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3,3,3-Tribromo-1-nitropropene: Synthesis and Structure

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Abstract—3,3,3-Tribromo-1-nitropropene and its precursors such as 2-hydroxy- and 2-acetoxy-1,1,1-tribromo-1-nitropropanes were prepared and characterized by IR, UV, ^{1}H, ^{13}C, HMQC, and HMBC NMR spectroscopy methods. Structure of tribromomethylnitroalkene was studied by X-ray diffraction.

Keywords: conjugated nitroalkenes, tribromomethyl group, synthesis, condensation structure

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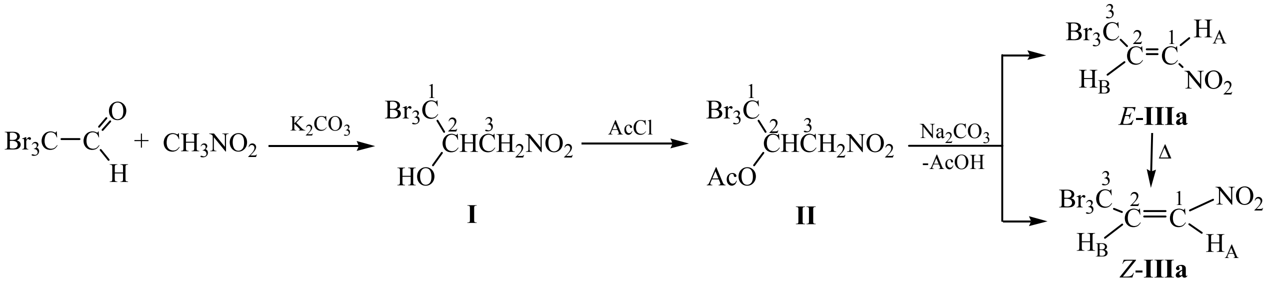
Conjugated nitroalkenes containing trihalomethyl group vicinal with respect to the nitro group are promising and intensively studied compounds [1–3].

First vicinal trihalomethylnitroalkenes (trifluoro- [4], trichloro- [5, 6], and tribromomethylnitroethenes [7]) have been synthesized in the second half of the last century. Compounds of this type are potential physiologically active substances: trichloromethylnitroethene is known for fumigant [8] and nematocidal [9] activity. Furthermore, highly reactive trihalomethylnitroethenes are used as building blocks for preparation of pharmacologically active peptides [10] and various classes of organic compounds. A wide range of linear [11–13], carbocyclic (cyclobutane [1] and norbornene [14]), and heterocyclic (benzopyran [15], chromen [16], oxazoline [17], and oxanorbornene [18, 19]) compounds have been obtained using trifluoro- and trichloromethylnitroalkenes.

Unlike trifluoro- and trichloromethylnitroethenes, structure and chemical properties of tribromomethylnitroethene have not been studied so far. The only data available concerning this compound have been its preparation method, melting point, and UV spectrum [7].

In this work, 3,3,3-tribromo-1-nitropropene was synthesized by one of the known methods starting from the corresponding nitro alcohol [7]. At the first stage, condensation of tribromoacetic aldehyde with nitromethane afforded 1,1,1-tribromo-2-hydroxy-3-nitropropane **I**. The second stage, reaction of nitro alcohol **I** with acetyl chloride, resulted in 2-acetoxy-1,1,1-tribromo-3-nitropropane **II** with yield of 81%. Deacylation of **II** (80°C, benzene, Na_2CO_3) gave a mixture of

Scheme 1.



Z- and *E*-isomers of 3,3,3-tribromo-1-nitropropene *E*-**IIIa** and *Z*-**IIIb** with overall yield of 83% (Scheme 1).

According to the ^{1}H NMR spectrum, the molar ratio of **IIIa** to **IIIb** in the reaction mixture was of 12 : 1 (Fig. 1). *E*-Isomer **IIIa** was isolated by flash chromatography (silica gel, carbon tetrachloride as eluent); it was a crystalline solid melting at 48–49°C. Melting point data and UV spectrum parameters (λ_{max} 225 nm, ε 11570) of nitroalkene **IIIa** obtained in this work coincided with those of the reference sample (mp 50°C, λ_{max} 225 nm [7]).

