United States Patent [19]

Rosher

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[45] **May 13, 1975**

[54] **DOUBLE-BASE PROPELLANT CONTAINING ORGANIC AZIDE**

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[73] Assignee: **The United States of America as represented by the Secretary of the Navy**, Washington, D.C.

[22] Filed: **Apr. 26, 1972**

[21] Appl. No.: **249,444**

Related U.S. Application Data

[62] Division of Ser. No. 851,765, Aug. 20, 1969.

[52] **U.S. Cl.** **149/19.8;** 149/38; 149/92; 149/98; 149/20

[51] **Int. Cl.** **C06d 5/06**

[58] **Field of Search** 149/851, 765, 92, 38, 98, 149/18, 76, 19.8, 20; 260/349

[56] **References Cited**

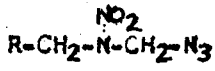
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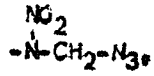
Primary Examiner—Benjamin R. Padgett
Assistant Examiner—E. A. Miller

[57] **ABSTRACT**

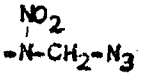
Compounds of the formula



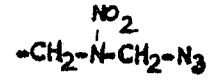
where R represents H,



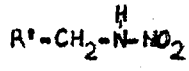
and alkyl group of 1 to 6 carbon atoms or an alkyl group of 1 to 6 carbon atoms where at least one hydrogen atom has been replaced by the group



to form a group of the formula



are prepared by reacting an amine of the formula



where R′ represents H, —NH-NO_2, alkyl of 1 to 6 carbon atoms or alkyl of 1 to 6 carbon atoms where at least one hydrogen atom has been replaced by —NH-NO_2 to form the group —CH_2NH-NO_2 with formaldehyde and HCl to effect a chloromethylation and thereafter reacting an ionic azide with the chloromethylated product.

The compounds are used in double-base propellents as a partial or total substitute for the nitroglycerin portion of the propellant.

11 Claims, No Drawings

DOUBLE-BASE PROPELLANT CONTAINING ORGANIC AZIDE

This is a division of Application Serial No. 851,765 filed Aug. 20, 1969.

BACKGROUND OF THE INVENTION

This invention generally relates to the preparation and use of organic nitrogen containing compounds and more specifically to the preparation and use of organic azides.

Double-base propellants, which have become widely used in recent years, have two principle ingredients-nitrocellulose and nitroglycerine. In addition various other materials have been added to the above propellant to modify the properties thereof. Thus, plasticizers such as phthalates, triacetin or other well known plasticizers can be added to the principle ingredients. Stabilizers such as 2-nitrodiphenylamine, tert-butyl catechol, resorcinol or any other art recognized stabilizer can be added to the basic propellant as well. It has also been the practice to add burning-rate modifiers such as, for example, lead salts to the basic propellant as well as extrusion lubricants such as stearates and soaps. Flash supporters such as potassium salts have also been added to these propellants. More recently additional oxidizers have been added such as ammonium perchlorate, potassium perchlorate, lithium perchlorate, potassium nitrate as well as a host of others known in the art. Finally, a fuel, such as aluminum may also be added.

Thus, the basic composition can be modified as desired merely by adding any one or combination of the known additives for their known effect.

Recently attempts have been made to modify the doublebase propellants not only by the addition of specific modifying agents but by the replacement, either partially or totally, of one of the principle ingredients, the nitroglycerin in order to increase the specific impulse and the burning rate of the propellant.

SUMMARY OF THE INVENTION

Accordingly, one object of this invention is to provide materials which can successfully replace all or part of the nitroglycerine in double-base propellants.

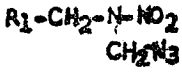
Another object of this invention is to provide compositions of double-base propellants in which all or part of the nitroglycerin has been replaced without a loss of the desired properties of the composition.

Another object of this invention is to effect an increase in both specific impulse and burning rate of double-base propellant compositions.

A still further object of this invention is to provide organic azides compounds.

A further object of this invention is to provide a method for the production of organic azides from amines.

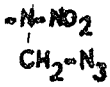
These and other objects of this invention are accomplished by providing organic azides of the formula



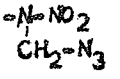
wherein R is selected from the group consisting of H, alkyl of 1 to 6 carbon atoms,



and alkyl of 1 to 6 carbon atoms wherein at least one of the hydrogen atoms has been replaced by the



radical. These organic azides, and all similar azides which contain the group

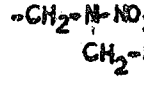


can be prepared from amines containing the radical $-NH-NO_2$ by reacting said amine with HCl and formaldehyde to obtain the chloromethylation product and thereafter reacting said chloromethylated product with an ionic azide.

