ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 5, pp. 954–962. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.M. Berestovitskaya, N.A. Anisimova, O.N. Kataeva, G.A. Berkova, A. Jager, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 5, pp. 811–819.

Reaction of Alkyl-3-nitro- and -3-Bromo-3-nitroacrylates with 2-(2-Nitroethenyl)furan

V. M. Berestovitskaya[a], N. A. Anisimova[a], O. N. Kataeva[b], G. A. Berkova[a], and A. Jager[c]

[a] *Hertzen Russian State Pedagogical University,*
nab. r. Moiki 48, St. Petersburg, 191186 Russia
e-mail:kohrgpu@yandex.ru

[b]*Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center,*
Russian Academy of Sciences, Tatarstan, Russia

[c] *Technical University, Drezden, Germany*

Received July 31, 2007

Abstract—The diene condensation of β-nitro and β-bromo-β-nitroacrylates with 2-(2-nitroethenyl)furan as 1,3-diene leads to a mixture of regioisomeric tetrahydrobenzofurans transforming under the reaction conditions into benzofurancarboxylates due to the easy dehydrohalogenation, denitration, and dehydration. In the case of a *gem*-bromonitroacrylate reaction takes two routes: diene synthesis and alkylation of the furan ring, the latter process prevailing. The structure of products formed was established by spectral methods. The investigation of geometry of 2-(1-methoxycarbonyl-2-nitroethenyl)-5-(2-nitroethenyl)furan by XRD analysis showed that its vinyl fragments have the coplanar chelate-like structure with the cisoid orientation of the CO_2Me and NO_2 groups. The ester group deviates from the plane of the the carbon–carbon multiple bond.

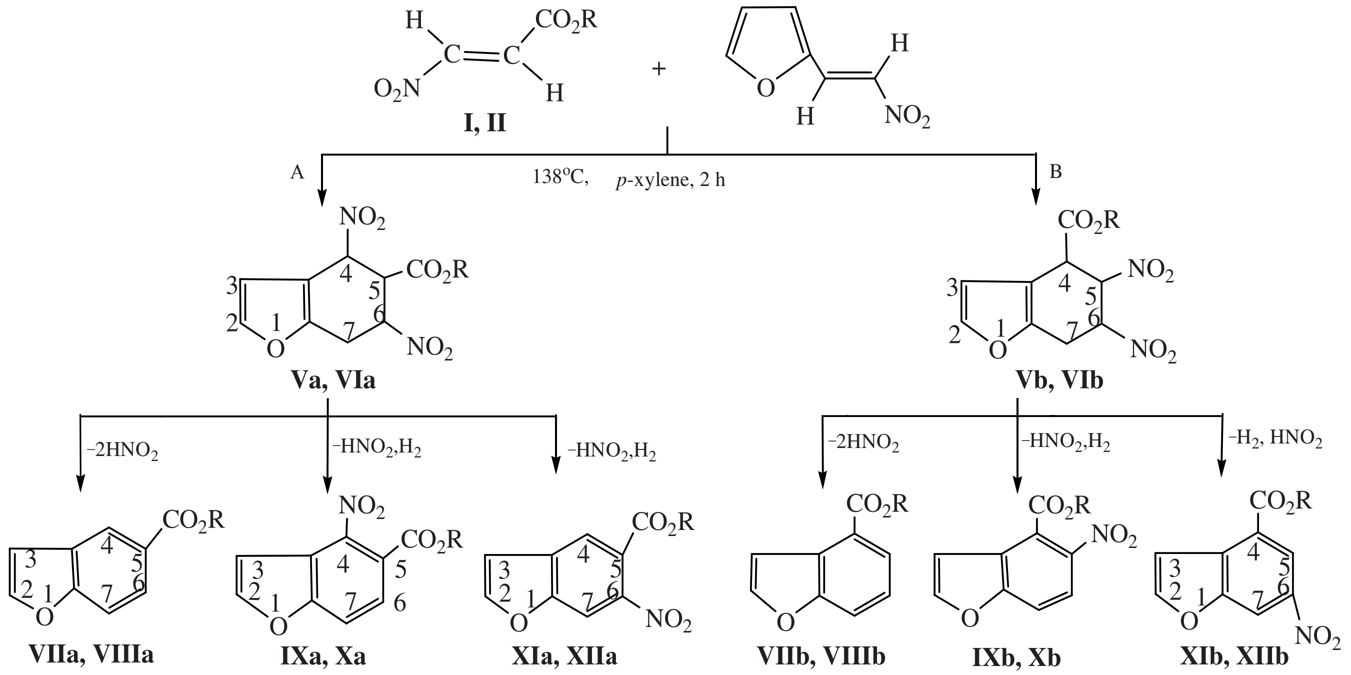
DOI: 10.1134/S1070363208050216

The interest to benzofuran derivatives is due to the wide spread of this bicyclic framework in nature. It is present in the structure of substances from vegetable (carotinoids, alkaloids [1, 2]) and animal kingdoms playing the role of plant growth regulators [3], enzyme inhibitors [4, 5], etc. The benzofuran derivatives are widely used in the cosmetics [6], in the agricultural chemistry, and in the pharmacology [7–9]. The benzofuran ring forms a basis of a series of drugs structures like benzofurocaine (local anesthetic and analgesic), amiodarone (antiarrhythmic), phenycaberon, grizeofulvin, etc. [10].

According to published data one of the methods of preparation of the benzofuran derivatives is Diels–Alder reaction of β-furylnitroethene (the diene component) with methyl acrylate or acrylonitrile (the dienophiles) [1]. The reaction proceeds under rigid conditions (100–140°C, pressure reactor) to give disubstituted tetrahydrobenzofurans that under treating with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) undergo aromatization to the corresponding benzofurans.

We have for the first time investigated the reaction of 3-nitro- and 3-bromo-3-nitroacrylates **I–IV** with 2-(2-nitrovinyl)furan. It was found that 3-nitroacrylates **I, II** enter the diene synthesis with 2-(2-nitrovinyl) furan under boiling in *p*-xylene for 2 h in the presence of aluminum chloride. At first the regioisomeric tetrahydrobenzofurans **Va, Vb**, **VIa**, and **VIb** are formed and under the conditions of diene synthesis they undergo further transformations including the elimination of both nitro groups or the simultaneous dehydration and denitration to corresponding benzofurans having no nitro groups (compounds **VIIa, VIIb, VIIIa**, and **VIIIb**) or to nitro derivatives **IXa, IXb–XIIa, XIIb**.

