

Synthesis and Structure of Cyclohexenes Functionalized by Nitro and Trifluoro(chloro)methyl Groups

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Abstract—Cyclohexenes functionalized by nitro and trihalomethyl groups were produced by condensation of 1-nitro- and 1-bromo-1-nitro-3,3,3-trifluoro(chloro)propenes with 2-methyl- and 2,3-dimethyl-1,3-butadienes; their structure was characterized by IR, ¹H, ¹³C, ¹⁹F NMR spectroscopy, and X-ray diffraction method.

Keywords: 1-nitro-3,3,3-trifluoro(chloro)propenes, cyclohexenes, Diels–Alder reaction, acyclic dienes, trihalomethyl group

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The cyclohexane ring is widespread in nature; it is a structural fragment of vitamins, terpenes, hormones, alkaloids, shikimic acid, and other practically significant substances [1, 2]. The growing interest in natural compounds containing a cyclohexene or cyclohexadiene ring is driven by the importance of the functions they perform (inhibitors of enzymes [3, 4]) and their usability as key compounds for the production of anticancer [5], narcotic [6, 7], and antiviral [8, 9] drugs, as well as promising anti-AIDS drugs [10].

One convenient and affordable method for the synthesis of functionalized cyclohexenes is the Diels–Alder reaction involving as a dienophile the vicinal-substituted nitroalkenes containing the second easily modifiable group (CO₂R, SO₂Ph, CHI₃) [11, 12]. Exactly these dienophiles are used for the synthesis of natural biologically active compounds, including the preparation of natural analgesic epibatidine [13, 14], morphine derivatives [15], and conduritols [10].

Of particular interest are nitrocyclohexenes containing a trihalomethyl group, which is known to allow

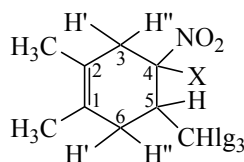
further modification of the cyclic structure and to enhance the pharmacological activity [14].

According to available public references, 1-nitro-3,3,3-trichloropropene enters into diene condensation with alkadienes like 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, isoprene, or piperylene, usually under severe conditions (multi-hour heating in an ampule in the medium of a high-boiling solvent) [16–18].

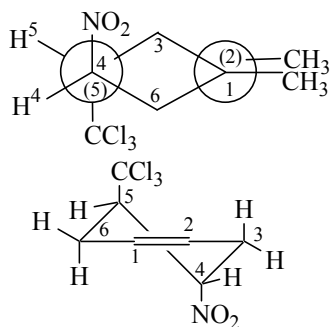
To obtain cyclohexenes containing CCl₃ or CF₃ groups, we studied the diene condensation of 1-nitro-3,3,3-trifluoro(chloro)propenes **1** and **2** and 1-bromo-1-nitro-3,3,3-trifluoro(chloro)propenes **3** and **4** with aliphatic dienes.

The reactions of nitroalkenes (**1** and **2**) and bromo-nitroalkenes (**3** and **4**) with 2,3-dimethyl-1,3-butadiene and isoprene have showed that these dienophiles are reactive with acyclic dienes even without heating (at 4–20°C, in the absence of a solvent, within 1–7 days). Nitroalkenes **1–4**, when reacted with 2,3-dimethyl-1,3-butadiene, produced the corresponding cyclohexenes **5–8** in good yields (92–98%).

[†] Deceased.

