

SHORT
COMMUNICATIONS

Synthesis of New Polynitro Dicarboxylic Acid Esters

A. S. Ermakov, P. V. Bulatov, D. B. Vinogradov, and V. A. Tartakovskii

Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Leninskii pr. 47, Moscow, 117913 Russia
e-mail: secretary@ioc.ac.ru

Received February 8, 2004

Development of new compositions for car airbags imposes a number of requirements on potential components. These substances should be characterized by a low combustion temperature, nearly 100% oxygen balance, sufficient thermal stability, and low enthalpy of formation. We anticipated that 2,2,2-trinitroethyl dicarboxylic acid esters could possess the required properties.

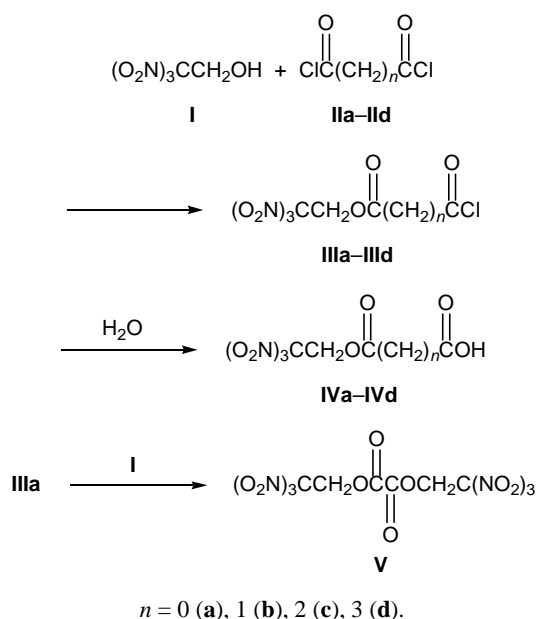
Taking into account the low nucleophilicity of 2,2,2-trinitroethanol, in order to synthesize the corresponding aliphatic carboxylic acid esters specific condensing agents and reaction conditions are used: transesterification of methyl esters in oleum [1]; esterification of carboxylic acids with 2,2,2-trinitroethanol in oleum [2], polyphosphoric acid [1], or trifluoroacetic anhydride [3]; and catalysis by aluminum chloride [2]. It should be emphasized that only bis-(2,2,2-trinitroethyl) dicarboxylates were obtained by the above methods while the synthesis of the corre-

sponding monoesters was not reported. Furthermore, Cochoy and McGuire [3] failed to obtain bis(2,2,2-trinitroethyl) oxalate because of decomposition of oxalic acid under the esterification conditions [3].

We propose a simple procedure for synthesizing a series of 2,2,2-trinitroethyl hydrogen dicarboxylates, which is analogous to the known synthesis of 2,2,2-trinitroethyl acetate [4]. The procedure is based on the reaction of the corresponding dicarboxylic acid dichloride **IIa–IIId** with 2,2,2-trinitroethanol (**I**) at 50–60°C over a period of several hours. In the synthesis of monoesters we used a threefold excess of the dichloride in order to suppress side formation of the respective diester. A commonly known method involving reaction of an alcohol with dicarboxylic acid anhydride is ineffective when the alcohol is 2,2,2-trinitroethanol. We have found that succinic anhydride does not react with 2,2,2-trinitroethanol, obviously because of the low nucleophilicity of the latter.

Using the proposed procedure, we obtained 2,2,2-trinitroethyl hydrogen malonate, succinate, and glutarate, as well as 2,2,2-trinitroethyl chloro(oxo)acetate (**IIIa**). The latter may be used as synthon in subsequent preparation of high-melting components for airbag compositions. Compound **IIIa** is unstable; therefore, it was characterized by the NMR spectra and conversion into bis(2,2,2-trinitroethyl) oxalate (**V**). Compound **V** was not described previously; only a single publication is available, where its detonation pressure is calculated [5].

