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Report 9
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H. Shechter
March 15, 1953

THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION

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THE OHIO STATE UNIVERSITY
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INVESTIGATION OF: Research in Nitromonomers and Their Application to Solid Smokeless Propellants

SUBJECT OF REPORT: Status Report for the Period August 15, 1952 to March 1, 1953

SUBMITTED BY: L. Zeldin, D. Ley, E. Roberson, D. Brain, T. Moritsugu and H. Shechter.

DATE: March 15, 1953

Abstract

1. Oxidation of propargyl alcohol with chromic acid-sulfuric acid in acetone gives propiolic acid in 33% yield. Base-catalyzed reactions of methyl propiolate with 1,1-dinitroethane, nitroethane, 1,1-dinitrobutane, and methyl 4,4-dinitrobutyrate result in methyl 4,4-dinitro-2-pentenoate, methyl 4-methyl-4-nitro-2,5-heptadienoate, methyl 4,4-dinitro-2-heptenoate and methyl 4,4-dinitro-2-heptenedioate (tent.) in 73, 13, 75.5 and 38 per cent yields, respectively. Hydrolysis of methyl 4,4-dinitro-2-pentenoate with dilute hydrochloric acid at 60° yields 4,4-dinitro-2-pentenoic acid; hydrolysis of methyl 4-methyl-4-nitro-2,5-heptadienoate with dilute hydrochloric acid gives 5-hydroxy-4-methyl-4-nitro-2-hepten.dioic acid lactone (tent.).

2. Selective reduction of 2-nitro-1-butene with lithium borohydride in ethyl ether-tetrahydrofuran at -70° yields 2-nitrobutane (59.3%) and 3-methyl-3,5-dinitroheptane (14.2%). Reduction of 1-nitropropene gives 1-nitropropane (50%) and 2-methyl-1,3-dinitropentane (2.4%). 2-Phenyl-1-nitroethane is formed in 55.3% yield upon reduction of omega-nitrostyrene with lithium borohydride in ethyl ether-tetrahydrofuran at -70°. A study of the variables on the reduction of conjugate nitroolefins has been made. Secondary addition of the nitroalkanes formed to unreduced nitroolefins may be minimized at lower temperatures.

3. Selective reduction of 2-nitro-1-butene with sodium trimethoxyborohydride in ethyl ether-tetrahydrofuran at -70° results in 2-nitrobutane (45%) and 3-methyl-3,5-dinitroheptane (35%); 3-methyl-3,5-dinitroheptane was converted to 3-methyl-3-nitro-5-heptanone by the Nef reaction and then characterized as 3-methyl-3-nitro-5-heptanone 2,4-dinitrophenylhydrazone. Reduction of 1-nitropropene gave 1-nitropropane (81.7%) and 2-methyl-1,3-dinitropentane (11.4%); 2-nitrobutane (62.6%) and 3,4-dimethyl-2,4-dinitrohexane (62.6%) were obtained by reaction of 2-nitro-2-butene with sodium trimethoxyborohydride. Selective reduction of omega-nitrostyrene at -3° is believed to have given 2,4-diphenyl-1,3-dinitrobutane.

4. 3-Nitro-1-propanol has been prepared by reaction of silver nitrite and 3-bromo-1-propanol; oxidative-nitration of 3-nitro-1-propanol gave 3,3-dinitro-1-propanol. Potassium 3,3-dinitro-1-propanol and silver 3,3-dinitro-1-propanol have been prepared and characterized.

Oxidative-nitration of cyclopentylnitromethane results in formation of cyclopentyldinitromethane (50.9%); silver and potassium salts of cyclopentyldinitromethane have been prepared and characterized.

Reaction of 1-bromo-3,3-dimethylbutane and silver nitrite gave 3,3-dimethyl-1-nitrobutane, characterized as 3,3-dimethylbutanal 2,4-dinitrophenylhydrazone. 3,3-Dimethyl-1,1-dinitrobutane was prepared in 43.3% yield by oxidative nitration of 3,3-dimethyl-1-nitrobutane. Physical and analytical properties of potassium and silver 3,3-dimethyl-1,1-dinitrobutane have been determined.

5. Reaction of silver 1,1-dinitroethane with methyl iodide in acetonitrile yields 2,2-dinitropropane (38.4-51.7%) and 1,1-dinitroethane (12.3%). 4,4-Dinitro-1-pentene (22-25%) was obtained from allyl bromide and silver 1,1-dinitroethane in acetonitrile at 0°; a study has been made of reaction variables on this system.

6. 1-Bromo-1,1-dinitroethane has been prepared by reaction of bromine and sodium 1,1-dinitroethane in water at 0-5°. Reaction of piperidine with 1-bromo-1,1-dinitroethane yielded piperidinium 1,1-dinitroethane (64.3%), piperidinium bromide (74.7%), and a high molecular weight product containing piperidine units.

Reaction of 1,1,1-trinitroethane with guanidine in ethanol at 0-5° resulted in formation of 2,2-dinitroethylguanidine (72.8%) and guanidine nitrite (82.3%). A proof of structure and method of analysis have been developed for guanidine nitrite.

7. The solubilities of the potassium salts of 1,1-dinitroethane, 1,1-dinitropentane, 1,1-dinitro-3-methylbutane, 3,3-dimethyl-1,1-dinitrobutane, cyclopentyldinitromethane, and cyclohexyldinitromethane in water at 25.00°±0.01° have been accurately determined. Ionization constants for substituted 1,1-dinitroalkanes have been determined at 25° in methanol (17.8%) - water, methanol (41.9%)-water, and dioxane (36.0%)-water (see Discussion). The effect of dielectric properties of the solvent medium on the ionization constant of 1,1-dinitroethane has been investigated (see Discussion).

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DISCUSSION

1. BASE-CATALYZED ADDITION REACTIONS OF MONONITROALKANES AND PRIMARY GEM-DINITROALKANES WITH METHYL PROPIOLATE. SYNTHESIS OF PROPIOLIC ACID, METHYL 4,4-DINITRO-2-PENTENOATE, 4,4-DINITRO-2-PENTENOIC ACID, METHYL 4-METHYL-4-NITRO-2,5-HEPTADIENOATE, 5-HYDROXY-4-METHYL-4-NITRO-2-HEPTENEDIOIC ACID LACTONE, METHYL 4,4-DINITRO-2-HEPTENOATE AND METHYL 4,4-DINITRO-2-HEPTENEDIOATE.

A study of base-catalyzed addition reactions of acidic mono and dinitroalkanes with methyl propiolate is being continued as new Michael systems which may be of value in the nitropolymer program. Addition of alpha-omega dinitro or polynitroalkanes to methyl propiolate should lead to a series of difunctional intermediates which may be of particular value in the synthesis of solid propellants.

It has been previously reported[1] that reaction of 2-nitropropane and methyl propiolate in the presence of methanolic sodium methoxide occurs readily at 0-25° to give methyl 4-methyl-4-nitro-2-pentenoate in 55.4 per cent yield. It was also observed[1] that addition of 1,1-dinitroethane and methyl propiolate in the presence of benzyltrimethylammonium hydroxide occurs readily; however, the adduct could not be readily purified because of its instability. It is now reported that methyl 4,4-dinitro-2-pentenoate is produced in 33 per cent yield by reaction of methyl propiolate and 1,1-dinitroethane catalyzed by methanolic benzyltrimethylammonium hydroxide (Equation 1). It has also been found that reaction of 1,1-dinitroethane and methyl propiolate occurs in much higher yield in tetrahydrofuran (73%) than in methanol. Methyl 4,4-dinitro-2-pentenoate is best isolated by molecular distillation technics; excessive decomposition of the ester occurs when distillation is attempted at higher pressures. Methyl 4,4-dinitro-2-pentenoate was identified by its chemical properties, infrared spectra, quantitative analysis and by hydrolysis with dilute hydrochloric acid to 4,4'-dinitro-2-pentenoic acid (Equation 2). 4,4-Dinitro-2-pentenoic acid is a stable

$$CH_3\text{-}CH(NO_2)_2 + HC{\equiv}C\text{-}CO_2\text{-}CH_3 \xrightarrow{^-OCH_3} CH_3\text{-}C(NO_2)_2\text{-}CH{=}CH\text{-}CO_2\text{-}CH_3 \quad (1)$$

$$CH_3\text{-}C(NO_2)_2\text{-}CH{=}CH\text{-}CO_2\text{-}CH_3 + H_2O \xrightarrow{HCl} CH_3\text{-}C(NO_2)_2\text{-}CH{=}CH\text{-}CO_2H + CH_3OH \quad (2)$$

white solid which was characterized by its chemical and physical properties, its infrared absorption and by quantitative analysis.

The addition reactions of methyl propiolate with primary gem-dinitroalkanes has been extended to 1,1-dinitrobutane (Equation 3) and methyl 4,4-dinitrobutyrate (Equation 4) to give methyl 4,4-dinitro-2-heptenoate (63% yield) and methyl 4,4-dinitro-2-heptenedioate (60%, tentative). In reaction of 1,1-dinitrobutane in the presence of

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH(NO_2)_2 + HC{\equiv}C\text{-}CO_2CH_3 \xrightarrow{^-OCH_3}$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}C(NO_2)_2\text{-}CH{=}CH\text{-}CO_2\text{-}CH_3 \quad (3)$$

$$HC(NO_2)_2\text{-}CH_2\text{-}CH_2\text{-}CO_2\text{-}CH_3 + HC{\equiv}C\text{-}CO_2\text{-}CH_3 \xrightarrow{^-OCH_3}$$

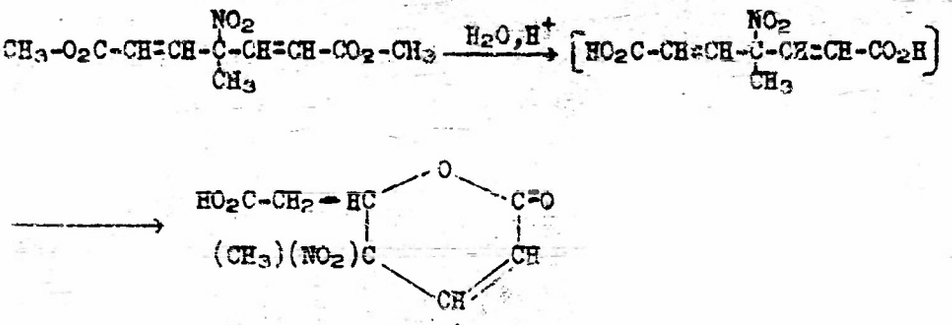
$$CH_3\text{-}O_2C\text{-}CH_2\text{-}CH_2\text{-}C(NO_2)_2\text{-}CH{=}CH\text{-}CO_2\text{-}CH_3 \quad (4)$$

benzyltrimethylammonium hydroxide, it was also observed that the product was of higher purity and the yield was greater when anhydrous tetrahydrofuran was used as solvent (75.5% yield) rather than methanol.

The addition reactions of methyl propiolate have been extended to the primary mononitroalkane, nitroethane. Considerable difficulty has been experienced in controlling and reproducing this reaction; however, in the presence of excess methyl propiolate (> 2:1), addition occurs to give methyl 4-methyl-4-nitro-2,5-heptadienoate (Equation 5) in 13 per cent yield. The intermediate 1:1 adduct, methyl 4-nitro-2-pentenoate, has, as yet, not been isolated in pure state. The structure of methyl 4-methyl-4-nitro-2,5-heptadienoate has been based on the

$$CH_3\text{-}CH_2NO_2 + 2HC{\equiv}C\text{-}CO_2\text{-}CH_3 \longrightarrow CH_3\text{-}O_2C\text{-}HC{=}CH\text{-}\underset{CH_3}{C}(NO_2)\text{-}CH{=}CH\text{-}CO_2\text{-}CH_3 \quad (5)$$

physical, chemical and infrared properties and qualitative analysis of the adduct. Acid hydrolysis of methyl 4-methyl-4-nitro-2,5-heptadienoate is believed to yield 5-hydroxy-4-methyl-4-nitro-2-heptenedioic acid lactone rather than 4-methyl-4-nitro-2,5-heptadienoic acid (Equation 6).



(6)

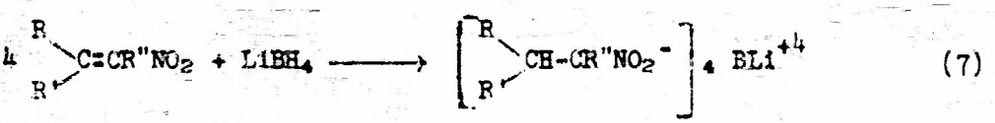
The structural assignment is based on (1) its physical, chemical, infrared and quantitative analysis characteristics, (2) its neutralization equivalent (titration as a monobasic acid), and (3) its eventual saponification with excess alkali. Further proof of structure of this product is now in progress.