Table 1. ^1H NMR spectra of nitrocyclohexenes **5–8**

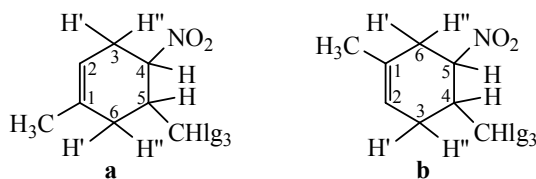
Comp. no.	Hlg	X	δ , ppm (J , Hz)							
			CH ₃	CH ₃	C ³ H		C ⁶ H		H ⁴	H ⁵
					H ^{3'}	H ^{3''}	H ^{6'}	H ^{6''}		
5	F	H	1.66 s	1.65 s	2.73 d.d ($^3J_{\text{H}^3\text{H}^4} = 9.7$, $^2J_{\text{H}^3\text{H}^3''} = 16.8$)	2.58 d.d ($^3J_{\text{H}^3\text{H}^4} = 5.6$, $^2J_{\text{H}^3\text{H}^3''} = 16.8$)	2.35 d.d ($^3J_{\text{H}^6\text{H}^5} = 6.9$, $^2J_{\text{H}^6\text{H}^6''} = 18.0$)	2.24 d.d ($^3J_{\text{H}^6\text{H}^5} = 10.1$, $^2J_{\text{H}^6\text{H}^6''} = 18.0$)	4.78 d.d.d ($^3J_{\text{H}^3\text{H}^4} = 9.7$, $^3J_{\text{H}^4\text{H}^3''} = 16.8$, $^3J_{\text{H}^4\text{H}^5} = 14.0$)	3.17 m
6	Cl	H	1.71 s	1.68 s	2.78 d.d ($^3J_{\text{H}^3\text{H}^4} = 6.8$, $^2J_{\text{H}^3\text{H}^3''} = 16.5$)	2.64 d.d ($^3J_{\text{H}^3\text{H}^4} = 6.8$, $^2J_{\text{H}^3\text{H}^3''} = 16.5$)	2.66 d.d ($^3J_{\text{H}^6\text{H}^5} = 7.2$, $^2J_{\text{H}^6\text{H}^6''} = 16.8$)	2.38 d.d ($^3J_{\text{H}^6\text{H}^5} = 7.2$, $^2J_{\text{H}^6\text{H}^6''} = 16.8$)	5.00 d.t ($^3J_{\text{H}^3\text{H}^4} = 6.8$, $^3J_{\text{H}^4\text{H}^3''} = 6.8$, $^3J_{\text{H}^4\text{H}^5} = 5.6$)	3.70 d.t ($^3J_{\text{H}^6\text{H}^5} = 7.2$, $^3J_{\text{H}^5\text{H}^6''} = 10.1$, $^3J_{\text{H}^4\text{H}^5} = 5.6$)
7	F	Br	1.69 s	1.65 s	3.46 d ($^2J_{\text{H}^3\text{H}^3''} = 17.5$)	2.88 d ($^2J_{\text{H}^3\text{H}^3''} = 17.5$)	2.46 d.d ($^3J_{\text{H}^6\text{H}^5} = 7.3$, $^2J_{\text{H}^6\text{H}^6''} = 18.3$)	2.50 d.d ($^3J_{\text{H}^6\text{H}^5} = 7.3$, $^2J_{\text{H}^6\text{H}^6''} = 18.3$)	–	3.60 d.t ($^3J_{\text{H}^6\text{H}^5} = 7.3$, $^3J_{\text{H}^5\text{H}^6''} = 7.3$, $^3J_{\text{H}^5\text{F}} = 8.5$)
8	Cl	Br	1.73 s	1.66 s	3.53 d ($^2J_{\text{H}^3\text{H}^3''} = 17.4$)	2.80 d ($^2J_{\text{H}^3\text{H}^3''} = 17.4$)	2.84 d.d ($^3J_{\text{H}^6\text{H}^5} = 6.0$, $^2J_{\text{H}^6\text{H}^6''} = 16.6$)	2.77 d.d ($^3J_{\text{H}^6\text{H}^5} = 10.3$, $^2J_{\text{H}^6\text{H}^6''} = 16.6$)	–	3.91 d.d ($^3J_{\text{H}^6\text{H}^5} = 6.0$, $^3J_{\text{H}^5\text{H}^6''} = 10.3$)



To ascertain the mutual disposition of the CHlg_3 and NO_2 groups in the molecules of cyclohexenes obtained, the spin-spin coupling constants characterizing the interaction of vicinal protons H^4 and H^5 with one another and with the protons of adjacent methylene groups ($\text{H}^{3'}$, $\text{H}^{3''}$ and $\text{H}^{6'}$, $\text{H}^{6''}$) were used as an analytical criterion. The analysis of the coupling constants (Tables 1 and 2) of these protons discovered that cyclohexenes **6**, **9a**, and **9b** with equal constants of methine ($^3J_{\text{H}^4\text{H}^5}$) and methylene protons ($^3J_{\text{H}^5\text{H}^6'} = ^3J_{\text{H}^5\text{H}^6''}$, $^3J_{\text{H}^4\text{H}^3'} = ^3J_{\text{H}^4\text{H}^3''}$) have an axial orientation of CHlg_3 and NO_2 groups, while compounds **5**, **10a**, and **10b** with different values of these constants have an

equatorial orientation of the same groups. This fact is confirmed by the coupling constants of methine protons $^3J_{\text{H}^4\text{H}^5}$, which range between 5.6–7.7 Hz for **5**, **9a**, and **9b** and 13.2–14.0 Hz for **6**, **10a**, and **10b** [21].

In the ^1H NMR spectra of all cyclohexenes obtained, the olefin protons appear in the range of 5.38 to 5.58 ppm. Regioisomers **a** and **b** of cyclohexenes **9–12** were identified from the position of the methyl group signal (Fig. 1). The CH_3 group signal in isomer **b** predictably appears downfield (1.80–1.86 ppm) as compared to isomer **a** (1.72–1.75 ppm). Such assignment of CH_3 group signals is additionally confirmed by the data of heteronuclear experiments, specifically ^1H – ^{13}C HMBC (correlation of signals of CH_3 group protons with those of the carbon atoms C^3 of multiple bond and methylene groups). For example, in the ^1H – ^{13}C HMBC spectrum of a **12a/12b** mixture (**12a** : **12b** = 1.0 : 4.0) a clear correlation between proton signals and the corresponding signals of carbon atoms is observed: for isomer **a**, CH_3 (1.74 ppm)/ C^1 (128.83 ppm), C^2 (118.42 ppm), C^3 (51.03 ppm); for isomer **b**, CH_3 (1.80 ppm)/ C^1 (132.34 ppm), C^2 (115.37 ppm), C^3 (34.34 ppm), C^4 (59.31 ppm); $\text{H}^{3',3''}$ (2.77 and 2.84 ppm)/

