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Division 8
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

CERTAIN ALIPHATIC NITRAMINES AND RELATED COMPOUNDS

by
Alfred T. Blomquist

Report OSRD No. 4134
Copy No. 45
Date: November 29, 1944

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Division 8
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Section 8.2

CERTAIN ALIPHATIC NITRAMINES AND RELATED COMPOUNDS

Service Project: OD-6

Endorsement (1) Dr. John R. Johnson, Chief, Section 8.2 to Dr. Ralph Connor, Chief, Division 8.

Forwarding report and noting:

"The excellent explosive properties of the cyclic nitramine RDX have prompted investigations of other nitramines, particularly those of open-chain aliphatic type. Under Service Project OD-68 methods for the large scale production of ethylenedinitramine (Haleite) were studied and a satisfactory process was developed through the pilot plant stage (OSRD-3466, 3851, 3857).

"Exploratory laboratory studies of a wide variety of nitramines were initiated in 1941 and several progress reports have appeared (OSRD-152, 819, 915, 2054, 3565, 3567). The present report covers work carried out at Cornell University for the period September 15, 1942 to September 30, 1944, including tests of explosive properties carried out at the Explosives Research Laboratory at Bruceton.

"One of the objects of this study was to prepare the nitramine analogs of several known nitrate-ester explosives. This was accomplished for the following: 1,2,3-trinitraminopropane and 2-nitroxy-1,3-dinitraminopropane (analogs of nitroglycerine), pentaerythritol tetranitramine (analog of PETN), pentaglyceryl trinitramine (analog of pentaglycerine trinitrate), nitroxyethylnitramine (related to glycol dinitrate and Haleite), dinitroxyethylnitramine (related to diglycol dinitrate). In general the nitramine analogs have excellent explosive properties and are usually somewhat less sensitive to impact, but they have higher melting-points and most of them are much more difficult to prepare.

Endorsement (1) (Continued)

"The most important outgrowth of the research on new nitramines has been the development of mixed nitramine nitrate esters, such as N-alkyl nitroxyethylnitramines (Alkyl NENA's) and dinitroxyethylnitramine (DINA), which are promising candidates as ingredients of special propellants (OSRD-3726). Compounds of the NENA type, including the dinitroxyethyl derivative of Haleite are being investigated as plasticizers for nitrocellulose. Laboratory and semi-works studies of the production of DINA are now being carried forward intensively and a pilot plant for the production of flashless powder containing DINA in place of nitroglycerin (Albanite) is expected to be in operation in the near future."

(2) from Dr. Ralph Connor, Chief, Division 8 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and concurring in the above endorsement.

This is a progress report under Contract OEMsr-193 with Cornell University.

ACKNOWLEGMENT

The studies presented in this report represent the researches of Dr. Fred T. Fiedorek carried out during the past two years. A certain amount of related material which has been included is due to the efforts of Dr. J. F. Ryan, Jr., and Dr. S. M. Tsang.

All data on the explosives properties of compounds described in this report were obtained by the research group at the Explosives Research Laboratory at Bruceton, Pa.

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CERTAIN ALIPHATIC NITRAMINES AND RELATED COMPOUNDS

by

Alfred T. Blomquist

ABSTRACT

This report presents the results of investigations dealing with the preparation and properties of some aliphatic nitramines.

Several compounds related to ethylenedinitramine (Haleite) were prepared. N-methyl-ethylenedinitramine, N,N'-dimethyl-ethylenedinitramine and dinitropiperazine were obtained by alkylating ethylenedinitramine. When N-methyl-ethylenedinitramine was reacted with ethylene dibromide two isomeric compounds, N^1,N^4-dimethyltriethylenetetranitramine and iso-N^1,N^4-dimethyltriethylenetetranitramine were isolated. The latter substance was shown to have a single isonitramino linkage.

The effect of cold absolute nitric acid on nitramines was studied. In general, primary nitramines are converted into the corresponding nitrates, secondary nitramines are unaffected, and isonitramines are cleaved at the isonitramino linkage to give nitrates.

Halogenation of ethylenedinitramine and its monomethyl derivative with iodine was unsuccessful. However, these

compounds could be successfully brominated to give N-bromo derivatives.

Propylenedinitramine was prepared using the procedure of Franchimont which involved nitration of the urethane followed by ammonolysis of the nitrourethane.

Nitramino derivatives of neopentane, including pentaerythrityl tetranitramine and pentaglyceryl trinitramine, were synthesized from pentaerythritol and pentaglycerine. Pentaglycol dinitramine was not prepared because of the difficulty of obtaining the corresponding diamine.

The nitramino analog of nitroglycerine, 1,2,3-trinitraminopropane, was synthesized in small yields following a procedure outlined by Bachmann.

The synthesis of tris(nitraminomethyl)amine was attempted but not accomplished. Several methods were employed but in no case could the desired product be obtained.

Nitroxyalkyl nitramines were prepared from a variety alkylol amines, some of which are commercially available, through the application of the catalyzed Bamberger reaction. This reaction, discovered by Dr. George F. Wright at Toronto, may be represented as the conversion of secondary amine nitrates into nitramines by means of acetic anhydride in the presence of a chloride ion catalyst.

$$R_1R_2NH_2^{+}NO_3^{-} \xrightarrow[Cl^{-}]{Ac_2O} R_1R_2N\text{-}NO_2 + H_2O$$

N-(β-nitroxyethyl)methylnitramine, N-(β-nitroxyethyl)ethylnitramine, N-(β-nitroxypropyl)methylnitramine, N,N'-bis(β-nitroxyethyl)ethylenedinitramine, and N,N-bis(β-nitroxypropyl nitramine were obtained from the corresponding amino-alcohol. Other nitroxyalkyl nitramines were prepared by the Franchimont technique. These include N-(β-nitroxyethyl)nitramine, N-(β-nitroxypropyl)nitramine, and dinitraminoisopropyl nitrate. From trimethylol aminomethane two nitrated compounds were obtained, 4,4-bis-(nitroxymethyl)oxazolidone and 3-nitro-4,4-bis(nitroxymethyl)oxazolidone.

The synthesis of pentaglycerine from propionaldehyde and formaldehyde was studied in light of its application to the preparation of pentaglyceryl trinitramine, and pentaglyceryl trinitrate. As side products there were isolated acetals whose structures we have ascertained.

Also, presented in this report is a detailed account of experiments conducted on the ammonolysis of pentaerythrityl bromide.

The explosive properties of several alkyl nitramines and nitroxyalkyl nitramines are presented.

INTRODUCTION

Investigations of aliphatic nitramines have, until recently, occupied the attention of relatively few chemists through whose efforts the principal facts concerning their preparation, chemical behavior, and properties have been determined. The most intensive study of this class of compounds was made during the first thirty-five years following their discovery. These studies laid the foundation for a new field of chemical compounds of great value because of their potentially high explosive character.

With advancements in production methods, the industrial manufacture of a great variety of aliphatic amines, alkylol amines, and related compounds reached great proportions, and a new source of intermediates for the manufacture of explosives was opened. In light of this fact it is not surprising that at the present time investigations of aliphatic nitramines should receive renewed and exhaustive studies on their possible utilization as explosives.

Belonging to this class of compounds are the greatly important RDX and Haleite whose advantages as modern military explosives are well recognized. Moreover, the applications of aliphatic nitramines are not limited to the field of high explosives for many nitramines such as DINA (bis-β-nitroxyethylnitramine) have properties which indicate that they may be important components of flashless propellants.

The purpose of our investigation originally centered on the study of the preparation and properties of certain aliphatic nitramines so that data relating the structures of various nitramino compounds with their explosive properties might be obtained.

While this work was in progress, investigations by Dr. L. J. Hoard at Cornell and by ERL at Bruceton indicated that some of the aliphatic nitramines, in particular the nitroxyalkyl nitramines, might be of interest as plasticizers for nitrocellulose in special propellants. As a result of this practical application the purpose of the investigation was somewhat broader in scope than originally planned.

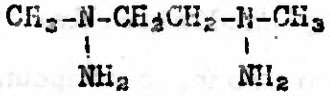
DISCUSSION

Compounds Related to Ethylenedinitramine

Derivatives of ethylenedinitramine have important theoretical significance in establishing the effect of constitution and configuration of an isomeric series of nitramine upon its physico-chemical properties and an equally important correlation can be obtained through a study of compounds containing various substituents attached to the parent molecule. A study of the synthesis of such compounds upon which is contingent such a survey is described.

Alkylation Studies of Ethylenedinitramine.

Several alkyl derivatives of ethylenedinitramine have been known for some time. Franchimont and Klobbie[1] prepared N-methyl-ethylenedinitramine (m.p., 121-2°C.) and N,N-dimethyl-ethylenedinitramine (m.p., 137°C.) by alkylating ethylenedinitramine with methyl iodide and somewhat later the latter was also prepared by alkylation with an excess of methyl sulfate. At the time of their first preparation the structures of these two compounds were uncertain. Employing electrolytic reduction Backer[2] showed that the dimethyl derivative of ethylenedinitramine was transformed into a hydrazine derivative of the following structure:

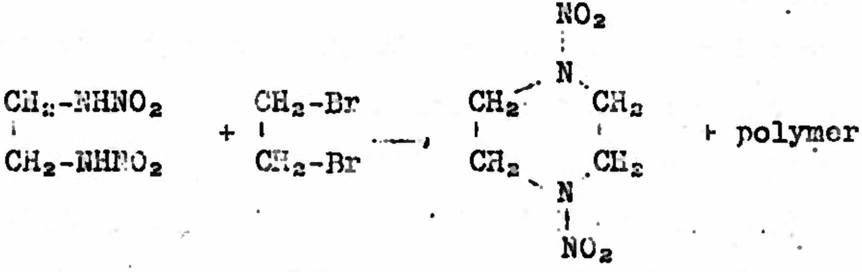


$$CH_3-\underset{NH_2}{\underset{|}{N}}-CH_2CH_2-\underset{NH_2}{\underset{|}{N}}-CH_3$$

This left no uncertainty as to the structure of the unreduced compound.

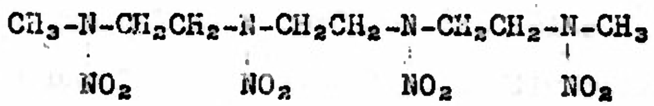
We repeated the preparation of N-methyl and N,N'-dimethylethylenedinitramine, paralleling the procedure of Franchimont using methyl bromide and obtained satisfactory yields. However, alkylation with methyl sulfate was found to be more efficacious. Using ratios of two moles of ethylenedinitramine to three moles of methyl sulfate there were obtained 34.9 per cent yields of the dimethyl derivative and 30.3 per cent of the monomethyl compound.

The reaction of ethylenedinitramine and ethylenedibromide yielded a cyclic compound, which was shown to be N,N'-dinitropiperazine, and a mixture of other compounds of a polymeric nature. The latter were not studied in detail. The equation for this reaction is the following:



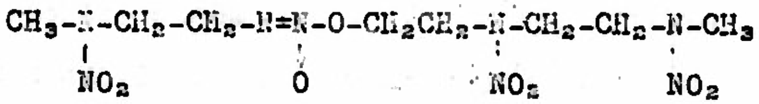
Alkylation Studies of N-Methyl-ethylenedinitramine.

When N-methyl-ethylenedinitramine was alkylated, using ethylene dibromide, two isomeric compounds of the empirical formula, $C_8H_{18}O_8N_8$, were isolated. These compounds melted at 211.5 -213° C., d, and 88.5-90°C. From an examination of the molecular formula it was concluded that each of the two isomers possessed one of the following three structures:



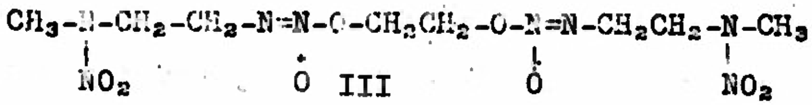
$$\mathrm{CH_3-\underset{NO_2}{N}-CH_2CH_2-\underset{NO_2}{N}-CH_2CH_2-\underset{NO_2}{N}-CH_2CH_2-\underset{NO_2}{N}-CH_3}$$

I



$$\mathrm{CH_3-\underset{NO_2}{N}-CH_2-CH_2-N=\underset{O}{N}-O-CH_2CH_2-\underset{NO_2}{N}-CH_2-CH_2-\underset{NO_2}{N}-CH_3}$$

II



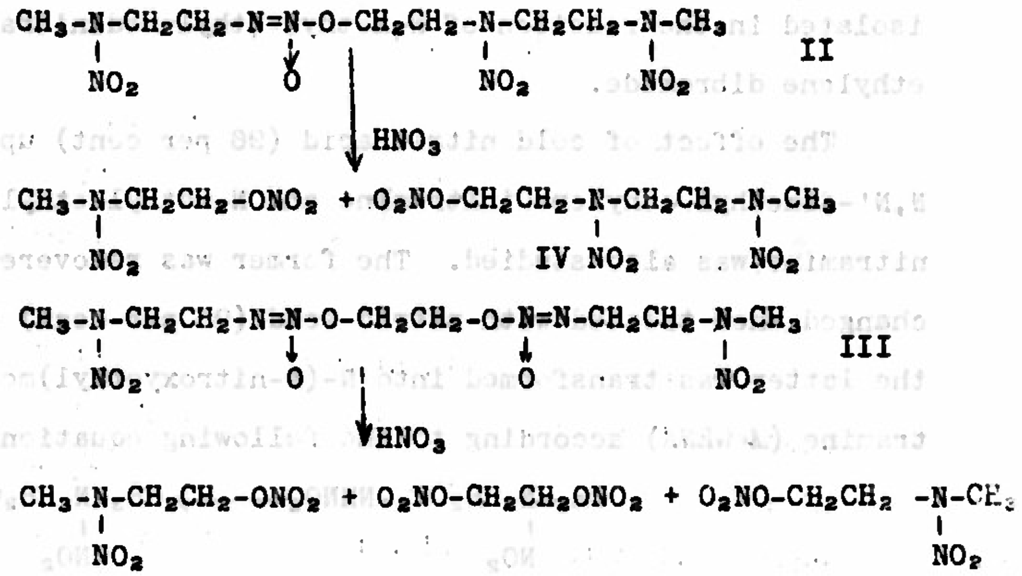
$$\mathrm{CH_3-\underset{NO_2}{N}-CH_2-CH_2-N=\underset{O}{N}-O-CH_2CH_2-O-\underset{O}{N}=N-CH_2CH_2-\underset{NO_2}{N}-CH_3}$$

III

The latter two formulae it is observed represent molecules containing an isonitramine type of linkage.

In ascertaining the structure of the two isomers which were isolated, nitric acid (98 per cent) was employed. It is observed that the formula indicated as I should be unaffected by nitric acid; II should be cleaved to give N-(β-nitroxyethyl)methylnitramine and N-methyl-N'-(β-nitroxyethyl)ethylenedinitramine; III should be cleaved to yield N-(β-nitroxyethyl)methylnitramine and glycol dinitrate.

These transformations can be represented by the following equations:



$$CH_3-\underset{\substack{|\\NO_2}}{N}-CH_2CH_2-N=\underset{\substack{\downarrow\\O}}{N}-O-CH_2CH_2-\underset{\substack{|\\NO_2}}{N}-CH_2CH_2-\underset{\substack{|\\NO_2}}{N}-CH_3 \quad \text{II}$$

$$\Big\downarrow HNO_3$$

$$CH_3-\underset{\substack{|\\NO_2}}{N}-CH_2CH_2-ONO_2 + O_2NO-CH_2CH_2-\underset{\substack{|\\NO_2}}{N}-CH_2CH_2-\underset{\substack{|\\NO_2}}{N}-CH_3 \quad \text{IV}$$

$$CH_3-\underset{\substack{|\\NO_2}}{N}-CH_2CH_2-N=\underset{\substack{\downarrow\\O}}{N}-O-CH_2CH_2-O-\underset{\substack{\downarrow\\O}}{N}=N-CH_2CH_2-\underset{\substack{|\\NO_2}}{N}-CH_3 \quad \text{III}$$

$$\Big\downarrow HNO_3$$

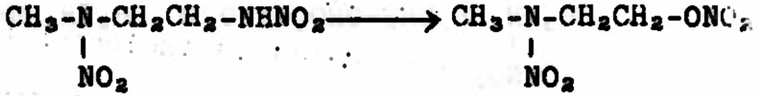
$$CH_3-\underset{\substack{|\\NO_2}}{N}-CH_2CH_2-ONO_2 + O_2NO-CH_2CH_2ONO_2 + O_2NO-CH_2CH_2-\underset{\substack{|\\NO_2}}{N}-CH_3$$

Actually, when the high melting isomer was treated with nitric acid, it was recovered unchanged, thus this compound must be of the structure indicated by formula I, e.g., N^1,N^4-dimethyl-triethylenetetranitramine. Two products were isolated when the low melting alkylation product was treated with nitric acid. One of these was shown to be identical with N-(β-nitroxyethyl)methylnitramine and analysis of the other product was in agreement with the formula, $C_5H_{11}O_7N_5$(IV). The low melting isomer was thus shown to be II.

The Effect of Nitric Acid on Some Alkyl Derivatives of Ethylenedinitramine.

The usefulness of nitric acid (98 per cent) as a reagent for aiding in the determination of the structure of nitramines and isonitramines is already somewhat apparent in light of its application in ascertaining the configuration of the isomers isolated in the reaction of N-methyl-ethylenedinitramine and ethylene dibromide.

The effect of cold nitric acid (96 per cent) upon N,N'-dimethyl-ethylenedinitramine and N-methyl-ethylenedinitramine was also studied. The former was recovered unchanged when treated with nitric acid (98 per cent) at 10°C.; the latter was transformed into N-(β-nitroxyethyl)methylnitramine (MeNENA) according to the following equation:



$$\underset{\displaystyle NO_2}{CH_3\text{-}\underset{|}{N}}\text{-}CH_2CH_2\text{-}NHNO_2 \longrightarrow \underset{\displaystyle NO_2}{CH_3\text{-}\underset{|}{N}}\text{-}CH_2CH_2\text{-}ONO_2$$

This reaction served in positively establishing the nature of the alkyl group attachment as N-methyl and not O-methyl. Also N-(β-nitroxyethyl)methylnitramine has been prepared by other more direct means (see page 31).

The effect of cold nitric acid (98 per cent) on these nitramines can be expressed by the following equations:

$$RNHNO_2 \longrightarrow RONO_2$$

$$R_2NNO_2 \longrightarrow \text{No Reaction}$$

$$RN{=}NO_2R' \longrightarrow RONO_2 + R'ONO_2$$

Salts of Ethylenedinitramine and Its Derivatives

Primary nitramines behave as acids and thus form salts with bases but the constitution of these metallic derivatives is questionable. The original formula, $R\text{-}N\overset{*}{Me}\text{-}NO_2$, as well as a somewhat more recent formulation, $R\text{-}N{=}NO_2Me$, have been used for these salts. These representations, we believe, are somewhat misleading in that they tend to localize the negative charge of the anion. A more preferable representation would be the following:

$$[R\text{-}NNO_2]^{-}\ Me^{+}$$

By this designation the site of the negative charge would not be attributed to any fixed atom and would be more commendable in light of the modern resonance theories.

In studying ethylenedinitramine, Franchimont and Klobbie[2] prepared several of its salts. We likewise have prepared a few salts, some of which were used in absorption spectra studies at the University of Pennsylvania. The compounds which were prepared included the diammonium and dipotassium salts.

The same metal salts of N-methyl-ethylenedinitramine were also prepared for like studies. In addition, the silver salt of N-methyl-ethylenedinitramine was prepared. This compound was decomposed by light and detonates when struck a heavy blow with a hammer.

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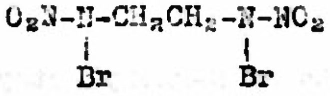
* Me= Metal

Halogen Derivatives of Ethylenedinitramine and Related Compounds.

N-halogen derivatives of aromatic nitramines have been purported to exist[4], but are extremely unstable. Mention regarding N-haloalkylnitramines, however has received no publication.

Some interest had been shown in the synthesis of halogenated aliphatic nitramines, particularly N-iodonitramines. These compounds would have possible uses as tracer compounds and might, if stable enough, be used as detonators. The results of the studies which have been carried out, however, indicate that the compounds are quite unstable. It has been impossible to prepare N-iodonitramines by any synthesis thus far attempted and the N-bromonitramines which have been prepared decompose very easily.

When ethylenedinitramine was allowed to react with bromine a compound was obtained for which a quantitative elementary analysis indicated the following structure.



$$O_2N-\underset{\displaystyle Br}{\underset{|}{N}}-CH_2CH_2-\underset{\displaystyle Br}{\underset{|}{N}}-NO_2$$

This compound, N,N'-dibromo-ethylenedinitramine, was quite unstable. On standing overnight in a dessicator the odor and color of bromine were noticeable. It liberated free iodine from an aqueous solution of potassium iodide although the reaction slowed down finally so that it could not be used quantitatively. When heated on platinum foil it flashed and completely decomposed. A small sample wrapped in tinfoil detonated very loudly when struck on the anvil with a three-inch hammer blow.

All attempts to prepare N,N'-diiodo-ethylenedinitramine were unsuccessful. It is believed that the iodo compound, if formed, is to unstable to be isolated and purified. The procedures tried are described below.

The potassium salt of ethylenedinitramine in aqueous solution was treated with solid iodine in one attempt and with a solution of iodine in potassium iodide in a second. Both gave no products. The potassium salt of ethylenedinitramine in aqueous solution was treated with iodine monochloride. The iodine monochloride decomposed in water liberating free iodine. A similar reaction was carried out in methanol and again no water-insoluble products were obtained. The ammonium salt of ethylenedinitramine in aqueous ammonia solution was treated with iodine in the hope that nitrogen triiodide might undergo an exchange reaction with ethylenedinitramine. Only a brown precipitate of nitrogen triiodide formed. Finally, N,N'-dibromo-ethylenedinitramine was treated with a saturated methanol solution of potassium iodide. Iodine was liberated and the potassium salt of ethylenedinitramine precipitated. No water insoluble products were formed in any of these experiments and there appeared to be no evidence for the formation of N,N'diiodo-ethylenedinitramine.

Halogenation of N-methyl-ethylenedinitramine (MeEDNA) was also attempted. As in the previous experiments a bromo derivative formed easily when an aqueous solution of the potassium salt of N-methyl-ethylenedinitramine was treated with a theoretical amount of pure bromine. However, attempts to prepare the iodo derivative appeared fruitless.

N-methyl-N'-bromo-ethylenedinitramine did not give an immediate precipitate of silver bromide when treated with cold alcoholic silver nitrate. When the solution was heated, however, the silver halide precipitated.

Nitromethane and acetone dissolved N-methyl-N'-bromo-ethylenedinitramine very readily at room temperature. When the compound was treated with boiling ether decomposition occurred, an odor of bromine was detectable and the residue after removing all the ether was shown to be N-methyl-ethylenedinitramine.

N-methyl-N'-bromo-ethylenedinitramine in the dry state was, as might be expected, somewhat more stable than N,N'-dibromo-ethylenedinitramine. There was no evidence of spontaneous decomposition at room temperature, and the substance coul not be detonated when struck on an anvil with a hammer.

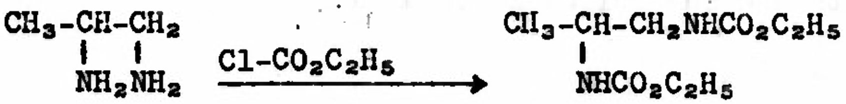
In attempting to prepare the iodo derivative of N-methyl-ethylenedinitramine an aqueous solution of the potassium salt was treated with a theoretical quantity of aqueous iodine-potassium iodide solution. Precipitation of the starting material, N-methyl-ethylenedinitramine occurred. As in the case of ethylenedinitramine the iodo derivative, if formed, probably decomposed very easily and therefore could not be isolated.

Propylenedinitramine.

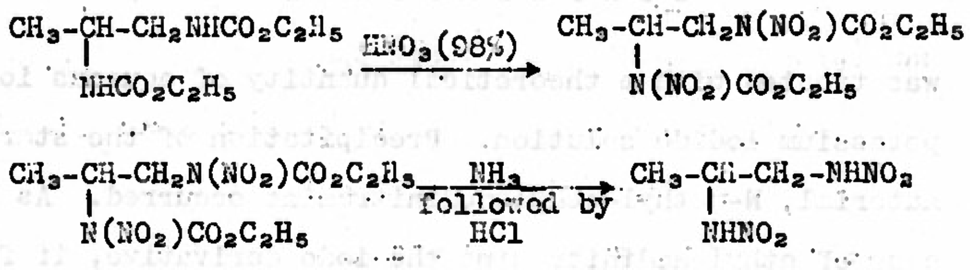
Because it is isomeric with N-methyl-ethylenedinitramine, the synthesis of propylenedinitramine (PDNA) was undertaken in the hope that some data could be gathered relating the molecular properties to the explosive properties.

Bachmann[5] first prepared propylenedinitramine by the hydrolysis of propylenedinitrourethane using a solution of sodium hydroxide as the hydrolytic agent but he reported very poor yields of the product. We have conducted some experiments on this preparation employing dry ammonia as the hydrolytic reagent and have obtained yields of propylenedinitramine as high as 61 per cent based on propylenediurethane.

The synthesis of propylenedinitramine was carried out according to the following equations:



$$\begin{array}{l} CH_3-CH-CH_2 \\ \quad\ \ | \quad\ \ | \\ \quad NH_2\,NH_2 \end{array} \xrightarrow{Cl-CO_2C_2H_5} \begin{array}{l} CH_3-CH-CH_2NHCO_2C_2H_5 \\ \qquad\ \ | \\ \quad NHCO_2C_2H_5 \end{array}$$



$$CH_3\text{-}\underset{\underset{\displaystyle NHCO_2C_2H_5}{|}}{CH}\text{-}CH_2NHCO_2C_2H_5 \xrightarrow{HNO_3(98\%)} CH_3\text{-}\underset{\underset{\displaystyle N(NO_2)CO_2C_2H_5}{|}}{CH}\text{-}CH_2N(NO_2)CO_2C_2H_5$$

$$CH_3\text{-}\underset{\underset{\displaystyle N(NO_2)CO_2C_2H_5}{|}}{CH}\text{-}CH_2N(NO_2)CO_2C_2H_5 \xrightarrow[\text{followed by } HCl]{NH_3} CH_3\text{-}\underset{\underset{\displaystyle NHNO_2}{|}}{CH}\text{-}CH_2\text{-}NHNO_2$$

Bachmann's procedure for the preparation of propylenediurethane gave very unsatisfactory yields (see page 86). Employing different conditions for this reaction yields of 92.5 per cent were realized. The dinitrourethane, which is an oil, was easily prepared and used directly for ammonolysis. Upon treatment of an aqueous solution of the diammonium salt (obtained from the ammonolysis) with concentrated hydrochloric acid good yields of propylenedinitramine were obtained. Only slight difficulty was encountered from the water solubility of this compound.

Melting Points of Binary Mixtures of Compounds Related to Ethylenedinitramine.

It was hoped to find a convenient diluent to lower the melting point of ethylenedinitramine and some of its derivatives. Accordingly several samples were prepared (see pp. 89 for procedure) and their melting points were taken. The results are summarized in Table I.

Table I

Melting Points of Mixtures

Sample[x]	M.P., °C (corr.) Flowed	M.P., °C (corr.) Cleared
25% EDNA-75% MeEDNA	114-115	135
50% EDNA-50% MeEDNA	115-116	148 (gas)
75% EDNA-25% MeEDNA	133-137	157 (gas)
25% EDNA-75% Me_2EDNA	124-125	126
50% EDNA-50% Me_2EDNA	125-126	152 (gas)
75% EDNA-25% Me_2EDNA	145-146	160 (gas)
25% MeEDNA-75% Me_2EDNA	102-103	114
50% MeEDNA-50% Me_2EDNA	103-104	108
75% MeEDNA-25% Me_2EDNA	120-122	126
25% EDNA-75% PDNA	106	126
50% EDNA-50% PDNA	107	147 (gas)
75% EDNA-25% PDNA	136	163 (gas)

[x] EDNA = ethylenedinitramine; MeEDNA = N-methyl-ethylenedinitramine; Me_2EDNA = N,N'-dimethyl-ethylenedinitramine; PDNA = propylenedinitramine.