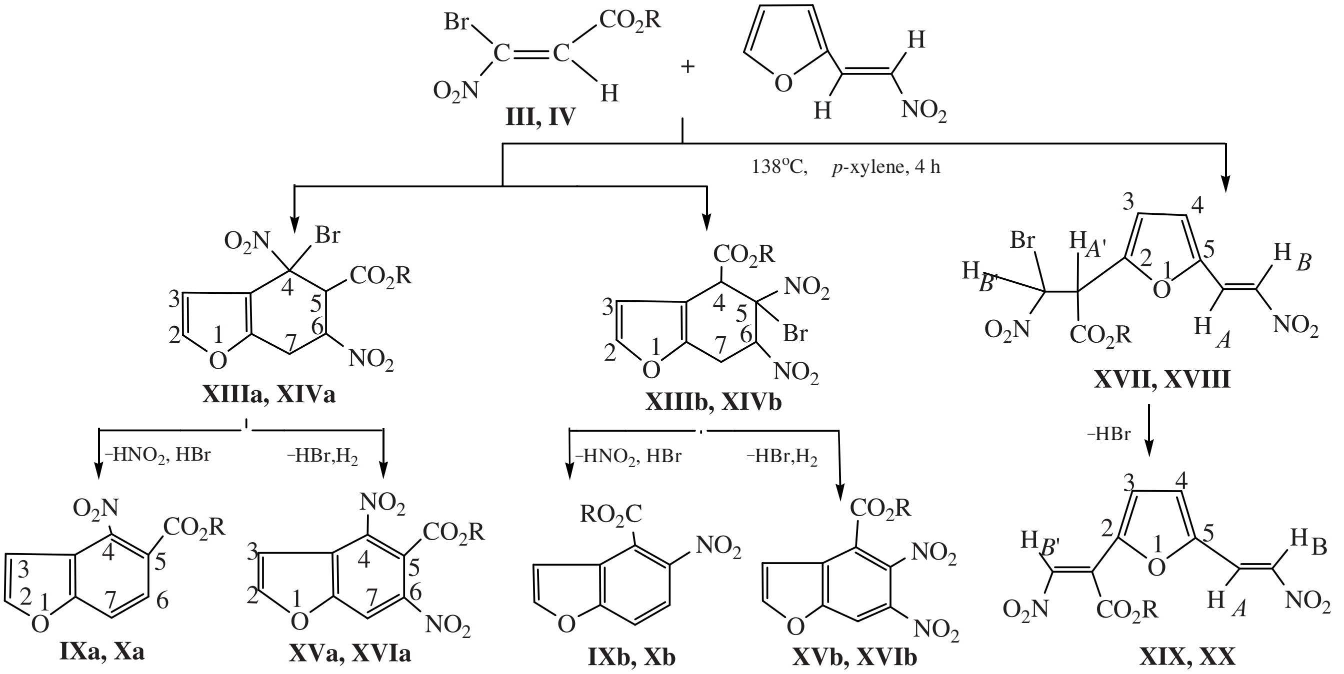
Alkyl 3-bromo-3-nitroacrylates **III, IV** react with 2-(2-nitrovilyl)furan (*p*-xylene, 138°C, 4 h) by two competing pathways to give regioisomeric tetrahydrobenzofurans **XIIIa, XIIIb, XIVa**, and **XIVb**, the products of the diene synthesis, and 2,5-disubstituted furans **XVII, XVIII** resulting from the alkylation with nitroalkenes. Simultaneous proceeding of the Diels–Alder reaction and the alkylation with the activated



R = Me (**I, Va, Vb, VIIa, VIIb, IXa, IXb, XIa, XIb**), Et (**II, VIa, VIb, VIIIa, VIIIb, Xa, Xb, XIIa, XIIb**).

alkene while using vicinal β-bromo-β- nitroalkenes we observed for the first time in reaction with furan [11]. The initially formed tetrahydro-benzofurans **XIIIa, XIIIb, XIVa**, and **XIVb** because of the presence of several electron-acceptor groups (CO_2R,NO_2, Br) easily undergo aromatization to the corresponding regioisomeric mono- (**IXa, IXb–XIIa, XIIb**) and dinitrobenzofurans **XVa,XVb,XVIa**, and **XVIb**.

The products **XVII, XVIII** under the reaction conditions eliminate hydrogen bromide to give 2,5-di-(nitrovinyl)furans **XIX, XX**. More rigid reaction



R = Me (**III, IXa, IXb, XIIIa, XIIIb, XVa, XVb, XVII, XIX**), Et (**IV, Xa, Xb, XIVa, XIVb, XVIa, XVIb, XVIII, XX**).

Table 1. Yields, R_f, and elemental analyses of compounds **Va, Vb–Xa, Xb, XIIIa, XIIIb–XVIa, XVIb, XIX,** and **XX**

Comp. no.	Yield, %	R_f, (mp, °C)	a:b ratio	Found, %			Formula	Calculated, %		
				C	H	N		C	H	N
Va, Vb	13	0.52, 0.58	8:1	–	–	10.00, 10.03	$C_{10}H_{10}N_2O_7$	–	–	10.37
VIa, VIb	30	0.66, 0.71	9:1	46.28, 46.32	4.00, 4.11	9.77, 9.81	$C_{11}H_{12}N_2O_7$	46.48	4.23	9.86
VIIa, VIIb	7	0.60, 0.65	1:3	68.01, 68.03	4.43, 4.47	–	$C_{10}H_8O_3$	68.18	4.54	–
VIIIa, VIIIb	26	0.55, 0.65	1:2	69.51, 69.55	5.30, 5.31	–	$C_{11}H_{10}O_3$	69.47	5.26	–
IXa, IXb	16	0.64, 0.68	1:4	53.99, 54.10	3.13, 3.17	6.03, 6.09	$C_{10}H_7NO_5$	54.30	3.16	6.33
Xa, Xb	9	0.52, 0.56	1:3	56.22, 56.23	4.23, 4.24	5.78, 5.81	$C_{11}H_9NO_5$	56.17	3.83	5.96
XIIIa, XIIIb	8	0.61, 0.66	9:1	–	–	8.00, 8.05	$C_{10}H_9BrN_2O_7$	–	–	8.02
XIVa, XIVb	6	0.71, 0.65	7:1	36.89, 36.90	3.15, 3.35	7.32, 7.33	$C_{11}H_{11}BrN_2O_7$	36.36	3.03	7.71
XVa, XVb	7	(132–134)	1:2	45.62, 45.64	2.62, 2.65	10.91, 10.95	$C_{10}H_6N_2O_7$	45.11	2.26	10.53
XVIa, XVIb	9	0.65, 0.70	1:2	–	–	9.81, 9.82	$C_{11}H_8N_2O_7$	–	–	10.00
XIX	40	(68–70)	–	44.52, 44.56	2.64, 2.68	10.61, 10.65	$C_{10}H_8N_2O_7$	44.77	2.98	10.45
XX	38	0.53	–	46.75, 46.78	3.60, 3.61	9.90, 9.95	$C_{11}H_{10}N_2O_7$	46.81	3.55	9.93

