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To the 80th Anniversary of B.I. Ionin

Aryl(hetaryl)-Containing *gem*-Cyanonitroethenes: Synthesis, Structure, and Reactions with 2,3-Dimethyl-1,3-butadiene

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Abstract—Methods of aryl(hetaryl)-substituted *gem*-cyanonitroethenes preparation are summarized, and the products structure elucidation by means of ^{1}H, ^{13}C NMR, IR, and UV spectroscopy methods is discussed. *E*-Configuration of the compounds obtained has been proved. Reaction of the studied *gem*-cyanonitroethenes with 2,3-dimethyl-1,3-butadiene affords the diene synthesis adducts – 6-aryl(hetaryl)-3,4-dimethyl-1-nitro-1-cyano-3-cyclohexenes .

Keywords: 1-cyano-1-nitroethene, α-nitroacrylonitrile, nitrile of α-nitrocinnamic acid, Diels–Alder reaction

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Geminal cyanonitroethenes are synthetically accessible convenient synthons for preparation of various organic compounds [1].

Aryl(hetaryl)-containing *gem*-cyanonitroethenes have been prepared via condensation of the corresponding aldehydes with nitroacetonitrile under various conditions: in the presence of methylamine or ethylamine hydrochlorides and sodium carbonate [2–7], β-alanine [8], *n*-propylamine [9], Iran dolomite [10], and on silica gel [11]. Preparation of nitrile of α-nitrocinnamic acid and its analogs via alkenylation of nitroacetonitrile with aldehydes in aqueous medium [12], solvent free conditions [13], in ionic liquids [14a], and under microwave irradiation [14b] has been reported. Unfortunately, most of the mentioned papers lack information about the quality grade of nitroacetonitrile introduced to the reaction. Most likely, crude nitroacetonitrile has been initially converted into the ammonium salt that was acidified afterwards [15]; therefore, synthesis of *gem*-cyanonitroethenes via the described procedure requires two additional steps.

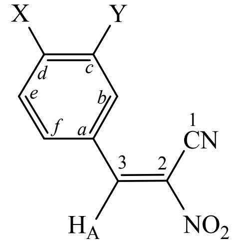
Other studies devoted to the reactions of nitro-containing methylene compounds with aryl(hetaryl) aldehydes under acidic catalysis [16–18] have demonstrated that *gem*-cyanonitroethenes can be synthesized using crude (not purified) nitroacetonitrile obtained via the reaction of methazonic acid with thionyl chloride [2] in the absence of any catalytic agents [16, 18, 19]. Purified nitroacetonitrile has been introduced in the reactions with furfural, 2-formylthiophene, 2-formylpyrrole, and 1-methyl-2-formylpyrrole [19–21]. The nitroacetonitrile can be purified via the two methods: fractional distillation under reduced pressure and column chromatography on silicic acid [21]. The reaction of the so purified nitroacetonitrile with heterocyclic aldehydes proceed in anhydrous ethanol or in an ethanol–diethyl ether mixture at 20°C without any catalytic agents to give the corresponding *gem*-cyanonitroethenes with up to 77% yield.

We prepared a number of aryl- and hetaryl-substituted *gem*-cyanonitroethenes **I–VI** via condensation of crude nitroacetonitrile [2] with the corresponding aldehydes; the nitroalkenes were isolated in up to 90% yield (Scheme 1).

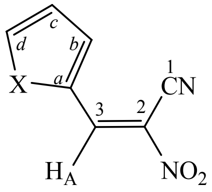
Structures of the synthesized 2-aryl(hetaryl)-1-cyano-1-nitroethenes **I–VI** were studied by IR, UV, and NMR spectroscopy methods.

The value of the olefinic proton chemical shift served as the main indication of the geometry con-

Table 1. ^{1}H NMR spectral parameters of *gem*-*E*-cyanonitroethenes **I–VI** (δ, ppm; *J*, Hz)



I–IV



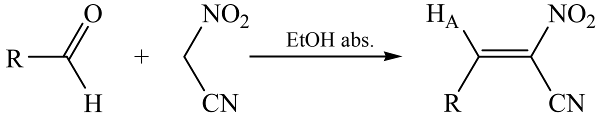
V, VI

Comp. no.	X	Y	H_A	CH_3 (OH) [H_B]	Ar, Het				
					H^b	H^f	H^c	H^e	H^d
I	H	H	8.66 s	–	8.01 d.d		7.59 d.d		7.69 t.t
					$^3J_{b,c}$ 8.24, $^3J_{c,d}$ 7.45, $^4J_{b,d}$ 1.20				
II	MeO	H	8.58 s	3.94 s	8.01 d		7.06 d		–
					$^3J_{b,c}$ 9.00				
III	OH	MeO	8.57 s	4.01 (6.50 s)	7.78 d	7.49 d.d	–	7.08 d	–
					$^3J_{e,f}$ 8.24, $^4J_{b,f}$ 1.83				
IV	Me_2N	H	8.42 s	3.19 s	7.90 br.d		6.74 d		–
					$^3J_{b,c}$ 9.22				
V	O	–	8.43 s	–	7.54 d	–	6.81 d.d	–	7.93 d
					$^3J_{b,c}$ 3.43, $^3J_{c,d}$ 1.55				
VI	S	–	8.81 s	–	8.00 d	–	7.36 d.d	–	8.04 d
					$^3J_{b,c}$ 4.02, $^3J_{c,d}$ 4.91				
Model compound [24]									
$Ph–CH_A=CH_B–NO_2$			7.87 d	[7.60 d]					
			$^3J_{AB}$ 14.0						

figuration of the discussed *gem*-functionalized nitroethenes as assessed by means of ^{1}H NMR spectroscopy: in the case of the *cis*-orientation towards to the nitro group, the corresponding signal was shifted downfield (due to the anisotropic effect of the nitro group [22, 23]) as compared to the *trans*-orientation case.

^{1}H NMR spectra of the *gem*-cyanonitroethenes **I–VI** recorded in $CDCl_3$ solution confirmed their stereo homogeneity (Table 1). The chemical shift of the olefinic proton H_A was of 8.42–8.81 ppm, being shifted downfield compared to that in the model *E*-nitroethenes. For example, the chemical shifts of H_A and H_B protons were of 7.87 and 7.60 ppm, respectively, in ^{1}H NMR spectrum of β-nitrostyrene ($CDCl_3$), the coupling constant being of $^3J_{AB}$ 14.0 Hz [24]; in the spectrum of nitrile of α-nitrocinnamic acid **I**, the chemical shift of H_A proton was of 8.66 ppm leading to the conclusion about *E*-configuration of compound **I**. Similarly, the *E*-configuration of other *gem*-cyanonitroethenes **II–VI** was confirmed.

