ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 2, pp. 242–254. © Pleiades Publishing, Ltd., 2014.
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Synthesis and Structure of Oxanorbornenes Functionalized by Nitro- and Trichloromethyl Groups

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Received June 10, 2013

Abstract—The reactions of furan and 2-methylfuran with 3,3,3-trichloro-1-nitro- and 1-bromo-3,3,3-trichloro-1-nitropropenes were studied to show that furan reacts by the diene condensation pathway, whereas the reactions with 2-methylfuran take two pathways: the diene synthesis and electrophilic substitution by C^5.

DOI: 10.1134/S1070363214020145

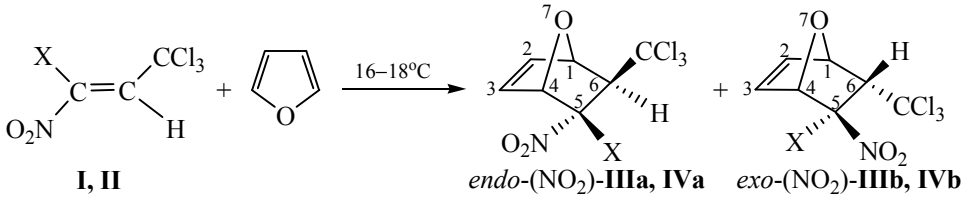
The increased interest to the Diels–Alder reaction with furan as the diene component is associated with the fact that such reactions can provide a synthetic approach to oxanorbornenes—compounds which are used as intermediates in the design of analogs of natural C-nucleosides [1, 2], monoterpenoids with pheromone activity [3], and other biologically active compounds [4, 5].

According to published data, the condensation of nitroalkenes with furan and its homologs can proceed, depending on the nature of substituents in the diene [6] and dienophile [7–9], either by the way of the diene synthesis or by the way of electrophilic substitution of the C^2 atom of the furan ring. Thus, nitroalkenes containing electron-acceptor substituents (for example, CO_2R, CN, SO_3Ph, CCl_3, P(O)OR, and CF_3) in the β position to the nitro group take exclusively the diene synthesis pathway [9–12].

Electrophic substitution products are formed by furan reactions with nitroethylene [9, 13–15] and *hem*-bromonitroalkenes (β-bromo-β-nitroethenyl phosphonates and carboxylates) [16–18]. Electron-donor substituents in the 2 position of furan (CH_3, OCH_3) direct the reaction to both cycloaddition and electrophilic substitution mechanisms [6].

In the present work we studied the reactions of vicinally substituted nitroalkenes—3,3,3-trichloro-1-nitro- and 1-bromo-3,3,3-trichloro-1-nitropropenes (**I**, **II**)—with furan and 2-methylfuran, as well compared the behavior of compounds **I** and **II** with that of nitro-

Scheme 1.



I, II *endo*-(NO_2)-**IIIa, IVa** *exo*-(NO_2)-**IIIb, IVb**

X = H (**I, IIIa, IIIb**); Br (**II, IVa, IVb**).

ethenes containing other electron-acceptor substituents in the β position.

Previously Balthazor et al. [19] established that 3,3,3-trichloro1-1-nitropropene reacts with furan at room temperature for 22 days, giving a mixture of the corresponding diastereomeric oxanorbornenes.

