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11

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Report No. 7
on

CONFIDENT No. N6onr-22524

L. Friedman, D. Icy, L. Zeldin
H. Shechter
February 15, 1952

**THE OHIO STATE UNIVERSITY
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R E P O R T

by

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

Columbus 10, Ohio

COOPERATOR: OFFICE OF NAVAL RESEARCH
Contract No. N6onr-22524

INVESTIGATION OF: Research in Nitromonomers and
Their Application to Solid
Smokeless Propellants

SUBJECT OF REPORT: Status Report, for the period
September 15, 1951 to February 1, 1952

SUBMITTED BY: I. Friedman, D. Ley, L. Zeldin
and H. Shechter

DATE: February 15, 1952

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ABSTRACT

1. The reaction of 1,1,1-trinitroethane with potassium diethyl malonate has been repeated. The yield of ethyl 2-carbethoxy-4,4-dinitrobutyrate was improved to 36.3%. The structure of this compound was verified by conversion to 4,4-dinitroheptanedioic acid.

2. The structure of trimethylammonium-N-(2-nitroethyl-2-nitronate) was proven by a successful displacement reaction with piperidine. The N-(2,2-dinitroethyl)-piperidine prepared (in 93.6% yield) by this reaction is identical with that produced by the reaction of piperidine with 1,1,1-trinitroethane. N-(2,2-dinitroethyl)-piperidine was also synthesized from dinitromethane and N-methylolpiperidine by the procedure of Duden, Bock and Reid.

3. Guanidine reacts with 1,1,1-trinitroethane to give the elimination-addition product, 2,2-dinitroethylguanidine, in 92% (crude) yield. The structure of this compound was established by an alternate synthesis: Guanidine undergoes a displacement reaction with N-(2,2-dinitroethyl)-piperidine to give 2,2-dinitroethylguanidine in 28% yield.

4. Trimethylammonium-N-(2-nitroethyl-2-nitronate) reacts with bromine to give an orange solid melting at 77.5° (evolution of bromine vapors). Attempts at recrystallization have yielded traces of trimethylammonium bromide, m.p. 244-246°; characterization of the other components of this reaction is still in progress.

5. To complete the work on selective reduction of nitrocarbonyl compounds, the action of sodium borohydride on 4,4-dinitropentanal (67.6% yield of alcohol using neutral-basic medium) and 5,5-dinitro-2-hexanone (78.2% yield of alcohol using acid medium; 54.5% using neutral-basic medium) was studied.

6. 1-Nitromethylcyclohexene was prepared in 62% yield using the procedure of Dauben, et al. Methyl 4-nitropentanoate (54-65%) and dimethyl 4-methyl-4-nitroheptanedioate (20-35%) were obtained in the reaction of nitroethane with methyl acrylate in the presence of trimethylamine or Triton B. Oxidative-nitration of methyl 4-nitropentanoate yielded methyl 4,4-dinitropentanoate.

7. Selective reduction of certain nitro esters to their corresponding nitro alcohols has been accomplished by the use of lithium borohydride in refluxing ethyl ether-tetrahydrofuran. Reaction of methyl 4-nitrobutyrate, methyl 4-methyl-4-nitropentanoate, methyl 4,4-dinitropentanoate, and methyl 4-nitropentanoate with lithium borohydride gave 4-nitro-1-butanol, 4-methyl-4-nitro-1-pentanol, 4,4-dinitro-1-pentanol, and 4-nitro-1-pentanol in 53, 96, 74 and 72 per cent yields, respectively.

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8. Reaction of methyl magnesium iodide with 2-methyl-1-nitropropene in the absence of free magnesium gave 2,2-dimethyl-1-nitropropane (52.2%) and 2,2,3,3-tetramethyl-1,4-dinitrobutane (6.4%). Reaction of methyl magnesium iodide with 2-methyl-1-nitropropene in the presence of excess magnesium gave 2,2-dimethyl-1-nitropropane (43.1%) and 2,2,3,3-tetramethyl-1,4-dinitrobutane (6.2%). It was concluded that the presence or absence of magnesium had no important effect on reductive-dimerization of nitroolefins.

Reaction of magnesium subiodide (magnesium-magnesium iodide) and 2-methyl-1-nitropropene resulted in extensive decomposition of the nitroolefin.

CONFIDENTIAL

CONFIDENTIAL
SECURITY INFORMATION

CONFIDENTIAL

TABLE OF CONTENTS

<u>DISCUSSION</u>	<u>Page</u>
1. REACTION OF 1,1,1-TRINITROETHANE AND POTASSIUM DIETHYL MALONATE	1
2. REACTION OF GUANIDINE AND 1,1,1-TRINITROETHANE	1
3. PROOF OF STRUCTURE OF N-(2,2-DINITROETHYL)-PIPERIDINE	2
4. PROOF OF STRUCTURE OF TRIMETHYLAMMONIUM-N-(2-NITROETHYL-2-NITRONATE).	3
5. PROOF OF STRUCTURE OF 2,2-DINITROETHYLGUANIDINE	3
6. SELECTIVE REDUCTION OF NITROCARBONYL COMPOUNDS WITH SODIUM BOROHYDRIDE	4
7. REDUCTION OF NITROESTERS WITH LITHIUM BOROHYDRIDE; NITROALCOHOLS	4
8. REACTION OF GRIGNARD REAGENTS WITH α , β -NITRO-OLEFINS; REDUCTIVE-DIMERIZATION	5

CONFIDENTIAL

TABLE OF CONTENTS Cont'd.

	<u>Page</u>
<u>EXPERIMENTAL</u>	
1. PREPARATION OF ETHYL 2-CARBETHOXY-4,4-DINITRO-BUTYRATE	7
2. PROOF OF STRUCTURE OF ETHYL 2-CARBETHOXY-4,4-DINITROBUTYRATE. CONVERSION TO 4,4-DINITROHEPTANEDIOIC ACID	7
3. PROOF OF STRUCTURE OF N-(2,2-DINITROETHYL)-PIPERIDINE	8
4. PROOF OF STRUCTURE OF TRIMETHYLAMMONIUM-N-(2-NITROETHYL-2-NITRONATE). EXCHANGE REACTION WITH PIPERIDINE	8
5. REACTION OF 1,1,1-TRINITROETHANE WITH GUANIDINE. SYNTHESIS OF 2,2-DINITROETHYLGUANIDINE	8
6. PROOF OF STRUCTURE OF 2,2-DINITROETHYLGUANIDINE	9
7. REACTION OF TRIMETHYLAMMONIUM-N-(2-NITROETHYL-2-NITRONATE) WITH BROMINE	10
8. SELECTIVE REDUCTION OF 5,5-DINITRO-2-HEXANONE TO 5,5-DINITRO-2-HEXANOL WITH SODIUM BOROHYDRIDE	10
9. SELECTIVE REDUCTION OF 4,4-DINITRO-1-PENTANAL TO 4,4-DINITRO-1-PENTANOL USING SODIUM BOROHYDRIDE	11
10. PREPARATION OF 1-NITROMETHYLCYCLOHEXENE	11
11. PREPARATION OF METHYL 4-NITROPENTANOATE AND DIMETHYL 4-METHYL-4-NITROHEPTANEDIOATE	11
12. OXIDATIVE-NITRATION OF METHYL 4-NITROPENTANOATE; METHYL 4,4-DINITROPENTANOATE	12
13. REDUCTION OF METHYL 4-NITROBUTYRATE WITH LITHIUM BOROHYDRIDE; 4-NITRO-1-BUTANOL	12
14. REDUCTION OF METHYL 4-METHYL-4-NITROPENTANOATE WITH LITHIUM BOROHYDRIDE; 4-METHYL-4-NITRO-1-PENTANOL	13
15. REDUCTION OF METHYL 4,4-DINITROPENTANOATE WITH LITHIUM BOROHYDRIDE; 4,4-DINITRO-1-PENTANOL	13
16. REDUCTION OF METHYL 4-NITROPENTANOATE WITH LITHIUM BOROHYDRIDE; 4-METHYL-4-NITRO-1-PENTANOL	13

CONFIDENTIAL

CONFIDENTIAL

TABLE OF CONTENTS Cont'd.