Propiolic acid,[1] previously prepared by decarboxylation of monopotassium acetylenedicarboxylic acid, has now been prepared by oxidation of propargyl alcohol with chromic acid in acetone at 0°C (33% yield). This investigation has been terminated because propiolic acid is now readily available from Fairfield Laboratories, Detroit, Michigan.

2. REDUCTION OF CONJUGATED NITROOLEFINS WITH LITHIUM BOROHYDRIDE

It has previously been reported [1] that selective reduction of the olefinic double bond in 2-methyl-1-nitropropene with lithium borohydride in ethyl ether-tetrahydrofuran at 0 to -5° gave the corresponding nitroalkane, 2-methyl-1-nitropropane in 48.4% yield upon acidification with urea-acetic acid solution. More recent work has shown this reaction to be of general applicability; 2-nitro-1-butene, 1-nitropropene and omega-nitrostyrene have been reduced to the corresponding saturated nitro compounds in yields of 59.3%, 49.9% and 55.3% respectively.

The reduction reaction proceeds according to Equations 7 and 8; however a secondary reaction (Equation 9) occurs by reaction of the



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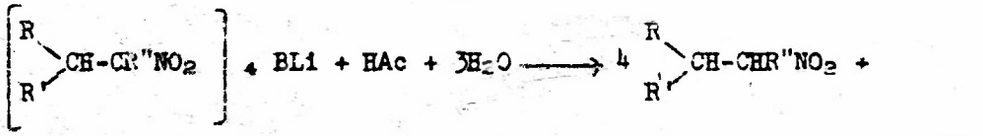

(8)

Michael type of the nitroolefin with the reduced product, the nitroalkane, to give 1,3-dinitroalkanes. This yield-lowering

$$RR'CH\text{-}CR''NO_2^- + RR'C{=}CR''NO_2 \longrightarrow RR'CH\text{-}\underset{\displaystyle R''}{\overset{\displaystyle NO_2}{C}}\text{-}CRR'\text{-}NO_2^- \qquad (9)$$

reaction can be minimized by lowering the temperature of the reduction to -70°.

A study of the effect of temperature and reaction time on the reduction (see Experimental) has shown that the desired reaction proceeds optimally at lower temperatures. Higher yields and complete reduction have also been realized by use of a 100% excess of the lithium borohydride. The results of this study are summarized in Table 1.

Table 1

REDUCTION OF 2-NITRO-1-BUTENE WITH LITHIUM BOROHYDRIDE

Temp.°	Time, hrs.	Moles $LiBH_4$/ moles Olefin	Yield 2-Nitro-1-butene	2-Nitro-butane	3-Methyl-3,5-dinitroheptane	Residue
-1 to +1	2.5	1/4	20.3%	16.2%	22.8%	15.7%
-50 to -55	1.08	1/4	*	24.0%	5.76%	3.27%
-68 to -70	5.5	1/4	23.7%	39.0%	9.2%	11.8%
-68 to -70	5.5	1/2	None	59.3%	14.2%	9.15%

*Products were washed with sodium bisulfite solution.

All products were identified by their physical constants, infrared spectra, and by conversion to the corresponding carbonyl compound via the Nef reaction [5] and thence to the 2,4-dinitrophenylhydrazone derivative.

3. REDUCTION OF CONJUGATED NITROOLEFINS WITH SODIUM TRIMETHOXY-BOROHYDRIDE.

The study of the selective reduction of the carbon-carbon double bond of conjugated nitroolefins with sodium trimethoxyborohydride has been continued. It was previously reported [1] that 2-methyl-1-nitropropene could be reduced to 2-methyl-1-nitropropane in 63.4% yield; it is now reported that 2-nitro-1-butene, 1-nitropropene and 2-nitro-2-butene have been reduced to the corresponding nitroalkanes in yields of

45%, 81.7% and 62.6% respectively. Reduction of omega-nitrostyrene resulted in the isolation of a high melting solid, as yet unidentified (see Experimental).

Two reactions occur in these systems; (1) the desired reduction reaction to give the saturated nitro compound (Equations 10 and 11) and (2) Michael condensation of the nitroolefin with the salt of the reduced product (Equation 12) to give the 1,3-dinitroalkane. Formation of the Michael condensation product may be minimized by effecting the reduction at -70°.

$$RR'C{=}CR''NO_2 + NaBH(OCH_3)_3 \longrightarrow RR'CH\text{-}CR''NO_2Na + (OCH_3)_3B \quad (10)$$

$$RR'CH\text{-}CR''NO_2Na + H^+ \longrightarrow RR'CH\text{-}CHR''NO_2 + Na^+ \quad (11)$$

$$RR'CH\text{-}CR''NO_2^- + RR'C{=}CR''NO_2 \longrightarrow RR'CH\text{-}CR''(NO_2)\text{-}CHR'\text{-}NO_2^- \quad (12)$$

Complete reduction of the conjugated nitroolefins may be realized if a 50% excess of sodium trimethoxyborohydride is employed. The effects of time and temperature on these reduction systems have been studied (Table II as an example); the optimum conditions include a short reaction time and low temperature.

Table 2

REDUCTION OF 2-NITRO-1-BUTENE WITH SODIUM TRIMETHOXYBOROHYDRIDE

Temp.	Time Min.	Moles $NaBH(OCH_3)_3$/ moles Olefin	Yield 2-Nitro-1-butene	2-Nitro-butane	3-Methyl-1,3-dinitroheptane	Residue
-1 to -2°	180	1/1	*	9.2%	5.03%	68%
-55 to -60°	100	1/1	*	29.7%	46.2%	7.2%
-60 to -65°	100	1.5/1	None	45%	35%	8.5%

* Product was washed with sodium bisulfite solution.

All products were identified by their physical constants, infrared spectra and by conversion to the corresponding carbonyl compound via the Nef reaction[3] and thence to the 2,4-dinitrophenylhydrazone derivative.

4. REACTIONS OF SILVER 1,1-DINITROETHANE WITH METHYL IODIDE AND ALLYL BROMIDE.

Reaction of silver salts of acidic nitroalkanes with alkyl halides may lead to carbon and oxygen-alkylated products. Methyl iodide reacts with silver 1,1-dinitroethane[4] in the absence of a solvent to give 2,2-dinitropropane (9.5%), 1,1-dinitroethane (15.2%), ethylnitrolic acid (6.1%), formaldehyde and methyl ethanenitrolate (tent). Since it has been found that 1,1,1-trinitroalkanes are formed in reactions of primary alkyl halides with silver trinitromethane,[5] an investigation has been initiated of the effects of temperature and solvents of high dielectric constants on the displacement reactions of silver salts of 1,1-dinitroalkanes with alkyl halides. It has been previously reported[1] from this laboratory that reaction of methyl iodide and silver 1,1-dinitroethane in anhydrous acetonitrile at 0-5° gave 2,2-dinitropropane (13.7%), 1,1-dinitroethane (9.8%) and formaldehyde; no ethylnitrolic acid could be isolated. It is now reported that addition of methyl iodide to a solution of silver 1,1-dinitroethane in acetonitrile at 0-5° results in the formation of acidic and neutral products. Separation and purification of the neutral components result in isolation of 2,2-dinitropropane in 51.7% crude yield; further purification of the 2,2-dinitropropane by chromatography on magnesol-Celite and vacuum sublimation gave pure 2,2-dinitropropane in 38.4% yield. Characterization of the acidic components result in the isolation of 1,1-dinitroethane as its potassium salt in 12.3% yield; no evidence was found for the presence of ethylnitrolic acid in the reaction product.

Reaction of allyl bromide with silver 1,1-dinitroethane in anhydrous acetonitrile at 0° resulted in formation of 4,4-dinitro-1-pentene (Equation 10) in 22% yield; the acidic reaction products have not been characterized.

$$CH_2{=}CH\text{-}CH_2Br + Ag(O_2N)_2C\text{-}CH_3 \longrightarrow CH_2{=}CH\text{-}CH_2\text{-}C(NO_2)_2\text{-}CH_3 \qquad (10)$$

4,4-Dinitro-1-pentene slowly decolorizes bromine in carbon tetrachloride and an aqueous solution of lithium permanganate; the structural assignment for the product is based on its quantitative analysis, its infrared spectra and its lack of reactivity with aqueous bases.

A study of the effect of temperature on reaction of allyl bromide with silver 1,1-dinitroethane at -40°, 0°, and 60° in acetonitrile resulted in formation of 4,4-dinitro-1-pentene in 22.7%, 22.0%, and 9% yields, respectively. Inversion of the reaction procedure in that an acetonitrile solution of silver 1,1-dinitroethane was added to allyl bromide at 0° gave 4,4-dinitro-1-pentene in 25.6% yield . No evidence has been obtained for oxygen-alkylation in this system. Heterogeneous reaction of silver 1,1-dinitroethane and allyl bromide in ethyl ether at 26° yielded a very sensitive reaction product which decomposed violently upon attempted distillation.

5. REACTION OF PIPERIDINE AND 1-BROMO-1,1-DINITROETHANE.

The reactions of various bases with 1-bromo-1,1-dinitroethane are being investigated (1) as methods for preparation of 1,1-dinitroethylene and its addition products and (2) in order to obtain information concerning

the behavior of halodinitroalkanes during reduction. It has been previously reported[1] that piperidine reacts with 1-bromo-1,1-dinitroethane by oxidation-reduction involving displacement of bromonium ion to give the piperidine salt of 1,1-dinitroethane; the other products of reaction were not identified. It is now reported that piperidine and 1-bromo-1,1-dinitroethane in ethyl ether at 0° react to give piperidinium 1,1-dinitroethane (64.3%), piperidinium hydrobromide (74.7%), and a high-molecular weight product (presumably a trimer) derived from 3,4,5,6-tetrahydropyridine (Equations 11 and 12). Piperidinium 1,1-dinitroethane was identified by

$$3\ C_5H_{10}NH + CH_3\text{-}CBr(NO_2)_2 \longrightarrow C_5H_{10}\overset{+}{N}H_2(O_2N)_2\bar{C}\text{-}CH_3 + C_5H_{10}\overset{+}{N}H_2\bar{Br} + [C_5H_9N] \qquad (11)$$

$$3\ [C_5H_9N] \longrightarrow (C_5H_9N)_3 \qquad (12)$$

comparison with an authentic sample prepared from piperidine and 1,1-dinitroethane and by its ultraviolet spectrum. Piperidinium hydrobromide was identified by its physical and chemical properties and by comparison with an authentic sample. The unidentified basic product is believed to be a mixture of stereoisomeric saturated 1,3,5-triazines resulting from trimerization of 3,4,5,6-tetrahydropyridine (Equation 12).

6. REACTION OF 1,1,1-TRINITROETHANE AND GUANIDINE.

It has been previously reported[1] that reaction of guanidine (excess, > two equivalents) and 1,1,1-trinitroethane in ethanol at 0-5° results in elimination-addition to give 2,2-dinitroethylguanidine in 77.7% yield; the other products of reaction were not identified. It is now reported that reaction of guanidine and 1,1,1-trinitroethane in ethanol at 0-5° gives 2,2-dinitroethylguanidine (72.8%) and guanidinium nitrite (82.3%, Equation 13). An ultraviolet absorption method has been

$$2\ H_2N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}NH_2 + CH_3\text{-}C(NO_2)_3 \longrightarrow H_2N\text{-}\overset{NH_2^+}{\overset{|}{\overset{\|}{C}}}\text{-}NH_2\text{-}CH_2\text{-}C(NO_2)_2^- + H_2N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}NH_2\cdot HNO_2$$

developed for estimating the concentrations and the yield of 2,2-dinitroethylguanidine produced in this reaction. Guanidine nitrite was identified by its chemical and physical properties and by its conversion to guanidinium picrate and silver nitrite.

7. OXIDATIVE-NITRATION OF 3,3-DIMETHYL-1-NITROBUTANE AND CYCLOPENTYLNITROMETHANE; 3,3-DIMETHYL-1,1-DINITROBUTANE AND CYCLOPENTYLDINITROMETHANE.

3,3-Dimethyl-1-nitrobutane has been prepared by reaction of silver nitrite and 1-bromo-3,3-dimethylbutane. 3,3-Dimethyl-1-nitrobutane did not

give a completely satisfactory quantitative analysis and thus it was converted to 3,3-dimethylbutanal via its sodium salt and the Nef reaction. 3,3-Dimethylbutanal was characterized as its 2,4-dinitrophenylhydrazone and these quantitatively analyzed.