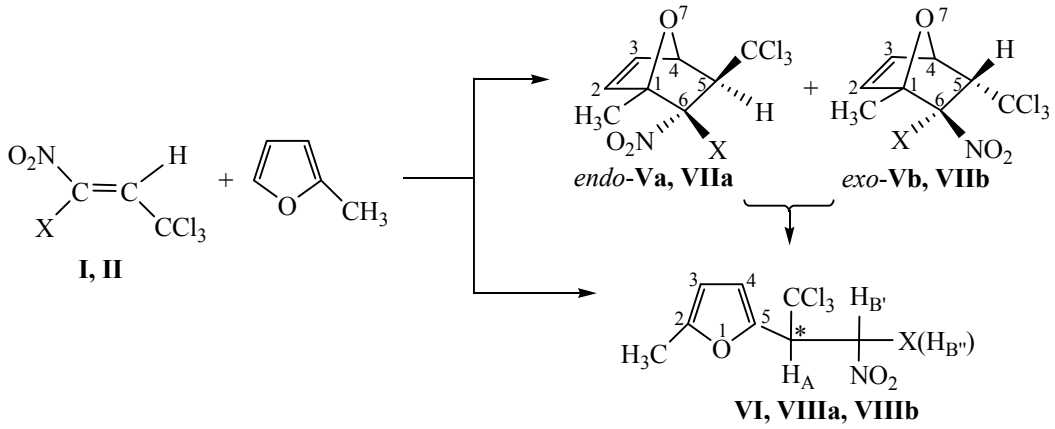
Our experiments showed nitroalkenes **I** and **II** best react with furan in mild conditions (16–18°C, no solvent) to form mixtures of diastereomeric *endo*-NO_2- and *exo*-NO_2-oxanorbornenes **IIIa**, **IIIb** and **IVa**, **IVb** with a total yield of 86–88%. The **IIIa** : **IIIb** *endo : exo* isomer ratio with nitroalkene **I** was 1 : 1, in agreement with published data [19] (see Scheme 1).

The reaction with *hem*-bromonitroalkene **II** showed improved selectivity, and, therewith, the ratio of the resulting *endo*- and *exo*-norbornenes **IVa** : **IVb** was 6 : 1. The isomer ratios in both cases were invariable for 19 days (reagent conversion ~90%), after which the *endo* isomers **IIIa** and **IVa** underwent the retrodiene reaction, which led to accumulation of the starting nitroalkenes **I** and **II** in the reaction mixture. Attempts to drive the reaction by heating the starting mixture (1 h, 80°C, C_6H_6) favored the retro-Diels–Alder reaction and, as a result, reduced the yield of oxanorbornenes **IIIa**, **IIIb**, **IVa**, and **IVb** to 10–15%. Note that *hem*-bromonitroalkene **II**, unlike *hem*-bromonitroacrylate and -phosphonate [16–18], gave no electrophilic substitution products when react with furan.

The condensation of nitroalkenes **I** and **II** with 2-methylfuran led to ambiguous results, which prompted us to study it in more detail. According to [19], nitroalkene **I** reacted with 2-methylfuran (room temperature, 4 h) to form the corresponding *endo*- and *exo*-oxanorbornenes **Va** and **Vb** (1 : 3) that transformed to an electrophilic substitution product only under the action of trifluoroacetic acid or upon long-term (2 months) standing of the reaction mixture. However, ^{1}H NMR monitoring of the reaction of nitroalkene **I** with 2-methylfuran (5 days, 16–18°C, no solvent) revealed formation of not only Diels–Alder adducts oxanorbornenes **Va** and **Vb**, but also 2,5-disubstituted furan **VI**, an electrophilic substitution product (Scheme 2).

The maximum conversion of the starting compounds (~85%) is observed after ~5 days, and the product ratio constantly varies over the course of the reaction. Thus, *exo*-oxanorbornene **Vb** prevails (by a factor of 1.5–2) for 5 days, which allows it to be considered as a kinetically controlled product [20]. The thermodynamically controlled *endo* isomer (compound **Va**) starts to accumulate until it becomes the major

Scheme 2.



X = H (**I, Va, Vb, VIa, VIb**); Br (I**I, VIIa, VIIb, VIIIa, VIIIb**).