Table 2. ^{1}H NMR and IR spectral data of tetrahydrobenzofurans **Va, Vb, VIa, VIb, XIIIa, XIIIb, XIVa**, and **XIVb**

Comp. no.	^{1}H NMR spectra, δ, ppm, J, Hz ($CDCl_3$)						IR spectra, ν, cm^{-1} ($CHCl_3$)		
	H^2	H^3	H^4 (H^5)	H^6	H^7	CO_2R	NO_2	C=O	C–O–C
Va	7.05 d	6.95 d	4.40 m (4.45 m)	4.10 m	3.40–3.50 m	4.10 s	1360, 1565	1750	1025, 1115
Vb	$J_{2,3}$ 7.5		3.90 m (4.60 m)	4.25 m	3.50–3.70 m	3.90 s			
VIa	7.05 d	6.92 d	4.36 m (4.43 m)	4.11 m	3.40–3.50 m	1.33 t 4.20 q	1360, 1565	1750	1025, 1115
VIb	$J_{2,3}$ 7.5		3.85 m (4.50 m)	4.15 m	3.45–3.60 m	1.40 t 4.35 q			
XIIIa	7.10 d	6.95 d	(4.40 m)	4.80 m	3.50 m	4.10 s	1360, 1560	1740	1025, 1115
XIIIb	$J_{2,3}$ 7.5		4.30 m	5.20 m	3.80 m	3.85 s			
XIVa	7.10 d	6.97 d	(4.30 m)	4.75 m	3.50 m	1.35 t 4.30 q	1375, 1560	1730	1035, 1128
XIVb	$J_{2,3}$ 7.5		4.20 m	5.20 m	3.80 m	1.25 t 4.20 q			

conditions (boiling in *p*-xylene for 24 h without a catalyst) favor the increase in the yield of the furan-containing dinitrotetraenic derivatives **XIX, XX** from 20% to 40%.

The chromatographic separation of tetrahydrobenzofurans and benzofurans yielded mixtures of regioisomers "a, b," and the final alkylation products **XIX, XX** were obtained as individual compounds.

The composition of compounds **Va, Vb–Xa, Xb, XIIIa, XIIIb–XVIa, XVIb, XIX, XX** was confirmed by elemental analyses (Table 1), and the structure of all the compounds obtained was established by the spectral methods including the regioisomeric attribution (Tables 2–4). For instance, the IR spectra contain absorption bands at 1730–1750 cm^{-1} belonging to ester carbonyl groups. The unconjugated nitro groups of the compounds **Va, Vb, VIa, VIb, XIIIa, XIIIb,**

Table 3. ^{1}H NMR and IR spectral data of benzofurans **VIIa, VIIb–XIIa, XIIb, XVa, XVb, XVIa, XVIb**

Comp. no.	^{1}H NMR spectra, δ, ppm, *J*, Hz ($CDCl_3$)						IR spectra, ν, cm^{-1} ($CHCl_3$)		
	H^2	H^3	H^4 (H^5)	H^6	H^7	CO_2R	NO_2	C=O	C–O–C
VIIa	7.12 d	7.03 d	7.30–7.5 m			3.80 s	–	1735	1030, 1110
VIIb	$J_{2,3}$ 7.5					3.96 s			
VIIIa	7.10 d	7.00 d	7.28–7.45 m			1.30 t, 4.40 q	–	1735	1030, 1110
VIIIb	$J_{2,3}$ 7.5					1.40 t, 4.25 q			
IXa	7.15 d	7.05 d	–	7.98 d	7.50 d	3.90 s	1355, 1525	1740	1025, 1120
				$J_{6,7}$ 7.9					
IXb	$J_{2,3}$ 7.5			8.10 d	7.54 d	4.00 s			
				$J_{6,7}$ 8.1					
Xa	7.15 d	7.05 d	–	7.88 d	7.50 d	1.30 t, 4.40 q	1360, 1520	1740	1020, 1095
	$J_{2,3}$ 7.5			$J_{6,7}$ 7.6					
Xb			–	8.08 d	7.53 d	1.40 t, 4.25 q			
				$J_{6,7}$ 8.0					
XIa	7.15 d	7.10 d	7.55	–	8.52	3.80 s	–	–	–
XIb	$J_{2,3}$ 7.5		(7.70 d)	–	8.36 d	3.75 s			
					$J_{5,7}$ 1.47				
XIIa	7.15 d	7.10 d	7.59	–	8.38 d	1.30 t, 4.40 q	–	–	–
XIIb	$J_{2,3}$ 7.5		(7.68 d)	–	8.34 d	1.25 t, 4.30 q			
					$J_{5,7}$ 1.5				
XVa[a]	7.40 d	7.25 d	–	–	8.80 s	3.9 s	1360, 1525	1740	1020, 1095
XVb[a]	$J_{2,3}$ 7.5		–	–	8.90 s	4.0 s			
XVIa[a]	7.50 d	7.30 d	–	–	8.70 s	1.40 t, 4.50 q	1360, 1520	1735	1030, 1125
XVIb[a]	$J_{2,3}$ 7.5		–	–	8.90 s	1.30 t, 4.25 q			

[a] ^{1}H NMR spectra of compounds **XVa, XVb, XVIa,** and **XVIb** were registered in DMSO-d_6.

Table 4. ^{1}H NMR spectral data of the furylnitroethene derivatives **XVII-XX**

Comp. no.	^{1}H NMR spectra, δ, ppm, *J*, Hz ($CDCl_3$)					
	H^3	H^4	H_A	H_B	$H_{B'}$ ($H_{A'}$)	CO_2R
XVII	6.92 d	7.10 d	7.70 d	7.61 d	5.70 d (5.20 d)	3.90 s
			J_{AB} 13.0			
XVIII	6.70 d	6.95 d	7.60 d	7.45 d	5.50 d (5.10 d)	1.30 t, 4.25 q
			J_{AB} 13.0			
XIX	6.91 d	7.00 d	7.75 d	7.63 d	7.56 s	4.0 s
	$J_{3,4}$ 3.4		J_{AB} 13.1			
XX	6.85 d	6.95 d	7.65 d	7.60	7.48 s	1.25 t, 4.30 q
	$J_{3,4}$ 3.4		J_{AB} 12.6			

XIVa, XIVb are characterized by the bands at 1560–1565 and 1360–1375 cm^{-1}, while the bands of conjugated nitro groups of compounds **IXa, IXb–Xa, Xb, XVa, XVb, XVIa, XVIb, XIX, XX** appear at 1525–1535 and 1355–1360 cm^{-1}.