In this work, structure of the intermediates **I** and **II** as well as of the final products **IIIa** and **IIIb** was studied for the first time using UV, IR, ^{1}H, ^{13}C, and heteronuclear (HMQC, HMBC) NMR spectroscopy methods, involving comparison with the structurally similar fluoro- and chloro-substituted species [20, 21].

In the ^{1}H and ^{13}C NMR spectra of compounds **I**–**III**, signals of the hydrogen and carbon atoms of all structural fragments of the molecules were identified; the assignments were performed taking advantage of HMQC and HMBC methods.

In the ^{1}H NMR spectrum of nitro alcohol **I**, magnetically nonequivalent protons of the methylene group gave rise to two signals at 4.70 (H^{a}) and 5.14 ppm (H^{b}) with the geminal constant of $^{2}J_{HH}^{a\,b}$ 13.43 Hz. The methine proton resonated at 4.95 ppm and was coupled with the methylene protons ($^{3}J_{HH}^{a}$ 1.93 and $^{3}J_{HH}^{b}$ 9.16 Hz). The signal at 3.77 ppm corresponded to the hydroxyl group. In the HMQC spectrum of **I**, a correlation was revealed between signals of methylene protons and of the corresponding carbon atoms (H^{a}/C^{3} 77.04 ppm, H^{b}/C^{3}), as well as between signals of methine proton and C^{2} (80.54 ppm). Carbon atom of tribromomethyl group resonated at 45.22 ppm.

The presence of additional electron-withdrawing substituent (acetoxy moiety) in the molecule of **II** led to a downfield shift of all the signals: methylene protons H^{a} and H^{b} manifested at 4.83 and 5.21 ppm with the geminal constant $^{2}J_{HH}^{a\,b}$ of 13.90 Hz; the methine proton signal was observed at 6.28 ppm with the spin-spin coupling constants $^{3}J_{HH}^{a}$ 8.85 and $^{3}J_{HH}^{b}$ 2.14 Hz. The methyl protons of acetoxy group resonated as a singlet at 2.21 ppm. The HMQC spectrum of compound **II** contained the following cross-peaks: H^{a}/C^{3} (76.13 ppm), H^{b}/C^{3}; H^{2}/C^{2} (77.64 ppm), and C$\underline{H}_3$ (2.21 ppm)/$\underline{C}H_3$ (20.61 ppm). The signals at 37.41 and 168.29 ppm corresponded to tribromomethyl and carbonyl groups, respectively.

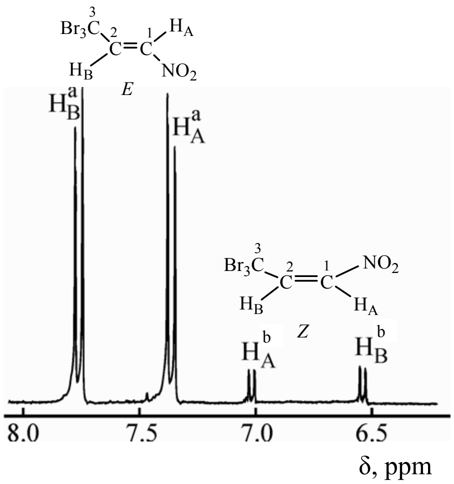
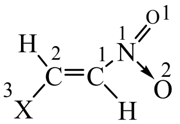


Fig. 1. Fragment of ^{1}H NMR spectrum of the 10 : 1 mixture of isomers *E*-**IIIa** and *Z*-**IIIb**.

In the IR spectra of compounds **I** and **II**, the nonconjugated nitro group resulted in absorption bands at 1557–1560 and 1372–1379 cm^{-1}. The absorbance band at 3445 cm^{-1} corresponded to hydroxyl group of **I**. Strong absorption band at 1767 cm^{-1} was due to carbonyl group stretching.