Oxidative-nitration of 3,3-dimethyl-1-nitrobutane resulted in the formation of 3,3-dimethyl-1,1-dinitrobutane in 43.5% yield. 3,3-Dimethyl-1,1-dinitrobutane was characterized by its infrared spectra, by conversion into its potassium and its silver salts, and by analysis as silver 3,3-dimethyl-1,1-dinitrobutane.

Reaction of the sodium salt of cyclopentylnitromethane with silver nitrate and sodium nitrite yielded cyclopentyldinitromethane (50.9%). Identification of cyclopentyldinitromethane was based on its infrared and its quantitative analyses, conversion to the potassium salt and its ultraviolet spectra, and by preparation and analysis of its silver salt.

B. THE INFLUENCES OF SOLVENTS ON THE IONIZATION CONSTANTS OF SUBSTITUTED 1,1-DINITROALKANES.

A study has been made of the apparent ionization constants of eleven 1,1-dinitroalkanes in various solvent systems (Table 3) in order to determine the influence of steric and electrical factors on the acid properties of this class of compounds. The solvent systems which have been studied at 25° are methanol (17.8%)-water, methanol (41.9%)-water and dioxane (56%)-water. In general, the same order of relative acidities for the substituted 1,1-dinitroalkanes was found in each of the three solvent systems. The only exception that has been found are the relative ionization constants of cyclopentyldinitromethane and cyclohexyldinitromethane in methanol (17.8%)-water. Excellent agreement has been obtained from the studies of ionization constants of 1,1-dinitroalkanes and the solubilities and ultraviolet spectra of their potassium salts for the general concept that the structures of nitronitronate ions are markedly influenced by the steric requirements of their alkyl substituents.

It has been previously reported[1] that the ionization constant of phenyldinitromethane can be correlated with the dielectric properties of the solvent medium; over the dielectric constant range 71.0-59.0, the ionization constants of phenyldinitromethane decreases almost linearly. A study is now reported (Table 4) of the influence of the dielectric nature of the solvent on the ionization constant of 1,1-dinitroethane in methanol-water. Over the dielectric range: 78.5 to 49.4 a plot of the ionization constant of 1,1-dinitroethane against the reciprocal of the dielectric constant of the solvent medium is essentially that of a straight line; at lower dielectric values, the decrease in ionization constant of 1,1-dinitroethane becomes accelerated.

IONIZATION CONSTANTS AND NEUTRALIZATION DATA FOR SUBSTITUTED 1,1-DINITROALKANES[a]

	Neut. Equiv.		Water Solvent		Titrations in Methanol (17.8%)[c] - water solvent[b]		Titrations in Methanol (41.9%)[c] - water solvent[d]		Titrations in Dioxane (36.0%[f])-water solvent[e]	
	Calcd.	Found	pKa	Ka	pKa	Ka	pKa	Ka	pKa	Ka
$CH_2-CH(NO_2)_2$[g]	120	120	5.177	$6.65\pm0.05 \times 10^{-6}$	5.390	$4.07\pm0.1 \times 10^{-6}$	5.824	$1.50\pm0.02 \times 10^{-6}$	5.775	$1.68\pm0.02 \times 10^{-6}$
$CH_3-CH_2-CH(NO_2)_2$	134	135			5.68	$2.09\pm0.1 \times 10^{-6}$	6.05	$8.90\pm0.02 \times 10^{-7}$	6.071	$8.49\pm0.1 \times 10^{-7}$
$CH_3CH_2CH_2CH(NO_2)_2$	148	150			5.456	$3.50\pm0.02 \times 10^{-6}$	5.873	$1.34\pm0.05 \times 10^{-6}$	5.872	$1.34\pm0.1 \times 10^{-6}$
$CH_3CH_2CH_2CH_2CH(NO_2)_2$[g]	162	163			5.511	$3.08\pm0.1 \times 10^{-6}$	5.914	$1.22\pm0.1 \times 10^{-6}$	5.886	$1.30\pm0.1 \times 10^{-6}$
$CH_3-\underset{CH_3}{CH}-CH(NO_2)_2$	148	149			6.903	$1.25\pm0.1 \times 10^{-7}$	7.311	$4.89\pm0.1 \times 10^{-8}$	7.374	$4.23\pm0.1 \times 10^{-8}$
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH(NO_2)_2$	162	164			8.228	$5.91\pm0.1 \times 10^{-9}$	8.804	$1.57\pm0.05 \times 10^{-9}$	9.028	$9.39\pm0.05 \times 10^{-10}$
$CH_3-\underset{H}{\overset{CH_3}{C}}-CH_2-CH(NO_2)_2$[g]	162	162			5.583	$2.55\pm0.5 \times 10^{-6}$	5.94	$1.15\pm0.15 \times 10^{-6}$	6.025	$9.43\pm0.1 \times 10^{-7}$
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH(NO_2)_2$	176	178			5.386	$4.11\pm0.15 \times 10^{-6}$	5.574	$2.67\pm0.15 \times 10^{-6}$	5.592	$2.56\pm0.1 \times 10^{-6}$
$C_5H_8-CH(NO_2)_2$[g]	174	173			7.40	$6.50\pm0.5 \times 10^{-8}$	7.463	$3.44\pm0.1 \times 10^{-8}$	7.431	$3.30\pm0.1 \times 10^{-8}$
$C_6H_{11}-CH(NO_2)_2$[g]	188	187			7.381	$4.16\pm0.5 \times 10^{-8}$	7.398	$4.00\pm0.1 \times 10^{-8}$	7.444	$3.60\pm0.15 \times 10^{-8}$
$C_6H_5-CH(NO_2)_2$[g]	182	182			4.32	$4.8\pm0.1 \times 10^{-5}$	4.78	$1.70\pm0.1 \times 10^{-5}$		
$C_6H_5-CO_2H$	122	122	4.18	$6.66\pm0.02 \times 10^{-5}$	4.444	$3.60\pm0.2 \times 10^{-5}$	5.15	$7.10\pm0.02 \times 10^{16}$	5.25	$5.60\pm0.02 \times 10^{-6}$

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a. The temperature of all solutions was 25.0 ± 0.1°C. Titrations were conducted with a Beckman pH meter with glass electrode, standardized with sodium acetate-acetic acid (pH = 4) buffer in water.

b. Neutralizations were carried out by adding 0.1000 N aqueous sodium hydroxide to a solution of the 1,1-dinitroalkane in a mixture of 15 ml. of C.p. methanol and 50 ml. of distilled water.

c. Per cent methanol by weight at half titre.

c. Titrations were conducted by adding 0.1000 N aq. sodium hydroxide to a solution of the 1,1-dinitroalkane in 50 ml. of methanol and 50 ml. of water. Titration of 1,1-dinitroethane in aqueous methanol (41.9% methanol by weight) with 0.1000 N sodium hydroxide in aqueous methanol of the same composition gave an ionization constant of 1.50×10^{-6}; this is in excellent agreement, within experimental error, for the ionization constant determined by titration of 50:50 methanol-water with aqueous sodium hydroxide (% methanol at neutralization:41.9%).

e. This set of titrations was run by adding 0.1000 N aqueous sodium hydroxide to a solution of the 1,1-dinitroalkane in 30 ml. of purified dioxane and 50 ml. of water.

f. Per cent dioxane by weight at half titre.

g. These compounds were not completely soluble in the methanol (17.8%) - water at the outset of the titrations.

Table 4

The Effect of Solvent Composition and Dielectric Constant on the Ionization Constant of 1,1-Dinitroethane at 25.0° ± 0.1°.[a]

% MeOH(wt.)	Dielectric Constant	Kion	$K_{ion} \times 10^8$
0	78.48	6.65×10^{-6}	665
17.8[b]	70.8	4.07×10^{-6}	407
25.34	67.50	2.91×10^{-6}	291
41.90	59.90	1.45×10^{-5}	145
41.90[b]	59.90	1.50×10^{-6}	150
44.20	58.85	1.25×10^{-6}	125
64.89	49.40	3.54×10^{-7}	35.4
87.77	38.80	5.71×10^{-8}	5.71

[a] Apparent ionization constants were determined from pH at half-titre of methanol - water solutions of 1,1-dinitroethane with methanolic aqueous sodium hydroxide solution of identical solvent composition. Titration of methanolic-aqueous 1,1-dinitroethane with aqueous sodium hydroxide; per cent methanol of solution at half-titre was calculated.

Experimental

1. OXIDATION OF PROPARGYL ALCOHOL; PROPIOLIC ACID

An aqueous solution of chromic acid (70.0 g., 0.70 moles in 350 ml. of water and 112 g., 1.17 moles of sulfuric acid) was added in 3 hours to a stirred solution of propargyl alcohol (31.0 g., 22.0 ml., 0.54 moles) in acetone at 0°. The reaction mixture was allowed to warm to room temperature overnight, then poured into iced water, and extracted with ethyl ether. The combined ether extracts were dried over sodium sulfate and then over calcium chloride. The ether solution was concentrated at atmospheric pressure and then distilled under vacuum to give propiolic acid (12.58 g., 33% yield): b.p. 83-85° (50 mm.), n_D^{20} 1.4308, 96.5% assay; lit.[6] b.p. 83-84° (50 mm.), n_D^{20} 1.4302.

2. REACTION OF 1,1-DINITROETHANE AND METHYL PROPIOLATE; METHYL 4,4-DINITRO-2-PENTENOATE.

Procedure 1 - Benzyltrimethylammonium hydroxide, (Triton B, 10 ml. of a 35% solution in methanol) was added slowly to a cold, stirred solution of methyl propiolate (5.0 g., 0.06 moles) and 1,1-dinitroethane (8.4 g., 0.07 moles) in anhydrous methanol (30 ml.). The solution was stirred overnight, warmed to room temperature and then poured into cold, dilute hydrochloric acid (1 N). The dark-red mixture was extracted with ethyl ether; the combined ether extracts were washed with dilute sodium bicarbonate solution and with water and then dried over calcium chloride. Upon removal of the ether at reduced pressure the yellow residue (6.0 g.) was distilled twice in a molecular still to give methyl 4,4-dinitro-2-pentenoate; 4.0 g., 33% yield, n_D^{20} 1.4728, d_4^{20} 1.332, MR_D^{20} (calc.) 42.33, MR_D^{20} (found) 42.98. Infrared analysis of the product indicates the presence of ester (5.8 microns), conjugated double bond (6.1 microns) and gem-dinitro (6.2 microns) groups.

Anal. Calc. for $C_6H_8N_2O_6$: C, 35.29; H, 3.95; N, 13.72.
Found: C, 35.59; H, 3.89; N, 13.28.

Procedure 2 - A solution of 1,1-dinitroethane (12.0 g., 0.1 mole), methyl propiolate (9.0 g., 0.11 mole) and anhydrous tetrahydrofuran (60 ml.) was placed in an Erlenmeyer flask equipped with a magnetic stirrer, an ice bath and a drying tube. Triton B (5 ml., 35% in methanol) was added in small portions (2 hrs.) to the cold, well stirred solution. The mixture was then allowed to warm to room temperature overnight. The dark-red reaction mixture was shaken with saturated sodium chloride solution containing a few drops of concentrated hydrochloric acid until the organic layer was acid. The tetrahydrofuran was removed at reduced pressure; the residual red oil was then dissolved in ether. The ether solution was washed twice with aqueous sodium hydroxide (5%), once with hydrochloric acid (1 N), several times with water and then dried over calcium chloride. After the ether had been vacuum distilled, the red residue (19 g., 93% yield)

was purified by molecular distillation to give nearly colorless methyl 4,4-dinitro-2-pentenoate: 14.9 g., 73% yield, n_D^{20} 1.4754.

3. HYDROLYSIS OF METHYL 4,4-DINITRO-2-PENTENOATE; 4,4-DINITRO-2-PENTENOIC ACID

Methyl 4,4-dinitro-2-pentenoate (0.62 g., 0.003 moles) was added to dilute hydrochloric acid (30 ml., 2 N) and stirred at 60° for 2 days. The clear solution was cooled and extracted with ethyl ether. The ether extract was dried and evaporated at reduced pressure; a white crystalline solid, 4,4-dinitro-2-pentenoic acid (0.36 g., 66% yield), remained which melted at 118-119° upon being washed with several portions of cold ethyl ether; neut. equiv. (calc.) 190, neut. equiv. (found) 191.