T, °C	Time, h	**Va** : **Vb** : **VI** ratio by ^{1}H NMR data
20	12	1.0 : 2.0 : 0.1
20	120	1.0 : 1.5 : 0.2
20	240	2.0 : 1.0 : 0.4
20	960	4.0 : 1.0 : 0.6
80 (C_6H_6)	12	5.0 : 1.0 : 5.0

product (**Va** : **Vb** = 5 : 1) with time and at an elevated temperature (80°C, C_6H_6, 5 h). However, attempted isolation of *endo* isomer **Va** by column chromatography led to formation of substituted furan **VI**. This result agrees with published data showing that *endo*-NO_2 isomers are more labile and tend for intramolecular transformation (retrodiene synthesis, opening of the oxanorbornene ring to form substituted furans, oxanorbornadienes, and arenes) even in mild conditions [21, 22].

hem-Bromonitroalkene (**II**) reacted with 2-methylfuran under the sme conditions to form a mixture of *endo*- and *exo*-NO_2-oxanorbornenes **VIIa** and **Vb** in a 10 : 1 ratio, as well as 2,5-dialkylfurans **VIIIa** and **VIIIb** in a 1 : 2 ratio. According to ^{1}H NMR data, oxanorbornenes **VIIa** and **VIIb** completely transformed into open forms **VIIIa** and **VIIIb** within 10 days. Note that oxanorbornenes **Va**, **Vb**, **VIIa**, and **VIIb** transformed exclusively to open forms **VI**, **VIIIa**, and **VIIb** and underwent no secondary dehydrohalogenation reactions, like those we observed previously with oxanorbornenes containing the carboxylate and phosphonate functions instead of the trichloromethyl group [10, 16, 18]. The lack of secondary intramolecular processes (first of all, dehydrohalogenation) can be explained by milder reaction conditions and another electronic nature of the trichloromethyl group compared to alkoxycarbonyl and dialkoxyphosphoryl [23]. The reaction of nitroalkene **II** with 2-methylfuran under heating in benzene (5 h) resulted in exclusive formation of furans **VIIIa** and **Vb** in a 1 : 1 ratio.

The fact that oxanorbornenes **Va**, **Vb**, **VIIa**, and **VIIb** formed by the reactions in study transformed into open forms **VI**, **VIIIa**, and **VIIIb** both on prolonged standing of the reaction mixture and on attempted isolation on silica gel suggests that the latter are formed by ring opening in the sterically congested oxanorbornenes; it is logical that this reaction pathway is characteristic of 2-methylfuran.

The structure of compounds **III**–**VIII** was established by IR, ^{1}H and ^{13}C NMR spectroscopy using heteronuclear correlation experiments (^{1}H–^{13}C HMQC, ^{1}H–^{13}C HMBC), as well as X-ray diffraction analysis.

In the ^{1}H spectra, the cyclic (oxanorbornenes) and open-chain (substituted furans) forms are best differentiated by methyl proton signals that appear as singlets and do not overlap with other signals. The proton chemical shifts of the oxanorbornene methyl groups attached to the bridgehead sp^3-carbon atom are 1.58 and 1.84 ppm, whereas those of the open-chain forms, belonging to protons at the furan C=C bond expectedly resonate downfield (2.20 and 2.29 ppm).

The ^{1}H NMR spectra of oxanorbornenes **III**–**V** and **VII** show signals of all ring protons, specifically bridgehead (H^1, H^4), olefin (H^2, H^3), and methine [$H^{5(6)}$ NO_2, $H^{6(5)}$ CCl_3]. The bridgehead protons H^1 and H^4, being located in the vicinity of the electronegative bridging oxygen atom, give downfield signals at 5.11–5.38 (H^1) and 5.36–5.79 ppm (H^4) (Fig. 1, Tables 1 and 2).

