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NITRAMINES

Alfred T. Blomquist and Fred T. Fiedorek, Ithaca, N. Y., assignors to the United States of America as represented by the Secretary of the Navy

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2 Claims. (Cl. 260—467)

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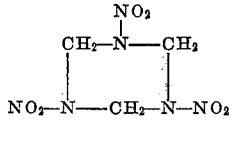
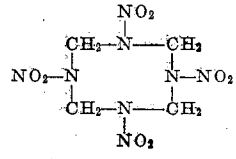
The present invention relates to nitramines and more particularly to a new series of nitramines derivable from certain types of aliphatic amines.

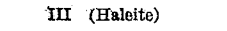
The aliphatic nitramines comprise a group of organic explosives of increasing interest at the present time because of the outstanding explosive properties of several members of the class that have come into prominence during the current World War. Of these nitramines, the most outstanding are cyclonite (I), homocyclonite (II), Haleite (III) and DINA (IV).



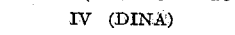
I (Cyclonite)



II (Homocyclonite)



III (Haleite)



IV (DINA)

It will be noted that one of these four nitramines (DINA) contains two nitroxyalkyl groups in addition to a nitramine group. Possibly because of the presence of these nitroxyalkyl groups, DINA is capable of plasticizing nitrocellulose and is therefore of interest as a replacement for the undesirably volatile nitroglycerine used in propellants of the double base type (cf. Wright et al. application Ser. No. 570,813, now Patent No. 2,461,582, and Kincaid et al. application Ser. No. 570,808, both filed of even date herewith). DINA, however, tends to crystallize out of the colloided nitrocellulose matrix of propellant compositions. For this and other reasons, DINA in itself is not entirely unobjectionable as a nitrocellulose plasticizer for use in propellant compositions.

Broadly speaking, the object of the present invention is to provide a new series of nitramines containing a nitroxyalkyl group in addition to one or more nitramino groups.

A further object is the provision of a novel series of nitroxyalkylnitramines suitable for various industrial uses but of particular interest in connection with the manufacture of industrial and military explosives.

A more particular object is to provide a new series of nitroxyalkylnitramines that are capable of plasticizing nitrocellulose, and are therefore adaptable for use in the production of propellants.

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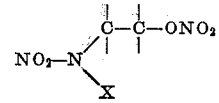
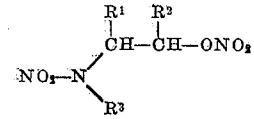
Another object is to provide commercially feasible methods for the synthesis of such compounds.

Still further objects and advantages will be apparent as the invention is hereinafter more fully described.

The nitramines with which the present invention is primarily concerned comprise a novel class of compounds having the general structural formula:



where X is either hydrogen or alkyl or carbalkoxy. More particularly, the nitramines of the present invention are characterized by the formula:

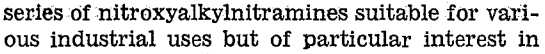


where R^1 and R^2 are either hydrogen, alkyl or nitramino-alkyl and R^3 is either hydrogen, alkyl or carbalkoxy. Such compounds are of interest as plasticizers for nitrocellulose. Moreover, because of the relatively low volatility of many of the class members, they provide a series of relatively non-volatile explosive or semi-explosive compounds adaptable for use in the preparation of propellants.

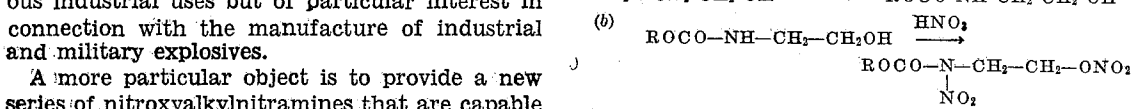
The novel nitroxyalkylnitramines of the present invention may conveniently be classified into two subclasses, namely (1) those wherein the R^3 radical is hydrogen or carbalkoxyl; and (2) those wherein the R^3 radical is alkyl. The first subclass (R^3=H or —COOR) may be prepared from the appropriate primary alkanol amine whereas the second subclass (R^3=alkyl) may be prepared from the appropriate secondary alkanol alkyl amine.