Table 2. ^1H NMR spectra of nitrocyclohexenes **9a**, **9b**, **10a**, and **10b**

Comp. no.	Hlg	δ , ppm (J , Hz)							
		CH_3	C^2H	C^3H		C^6H		H^4	H^5
				$\text{H}^{3'}$	$\text{H}^{3''}$	$\text{H}^{6'}$	$\text{H}^{6''}$		
9a	F	1.72 s	5.38 br.s	2.80 d.d ($^3J_{\text{H}^3\text{H}^4} = 3.2$, $^2J_{\text{H}^3\text{H}^{3'}} = 18.6$)	2.70 d.d ($^3J_{\text{H}^3\text{H}^4} = 3.2$, $^2J_{\text{H}^3\text{H}^{3''}} = 18.6$)	2.60 d.d ($^3J_{\text{H}^6\text{H}^5} = 8.1$, $^2J_{\text{H}^6\text{H}^{6''}} = 17.2$)	2.45 d.d ($^3J_{\text{H}^6\text{H}^5} = 8.1$, $^2J_{\text{H}^6\text{H}^{6''}} = 17.2$)	4.75 d.t ($^3J_{\text{H}^3\text{H}^4} = 3.2$, $^3J_{\text{H}^4\text{H}^5} = 3.2$, $^3J_{\text{H}^4\text{H}^5} = 7.7$)	3.10 m
9b	F	1.82 s	5.38 br.s	2.70 d.d ($^3J_{\text{H}^3\text{H}^4} = 9.3$, $^2J_{\text{H}^3\text{H}^{3'}} = 17.9$)	2.22 d.d ($^3J_{\text{H}^3\text{H}^4} = 9.3$, $^2J_{\text{H}^3\text{H}^{3''}} = 17.9$)	2.65 d.d ($^3J_{\text{H}^6\text{H}^5} = 2.8$, $^2J_{\text{H}^6\text{H}^{6''}} = 18.0$)	2.40 d.d ($^3J_{\text{H}^6\text{H}^5} = 2.3$, $^2J_{\text{H}^6\text{H}^{6''}} = 18.0$)	3.23 m	4.74 d.t ($^3J_{\text{H}^6\text{H}^5} = 2.3$, $^3J_{\text{H}^5\text{H}^6} = 2.3$, $^3J_{\text{H}^4\text{H}^5} = 7.3$)
10a	Cl	1.75 s	5.58 m	2.83 d.d ($^3J_{\text{H}^3\text{H}^4} = 6.2$, $^2J_{\text{H}^3\text{H}^{3'}} = 18.0$)	2.42 d.d ($^3J_{\text{H}^3\text{H}^4} = 6.2$, $^2J_{\text{H}^3\text{H}^{3''}} = 18.0$)	2.68 d.d ($^3J_{\text{H}^6\text{H}^5} = 7.1$, $^2J_{\text{H}^6\text{H}^{6''}} = 17.6$)	2.60 d.d ($^3J_{\text{H}^6\text{H}^5} = 7.1$, $^2J_{\text{H}^6\text{H}^{6''}} = 17.6$)	5.10 d.t ($^3J_{\text{H}^3\text{H}^4} = 6.2$, $^3J_{\text{H}^4\text{H}^5} = 6.2$, $^3J_{\text{H}^4\text{H}^5} = 13.2$)	3.67 d.t ($^3J_{\text{H}^6\text{H}^5} = 7.1$, $^3J_{\text{H}^5\text{H}^6} = 7.1$, $^3J_{\text{H}^4\text{H}^5} = 13.2$)
10b	Cl	1.86 s	5.43 m	2.70 d.d ($^3J_{\text{H}^3\text{H}^4} = 6.9$, $^2J_{\text{H}^3\text{H}^{3'}} = 16.9$)	2.66 d.d ($^3J_{\text{H}^3\text{H}^4} = 6.9$, $^2J_{\text{H}^3\text{H}^{3''}} = 16.9$)	2.80 d.d ($^3J_{\text{H}^6\text{H}^5} = 6.3$, $^2J_{\text{H}^6\text{H}^{6''}} = 18.3$)	2.40 d.d ($^3J_{\text{H}^6\text{H}^5} = 6.3$, $^2J_{\text{H}^6\text{H}^{6''}} = 18.3$)	3.74 d.t ($^3J_{\text{H}^3\text{H}^4} = 6.9$, $^3J_{\text{H}^4\text{H}^5} = 6.9$, $^3J_{\text{H}^4\text{H}^5} = 13.2$)	4.99 d.t ($^3J_{\text{H}^6\text{H}^5} = 6.3$, $^3J_{\text{H}^5\text{H}^6} = 6.3$, $^3J_{\text{H}^4\text{H}^5} = 13.2$)

CH_3 (22.56 ppm), C^1 (132.34 ppm), C^2 (115.37 ppm), C^4 (59.31 ppm), C^5 (96.24 ppm).

