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Synthesis and Structure of Nitrocyclohexenylcarboxylates

N. A. Anisimova, A. A. Kuzhaeva, G. A. Berkova, and V. M. Berestovitskaya

Herzen Russian State Pedagogical University, nab. r. Moiki 48, St. Petersburg, 191186 Russia
e-mail: kohrgpu@yandex.ru

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Abstract—The diene condensation of 3-nitro- and 3-bromo-3-nitroacrylates with 2,3-dimethyl-1,3-butadiene and isoprene obtained under the reaction condition from 3-methyl-3-thiolene-1,1-dioxide was investigated. The formed 6-nitro-3-cyclohexenylcarboxylates were subjected to the intramolecular transformation (dehydration and dehydrohalogenation) to give the corresponding nitrocyclohexadienyl- and arylcarboxylates. The structure of the obtained compounds was established from the IR, ^{1}H NMR spectra and independent synthesis.

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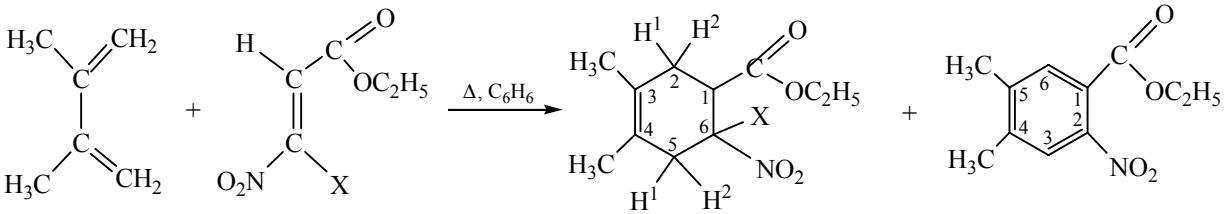
The cyclohexane ring is very common in the nature as a structural fragment of vitamins, terpenes, hormones, alkaloids, and other practically important substances [1, 2]. The interest in natural compounds containing cyclohexene or cyclohexadiene ring is due to the importance of their functions (enzyme inhibitors [3, 4]) and the possibility of their use as key compounds in the synthesis of drugs possessing anticancer [5], narcotic [6, 7], and antiviral [8, 9] activity as well as a promising therapeutic means in the AIDS treatement [10].

One of convenient and accessible methods of the synthesis of functionalized cyclohexenes is the Diels–Alder reaction involving as a dienophile the vicinal substituted nitroalkenes containing the second easily modifiable group (CO_2R, SO_2Ph) [11, 12]. These dienophiles are used for the synthesis of the biologically active compounds, including natural analgesic epibatidine [13, 14], morphine derivatives [15], and conduritols [10].

According to the literature, nitroalkenes enter the condensation with dienes usually in rigid conditions (prolonged heating in a pressure reactor) [16, 17]. The introduction of the second electro-withdrawing substituent (CO_2R, CCl_3, SO_2Ph) into the β-position of nitroalkenes regularly makes the reaction conditions milder [11, 12].

Previously, a 3-nitroacrilate was found to react successfully with some open-chain [18] and cyclic dienes [19], as well as with the diene systems of heterocyclic structure [20–22]. Note that the 3-bromo-3-nitroacrylate was not introduced into the diene condensation before our research.

In this work we studied the reaction of 3-nitro- and 3-bromo-3-nitroacrylates **I** and **II** with 2,3-dimethyl-1,3-butadiene and isoprene. The reaction of the nitroalkene **I** with 2,3-dimethyl-1,3-butadiene occurs in a boiling benzene in 1 h and affords the corresponding 3,4-dimethyl-6-nitro-3-cyclohexen-1-ylcarboxylate **III** in 90% yield (Table 1). The reaction of bromonitroalkene **II** with the same diene proceeds only at boiling the reaction mixture in benzene for 2 h. Ethyl 4,5-dimethyl-2-nitrophenylcarboxylate **V** was isolated along with cyclohexene **IV** in a low yield (5%).



