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N-NITRO-N-TRINITROALKYLAMINE ALCOHOLS AND DERIVATIVES THEREOF

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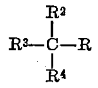
No Drawing. Filed Oct. 16, 1958, Ser. No. 767,746
10 Claims. (Cl. 260—584)

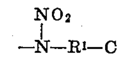
Our invention relates to novel nitro compounds and more particularly it relates to polynitro amino alcohols and to a process for producing same.

Our new compounds have the following structural formula:



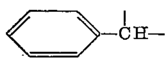
$$R^3-\overset{\overset{R^2}{|}}{\underset{\underset{R^4}{|}}{C}}-R$$

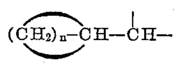
where R is the radical



$$-\overset{\overset{NO_2}{|}}{N}-R^1-C(NO_2)_3$$

R^1 is selected from the group consisting of

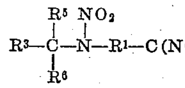




and alkylene having up to five carbon atoms; R^2 is hydroxyalkyl having up to five carbon atoms; R^3 is selected from the group consisting of hydrogen, alkyl having up to five carbon atoms; R^4 is selected from the group consisting of hydrogen, alkyl having up to five carbon atoms, R-substituted alkyl, hydroxyalkyl having up to ten carbon atoms and R-and hydroxy-substituted alkyl having up to ten carbon atoms; and *n* is a number from 3 to 9.

Compounds which come within the above structural formula include: 2-(N-nitro-N-trinitroethylamino)-ethanol, 3-(N-nitro-N-trinitroethylamino)-1-propanol, 2-methyl-2-(N-nitro-N-trinitroethylamino)-1,3-propanediol, 2-(N-nitro-N-trinitroethylamino)-1,4-butanediol, 2,3-bis(2-trinitroethylamino)-1,4-butanedoil, 2-propyl-2-[N-nitro-N-(2-phenyl-2-trinitropropylamino)] 1,3-propanediol, 3-methyl-3-[N-nitro-N-(2-cyclohexyl-2-trinitroethylamino)]heptanol, 6-(N-nitro-N-trinitroethylamino)-1-undecanol, 2-[N-nitro-N-(2-trinitrobutylamino)]-1-pentanol, 2,6-bis[N-nitro-N-(2-phenyl-2-trinitroethylamino)]1,7-heptanedoil, 2,4-bis[N-nitro-N-(2-cyclopentyl-2-trinitroethylamino)]-2-ethyl-1-hexanol, 5,9-dihydroxymethyl-3,5,9,11-tetra(N-nitro-N-trinitroethylamino)tridecane, 2-hydroxybutyl-2,4-bis(N-nitro-N-trinitroethylamino)-1-hexanol, 2,9-diethyl-2,4,7,9-tetra[N-nitro-N-(2-trinitropropyl)amino]-1-10-decanedoil, etc.

Generally our process for producing our new compounds consists of esterifying a nitrate having the following structural formula:



$$R^3-\overset{\overset{R^5}{|}}{\underset{\underset{R^6}{|}}{C}}-\overset{\overset{NO_2}{|}}{N}-R^1-C(NO_2)_3$$

where R^5 is the nitrate ester of hydroxyalkyl having up to five carbon atoms and R^6 is selected from the group consisting of hydrogen, alkyl having up to five carbon atoms, R-stubstituted alkyl having up to ten carbon atoms, the nitrate ester of hydroxyalkyl having up to 10 carbon atoms and R and the nitrate ester of hydroxy substituted alkyl having up to 10 carbon atoms. The ester is in turn converted to the alcohol by subjecting it to acid hydrolysis. Our process appears to be operable for all nitrates of this type.

The nitrates untilized in forming the alcohols of our invention are easily prepared by the process of our copending application, U.S. Serial No. 713,512, now abandoned. In this application we claim a process wherein polynitroamino alcohols are nitrated to form the above-described polynitroamino nitrate.

The nitration of the N-trinitroalkylamino alcohol is carried out using nitric acid as the nitrating agent, generally in the form of a nitrating mix with sulfuric acid, acetic anhydride, phosphorus pentoxide or other dehydrating agent which will not react with the reactants or products to destroy the desired nitrate. Generally we prefer to carry out the nitration reaction at temperatures ranging from about 5 to 25° C. Following completion of the nitration reaction, we can generally obtain the N-nitro-N-trinitroalkylaminoalkyl nitrate as a solid by cooling the reaction mixture to a temperature of about 0° or below as by pouring the reaction mixture over ice. The resulting product can be recrystallized by dissolving in cold fuming nitric acid and then cooling to the low temperatures indicated by any means, including pouring the nitric acid solution over ice.