The synthesis of the first subclass may be illustrated by the following series of reactions:

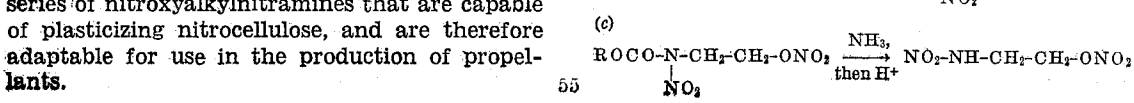
(a)



(b)



(c)



The synthesis of the second subclass of nitramines (R or R^3=alkyl) may be accomplished somewhat more readily by the catalytic "dehydration" of the corresponding nitroxyalkylamine nitrate salt, as illustrated by the following equations:

(a)

$$R{-}NH{-}CH_2CH_2{-}OH \longrightarrow R{-}\overset{+}{N}H_2{-}CH_2CH_2ONO_2 \quad \overset{-}{N}O_3$$

(b)

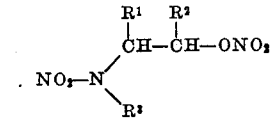
$$R{-}\overset{+}{N}H_2{-}CH_2CH_2ONO_2 \quad \overset{-}{N}O_3 \xrightarrow[(CH_3CO)_2O]{-H_2O} R{-}N{-}CH_2{-}CH_2ONO_2$$
$$(Cl^- \text{ or } Br^-)$$

Before describing in detail the procedures used for preparing the various nitramines of the present invention, a brief description of the preparation and properties of several specific compounds in this series may be of interest. Purely as a matter of convenience these will be discussed as members of a homologous series, the parent compound of which is N-(2-nitroxyethyl) nitramine,

$$NO_2{-}NH{-}CH_2CH_2ONO_2$$

hereinafter referred to by the trivial name, NENA. The N-alkyl homologues (R^3=alkyl) of this parent compound may conventently be designated Alkyl-NENA's, the N-methyl homologue being called Me-NENA, the N-ethyl homologue, Et-NENA, etc.

N-(2-nitroxyethyl) nitramine (NENA) and the corresponding urethane



R^1 and R^2 are H; R^3 is either H or $-COOC_2H_5$.

Of interest from a standpoint of explosive properties, because it possesses a structure intermediate to glycol dinitrate and ethylenedinitramine is the compound N-(2-nitroxyethyl) nitramine ("NENA") having the following formula:

$$O_2NO_2{-}CH_2CH_2{-}NHNO_2$$

This substance is a liquid at room temperature and melts at 15° C. Its explosive properties are as follows:

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).
Impact sensitivity (50% pt.): 191, 107 cm.

The synthesis of NENA may be carried out according to the following equations:

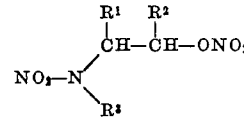
$$HOCH_2CH_2NH_2 \xrightarrow{ClCO_2R} HOCH_2CH_2NHCO_2R$$

$$HOCH_2CH_2NHCO_2R \xrightarrow{HNO_3} O_2NOCH_2CH_2N(NO_2)CO_2R$$

$$O_2NOCH_2CH_2N(NO_2)CO_2R \xrightarrow[H_2SO_4]{NH_3} O_2NOCH_2CH_2NHNO_2$$

N-(2-ethanol) urethane was obtained from ethanolamine and ethyl chlorocarbonate by employing a modification of the method used by Franchimont and Lublin, Rec. trav. chem. 21, 48 (1902). Yields as high as 96 per cent of theoretical were obtained. The nitration of N-(2-ethanol) urethane proceeded smoothly and ammonolysis of the resulting nitrourethane yielded the ammonium salt of N-(2-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-(2-nitroxyethyl) nitramine by the neutralization of the ammonium salt is preferably carried out as rapidly as possible. By this technique, yields of 93.3 per cent of the theoretical were realized for the free nitramine.

N-(2-nitroxyethyl) methylnitramine (Me-NENA)



R^1 and R^2 are H; R^3 is methyl.

With a view to developing an essentially nonvolatile nitrocellulose plasticizer for use in double base-type powders in lieu of nitroglycerine, the preparation of N-(2-nitroxyethyl) methylnitramine was undertaken.

The properties of Me-NENA are as follows:

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).
Impact sensitivity: Greater than 90 cm. (Cyclonite=48–50 cm.).
Density (by picnometer):
Liquid: D_4^{25}=1.40.
Solid: D_4^{25}=1.53.