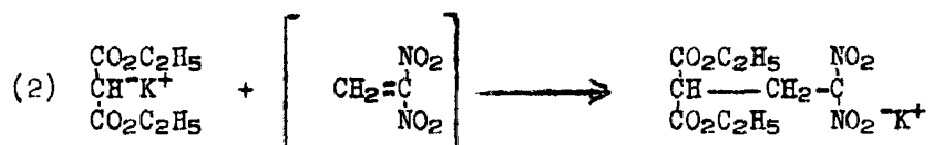
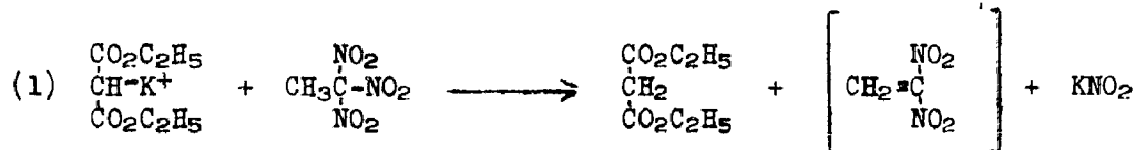
	<u>Page</u>
17. REACTION OF METHYL MAGNESIUM IODIDE WITH 2-METHYL-1-NITROPROPENE IN THE ABSENCE OF MAGNESIUM	14
18. REACTION OF METHYL MAGNESIUM IODIDE WITH 2-METHYL- 1-NITROPROPENE IN THE PRESENCE OF MAGNESIUM	15
<u>REFERENCES</u>	16

CONFIDENTIAL

DISCUSSION

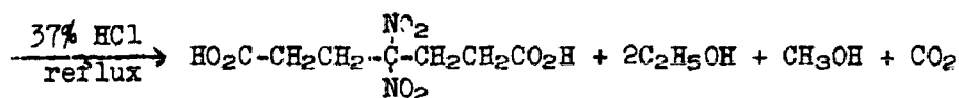
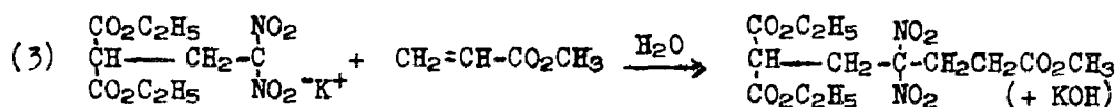
(1) Reaction of 1,1,1-Trinitroethane and Potassium diethyl malonate.

Reaction of potassium diethyl malonate with 1,1,1-trinitroethane gives ethyl 2-carbethoxy-4,4-dinitrobutyrate as the principal product. This reaction proceeds via an "elimination-addition" mechanism¹; the equation follows:



The reaction was repeated in an effort to increase the yield of alkylation product (the early run gave 24.4% yield of acidified and distilled material). The modified acidification procedure of Kornblum and Graham² was employed; the yield of distilled ethyl 2-carbethoxy-4,4-dinitrobutyrate was improved to 36.3%.

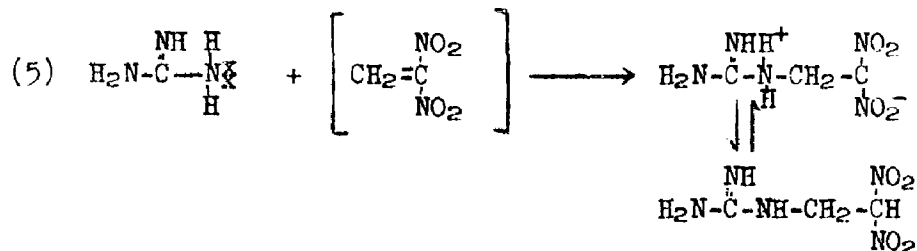
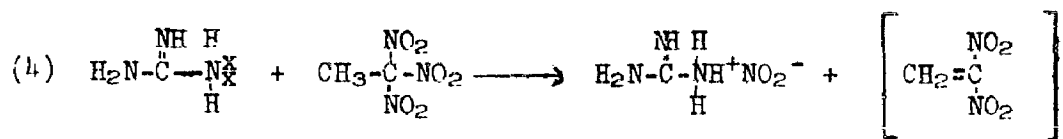
The structure of the product was proven by conversion of its potassium salt to 4,4-dinitroheptanedioic acid (30% overall yield) by reaction with methyl acrylate and subsequent hydrolysis of the adduct with hydrochloric acid:



The 4,4-dinitroheptanedioic acid had a neutralization equivalent of 127 (calcd., 125) and melted at 138.5-140° (an authentic sample³ melted at 138-140° and mixing produced no depression). The intermediate methyl ethyl 2-carbethoxy-4,4-dinitroheptanedioate was not isolated.

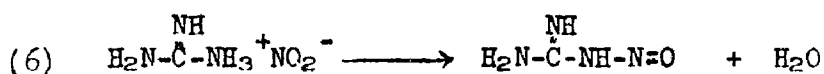
(2) Reaction of Guanidine and 1,1,1-Trinitroethane.

Guanidine, a strong organic base, reacts exothermally with 1,1,1-trinitroethane via an "elimination-addition" mechanism to give the alkylation product, 2,2-dinitroethylguanidine in 92% yield (crude):



The ultraviolet absorption spectrum of 2,2-dinitroethylguanidine (in excess base) shows the characteristic strong absorption band attributed to the gem-dinitro anion at $364 \text{ m}\mu$ ($\log \epsilon = 4.23$); the spectrum is quite similar to those of N-(2,2-dinitroethyl)-piperidine and trimethylammonium-N-(2-nitroethyl-2-nitronate). The infrared spectra of the three amino-dinitro compounds (in Nujol suspension) do not show the sharp, strong band at 6.3μ , normally observed for compounds containing the gem-dinitro group; weak bands are observed at $6.6-6.7 \mu$ and $7.4-7.5 \mu$ (but these are obscured by the powerful absorption of Nujol at $6.7-6.9 \mu$ and $7.2-7.3 \mu$). This evidence indicates that 2,2-dinitroethylguanidine may exist preferentially in the "zwitterion" (or "betaine") form. This supposition is further supported by the salt-like characteristics of this product. It is also of interest that dilute aqueous solutions of 2,2-dinitroethylguanidine are slightly acidic.