Nitramino Derivatives of Neopentane

It was of interest to obtain data relating the molecular properties of a series of nitramino derivatives of neopentane with the explosive properties of the compounds. The members of this series which were considered include pentaerythrityl tetranitramine, pentaglyceryl trinitramine and 2,2-dimethyl-1,3-dinitraminopropane. Because of the relation that these nitramines bear to the corresponding nitrates correlations of the relative effect on explosive properties of the nitramino and nitrate groups attached to neopentane could be made. The preparative studies of nitramino derivatives of neopentane upon which is contingent the determination of their explosive properties are described.

Pentaerythrityl Tetranitramine.

We have carried out the synthesis of pentaerythrityl tetranitramine starting with pentaerythritol by the following series of reactions:

$$C(CH_2OH)_4 \xrightarrow{PBr_3} C(CH_2Br)_4$$

$$C(CH_2Br)_4 \xrightarrow{NH_3} C(CH_2NH_2)_4$$

$$C(CH_2NH_2)_4 \xrightarrow{ClCO_2C_2H_5} C(CH_2NHCO_2C_2H_5)_4$$

$$C(CH_2NHCO_2C_2H_5)_4 \xrightarrow{HNO_3} C[CH_2N(NO_2)CO_2C_2H_5]_4$$

$$C[CH_2N(NO_2)CO_2C_2H_5]_4 \xrightarrow[HCl]{NH_3} C(CH_2NHNO_2)_4$$

Pentaerythritol was converted progressively into the corresponding tetrabromide, tetramine, and thence into the tetraurethane. Employing a mixture of acetic anhydride and nitric acid pentaerythrityl tetraurethane was nitrated to give the tetranitrourethane which was easily ammonolyzed to the tetranitramine.

Pentaerythrityl tetramine was obtained by the ammonolysis of pentaerythrityl bromide as described in a following section under the title "Ammonolysis of Pentaerythrityl Bromide".

Absolute nitric acid, 98 per cent, used alone was not a good nitrating agent for the nitration of the tetraurethane. Even with a ratio of one gram of the tetraurethane to eight cubic centimeters of nitric acid the nitration was incomplete. However, a mixture of absolute nitric acid and acetic anhydride gave the tetranitrourethane which was subsequently hydrolyzed to the tetranitramine.

Pentaglyceryl Trinitramine.

The synthesis of pentaglyceryl trinitramine was accomplished through reactions paralleling those employed for the synthesis of pentaerythrityl tetranitramine and is shown by the following equations:

$$CH_3C(CH_2OH)_3 \xrightarrow{PBr_3} CH_3C(CH_2Br)_3$$

$$CH_3C(CH_2Br)_3 \xrightarrow{NH_3} CH_3C(CH_2NH_2)_3$$

$$CH_3C(CH_2NH_2)_3 \xrightarrow{ClCO_2C_2H_5} CH_3C(CH_2NHCO_2C_2H_5)_3$$

$$CH_3C(CH_2NHCO_2C_2H_5)_3 \xrightarrow{HNO_3} CH_3C[CH_2N(NO_2)CO_2C_2H_5]_3$$

$$CH_3C[CH_2N(NO_2)CO_2C_2H_5]_3 \xrightarrow[HCl]{NH_3} CH_3C(CH_2NHNO_2)_3$$

The preparations of the starting material, pentaglycerine, and its tribromo derivative are discussed in a following section of this report under the title, "Pentaglycerine and Its Reactions".

Several experiments on the ammonolysis of pentaglyceryl tribromide were carried out. Early experiments centered around the use of ammonium chloride, aqueous alcohol, and liquid ammonia at 160° with subsequent evaporation of ammonia followed by acidification. Unlike pentaerythrityl tetramine, pentaglyceryl triamine failed to form a sulfate when an equivalent quantity of sulfuric acid was added to the reaction products; instead the trihydrobromide was formed.

In later experiments it was found that the isolation of pentaglyceryl triamine was facilitated by using ammonium bromide, aqueous alcohol, and liquid ammonia at 160° followed by removal of excess ammonia and acidification with hydrobromic acid. In this way yields of 74.7 per cent have been realized. The triamine readily underwent an acylation reaction with ethyl chlorocarbonate to give the triurethane in yields of 89 per cent.

In early experiments on the nitration of pentaglyceryl triurethane, a solution of acetic anhydride and nitric acid was employed. In later experiments it was found that nitration with 98 per cent nitric acid alone was more efficacious and yields of 75 per cent of pentaglyceryl trinitramine were obtained.

<u>2,2-Dimethyl-1,3-dinitraminopropane</u>.

The synthesis of 2,2-dimethyl-1,3-dinitraminopropane was undertaken but was not completed because of the difficulty of obtaining 2,2-dimethyl-1,3-diaminopropane in good yields. The proposed synthesis of this dinitramine parallels the reactions used for the preparation of pentaerythrityl tetranitramine and pentaglyceryl trinitramine, and is represented by the following equations:

$$(CH_3)_2CHCHO \xrightarrow{CH_2O} (CH_3)_2C(CH_2OH)_2$$

$$(CH_3)_2C(CH_2OH)_2 \xrightarrow{PBr_3} (CH_3)_2C(CH_2Br)_2$$

$$(CH_3)_2C(CH_2Br)_2 \xrightarrow{NH_3} (CH_3)_2C(CH_2NH_2)_2$$

$$(CH_3)_2C(CH_2NH_2)_2 \xrightarrow{ClCOOC_2H_5} (CH_3)_2C(CH_2NHCOOC_2H_5)_2$$

$$(CH_3)_2C(CH_2NHCOOC_2H_5)_2 \xrightarrow{HNO_3} (CH_3)_2C\left[CH_2N(NO_2)COOC_2H_5\right]_2$$

$$(CH_3)_2C\left[CH_2N(NO_2)COOC_2H_5\right]_2 \xrightarrow[HCl]{NH_3} (CH_3)_2C(CH_2NHNO_2)_2$$

In this connection we have prepared 2,2-dimethyl-1,3-propandiol following the procedure of Meyersberg[6] in rather unsatisfactory yields. Through the courtesy of Dr. W. E. Lawson, E. I. duPont deNemours and Company, we obtained additional quantities of the glycol. By employing a slight modification of Franke's[7] procedure we were able to obtain 2-2-dimethyl-1,3-dibromopropane in yields of 50 per cent from the corresponding glycol.

The conversion of 2,2-dimethyl-1,3-dibromopropane into the corresponding diamino has been attempted in a single experiment. A liquid of ammoniacal odor was obtained from which the sulfate was prepared. However the identity of this salt is questionable.

A synthesis which might give the desired diamine in good yields has been outlined by Hass[8] however no experimental procedure was given. The preparation involves a condensation of acetone and nitromethane followed by a reduction of the resulting dinitroparaffin.

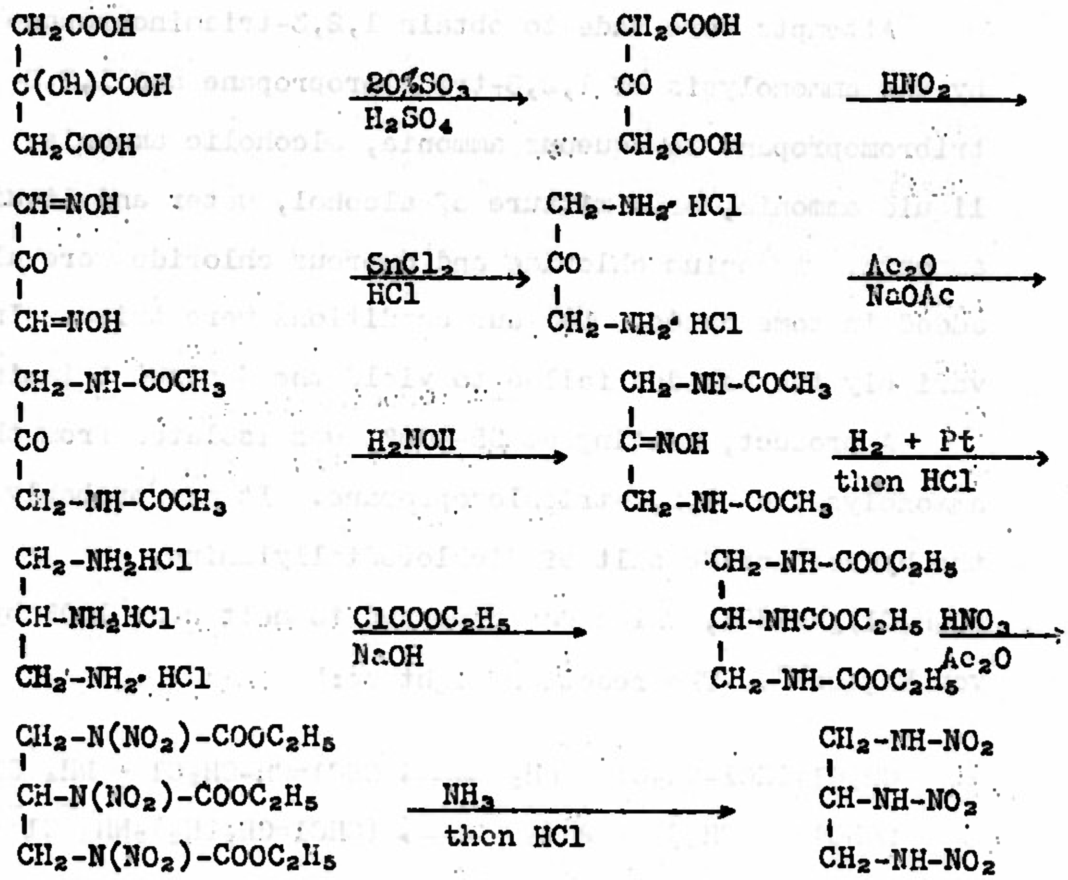
$$2CH_3NO_2 + CH_3COCH_3 \longrightarrow (CH_3)_2C(CH_2NO_2)_2$$

$$(CH_3)_2C(CH_2NO_2)_2 \xrightarrow{[H]} (CH_3)_2C(CH_2NH_2)_2$$

This synthesis was not tried, however, it does appear to be a promising method.

1,2,3-Trinitraminopropane.

The synthesis of 1,2,3-trinitraminopropane involved a long series of transformations shown below:



$$\begin{array}{l}\mathrm{CH_2COOH}\\ \vert\\ \mathrm{C(OH)COOH}\\ \vert\\ \mathrm{CH_2COOH}\end{array} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{20\%SO_3}} \begin{array}{l}\mathrm{CH_2COOH}\\ \vert\\ \mathrm{CO}\\ \vert\\ \mathrm{CH_2COOH}\end{array} \xrightarrow{\mathrm{HNO_2}}$$

$$\begin{array}{l}\mathrm{CH{=}NOH}\\ \vert\\ \mathrm{CO}\\ \vert\\ \mathrm{CH{=}NOH}\end{array} \xrightarrow[\mathrm{HCl}]{\mathrm{SnCl_2}} \begin{array}{l}\mathrm{CH_2\text{-}NH_2\cdot HCl}\\ \vert\\ \mathrm{CO}\\ \vert\\ \mathrm{CH_2\text{-}NH_2\cdot HCl}\end{array} \xrightarrow[\mathrm{NaOAc}]{\mathrm{Ac_2O}}$$

$$\begin{array}{l}\mathrm{CH_2\text{-}NH\text{-}COCH_3}\\ \vert\\ \mathrm{CO}\\ \vert\\ \mathrm{CH_2\text{-}NH\text{-}COCH_3}\end{array} \xrightarrow{\mathrm{H_2NOH}} \begin{array}{l}\mathrm{CH_2\text{-}NH\text{-}COCH_3}\\ \vert\\ \mathrm{C{=}NOH}\\ \vert\\ \mathrm{CH_2\text{-}NH\text{-}COCH_3}\end{array} \xrightarrow[\text{then HCl}]{\mathrm{H_2 + Pt}}$$

$$\begin{array}{l}\mathrm{CH_2\text{-}NH_2HCl}\\ \vert\\ \mathrm{CH\text{-}NH_2HCl}\\ \vert\\ \mathrm{CH_2\text{-}NH_2\cdot HCl}\end{array} \xrightarrow[\mathrm{NaOH}]{\mathrm{ClCOOC_2H_5}} \begin{array}{l}\mathrm{CH_2\text{-}NH\text{-}COOC_2H_5}\\ \vert\\ \mathrm{CH\text{-}NHCOOC_2H_5}\\ \vert\\ \mathrm{CH_2\text{-}NH\text{-}COOC_2H_5}\end{array} \xrightarrow[\mathrm{Ac_2O}]{\mathrm{HNO_3}}$$

$$\begin{array}{l}\mathrm{CH_2\text{-}N(NO_2)\text{-}COOC_2H_5}\\ \vert\\ \mathrm{CH\text{-}N(NO_2)\text{-}COOC_2H_5}\\ \vert\\ \mathrm{CH_2\text{-}N(NO_2)\text{-}COOC_2H_5}\end{array} \xrightarrow[\text{then HCl}]{\mathrm{NH_3}} \begin{array}{l}\mathrm{CH_2\text{-}NH\text{-}NO_2}\\ \vert\\ \mathrm{CH\text{-}NH\text{-}NO_2}\\ \vert\\ \mathrm{CH_2\text{-}NH\text{-}NO_2}\end{array}$$

1,2,3-Triaminopropane trihydrochloride was synthesized according to the directions given by Bachmann[9], except for the intermediate preparation of acetonedicarboxylic acid, which was done according to the method described in "Organic Syntheses" (Volume I, Second Edition, page 10).

1,2,3-Trinitraminopropane precipitates from aqueous solutions only after long standing at 0°. It is probably for this reason that Bachmann was unable to obtain the trinitramine from the corresponding triurethane.

Attempts were made to obtain 1,2,3-triaminopropane by the ammonolysis of 1,2,3-trichloropropane and 1,2,3-tribromopropane in aqueous ammonia, alcoholic ammonia, liquid ammonia, or a mixture of alcohol, water and liquid ammonia. Ammonium chloride and cuprous chloride were also added in some cases. Various conditions were tried. Invariably the halides failed to yield the desired triamine.

A product, melting at 95-100°, was isolated from the ammonolysis of 1,2,3-trichloropropane. It was probably the hydrochloride salt of dichlorodiallylamine, $(C_3H_4Cl)_2NH\cdot HCl$, which was reported to melt near 100° by von Engler[10]. The reaction might be:

$$CH_2Cl{=}CHCl{-}CH_2Cl + NH_3 \longrightarrow CHCl{=}CH{-}CH_2Cl + NH_4^{+}Cl^{-}$$

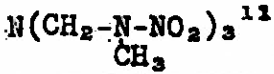
$$2CHCl{=}CH{-}CH_2Cl + 2NH_3 \longrightarrow (CHCl{=}CH{-}CH_2)_2NH_2^{+}Cl^{-} + NH_4^{+}C$$

From the product of the ammonolysis of 1,2,3-tribromopropane a salt was obtained. It melts at 140°. Probably it was the hydrochloride salt of dibromodiallylamine, $(C_3H_4Br)_2NH\cdot HCl$.

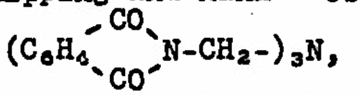
The formation of the diallylamines instead of the triamine probably is due to ease of ionization of the trihalogen compounds under the inductive influence of two halogen atoms at position 1 and 3. The resulting carbonium ion is stabilized by the splitting off of a proton. The resulting γ-haloallyl halide reacts with ammonia to give the diallylamine.

Attempts to Synthesize Tris(nitraminomethyl)amine

An Attempt to Obtain Tris(nitraminomethyl)amine by the Condensation of Ammonia, Formaldehyde and Nitrourethane.

In view of the fact that the condensation of methylnitramine, formaldehyde, and ammonia led to the formation of tris(methylnitraminomethyl)amine,  $N(CH_2-\underset{CH_3}{N}-NO_2)_3$[11], the analogous condensation between ammonia, formaldehyde, and ethyl nitrocarbamate as well as methyl nitrocarbamate was studied. The only products that could be isolated were hexamine and the nitrourethanes.

Hydrolysis of Tris(phthalimidomethyl)amine.

Kipping and Mann[12] obtained tris(phthalimidomethyl)amine,  $(C_6H_4\begin{smallmatrix}CO\\ \\CO\end{smallmatrix}N-CH_2-)_3N$, by passing dry ammonia gas through a solution of N-(bromomethyl)phthalimide in dry xylene at reflux temperature. However, they failed to get tris(aminomethyl)amine, $N(CH_2NH_3)_3$, when they hydrolyzed tris-

(phthalimidomethyl)amine with 6 N. hydrochloric acid. It was of interest to see whether or not the phthalimide derivative could be partially hydrolyzed to the acid-amide derivative,  $(\underset{\text{COOH}}{C_6H_4}\text{-}CONHCH_2)_3N$, which might subsequently be nitrated. However, the attempt was unsuccessful. The compound seemed to be hydrolyzed completely even in the presence of a small amount of potassium hydroxide.

The Condensation of Urethane with Hexamine.

Reactions of hexamine in some instances yield compounds which are symmetrically substituted tertiary amines. Thus the preparation of tris(cyanomethyl)amine, $N(CH_2CN)_3$, from hexamine and hydrogen cyanide[13] may be cited as an example. It was thought that hexamine might undergo a similar reaction with urethane to yield the triurethane of tris(aminomethyl)amine, $N(CH_2NHCO_2Et)_3$. However, only methylene diurethane, $CH_2(NH_2COOC_2H_5)_2$, was obtained.

An Attempt to Prepare Tris(nitraminomethyl)amine from Tris(cyanomethyl)amine.

An attempt to prepare tris(nitraminomethyl)amine from tris(cyanomethyl)amine was made according to the proposed scheme given below:

$$(CH_2)_6N_4 + 6HCN \xrightarrow{HCl} 2\ N(CH_2CN)_3$$

$$N(CH_2CN)_3 \xrightarrow[\text{then HCl}]{\text{NaOH}} N(CH_2CO_2H)_3$$

$$N(CH_2CO_2H)_3 \xrightarrow[\text{HCl}]{C_2H_5OH} N(CH_2CO_2Et)_3$$

$$N(CH_2CO_2Et)_3 \xrightarrow{NH_2NH_2} N(CH_2CONHNH_2)_3$$

$$N(CH_2CONHNH_2)_3 \xrightarrow{HNO_2} N(CH_2CON_3)_3$$

$$N(CH_2CON_3)_3 \xrightarrow[\text{heat}]{C_2H_5OH} N(CH_2NHCO_2Et)_3$$

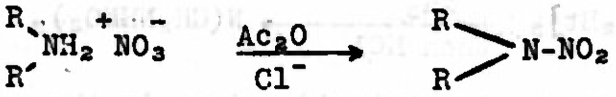
$$N(CH_2NHCO_2Et)_3 \xrightarrow{98\%\ HNO_3} N[CH_2N(NO_2)CO_2Et]_3$$

$$N[CH_2N(NO_2)CO_2Et]_3 \xrightarrow[\text{then HCl}]{NH_3} N(CH_2NHNO_2)_3$$

Curtius[13] prepared the triazide given in the reactions listed above. It was planned to use this triazide as a means of obtaining the desired tris(nitraminomethyl)amine. However, his synthesis of the triazide could not be duplicated.

Explosive Derivatives of Some Amino-Alcohols

In a continuation of the study of the preparation and properties of aliphatic nitramines the synthesis of explosive deivatives of some β-alkylolamines was undertaken. N-β-nitroxyethyl)nitramine (NENA) was prepared and a detailed investigation was made of N-(β-nitroxyethyl)methylnitramine (MeNENA). Also, the synthesis of several related compounds which include N-(β-nitroxyethyl)ethylnitramine (EtNENA), N-(β-nitroxypropyl)methylnitramine (Me$_2$NENA), N-(β-nitroxypropyl)nitramine (IsoMeNENA), dinitraminoisopropyl nitrate, N,N-bis(β-nitroxyethyl)nitramine (DINA), N, N'-bis(β-nitroxyethyl)ethylenedinitramine, and N,N-bis(β-nitroxypropyl)nitramine was accomplished. All of the compounds with the exception of N-(β-nitroxyethyl)nitramine (NENA), N-(β-nitroxypropyl)nitramine (IsoMeNENA), and dinitramino-isopropyl nitrate were prepared by the catalyzed Bamberger reaction. This reaction which appears to be generally applicable for preparing secondary nitramines is indicated by the following equation.



Possible Mechanism for the Catalyzed Bamberger Reaction.

In the course of the survey of possible catalysts for the production of N,N-bis(β-nitroxyethyl)nitramine (DINA) and N-(β-nitroxyethyl)methylnitramine (MeNENA) by the Bamberger reaction, it became apparent that compounds containing ionic or reactive chlorine were unique in their catalytic effect. The only substances which seemed to be exceptions were calcium hypochlorite and potassium chlorate. However, it was observed that chloride ion was present in the filtrates from the DINA preparations using potassium chlorate so the catalysis may have been due to the chloride produced by the reduction of the chlorate in the reaction mixture.

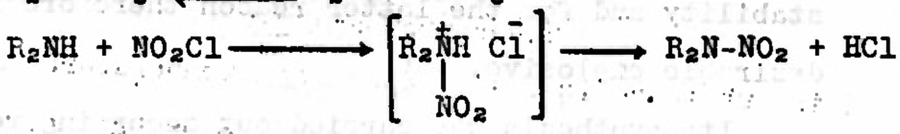
This special effect of ionic or reactive chlorine led to the postulation that the chlorine is involved in some active intermediate. The intermediate which could quite conceivably be formed is NO_2Cl, nitryl chloride or nitroxyl chloride.

A possible course of the reaction would then be the following series of reactions:

(1) $(CH_3CO)_2O + HNO_3 \rightleftarrows CH_3CO\text{-}ONO_2$

(2) $CH_3CO\text{-}ONO_2 + HCl \rightleftarrows NO_2Cl + CH_3CO_2H$

(3) $R_2\overset{+}{N}H\,NO_3^- \rightleftarrows R_2NH + HNO_3$

(4) 

$$R_2NH + NO_2Cl \longrightarrow \left[\begin{array}{l} R_2\overset{+}{N}H\ \overset{-}{Cl} \\ \quad | \\ \ \ NO_2 \end{array}\right] \longrightarrow R_2N\text{-}NO_2 + HCl$$

The HCl produced in step (4) could react again as in step (2) and the HNO_3 produced in step (3) could form more acetyl nitrate in step (1).

These reactions offer a working hypothesis for the reaction mechanism although at present very little proof is available. The reaction of nitrosyl chloride (NOCl) which is analogous to steps (3) and (4) has been carried out using 0.5 mole of the pure trinitrate of diethanolamine and 0.5 mole of NOCl in acetic anhydride. A yield of 97 per cent of bis-β-nitroxyethylnitrosamine was obtained and identified by mixed melting point and by a mixed fusion on a microscope slide.

N-(β-nitroxyethyl)nitramine (NENA).

Of interest from a standpoint of explosive properties, because it possesses a structure intermediate to glycol dinitrate and ethylenedinitramine is the compound N-(β-nitroxyethyl)nitramine (NENA) whose formula is the following:

$$O_2NO_2\text{-}CH_2CH_2\text{-}NHNO_2$$

This substance is a liquid at room temperature and melts at 15°C. It is an explosive of high power but very poor stability and for the latter reason therefore is not a desirable explosive.

Its synthesis was carried out according to the following equations:

$$HOCH_2CH_2NH_2 \xrightarrow{ClCO_2C_2H_5} HOCH_2CH_2NHCO_2C_2H_5$$

$$HOCH_2CH_2NHCO_2C_2H_5 \xrightarrow{HNO_3} O_2NOCH_2CH_2N(NO_2)CO_2C_2H_5$$

$$O_2NOCH_2CH_2N(NO_2)CO_2C_2H_5 \xrightarrow[H_2SO_4]{NH_3} O_2NOCH_2CH_2NHNO_2$$

N-(β-ethanol)urethane was obtained from ethanolamine and ethyl chlorocarbonate by employing a modification of the method used by Franchimont and Lublin.[14] Yields as high as 96 per cent of theoretical were obtained. The nitration of N-(β-ethanol)urethane proceeded smoothly and ammonolysis of the resulting nitrourethane yielded the ammonium salt of

N-(β-nitroxyethyl)nitramine in yields of 97 per cent. This salt decomposed slowly at room temperature. The decomposition proceeded more rapidly in aqueous solution and because of this, the isolation of N-(β-nitroxyethyl)-nitramine by the neutralization of the ammonium salt should be carried out as rapidly as possible. By so doing, yields of 93.3 per cent of theoretical were realized for the free nitramine. The silver salt of N-(β-nitroxyethyl)nitramine was precipitated almost quantitatively by adding silver nitrate to a freshly prepared aqueous solution of the ammonium salt. It was unstable to light and decomposed when heated.

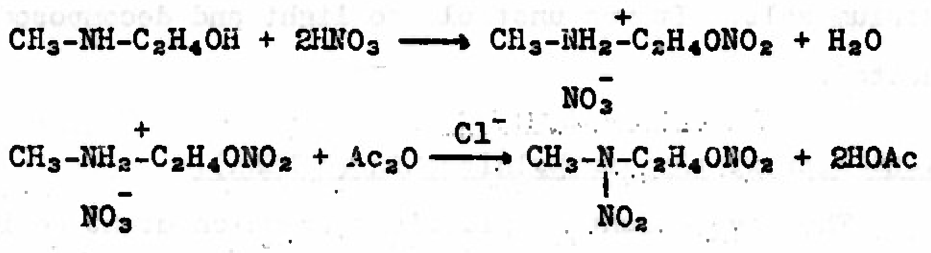
N-(β-nitroxyethyl)methylnitramine(MeNENA).

The development of plasticizers which might be incorporated into powders in place of the undesireable nitroglycerine was sought so that the disadvantages of nitroglycerine might be obviated. Early indications pointed to the possible use of N-(β-nitroxyethyl)methylnitramine for such purposes. It was with this in mind that a detailed study of the preparation and properties of MeNENA was undertaken.

This compound it will be recalled was first prepared by the action of nitric acid on N-methyl-ethylenedinitramine (page 9) and also by the action of nitric acid on the low melting isomer, iso-N^1,N^4-dimethyl-triethylenetetranitramine, obtained from the reaction of N-methyl-ethylenedinitramine and ethylene dibromide (page 8).

MeNENA can be prepared by the catalyzed Bamberger reaction starting from methyl ethanolamine by either a one stage or two stage process.

The method for preparing MeNENA which was employed in these studies was the two stage reaction shown by the following equations:



$$CH_3\text{-}NH\text{-}C_2H_4OH + 2HNO_3 \longrightarrow CH_3\text{-}\underset{NO_3^-}{\overset{+}{N}H_2}\text{-}C_2H_4ONO_2 + H_2O$$

$$CH_3\text{-}\underset{NO_3^-}{\overset{+}{N}H_2}\text{-}C_2H_4ONO_2 + Ac_2O \xrightarrow{Cl^-} CH_3\text{-}\underset{NO_2}{\underset{|}{N}}\text{-}C_2H_4ONO_2 + 2HOAc$$

We reported at one time that the one stage reaction whereby N-methyl-β-ethanolamine and nitric acid were added concurrently and simultaneously to acetic anhydride containing a trace of chloride catalyst was superior to the two stage reaction. If however, instead of isolating the dinitrate in stage one, as was customary in early studies, on the two stage process, a solution of the amine and nitric acid was employed, excellent results were obtained.

The following factors were studied in relation to their influence upon the yield and quality of MeNENA produced in the two stage reaction: (1) Conditions of the reaction such as temperature and catalysts; (2) Relative proportion of reactants. Furthermore, the stabilization of McNENA and the properties of the stabilized product were studied.

Experiments on the Preparation of McNENA

Since McNENA is very soluble in both glacial acetic acid and aqueous acetic acid and is slightly soluble in water (.76 g./100 cc.), the isolation of this substance in the maximum possible yield from the reaction mixture is dependent upon a knowledge of the solubility of McNENA in aqueous acetic acid. Table II and Figure I show the solubility of McNENA in various concentrations of aqueous acetic acid (0-50 per cent).

Table II

Solubility of McNENA in Aqueous Acetic Acid at 25°C.