Scheme 1.

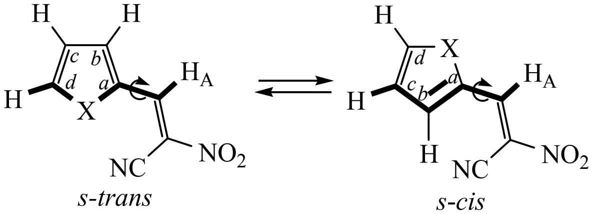


I–VI

R = Ph (**I**), 4-$MeOC_6H_4$ (**II**), 4-HO-3-$MeOC_6H_3$ (**III**), 4-$Me_2NC_6H_4$ (**IV**), 2-furyl (**V**), 2-thienyl (**VI**).

Analysis of the long-range spin-spin coupling constants in ^{1}H NMR spectra of furan-, thiophene-, and pyrrole-based *gem*-cyanonitroethenes allowed investigation of their conformational isomerism with respect to the heterocycle–ethylene fragment single bond [19]. That approach has been described in view of elucidation of the conformation of 2-vinylfuran-(thiophene) and their nitro- and formyl-containing derivatives. In detail, the coupling constant between

Scheme 2.



X = O, S, NMe.

the olefinic proton and the H^d proton evidences about the presence of the *s-trans*-conformer, and the nonzero constant between the olefinic proton and the H^c proton confirms the presence of the *s-cis*-conformer [25–27]. The both mentioned coupling constants [${}^5J(H_AH^d)$ 0.5–1.0 and ${}^5J(H_AH^c)$ 0.3–0.5 Hz] were found in the ${}^1H$ NMR spectra ($CDCl_3$) of 1-nitro-2-furyl(thienyl; 1-cyano-2-furyl(thienyl; 1-methylpyrrolyl)-1-nitroethenes, thus revealing the coexistence of the *s-trans*- and *s-cis*-conformers and indicating the possibility of free rotation around the heterocycle–ethylene fragment ordinary bond (Scheme 2).

The example of the thiophene-containing *gem*-cyanonitroethene **VI** showed that replacement of $CDCl_3$ on the more polar $(CD_3)_2CO$ shifted the conformational equilibrium: compound **VI** existed exclusively in the form of the *s-trans*-conformer in the $(CD_3)_2CO$ solution [19].

The ${}^{13}C$ NMR spectra of certain representatives of *gem*-cyanonitroethenes have been reported earlier [10, 12–14, 28] but the signal assignment has not been accomplished; complete assignment of the ${}^{13}C$ NMR signals has been performed only for β-(2-methoxycarbonylphenyl)-α-nitroacrylonitrile [8].

${}^{13}C$ NMR spectra of *gem*-cyanonitroethenes **I–VI** recorded in this work (Table 2) contained the signals of all the carbon atoms present in the structures. In particular, the signals of the carbon atom adjacent to the two electron withdrawing nitro and cyano groups were found to be upfield shifted (116.17–131.09 ppm) as compared to the carbon atom in β-position with

Table 2. ${}^{13}C$ NMR spectral parameters of *gem*-*E*-cyanonitroethenes **I–VI** (δ, ppm; *J*, Hz)

Comp. no.	X	Y	C^3	C^2	CH_3	C^1	C^a	C^b	C^f	C^c	C^e	C^d
I	H	H	148.65 (${}^1J_{CH}$ 160.05)	123.33	–	111.03 (${}^3JC^1H_A$ 11.26)	127.40	132.34 (${}^1J_{CH}$ 161.54)		130.03 (${}^1J_{CH}$ 163.70)		135.63 (${}^1J_{CH}$ 163.10)
II	MeO	H	148.19 (${}^1J_{CH}$ 158.55)	120.54	56.06 (${}^1J_{CH}$ 158.55)	111.86 (${}^3JC^1H_A$ 11.10)	120.00	135.34 (${}^1J_{CH}$ 161.66)		115.73 (${}^1J_{CH}$ 163.38)		165.98
III	OH	MeO	148.71 (${}^1J_{CH}$ 158.39)	120.40	56.45 (${}^1J_{CH}$ 145.69)	112.20 (${}^3JC^1H_A$ 11.50)	120.06	111.57 (${}^1J_{CH}$ 159.11)	131.55 (${}^1J_{CH}$ 162.94)	147.46	115.83 (${}^1J_{CH}$ 164.86)	153.43
IV	Me_2N	H	147.92 (${}^1J_{CH}$ 156.43)	116.17	40.43 (${}^1J_{CH}$ 137.83)	113.59 (${}^3JC^1H_A$ 10.86)	115.05	136.06 (${}^1J_{CH}$ 157.35)		112.41 (${}^1J_{CH}$ 161.18)		155.38
V	O	–	132.99 (${}^1J_{CH}$ 163.57)	119.73	–	110.75 (${}^3JC^1H_A$ 11.70)	144.75	127.30 (${}^1J_{CH}$ 181.47)	–	115.42 (${}^1J_{CH}$ 180.71)	–	151.52 (${}^1J_{CH}$ 206.87)
VI	S	–	140.95 (${}^1J_{CH}$ 162.63)	120.28	–	111.14 (${}^3JC^1H_A$ 11.50)	131.55	140.80 (${}^1J_{CH}$ 173.48)	–	129.91 (${}^1J_{CH}$ 172.68)	–	139.40 (${}^1J_{CH}$ 187.86)