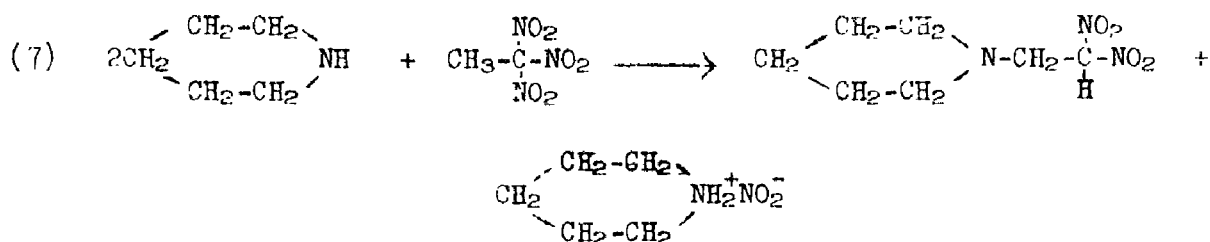
2,2-Dinitroethylguanidine gives a positive nitrosamine (Liebermann) test. At first, it was believed that nitrosoguanidine might be present as an impurity (this could arise from the decomposition of guanidine hydronitrite):



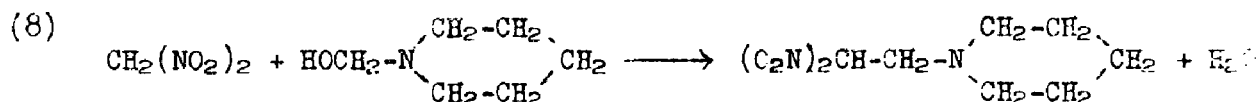
When recrystallized samples of 2,2-dinitroethylguanidine gave positive tests, it was concluded that the action of concentrated sulfuric acid on 2,2-dinitroethylguanidine results in the elimination of nitrous acid (as also happens when alkali metal salts of 1,1-dinitroalkanes are acidified); the nitrous acid reacts with phenol to give the colored nitrosophenol derivative. To substantiate these observations, the Liebermann test was run on trimethylammonium-N-(2-nitroethyl-2-nitronate) and on two samples of N-(2,2-dinitroethyl)-piperidine (one sample was the product of the reaction of piperidine and 1,1,1-trinitroethane, the other was prepared from N-methylolpiperidine and dinitromethane; see below). In each case, a positive test was obtained. As a control, the test was run on 1,1-dinitrobutane; the result was negative.

(3) Proof of Structure of N-(2,2-dinitroethyl)-piperidine.

It has been previously reported⁴ that reaction of piperidine and 1,1,1-trinitroethane yields N-(2,2-dinitroethyl)-piperidine and piperidine hydronitrite:

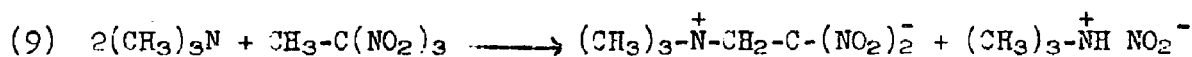


Proof of structure of N-(2,2-dinitroethyl)-piperidine has now been completed by synthesis of this compound by the method of Duden, Bock, and Reid⁵ (the previous investigators did not report any physical constants for N-(2,2-dinitroethyl)-piperidine): dinitromethane (prepared in 31% overall yield from nitromethane via 1-nitro-2-propanol and 1,1-dinitro-2-propanol) in cold ethyl ether was shaken with N-methylolpiperidine in aqueous suspension. N-(2,2-dinitroethyl)-piperidine separated as a yellow salt (93.6%), m.p. 108.0-108.5°; this material did not depress the melting point of the product of reaction of piperidine and 1,1,1-trinitroethane.

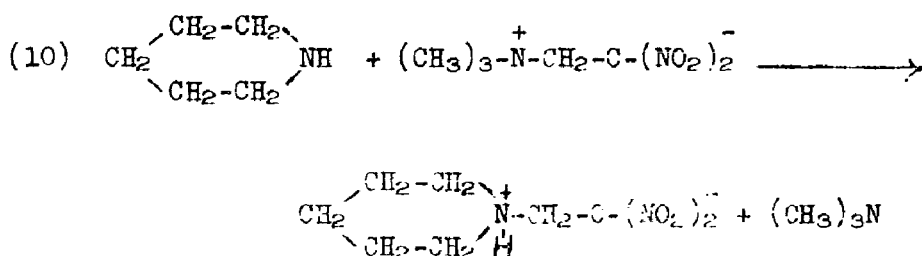


(4) Proof of Structure of Trimethylammonium-N-(2-nitroethyl-2-nitronate)

It has been previously reported⁶ that reaction of trimethylamine and 1,1,1-trinitroethane yields trimethylammonium -N-(2-nitroethyl-2-nitronate):

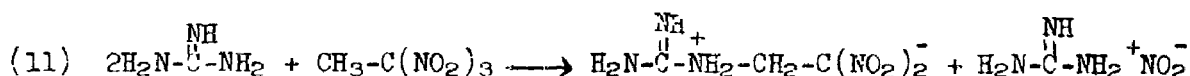


Proof of structure of trimethylammonium-N-(2-nitroethyl-2-nitronate) has now been established by displacement with piperidine in warm water to yield N-(2,2-dinitroethyl)-piperidine in 95.6% yield; N-(2,2-dinitroethyl)-piperidine was verified by its melting point and by mixed melting point with an authentic sample.



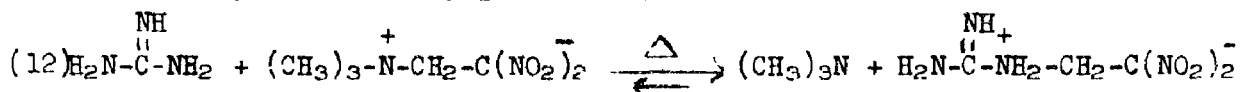
(5) Proof of Structure of 2,2-Dinitroethylguanidine

Reaction of guanidine and 1,1,1-trinitroethane has been reported (page 1) to give 2,2-dinitroethylguanidine and guanidine hydronitrite:



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Proof of structure of 2,2-dinitroethylguanidine has been obtained by exchange of guanidine with trimethylammonium-N-(2-nitroethyl-2-nitronate); 2,2-dinitroethylguanidine was obtained in 28% yield. X-ray diffraction patterns of 2,2-dinitroethylguanidine prepared by both reactions are identical.



(6) Selective Reduction of Nitrocarbonyl Compounds with Sodium Borohydride.

It was previously reported^{7,8,9} that 5-methyl-5-nitro-2-hexanone, 5-nitro-2-hexanone, 5-nitro-2-pentanone, 4-methyl-4-nitropentanal, 5,5-dinitro-2-hexanone, and 4,4-dinitropentanal are reduced to their corresponding alcohols by the action of aluminum isopropoxide in 93.3, 48.0, 24.0, 69.3, 26.7, 87.9 and 62.8 percent yields, respectively. Similarly, 5-methyl-5-nitro-2-hexanone, 5-nitro-2-hexanone, 5-nitro-2-pentanone, 4-methyl-4-nitropentanal, 4-nitrobutanal, 5,5-dinitro-2-pentanone, 4,4,4-trinitrobutanal,¹⁰ and 5,5,5-trinitro-2-pentanone¹⁰ are reduced to their corresponding alcohols by acidic sodium borohydride in 98.7, 50.7, 66.6, 54.8, 33.4, 48.5, 72, and 60 per cent yields.

