The First Synthesis of 1,1-Dinitrocyclopropane

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Abstract: 1,1-Dinitrocyclopropane was prepared in 62% yield. This high energetic compound was previously unknown. Herein its preparation via tandem reaction between nitroform and diazomethane in benzene is described.

Key words: 1,1-dinitrocyclopropane, trinitromethane, diazomethane, tandem reactions, alicyclic nitro compounds

Strained-ring compounds substituted with multiple nitro groups are of considerable interest as high-energy and high-density materials.[1] Polynitrocyclopropanes are of particular interest as compounds with heightened energy, molecular compactness, high ratio of nitro groups to carbon atoms and a remarkable synthetic potential.[2] However, even the synthesis of dinitrocyclopropanes is still complicated problem.[3] Thus, the simplest representative of *gem*-dinitrocyclopropanes, namely 1,1-dinitrocyclopropane, which is expected to have unusual chemical reactivity and useful properties has not been synthesized yet while at least three unsuccessful attempts of its synthesis were documented in the literature.[4–6]

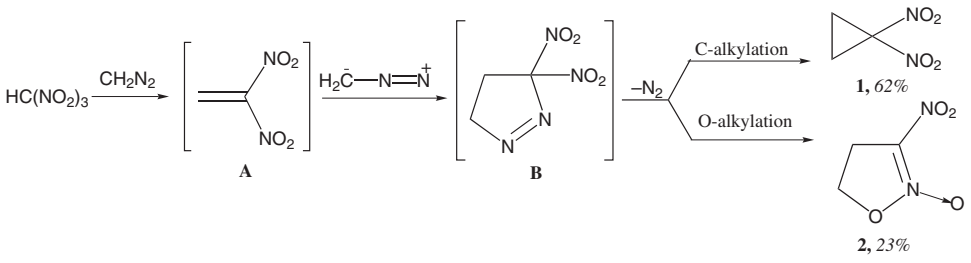
For example, the cyclization reaction of 1-bromo-3,3-dinitropropane under the action of bases leads exclusively to the product of intramolecular O-alkylation, namely 3-nitroisoxazoline *N*-oxide.[4] Attempts of electrophilic nitration of nitrocyclopropanes at the α-carbon atom were not successful and only dimeric coupling products were observed after cyclopropyl anion generation.[5] Dinitrocarbene generation from different precursors also did not bring positive results.[6] There exists only one brief report[7] declaring the fact of generation of the dinitrocarbene from trinitromethane salts. However, this carbene reacted with alkenes as 1,3-dipole to give 3-nitroisoxazoline *N*-oxide in only 1–15% yield.[7]

In the course of our study of the reactions of acetylenes and nitronates[8] we obtained 1,1-dinitrocyclopropane (**1**) as a by-product. Because it was evident that the formation of **1** was due to the reaction of nitroform and diazomethane, we have examined this reaction in detail. We have found that the treatment of nitroform with diazomethane (in the ratio 1:4) in benzene at 5 °C gave 1,1-dinitrocyclopropane (**1**) as a major product together with isoxazoline *N*-oxide (**2**) (ratio 7:3, NMR data). The reaction products were isolated after distillation or column chromatographic purification.

The ^{1}H NMR spectrum of **1** shows one singlet at δ 2.29 ppm; its ^{13}C NMR spectrum exhibits two signals at δ 19.1 ppm (J_{C-H} = 172 Hz) and δ 94.9 ppm, which are typical values for cyclopropane rings. Mass spectrum and microanalysis also confirm the structure and composition for **1**. 1,1-Dinitrocyclopropane (**1**) is a stable compound. Heating of **1** to 150 °C (40 min) did not lead to any change of its NMR spectrum.

It is necessary to emphasize that the reaction of nitroform with diazomethane in benzene, as it has been reported previously,[9] proceeded to give the *O*-methyl ether of nitroform (this pathway has been proven by the formation of corresponding adducts with olefins). However, the formation of *gem*-1,1-dinitrocyclopropane (**1**) was not observed in all these experiments.

Taking into consideration the literature data[7,9] and our results, the scheme of the formation of **1** may be represented in the following way (Scheme 1). The key step of the reaction of nitroform with diazomethane (in the absence of



Scheme 1

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unsaturated compounds) is the transient formation of 1,1-dinitroethylene (**A**) as the principle intermediate (for different possible pathways of its formation see ref.[10]). Dinitroethylene (**A**) can add diazomethane as 1,3-dipolarophile yielding the intermediate dinitropyrazoline (**B**) which, in turn, eliminates nitrogen to give either the product of intermolecular C-alkylation, namely 1,1-dinitrocyclopropane (**1**), or the product of O-alkylation, namely 3-nitroisoxazoline *N*-oxide (**2**).

In summary, we have demonstrated that the reaction of trinitromethane with diazomethane under mild conditions provides the first synthesis of *gem*-dinitrocyclopropane (**1**). The study of this reaction in detail is in a progress now.

NMR spectra were performed on a Varian VXR-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) and a Bruker DPX-300 (300 MHz for ^{1}H, 75 MHz for ^{13}C) spectrometer using $CDCl_3$ as solvent. Melting points were determined on a Electrotermal apparatus and are uncorrected. Mass spectra were obtained on a Varian MAT 311 (electron impact) spectrometer. Merck silica gel 60 (0.063–0.200 mm) was used for column chromatography. Analytical TLC was performed on Silufol silica gel plates.

Reaction of Diazomethane with Trinitromethane; Typical Procedure

The solution of diazomethane obtained from *N*-nitroso-*N*-methylurea (1.03 g, 10 mmol) in benzene (10 mL) was added over 1 h to a solution of trinitromethane (380 mg, 2.5 mmol) in benzene (10 mL) at 5 °C and the resulting mixture was stirred at 5 °C for additional 30 min. Then the mixture was concentrated to give 1.30 g of a yellow oil consisting of **1** and **2** in the ratio 7:3 (as shown by ^{1}H NMR). *N*-Oxide **2** was isolated from the reaction mixture by freezing at –20 °C to give 300 mg (23%) of the product; mp 92 °C (EtOH).[4] Distillation of the residue gave pure **1** (820 mg, 62%); bp 80 °C (9 mm); d_4^{20} 1.423 g/cm^3; R_f = 0.66 ($CHCl_3$).[11]

Caution: Although we have not experienced any problems in handling these compounds, full safety precautions should be taken due to their potential explosive nature.

1,1-Dinitrocyclopropane (1)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.11 (2 × CH_2, J = 172 Hz), 94.92 [$C(NO_2)_2$].

MS (EI, 70 eV): *m*/*z* (%) = 133 $[M + 1]^+$ (0.1), 132 $[M]^+$ (0.1), 86 $[M – NO_2]^+$ (0.4), 56 $[M – NO_2 – NO]^+$ (6.4), 46 $[NO_2]^+$ (12.3), 40 $[M – 2NO_2]^+$ (32.5), 31 (100.0), 30 (87.3).

Anal. Calcd for $C_3H_4N_2O_4$: C, 27.28; H, 3.05; N, 21.21. Found: C, 27.20; H, 3.23; N 21.22.

3-Nitroisoxazoline *N*-Oxide (2)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (t, 2 H, J = 9.0 Hz, CH_2), 4.73 (t, 2 H, J = 9.0 Hz, CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.57 (CH_2), 64.60 (CH_2), 127.32 (CNO_2).

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(11) Separation of the reaction mixture by column chromatography (silica gel, *n*-hexane–$CHCl_3$, 3:1) led to partial decomposition of **1**.

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