Anal. Calc. for $C_5H_6N_2O_6$: C, 31.59; H, 3.13; N, 14.74
Found: C, 31.84; H, 3.26; N, 14.56

4. REACTION OF NITROETHANE AND METHYL PROPIOLATE; METHYL 4-METHYL-4-NITRO-2,5-HEPTADIENOATE

Benzyltrimethylammonium hydroxide (Triton B, 16 ml., 35% in methanol) was added in small portions to a stirred mixture of methyl propiolate (16.8 g., 0.20 moles) and nitroethane (7.5 g., 0.10 moles) in anhydrous methanol (40 ml.) at 0°. The reaction mixture was warmed to room temperature overnight and then poured into dilute hydrochloric acid (1 N). The mixture was extracted with ethyl ether; the ether extracts were combined and dried over calcium chloride. Upon distillation of the ether extract a mixture of a yellow oil and white crystals (total 10 g.) remained. The residue mixture was dissolved in ethyl ether and fractionally crystallized by partially removing the ether and then filtering the product, and repeating these processes until the oily product began separating. The crystalline product was identified as methyl 4-methyl-4-nitro-2,5-heptadienoate (3.0 g., 13% yield) by quantitative and infrared analysis. Its infrared spectrum indicates the presence of nitro (6.4 microns), ester (5.8 microns), and conjugated double bond (6.1 microns) groups. The liquid product of reaction was not identified.

Anal. Calc. for $C_{10}H_{13}O_4N$: C, 49.39; H, 5.39; N, 5.76.
Found: C, 49.40; H, 5.25; N, 5.79

5. HYDROLYSIS OF METHYL 4-METHYL-4-NITRO-2,5-HEPTADIENOATE; 5-HYDROXY-4-METHYL-4-NITRO-2-HEPTENEDIOIC ACID LACTONE (tent).

Methyl 4-methyl-4-nitro-2,5-heptadienoate (0.30 g., 0.0012 moles) was stirred in dilute hydrochloric acid (2 N) at 60° for two days. The clear solution was extracted with ethyl ether; the combined ether extracts were dried over calcium chloride. Upon partial distillation of the ether extract, successive crops of a white, amorphous powder separated from solution. The product was tentatively

identified as 5-hydroxy-4-methyl-4-nitro-2-heptenedioic acid lactone (0.170 g., 65% yield); neut. equiv. (calc.) 215 g., neut. equiv. (found) 209 and 219. The product did not have a definite melting point, decomposing slowly above 120°, and rapidly about 160°.

Anal. Calc. for $C_8H_9O_6N$: C, 44.65; H, 4.21; N, 6.51
Found: C, 44.90; H, 4.20; N, 6.34

6. REACTION OF 1,1-DINITROBUTANE AND METHYL PROPIOLATE; METHYL 4,4-DINITRO-2-HEPTENOATE

Procedure 1 - Benzyltrimethylammonium hydroxide (Triton B, 10 ml., 35% in methanol) was added in small portions to a cold stirred mixture of methyl propiolate (3.36 g., 0.04 moles) in anhydrous methanol (50 ml.). The solution was allowed to warm to room temperature overnight and then poured into dilute hydrochloric acid (1 N). The reaction mixture was extracted with ethyl ether; the ether extract was dried over sodium sulfate, concentrated at reduced pressure, redried over calcium chloride, and then vacuum-evaporated for one hour at a pressure of 1 mm. The pale yellow liquid residue (4.3 g.) was distilled through a molecular still to give a pale yellow liquid, methyl 4,4-dinitro-2-heptenoate (1.4 g., excessive manipulative loss), n_D^{20} 1.4682, d_4^{20} 1.239, MR_D^{20} (calc.) 51.57, MR_D^{20} (found) 52.11. The infrared spectrum of the product indicated absorption for ester (5.8 microns), conjugated double bond (6.1 microns, weak) and gem-dinitro(6.2 microns) groups.

Anal. Calc. for $C_8H_{12}N_2O_6$: C, 41.38; H, 5.21; N, 12.07
Found: C, 41.43; H, 5.18; N, 11.19

Procedure 2 - A solution of 1,1-dinitrobutane (14.8 g., 0.10 mole) and methyl propiolate (9.0 g., 0.11 mole) in anhydrous tetrahydrofuran (70 ml.) was placed in an Erlenmeyer flask equipped with a magnetic stirrer, drying tube and ice bath. Triton B (4 ml., 35% in methanol) was added in small amounts to the stirred mixture over the course of one hour (Caution - The reaction mixture may fume off if the base is added too rapidly). The mixture was then allowed to come to room temperature over the course of two hours. The dark-red solution was then washed until acidic with a saturated sodium chloride solution containing a few drops of concentrated hydrochloric acid. The tetrahydrofuran was removed under vacuum; the residue was then dissolved in ether. The ether solution was extracted several times with aqueous potassium hydroxide (5%) and then with hydrochloric acid (0.1 N) until the ether layer was acidic. After the extract was dried over calcium chloride and vacuum distilled, there remained a slightly yellow oil, nearly pure methyl 4,4-dinitro-2-heptenoate; 17.5 g., 75.5% yield, n_D^{20} 1.4728. This product was then purified by molecular distillation to give pure, nearly colorless methyl 4,4-dinitro-2-heptenoate, 14.68 g., 63.3% yield, n_D^{20} 1.4721, d_4^{20} 1.242, MR_D (calc.) 52.12,

MR_D (found) 52.36.

Anal. Calc. for $C_8H_{12}N_2O_8$: C, 41.38; H, 5.21; N, 12.07
Found: C, 41.83; H, 4.92; N, 11.95

7. REACTION OF METHYL 4,4-DINITROBUTYRATE AND METHYL PROPIOLATE; METHYL 4,4-DINITRO-2-HEPTENEDIOATE (Tent.)

Benzyltrimethylammonium hydroxide (Triton B, 10 ml., 35% in methanol) was added in portions to a solution of methyl propiolate (5.5 g., 0.065 moles) and methyl 4,4-dinitrobutyrate (9.6 g., 0.050 moles) in methanol (60 ml.). The reaction mixture was allowed to warm to room temperature overnight and then poured into cold hydrochloric acid (1 N). The mixture was extracted with ethyl ether; the combined ether extracts were dried over calcium chloride and distilled. Molecular distillation of the yellow liquid distillation residue (8.1 g., 60% crude yield, n_D^{20} 1.4672) gave methyl 4,4-dinitro-2-heptenedioate as a pale yellow liquid (5.0 g., 38% yield); n_D^{20} 1.4560, d_4^{20} 1.295, MR_D^{20} (calc.) 57.84, MR_D^{20} (found) 57.98.

8. REDUCTION OF 2-NITRO-1-BUTENE WITH LITHIUM BOROHYDRIDE; 2-NITROBUTANE, 3-METHYL-3,5-DINITROHEPTANE (Tent.)

Procedure 1 - A solution of 2-nitro-1-butene (15.2 g., 0.15 mole) in ethyl ether (25 ml.) was added dropwise in 3 hours to a stirred suspension of lithium borohydride (1.72 g., 0.075 mole + 5%) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.) contained in a 500 ml., three-necked flask equipped with a stirrer, a dropping funnel, a thermometer and a drying tube. During addition the reaction mixture was kept at -68 to -70°; after addition was completed the mixture was stirred for 2.5 hours at -70°. The mixture was then acidified in one hour at 0° with urea-acetic acid solution (75 ml.). The mixture was transferred to a separatory funnel and saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The ether extract was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvent on a steam bath, distillation of the product gave: (a) 2-nitrobutane (9.17 g., 0.089 mole, 59.3%) as a colorless liquid, b.p. 67-70° (80 mm.), n_D^{20} 1.4058 - 1.4098, d_{20}^{20} 0.968; MR_D (calcd.) 26.33, MR_D (found) 26.30; lit.[7] b.p. 140°C., d_{20}^{20} 0.968, n_D^{20} 1.4036, (b) 3-methyl-3,5-dinitroheptane (tent.) (2.16 g., 0.0106 mole, 14.2%), b.p. 72-92° (1.4 mm.), n_D^{20} 1.4564, and (c) a brown residue (1.4 g.).

The structure of 2-nitrobutane was proven by its conversion to methyl ethyl ketone via the Nef reaction[3] followed by preparation of methyl ethyl ketone 2,4-dinitrophenylhydrazone, m.p. 115-116.5°. The melting point of the derivative was not depressed when mixed with an authentic sample.

An infrared spectrum of the 2-nitrobutane (sandwich cell) contained a strong band for the mononitro (6.4 microns) group and no bands for a carbonyl group (5.7 microns), a mononitro group attached to an unsaturated carbon atom (6.5 microns) or a carbon-carbon double bond (6.0 microns).

9. REDUCTION OF 1-NITROPROPENE WITH LITHIUM BOROHYDRIDE; 1-NITROPROPANE, 2-METHYL-1,3-DINITROPENTANE (Tent.)

A solution of 1-nitropropene (15.2 g., 0.175 mole) in ethyl ether (25 ml.) was added dropwise in 3 hours to a stirred suspension of lithium borohydride (1.92 g., 0.088 mole) in ethyl ether (175 ml.) contained in a 500 ml., three-necked flask equipped with a stirrer, a dropping funnel, a thermometer and a drying tube. During addition the reaction mixture was kept at -70° ± 1°; after addition was completed the mixture was stirred for 2 hours at -70°. The mixture was then acidified in 1 hour at 0° with urea-acetic acid solution (200 ml.). The mixture was transferred to a separatory funnel and saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and concentration of the filtrate on a steam bath, distillation gave: (a) 1-nitropropane (7.77 g., 0.0873 mole, 49.8%) as a colorless liquid, b.p. 65-69.5° (100 mm.), n_D^{20} 1.4035-1.4045, d_{20}^{20} 0.9989; MR_D (calcd.) 21.68, MR_D (found) 22.12; lit.[8] b.p. 132°, d_{20}^{20} 1.003, n_D^{20} 1.4015, (b) 2-methyl-1,3-dinitropentane (tent.)(0.37 g., 0.0021 mole, 2.4%) as a yellow liquid, b.p. ca. 105° (1 mm.), n_{20}^{20} 1.4577 and (c) a brown residue (0.9 g.).

The structure of 1-nitropropane was proven by its conversion to propionaldehyde via the Nef reaction[5] followed by preparation of propionaldehyde 2,4-dinitrophenylhydrazone, m.p. 153.5-155.5°. The melting point of the derivative was not depressed when mixed with an authentic sample.

An infrared spectrum of the 1-nitropropane (sandwich cell) contained a strong band for the mononitro (6.4 microns) group and no bands for a carbonyl group (5.7 microns), a mononitro group attached to an unsaturated carbon atom (6.5 microns) or a carbon-carbon double bond (6.0 microns).

Procedure 2 - The experiment was conducted as above except 0.86 g., 0.0375 mole of lithium borohydride was used. Distillation of the product gave: (a) 2-nitro-1-butene (3.60 g., 0.0356 m., 23.7%) and 2-nitrobutane (6.03 g., 0.0585 mole, 39%) as a mixture (analyzed by refractive index), b.p. 53-70° (82-83 mm.), (b) crude 3-methyl-3,5-dinitroheptane (tent.) (1.41 g., 0.0068 mole, 9.2%), b.p. 55-92° (1.3 mm.), n_D^{20} 1.4525, and (c) a brown residue (1.8 g.).

Procedure 3 - The experiment was conducted as above (Procedure 1) except the 2-nitro-1-butene solution was added to lithium borohydride (0.86 g., 0.0375 mole) in 1.5 hours. During addition the mixture was kept at -1 to +1°; after addition was completed the mixture was stirred for 1 hour at 0°. Distillation of the product gave: (a) 2-nitro-1-butene (3.07 g., 0.0304 mole, 20.3%) and 2-nitrobutane (2.50 g., 0.0243 mole, 16.2%) as a mixture (analysis by refractive index), b.p. 60-70° (80 mm.), (b) 3-methyl-3,5-dinitroheptane (tent.) (3.49 g., 0.0171 mole, 22.8%), b.p. 96-98° (1.3 mm.), n_D^{20} 1.4594, and (c) a brown residue (2.4 g.).

Procedure 4 - The experiment was conducted as above (Procedure 1) except the 2-nitro-1-butene solution was added to the lithium borohydride (0.86 g., 0.0375 mole) in 50 minutes. During addition the reaction mixture was kept at -50 to -55°; after addition was completed the mixture was stirred for 15 min. at -55°. The combined ether extract was also washed with saturated sodium bisulfite solution (3 x 200 ml., 5 minutes with each portion). Distillation of the product gave: (a) 2-nitro-1-butene (0.78 g., 0.0077 mole, 5.13%) and 2-nitrobutane (3.72 g., 0.0361 mole, 24%) as a mixture (analysis by refractive index), b.p. 63-70° (80 mm.), (b) 3-methyl-3,5-dinitroheptane (tent.) (0.88 g., 0.00432 mole, 5.76%), b.p. 89-91.5° (1.2 mm.), n_D^{20} 1.4503, and (c) a black residue (0.5 g.).