The ^{1}H NMR spectrum of nitroalkene **IIIa** contained two doublets corresponding to vicinal protons H$_A$ and H$_B$ at 7.36 and 7.76 ppm, respectively, with the

Bonds lengths (*d*, Å) in the nitroethene fragments of molecules of **IIIa** and model compound **A** [24]



X = CBr$_3$ (**IIIa**), carbohydrate residue (**A**).

Bond	**IIIa**	**A**
N^{1}=O^{1}	1.212(9)	1.217
N^{1}=O^{2}	1.228(8)	1.227
N^{1}–C^{1}	1.453(9)	1.455
C^{1}=C^{2}	1.306(8)	1.305
C^{2}–C^{3}	1.486(9)	1.501
C^{3}–Br^{1}	1.941(7)	–
C^{3}–Br^{2}	1.961(6)	–
C^{3}–Br^{3}	1.932(6)	–

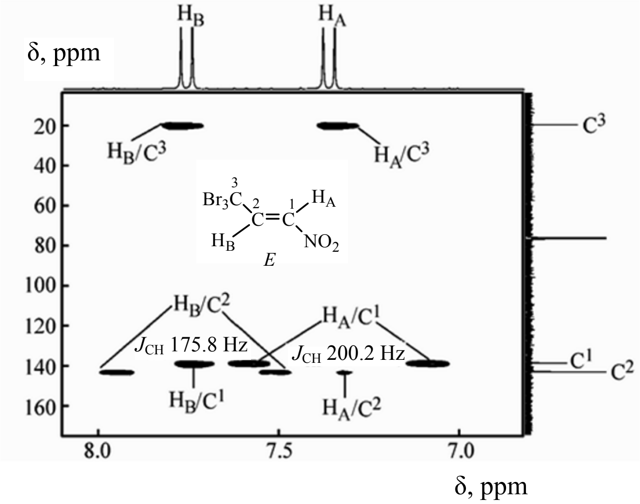


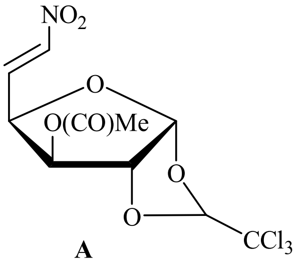
Fig. 2. ^{1}H–^{13}C HMBC spectrum of compound **IIIa**.

spin-spin coupling constant $^3J(H_AH_B)$ of 12.51 Hz, confirming the *E*-configuration of the compound (Fig. 1). In the HMBC spectrum of **IIIa** (Fig. 2) the olefinic protons signals correlated with the signals of the corresponding carbon atoms: H_A/C^1 (139.74 ppm) $J(C^1H_A)$ 200.21 Hz; H_A/C^2 (144.12 ppm); H_A/C^3 (20.24 ppm) and H_B/C^1; H_B/C^2 $J(C^2H_B)$ 175.80 Hz; H_B/C^3. Apparently, unusual position (20.24 ppm) of the tribromomethyl group carbon signal (as compared to the signal of the CCl_3 fragment of trichloromethylnitroalkene, δ 88.1 ppm [20]) can be explained by the "heavy atom" effect [22]. In the IR spectrum of the *E*-nitroalkene **IIIa**, vibration bands of the conjugated nitro group appeared at 1543 and 1347 cm^{-1}; the absorption band at 1658 cm^{-1} was assigned to stretching of the C=C bond.

In the ^{1}H NMR spectrum of the mixture of the nitroalkene isomers (Fig. 1), the signals at 7.01 and 6.56 ppm corresponded to olefinic protons H_A and H_B, respectively, of compound **IIIb**; the value of spin-spin coupling constant (9.46 Hz) confirming their *cis*-orientation. Similar value of the coupling constant was found in the case of *Z*-nitrostyrene [23]. In the HMBC spectrum of the mixture of compounds **IIIa** and **IIIb**, besides the cross-peaks corresponding to *E*-isomer **IIIa** (Fig. 2), the correlation signals of *Z*-isomer **IIIb** were found: H_A/C^1 (129.86 ppm), $J(C^1H_A)$ 177.91 Hz; H_A/C^2 (75.72 ppm); H_A/C^3 (20.38 ppm) and H_B/C^1; H_B/C^2 $J(C^2H_B)$ 177.09 Hz; H_B/C^3.