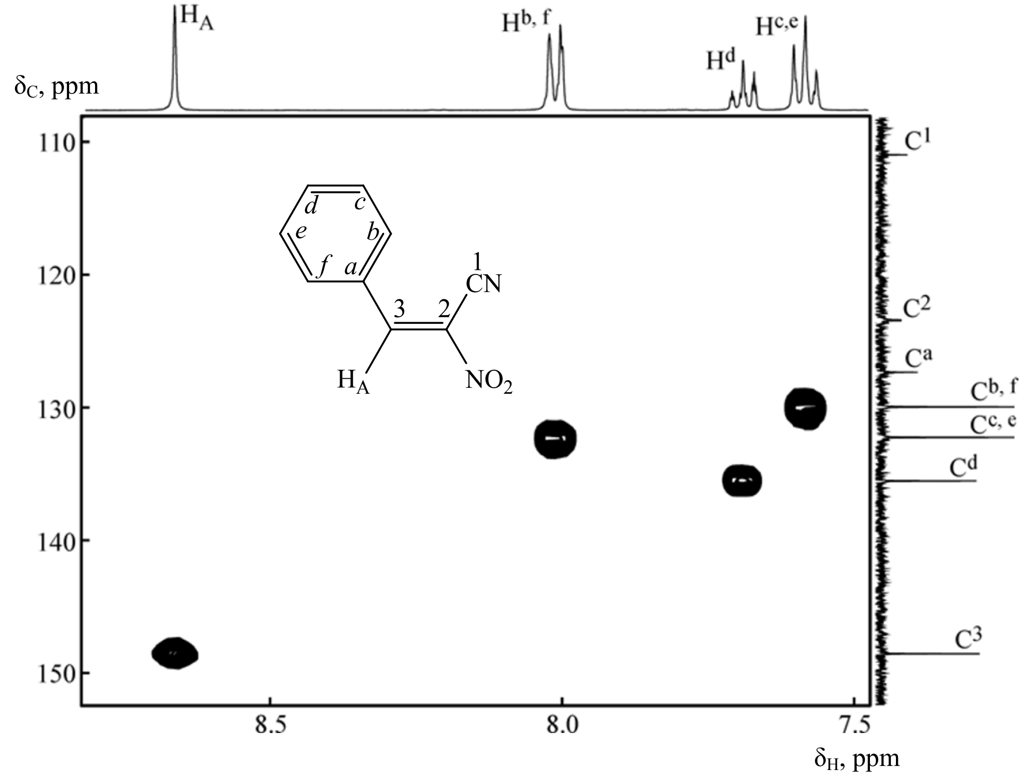


Fig. 1. ^{1}H–^{13}C HMQC spectrum of (*E*)-1-cyano-1-nitro-2-phenylethene **I** in $CDCl_3$.

respect to the nitro group (132.99–160.04 ppm) {in contrast to the *gem*-alkoxycarbonyl(acetyl)nitroethenes analogs [29, 30]}. That was in line with to the well known anisotropic effect of cyano group [23].

Validity of the proton and carbon signals assignment in the ^{1}H and ^{13}C NMR spectra of *gem*-cyanonitroethenes **I–VI** was confirmed by the data of two-dimensional NMR experiments (HMQC and HMBC). In detail, the H_A olefinic proton (δ = 8.66 ppm) was correlated with the C^3 carbon atom (δ = 148.65 ppm) in the ^{1}H–^{13}C HMQC spectrum of *gem*-cyanonitrostyrene **I** (Fig. 1). The HMBC data allowed unambiguous assignment of the signals of hydrogen and carbon atoms at *ortho*- and *meta*-positions of benzene ring and the C^2 atom signal in the case of 2-(4-*N*,*N*-dimethylaminophenyl)-1-cyano-1-nitroethene **IV** basing on the presence of the corresponding cross-peaks of the H_A proton and the C^3 carbon atom (Fig. 2).

E-Configuration of one of the *gem*-cyanonitroethenes, 2-(2-methoxycarbonylphenyl)-1-nitro-1-cyanoethene (δ_{HA} = 9.49 ppm), stated earlier [8] was additionally confirmed by the value of the heteronuclear coupling constant between the H_A proton and the carbon atom of cyano group [$^3J(H_AC^1) \approx 14$ Hz] corresponding to their *trans*-location. That constant was observed in the proton-coupled ^{13}C NMR spectra of *E-gem*-cyanonitroethenes **I–VI** recorded in this work [$^3J(H_AC^1)$ = 10.86–11.70 Hz].

IR and electronic absorption spectra of compounds **I–VI** were similar to the earlier described ones [19, 31–34] (Table 3).

The electronic spectroscopy data did not contradict the conclusion about *E*-configuration of *gem*-cyanonitroethenes **I–VI** suggested above based on the NMR data. Indeed, comparison of the electronic spectra data for the simplest 2-aryl(hetaryl)-1-nitroethenes [24, 34] with the data listed in Table 3 indicated that introduction of the cyano group led to bathochromic shift of the long-wave absorption band, thus strongly confirming the existence of *gem*-cyanonitroethenes **I–VI** in the *E*-form. Let us give a typical example of the spectral parameters change due to the presence of the cyano group: 2-(*para*-dimethylaminophenyl)-1-nitroethene (λ_{max} = 437 nm, ε = 28700 L mol^{-1} cm^{-1}) and compound **IV** (λ_{max} = 485 nm, ε = 46300 L mol^{-1} cm^{-1}) [31].

IR spectrum of the simplest *E-gem*-cyanonitrostyrene **I** contained the absorption bands typical of the covalently bound conjugated nitro group, ν_{as} = 1537 and ν_s = 1317 cm^{-1}. However, the spectra of its analogs, *E*-