DESCRIPTION OF PREFERRED EMBODIMENT

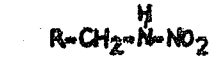
The compounds of this invention are readily prepared by reacting a nitramine with formaldehyde and HCl, thus forming a nitramine chloride. This intermediate is then converted to the desired product by reacting it with an ionic azide. This general method is applicable to produce azides from any amine of Formula I hereinafter defined, as long as the starting materials do not contain groups that will react with the other reagents present in the reaction.

Thus, the process itself can be looked on generally as a process for converting a compound containing the radical $-CH_2-NH-NO_2$ (I) to a compound containing the radical



(II) by means fo reacting (I) with formaldehyde and HCl to obtain the chloromethylated product and thereafter reacting said chloromethylated product with an ionic azide to obtain (II). The only limit on this reaction is that the groups attached to the carbon atom of Formula I must not react with any of the reagents that are being used to bring about the desired transformation. Thus, any amine as in Formula (I) can be converted so long as the above limitation with respect to the other functional groups in the molecule is kept in mind.

The primary nitramines which are used as starting materials can contain cyclic, acyclic or aromatic radicals as well as various other substituents as long as these substituents do not react with the other reagents which will be used in this reaction as hereinbefore disclosed. Some typical nitramines that can be used in the instant process are



wherein R represents H, an aliphatic radical, an aromatic radical, a cyclic radical, $-NH-NO_2$, or an aliphatic, aromatic or cyclic radical wherein at least one of the hydrogen atoms is replaced by the $-NH-NO_2$

group to form the radical $—CH_2-NH-NO_2$. The preferred starting materials are those wherein R represents H, alkyl of 1 to 6 carbon atoms, $—NH-NO_2$ and alkyl of 1 to 6 carbon atoms wherein at least one of the hydrogen atoms has been replaced by the $—NH-NO_2$ radical to form the radical $—CH_2-NH-NO_2$ (i.e. R represents $—CH_2-NH-NO_2$, $—CH_2-CH_2-NH-NO_2$ etc).

The formaldehyde used in this reaction can be from any of the known sources of formaldehyde and may be generated in situ using any the the conventional techniques.

The reaction temperature at which the chloromethylation takes place is not critical but is preferably kept below about 60° C although other temperatures can be used.

The final reaction needed to obtain the products of this invention consists of reacting the chloromethylation product obtained above with an ionic azide, such as for example sodium azide or other alkali metal azides at a temperature below about 20° C and preferably under a dry nitrogen atmosphere.

The compositions contemplated by this invention include the known compositions of all double base propellants where some or all of the nitroglycerin has been replaced by the compounds of this invention.

The simplest composition contemplated by this invention is merely a mixture of an organic azide of this invention and nitrocellulose. A composition such as this when used as a gun propellant serves to increase impetus without increasing the flame temperature significantly by virtue of the fact that this composition produces more gas per unit weight on decomposition than does the nitrocellulose nitroglycerin propellant.

To the basic ingredients, nitrocellulose and nitroglycerine which is totally or partially replaced by the azides defined by Formula (III) may be added various other ingredients such as plasticizers, stabilizers, burning-rate modifiers, extrusion lubricants, flash supporters as well as additional oxidizers and fuels. Thus, any double-base propellant can be converted merely by the substitution with the azides of Formula III for either all or part of the nitroglycerin.

The instant compositions can be processed in any of the art recognized manners. For example one can prepare a composition by the slurry process and then cure it to obtain the final composition or one can produce a product by means of the well known cast powder process.

The general nature of the invention having been set forth, the following examples are presented as specific illustrations thereof. It will be understood that the invention is not limited to these specific examples but is susceptible to various modifications that will be recognized by one of ordinary skill in the art.

EXAMPLE I

Preparation of 1,6-Diazide-2,5-Dinitrazahexane

Five hundred ml. of glacial acetic acid and 150 g of trioxymethylene were placed in a flash equipped with a gas inlet tube, a mechanical stirrer and a reflux condenser fitted with a drying tube. Dry HCl gas was passed through the suspension until only a slight turbidity remained.

The HCl treatment was interrupted while 150 g of dry powdered ethylene dinitramine was added over a period of several minutes. Treatment with HCl was then resumed and the temperature rose slowly to 40° C. After approximately two hours a white preipitate began to form and the addition of HCl was continued for 2 hours. Then the mixture was stirred for 16 hours after which the product was separated by filtration. It was washed first with cold glacial acetic acid and was then slurried with benzene prior to drying in a desiccator at ambient temperature. A yield of 80–85% was obtained.

Twenty grams of the chloromethylated product was dissolved in 100 ml of acetone. The solution was stirred while nitrogen was passed over its surface and it was cooled by immersion in an ice-salt bath. A solution of 21 g of sodium azide in 100 ml of water was added at such a rate that the temperature did not exceed 10° C. The crystalline product was allowed to stand in contact with the mother liquor for 16 hours prior to filtration after which it was washed with water and air dired for two hours.

The product was recrystallized from hot benzene, separated and slurried with ether. After drying a yield of 75 percent was obtained.