10. REDUCTION OF OMEGA-NITROSTYRENE WITH LITHIUM BORCHYDRIDE; 2-PHENYL-1-NITROETHANE.

A solution of omega-nitrostyrene (14.9 g., 0.1 mole) in ethyl ether (75 ml.) and tetrahydrofuran (25 ml.) was added dropwise in 3 hours to a stirred suspension of lithium borchydride (1.1 g., 0.05 mole) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.) contained in a 500 ml., round-bottomed, three-necked flask equipped with a stirrer, a dropping funnel, a thermometer, and a drying tube. During addition the reaction mixture was kept at -70 to -72°; after addition was completed the mixture was warmed to -15°; suddenly the temperature rose to +18° and the mixture turned from an opaque yellow to a white color. The mixture was then cooled to 0° and acidified in 55 minutes at 0° with urea-acetic acid solution (90 ml.). The mixture was transferred to a separatory funnel and saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and concentration of the filtrate on a steam bath, distillation gave: (a) 2-phenyl-1-nitroethane (8.36 g., 0.0553 mole, 55.3%) as a colorless liquid, b.p. 80-85.5° (0.8 - 1.2 mm.), n_D^{20} 1.5291 - 1.5296; redistillation of this fraction gives very pure 2-phenyl-1-nitroethane in slightly lower yield, b.p. 68.5-70.8° (0.4 mm.), n_D^{20} 1.5290-1.5296, d_{20}^{20} 1.1225; MR_D (calcd.) 41.37, MR_D (found) 41.52; lit.[9a] b.p. 128-135° (14 mm.); lit.[9b] b.p. 249-251° (763 mm.); lit.[9c] 125-135° (1 mm.), and (b) a yellow residue (5.7 g.) which will be investigated.

The structure of 2-phenyl-1-nitroethane was proven by its conversion to phenylacetaldehyde via the Nef reaction[3] followed by preparation of phenylacetaldehyde 2,4-dinitrophenylhydrazone, m.p. 123.5-124.5°. The melting point of the derivative was not depressed when mixed with an authentic sample.

An infrared spectrum of the 2-phenyl-1-nitroethane (sandwich cell) contained strong bands for the mononitro (6.4 microns) group and a mono-substituted benzene ring (13.3 and 14.35 microns).

11. REDUCTION OF 2-NITRO-1-BUTENE WITH SODIUM TRIMETHOXYBORCHYDRIDE; 2-NITROBUTANE, 3-METHYL-3,5-DINITROHEPTANE.

Procedure 1 - A solution of 2-nitro-1-butene (15.2 g., 0.15 mole) in ethyl ether (25 ml.) was added dropwise in 70 minutes to a stirred suspension of sodium trimethoxyborohydride (28.8 g., 0.15 mole plus 50% excess) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.) contained in a 500 ml., three-necked flask equipped with a stirrer, a dropping funnel, a thermometer and a drying tube. During addition the reaction mixture was kept at -60 to -65°; after addition was completed, the mixture was stirred for 30 minutes at -65°. The mixture was then acidified in one hour at 0° with urea-acetic acid solution (100 ml.). The mixture was transferred to a separatory funnel and saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and evaporation of the solvent on a steam bath, distillation of the product gave: (a) 2-nitrobutane (6.95 g., 0.0675 mole, 45%) as a colorless liquid, b.p. 60-70° (80 mm.), n_D^{20} 1.4048-1.4050, d_{20}^{20} 0.9652; MR_D (calcd.) 26.33, MR_D (found) 26.19; lit.[7] b.p. 140°, d_{20}^{20} 0.968, n_D 1.4036, and (b) 3-methyl-3,5-dinitroheptane (5.34 g., 0.0262 mole, 35%), b.p. 86-90° (0.5 mm.), n_D^{20} 1.4568-1.4577; redistillation of this fraction gives very pure 3-methyl-3,5-dinitroheptane in slightly lower yield, b.p. 92-94° (0.6 mm.), n_D^{20} 1.4582, and (c) a residue (1.3 g.). The 3-methyl-3,5-dinitroheptane was analyzed.

Anal. Calcd. for $C_8H_{16}N_2O_4$: C, 47.05; H, 7.90; N, 13.70.
Found: C, 47.98; H, 7.30; N, 13.07.

Another sample will be analyzed.

The structure of 2-nitrobutane was proven by its conversion to methyl ethyl ketone via the Nef reaction[3] followed by preparation of methyl ethyl ketone 2,4-dinitrophenylhydrazone, m.p. 113.5-114°. The melting point of the derivative was not depressed when mixed with an authentic sample.

A derivative of 3-methyl-3,5-dinitroheptane was prepared by its conversion to 3-methyl-3-nitro-5-heptanone via the Nef reaction followed by preparation of 3-methyl-3-nitro-5-heptanone 2,4-dinitrophenylhydrazone, m.p. 131.5-132.5°.

Anal. Calcd. for $C_{14}H_{18}N_5O_6$: C, 47.59; H, 5.42; N, 19.82.
Found: C, 47.48; H, 5.29; N, 19.96.

An infrared spectrum of the 2-nitrobutane (sandwich cell) contained only a strong band for a mononitro group (6.4 microns). An infrared spectrum of the 3-methyl-3,5-dinitroheptane contained a strong band for a mononitro group (6.4 microns) and a very weak band for a carbonyl group (5.8 microns).

Procedure 2 - The experiment was conducted as above except 2-nitro-1-butene (12.1 g., 0.12 mole) was added to sodium trimethoxyborohydride (16.9 g., 0.12 mole + 10%) in 70 minutes at -55 to -60°; after addition was completed the mixture was stirred for 30 minutes at -60°. The ether extract was also washed with saturated sodium bisulfite solution (3 x 150 ml.). Distillation of the product gave: (a) 2-nitrobutane (3.67 g., 0.0357 mole, 29.7%) as a colorless liquid, b.p. 44-62° (60 mm.), n_D^{20} 1.4047-1.4055, (b) 3-methyl-3,5-dinitroheptane (5.65 g., 0.0277 mole, 46.2%) as a yellow liquid, b.p. 99-100° (1 mm.), n_D^{20} 1.4559-1.4580, and (c) a residue (1.1 g.).

Procedure 3 - The experiment was conducted as previously (Procedure 1) except the 2-nitro-1-butene was added dropwise in 1.5 hours to sodium trimethoxyborohydride (21.1 g., 0.15 mole + 10% excess). During addition the reaction mixture was kept at -1 to -2°; after addition was completed the mixture was stirred for 1.5 hours at 0°. The ether extract was also washed with sodium bisulfite solution (3 x 150 ml.). Distillation of the product gave: (a) 2-nitrobutane (1.42 g., 0.0138 mole, 9.2%) as a pale yellow liquid, b.p. 45 53° (50 mm.), n_D^{20} 1.4048-1.4061, (b) 3-methyl-3,5-dinitroheptane (0.77 g., 0.00377 mole, 5.03%) as an amber liquid, b.p. 40-90° (0.6 mm.), n_D^{20} 1.4570 and (c) a residue (10.41 g.).

12. REDUCTION OF 1-NITROPROPENE WITH SODIUM TRIMETHOXYBOROHYDRIDE; 1-NITROPROPANE, 2-METHYL-1,3-DINITROPENTANE (Tent.).

A solution of 1-nitropropene (15.2 g., 0.175 mole) in ethyl ether (25 ml.) was added dropwise in 70 minutes to a stirred suspension of sodium trimethoxyborohydride (33.58 g., 0.175 mole + 50% excess) in ethyl ether (150 ml.) and tetrahydrofuran (50 ml.). During addition the reaction mixture was kept at -70° ± 1°; after addition was completed the mixture was stirred for 30 minutes at -72°. The mixture was then acidified in 1 hour at 0° with urea-acetic acid solution (100 ml.).

The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration, distillation gave, after removal of ether: (a) 1-nitropropane (12.73 g., 0.143 mole, 81.7%) as a colorless liquid, b.p. 40-72° (100 mm.), n_D^{20} 1.4025-1.4046, d_{20}^{20} 1.0006; MR_D (calcd.) 21.68, MR_D (found) 21.96; lit.[8] b.p. 132°, d_{20}^{20} 1.003, n_D 1.4015, (b) 2-methyl-1,3-dinitropentane (tent.)(1.75 g., 0.00994 mole, 11.4%) as a yellow liquid, b.p. 105-108.5° (2 mm.), n_D^{20} 1.4563, and (c) residue (0.9 g.).

The structure of 1-nitropropane was proven by its conversion to propionaldehyde via the Nef reaction[3] followed by preparation of propionaldehyde 2,4-dinitrophenylhydrazone, m.p. 153-155°. The melting point of the derivative was not depressed when mixed with an authentic sample.

An infrared spectrum of the 1-nitropropane (sandwich cell) contained a strong band for the mononitro (6.4 microns) group and no bands for a carbonyl group (5.7 microns), a moninitro group attached to an unsaturated carbon atom (6.5 microns) or a carbon-carbon double bond (6.0 microns).

13. REDUCTION OF 2-NITRO-2-BUTENE WITH SODIUM TRIMETHOXYBOROHYDRIDE; 2-NITROBUTANE, 3,4-DIMETHYL-2,4-DINITROHEXANE (Tent.).

Procedure 1 - A solution of 2-nitro-2-butene (15.2 g., 0.15 mole) in ethyl ether (25 ml.) was added dropwise in 65 minutes to a stirred suspension of sodium trimethoxyborohydride (28.8 g., 0.15 mole, + 50% excess) in ethyl ether (150 ml.) and tetrahydrofuran (50 ml.). During addition the reaction mixture was kept at -70°; after addition was completed the mixture was stirred for 35 minutes at -70°. The mixture was then warmed to ca. -20°; suddenly a grey precipitate separated and the temperature rose to ca. + 20°. The mixture was cooled to 0° and acidified in 1.5 hours at 0° with urea-acetic acid solution (100 ml.). The mixture was transferred to a separatory funnel and saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over anhydrous sodium sulfate. The sodium sulfate was removed by filtration; distillation gave: (a) 2-nitrobutane (9.49 g., 0.0939 mole, 62.6%) as a colorless liquid, b.p. 70-73° (80 mm.), n_D^{20} 1.4038-1.4057, d_{20}^{20} 0.9674; MR_D (calcd.) 26.33, MR_D (found) 26.13; lit.[7] b.p. 140°, d_{20}^{20} 0.968, n_D 1.4036, (b) 3,4-dimethyl-2,4-dinitrohexane (tent.) (1.74 g., 0.0085 mole, 11.4%) as a green liquid, b.p. 111-112° (1.3 mm.), n_D^{20} 1.4642-1.4647, and (c) a residue (0.8 g.).

The structure of 2-nitrobutane was proven by its conversion to methyl ethyl ketone via the Nef reaction[5] followed by preparation of methyl ethyl ketone 2,4-dinitrophenylhydrazone, m.p. 115-116.5°. The melting point of the derivative was not depressed when mixed with an authentic sample.

An infrared spectrum of the 2-nitrobutane (sandwich cell) contained a strong band for the mononitro (6.4 microns) group and no bands for a carbonyl group (5.7 microns), a moninitro group attached to an unsaturated carbon atom (6.5 microns) or a carbon-carbon double bond (6.0 microns).

Procedure 2 - The experiment was conducted as previously except the sodium trimethoxyborohydride was suspended in 200 ml. of ethyl ether. The same rapid rise in temperature was noted when the reaction mixture was warmed to -30°. Distillation of the product gave: (a) 2-nitro-2-butene (3.19 g., 0.0315 mole, 21%) and 2-nitrobutane (9.72 g., 0.0942 mole, 62.8%) as a mixture (analysis by refractive index), b.p. 72.5-78° (80 mm.), and (b) a residue (0.5 g.).

Procedure 3 - The experiment was conducted as previously (Procedure 1) except the sodium trimethoxyborohydride was suspended in 200 ml. of ethyl ether. The olefin was added in 75 minutes and after addition was completed the mixture was stirred for 125 minutes. The same rapid temperature rise was noted when the reaction mixture was warmed to -30°. Distillation of the product gave: (a) 2-nitro-2-butene (2.53 g., 0.0251 mole, 16.7%) and 2-nitrobutane (9.56 g., 0.0928 mole, 61.9%) as a mixture (analysis by refractive index), b.p. 72-80° (80 mm.), and (b) a residue (0.6 g.).

