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Inventor Horst G. Adolph

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Navy Case No. 66,305

3,3,3-TRINITROPROPANOL AND METHOD OF PREPARATION

BACKGROUND OF THE INVENTION

This invention relates to alcohols and more particularly to polynitroalcohols.

Polynitro alcohols of the formula $XC(NO_2)_2CH_2OH$ wherein $X = CH_3$, NO_2, or halogen are extensively used as intermediates for the synthesis of polynitroaliphatic high energy compounds. Examples are 2,2,2-trinitroethanol, 2,2-dinitropropanol, 2-fluoro-2,2-dinitroethanol, and 2,2-dinitro-1,3-propanediol. Unfortunately, these alcohols undergo Henry deformulation in strong base. This limits the number of new energetic compounds which may be synthesized. Therefore, it would be desirable to provide a polynitroalcohol which does not deformylate in the presence of a base.

SUMMARY OF THE INVENTION

→ Accordingly, an object of this invention is to provide a new organic compound.

Another object of this invention is to provide a new polynitro alcohol.

A further object of this invention is to provide a polynitro alcohol which does not deformylate in the presence of base,

Yet another object of this invention is to provide a polynitro alcohol which is useful as an intermediate for the synthesis of new novel energetic compounds. ←

These and other objects of this invention are accomplished by providing 3,3,3-trinitropropanol. 3,3,3-trinitropropanol is useful as an energetic additive to propellants and explosives.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

3,3,3-trinitropropanol is prepared by the following reaction sequence:

$$\begin{array}{l}
CH(NO_2)_3 + CH_2{=}CHCOOCH_3 \\
\quad\downarrow \\
C(NO_2)_3CH_2CH_2COOCH_3 \\
\quad\downarrow \; H_2O,\ H^+ \\
C(NO_2)_3CH_2CH_2COOH \\
\quad\downarrow \; SOCl_2 \text{ reflux} \\
C(NO_2)_3CH_2CH_2COCl \\
\quad\downarrow \; NaN_3 \\
C(NO_2)_3CH_2CH_2CON_3 \\
\quad\downarrow \\
C(NO_2)_3CH_2CH_2NCO \\
\quad\downarrow \; H_2O,\ H^+ \\
C(NO_2)_3CH_2CH_2NH_3^{\,+}HSO_4^- \\
\quad\downarrow \; NaNO_2 \\
C(NO_2)_3CH_2CH_2OH.
\end{array}$$

The details of the reactin conditions are illustrated in the example.

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

EXAMPLE

Preparation of 3,3,3-Trinitropropanol via 4,4,4-Trinitrobutyryl Azide

54.6 g of nitroform as 33% aqueous solution (0.36 mol), 33.0 g of methyl acrylate (0.38 mol) and 90 ml methanol were heated for 3 hours at 70°C, then cooled in an ice bath. The precipitate was filtered off, added to 200 ml of concentrated hydrochloric acid, and the mixture was refluxed for 20 hours. An oil was formed which was cooled and about 50 g trinitrobutyric acid, m.p. 50-68°C,crystallized out. The crude trinitrobutyric acid was collected and then refluxed with thionyl chloride for about six hours to form trinitrobutyric acid chloride. The excess thionyl chloride was removed in vacuo. The crude 3,3,3-trinitrobutyric acid chloride was dissolved in acetone and then added dropwise to a solution of sodium azide in water at a temperature of 10-20°C. The solution became cloudy and deposited crystals of the azide. The reaction mixture was stirred for 30 minutes and extracted with chloroform. The chloroform solution was washed with water, dilute sodium bisulfite solution, water, and dried over sodium sulfate. The solution was partially concentrated in vacuo to remove the last traces of water and then heated to reflux until the evolution of nitrogen had ceased.

The solution was concentrated in vacuo and the residual oil, 3,3,3-trinitropropyl isocyanate, was separated by distillation. The crude 3,3,3-trinitropropyl isocyanate was added dropwise with good agitation to 2250 ml of concentrated hydrochloric acid. The temperature rise was observed and the rate of addition was adjusted to keep the temperature of the reaction mixture below 60°C. Carbon dioxide was evolved immediately during the addition of the isocyanate. After the addition was completed, the temperature of the reaction mixture was raised to 85°C and held there for one hour. The reaction mixture was then concentrated to dryness in vacuo to yield about 35 g of crude trinitropropylamine hydrochloride. The NMR spectrum in D_2O showed the expeted triplets at 2.81 and 3.06. The hydrochloride was converted to the sulfate by stirring with an aqueous suspension of Ag_2SO_4 at 50°C for several hours, filtering, and removing the water. The salt was redissolved in 350 ml water, the pH was brought to 1-2 with $NaHCO_3$ (any precipitate appearing at this point is redissolved by addition of dilute H_2SO_4), and over 1 hour at about 45°C a solution of 20 g sodium nitrite in 75 ml water was added. After complete addition, the mixture was stirred 1.5 hours with the temperature raised gradually to 55°C, then cooled with ice and extracted with CH_2Cl_2. Sodium chloride was added to the aqueous phase which was then extracted 3 more times with dichloromethane. The combined extracts were washed once with water and dried. Removal of the solvent gave 20 g of yellow oil which by thin-layer chromatography (TLC) analysis was shown to consist of one major and one minor component. The pure 3,3,3-trinitropropanol was isolated readily by chromatography on silica gel with CH_2Cl_2/hexane solvent; m.p. 24-25°C.

NMR ($CDCl_3$): δ 1.87 (t, OH), 3.30 (s, C-$\underline{CH}_2$-C), 4.1 (m, $\underline{CH}_2$-O).

MS (CI, CH_4): 196 (M+1, 7.29%); 178 (M-17; 100%); 132 (M-53; 17.48%).

Anal. Calcd. for $C_3H_5N_3O_7$(195.1): C, 18.47; H, 2.58; N, 21.54. Found: C, 18.40; H, 2.62; N, 19.72.

To those skilled in the art, many modifications and variations of the present invention are possible in light of the above teachings.

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ABSTRACT OF THE DISCLOSURE

3,3,3-trinitropropanol which is prepared via the following reaction sequence:

$$
\begin{array}{l}
CH(NO_2)_3 + CH_2{=}CHCOOCH_3 \\
\big\downarrow \\
C(NO_2)_3CH_2CH_2COOCH_3 \\
\big\downarrow\ H_2O,\ H^+ \\
C(NO_2)_3CH_2CH_2COOH \\
\Big\downarrow\ \begin{array}{l} SOCl_2 \\ \text{reflux} \end{array} \\
C(NO_2)_3CH_2CH_2COCl \\
\big\downarrow\ NaN_3 \\
C(NO_2)_3CH_2CH_2CON_3 \\
\big\downarrow \\
C(NO_2)_3CH_2CH_2NCO \\
\big\downarrow\ H_2O,\ H^+ \\
C(NO_2)_3CH_2CH_2NH_3{}^+HSO_4^- \\
\big\downarrow\ NaNO_2 \\
C(NO_2)_3CH_2CH_2OH.
\end{array}
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