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On the 100th anniversary of V.V. Perekalin

Alkyl-2,3-dibromo-3-nitroacrylates in the Reactions with Substituted Hydrazines

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Abstract—The interaction of alkyl 2,3-dibromo-3-nitroacrylates with aroylhydrazines at room temperature or with 2,4-dinitrophenylhydrazine under reflux gives the corresponding 2-aroyl(aryl)hydrazono-3-bromo-3-nitropropanoates. Refluxing of ethyl 2,3-dibromo-3-nitroacrylate with a fourfold excess of benzoylhydrazine results in ethyl-2,3-bis(benzoylhydrazono)propanoate. The structure of compounds obtained has been proved by IR, ^{1}H NMR, ^{13}C–{^{1}H} NMR, and electron spectroscopy methods.

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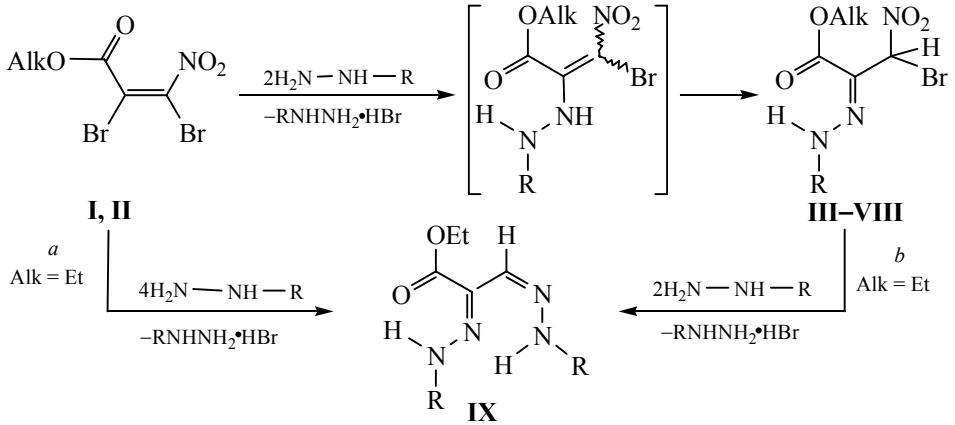
Studies of alkyl 2,3-dibromo-3-nitroacrylates [1] reactions with primary arylamines [2] and *o*-phenylenediamine [3] have revealed high reactivity of these dihalonitroalkenes, acting as both mono- and bielectrophiles. It seems interesting to examine their behavior in the reactions with substituted hydrazines, as the latter have never been involved in the reactions of this type [4, 5]. Theoretically, such interaction can result in the substituted 2-hydrazino-1-bromo-1-nitroethenes prone to the enamine–imine tautomerism [6]. Indeed, the reaction of α-chloro-β-nitrostyrene, the closest analogue of the discussed dihalonitroalkenes, with phenylhydrazine gives the product existing in the imine form, nitroacetophenone phenylhydrazone [7]. Depending on the substituents nature, known hydrazine-containing nitroethenes exist in the imine form or in the form of enamine ⇄ imine isomers mixture [6–8].

In this study we found that the interaction of methyl and ethyl 2,3-dibromo-3-nitroacrylates (**I** and **II**) with benzoyl- and 4-chlorobenzoylhydrazines at the reagents ratio of 1:2 gave aroylhydrazones of β-bromo-β-nitropyruvates **III**–**VI** at room temperature in anhydrous benzene within 2 h.



Alk = Me (**I**), Et (**II**); R = benzoyl: Alk = Me (**III**), Et (**IV**, **IX**); R = 4-chlorobenzoyl: Alk = Me (**V**), Et (**VI**); R = 2,4-dinitrophenyl: Alk = Me (**VII**), Et (**VIII**).

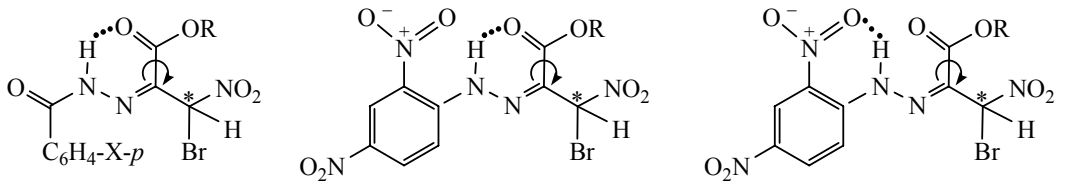
The interaction of **I** and **II** with 2,4-dinitrophenylhydrazine required more severe conditions. The reactions occurred upon refluxing the reactants in anhydrous benzene for 7 h to yield esters of 2,4-dinitrophenylhydrazones of β-bromo-β-nitropyruvates **VII** and **VIII**.