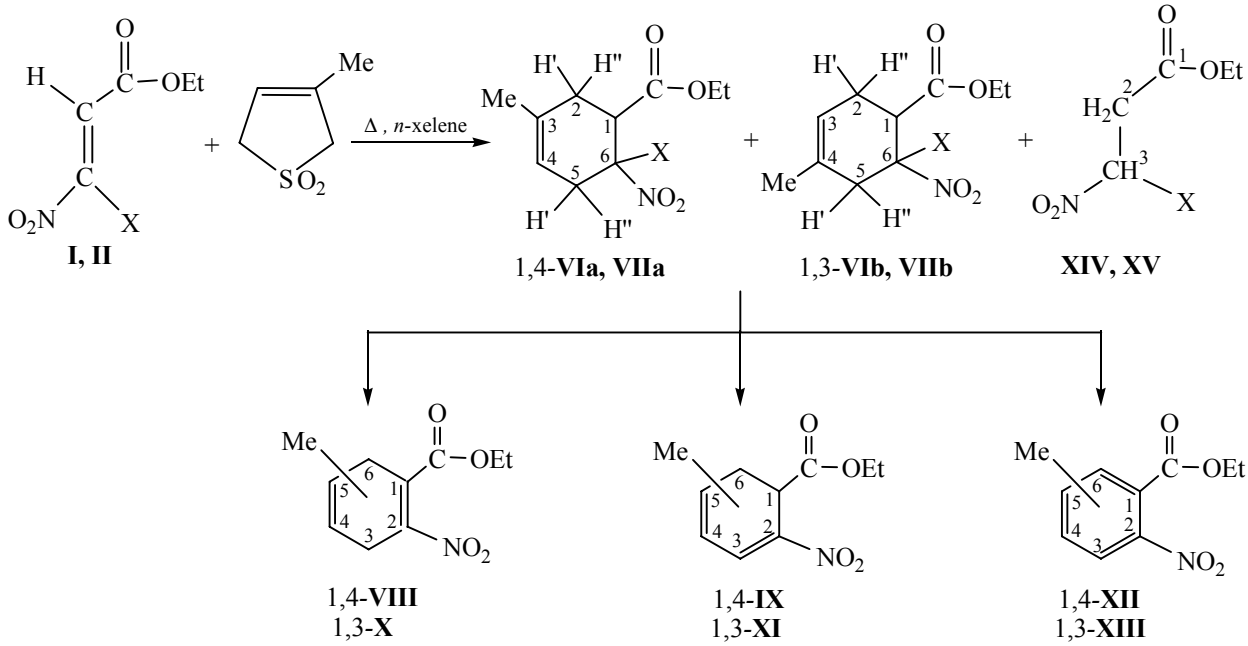
I, II **III, IV** **V**

X = H (**I, III**), Br (**II, IV**).

Table 1. Yields, R_f, and elemental analysis data for nitrocyclohexenes **III**, **IV**, **VIa**, **VIIa**, **VIIb**, nitrocyclohexadienes **IX**, **XI**, **XVI**, **XVII**, and nitroarenes **V**, **XII**, **XIII**

Comp. no.	Yield, %	R_f	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
III	90	0.33	58.01	7.07	6.04	$C_{11}H_{17}NO_4$	58.15	7.49	6.17
			58.06	7.09	6.12				
IV	91	0.48	43.16	5.28	4.61	$C_{11}H_{16}BrNO_4$	43.14	5.23	4.58
			43.19	5.30	4.65				
V	25	0.29	59.21	5.85	6.30	$C_{11}H_{13}NO_4$	59.19	5.83	6.28
			59.24	5.88	6.35				
VIa	33	0.43	56.36	7.06	6.61	$C_{10}H_{15}NO_4$	56.34	7.04	6.57
			56.39	7.09	6.63				
VIIa,	62	0.38	41.13	4.81	4.83	$C_{10}H_{14}BrNO_4$	41.10	4.79	4.79
VIIb		0.45	41.15	4.84	4.84				
IX,	6	0.37	56.88	6.19	6.67	$C_{10}H_{13}NO_4$	56.87	6.16	6.64
XI		0.45	56.91	6.21	6.70				
XII,	12	0.39	57.45	5.30	6.65	$C_{10}H_{11}NO_4$	57.42	5.26	6.70
XIII		0.48	57.49	5.35	6.68				
XVI,	30	0.18	58.69	6.65	6.30	$C_{11}H_{15}NO_4$	58.67	6.67	6.22
XVII		0.24	58.71	6.69	6.35				

The condensation of nitroalkenes **I** and **II** with 3-methyl-3-thiolene-1,1-dioxide was carried out under more rigid conditions (reflux for 13 h in *p*-xylene) due to preliminary desulfonylation of the reagent and isoprene formation *in situ* directly under the reaction conditions. According to the literature [11, 12, 23], the reaction of nitroalkenes with asymmetric 1,3-dienes affords the regioisomeric cyclohexenes. In the simultaneous presence of nitro- and an other electron-withdrawing groups (SO_2Ph, $C{\equiv}N$, CO_2R) in the dienophile it is the nitro moiety that defines the cycloaddition regioselectivity. This fact was also observed



X = H (**I, VIa, VIb, XIV**), Br (**II, VIIa, VIIb, XV**).

in our case [24]. Isoprene formed *in situ* reacts with nitroalkenes **I** and **II** to form a mixture of regioisomers **VIa**, **VIb** and **VIIa**, **VIIb** with the methyl substituents in the 3 and 4 positions of the cyclohexene ring with respect to the nitro group. The yields of cyclohexenes **VIa**, **VIb** and **VIIa**, **VIIb** were 52 and 62%, respectively.