Me-NENA may be prepared from methyl ethanolamine by the reactions shown in the following equations:

$$CH_3{-}NH{-}C_2H_4OH + 2HNO_3 \rightarrow CH_3{-}\overset{+}{N}H_2{-}C_2H_4ONO_2 + H_2O \quad \overset{-}{N}O_3$$

$$CH_3{-}\overset{+}{N}H_2{-}C_2H_4ONO_2 \quad \overset{-}{N}O_3 + Ac_2O \xrightarrow{Cl^-} CH_3{-}\underset{\underset{NO_2}{|}}{N}{-}C_2H_4ONO_2 + 2HOAc$$

This preparation may be carried out in one stage by adding N-methyl-2-ethanolamine and nitric acid concurrently and simultaneously to acetic anhydride containing a trace of chloride catalyst. If preferred, however, the process may be carried out in two-stages, one of which involves the formation of a solution of the amine and nitric acid, while the second involves the addition of this solution to the acetic anhydride and the chloride catalyst. The Me-NENA is separated from the reaction mixture produced by either the one-stage or the two-stage process by diluting the mixture with water, and then filtering off the Me-NENA precipitate from the mother liquor.

Stability of Me-NENA

The stability of Me-NENA may be considerably enhanced by the agitation of molten Me-NENA with dilute base followed by subsequent precipitation of the substance from an acetone solution.

Table I lists results of tests on the vacuum stability of Me-NENA. The vacuum stabilities of

DINA and nitroglycerine are presented to provide a basis for comparison. Me-NENA, it is observed, is far superior to either DINA or nitroglycerine in this respect.

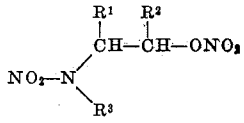
TABLE

Vacuum stability of Me-NENA, DINA and nitroglycerine at 100° C.[1]

Sample	Time (hrs.)
Me-NENA	144, 144.
DINA	10, 42.
N. G	12¾, 12¾.

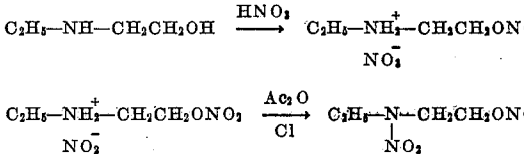
[1] 2.4 g. samples were used in these tests. The time represents the number of hours required to exceed the capacity of the apparatus (12 cc.).

N-(2-nitroxyethyl) ethylnitramine (Et-NENA)

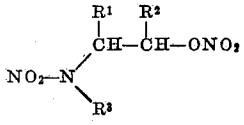


R^1 and R^2 are H; R^3 is ethyl.

A nitroxylalkyl nitramine homologous to N-(2-nitroxyethyl) nitramine, (NENA), and N-(2-nitroxyethyl) methylnitramine (Me-NENA) is the compound N-(2-nitroxyethyl) ethylnitramine or Et-NENA. This substance was prepared by a process indicated by the following equations:



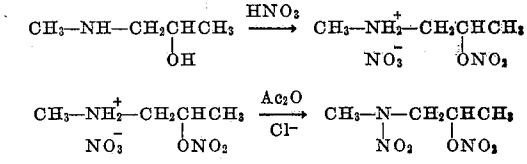
N-(2-nitroxypropyl) methylnitramine (Me$_2$-NENA)



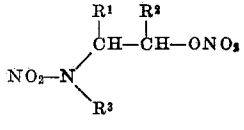
R^1 is H; R^2 and R^3 are methyl.

A compound that is structurally related to the previously discussed nitroxyalkyl nitramines is N-(2-nitroxypropyl) methylnitramine. This compound is isomeric with N-(2-nitroxyethyl) ethylnitramine (Et-NENA).

The preparation of N-(2-nitroxypropyl) methylnitramine was carried out using methyl isopropanolamine as a starting material, as indicated by the following equations:

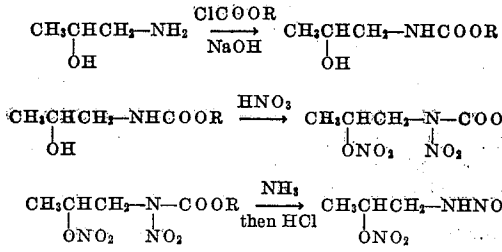


N-(2-nitroxypropyl) nitramine (Iso-Me-NENA) and the corresponding urethane



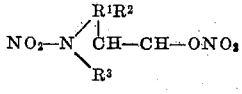
R^1 is H; R^2 is methyl; R^3 is H or —$COOC_2H_5$.