The N-nitro-N-trinitroalkylaminoalkyl nitrate can be converted to an N-nitro-N-trinitroalkylaminoalkyl ester by reacting the same with an esterifying agent such as acetic anhydride, phthalic anhydride, lower aliphatic acid chlorides, etc., in the presence of an acid esterification catalyst, such as sulfuric acid, benzenesulfonic acid, toluenesulfonic acid, etc. The reaction is carried out at low temperatures ranging from about 0 to about 30° C. The ester can ordinarily be recovered by cooling the reaction mixture to a temperature of about 0° or below as by pouring the reaction mixture over ice. Generally the ester is obtained as an oily liquid and it is generally desirable to dry the same by any convenient means such as, for example, dissolving the oily layer in ether, adding magnesium sulfate as a drying agent, removing the drying agent, and then removing the ether by distillation.

The N-nitro-N-trinitroalkylaminoalkyl ester can be converted to the corresponding alcohol by hydrolysis in the usual manner. Acids such as hydrochloric, sulfuric, etc. can be employed and generally we prefer to employ reflux temperatures for carrying out the hydrolysis of the ester to obtain the alcohol. Generally we prefer to conduct the hydrolysis in the presence of an inert solvent, such as a lower alkyl alcohol. Following the reaction, the solvent can be removed by distilling in vacuo to obtain the alcohol as an oily liquid which in some instances crystallizes upon cooling. In some instances it is necessary to dissolve the oily product in a suitable solvent such as ether, and then remove the solvent by distillation in vacuo to obtain a product oil which crystallizes upon cooling. In other instances, it is necessary to dissolve the oily product in a suitable solvent such as, for example, ether and then crystallize the same by addition of hexane or other suitable material to the ether solution. Ordinarily, the product can be recrystallized from any suitable solvent such as, for example, carbon tetrachloride, ethylene dichloride, etc.

Our polynitroamino alcohols can be utilized to form polymers useful as both solid and liquid propellants for reaction motors. These polymers can be fluids or solids, depending upon the chain length of the polymer, the nature of the cross-linking agent, etc. These polymers are also stable to shock, heat, etc., to the extent that, as a general rule, additional stabilizers are not required in the propellant mixtures. Our monomers are also plasticizers for polymers prepared from our monomer alcohols.

As previously indicated, low molecular weight polymers prepared from the monomers of our invention are fluids. These propellants are generally rich in fuel elements and as such can be utilized as a fuel in the process of U.S. Patent 2,537,526 where tetranitromethane and hexanitroethane are used as oxidants and liquid nitro paraffins are used as fuels; in the processes described in U.S. Patents 2,582,048 and 2,548,803 wherein nitro substituted aliphatic compounds having more than one nitro group per carbon atom were used as oxidants and nitro-substituted compounds having less than one nitro group per carbon atom were used as fuels in monopropellant systems; or in the similar process of U.S. Patent 2,590,009.

We have discovered that generally solid polymers prepared from our alcohols and various isocyanates and amines can be dissolved in polar solvents, such as dimethylformamide and lower nitro alkanes, such as tetranitromethane, and, as such, are operative as fuels in the above-described processes. Other solvents which can be used to liquify our polymers include dimethylsulfoxide, Cellosolve, acetonitrile, lower alkanols, nitro esters and nitro ethers.

Rubber-like materials can be prepared by interaction of our alcohols with cross-linking agents such as diisocyanates, various polycarboxylic acids, such as succinic acid, tartaric acid, maleic acid, malic acid, etc.

Our monomers form polymers with tetranitrodicarboxylic acids which can be prepared by interacting a tetranitro compound with methylacrylate, and hydrolyzing the resulting tetranitro ester to form the acid.

Our solid polymers can be mixed wih various oxidant salts, such as ammonium nitrate, ammonium perchlorate, lithium perchlorate, etc. to obtain solid heterogeneous propellants having specific impulses on the order of that of Ballistite.

The following examples are offered to illustrate the production of our new compounds. We do not intend to be limited to the specific materials, proportions, conditions, etc. shown, rather we intend to include all equivalents obvious to those skilled in the art.