The formation of regioisomeric cyclohexenes **VIa**, **VIb** and **VIIa**, **VIIb** is confirmed by the double set of signals of the ring and methyl protons in the ^{1}H NMR spectra. The ratio of 1,4- (**VIa**, **VIIa**) and 1,3-isomers (**VIb**, **VIIb**) was determined from the the ^{1}H NMR spectra: **VIa**:**VIb** = 4:1, **VIIa**: **VIIb** = 3:1. Only the 1,4-isomer **VIa** was individually isolated by the column chromatography (Table 1).

The rigid conditions of the isoprene condensation with nitroalkenes **I** and **II** promote further intramolecular transformation of the formed nitrocyclohexenes **VIa**, **VIb** and **VIIa**, **VIIb**. In the ^{1}H NMR spectra of the reaction mixtures along with the signals of compounds **VIa**, **VIb** and **VIIa**, **VIIb**, there are the proton signals of the conjugated and nonconjugated cyclohexadienes and substituted benzenes. The reaction is complicated because each nitrocyclohexene regioisomer suffers intramolecular transformations, hence, 1,4- and 1,3-isomers each react to form a pairs of the corresponding nitrocyclohexadienes and nitroarenes, respectively. The reaction of nitroalkene **I** with isoprene formed from 3-methyl-3-thiolene-1,1-dioxide affords not only nitrocyclohexenes **VIa** and **VIb**, but also the dehydration and aromatization products: 1,4 - and 2,4-cyclohexadienes **VIII**–**XI** and 2-nitrophenylcarboxylates **XII** and **XIII**, respectively.

The formation of the conjugated and nonconjugated cyclohexadienes **VIII**, **IX** and **X**, **XI**, and the substituted benzenes **XII** and **XIII** in the case of the reaction of nitroalkenes **I**, **II** with 2,3-dimethyl-1,3-butadiene and isoprene can be described as the simultaneous or successive processes of dehydrohalogenation and dehydrogenation.

In addition to the compounds mentioned above, β-nitro- and β-bromo-β-nitropropanoate **XIV**, **XV** were isolated from the reaction mixture, whose formation can result from the hydrogenation of the carbon-carbon double bond of nitroalkenes **I**, **II** unreacted or formed in a retrodiene process. A similar example of the nitroalkenes hydrogenation with a hydrogen eliminating from the formed reaction product was noted in [24, 25].

The structure of the obtained nitrocyclohexenes **III**, **IV**, **VIa**, **VIb**, **VIIa**, **VIIb** was established from the IR and ^{1}H NMR spectra (Table 2), as well as by comparing their spectral characteristics with those in the spectra of the structurally similar compounds described in [18, 24, 26].

The IR spectra of nitrocyclohexenes **III**, **IV**, **VIa**, **VIb** and **VIIa**, **VIIb** contain the characteristic bands of all functional groups. The ester group vibrations appear as strong bands in the regions of 1735–1745 (C=O), 1025–1030, and 1090–1195 cm^{-1} (C–O–C). The two bands of moderate and high intensity correspond to the symmetric (1350–1340 cm^{-1}) and antisymmetric (1570–1560 cm^{-1}) vibrations of the nitro groups. A weak band at 1620 cm^{-1} in the spectra of compounds **VIa**, **VIb** and **VIIa**, **VIIb** corresponds to the double bond of the cyclohexene ring. This band is absent in the spectra of compounds **III**, **IV** with the symmetrically substituted C=C bond.

According to the ^{1}H NMR spectroscopy (Table 2), compounds **III**, **IV**, **VI**, **VII** are sterically uniform. The formation of two 1,4- (**VIa**, **VIIa**) and 1,3-regioisomers (**VIb**, **VIIb**) is proved by a double set of the methyl group signals at 1.70 and 1.88 ppm (**VIa**, **VIb**), 1.70 and 1.72 ppm (**VIIa**, **VIIb**), and of cyclic protons H^1 at 3.21 and 3.50 ppm (**VIa**, **VIIa**), 3.29 and 3.70 ppm (**VIb**, **VIIb**) and H^6 at 4.88 (**VIa**) and 4.70 ppm (**VIb**). The methylene protons at the atom C^2 in the spectra of nitrocyclohexenes **III**, **IV**, **VIa**, **VIb** and **VIIa**, **VIIb** appear as multiplets at 2.10–2.65 ppm. Owing to the effect of NO_2-group, the signals of methylene protons H^5 are shifted downfield (2.32–3.45 ppm) in comparison with the signals of H^2 (2.10–2.65 ppm). The chemical shift values are close to those in the published spectra of analogs [12, 24].