HOAc (%)	Sol. of McNENA (g./100 cc. of solvent)	Sol. of McNENA (g./100 g. of solvent)
0	0.759	0.759
10	1.18	1.17
20	1.46	1.42
30	3.67	3.53
40	6.92	6.60
50	11.9	11.2

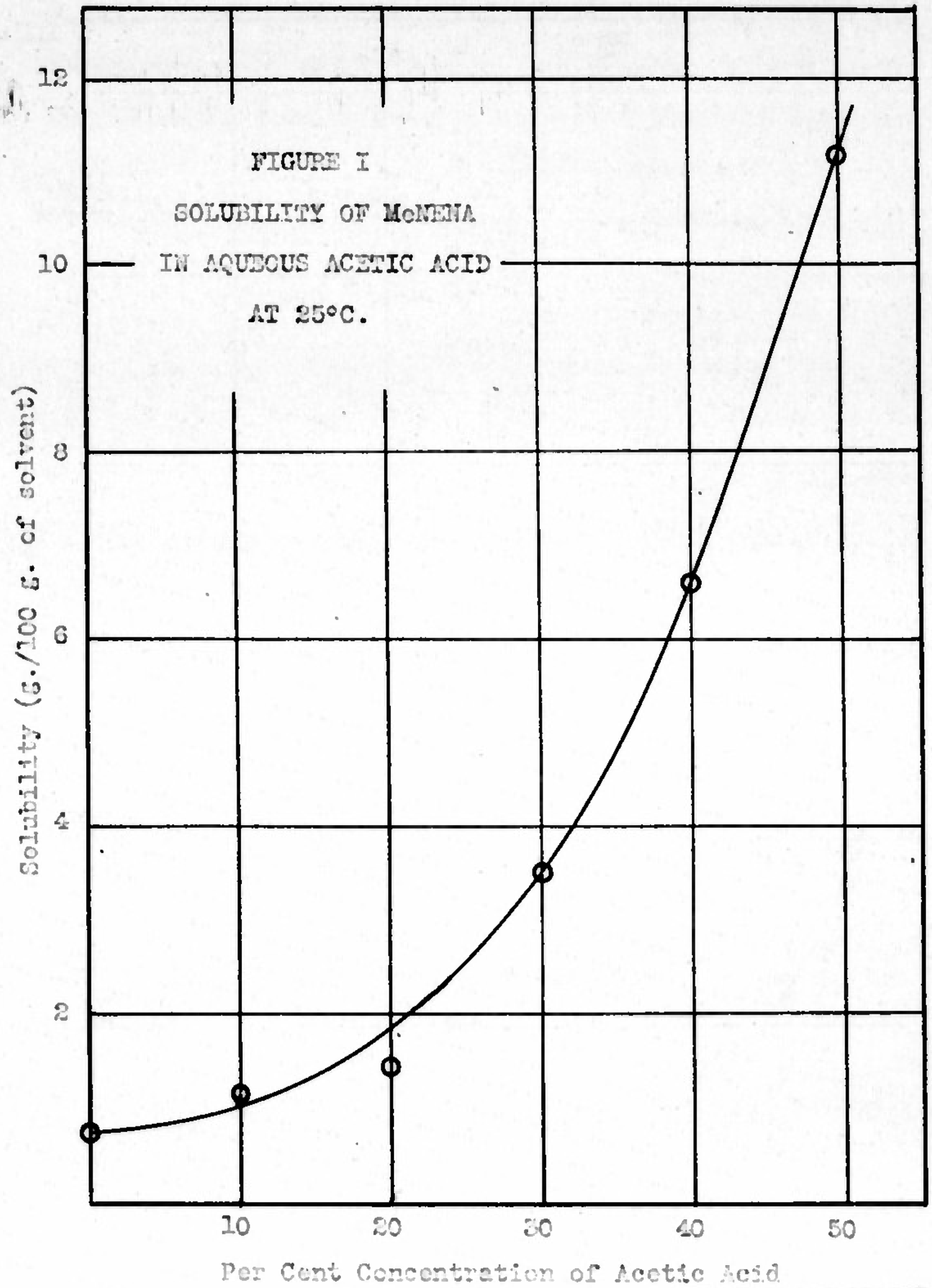


FIGURE I

SOLUBILITY OF McNENA IN AQUEOUS ACETIC ACID AT 25°C.

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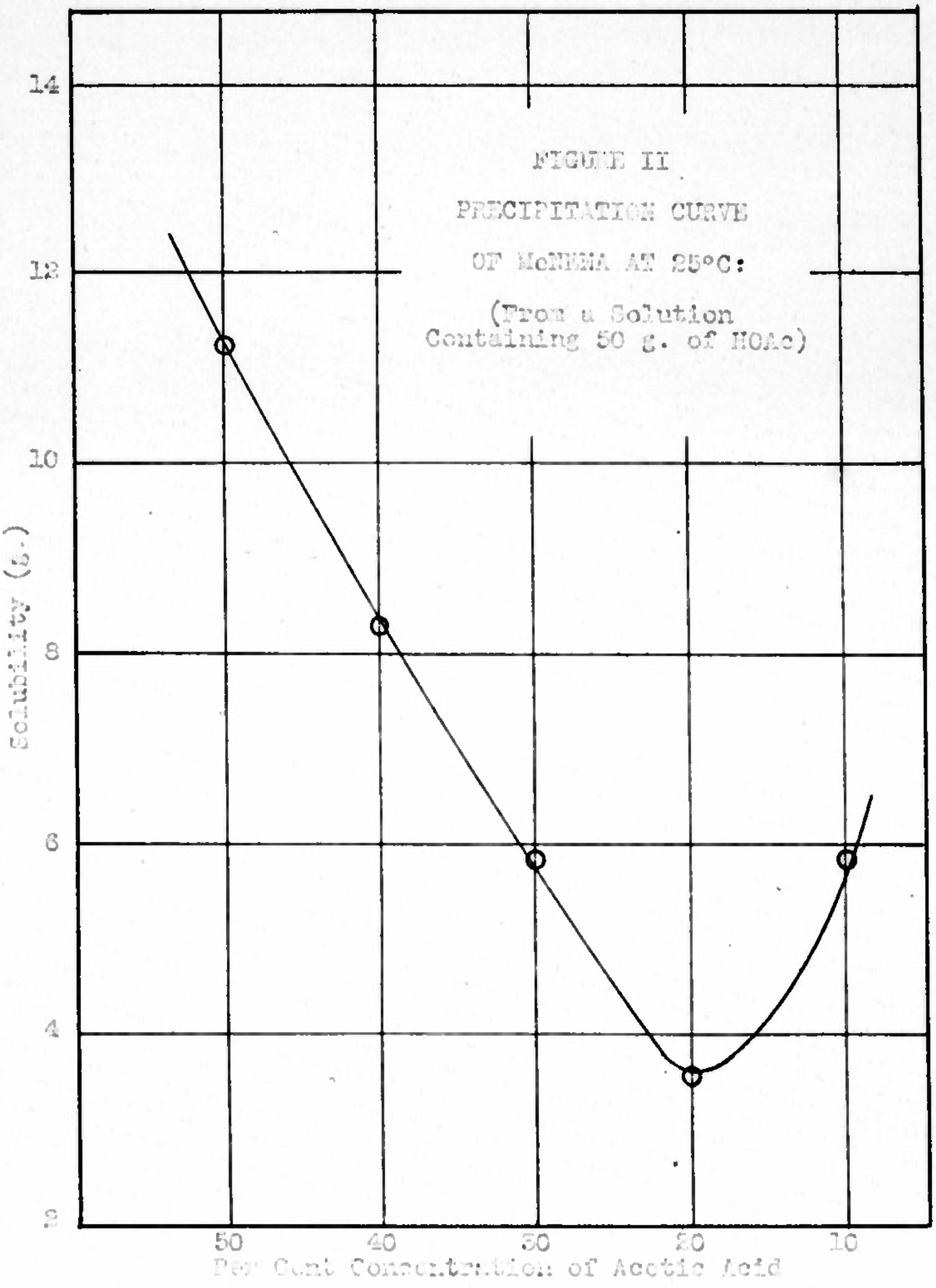


FIGURE II

PRECIPITATION CURVE

OF McNENA AT 25°C:

(From a Solution
Containing 50 g. of HOAc)

From the above data the precipitation curve of MeNENA from acetic acid solution, shown in Figure II, was determined. It is to be noted that the maximum precipitation of MeNENA occurs at approximately 20 per cent acetic acid. Consequently, the isolation of MeNENA from the reaction mixture was carried out by quenching with sufficient water to give a 20 per cent acetic acid solution.

Optimum Temperature. A series of experiments employing theoretical quantities of methyl ethanolamine and nitric acid with a 10 per cent excess of acetic anhydride showed clearly that the optimum temperature for the preparation of MeNENA to be about 25-35°C. The results of experiments carried out at different temperatures are listed in Table III

Table III

Effect of Varying the Temperature in the Preparation of MeNENA

Run No.*	Temp. (°C.)	MeNENA Crop I (g.)	% Yield	m.p. (°C.)
F-XII	5	0	0	--
F-XI	15	35.5	43.0	37-38
F-X	25	66.4	80.5	37.5-38
F-VII	35	66.1	80.1	38-39
F-VIII	45	63.2	76.6	37.5-38.5
F-IX	55	60.0	72.7	38-38.5

* Procedure F-VII was followed employing the temperatures indicated in the table. (See page 114).

Table IV lists the results of experiments in which the addition of the amine-nitric acid solution to acetic anhydride was carried out at different temperatures and then allowed to remain at 40°C. for twenty minutes. The yields in all cases were fairly uniform, falling off somewhat at higher temperatures.

Table IV

Preparation of McNENA at Various Temperatures Followed by "Digestion" at 40°C.*

Run No.	Addition Temp. (°C.)	Holding Temp. (°C.)	McNENA Crop I (g.)	% Yield	m.p. (°C.)
F-II	5	40	58.6	71.0	37-38
F-I	15	40	64.6	78.3	38-39
F-III	25	40	64.6	78.3	37.5-38.5
F-IV	35	40	66.2	80.3	37-37.5
F-V	45	40	63.4	76.9	38-39
F-VI	55	40	57.3	69.5	38-39

* Procedure F-I was employed. (See page 112).

The Bamberger "dehydration" reaction, as is shown in Table V, is subject to the influence of temperature and time. Run F-XI and F-XIV in which the holding time or "digestion period" was 15 minutes and 120 minutes, respectively, at 15°C. showed a marked difference in the yields of McNENA. The yield in the former was 43 per cent, whereas the yield in the latter was 68.4 per cent. At a higher temperature the reaction was completed in a relatively short time. Runs F-VIII and F-XIII showed slight variations in the yield when the holding time was 15 and 0 minutes. It is quite probable that at moderately elevated temperatures some decomposition of MeNENA by the acid solution occurs.

Table V

Effect of Holding Time in the Preparation of MeNENA

Run No.*	Temp. (°C.)	Holding Time(min.)	MeNENA Crop I(g.)	% Yield	m.p.(°C.)
F-XI	15	15	35.5	43.0	38-39
F-XIV	15	120	68.4	82.9	37-38
F-VIII	45	15	63.2	76.6	37.5-38.5
F-XIII	45	0	63.9	77.5	37-38

* Procedure F-VII was followed subject to the variation in temperature and holding time, indicated in the table. (see page 114).

Influence of Varying Amounts of Acetic Anhydride. The results of several experiments disclosed that a slight excess of acetic anhydride over the theoretical requirement (about 10 per cent) gave somewhat better yields. Increasing the quantity of acetic anhydride from 1.1 mole to 1.4 mole per 0.5 mole methyl ethanolamine did not improve the recovery. The results of the experiments are given in Table VI.

Table VI

Variation of Acetic Anhydride in the Preparation of MeNENA

Run* No.	Ac_2O (moles)	MeNENA Crop I(g.)	% Yield	m.p.(°C.)
F-XX	0.9	53.7	65.1	37-38.5
F-XVII	1.0	62.5	75.8	37-38
F-VII	1.1	66.1	80.1	38-39
F-XV	1.2	65.8	79.8	37-38
F-XVI	1.3	64.9	78.7	37.5-38
F-XVIII	1.4	65.0	78.8	37.5-38.5

* Procedure F-VII (0.5 mole run) was followed, varying only the moles of acetic anhydride. In isolating the product the reaction was quenched with enough ice and water to give a 20 per cent solution of acetic acid. (See page 114).

Influence of Varying Amounts of Nitric Acid. The influence of varying amounts of nitric acid is summarized in Table VII. There is a very slight increase in the yield of MeNENA when the amount of nitric acid is varied from 1.00 mol to 1.20 moles per 0.50 mole of methyl ethanolamine.

Table VII

Effect of Nitric Acid in the Preparation of MeNENA*

Run No.	HNO_3 (moles)	MeNENA Crop I (g.)	% Yield	m.p.(°C.)
F-VII	1.00	66.1	80.1	38-39
F-XXIII	1.05	66.5	80.6	37-38
F-XIX	1.10	63.7	80.8	37-38
F-XXXV	1.20	67.5	81.8	37-38

* Procedure VII was followed. (See page 114).

Catalysts in the Preparation of MeNENA. It appears from an examination of Table VIII that the catalytic effect of the chloride ion is essential for the conversion of the nitrate of N-(β-nitroxyethyl)methylamine into MeNENA. This is borne out by Run F-XXII and F-XXXI. In the former no catalyst was employed; in the latter sulfuric acid was used. In each of these experiments no MeNENA was isolated.

The yield of MeNENA is also subject to the influence of the concentration of chloride ion and as it is observed in Table VIII, in experiments employing zinc chloride, there is an optimum concentration at which the catalyst is most effective. The highest yield was obtained when 0.011 mole of zinc chloride per 0.50 mole of methyl ethanolamine was used.

Other chlorides, it was found, were equally as effective as zinc chloride. Acetyl chloride, aluminum chloride, ammonium chloride, sodium chloride, hydrochloric acid gave excellent results, and ferric chloride was somewhat less effective. The results also showed that potassium chlorate and sodium hypochlorite were effective catalysts while potassium dichromate and sodium sulfite were without effect.

Table VIII

Catalytic Studies on MeNENA[**]

Exp. No.	Catalyst	Catalyst (moles)	MeNENA (g.)	Yield (%)	m.p. (°C.)
F-XXII	--	0	0	0	--
F-XXVI	$ZnCl_2$	0.0007	14.4	17.5	37-38
F-XXV	$ZnCl_2$	0.0037	69.3	84.0	37-38
F-XXIV	$ZnCl_2$	0.011	70.1	85.0	37.5-38
F-XXIII	$ZnCl_2$	0.022	66.5	80.6	37-38
F-XXVII	$ZnCl_2$	0.074	57.6	72.2	37-38
F-XXVIII	AcCl	0.011	71.4	86.5	37.5-38.5
F-XXIX	$AlCl_3$	0.011	69.1	83.8	37-38
F-XXX	NH_4Cl	0.011	70.4	85.3	37-38
F-XXXI	H_2SO_4	0.011	0	0	--
F-XXXII	NaCl	0.011	70.6	85.6	37.5-38.5
F-XXXIII	HCl	0.011	67.9	82.3	37-38
F-XXXIV	$FeCl_3$	0.011	64.4	78.1	37-38
A	$KClO_3$	0.011	67.2	81.5	37.5-38.5
D[*]	$KClO_3$	0.011	5.7	6.9	38-39
C	$KClO_3$	0.0007	0	0	--
E	NaOCl	0.011	55.2	67.0	37.5-38.5
B	Na_2SO_3	0.011	0	0	--
F	$K_2Cr_2O_7$	0.011	0	0	--

---

[*] Exp. D was run at 15°C whereas the other runs were at 35°C.

[**] Procedure F-XXIV was used. (See page 114).

Stabilization of MeNENA.

The stabilization of MeNENA is described in the experimental part of this work (see page 116). The treatment, which involves agitation of molten MeNENA with dilute base followed by subsequent precipitation of the substance from an acetone solution, enhances the stability of MeNENA considerably.

Table IX lists results on the vacuum stability of MeNENA.

Table IX

<u>Vacuum Stability of MeNENA at 100°C.</u>

Sample [a]	Vol. of gas (cc) after 48 hrs.
CU-F-15 [b]	3.85, 3.78
CU-F-15 [c]	6.30, 7.38
CU-F-16 [b]	4.38, 4.55
CU-F-16 [c]	6.24, 7.23

[b] Test made at Cornell on 2.3 g. samples.

[c] Test made at ERL on 5 g. samples

[a] Samples were stabilized prior to testing as described on pages 116-117 of this report

<u>Properties of MeNENA</u>.

The explosive properties of MeNENA are given on page 72.

<u>Density of MeNENA</u>. A determination of the density of MeNENA by the picnometer method gave the following results:

Solid MeNENA: $d_4^{25} = 1.53$

Liquid MeNENA: $d_4^{25} = 1.40$

Volatility of MeNENA. A study of the relative volatility of MeNENA as compared to DINA and nitroglycerine was made and inconsistent results were obtained depending on how the tests were carried out.

The results tabulated in Table X were obtained by carrying out the determinations as described by Marshall[15] at 100°C.

Table X

International Tests[x]

	Time	Per Cent Loss in Weight MeNENA	DINA	N.G.
	24 hrs.	.14	.56	.14
Addn.	24 hrs.	.025	.016	.60
Addn.	24 hrs.	.053	.055	1.53
Addn.	24 hrs.	.010	.123	1.43
Addn.	24 hrs.	.14	.069	4.86

[x] 10 g. samples were used in these tests.

The results obtained by heating samples of MeNENA, DINA, and nitroglycerine in an open beaker at 50 C. showed MeNENA and nitroglycerine to be of comparable volatility while that of DINA was almost negligible. The data are summarized in Table XI.

Table XI

Volatility Tests in Open Beakers*

Time	Per Cent Loss in Weight		
	MeNENA	DINA	N.G.
24 hrs.	.19	.30	.60
Addn. 72 hrs.	.32	.01	.38
Addn. 216 hrs.	1.34	.02	1.33

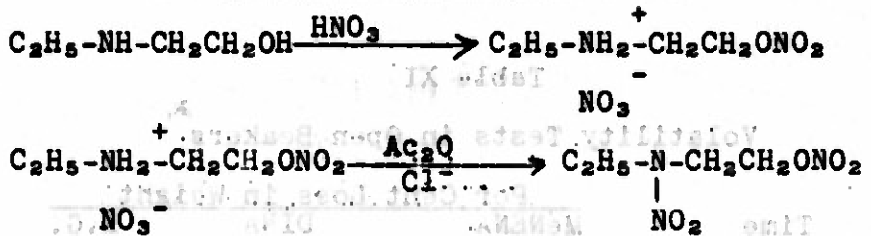
* 10 g. samples were used in these tests.

The reason for disagreement in the results on the volatility of MeNENA as compared to nitroglycerine is not quite clear, but it should be pointed out that the tests performed in the open beakers appear to be more significant than the tests carried out in a loosely covered beaker as described by Marshall.[15]

In view of the more significant work of Dr. J. L. Hoard on the volatility of DINA, MeNENA, and etc. in films of plasticized nitrocellulose the foregoing results do not appear to be particularly important.

N-(-nitroxyethyl)ethylnitramine(EtNENA).

A nitroxyalkyl nitramine related through homology, to N-(β-nitroxyethyl)nitramine and N-(β nitroxyethyl)methylnitramine is the compound N-(β-nitroxyethyl)ethylnitramine. This substance was prepared paralleling the technique usually employed in the catalyzed Bamberger reaction. The following equations represent its synthesis:



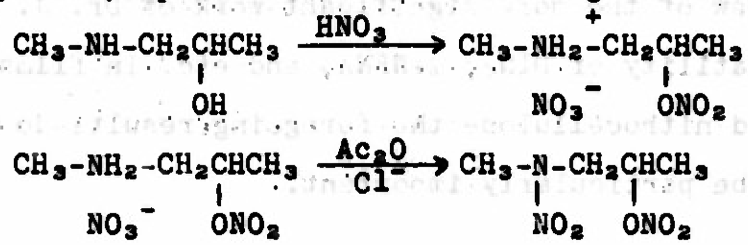
$$C_2H_5-NH-CH_2CH_2OH \xrightarrow{HNO_3} C_2H_5-\overset{+}{N}H_2-CH_2CH_2ONO_2 \quad NO_3^-$$

$$C_2H_5-\overset{+}{N}H_2-CH_2CH_2ONO_2 \quad NO_3^- \xrightarrow[Cl^-]{Ac_2O} C_2H_5-\underset{NO_2}{N}-CH_2CH_2ONO_2$$

N-(β-nitroxypropyl)methylnitramine (MeNENA).

A compound which is structurally related to several previously discussed nitroxyalkyl nitramines is N-(β-nitroxypropyl)methylnitramine. This compound is isomeric with N-(β-nitroxyethyl)ethylnitramine, differing from it only in the manner of the disposition of the alkyl groups. Furthermore it is observed that N-(β-nitroxypropyl)methylnitramine is an N-methyl derivative of N-(β-nitroxypropyl)nitramine.

The preparation of N-(β-nitroxypropyl)methylnitramine was carried out through a catalyzed Bamberger reaction using methyl isopropanolamine[x] as a starting material.



$$CH_3-NH-CH_2\underset{OH}{C}HCH_3 \xrightarrow{HNO_3} CH_3-\overset{+}{N}H_2-CH_2\underset{ONO_2}{C}HCH_3 \quad NO_3^-$$

$$CH_3-NH_2-CH_2\underset{ONO_2}{C}HCH_3 \quad NO_3^- \xrightarrow[Cl^-]{Ac_2O} CH_3-\underset{NO_2}{N}-CH_2\underset{ONO_2}{C}HCH_3$$

N-(β-nitroxypropyl)nitramine(IsoMeNENA).

Earlier in this report the preparation and properties of N-(β-nitroxyethyl)nitramine were described (see page 30). This compound it will be recalled was prepared by nitrating

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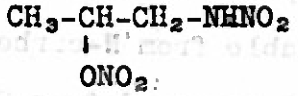
[x] This compound was obtained from the reaction of methylamine and propyleneoxide. It distilled at 56-65°C/15 mm.

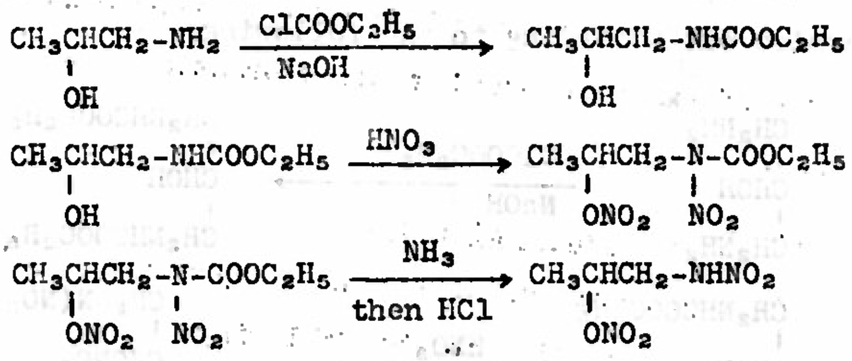
N-(β-ethanol)urethane to the corresponding nitroxyalkyl nitrourethane followed by ammonolysis to give the ammonium salt of N-(β-nitroxyethyl)nitramine. The nitramine was then obtained by acidifying an aqueous solution of the ammonium salt.

A nitroxyalkylnitramine related to N-(β-nitroxyethyl)-nitramine is N-(β-nitroxypropyl)nitramine,



$$CH_3-\underset{ONO_2}{CH}-CH_2-NHNO_2$$

This compound is isomeric with N-(β-nitroxyethyl)methylnitramine, differing from it only in the manner of disposition of the methyl group. Its synthesis was carried out in a manner analagous to N-(β-nitroxyethyl)nitramine and is given by the following equations:



$$CH_3\underset{OH}{CH}CH_2-NH_2 \xrightarrow[NaOH]{ClCOOC_2H_5} CH_3\underset{OH}{CH}CH_2-NHCOOC_2H_5$$

$$CH_3\underset{OH}{CH}CH_2-NHCOOC_2H_5 \xrightarrow{HNO_3} CH_3\underset{ONO_2}{CH}CH_2-\underset{NO_2}{N}-COOC_2H_5$$

$$CH_3\underset{ONO_2}{CH}CH_2-\underset{NO_2}{N}-COOC_2H_5 \xrightarrow[\text{then } HCl]{NH_3} CH_3\underset{ONO_2}{CH}CH_2-NHNO_2$$

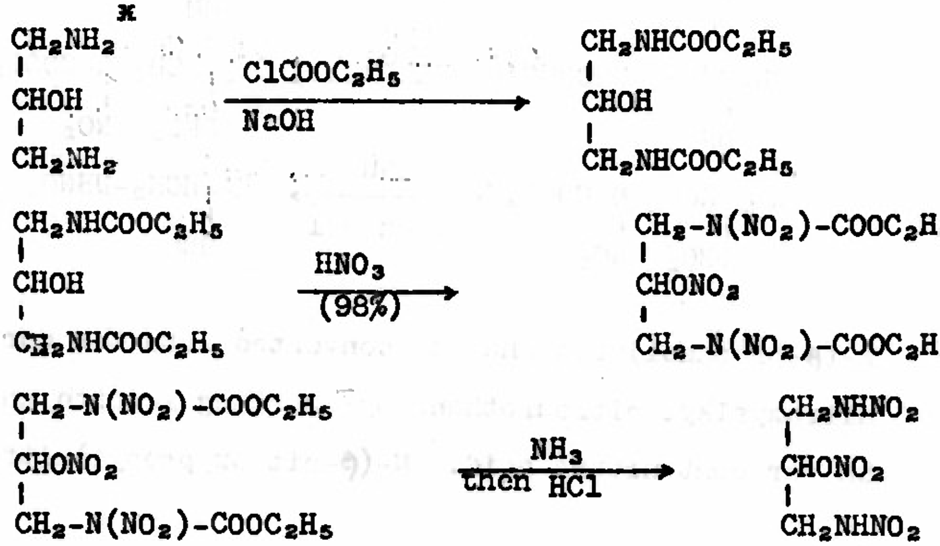
N-(β-propanol)urethane was converted into the corresponding nitroxyalkyl nitrourethane by treating it with an excess of 98 per cent nitric acid. N-(β-nitroxypropyl)nitrourethane is soluble in ether and when the extract was treated with dry ammonia the ammonium salt of N-(β-nitroxypropyl)nitramine was obtained as an oil which solidified upon standing a short while. The free nitroxyalkylnitramine was obtained simply by acidifying an aqueous solution of the ammonium salt.

2-Nitramino-1-butanol Nitrate.

Another compound related to N-(β-nitroxyethyl)nitramine should be obtainable from N-carbethoxy-2 amino-1-butanol. This urethane was prepared from 2-amino-1-butanol and ethyl chlorocarbonate but further transformations were not concluded.

Dinitraminoisopropyl Nitrate.

The synthesis of dinitraminoisopropyl nitrate was carried out according to the following:



$$\begin{array}{l} CH_2NH_2^{*} \\ | \\ CHOH \\ | \\ CH_2NH_2 \end{array} \xrightarrow[NaOH]{ClCOOC_2H_5} \begin{array}{l} CH_2NHCOOC_2H_5 \\ | \\ CHOH \\ | \\ CH_2NHCOOC_2H_5 \end{array}$$

$$\begin{array}{l} CH_2NHCOOC_2H_5 \\ | \\ CHOH \\ | \\ CH_2NHCOOC_2H_5 \end{array} \xrightarrow[(98\%)]{HNO_3} \begin{array}{l} CH_2-N(NO_2)-COOC_2H_5 \\ | \\ CHONO_2 \\ | \\ CH_2-N(NO_2)-COOC_2H_5 \end{array}$$

$$\begin{array}{l} CH_2-N(NO_2)-COOC_2H_5 \\ | \\ CHONO_2 \\ | \\ CH_2-N(NO_2)-COOC_2H_5 \end{array} \xrightarrow[\text{then } HCl]{NH_3} \begin{array}{l} CH_2NHNO_2 \\ | \\ CHONO_2 \\ | \\ CH_2NHNO_2 \end{array}$$

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[*] Obtained through the courtesy of Dr. A. L. Wilson, Carbide and Carbon Chem.Corp.Fellowship,Mellon Institute,Pittsburgh, Pa.

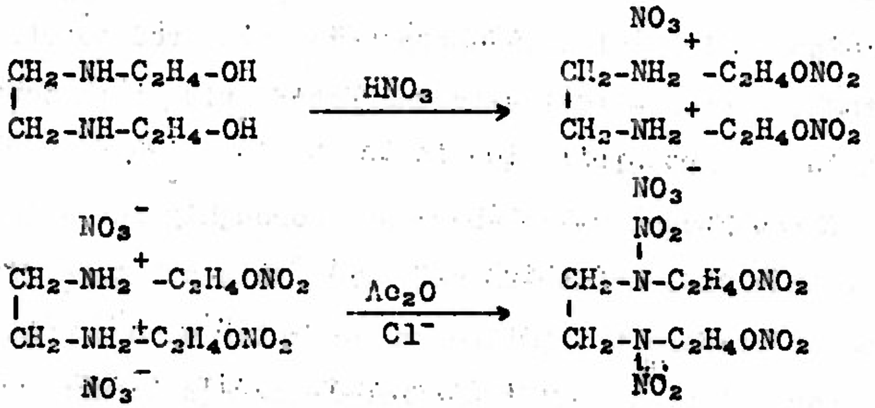
The overall yield from diaminoisopropanol was 74.8 per cent.