To complete these studies, reductions of 5,5-dinitro-2-hexanone and 4,4-dinitro-1-pentanal with both acidic and neutral-basic sodium borohydride were investigated. 5,5-Dinitro-2-hexanol and 4,4-dinitro-1-pentanol were obtained in 54.5 and 67.6 per cent yields, respectively, from their corresponding carbonyl compounds by the action of neutral-basic sodium borohydride; 5,5-Dinitro-2-hexanone is reduced in 78.2 per cent yield to 5,5-dinitro-2-hexanol by acidic sodium borohydride. The neutral-basic reaction is more convenient and can be completed in a few minutes; this technic is to be recommended for compounds that are not sensitive to the action of mild bases.

(7) Reduction of Nitroesters with Lithium Borohydride; Nitroalcohols

The selective reduction of nitroaliphatic acid derivatives has been previously limited to the conversion of nitro acid chlorides into nitroalcohols with sodium borohydride.¹¹ Recently, it has been reported that certain nitro esters may be converted into nitroalcohols by lithium aluminum hydride at low temperatures. In order to develop a more general and convenient method for reducing nitroaliphatic acid derivatives, reactions of nitro esters with lithium borohydride have been studied.

Lithium borohydride has a higher reduction potential than sodium borohydride. Lithium borohydride will reduce ester groups to alcohols; however, nitro groups are unattacked. The advantages of lithium borohydride thus are: (1) it reduces esters, acid chlorides, and other carbonyl compounds without affecting the nitro group and (2) it is soluble in organic solvents such as ethyl ether and tetrahydrofuran. It is also soluble in water and methanol and, with proper buffering, can be used in these solvents in much the same manner as sodium borohydride.

Methyl 4-nitrobutyrate, methyl 4-nitropentanoate, methyl 4-methyl-4-nitropentanoate, and methyl 4,4-dinitropentanoate have been reduced to

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their corresponding alcohols in 55, 72, 96 and 84 per cent yields, respectively, with lithium borohydride (methyl 4,4-dinitropentanoate was prepared by oxidative-nitration of methyl 4-nitropentanoate). The reaction technic for small scale reductions, i.e., 0.1 to 0.3 mole, is simply mixing the nitro ester with a standardized solution of lithium borohydride solution and then refluxing the mixture for 2-4 hours. Refinements will probably be advisable for larger scale reductions.

The reduction of esters with lithium borohydride yields a mixture of alkyl borates and lithium alkoxide; thus methyl esters give borate esters of methanol and the nitro alcohols produced and lithium methoxide. If the nitro group present is capable of existing in the aci-form, the lithium alkoxide will convert such nitro groups to their lithium salts. This occurrence is noted in the reduction of methyl 4-nitrobutyrate and methyl 4-nitropentanoate; white insoluble nitronate salts are formed which may undergo the Nef reaction upon acidification. The rate of salt formation is greater with methyl 4-nitrobutyrate than with methyl 4-nitropentanoate.

While nitro groups are not reduced rapidly by lithium borohydride solution, in the reduction of methyl 4-nitrobutyrate, appreciable quantities of colorless, flammable gas were evolved. This may result from the alkoxide formed by reduction of the ester group; the nitronate ion produced may react with lithium borohydride to form the lithium nitronate salt with subsequent exchange and decomposition of the borohydride ion into hydrogen and diborane (tentative). Thus, in cases when decomposition of the reducing agent via salt formation is faster than reduction of the ester, excess hydride is used to compensate for the loss incurred by neutralization of the nitro group.

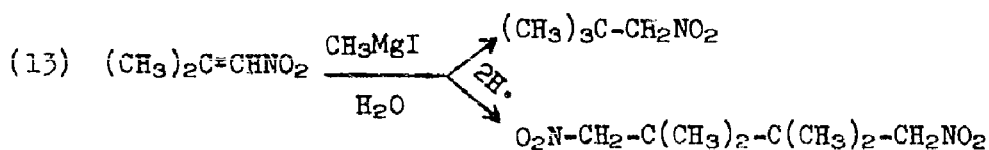
Decomposition of reaction mixtures in which nitronate salts have formed should be effected at low temperatures using reagents such as urea-phosphoric acid that will minimize the Nef and other side reactions.

Initial decomposition of the reaction products yields an aqueous ethereal mixture containing lithium phosphate, nitro alcohol and borate esters of the nitro alcohols. Hydrolysis of the borate esters is conveniently accomplished by acidifying the mixture to pH 1 with hydrochloric acid and refluxing for 15 to 30 minutes. It is convenient to remove the solvent at this point by distillation. The hydrolyzed residue is cooled to room temperature, saturated with salt and extracted with ether. The ether extracts contain the nitro alcohol; the nitro alcohol may be obtained after removal of solvent and distillation.

(8) Reaction of Grignard Reagents with α,β -Nitroolefins;
Reductive-Dimerization.

It has been previously shown in this laboratory⁶ that reaction of methyl magnesium iodide with 2-methyl-1-nitropropene yields 2,2,3,3-tetramethyl-1,4-dinitrobutane along with 2,2-dimethyl-1-nitropropane (Equation 13). Similarly,⁶ reaction of

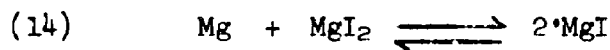
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methyl magnesium iodide with 1-nitro-1-propene gives d,l and meso 2,3-dimethyl-1,4-dinitrobutane along with 2-methyl-1-nitropropane. The formation of dimeric adducts from reactions of alkyl Grignard reagents with conjugated nitroolefins appears general and thus reactions of this type have been classified as involving reductive-dimerization. A study has been initiated therefore to develop a general method for reductive-dimerization of conjugated nitroolefins.

There have been reported many cases in which the presence of free magnesium in a Grignard reaction promotes reduction. In order to study the influence of this variable on the course of the dimerization reaction, reactions of methyl magnesium iodide and 2-methyl-1-nitropropene were conducted in the presence and the absence of free magnesium. It was found that yields in the two reactions were almost identical (ca. 45% 2,2-dimethyl-1-nitropropane and 6% 2,2,3,3-tetramethyl-1,4-dinitrobutane); it was concluded therefore that reductive-dimerization is not greatly influenced by free magnesium.

Gomberg and Bachmann¹⁴ have shown that magnesium sub-iodide promotes reduction of various conjugated unsaturated compounds. Magnesium and magnesium iodide are in equilibrium with magnesium sub-iodide (Equation 14);



even though the concentration of MgI is very low at equilibrium, it has been proposed that the concentration of MgI is sufficiently great to effect reduction of conjugated unsaturates. Since MgI is probably present to some extent in Grignard reactions of methyl iodide, a study of the effect of Mg-MgI₂ on 2-methyl-1-nitropropene has been started. In the initial experiments, 2-methyl-1-nitropropene has been found to be decomposed and no identifiable products have been isolated as yet. Further results of studies of reactions of this type will be reported at a later date.