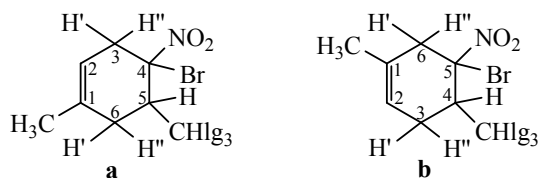
In the ^{13}C NMR spectra (Table 4) of cyclohexenes **5–8**, **9a–11a**, and **9b–11b**, there are signals of all carbon atoms of the $\text{C}^1\text{--C}^6$ cycle and CHlg_3 groups. The most upfield signals are from carbon atoms of methyl groups (18.16–22.88 ppm) and methylene groups C^3H_2 and C^6H_2 (25.29–52.18 ppm). The signals of carbon atoms of methine groups C^4H and C^5H influenced by NO_2 and CHlg_3 groups appear more downfield, in the ranges of 41.90–59.44 ppm [$\text{C}^{5(4)}\text{HCHlg}_3$] and 81.08–99.17 ppm [$\text{C}^{4(5)}\text{HNO}_2$]. The signals of carbon atoms in the $\text{C}^1=\text{C}^2$ bond of the ring appear in the region of 115.91–133.85 ppm. The carbon atoms of CF_3 and CCl_3 groups have signals in the regions of 123.25–126.05 and 77.12–101.47 ppm, respectively [21].

The molecular structure of compound **8** was studied by X-ray diffraction. The spatial structure of one of the two independent molecules of compound **8** is shown in

Fig. 2a¹. The geometries of the two independent molecules of compound **8** are substantially the same, the maximum difference in the length being observed for the $\text{N}^1\text{--O}^1$ bond: 1.236(3) and 1.219(3) Å. The unsaturated six-membered cycle has typical distorted *semi-chair* geometry. The almost flat (within ± 0.01 Å accuracy) fixed part of the cycle consists of carbon atoms C^2 , C^3 , C^4 , and C^5 [the torsion angle $\text{C}^2\text{C}^3\text{C}^4\text{C}^5$ is $2.3(4)^\circ$ and $-2.0(4)^\circ$ for the two independent molecules], which implies that the $\text{C}^3=\text{C}^4$ double bond is not twisted, its length is 1.322(4) and is the same for both independent molecules. The carbon atoms C^1 and C^6 deviate from the coplanar part of the cycle by 0.326(3) and 0.377(3) Å in the first independent molecule and by 0.370(3) and 0.346(3) Å in the second.

The Br atom is in the axial position, one oxygen atom of the nitro group is almost eclipsed by the Br atom, the torsion angle $\text{Br}^1\text{C}^1\text{N}^1\text{O}^2$ is 11.3° and the

¹ The atom numbering in Fig. 2 is different from the indexes provided above, which correspond to the nomenclature.

