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UNITED STATES PATENT OFFICE

2,481,283

PREPARATION OF NITRATOALKYL NITRAMINES

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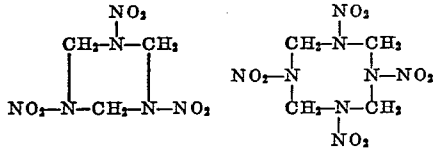
No Drawing. Application December 30, 1944, Serial No. 570,805

1 Claim. (Cl. 260—467)

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The present invention relates to nitramines and more particularly to a new series of aliphatic nitramines having a plurality of nitramine groups.

The aliphatic nitramines comprises a group of organic explosives of increasing importance at the present time because of the outstanding explosive properties of several class members that have recently come into prominence. Possibly the four most important representatives of this class are cyclonite (I), homocyclonite (II), Haleite (III) and DINA (IV).



I (Cyclonite) II (Homocyclonite)

$NO_2-NH-CH_2CH_2-NH-NO_2$ $NO_2-N(CH_2CH_2ONO_2)_2$

III (Haleite) IV (DINA)

It will be noted that one of the compounds in this group (i. e., DINA) contains two nitroxyalkyl groups in addition to a nitramine group. Possibly because of the presence of these nitroxyalkyl groups, DINA differs from the other three nitramines in that it is capable of plasticizing nitrocellulose. Since DINA is a solid compound of very low volatility, it is therefore of interest as a replacement for the objectionably volatile nitroglycerine heretofore used in propellant powders of the double-base type. However, DINA exhibits a tendency to crystallize in the colloided nitrocellulose matrix and for this and other reasons it is not entirely without its objectionable characteristics for such applications.

One of the objects of the present invention is to provide a new series of nitramines that may be regarded as derivatives of Haleite.

A more particular object is the provision of a new series of nitramines containing one or more nitroxyalkyl groups in addition to an ethylenedinitramine unit.

Another object is to provide a series of compounds containing a plurality of ethylenedinitramine units.

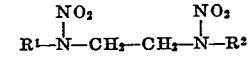
A further object is to provide feasible methods of manufacturing the amines of the character defined above.

Other objects and advantages will be apparent as the invention is hereinafter more particularly described.

The nitramines with which the present invention is primarily concerned may be regarded as

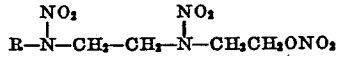
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mono or disubstituted derivatives of ethylenedinitramine, having the general structural formula:

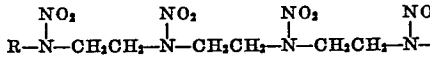


where R^1 is either an alkyl, or a nitroxyalkyl or a nitraminoalkyl group, and R^2 is either a nitroxyalkyl or a nitraminoalkyl group.

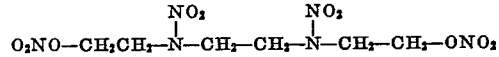
As typical examples of this class of compounds, the following types may be mentioned: N-alkyl-N'-(nitroxyethyl) ethylenedinitramines (V), N^1, N^4-dialkyltriethylenetetranitramines (VI) and N,N' - bis(nitroxyethyl) ethylenedinitramines (VII):



V



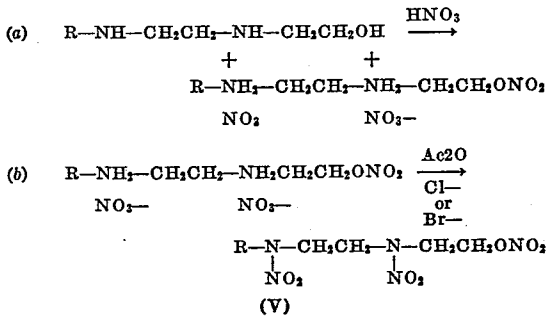
VI



VII

N-Alkyl-N'-(2-Nitroxyethyl) Ethylene-dinitramine (V)

The first of these compounds (V) may be prepared by converting N-alkyl-ethylendiamine by means of ethylene oxide to the N-alkyl-N'-(2-ethanol) ethylenediamine and then treating this latter secondary amine according to the general procedure described and claimed in the copending application of Wright and Chute, Serial No. 570,814, now U. S. Patent 2,426,052, or Cason, Serial No. 570,811, or our copending application Serial No. 570,804, all filed of even date herewith. The reaction involved in the latter stage of its preparation may be represented as follows:

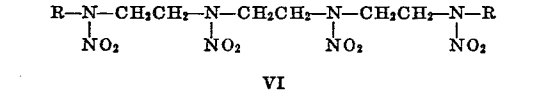


N^1,N^4-Dimethyl-Triethylenetetranitramine (VI)

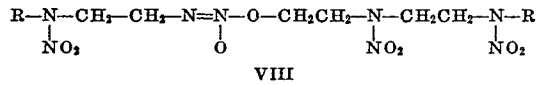
An alternate method of preparing compounds of type V also involves the formation of compounds of type VI. According to this alternate procedure, N-alkylethylenedinitramine (Franchimont and Klobbie, Rec. trav. chim. 7, 346; 347 (1888)) is treated with ethylene dibromide. Two isomeric compounds are obtained. The higher melting compound appears to have the structure VI and is therefore an alkyl-nitraminoalkyl derivative of ethylenedinitramine (i. e., R^1=CH_3 and

$$R^2{=}CH_3{-}N(NO_2){-}CH_2CH_2{-}N(NO_2){-}CH_2CH_2{-})$$

The lower melting compound appears to have the structure VIII:



VI



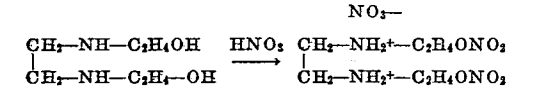
VIII

The first type of compound (VI) is unaffected by nitric acid, as would be expected from its formula.

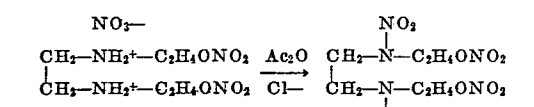
The second type of compound (VIII) when treated with nitric acid cleaves to give two types of products: (a) N-(2-nitroxyethyl) alkylnitramines, described and claimed in our copending application, Serial No. 570,806, filed of even date herewith; and (b) N-alkyl-N'(-2-nitroxyethyl)-ethylenedinitramines (V), thereby proving the formula for the compound of the type (VIII) and at the same time providing an alternate route for the synthesis of compounds of type V.

N,N'-Bis(2-Nitroxyethyl) Ethylene-dinitramine (VII)

Another example of the novel series of nitramines in accordance with the present invention is bis(2-nitroxyethyl) ethylenedinitramine (VII). This type of compound may be conveniently prepared from diethanolethylenediamine (IX), according to the procedure indicated by the following equations:



IX



VII

The foregoing typical examples of the class of nitramines represented by the formula:

$$R^1{-}N(NO_2){-}CH_2CH_2{-}N(NO_2){-}R^2$$

will be sufficient to enable those skilled in the art to prepare their higher homologues and analogues, using procedures similar to those briefly mentioned above.

All representative members of the class that

contain one or more nitroxyalkyl groups are characterized by the ability to plasticize nitrocellulose and because of their very low volatility, provide a group of essentially non-volatile high-potential plasticizers for nitrocellulose adaptable for use in the manufacture of double-base type of powders.

In order more clearly to disclose the nature of the present invention, several specific examples will hereinafter be described in considerable detail. It is to be clearly understood, however, that this is done solely by way of example and not for the purpose of delineating the scope of the present invention, or of restricting the ambit of the present claim.

Example I

Preparation of N-methyl-N^1-(2-nitroxyethyl)-ethylenedinitramine (V) and N^1,N^4-dimethyl-triethylenetetranitramine (VI)

$$R^1{-}N(NO_2){-}CH_2CH_2{-}N(NO_2){-}R^2$$

(V): R^1 is methyl: R^2 is 2-nitroxyethyl.

(VI): R^1 and R^2 are $-CH_2CH_2-N(NO_2)CH_3$.

(A) *Reaction of N-methyl-ethylene dinitramine and ethylene dibromide*

In a 2–1 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-dimethyltriethylenetetranitramine began to take place after two hours refluxing.

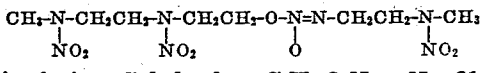
After completion of the reflux period the mixture was filtered at 70° C., and the crude solid washed with 100 cc. of hot alcohol. The washings were combined with the main filtrate. The yield of crude product from several runs varied from 12.1 g.–13.6 g. and melted at 210–213° C. d. (uncorr.). The pure N^1,N^4-dimethyl-triethylenetetranitramine (m. p. 211.5–213° C. d. (uncorr.) was obtained by recrystallizing the crude product from nitromethane.