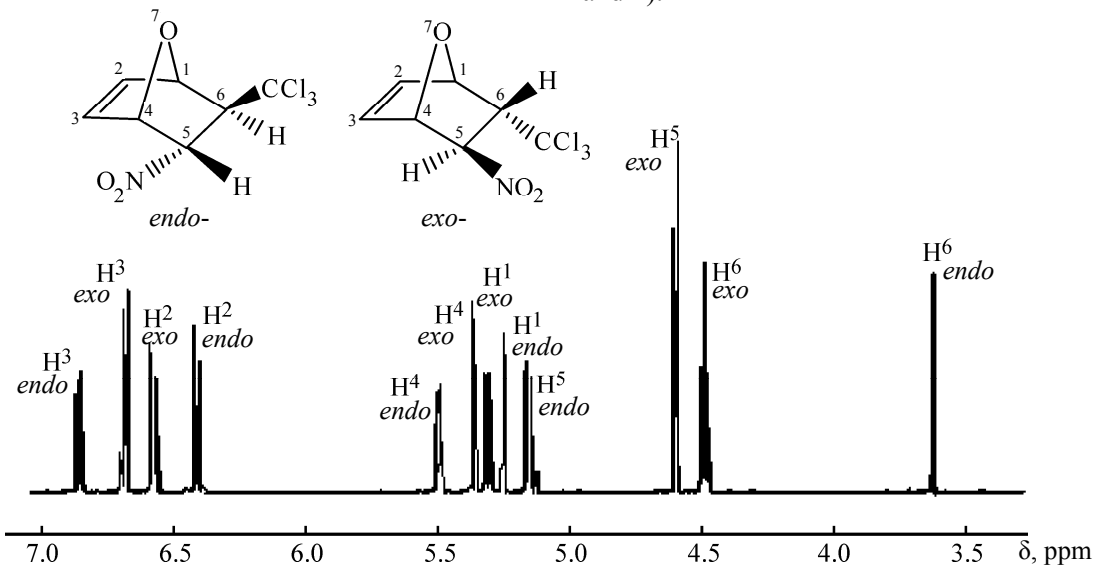
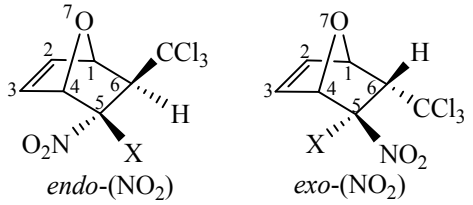


Fig. 1. ^{1}H ($CDCl_3$) NMR spectrum of the mixture of *endo* and *exo* isomers **IIIa** and **IIIb**, taken immediately after reaction sompletion.

Table 1. ^{1}H and ^{13}C NMR spectra of nitrooxanorbornenes **IIIa**, **IIIb**, **IVa**, and **IVb**



Comp. no.	X	Yield, % (**a** : **b**)	^{1}H NMR spectrum, δ, ppm (*J*, Hz)						^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm[a]					
			H^1	H^2	H^3	H^4	H^5	H^6	C^1	C^2	C^3	C^4	C^5	C^6
IIIa	H	88 (1 : 1)	5.23 d.d $^{4}J_{H^1H^3}$ 1.93 $^{3}J_{H^1H^6}$ 1.86	6.43 d.d $^{4}J_{H^2H^4}$ 1.27 $^{3}J_{H^2H^3}$ 5.65	6.85 d.d $^{4}J_{H^3H^1}$ 1.93	5.49 d.t $^{4}J_{H^4H^2}$ 1.27 $^{3}J_{H^4H^5}$ 4.74	5.13 d.d $^{3}J_{H^5H^6}$ 3.97	3.61 d $^{3}J_{H^6H^5}$ 3.97 $^{3}J_{H^6H^1}$ 1.86	83.10	134.06	139.70	80.02	84.46	64.52
IIIb	H		5.30 d $^{4}J_{H^1H^3}$ 1.67 $^{3}J_{H^1H^6}$ 4.12	6.59 d.d $^{4}J_{H^2H^4}$ 1.92 $^{3}J_{H^2H^3}$ 5.62	6.69 d.d $^{4}J_{H^3H^1}$ 1.67	5.36 t $^{4}J_{H^4H^2}$ 1.92 $^{3}J_{H^4H^5}$ 0.56	4.59 d.d $^{3}J_{H^5H^6}$ 4.63	4.50 t $^{3}J_{H^6H^5}$ 4.63 $^{3}J_{H^6H^1}$ 4.12	86.21	133.63	137.63	80.83	87.44	64.16
IVa	Br	86 (6 : 1)	5.34 d.d $^{4}J_{H^1H^3}$ 1.62 $^{3}J_{H^1H^6}$ 1.83	6.46 d.d $^{4}J_{H^2H^4}$ 1.86 $^{3}J_{H^2H^3}$ 5.72	6.87 d.d $^{4}J_{H^3H^1}$ 1.62	5.49 t $^{3}J_{H^4H^2}$ 1.86	–	3.84 s	84.62	135.30	141.06	89.90	89.57	65.71
IVb	Br		5.38 d.d $^{3}J_{H^1H^6}$ 3.99 $^{4}J_{H^1H^3}$ 1.53	6.62 d.d $^{4}J_{H^2H^4}$ 1.98 $^{3}J_{H^2H^3}$ 5.78	6.85 d.d	5.79 d.d $^{4}J_{H^4H^2}$ 1.98	–	4.68 d $^{3}J_{H^6H^1}$ 3.99	–	–	–	–	–	–