Example I

A solution composed of 10.5 grams of 2-methyl-2-amino-1,3-propanediol, 15.1 grams of trinitromethane, and 8.5 ml. of 37% formalin solution in 35 ml. of distilled water was prepared and held at ice bath temperature for several hours after which the water was removed by aerating the solution at 25° C. The residual oil was dissolved in ethyl alcohol and the solution dried over magnesium sulfate, after which the ethyl alcohol was removed by distillation in vacuo leaving 2-methyl-2-(N-trinitroethylamino)-1,3-propanediol as a heavy oil. The oily product was dissolved in 50 ml. of acetic anhydride and the solution cooled to 5° C. after which 30 ml. of fuming nitric acid was added to the cooled solution over a period of one and one-half hours, the temperature being kept below 20° C. at all times. The mixture was then stirred at 5 to 15° C. for two hours and poured over crushed ice to precipitate 2-methyl-2-(N-nitro-N-trinitroethylamino)-1,3-propyl dinitrate as a heavy oil. The oily nitrate product was dissolved in 100 ml. of ether, the solution washed with two 100 ml. portions of water and dried with magnesium sulfate after which the ether was removed in vacuo and the oily dinitrate dissolved in 100 ml. of acetic anhydride, cooled to 5° C. and stirred vigorously while 6 ml. of concentrated sulfuric acid was added in small portions maintaining the temperature blow 20° C. The mixture was poured over crushed ice to give a red oil which was dissolved in 100 ml. of ethylene dichloride and the solution washed with water and dried with magnesium sulfate. The solvent was then removed in vacuo to give a reddish impure solid which was triturated with methanol and the solid 2-methyl-2-(N-nitro-N-trinitroethylamino)-1,3-propyl diacetate removed. Melting point 75–75.5° C. Analysis—calculated: N=17.6; found: N=17.65. A 7.2 gram portion of crude 2-methyl-2-(N-nitro-N-trinitroethylamino)-1,3-propyl diacetate was dissolved in a mixture of 100 ml. of methanol and 5 ml. of concentrated hydrochloric acid and the solution heated under reflux for two hours. Removal of the solvents in vacuo left a solid that was recrystallized from carbon terachloride to yield pure white 2-methyl-2-(N-nitro-N-trinitroethylamino)-1,3-propanediol having a melting point of 115–117° C. with decomposition. Analysis—calculated: N=22.4; found: N=22.2.

Example II

A mixture of 25 ml. of concentrated sulfuric acid and 25 ml. of fuming nitric acid was cooled to approximately 15° C. and to the mixture was added 7.6 grams of 2-(N-trinitroethylamino)ethanol. The mixture was stirred at 15–25° C. for approximately two hours after which it was poured over crushed ice to produce a solid that was purified by dissolving in cold fuming nitric acid followed by precipitation over crushed ice. The product was dried in vacuo at 25–30° C. and recrystallized from 30 ml. of ethylene dichloride. The product 2-(N-nitro-N-trinitroethylamino)ethyl nitrate had a melting point of 105–106° C. with decomposition. Analysis—calculated: N=26.8; found: N=26.4. A 3-gram portion of 2-(N-nitro-N-trinitroethylamino)ethyl nitrate was dissolved in 30 ml. of acetic anhydride and the solution cooled and stirred vigorously. To the solution 3 ml. of concentrated sulfuric acid was added so that the temperature never exceeded 15° C. and after the addition of the acid was complete the mixture was allowed to stand for approximately 5 hours at 0–5° C. and then for an additional hour while the temperature rose to about 30° C. The mixture was then poured over crushed ice to obtain an oil which was taken up in 100 ml. of ether, the solution washed with four 50 ml. portions of distilled water, dried over magnesium sulfate, and the ether then removed in vacuo to leave the oily 2-(N-nitro-N-trinitroethylamino)ethyl acetate. The ester was dissolved in a mixture of 30 ml. of methanol and 3 ml. of concentrated hydrochloric acid and the solution refluxed for about two hours. The solvent was then removed in vacuo to leave an oil that solidified when two 10–15 ml. portions of ether were added and subsequently removed in vacuo. The material was recrystallized from carbon tetrachloride to give 2-(N-nitro-N-trinitroethylamino)ethanol as a white solid, melting point 74° C. Analysis—calculated: N=26.0%; found: N=26.2%.

The following example is offered to illustrate the conversion of our new N-nitro-N-trinitroalkylamino alcohols into further very powerful explosives.

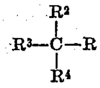
Example III

A 1.07 gram portion of 2-(N-nitro-N-trinitroethylamino)ethanol, 1.0 gram of 4,4,4-trinitrobutyryl chloride and 0.55 gram of aluminum chloride were dissolved in 30 ml. of ethylene dichloride and the solution heated at about 50° C. for about 18 hours. The solution was then poured over a mixture of 16 ml. of concentrated hydrochloric acid and 30 grams of crushed ice. After the ice had melted, the aqueous layer was washed with six 15 ml. portions of ethylene dichloride and these extracts combined with the original ethylene dichloride layer which was then washed with three 20 ml. portions of water, dried with magnesium sulfate and concentrated to 15 ml. in vacuo. An oil remained which after addition of hexane solidified at −10° C. to produce 2-(N-nitro-N-trinitroethylamino)ethyl-4,4,4-trinitrobutyrate melting at 40–43° C. This explosive has the sensitivity and explosive properties of PETN (pentaerythritoltetranitrate).