Structure of nitroalkene **IIIa** was studied by X-ray diffraction. General view of the molecule of **IIIa** is shown in Fig. 3, some bond lengths are collected in table.

The $O_2NC^1{=}C^2{-}C^3{-}Br^1$ fragment was planar within ±0.018(6) Å; the nitro and tribromomethyl groups were *trans*-positioned. Within experimental accuracy, bond lengths of nitroethene fragment of **IIIa** were equal to those of the same fragment with the *trans*-positioned substituents (nitro and furanose ring) in the molecule of compound **A** [24] (see Table) reported in the Cambridge Structural Database (CCDC 109502) [25].



A

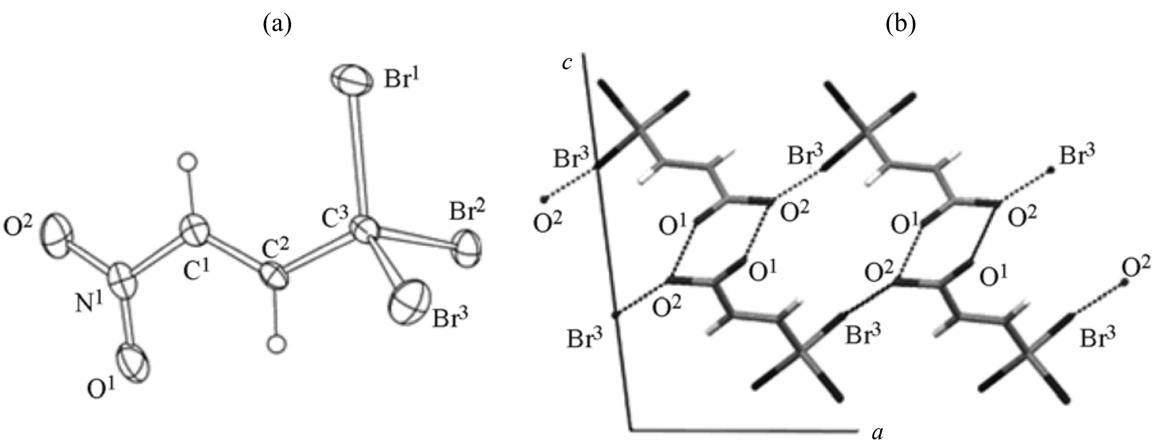


Fig. 3. General view (a) and crystal packing (b) of the molecule of **IIIa**.

Interestingly, the Cambridge Structural Database includes only eight compounds containing CBr_3 group, and none of them contained CBr_3 group adjacent to the C=C double bond. Hence, in this work we have presented the first example of such structure.

In the crystal structure of compound **IIIa**, chains were present along the axis *b* owing to interaction of the NO_2 groups: $O^1\cdots O^2$ 3.034(9), $O^1\cdots N^1$ 2.212(9), $O^1\cdots C^1$ 3.037(9) Å, the sum of Van der Waals radii being of about 3.16 (O···O), 3.22 (O···N), and 3.35 (O···C) Å [26]). The chains were stacked into layers parallel to the *b*, *c–a* plane due to interaction between the NO_2 and CBr_3 groups with contracted $O^2\cdots Br^3$ 2.938(6) contacts {interlayer contacts $Br^2\cdots Br^2$ 3.611(1), the sum of Van der Waals radii being of 3.45 (O···Br) and 3.74 (Br···Br) Å [26]}.

EXPERIMENTAL

IR spectra of the solutions in chloroform were recorded with the Shimadzu IRPrestige-21 spectrophotometer. ^1H NMR spectra of the solutions in $CDCl_3$ were registered with the Jeol ECX400A spectrometer [399.78 (^1H), 100.525 MHz (^{13}C)] relative to the signal of residual solvent protons.

E-Isomer of the final product was isolated by column chromatography on silica gel Macherey-Negel (L 140/270 μ, Germany) at the material to medium ratio of 1 : 10 (w/w) using the Trappe eluotropic series of solvents [27].