The ^{1}H NMR spectra of the products **Va, Vb–XVIa, XVIb** contain two sets of signals with different ratio of the integral intensities indicating the formation of adducts as a mixtures of regioisomers.

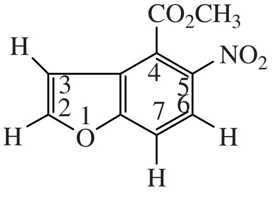
The signals of nitromethine protons $H^{4,6}$ of the isomer “a” in tetrahydrobenzofurans **Va, Vb, VIa**, and **VIb** are located upfield (4.36–4.40 ppm and 4.10–4.11 ppm, respectively) as compared to the analogous protons $H^{5,6}$ of the isomer “b” giving rise to signals at

4.43–4.60 ppm and 4.15–4.25 ppm (Table 2). Similar approach permits to attribute the $H^{5,4}$ protons at the ester function (4.43–4.45 ppm for the compounds **Va, VIa** and 3.85–3.90 ppm for the isomers **Vb, VIb**), and also the protons of the cyclic methylene group (3.40–3.50 ppm for the isomer "a" and 3.45–3.70 ppm for the isomer "b").

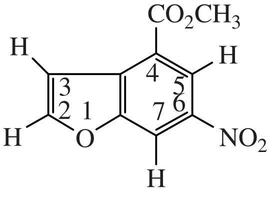
In the bromine-containing tetrahydrobenzofurans **XIIIa, XIIIb, XIVa, XIVb** the signals of the cyclic nitromethine protons H^6 are evidently located downfield (5.20 ppm for the isomers **XIIIb, XIVb** as compared to 4.80 ppm for the compound **XIIIa** and 4.75 ppm for substance **XIVa**). Presence of the electron-acceptor substituents from both sides leads to the downfield position of signals of the protons H^5 (4.40 ppm for the product **XIIIa** and 4.30 ppm for substance **XIVa**) as compared to the protons H^4 in the isomers "b" (4.30 ppm for the product **XIIIb** and 4.20 ppm for compound **XIVb**).

Spectral characteristics of compounds **VIIa, VIIIa** coincide with the published data for these compounds prepared by another method [1] (Table 3). In our case the signal of protons of the methoxycarbonyl group in ^1H NMR spectrum of a mixture of the products **VIIa, VIIb** (the a:b ratio 1:3) is doubled (3.80 and 3.96 ppm), the downfield part belonging to the isomer **VIIb**.

Chemical shifts of the aromatic protons $H^{6,7}$ in compounds **IXa, IXb, Xa**, and **Xb** and $H^{4,5,7}$ in substances **XIa, XIb, XIIa**, and **XIIb** were used for assignment of the structure of isomers because these values depend on the mutual location of the proton and the electron-acceptor nitro group [12–14]. Due to the effect of the latter substituent the signals of the protons $H^{6,7}$ in the ^1H NMR spectrum of compound **IXb** are located downfield at 8.10 and 7.54 ppm respectively as compared to location of the analogous protons (7.98 and 7.50 ppm) in the isomer **IXa**. Reciprocal location of the aromatic protons in the molecules of benzofurans **IXa, IXb–XIIa, XIIb** was determined on the basis of values of the coupling constants of these protons [15]. The coupling constants of the protons $H^{6,7}$ 7.9 Hz in the compound **IXa** and 8.1 Hz in the substance **IXb** indicate their *ortho*-location [15]. Analogously to [1] the signal of the ester methoxy group at 4.0 ppm was attributed to product **IXb**, and the signal at 3.9 ppm, to isomer **IXa**.



IXb



XIb

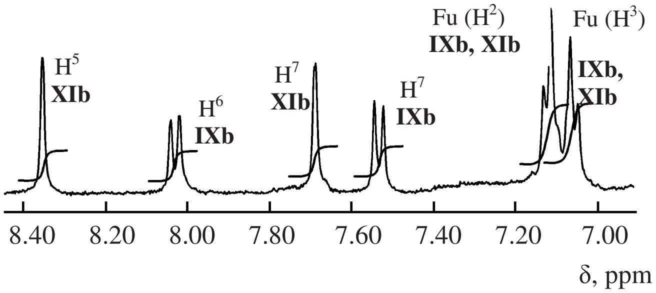


Fig. 1. Fragment of the ^1H NMR spectrum of a mixture of 4-methoxycarbonyl-5-nitro- and 4-methoxycarbonyl-6-nitrobenzofurans **IXb** and **XIb** in $CDCl_3$.

The aromatic protons $H^{5,7}$ of isomer **XIb** give signals at 7.70 and 8.36 ppm with the characteristic coupling constant 1.47 Hz showing their *meta*-location. Spectral difference of *ortho*- and *meta*-isomers in the series of structures under investigation is illustrated by ^1H NMR spectrum of a mixture of substances **IXb** and **XIb** isolated by column chromatography (Fig.1).

Analogous rules are observed in the appearance of signals of the protons $H^{4–7}$ in nitrobenzofurans **Xa, Xb, XIIa**, and **XIIb** (Table 3). Benzofurans **XVa, XVb, XVIa**, and **XVIb** alongside the alkoxycarbonyl group contain two nitro groups, and in the ^1H NMR spectrum the singlet of the aromatic proton H^7 is observed at 8.80 ppm and 8.70 ppm for isomers **XVa, XVIa**, and at 8.90 ppm for isomers **XVb, XVIb**.

^1H NMR spectral data of compounds **XVII, XVIII** correspond to the assumed structures. The coupling constant values for the olefin protons of the nitrovinyl fragment (13 Hz) show that they have *E*-configuration (Table 4).

