

Synthesis of Nitroesters Based on Methylol Derivatives of Parabanic and Isocyanuric Acids

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Abstract—Nitroesters synthesis based on methylol derivatives of parabanic and cyanuric acids was performed. The corresponding alloxan nitroxymethyl derivative was unstable.

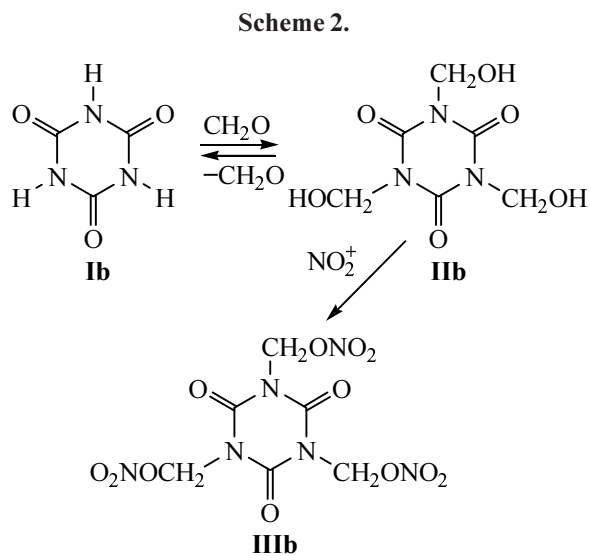
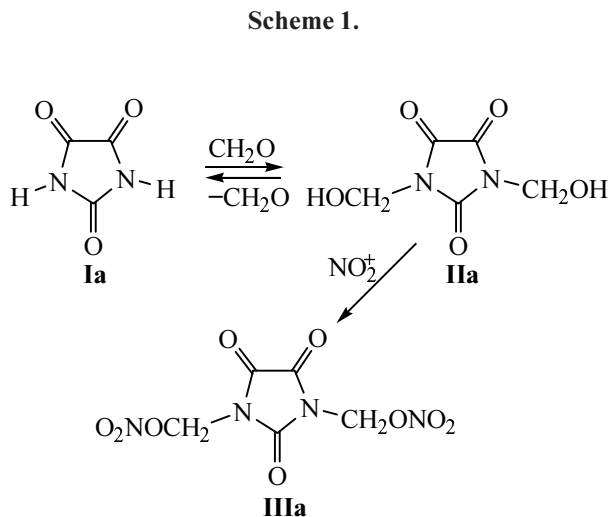
In recent years gas generating compositions for widespread uses, in particular, for airbags, are intensively developed. The components of the pyrocompounds should possess high oxygen balance, low combustion temperature, high heat resistance, low sensitivity to mechanical impact, and a number of other qualities.

The search for compounds with properties fitting to all above requirements was started with the derivatives of cyclic polycarboimides [1]. The latter substances have been first discovered at the beginning of the previous century and nowadays quite a number of these compounds are known. These compounds have high melting points and possess high heat resistance. The modification of these compounds for improvement of their oxygen balance was apparently promising. The most simple way to this target was an introduction of nitrate groups into methylol derivatives.

Although the polycarboimides reactions with aldehydes were long known [2, 3], no publications appeared on nitrates of their methylol derivatives.

The work was started by optimizing the formaldehyde reaction with parabanic acid (**Ia**). We found reaction conditions affording dimethylol derivative **IIa** that further was subjected to nitration in a mixture of nitric acid and acetic anhydride to obtain 1,3-di(nitroxymethyl)imidazolidine-2,4,5-trione (**IIIa**) in a ~56% yield (Scheme 1). Compound **IIIa** was a crystalline substance melting at ~105°C.

The study was continued by performing a similar reaction sequence with cyanuric acid reacting in the isomeric form **Ib**. As a result 1,3,5-tri(nitroxymethyl)-1,3,5-triaza-2,4,6-cyclohexanetrione (**IIIb**) was obtained in a ~30% yield. Compound **IIIa** was a crystalline substance melting at ~150°C (Scheme 2).