Apparently, the reaction proceeded as a nucleophilic vinyl substitution (S_NVin), but under those conditions the initially formed α-hydrazino-β-bromo-β-nitroacrylate was converted into the imine tautomeric form, hydrazone of β-bromo-β-nitropyruvate. This transformation was likely caused by high acidity of the NH-amino group located at the double bond C=C and by low steric strain of the hydrazone fragment that could be stabilized by the intramolecular hydrogen bonding.

The result of ethyl 2,3-dibromo-3-nitroacrylate **II** reaction with a fourfold excess of benzoylhydrazine was quite surprising. According to TLC, at room temperature only the starting compounds and hydrazone **IV** were found in the reaction mixture. However, under reflux the reaction proceeded within 6 h to give bishydrazone **IX** (method *a*, yield of 69%). The product **IX** was prepared also starting from compound **IV** by refluxing with a twofold excess of benzoylhydrazine in anhydrous benzene (method *b*, yield 79%). The bishydrazone **IX** was previously synthesized from ethyl 3-diazo-2-oxo-propanoate with yield of 61% [9].

In the ^{1}H NMR spectra of hydrazones **III**–**VIII** recorded in $CDCl_3$, the following signals were observed: 7.47–9.17 ppm (benzene ring), 13.38–13.49 ppm (amino group, in the case of **III**–**VI**), 14.40, 14.38 ppm (amino group, in the case of **VII** and **VIII**), 6.95–7.03 ppm (methyne proton of bromo-nitromethyl group), and 3.93–4.01 ppm (OCH_3 in ester) or 1.34–1.40, and 4.39–4.48 ppm (OC_2H_5 in ester) (see table for details).

In the ^{1}H NMR spectra of compounds **IV**, **VI**, and **VIII**, the signals of methylene protons of the ester group appeared as a doublet of quartets with ^2J 10.7–10.9 and ^3J 7.0–7.2 Hz (Fig. 1). Apparently, the observed magnetic non-equivalence (diastereotopicity) of these protons was due to the chirality of the carbon atom of bromonitromethyl group and due to formation of quasi six-membered ring via the intramolecular hydrogen bonding between the NH and C=O groups.



s-cis-Conformers of benzoylhydrazones **III**–**VI** and 2,4-dinitrophenylhydrazones **VII**, **VIII**.

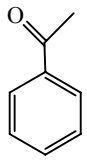
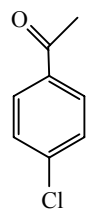
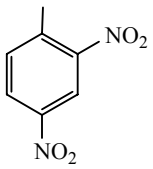
A relatively downfield position of the amino group proton signal in the ^{1}H NMR spectra of **III**–**VIII** was in accordance with the compounds structures, and the difference in the signal positions in the cases of benzoylhydrazones **III**–**VI** and of 2,4-dinitrophenylhydrazones **VII** and **VIII** was due to the influence of two strong electron withdrawing substituents in the benzene ring (**VII** and **VIII**).

The ^{1}H NMR spectrum (δ, ppm) of **VI** recorded in acetonitrile-d_3 solution [1.28 ($C\underline{H}_3$, t, ^3J 7.1 Hz), 4.34, 4.37 ($C\underline{H}_2O$, d. q, ^2J 10.8, ^3J 7.1 Hz), 7.22 ($C\underline{H}BrNO_2$, s), 7.56, 7.83 ($C_6\underline{H}_4$, d, ^3J 8.8 Hz), and 13.02 ($N\underline{H}$, br.s)] was substantially the same as that of **VI** in the $CDCl_3$ solution. Thus, no transformation of **VI** into other isomeric form occurred under the action of CD_3CN.

The signals of all the carbon atoms of **III**–**VIII** were identified in the $^{13}C-\{^1H\}$ NMR spectra; the signals assignment was performed on the basis of heteronuclear correlation experiments (see table and Fig. 2). In the case of **VI**, the $^1H-^{13}C$ HMQC cross-peak (δ_H = 6.95 and δ_C = 78.16 ppm) indicated the presence of bromonitromethyl group in its structure. Two cross-peaks of the aromatic protons doublets at 7.47 and 7.86 ppm with a broadened signal at 129.45 ppm indicated that the latter signal should be assigned to the carbon atoms of the aromatic ring (Fig. 3).