Analysis of the ^1H NMR spectrum of compound **XIX** (Fig. 2, Table 4) shows that the signal of the proton H_A is shifted downfield due to the *cis*-located nitro group exhibiting the largest deshielding effect [16]. The signal of the proton H_A is doublet with the coupling constant $^3J_{AB}$ 13.1 Hz because of the interaction with the proton H_B. These protons are *trans*-located with respect to the C=C bond. The signal of the proton $H_{B'}$ is a singlet at 7.56 ppm. Close values of chemical shifts of the H_B and $H_{B'}$ olefin protons show that both of them are *gem*-located with respect to the nitro group. The protons H^3 and H^4 of the furan ring

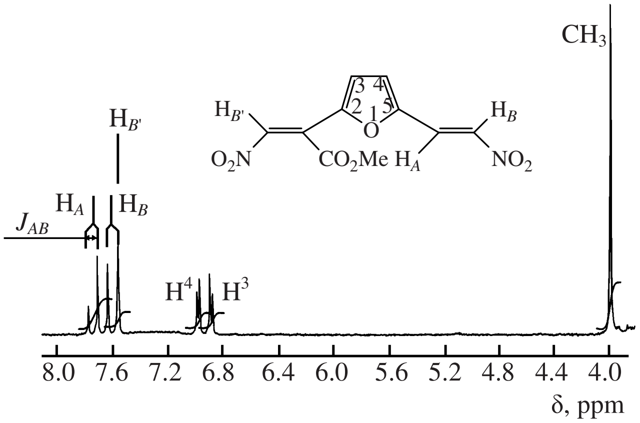


Fig. 2. ^{1}H NMR spectrum of 2-(1-methoxycarbonyl-2-nitroethenyl)-5-(2-nitroethenyl)furan **XIX** in $CDCl_3$.

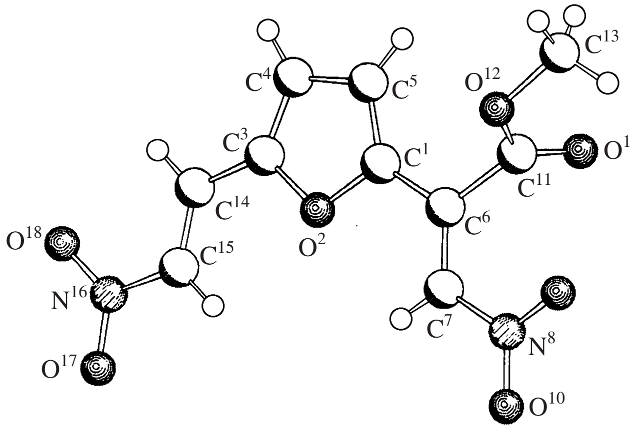


Fig. 3. General view of the molecule of 2-(1-methoxycarbonyl-2-nitroethenyl)-5-(2-nitroethenyl)furan **XIX** according to the XRD analysis.

form the *AB*-system with the coupling constant 3.66 Hz, their chemical shifts are 6.91 ppm and 7.00 ppm respectively (Table 4).

The crystals of compound **XIX** were analyzed by XRD method. General view of the molecule is presented in Fig. 3, and its geometric parameters in Tables 5–7. The nitrovinyl substituents located in the positions 2 and 5 of the furan ring of compound **XIX** have *Z*- and *E*-configuration respectively. The tetraene conjugated system consisting of two endocyclic and two exocyclic multiple bonds is practically coplanar. It

Table 5. Interatomic distances (*d*, Å) in the molecule of compound **XIX**

Bond	*d*	Bond	*d*
$C^1–C^5$	1.3593(19)	$N^8–O^9$	1.2216(16)
$C^1–O^2$	1.3657(15)	$C^{11}–O^{11}$	1.1915(18)
$C^1–C^6$	1.4387(19)	$C^{11}–O^{12}$	1.3172(18)
$O^2–C^3$	1.3708(16)	$O^{12}–C^{13}$	1.4518(18)
$C^3–C^4$	1.357(2)	$C^{13}–H^{13A}$	0.9600
$C^3–C^{14}$	1.4272(19)	$C^{13}–H^{13B}$	0.9600
$C^4–C^5$	1.406(2)	$C^{13}–H^{13C}$	0.9600
$C^4–H^4$	0.9300	$C^{14}–C^{15}$	1.321(2)
$C^5–H^5$	0.9300	$C^{14}–H^{14}$	0.9300
$C^6–C^7$	1.3327(19)	$C^{15}–N^{16}$	1.4325(17)
$C^6–C^{11}$	1.5139(17)	$C^{15}–H^{15}$	0.9300
$C^7–N^8$	1.4342(18)	$N^{16}–O^{17}$	1.2214(17)
$C^7–H^7$	0.9300	$N^{16}–O^{18}$	1.2242(16)
$N^8–O^{10}$	1.2183(16)		

Table 6. Bond angles (ω, deg) in the molecule of compound **XIX**

Angle	ω	Angle	ω
$C^5C^1O^2$	110.13(12)	$O^9N^8C^7$	119.58(12)
$C^5C^1C^6$	132.56(12)	$O^{11}C^{11}O^{12}$	126.85(12)
$C^5C^1C^6$	132.56(12)	$O^{11}C^{11}C^{16}$	122.44(13)
$C^1O^2C^3$	106.27(10)	$O^{12}C^{11}C^6$	110.58(12)
$C^4C^3O^2$	110.07(12)	$C^{11}O^{12}C^{13}$	115.65(13)
$C^4C^3C^{14}$	131.40(14)	$O^{12}C^{13}H^{13A}$	109.5
$O^2C^3C^{14}$	118.43(12)	$O^{12}C^{13}H^{13B}$	109.5
$C^3C^4C^5$	106.78(13)	$O^{12}C^{13}H^{13C}$	109.5
$C^3C^4H^4$	126.6	$H^{13A}C^{13}H^{13B}$	109.5
$C^5C^4H^4$	126.6	$H^{13A}C^{13}H^{13C}$	109.5
$C^1C^5C^4$	106.74(12)	$H^{13B}C^{13}H^{13C}$	109.5
$C^1C^5H^5$	126.6	$C^{15}C^{14}C^3$	124.57(13)
$C^4C^5H^5$	126.6	$C^{15}C^{14}H^{14}$	117.7
$C^7C^6C^1$	121.86(11)	$C^3C^{14}H^{14}$	117.7
$C^7C^6C^{11}$	123.13(12)	$C^{14}C^{15}N^{16}$	120.70(13)
$C^1C^6C^{11}$	114.86(11)	$C^{14}C^{15}H^{15}$	119.7
$C^6C^7N^8$	121.96(12)	$N^{16}C^{15}H^{15}$	119.7
$C^6C^7H^7$	119.0	$O^{17}N^{16}O^{18}$	122.73(13)
$N^8C^7H^7$	119.0	$O^{17}N^{16}C^{15}$	116.86(13)
$O^{10}N^8O^9$	123.66(13)	$O^{18}N^{16}O^{15}$	120.39(12)
$O^{10}N^8C^7$	116.75(12)		