Table 3. ^1H NMR spectra of cyclohexenes **11a**, **11b**, **12a**, and **12b**

Comp. no.	Hlg	δ , ppm (J , Hz)							
		CH_3	CH^2	C^3H		C^6H		H^4	H^5
				$\text{H}^{3'}$	$\text{H}^{3''}$	$\text{H}^{6'}$	$\text{H}^{6''}$		
11a	F	1.75 s	5.46 s	3.43 d ($^2J_{\text{H}^{3'}\text{H}^{3''}} = 17.7$)	2.86 d.d ($^3J_{\text{H}^{3'}\text{H}^5} = 2.1$, $^2J_{\text{H}^{3'}\text{H}^{3''}} = 17.7$)	2.40 d.d ($^3J_{\text{H}^{6'}\text{H}^5} = 7.3$, $^2J_{\text{H}^{6'}\text{H}^{6''}} = 16.6$)	2.52 d.d ($^3J_{\text{H}^{6''}\text{H}^5} = 7.3$, $^2J_{\text{H}^{6''}\text{H}^{6'}} = 16.6$)	—	3.55 m
11b	F	1.78 s	5.34 d ($^4J_{\text{H}^2\text{H}^4} = 2.1$)	2.50 d.d ($^3J_{\text{H}^{3'}\text{H}^4} = 5.3$, $^2J_{\text{H}^{3'}\text{H}^{3''}} = 17.2$)	2.45 d.d ($^3J_{\text{H}^{3''}\text{H}^5} = 5.3$, $^2J_{\text{H}^{3''}\text{H}^{3'}} = 17.2$)	3.00 d.d ($^5J_{\text{H}^{6'}\text{F}} = 4.6$, $^2J_{\text{H}^{6'}\text{H}^{6''}} = 17.9$)	3.43 d.d ($^5J_{\text{H}^{6''}\text{F}} = 4.6$, $^2J_{\text{H}^{6''}\text{H}^{6'}} = 17.9$)	3.65 m	—
12a	Cl	1.74 s	5.50 d ($^3J_{\text{H}^2\text{H}^3} = 6.4$)	2.88 d.d ($^3J_{\text{H}^{3'}\text{H}^2} = 6.4$, $^2J_{\text{H}^{3'}\text{H}^{3''}} = 17.9$)	3.57 d ($^2J_{\text{H}^{3'}\text{H}^{3''}} = 17.9$)	2.73 d.d ($^3J_{\text{H}^{6'}\text{H}^5} = 6.3$, $^2J_{\text{H}^{6'}\text{H}^{6''}} = 17.6$)	2.92 d.d ($^3J_{\text{H}^{6''}\text{H}^5} = 6.3$, $^2J_{\text{H}^{6''}\text{H}^{6'}} = 17.6$)	—	3.82 d.d ($^3J_{\text{H}^5\text{H}^{6'}} = 6.3$, $^3J_{\text{H}^5\text{H}^{6''}} = 6.3$)
12b	Cl	1.80 s	5.33 d ($^3J_{\text{H}^2\text{H}^{3''}} = 6.1$)	2.77 d.d ($^3J_{\text{H}^{3'}\text{H}^2} = 5.2$, $^2J_{\text{H}^{3'}\text{H}^{3''}} = 17.6$)	2.84 d.d ($^3J_{\text{H}^{3''}\text{H}^2} = 6.1$, $^2J_{\text{H}^4\text{H}^{3''}} = 5.2$, $^2J_{\text{H}^{3'}\text{H}^{3''}} = 17.6$)	2.98 d ($^2J_{\text{H}^{6'}\text{H}^{6''}} = 17.6$)	3.52 d ($^2J_{\text{H}^{6'}\text{H}^{6''}} = 17.6$)	3.92 d.d ($^3J_{\text{H}^4\text{H}^{3'}} = 5.2$, $^3J_{\text{H}^4\text{H}^{3''}} = 5.2$)	—

corresponding angle in the second molecule is 7.5° . The trichloromethyl group is in the equatorial position and its rotation is retarded with respect to the $\text{C}^6\text{--C}^1$ bond, the torsion angle $\text{C}^1\text{C}^6\text{C}^7\text{Cl}^3$ is -82.3° and

-76.7° . This group is in the *gauche*(+) position with respect to the Br atom and in the *gauche*(-) position with respect to the nitro group. The torsion angles $\text{C}^7\text{C}^6\text{C}^1\text{Br}^1$ are $60.5(2)^\circ$ and $62.9(2)^\circ$ and $\text{C}^7\text{C}^6\text{C}^1\text{N}^1$ are

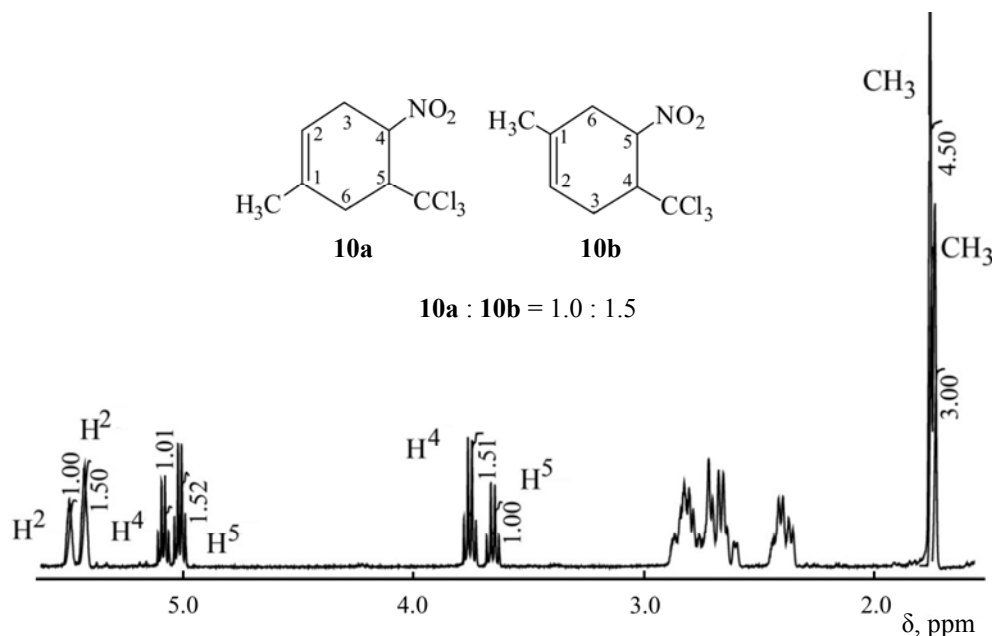
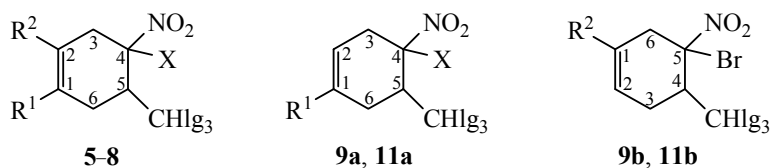
**Fig. 1.** ^1H NMR spectrum of mixture of regioisomeric cyclohexenes **10a**, **10b**.