[a] CCl_3 carbon signal; δ_C, ppm: 98.22 (**IIIa**), 96.21 (**IIIb**), 97.85 (**IVa**).

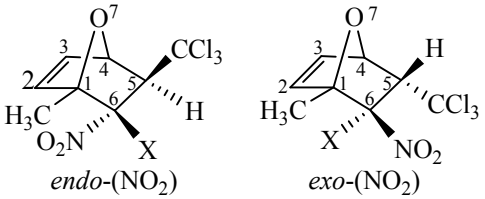
The assignment of the products to the *endo* or *exo* series was based on the analytical criteria for structurally related compounds, described in [10, 24–26]. One of such criteria is the chemical shift of the nitromethine proton $H^{5(6)}$. The difference in the chemical shifts of $H^{5(6)}$ in the *endo*-NO_2 and *exo*-NO_2 isomers is explained by different spacial arrangements of this atom with respect to the magnetically anisotropic ring C=C bond. As seen from the data in Table 1 and Fig. 2, the H^5 proton in the *endo* isomer have larger chemical shift (5.13 ppm) and vicinal coupling constant $^{3}J_{H^4H^5}$ 4.74 Hz, which is expected by its *exo* orientation in compound **IIIa**. The smaller chemical shifts (4.59 ppm) and coupling constants ($^{3}J_{H^4H^5}$ 0.56 Hz) of this proton relate to the *endo* arrangement of H^5 in compound **IIIb**, which is consistent with published data for bicyclic structures [27].

The methane protons H^6 in compounds **IIIa**, **IIIb**, **IVa**, and **IVb** and H^5 in compounds **Va**, **Vb**, **VIIa**, and **VIIb** appear at 3.61–4.68 ppm. The H^6 proton in oxanorbornenes **IIIa**, **IIIb**, **IVa**, and **IVb** is vicinally coupled to H^1, which, too, characterizes its spacial arrangement. Smaller chemical shifts and coupling constants of H^6 (3.61 ppm and $^{3}J_{H^1H^6}$ 1.86 Hz for **IIIa** and 3.84 ppm for **IVa**) relate to the *endo* arrangement of this proton, while larger chemical shifts and coupling constants (4.50 ppm and $^{3}J_{H^1H^6}$ 4.12 Hz for **IIIb** and 4.68 ppm and $^{3}J_{H^1H^6}$ 3.99 Hz for **IVb**) to its *exo* arrangement.