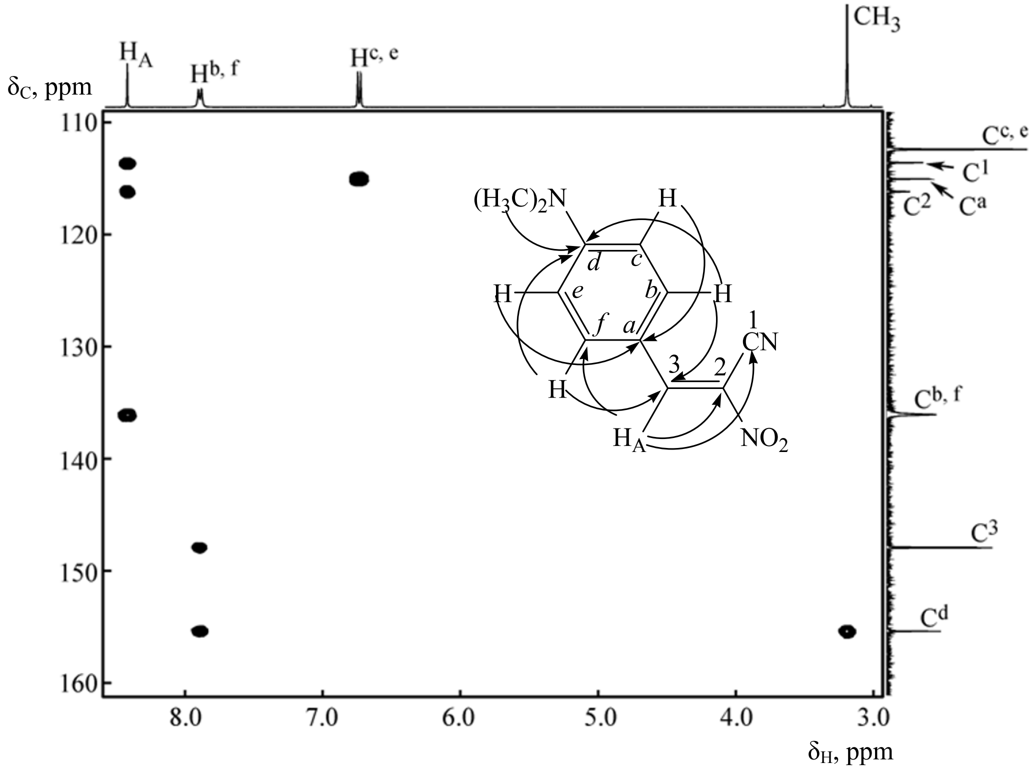
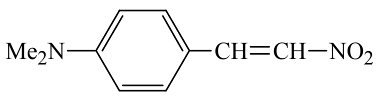


Fig. 2. ^{1}H–^{13}C HMBC spectrum of (*E*)-2-(4-*N,N*-dimethylaminophenyl)-1-cyano-1-nitroethene **IV** in $CDCl_3$.

II–VI containing electron-donating substituents (such as methoxy, hydroxyl, or dimethyamino groups) at the benzene ring or furan (thiophene) components revealed the spectra similar to that of the model *E*-2-aryl(hetaryl)-1-nitroethenes;[1] in particular, the recorded spectra contained no typical bands of the covalently bound nitro group whereas the extraordinarily strong bands at 1595–1640 (C=C, $C=N^+$) and 1315–1335, 1300–1305 cm $^{-1}$ (NOO^-) were observed (cf. [19–21, 32, 33]). The spectral features evidenced about high

Table 3. IR and electronic spectra parameters of *gem-E*-cyanonitroethenes **I–VI**

Comp. no.	R	ν, cm $^{-1}$			λ_{max}, nm[a]	ε, L mol^{-1} cm^{-1}
		NO_2 (NOO^-)	CN	C=C ($C=N^+$)		
I	Ph	1537, 1317	2225	1618	328	17000
II	4-$MeOC_6H_4$	(1320, 1305)	2230	(1595, 1640)	390	30000
III	4-HO-3-$MeOC_6H_4$	(1320, 1305)	2225	(1595, 1620)	390	28500
IV	4-$Me_2NC_6H_4$	(1315, 1300)	2230	(1595, 1640)	485	46300
V	2-Furyl	(1335, 1305)	2225	(1620)	371	21500
VI	2-Thienyl	(1335, 1305)	2225	(1615)	375	17900
Model compound 		(1320, 1298, 1267)	–	(1600)	437	28700

[a] The absorption bands at λ > 270 nm (EtOH) are given.

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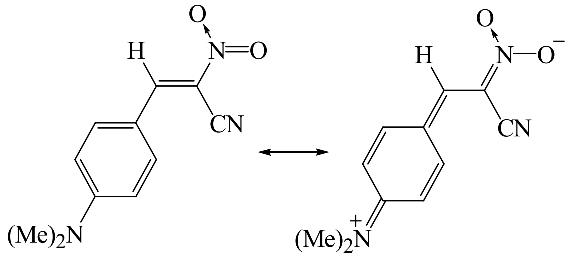
[1] In the review [25] the absorption bands at 1510–1550 and 1340 cm^{-1} in IR spectra of furylnitroethenes have been attributed to the asymmetric and symmetric stretching, respectively, of nitro group.

polarity of the molecules due to the efficient conjugation involving *p*-electrons of nitrogen, oxygen or sulfur, double carbon-carbon bond, and the nitro group.



The high polarity of *E*-*gem*-cyanonitroethenes was confirmed using the dipole moments method with nitrile of α-nitrocinnamic acid (μ_{exp}, 5.46 D) as an example; the molecule was completely coplanar, and the both substituents (nitro and cyano groups) participated in the conjugation [35].

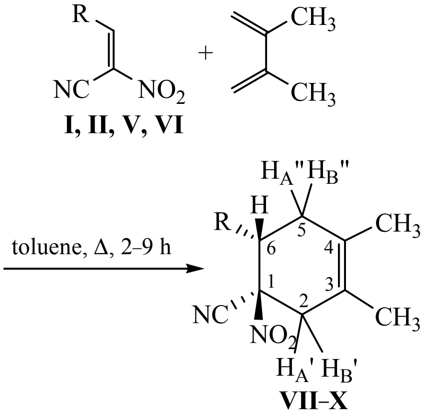
The X-ray analysis data of α-nitrocinnamic acid nitrile, its derivatives (*ortho*- and *para*-methoxy-substituted at the benzene ring), and *gem*-cyano-nitroethene of ferrocene type available in the literature have confirmed the molecules *E*-configuration in the crystal [7, 28, 36, 37].

Nitriles of α-nitrocinnamic acids and their hetero-analogs have been recognized as highly reactive species: they easily react with *C*-, *N*-, and *P*-nucleophiles [1]. Their reactions with 1,3-dipoles [7, 38–42] and vinyl ethers [43–45] yielding practically important cyclic compounds are of the particular interest.

Due to the presence of the electron-deficient C=C bond in the molecules of *gem*-cyanonitroethenes, they can be used as dienophile components in the Diels–Alder reactions. However, the information about preparation of the diene synthesis adducts based on aryl(hetaryl)-containing cyanonitroethenes has only appeared recently. The available examples include the interaction of these nitroalkenes with cyclo-pentadiene [46]; the reactions have been performed in anhydrous nitromethane at room temperature during 24 h and have yielded a mixture of *endo*(NO_2)- and *exo*(NO_2)-isomers of *gem*-cyanonitronorbornenes, with a predominance of first. Structure of the *endo*(NO_2)-isomers has been confirmed by NOESY spectroscopy [46] and X-ray diffraction analysis [47]; the kinetic [48] and quantum-chemical studies of the reactions have been performed [49–51].