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EXPERIMENTAL

(1) Preparation of Ethyl 2-Carbethoxy-4,4-dinitrobutyrate
(Improved Procedure)¹

Diethyl malonate (35.2 g., 0.22 mole) was added to a solution of potassium (8.6 g., 0.22 mole) in absolute ethanol (400 ml.). Upon heating the mixture to 79°, the white precipitate of potassium diethyl malonate dissolved. 1,1,1-Trinitroethane (16.5 g., 0.10 mole) in absolute ethanol (50 ml.) was then added at a rate such that ebullition was maintained (0.5 hour). The solution color changed to deep red. Toward the end of the addition, heat had to be applied to keep the solution refluxing. A yellow-orange salt soon precipitated. The reaction mixture was cooled and stirred in an ice-water mixture (3 hours), then filtered. The powdery, yellow-orange salt obtained weighed 27.5 g. A sample of this salt gave a positive test for nitrite ion (liberation of iodine from a solution of sodium iodide acidified with acetic acid).

The salt was suspended in water (100 ml.) with stirring and the mixture was cooled to 0-3°. Urea-acetic acid reagent (84 g., 0.23 mole each of urea and acetic acid)² was precooled to 0-3°, then added dropwise, in 45 minutes, to the salt solution. The acidified solution was extracted with ether; the ether extract was then dried with calcium sulfate. Distillation of the product at reduced pressure, gave ethyl 2-carbethoxy-4,4-dinitrobutyrate¹ (10.09 g., 36.3% conversion), b.p. 126-130° (1.1 mm.).

(2) Proof of Structure of Ethyl 2-Carbethoxy-4,4-dinitrobutyrate.
Conversion to 4,4-Dinitroheptanedioic Acid.

Methyl acrylate (1.30 g., 0.015 mole) was added to a stirred mixture of ethyl 2-carbethoxy-4,4-dinitrobutyrate,* potassium hydroxide (0.434 N, 11.5 ml., 0.00499 mole), and water (14 ml.) at 0-5°. The solution was stirred at 0-5° for 2 hours, then at room temperature for 18 hours. The color of the mixture changed slowly from light yellow to deep amber, and a dense oil settled out. The mixture was extracted with ether; the organic extract was concentrated by distillation. Concentrated hydrochloric acid (30 ml.) was added to the residue, and the mixture was heated to 135-140°. After 4 hours, the oil had dissolved. Heating was continued for another hour. Charcoal was added to the hot, red solution, and the mixture was immediately filtered. After evaporation of most of the aqueous solution, crude 4,4-dinitroheptanedioic acid (0.375 g., 30% conversion), m.p. 135-137.5°, crystallized. After recrystallization from hot water, the acid melted at 138.5-140°; neut. equiv. (calcd.) 125, neut. equiv. (found) 127. An authentic sample, prepared by the hydrolysis of dimethyl 4,4-dinitroheptanedioate,³ melted at 138.5-139.5°. Admixture of the two samples resulted in no depression of the melting point.

* 1.39 g., 0.005 mole.

CONFIDENTIAL

(3) Proof of Structure of N-(2,2-Dinitroethyl)-piperidine.⁵

Potassium dinitromethane (1.44 g., 0.01 mole; this material was prepared in 31% overall yield from nitromethane via 1-nitro-2-propanol and 1,1-dinitro-2-propanol according to the procedure of Kaplan)⁵ was suspended in a mixture of water (7 ml.) and ethyl ether (40 ml.). The mixture was stirred at 0° while sulfuric acid (0.50 N, 25 ml., 0.0125 equiv.) was added dropwise. The pale-yellow ether solution of dinitromethane was separated.

N-Methylolpiperidine was prepared by adding aqueous formaldehyde (36%, 2.0 g., 0.024 mole) to piperidine (1.2 g., 0.14 mole) in water (3 ml.) at 0°. The product separated as an oil.

The ether solution of dinitromethane was added to the aqueous suspension of N-methylolpiperidine; the stirred mixture was cooled in an ice-water bath. The pale-yellow product which separated was filtered, washed with ethanol and ethyl ether, and dried. N-(2,2-Dinitroethyl)-piperidine (1.90 g.) was obtained in 93.6% yield, m.p. 108.0-108.5° (dec.); recrystallization from hot water did not change the melting point of the product. Admixture with a sample of N-(2,2-dinitroethyl)-piperidine prepared from 1,1,1-trinitroethane and piperidine⁴ produced no depression in the melting point.

(4) Proof of Structure of Trimethylammonium-N-(2-nitroethyl-2-nitronate). Exchange Reaction with Piperidine.

Piperidine (0.85 g., 0.01 mole) was added to a stirred mixture of trimethylammonium-N-(2-nitroethyl-2-nitronate) (0.885 g., 0.005 mole) in water (13 ml.) at 50-60°. The solution was stirred at 50-60° for 5 hours, then evaporated at reduced pressure. The yellow solid that remained was covered with absolute ethanol, crushed and filtered. The yield of N-(2,2-dinitroethyl)-piperidine was 0.970 g. (95.6%), m.p. Admixture of this material with the samples of N-(2,2-dinitroethyl)-piperidine previously prepared resulted in no depression of the melting point.

(5) The Reaction of 1,1,1-Trinitroethane with Guanidine.
The Synthesis of 2,2-Dinitroethylguanidine.

A solution of guanidine in absolute alcohol was prepared in the following manner:¹⁷ Sodium ethoxide was prepared from sodium (4.6 g., 0.20 mole) and absolute ethanol (100 ml.). Guanidine carbonate (18.0 g., 0.10 mole = 0.20 mole guanidine) was added; the walls of the flask were then washed with ethanol (25 ml.). The mixture was stirred for 15 minutes, cooled in ice-water for 10 minutes, then filtered. The precipitate of sodium carbonate was washed with several portions of ethanol.

1,1,1-Trinitroethane (8.25 g., 0.05 mole) in absolute ethyl ether (50 ml.) was added dropwise to the ethanolic solution of guanidine. The

CONFIDENTIAL

CONFIDENTIAL

solution turned red, and heat was evolved. The reaction mixture was then stored at 0° for several days. The orange salt that formed was filtered, washed with ethyl ether and sucked dry. The yield of crude 2,2-dinitroethylguanidine was 8.1 g. (92%). The product was recrystallized from boiling water; the yellow needles obtained decomposed at 196-199° (the material darkens slowly and no gas is evolved; determination of the decomposition point is rather arbitrary).

The pure product is very slightly soluble in cold water (pale-yellow solution) and only slightly soluble in boiling water (1 part in 103 parts of water at 100°); it is insoluble in hot or cold acetone, acetonitrile, methanol or piperidine. The compound is soluble in acids (colorless solution) and in dilute base (yellow solution). The pH of the cold aqueous solution is 5.4-5.5. Its ultraviolet spectrogram showed absorption maxima attributed to gem-dinitro resonance at $364\text{m}\mu$ ($\log \epsilon = 4.23$) and to nitro group resonance at $225\text{m}\mu$ ($\log \epsilon = 3.88$); the pattern is similar to those observed for other 1,1-dinitro compounds.⁶ The infrared spectrum was determined in Nujol; the sharp peak observed for most gem-dinitro groups at 6.3μ is absent. Two bands were observed at 5.98μ and 6.08μ ; these are usually attributed to the C=N group¹⁸ and may indicate an aci-nitro as well as the imino group. Weak bands observed at 6.63μ , 7.5μ and 11.9μ are, most likely, nitro group frequencies.

This compound gave a positive nitrosamine (Liebermann) test (see Discussion). This chemical evidence, coupled with the infrared and pH data, suggests that 2,2-dinitroethylguanidine exists mainly in the form of the "zwitterion."

