

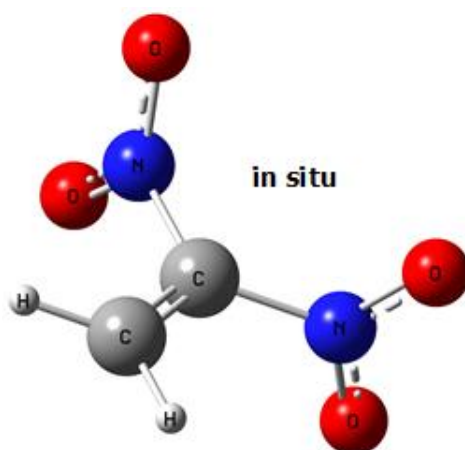
Unsuccessful synthesis of individual 1,1-dinitroethene

Jowita Kras ⁽¹⁾, Maria Mikulska ⁽¹⁾, Radwan Allnajar ⁽²⁾, Karolina Kula ⁽¹⁾ ✉

⁽¹⁾ Department of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow (Poland),

⁽²⁾ PharmD, Faculty of Pharmacy, Libyan International Medical University, Benghazi, Libya

✉ Correspondence to: karolina.kula@pk.edu.pl



Abstract: The possibility of the preparation of free 1,1-dinitroethene was examined experimentally on the basis of procedures described earlier for other examples of 1-R-1-nitroethenes. It was found, that these types of protocols are non-usable for the preparation of the title compound due to its high reactivity and tendency to decomposition and oligomerization.

Keywords: nitroalkenes, nitroalcohols, dehydration

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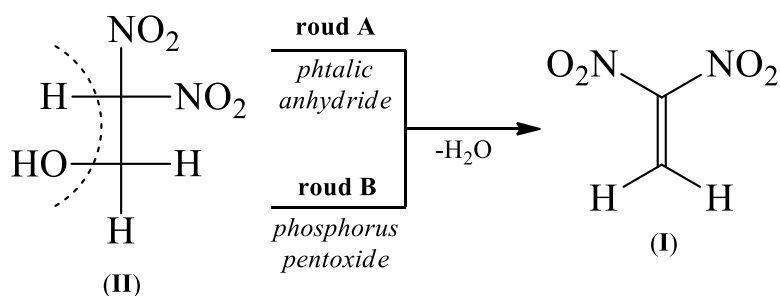
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Introduction

Conjugated nitroalkenes are very universal build block in the organic synthesis [1,2]. In general however, most great known are 2-substituted analogs of the nitroethene. The preparation of 1-substituted nitroethenes is relatively more difficult, and in the consequence, the applications of this group of nitroalkenes are substantially more rare [3]. Especial example of 1-R-1-nitroethene analog is 1,1-dinitroethene (gem-dinitroethene) (**I**). Only some, incidental notes regarding to the preparation and properties of this compound are available. So, the participation of it's in the [3+2] cycloaddition reactions with nitrones [4] and nitrile N-oxides [5] were recently discussed on the basis of DFT calculations. Next, in some cases, generated *in situ* 1,1-dinitroethene (**I**) was immediately trapped to some nucleophilic agents such as cyclopentadiene [6] or diazomethane [7].

In any cases however, authors not described attempts for the preparation of free 1,1-dinitroethene (**I**). So, within this work we decided to perform test of the process of the preparation of this nitroalkene (**I**), based on the analogous procedures verified for 2-nitropropan-1-ol (with phthalic anhydride) [8] and 1-halo-1-nitroethenes (with phosphorus pentoxide) [9]. This article is a short summary of potentially possible synthesis routes of the simplest gem-dinitroalkene (**I**) via dehydration of 2,2-dinitroethanol (**II**) (**Scheme 1**).



Sch. 1. The general scheme of synthesis of the 1,1-dinitroethene (**I**) via dehydration of reaction of 2,2-dinitroethanol (**II**), investigated in this study.

Results and discussion

From thermodynamically point of view, the decomposition of the 2,2-dinitroethanol should be treatment as full allowed, because the Gibbs free energy of the transformation is evidently negative. (see Supplementary Material). Firstly we initiated tests of the dehydration reaction using phthalic anhydride, using different temperatures of preparation of the phthalic ester and different temperatures of this ester decomposition. Unfortunately, along all tests, only explosive residues were obtained. Next, the series of test with the participation of phosphorus pentoxide as dehydrating agent were conducted. These test were also unsuccessful.

