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1 Navy Case No. 66,305

2 3,3,3-TRINITROPROPANOL AND METHOD OF PREPARATION

3 BACKGROUND OF THE INVENTION

4 This invention relates to alcohols and more particularly
5 to polynitroalcohols.

6 Polynitro alcohols of the formula $XC(NO_2)_2CH_2OH$
7 wherein X = CH_3 , NO_2 , or halogen are extensively used as
8 intermediates for the synthesis of polynitroaliphatic high
9 energy compounds. Examples are 2,2,2-trinitroethanol, 2,2-
10 dinitropropanol, 2-fluoro-2,2-dinitroethanol, and 2,2-dinitro-
11 1,3-propanediol. Unfortunately, these alcohols undergo Henry
12 deformation in strong base. This limits the number of new
13 energetic compounds which may be synthesized. Therefore, it
14 would be desirable to provide a polynitroalcohol which does not
15 deformylate in the presence of a base.

16 SUMMARY OF THE INVENTION

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

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

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

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

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

5 EXAMPLE

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

8 54.6 g of nitroform as 33% aqueous solution (0.36 mol),
9 33.0 g of methyl acrylate (0.38 mol) and 90 ml methanol were
10 heated for 3 hours at 70°C, then cooled in an ice bath. The
11 precipitate was filtered off, added to 200 ml of concentrated
12 hydrochloric acid, and the mixture was refluxed for 20 hours.
13 An oil was formed which was cooled and about 50 g
14 trinitrobutyric acid, m.p. 50-68°C, crystallized out. The crude
15 trinitrobutyric acid was collected and then refluxed with
16 thionyl chloride for about six hours to form trinitrobutyric
17 acid chloride. The excess thionyl chloride was removed in
18 vacuo. The crude 3,3,3-trinitrobutyric acid chloride was
19 dissolved in acetone and then added dropwise to a solution of
20 sodium azide in water at a temperature of 10-20°C. The
21 solution became cloudy and deposited crystals of the azide.
22 The reaction mixture was stirred for 30 minutes and extracted
23 with chloroform. The chloroform solution was washed with
24 water, dilute sodium bisulfite solution, water, and dried over
25 sodium sulfate. The solution was partially concentrated in
26 vacuo to remove the last traces of water and then heated to
27 reflux until the evolution of nitrogen had ceased.

1 The solution was concentrated in vacuo and the residual oil,
2 3,3,3-trinitropropyl isocyanate, was separated by distillation.
3 The crude 3,3,3-trinitropropyl isocyanate was added dropwise
4 with good agitation to 2250 ml of concentrated hydrochloric
5 acid. The temperature rise was observed and the rate of
6 addition was adjusted to keep the temperature of the reaction
7 mixture below 60°C. Carbon dioxide was evolved immediately
8 during the addition of the isocyanate. After the addition was
9 completed, the temperature of the reaction mixture was raised
10 to 85°C and held there for one hour. The reaction mixture was
11 then concentrated to dryness in vacuo to yield about 35 g of
12 crude trinitropropylamine hydrochloride. The NMR spectrum in
13 D₂O showed the expected triplets at 2.81 and 3.06. The
14 hydrochloride was converted to the sulfate by stirring with an
15 aqueous suspension of Ag₂SO₄ at 50°C for several hours,
16 filtering, and removing the water. The salt was redissolved in
17 350 ml water, the pH was brought to 1-2 with NaHCO₃ (any
18 precipitate appearing at this point is redissolved by addition
19 of dilute H₂SO₄), and over 1 hour at about 45°C a solution of
20 20 g sodium nitrite in 75 ml water was added. After complete
21 addition, the mixture was stirred 1.5 hours with the
22 temperature raised gradually to 55°C, then cooled with ice and
23 extracted with CH₂Cl₂. Sodium chloride was added to the
24 aqueous phase which was then extracted 3 more times with
25 dichloromethane. The combined extracts were washed once with
26 water and dried. Removal of the solvent gave 20 g of yellow
27 oil which by thin-layer chromatography (TLC)

1 analysis was shown to consist of one major and one minor
2 component. The pure 3,3,3-trinitropropanol was isolated readily
3 by chromatography on silica gel with CH_2Cl_2 /hexane solvent;
4 m.p. 24-25°C.

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

6 MS (CI, CH_4): 196 (M+1, 7.29%); 178 (M-17; 100%); 132 (M-53;
7 17.48%).

8 Anal. Calcd. for $\text{C}_3\text{H}_5\text{N}_3\text{O}_7$ (195.1): C, 18.47; H, 2.58; N, 21.54.
9 Found: C, 18.40; H, 2.62; N, 19.72.

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

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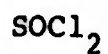
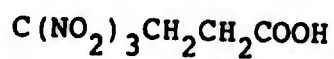
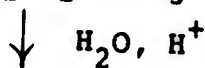
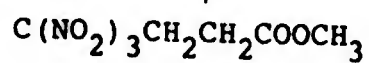
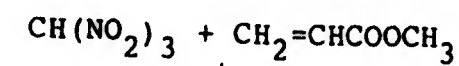
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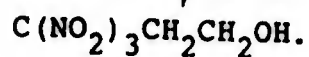
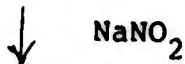
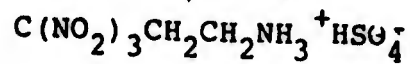
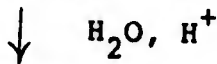
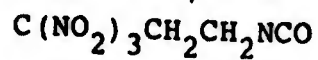
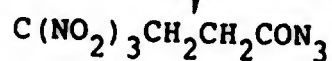
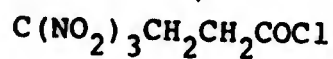
2 3,3,3-TRINITROPROPANOL AND METHOD OF PREPARATION

3 ABSTRACT OF THE DISCLOSURE

4 3,3,3-trinitropropanol which is prepared via the following
5 reaction sequence:



12 reflux



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26
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