Another nitroxyalkylnitramine related to N-(2-nitroxyethyl) nitramine (NENA) is N-(2-nitroxypropyl) nitramine (iso-Me-NENA). This compound is isomeric with N-(2-nitroxyethyl) methylnitramine (Me-NENA) differing from it only in the position of the methyl group. Its synthesis was carried out as indicated by the following equations:



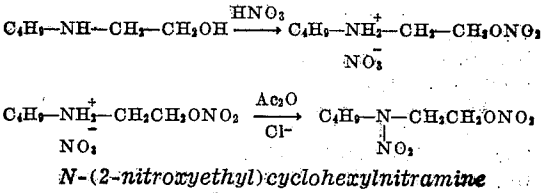
N-(2-propanol) urethane was converted into the corresponding nitroxyalkyl nitrourethane by treating it with an excess of 98 per cent nitric acid. N-(2-nitroxypropyl) nitrourethane is soluble in ether and when the extract was treated with dry ammonia the ammonium salt of N-(2-nitroxypropyl) nitramine 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.

N-(2-nitroxyethyl) butylnitramine (Bu-NENA)

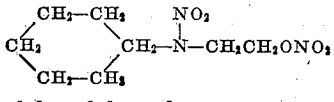


R^1 and R^2 are H; R^3 is n-butyl.

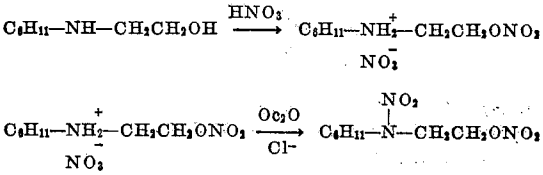
The butyl homologue (Bu-NENA) of Me-NENA may be obtained from 2-ethanol butylamine by the reactions indicated by the following equations:



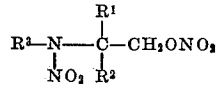
N-(2-nitroxyethyl) cyclohexylnitramine (cyclohexyl-NENA)



The cyclohexyl homologue of Me-NENA may be prepared from cyclohexylethanolamine by the reactions indicated by the following equations:



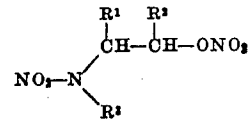
2-nitramino-1-butanol nitrate and corresponding urethane



R^1 and/or R^2 is H, CH_3, or C_2H_5; R^3 is H or —$CO_2C_2H_5$.

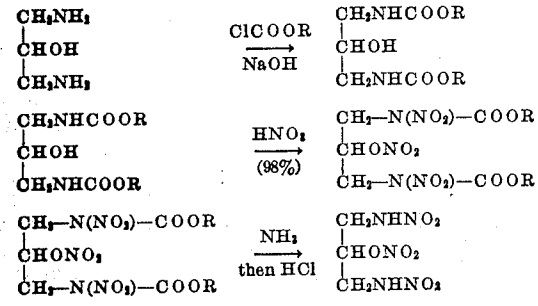
Another compound related to NENA is obtainable by nitration of N-carbethoxy-2-amino-1-butanol. This urethane was obtained from 2-amino-1-butanol and chloroethyl carbonate. A similar compound (R^1 and R^2=methyl) may be obtained from 2-amino-2-methyl-1-propanol via the urethane.

Dinitraminoisopropyl nitrate and the corresponding urethane



R^1 is H; R^2 is $-CH_2N(NO_2)COOC_2H_5$ or $-CH_2NHNO_2$; R^3 is H or $-COOC_2H_5$.

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

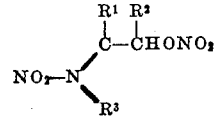


The latter compound is a nitramino analogue of nitroglycerine wherein two nitroxy groups are replaced by two nitramino groups. Its explosive properties are as follows:

M. P.: 164–154 (decomp.).
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).
Impact sensitivity: 24.4 cm. (Cyclonite=48–50 cm.).