2,2,2-Trinitroethyl hydrogen malonate (IVb). Compound **IIb**, 2.82 g (20 mmol), was added to a solution of 1.27 g (7 mmol) of 2,2,2-trinitroethanol (**I**) in 3 ml of diethyl ether, and the mixture was heated to remove diethyl ether and was then kept for 10 h at 50°C. Excess malonyl dichloride was distilled off on a rotary evaporator, and the residue was recrystallized from water. Yield 0.65 g (35%), mp 78°C. ¹H NMR



spectrum (acetone- d_6), δ , ppm: 3.61 s (2H, COCH₂CO), 5.89 s (2H, CH₂O). Found, %: C 22.66; H 2.01; N 15.48. C₅H₅N₃O₁₀. Calculated, %: C 22.48; H 1.89; N 15.73.

2,2,2-Trinitroethyl hydrogen succinate (IVc) was synthesized in a similar way. Yield 30%, mp 126°C. ¹H NMR spectrum (acetone- d_6), δ , ppm: 2.65 t [2H, CH₂OC(O)CH₂CH₂, $J = 15$ Hz]; 2.73 t [CH₂C(O)OH, $J = 15$ Hz]. Found, %: C 25.87; H 3.12; N 15.82. C₆H₇N₃O₁₀. Calculated, %: C 25.63; H 2.51; N 14.95.

2,2,2-Trinitroethyl hydrogen glutarate (IVd) was synthesized in a similar way. Yield 30%, mp 57°C. ¹H NMR spectrum (acetone- d_6), δ , ppm: 1.90 m (2H, CH₂CH₂CH₂), 2.41 t [2H, CH₂OC(O)CH₂CH₂, $J = 19.5$ Hz], 2.58 t (2H), 5.89 s (2H, CH₂O). Found, %: C 28.61; H 3.04; N 14.21. C₇H₉N₃O₁₀. Calculated, %: C 28.49; H 3.07; N 14.24.

Bis(2,2,2-trinitroethyl) oxalate (V). *a.* Oxalyl dichloride, 13 g (100 mmol), was added to a solution of 4.53 g (25 mmol) of alcohol **I** in 6 ml of diethyl ether, and the mixture was heated to remove diethyl ether and was kept for 12 h at 50°C. Excess oxalyl dichloride was distilled off on a rotary evaporator. The residue was 2,2,2-trinitroethyl chloro(oxo)acetate (**IIIa**). Yield 6.73 g (97%), mp 26–28°C. ¹H NMR spectrum (CDCl₃), δ , ppm: 5.62 s (2H). ¹³C NMR spectrum (CDCl₃), δ_C , ppm: 62.88 (C³), 154.54 (C²), 156.17 (C¹), 158.36 (C⁴).

b. Compound **IIIa**, 2.72 g (10 mmol), was dissolved in 2 ml of diethyl ether, 1.81 g (10 mmol) of

2,2,2-trinitroethanol (**I**) was added, and the mixture was heated to remove diethyl ether, kept for 12 h at 50°C, and treated with water. The precipitate was dried, dissolved in diethyl ether, and precipitated with hexane. Yield 2.41 g (58%), mp 116°C. IR spectrum (KBr), ν , cm⁻¹: 1780 (C=O); 1592, 1304 (NO₂); 1172 (COC). ¹H NMR spectrum (acetone- d_6), δ , ppm: 6.11 s (2H). Found, %: C 17.36; H 1.07; N 20.31. C₇H₉N₃O₁₀. * Calculated, %: C 17.32; H 0.97; N 20.20.

The ¹H NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 MHz), and the ¹³C NMR spectra were measured on a Bruker AC-200 instrument (50.32 MHz).

This study was performed under financial support by the International Scientific–Technical Center (grant no. 1882).

REFERENCES

1. Gold, M.H. and Klager, K., *Tetrahedron, Suppl. 1*, 1963, vol. 19, p. 81.
2. Frankel, M.B., *J. Org. Chem.*, 1961, vol. 27, p. 331.
3. Cochoy, R.E. and McGuire, R.R., *J. Org. Chem.*, 1972, vol. 37, p. 3041.
4. Ludwig, B.J., *J. Am. Chem. Soc.*, 1950, vol. 72, p. 5329.
5. Zerilli, F.J., Doherty, R.M., Short, J.M., McGuire, R.R., and Kamlet, M.J., *Combust. Flame*, 1988, vol. 74, p. 295.

* As in Russian original.—*Publisher*.