14. REACTION OF OMEGA-NITROSTYRENE WITH SODIUM TRIMETHOXYBOROHYDRIDE.

A solution of omega-nitrostyrene (14.9 g., 0.1 mole) in ether (75 ml.) was added dropwise in 1.5 hours to a stirred suspension of sodium trimethoxyborohydride (14.1 g., 0.1 mole + 10% excess) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.). During addition the reaction mixture was kept at -2 to -3°; after addition was completed the mixture was stirred for 1.5 hours at 0°. The mixture was then acidified in one hour at 0° with urea-acetic acid solution (60 ml.). The ether phase contained a white solid. The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.) The white solid was filtered from the combined ether extract and air dried to constant weight (13.2 g.); the filtrate was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and saturated sodium bisulfite solution (3 x 150 ml.). The ether layer was dried over anhydrous sodium sulfate and then evaporated; no residue was obtained.

The following tests were made on the white solid isolated from the reduction reaction:

(1) The white solid (1 g.) was refluxed for 2 hours with 1:1 hydrochloric acid (20 ml.); the solid was recovered unchanged.

(2) A mixture of potassium hydroxide (2 g.) and the reduction product (1 g.) in ethyl alcohol (25 ml.) and water (25 ml.) was heated on a steam bath for 5 minutes. The white solid dissolved producing a dark red solution; a small amount of charred material settled from solution. Half of the solution was acidified at 0° with urea-acetic acid solution and then extracted with ethyl ether (50 ml.). No residue was obtained upon evaporation of the ether extract. The second half of the basic solution was dropped slowly at 0° into 50% sulfuric acid (excess) (Nef reaction[3]). This solution was treated with 2,4-dinitrophenylhydrazine solution; however, no derivative precipitated.

(3) An infrared spectrum of the white solid in Nujol contained strong bands for a mononitro group (6.4 microns) and a mono-substituted benzene ring (13.6 and 14.35 microns).

(4) The product was insoluble in the following solvents at their boiling points: ether, Skellysolves, benzene, methanol, ethanol, water, carbon tetrachloride, chloroform, acetone and acetic acid.

(5) The white solid (0.75 g.) was dissolved in hot aqueous sodium hydroxide (0.025 gram in 5 ml.). The red solution was cooled and added dropwise to aqueous sodium permanganate-$3H_2O$ (1.4 g. in 25 ml.). The mixture was heated on a steam bath until most of the permanganate color was gone. The mixture was then cooled in ice and made strongly acid; manganese dioxide was dissolved by adding sodium bisulfite (solid). (Note: Since sodium bisulfite is basic, sufficient acid must be present to generate -COOH from $-COO^-$ ion). The white solid present was contaminated with charred material. The mixture was filtered and the solid was dissolved in sodium hydroxide solution, filtered from charred material, and reprecipitated by adding dilute hydrochloric acid. The solid, benzoic acid, was filtered and recrystallized from hot water, m.p. 118-120°. No depression in melting point was observed when the oxidized product was mixed with an authentic sample of benzoic acid.

(6) The white solid was analyzed: Anal: C, 64.05, 64.21; H, 4.94, 5.01; N, 9.28, 9.24. The product from a condensation of omega-nitrostyrene with 2-phenyl-1-nitroethane, 2,4-diphenyl-1,3-dinitrobutane, has the following analysis: C, 63.99; H, 5.37; N, 9.33.

15. OXIDATIVE-NITRATION OF 3-NITRO-1-PROPANOL. 3,3-DINITRO-1-PROPANOL.

(a) 3-Nitro-1-propanol. Silver nitrite (78 g., 0.51 mole) was introduced into a 500 ml. round-bottomed flask equipped with a condenser, a stirrer and a dropping funnel. The flask was cooled to 0° and trimethylene bromohydrin (66 g., 0.48 mole, b.p. 60-65° (5 mm.), n_D^{25} 1.4842, d_4^{20} 1.5777, Columbia Organic Chemicals) was added dropwise in the course

of one hour with continuous stirring. The stirring at 0° was continued for 4 hours, after which the mixture was brought to room temperature and left overnight. The reaction mixture was warmed gently (50°) for 4 hours (higher temperature resulted in evolution of brown fumes). Ethyl ether (100 ml.) was then added; the insoluble silver bromide was filtered and washed repeatedly with ether. Distillation of the filtrate gave: volatile Fraction 1, 3.0 g., b.p. 50-65° (2 mm.), n_D^{25} 1.4231; Fraction 2, 3.5 g., b.p. 65-80° (2 mm.), n_D^{25} 1.4285; Fraction 3, 13.9 g., b.p. 80-85° (2 mm.), n_D^{25} 1.4378, d_4^{20} 1.1828; lit.[10] b.p. 138-140° (32 mm.), d^{13} 1.773. Additional low boiling material (4 g.) was condensed in the trap; higher boiling product (3 g.) remained in the pot.

Crude 3-nitro-1-propanol (fraction 3, b.p. 80-85° (2 mm.), n_D^{25} 1.4378, d_4^{20} 1.1828) was rectified in a helix-packed column (1.5 x 13 cm.) to give a product of b.p. 82-84° (3 mm.), n_D^{25} 1.4403.

(b) 3,3-Dinitro-1-propanol. 3-Nitro-1-propanol (6.73 g., 0.045 mole, b.p. 82-84° (3 mm.), n_D^{25} 1.4405) in methanol (50 ml.) was slowly mixed with aqueous sodium hydroxide (2.0 g., 0.050 mole in 20 ml. of water); the solution was allowed to stand for 20 minutes at temperatures below 15°. Sodium nitrite (3.5 g., 0.05 mole, 97% assay) was added and the mixture was cooled in an ice bath and poured into stirred silver nitrate (15.3 g., 0.90 mole) in water (35 ml.) and ether (50 ml.) at 5°. After 30 minutes the cooling bath was removed; brine (5 ml.) was added, and the mixture was filtered by suction. The silver deposit was washed freely with ether; the filtrate was separated and the aqueous layer was extracted with ether. The combined ether extract was washed with saturated sodium chloride and water. Distillation of the dried filtrate gave 3,3-dinitro-1-propanol boiling at 105-106° (1.5 mm.), n_D^{25} 1.4590. The infrared spectrogram of 3,3-dinitro-1-propanol (sandwich cell) indicated absorption at 3.0 microns (OH group) and strong absorption at 6.3 microns and medium-strong absorption at 7.5 microns in agreement with values observed for other gem dinitrocompounds.

Potassium 3,3-dinitro-1-propanol (0.85 g., 83.9% theory) was obtained as a yellow salt by treating 3,3-dinitro-1-propanol (0.710 g., 0.00675 mole) in methanol with methanolic potassium hydroxide and washing the filtered product several times with methanol. The salt, after recrystallization from hot water, melted at 156-162° (explosion).

The solubility of potassium 3,3-dinitro-1-propanol at 25 ± 0.01° in water was found to be 1 part in 6.62.

Silver 3,3-dinitro-1-propanol was obtained as a water insoluble yellow solid on mixing aqueous silver nitrate and an aqueous solution of potassium 3,3-dinitro-1-propanol, m.p. 140-155°.

16. REACTION OF SILVER 1,1-DINITROETHANE WITH METHYL IODIDE IN ACETONITRILE, 2,2-DINITROPROPANE.

Silver 1,1-dinitroethane (45.4 g., 0.20 mole; dried in vacuum desiccator at 0.5 mm. for 2 hours) was dissolved in anhydrous acetonitrile (200 ml.; heat of solution was detected) in a dry flask which had been flushed with nitrogen. The slightly murky, amber solution was cooled in an ice-water mixture and stirred while methyl iodide (35.0 g., 0.248 mole; 24% excess) was added dropwise (30 min.). A grey-white precipitate (silver iodide) was formed during the addition. The mixture was then stirred at 0-15° for 3 hours. The silver iodide was filtered and then thoroughly washed with ether. The recovery of dried silver iodide was practically quantitative (46.0 g. recovered; theoretical yield, 46.8 g.). Traces of silver iodide settled from the filtrate when ether was added; the yellow filtrate was filtered through a sintered-glass funnel.

The filtrate was evaporated under reduced pressure. A light-red residue remained which weighed 23.4 g. The product was separated into neutral and acidic fractions by the following procedure: The residue was dissolved in ether and washed with dilute sodium thiosulfate solution to remove the trace of iodine present. The yellow solution was then extracted with 1.2 N sodium hydroxide (ca. 0.20 mole); the orange aqueous layer was immediately acidified by pouring into excess sulfuric acid solution (ca. 0.25 mole) covered with a layer of ether. The amber acidic extract was dried with calcium chloride and saved.

The neutral (ether) solution was dried over calcium chloride. The solution was then filtered through calcium chloride; the salt residue was washed thoroughly with ether. Ether was distilled from the filtrate at a reflux ratio of ca. 3:1. The last traces of solvent were removed by passing a stream of dry air over the surface of the solution until ether fumes could not be detected. The viscous yellow oil remaining weighed 13.87 g. (51.7% crude yield of 2,2-dinitropropane).

A 20% aliquot portion of the product (2.775 g.) was chromatographed on a 32 x 180 mm. column of magnesol-Celite (5:1) in an effort to separate 2,2-dinitropropane from its impurities. The sample was dissolved in Skellysolve F (100 ml.); a yellow, insoluble residue weighing 0.195 g. remained (thus 2.580 g. of soluble material, essentially all 2,2-dinitropropane, was present). The solution was placed on the chromatographic column (previously wet with Skellysolve F); the adsorbate was eluted with Skellysolve F (1200 ml.). The solvent was removed by fractionation; a colorless, oily residue remained which solidified to a white solid upon being chilled. On being warmed to 32°, the solid melted. The oil was vacuum sublimed to give white, crystalline 2,2-dinitropropane (1.07 g.; 38.6% of the aliquot; 19.6% overall yield). Considerable loss of material resulted in the chromatographic and sublimation processes.

The remaining oil (13.87 g. - 2.775 g. = 11.095 g.) was dissolved in Skellysolve F (250 ml.) to remove the yellow, gummy, insoluble material (0.66 g. of tar recovered). The solvent was removed by distillation; the residual oil solidified on refrigeration, but melted on warming to room temperature (34°). Upon vacuum sublimation the oil gave white, waxy 2,2-dinitropropane (8.24 g.; 74.3% of the aliquot; 38.4% overall yield), melting range 47-51°.

The acidic extract was filtered through calcium chloride. The solvent was removed at reduced pressure to give a residual oil weighing 3.2 g. No solid precipitated (Nef[4] reported that ethylnitrolic acid separated as a solid from the acidic fraction at this point). The residue was dissolved in methanol and added slowly at 0-10° to excess methanolic potassium hydroxide. A bright yellow salt, weighing 3.90 g., precipitated which is essentially pure potassium 1,1-dinitroethane and represents a recovery of 12.3%.

17. REACTION OF SILVER 1,1-DINITROETHANE WITH ALLYL BROMIDE. 4,4-DINITRO-1-PENTENE.

Procedure A: Silver 1,1-dinitroethane (45.4 g., 0.20 mole) was dissolved in anhydrous acetonitrile (25 ml.) at 0-10°. Allyl bromide (27.0 g., 0.22 mole) was added dropwise (1 hour) at 0° to the stirred, orange-amber acetonitrile solution. A brownish-grey precipitate (silver bromide, contaminated by silver oxide and/or other impurities) formed rapidly. After the mixture had been stirred at room temperature for 48 hours, the silver bromide was filtered. The precipitate was thoroughly washed with acetonitrile and ether (the weight of silver bromide was not determined). The filtrates were combined and evaporated at reduced pressure. The residue was separated into acidic and neutral fractions as previously described (Experiment 16). The neutral fraction was vacuum distilled to give a greenish oil at 65-67° (4.3 mm.); $n_D^{19.5}$ 1.4541; yield, 7.06 g. (22%). This oil slowly decolorized (a) a solution of bromine in carbon tetrachloride and (b) a solution of lithium permanganate, indicating the presence of a carbon-carbon double bond. The compound was not affected by aqueous sodium hydroxide. Infrared spectra of the crude and redistilled oil confirm the presence of a gem-dinitro group (absorption bands at 6.3, 7.5 and 11.8 mu's) and a carbon-carbon double bond (bands at 5.3 - weak , 6.0 - medium , 10.0 - strong and 10.7 microns - strong ; the latter two bands indicate that the compound has a terminal double bond). Additional physical data (molar refraction and element analysis) establish the product as 4,4-dinitro-1-pentene.

The oil was redistilled; b.p. 74-75° (6.2 mm.); n_D^{20} 1.4535; d_{20}^{20} 1.208; MR_D (calcd.) 36.19; MR_D (found) 35.84. 4,4-Dinitro-1-pentene is a water-white, slightly viscous oil possessing a distinct camphoraceous odor.

Anal. Calcd. for $C_5H_8N_2O_4$: C, 37.50; H, 5.04; N, 17.50.
Found: C, 37.64, 37.69; H, 4.85, 4.89; N, 17.30, 17.42.