Assignment of C=O and C=N carbon atoms signals was confirmed by the $^1H-^{13}C$ HMBC data (Fig. 4). In particular, hydrazone **VI** cross-peaks of OCH_2 protons signal (4.39 ppm) with the δ_C = 160.09 ppm signal (^3J),

Spectral characteristics of substituted 2-aroyl(aryl)hydrazono-3-bromo-3-nitropropanoates **III–VIII**

Comp. no.	Alk	R	NMR spectra ($CDCl_3$), δ, ppm (*J*, Hz)						IR spectrum ($CHCl_3$), ν, cm^{-1}			Electronic spectrum ($CHCl_3$), λ_{max}, nm [ε, $l\ mol^{-1}\ cm^{-1}$]
			^1H			^{13}C						
			CH_3 (C_2H_5)	CH (NH)	Ar	CH_3 (C_2H_5)	CH (C=N) [C=O]	Ar	C=O (NH)	C=N (Ar)	NO_2[c]	
III	Me		3.93 s	6.97 s (13.42 br.s)	7.52 t (^3J 7.4), 7.63 t (^3J 7.4), 7.93 d (^3J 7.4)	53.56	78.10 (131.08) [160.64, 164.16[a]]	128.23–133.61	1716, 1703[b] (3265)	1600 (1506, 1481)	1577, 1346	288 (18200)
IV	Et		(1.35 t, ^3J 7.0, 4.37 d.q, ^2J 10.7, ^3J 7.0, 4.42 d.q, ^2J 10.7, ^3J 7.0)	6.96 s (13.49 br.s)	7.53 t (^3J 7.3), 7.63 t (^3J 7.3), 7.93 d (^3J 7.3)	(13.71, 63.54)	78.34 (131.44) [160.13, 164.24[a]]	128.21–133.55	1710, 1700[b] (3262)	1601 (1506, 1481)	1577, 1347	289 (17800)
V	Me		3.94 s	6.95 s (13.38 br.s)	7.50 d (^3J 8.5), 7. 87 d (^3J 8.5)	53.62	77.87 (131.16) [160.58, 163.34[a]]	129.44–140.07	1715, 1705[b] (3260)	1595 (1506, 1478)	1578, 1346	297 (22500)
VI	Et		(1.34 t, ^3J 7.3, 4.37 d.q, ^2J 10.9, ^3J 7.3, 4.42 d.q, ^2J 10.9, ^3J 7.3)	6.95 s (13.41 br.s)	7.47 d (^3J 8.5), 7.86 d (^3J 8.5)	(13.70, 63.66)	78.16 (131.65) [160.09, 163.36[a]]	129.45–140.01	1712, 1700[b] (3256)	1594 (1505, 1477)	1578, 1346	296 (20300)
VII	Me		4.01 s	7.03 s (14.40 br.s)	8.12 d (^3J 9.4), 8.48 d.d (^3J 9.4, ^4J 2.5), 9.17 d (^4J 2.5)	53.89	77.65 (129.52) [159.67]	117.74–142.67	1714 (3196, 3100)	1618, 1602 (1502)	1577, 1342	271 (9800) 349 (23400) 377 (26600)
VIII	Et		(1.40 t, ^3J 7.1, 4.46 d.q, ^2J 10.9, ^3J 7.1, 4.50 d.q, ^2J 10.9, ^3J 7.1)	7.01 s (14.39 br.s)	8.12 d (^3J 9.1), 8.47 d.d (^3J 9.1, ^4J 2.5), 9.17 d (^4J 2.5)	(13.95, 63.82)	77.70 (129.88) [159.23]	117.71–142.75	1709 (3196, 3101)	1618, 1602 (1502)	1577, 1342	270 (9500) 347 (23200) 376 (26000)

[a] The signal of the carbon atom of amide moiety. [b] Absorption band of amide carbonyl moiety. [c] Absorption bands of the nitro groups of aromatic rings in the spectra of compounds **VII** and **VIII** were observed at 1529, 1316 and 1528, 1315 cm^{-1} respectively.

and of methyne proton signal (6.95 ppm) with the same signal (^3J) led to assignment of the latter signal to the carbonyl carbon atom of ester. The second cross-peak of methyne proton signal with the broadened weak signal at 131.65 ppm indicated that the latter corresponded to the carbon atom of imino group (^2J). The signal of amide fragment carbonyl carbon atom (at 163.36 ppm) was assigned taking into account the only cross-peak of it with the downfield doublet of aromatic *ortho*-protons at 7.86 ppm (^3J).