The diene condensations between 1-cyano-1-nitro-2-(4-cyanophenyl)ethene and 2,3-dimethyl-1,3-butadiene (in bulk, 30°C, 10 h) as well as between 2-(4-methylphenyl)-1-cyano-1-nitroethene and divinyl [the latter being generated in situ from 3-sulfolene under the reaction conditions (110°C, 12 h)] have been described in [13].

We found that *gem*-cyanonitroethenes **I**, **II**, **V**, and **VI** reacted smoothly with 2,3-dimethyl-1,3-butadiene; the reactions proceeded in toluene under reflux during 2–9 h in the absence of any catalyst. The functionalized cyclohexenes **VII–X** were obtained in up to 94% yield.



I, II, V, VI

VII–X

R = Ph (**I**, **VII**), 4-$MeOC_6H_4$ (**II**, **VIII**), 2-furyl (**V**, **IX**), 2-thienyl (**VI**, **X**).

The prepared *gem*-cyanonitrocyclohexenes were crystalline solids. Compound **VII** has been earlier synthesized via the three-component solvent-free reaction from benzaldehyde, nitroacetonitrile, and 2,3-dimethyl-1,3-butadiene (60°C, 5 h) [13].

Structure of the products **VII–X** was confirmed by IR and ^{1}H NMR spectroscopy data (Table 4). In particular, the IR spectra contained strong absorption bands assigned to stretching of non-conjugated nitro group (ν_{as} = 1565–1570 and ν_s = 1355–1370 cm^{-1}). Stretching vibrations of the cyano group were not registered in the IR spectra; that feature of the non-conjugated *gem*-nitro nitrile fragment could be probably explained by the electronic effect of the neighboring nitro group [52]. Similarly, the cyano group has been inactive in IR spectrum of nitroacetonitrile; however, the corresponding band in the Raman spectrum (2270 cm^{-1}) is strong [19].

^{1}H NMR spectra of cyanonitrocyclohexenes **VII–X** contained the signals of all the protons present in the molecules. In detail, the spectrum of compound **X** solution in $CDCl_3$ (Fig. 3) contained a singlet of the protons of the CH_3 groups at the double bond of the

Table 4. Spectral parameters of *gem*-cyanonitrocyclohexenes **VII–X**

Comp. no.	R	ν, cm^{-1}	δ_H, ppm (*J*, Hz)						
		NO_2	CH_3	$H_{A'}$	$H_{B'}$	$H_{A''}$	$H_{B''}$	H	Ar, Het [OCH_3]
VII	Ph	1570, 1360	1.75 s	3.27 d $^2J_{A'B'}$ 16.5	2.82 d	2.78 m $^2J_{A''B''}$ 17.94 $^3J_{A''H}$ 11.84, $^3J_{B''H}$ 5.55	2.47 d.d	3.65 d.d	7.30–7.40 m
VIII	4-$MeOC_6H_4$	1565, 1360	1.73 s	3.26 d $^2J_{A'B'}$ 17.0	2.80 d	2.74 m $J_{A''B''}$ 18.00 $^3J_{A''H}$ 11.90, $^3J_{B''H}$ 5.80	2.42 d.d	3.65 d.d	6.85d, 7.27d $^3J_{b,c}$ 8.85 [3.78 s]
IX	2-Furyl	1565, 1355	1.75 s	3.27 d $^2J_{A'B'}$ 16.5	2.82 d	2.78 m $^2J_{A''B''}$ 18.16 $^3J_{A''H}$ 12.0, $^3J_{B''H}$ 5.45	2.46 d.d	3.65 d.d	6.30–7.35 m
X	2-Thienyl	1570, 1370	1.74 s	3.24 d $^2J_{A'B'}$ 16.0	2.84 d	2.74 m $^2J_{A''B''}$ 17.33 $^3J_{A''H}$ 11.52, $^3J_{B''H}$ 5.70	2.59 d.d	4.01 d.d	6.98 d (H^c), 7.04 d.d (H^b) 7.27 d (H^d) $^3J_{b,c}$ 3.68, $^3J_{c,d}$ 5.06

ring (δ = 1.74 ppm); the cyclic methylene protons $C^2H_{A'}$ and $C^2H_{B'}$ resonated as an AB-system and were detected as doublets at 3.24 and 2.84 ppm [$^2J(H_{A'}H_{B'})$ = 16.00 Hz]; the $C^5H_{A''}$, $C^5H_{B''}$, and C^6H protons of a three-spin ABX-system were observed at 2.74, 2.59, and 4.01 ppm, respectively; the protons of thiophene ring resonated as two doublets (6.98 and 7.27 ppm) and a doublet of doublets (7.04 ppm).

Availability of the starting reagents, simplicity of the procedure, and good yields of the products suggested that the proposed method was a convenient approach towards synthesis of *gem*-cyanonitrocyclohexenes.

The new nitro- and cyano-substituted cyclohexenes obtained in this work are of definite practical interest in view of the application as synthetic intermediates for preparation of pharmacologically active compounds. Substituted cyclohexanes and cyclohexenes have been recognized as the key parts of a number of practically important compounds or intermediates for their preparation [53–56]. *gem*-Cyanonitrocyclohexenes containing pharmacophore furan or thiophene fragments are of special significance since many derivatives of these heterocycles (such as furacilin, furazolidone, furagin, furosemid, pyrantel, ketotifen, and others) have been widely used in the medicine [57].

EXPERIMENTAL

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

^1H, ^{13}C–{^1H} NMR, ^1H–^{13}C HMQC, and ^1H–^{13}C HMBC spectra of the solutions in deuterated chloroform were registered with a Jeol JNM-ECX400A spectrometer operating at 399.78 (^1H) and 100.53 (^{13}C) MHz. The residual proton signals of the non-deuterated solvent served as the internal reference. IR spectra were recorded with a Shimadzu IR-Prestige-21 Fourier spectrometer in the chloroform solution (*c* = 40 mg mL^{-1}). Electronic absorption spectra of the ethanolic solutions were recorded using a Shimadzu UV 2401PC instrument (quarts cell, *l* = 1.01 mm). Elemental analysis was performed with a EuroVector analyzer (EA 3000, the CHN Dual configuration).