3-nitro-4,4-bis(nitroxymethyl) oxazolidone

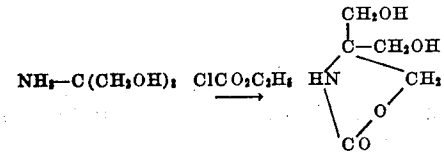
A cyclic urethane related to the urethane from which NENA was prepared is 3-nitro-4,4-bis(nitroxymethyl) oxazolidone, having the structure:



where R^1 is nitroxymethyl; R^2 is H; and R^3 is the cyclic urethane group, $-COOCH_2-$.

This compound was prepared from trimethyl aminomethane, (Commercial Solvents Corporation), by the following series of reactions:

(a)



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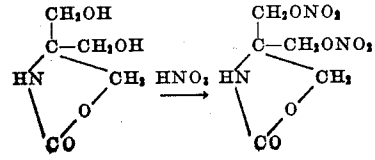
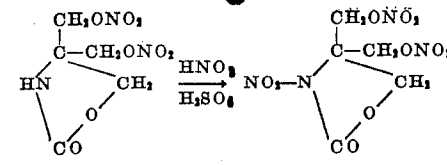
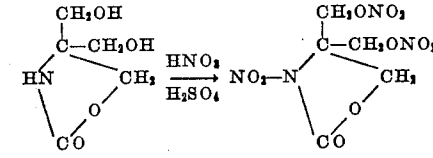


(c)



or

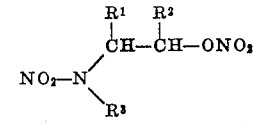
(d)



In order more clearly to describe the new and improved nitramines of the present invention several specific examples will hereinafter be described in considerable detail. It should be clearly understood, however, that this is done solely by way of example, and not for the purpose of delineating the scope of the invention or limiting the ambit of the appended claims.

EXAMPLE I

Preparation of N-(2-nitroxyethyl) nitramine ("NENA") and N-(2-nitroxyethyl) nitrourethane



R^1 and R^2 are H; R^3 is H or $-COOC_2H_5$.

A. *Preparation of N-(2-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° C. (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° C. 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.

B. *Nitration of N-(2-ethanol) urethane*

The nitration of N-(2-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° C., 50 g. (0.376 mole) of N-(2-ethanol) urethane was added dropwise. The temperature of the reaction mixture was maintained at 5–10° C. 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 rapid-

ly with 75 g. of anhydrous magnesium sulfate. The ether solution of N-(2-nitroxyethyl) nitrourethane was used directly for the ammonolysis.

C. *Ammonolysis of N-(2-nitroxyethyl) nitrourethane*

The ammonolysis of N-(2-nitroxyethyl) nitrourethane was carried out using the ether solution that was prepared above. The ammonium salt of N-(2-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-(2-nitroxyethyl) nitramine precipitated and was filtered and washed with dry ether. The product (61.3 g., 97% yield) melted with decomposition at 78–79° C.

The ammonium salt of N-(2-nitroxyethyl)-nitramine decomposes slowly at room temperature. The decomposition of the salt proceeds more rapidly in aqueous solution.

D. *Isolation of N-(2-nitroxyethyl) nitramine (NENA)*

The ammonium salt of N-(2-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° C. at 9 mm. The product was a pale yellow, water-insoluble oil melting at 15° C. 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-(2-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-(2-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° C. and acidified immediately, giving a 95 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-(2-nitroxyethyl) nitramine, should be handled carefully as it appears to be a skin irritant. It produces inflammation and itching.

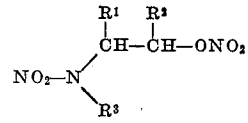
E. *The silver salt of N-(2-nitroxyethyl) nitramine*

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-(2-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° C. It darkens on exposure to light.

Analysis: Calcd. for $C_2H_4O_5N_3Ag$: N, 16.29. Found: N, 16.28, 16.49.

EXAMPLE II

Preparation of N-(2-nitroxyethyl) methylnitramine ("Me-NENA")



R^1 and R^2 are H; R^3 is methyl.

A. *One-stage preparation of Me-NENA*

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° C. 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° C. After all of the amine 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° C. The contents of the flask were poured on 500 g. of cracked ice. A precipitate of N-(2-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° C. was recrystallized from 1000 cc. of anhydrous ether and gave 93.8 g. of a crystalline solid melting at 39–40.5° C. (corr.). An additional 9.4 g. of product was obtained upon concentrating the ether solution. The yield of purified product was 63 per cent.