N, N-bis(β-nitroxyethyl)nitramine (DINA).

A separate report will be issued shortly describing the work carried out in this laboratory on this compound.

N,N'-bis(β-nitroxyethyl)ethylenedinitramine.

The synthesis of N,N'-bis(β-nitroxyethyl)ethylenedinitramine parallels the technique employed by Wright[16] on the preparation of bis(β- nitroxyethyl)nitramine (DINA) by the two stage method. The equations for these reactions are the following:



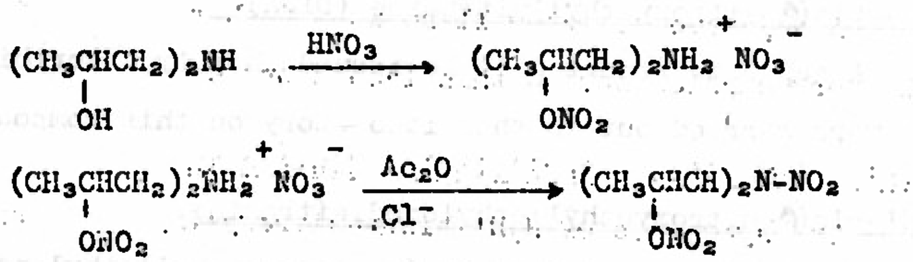
$$\begin{array}{l} CH_2\text{-}NH\text{-}C_2H_4\text{-}OH \\ | \\ CH_2\text{-}NH\text{-}C_2H_4\text{-}OH \end{array} \xrightarrow{HNO_3} \begin{array}{l} \quad NO_3^- \\ CH_2\text{-}NH_2^+\text{-}C_2H_4ONO_2 \\ | \\ CH_2\text{-}NH_2^+\text{-}C_2H_4ONO_2 \\ \quad NO_3^- \end{array}$$

$$\begin{array}{l} \quad NO_3^- \\ CH_2\text{-}NH_2^+\text{-}C_2H_4ONO_2 \\ | \\ CH_2\text{-}NH_2^+\text{-}C_2H_4ONO_2 \\ \quad NO_3^- \end{array} \xrightarrow[Cl^-]{Ac_2O} \begin{array}{l} \quad NO_2 \\ \quad | \\ CH_2\text{-}N\text{-}C_2H_4ONO_2 \\ | \\ CH_2\text{-}N\text{-}C_2H_4ONO_2 \\ \quad | \\ \quad NO_2 \end{array}$$

N,N-bis(β-nitroxypropyl)nitramine.

A compound related to the primary nitramine, N-(β-nitroxypropyl)nitramine, is N,N-bis(β-nitroxypropyl) nitramine, a secondary nitramine which was prepared by a

Bamberger "dehydration" of bis(β-nitroxyethyl)amine nitrate using acetic anhydride and a chloride catalyst. The following are the reactions employed in its preparation.



$$(\mathrm{CH_3}\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH}}\mathrm{CH_2})_2\mathrm{NH} \xrightarrow{\mathrm{HNO_3}} (\mathrm{CH_3}\underset{\substack{|\\ \mathrm{ONO_2}}}{\mathrm{CH}}\mathrm{CH_2})_2\overset{+}{\mathrm{NH_2}}\ \overset{-}{\mathrm{NO_3}}$$

$$(\mathrm{CH_3}\underset{\substack{|\\ \mathrm{ONO_2}}}{\mathrm{CH}}\mathrm{CH_2})_2\overset{+}{\mathrm{NH_2}}\ \overset{-}{\mathrm{NO_3}} \xrightarrow[\mathrm{Cl^-}]{\mathrm{Ac_2O}} (\mathrm{CH_3}\underset{\substack{|\\ \mathrm{ONO_2}}}{\mathrm{CH}}\mathrm{CH})_2\mathrm{N{-}NO_2}$$

Explosive Derivatives of Trimethylol Aminomethane and Related Compounds.

Trimethylol aminomethane, 2-amino-2-methyl-1,3-propanediol, and 2-amino-2-methyl-1-propanol which are available from Commercial Solvents Corporation appeared to offer worthwhile possibilities in the preparation of a new series of nitroxyalkyl nitramines.

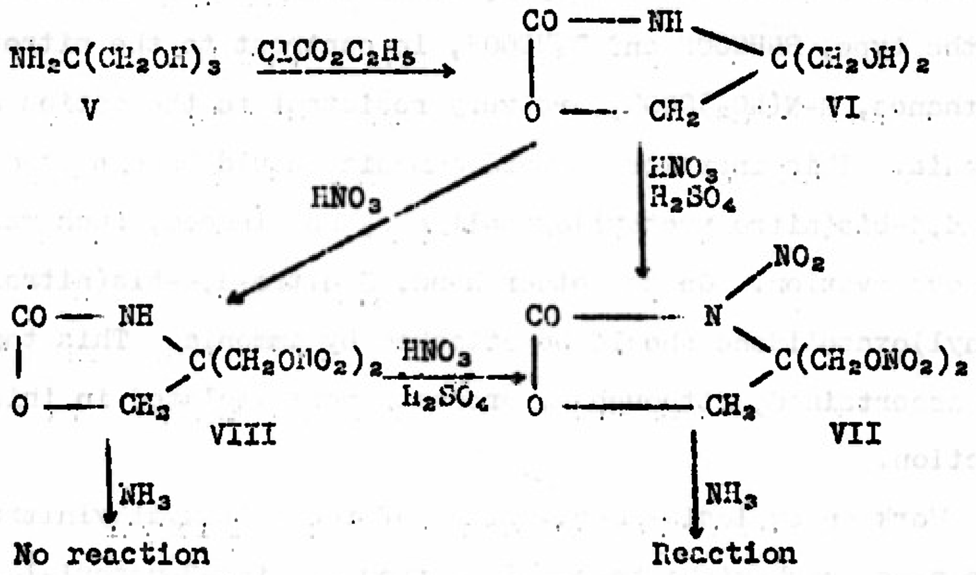
The compound which was most thoroughly investigated was trimethylol aminomethane. From this substance it was hoped to prepare tris(nitroxymethyl)nitraminomethane by transformations given by the following equations:

$$\mathrm{NH_2C(CH_2OH)_3} \xrightarrow{\mathrm{Cl{\cdot}COOEt}} \mathrm{EtOOC{-}NHC(CH_2OH)_3}$$

$$\mathrm{EtOOC{-}NH{-}C(CH_2OH)_3} \xrightarrow{\mathrm{HNO_3}} \mathrm{EtOOC{-}N(NO_2)C(CH_2ONO_2)_3}$$

$$\mathrm{EtOOCN(NO_2)C(CH_2ONO_2)_3} \xrightarrow[\mathrm{HCl}]{\mathrm{NH_3}} \mathrm{O_2N{-}NH{-}C(CH_2ONO_2)_3}$$

This synthesis however was not realized. Instead, reactions occurred which are best summarized as follows:



Trimethylol aminomethane (V) and ethyl chlorocarbonate reacted to give a cyclic urethane, 4,4-dimethylol oxazolidone (VI) instead of the expected N-(trimethylolmethyl)urethane, $C_2H_5OOCNHC(CH_2OH)_3$. From 4,4-dimethylol oxazolidone two nitrated derivatives were isolated. With 98 per cent nitric acid there was obtained 4,4-bis(nitroxymethyl)oxazolidone (VIII). Employing more drastic conditions, i.e., using mixed acids and higher temperatures, 4,4-dimethylol oxazolidone yielded a more highly nitrated compound, 3-nitro-4,4-bis(nitroxymethyl)oxazolidone (VII). The latter compound was also obtained by treating 4,4-bis(nitroxymethyl)oxazolidone with mixed acids at slightly elevated temperatures.

The behavior of the nitrated derivatives toward ammonia served as a means for verifying their structures. Urethanes of the type, RNHCOOR and R_2NCOOR, in contrast to the nitrourethanes, $R-N(NO_2)COOR$, are very resistant to the action of ammonia. This inertness toward ammonia should be expected for 4,4-bis(nitroxymethyl)oxazolidone, and indeed, such was our observation. On the other hand, 3-nitro-4,4-bis(nitroxymethyl)oxazolidone should be attacked by ammonia. This too was ascertained, although no products were isolated in this reaction.

Work on explosive derivatives of the nitroxyalkylnitramine type which might be obtained from 2-amino-2-methyl-1-propanol and 2-amino-2-methyl-1,3-propanediol was not concluded. Only the urethane of the former, N-carbethoxy-2-amino-2-methyl-1-propanol was prepared. It is to be noted that cyclization to give an imidazolidone derivative did not occur as was the case when trimethylol aminomethane and ethyl chlorocarbonate were reacted.

Experiments on
Trimethylol Nitromethane.

The object of these experiments was the synthesis of tris(nitraminomethyl)nitromethane, $O_2NC(CH_2NHNO_2)_3$, according to the following:

$$O_2N\text{-}C(CH_2OH)_3 \xrightarrow{SOCl_2} O_2N\text{-}C(CH_2Cl)_3$$

$$O_2N\text{-}C(CH_2Cl)_3 \xrightarrow{NH_3} O_2N\text{-}C(CH_2NH_2)_3$$

$$O_2N\text{-}C(CH_2NH_2)_3 \xrightarrow{ClCOOEt} O_2N\text{-}C(CH_2NHCOOEt)_3$$

$$O_2N\text{-}C(CH_2NHCOOEt)_3 \xrightarrow{HNO_3} O_2N\text{-}C\left[CH_2N(NO_2)COOEt\right]_3$$

$$O_2N\text{-}C\left[CH_2N(NO_2)COOEt\right]_3 \xrightarrow[HCl]{NH_3} O_2N\text{-}C(CH_2NHNO_2)_3$$

In this connection we prepared tris(chloromethyl) nitromethane in yields considerably better than those reported by Kleinfeller[17], who carried out the chlorination by replacement with phosphorous pentachloride, and obtained only a 30 per cent yield.

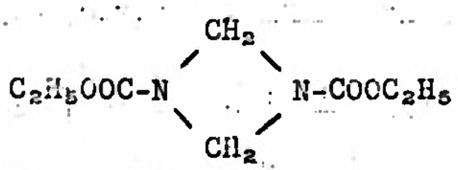
The ammonolysis of tris(chloromethyl)nitromethane was not successful in the single attempt which was made. The reaction should presumably be carried out at lower temperatures than that which was attempted.

Experiments on the Reaction of Urethane with Formaldehyde.

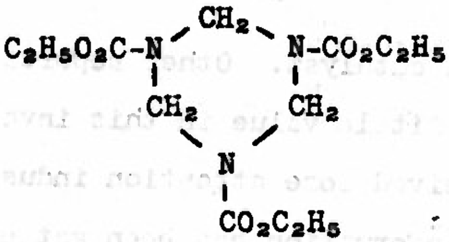
Nitration of the Methylene Urethanes.

The condensations of urethane with formaldehyde lead to several products which appear to offer interesting possibilities in nitration reactions.

The reaction between urethane and formaldehyde was first reported by Bischoff and Reinfeld[18], who isolated a compound which they called anhydroformaldehydeurethane, melting at 100° and to which they ascribed the formula;



the dimer of methylene urethane. In the same year Conrad and Hock[19] carried out additional experiments in which they varied the proportions of formaldehyde and urethane. From a two to one mole ratio of urethane to formaldehyde they were able to obtain in good yields methylene diurethane. When the ratio was changed to unity they obtained an oil which when treated with a mixture of acetic acid and acetic anhydride yielded anhydroformaldehydeurethane (m.p. 102°). On the basis of molecular weight measurements they concluded that the dimeric structure was correct. Gina and Racciu[20] in 1929 carried out additional experiments, and they reported the isolation of a trimer and tetramer in addition to anhydroformaldehydeurethane. More recently C. S. Marvel in a communication to J. R. Johnson reported that cryoscopic measurements in benzene indicate that the dimeric structure proposed by former workers was really a trimer, vis. trimethylenetriurethane of the formula,



and not anhydroformaldehydeurethane. The molecular weight, as determined by Marvel, was 275. The theoretical molecular weight of the trimer of methylene urethane is 303. In addition, Marvel also claims to have isolated the tetramer, a "grainy oil" which on a basis of cryoscopic measurements has a molecular weight of 375.

We prepared a considerable amount of methylene diurethane from which we hoped to prepare methylene dinitramine. An ammonium salt was prepared upon ammonolysis of the nitration product of methylene diurethane. This however could not be repeated in subsequent attempts.

Likewise, a small amount of cyclotrimethylenetriurethane (m.p. 100-2°) was prepared from which it was hoped that cyclotrimethylenetrinitramine (RDX) could be prepared by nitrolysis. However, this proved unsuccessful.

Pentaglycerine and Its Reactions.

Pentaglycerine was first prepared by Hosaeus[21] in 1893 through the reaction of propionaldehyde and formaldehyde using calcium hydroxide as a catalyst. Other reports of it preparation have been of little value in this investigation. The synthesis has received some attention industrially, although little useful information has been gathered from this source.

Koch and Zorner[22] have studied the condensation of propionaldehyde and formaldehyde using potassium carbonate and also potassium hydroxide as the condensing agent. In their studies they employed ratios of formaldehyde to propionaldehyde lower than that theoretically required for the formation of pentaglycerine.

More recently Cooper, O'Neill, and Clark[23], and Metcalfe and Clark[24] have studied its preparation in conjunction with its possible use as an explosives intermediate.

Synthesis of Pentaglycerine.

Our primary interest in the preparation of pentaglycerine was in its use in the synthesis of pentaglyceryl trinitramine, $CH_3C(CH_2NHNO_2)_3$ (see page 19). However, in its preparation we encountered some new products which might be of interest in connection with its possible importance in the synthesis of trimethylolmethylmethane trinitrate described by Cooper, O'Neill, and Clark[23], and by Metcalfe and Clark[24].

In our experiments on the condensation of propionaldehyde and formaldehyde we employed ratios which were in equivalence and also ratios in which formaldehyde was present in ratios greater than equivalence. The results of the most striking experiments are tabulated below.

Table XII

Summary of Experiments on Preparation of Pentaglycerine

Procedure Number	PFA Moles	PA Moles	H_2O Liters	$Ca(OH)_2$ Moles	P.G. % Yield	Color of Reaction
I	3.12	1.04	3.3	2.00	29	brown
II[a]	20	4.77	5.5	2.43	46	clear
III[b]	20	4.77	4.0	2.43	25[d]	clear
IV[c]	15	4.77	4.0	2.43	46	brown
V[c]	15	4.77	4.0	3.22	46	brown

PFA = paraformaldehyde, PA = propionaldehyde, P.G. = pentaglycerine

a. Reaction acidified with hydrochloric acid and then concentrated.

b. Concentrated without acidification.

c. Reaction acidified with sulfuric acid, filtered and then concentrated.

d. Other products, i.e., 5-methyl-5-methylol-1,3-dioxane and its formal derivative were also obtained.

Procedure I was a duplication of Hosaeus'[24] method and represents an average of several runs. The reaction was characterized by low yields of pentaglycerine and by the presence of great amounts of "formose" sugars.

From a comparison of the yields in procedures II, IV, and V, one must conclude that the reaction is relatively independent of moderate dilutions, great excesses of paraformaldehyde and calcium hydroxide. However, the influence of an excess of paraformaldehyde is clearly seen in procedure II and III. In these experiments the solutions maintained their clarity and an absence of sugary odor throughout the preparation. This is in striking contrast to procedures I, IV, and V, which were characterized by extensive formation of "formoso" sugars.

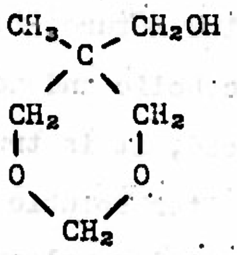
Of importance in the condensation of propionaldehyde and formaldehyde is the manner in which the solution is treated after the completion of the reaction. Whether the solution is acidified with hydrochloric acid, or with sulfuric acid (which is more desirablo, since calcium may be precipitated and removed), makes little difference in the yield. However, in procedure II which was not acidified before working up the product thero was extensive acetal formation.

It is inferred through this latter comparison then, that there proceeds in the reaction of propionaldehyde and formaldehyde in which an excess of the latter is used, not only the condensations and disproportionations characteristic of a Tollen's condensation but also extensive acetal formatior

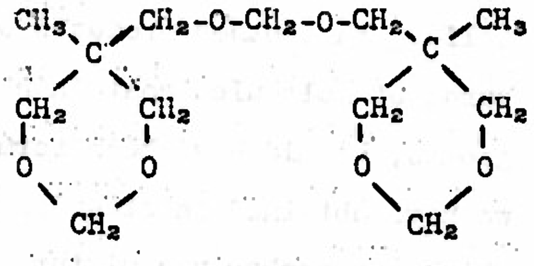
Acidification, therefore, in the case where sulfuric acid is used, performs a dual role, (1) that of precipitating the calcium, and (2) of hydrolyzing the acetals. Hydrochloric acid functions only as the latter.

Acetals of Pentaglycerine.

The reaction of propionaldehyde and formaldehyde, under conditions mentioned in the previous section, produces in addition to pentaglycerine, certain acetals which we have been able to isolate. Work on these compounds indicated that they were derivatives of 1,3-dioxane of the following structures:

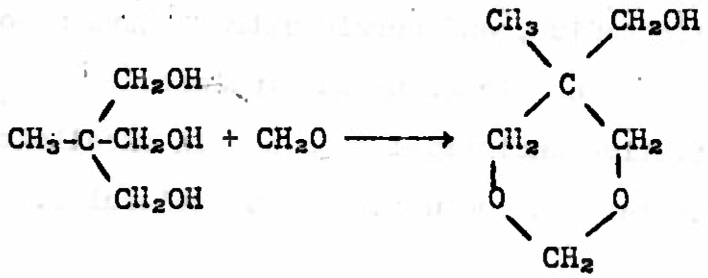


IX

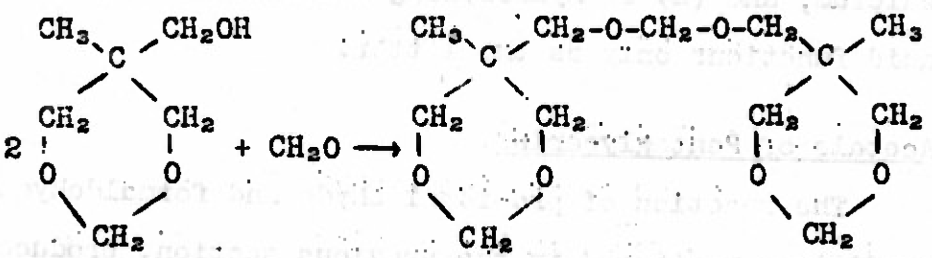


X

The compound IX, 5-methyl-5-methylol-1,3-dioxane arises from the acetalization of pentaglycerine by formaldehyde according to the following equation:



The compound X may arise either through an acetalization of 5-methyl-5-methylol-1,3-dioxane by formaldehyde according to the equation,



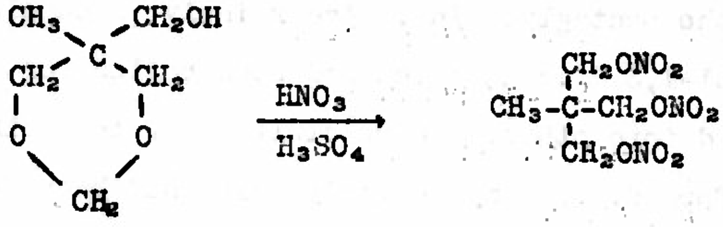
or through an acetal interchange between molecules of 5-methyl-5-methylol-1,3-dioxane. This latter possibility is discussed later on.

In addition to the acetals described we have reason to believe that other products of a complex nature, i.e., mixtures of molecules containing both alcoholic and acetal groups, should have been formed. Indeed, it is true that we have obtained an ether insoluble, water soluble residue which was probably a mixture of some complex molecules. This, however, was not investigated further.

Qualitative analytical tests on IX indicated no unsaturation and gave a negative Tollen's test. A sample dissolved in dry xylene produced a slow evolution of gas with metallic sodium, and cerric nitrate gave a positive test; thus an alcoholic group was indicated.

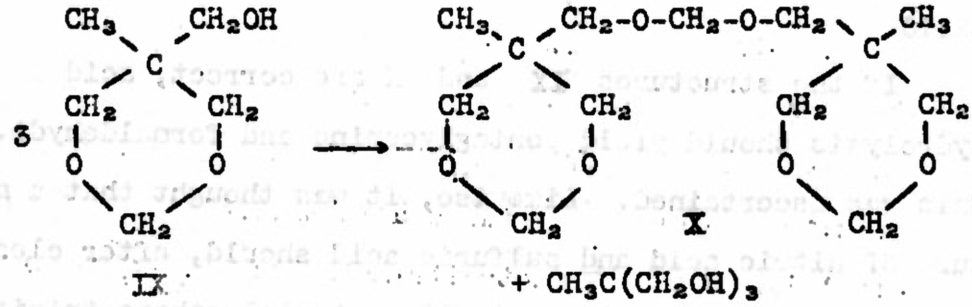
Quantitative analytical data was in excellent agreement for the postulated structures of both molecules. A comparison of the calculated and theoretical molecular refractivities for IX. was satisfactory. From the values for the atomic factors for calculating the molecular refraction a value of 32.52 was obtained, whereas the observed value was 32.10.

If the structures IX and X are correct, acid hydrolysis should yield pentaglycerine and formaldehyde. This was ascertained. Likewise, it was thought that a mixture of nitric acid and sulfuric acid should, after cleaving the formal linkage, give methyltrimethylolmethane trinitrate according to the following equation:



The formation of trimethylolmethylmethane trinitrate was confirmed for not only 5-methyl-5-methylol-1,3-dioxane but also for the acetal of 5-methyl-5-methylol-1,3-dioxane.

Atmospheric distillation of the liquid, 5-methyl-5-methylol 1,3-dioxane occurred at a temperature of 214-215°, accompanied by an intermolecular transformation. A water insoluble solid, melting at 99-100°, was formed which was identical with X, isolated in the pentaglycerine reaction. This transformation might best be interpreted as having occurred through an acetal interchange to yield finally the relatively more stable bimolecular derivative. The equation for this overall transformation then becomes:



It was hoped to verify this reaction by attempting to isolate the pentaglycerine. Accordingly, a sample of 5-methyl-5-methylol-1,3-dioxane which had been boiled for two hours was poured into ether. No precipitate of the trihydric alcohol formed. If any pentaglycerine had been formed, it might well be that the excess 1,3-dioxane derivative exerted a solubilizing effect on it.

Nitration of Pentaglycerine and Its Derivatives.

From the nitrations of 5-methyl-5-methylol-1,3-dioxane and its bimolecular formal derivative, there was obtained upon treatment of each with mixed acids the same product, trimethylolmethylmethane trinitrate. This substance was a clear oily liquid at room temperature and froze to a white solid at +7.5°C. The same solid melted at approximately

+9°C., a somewhat higher temperature than the observed freezing point. This slight discrepancy of melting point and freezing point is explained by the fact that the liquid has a great tendency to supercool, becoming very viscous and sticky near its freezing point.

Previously reported melting points for trimethylolmethylmethane trinitrate were variable. Cooper, O'Neill, and Clark[23] gave -17.5°C., Metcalfe and Clark[24] gave -2.9°C. Other sources gave -15°C.[25] and -3°C.[26]. These values were observed for the trinitrate obtained through the action of nitric acid and sulfuric acid on pentaglycorine. We repeated the preparation of trimethylolmethylmethane trinitrate by reacting pentaglycerine with mixed acids and obtained a melting point of +9°C. for the product.

That the compound which we isolated through the nitration of the acetals of pentaglycerine was methyltrimethylolmethane trinitrate is substantiated by analytical data and molecular weight determination. In addition, the physical constants, i.e., the density and refractive index, of the trinitrate prepared from the nitration of pentaglycerine and from the nitration of the acetal derivatives of pentaglycerine are in excellent agreement. Further proof was offered through a comparison of the calculated and theoretical molecular refractivities. From the values for atomic factors for calculating the molecular refraction a value of 49.69 was obtained whereas the observed value was 49.4.

Possibly there existed in trimethylolmethylmethane trinitrate, prepared from pentaglycerine and mixed acids by other investigators an impurity which lowered the true melting point, accounting for the variable and low values for this constant.

We have made some progress in elucidating the possible nature of this contaminant. When recrystallized pentaglycerine was brominated by replacement using phosphorous tribromide there was obtained in addition to the main product, pentaglyceryl tribromide, a residue which was shown to be pentaerythrityl bromide. This leads us to suspect that there exists in pentaglycerine a small percentage of pentaerythritol as an impurity. Its introduction as an impurity is quite possible since it seems not unlikely that propionaldehyde may be contaminated with some acetaldehyde which may not be removed completely through distillation. By analogy, then, the impurity present in trimethylolmethylmethane trinitrate was undoubtedly pentaerythritol tetranitrate (PETN). Thus this may account for the low values obtained for the melting point of the trinitrate prepared from pentaglycerine and mixed acids by previous workers.

The likelihood of the existence of polymorphic forms for trimethylolmethylmethane trinitrate may also offer an explanation for the variance of its melting point as observed by different workers.

Ammonolysis of Pentaerythrityl Bromide

Ammonolysis with Alcoholic Ammonia.

Pentaerythrityl bromide did not react with alcoholic ammonia (95 per cent ethyl alcohol saturated with ammonia) at room temperature after standing for sixty days. It reacted slowly at 130° to yield only about two per cent of pentaerythrityl tetramine, $C(CH_2NH_2)_4$, based on the reacted bromide. At 160°, the ammonolysis was practically complete in twelve hours (one per cent of the bromide unreacted).

When the ammonolysis was carried out at 160° for twelve hours, the yields of the tetramine increased slightly but regularly as the percentage of water in the reaction mixture was increased (see Table XIII). This effect may be explained by the fact that water acts as an acid in the mixture.

Table XIII

The Effect of Water Content on the Yield of Pentaerythrityl Tetramine.

Percentage of water	0	5	10	25
Yields of the amine	16.6	19.9	22.5	23.3

Ammonolysis with Liquid Ammonia.

Pentaerythrityl bromide did not react with liquid ammonia at room temperature in five days. At 80°, 64 per cent of the total bromide used reacted with ammonia in six hours, but no tetramine could be isolated. It reacted completely with liquid ammonia at 100-110° and 125°-130°, but in both cases no primary tetramine was formed.

Ammonolysis with a Mixture of Liquid Ammonia and Ethanol.

Pentaerythrityl bromide reacted with a mixture of 67 per cent of ammonia and 33 per cent of absolute alcohol (by volume) at 150-155° in six hours and gave 6.6 per cent of the amino. The yield was lowered to 2.4 per cent when the reaction was carried out at 175-180° for six hours. With ethanol containing 30 per cent of water, the yield increased to 15.6 per cent. With high concentration of ammonia the rate of reaction increased greatly. The ammonolysis was complete in one hour at 140-160°, whereas the reaction with alcoholic ammonia required twelve hours at 160°.

Ammonolysis with a Mixture of Liquid Ammonia, Ethanol and Ammonium Chloride.

Ammonium chloride acts as an acid in liquid ammonia, donating a proton to an amine and hence protecting it from further reaction with the alkyl halide. This effect was confirmed as the yield of the tetramine was increased from 34 per cent to 50 per cent. A ratio of four moles of ammonium chloride to each atom of bromine in the tetrabromide appeared to be moxt favorable. Further increase in concentration of ammonium chloride did not increase the yield of the tetramine. It was also found that ethanol containing 50 per cent of water improved the yield slightly (four per cent). In a large run using 60 g. of the tetrabromide, a yield as high as 67.2 per cent was obtained.

Ammonolysis with Liquid Ammonia and Pyridine.

A mixture of ammonia and pyridine was tried in the ammonolysis. This mixture did not show much improvement over an alcohol mixture.