1-Cyano-1-nitro-2-phenylethene **I** was prepared as described in [2] from benzaldehyde and nitroacetonitrile in the presence of $MeNH_2{\cdot}HCl$ and Na_2CO_3; other *gem*-cyanonitroethenes **II–VI** were synthesized from crude nitroacetonitrile without any catalyst [18, 19].

3,4-Dimethyl-1-cyano-1-nitro-6-phenyl-3-cyclohexene (VII). 2,3-Dimethyl-1,3-butadiene (0.33 mL, 0.003 mol) and approximately 0.05 g of hydroquinone as polymerization inhibitor were added to a suspension

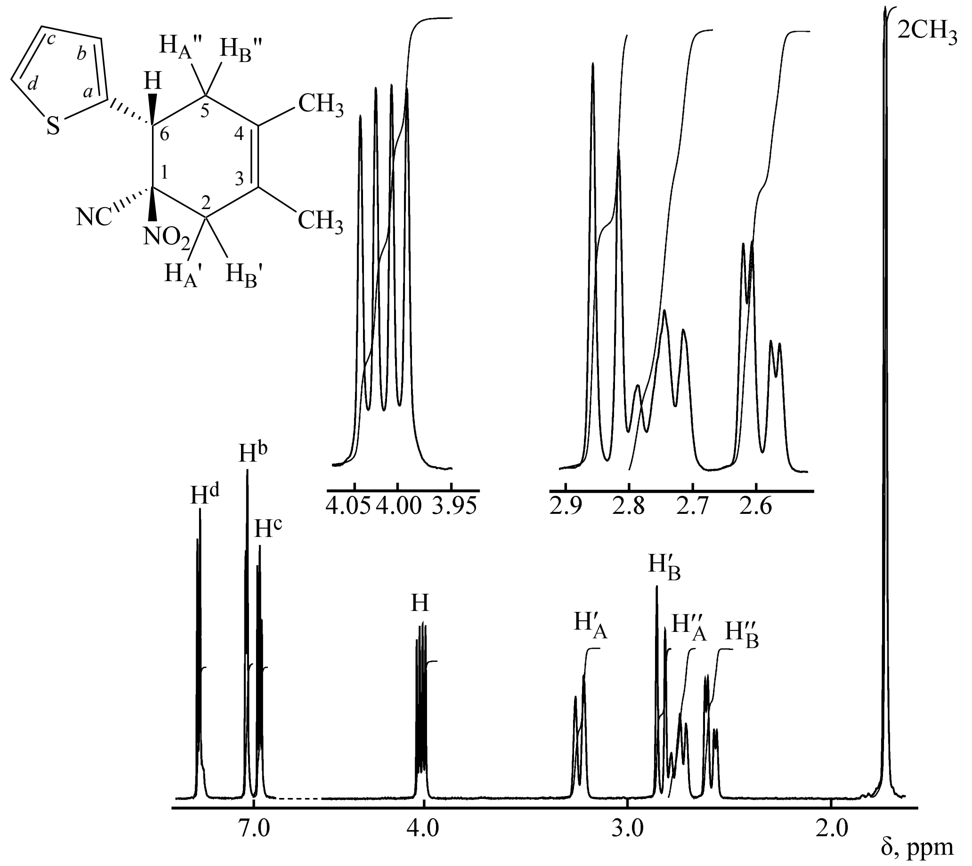


Fig. 3. ^{1}H NMR spectrum of 3,4-dimethyl-1-cyano-1-nitro-6-(2-thienyl)-3-cyclohexene **X** in $CDCl_3$.

of 1-cyano-1-nitro-2-phenylethene **I** (0.174 g, 0.001 mol) in 3.3 mL of toluene. The reaction mixture was refluxed during 3 h. After cooling, the solvent and excess of 2,3-dimethyl-1,3-butadiene were removed; the residue was treated with ethanol. Yield 0.192 g (75%), colorless crystals, mp 90–92°C (ethanol) (mp 98–100°C (Et_2O) [13]). Found, %: C 70.34, 70.48; H 6.31, 6.38; N 10.79. $C_{15}H_{16}N_2O_2$. Calculated: C 70.31; H 6.25; N 10.94.

3,4-Dimethyl-6-(4-methoxyphenyl)-1-cyano-1-nitro-3-cyclohexene (VIII) was prepared similarly from 2-(4-methoxyphenyl)-1-cyano-1-nitroethene **II** and 2,3-dimethyl-1,3-butadiene; the reaction mixture was refluxed with toluene during 9 h. Yield 94%, colorless crystals, mp 108–110°C (ethanol). Found N, %: 9.63. $C_{16}H_{17}N_2O_3$. Calculated N, %: 9.79.

3,4-Dimethyl-6-(2-furyl)-1-cyano-1-nitro-3-cyclohexene (IX) was prepared similarly from 1-cyano-1-nitro-2-(2-furyl)ethene **V** and 2,3-dimethyl-1,3-butadiene; the reaction mixture was refluxed with toluene during 2 h. Yield 54%, colorless crystals, mp 93–94°C (ethanol). Found N, %: 11.53. $C_{13}H_{14}N_2O_3$. Calculated N, %: 11.38.

3,4-Dimethyl-1-cyano-1-nitro-6-(2-thienyl)-3-cyclohexene (X) was prepared similarly from 1-cyano-1-nitro-2-(2-thienyl)ethene **VI** and 2,3-dimethyl-1,3-butadiene; the reaction mixture was refluxed with toluene during 4 h. Yield 83%, colorless crystals, mp 122–124°C (ethanol). $^{13}C-\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 18.52, 18.56, 38.34, 42.04, 43.18, 90.85, 113.45, 120.32, 126.00, 126.63, 127.05, 127.27, 137.60. Found, %: C 59.77; H 5.29; N 10.48. $C_{13}H_{14}N_2SO_2$. Calculated, %: C 59.54; H 5.34; N 10.68.