EXAMPLE 2

Preparation of 1,5-Diazido-2,4-Dinitrazapentane

The above procedure was repeated except that 136 g of methylene dinitramine was chloromethylated instead of 150 g ethylene dinitramine. Occasionally, it was necessary to cool the flask to initiate crystallization of the chloromethylated product which was obtained in 75 percent yield. The yield of the diazide was 60 percent.

EXAMPLE 3

Preparation of 2-Nitrazapropyl Azide

Two hundred and fifty ml. of redistilled dioxane and 62.4g. of trioxylmethylene were placed in a 1 liter three necked flask having a gas inlet tube, a mechanical stirrer, a thermometer and a drying tube. Dry HCl gas was passed into the mixture until it was almost clear.

The addition of HCl was stopped and the temperature of the reaction mixture was allowed to drop to 35° C before 39.6 g. of dry, powdered methyl nitramine has added. The rate of addition was such that the temperature did not rise above 40° C. After the addition was complete, the passage of HCl was resumed and continued for 3 hours. The reaction mixture was allowed to stand for 13 hours at ambient temperature. The solvent was then removed on a rotary evaporator. The product was a greenish-yellow oil.

15.7 g. of the oil was dissolved in 100 ml of acetone in a beaker and the beaker was immersed in an ice-salt bath. A solution of 25.2 g. of sodium azide in 75 ml of water was added with mechanical stirring. The reaction mixture was blanketed with dry nitrogen during this operation and the temperature was maintained below 10° C.

After standing 64 hours the reaction mixture was extracted with ether and the extract was dried over $MGSO_4$. The ether was evaporated leaving a greenish-yellow product in an amount equivalent to an 80 percent yield. Distillation under reduced pressure gave a clear liquid $n_D^{25°}$ 1.4828.

EXAMPLE 4

Typical Compositions

A composite made up of the following materials was mixed by conventional slurry techniques and cured in the conventional manner.

Nitrocellulose	12.0%
Nitroglycerine	25.3
1,6-diazido-2,5-dinitrazahexane	8.0
Ammonium Perchlorate	34.8
Aluminum	16.0
2-Nitrodiphenylamine	1.0
Resorcinol	1.3
Triacetin	1.6

A casting powdered was also prepared by the conventional methods. It was cast with 90 percent casting solvent giving a product of the following composition:

Nitrocellulose	18.0%
Nitroglycerine	25.2
1,6-diazido-2,5-dinitrazahexane	9.0
Ammonium Perchlorate	36.0
Aluminum	7.2
2-Nitrodiphenylamine	1.0
Resorcinol	1.1
Triacetin	2.5

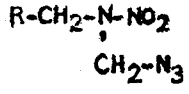
EXAMPLE 5

Compositions containing 1,5-diazide-2,4-dinitrazapentane (D DZP) were also prepared. Column A lists the percentage of each material in the slurry that was prepared as in example 4 above and column B lists the percentage of each material in the casting power process prepared as in Example 4 above.

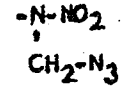
	A	B
Nitrocellulose	12.0%	18.0%
Nitroglycerine	23.9	25.2
DADZP	13.0	9.0
Ammonium Perchlorate	13.0	36.0
HMX	13.0	—
Aluminum	15.0	7.2
2-Nitrodephenylanine	1.0	1.0
Resorcinol	1.5	1.1
Triacetin	7.6	2.5

What is claimed and desired to be secured by Letters Patent of the United States is:

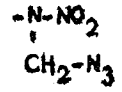
1. A propellant composition comprising nitrocellulose and an organic azide represented by the formula



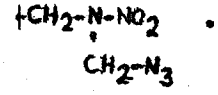
wherein R is selected from the group consisting of H, alkyl of 1 to 6 carbon atoms,



and alkyl of 1 to 6 carbon atoms wherein at least one hydrogen atom has been replaced by the



radical to form the radical



2. A composition according to claim **1** which additionally contains nitroglycerin.

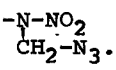
3. The composition of claim **2** which additionally contains plasticizers, stabilizers, rate burning modifiers, extrusion lubricants, flash supporters, additional oxidizers and fuels.

4. The composition of claim **2** which additionally contains a fuel, an oxidizer, a stabilizer and a plasticizer.

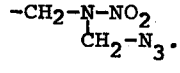
5. The composition of claim **4** wherein said oxidizer is ammonium perchlorate said fuel is aluminum, said stabilizer is a mixture of resorcinol and 2-nitrodiphenylamine and said plasticizer is triacetin.

6. The propellant of claim **1** wherein R of the organic azide is H.

7. The propellant of claim **1** wherein R of the organic azide is



8. The propellant of claim **1** wherein R of the organic azide is



9. The propellant of claim **6** which additionally contains nitroglycerin.

10. The propellant of claim **7** which additionally contains nitroglycerin.

11. The propellant of claim **8** which additionally contains nitroglycerin.

* * * * *