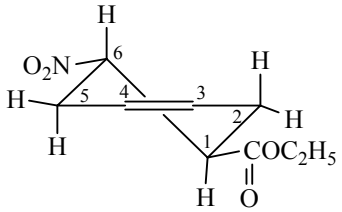
The presence of the bromine atom at the *gem*-position to the NO_2 group in the molecules of compounds **IV**, **VIIa**, and **VIIb** causes a downfield shift of the methylene protons (H^2, H^5) signals at 0.23 and 0.65 ppm, respectively. The methyne protons H^1 give rise in the spectra of compounds **III**, **VIa**, **VIb** to a multiplet in the range of 3.05–3.29 ppm. In the case of the compounds **IV**, **VIIa**, **VIIb** this signal is shifted downfield to 3.50–3.70 due to the influence of the bromine atom. A multiplet at 4.70–4.88 ppm in the spectra of compounds **III**, **VIa**, and **VIb** belongs to the methine proton H^6. The signals of the ring olefin protons in the spectra of compounds **VIa**, **VIb**, **VIIa**, **VIIb** appear at 5.39 and 5.45 ppm (H^3), 5.65 and

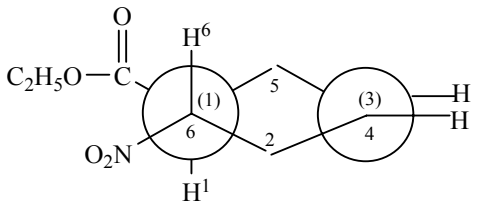
Table 2. ^{1}H NMR spectral parameters for nitrocyclohexenylcarboxylates **III**, **IV**, **VIa**, **VIb**, **VIIa**, **VIIb**

Comp. no.	δ, ppm ($CDCl_3$), J (Hz)									
	C^3H (CH_3)	C^4H (CH_3)	C^2H		C^5H		H^1	H^6	CO_2Et	
			$H^{2'}$	$H^{2''}$	$H^{5'}$	$H^{5''}$			OCH_2	Me
III	(1.52 s)	1.52 s	2.30	2.10 m	2.55	2.32	3.05	4.70	4.25 q	1.30 t
			$J_{H1H2'}$ 5.1	$J_{H1H2''}$ 12.0	$J_{H6H5'}$ 9.5	$J_{H6H5''}$ 7.0	$J_{H1H2'}$ 5.1	$J_{H5'H6}$ 9.5		
			$J_{H2'H2''}$ 13.6		$J_{H5'H5''}$ 14.0		$J_{H1H2''}$ 12.0	$J_{H5''H6}$ 7.0		
							J_{H1H6} 10.2			
IV	(1.68 s)	1.68 s	2.65	2.36	3.25	3.04	3.70 d.d	–	4.19 q	1.32 t
			$J_{H1H2'}$ 6.25	$J_{H1H2'}$ 8.75	$J_{H5'H5''}$ 18.0		$J_{H1H2'}$ 6.25			
VIa	(1.70 s)	5.65	2.25	2.21	2.80	2.70	3.21	4.88	4.16 q	1.24 t
		$J_{H4H5'}$ 1.2	$J_{H1H2'}$ 5.9	$J_{H1H2'}$ 9. 5	$J_{H5'H6}$ 11.5	$J_{H5''H6}$ 6.6	$J_{H1H2'}$ 5.9	$J_{H6H5'}$ 11.5		
		$J_{H4H5''}$ 1.0	$J_{H2'H2'}$ 13.5		$J_{H5'H4}$ 1.2	$J_{H5''H4}$ 1.0	$J_{H1H2''}$ 9.5	$J_{H6H5'}$ 6.6		
					$J_{H5'H5''}$ 16.0		J_{H1H6} 10.0			
VIb	5.39	(1.88 s)	2.42	2.38	2.50	2.41	3.29	4.70	4.32 q	1.36 t
	$J_{H3H2'}$ 1.6		$J_{H1H2'}$ 6.4	$J_{H1H2''}$ 7.0	$J_{H5'H6}$ 8.0	$J_{H5''}$ 6 7.3	$J_{H1H2'}$ 6.4	J_{H6H5} 8.0		
	$J_{H3H2''}$ 1.2		$J_{H2'H2''}$ 16.0		$J_{H5'H5''}$ 10.0		$J_{H1H2''}$ 7.0	$J_{H6H5''}$ 7.3		
							J_{H1H6} 12.8			
VIIa	(1.70 s)	5.70	2.58 m		3.45 m		3.50 m	–	4.35 q	1.25 t
VIIb	5.45	(1.72 s)	2.65 m		3.35 m		3.70 m	–	4.30 q	1.27 t