(6) Proof of Structure of 2,2-Dinitroethylguanidine. Alternate Synthesis by Exchange Reaction of Guanidine with Trimethylammonium-N-(2-nitroethyl-2-nitronate).

Guanidine carbonate (1.10 g., 0.006 mole) was dissolved in water (10 ml.) and treated with 0.999 N sodium hydroxide (12.0 ml., 0.012 mole). To this solution was added trimethylammonium-N-(2-nitroethyl-2-nitronate) (1.77 g., 0.01 mole) and water (15 ml.). The clear yellow solution was stirred at 40-45° for 5 hours. The temperature of the mixture was then slowly raised over a three hour period (max. temp. = 80°); heating was then discontinued. On cooling, a yellow salt precipitated. The product was filtered, washed with ethanol and ethyl ether and dried. 2,2-Dinitroethylguanidine was recovered in 0.24 g. yield, dec. range 185-192°. On evaporation of the filtrate to ca. half its original volume, another 0.26 g. of product was obtained; total yield 0.50 g. (28%). Further evaporation yielded a mixture of water-soluble salts composed principally of sodium carbonate.

The product of this reaction will be compared directly with that from reaction of guanidine and 1,1,1-trinitroethane by means of X-ray diffraction patterns. Further proof of identity will be furnished by the preparation and analysis of suitable derivatives.

CONFIDENTIAL

CONFIDENTIAL

(7) Reaction of Trimethylammonium-N-(2-nitroethyl-2-nitronate) with Bromine.

Trimethylammonium-N-(2-nitroethyl-2-nitronate) (0.50 g., 0.0029 mole) was dissolved in water (5 ml.). The solution was vigorously stirred while bromine (0.41 g., 0.00256 mole) was added dropwise. The bromine layer gradually disappeared as orange crystals formed. The mixture was stirred in an ice-water bath for 15 minutes, then filtered. The waxy solid was pressed dry between sheets of filter paper; 0.76 g. (88% calcd. as "dibromide") was obtained, m.p. 77.5° (dec. with evolution of bromine vapors).

The product is insoluble in ether, cold ethanol and cold water (the waxy material is not wet by water). On warming in ethanol or water, the "dibromide" dissolves; on cooling, the salt is not reprecipitated. The product is soluble in cold acetonitrile. When ether is added to the warm ethanol solution of the "dibromide", a white precipitate is formed. This appears to be trimethylammonium bromide; m.p. 244-246° (Fischer m.p. block; sublimation below the melting point was observed). The literature values¹⁹ for this compound are m.p. 243-245°; sublimation about 200°.

(8) Selective Reduction of 5,5-Dinitro-2-hexanone to 5,5-Dinitro-2-hexanol using Sodium Borohydride.

a. Acid Medium: 5,5-Dinitro-2-hexanone (19.0 g., 0.10 mole) was dissolved in a solution of methanol (90 ml.) and water (45 ml.); sodium borohydride (2.00 g., 0.05 mole) in water (50 ml., one drop of 6 N sodium hydroxide added) was added dropwise in 3 hours. The reaction solution was kept at 20-25° during the addition and the pH was maintained below 5 by adding 3M sulfuric acid when needed. When the addition of the hydride was completed, the pH of the solution was adjusted to 2, and water (50 ml.) was added to decompose any salts formed. The reaction mixture was extracted with ethyl ether while salting out the organic material with sodium chloride. The ether extract was washed with brine, dried with sodium sulfate and distilled to yield 5,5-dinitro-2-hexanol⁸ (15.01 g., 78.2% conversion), b.p. 114° (1.1 mm.), $n_D^{20.5}$ 1.4630. The forerun (0.74 g.), b.p. 110-114° (1.3 mm.), $n_D^{20.5}$ 1.4614, was a mixture of product and starting material.

b. Neutral-basic Medium: 5,5-Dinitro-2-hexanone (19.0 g., 0.10 mole) was dissolved in methanol (70 ml.) and water (30 ml.); sodium borohydride (2.00 g., 0.05 mole) in water (30 ml., one drop of 6 N sodium hydroxide was added) was added dropwise (15 minutes) while the reaction mixture was shaken in an ice-water bath. The solution was yellow and considerable gas was evolved near the end of the addition. The pH of the solution at this point was 8.7. Sulfuric acid (3M) was added to the cold reaction solution until the pH was 2. The color changed to blue-green during the acidification step. The mixture was extracted with ethyl ether; the organic matter was salted out with sodium chloride. The ether extract was dried with sodium sulfate, then distilled to yield 5,5-dinitro-2-hexanol⁸ (10.46 g., 54.5% conversion), b.p. 114-116° (1.3 mm.). The forerun (0.27 g.), b.p. to 114° (1.3 mm.), was a mixture of product and starting material.

CONFIDENTIAL

(9) Selective Reduction of 4,4-Dinitro-1-pentanal to 4,4-Pinitro-1-pentanol using Sodium Borohydride.

Sodium borohydride solution (0.795 g., 0.021 mole, in 10 ml. of water containing one drop of 6N sodium hydroxide) was added dropwise (15 minutes) to a stirred solution of 4,4-dinitro-1-pentanal (7.27 g., 0.0413 mole), methanol (25 ml.) and water (10 ml.) cooled in an ice-water mixture. The pH of the mixture, after the reaction was completed, was 9.2. The solution was partially neutralized with urea-acetic acid solution (10 ml., 0.028 mole each of acetic acid and urea; the pH after the addition was 6); the pH was then adjusted to 3 by adding 18 N sulfuric acid (2 ml.). The blue-green acidic solution was extracted with ethyl ether; the ether extract was dried with sodium sulfate and distilled to give 4,4-dinitro-1-pentanol⁸ (4.97 g., 67.6% yield), b.p. 114-118° (1.2 mm.).

(10) Preparation of 1-(Nitromethyl)-cyclohexene.

The procedure of Dauben, et al,²⁰ was employed. Cyclohexanone (56.7 g., 0.58 mole), nitromethane (66.7 g., 1.09 moles) and piperidine (3 g.) were allowed to stand, with occasional shaking, over anhydrous magnesium sulfate (30 g.) for 7 days at room temperature. The red solution was filtered through anhydrous magnesium sulfate. Distillation of the filtrate yielded the following fractions:

<u>Fract.</u>	<u>Boiling Range</u>	<u>Weight</u>	<u>$n_D^{20.5}$</u>	<u>Composition</u>
1	35-55° (40 mm.)	25.7 g.	1.3900	Nitromethane
2	55-80° (20-40 mm.)	8.9 g.	1.4460	Nitromethane and Cyclohexanone
3	80-103° (19-20 mm.)	9.8 g.	1.4695	Cyclohexanone and 1-(Nitromethyl)-cyclohexene
4	103-105 (19 mm.)	40.9 g.	1.4815	1-(Nitromethyl)-cyclohexene

The crude yield of 1-(nitromethyl)cyclohexene is 50.7 g. (62%). The infrared spectrogram of this compound shows that the double bond is not conjugated with the nitro group;²¹ this verifies the chemical evidence given by Fraser and Kon²² and others.²³

(11) Preparation of Methyl 4-Nitropentanoate and Dimethyl 4-Methyl-4-nitroheptanedioate.

a. Triethylamine Catalyst: With minor variations, the procedure of Kloetzel²⁴ was used. Nitroethane (675 g., 9 moles), methyl acrylate (264 g., 3 moles) and triethylamine (152.5 g., 1.5 moles) were mixed at room temperature. On standing for 4 hours, the temperature of the mixture

CONFIDENTIAL

rose to 44° and the color was green. The solution was placed in a water bath to moderate the temperature; the solution was stored at 28-32° for 4 days.

