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Synthesis and Structure of 1,3,3,3-Tetrabromo-1-nitropropene

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Abstract—Preparation of a previously unexplored *gem*-bromonitroethene compound, 1,3,3,3-tetrabromo-1-nitropropene, is reported. The product structure has been confirmed by IR, UV, ^{1}H and ^{13}C NMR spectroscopy (including HMBC).

Keywords: conjugated nitroalkene, *gem*-halonitroethene, 1,3,3,3-tetrabromo-1-nitropropene, bromination, dehydrobromination

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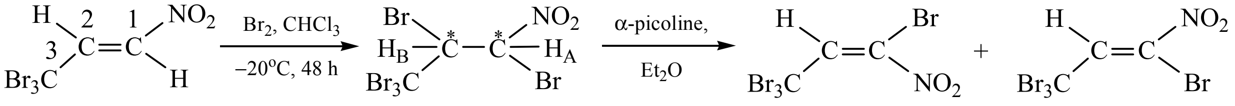
Highly reactive conjugated nitroalkenes can be used as starting materials for preparation of organic compounds of different classes [1, 2]. Due to the presence of halogen atom, *gem*-halonitroethenes are of special interest [2, 3]. The only representative of *gem*-halonitroethenes containing the trihalomethyl group, 1-bromo-1-nitro-2-trichloromethylethene (1-bromo-1-nitro-3,3,3-trichloropropene) exhibits bactericidal properties [4] and is considered a promising reagent for preparation of functionalized carbocyclic [5] and heterocyclic [6–10] compounds such as aziridines, benzodioxoles, hydrogenated benzofurans, oxanorbornenes, etc.

We developed a method to prepare a new representative of the trihalomethyl-containing *gem*-bromonitroethenes family, 1,3,3,3-tetrabromo-1-nitropropene, starting from 3,3,3-tribromo-1-nitropropene [11]. Bromination of the latter was carried out at –20°C during 48 h using equimolar amounts of nitroalkene **I** and bromine (solution in chloroform). The so obtained 1,2,3,3,3-pentabromo-1-nitropropane **IIa**, **IIb** was a volatile oily substance (Scheme 1).

The bromination product was then dehydrobrominated with equimolar amount of α-picoline solution in diethyl ether to give 1,3,3,3-tetrabromo-1-nitropropene (mixture of the *E*-**IIIa** and *Z*-**IIIb** isomers, 8 : 1 ratio with total yield of 82%). The individual *E*-isomer **IIIa** was isolated by column chromatography (silica gel, heptane as eluent).

^{1}H NMR spectrum of 1,2,3,3,3-pentabromo-1-nitropropane **II** contained two sets of doublet signals of methine protons, indicating the presence of two diastereomers **IIa** and **IIb** in the mixture (the ratio of 20 : 1). The signals at 7.00 (H$_A$, $^3J_{HH}$ 1.95 Hz) and 5.76 ppm (H$_B$, $^3J_{HH}$ 1.95 Hz) were assigned to the **IIa** isomer; the signals at 6.73 (H$_A$, $^3J_{HH}$ 5.68 Hz) and 5.31 ppm (H$_B$, $^3J_{HH}$ 5.68 Hz) were assigned to the **IIb** isomer. The following correlations were revealed between the signals of methine protons and the signals of carbon atoms in ^{1}H–^{13}C HMBC spectrum of **IIa**, **IIb** (Fig. 1): **IIa,** H$_A$ (7.00 ppm)/C^1 (84.54 ppm, J_{CH} 170.86 Hz), H$_B$ (5.76 ppm)/C^2 (65.34 ppm, J_{CH} 157.80 Hz), H$_A$/C^3 (35.66 ppm), and H$_B$/C^3 (35.66 ppm); **IIb,** H$_A$ (6.73 ppm)/C^1 (77.50 ppm, J_{CH} 165.02 Hz), H$_B$

Scheme 1.