B. *Two-stage preparation of Me-NENA*

N-(2-nitroxyethyl) methylnitramine has been prepared by treating N-methyl-2-ethanolamine dinitrate with acetic anhydride,, zinc chloride, and hydrochloric acid at 40° C. The intermediate dinitrate is a crystalline salt and is best obtained by adding N-methyl-2-ethanolamine to 98 per cent nitric acid and pouring the reaction mixture into ether.

1. *Preparation of N-methyl-2-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° C., 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-2-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° C. No further purification was necessary preparatory to the next step. Yield, 95 per cent.

2. *Conversion of N-methyl-2-ethanolamine dinitrate into N-(2-nitroxyethyl) methylnitra-*

mine.—A mixture of 100 cc. of acetic anhydride, 1 g. of zinc chloride and 1 cc. of concentrated hydrochloric acid was warmed to 40° C. To the solution there was added in portions 17.3 g. (.095 mole) of N-methyl-2-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° C. After one recrystallization from ether the melting point was unchanged.

C. *The stabilization of Me-NENA*

A 200 g. sample of crude Me-NENA (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° C. The charge was then agitated by bubbling air through the suspension until the temperature had dropped to 50° C. The agitation was continued and pieces of ice added until precipitation occurred. The Me-NENA 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° C.

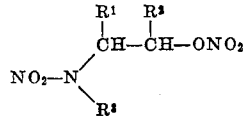
An 80 g. sample of Me-NENA was recrystallized from 720 cc. of ether using vigorous stirring and cooling in an ice bath. After filtration there was obtained 74.8 g. of product melting at 39.5°–40.5° C.

The ether recrystallized Me-NENA 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.

EXAMPLE III

Preparation of N-(2-nitroxyethyl) ethylnitramine (Et-NENA)



R^1 and R^2 are H; R^3 is ethyl.

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 contents of the flask were cooled externally and the temperature maintained below 10° C. during the addition.

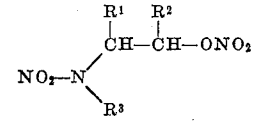
The amine-nitric acid mixture was transferred to a dropping funnel and added dropwise to a solution of 118 g. (1.1 moles) of 95 per cent acetic anhydride and 0.86 g. (0.011 mole) of acetyl chloride contained in a 500 cc., three-necked flask. Moderate stirring was employed and the reaction was maintained at 35° C. After the addition of the amine-nitric acid mixture which required fifteen minutes, the reaction was kept at 35° C. 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 obtained 73.4 g. (82 per cent of theoretical) of N-(2-nitroxyethyl) ethyl-nitramine melting at 4–5.5° C.

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

Theoretical molecular refraction=38.75.
Observed molecular refraction=38.4.

EXAMPLE IV

Preparation of N-(2-nitroxypropyl) methylnitramine (Me2—NENA)



R^1=H; R^2 and R^3 are methyl.

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 contents of the flask were externally cooled to a temperature below 10° C. and there maintained during the addition.

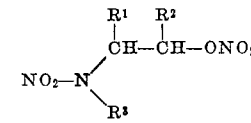
The amine-nitric acid mixture was transferred to a dropping funnel and added dropwise to a solution of 118 g. (1.1 moles) of 95 per cent acetic anhydride and 0.86 g. (0.011 mole) of acetyl chloride contained in a 500 cc., three-necked flask. Moderate stirring was employed and the reaction was maintained at 35° C. After the addition of the amine-nitric acid mixture which required fifteen minutes, the reaction was kept at 35° C. 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-(2-nitroxypropyl) methylnitramine as a pale yellow oil, melting at 22–23° C.

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

Theoretical molecular refraction=38.75.
Observed molecular refraction=38.5.

EXAMPLE V

Preparation of N-(2-nitroxypropyl) nitrourethane and N-(2-nitroxypropyl nitramine ("iso-Me-NENA")



R^1 is H; R^2 is methyl; R^3 is —$COOC_2H_5$ or H.

A. *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 mole) of 1-amino-2-propanol, 150 cc. of water, and 200 cc. of ether. While maintaining the temperature of the reaction at 5–10° C. 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° C./1 mm. Yield, 87 per cent.

$n_D^{20}=1.4492$; $D_4^{20}=1.082$

Theoretical molecular refraction=36.46.
Observed=36.4.