Table 7. Torsion angles (τ, deg) in the molecule of compound **XIX**

Angle	τ	Angle	τ
$C^5C^1O^2C^3$	0.47 (16)	$C^6C^7N^8O^{10}$	–171.31 (14)
$C^6C^1O^2C^3$	–179.44 (12)	$C^6C^7N^8O^9$	9.7 (2)
$C^1O^2C^3C^4$	–0.66 (16)	$C^7C^6C^{11}O^{11}$	75.30 (19)
$C^1O^2C^3C^{14}$	176.19 (12)	$C^1C^6C^{11}O^{11}$	–100.23 (17)
$O^2C^3C^4C^5$	0.59 (18)	$C^7C^6C^{11}O^{12}$	–108.57 (16)
$C^{14}C^3C^4C^5$	–179.71 (16)	$C^1C^6C^{11}O^{12}$	75.90 (15)
$O^2C^1C^5C^4$	–0.12 (17)	$O^{11}C^{11}O^{12}C^{13}$	–1.2 (2)
$C^6C^1C^5C^4$	179.77 (15)	$C^6C^{11}O^{12}O^{13}$	–177.10 (14)
$C^3C^4C^5C^1$	–0.29 (18)	$C^4C^3C^{14}C^{15}$	172.96 (17)
$C^5C^1C^6C^7$	179.22 (16)	$O^2C^3C^{14}C^{15}$	–3.1 (2)
$O^2C^1C^6C^7$	–0.9 (2)	$C^3C^{14}C^{15}N^{16}$	–177.08 (14)
$O^2C^1C^6C^{11}$	174.70 (11)	$C^{14}C^{15}N^{16}O^{17}$	–179.75 (16)
$C^1C^6C^7N^8$	–178.41 (12)	$C^{14}C^{15}N^{16}O^{18}$	–0.8 (2)
$C^{11}C^6C^7N^8$	6.4 (2)		

is confirmed by the values of torsion angles of the main structural fragments of the molecule under study: the $C^{14}C^3C^4C^5$ angle is –179.71°, the $C^6C^1C^5C^6$ angle is 179.77°, the $C^3C^4C^5C^1$ angle is –0.29°, the $C^5C^1C^6C^7$ angle is 179.22°. The values of the torsion angles $C^1C^6C^7N^8$ (–177.41°) and $C^3C^1C^4C^1C^5N^1N^6$ (–177.08°) show that both nitro groups of the vinyl fragment have *trans*-orientation with respect to the furan ring and are coplanar with it [$C^6C^7N^8O^{10}$ angle (–171.77°), $C^6C^7N^8O^9$ angle (9.7°), $C^{14}C^{15}N^{16}O^{17}$ angle (–179.75°), $C^{14}C^{15}N^{16}O^{18}$ angle (–0.8°)]. It is characteristic that the ester function having *cis*-location to the nitro group and compelled to occupy the space between the furan ring and the nitro group deviates from the plain of the double bonds [$C^1C^6C^{11}O^{11}$ angle (–100.23°), $C^1C^6C^{11}O^{12}$ angle (75.90°), $C^7C^6C^{11}O^{11}$ angle (75.30°), $C^7C^6C^{11}O^{12}$ angle (–108.57°)]. Hence, in the molecule of compound **XIX** vinyl fragments have the coplanar chelate-like structure. Its nitro and methoxycarbonyl groups are *cis*-located with respect to one another, and the ester function deviates from the plain of the multiple carbon–carbon bond. In crystal the hydrogen atoms of vinyl group are bound by weak H-bonds with the oxygen atoms of nitro groups belonging to the adjacent molecules.

EXPERIMENTAL

The IR spectra were obtained on an Infra-LYUM FT-02 spectrometer in chloroform, *c* 0.1–0.001 mol l^{-1}.

Table 8. Atomic coordinates of the structure **XIX**, their equivalent temperature parameters (×10^4), and the isotropic parameters of hydrogen atoms ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	U_{eq}
C^1	2600 (1)	–110 (1)	–24 (2)	36 (1)
O^2	1785 (1)	–80 (1)	587 (1)	37 (1)
C^3	1641 (1)	–1414 (1)	1035 (2)	40 (1)
C^4	2339 (1)	–2261 (2)	700 (2)	49 (1)
C^5	2958 (1)	–1424 (1)	23 (2)	46 (1)
C^6	2916 (1)	1182 (1)	–575 (2)	35 (1)
C^7	2432 (1)	2363 (1)	–516 (2)	38 (1)
N^8	2732 (1)	3645 (1)	–1100 (1)	42 (1)
O^9	3368 (1)	3638 (1)	–1854 (2)	61 (1)
O^{10}	2313 (1)	4693 (1)	–822 (2)	66 (1)
C^{11}	3871 (1)	1108 (2)	–1104 (2)	39 (1)
O^{11}	4617 (1)	1484 (1)	–307 (1)	55 (1)
O^{12}	3753 (1)	508 (1)	–2476 (1)	55 (1)
C^{13}	4630 (1)	317 (3)	–3073 (2)	75 (1)
C^{14}	864 (1)	–1674 (1)	1810 (2)	41 (1)
C^{15}	292 (1)	–706 (1)	2192 (2)	42 (1)
N^{16}	–443 (1)	–1056 (1)	3034 (2)	46 (1)
O^{17}	–946 (1)	–105 (1)	3339 (2)	74 (1)
O^{18}	–557 (1)	–2263 (1)	3395 (2)	64 (1)

The ^1H NMR spectra of compounds **Va, Vb–XIVa, XIVb, XVII–XX** were registered on a Bruker AC-200 spectrometer (200 MHz) in $CDCl_3$, and of compounds **XVa, XVb, XVIa**, and **XVIb** in DMSO-d_6, external reference HMDS.