5.70 ppm (H^4). Depending on the compound structure the signals of methyl groups are differently located in the spectrum. For example, the methyl group signals in the spectra of compounds **III** and **IV** containing two methyl substituents are shifted more upfield (chemical shifts 1.52 and 1.68 ppm), compared with the compounds **VIa**, **VIb** and **VIIa**, **VIIb** containing only one methyl substituent (1.70–1.88 ppm).

To reveal the relative position of the nitro and ester groups in the nitrocyclohexenylcarboxylate molecule and conformational characteristics of the six-membered ring we have considered the spin-spin coupling constant of the vicinal protons H^1 and H^6. For the studied compounds its value lies in the range of $^3J_{1,6}$ 10.0–12.8 Hz (Table 2), which corresponds to the dihedral angle between the vicinal protons (~180°C) or axial arrangement of vicinal protons [27, 28]. Consequently, the molecules of the compounds **III**, **VIa**, **VIb** contain a six-membered ring in a *semi-chair* form with the equatorial location of the bulky substituents (NO_2 and $CO_2C_2H_5$) and *anti*-orientation of the vicinal protons along the C^1–C^6 bond, as shows the Newman projection.



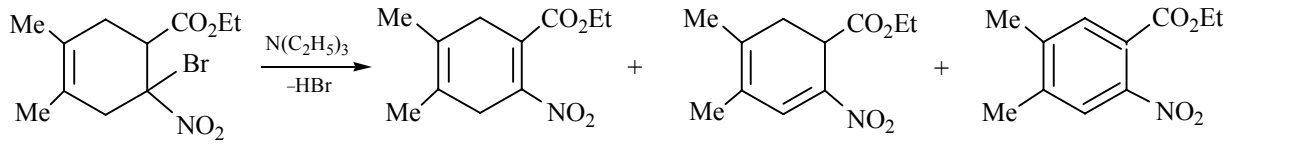


To determine the structure of nitrocyclohexadienyl- and nitroarylcarboxylates isolated from the products mixture obtained by the Diels–Alder reaction an attempt was made of their synthesis directly from the bromonitrocyclohexene **IV** by the dehydrohalogenation. The halonitrocyclohexene **IV** was found to eliminate HBr already at boiling in benzene and to convert into a mixture of the nitro-containing 1,4 - and

Table 3. ^{1}H NMR spectral parameters for nitrocyclohexadienylcarboxylates **VIII**–**XI**, **XVI**, **XVII** and nitroarylcarboxylates **V**, **XII**, **XIII**

Comp. no.	δ, ppm ($CDCl_3$), *J* (Hz)						
	C^1H	C^3H	C^4H, (CH_3)	C^5H, (CH_3)	C^6H	OCH_2	CH_3
Nitrocyclohexadienes							
VIII	–	2.40 m	5.50 m	(1.70 s)	2.35 m	4.20 q	1.30 t
IX	3.25 m	8.00 m	7.35 m	(1.75 s)	2.45 m	4.20 q	1.30 t
X	–	2.30 m	(2.30 s)	5.30 m	2.40 m	4.30 q	1.30 t
XI	3.25 m	7.92	(2.40 s)	7.45 m	2.50 m	4.30 q	1.30 t
XVI	–	2.28 m	(1.75 s)	(1.70 s)	2.10 m	4.15 q	1.30 t
XVII	3.45 m	7.50 m	(2.35 s)	(2.28 s)	2.80 m	4.25 q	1.30 t
Nitroarenes							
V	–	7.70 s	(2.38 s)	(2.35 s)	7.50 m	4.36 q	1.34 t
XII	–	8.20 m	7.15 m	(2.20 s)	6.50 m	4.40 q	1.40 t
XIII	–	8.15 m	(2.45 s)	7.25	6.70 m	4.40 q	1.40 t

2,4-cyclohexadienes **XVI** and **XVII** and aromatic derivative **V**. The dehydrohalogenation of bromonitrocyclohexene **IV** in the presence of triethylamine leads to the formation of nitroarene **V** in a 62% yield.