B. *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.

C. *Ammonolysis of N-(2-nitroxypropyl) nitrourethane; isolation of N-(2-nitroxypropyl)-nitramine*

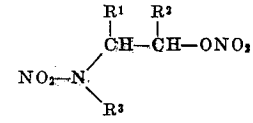
The dried ether solution of the nitroxyalkyl nitrourethane was cooled in an ice bath and saturated with dry ammonia. An oil separated, which on standing solidified to a white crystalline solid, the ammonium salt of N-(2-nitroxypropyl) nitramine. The salt was filtered and washed with several portions 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 133.1 g. (81 per cent of the theoretical) of a N-(2-nitroxypropyl) nitramine melting at 84–85° C. 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 purified product was 86–87° C.

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.

EXAMPLE VI

Preparation of N-(2-nitroxyethyl) butylnitramine ("Bu-NENA")



R^1 and R^2 are H; R^3 is butyl.

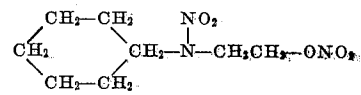
The nitration of N-n-butylmonoethanolamine (Sharples) was carried out by a modification of the procedure described in Example II for the one-step preparation of Me-NENA.

Acetic anhydride (610 g.), 98.3% nitric acid (207.5 cc.) and zinc chloride (15 g.) were mixed in a covered stainless steel beaker and cooled to 10–13° C. The mixture was stirred mechanically and 230 g. of purified butylmonoethanolamine (B. P. 109.5±0.5° C./27 mm.) was added under the surface of the liquid through a dropping funnel with a constricted tip. The amine was introduced over a period of one and one-half hours, while the temperature was maintained at 10–13° C. The solution was further stirred at 10–13° C. for half an hour and then for half an hour at 40–45° C. The nitration mixture was drowned in excess ice water. The pale yellow oil which separated was washed thoroughly with water, with aqueous bicarbonate solution and then steamed by agitating the material violently with live steam at 100° C. for 15 minutes. Finally the Butyl-NENA was washed twice with water, dried over calcium chloride and filtered. The yield of purified product was 370 g. (91 per cent of theory). It froze at −9.9° C. and melted at −9.1° C.; $n_D^{20°}=1.4750$.

Analysis by nitrometer: Nitrate N: calc. 6.76; found, 6.68.

EXAMPLE VII

Preparation of N-(2-nitroxyethyl) cyclohexylnitramine (cyclohexyl-NENA)



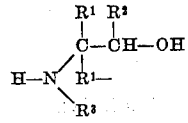
Into a 200 ml. flask fitted with stirrer, thermometer, addition funnel, and outside cooling bath, was placed 27.1 grams of 98.5% nitric acid. To this was added, with stirring, at 10–15° C., 14.2 grams of pure cyclohexylmonoethanolamine. This melts at 39° C., was warmed prior to addition and then added to the nitric acid in the form of a supercooled liquid.

The nitric acid solution thus prepared was transferred to an addition funnel, and then added to a stirred mixture of 47.2 grams of 95% acetic anhydride and 0.3 grams of powdered anhydrous zinc chloride in a 200 ml. flask, while maintaining the temperature in the flask at 35° C. When addition was complete, stirring was continued for 100 minutes at 35 to 40° C.

The nitration mixture was then drowned in an excess of chipped ice. A crystalline product was thus formed. This was removed by filtration, washed with cold water, washed with hot water (which caused the product to melt), cooled, filtered, washed again with cold water and dried in a vacuum desiccator over calcium chloride. The yield was 10 grams (43% of theoretical) of pale yellow crystals, M. P. 36.0–36.6° C. This may be recrystallized from an acetone-ligroin mixture to yield white crystals, M. P. 37.8–38.4° C.

EXAMPLE VIII

Preparation of N-carbethoxy-2-amino-butanol and N-carbethoxy-2-amino-2-methyl-1-propanol



(A) R^1 is ethyl; R^{1-} is H; R^2 is H; R^3 is $-COOC_2H_5$; and (B) R^1 and R^{1-} are methyl; R^2 is H; R^3 is $-COOC_2H_5$.

A. *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 mole) of 2-amino-1-butanol, 150 cc. of water, and 200 cc. of ether. After cooling the contents of the flask to 5–10° C., and maintaining this temperature, 54.3 g. (0.5 mole) of ethyl chlorocarbonate was added dropwise. Next there was added concurrently a solution of 40 g. (10 mole) of sodium hydroxide in 100 cc. of water and 54.3 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° C. (yield 42 per cent). The substance can also be distilled at reduced pressure. It boils at 115–117° C./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.