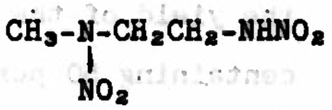
From the foregoing it is possible to make the following conclusions:

1. The optimum temperature for the ammonolysis of pentaerythrityl bromide is about 160°.
2. Alcohol must be present to act as a solvent for the pentaerythrityl bromide.
3. A high concentration of ammonia favors the tetramine formation.
4. Ammonium chloride and water increase the yields of the tetramine markedly.

EXPLOSIVE PROPERTIES OF SOME ALIPHATIC NITRAMINES AND RELATED COMPOUNDS

A summary of the explosive properties of a number of compounds prepared in our investigations is presented. The results contained herein were determined by the Explosives Research Laboratory, Bruceton, Pa.

N-methyl-ethylenedinitramine



$CH_3-\underset{NO_2}{\underset{|}{N}}-CH_2CH_2-NHNO_2$

M.P. 120.5-122.5°C.

Oxygen Balance to CO_2: -58.5%

pH: 3.7

Explosion Temperature: No explosion 360°C.

Thermal Stability (135°C.): Not acid in 300 min.

Vacuum Stability (120°C.): E.C. in 26-48 hrs.

International Test (75°C.): Volatility, 0.1%

Hygroscopicity

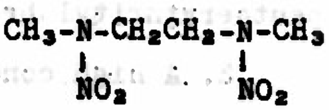
90% R.H.: 0.00%

100% R.H.: 3.77%

Power: 119.7 (TNT = 100)

Sensitivity: Greater than 90 cm. (RDX = 48-50 cm.)

N,N'-dimethyl-ethylenedinitramine



$CH_3-\underset{NO_2}{\underset{|}{N}}-CH_2CH_2-\underset{NO_2}{\underset{|}{N}}-CH_3$

M.P. 137.5-138°C.

Oxygen balance to CO_2: -80.9%

pH: 6.6

Explosion Temperature: No explosion 360°C.

Thermal Stability: (135°C.): Not acid in 300 min.

Vacuum Stability (120°C): 0.31 cc., 0.32 cc. in 48 hrs.

International Test (75°C): Volatility, 0.1% in 24 hrs.

Hygroscopicity

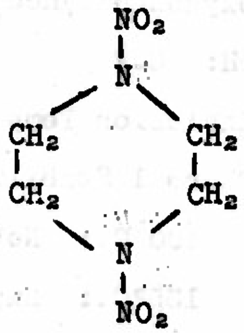
90% R.H.: 0.02%

100% R.H.: 1.92%

Power: 95, 103.4 (TNT = 100)

Sensitivity: Greater than 90 cm. (RDX = 48-50 cm.); 51 (50% point) RDX (50%pt.= 35 cm.)

N,N'-dinitropiperazine

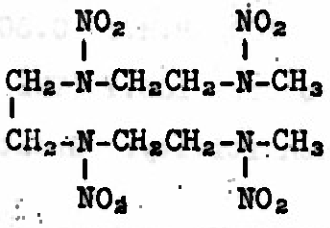


M.P 214-216°C. d.

Oxygen Balance to CO$_2$: -72.6%

Power: Lead Block = 105

N^{1}N^4-dimethyl-triethylenetetranitramine



$$\begin{array}{l}\mathrm{CH_2{-}\overset{NO_2}{N}{-}CH_2CH_2{-}\overset{NO_2}{N}{-}CH_3}\\ \;|\\ \mathrm{CH_2{-}\underset{NO_2}{N}{-}CH_2CH_2{-}\underset{NO_2}{N}{-}CH_3}\end{array}$$

M.P. 211.5-213°C., d.

Oxygen balance to CO$_2$: -76.8%

pH: 6.9

Explosion Temperature: No explosion 360°C.

Thermal Stability (135°C.): Not acid in 300 min.

Vacuum Stability (120°C.): 10.49, 5.39 cc. in 90 min.

International Test (75°C.): Volatility, 0.1%

Hygroscopicity

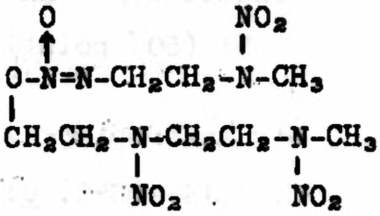
90% R.H.: 0.2%

100% R.H.: 0.95%

Power: 90.4 (TNT = 100)

Sensitivity: Greater than 90 cm. (RDX = 48-50 cm.)

Iso-N^1,N^4-dimethyl-triethylenetetranitramine



M.P. 88.5-90°C.

Oxygen Balance to CO_2: -76.8%

pH: 6.2

Explosion Temperature: Ignited, 325°C.

Thermal Stability

100°C.: Not acid in 300 min.

135°C.: Exploded in 10 min.

Hygroscopicity

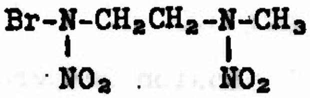
90% R.H.: 0.02%

100% R.H.: 0.36%

Power: 109.1 (TNT = 100)

Sensitivity: Greater than 90 cm. (RDX = 48-50 cm.)

N-bromo-N'-methyl-ethylenedinitramine



$Br-\underset{NO_2}{N}-CH_2CH_2-\underset{NO_2}{N}-CH_3$

M.P. 118-119°C., d.

Oxygen Balance to CO_2: -29.6%

pH: 3.9

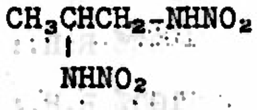
Explosion Temperature: No explosion 360°C.

Thermal Stability (135°C.): Ignited in 4 min.

Power: 101.2 (TNT = 100)

Sensitivity: 6.6 cm (50% pt.; RDX = 35 cm.)

Propylenedinitramine (PDNA)



$CH_3\underset{\displaystyle NHNO_2}{\underset{|}{C}}HCH_2-NHNO_2$

M.P. 111-112°C.

Oxygen Balance to CO_2: -58.5%

pH: 3.3

Explosion Temperature: Ignited 355°C.

Thermal Stability (100°C.): Not acid in 300 min.

Vacuum Stability (100°C.): E.C. in 24 hrs.

International Test (75°C.): Volatility, 2.0% in 24 hrs.

Hygroscopicity

90% R.H.: 0.76%

100% R.H.: 2.42%

Power: 115.9 (TNT = 100)

Sensitivity: 63.1 cm (RDX = 48-50 cm.)

Pentaerythrityl tetranitramine $C(CH_2NHNO_2)_4$

M.P. 166.8-167.4°C. d.

Oxygen Balance to CO_2: -41.0%

pH: 3.2

Explosion Temperature: Deflagrated 295°C.

Thermal Stability

100°C: Not acid in 300 min.

135°C: Ignited in 240 min.

Vacuum Stability (100°C.): 8.76, 10.20 cc. in 48 hrs.

International Test (75°C.): Volatility 0.0%

Hygroscopicity

90% R.H.: 0.01%

100% R.H.: 0.06%

Power: 129 (TNT = 100)

Sensitivity: 26.8 cm. (RDX = 48-50 cm.)

Pentaglyceryl trinitramine (PGX) $CH_3C(CH_2NHNO_2)_3$

M.P. 130-131°C., d.

Oxygen Balance to CO_2: -64.0%

pH: 3.0

Explosion Temperature: Ignited, 335°C.

International Test (75°C.): 0.0%

Thermal Stability (135°C.): Ignited in 10 min.

Vacuum Stability (100°C.): E.C. (12 cc.) in 25 hrs.

Power: 111.8 (TNT = 100)

Sensitivity (50% pt.): 30

N-(β-nitroxyethyl)nitramine (NENA) $O_2NO-CH_2CH_2-NHNO_2$

M.P. 15°C.

Oxygen Balance to CO_2: -15.9%

pH: 2.7

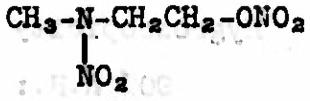
Explosion Temperature: No explosion, 360°C; Volatilizes rapidly

Thermal Stability (135°C.): Acid in 75 min.

Power: 133.9 (TNT = 100)

Sensitivity (50% pt.): 191, 107

N-(β-nitroxyethyl)methylnitramine (MeNENA)



$CH_3-N(NO_2)-CH_2CH_2-ONO_2$

M.P. 38-40°C.

Oxygen Balance to CO_2: -43.6%

pH: 7.2

Explosion Temperature: No explosion 360°C.

Thermal Stability (135°C.): Volatilizes rapidly; acid in 65 min.

Vacuum Stability (100°C.): 6.30; 7.38 cc./5 g./48 hrs.

International Test (75°C.): Volatility, 0.13%; 0.10%

Hygroscopicity

90% R.H.: 0.00%

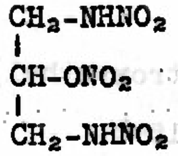
100% R.H.: 0.01%

Power = 135.5;137.2 (TNT = 100)

Sensitivity: Greater than 90 cm.

(RDX = 48-50 cm.)

Dinitraminoisopropyl Nitrate



$$\begin{array}{l} CH_2\text{-}NHNO_2 \\ | \\ CH\text{-}ONO_2 \\ | \\ CH_2\text{-}NHNO_2 \end{array}$$

M.P. 164-165°C. d.

Oxygen Balance to CO_2: -17.8%

pH: 3.5

Explosion Temperature: Deflagrated, 230°C.

Thermal Stability

100°C.: Not acid in 300 min.

135°C.: Acid in 105 min.

Vacuum Stability (100°C.): 1.99, 4.36 cc. in 48 hrs.

International Test (75°C.): 0.0%

Hygroscopicity

90% R.H.: 0.02%

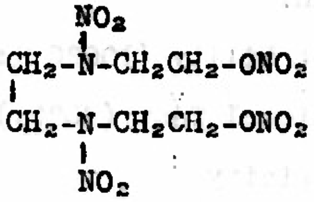
100% R.H.: 0.02%

Power: 141.5 (TNT = 100)

Sensitivity: 24.4 cm. (RDX = 48-50 cm.)

N,N'-bis(β-nitroxyethyl)ethylenedinitramine

M.P. 60-62°C.



$$\begin{array}{l} \quad\;\; NO_2 \\ \quad\;\; | \\ CH_2\text{-}N\text{-}CH_2CH_2\text{-}ONO_2 \\ | \\ CH_2\text{-}N\text{-}CH_2CH_2\text{-}ONO_2 \\ \quad\;\; | \\ \quad\;\; NO_2 \end{array}$$

Oxygen Balance to CO_2: -39.0%

pH: 6.9

Explosion Temperature: No explosion, 360°C.

International test (75°C.): 2.2%

Thermal Stability (135°C.): Acid in 10 min.

Vacuum Stability (100°C): E.C. in 20 min.

Power: 134.5 (TNT = 100)

Sensitivity (50% pt.): 83

EXPERIMENTAL PART

Methylation of Ethylenedinitramine.

Procedure A. In a 1000-cc. three-necked flask equipped with stirrer, thermometer, and dropping funnel there were placed 250 cc. of water, 100 cc. of alcohol, 15 g. (0.1 mole) of ethylenedinitramine, and 16.8 g. (0.3 mole) of potassium hydroxide. A solution of 28.5 g. (0.3 mole) of methyl bromide in 150 cc. of alcohol was added through the dropping funnel and the mixture was stirred for eight hours at room temperature. After stirring, the reaction was allowed to stand for three days. The precipitate which formed was filtered and dried. The crude product amounting to 5.2 g. and melting at 135-136° (uncorr.) was recrystallized from 200 cc. of water and gave 3.7 g. of pure product melting at 136-138°. This corresponds to the N,N-dimethyl-ethylenedinitramine prepared by Franchimont.

The filtrate from the reaction mixture was concentrated to a volume of 130 cc. No further precipitation occurred when this solution was cooled. Upon acidification with dilute nitric acid a copious precipitate formed which was filtered and dried. This crude product (6.5 g.) melted at 108-110° (uncorr.). After two recrystallizations from water (100 cc., and 50 cc.) there was obtained 4.4 g. of a crystalline solid melting at 120-121° (uncorr.). This corresponds to N-methyl-ethylenedinitramine prepared by Franchimont.

Procedure B. The methylation of ethylenedinitramine was also carried out using dimethyl sulfate. As in Procedure A above, both the monomethyl and dimethyl derivatives were obtained.

In a 5-l., three-necked flask equipped with stirrer, thermometer, and dropping funnel were placed 300 g. (2 moles) of ethylenedinitramine, 168.3 g. (3 moles) of potassium hydroxide, 200 g. (2 moles) of potassium bicarbonate and a solvent consisting of 1250 cc. of alcohol and 1250 cc. of water. The mixture was stirred until there was complete solution of the solids. Methyl sulfate (378.3 g., 3 moles) was added dropwise to the reaction mixture over a period of four hours; the temperature of the reaction mixture remained slightly above room temperature during this time because of the heat of the reaction. When the addition of methyl sulfate had been completed the entire mixture was heated to boiling and 800 cc. of solvent distilled off. The reaction mixture was cooled to 0° and the precipitate of N,N'-dimethyl-ethylenedinitramine which separated was filtered. The crude product, weighing 105.3 g. and melting at 134-137° (corr.), was recrystallized from 2500 cc. of water. There was obtained 88.5 g. of a light flaky crystalline material melting at 137.5-138° (corr.) corresponding to a yield of 24.8 per cent.

The filtrate obtained after filtering off the crude dimethyl derivative was made distinctly acid to Congo Red paper by adding approximately 115 cc. of 70 per cent nitric acid.

The acidified solution was cooled to 0° and the crystalline precipitate which separated was filtered and dried in the air. A yield of 179.4 g. of crude material melting at 110-113° (corr.) was obtained. Recrystallization of the crude product from 1100 cc. of water gave 90.2 g. of crystalline N-methylethylenedinitramine melting at 120.5-122.5° (corr.). This was a yield of 30.3 per cent.

Very little additional product was obtained when the filtrates from the recrystallizations were concentrated. An additional 1.5 g. of the dimethyl derivative was obtained by concentrating the filtrate from the recrystallization of the first crop of material. Potassium methyl sulfate made up the bulk of the material remaining in the aqueous filtrate in recrystallizing the monomethyl derivative.

Preparation of N,N'-dinitropiperazine.

In a two-liter, three necked flask, provided with stirrer, condenser, and dropping funnels there were placed 37.5 g. (0.25 mole) of ethylenedinitramine, 500 cc. of ethanol, and 500 cc. of water. There were also prepared two solutions, 200 cc. of aqueous potassium hydroxide containing 28.0 g. (0.5 mole) of the solid base, and 100 cc. of an alcoholic solution containing 47 g. (0.25 mole) of ethylene dibromide.

There were added every hour to the refluxing reaction mixture 10 cc. of alcoholic ethylene dibromide and 20 cc. of aqueous potassium hydroxide. The heating was continued for a total of twenty-four hours and then cooled whereupon a precipitate formed.

The crystalline deposit was filtered off and there was obtained 10.5 g. of crude N,N'-dinitropiperazine, melting at 208-210°C. d. This was further purified by treating it with 80 g. of 10 per cent sodium hydroxide to remove any alkali soluble products, filtered, and finally recrystallized from ethyl acetate. The final product was a white glistening, crystalline solid (8.5 g.) melting at 214-216° d. (uncorr.).

Analysis: Calcd. for $C_4H_8O_4N_4$: N, 31.82.

Found: N, 31.85.

The aqueous filtrate contained unreacted ethylenedinitramine together with other products of a polymeric nature. The separation of these various by-products was difficult and was not therefore studied further.

Other experiments were carried out employing ratios of two moles of ethylenedinitramine to one mole of ethylene dibromide; likewise some reactions were carried out using less solvent, thus increasing the concentration of the reactants. It is interesting to note that the yields of N,N'-dinitropiperazine were less in both cases; the formation of side-products was enhanced but these were difficult to separate. Undoubtedly they were a mixture of linear molecules of a polymeric nature.

Reaction of N-methyl-ethylenedinitramine and Ethylene Dibromide.

In a 2-l. flask fitted with stirrer, thermometer, and reflux condenser there were placed 82.0 g. (0.5 mole) of N-methylethylenedinitramine, 500 cc. of alcohol, 500 cc. of water, 28.1 g. (0.5 mole) of potassium hydroxide, and 47.0 g. (0.25 mole) of ethylene bromide. The mixture was stirred and refluxed for twenty-four hours. Precipitation of N^1,N^4-dimethyl-triethylenetetranitramine began to take place after two hours refluxing.

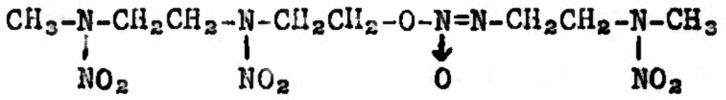
After completion of the reflux period the mixture was filtered at 70° and the crude solid washed with 100 cc. of hot alcohol. The washings were combined with the main filtrate. The yield of crude product from several runs varied from 12.1 g.-15.6 g. and melted at 210-213° *d.*(uncorr.). The pure N^1,N^4-dimethyl-triethylenetetranitramine (m.p. 211.5-213° *d.* (uncorr.)) was obtained by recrystallizing the crude product from nitromethane.

Analysis: Calcd. for $C_8H_{18}O_8N_8$: N, 31.64.

Found: N, 31.62.

The combined filtrate and washings obtained above were cooled in the refrigerator overnight and gave a second crop of crystalline material (15.4 g.-19.5 g.) melting at 83.5-85.5° (corr.). This impure material was purified by dissolving in the minimum amount of hot acetone, treating with decolorizing charcoal, filtering, and allowing the solution to cool. The crystalline precipitate was separated and recrystallized from aqueous acetone (5 volmes of water to 8 volumes of acetone). There separated on cooling two solid species, one of which was a small, plate-like, well crystallized solid whereas the other was a light amorphous material. It was possible to separate the two materials mechanically. The mixture in the cold acetone was swirled and the liquid containing the amorphous material was decanted from the crystalline solid. The process was repeated several times and complete separation was obtained. The amorphous solid (1.8-2.3 g.) melted at approximately 150°. This substance was not invesigated further.

The crystalline solid (11.2-14.2 g.) melted at 88.5-90° (corr.) and recrystallization from aqueous acetone did not raise the melting point. The experimental evidence indicates that this product is isomeric with N^1,N^4-dimethyl-triethylenetetranitramine and probably has the structure:



$$CH_3-\underset{\substack{|\\NO_2}}{N}-CH_2CH_2-\underset{\substack{|\\NO_2}}{N}-CH_2CH_2-O-\underset{\substack{\downarrow\\O}}{N}=N-CH_2CH_2-\underset{\substack{|\\NO_2}}{N}-CH_3$$

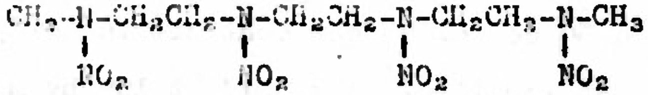
Analysis: Calcd. for $C_6H_{18}O_8N_8$: N, 31.64.

Found: N, 31.58, 31.61.

When the filtrate from the second crop was acidified with 70 per cent nitric acid a precipitate of impure unreacted N-methyl-ethylenedinitramine separated. From 28-35 g. of unreacted material was recovered.

Structure of High-melting Compound Formed in Alkylation of N-methyl-ethylenedinitramine.

If the high melting compound formed in the reaction of N-methyl-ethylenedinitramine has the structure proposed,



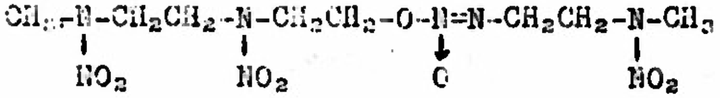
$$CH_3-\underset{\substack{|\\ NO_2}}{N}-CH_2CH_2-\underset{\substack{|\\ NO_2}}{N}-CH_2CH_2-\underset{\substack{|\\ NO_2}}{N}-CH_2CH_2-\underset{\substack{|\\ NO_2}}{N}-CH_3$$

treatment with 98 per cent nitric acid should not affect the compound.

Actually the compound can be recovered unchanged when it is dissolved in 98 per cent nitric acid by quenching with water.

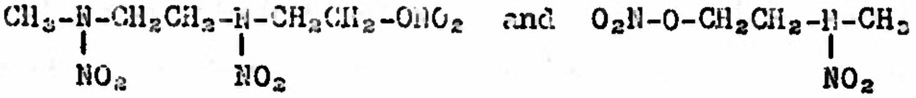
Structure of Low-melting Compound Formed in Alkylation of N-methyl-ethylenedinitramine.

If the low melting compound formed in the alkylation of N-methyl-ethylenedinitramine with ethylene bromide has the structure proposed,



$$CH_3-\underset{\substack{|\\ NO_2}}{N}-CH_2CH_2-\underset{\substack{|\\ NO_2}}{N}-CH_2CH_2-O-\underset{\substack{\downarrow\\ O}}{N}=N-CH_2CH_2-\underset{\substack{|\\ NO_2}}{N}-CH_3$$

treatment with 98 per cent nitric acid should cleave the compound to give two products, namely:



$$CH_3-\underset{\substack{|\\ NO_2}}{N}-CH_2CH_2-\underset{\substack{|\\ NO_2}}{N}-CH_2CH_2-ONO_2 \quad \text{and} \quad O_2N-O-CH_2CH_2-\underset{\substack{|\\ NO_2}}{N}-CH_3$$

Actually two products were isolated when the low melting alkylation product was treated with nitric acid. One of these was shown to be identical with N-(β-nitroxyethyl)-

methylnitramine and analysis of the other product was in agreement with the formula $C_5H_{11}O_7N_5$. The experimental details are given in the following.

In a 200-cc. flask fitted with stirrer and thermometer there was placed 50 cc. of 98 per cent nitric acid and while the temperature of the liquid was held at 10° by means of external cooling 10 g. of the low melting alkylation product was slowly added. The mixture was stirred for fifteen minutes after addition had been complete and then poured on 150 g. of cracked ice. The crystalline precipitate which formed was filtered, washed with two 50-cc. portions of water, and air-dried. The crude solid (Crop I, 6.1 g.) melted at 90-92°.

The acid filtrate from Crop I was neutralized with sodium bicarbonate and a second crop precipitated which was filtered, washed with a small amount of water and dried in the air. The crude Crop II (2.5 g.) melted at approximately 35°. Extraction of this crude material with 150 cc. of ether left a residue of 1.1 g. melting at 85°.

The alkaline filtrate from Crop II was extracted with three 100-cc. portions of ether and the ether extracts were combined with the ether extract of Crop II. After drying over 30 g. of magnesium sulfate the ether was removed and there was obtained 2.8 g. of N-(β-nitroxyethyl)methylnitramine melting at 35.5-37° (uncorr.). No depression of melting point was observed when it was mixed with an authentic sample melting at

38-40°.

Crop I and the ether insoluble residue from Crop II were combined and recrystallized from 50 per cent aqueous acetone. The material crystallized as small glistening plates melting at 90.5-92° (corr.). Yield, 6.4 g. This material was proved to be different from the starting material by taking a mixed melting point.

Analysis: Calcd. for $C_5H_{11}O_7N_5$: N, 27.67.

Found: N, 27.65.

Effect of Nitric Acid on N,N'-dimethyl-ethylenedinitramine.

N,N'-dimethyl-ethylenedinitramine dissolved in a large excess of 98 per cent nitric acid at 10° without any noticeable evolution of heat. Warming the nitric acid solution to room temperature and pouring over ice precipitated the N,N'-dimethyl-ethylenedinitramine unchanged.

Effect of Nitric Acid on N-methyl-ethylenedinitramine.

To 25 cc. of 98 per cent nitric acid cooled to 10° there was slowly added 5 g. of N-methyl-ethylenedinitramine. It was necessary to apply external cooling in order to maintain the temperature at 10° during the addition. After the addition had been completed the mixture was allowed to warm up to room temperature. The charge was poured over 150 g. of cracked ice and the acid mixture neutralized by adding approximately 45 g. of sodium bicarbonate. A solid precipitate formed which was extracted with three 100-cc. portions of ethyl ether. The combined ether extracts were dried over 20 g. of magnesium sulfate, filtered, and concentrated to near dryness and cooled. Precipitation of a crystalline material occurred almost immediately. The solid was filtered and the filtrate concentrated again to give a second crop of crystals. The combined crops weighed 4.2 g. and melted at 39-40° (corr.). This corresponded to an 84 per cent yield of N-(β-nitroxyethyl)-methylnitramine, $CH_3-N(NO_2)-CH_2CH_2ONO_2$.

Analysis: Calcd. for $C_3H_7O_5N_3$: N, 25.45

Found: N, 25.30.

Dipotassium Salt of Ethylenedinitramine.

To a solution of 7.5 g. (0.13 mole) of potassium hydroxide in 75 cc. of aqueous alcohol (50 cc. alc.-35 cc. water) there was added 10 g. (0.067 mole) of ethylenedinitramine. The mixture was warmed until solution occurred. The crystals which precipitated on cooling were filtered and washed with alcohol and ether. After recrystallization from aqueous alcohol there was obtained 12.9 g. of the salt. This salt detonated when heated.

Diammonium Salt of Ethylenedinitramine.

A mixture of 10 g. (0.67 mole) of ethylenedinitramine in 250 cc. of alcohol was heated until solution occurred and then approximately 50 cc. of concentrated aqueous ammonia was added. A precipitate of the ammonium salt of ethylenedinitramine formed immediately. After cooling, the precipitate was filtered and washed with ether. The diammonium salt was recrystallized from an aqueous alcohol solution to which a small amount of ammonia had been added. The salt (8.4 g.) melted at 182-184° (uncorr.).

Potassium Salt of N-methyl-ethylenedinitramine.

Solutions of 10 g. (0.06 mole) of N-methyl-ethylenedinitramine in 250 cc. of alcohol and 3.4 g. (0.06 mole) of potassium hydroxide in 100 cc. of alcohol were mixed together. Upon cooling a precipitate formed which was filtered. Recrystallization from aqueous alcohol gave a crystalline product (6.7 g.) which detonated on heating.

Ammonium Salt of N-methyl-ethylenedinitramine.

A mixture of 10 g. (0.06 mole) of N-methyl-ethylenedinitramine and 250 cc. of alcohol was heated until solution occurred. To this solution there were added 50 cc. of alcohol saturated with dry ammonia, and 100 cc. of ether. The mixture was cooled and the precipitate filtered and washed with ether. The salt (7.0 g.) melted at 158-159°C. (uncorr.).

Silver Salt of N-methyl-ethylenedinitramine.

The silver salt of N-methyl-ethylenedinitramine was prepared by dissolving 16.4 g. (0.1 mole) of N-methyl-ethylenedinitramine in 100 cc. of water and 97.1 ml. of 1.03 N. sodium hydroxide. A solution of 17.0 g. (0.1 mole) of silver nitrate in 200 cc. of water was then added. A copious precipitate formed which was filtered off, and washed with water and finally with alcohol. There was obtained 26.0 g. of the salt Upon exposure to light it darkens.

Analysis: Calcd. for $C_3H_7O_4N_4Ag$: N, 20.68.

Found: N, 20.67.

Preparation of N,N'-dibromo-ethylenedinitramine.

The procedure for this preparation was to dissolve 12.0 g. (0.08 mole) of ethylenedinitramine in 150 cc. of water containing 9.0 g. (0.16 mole) of potassium hydroxide. This solution was cooled in an ice bath, then 8.5 cc. (25.6 g., 0.16 mole) of bromine added and the mixture stirred for several minutes until all the bromine reacted. The brownish-yellow precipitate of N,N'-dibromo-ethylenedinitramine was filtered off and sucked dry on the filter. This crude product was purified by dissolving in acetone to form a nearly saturated solution and then precipitating by the addition of an equal volume of water. This material was dried and for the final purification recrystallized from nitromethane. The final product consisted of nearly colorless needles, m.p. 138.0-138.5°C (corr.). Yield 50-60 per cent.

Analysis: Calcd. for $C_2H_4O_4N_4Br_2$: N, 18.18; Br, 51.92.

Found: N, 18.32, 18.38; Br, 50.94, 52.39.

Preparation of N-methyl-N'-bromo-ethylenedinitramine.

The preparation of N-methyl-N'-bromo-ethylenedinitramine was carried out by dissolving 1.64 g. (0.01 mole) of N-methyl ethylenedinitramine in 25 cc. of water containing 0.56 g. (0.01 mole) of potassium hydroxide. To this solution there was added dropwise and with stirring 0.55 cc. (1.60 g., 0.01 mole) of liquid bromine. A solid precipitate formed in the reaction and after stirring for several minutes with subsequent cooling, the pale yellow crystals were filtered off and washed well with water. There was recovered 2.2 g. of product melting at 118-119° d. (uncorr.). Yield 90 per cent.

The product can be reprecipitated as small shining crystals from an acetone solution by adding an excess of water. The melting point, however, remains unchanged.