I **IIa, IIb** *E*-**IIIa** *Z*-**IIIb**

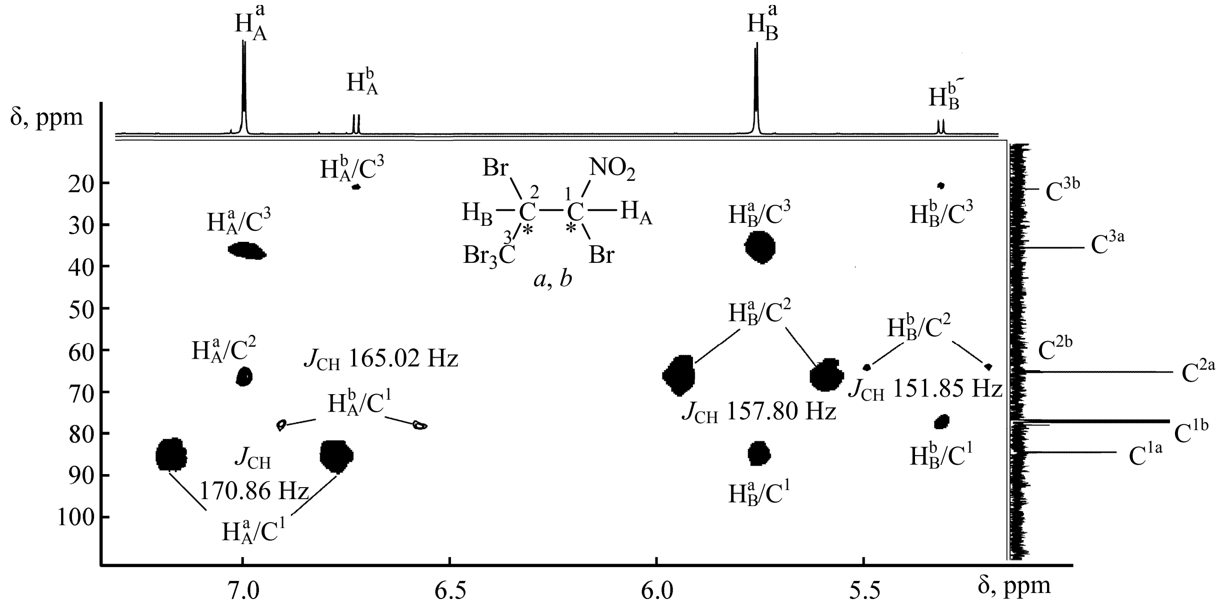


Fig. 1. ^{1}H–^{13}C HMBC spectrum of **IIa**, **IIb**.

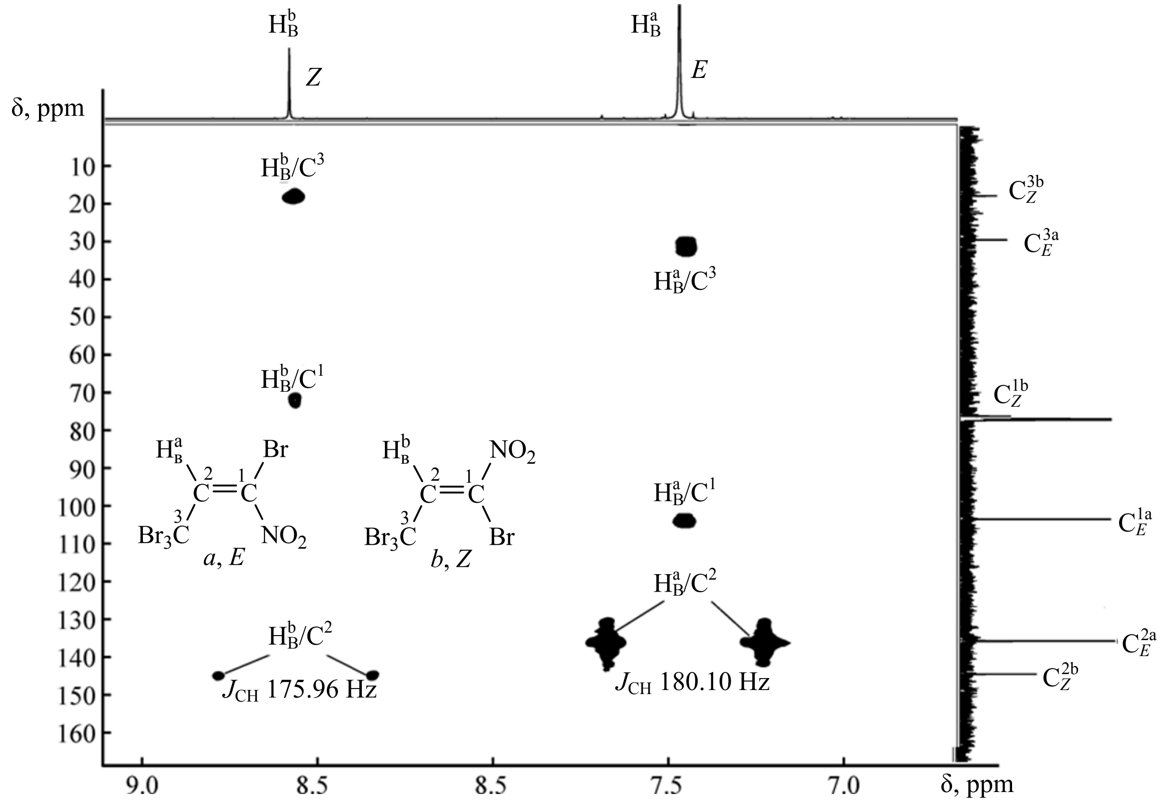


Fig. 2. ^{1}H–^{13}C HMBC spectrum of **IIIa**, **IIIb**.

(5.31 ppm)/C^2 (65.11 ppm, J_{CH} 151.85 Hz), H$_A$/C^3 (20.28 ppm), and H$_B$/C^3 (20.28 ppm).