Table 4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of cyclohexenes **5–8**, **9a**, **9b**, **11a**, **11b** (δ_{C} , ppm)

Comp. no.	Hlg	X	R ¹ , R ² (CH ₃)	C ¹	C ²	C ³	C ⁴	C ⁵	C ⁶	CHlg ₃
5	F	H	18.40, 18.54	122.03	122.97	35.74	81.08 d (³ J _{C⁴F} = 1.1)	41.90 d (² J _{C⁵F} = 27.5)	29.18 d (³ J _{C⁶F} = 2.5)	125.96 d (¹ J _{CF} = 280.0)
6	Cl	H	18.57, 18.69	122.89	125.36	36.23	84.23	56.29	33.49	77.12
7	F	Br	18.27, 18.48	121.57	122.8	48.46	94.66	47.81 (² J _{C⁵F} = 26.8)	31.00	124.80
8	Cl	Br	18.16, 18.29	120.91	123.88	52.18	99.17	59.44	35.46	98.95
9a	Cl	H	22.63	130.89	119.12	34.20	83.98	55.19	26.90	95.50
9b	Cl		22.88	133.85	116.58	30.01	55.67	83.55	31.45	101.47
11a	F	Br	22.50	129.66	117.25	46.94	94.33	46.67	25.29	123.25
11b	F		22.52	131.34	115.91	29.88	47.53	94.45	43.44	126.05

–61.8(2)° and –60.3(2)°. A shortened intramolecular contact O¹...Cl² of 3.09 and 3.06 Å (the sum of the van der Waals radii equal to 3.34 Å [22]) leads to deviations in the bond angles in the O¹N¹C¹C⁶C⁷Cl² chain from the ideal values. The O¹N¹C¹ angle is 113.2(2)° and 114.7(2)°, and C¹C⁶C⁷ is 119.7(2)° in both molecules, while the C⁶C⁷Cl² angle is 114.3(2)° and 113.7(2)°. The weak intramolecular hydrogen bonds are compiled in Table 5.

In the crystalline structure molecular layers are distinguished in the (*a* + *c*, *b* + *c*) plane (Fig. 2b). The symmetrically independent molecules of cyclohexene **8** form pairs of associates due to intermolecular hydrogen bonds of the C–H...O type with H...O distances of 2.609 Å (C⁶–H...O²–N¹) and 2.715 Å (C^{6A}–H...O^{2A}–N^{1A}). The paired associates of molecules **8** are interconnected into layers in one direction by shortened contacts Cl³...Br^{1A} 3.407(2) Å and in the other by Cl^{1A}...O¹ 3.232(3) Å (the sums of the Van der Waals radii, Cl...Br and Cl...O, amount to 3.63 Å [22]).

Thus, the study has demonstrated that 1-nitro- and 1-bromo-1-nitro-3,3,3-trifluoro(chloro)propenes are active dienophiles. They successfully react with acyclic dienes to form the corresponding cyclohexenes with good yields. As such, the CHlg₃ group effectively

competes with the NO₂ group for the regio- and stereodirectivity of diene condensation.

EXPERIMENTAL

¹H, ¹³C{¹H}, ¹H–¹³C HMQC, and ¹H–¹³C HMBC NMR spectra were recorded on a Jeol ECX400A spectrometer at operating frequencies of 100.52 MHz (¹³C) and 399.78 MHz (¹H) in deuteriochloroform-*d* using the residual signal of an undeuterated solvent as an internal reference. IR spectra were obtained on a Shimadzu IR Prestige-21 Fourier spectrometer in chloroform. Spectral studies were performed at the Center for Joint Use of the Faculty of Chemistry of the Herzen State Pedagogical University of Russia, St. Petersburg.

Separation of the individual compounds was carried out by column chromatography on Chemapol 100/200 silica gel using solvents according to the procedure described in [23]. The TLC test was performed on Silufol 254 plates, eluent a 3 : 2 hexane–acetone mixture, development under UV light. The ratios of isomers **9a–12a** and **9b–12b** were determined by ¹H NMR spectroscopy prior to chromatography of the reaction mixture.