The IR spectra gave additional information on the structure of β-bromo-β-nitropyruvic acid hydrazones **III–VIII** (see table). The absorption band of the ester carbonyl appeared as a shoulder in the lower frequency region (1709–1716 cm^{-1}) as compared with the IR spectra of α-arylamino-β-bromo-β-nitroacrylates {ν(C=O) 1748–1755 cm^{-1} [2]}. Likely, that shift was due to formation of hydrogen bonds involving the amino and carbonyl groups of **III–VIII** [10]. That was additionally supported by the position and the shape of the amino group absorption bands (3100–3265 cm^{-1}). The absorption bands at ν_{as} 1577–1578 cm^{-1} and ν_s 1342–1347 cm^{-1} in the IR spectra of **III–VIII** were assigned to the non-conjugated nitro group. The observed value of $\Delta\nu$ = 230–235 cm^{-1}, quite high, was characteristic of the nitro group containing an electron-withdrawing sub-stituent in the *gem*-position [11–13], in the considered cases those were bromine atom and imine group.

The spectra of benzoylhydrazones **III–VI** contained the absorption band of amide carbonyl moiety (1700–1705 cm^{-1}) in addition to the above-mentioned ones. In

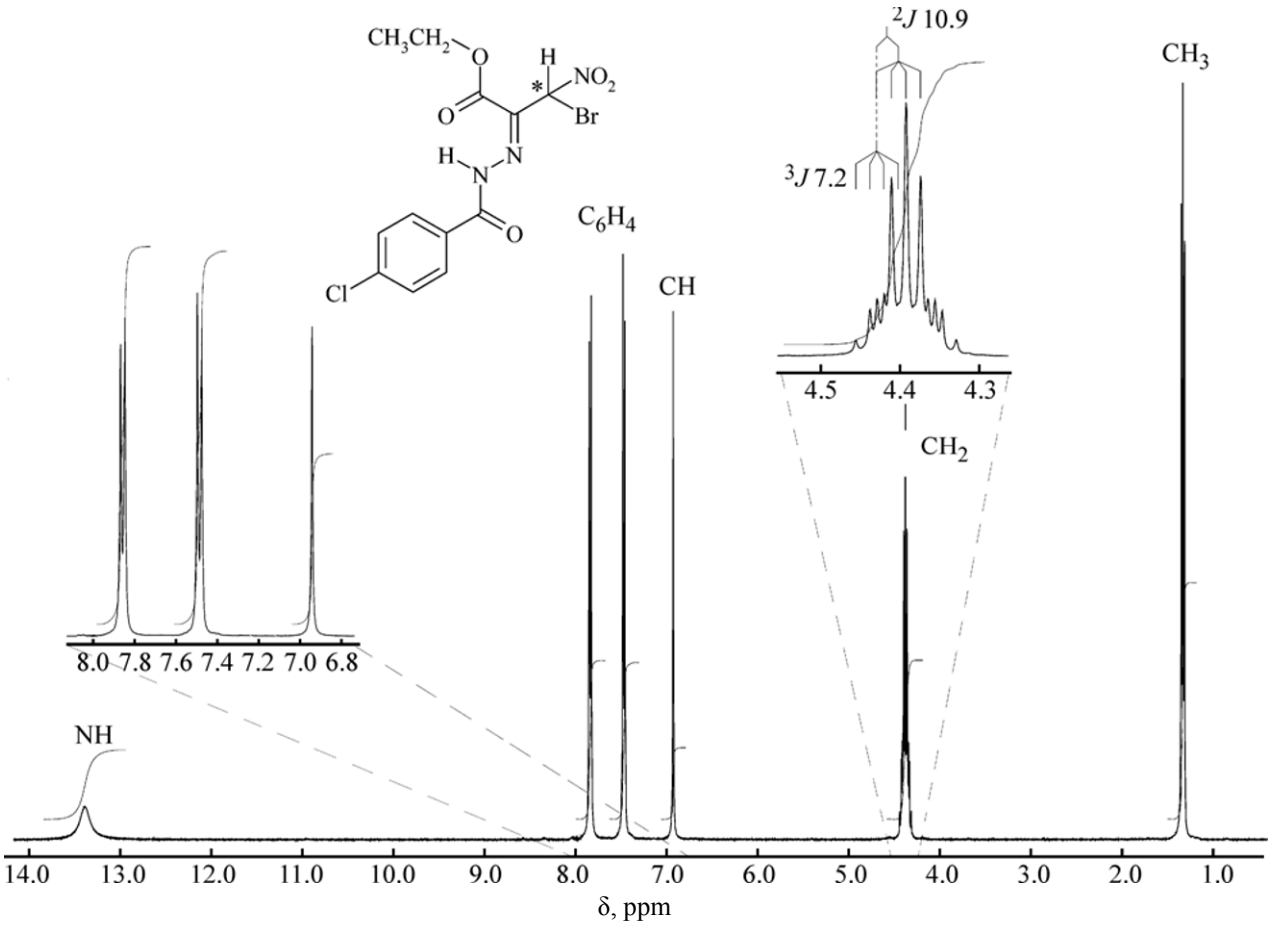


Fig. 1. ^{1}H NMR spectrum of compound **VI** in $CDCl_3$.

contrast, the spectra of hydrazones **VII** and **VIII** contained additionally the absorption bands (1529, 1528 and 1316–1315 cm^{-1}) assigned to the nitro groups of benzene ring. Probably, the electronic effects of imine and alkoxy groups caused the specific shape of intense broadened absorption bands characteristic of an aliphaticconjugated nitro group rather than an aromatic one (compare, for instance, with the spectrum of dinitroaniline [14]).