The solution was extracted with 13% hydrochloric acid (400 ml.). Ethyl ether and brine were added to aid in separation of the organic and aqueous layers. The organic layer was distilled to yield (a) methyl 4-nitropentanoate (314.8 g., 65.1% conversion), b.p. 88-91° (2-3 mm.), n_D^{20} 1.4345-1.4366, d_4^{20} 1.128, and (b) dimethyl 4-methyl-4-nitroheptanedioate (74.5 g., 20.1% conversion), b.p. 125-140° (0.8-1.1 mm.). The latter product was not reported by Klotzel.

(12). Oxidative-Nitration of Methyl 4-Nitropentanoate; Methyl 4,4-Dinitropentanoate.

Methyl 4,4-Dinitropentanoate - Methyl 4-nitropentanoate (113 g., .70 mole) in methanol (140 ml.) was added in 30 minutes to a solution of sodium (18g., 0.78 mole) in methanol (450 ml.) at 0-2° in a 2-liter, 3-necked flask equipped with a mechanical stirrer, dropping funnel, and thermometer. A solution of ice cold sodium nitrite (53 g., 0.77 mole in 500 ml. water) was then added to the mixture at temperatures below 5°. The resulting solution was then poured into a stirred mixture of silver nitrate (218g., .13 mole), ethyl ether (200 ml.) and water (100 ml.) at 0-5°. A complex formed which quickly turned black; gases were evolved and the temperature of the mixture rose. After the suspension had been stirred for 10 minutes, hydrochloric acid (a few ml.) was added and the mixture was filtered. The aqueous filtrates were extracted with ethyl ether; the filter residue was washed with methanol (3 x 200 ml.) After the methanolic extracts had been distilled ~~on~~ a steam bath to remove methanol, the cooled residue was dissolved in ethyl ether. The ether extracts were dried with sodium sulfate; the ether was evaporated; and the residue was distilled at reduced pressure to give methyl 4,4-dinitropentanoate (107 g., 72% yield); b.p. 90-91° (0.5 mm), lit.²⁵ 94-97° (0.6-0.7 mm.); $n_D^{19.5}$ 1.4457, lit.²⁵ n_D 1.4456

(13). Reduction of Methyl 4-Nitrobutyrate with Lithium Borohydride; 4-Nitro-1-butanol.

4-Nitro-1-butanol. - A solution of methyl 4-nitrobutyrate (18.84g., .125 mole) and ethyl ether (50 ml.) was added to a 0.57 molar solution (310 ml) of lithium borohydride in ethyl ether. An exothermic reaction occurred which resulted in the formation of a white precipitate and the evolution of a flammable gas (probably hydrogen or diborane). After the initial reaction had subsided, the mixture was refluxed for 4 hours. The mixture was then cooled to 0-2° and a solution of phosphoric acid (85%, 30 ml.), urea (10g.) and water (120 ml.) was added at a rate such that the temperature was maintained below 5°. The mixture then consisted of a lower aqueous layer containing some insoluble matter (which dissolves on further dilution) and an upper colorless layer of tetrahydrofuran which contains the reduction products. Hydrochloric acid was added to raise the pH of the mixture to 1;

CONFIDENTIAL

the mixture was distilled from a steam bath to remove tetrahydrofuran and to hydrolyze the borate esters. The residue was cooled to room temperature, saturated with sodium chloride, and extracted with ethyl ether (3 x 70 ml.). After the extracts had been dried with sodium sulfate and then evaporated, the residue was distilled at reduced pressure to yield 4-nitro-1-butanol (7.92 g., 53% yield), b.p. 74-75° (0.5 mm.), lit.^{7,9} b.p. 103-103.5° (2 mm.); $n_D^{19.5}$ 1.4508, $n_D^{19.5}$ 1.4510. A small quantity of red residue which contained boron compounds remained in the distilling flask.

The ratio of lithium borohydride to nitro ester in this experiment was 1.5:1. The use of smaller ratios resulted in the recovery of some unreduced starting material.

(14) Reduction of Methyl 4-Methyl-4-nitropentanoate with Lithium Borohydride; 4-Methyl-4-nitro-1-pentanol.

4-Methyl-4-nitro-1-pentanol. - A mixture of methyl 4-methyl-4-nitropentanoate (21 g., 0.12 mole) in ethyl ether (50 ml.) was added to a 0.57 M solution (125 ml., .071 mole) of lithium borohydride in tetrahydrofuran. After a mild exothermic reaction had occurred, the mixture was refluxed for 3 hours. The mixture then consisted of a clear solution containing a small amount of suspended gelatinous matter. The mixture was cooled to room temperature and hydrochloric acid (100 ml., 6 N) was added. The resulting two-layer system was distilled to remove the solvents and hydrolyze any borate esters that were present. The residue was cooled to room temperature saturated with sodium chloride, and extracted with ethyl ether (3 x 60 ml.). After the ether extracts had been dried over sodium sulfate and evaporated, the residue was distilled at reduced pressure to yield 4-methyl-4-nitro-1-pentanol (17.0 g., 96% yield); b.p. 83-84° (0.3 mm.), lit.^{7,9} 111-115° (3 mm.), $n_D^{19.5}$ 1.4505, lit.^{7,9} $n_D^{19.5}$ 1.4507.

(15) Reduction of Methyl 4,4-Dinitropentanoate with Lithium Borohydride; 4,4-Dinitro-1-pentanol.

By using the preceding procedure, methyl 4,4-dinitropentanoate (26 g., .12 moles) was reduced with 0.57 M lithium borohydride-tetrahydrofuran (125 ml., .071 moles) to give 4,4-dinitro-1-pentanol (17 g.) in 74% yield; b.p. 102-104° (0.3 mm.), lit.^{8,9} 109-110° (0.8 mm.); $n_D^{19.5}$ 1.4670, lit.^{8,9} $n_D^{20.0}$ 1.4669.

(16) Reduction of Methyl 4-Nitropentanoate with Lithium Borohydride; 4-Methyl-4-nitro-1-pentanol.

4-Nitropentanol. - A mixture of methyl 4-nitropentanoate (19.21 g., 0.21 mole) in ethyl ether (50 ml.) was added to a 0.57 M solution (135 ml., .078 moles) of lithium borohydride in tetrahydrofuran. A mild exothermic reaction occurred and the mixture was refluxed for 3 hours. A white precipitate formed slowly. The mixture was then cooled to 0-2° and a solution of phosphoric acid (85%, 10 ml.), urea (5 g.) and water (40 ml.) was added at a rate such that the temperature was maintained below 5°. A small

CONFIDENTIAL

quantity of hydrogen was evolved. The mixture then consisted of a lower aqueous layer and an upper colorless layer of tetrahydrofuran containing the reduction products. Hydrochloric acid was added to raise the pH of the mixture to 1 and the mixture was distilled from a steam bath to remove the tetrahydrofuran and to hydrolyze the borate esters. The residue was cooled to room temperature, saturated with sodium chloride, and extracted with ethyl ether (3 x 60 ml.). After the extracts had been dried with sodium sulfate and then evaporated, the residue was distilled at reduced pressure to yield 4-nitro-1-pentanol (9.6g., 72% yield); b.p. 72-73° (0.5mm.), lit.^{7,9} b.p. 91-92° (1mm.); n_D^{20} 1.4480, lit.^{7,9} n_D^{20} 1.4475.