Analysis: Calcd. for $C_3H_7O_4N_4Br$: N, 23.06.

Found: N, 23.00.

Preparation of Propylenediurethane.

Procedure A. In a 2-1., three-necked flask provided with a mechanical stirrer, reflux condenser, and dropping funnel were placed a solution of 161 cc. (1.0 mole) of aqueous propylenediamine,[*] 650 cc. of water, and 233.2 g. of anhydrous

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[*] The propylenediamine was obtained through the courtesty of Mr. A. L. Wilson, Carbide and Carbon Chem. Corp. Fellowship, Mellon Institute, Pittsburgh, Pa.

sodium carbonate. The mixture was heated to 85° by means of a water bath and 220 g. (2 moles) of ethyl chlorocarbonate was added dropwise with vigorous stirring. After all of the ethyl chlorocarbonate had been added, the mixture was stirred and heated for half an hour. After the mixture had been cooled by an ice-bath, the urethane crystallized and was filtered. The product was contaminated with large amounts of sodium bicarbonate. This was removed by washing with warm water. The crude product melted at 80-82° when dried in the air. The crude urethane (160 g.) was purified by recrystallization from an alcohol-water mixture (four volumes of alcohol to nine volumes of water). The purified urethane (105 g., 48 per cent of the theoretical yield) melted at 81-82°.

Procedure B. In a 5-l., three-necked flask equipped with stirrer, thermometer, and two dropping funnels there were placed 502.8 g. (2 moles) of 49.5 per cent propylene diamine[x] solution, 450 cc. of water, and 1200 cc. of ether. While the temperature of the mixture was kept at 0-5° (external cooling) 217 g. (2 moles) of ethyl chlorocarbonate was added dropwise with vigorous stirring. Following this addition an additional 217 g. (2 moles) of ethyl chlorocarbonate was added simultaneously with a solution of 166 g. (4.0 moles) of sodium hydroxide in 400 cc. of water. It was necessary to add an additional 80 cc. of ether before all of the reactants had been added in

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[x] Obtained through the courtesy of Mr. A. L. Wilson, Carbide and Carbon Chem. Corp. Fellowship, Mellon Institute, Pittsburgh, Pa.

order to break up the solid cake. At the completion of the reaction 1500 cc. of ether was added completely dissolving the urethane. The ether layer was separated and the aqueous solution was extracted with two portions of ether (500 and 200 cc.). The combined ether solutions were dried over anhydrous potassium carbonate and 3000 cc. of ether distilled off. The solution was cooled and the crystalline propylenediurethane which precipitated was filtered. There was obtained 356 g. of material melting at 79-80°. A second crop of 47 g. of slightly lower melting product was recovered from the filtrate. The yield of the combined crops was 92.5 per cent of the theoretical amount.

Nitration of Propylenediurethane.

In a 500-cc., three-necked flask fitted with stirrer and thermometer there was placed 125 cc. of 98 per cent nitric acid. The temperature of the acid was maintained at 5-10° and 25 g. (0.115 mole) of propylenediurethane was added slowly with continuous stirring. After addition had been completed (fifteen minutes) the reaction mixture was stirred for an additional fifteen minutes. The charge was poured over 350 g. of cracked ice and the acid neutralized with approximately 230 g. of sodium bicarbonate. The oil which separated was extracted with three portions of ether (200, 200 and 100 cc.) and the combined extracts were dried with 50 g. of magnesium sulfate. The extract was used directly in the next step.

Isolation of Propylenedinitramine.

The dried ether solution from above, containing the nitrourethane, was saturated with dry gaseous ammonia and a gummy solid separated. The ether was removed from the gummy precipitate by decantation. The sticky mass was dissolved in 100 cc. of water and acidified with concentrated hydrochloric acid (Congo Red). Upon cooling, a crystalline precipitate separated which was filtered and washed with a small amount of cold water. Yield, 8.9 g. melting at 107-110°.

The crude product was recrystallized from water and gave 6.3 g. of material melting at 111-112° (corr.). Yield, 40 per cent[x], based on propylenediurethane.

Analysis: Calcd. for $C_3H_8O_4N_4$: N, 34.14.

Found: N, 34.23, 34.40.

Preparation of Binary Mixtures of Compounds Related to Ethylenedinitramine.

Mixtures of MeEDNA-EDNA, Me_2EDNA-EDNA, MeEDNA-Me_2EDNA, and EDNA-PDNA were accurately prepared having the following percentages; 25 per cent, 50 per cent, and 75 per cent. One gram of each mixture was placed in a separate vial and the vials were heated in an oil bath to 160°. After cooling, the melts were removed and broken up in a mortar and the melting points taken (see page 16).

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[x] Using the same conditions but working on a somewhat larger scale, yields of 61 per cent for this preparation have been realized.

Preparation of Pentaerythrityl Tetraurethane.

In a 3 liter, 3-necked flask fitted with stirrer, thermometer, and dropping funnel, there was placed 82 g. (0.25 mole) of pentaerythrityl tetramine disulfate, 80 g. (2 moles) of sodium hydroxide, and 500 cc. of water. When solution was complete, 1000 cc. of ether was added, and the mixture was cooled to 0° to -5° by means of an ice-salt mixture. To the vigorously stirred mixture there was added dropwise 108.5 g. (1 mole) of ethyl chloroformate over a period of 30 minutes. Stirring at 0° was continued for two hours after all of the ethyl chloroformate had been added. The ether layer was separated. The tetraurethane suspended in the aqueous layer was extracted with ether. The combined ether extracts (about four liters) was dried over anhydrous calcium chloride. The ether was removed on a steam bath, and the colorless residue was recrystallized from 250 cc. of ethanol (95 per cent). There was obtained 80.3 g. of pure tetraurethane melting at 167-167.5°. The yield was 76.5 per cent of the theoretical.

Analysis: Calcd. for $C_{17}H_{32}O_8N_4$: N, 13.33.

Found: N, 13.70, 13.71.

Nitration of Pentaerythrityl Tetraurethane.

To a mixture of 100 cc. of nitric acid (98 per cent) and 100 cc. of acetic anhydride cooled to 0°, there was added

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[*] See page 146 for the preparation of pentaerythrityl tetramine disulfate.

in portions over a fifteen minute period 25 g. of pentaerythrityl tetraurethane. During this addition the mixture was stirred and the temperature was maintained at 0° by means of an ice-salt bath. Stirring was continued for an hour and a half at 0-5° after the addition was complete. The clear solution was poured on 500 g. of crushed ice and a colorless gummy precipitate separated. The acid solution was separated from the precipitate by decantation. The crude gummy nitrourethane was then washed with cold water and hydrolyzed immediately with aqueous ammonia.

Ammonolysis of Pentaerythrityl Tetranitrourethane.

The gummy nitrourethane described in the preceding paragraph was treated with 50 cc. of water and 100 cc. of aqueous ammonia (28 per cent). The mixture was heated on a steam bath, solution being complete within ten minutes. The reaction was strongly exothermic and it was necessary to apply external cooling. The clear solution was cooled and acidified with concentrated hydrochloric acid (about 90 cc. was required). Colorless crystals separated slowly. The mixture was kept at 0° overnight and the crystals filtered, washed with water, and dried in the air. The yield of pure tetranitramine was 16.3 g. (88 per cent of the theoretical amount). It melted with decomposition at 175° (corr.). Recrystallization from nitromethane did not improve its melting point.

Analysis: Calcd. for $C_5H_{12}O_8N_8$: N, 35.90.

Found: N, 36.01, 36.15, 36.03.

The Preparation of Pentaglyceryl Triamine Trihydrobromide.

The ammonolysis of pentaglyceryl tribomide was effected by heating in a pressure reactor the following substances: 103 g. (0.333 mole) of pentaglyceryl tribromide, 196 g. (2 moles) of ammonium bromide, 150 cc. of alcohol, 150 cc. of water, and 600 cc. of liquid ammonia. It required one hour and twenty-five minutes to heat the bomb to 150°. The temperature was then maintained at 150-160° for one hour. After cooling, the solution was evaporated almost to dryness, then taken up in 400 cc. of water and heated until the solid was dissolved. The solution was then made distinctly acid to congo red paper by adding concentrated hydrobromic acid. The acidified solution was cooled overnight in a refrigerator, and the solid which formed was filtered off and washed well with alcohol, and ether. The pentaglyceryl triamine trihydrobromide (83.1 g.) so obtained, melted at 327° d. (uncorr.).

An additional quantity of the product was obtained from the filtrate, which was treated with 100 g. (2.5 moles) of sodium hydroxide. The solution was evaporated to nearly dryness and 250 cc. of alcohol added. The inorganic salts were filtered off. After evaporating off the alcohol the residue was dissolved in a minimum amount of water and made distinctly acid to congo red paper by adding hydrobromic acid. After cooling, the solid which formed was filtered and washed with alcohol and ether. Thus an additional quantity (6.5 g.) of the trihydrobromide melting at 326° d. was obtained. Total yield, 74.7 per cent.

A small quantity of pentaglyceryl triamine trihydrobromide was recrystallized from water for analysis. The melting point was unchanged.

Analysis: Calcd. for $C_5H_{18}N_3Br_3$: N, 11.67; Br. 66.60.

Found: N, 12.35, 11.73, 12.22; Br, 66.58, 66.54.

The Preparation of Pentaglyceryl Triurethane.

Into a three-liter, three-necked flask provided with a thermometer, two dropping funnels and a stirrer there were added 72 g. (0. 2 mole) of pentaglyceryl triamine trihydrobromide, 120 cc. of water and 900 cc. of ether. The free amine was liberated by adding 240 g. of 10 per cent sodium hydroxide (0.6 mole). The mixture was cooled to 0° by means of a salt-ice bath and this temperature was maintained while 32.7 g. (0. 3 mole) of ethyl chlorocarbonate was added dropwise. Another 32.7 g. (0.3 mole) of ethyl chlorocarbonate was added concurrently with 240 g. of 10 per cent sodium hydroxide solution (0.6 mole) while maintaining the same temperature. After stirring for two hours the ether layer was separated and the aqueous layer extracted with two 300 cc. portions of ether. The extracts were combined and dried with magnesium sulfate. After distilling off almost all of the ether, the residue was cooled in an acetone-dry ice mixture causing the triurethane to crystallize. After adding 400 cc. of petroleum ether (30°-60°) to the suspension and cooling again, the product was filtered. When recrystallized from an ether-petroleum ether mixture, a solid (61.5 g.) melting at 54.6° was obtained. Yield 89 per cent.

Analysis: Calcd. for $C_{14}H_{27}O_6N_3$: N, 12.60.

Found: N, 12.47, 12.23, 12.17, 12.82.

<u>Preparation of Pentaglyceryl Trinitramine (PGX).</u>

Procedure A. Into a 500 cc. three-necked flask equipped with stirrer, dropping funnel, and thermometer there was added 122.4 g. (1.2 moles) of acetic anhydride. A nitrating mixture was prepared by slowly adding 50.4 g. (0.8 mole) of 98 per cent nitric acid to the anhydride while employing a temperature of 5-10°. Then 40 g. (0.116 moles) of pentaglyceryl triurethane was added at 0-5°. After the addition the reaction was stirred for one-half hour and was followed by the dropwise addition of 72 g. (1.14 moles) of 98 per cent nitric acid while maintaining the same temperature. Stirring was continued for two hours. The reaction was poured over 600 g. of cracked ice whereupon a sticky solid formed. The aqueous solution was decanted and the residue was treated with 200 cc. of water and 160 cc. of aqueous ammonia (28 per cent). It was necessary to boil the mixture a short while in order to cause the complete hydrolysis of the trinitrourethane. The clear solution was filtered and made distinctly acid to congo red paper with concentrated hydrochloric acid. Precipitation of the trinitramine was very slow. After standing for two days the precipitate which formed was filtered and washed with a small quantity of water. The solid (18.5 g.) melted at 128-9° <u>d</u>. (uncorr.). Two recrystallizations, one from ethyl acetate and one from nitromethane raised the melting point to 130-1° <u>d</u>. (uncorr.).

Procedure B. A more satisfactory procedure for this preparation is the following:

This reaction was carried out by adding 60 g. (.18 mole) of pentaglyceryl triurethane to 500 cc. of 98 per cent nitric acid while maintaining the temperature at 0-5°. After stirring for one-half hour the reaction was heated to room temperature and stirred another one-half hour. At the end of this time the solution was poured over 1500 g. of cracked ice and neutralized with about 600 g. of sodium bicarbonate. After extraction of the gummy solid with three portions of ether (1000, 500, and 250 cc.) and drying the extract with magnesium sulfate the ether was removed by distillation. The residue was divided in half and each portion was treated with 150 cc. of 8 per cent alcoholic ammonia. A vigorous reaction occurred immediately giving a sticky solid. The liquid was removed by decanting and the solid dissolved in 75 cc. of water and neutralized with hydrochloric acid (1:1). Precipitation of the nitramine occurred in about ten minutes. After standing overnight in a refrigerator the product was filtered and washed with cold water. The crude product (33.5 g.) melted at 128-9°. Yield, 75 per cent. The product can be recrystallized well from nitromethane. After three recrystallizations the melting point was 129-130° d.

Analysis: Calcd. for $C_5H_{12}O_6N_6$: N, 33.33.

Found: N, 33.50, 33.52, 33.85.

Nitration of Pentaglyceryl Triurethane; Preparation of the Silver Salt of Pentaglyceryl Trinitramine.

Into a 100 cc., three-necked flask provided with thermometer, dropping funnel and stirrer, there was added 30.6 g. (0.3 mole) of acetic anhydride. While the temperature of the reaction was maintained at 5-10°, 12.6 g. (0.2 mole) of 98 per cent nitric acid was added dropwise. This was followed by the addition of 10 g. (0.029 mole) of pentaglyceryl triurethane. The temperature during the latter addition was kept below 0°. Following this addition the reaction was stirred for one-half hour and then 28 g. (0.45 mole) of 98 per cent nitric acid was added dropwise while the temperature was maintained below 0°. The reaction was stirred for one and one-half hours and then poured over 150 g. of crushed ice. A sticky solid separated. After decanting off the aqueous acid solution, the product was treated with 50 cc. of water and 40 cc. of 28 per cent ammonium hydroxide. It was necessary to boil the mixture in order to cause the hydrolysis of the trinitrourethane. The clear solution was filtered. To the ammoniacal solution there was added an aqueous solution containing 15.3 g. (0.09 mole) of silver nitrate and enough acetic acid to give a distinctly acid reaction toward litmus. A precipitate formed immediately which was filtered off and washed well with water, alcohol and ether. There was recovered 14.5 g. of the silver salt. When heated the substance detonates.

Analysis: Calcd. for $C_5H_9O_6N_6Ag_3$: N, 14.67, Ag, 56.50.

Found: N, 14.91; Ag, 55.43, 55.37.

Preparation of 2,2-Dimethyl-1,3-propanediol.

In a two-liter, three-necked flask provided with stirrer, thermometer, dropping funnel, and condenser, there was placed 144 g. (2.0 moles) of isobutyraldehyde, and 331 cc. (4.0 moles) of 36.3 per cent formalin. While maintaining the temperature of the reaction below 20°, there was added in a steady stream a solution of 112 g. (2.0 moles) of potassium hydroxide in 1040 cc. of absolute alcohol. The reaction was stirred for 48 hours and then refluxed for two hours. After cooling, solid carbon dioxide was added and the precipitated salts filtered off. The reaction mixture was then concentrated at reduced pressure until a syrup remained. This was extracted with ether, and the extract dried with magnesium sulfate. Upon concentrating the extract a precipitate formed which was filtered off. After two recrystallizations, one from benzene, and another from ether there was obtained a solid (73 g.) melting at 127-9°. Yield 35 per cent.

Preparation of 2,2-Dimethyl-1,3-dibromopropane.

In a 200 cc., three-necked flask fitted with thermometer, dropping funnel, and a condenser to which there was attached a trap for absorbing gases, there was placed 20.8 g. (0.2 mole) of 2,2-dimethyl-1,3-propandiol. The contents of the flask was heated over a steam bath and 54.2 g. (0.2 mole) of phosphorous tribromide added dropwise. This addition required four hours. The reaction was slowly heated to 150° by means of an oil bath and allowed to remain at this temperature for seventeen hours. After cooling, the mixture was poured into water and 200 cc. of ether added. After filtering to remove insoluble substances, the extract was separated and the aqueous solution was extracted with two additional 100 cc. portions of ether. The combined extract was dried with magnesium sulfate. After removing the ether the residue was vacuum distilled. There was obtained a liquid (22.9 g.) boiling at 75-7°/20 mm. Yield, 50 per cent. D_4^{20} = 1.686; n_D^{20} = 1.5053. Observed molecular refraction was 40.5; calculated, 40.8.

Ammonolysis of 2,2-Dimethyl-1,3-dibromopropane.

Into a steel bomb of 400 cc. capacity there was added 10 g. (0.044 mole) of 2,2-dimethyl-1,3-dibromopropane, 17.1 g. (0.174 mole) of ammonium bromide, 15 cc. of alcohol, 15 cc. of water, and 60 cc. of liquid ammonia. The bomb was shaken in a rocker type agitator and slowly heated to a temperature of 150° over a period of one hour. The reaction was maintained at this temperature for one hour. After cooling and releasing the gases the solution was evaporated to dryness. The salts were dissolved in 40 cc. of water and 50 g. of solid sodium hydroxide was slowly added. A small amount of oil separated which was removed and placed in a small distilling flask. Upon distillation a small quantity of liquid of ammoniacal odor, boiling at 115°-127° was obtained. This was dissolved in absolute alcohol and acidified to methyl orange with concentrated sulfuric acid. A precipitate formed which was filtered and washed with alcohol. There was obtained a small quantity of crystalline solid (0.4 g.) melting at 233-9°. This substance was not identified.

Preparation of the Triurethane of 1,2,3-Triaminopropane.

In a 1-liter three-necked flask fitted with a mechanical stirrer, a thermometer and two dropping funnels, there were placed 18.0 g. (0.091 mole) of 1,2,3-triaminopropane trihydrochloride[*], a solution of 12 g. (0.3 mole) of sodium hydroxide in 50 cc. of water and 500 cc. of ether. The mixture was cooled to 5-10° by means of ice. To the vigorously stirred mixture, there was added dropwise 13.6 g. (0.15 mole) of ethyl chloroformate over a period of half an hour. Following this addition, 16.3 g. (0.15 mole) of ethyl chloroformate and a solution of 12 g. (0.3 mole) of sodium hydroxide in 40 cc. of water were added separately and concurrently during half an hour. After the addition, stirring was continued overnight at room temperature. Sufficient ether was added to dissolve the precipitated triurethane. The ether layer was separated, and the water layer extracted three times with 100 cc. portions of ether. The combined ether solutions were dried over anhydrous calcium chloride. The ether was removed on a steam bath and the viscous residue was recrystallized from a mixture of benzene and petroleum ether (b.p. 60-70°). There was obtained 16.5 g. of the pure triurethane, melting at 105.5-106°. The yield was 53.6 per cent of the theoretical.

Nitration of the Triurethane of 1,2,3-Triaminopropane.

To a mixture of 30 cc. of 98 per cent nitric acid and 30 cc. of acetic anhydride cooled to -5°, 6.0 g. of the

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[*] 1,2,3-Triaminopropane trihydrochloride was prepared according to the directions given by W. E. Bachmann in his report on "The Preparation of Explosives from Ethylenediamine".

triurethane of 1,2,3-triaminopropane was added in portions over a period of fifteen minutes. After the addition, stirring was continued for one hour at 0°. The clear solution was poured on 200 g. of crushed ice and a gummy precipitate separated. The acid solution was separated from the precipitate by decantation. The crude gummy nitrourethane was washed with water and dissolved in 200 cc. of ether. The ether solution was dried over anhydrous magnesium sulfate.

Preparation of 1,2,3-Trinitraminopropane.

The dried ether solution containing the nitration product of the triurethane was treated with anhydrous gaseous ammonia at 10-20°. The oily precipitate was separated by decantation and dissolved in 25 cc. of water. The aqueous solution was acidified to Congo red paper with concentrated hydrochloric acid. The solution was allowed to stand two days in a refrigerator. The trinitramine which separated slowly was filtered, and washed with ice water. It amounted to 2.2 g. (50 per cent of the theoretical amount). By recrystallization from 10 cc. of nitromethane, 1.8 g. of the trinitramine melting at 132-133° (uncorr.) d. was obtained. It is fairly soluble in acetone, slightly so in nitromethane, ethanol, or water and insoluble in ether.

The nitrogen analyses were unsatisfactory. The observed values ranged from 38.7 to 39.2 per cent, whereas the calculated percentage of nitrogen for $C_3H_8O_6N_6$ is 37.4. However, the values for the equivalent weight obtained by titrating with standard sodium hydroxide showed that the product was the trinitraminopropane.

Analysis: Calcd. for $C_3H_8O_6N_6$: Equiv. weight, 74.7.

Found: Equiv. weight, 75.6, 75.4.

Reaction between Ammonia, Formaldehyde and Nitrourethanes.

To a solution of 5 cc. of 28 per cent aqueous ammonia (0.021 mole) in 7 cc. of commercial 34 per cent formalin (0.055 mole), 6.7 g. (0.05 mole) of nitrourethane, $O_2N\text{-}NHCOOC_2H_5$, was added. The mixture was allowed to stand at room temperature for nine days. During this period, no precipitate formed. The reaction mixture was evaporated to dryness in a vacuum dessicator over phosphorus pentoxide. The residue was recrystallized from absolute alcohol. The colorless product obtained melted with decomposition at 137°.

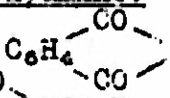
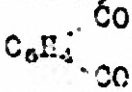
Analysis: Calcd. for $C_9H_{18}N_6O_4$; N, 30.66.

Found: N, 30.6.

In the report, "The Condensation of Nitroeurethane and Formaldehyde in the Presence of Ammonia", by Garwood and Springall, the University, Bristol, 1945, the authors found that this compound was the nitrourethane salt of hexamine.

The condensation of methyl nitrourethane with formaldehyde in aqueous ammonia was carried out in the same manner as that of nitrourethane. By treating the product with aqueous ammonia and then with dilute hydrochloric acid, a small amount of methyl nitrourethane was obtained.

Hydrolysis of Tris(phthalimidomethyl)amine.

N-(hydroxymethyl)phthalimide,  $C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}NCH_2OH$, and N-(bromomethyl)phthalimide,  $C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}NCH_2Br$, were prepared according to the method described by Pucher and Johnson[27]. When 75.8 g. of N-(bromomethyl)phthalimide was refluxed in 400 cc. of dry xylene, and dry ammonia was passed through the solution for eight hours, there was obtained 17.0 g. of the pure tris(phthalimidomethyl)amine as the acetate[12]. This corresponds to a 30 per cent yield.

An attempt to effect partial hydrolysis of the phthalimido derivative was unsuccessful. A mixture of 17.0 g. (0.031 mole) of tris(phthalimidomethyl)amine acetate, 3.4 g. (0.062 mole) of potassium hydroxide, and 300 cc. of water was refluxed with stirring for two days. Almost complete solution occurred. The solution was filtered to remove the insoluble amorphous material and then acidified with concentrated hydrochloric acid. There was obtained 15.2 g. of phthalic acid, melting at 205-206°. The filtrate was not examined.

The Condensation of Urethane with Hexamine.

A mixture of 14 g. (0.1 mole) of hexamine, 58.8 g. (0.66 mole) of urethane, and 35 cc. of hydrochloric acid (12 N) in 150 cc. of water was heated at 40° for five hours and allowed to stand at room temperature for four days. The crystalline precipitate which formed was filtered and washed with water. There was obtained 18.7 g. of methylene diurethane melting at 130-131°. The identity of the product was confirmed by a mixed melting point with an authentic sample of methylene diurethane. No depression in melting point was noted.

In another experiment, two equivalents of citric acid were used in place of the excess hydrochloric acid. No products other than the starting materials could be isolated.

Syntheses of Some Symmetrically Substituted Amines.

Tris(cyanomethyl)amine. To a solution of 454 g. of sodium cyanide (96 per cent pure) and 200 g. of hexamine in 1800 cc. of water there was added 1250 cc. of concentrated hydrochloric acid with agitation over a period of one hour. During the addition, the temperature of the solution was maintained below 40° by external cooling with ice water. Subsequently the mixture was allowed to stand at 40° for three hours, at room temperature for two days, and finally in the refrigerator for one day. The resulting precipitate was filtered, washed with water, and recrystallized from two liters of water. There was obtained 199.5 g. of tris-(cyanomethyl)amine, melting at 127-128°. This corresponds to a yield of 52 per cent of the theoretical amount.

Tris(carboxymethyl)amine. To 150 g. of tris(cyanomethyl)-amine there was added a solution of 150 g. of sodium hydroxide in 1000 cc. of water. Hydrolysis started spontaneously with the solution boiling within five minutes. After cooling the mixture to 60° it was allowed to stand for fifteen minutes with occasional shaking. The reaction mixture was then refluxed for half an hour, cooled to room temperature, and acidified with concentrated hydrochloric acid (Congo). The resulting crystalline precipitate was filtered, washed with water and dried at 95°. There was obtained 203.7 g. of the acid melting with decomposition at 241-242°. A 95 per cent yield was obtained.

Tris(carbethyoxymethyl)amine. The acid described above was esterified by suspending the acid in absolute ethyl alcohol and passing in dry hydrogen chloride gas until all of the acid had gone into solution. The ester was isolated and purified by vacuum distillation, b.p. 161-162° at 5 mm. An 85 per cent yield of the ester was obtained.

Tris(carbhydrazidomethyl)amine. The trihydrazide was prepared from tris(carbethoxymethyl)amine and hydrazine according to the Curtius' method[13].

Tris(carbazidomethyl)amine. The trihydrazide of tris-(carboxymethyl)amine was treated with nitrous acid according to the procedure given by Curtius[13]. None of the triazide could be obtained from the reaction mixture.

Preparation of N-(β-ethanol)urethane.

In a three liter, three-necked flask provided with a mechanical stirrer, thermometer, and two dropping funnels there were placed 244 g. (4.0 moles) of ethanolamine, 600 cc. of water, and 750 cc. of ether. The reaction mixture was cooled to 5-10° (external cooling) and 217 g. (2.0 moles) of ethyl chlorocarbonate was added slowly with stirring. The temperature of the reaction mixture was maintained at 5-10° during the addition. Following this addition there was added simultaneously 217 g. (2 moles) of ethyl chlorocarbonate and a solution of 160 g. (4 moles) of sodium hydroxide in 400 cc. of water. When the addition was complete, 500 cc. of ether was added and the reaction mixture stirred for one-half hour. The ether layer was separated and the aqueous solution was extracted with eight 100-cc. portions of ether. The combined ether extracts were dried with anhydrous magnesium sulfate and the ether removed by distillation. The residue was distilled under reduced pressure. There was obtained 510 g. (96% yield) of the colorless liquid urethane; b.p. 132-134° at 5 mm.

Nitration of N-(β-ethanol)urethane.

The nitration of N-(β-ethanol)urethane was carried out in a 1000 cc., three-necked flask equipped with thermometer and stirrer. After adding 250 cc. of 98 per cent nitric acid to the flask and cooling to 5°, 50 g. (0.376 mole) of N-(β-ethanol)urethane was added dropwise. The temperature of the reaction mixture was maintained at 5-10° during the addition. After stirring for fifteen minutes the reaction mixture was poured over 750 g. of cracked ice. The product separated as an oil and was extracted with three 250-cc. portions of ether after the mixture had been neutralized with sodium bicarbonate. The ether extract was dried rapidly with 75 g. of anhydrous magnesium sulfate. The ether solution of N-(β-nitroxyethyl)nitrourethane was used directly for the ammonolysis.

Ammonolysis of N-(β-nitroxyethyl)nitrourethane.

The ammonolysis of N-(β-nitroxyethyl)nitrourethane was carried out using the ether solution which was prepared above. The ammonium salt of N-(β nitroxyethyl)nitramine was isolated employing the following procedure. Dry ammonia was bubbled through the dried ether solution, keeping the solution cool with an ice-water bath, until the ether was saturated. The ammonium salt of N-(β-nitroxyethyl)nitramine precipitated and was filtered and washed with dry ether. The product (61.3 g., 97% yield) melted with decomposition at 78-79°.

The ammonium salt of N-(β-nitroxyethyl)nitramine decomposes slowly at room temperature. The decomposition of the salt proceeds more rapidly in aqueous solution.

