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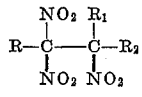
3,000,971

METHOD OF PREPARING POLYNITRO COMPOUNDS

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15 Claims. (Cl. 260—644)

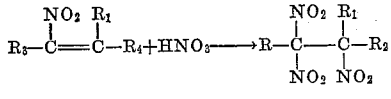
This invention relates to a new and improved method for nitrating nitroolefins to prepare polynitro compounds. In particular this invention relates to a new method for preparing polynitro compounds having the general formula:



wherein R is a hydrogen, alkyl, or nitroalkyl radical; R_1 is a hydrogen or alkyl radical; and R_2 is a hydrogen, alkyl, or nitroalkyl radical which may or may not be the same as R.

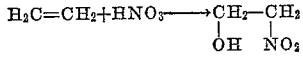
Polynitro compounds, prepared according to the method of our invention, are useful diesel fuel oil additives. When added to diesel fuel oils in amounts on the order of from about 0.5 to about 1.0 percent by weight they increase the cetane number of the oil and hence increase its utility. In addition, these compounds 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 U.S. Patent No. 2,470,162, issued May 17, 1949. One way of using the high explosives in a device such as that disclosed in U.S. 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 new method of our invention comprises nitrating a nitroolefin with nitric acid to obtain corresponding polynitro compounds, in accordance with the general reaction scheme set forth below:



wherein R, R_1, and R_2 are as defined above; R_3 is a hydrogen, alkyl, nitroalkyl, or nitroalkenyl radical; and R_4 is a hydrogen, alkyl, nitroalkyl, or nitroalkenyl radical which may or may not be the same as R_3.

It is known to those skilled in the art that alkenes, such as ethylene, react with nitric acid to yield the corresponding nitroalcohols, such as 2-nitroethanol, in accordance with the reaction scheme set forth below:



We have now discovered, however, that nitroolefins having a nitro group attached to an unsaturated carbon atom react with nitric acid to yield polynitro compounds useful as high explosives, rather than nitroalcohols as suggested by the prior art.

To more clearly illustrate our invention, the following

example is presented. It is to be understood, however, that this example is presented merely as a means of illustration and is not intended to limit the scope of our invention in any way.

EXAMPLE

Nitration of 2-nitro-2-butene.—In a 500 ml. 3-necked flask, fitted with a stirrer, thermometer, and dropping funnel, was placed 150 ml. of 70% nitric acid. The acid was warmed to 40° C. and 25 g. (0.25 mole) of 2-nitro-2-butene was added dropwise in 90 minutes. The temperature was maintained at 39 to 41° C. by intermittent cooling during the addition and for one hour after the addition was completed. (When 2-nitro-2-butene and 70% nitric acid were mixed at 5–10° C. and then allowed to warm up, a fume off occurred.) At the end of this time, the temperature began to drop indicating that the reaction was completed. The mixture was cooled to 5° C., causing a white solid to separate, and poured onto ice. The white solid was collected, washed thoroughly with water, and dried in vacuo, over potassium hydroxide. The yield of 2,2,3-trinitrobutane was 12.1 g. (25.3%), M.P. 42–45° C. Recrystallization from isopropyl ether raised the melting point to 46–48° C. A Lieberman test for the nitrite group was negative.

Analysis.—Cal'd for $C_4H_7N_3O_6$: C,24.88; H, 3.65; N, 21.76; M.W., 193. Found: C, 24.85; H, 3.75; N, 22.00; M.W., 211.

The reaction of our invention is preferably conducted within the temperature range from about 25° to about 50° C. although lower or higher temperatures can be used if desired. For optimum results we prefer to use a temperature of about 40° C.

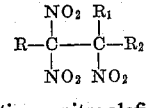
The nitric acid starting material of this invention is preferably employed in the form of an aqueous solution of from about 35 to about 90 percent concentration. For optimum results an acid of about 70 percent concentration should be used.

It will be appreciated that the polynitro compounds can be prepared from a wide variety of nitroolefins in accordance with the method of this invention. For example, 2-nitro-1-propene; 2-nitro-1-butene; 1,4-dinitro-1,3-butadiene; 2,5-dinitro-2,4-hexadiene; 2,5-dinitro-2-pentene; and 2,4-dinitro-2,4-hexadiene react with nitric acid to yield 1,2,2-trinitropropane; 1,2,2-trinitrobutane; 1,1,2,-3,4,4-hexanitrobutane; 2,2,3,4,5,5-hexanitrohexane; 2,2,3,-5,5-pentanitropentane; and 2,2,3,4,4,5-hexanitrohexane, respectively.