The electronic spectra of compounds **III**–**VIII** were in agreement with the elucidated structures [15, 16] (see table). The presence of absorption bands at λ_{max} = 347–377 nm in the spectra of **VII** and **VIII** coincided with the spectra of the previously described dinitrophenylhydrazones of ketones (λ_{max} of 360–380 nm, ε 20000–25000) [17]. Probably, those bands corresponded to the electronic transitions involving the imino and dinitrophenylamino groups.

Spectral characteristics of bishydrazone **IX** corresponded to those of the reference spectrum [9].

EXPERIMENTAL

The ^{1}H, ^{13}C–{^{1}H} NMR, ^{1}H–^{13}C HMQC, and ^{1}H–^{13}C HMBC spectra were recorded with Jeol ECX-400A spectrometer [100.52 (^{13}C) and 399.78 MHz (^{1}H)] in deuterochloroform-d_1, acetonitrile-d_3, and DMSO-d_6 using the nondeutarated solvents residual signals as internal reference. The IR spectra were recorded with Shimadzu IRPrestige-21 Fourier spectrometer in KBr pellets. The electronic spectra were recorded with Shimadzu UV2401 spectrophotometer in quartz cuvettes (l = 0.101 cm, c = 0.0004–0.0006 mol l^{-1}), in $CHCl_3$ solutions. Elemental analysis was performed with Eurovector EA3000 (CHN Dual) analyzer. The reaction progress was monitored by thin layer chromatography with Silufol UV-254 plates developed in iodine vapor or by chromatoscope.

Starting methyl and ethyl 2,3-dibromo-3-nitroacrylates **I** and **II** were obtained as described in [1].

Methyl 2-benzoylhydrazono-3-bromo-3-nitropropanoate (III). A solution of 0.25 g (0.85 mmol) of