X-ray diffraction analysis of compound (XIX). The crystals of compound **XIX** are monoclinic, space group $P2_1/c$. Unit cell parameters at 20°C are a follows: *a* 14.086(1), *b* 9.628(1), *c* 8.799(1) Å, β 104.04 (1)°, *V* 1167.1(3) $Å^3$, *Z* 4, d_{calc} 1.526 g cm^{-3}. Unit cell parameters and the intensities of 45603 reflections among which 2998 independent (R_{int} 0.037) were measured on an automatic Nonius KappaCCD X-ray diffractometer (λMoK_α irradiation, graphite monochromator, $\theta < 30°$) at room temperature using the COLLECT (Nonius B.V., 1998), Dirax/Isl (Duisenberg & Schreurs, 1989–2000) and EvalCCD (Duisenberg & Schreurs 1990–2000) programs. The extinction was accounted for empirically. The structure was solved by the direct method using SHELXS-97 program [17] and refined with the help of the SHELXL-97 program (G.M.Sheldrick, Universitat

Göttingen, 1997). Final values of the diversion factors R 0.040, R_W 0.095 by 2174 independent reflections with $F^2 > 2\sigma$.

The separation and purification of the individual compounds was carried out by column chromatography on the Chemapol (100/200 μm) silica gel and on aluminum oxide. The reaction progress was monitored by TLC on Silufol-254 plates, elution with 3:2 hexane-acetone, development with iodine vapour. Initial β-nitro- and β-bromo-β-nitroacrylates **I–IV** were prepared according to the procedures [18,19], and β - furylnitroethylene, to the procedure [20].

4,6(5,6)-Dinitro-5(4)-methoxycarbonyl-4,5,6,7-tetrahydrobenzofurans (Va, Vb), 5(4)-methoxycarbonylbenzofurans (VIIa, VIIb), 5(4)-methoxycarbonyl-4(5)nitrobenzofurans (IXa, IXb), and 5 (4)-methoxycarbonyl-6-nitrobenzofurans (XIa, XIb). To a solution of 0.68 g of methyl 3-nitroacrylate **I** in 10 ml of anhydrous *p*-xylene were added 0.15 g of aluminum chloride and 0.70 g of 2-(2-nitroethenyl) furan. The reaction mixture was refluxed for 2 h, solvent was removed on a rotary evaporator, and the residue was subjected to chromatography on silica gel.

Elution with carbon tetrachloride permitted isolation of 0.66 g of a mixture of nitrobenzofurans **IXa, IXb, XIa**, and **XIb**, and by elution with benzene 0.5 g of a mixture of tetrahydrobenzofurans **Va, Vb** and benzofurans **VIIa, VIIb** was obtained.

By repeated chromatography of a mixture of compounds **IXa, IXb, XIa**, and **XIb** elution with carbon tetrachloride gave 0.39 g (35%) of a mixture of isomeric benzofurans **IXb** and **XIb** in 1:1 ratio, R_f 0.64 and 0.72 respectively. Elution with benzene (first portion ~200 ml) gave 0.03 g (3%) of a mixture of compounds **IXb, XIa**, and **XIb**, R_f 0.64, 0.72, and 0.75. The second portion of benzene (~200 ml) gave 0.06 g (6%) of a mixture of compounds **IXa** and **IXb** in 1:4 ratio, R_f 0.64 and 0.68 respectively.

By repeated chromatography of a mixture of compounds **Va, Vb, VIIa**, and **VIIb** elution with benzene gave 0.06 g (7%) of benzofurans **VIIa** and **VIIb** in 1:3 ratio, R_f 0.60 and 0.65. The fraction eluted with chloroform gave 0.18 g (13%) of oil consisting of tetrahydrobenzofurans **Va, Vb** in 1:8 ratio, R_f 0.52 and 0.58.

4,6(5,6)-Dinitro-5(4)-ethoxycarbonyl-4,5,6,7-tetrahydrobenzofurans (VIa, VIb), 5(4)-ethoxycarbonylbenzofurans (VIIIa, VIIIb), 4(5)nitro-5(4)-ethoxycarbonylbenzofurans (Xa, Xb) and 6-nitro-5(4)ethoxycarbonylbenzofurans (XIIa, XIIb). To a solution of 0.70 g of ethyl 3-nitroacrylate **II** in 10 ml of the anhydrous *p*-xylene were added 0.15 g of the aluminum chloride and 0.67 g of 2-(2-nitroethenyl) furan. The mixture obtained was refluxed for 2 h, solvent was removed on a rotary evaporator, and the residue was chromatographed on silica gel.

Elution with carbon tetrachloride gave 0.15 g (13%) of a mixture of compounds **Xa, Xb, XIIa**, and **XIIb**, and elution with benzene yielded 1.20 g of a mixture of tetrahydrobenzofurans **VIa, VIb** and benzofurans **VIIIa, VIIIb**.

Repeated chromatography of a mixture of compounds **VIa, VIb, VIIa**, and **VIIb** gave the benzene-eluted fraction containing 0.24 g (26%) of a mixture of benzofurans **VIIIa, VIIIb** in 1:2 ratio, R_f 0.55 and 0.65. Elution with chloroform gave 0.41 g (30%) of oil containing tetrahydrobenzofurans **VIa, VIb** in 9:1 ratio, R_f 0.66 and 0.71.

Repeated chromatography of a mixture of compounds **Xa, Xb, XIIa, XIIb** (elution with benzene) gave 0.1 g (9%) of a mixture of compounds **Xa, Xb** in 1:3 ratio, R_f 0.52 and 0.56 respectively.

5-(4)-Methoxycarbonyl-4(5)-nitrobenzofurans (IXa, IXb), 4(5)-bromo-4,6(5,6)-dinitro-5(4)-methoxycarbonyltetrahydrobenzofurans (XIIIa, XIIIb),4,6(5,6)-dinitro-5(4)-methoxycarbonyl-benzofurans (XVa, XVb), 2-(2-bromo-1-methoxycarbonyl-2-nitroethyl)-5-(2-nitroethenyl)furan (XVII), 2-(1-methoxycarbonyl-2-nitroethenyl)-5-(2-nitroethenyl)furan (XIX). To a solution of 0.73 g of methyl 3-bromo-3-nitroacrylate **III** in 10 ml of *p*-xylene were added 0.15 g of aluminum chloride and 0.48 g of 2-(2-nitrovinyl)furan. The reaction mixture was boiled for 4 h, solvent was evaporated on a rotary evaporator, and the residue was subjected to chromatography on silica gel. Elution with benzene gave 0.94 g of a mixture of compounds **IXa, IXb, XVa, XVb, XVII,** and **XIX**, and elution with chloroform yielded 0.1 g (8%) of regioisomeric tetrahydrobenzofurans **XIIIa, XIIIb**, R_f 0.61 and 0.66 respectively. According to ^{1}H NMR data the ratio of compounds **XIIIa, XIIIb** was 9:1.