The vicinal coupling constants of methine protons (H^5, H^6) in compounds **IIIa**, **IIIb**, **Va**, and **Vb** [$^{3}J_{H^5H^6}$ 3.97 and 4.63 Hz] correspond to their *trans* arrangement, which is characteristic of the geometry of structurally related compounds [27, 28].

Additional analytical criteria sensitive to the steric structure are provided by the chemical shifts and coupling constants the olefin protons at the ring C^2=C^3 bond for the *endo*-NO_2- and *exo*-NO_2 isomers. The H^2 and H^3 olefin in oxanorbornenes **III–V** and **VIIa** appear at 6.05–6.87 ppm with characteristic vicinal coupling constants of $^{3}J_{H^2H^6}$ 5.62–5.78 Hz. Like with

Table 2. [1]H NMR spectra of nitrooxanorbornenes **Va**, **Vb**, **VIIa**, and **VIIb**



Comp. no.	X	**a** : **b** ratio[a]	[1]H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz)					
			$C\underline{H}_3$	H^2	H^3	H^4	H^5	H^6
Va	H	1 : 2	1.81 s	6.82 d.d $^4J_{H2H4}$ 1.85 $^3J_{H2H3}$ 5.65	6.21 d	5.11 d $^4J_{H4H2}$ 1.85	3.72 d $^3J_{H5H6}$ 3.97	4.81 d
Vb	H		1.56 s	6.67 d.d $^4J_{H2H4}$ 1.68 $^3J_{H2H3}$ 5.62	6.32 d	5.22 d.d $^4J_{H4H2}$ 1.68 $^3J_{H4H5}$ 4.11	4.51 d.d $^3J_{H5H4}$ 4.11 $^3J_{H5H6}$ 4.63	4.64 d
VIIa	Br	10 : 1	1.85 s	6.60 m	6.05 m	5.25 m	3.74 m	–
VIIb	Br		1.59 s	6.59 m	6.25 m	5.30 m	4.35 m	–

[a] Compounds **Va**, **Vb**, **VIIa**, and **VIIb** were detected spectrally; the a:b ratio in the reaction mixture after 5 days.

previously described norbornenes [25, 26], the larger difference in the proton chemical shifts correspond to *endo* arrangement of the nitro group: the ΔH^2H^3 for *endo* isomers **IIIa**–**Va** and **VIIa** is 0.41–0.61 ppm and the ΔH^2H^3 for *exo* isomers **IIIb**–**Vb** and **VIIb** is 0.10–0.35 ppm.

The physicochemical characteristics of compounds **IIIa** and **IIIb**, obtained in the present work, are close in general to published values [19].

The [1]H NMR spectra of oxanorbornenes **Va**, **Vb**, **VIIa**, and **Vb**, which contain the methyl group at the bridgehead C^1 atom, show different chemical shifts for methyl protons: 1.56 and 1.59 ppm for *exo* isomers **Vb** and **VIIb** and 1.81 and 1.85 ppm for *endo* isomers **Va** and **VIIa** (Table 2). The downfield shift of the signal for the latter isomers is likely to be explained by the special proximity of the methyl and nitro groups at the ring fold.

The [1]H NMR spectra of **IIIa**, **IIIb**, **IVa**, and **IVb** show long-range vicinal coupling between H^1 and H^3 and H^2 and H^4 protons [28] with the constants 1.27–1.98 and 1.62–1.93 Hz, respectively. Compounds **Va**, **Vb**, **VIIa**, and **VIIIb** have a CH_3 group at the bridgehead C^1 atom, which explains the lack of vicinal coupling constant for H^3 and provides evidence for correct assignment of the signals of the proton at the bridgehead C^4 atom and ring olefin protons.