B. *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 were placed 89 g. (1.0 mole) of 2-amino-2-methyl-1-propanol, 150 cc. of water, and 200 cc. of ether. While maintaining the temperature at 5–10° C. 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 mole) 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 the 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 97–97° C./2 mm. Yield, 88 per cent.

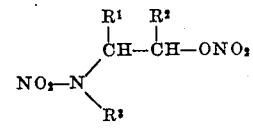
$$D_4^{20}=1.066,\ n_D^{20}=1.451$$

Observed molecular refraction, 40.7; calculated, 41.1.

Analysis: Calculated for $C_7H_{15}O_2N$: C, 52.15; H, 9.38; N, 8.69. Found: C, 51.74; H, 9.42; N, 8.12.

EXAMPLE IX

Preparation of the dinitrourethane of diaminoisopropanol nitrate and dinitraminoisopropyl nitrate



R^1 is H; R^2 is $-CH_2NHNO_2$ or $-CH_2N(NO_2)COOC_2H_5$ and R^3 is H or $-COOC_2H_5$

A. *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. 45–57° C.), 100 cc. of water, and 400 cc. of ether. The mixture was cooled to 0–5° C. 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° C. 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 yellow viscous residue. All attempts to crystallize the urethane failed. Also, it could not be distilled at a pressure of 1.5 mm.

B. *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° C. 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.

C. *Isolation of dinitraminoisopropyl nitrate*

The dried ether solution containing the nitraction product of the diurethane was treated with anhydrous gaseous ammonia at 5–10° C. A gummy precipitate was 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 (71.8 g.) melted with decomposition at 161–163° C. (corr.). One recrystallization from 600 cc. of nitromethane gave 56.3 g. of a product melting at 164–165° C. (corr.) with decomposition. The overall yield from diaminoisopropanol was 74.8 per cent.

Analysis of the silver salt:

Calcd. for $CH_2—N(Ag)NO_2$: N, 15.95; neutral equivalent, 112.5.

$CHONO_2$
$CH_2—N(Ag)NO_2$

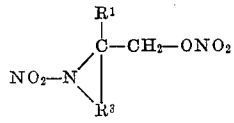
Calcd. for $CH_2—N(Ag)NO_2$: N, 14.22; neutral equivalent, 90.0.

$CHOH$
$CH_2—N(Ag)NO_2$

Found: N, 15.67, 15.27, 15.31; neutral equivalent, 112.0, 112.4.

EXAMPLE X

Preparation of 3-nitro-4,4-bis(nitroxymethyl) oxazolidone



R^1 is nitroxymethyl; R^3 is —CO—OCH_2—

A. *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° C., 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° C. By working up the filtrate 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, 40.73; H, 5.57, 5.72; N, 9.64, 9.85.

B. *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(nitroxymethyl) oxazolidone (11.0 g.), melting at 106–7° C.

Analysis: Calculated for $C_5H_7O_8N_3$: C, 25.40; H, 2.95; N, 17.72. Found; C, 25.57, 25.39, 25.89, 25.86; H, 3.46, 3.25, 3.28, 3.27; N, 17.59, 17.54.

C. *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° C., 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° C. 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° C. was obtained. Yield, 30 per cent.

Analysis: Calculated for $C_5H_6O_{10}N_4$: C, 21.28; H, 2.13; N, 19.86. Found: C, 21.25, 21.35; H, 2.12, 2.01; N, 19.49, 19.38.

D. *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° C., 3.28 g. (0.014 mole) of 4,4-bis(nitroxymethyl) oxazolidone was added. The reaction was heated to 50° C. 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° C. Yield, 28 per cent.

It will be apparent to those skilled in the art that many variations, modifications and extensions of the processes described in the foregoing examples may be made without departing from the spirit and scope of the present invention. All such variations, modifications and extensions are to be understood as included within the scope of the appended claims.

We claim:

1. As a new composition of matter, N-(2-nitroxyalkyl) alkylnitramine.

2. As a new composition of matter, N-(2-nitroxyethyl) alkyl nitramine.

ALFRED T. BLOMQUIST.
FRED T. FIEDOREK.

REFERENCES CITED

The following references are of record in the file of this patent:

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