IV **XVI** **XVII** **V**

The structure of the synthesized nitroaromatic compounds **V**, **XII**, **XIII** was established on the basis of the spectral characteristics in comparison with the structurally identical compounds [24]. In the ^{1}H NMR spectra of these compounds the proton signal of C^6H is observed in the range of 6.50–7.50 ppm, and the signal of the C^3H proton is shifted downfield (~7.70–8.20 ppm) due to the effect of an electron-withdrawing nitro group (Table 3).

The IR spectra of nitroarylcarboxylates **V**, **XII**, **XIII** contain characteristic absorption bands corresponding to the functional groups present in the molecule: to the ester group belong three bands in the range of 1745–1750 ($\nu_{C=O}$), 1025–1035 and 1055–1110 cm^{-1} (ν_{C-O-C}), and two bands at 1550–1560 and 1360–1380 cm^{-1} correspond to the conjugated nitro groups.

The assignement of nitrocyclohexadienylcarboxylates to the conjugate (**IX**, **XI**, **XVII**) and nonconjugated (**VIII**, **X**, **XVI**) systems were carried out on the basis of analysis of their ^{1}H NMR spectra, as well as by comparison with the corresponding characteristics of the model nitrocyclohexadienes [12]. For the nonconjugated cyclohexadienes **VIII**, **X**, **XVI** the ^{1}H NMR spectrum is characteristed by the presence of the methylene protons signals at the atoms C^3, C^6 (2.10–2.40 ppm) and of the olefin protons of the isolated C=C bond at 5.30–5.50 ppm. This is consistent with the corresponding parameters of the structurally identical compounds [12, 29] (Table 3). The presence of two conjugated C=C bonds in the six-membered ring causes a downfield shift of the signals of methylene and olefin protons compared with those of the similar protons in the corresponding initial cyclohexenes and nonconjugated cyclohexadienes.

Thus, in the ^{1}H NMR spectrum of cyclohexadienes **IX**, **XI** and **XVII** the olefin proton at C^3H appears at 7.50–8.00 ppm, the signals of the methylene and ring protons appear at 2.45–2.80 ppm (Table 3).

An important criterion in the structural analysis of the compounds is the value of chemical shift of the methyl protons. The signal of the CH_3 groups at C=C bond in the nonconjugated dienes **VIII**, **X**, **XVI** has chemical shift in the range of 1.70–1.75 ppm. In the spectra of the conjugated (**IX**, **XI**, **XVII**) and aromatic (**V**, **XII**, **XIII**) structures it is shifted downfield (2.20–2.45 ppm).

The 1,4- and 1,3-isomers of methylnitrocyclohexadienes were identified by considering the methyl groups signal. The downfield signal $\delta(CH_3)$ 2.30–2.40 ppm corresponds to the mutual location of the methyl and nitro groups in the 1,3-isomers (**X**, **XI**). In the spectrum of 1,4-isomers (**VIII**, **IX**) the methyl group signal appears in a stronger field (1.70–1.75 ppm) due to the weaker electron-withdrawing effect of the nitro group.

The spectral (IR and ^{1}H NMR) characteristics of β-nitro- and β-bromo-β-nitropropanoates **XIV**, **XV** conform fully the proposed structures. Thus, in the ^{1}H NMR spectrum of compound **XIV** the methylene protons appear at 4.50 (C^2H_2) and 4.80 ppm (C^3H_2). The presence of Br atom in compound **XV** contributes to the downfield shift of the signals of C^3H_2. The signals appear at 4.85 ppm, and the methine proton C^3H resonates at 5.20 ppm

Thus, as a result of our study the reaction conditions of 3-nitro- and 3-bromo-3-nitroacrylates with 2,3-dimethyl-1,3-butadiene, as well as with 3-methyl-3-thiolene-1,1-dioxide, a source of the synthetic 1,3-alkadiene, were found. The nitro- and *gem*-bromonitrocyclohexenes are shown to exhibit an increased tendency to the intramolecular transformations under the conditions of their synthesis (dehydrobromination, dehydrogenation, aromatization). The largest mobility is characteristic of the bromine-containing nitrocycloalkenylcarboxylates.

The Diels–Alder reaction involving 3-nitroacrylates and acyclic 1,3-alkadienes can be considered as an accessible preparative method for the synthesis of nitrocyclohexenylcarboxylates, the nitro precursors of the potentially biologically active compounds and, in particular, cyclohexane β-amino acids [30–32].