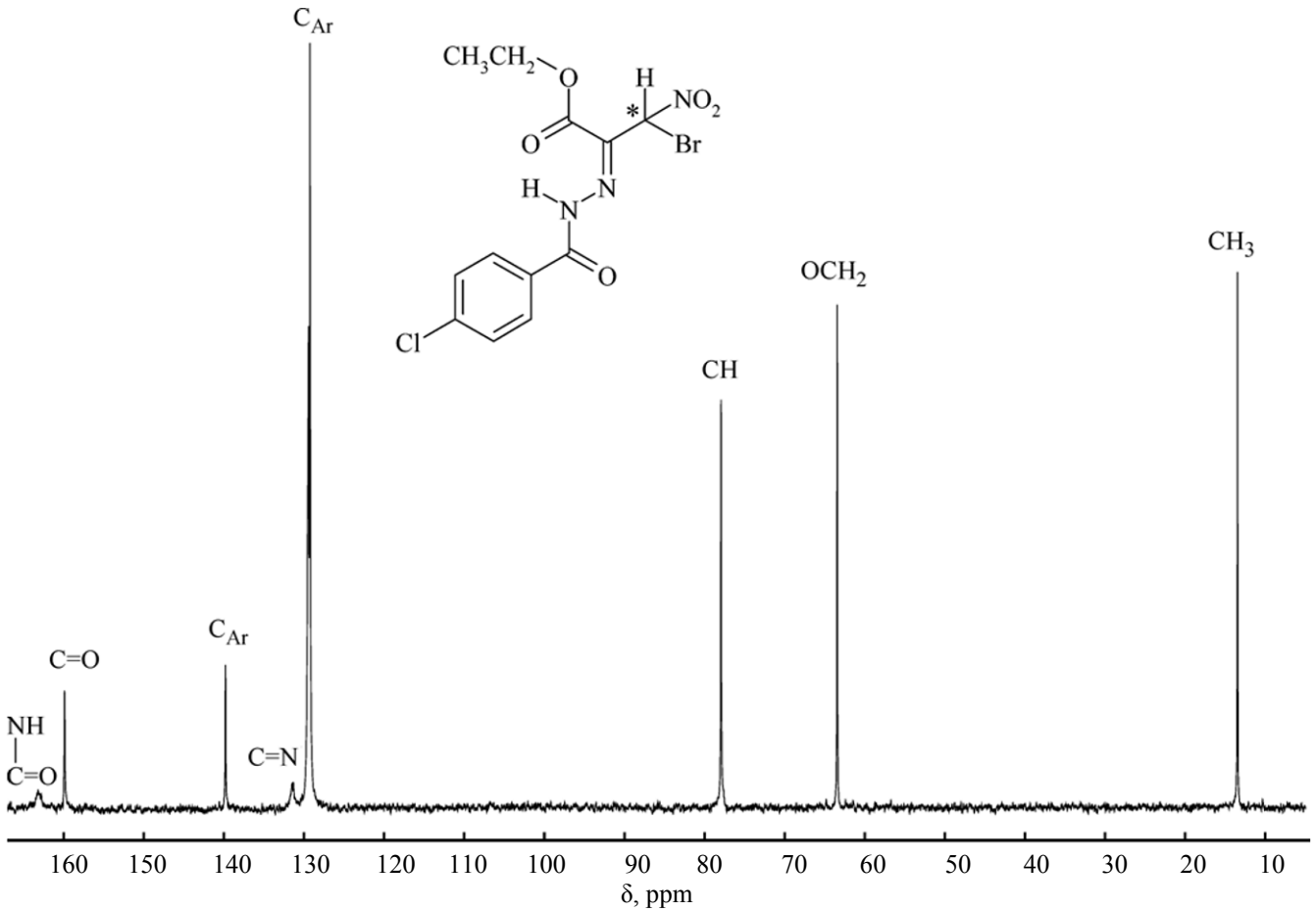


Fig. 2. $^{13}C-\{^1H\}$ NMR spectrum of compound **VI** in $CDCl_3$.

methyl 2,3-dibromo-3-nitroacrylate **I** in 12 ml of anhydrous benzene was added dropwise during 10 min to a suspension of 0.23 g (1.7 mmol) of benzohydrazide in 13 ml of anhydrous benzene. The reaction mixture was stirred at room temperature for 90 min. The precipitated benzohydrazide hydrobromide was filtered off, and solvent was evaporated from the filtrate in a Petri dish. Yield 0.17 g (58%) of colorless crystals, mp 95–97°C (methanol). Found, %: C 38.50, 38.45, H, 3.05, 3.06; N 12.18, 12.17. $C_{11}H_{10}BrN_3O_5$. Calculated, %: C 38.39, H 2.93; N 12.21.

Ethyl 2-benzoylhydrazono-3-bromo-3-nitropropanoate (IV) was prepared similarly to **III**, from 0.37 g (2.76 mmol) of benzohydrazide and 0.42 g (1.38 mmol) of ethyl 2,3-dibromo-3-nitroacrylate **II** in 15 ml of anhydrous benzene. The reaction mixture was stirred for 80 min at 18–20ºC. Yield 0.33 g (67%), colorless crystals, mp 107–108°C (methanol). Found, %: C 40.21, 40.38; H, 3.31, 3.32; N 11.63, 11.59. $C_{12}H_{12}BrN_3O_5$. Calculated, %: C 40.24; H 3.38; N 11.73.

Methyl 3-bromo-2-(4-chlorobenzoylhydrazono)-3-nitropropanoate (V) was prepared similarly to **III**, from 0.52 g (3 mmol) of 4-chlorobenzohydrazide and 0.44 g (1.5 mmol) of methyl 2,3-dibromo-3-nitroacrylate **I** in 20 ml of anhydrous benzene. The reaction mixture was stirred for 120 min at 18–20ºC. After evaporation of the solvent in a Petri dish, the residue was treated with ether. Yield 0.4 g (70%), pale yellow crystals, mp 123–125°C (hexane:ethanol = 1:1). Found, %: C 35.05; H 2.49; N 11.05. $C_{11}H_9BrClN_3O_5$. Calculated, %: C 34.90; H 2.40; N 11.10.

Ethyl 3-bromo-2-(4-chlorobenzoylhydrazono)-3-nitropropanoate (VI) was prepared similarly to **III**, from 0.52 g (3 mmol) of 4-chlorobenzohydrazide and 0.46 g (1.5 mmol) of ethyl 2,3-dibromo-3-nitroacrylate **II** in 20 ml of anhydrous benzene. The reaction mixture was stirred for 120 min at 18–20ºC. Yield 0.49 g (83%), pale yellow crystals, mp 141–142°C (hexane:ethanol = 1:1). Found, %: C 36.81; H 3.23; N 10.53. $C_{12}H_{11}BrClN_3O_5$. Calculated, %: C 36.71; H 2.82; N 10.70.