(17) Reaction of Methyl Magnesium Iodide with 2-Methyl-1-nitropropene in the Absence of Free Magnesium; Isolation of 2,2-Dimethyl-1-nitropropane and 2,2,3,3-Tetramethyl-1,4-dinitrobutane.

Methyl magnesium iodide (0.15 mole) in dry ethyl ether (70 ml.) was prepared in the usual manner: magnesium turnings (3.7 g., 0.15 mole) were added to a 300 ml., three-necked flask equipped with a reflux condenser and drying tube, a sealed stirrer, and a dropping funnel. After flaming and cooling the flask under a flow of nitrogen, a solution of methyl iodide (21.3 g., 0.15 mole) in dry ether (70 ml.) was added to the magnesium. The methyl iodide was added slowly at first until a reaction was initiated and then more rapidly with occasional cooling. The mixture was refluxed on a water bath for 30 minutes and filtered through a sintered glass disc into a flask containing the same equipment as above.

The Grignard reagent was cooled to 0° and 2-methyl-1-nitropropene (15.2 g., 0.15 mole) in dry ether (25 ml.) was added dropwise in 2 hours at 0°. A vigorous reaction and formation of a solid complex occurred upon introduction of each drop of 2-methyl-1-nitropropene. The mixture was acidified at 0° with aqueous acetic acid (15 ml. of glacial acetic acid in 100 ml. of water); stirring was difficult until the complex had dissolved. The ether layer was separated; the aqueous layer was extracted with ether (100 ml.). The combined ether extract was neutralized with sodium bicarbonate and washed with 5% sodium bicarbonate solution (2 x 100 ml.), water (100 ml.) and saturated sodium chloride solution (100 ml.). The ether solution was dried over anhydrous sodium sulfate. Distillation of the product at reduced pressures, after removal of the solvent, gave crude 2,2-dimethyl-1-nitropropane (9.18 g., 0.0783 mole, 52.2% theory) b.p. 76-78° (65 mm.), n_D^{20} 1.4213-1.4256. Redistillation of this volatile product gave the following fractions:

b.p.	Weight	n_D^{20}	d_{20}^{20}	MR _D (found)
(1) 35-72° (63 mm.)	0.74 g.	1.4180	0.9524	31.01
(2) 72-74° (60-63 mm.)	1.41	1.4209		
(3) 74-74.5° (60 mm.)	2.80	1.4219	0.9569	31.11
(4) 74.5-74° (60 mm.)	1.82	1.4239		
(5) 74-72° (58-60 mm.)	1.05	1.4291	0.9681	31.20
			MR _D (calcd.)	30.92

The 2,2-dimethyl-1-nitropropane is not pure and infrared analyses are being made to identify the contaminant (presumably 2-methyl-1-nitropropene): lit.²⁶ b.p. 77-78° (65 mm.); 150-151°; m.p. 13-14°; n_D^{30} 1.4099, d_4^{20} 0.9494.

The residue from the first distillation solidified and was recrystallized once from ethanol to give crude 2,2,3,3-tetramethyl-1,4-dinitrobutane (0.98 g., 0.0048 mole, 6.4% theory), m.p. 135-137°. Four recrystallizations from ethanol gave a very pure product, m.p. 141-142°, which gave no depression in melting point when mixed with an authentic sample.⁶

(18) Reaction of Methyl Magnesium Iodide with 2-Methyl-1-nitropropene in the Presence of Free Magnesium; Isolation of 2,2-Dimethyl-1-Nitropropane and 2,2,3,3-Tetramethyl-1,4-dinitrobutane.

2-Methyl-1-nitropropene (15.2 g., 0.15 mole) in ether (25 ml.) was added in 1.5 hours at 0° to methyl magnesium iodide (24.9 g., 0.15 mole, 1.87 N in ethyl ether) and magnesium (3.65 g., 0.15 mole) contained in a dry (flamed) 300 ml., three-necked flask equipped with a reflux condenser and drying tube, a sealed stirrer, and a dropping funnel. A vigorous reaction and the formation of a complex occurred upon the introduction of each drop of 2-methyl-1-nitropropene. After addition was completed, the mixture was stirred for 15 minutes at 0° and then acidified at 0° with aqueous acetic acid (15 ml. of glacial acetic acid in 100 ml. of water); stirring was difficult until the complex had dissolved. The reaction mixture was then filtered from the magnesium. The ether layer was separated; the aqueous layer was extracted with ether (100 ml.). The combined ether extract was washed with 5% sodium bicarbonate solution until evolution of carbon dioxide was complete, then with water (100 ml.) and finally with saturated sodium chloride solution (100 ml.). The ether solution was dried over anhydrous sodium sulfate. Distillation of the product at reduced pressures, after removal of the solvent on a steam bath, gave 2,2-dimethyl-1-nitropropane (7.57 g., 0.0646 mole, 43.1% theory) as a light yellow liquid, b.p. 76-77.5° (65 mm.), n_D^{20} 1.4191-1.4222.

The residue from the distillation was recrystallized once from ethanol to give crude 2,2,3,3-tetramethyl-1,4-dinitrobutane (0.95 g., 0.0045 mole, 6.2% theory). Four recrystallizations from ethanol gave a very pure product, m.p. 141-142°, which did not depress the melting point of an authentic sample.⁶

(19) Reaction of Methyl Magnesium Iodide and 2-Methyl-1-Nitropropene.

Dry ethyl ether (70 ml.), dry benzene (55 ml.) and powdered magnesium (0.14 mole, 3.40 g.) were placed in a 300 ml., round-bottomed flask equipped with a dropping funnel, a sealed stirrer and a reflux condenser with drying tube. Iodine (8.88 g., 0.07 mole, dried over sulfuric acid) was added in small portions such that the mixture refluxed gently. The clear solution (powdered magnesium was present) was cooled to 0°, and a solution of 2-methyl-1-nitropropene (7.08 g., 0.07 mole) in benzene (25 ml.) was added dropwise in 30 minutes at 0°. As the nitroolefin was added, the solution

turned brownish-red in color. After stirring overnight in an ice bath, a black gum was present. Aqueous acetic acid (6 ml. of glacial acetic acid in 20 ml. of water) was added at 0°. The solvent layer was separated from the black gum and magnesium; the gummy product was dissolved in ethanol and quickly filtered from the magnesium. The solvent layers were combined and washed with 5% sodium bicarbonate (2 x 100 ml.), water (100 ml.) and saturated sodium chloride solution (100 ml.). After drying the solution over anhydrous sodium sulfate and removal of the solvents on a steam bath, a brown oil (2.7 g.) remained which could neither be distilled at reduced pressures nor recrystallized.

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Investigators L. Friedman, D. L. & L. Zeldin Date April 10, 1951
Supervisor H. E. Hechter Date 4.10.51

FOR THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION

Executive Director Oran C. Woolpert Date 12 AUG 1951
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