Procedure B: To silver 1,1-dinitroethane (45.4 g., 0.20 mole) in anhydrous acetonitrile (600 ml.) was added allyl bromide (26.0 g., 0.21 mole, in 100 ml. acetonitrile) at -40°. The reaction mixture was pale-yellow before and after the addition. Stirring at -30 to -40° was continued for 21 hours. On warming the mixture to room temperature, the salt turned dark brown and the solution was red. The mixture was then refluxed; 30 ml. of distillate (b.p. 70-75°) was collected in an effort to determine if any acrolein was formed in the reaction. A negative 2,4-dinitrophenylhydrazine test was obtained. The mixture was cooled and filtered; silver bromide (35.6 g.; theoretical quantity is 37.6 g.) was recovered. The usual solvent removal and separation of acidic and neutral fractions procedure was employed. The neutral fraction, on distillation, gave 4,4-dinitro-1-pentene (7.26 g., 22.7% yield).

Procedure C: Allyl bromide (27.0 g., 0.22 mole) in anhydrous acetonitrile (100 ml.) was added to a stirred solution of silver 1,1-dinitroethane (45.4 g., 0.20 mole) in acetonitrile (500 ml.; this solution was filtered before use) at 55-60° during 1.5 hours. On stirring and heating the mixture at 60°, oxides of nitrogen were evolved. No distillate was obtained under these conditions; thus acrolein was not formed at this stage. After heating the mixture for three hours, it was cooled and filtered to yield silver bromide (quantitative recovery) and a wine-colored filtrate. Acetonitrile was removed at reduced pressure; on addition of ether to the residue, a tar (1.8 g.) separated. The ether solution was extracted with 105 ml. of 2 N sodium hydroxide. The ether fraction was distilled at reduced pressure to yield 4,4-dinitro-1-pentene (2.89 g., 9.0% yield), b.p. 68-70° (4.5 mm.).

Procedure D: The same proportions of reagents and the same temperature conditions as reported in Procedure A were employed. The order of addition, however, was reversed, the silver 1,1-dinitroethane solution being added to the allyl bromide solution during 21 hours. After being stirred at room temperature for another 24 hours, the mixture was filtered; 36.5 g. of powdery, dark silver bromide (theoretical recovery, 37.6 g.) was obtained. The isolation procedure previously described was employed, and 8.19 g. of 4,4-dinitro-1-pentene (25.6% yield) was obtained. The distillation residue weighed 1.91 g.

Procedure E: The same proportions of reagents and the same temperature conditions as reported in Procedure A were employed. Instead of using acetonitrile as solvent, however, heterogeneous conditions using ethyl ether as diluent were employed. Upon warming and stirring at room temperature (26°), the reaction mixture evolved heat (temperature increased slowly to 31°; temperature maintained at 20-30° by external cooling). After stirring the reaction mixture for 18 hours, the silver bromide was filtered. The filtrate was subjected to vacuum distillation without prior washing with base. The first fraction distilled at 54-60° (2.5-4.5 mm.) and the second fraction at 99-105° (1.3-4 mm.). Violent decomposition of the residue near the end of the distillation completely destroyed the apparatus. None of the distilled material could be recovered.

18. THE REACTION OF 1-BROMO-1,1-DINITROETHANE WITH PIPERIDINE.

(a) Preparation of 1-Bromo-1,1-dinitroethane: 1,1-Dinitroethane (42.3 g., 0.35 mole) was added dropwise to a stirred solution of sodium hydroxide in water (14.6 g., 0.36 mole, in 300 ml. of water) at 5°. To the cold, aqueous solution of sodium 1,1-dinitroethane was added (dropwise; one hour) bromine (58 g., ca. 0.36 mole); a yellow oil separated during the addition. The crude reaction mixture was steam distilled; this did not completely purify the product because bromine (excess) also co-distilled. The contaminating bromine was removed by washing the product with a dilute solution of sodium thiosulfate. The aqueous material was extracted with methylene chloride. The combined organic fractions were dried with calcium chloride; the solvent was then removed at reduced pressure. The yellow, lachrymatory 1-bromo-1,1-dinitroethane remaining weighed 62.7 g. (89.3% yield). A portion of this material (25.7 g.) was vacuum distilled; 1-bromo-1,1-dinitroethane was obtained as a colorless oil, b.p. 49-50° (4.7-4.8 mm.); n_D^{20} 1.4752-1.4763 (4 fractions); d_{20}^{20} 1.851; MR_D (calcd.) 30.41; MR_D (found) 30.64. The recovery was 24.3 g. (94.3% of charge; 84.2% overall yield). The bromine content was determined by reaction with potassium iodide and by titration of the liberated iodine with standard sodium thiosulfate.

Anal. Calcd. for $C_2H_3N_2O_4Br$: Br, 40.16. Found: Br, 37.02 (20 min.), 37.29 (20 min.), 37.39 (30 min.), 37.81 (30 min.), 38.40 (90 min.), 38.68 (3.5 hours).

Time in parentheses refers to time of shaking with potassium iodide before titration.

(b) Reaction with Piperidine: Piperidine (17.0 g., 0.20 mole) was dissolved in ethyl ether (60 ml.) and cooled in an ice-water mixture. 1-Bromo-1,1-dinitroethane (19.9 g., 0.10 mole) in ether (70 ml.) was added dropwise (40 min.) to the stirred piperidine solution. The solution immediately turned yellow and a yellow, crystalline solid soon precipitated. The precipitate was filtered, washed with several portions of anhydrous ether and sucked dry. Essentially pure piperidinium 1,1-dinitroethane (13.2 g., 64.3% yield) was recovered, m.p. 111-113°. Two recrystallizations (from ethanol) raised the m.p. to 113-114°; authentic piperidinium 1,1-dinitroethane melts at 114.5-115.5°; mixed m.p. 113.5-114.5°. The ultraviolet spectrum of the authentic salt exhibited a maximum at 381-382 mμ (E_{max} 1.658, 1.640); the salt from reaction of 1-bromo-1,1-dinitroethane and piperidine had an absorption maximum at 381-382 mμ (E_{max} 1.635, 1.632); the overall spectra were identical.

The filtrate, on storage overnight, yielded a second crystalline mass containing an ether-insoluble red oil. The product was purified by adding absolute ethanol, heating on the steam bath to remove ether and to dissolve the oil and salt, and then cooling in a refrigerator

for several days. The crystals obtained were filtered, washed with ethanol-ether and ether, and dried. The product was identified as piperidinium bromide (8.3 g., 50% of the theoretical yield), off-white needles, m.p. 240.5-241.5°. Evaporation of the filtrate nearly to dryness followed by addition of ether (then ethanol until the red oil all dissolved) resulted in the isolation of another 2.4 g. of piperidinium bromide, m.p. 240-242°. An authentic sample was prepared from piperidine and hydrogen bromide. Both samples were ground and dried at 1 mm. and 56°; m.p. (authentic salt) 238.5-239.5°; m.p. (prepared salt) 239.0-239.5°; mixed m.p. 238.5-239.5°.

The filtrate was evaporated at reduced pressure to leave tarry red oily residue containing crystals and weighing 10.3 g. The residue was washed repeatedly with water to remove the soluble hydrobromide salt. The aqueous solution was evaporated at reduced pressure . On addition of ethanol to the residual oil, 0.51 g. of brown crystals were recovered. Attempts to crystallize additional material from the filtrate (by evaporation, freezing, addition of ether) were unsuccessful; only tars separated. The hydrobromide content of this mixture was determined by dissolving the tar and ethanolic solution in water and treating the mixture with excess aqueous silver nitrate. The silver bromide recovered weighed 1.48 g. Thus 0.0079 mole (1.31 g.) of piperidinium bromide was present in the filtrate. The brown crystals were dissolved in warm ethanol and reprecipitated by addition of ether. Recovered 0.43 g. of tan salt, m.p. 226-233°. The total amount of piperidinium bromide present in the tarry residue, therefore, was 1.74 g. (10.5% of the theoretical yield).

The products of reaction of 1,1,1-trinitroethane and piperidine are thus summarized: piperidinium 1,1-dinitroethane (64.3%), piperidinium bromide (74.7%, 12.4 g.) and an unidentified residue (a polymer probably composed of piperidine units; yield based on piperidine 29.4%).

19. REACTION OF 1,1,1-TRINITROETHANE WITH GUANIDINE.

Sodium ethoxide was prepared from sodium (2.76 g., 0.12 g.-equiv.) and absolute ethanol (50 ml.). To this solution was added guanidine carbonate (12.60 g., 0.07 mole, 0.14 equiv.; ground in mortar) with vigorous stirring at room temperature; the walls of the reaction flask were washed down with absolute ethanol (20 ml.). After 15 min., the suspension was cooled to 0-5° and stirred for 30 min. The sodium carbonate and excess guanidine carbonate were filtered and washed with absolute ethanol (ca. 50 ml.) and then with ethanol-ether; the washings were combined with the filtrate.

The alcoholic guanidine solution was cooled to 0-5° and 1,1,1-trinitroethane (8.25 g., 0.05 mole) in absolute ethanol (40 ml.) was added dropwise with stirring (90 min.). The mixture was stirred at room temperature for 10 hours. The suspension was cooled to 0° and filtered to isolate the orange salt (9.16 g.) that had precipitated. This salt was freed of impurities (guanidinium nitrite)

soluble in ethanol by suspension in 95% alcohol (35 ml.) and then refluxing; the suspension was cooled to 0-5°, filtered, washed with absolute ethanol and ether, and dried. Powdery, orange 2,2-dinitroethylguanidine was recovered in 84.8% crude yield (7.50 g.). Ultraviolet analysis of a 1 x 10^{-4} M solution of this salt (in 10^{-3} M NaOH) showed it to be 88.3% pure (E_{max} (365 mμ) 1.435; c, 0.883 x 10^{-4} M). The impurity present is presumably guanidine carbonate.

On standing, the filtrate deposited a red, crystalline salt (0.22 g.). On the basis of its ultraviolet analysis, this product contains 30.8% 2,2-dinitroethylguanidine; the remaining material is largely guanidinium nitrite.

The filtrate was evaporated to dryness at reduced pressure. A gummy, red solid remained. A homogeneous, crystalline salt could not be obtained by adding either ether or acetone to an alcohol solution of the solid product. The solvents were removed by aspiration at room temperature. The gummy solid remaining weighed 7.41 g. This was stored in a vacuum desiccator over Drierite at 1 mm. for three days. The weight of this product when dried was 7.06 g. (theoretical yield for guanidinium nitrite is 5.30 g.; the impurities present include 2,2-dinitroethylguanidine and guanidine as its hydrate or alcoholate). Ultraviolet analysis of a 1 x 10^{-4} M solution of this product (in 10^{-3} M NaOH) indicates that 2,2-dinitroethylguanidine is present to the extent of 8.2-9.7%, (a background absorption of 0.025 was observed (guanidine carbonate in excess base shows no absorption in the 300-400 mμ region); if this is taken into account, the lower value is more accurate).

Identification of the salt as guanidine nitrite was accomplished as follows:

(I) A sample weighing 0.5026 g. was dissolved in ethanol-water (10:3 ml.) and added to a solution of picric acid (2.2 g.) in absolute ethanol (ca. 40 ml.). The orange-yellow picrate was filtered, washed with ethanol and ether and dried to give guanidine picrate (1.01 g.), m.p. 317° (dec.); an authentic sample melted at 319-320° (dec.). On the basis of the yield of guanidine picrate, 0.207 g. of guanidine was present in the sample. If it is assumed that all of the guanidine were present as its nitrite, the original salt crop contains 5.23 g. of guanidinium nitrite (5.30 g. = theoretical yield).

(II) On treating the salt with acid, copious quantities of nitrogen oxides were evolved; the salt also liberated iodine from a solution of potassium iodide and acetic acid. A solution of 1.006 g. of the impure salt in ca. 40 ml. of distilled water (pH of solution = 9.6) was neutralized with dilute nitric acid (to pH = 6.9) to bind any free guanidine. A concentrated solution of silver nitrate (3.995 g. in ca. 6 ml. of water) was then added. The crude grey-brown salt obtained weighed 1.15 g. (theoretical yield of silver nitrite = 1.54 g.) A portion of this product (1.05 g.) was recrystallized upon heating in 80 ml. of water at 60-70°, filtering, and cooling the filtrate to 0°. The brown,

insoluble material weighed 0.09 g. The remaining material, silver nitrate (0.96 g.), upon filtration was isolated as a powdery orange salt (0.95 g.). The salt gave a strong positive test for nitrite ion (iodide to iodine in acetic acid solution).