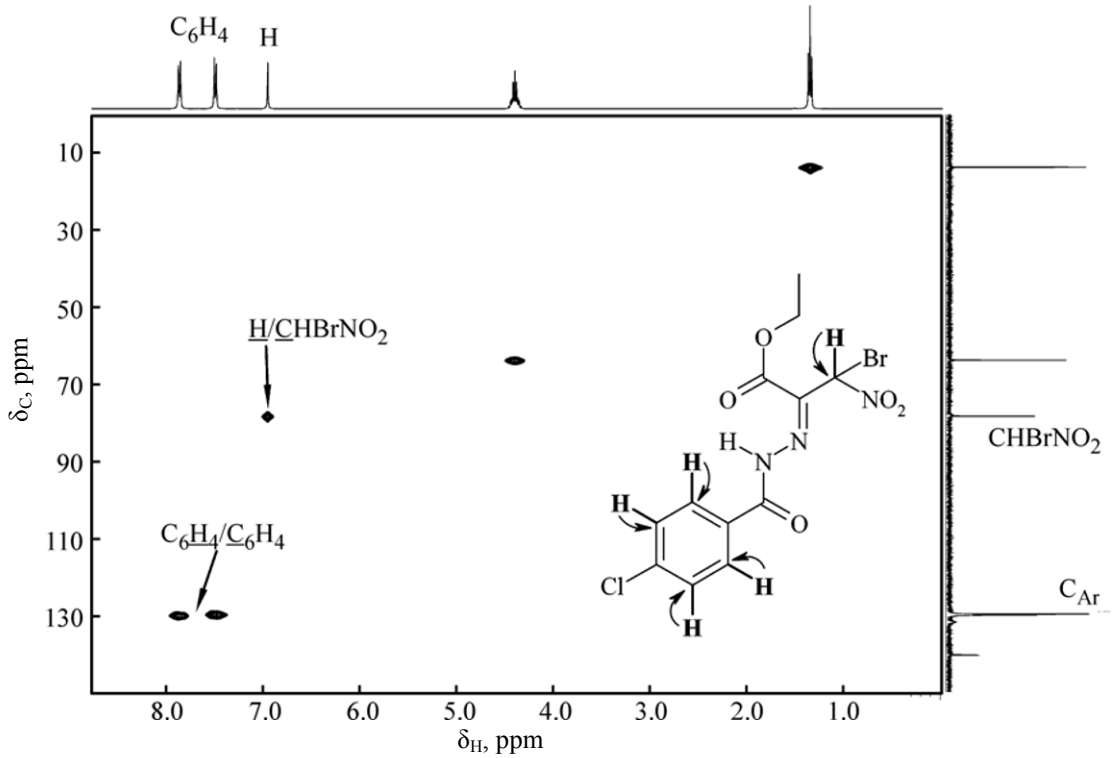


Fig. 3. $^{1}H–^{13}C$ HMQC NMR spectrum of compound **VI** in $CDCl_3$.