Isolation of N-(β-nitroxyethyl)nitramine (NENA).

The ammonium salt of N-(β-nitroxyethyl)nitramine (61.3 g., 0.365 mole) was dissolved in 250 cc. of ice water and immediately neutralized to Congo Red by adding concentrated sulfuric acid (10.3 cc.) dropwise with stirring. The oil which separated was extracted with three portions of ether (150, 100, and 100 cc.) and the combined extracts were dried over 25 g. of anhydrous magnesium sulfate. The ether was removed from the dried solution by vacuum distillation at room temperature. The last traces of ether were removed by heating to 100° at 9 mm. The product was a pale yellow, water insoluble oil melting at 15°. The yield (51.4 g.) was 93.3 per cent of the theoretical amount.

Titration with standard alkali gave an equivalent weight of 155. Calculated equivalent weight for N-(β-nitroxyethyl)-nitramine is 151.

Analysis: Calcd. for $C_2H_5O_5N_3$: N, 27.81.

Found: N, 27.52, 27.64, 27.23, 27.36.

Because of the speed with which the ammonium salt of N-(β-nitroxyethyl)nitramine decomposes in aqueous solution, acidification of the cold aqueous solution with sulfuric acid should be carried out as quickly as possible. In one experiment the aqueous solution of the ammonium salt was cooled to 5-10° and acidified immediately, giving a 93 per cent yield of the nitramine. In another experiment the acidification was carried out at room temperature and gave a 76 per cent yield. Finally in a third experiment the aqueous solution of the salt was allowed to stand at room temperature for one hour before acidifying. In this case the yield fell to 61 per cent. A considerable evolution of gas accompanied the acidification in the last experiment.

The compound, N-(β-nitroxyethyl)nitramine, should be handled carefully as it appears to be a skin irritant. It produces inflammation and itching.

The Silver Salt of N-(β-nitroxyethyl)nitramine.

An aqueous solution of 42.5 g. (0.25 mole) of silver nitrate in 500-cc. of water was added with stirring to a solution of 42 g. (0.25 mole) of the ammonium salt of N-(β-nitroxyethyl)nitramine. A gummy precipitate separated which solidified to a chalky white solid. After filtering, the product was washed with water, alcohol, and ether. The solid product (62.0 g., 96.1 per cent yield) decomposed when heated to about 120°. It darkens on exposure to light.

Analysis: Calcd. for $C_2H_4O_5N_3Ag$: N, 16.29.

Found: N, 16.28, 16.49.

The One Stage Synthesis of N-(β-nitroxyethyl)methylnitramine.

In a 1000-cc., three-necked flask fitted with stirrer, thermometer, and dropping funnel there was placed 245 g. (2.4 moles) of acetic anhydride. While maintaining the temperature at 10-12° by means of external cooling, 126 g. (2 moles) of nitric acid (98 per cent) was added with vigorous stirring. After addition of the acid, 6.0 g. (0.044 mole) of anhydrous zinc chloride was added.

To the nitrating mixture there was added 75 g. (1.0 mole) of methylethanolamine[+] through a capillary-tipped dropping funnel whose end was immersed below the surface of the nitrating solution. During the addition which required two hours the temperature was held at 10-12°. After all of the amino had been added the charge was stirred for an additional period of one hour at the same temperature followed by stirring for half an hour at 40°. The contents of the flask were poured on 500 g. of cracked ice. A precipitate of N-(β-nitroxyethyl)-methylnitramine separated and was filtered and washed with two 100-cc. portions of water.

The crude product (111.6 g.) melting at 36.5-38° was recrystallized from 1000 cc. of anhydrous ether and gave 95.8 g. of a crystalline solid melting at 39-40.5° (corr.). An additional 9.4 g. of product was obtained upon concentrating the ether solution. The yield of purified product was 65 per cent.

[+] Obtained through the courtesty of Dr. A. L. Wilson, Carbide an
Carbon Chem.Corp.Fellowship,Mellon Institute,Pittsburgh, Pa.

The Two Stage Synthesis of N-(β-nitroxyethyl)methylnitramine.

N-(β-nitroxyethyl)methylnitramine has been prepared by treating N-methyl-β-ethanolamine dinitrate with acetic anhydride, zinc chloride, and hydrochloric acid at 40°. The intermediate dinitrate is a crystalline salt and is best obtained by adding N-methyl-β-ethanolamine to 98 per cent nitric acid and pouring the reaction mixture into ether.

Preparation of N-methyl-β-ethanolamine Dinitrate. In a 200 cc., three-necked flask provided with stirrer, thermometer, and dropping funnel, there was placed 45 cc. (1.07 moles) of 98 per cent nitric acid. While maintaining the temperature of the reaction below 25°, there was added slowly through a capillary tipped dropping funnel, whose end was immersed below the surface of the acid, 7.5 g. (0.1 mole) of N-methyl-β-ethanolamine. The reaction was stirred for one hour and then added dropwise to 500 cc. of ether while employing vigorous stirring. A crystalline precipitate formed which was filtered off and washed well with ether. There was obtained a solid (17.5 g.) melting at 76-8°. No further purification was necessary preparatory to the next step. Yield, 95 per cent.

Conversion of N-methyl-β-ethanolamine Dinitrate into N-(β-nitroxyethyl)methylnitramine. A mixture of 100 cc. of acetic anhydride, 1 g. of zinc chloride and 1 cc. of concentrated hydrochloric acid was warmed to 40°. To the solution there was added in portions 17.5 g. (.095 mole) of N-methyl-β-ethanolamine dinitrate while maintaining the same temperature. After stirring for 15 minutes the reaction was poured into 500 cc. of water. After a short time complete miscibility occurred and when the acid was neutralized with a calculated amount of sodium bicarbonate a precipitate formed which was filtered off and washed well with water. There was obtained a crystalline solid (10 g.) melting at 38-40°. After one recrystallization from ether the melting point was unchanged.

The following procedures are typical of the two stage preparation of MeNENA, using a mixture of nitric acid (98 per cent) and methyl ethanolamine instead of the solid dinitrate.

Procedure F-I: A mixture of methyl ethanolamine and nitric acid was prepared by slowly adding 37.5 g. (0.5 mole) of methyl ethanolamine to 64.5 g. (1.0 mole) of 98 per cent nitric acid, while maintaining the temperature of the reaction below 10° by means of external cooling. This reaction was carried out in a 500 cc. three-necked flask, provided with stirrer, thermometer, and a capillary tipped dropping funnel, the end of which was immersed below the surface of the nitric acid. Moderate stirring was employed throughout the addition.

The mixture of methyl ethanolamine and nitric acid was transferred to another dropping funnel and added dropwise to a solution of 3 g. (0.022 mole) of zinc chloride and 113 g. (1.1 mole) of 95 per cent acetic anhydride, contained in a 500 cc., three-necked flask. Stirring was employed throughout the addition which required fifteen minutes and the temperature maintained at 15° by means of intermittent cooling in an ice or water bath. After stirring for an additional ten minutes the solution was heated to 40° and kept at this temperature for twenty minutes.[x] The reaction was quickly cooled to room temperature and then poured slowly over 550 g. of ice and water, employing vigorous stirring. A sandy precipitate of McNENA formed which was filtered off and washed with two 50 cc. portions of water. After air drying for twenty-four hours, it was desiccated in vacuum over phosphorus pentoxide for another twenty-four hours. The crude material (Crop 1) weighed 64.6 g. and melted at 38-39°.

A second crop of McNENA can be obtained by neutralizing the filtrate from the first crop. When the above filtrate was neutralized with approximately 195 g. of sodium bicarbonate, a small amount of precipitate formed which was filtered and washed with two 25 cc. portions of water. There was obtained 7.8 g. of solid (Crop 2) melting at 37-38°.

The combined yield of crude McNENA by this procedure was 72.4 g. or 88 per cent of theoretical.

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[x] Little heat evolution occurs at this temperature when the addition is carried out at room temperature or higher. However, if the addition is carried out below room temperature there is considerable heat evolution upon heating.

Procedure F-VII: A mixture of 37.5 g. (0.5 mole) of methyl ethanolamine and 64.5 g. (1.0 mole) of 98 per cent nitric acid was prepared employing the directions given in Procedure F-I.

The second step in the preparation of McNENA is best carried out in a 500 cc., three-necked flask fitted with stirrer, thermometer, and dropping funnel. The mixture of methyl ethanolamine and nitric acid was added dropwise with stirring to a solution of 3 g. (0.022 mole) of zinc chloride and 118 g. (1.1 mole) of acetic anhydride maintaining the temperature of the reaction at 35° by means of intermittent cooling. The addition required 15 minutes and after it was completed, the reaction was stirred for an additional fifteen minutes at the same temperature and then poured over 550 g. of ice and water employing vigorous stirring. McNENA precipitated and was filtered. After washing twice with 50 cc. portions of water the product was air dried. The final trace of moisture was removed by vacuum desiccation over phosphorus pentoxide. The crude product (Crop 1) weighing 68.1 g. melted at 38-39°.

Procedure XXIV: A mixture of methyl ethanolamine and 98 per cent nitric acid was prepared following the directions of Procedure I using in this case 37.5 g. (0.5 mole) of the amine and 67.7 g. (1.05 moles) of acid.

The subsequent step was carried out in a 500 cc. three-necked flask, provided with stirrer, thermometer, and dropping funnel. The amino-nitric acid solution was added dropwise to a solution of 1.5 g. (0.011 mole) of zinc chloride in 118 g. (1.1 moles) of acetic anhydride, keeping the temperature of the reaction at 35°. After the addition, which required fifteen minutes, the reaction was stirred for an additional fifteen minutes at the same temperature and immediately poured into 550 g. of ice and water. Vigorous stirring was employed. The precipitate was filtered off and washed with two 50 cc. portions of water and then allowed to dry in air. The final trace of moisture was removed by drying in vacuum over phosphorus pentoxide. The crude product (Crop 1) weighed 70.1 g. and melted at 37.5-38°.

An additional quantity of MeNENA can be isolated from the filtrate from Crop 1 by neutralizing the acid with a calculated amount of sodium bicarbonate. By so doing, 5.3 g. (Crop 2) of MeNENA, melting at 37-38° was obtained.

The combined crops totaled 75.4 g. which is 91.4 per cent of the theoretical yield.

The Large Scale Preparation of MeNENA.

Into a one-liter four-necked flask provided with stirrer, thermometer, and two dropping funnels there was placed a solution consisting of 37.5 g. (0.5 mole) methyl ethanolamine and 67.7 g. (1.05 mole) of 98 per cent nitric acid. This mixture was prepared as described in Procedure XXIV. There was then added concurrently and simultaneously 187.5 g. (2.5 moles) of methyl ethanolamine and 338.5 g. (5.25 moles) of 98 per cent nitric acid. The temperature throughout the addition was kept at 10-15°.

The three mole mixture of alkamine dinitrate was transferred to a dropping funnel and added to a solution of 708 g. (6.6 moles) of acetic anhydride and 5.2 g. (0.066 mole) of acetyl chloride contained in a three-liter flask. Moderate stirring was employed and the reaction maintained at 35°. The addition required twenty minutes. After the addition the reaction was stirred for fifteen minutes at the same temperature and then poured over 3300 cc. of ice and water. MeNENA precipitated and was filtered and washed with three 300 cc. portions of water. There was obtained 416 g. of the substance, melting at 37-38°.

The filtrate containing the washings was neutralized with a calculated amount of sodium carbonate. Approximately 20 g. of additional product was obtained. This was recrystallized from ether and there was obtained 14 g. of second crop MeNENA, m.p. 38-39°.

Total Yield: 86.9 per cent.

The Stabilization of MeNENA.

A 200 g. sample of crude MeNENA (m.p. 36.5-37.5°C) was suspended in 800 cc. of water containing 8 g. of sodium bicarbonate and steam bubbled into the mixture until the temperature had risen to 75°. The charge was then agitated by bubbling air through the suspension until the temperature had dropped to 50°. The agitation was continued and pieces of ice added until precipitation occurred. The McNENA was separated and the entire process of steaming, agitation and cooling was repeated and the product finally filtered.

The solid obtained was dissolved in 400 cc. of acetone, then cooled in an ice bath, and three liters of water added dropwise to the acetone solution. Further cooling and vigorous stirring were employed. When the mixture became milky it was seeded to induce crystallization. The product was filtered by suction, air dried, and the final traces of moisture were removed by drying in vacuo over phosphorus pentoxide for 24 hours. The product (161.g.) melted at 39-40°. (Code No. CU-F-15).

An 80 g. sample of McNENA (CU-F-15) was recrystallized from 720 cc. of ether using vigorous stirring and cooling in an ice bath. After filtration there was obtained 74.8 g. of product melting at 39.5°-40.5°. (Code No. CU-F-16).

The ether recrystallized McNENA was analyzed.

Analysis: Calcd. for $C_3H_7O_5N_3$: C, 21.82; H, 4.27; N, 25.45

Found: C, 21.74; H, 3.79; N, 24.49, 24.68 (See also page 83).

Preparation of N-(β-nitroxyethyl)ethylnitramine (EtNENA).

Into a 500 cc., three-necked flask containing 67.7 g. (1.05 moles) of 98 per cent nitric acid and equipped with stirrer, thermometer, and a capillary tipped dropping funnel whose end was immersed below the surface of the acid, there was added 44.5 g. (0.5 mole) of ethyl ethanolamine. The content of the flask was cooled externally and the temperature maintained below 10° during the addition.

The amine-nitric acid mixture was transferred to a dropping funnel and added dropwise to a solution of 118 g. (1.1 moles) of 95 per cent acetic anhydride and 0.86 g. (0.011 mole) of acetyl chloride contained in a 500 cc., three-necked flask. Moderate stirring was employed and the reaction was maintained at 35°. After the addition of the amine-nitric acid mixture which required fifteen minutes, the reaction was kept at 35° for an additional fifteen minutes. After pouring the contents of the flask into 550 cc. of ice and water there was obtained an oil which was separated and washed successively with two 100 cc. portions of 5 per cent sodium bicarbonate and two 100 cc. portion of water. After filtering, the pale yellow oil was dried by bubbling dry air through it. There was obtained 73.4 g. (82 per cent of theoretical) of N-(β-nitroxyethyl)ethylnitramine melting at 4-5.5°.

$D_4^{25} = 1.32$; $n_D^{25} = 1.479$.

Theoretical molecular refraction = 38.75.

Observed molecular refraction = 38.4.

Preparation of N-(β-nitroxypropyl)methylnitramine.

Into a 500 cc. three-necked flask equipped with stirrer, thermometer, and a capillary tipped dropping funnel whose end could be immersed well below the surface of the reaction mixture there was placed 67.7 g. (1.05 moles) of 98 per cent nitric acid. To this there was added by means of the dropping funnel 44.5 g. (0.5 mole) of 2-hydroxypropylmethylamine. The content of the flask was externally cooled to a temperature below 10° and here maintained during the addition.

The amine-nitric acid mixture was transferred to a dropping funnel and added dropwise to a solution of 118 g. (1.1 moles) of 95 per cent acetic anhydride and 0.86 g. (0.011 mole) of acetyl chloride contained in a 500 cc., three-necked flask. Moderate stirring was employed and the reaction was maintained at 35°. After the addition of the amine-nitric acid mixture which required fifteen minutes, the reaction was kept at 35° for an additional fifteen minutes. After pouring the contents of the flask into 550 cc. of ice and water there was obtained an oil which was separated and washed successively with two 100 cc. portions of 5 per cent sodium bicarbonate and two 100 cc. portions of water. After filtering, the pale yellow oil was dried by bubbling dry air through it. There was 65.8 g. (74 per cent of theoretical) of N-(β-nitroxypropyl)methylnitramine as a pale yellow oil, melting at 22-23°.

$D_4^{25} = 1.32$; $n_D^{25} = 1.478$.

Theoretical molecular refraction = 33.75.

Observed molecular refraction = 38.5.

Preparation of N-carbethoxy-1-amino-2-propanol.

Into a one-liter, four-necked flask provided with stirrer, thermometer, and two dropping funnels there was placed 75 g. (1.0 moles) of 1-amino-2-propanol, 150 cc. of water, and 200 cc. of ether. While maintaining the temperature of the reaction at 5-10° there was added dropwise 54.3 g. (0.5 mole) of ethyl chlorocarbonate, followed by a concurrent addition of 54.3 g. (0.5 mole) more ethyl chlorocarbonate and a solution of 40 g. (1.0 mole) of sodium hydroxide in 100 cc. of water. Vigorous stirring was employed throughout the addition. After stirring for an additional one-half hour, the ether extract was separated. The aqueous solution was extracted with three portions of ether (200, 200, and 100 cc.). The combined extract was dried with magnesium sulfate and then distilled to remove the ether. The oily residue was distilled at reduced pressure. There was obtained a clear liquid (127.4 g.) boiling at 107.5-110°/1 mm. Yield, 37 per cent. $n_D^{20} = 1.4492$; $D_4^{20} = 1.082$. Theoretical molecular refraction = 36.46, Observed = 36.4.

Nitration of N-carbethoxy-1-amino-2-propanol.

In a two liter, three-necked flask provided with stirrer, thermometer, and dropping funnel, there was placed 735 cc. (17.5 moles) of 98 per cent nitric acid. While employing moderate stirring and maintaining a temperature of 10° by external cooling, there was added dropwise 147 g. (1.0 mole) of N-carbethoxy-1-amino-2-propanol. After completion of the addition the reaction was maintained at 10° for one-half hour and then poured over 3700 g. of ice and water. The excess acid in the mixture was neutralized with 1310 g. of sodium bicarbonate and the product extracted with two portions (750 cc., 750 cc.) of ether. The extract was dried with anhydrous magnesium sulfate and used directly in the next step.

Ammonolysis of N-(β-nitroxypropyl)nitrourethane. Isolation of N-(β-nitroxypropyl)nitramine.

The dried ether solution of the nitroxyalkyl nitrourethane was cooled in an ice bath and saturated with dry ammonia. An oil separated, which on standing solidified to a white crystalline solid, the ammonium salt of N-(β-nitroxypropyl)-nitramine. The salt was filtered and washed with several portions of dry ether.

The ammonium salt obtained in the ammonolysis was dissolved in one liter of ice water and neutralized to congo red with concentrated hydrochloric acid. The nitroxyalkyl nitramine precipitated instantaneously and after filtering, the solid was washed with two 100 cc. portions of water. There was obtained 135.1 g. (81 per cent of theoretical) of N-(β-nitroxypropyl)nitramine melting at 84-85°. The product was recrystallized once from ether, and for the final purification it was precipitated from acetone by the addition of water. The melting point of the purified product was 86-87°.

Analysis: Calcd. for $C_3H_7O_5N_3$: C, 21.82; H, 4.27; N, 25.45; Neutral Equivalent, 165.1

Found: C, 21.54; H, 4.04; N, 24.40, 24.70; Neutral Equivalent, 165.

Preparation of N-carbethoxy-2-amino-1-butanol.

Into a one-liter, four-necked flask fitted with stirrer, thermometer, and two dropping funnels, there was added 89 g. (1.0 moles) of 2-amino-1-butanol, 150 cc. of water, and 200 cc. of ether. After cooling the contents of the flask to 5-10°, and maintaining this temperature, 54.5 g. (0.5 mole) of ethyl chlorocarbonate was added dropwise. Next there was added concurrently a solution of 40 g. (1.0 moles) of sodium hydroxide in 100 cc. of water and 54.5 g. (0.5 mole) more ethyl chlorocarbonate. Vigorous stirring was employed throughout the addition. The reaction was stirred one-half hour. After separation of the ether layer, the aqueous solution was extracted with two portions of ether (200 and 200 cc.). The combined extract was dried with 80 g. of magnesium sulfate. The extract was concentrated through distillation until a thick oil remained. Upon standing the oil crystallized. The crude product weighed 147 g. After two recrystallizations, the first from benzene, and the second from ether, the product (68 g.) melted at 54-5° (yield, 42 per cent). The substance can also be distilled at reduced pressure. It boils at 115-117°/2 mm.

Analysis: Calculated for $C_7H_{15}O_3N$: C, 52.15; H, 9.38; N, 8.69.

Found: C, 51.98; H, 9.44; N, 8.40.

Preparation of Diurethane of Diaminoisopropanol.

In a 2000-cc. three-necked flask fitted with a mechanical stirrer, thermometer, and two dropping funnels, there were placed 45 g. (0.5 mole) of diaminoisopropanol* (m.p. 45-47°), 100 cc. of water, and 400 cc. of ether. The mixture was cooled to 0-5° by means of an ice-salt bath. To the vigorously stirred mixture there was added dropwise 54.8 g. (0.5 mole) of ethyl chloroformate over a period of one hour. Following this addition, a further quantity of ethyl chloroformate (54.8 g.) and a solution of 40 g. of sodium hydroxide in 100 cc. of water were added separately and concurrently during one hour. After the addition, stirring was continued for two hours at 0-5°. The ether layer was separated and the water layer extracted with three 100-cc. portions of ether. The ether solutions were combined and dried over anhydrous magnesium sulfate. After removal of the ether by distillation under vacuum there was obtained 118 g. of a

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* Obtained from Dr. A. L. Wilson, Mellon Institute, Pittsburgh, Pa.

yellow viscous residue. All attempts to crystallize the urethane failed. Also, it could not be distilled at a pressure of 1.5 mm.

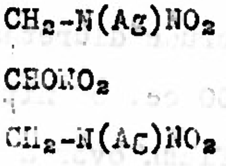
Nitration of the Diurethane of Diaminoisopropanol.

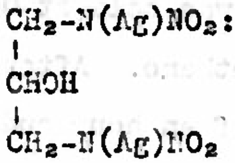
One hundred grams of the crude diurethane prepared as described above was added to 500 cc. of nitric acid (98 per cent) contained in a 1000-cc. flask over a fifteen minute period. The reaction mixture was held at 0-5° and stirred during the addition of the urethane. After the addition, the mixture was stirred for half an hour and then poured over 2,000 g. of cracked ice. A colorless gummy precipitate was obtained which was separated by decantation, washed with water, and dissolved in ether. The ether solution was washed first with dilute sodium bicarbonate solution then with water and finally dried over anhydrous magnesium sulfate.

Isolation of Dinitraminoisopropyl nitrate.

The dried ether solution containing the nitration product of the diurethane was treated with anhydrous gaseous ammonia at 5-10°. A gummy precipitate formed which was separated by decantation, washed with ether, and dissolved in 500 cc. of water. The aqueous solution was filtered and acidified to Congo red with dilute hydrochloric acid. The colorless crystalline precipitate was filtered, washed thoroughly with water and dried in the air. The product (71.3 g.) melted with decomposition at 161-163° (corr.). One recrystallization from 600 cc. of nitromethane gave 53.8 g. of a product melting at 164-165° (corr.) with decomposition. The overall yield from diaminoisopropanol was 74.8 per cent.

Analysis of the silver salt.

Calcd. for  $CH_2-N(Ag)NO_2 - CHONO_2 - CH_2-N(Ag)NO_2$: N, 15.95; Neutral Equivalent, 112.5

Calcd. for  $CH_2-N(Ag)NO_2 - CHOH - CH_2-N(Ag)NO_2$: N, 14.22; Neutral Equivalent, 90.0

Found: N, 15.67, 15.27, 15.51; Neutral Equivalent, 112.0, 112.4

Preparation of N,N'-di-(β-ethanol)ethylenediamine Tetranitrate.

In a 1000-cc. flask fitted with stirrer and thermometer there was placed 250 cc. of 98 per cent nitric acid. The acid was cooled to 10-15° by means of external cooling and 48.8 g. (0.33 mole) of N,N'-diethanol-ethylenediamine* was added slowly with stirring. The temperature was maintained at 10-15° during this addition. After all of the amine had been added the mixture was warmed to 35° and stirred at this temperature for an additional fifteen minutes. The clear solution was poured over 750 g. of cracked ice and the resulting aqueous solution was diluted with 500 cc. of 95 per cent

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* The N,N'-diethanol-ethylenediamine was obtained through the courtesy of Dr. A. L. Wilson, Carbide and Carbon Chem. Corp. Fellowship, Mellon Institute, Pittsburgh, Pa. After one crystallization it melted at 99-102°.

alcohol. The crystalline solid which precipitated was filtered, washed with two 100-cc. portions of alcohol and dried in the air.

The crude product (97.8 g.) melted with decomposition at 157.5° (corr.) and was purified by crystallization from aqueous alcohol. There was obtained 80.1 g. (75.5 per cent of the theoretical yield) of a white crystalline solid melting with decomposition at 170-171° (corr.). This product proved to be identical with the substance prepared by various other methods.

Preparation of N,N'-bis(β-nitroxyethyl)ethylenedinitramine.

In a 500-cc. flask fitted with a stirrer and thermometer there was placed 18.4 g. (0.05 mole) of N,N'-di(β-ethanol) ethylenediamine tetranitrate, 100 cc. of acetic anhydride, and 1 cc. of concentrated hydrochloric acid. The mixture was heated by a water bath to 50° and 1 g. of anhydrous zinc chloride was added to the slurry. An exothermic reaction took place within a minute and it was necessary to apply external cooling in order to maintain a reaction temperature of 50°.[x] After stirring at 50° for half an hour the mixture was poured slowly into 500 cc. of water. In a short while an oil separated which solidified upon cooling. The crude solid

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[x] No reaction occurred when the tetranitrate was heated for fifteen minutes with acetic anhydride alone or with acetic anhydride and a small amount of hydrochloric acid.

was filtered, washed with water, and dried in the air. The impure product (13.7 g.) melted at 58.5-60.5°(corr.).

The product was purified by precipitating an acetone solution of the crude material with cold water. The product obtained in this way (13 g) melted at 60-62° (corr.). Yield, 80 per cent.

Analysis: Calcd. for $C_6H_{12}O_{10}N_6$; N, 25.81

Found: N, 25.62, 25.50.

Preparation of N,N-bis(β-nitroxypropyl)amine Nitrate.

In a 200-cc., three-necked flask provided with stirrer and thermometer, there was added 60 cc. of 98 per cent nitric acid. While the temperature was kept below 15° there was slowly added 12.3 g. (0.1 mole) of di-(β-hydroxypropyl)amine. After the addition, the reaction was warmed to 35° and stirred for 15 minutes. The content of the flask was then poured over 180 g. of cracked ice. A precipitate settled out which was filtered off and washed with water. The crude product (20.3 g.) was recrystallized from 500 cc. of water and there was obtained a crystalline solid (17.6 g.) melting at 144° d.

Preparation of N,N-bis(β-nitroxypropyl)nitramine.

To a 100 cc. three-necked flask provided with stirrer and thermometer there was placed 50 cc. of acetic anhydride, 0.5 cc. of concentrated hydrochloric acid, and 0.5 g. of zinc chloride. The content of the flask was warmed to 45° and 10 g. of bis(β-nitroxypropyl)amine nitrate added, the temperature being maintained at 45-50°. After stirring for fifteen minutes at this temperature the reaction was poured into 250 cc. of water and stirred until the hydrolysis of the excess anhydride was completed. The solid which was formed was filtered off and washed with water. There was obtained 8.5 g. of substance, melting at approximately 75°. After a single recrystallization from ether the melting point was raised to 103-4°. A better technique for obtaining a purified compound seems to be its reprecipitation from an acetone solution through the addition of water.

Preparation of 4,4-Dimethylol Oxazolidone. Reaction of Trimethylol Aminomethane with Ethyl Chlorocarbonate.

Into a one-liter, three-necked flask provided with a stirrer, thermometer, and two dropping funnels there were added 121 g. (1.0 mole) of trimethylol aminomethane and 200 cc. of water. While maintaining the temperature at 5-10°, 54.3 g. (0.5 mole) of ethyl chlorocarbonate was added dropwise. Next there were added concurrently 54.3 g. (0.5 mole) additional ethyl chlorocarbonate and a solution of 40 g. (1.0 mole) of sodium hydroxide in 360 cc. of water. The temperature was allowed to rise to room temperature and the stirring was continued overnight. The solution was distilled at reduced pressure until almost all of the water was removed and the residue was taken up in absolute alcohol. The inorganic salts were filtered off and the alcoholic filtrate was concentrated at reduced pressure. The oily residue was dissolved in 125 cc. of methyl alcohol and cooled overnight. The crystalline deposit was filtered off, washed with 50 cc. of cold methyl alcohol and again with ether. There was obtained a solid (40.0 g.) melting at 108-9°. By working up the filtrates and again recrystallizing, an additional 28.1 g. of 4,4-dimethylol oxazolidone was obtained. Yield, 46 per cent.

Analysis: Calculated for $C_5H_9O_4N$: C, 40.82; H, 6.12; N, 9.52.

