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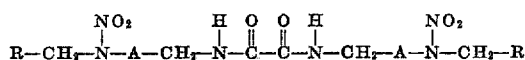
3,000,942

N,N'-(NITRAZAALKYL) OXAMIDES

Milton B. Frankel, Pasadena, Calif., assignor to Aerojet-General Corporation, Azusa, Calif., a corporation of Ohio

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12 Claims. (Cl. 260—561)

This invention relates to new compositions of matter and to their preparation. In particular, the invention relates to N,N'-bis (nitrazaalkyl) oxamides having the general formula:

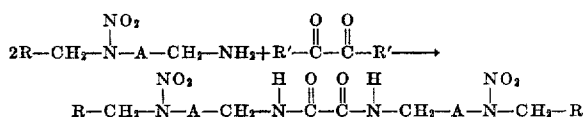


wherein each R is a hydrogen, alkyl, or nitroalkyl radical and each A is an alkylene radical.

The oxamides of the present invention are particularly valuable as starting materials for preparing high energy oxamide compounds, such as, for example, N,N'-bis (3-nitraza-1-butyl)-N,N'-dinitro oxamide, as more fully disclosed in my copending U.S. patent application Serial No. 666,270, filed concurrently with the present application.

The high energy oxamide compounds of the copending application are useful as high explosives, and can be used in any conventional explosive missile, projectile, rocket, or the like, as the main explosive charge. An example of such a missile is disclosed in United States Patent No. 2,470,162, issued May 17, 1949. One way of using the high explosives of this invention in a device such as that disclosed in United States Patent No. 2,470,162, is to pack the crystalline explosive in powder form into the warhead of the missile. Alternatively, the crystals can be first pelletized and then packed. A charge thus prepared is sufficiently insensitive to withstand the shock entailed in the ejection of a shell from a gun barrel or from a rocket launching tube under the pressure developed from ignition of a propellant charge, and can be caused to explode on operation of an impact- or time fuse-mechanism firing a detonating explosive such as lead azide or mercury fulminate.

The oxamide compounds of this invention are readily prepared by condensing nitraza amines with oxalyl compounds in accordance with the general reaction scheme set forth below:



wherein each R and each A is as previously defined and each R' is a halogen or alkoxy radical.

To more clearly illustrate my invention, the following example is presented. It is to be understood, however, that this example is intended merely as a means of illustrating my invention and that it should not be construed as limiting the scope of said invention in any way.

Example I.—Preparation of N,N'-bis (3-nitraza-1-butyl) oxamide

To a solution of 11.9 g. (0.1 mole) of 3-nitraza-1-butylamine in 50 ml. of chloroform was added 7.3 (0.05 mole) of ethyl oxalate. An immediate exothermic reaction occurred with the precipitation of a white solid. The solid was collected and dried to produce 9.9 g. (67.8%) of final product having a melting point of 225°–230° C.

Reaction temperature is non-critical in the practice of this invention, the only effect of temperature variation being a corresponding increase or decrease in reaction rate.

The nitraza amines useful as starting materials in the

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practice of this invention are generated from their corresponding strong mineral acid salt by neutralizing the strong mineral acid salts with inorganic basic salts, as for example hydroxides or carbonates, or weak organic acid salts, such as acetates, of alkali or alkaline earth metals such as sodium, calcium, etc. This method of generating ditraza amines from their strong mineral acid, i.e., hydrochloric acid, nitric acid, or the like, salts is more fully disclosed in my copending U.S. patent application Serial No. 666,273, filed concurrently with the present application.

The strong mineral acid salts of the nitraza amines, suitable for use in the present invention, are prepared by reacting corresponding nitraza isocyanates, such as 3-nitraza-1-butyl isocyanate, with aqueous strong mineral acid solutions, as more fully disclosed in my copending U.S. patent application Serial No. 666,273.

The above-mentioned nitraza isocyanates are prepared by reacting nitraza-acid halides, such as 4-nitrazapentanoil chloride, with alkali or alkaline earth metal azides, as for example sodium azide, to form the corresponding nitraza azides and then heating said nitraza azides under anhydrous conditions to effect rearrangement to the desired nitraza isocyanates. This method of preparing nitraza isocyanates is more fully disclosed in my copending U.S. patent application Serial No. 514,384, filed June 9, 1955.

The nitraza-acid halides from which the nitraza isocyanates are prepared are obtained by reacting thionyl halides, such as thionyl chloride, with appropriate nitraza-acids, as more fully disclosed in my copending U.S. patent application Serial No. 514,384. The nitraza-acids can be nitroalkyl-aza-acids which are prepared by condensing nitroalcohols with amino acids, as more fully disclosed in assignee's copending U.S. patent application Serial No. 416,385, filed March 15, 1954, or alkyl-nitraza-acids which are prepared by the acid hydrolysis of nitraza-nitriles, as disclosed in my copending U.S. patent application Serial No. 514,386, filed June 9, 1955.

It should be pointed out that mixtures of suitable nitraza amines can be employed in the preparation of the oxamide compounds of this invention. It is thus within the purview of the invention to condense such mixtures of nitraza amines with suitable oxalyl compounds and thereby obtain oxamide compounds of the general formula shown hereinbefore in which the two R's and/or the two A's are respectively different. For reasons of convenience and economy, however, I prefer to employ relatively pure nitraza amines as starting materials, in which case symmetrical oxamide compounds having identical R's and identical A's are produced.