A mixture of compounds **IXa, IXb, XVa, XVb, XVII,** and **XIX** was washed with benzene, and the crystals were filtered off to give 0.065 g (7%) of dinitrobenzofurans **XVa, XVb** in 1:2 ratio, mp 132–

134°C. The filtrate was evaporated and subjected to chromatography on silica gel. The first portion of benzene eluate (~150 ml) gave 0.63 g of a mixture of compounds **XVII, XIX** in 1:8 ratio as a brown oil, R_f 0.60 and 0.68 respectively. The chloroform eluate gave 0.05 g (16%) of mononitrobenzofurans **IXa, IXb** in 1:4 ratio, R_f 0.64 and 0.68 respectively.

Repeated chromatography of a mixture of compounds **XVII, XIX** (elution with benzene) gave 0.38 g (40%) of compound **XIX**, mp 68–70°C.

4(5)-Nitro-5(4)ethoxycarbonylbenzofurans (Xa, Xb), 4(5)-bromo-4,6(5,6)-dinitro-5(4)-ethoxycarbonylbenzofurans (XIVa, XIVb), 4,6(5,6)-dinitro-5(4)ethoxycarbonyltetrahydrobenzofurans (XIVa, XIVb), 4,6(5,6)-dinitro-5(4)-ethoxycarbonylbenzofurans (XVIa, XVIb), 2-(2-bromo-2-nitro-1-ethoxycarbonylethyl)-5-(2-nitroethenyl) furan (XVIII), 2-(2-nitro-1-ethoxycarbonylethenyl)-5-(2-nitroethenyl)furan (XX). To a solution of 0.7 g of ethyl 3-bromo-3-nitroacrylate **IV** in 10 ml of *p*-xylene was added 0.4 g of 2-(2-nitroethenyl)furan. The reaction mixture was refluxed for 4 h, solvent was removed on a rotary evaporator and subjected to chromatography on aluminum oxide.

The hexane eluate gave 0.46 g of a mixture of compounds **Xa, Xb, XVIa,** and **XVIb**, and the benzene one yielded 0.60 g of a mixture of compounds **XIVa, XIVb**, **XVIII,** and **XX.**

Repeated chromatography of a mixture of compounds **Xa, Xb, XVIa,** and **XVIb** (elution with benzene) gave 0.13 g (7%) of isomeric mononitrobenzofurans **Xa, Xb** in 2:3 ratio as an orange oil, R_f 0.52 and 0.56 respectively. Elution with chloroform yielded 0.08 g (9%) of dinitrobenzofurans **XVIa, XVIb** in 1:2 ratio, R_f 0.65 and 0.70 respectively.

Repeated chromatography of a mixture of compounds **XIVa, XIVb, XVIII,** and **XX** (elution with chloroform) gave 0.25 g of a mixture of compounds **XVIII, XX** in 1:6 ratio, R_f 0.48 and 0.53 respectively. The ether eluate yielded 0.07 g (6%) of tetrahydrobenzofurans **XIVa, XIVb** in 7:1 ratio, R_f 0.71 and 0.65 respectively.

Additional chromatography of a mixture of compounds **XVIII, XX** gave in the first portion of chloroform eluate (~200 ml) 0.32 g (38%) of compound **XX**, R_f 0.53.

REFERENCES

1. Kusurkar, R.S. and Bhosale, D.K., *Synth. Commun.,* 1990, vol. 20, no. 1, p. 101.
2. Gilkrist, T., *Khimiya geterotsiklicheskikh soedinenii* (Chemistry of Heterocyclic Compounds), Moscow: Mir, 1966, p. 280.
3. Baralti, P.G., Romagnoli, R., Beria, J., Cozzi, P., and Geroni, C., *J. Med. Chem*., 2000, vol. 43, no. 14, p. 2675.
4. Bertinano, P., Blize, A.E., Bronk, B.S., and Cheng, H., PCT Int. Appl. WO 032,533,2002; *C.A.,* 2003, vol. 138, no. 73533d.
5. Lombaert, S., Blanchard, L., Stamford, L., and Tan, J., *J. Med. Chem*., 2000, vol. 43, no. 3, p. 488.
6. Leung, A.Y. and Foster, S., *Encyclopedia of Common Natural Ingredients Used in Food, Drugs, and Cosmetics*, New York: Wiley, 1996, p. 268.
7. Joule, J. and Mills, K., *Khimiya geterotsiklicheskikh soedinenii* (Chemistry of Heterocyclic Compounds), Moscow: Mir, 2004, p. 479.
8. Boger, D.L., Fink, B.E., and Hetrick, M.P., *J. Am. Chem. Soc*., 2000, vol. 122, no. 27, p. 6382.
9. Walker, D.P., Piotrowski, D.W., and Jacobson, E.J., PCT Int. Appl. WO 03 70,731,2003; *C.A*., 2003, vol. 139, no. 214612x.
10. Mashkovskii, M.D., *Lekarstvennye sredstva* (Pharmaceuticals), Moscow: Meditsina, vol. 1, pp. 381, 481, 517; vol 2, p. 427.
11. Anisimova, N.A., Kuzhaeva, A.A., Berkova, G.A., Berestovitskaya, V.M., and Deiko, L.I., *Zh. Obshch. Khim*., 2005, vol. 75, no. 11, p. 1833.
12. Suzuki, T., *Bull. Chem. Soc. Japan*, 1985, vol. 58, no. 10, p. 821.
13. Tromelin, A., Demerseman, P., and Royer, R., *Synth*., 1985, vol. 11, p. 1074.
14. Einhorn, J., Demerseman, P., and Royer, R., *Can. J. Chem*., 1983, vol. 61, no. 10, p. 2287.
15. Ionin, B.I., Ershov, B.A., and Kol’tsov, A.I., *YaMR spektroskopiya v organicheskoi khimii NMR* (Spectroscopy in Organic Chemistry), Leningrad: Khimiya, 1983.
16. Trukhin, E.V., Makarenko, S.V., and Berestovitskaya, V.M., *Zh. Org. Khim*., 1998, vol. 34, no. 1, p. 72.
17. Sheldrick, G.M., *Acta Cryst*., 1990, vol. 46, p. 467.
18. Shechter, H. and Conrad, F., *J. Am. Chem. Soc*., 1953, vol. 75, no. 22, p. 5610.
19. Sarkisyan, Z.M., Sadikov, K.D., Smirnov, A.S., Makarenko, S.V., Anisimova, N.A., Kuzhaeva, A.A., and Berestovitskaya, V.M., *Zh. Org. Khim*., 2004, vol. 40, no. 6, p. 944.
20. Dornow, A. and Frese, C.D., *Lieb. Ann.*, 1953, p. 211.