Found: C, 40.75, 40.73; H, 5.57, 5.72; N, 9.64, 9.85.

Preparation of 4,4-Bis(nitroxymethyl)oxazolidone.

In a 200 cc., three-necked flask fitted with stirrer and thermometer there was placed 62.5 cc. (1.49 moles) of 98 per cent nitric acid. While maintaining the temperature at 5-10°C. there was added in portions 10 g. of 4,4-dimethylol oxazolidone. After stirring at this temperature for two hours, the reaction was quenched by pouring over 250 g. of cracked ice. A white crystalline precipitate separated which was filtered off and washed with two 50 cc. portions of water. A small additional quantity of the same substance was recovered by neutralizing the acid filtrate with sodium bicarbonate. The combined product was recrystallized from 35 cc. of methyl alcohol. There was obtained 4,4-bis(nitroxymethy)oxazolidone (11.0 g.), melting at 106-7°.

Analysis: Calculated for $C_5H_7O_8N_3$: C, 25.40; H, 2.95; N, 17.72.

Found: C, 25.57, 25.39, 25.09, 25.86; H, 3.46, 3.25, 3.23, 3.27; N, 17.59, 17.54.

Preparation of 3-Nitro-4,4-bis(nitroxymethyl)oxazolidone.

A nitrating mixture was prepared by adding 62.5 cc. (1.5 moles) of 98 per cent nitric acid to 62.5 cc. (1.17 moles) of concentrated sulfuric acid. After cooling the mixed acid to 5-10°, 10 g. (0.068 mole) of 4,4-dimethylol oxazolidone was added in portions, maintaining the same temperature. After the addition the temperature was raised to 50° and held there for one-half hour. After cooling, the reaction was poured over 350 g. of cracked ice. A precipitate was formed which was filtered and washed with two 50 cc. portions of water. After recrystallizing the resultant solid from 150 cc. of methyl alcohol a crystalline substance (4.9 g.), 3-nitro-4,4-bis(nitroxymethyl)oxazolidone, melting at 122-3° was obtained. Yield, 30 per cent.

Analysis: Calculated for $C_5H_3O_{10}N_4$: C, 21.28; H, 2.13; N, 19.86.

Found: C, 21.25, 21.36; H, 2.12, 2.01; N, 19.49, 19.38.

Conversion of 4,4-Bis(nitroxymethyl)oxazolidone into 3-Nitro-4,4-bis(nitroxymethyl)oxazolidone.

A nitrating mixture consisting of 5 cc. of 98 per cent nitric acid and 5 cc. of concentrated sulfuric acid was prepared. While stirring and maintaining a temperature of 5-10°, 3.33 g. (0.014 mole) of 4,4-bis(nitroxymethyl)oxazolidone was added. The reaction was heated to 50° and kept at this temperature for one-half hour. After cooling, the solution was poured over 30 g. of cracked ice. The precipitate which formed was filtered and washed with water. After one recrystallization from 30 cc. of methyl alcohol there was obtained a solid (1.11 g.), 3-nitro-4,4-bis(nitroxymethyl)oxazolidone, melting at 121-2°. Yield, 28 per cent.

Effect of Ammonia on 4,4-Bis(nitroxymethyl)oxazolidone and 3-Nitro-4,4-bis(nitroxymethyl)oxazolidone.

In one experiment, 3.3 g. of 4,4-bis(nitroxymethyl)-oxazolidone was dissolved in 30 cc. of methyl alcohol and dry ammonia gas bubbled through the solution for several minutes. The ammoniacal solution was boiled for several minutes. After removing the solvent only the original compound was isolated.

In another experiment, 4,4-bis(nitroxymethyl)oxazolidone was dissolved in 50 cc. of alcohol, 25 cc. of water, and 2.5 cc. of ammonium hydroxide and heated on a steam bath. Upon working up the solution only 4,4-bis(nitroxymethyl)oxazolidone was isolated.

When 3.7 g. of 3-nitro-4,4-bis(nitroxymethyl)oxazolidone was suspended in 35 cc. of methyl alcohol and 2.5 cc. of ammonium hydroxide added, solution of the solid occurred, accompanied by some heat. After standing for a few minutes, the solution was distilled at reduced pressure to remove the solvent. No product was isolated.

Preparation of N-carbethoxy-2-amino-2-methyl-1-propanol.

In a one-liter, four-necked flask provided with stirrer, thermometer and two dropping funnels, there wereplaced 89 g. (1.0 moles) of 2-amino-2-methyl-1-propanol, 150 cc. of water, and 200 cc. of ether. While maintaining the temperature at 5-10° there was added dropwise 54.3 g. (0.5 mole) of ethyl chlorocarbonate. Then there were added concurrently a solution of 40 g. (1.0 moles) of sodium hydroxide in 100 cc. of water and 54.3 g. (0.5 mole) additional ethyl chlorocarbonate. After the addition the reaction was stirred for one-half hour. The ether was separated and the aqueous layer extracted with two portions (200, 100 cc.) of ether. After drying the combined extract, the ether was removed by distillation. The residue was distilled at reduced pressure. There was obtained an oily liquid (141 g.) boiling at 96-97°/2 mm. Yield, 88 per cent. $D_4^{20} = 1.066$, $n_D^{20} = 1.451$. Observed molecular refraction, 40.7; calculated, 41.1.

Analysis: Calculated for $C_7H_{15}O_3N$: C, 52.15; H, 9.38; N, 8.69.

Found: C, 51.74; H, 9.42; N, 8.12.

Preparation of Tris(chloromethyl)nitromethane.

To a one-liter, 3-necked flask provided with stirrer, thermometer, dropping funnel, and a trap for absorbing gases, there were added 144 g. (0.95 mole) of trimethylol nitromethane and 237 g. (3.0 mole) of pyridine. To this mixture was added 357 g. (3.0 moles) of thionyl chloride, maintaining the temperature at 40-50°. The complete addition required six hours. The reaction was allowed to stand overnight and was next heate on a steam bath to 90° and maintained at this temperature for one-half hour. After cooling, the content of the flask was poured into 1000 cc. of ice-water. A precipitate formed which was filtered off and washed well with water. After one recrystallization from 500 cc. of absolute alcohol there was obtained a white crystalline product (145 g.) melting at 103-104°. Yield 75 per cent.

Attempted Ammonolysis of Tris(chloromethyl)nitromethane.

The ammonolysis of tris(chloromethyl)nitromethane was attempted by heating in a pressure reactor the following substances: 34.4 g. (.133 mole) of tris(chloromethyl)nitromethane, 75 cc. of alcohol, 75 cc. of water, 53.5 g. (1.0 mole) ammonium chloride, and 300 cc. of liquid ammonia. It required one hour to heat the reaction to 120-130°. This temperature was maintained for two hours. At the end of this time the mixture was cooled and then evaporated on a steam bath. The slurry was taken up in 200 cc. of water and made distinctly acid to congo with hydrochloric acid. Considerable gas evolution accompanied the neutralization. A sticky sludge formed but no pure substance could be isolated.

Preparation of Methylenediurethane.

Into a two-liter beaker containing 1000 cc. of water there were added 178 g. (2 moles) of urethane, 82.7 g. (1 mole) of 36.3 per cent formalin, and 2-3 cc. of concentrated hydrochloric acid. The reaction mixture was allowed to stand for a period of thirty days, allowing the solution to evaporate. From time to time the crystals which formed were filtered off and washed with a small amount of water. There was obtained 170 g. of methylenediurethane melting at 130-1°. Recrystallization from alcohol raised the melting point to 130-131.5°. Yield, 90 per cent.

Nitration of Methylenediurethane. Ammonolysis.

To a flask equipped with stirrer and thermometer, and containing 100 cc. of 98 per cent nitric acid there was added slowly 19 g. (0.1 mole) of methylenediurethane. The temperature was maintained at 0-5° during the addition. After stirring 15 minutes at the same temperature the reaction was poured over 300 g. of cracked ice and the acid neutralized with sodium bicarbonate. An oil formed which was extracted with four portions of ether (150 cc. each) and the extract was dried with magnesium sulfate. The ethereal solution was saturated with dry ammonia gas whereupon a precipitate formed. This was filtered off and washed with ether. Yield, 12.5 g. (74 per cent).

Preparation of Cyclo-trimethylenetriurethane.

Into a 500 cc. flask containing 50 cc. of water there were added 41.4 cc. (0.5 mole) of 36.3 per cent formalin and 10 cc. of concentrated hydrochloric acid. While the temperature was kept below 25°, 44.5 g. (0.5 mole) of urethane was added. Precipitation of methylenediurethane occurred and on standing changed to an oil. At this point, the reaction was refluxed for forty-five minutes and then allowed to cool. The acid was neutralized with sodium bicarbonate and the oil extracted with ether (500 cc.). The extract was dried with magnesium sulfate and evaporated. The oil failed to crystallize when cooled and allowed to stand. It was then refluxed with a mixture of 75 cc. of acetic acid and 75 cc. of acetic anhydride for twelve hours. The anhydride and acid were distilled off and the oily residue poured into water. A semi-solid formed which was recrystallized from alcohol. There was obtained 14 g. of cyclo-trimethylenetriurethane (m.p. 100-2°). Yield 28 per cent.

Attempted Nitration of Cyclo-trimethylenetriurethane.

All attempts to convert cyclo-trimethylenetriurethane into RDX failed. Cyclo-trimethylenetriurethane was added to nine times its weight of 98 per cent nitric acid while cooling at 0-5°. In one experiment the reaction was quenched with water giving a completely homogeneous solution. In another experiment the nitric acid was evaporated under reduced pressure. Only an oily residue was formed which failed to crystallize after many weeks of standing.

Preparation of Pentaglycerine.

Preparative Procedure I. Into a 5000-cc., three-necked flask equipped with stirror, thermometer, and condenser there were added 2700 cc. of water, 60 g. (1.04 moles) of propionaldehyde, 258 g. (3.12 moles) of 36.3 per cent formalin solution, and a suspension of 150 g. (2 moles) of calcium hydroxide in 600 cc. of water. The mixture was heated on a steam bath for twenty-four hours. The excess slaked lime was removed and the filtrate acidified with dilute sulfuric acid. The precipitate of calcium sulfate was filtered off by suction. Oxalic acid may also be used instead of sulfuric acid. The filtrate was evaporated to a syrup over a steam bath. Upon dissolving in cold absolute alcohol, the inorganic matter remained behind and when the alcoholic solution was concentrated and cooled, crystals of pentaglycerine separated.

The product was filtered and washed with ether. The filtrate yields an additional quantity of pentaglycerine upon further concentration. The combined solids were recrystallized from absolute alcohol. The product (55.0 g.) melted at 199-200° (uncorr.). Yield, 29 per cent.

Preparative Procedure II. Into a ten-liter earthenware crock, provided with suitable cover, stirring device, thermometer, and addition funnel there were added 5.5 liters of water, 277 g. (4.77 moles) of propionaldehyde, and 600 g. (20.0 moles) of paraformaldehyde. To this vigorously stirred suspension there was added 100 g. (2.43 moles) of powdered calcium hydroxide in small portions. The rate of addition was so adjusted that the temperature rose to 45° in thirty minutes. After the addition, the stirring was continued overnight, and on the following morning the excess calcium hydroxide was filtered off. The filtrate was made acid to litmus with dilute hydrochloric acid and then concentrated under vacuum. Crystals of calcium formate separated out and were filtered off. The concentration and filtration operations were repeated several times until there finally remained a clear viscous oil. This oil was dissolved in one liter of absolute alcohol and the remaining insoluble calcium salts filtered off. Several concentrations of the alcohol solution with subsequent cooling yielded several crops of solid pentaglycerine of inferior melting point. The combined crops were refluxed with ether in order to remove formaldehyde impurities. After filtering off the ether the solid was recrystallized from absolute alcohol. There was obtained 265 g. of pentaglycerine, m.p. 199-200°. Yield, 46 per cent.

Preparative Procedure III. In a five-liter, three-necked flask, fitted with stirrer and thermometer, there were placed four liters of water, 277 g. (4.77 moles) of redistilled propionaldehyde, and 600 g. (20 moles) of paraformaldehyde. While employing moderate stirring there was added in portions 180 g. (2.43 moles) of calcium hydroxide. The rate of addition was so adjusted that the temperature of the reaction rose to 50° in one-half hour. The remainder of the calcium hydroxide was added keeping the temperature below 55°. The reaction mixture was stirred for four hours and allowed to set overnight The excess solid was filtered off and the filtrate was concentrated by vacuum distillation. It was necessary to remove calcium formate which crystallized out during the distillation periodically. There finally remained a water white oil which was taken up in 100 cc. of absolute alcohol. The remainder of the insoluble salts was filtered off and the alcoholic filtrate concentrated at reduced pressure. Upon cooling the concentrate, several crops of crude pentaglycerine were obtained. The crude material was digested with ether and filtered. The partially purified pentaglycerine was recrystallized from absolute alcohol. A total of 141 g. of pentaglycerine, melting at 197-9° was obtained.

The ether solution used in the digestion operation was concentrated and a solid crystalline compound obtained. After a recrystallization from ether crystals of the formal derivative of 5-methyl-5-methylol-1, 3-dioxane (10 g.), melting at 99-100°, were obtained.

Analysis: Calculated for $C_{13}H_{24}O_6$: C, 56.50; H, 8.76; M.W., 276.

Found: C, 57.14, 56.73; H, 8.91, 8.67; M.W., 255, 256.

The alcoholic filtrate, obtained after removing the pentaglycerine, was heated on a steam bath to remove the last traces of solvent. One liter of ether was added to the residue. Most of the material went into solution. After the extract was dried with magnesium sulfate and then concentrated the residue was distilled at reduced pressure. There was obtained an oily liquid, 5-methyl-5-methylol-1,3-dioxane (145 g.) boiling at 86.5-87°/3 mm. D_4^{25}, 1.118; n_D^{25}, 1.4562.

Analysis: Calculated for $C_6H_{12}O_3$: C, 54.51; H, 9.15; M.W., 132.

Found: C, 54.45, 53.82; H, 9.32, 9.27; M.W. 134, 131.

The distillation residue (50 g.) was soluble in ether and consisted largely of the formal derivative of 5-methyl-5-methylol-1,3-dioxane.

The ether insoluble, water soluble residue (91 g.) from the extraction operation was not further studied. In all probability it was a complex mixture of products containing molecules with both alcoholic groups and acetal linkages.

Preparative Procedures IV and V. Into a five-liter, three-necked flask there were added 4000 cc. of water, 277 g. (4.77 moles) of propionaldehyde, and 450 g. (15 moles) of paraformaldehyde. To the mixture, employing moderate stirring, there was added in portions 180 g. (2.43 moles) of calcium hydroxide. The rate of addition was so adjusted that the temperature of the reaction rose to 50° in one-half hour. The remainder of the calcium hydroxide was added while keeping the temperature below 55°. The solution was stirred for twenty hours and developed a light brown color. The calcium was removed by adding 132 cc. of 98 per cent sulfuric acid. The precipitate of calcium sulfate was filtered off and the filtrate concentrated at reduced pressure until a syrup remained. The residue was taken up in methyl alcohol. The remainder of the inorganic salts was removed by filtration and the alcoholic filtrate concentrated over a steam bath. When allowed to cool overnight, crystals of crude pentaglycerine separated and were removed by filtration. Recrystallization from methyl alcohol yielded a solid (262 g.), melting at 197-9°.

No products similar to those obtained from Procedure III could be isolated. The final residue, a dark brown viscous syrup, possessed an odor reminiscent of burnt sugar. The probability that the residue consisted of "formose" sugars is not unlikely.

Hydrolysis of 5-Methyl-5-methylol-1,3-dioxane.

The hydrolysis of 5-methyl-5-methylol-1,3-dioxane was carried out by refluxing 13.2 g. (0.1 mole) of the liquid in 50 cc. of 1 N. hydrochloric acid for one-half hour. The odor of formaldehyde was unmistakeable; likewise, the solution gave a positive Tollen's test. The solution was evaporated over a steam bath and there remained an ether insoluble residue weighing 1.1 g. and melting at 180-2°. Two recrystallizations from methyl alcohol raised the melting point to 195-6° and a mixed melting point with an authentic sample of pentaglycerine showed no depression.

Hydrolysis of the Formal Derivative of 5-Methyl-5-methylol-1,3-dioxane.

The hydrolysis of the formal derivative of 5-methyl-5-methylol-1,3-dioxane was carried out paralleling the directions given for the hydrolysis of 5-methyl-5-methylol-1,3-dioxane. Similiar results were obtained.

Transformation Induced by Boiling 5-Methyl-5-methylol-1,3-dioxane.

Accordingly, 13.2 g. (0.1 mole) of 5-methyl-5-methylol-1,3-dioxane was boiled under reflux for two hours. After cooling, it was added to 100 cc. of water. A precipitate formed which was filtered off and washed with a small amount of water. After recrystallization from ether a solid (0.8 g.) melting at 97-8° was obtained. No depression of melting point was observed when mixed with a sample of the formal derivative of 5-methyl-5-methylol-1,3-dioxane.

Likewise, a similarly treated reaction was poured into ether. It was hoped that pentaglycerine might be precipitated. However, none was obtained.

Nitration of 5-Methyl-5-methylol-1,3-dioxane.

A nitrating mixture was prepared by adding 57.6 g. (0.90 mole) of 98 per cent nitric acid to 86.4 g. (0.88 mole) of concentrated sulfuric acid. While stirring the solution and maintaining the temperature at 20°, there was added dropwise 13.2 g. (0.1 mole) of 5-methyl-5-methylol-1,3-dioxane. After the addition, cooling was discontinued and the reaction was stirred for one and three-quarter hours. During this interval the temperature had risen to 60° and an oil formed on the surface. After cooling the reaction, the mixture was poured over cracked ice. The milky oil was separated and washed with several successive portions of water, sodium bicarbonate solution, and finally water. After drying the oil over calcium chloride and filtering, there was obtained 18.2 g. (85 per cent of theoretical) of a colorless liquid melting at +9°C.: $D_4^{22} = 1.46$; $n_D^{22} = 1.4760$. This product was shown to be trimethylolmethylmethane trinitrate.

A drop of the oil placed on an anvil, detonated sharply when struck with a hammer.

Analysis: Calculated $C_5H_9O_9N_3$: N, 16.47; M.W., 255.
Found: N, 16.61, 16.11, 16.13; M.W., 248, 249.

Nitration of the Formal Derivative of 5-Methyl-5-methylol-1,3-dioxane.

A nitrating mixture was prepared by adding 11.6 g. (0.18 mole) of 98 per cent nitric acid to 17.4 g. (0.17 mole) of concentrated sulfuric acid. While stirring and maintaining the temperature of the reaction at 20°, there was added 2.46 g. (.009 mole) of the formal derivative of 5-methyl-5-methylol-1,3-dioxane. The reaction was stirred at this temperature for three hours and then heated slowly to 60° and held at this temperature for a few minutes. After cooling, the reaction was poured over ice. The oil was separated and washed successively with portions of water, sodium bicarbonate solution and finally water. After drying with calcium chloride the liquid was filtered. There was obtained 2.30 g. of product, showing the same properties as the nitration product obtained from 5-methyl-5-methylol-1,3-dioxane. $D_4^{20} = 1.46$,

n_D^{20} = 1.4762. Molecular Weight = 244, 249.

Nitration of Pentaglycerine. Preparation of Trimethylolmethylmethane Trinitrate.

Into a 200 cc., three-necked flask, equipped with stirrer and thermometer there was added a nitrating mixture consisting of 28.8 g. (0.46 mole) of 98 per cent nitric acid and 43.2 g. (0.43 mole) of 98 per cent sulfuric acid. While maintaining the temperature at 20°, 12 g. (0.1 mole) of pentaglycerine was added. The reaction was allowed to stand for one-half hour and was then heated to 60° and held at this temperature for a few minutes. After cooling, the reaction was poured into cracked ice. The oil was separated and washed with portions of water, sodium bicarbonate solution, and finally water. The product was dried over calcium chloride. After filtering, a liquid (17.5 g.) was obtained. Yield 70 per cent. n_D^{22} = 1.4760; D_4^{22} = 1.46; m.p., +9°C.

Preparation of Pentaglyceryl Tribromide. Isolation of Pentaerythrityl Bromide as Impurity.

Into a 500 cc., 3-necked flask provided with a thermometer dropping funnel, and air condenser to which there was attached a suitable trap for absorbing gases, there was placed 120 g. (1.0 moles) of pentaglycerine. The flask was heated by means of a water bath to nearly 100° and 406 g. (1.5 moles) of phosphorus tribromide was added dropwise. After the addition was completed the water bath was replaced by an electrically heated oil bath and the reaction mixture was slowly heated to 160-170°. This temperature was maintained for twenty hours. The flask was then cooled and its contents poured into 1500 cc. of water. The pentaglyceryl tribromide settled to the bottom as an oil, which after filtering to remove insoluble solids, was extracted with four portions of ether (500, 500, 250, and 250 cc.). The extract was dried with magnesium sulfate and the solution was concentrated by distilling off the ether. The residue was fractionated through a 60 cm. column under a pressure of 8 mm. of Hg. A fraction (177.5 g.) boiling at 88-89° was collected, n_D^{20} = 1.558. Yield, 58 per cent.

Analysis: Calculated for $C_5H_9Br_3$: Br, 77.63.

Found: 77.92, 78.09.

The residue from distillation solidified upon standing and after recrystallization from ether there was obtained a small amount of solid melting at 159-160°. The compound gave no depression of melting point when mixed with an authentic sample of pentaerythrityl bromide, m.p., 159.5-160°.

Analysis: Calculated for $C_5H_8Br_4$: C, 15.49; H, 2.08; Br, 82.44.

Found: C, 15.54, 15.53; H, 2.07, 2.27; Br, 82.18 82.37.

Ammonolysis of Pentaerythrityl Bromide.

The ammonolysis of pentaerythrityl bromide was carried out using (1) alcoholic ammonia, (2) liquid ammonia, (3) a mixture of liquid ammonia and alcohol, (4) liquid ammonia, alcohol, and ammonium chloride, and (5) liquid ammonia and pyridine.

In the cases where liquid ammonia was used, the mixture was cooled down in the reactor (the liner) with acetone-dry ice mixture in order to prevent the evaporation of ammonia. After the reaction was finished, the reactor was cooled down to room temperature and the ammonia was allowed to escape slowly through the valve attached to the bomb.

Generally the reaction mixture was evaporated to dryness on the steam bath to remove excess ammonia. The residue was tested for unreacted pentaerythrityl bromide by noting the presence of any water insoluble material. Sufficient water was added to effect complete solution of the amine hydrobromide. The solution was filtered from any unreacted material and the filtrate treated with excess dilute sulfuric acid (Congo Red). The amine separated as the disulfate. To insure complete precipitation, the aqueous solution was diluted with an equal volume of 95 per cent ethyl alcohol and allowed to stand overnight. The disulfate salt was filtered and washed with 50 per cent ethyl alcohol. The crude sulfate was suspended in two to three times its weight of water, the mixture warmed and made alkaline with sodium hydroxide solution. The alkaline solution was filtered, heated to boiling, and acidified with dilute sulfuric acid (Congo Red). The resulting crystalline precipitate was filtered and washed with water or 50 per cent ethyl alcohol. The disulfate obtained melted with decomposition in the range of 296-300.5°. The disulfate of pentaerythrityl tetramine is insoluble in water and in 50 per cent ethyl alcohol containing dilute sulfuric acid. It is soluble in dilute sulfuric acid (12 N) alone. In the presence of impurities it is precipitated slowly from its solutions. The yields were calculated as the disulfate, $C(CH_2NH_2)_4 \cdot 2H_2SO_4$. The results are summarized in the tables which follow.

Table XIV

Ammonolysis of Pentaerythrityl Bromide with Alcoholic Ammonia

Amt. of Bromide	Amt. of Alcoholic Ammonia	Temp. (°C)	Time	Amt. of Unreacted Bromide(%)	Yield (%)
20 g.	600 cc (95%)	20-25	60 days	100	0
30 g.	300 cc (99.5%)	160	12 hrs.	1	16.6
30 g.	300 cc (95%)	160	12 hrs.	1	19.9
30 g.	300 cc (90%)	160	12 hrs.	1	22.5
30 g.	300 cc (75%)	160	12 hrs.	1	23.3
60 g.	600 cc (70%)	130	20 hrs.	12	1.8
60 g.	600 cc (75%)	130	12 hrs.	70	1.4

Table XV

Ammonolysis of Pentaerythrityl Bromide with Liquid Ammonia

Amt. of Bromide	Amt. of Liquid Ammonia	Temp. (°C)	Time	Amt. of Unreacted Bromide (g.)	Yield %
5 g.	18 cc.	20-25	5 days	5	None
25 g.	150 cc.	80	6 hrs.	9.1	"
50 g.	150 cc.	100-110	6 hrs.	None	"
25 g.	150 cc.	125-130	7 hrs.	None	"

Table XVI

Ammonolysis of Pentaerythrityl Bromide with Liquid Ammonia and Alcohol

Amt. of Bromide	Amt. of Liq. Ammonia	Amt. Alc.	Temp. (°C.)+	Time	Yield of Disulfate (%)
25 g.	100 cc.	50 cc. (absolute)	150-155	6 hrs.	6.6
25 g.	100 cc.	50 cc. (70%)	160-170	6 hrs.	15.6
25 g.	100 cc.	50 cc. (absolute)	175-180	6 hrs.	2.4
25 g.	100 cc.	50 cc. (70%)	160	1-1 1/2 hrs.	15.1
25 g.	100 cc.	50 cc. (70%)	140-160	1 hr.	31.2

+ Due to heat of reaction, the temperature rose about 20 degrees above the specified temperature for 10 minutes.

Table XVII

Ammonolysis of Pentaerythrityl Bromide with Liquid Ammonia, Ammonium Chloride, and Alcohol

Amt. of Bromide	Amt. of Liq. Ammonia	Amt. Alc. 75%(25% H_2O)	NH_4Cl	Temp.[+] (°C)	Time	Yield (%)
10 g.	100 cc.	50 cc.	none	160	1 hr.	34
10 g.	100 cc.	50 cc.	22.2 g.	160	1 hr	50
10 g.	100 cc.	50 cc.	22.2 g.	160	2 hrs.	52
10 g.	100 cc.	50 cc.	22.2 g.	160	3 hrs.	53
10 g.	100 cc.	50 cc.	44.4 g.	160	1 hr.	46[++]
10 g.	100 cc.	50 cc. (50% alc.)	22.2 g.	160	1 hr.	54

[+] When the temperature was raised to 140°, heating was discontinued for 15 min., during which time the temperature increased to 155° spontaneously. This was due to the heat of the reaction.

[++] The yield was slightly lower, because more water had to be used to dissolve the large amount of ammonium chloride.

Table XVIII

Ammonolysis of Pentaerythrityl Bromide with Liquid Ammonia, Ammonium Chloride, and Alcohol

Amt. of Bromide	Amt. of Liq. Ammonia	Amt. Alc. 50%(50% H_2O)	NH_4Cl	Temp. (°C)	Time	Yield (%)
60 g.	600 cc.	300 cc.	133.3 g.	160	1 hr.	56.3
"	"	"	"	"	"	56.5
"	"	"	"	"	"	58.0
"	"	"	"	"	"	60.3
"	"	"	"	"	"	66.6
"	"	"	"	"	"	67.2

Table XIX

Ammonolysis of Pentaerythrityl Bromide

with Liquid Ammonia and Pyridine

Amt. of Bromide	Amt. of Liq. Ammonia	Amt. of Pyridine	Temp. (°C.)	Time	Yield %
10 g.	50 cc.	25 cc.	160	8 hrs.	11.8

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FORMULA INDEX OF NITRAMINE DERIVATIVES

(References to experimental procedures are indicated by underlined figures).

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ABSTRACT:

Results are given of investigations dealing with the preparation and properties of some aliphatic nitramines. Several compounds related to Haleite were prepared. N-methyl-ethylene-dinitramine, N,N'-dimethyl-ethylenedinitramine, and dinitropiperazine were obtained by alkylating ethylenedinitramine. The effect of cold absolute nitric acid on nitramines was studied, and the halogenation of ethylenedinitramine and its monoethyl derivative with iodine proved to be unsuccessful. One of the objects of this study was to prepare the nitramine analogs of several known nitrate-ester explosives, and this was accomplished for several compounds listed. The most important outgrowth of the research on new nitramines has been the development of mixed nitrate esters and compounds of the NENA type, which are being investigated as plasticizers for nitrocellulose.

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