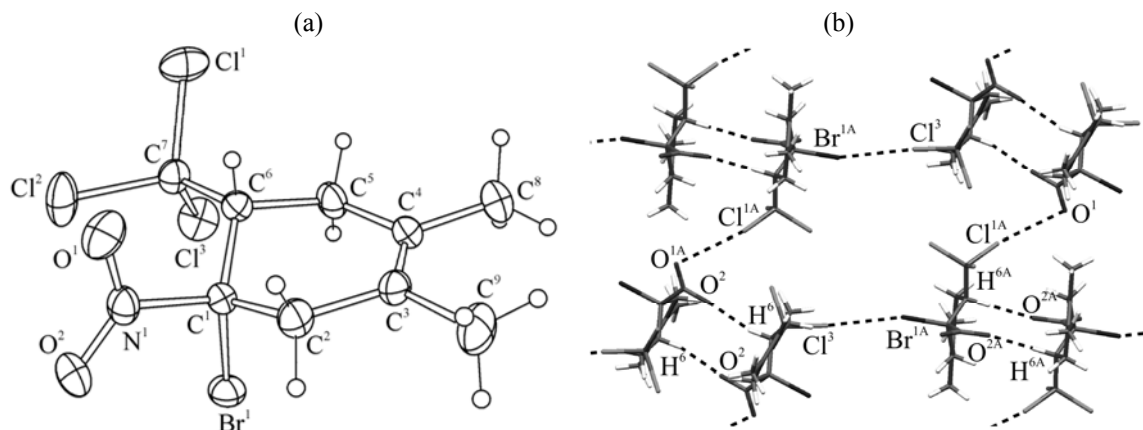


Fig. 2. General view of one of the two independent molecules (a) in the crystal and (b) the molecular layer parallel to $(a + c, b + c)$ plane in the crystals of compound **8**. (Dashed line) intermolecular hydrogen bonds and shortened contacts.

X-ray diffraction analysis of a single crystal of compound **8** was carried out by an X-ray diffraction analysis team of the Center for Spectral Information at the Vorozhtsov Novosibirsk Institute of Organic Chemistry (Siberian Branch, Russian Academy of Sciences). An X-ray diffraction experiment on crystals **8** grown from hexane was performed at 296(2) K on a Bruker Kappa APEX II diffractometer (MoK α radiation, graphite monochromator, CCD detector, 2θ 55.2°). Single crystals **8** are triclinic, unit cell parameters are as follows: a 8.720(5), b 10.832(6), c 14.546(8) Å, α 103.27(2)°, β 92.11(1)°, γ 99.18(1)°, V 1316.2(12) Å³, space group $P-1$, Z 4, C₉H₁₁BrCl₃NO₂, d_{calc} 1.774 g/cm³, μ 3.72 mm⁻¹, sample size 0.48×0.26×0.09 mm. The intensities of 7539 independent reflections were measured. A correction for extinction was introduced using the SADABS program (transmission 0.2685–0.7309). The structure was solved by the direct method by means of the SHELXS-97 program and refined in the anisotropic-isotropic (for H) approximation using the SHELXL-97 program. The hydrogen positions were calculated geometrically and the parameters of the H atoms were refined in the isotropic approximation using the *rider* model. The final refinement parameters are as follows: wR_2 0.0946, S 1.034, 293 parameters were refined (R 0.0349 for 5633 $F > 4\sigma$). The independent part of unit cell **8** contains two molecules. The atomic coordinates, bond lengths, and angles are deposited with the Cambridge Crystallographic Data Centre [24, 25] (CCDC 874993).

Nitroalkenes **1** and **2** were synthesized according to known literature methods through preliminary preparation of the corresponding nitro alcohols [26, 27] followed by further transformation (acylation and

elimination of H₂O, AcOH) [28, 29]. *gem*-Bromonitroalkenes **3** and **4** were prepared according to the procedures described in [30–32].

1,2-Dimethyl-4-nitro-5-trifluoromethyl-1-cyclohexene (5). 2.05 g (0.025 mol) of 2,3-dimethyl-1,3-butadiene was added to 3.50 g (0.025 mol) of 1-nitro-3,3,3-trifluoropropene **1**. The reaction mixture was held at 20°C for 24 h. The reaction mixture was chromatographed (eluent: hexane). Yield 5.43 g (98%), mp 38–40°C (hexane). Found, %: C, 47.80, 47.60; H 5.19, 5.23; N 6.25, 6.14; F 25.98, 25.83. C₉H₁₂F₃NO₂. Calculated: C 48.43; H 5.38; N 6.28; F 25.56.

1,2-Dimethyl-4-nitro-5-trichloromethyl-1-cyclohexene (6). 1.48 g (0.018 mol) of 2,3-dimethyl-1,3-butadiene was added to 3.50 g (0.018 mol) of 1-nitro-3,3,3-trichloropropene **2**. The reaction mixture was held at 20°C for 3 days. The reaction mixture was

Table 5. Weak intramolecular hydrogen bonds in the molecule of compound **8**

Hydrogen bond	H...A	D...A	D–H...A
C ^{2A} –H...O ^{1A}	2.43	2.843(3)	106
C ² –H...O ¹	2.45	2.869(4)	106
C ^{5A} –H ^A ...Cl ^{2A}	2.64	3.125(3)	111
C ^{5A} –H ^B ...Cl ^{1A}	2.72	3.154(3)	107
C ⁵ –H ^A ...Cl ²	2.59	3.068(3)	110
C ⁵ –H ^B ...Cl ¹	2.80	3.217	107
C ⁶ –H...O ¹	2.48	2.848(3)	100
C ^{6A} –H...O ^{1A}	2.54	2.862	99

chromatographed (eluent: hexane). Yield 4.61 g (92%), colorless oil, R_f 0.69. Found, %: C 39.65, 39.70; H 4.35, 4.38; N 5.16, 5.20. $C_9H_{12}Cl_3NO_2$. Calculated, %: C 39.63; H 4.41; N 5.14.