EXPERIMENTAL

The IR spectra were obtained on an Infralum FT-02 spectrometer (chloroform, *c* 0.1–0.001 M). The ^{1}H NMR spectra were registered on a Bruker AC-200 spectrometer (200 MHz) from solutions in $CDCl_3$. The chemical shifts were determined relative to external standard (HMDS) accurate to ±0.5 Hz.

The individual compounds were isolated by the column chromatography on a Chemapol 100\200 silica gel and aluminum oxide. The compounds individuality and the reaction progress were monitored by the TLC on Silufol-254 plates in hexane–acetone mixture (3:2) detecting with iodine vapor. The compounds ratio was determined by the ^{1}H NMR spectroscopy after the column chromatography.

The starting nitro- and *gem*-bromonitroacrylates **I** and **II** were prepared according to the procedures [33, 34], respectively.

Ethyl 3,4-dimethyl-6-nitro-3-cyclohexen-1-ylcarboxylate (III). To a solution of 0.86 g of ethyl 3-nitroacrylate **I** in 5 ml of benzene was added 0.1 g of hydroquinone and 1.1 ml of 2,3-dimethyl-1,3-butadiene. The reaction mixture was boiled for 1 h. The solvent was removed on a rotary evaporator, and the residue was chromatographed on alumina. From the fraction eluted with carbon tetrachloride was isolated 1.22 g (90%) of compound **III** as a yellow oil, R_f 0.33.

Ethyl 6-bromo-3,4-dimethyl-6-nitro-3-cyclohexen-1-ylcarboxylate (IV), ethyl 4,5-dimethyl-2-nitrophenylcarboxylate (V). To a solution of 0.8 g of ethyl 3-bromo-3-nitroacrylate **II** in 5 ml of benzene was added 0.1 g of hydroquinone and 0.84 ml of 2,3-dimethyl-1,3-butadiene in 1 ml of benzene. The reaction mixture was boiled for 2 h. The solvent was removed on a rotary evaporator, and the residue was chromatographed on alumina. From the fraction eluted with carbon tetrachloride was isolated 1.0 g (91%) of compound **IV** as a yellow oil, R_f 0.48. From the fraction eluted with benzene was obtained 0.05 g (5%) of compound **V**, R_f 0.29.

Ethyl 3(4)-methyl-6-nitro-3-cyclohexen-1-yl-carboxylate (VIa, VIb), ethyl 5(4)-methyl-2-nitro-1,4-cyclohexadien-1-ylcarboxylates (VIII, X), ethyl-5(4)-methyl-2-nitro-2,4-cyclohexadien-1-ylcarboxylates (IX, XI), ethyl 5(4)-methyl-2-nitrophenylcarboxylates (XII, XIII), ethyl 3-nitropropanoate (XIV). To a solution of 0.8 g of ethyl 3-nitroacrylate **I** in 5 ml of *p*-xylene was added 0.1 g of hydroquinone

and 1.46 g of 3-methyl-3-thiolene-1,1-dioxide. The reaction mixture was boiled for 13 h. The solvent was removed on a rotary evaporator, and the residual oil was chromatographed on a silica gel. From the fraction eluted with benzene was obtained 0.12 g of a yellow oil as a mixture of compounds **VIII–XI** in a 2:1:2:1 ratio. From the first chloroform portion (~100 ml) was obtained 0.25 g of a yellow oil as a mixture of compounds **IX**, **XI**, **XIV** in a 3:2:2 ratio. From the second chloroform portion (~150 ml) was obtained 0.61 g (52%) of a yellow oil as a mixture of compounds **VIa** and **VIb** in a 2:1 ratio, R_f 0.43, 0.33. The compounds **VIII–XI** were registered spectrally.

The repeated chromatographing compounds **VIa** and **VIb** mixture with benzene gave 0.39 g (33%) of compound **VIa** as an oil, R_f 0.43. From the first ether portion (~100 ml) was obtained 0.14 g (12%) of a mixture of compounds **XII** and **XIII** in a 2:1 ratio, R_f 0.39, 0.48. From the second ether portion (~150 ml) was obtained 0.07 g (9%) of compound **XIV**, R_f 0.42. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1570, 1375 (NO_2), 1740 (C=O), 1030, 1090 (C–O–C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.50 m (2H, CH_2CO_2R), 4.80 m (2H, CH_2NO_2), 4.25 q (2H, OCH_2), 1.15 t (3H, CH_3). Found, %: C 40.85, 40.89; H 6.15, 6.16; N 9.58, 9.61. $C_5H_9NO_4$. Calculated, %: C 40.82; H 6.12; N 9.52.