Analysis: Calcd. for $C_8H_{18}N_8$: 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° C. (corr.). This low melting 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 volumes 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 whirled 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° C. This substance was not investigated further.

The low melting crystalline solid (11.2–14.2 g.) melted at 88.5–90° C. (corr.); 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-tri-

ethylenetetramitramine and probably has the structure:

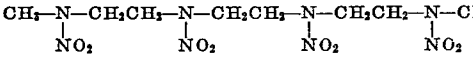


Analysis: Calcd. for $C_8H_{18}O_8N_8$: N, 31.64. Found: N, 31.58; 31.61.

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.

(B) *Structure of high-melting compound formed in alkylation of N–methylethylenedinitramine*

If the high melting compound formed in the reaction between N-methylethylenedinitramine and ethylene bromide has the structure:

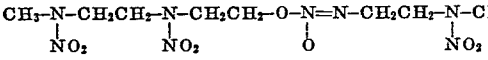


treatment with 98 per cent nitric acid should not affect the compound.

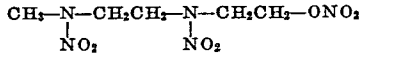
Actually the compound can be recovered unchanged when it is dissolved in 98 per cent nitric acid by quenching with water.

(C) *Structure of Low-Melting Compound Formed in Alkylation of N-methylethylenedinitramine*

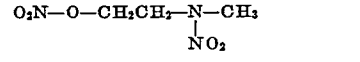
If the low melting compound formed in the alkylation of N-methylethylenedinitramine with ethylene bromide has the structure:



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



and



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 - (2 - nitroxyethyl) - methylnitramine (MeNENA) and analysis of the other product was in agreement with the formula $C_5H_{11}O_7N_5$. The experimental details are as follows:

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° C. 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° C.

The acid filtrate from Crop I was neutralized with sodium bicarbonate. A second crop precipitated and this was filtered, washed with a small amount of water and dried in the air. The crude Crop II (2.3 g.) melted at approximately 35° C. Extraction of this crude material with 150 cc. of ether left a residue of 1.1 g. melting at 85° C.

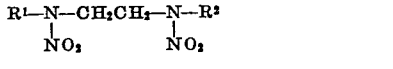
The alkaline filtrate from Crop II was extracted with three 100-cc. portions of ether and the ether extracts were combined with the ether extract of Crop II. After drying over 30 g. of magnesium sulfate the ether was removed and there was obtained 2.8 g. of N-(2-nitroxyethyl) methylnitramine (MeNENA) melting at 35.5–37° C. (uncorr.). No depression of melting point was observed when it was mixed with an authentic sample melting at 38–40° C.

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° C. (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, 27.63.

EXAMPLE II

Preparation of N,N'-(2-nitroxyethyl) ethylenedinitramine (VII)



(VI): R^1 and R^2 are 2-nitroxyethyl.

(A) *Preparation of N,N'-di-(2-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° C. by means of external cooling and 49.3 g. (0.35 mole) of N,N'-diethanolethylenediamine was slowly added with stirring. The temperature was maintained at 10–15° C. during this addition. After all of the amine had been added the mixture was warmed to 35° C. 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 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° C. (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° C. (corr.).

(B) *Preparation of N,N'-bis(2-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(2-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° C. 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° C. (No reaction occurred when the tetranitrate was heated for fifteen minutes with acetic anhydride or with acetic anhydride and a small amount of hydrochloric acid.) After stirring at 50° C. 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 was filtered, washed with water, and dried in the air. The impure product (13.7 g.) melted at 58.5–60.5° C. (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° C. (corr.). Yield, 80 per cent.

Analysis: Calcd. for $C_6H_{12}O_{16}N_6$: N, 25.61. Found: N, 25.62, 25.50.

It will be apparent to those skilled in the art that many variations, modifications and extensions of the foregoing specific 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 ambit of the appended claim.

We claim:

A process which comprises treating a compound selected from the group consisting of N-alkyl-N' and (2-alkanol) ethylenediamine and N,N'-bis(2-alkanol) ethylenediamine, with about an equivalent amount of nitric acid and about an equivalent amount of a dehydrating fatty acid anhydride in the presence of a halide-ion-forming catalyst, and then separating the nitroxyalkylnitramine from the resulting reaction mixture.

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FRED T. FIEDOREK.

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