At the same time we failed to obtain stable products by treating likewise alloxan. In the course of isolation of its methylol derivative dinitrate a complex mixture of compounds formed containing according to ^1H NMR data ~30% of the target product 1,3-di(nitroxymethyl)-1,3-diaza-2,4,5,6-cyclohexanetrione that gradually suffered decomposition.

It is significant that nitration of dimethylol derivatives of urea and oxamide also does not provide positive results, and the arising nitrates suffer decomposition.

Thus we synthesized compounds **IIIa**, **IIIb**, crystalline substances that were suggested for use as in pyrocompounds for airbags.

EXPERIMENTAL

^1H NMR spectra were registered on a spectrometer Bruker AM-300 (300.13 MHz) in $(\text{CD}_3)_2\text{CO}$, internal reference HMDS.

1,3-Di(hydroxymethyl)imidazolidine-2,4,5-trione (IIa). To a solution of 1 g (8.8 mmol) of parabanic acid in 10 ml of MeOH was added 2 g of 27.5% water solution of formaldehyde. The solution obtained was evaporated in a vacuum at 48°C. We obtained 1.54 g (~100%) of 1,3-di(hydroxymethyl)imidazolidine-2,4,5-trione (**IIa**), mp 128–130°C (publ: mp 130°C [2]).

1,3-Di(nitroxymethyl)imidazolidine-2,4,5-trione (IIIa). To 13 ml of Ac_2O at ~0°C was added 4.2 ml of 98% HNO_3 . To the mixture obtained was added at stirring 1.21 g (7 mmol) of 1,3-di(hydroxymethyl)imidazolidine-2,4,5-trione (**IIa**), and the reaction mixture was kept at –2–4°C for 1 h. Then it was poured into 30 ml of water with ice, the separated precipitate was filtered off and washed on the filter with water (2×8 ml). The precipitate was dried to furnish 1.5 g of crude product **IIIa**. The substance was recrystallized from 14 ml of MeOH to obtain 1.03 g (55.5%) of 1,3-di(nitroxymethyl)imidazo-

lidine-2,4,5-trione (**IIIa**), mp 103–105°C. IR spectrum (KBr), ν , cm^{-1} : 1674 (ONO_2), 1710 ($\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 6.15 s (4H, NCH_2ONO_2). Found, %: C 23.37; H 1.68; N 21.15. $\text{C}_5\text{H}_4\text{N}_4\text{O}_9$. Calculated, %: C 22.74; H 1.53; N 21.21.

1,3,5-Tri(nitroxymethyl)-1,3,5-triaza-2,4,6-cyclohexanetrione (IIIb). To a solution of 1.35 g (10.5 mmol) of cyanuric acid in 13 ml of water was added 2.51 g of 27.5% water solution of formaldehyde. The solution obtained was evaporated in a vacuum at 60–70°C. We obtained 2.32 g of 1,3,5-tri(hydroxymethyl)-1,3,5-triaza-2,4,6-cyclohexanetrione (**IIIb**).

To 13 ml of Ac_2O at ~0°C was added 4.2 ml of 98% HNO_3 . To the mixture obtained was added at –20°C while vigorous stirring 2.15 g (9.81 mmol) of 1,3,5-tri(hydroxymethyl)-1,3,5-triaza-2,4,6-cyclohexanetrione (**IIIb**). After keeping the reaction mixture at –20...–17°C for 1 h it was poured into 30 ml of water with ice, the separated precipitate was filtered off and washed on the filter with water (2×8 ml). The precipitate was dried and recrystallized from MeOH to obtain 1.05 g (31%) of 1,3,5-tri(nitroxymethyl)-1,3,5-triaza-2,4,6-cyclohexanetrione (**IIIb**), mp 149–150°C. ^1H NMR spectrum, δ , ppm: 6.45 s (6H, NCH_2ONO_2). Found, %: C 20.62; H 1.88; N 23.79. $\text{C}_6\text{H}_6\text{N}_6\text{O}_{12}$. Calculated, %: C 20.34; H 1.71; N 23.73.

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