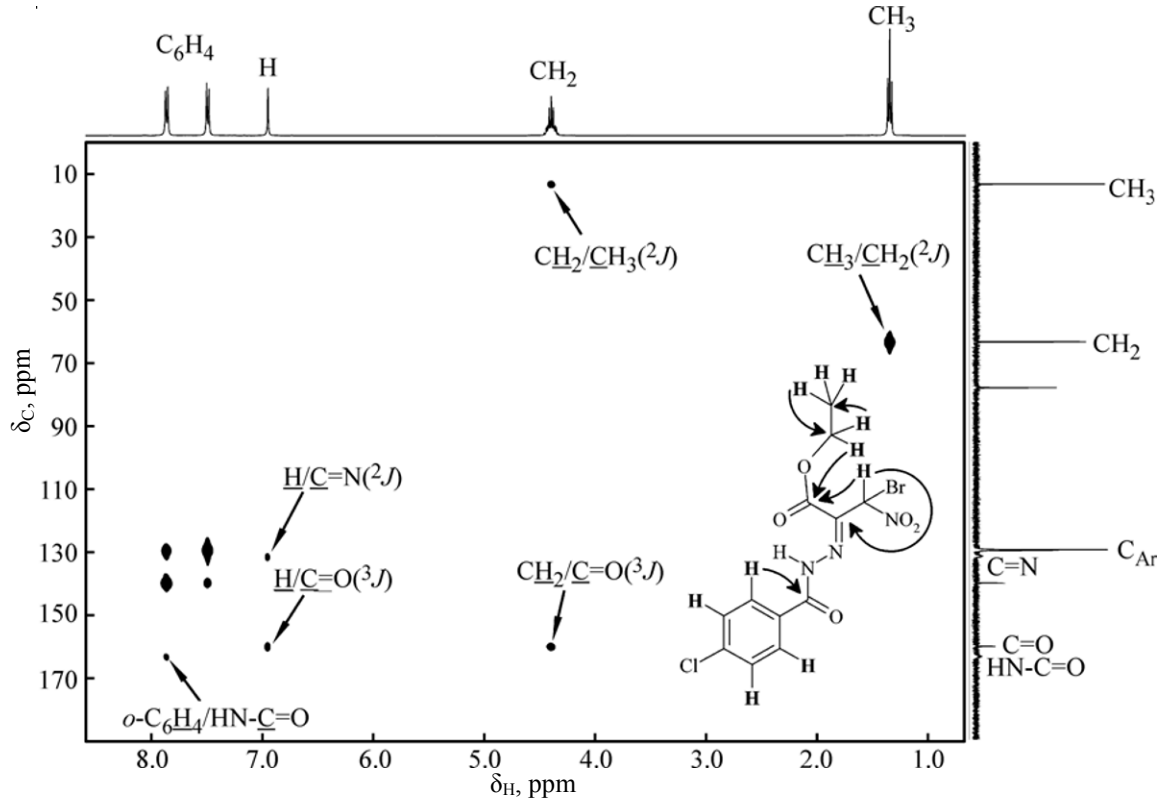


Fig. 4. $^{1}H–^{13}C$ HMBC NMR spectrum of compound **VI** in $CDCl_3$.

Methyl 3-bromo-2-(2,4-dinitrophenylhydrazono)-3-nitropropanoate (VII). A suspension of 0.69 g (3.5 mmol) of 2,4-dinitrophenylhydrazine and 0.5 g (1.7 mmol) of methyl 2,3-dibromo-3-nitroacrylate **I** in 30 ml of anhydrous benzene was refluxed for 7 h, then the precipitated 2,4-dinitrophenylhydrazine hydrobromide was filtered off, and solvent was evaporated from the filtrate in a Petri dish. The residue was treated with ethanol. Yield 0.51 g (72%), orange crystals, mp 154–158°C (methanol). Found, %: C 29.84; H 1.79; N 17.93. $C_{10}H_8BrN_5O_8$. Calculated, %: C 29.58; H 1.99; N 17.25.

Ethyl 3-bromo-2-(2,4-dinitrophenylhydrazono)-3-nitropropanoate (VIII) was prepared similarly to **VII**, from 0.44 g (2.2 mmol) of 2,4-dinitrophenylhydrazine and 0.34 g (1.1 mmol) of ethyl 2,3-dibromo-3-nitroacrylate **II** in 20 ml of anhydrous benzene. Yield 0.31 g (67%), orange crystals, mp 165–167°C (methanol). Found, %: C 31.52, 31.95; H 2.57, 2.64; N 16.10, 16.27. $C_{11}H_{10}BrN_5O_8$. Calculated, %: C 31.45; H 2.40; N 16.67.

Ethyl 2,3-bis(benzoylhydrazono)propanoate (IX). *a*. A mixture of 0.33 g (1.1 mmol) of ethyl 2,3-dibromo-3-nitroacrylate **II** and 0.60 g (4.4 mmol) of benzohydrazide in 35 ml of anhydrous benzene was refluxed for 6 h. After cooling the reaction mixture down to room temperature, the formed precipitate was filtered off and washed with water. Yield 0.28 g (69%), colorless powder, mp 227–228°C (ethanol) {yield 61%, mp 227–229°C (ethanol) [9]}. ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 1.30 t (3H, CH_3), 4.29 q (2H, OCH_2), 7.56–8.32 m (10H, $2C_6H_5$), 8.67 s (1H, =CH), 12.56 s, 14.70 s (2H, NH). IR spectrum (KBr), ν, cm^{-1}: 1512, 1547, 1582, 1600, 1679, 1685, 1711, 3281, 3127. Electronic spectrum (DMSO), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 260 (24800), 350 (15200). Found, %: C 62.44; H 4.98; N 14.78. $C_{19}H_{18}N_4O_4$. Calculated, %: C 62.29; H 4.95; N 15.29.

b. A mixture of 0.211 g (0.59 mmol) of hydrazone **IV** and 0.16 g (1.18 mmol) of benzohydrazide in 15 ml of anhydrous benzene was refluxed for 6 h. After cooling the reaction mixture down to room temperature, the formed precipitate was filtered off and washed with water. Yield 0.17 g (79%), colorless powder, mp 229–230°C (ethanol). The melting point of the mixture of products prepared by the both methods was not depressed.

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

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