This application is a continuation-in-part of our abandoned U.S. patent application Serial No. 646,176 filed March 14, 1957.

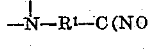
Now having described our invention what we claim is:

1. Compounds having the structural formula



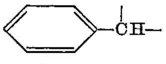
$$R^3-\overset{\displaystyle R^2}{\underset{\displaystyle R^4}{\overset{|}{\underset{|}{C}}}}-R$$

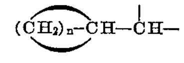
where R is the radical



$$-\overset{\displaystyle NO_2}{\overset{|}{N}}-R^1-C(NO_2)_3$$

R^1 is selected from the group consisting of





and alkylene having up to five carbon atoms; R^2 is hydroxyalkyl having up to five carbon atoms; R^3 is selected from the group consisting of hydrogen, alkyl having up to five carbon atoms, hydroxyalkyl having up to five carbon atoms; R^4 is selected from the group consisting of hydrogen, alkyl having up to five carbon atoms, R-substituted alkyl, hydroxyalkyl having up to ten carbon atoms; and *n* is a number from 3 to 9.

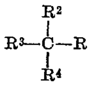
2. 2-(N-nitro-N-trinitroethylamino)ethanol.

3. 3-(N-nitro-N-trinitroethylamino)-1-propanol.

4. 2 - methyl - 2 - (N-nitro-N-trinitroethylamino)-1,3-propanediol.

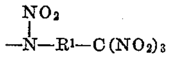
5. 2-(N-nitro-N-trinitroethylamino)-1,4-butanediol.

6. A process for the production of alcohols having the following structural formula



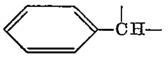
$$R^3-\underset{R^4}{\overset{R^2}{C}}-R$$

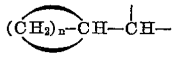
where R is the radical



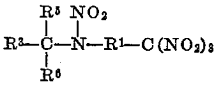
$$-\overset{NO_2}{N}-R^1-C(NO_2)_3$$

R^1 is selected from the group consisting of





and alkylene having up to five carbon atoms; R^2 is hydroxyalkyl having up to five carbon atoms; R^3 is selected from the group consisting of hydrogen, alkyl having up to five carbon atoms; R^4 is selected from the group consisting of hydrogen, alkyl having up to five carbon atoms, R-substituted alkyl, hydroxyalkyl having up to ten carbon atoms; and *n* is a number from 3 to 9 which consists of contacting a nitrate having the structural formula



$$R^3-\underset{R^6}{\overset{R^5}{C}}-\overset{NO_2}{N}-R^1-C(NO_2)_3$$

where R^5 is the nitrate ester of hydroxyalkyl having up to five carbon atoms and R^6 is selected from the group consisting of hydrogen, alkyl having up to five carbon atoms, R-substituted alkyl having up to ten carbon atoms, the nitrate ester of hydroxyalkyl having up to 10 carbon atoms and R and the nitrate ester of hydroxy substituted alkyl having up to 10 carbon atoms with an esterifying agent selected from the group consisting of acetic anhydride, phthalic anhydride and lower aliphatic acid chlorides in the presence of an acid esterifying catalyst to form an ester from the nitrate, contacting the ester with a mineral acid to form the alcohol.

7. The process which comprises reacting 2-(N-nitro-N-trinitroethylamino)ethyl nitrate with acetic anhydride in the presence of a mineral acid and hydrolyzing the product so obtained under acid conditions to obtain 2-(N-nitro-N-trinitroethylamino)ethanol.

8. The process which comprises reacting 3-(N-nitro-N-trinitroethylamino)-1-propyl nitrate with acetic anhydride in the presence of an acid and hydrolyzing the product so obtained under acid conditions to obtain 3-(N-nitro-N-trinitroethylamino)-1-propanol.

9. The process which comprises reacting 2-methyl-2-(N-nitro-N-trinitroethylamino)-1,3-propyl dinitrate with acetic anhydride in the presence of a mineral acid and hydrolyzing the product so obtained under acid conditions to obtain 2-methyl-2-(N-nitro-N-trinitroethylamino)-1,3-propanediol.

10. The process which comprises reacting 2-(N-nitro-N-trinitroethylamino)-1,4-butyl dinitrate with acetic anhydride in the presence of a mineral acid and hydrolyzing the product so obtained under acid conditions to obtain 2-(N-nitro-N-trinitroethylamino)-1,4-butanediol.

No references cited.