorolube oil.

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[22] L. J. Gillespie and E. H. Walters, THIS JOURNAL, **39**, 2027 (1917).

[23] R. C. Brasted, *J. Chem. Education*, **23**, 320 (1946).

[24] Prepared by the method of E. ter Meer, *Ann.*, **181**, 6 (1876), who reported b.p. 182° and $d^{22.5}_{22.5}$ 1.258 for 1,1-dinitropropane. We report b.p. 76–77° (10 mm.), d^{25}_{4} 1.2583, n^{25}_{D} 1.4316; MR_D calcd. 27.30, found 27.62.

[25] W. F. Barthel and F. B. LaForge, *Anal. Chem.*, **16**, 434 (1944).

[26] W. Seaman and E. Allen, *ibid.*, **23**, 592 (1951).

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[CONTRIBUTION FROM WYETH INSTITUTE OF APPLIED BIOCHEMISTRY]

The Use of the Disproportionation of Esters of 2-Propanenitronic Acid to Convert Halides to Carbonyl Compounds and Benzaldehyde to Benzamides

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A reaction between 2-nitropropane and benzylidene-bis-dimethylamine gave acetoxime and N,N-dimethylbenzamide. Benzylidene-bis-piperidine and 2-nitropropane gave acetoxime and benzoylpiperidine. The reactions appear to proceed by formation of aminobenzyl 2-propanenitronates which disproportionate into acetoxime and benzamides, thus establishing a relationship with the reaction of halides with sodium 2-propanenitronate to form esters with subsequent disproportionation. The latter reaction has been found to go well in wet solvents and even in water. The reaction has been extended to synthesize the aliphatic aldehydes, undecanal and dodecanal, as well as 3,4-methylenedioxyphenylacetone and cyclohexadione.

Among a number of routes that could conceivably lead to a phenyl substituted *t*-butylamine was a Mannich reaction involving benzaldehyde, dimethylamine and 2-nitropropane. When this reaction was attempted, no Mannich base formed. The products of the reaction were acetoxime and N,N-dimethylbenzamide. The same products, plus dimethylamine, resulted from an attempted abbreviated Mannich reaction[1] with preformed benzylidene-bis-dimethylamine and 2-nitropropane. The expected reaction, forming Mannich base, should have been carbon alkylation of the active hydrogen compound, 2-nitropropane, by the cation[1] resulting from the interaction of benzaldehyde and dimethylamine.

The unexpected formation of acetoxime and dimethylbenzamide is explicable only if the two result from the disproportionation of the ester, α-dimethylaminobenzyl 2-propanenitronate, arising from oxygen alkylation of 2-propanenitronic acid by the cation. Although this reaction has not been reported previously, it may be classified among a number of reported reactions[2,3] of halides and salts of nitronic acids giving rise to carbonyl compounds corresponding to the halides and oximes corresponding to the nitronic acids. Earlier examples of similar reactions involve mononitroparaffins other than 2-nitropropane. There can be little doubt that these

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[2] H. B. Hass and M. L. Bender, THIS JOURNAL, **71**, 1767, 3482 (1949); *Org. Syntheses*, **30**, 99 (1950).

[3] L. Weisler and R. W. Helmkamp, THIS JOURNAL, **67**, 1167 (1945).