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REFERENCES

1. Berestovitskaya, V.M., Baichurin, R.I., and Aboskalova, N.I., *Sopryazhennye nitroeteny, geminal'no aktivirovannye slozhnoefirnoi, tsiano-, i atsil'noi gruppami* (Conjugated Nitroethenes Geminally Activated by the Ester, Cyano, and Acyl Groups), St. Petersburg: Asterion, 2014.
2. Ried, W., and Köhler, E., *Lieb. Ann.*, 1956, vol. 598, no. 2, p. 145. DOI: 10.1002/jlac.19565980207.
3. Acheson, R.M., Dearnaley, D.P., Plunkett, A.O., and Porter, V.C., *J. Chem. Soc. (Resumed)*, 1963, p. 2085. DOI: 10.1039/JR9630002085.
4. Dore, J.C., and Viel, C., *Chim. Therapeutica*, 1973, vol. 8, no. 1, p. 80.
5. Metchkov, T., and Demireva, Z., *Z. Chem.*, 1985, vol. 25, no. 5, p. 169. DOI: 10.1002/zfch.19850250504.
6. Mechkov, Ts.D., and Demireva, Z.I., *J. Org. Chem. USSR*, 1985, vol. 21, no. 9, p. 1724.
7. Benhaoua, H., Piet, J.C., Danion-Bougot, R.D., Toupet, L., and Carrie, R., *Bull. Soc. Chim. Fr.*, 1987, no. 2, p. 325.
8. Troschütz, R., and Grün, L., *Archiv Pharm.*, 1993, vol. 326, no. 11, p. 857. DOI: 10.1002/ardp.19933261104.
9. Jasiński, R., Kwiatkowska, M., and Barański, A., *Czasopismo Techniczne. Chemie*, 2006, vol. 103, no. 4, p. 41.
10. Tamaddon, F., Tayefi, M., Hosseini, E., and Zare, E., *J. Mol. Catal. (A),* 2013, vol. 366, p. 36. DOI: 10.1016/j.molcata. 2012.08.027.
11. Brillon, D., and Sauve, G., *J. Org. Chem.*, 1992, vol. 57, no. 6, p. 1838. DOI: 10.1021/jo00032a042.
12. Amantini, D., Fringuelli, F., Piermatti, O., Pizzo, F., and Vaccaro, L., *Green Chem.*, 2001, vol. 3, no. 5, p. 229. DOI: 10.1039/B105522B.
13. Frinquelli, F., Girotti, R., Piermatti, O., Pizzo, F., and Yaccaro, L., *Org. Lett.*, 2006, vol. 8, no. 25, p. 5741. DOI: 10.1021/ol062253o.
14. (a) Boguszewska-Czubara, A, Łapczuk-Krygier, A., Rykała, K., Biernasiuk, A., Wnorowski, A, Popiołek, Ł., Maziarka, A., Hordyjewska, A., Jasiński, R., *J. Enzyme Inhibition and Medicinal Chemistry*, in press. DOI: 10.3109/14756366.2015.1070264. (b) Velizadeh, H., Mamaghani, M., and Badrian, A., *Synth. Comm.*, 2005, vol. 35, no. 6, p. 785. DOI: 10.1081/SCC-200050942.
15. Steinkopf, W., and Bohrmann, L., *Ber.*, 1908, vol. 41, no. 1, p. 1044. DOI: 10.1002/cber.190804101207.
16. Aboskalova, N.I., *Candidate Sci. (Chem.) Dissertation*, Leningrad, 1971.
17. Polyanskaya, A.S., Perekalin, V.V., Aboskalova, N.I., and Sokolova L.N., *USSR Author's Certificate* 335246 (1972); *Bull. Izobret.*, 1972, no. 13.
18. Aboskalova, N.I., Polyanskaya, A.S., Perekalin, V.V., Demireva, Z.I., and Sokolova, L.N., *J. Org. Chem. USSR*, 1972, vol. 8, no. 6, p. 1349.
19. Shadrin, V.Yu., *Candidate Sci. (Chem.) Dissertation*, Leningrad, 1987.
20. Sokolova L.N., Polyanskaya, A.S., Aboskalova, N.I., Demireva, Z.I., and Pyatnitskaya, I.A., *Sb. Nauchn. Dokl., XXX Gertsenovskie chteniya*, Leningrad, 1977, p. 59.
21. Polyanskaya, A.S., Perekalin, V.V., Aboskalova, N.I., Demireva, Z.I., Sokolova L.N., and Abdulkina, Z.A., *Zh. Org. Khim.*, 1979, vol. 15, no. 10, p. 2057.
22. Perekalin, V.V., Sopova, A.S., and Lipina, E.S., *Nepredel'nye nitrosoedineniya* (Unsaturated Nitrocompounds), Leningrad: Khimiya, 1982.
23. Ionin, B.I., Ershov, B.A., and Kol'tsov, A.I., *YaMR-spektroskopiya v organicheskoi khimii* (NMR Spectroscopy in Organic Chemistry), Leningrad: Khimiya, 1983.
24. Aboskalova, N.I., Smirnova, N.N., Kataeva, O.N., Baichurin, R.I., Fel'gendler, A.V., Berkova, G.A., and Berestovitskaya, V.M., *Russ. J. Gen. Chem.*, 2008, vol. 78, no. 9, p. 1711. DOI: 10.1134/S1070363208090120.
25. Karakhanov, R.A., Kelarev, V.I., and Polivin, Yu.N., *Russ. Chem. Rev.*, 1993, vol. 62, no. 2, p. 169. DOI: 10.1070/RC1993v062n02ABEH000011.
26. Arcoria, A., Bottino, F., and Sciotto, D., *J. Heterocycl. Chem.*, 1977, vol. 14, no. 8, p. 1353. DOI: 10.1002/jhet.5570140811.
27. Parr, W.J.E., Wasylishen, R.E., and Schaefer, T., *Can. J. Chem.*, 1976, vol. 54, no. 20, p. 3216. DOI: 10.1139/v76-459.
28. Nishiwaki, N., Tomoko, N., Tanaka, C., Nakashima, F., Inoue, Y., Asaka, N., Tohda, Y., and Ariga, M., *J. Org. Chem.*, 1999, vol. 64, no. 6, p. 2160. DOI: 10.1021/jo9818879.
29. Baichurin, R.I., Baichurina, L.V., Aboskalova, N.I., and Berestovitskaya, V.M., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 9, p. 1764. DOI: 10.1134/S1070363213090223.
30. Marçot, B., Rabaron, A., and Viel, C., *Can. J. Chem.*, 1981, vol. 59, no. 8, p. 1224. DOI: 10.1139/v81-179.
31. Paperno, T.Ya., Perekalin, V.V., and Sopova, A.S., *J. Appl. Spectr.*, 1973, vol. 19, no. 4, p. 1299. DOI: 10.1007/BF00604072.
32. Paperno, T.Ya., and Perekalin, V.V., *Infrakrasnye spektry nitrosoedinenii* (IR Spectra of Nitrocompounds), Leningrad: LGPI, 1974.
33. Ptichkina, I.P., Paperno, T.Ya., Demireva, Z.I., Aboskalova, N.I., and Shadrin, V.Yu., *Mezhvuz. sb. nauch. trudov "Metody sinteza, stroenie i khimicheskie prevrashcheniya nitrosoedinenii"* (Methods of Synthesis, Structure, and Chemical Reactions of Nitrocompounds), Leningrad, 1980, p. 61.
34. Pozdnyakov, V.P., and Shadrin, V.Yu., *Mezhvuz. sb. nauch. trudov "Metody sinteza, stroenie i khimicheskie prevrashcheniya nitrosoedinenii"* (Methods of