The recovery of silver nitrite, therefore, is 61.7% of the sample (not including that soluble in the original filtrate); the amount of guanidinium nitrite present, therefore, is approximately 4.36 g, (82.3% of theoretical amount). The amount of free guanidine present (considering quantity of picrate obtained) is approximately 0.8 g. The total yield of 2,2-dinitroethylguanidine is 72.8% (64.9 + 1.4 + 6.5%).

2C OXIDATIVE-NITRATION OF CYCLOPENTYLNITROMETHANE; CYCLOPENTYLDINITROMETHANE.

(a) Cyclopentyldinitromethane. Cyclopentylnitromethane (9.50 g., 0.043 mole, n_D^{30} 1.4565, d_4^{20} 1.0530, received from Dr. N. Kornblum, Purdue University) in methanol (125 ml.) was slowly mixed with aqueous sodium hydroxide (3.1 g., 0.078 mole, 97.9% assay, in 100 ml. of water) and the solution was allowed to stand for 15 minutes below 15°. Sodium nitrite (5.38 g., 0.078 mole, 97% assay, in 5 ml. of water) was added and the mixture was cooled in an ice-salt bath and poured into a stirred solution of silver nitrate (25.5 g., 0.15 mole, in 50 ml. of water), aqueous sodium hydroxide (5%, 1 drop) and ethyl ether (75 ml.) at 5°. After the precipitation of silver was complete, the cooling bath was removed and the mixture was allowed to stir for 30 minutes. Saturated sodium chloride (5 ml.) was added and the mixture was filtered by suction. The silver deposit was washed liberally with ether; the ether layer was washed with water, brine and dried with Drierite. Distillation under reduced pressure (nitrogen atmosphere) gave cyclopentyldinitromethane: 6.47 g., 50.9% yield, b.p. 95-96° (5 mm.), n_D^{25} 1.4689, d_4^{20} 1.2473.

(b) Purification of Cyclopentyldinitromethane. Potassium cyclopentyldinitromethane (4.069 g., 0.019 mole, recrystallized from hot water) was placed in a 500 ml. flask, fitted with a stirrer, a thermometer and a condenser. The potassium salt was dissolved in 250 ml. of water and cooled to 0°. With stirring, a solution (precooled to 0°) of urea (5.1 g., 0.085 mole) dissolved in 20% aqueous acetic acid (30 g., 0.10 mole acid) was added (by means of a medicine dropper) over a period of 20 minutes. The two phase system thus produced was extracted with petroleum ether (3 x 50 ml.); the extracts were combined, dried with Drierite and distilled under reduced pressure (nitrogen atmosphere) to give pure cyclopentyldinitromethane: 2.35 g., b.p. 95-96° (5 mm.), n_D^{25} 1.4686, d_4^{20} 1.2470.

Anal. for $C_6H_{10}N_2O_4$: Calcd. C, 41.38; H, 5.79; N, 16.09.

Found: C, 41.36; H, 5.30; N, 15.84.

Potassium cyclopentyldinitromethane (1.010 g., 79.2% theory) was obtained as a yellow salt by treating cyclopentyldinitromethane (1.046 g.) in methanol (10 ml.) with methanolic potassium hydroxide and washing the filtered product several times with ethyl ether; dec. range 134-151° after recrystallization from hot water. The ultraviolet absorption of potassium cyclopentyldinitromethane (conc. of anion: 1 x 10^{-4} moles/liter in 10^{-3} N sodium hydroxide. The sample was prepared by dissolution of the potassium salt in 1.0 x 10^{-3} N sodium hydroxide) are: Max. 1, 308 mμ, logε, 4.01; Min. 1, 306-308 mμ, log$\varepsilon_{min.}$ 2.76; Max. 2, 233 mμ, log ε 3.87.

Silver cyclopentyldinitromethane (0.491 g., 94.4% theory) was obtained as a water-insoluble solid on mixing aqueous solutions of potassium cyclopentyldinitromethane (0.393 g.) and silver nitrate; dec. range, 104-119° at which the silver salt began to deposit a silver mirror. The following analyses of silver cyclopentyldinitromethane were obtained: (1) 0.1088 g. of silver cyclopentyldinitromethane required 7.55 ml. of 0.05148 N ammonium thiocyanate; Ag 38.5%, (2) 0.1084 g. of silver cyclopentyldinitromethane required 7.50 ml. of 0.05148 N ammonium thiocyanate; Ag 38.4%. Theory, Ag 38.38%.

21. PREPARATION OF 3,3-DIMETHYL-1-NITROBUTANE.

Silver nitrite (54 g., 0.35 mole, freshly recrystallized from hot water) was introduced into a 1 liter round-bottomed three-necked flask fitted with a condenser, a stirrer, and a dropping funnel. The flask was cooled to 0° and 1-bromo-3,3-dimethylbutane (58.4 g., 0.35 mole, prepared by reaction of t-butyl bromide, ethylene, and aluminum bromide at -30 to -5°, b.p. 54-55° (40 mm.), n_D^{25} 1.4420, d_4^{20} 1.1592; lit.[11], b.p. 54° (40 mm.), n_D^{20} 1.4440, d_4^{20} 1.1556) was added dropwise in the course of 2 hours. Stirring at 0° was continued for an additional 4 hours. The mixture was brought to room temperature and left overnight while stirring. The mixture was then heated on a steam-bath for 6 hours. Ethyl ether (50 ml.) was added and the mixture was refluxed for an additional 2 hours. The insoluble silver bromide was filtered and washed repeatedly with ether. The combined ether washings were distilled to give: Fraction 1, 0.9 g., b.p. 45-60°(20 mm), n_D^{25} 1.4209; Fraction 2, 11.9 g., b.p. 60-69° (20 mm.), n_D^{25} 1.4212, d_4^{20} 0.9802; Fraction 3, 10.5 g., b.p. 69-70° (29 mm.), n_D^{25} 1.4212, d_4^{20} 0.9497.

Sulfuric acid (96%, 35 ml., precooled to 0°) was added to Fractions 2 and 3 (22.4 g., cooled to 0°) at a rate such that the temperature did not rise above 5°. The solution was then stirred for 15 minutes at 0° and then poured on ice (200 g.) which was covered with petroleum ether (75 ml., b.p. 30-60°). The aqueous layer was separated and extracted with fresh portions of petroleum ether. The ether extracts were combined, washed with water and dried over Drierite. The solvent was removed under reduced pressure and the residue was distilled under reduced pressure to give crude 1-nitro-3,3-dimethylbutane: Fraction 1, 3.74 g., b.p. 67-68° (20 mm.), n_D^{25} 1.4198, d_4^{20} 0.9551; Fraction 2, 6.71 g., b.p. 68-69° (20 mm.), n_D^{25} 1.4218, d_4^{20} 0.9467.

3,3-Dimethyl-1-nitrobutane did not analyze quite correctly. It was therefore converted to 3,3-dimethylbutanal and analyzed as its 2,4-dinitrophenylhydrazone. A solution of 3,3-dimethyl-1-nitrobutane (0.340 g.) and methanol (25 ml.) was added dropwise to sodium hydroxide (0.3 g.) in water (10 ml.) at 0-5°. The resulting mixture was added dropwise to a solution of sulfuric acid (2.5 ml. of 95% sulfuric acid in 12.5 ml. of water) cooled to 0-5°. The 2,4-dinitrophenylhydrazone of 3,3-dimethylbutanal resulted when a solution of 2,4-dinitrophenylhydrazine was added. After recrystallization from 95% ethanol, the 2,4-dinitrophenylhydrazone gave orange needles (0.208 g.), m.p. 148°

Anal. for $C_{12}H_{17}N_4O_4$: Calcd: C, 51.23; H, 6.09; N, 19.92.
Found: C, 51.23; H, 5.84; N, 20.17.

22. PREPARATION OF 3,3-DIMETHYL-1,1-DINITROBUTANE (Completed experiment)

3,3-Dimethyl-1-nitrobutane (10.45 g., 0.80 mole) was dissolved in methanol (100 ml.) and added to aqueous sodium hydroxide (3.6 g., 97.9% assay in 25 ml. of water) at 5°. Sodium nitrite (6.2 g., 0.09 mole, in 15 ml. of water) was added and the cold solution was poured rapidly into a stirred mixture of aqueous silver nitrate (30.6 g., 0.18 mole), aqueous sodium hydroxide (5%, 1 drop), water (70 ml.) and ether (125 ml.) at 0-5°. After the precipitation of silver was complete, the cooling bath was removed and the mixture was stirred for 0.5 hour. Saturated sodium chloride (5 ml.) was added and the mixture was filtered; the residue from the filtration was washed thoroughly with ethyl ether. The filtrate was separated and the aqueous layer was washed with ether. The ether washings were combined, washed with saturated sodium chloride solution, water and dried with Drierite. After ether was removed, the crude product was distilled under reduced pressure (nitrogen atmosphere) to give 3,3-dimethyl-1,1-dinitrobutane (6.10 g., 43.3% yield), b.p. 77° (5 mm.), n_D^{20} 1.4394, d_4^{20} 1.1190.

Potassium 3,3-dimethyl-1,1-dinitrobutane (1.66 g., 95.5% theory) was obtained as a yellow salt by treating 3,3-dimethyl-1,1-dinitrobutane (1.43 g., 0.0081 mole) in methanol (10 ml.) with methanolic potassium hydroxide and washing the filtered product several times with ethyl ether; dec. range, 260-273° after recrystallization from hot water. The solubility of potassium 3,3-dimethyl-1,1-dinitrobutane is 1 part in 15.3 parts of water at 32°.

Silver 3,3-dimethyl-1,1-dinitrobutane (0.271 g., 97.8% theory) was obtained as a water-insoluble orange solid on mixing aqueous solutions of potassium 3,3-dimethyl-1,1-dinitrobutane (0.268 g., 0.00098 mole) and silver nitrate; dec. range, 160-177°, deposition of a silver mirror. The following analyses of silver 3,3-dimethyl-1-dinitrobutane were obtained: (1) 0.0814 g. of silver 3,3-dimethyl-1,1-dinitrobutane required 5.60 ml. of 0.05148 N ammonium thiocyanate; Ag 38.2%, (2) 0.0888 g. of silver 3,3-dimethyl-1,1-dinitrobutane required 6.14 ml. of 0.05148 N ammonium thiocyanate; Ag 38.4%. Theory, Ag 38.11%.

Purification of 3,3-dimethyl-1,1-dinitrobutane. Potassium 3,3-dimethyl-1,1-dinitrobutane (42.7 g., 0.0201 mole, recrystallized twice from hot water) was placed in a 500 ml., round-bottomed, three necked flask equipped with a stirrer, a thermometer and a condenser. The potassium salt was dissolved in water (250 ml.) and cooled to 0°. While stirring, a solution of urea (5.1 g., 0.085 mole, precooled to 0°) in 20% aqueous acetic acid (30 g., 0.10 mole acid) was added (by means of a medicine dropper) over a period of 20 minutes. The two phase system thus produced was extracted with petroleum ether (3 x 50 ml.) and the extracts were combined and dried over Drierite. After petroleum ether was distilled, the residue was distilled under reduced pressure to give pure 3,3-dimethyl-1,1-dinitrobutane: 2.75 g., b.p. 78-79° (5 mm.), n_D^{20} 1.4398, d_4^{20} 1.1185, MR_D (calcd.) 41.50, MR_D (found) 41.24.

Anal. Calcd. for $C_6H_{12}N_2O_4$: Calcd.: C, 40.90; H, 6.86; N, 15.90.
Found: C, 41.38; H, 6.76; N, 15.38.

23. THE SOLUBILITIES OF POTASSIUM 1,1-DINITROALKANES (reexamination)

The solubilities of the various potassium 1,1-dintiroalkanes were determined in the following manner: Water was added from a buret into a weighed sample (0.1-0.3 g.) of potassium dinitroalkane in a weighed Erlenmeyer flask. The heterogeneous solution was shaken from time to time and left at room temperature bath (25 ± 0.01°) overnight. The insoluble potassium dinitroalkane was filtered rapidly (required not more than 1 minute) in a weighed glass sintered funnel and weighed after complete drying. The solubility of the salt was then calculated.

Compound: Potassium salt of	Solubility
1,1-Dinitroethane	(a) 1 part in 13.3 (b) 1 part in 13.6
1,1-Dinitropentane	(a) 1 part in 42.1 (b) 1 part in 42.1
1,1-Dinitro-3-methylbutane	1 part in 8.30
3,3-Dimethyl-1,1-dinitrobutane	1 part in 19.3
Cyclopentyldinitromethane	1 part in 13.2
Cyclohexyldinitromethane	(a) 1 part in 36.8 (b) 1 part in 36.6

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