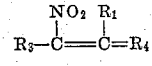
It is apparent that any member of the series of nitroolefins to which the method of the present invention is applicable can be treated with nitric acid, as taught herein, to yield the desired compounds.

We claim:

1. The method of preparing polynitro compounds having the formula:

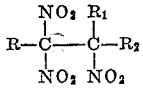


which comprises reacting a nitroolefin having the formula:

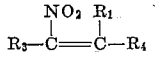


with nitric acid; wherein R_3 and R_4 are radicals selected from the group consisting of hydrogen, lower alkyl, lower nitroalkyl, and lower nitroalkenyl radicals; R_1 is a radical selected from the group consisting of hydrogen and lower alkyl radicals; and R and R_2 are radicals selected from the group consisting of hydrogen, lower alkyl, and lower nitroalkyl radicals.

2. The method of preparing polynitro compounds having the formula:



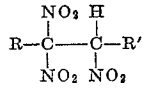
which comprises reacting a nitroolefin having the formula:



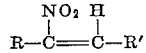
with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.; wherein R_3 and R_4 are radicals selected from the group consisting of hydrogen, lower alkyl, lower nitroalkyl, and lower nitroalkenyl radicals; R_1 is a radical selected from the group consisting of hydrogen and lower alkyl radicals; and R and R_2 are radicals selected from the group consisting of hydrogen, lower alkyl and lower nitroalkyl radicals.

3. The method of claim 2 in which the nitric acid is of about 70 percent concentration and the reaction temperautre is about 40° C.

4. The method of preparing polynitro compounds having the formula:

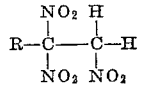


which comprises reacting a nitroolefin having the formula:

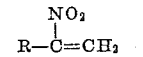


with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.; wherein R and R′ are lower alkyl radicals.

5. The method of preparing polynitro compounds having the formula:

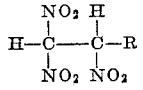


which comprises reacting a nitroolefin having the formula:

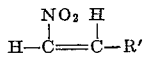


with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.; wherein R is a lower alkyl radical.

6. The method of preparing polynitro compounds having the formula:

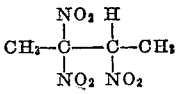


which comprises reacting a nitroolefin having the formula:

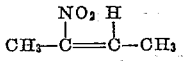


with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.; wherein R is a lower nitroalkyl radical and R′ is a lower nitroalkenyl radical.

7. The method of preparing 2,2,3-trinitrobutane having the structural formula:



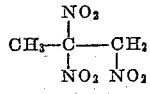
which comprises reacting 2-nitro-2-butene having the structural formula:



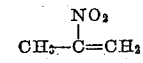
with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.

8. The method of claim 7 in which the nitric acid is of about 70 percent concentration and the reaction temperature is about 40° C.

9. The method of preparing 1,2,2-trinitropropane having the structural formula:



which comprises reacting 2-nitropropene having the structural formula:



with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.

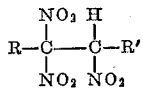
10. The method of preparing 1,2,2-trinitrobutane which comprises reacting 2-nitro-1-butene with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.

11. The method of preparing 1,1,2,3,4,4-hexanitrobutane which comprises reacting 1,4-dinitro-1,3-butadiene with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.

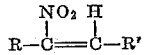
12. The method of preparing 2,2,3,4,5,5-hexanitrohexane which comprises reacting 2,5-dinitro-2,4-hexadiene with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.

13. The method of preparing 2,2,3,4,4,5-hexanitrohexane which comprises reacting 2,4-dinitro-2,4-hexadiene with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.

14. The method of preparing polynitro compounds having the formula:



which comprises reacting a nitroolefin having the formula:



with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.; wherein R is a lower alkyl radical and R′ is a lower nitroalkyl radical.

15. The method of preparing 2,2,3,5,5-pentanitropentane which comprises reacting 2,5-dinitro-2-pentene with nitric acid, of from about 35 to about 90 percent concentration, at a temperature of from about 25° to about 50° C.

No references cited.