4-Bromo-1,2-dimethyl-4-nitro-5-trifluoromethyl-1-cyclohexene (7). 0.90 g (0.011 mol) of 2,3-dimethyl-1,3-butadiene was added to a solution of about 2.50 g (0.011 mol) of 1-bromo-1-nitro-3,3,3-trifluoropropene **3** in diethyl ether under cooling ($-10^\circ C$). The resulting mixture was held at $4^\circ C$ for 10 h. The reaction mixture was chromatographed (eluent: hexane). Yield 3.12 g (97%), mp $40-42^\circ C$ (hexane). Found, %: C 35.60, 35.75; H 3.69, 3.65; N 4.71, 4.64; F 18.98, 18.75; Br 26.60, 26.63. $C_9H_{11}F_3NO_2Br$. Calculated, %: C 35.76; H 3.64; N 4.64; F 18.87; Br 26.49.

4-Bromo-1,2-dimethyl-4-nitro-5-trichloromethyl-1-cyclohexene (8). A mixture of 4.00 g (0.015 mol) of 1-bromo-1-nitro-3,3,3-trichloropropene **4** and 1.23 g (0.015 mol) of 2,3-dimethyl-1,3-butadiene was held at $20^\circ C$ for 6 days and then was chromatographed on silica gel. From a fraction washed with hexane, 4.46 g (85%) of cyclohexene **8** of mp $76-78^\circ C$ was separated. Found, %: C 30.78; 30.83; H 3.16, 3.26; N 4.03, 4.08. $C_9H_{11}Cl_3BrNO_2$. Calculated, %: C 30.73; H 3.13; N 3.98.

1-Methyl-4(5)-nitro-5(4)-trifluoromethyl-1-cyclohexene (9a, 9b). A mixture of 3.00 g (0.021 mol) of 1-nitro-3,3,3-trifluoropropene **1** and 1.45 g (0.021 mol) of 2-methyl-1,3-butadiene was held at $20^\circ C$ for 24 h and then was chromatographed on silica gel (eluent: hexane). Yield 3.82 g (87%), isomer ratio **9a** : **9b** = 1 : 4, R_f 0.91, 0.78.

1-Methyl-4(5)-nitro-5(4)-trichloromethyl-1-cyclohexene (10a, 10b). A mixture of 3.50 g (0.018 mol) of 1-nitro-3,3,3-trichloropropene **2** and 1.25 g (0.018 mol) of 2-methyl-1,3-butadiene was held at $20^\circ C$ for 6 days. The reaction mixture was chromatographed (eluent: hexane). Yield 4.42 g (95%), isomer ratio **10a** : **10b** = 1.0 : 2.5, R_f 0.84, 0.54. Found, %: C 37.13; 37.16; H 3.87, 3.86; N 5.41, 5.45. $C_8H_{10}Cl_3NO_2$. Calculated, %: C 37.14; H 3.87; N 5.42.

4(5)-Bromo-1-methyl-4(5)-nitro-5(4)-trifluoromethyl-1-cyclohexene (11a, 11b). 0.46 g (0.007 mol) of 2-methyl-1,3-butadiene was added to a solution of about 1.50 g (0.007 mol) of 1-bromo-1-nitro-3,3,3-trifluoropropene **3** in diethyl ether under cooling ($-10^\circ C$). The mixture was held at $4^\circ C$ for 10 h and then chromatographed on silica gel (eluent: hexane). Yield 1.31 g (65%), isomer ratio **11a** : **11b** = 1 : 4.

4(5)-Bromo-1-methyl-4(5)-nitro-5(4)-trichloromethyl-1-cyclohexene (12a, 12b). A mixture of 3.20 g (0.012 mol) of 1-bromo-1-nitro-3,3,3-trichloropropene **5** and 0.81 g (0.012 mole) of 2-methyl-1,3-butadiene was held at $20^\circ C$ for 6 days and then chromatographed on silica gel (eluent: hexane). Yield 2.27 g (56%), isomer ratio **12a** : **12b** = 1 : 3, R_f 0.82, 0.64. Found, %: C 28.42; 28.43; H 2.69, 2.65; N 4.17, 4.12. $C_8H_9BrCl_3NO_2$. Calculated, %: C 28.44; H 2.67; N 4.15.

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