Ethyl 6-bromo-3(4)-methyl-6-nitro-3-cyclohexen-1-ylcarboxylates (VIIa, VIIb), ethyl 5(4)-methyl-2-nitro-1,4-cyclohexadien-1-ylcarboxylates (VIII, X), ethyl 5(4)-methyl-2-nitro-2,4-cyclohexadien-1-ylcarboxylates (IX, XI), ethyl 5(4)-methyl-2-nitrophenylcarboxylates (XII, XIII), ethyl 3-bromo-3-nitropropanoate (XV). To a solution of 0.8 g of ethyl 3-bromo-3-nitroacrylate **II** in 5 ml of *p*-xylene was added 0.1 g of hydroquinone, 0.48 g of 3-methyl-3-thiolene-1,1-dioxide, and the reaction mixture was boiled for 13 h. After removing the solvent, the residue was chromatographed on a silica gel. From the first benzene portion (~150 ml) was obtained 0.06 g of a yellow oil as a mixture of compounds **VIII**, **IX**, **XI** in a 1:2:1 ratio. From the second benzene portion (~150 ml) was obtained 0.15 g of a yellow oil as a mixture of compounds **IX**, **XII**, **XIII** in a 1:2:1 ratio. From chloroform was obtained 0.65 g (62%) of a yellow oil as a mixture of compounds **VIIa**, **VIIb** in a 3:1 ratio, R_f 0.38, 0.45.

From the ether fraction was obtained 0.1 g (12%) of compound **XV** as a yellow oil, R_f 0.51. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1560, 1370 (NO_2), 1735 (C=O), 1030, 1080 (C–O–C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.85 m (2H, CH_2CO_2R), 5.20 m (1H, $CHNO_2$), 4.20 q (2H, OCH_2), 1.18 t (3H, CH_3). Found, %: C 26.58, 26.61; H 3.60, 3.58; N 6.25, 6.28. $C_5H_8BrNO_4$. Calculated, %: C 26.55; H 3.54; N 6.19.

The repeated chromatographing compounds **VIII**, **IX,** and **XI** mixture with benzene gave 0.05 g (6%) of a yellow oil as a mixture of compounds **IX** and **XI** in a 3:2 ratio, R_f 0.45, 0.37.

The repeated chromatographing compounds **IX**, **XII** and **XIII** mixture with benzene gave 0.05 g (7%) of a mixture of compounds **XII** and **XIII** in a 2:1 ratio, R_f 0.39, 0.48. The spectra of compounds **VIII** and **X** were recorded.

Ethyl 6-bromo-3,4-dimethyl-6-nitro-3-cyclohexen-1-ylcarboxylate (IV), ethyl 4,5-dimethyl-2-nitrophenylcarboxylate (V), ethyl 4,5-dimethyl-2-nitro-1,4-cyclohexadien-1-ylcarboxylate (XVI), ethyl 4,5-dimethyl-2-nitro-2,4-cyclohexadien-1-ylcarboxylate (XVII). *a.* To a solution of 0.8 g of ethyl 3-bromo-3-nitroacrylate **II** in 5 ml of benzene was added 0.1 g of hydroquinone and 0.84 ml of 2,3-dimethyl-1,3-butadiene in 1 ml of benzene. The reaction mixture was refluxed for 15 h. The solvent was removed on a rotary evaporator, and the residue was chromatographed on alumina. From the fraction, eluted with carbon tetrachloride was isolated 0.5 g of a mixture of compounds **IV**, **XVI** and **XVII** in a 1:2:1 ratio, respectively, and from the benzene fraction was obtained 0.9 g of a mixture of compounds **V**, **XVI,** and **XVII**. The repeated chromatographing compounds **IV**, **XVI,** and **XVII** mixture gave 0.31 g (30%) of a mixture of compounds **XVI** and **XVII** (eluent – benzene) in a 1:2 ratio, R_f 0.18, 0.24.

The repeated chromatographing the compounds **V**, **XVI,** and **XVII** mixture with benzene gave 0.27 g (25%) of compound **V** as a yellow oil, R_f 0.29.

b. To a solution of 0.80 g of compound **IV** in 4 ml of benzene was added 0.20 ml of triethylamine, and the reaction mixture was boiled for 20 h. The triethylamine hydrobromide was filtered off. The filtrate was diluted with 20 ml of benzene and washed with water. Benzene extract was dried over anhydrous magnesium sulfate, evaporated, and chromatographed on alumina. From the benzene fraction was obtained 0.67 g (62%) of compound **V** as a yellow oil, R_f 0.29.

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