IR spectrum of the **IIa**,**b** mixture contained the absorption bands assigned to vibrations of non-conjugated nitro group at 1586, 1561 and 1341, 1317 cm^{-1}.

^{1}H NMR spectrum of 1,3,3,3-tetrabromo-1-nitropropene **III** contained signals of two olefinic protons at 7.47 (*E*-**IIIa**) and 8.57 ppm (*Z*-**IIIb**), being in line with the data for structurally similar compounds [3, 12, 13]. ^{13}C NMR and ^{1}H–^{13}C HMBC spectra of 1,3,3,3-tetrabromo-1-nitropropene also contained two sets of signals of carbon atoms.

The proton signal of *E*-isomer **IIIa** (7.47 ppm) in ^{1}H–^{13}C HMBC spectrum (Fig. 2) was correlated with the signal of C^2 atom (135.96 ppm, direct constant J_{HC} of 180.10 Hz). The signals at 103.75 and 29.80 ppm were assigned to the C^1 and C^3 (CBr_3) carbon atoms, respectively. The *Z*-isomer **IIIb** proton signal at 8.57 ppm was correlated with the signal of C^2 atom at 144.72 ppm, having a direct constant J_{HC} of 175.96 Hz. The signals at 76.85 and 18.14 ppm were assigned to the C^1 and C^3 (CBr_3) carbon atoms, respectively. The unusual signal of the tribromomethyl carbon atom, upfield-shifted as compared with that in the $CC1_3$ group (87.90 ppm) was likely explained by "the heavy atom effect" [14]. IR spectrum of **IIIa** contained absorption bands at 1586 and 1319 cm^{-1}, assigned to the nitro group. UV spectrum of **IIIa** contained absorption band with λ_{max} of 263 nm (ε = 4925).

EXPERIMENTAL

IR spectra of the solutions in chloroform were obtained with the Shimadzu IRPrestige-21. UV spectra of the solutions in ethanol were recorded with the Shimadzu UV 2401 PC spectrophotometer (quartz cell, l = 0.1 cm, $c \approx 0.002$ mol L^{-1}). NMR spectra of the solutions in chloroform-d_1 were recorded with the Jeol ECX400A spectrometer operating at 399.78 MHz (^1H) and 100.53 MHz (^{13}C). The signals of residual non-deuterated solvent served as internal reference. Elemental analysis was performed with the Eurovector EA 3000 (CHN Dual mode) analyzer.

Column chromatography was performed at the Macherey-Negel (L 140/270 μ, Germany) silica gel using the Trappe eluotropic series of solvents with the gel to the medium ratio of 1 : 10 (w/w) [15]. The R_f values were determined using the Silufol UV 254 plates, via eluting with 2 : 1 hexane–acetone mixture and developing with iodine vapor or UV radiation (λ = 254 nm).

Nitroalkene **I** was prepared as described elsewhere [11].

1,2,3,3,3-Pentabromo-1-nitropropane (IIa, IIb). 0.7 mL (2.0 g, 0.0124 mol) of bromine was added to a solution of 4.0 g (0.0124 mol) of 3,3,3-tribromo-1-nitropropene in 4 mL of chloroform. The reaction mixture was incubated during 48 h at –20°C and then poured into a Petri dish. After removal of residual bromine, 5.41 g (90%) of 1,2,3,3,3-pentabromo-1-nitropropane **IIa,b** was obtained as colorless oily liquid (R_f 0.80, 0.68); the product was used in further reactions without purification. According to the ^1H and ^{13}C NMR spectra, the resulting substance was a 20 : 1 mixture of diastereomers **IIa** and **IIb**.

1,3,3,3-Tetrabromo-1-nitropropene (III). A solution of 1.1 mL (1.04 g, 0.0112 mol) of α-picoline in 5 mL of diethyl ether was added to a solution of 5.41 g (0.0112 mol) of **IIa, IIb** in 15 mL of diethyl ether. The reaction mixture was incubated at room temperature during 30 min and then diluted with 10 mL of water. The ether layer was separated off, dried over calcium chloride, and evaporated on a rotary evaporator. Yield 3.70 g (82%), dark-red oil, a mixture of *E*- and *Z*-isomers in the ratio of 8 : 1. The mixture was purified by silica gel chromatography (eluting with hexane) to give a yellow-green oily substance, a mixture of *E*- and *Z*-isomers, R_f 0.68, 0.54. Found, %: C 8.97, 8.99; H 0.28, 0.25; N 3.45, 3.41. $C_3HBr_4NO_2$. Calculated, %: C 8.93, H 0.25, N 3.47.

Repeated chromatography of the mixture of *E*- and *Z*-isomers yielded individual *E*-isomer **IIIa** (yellow oil, R_f 0.68). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.47 s (H_B). ^{13}C–{^1H} NMR spectrum ($CDCl_3$), δ_C, ppm: 29.80 (C^3), 135.96 (C^2, J_{CH} 180.1 Hz), 103.75 (C^1).

Physico-chemical studies were performed at the Center for Collective Use in Herzen State Pedagogical University of Russia.

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