The oxalyl compounds used as starting materials in the practice of the present invention can be acyl dihalides of oxalic acid, as for example, oxalyl chloride, or diesters of oxalic acid, as for example ethyl oxalate. I prefer to employ the diesters of oxalic acid, rather than the dihalides of oxalic acid, for purposes of my invention since when the former compounds are used alcohols are formed as by-products whereas when the latter compounds are used halogen acids are formed as by-products. The presence of the aforesaid alcohols has substantially no effect on the reaction of my invention but the presence of halogen acids interferes with the reaction since they form salts with the nitraza amine reactants present.

Diesters of oxalic acid other than ethyl oxalate are suitable for the practice of my invention. For example, diesters prepared from the lower alcohols, such as methyl, n-propyl, n-butyl, etc., alcohol, can be employed within the scope of the invention.

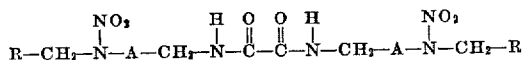
It will be appreciated that a wide variety of oxamide compounds can be prepared in accordance with the method of my invention. For example, 4-nitraza-1-hexyl-

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amine and 3-aza-3,5,5-trinitro-1-hexylamine react with diesters of oxalic acid and the lower alcohols to yield N,N'-bis (4-nitrazo-1-hexyl) oxamide and N,N'-bis (3-aza-3,5,5-trinitro-1-hexyl) oxamide, respectively. Other members of this new series of oxamide compounds are prepared simply by reacting appropriate starting materials as taught herein.

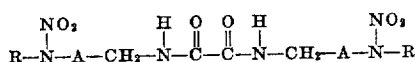
I claim:

1. As a new composition of matter, an N,N'-bis (nitrazalkyl) oxamide having the formula:



wherein each R is a radical selected from the group consisting of hydrogen, lower alkyl, and lower nitroalkyl radicals and each A is a lower alkylene radical.

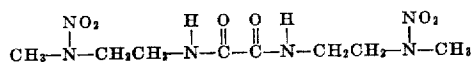
2. As a new composition of matter, an N,N'-bis (nitrazalkyl) oxamide having the formula:



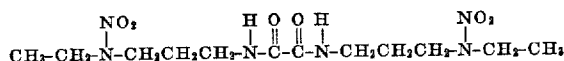
wherein each R is a lower alkyl radical and each A is a lower alkylene radical.

3. The composition of claim 1 in which each R is a lower nitroalkyl radical.

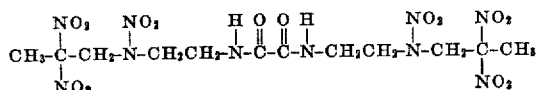
4. As a new composition of matter, N,N'-bis (3-nitrazabutyl) oxamide having the structural formula:



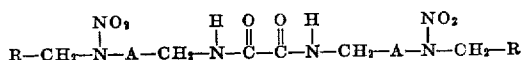
5. As a new composition of matter, N,N'-bis (4-nitrazahexyl) oxamide having the structural formula:



6. As a new composition of matter, N,N'-bis (3-aza-3,5,5-trinitrohexyl) oxamide having the structural formula:

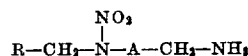


7. The method of preparing N,N'-bis (nitrazalkyl) oxamides having the formula:

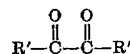


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which comprises condensing nitraza amines having the formula:

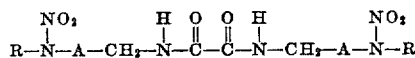


5 with oxalyl compounds having the formula:

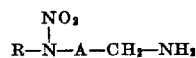


10 wherein each R is a radical selected from the group consisting of hydrogen, lower alkyl, and lower nitroalkyl radicals; each A is a lower alkylene radical; and each R' is a radical selected from the group consisting of halogen and alkoxy radicals.

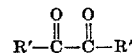
15 8. The method of preparing N,N'-bis (nitrazalkyl) oxamides having the formula:



20 which comprises condensing nitraza amines having the formula:



25 with oxalyl compounds having the formula:

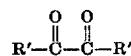


wherein each R is a lower alkyl radical; each A is a lower alkylene radical; and each R' is an alkoxy radical.

30 9. The method of claim 7 wherein each R is a lower nitroalkyl radical and each R' is an alkoxy radical.

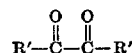
10. The method of preparing N,N'-bis (3-nitrazabutyl) oxamide which comprises condensing 3-nitrazo-1-butylamine with ethyl oxalate.

35 11. The method of preparing N,N'-bis (4-nitrazo-1-hexyl) oxamide which comprises condensing 4-nitrazo-1-hexylamine with an oxalyl compound having the formula:



40 wherein each R' is a lower alkoxy radical.

12. The method of preparing N,N'-bis (3-aza-3,5,5-trinitro-1-hexyl) oxamide which comprises condensing 3-aza-3,5,5-trinitro-1-hexylamine with an oxalyl compound having the formula:



50 wherein each R' is a lower alkoxy radical.

No references cited.