Conclusion and future perspective

Based on presented experimental study it should be concluded that probably is rather impossible to preparation of 1,1-dinitroethene (I) as individual compound. In the consequence this nitroalkene must be formed *in situ* and immediately trapped with the second component of respective reaction. This research is important both in an experimental and theoretical point of view due to synthesis of small alkenes and their application to preparation of organic heterocyclic compounds.

Experimental

General

The reactions and purity control of the compounds were monitored using a Knauer liquid chromatograph (UV detector, LiChrospher 100-10 RP18 4 × 240 mm column, eluent 70% (by volume) aqueous MeOH, the flow rate of the eluent 1.5 ml/min, detection at $\lambda = 254$ nm). IR spectra were registered on a FTS Nicolet IS 10 apparatus in KBr pellets. ^1H spectra were recorded on a Bruker AMX-500 spectrometer in CDCl_3 . TMS was used as the internal standard. The presented experimental procedure is a standard approach, common used in during laboratory research [10].

Preparation of the 2-bromo-2-nitroethanol (III)

For the suspense of the 63.0 g of natrium salt of the 2-nitroethanol (prepared using known procedure [11]) in 250 cm^3 od dry diethyl ether, a 29 cm^3 of bromine were added drop wise at the -8 - -5°C. The reaction mixture was intensively stirred. After 24 hours, the sodium bromide was filtered, and the liquid residue was evaporated on the rotary vapor evaporator. The residue was distilled under the reduced pressure. 73.0 g (77%) of the 2-bromo-2-nitroethanol was obtained.

B.p. 67-68°C/3mmHg (lit.: [12] 113°C/15mmHg); ^1H NMR: 5.97 ppm (1H, dd, $J=4.16\text{Hz}$, $J=7.52\text{Hz}$), 4.26 ppm (1H, dd, $J=7.52\text{Hz}$, $J=12.88\text{Hz}$), 4.10 ppm (1H, dd, $J=4.16\text{Hz}$, $J=12.88\text{Hz}$), 2.31 (1H, s,); IR, cm^{-1} : 1567, 1351 (NO_2), 3363 (OH).

Preparation of the potassium salt of the 2,2-dinitroethanol (IIa)

52.0 g of the 2-bromo-2-nitroethanol was dissolved in the 75 cm^3 of the methanol, and cooled to the -5°C using acetone/dry ice mixture. Next, the solution of 31.0 g of the potassium nitrite in the 45 cm^3 of the water was added drop wise. The reaction mixture was intensively stirred. Next, on similar way, the solution of 27.5 g KOH in the 20 cm^3 of the

water was added. The cooling mixture was removed, and when the temperature was increased to the 0°C, the crystalline yellow mass was filtered, washed using 2 x 10 cm³ of the cool methanol and dried in the exicator. The 14.0 g (27%) of the potassium salt of the 2,2-dinitroethanol was obtained. This salt was not stored and immediately used for the further transformation.

Preparation of the 2,2-dinitroethanol (II)

14 g of the potassium salt of the 2,2-dinitroethanol was added to the 47 cm³ of the water with ice at the 3°C. The reaction mixture was intensively stirred. Next, the solution of the 1.6 cm³ concentrated sulfuric acid in the 15 cm³ of the water was added drop wise. The obtained mass was extracted using 5 x 10 cm³ of the diethyl ether. The extract was mixed, and dried over anhydrous magnesium sulphate at -20°C. After filtration, the ether was removed. 10.0 g of the 2,2-dinitroethanol as yellow oil was obtained.

M.p.: 2-3°C. (lit.: b.p.: 50-60°C/0.2mmHg [6]).

Preparation of the 1,1-dinitroethene (I, procedure A)

5.0 g of 2,2-Ditroethanol and 10.0 g of phthalic anhydride were heated in a Claisen flask at 50°C under 80 mmHg until the phthalic anhydride melted. The temperature was then raised to 100°C. Any distilled product was not obtained. In the residue only oligomeric explosive mass was detected. Similar attempts were started using different temperatures in the range 50-150°C and different pressures in the range 40-100mmHg. In any case the free 1,1-dinitroethene was not obtained.

Preparation of the 1,1-dinitroethene (I, procedure B)

A Claisen flask was charged with the 5.0 g of the phosphorus pentoxide. The flask was heated to 100°C, after which the pressure in the distillation assembly was reduced to 100 mmHg. Then it has been slowly added drop wise to the flask the 4.0 g of the 2,2-dinitroethanol. Any distilled product was not obtained. In the residue only oligomeric explosive mass was detected. Similar attempts were started using different temperatures in the range 50-150°C, and different pressures in the range 40-100 mmHg. In any case the free 1,1-dinitroethene was not obtained.

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