X-Ray diffraction studies were performed at 200(2) K with the Bruker Kappa APEX II diffractometer (MoK_α, graphite monochromator, CCD detector, $2\theta_{max}$ 60.0°). Single crystals of compound **IIIa** were grown from solution in carbon tetrachloride. The crystals were monoclinic, the unit cell parameters were as follows: *a* 6.2735(6), *b* 5.8979(5), *c* 10.641(1) Å, β 97.389(4)°, *V* 390.46(6) $Å^3$, space group $P2_1$, *Z* 2, $C_3H_2Br_3NO_2$, d_{calc} 2.754 g cm^{-3}, μ 15.428 mm^{-1}, fragment size 0.45 × 0.40 × 0.10 mm. Intensity of 2245 independent reflections was measured. Absorption was corrected for in SADABS software (transmission 0.0237–0.1031). The structure was solved by the direct method and refined in the anisotropic-isotropic approximation (H atoms) using SHELXS-97 software. Positions of the hydrogen atoms were geometrically calculated; parameters of the hydrogen atoms were refined in the isotropic approximation by a *rider* model. Final refinement parameters: wR_2 0.1129, *S* 1.104, 82 refinements (*R* 0.0436 for 1900 $F > 4\sigma$). Atomic coordinates, bond lengths and angles were deposited in the Cambridge Structural Database (CCDC 947898).

1,1,1-Tribromo-2-hydroxy-3-nitropropane (I). Nitromethane (5.4 mL, 0.1 mol) was added upon stirring to a solution of 20 g (0.067 mol) of bromal in 30 mL of water. 0.8 g of K_2CO_3 was then added in several portions to the reaction mixture during 30 min upon heating (45–50°C) and stirring. The reaction mixture was neutralized with dilute hydrochloric acid. The resulting nitro alcohol was separated off in a separating funnel. The washings were extracted with chloroform (3 × 25 mL); the chloroform extracts were combined with the main fraction, dried over $CaCl_2$, and concentrated to yield 20.85 g (91%) of **I.** Colorless oil, crystallizing upon cooling, mp 76–78°C (mp 78°C [28]).

2-Acetoxy-1,1,1-tribromo-3-nitropropane (II). Acetyl chloride (8.7 mL, 0.122 mol) was added to 20.85 g (0.061 mol) of nitro alcohol **I**. The resulting mixture was heated at a water bath to dissolve the nitro alcohol and then incubated during 12 h at room temperature. Excess of acetyl chloride (about 3.0 mL) was distilled off. The residue was dissolved in 20 mL of hexane and cooled down. The precipitated crystals were filtered off. Yield 22.25 g (95%), mp 66–68°C (ethanol) (mp 66–67°C [7]).

3,3,3-Tribromo-1-nitropropene (III). A mixture of 22.25 g (0.058 mol) of compound **II** in 50 mL of benzene and 6.77 g (0.064 mol) of sodium carbonate was refluxed during 6 h. The resulting precipitate was filtered off, and the solvent was distilled off to give 17.28 g (92%) of dark-orange oil, which was a mixture of isomers *E*-**IIIa** and *Z*-**IIIb** in a ratio of 12:1. *E*-3,3,3-Tribromo-1-nitropropene **IIIa** was isolated by column chromatography (eluting with CCl_4). Yellowish crystals, mp 48–49°C {[mp 50°C, bp 92–95°C (2 mmHg) [7]}. Found, %: C 11.09, 11.15; H 0.65, 0.60; N 4.31, 4.35. $C_3H_2Br_3NO_2$. Calculated, %: C 11.11; H 0.62; N 4.32.

^1H, ^{13}C–{^1H}, ^1H–^{13}C HMQC, ^1H–^{13}C HMBC, and IR spectra were measured at the Center for Collective Use, Spectral Analytical Center, Herzen State Pedagogical University of Russia. X-ray diffraction analysis of single crystals of compound **IIIa** was performed at Department of X-ray diffraction studies, Center for Collective Use, Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences.

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