Synthesis, Structure, and Chemical reactions of Nitrocompounds), Leningrad, 1989, p. 105.

35. Demireva, Z.I., Polyanskaya, A.S., Mladenov, I., and Perekalin, V.V., *Zh. Org. Khim*., 1976, vol. 12, no. 6, p. 1192.
36. Nesterov, V.N., Kislyi, V.P., Timofeeva, T.V., Antipin, M.Yu., and Semenov, V.V., *Acta Cryst., Sect. C*, 2000, vol. 56, no. 3, p. e107. DOI: 10.1107/S0108270100001864.
37. Laus, G., Schottenberger, H., Schuler, N., Wurst, K., and Herber, R.H. *J. Chem. Soc., Perkin Trans. 2,* 2002, no. 8, p. 1445. DOI: 10.1039/B203395J.
38. Amantini, D., Fringuelli, F. Piermatti, O., Pizzo, F., Zunino, E., and Vaccaro, L., *J. Org. Chem*., 2005, vol. 70, no. 16, p. 6526. DOI: 10.1021/jo0507845.
39. Fringuelli, F., Lanari, D., Pizzo, F., and Vaccaro, L., *Eur. J. Org. Chem*., 2008, no. 23, p. 3928. DOI: 10.1002/ejoc.200800142.
40. Piet, J.C., Le Hetet, G., Cailleux, P., Benhaona, H., and Carrie, R., *Bull. Soc. Chim. Belg*., 1996, vol. 105, no. 1, p. 33. DOI: 10.1002/bscb.19961050107.
41. Nosachev, S.B., Shchurova, N.A., and Tyrkov, A.G., *Russ. J. Org. Chem*., 2011, vol. 47, no. 4, p. 577. DOI: 10.1134/S107042801104018X.
42. Nosachev, S.B., Del'netskaya, K.A., Solov'ev, N.A., and Tyrkov, A.G., *Russ. J. Org. Chem*., 2010, vol. 46, no. 9, p. 1427. DOI: 10.1134/S1070428010090319.
43. Fringuelli, F., Matteucci, M., Piermatti, O., Pizzo, F., and Burla, M.C., *J. Org. Chem*., 2001, vol. 66, no. 13, p. 4661. DOI: 10.1021/jo010182v.
44. Bellachioma, G., Castrica, L., Fringuelli, F., Pizzo, F., and Vaccaro, L., *Green Chem*., 2008, vol. 10, no. 3, p. 327. DOI: 10.1039/B712858D.
45. Jasiński, R., Kubik, M, Łapczuk-Krygier, A., Kącka, A., Dresler, E., and Boguszewska-Czubara, A., *Reac. Kinet. Mech. Cat*., 2014, vol. 113, no. 2, p. 333. DOI: 10.1007/s11144-014-0753-8.
46. Jasiński, R., Rzyman, M., and Barański, A., *Coll. Czech. Chem. Comm*., 2010, vol. 75, no. 9, p. 919. DOI: 10.1135/cccc2009562.
47. Łapczuk-Krygier, A., Ponikiewski, Ł., and Jasiński, R., *Cryst. Rep*., 2014, vol. 59, no. 7, p. 961. DOI: 10.1134/S1063774514070128.
48. Jasiński, R., Kwiatkowska, M., and Barański, A., *Monatsh. Chem. Chem. Monthly*, 2012, vol. 143, no. 6, p. 895. DOI: 10.1007/s00706-012-0735-3.
49. Jasiński, R., Kwiatkowska, M., and Barański, A., *J. Mol. Struct. (THEOCHEM)*, 2009, vol. 910, nos. 1–3, p. 80. DOI: 10.1016/j.theochem.2009.06.018.
50. Jasiński, R., and Barański, A., *J. Mol. Struct. (THEOCHEM)*, 2010, vol. 949, no. 1–3, p. 8. DOI: 10.1016/j.theochem. 2010.02.023.
51. Jasiński, R., Michorczyk, P., Jasińska, E., Koifman, O.I., and Barański, A., *Izv. Vuzov. Ser. Khim i Khim. Tekhnol*., 2011, vol. 54, no. 5, p. 89.
52. Bellamy, L.J., *The Infrared Spectra of Complex Molecules*, London: Methuen & Co., Ltd., 1958.
53. Anisimova, N.A., and Berestovitskaya, V.M., *Funktsionalizirovannye nitroalkeny v reaktsiyakh dienovogo sinteza i 1,3-dipolyarnogo tsikloprisoedineniya* (Functionalized Nitroalkenes in Reactions of the Diene Synthesis and 1,3-Dipolar Cycloaddition), St. Petersburg: Asterion, 2008.
54. Nicolaou, K.C., Snyder, S.A., Montagnon, T., and Vassilikogiannakis, G., *Angew. Chemie Int. Ed*., 2002, vol. 41, no. 10, p. 1668. DOI: 10.1002/1521-3773(20020517)41:10<1668::AID-ANIE1668>3.0.CO;2-Z.
55. Mackay, E. G., and Sherburn, M.S., *Synthesis*, 2015, vol. 47, no. 1, p. 1. DOI: 10.1055/s-0034-1378676.
56. Maltsev, O.V., Beletskaya, I.P., and Zlotin, S.G., *Russ. Chem. Rev*., 2011, vol. 80, no. 11, p. 1067. DOI: 10.1070/RC2011v080n11ABEH004249.
57. Mashkovskii, M.D., *Lekarstvennye sredstva* (Drugs), Moscow: RIA “Novaya Volna,” 2012.