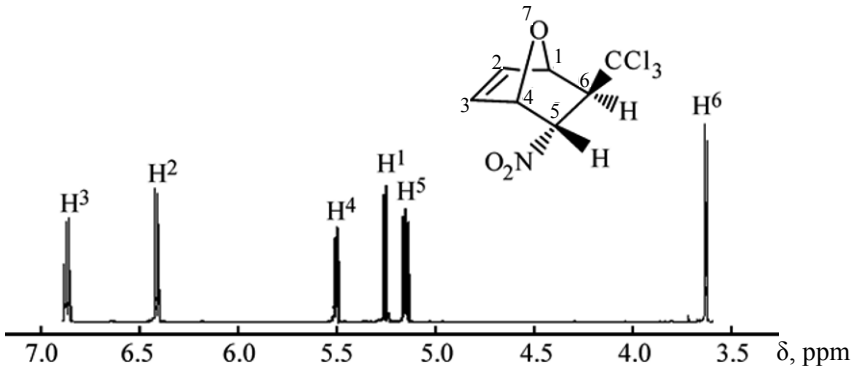


Fig. 2. [1]H ($CDCl_3$) NMR spectrum of the *endo* isomer of **IIIa**.

The assignement of the signals of the oxanorbornene methine and olefin protons in compounds **IIIa**, **IIIb**, **IVa**, and **IVb** was confirmed by 2D $^{1}H–^{13}C$ HMQC (Heteronuclear Multiple Quantum Correlation) spectroscopy. The $^{1}H–^{13}C$ HMQC spectrum of compound **IVa** (Fig. 3) shows cross-peaks between the bridgehead protons H^1 (5.34 ppm) and H^4 (5.49 ppm) and C^1 (84.62 ppm) and C^4 (89.90 ppm), respectively, between the methane proton H^6 (3.84 ppm) and C^6 (65.71 ppm), and between the olefin protons H^2 (6.46 ppm) and H^3 (6.87 ppm) with C^2 (135.30 ppm) and C^3 (141.06 ppm), respectively.

Analysis of the $^{1}H–^{13}C$ HMBC spectrum of compound **IVa** (Fig. 4) allowed us to correctly assign of the signals of the ring methine and olefin protons due to the observation of cross-peaks between H^2 (6.46 ppm) and C^1 (84.62 ppm), C^2 (135.30 ppm), and C^3(141.06 ppm), between H^3 (6.87 ppm) and C^4 (89.90 ppm), C^1 (84.62 ppm), C^3 (141.06 ppm), and C^2 (135.30 ppm), between H^1 (5.34 ppm) and CCl_3 carbon (97.85 ppm), C^1 (84.62 ppm) and C^2 (135.30 ppm), as well as between H^4 (5.49 ppm) and C^4 (89.90 ppm), C^1 (84.62 ppm), and C^3 (141.06 ppm).

The same approach based on the 2D spectra was also applied to assign the $^{1}H–^{13}C$ NMR spectra of compounds **IIIa**, **IIIb**, and **IVb**.

The IR spectra of oxanorbornenes **IIIa**, **IIIb**, **IVa**, and **IVb** and substituted furans contains NO_2 absorption bands at 1560–1575 and 1345–1373 cm^{-1}.

Complete information on the fine solid-phase structure of the synthesized oxanorbornenes was obtained from the X-ray diffraction analysis of compound **IVa**. Its spacial structure is shown in Fig. 5, and the geometric parameters are listed in Tables 3–5. The geometry of the bicyclic fragment is usual for norbornene: The five-membered rings have an O^7 *envelope* conformation, and the six-membered ring has a *boat* conformation.

The bulky trichloromethyl substituent at C^6 and the bromine substituent on C^5 have a cisoid equatorial orientation, whereas the nitro group on C^5 is axial [the $C^7C^6C^5Br^1$ and $C^7C^6C^5N^1$ torsion angles are –10.7(3)° and –111.4(2)°, respectively (Fig. 5)]. There is an eclipsed conformation along the $C^5–C^6$ bond [$C^1C^6C^5C^4$ 5.9(2)°]. No $C^2=C^3$ bond torsion in molecule

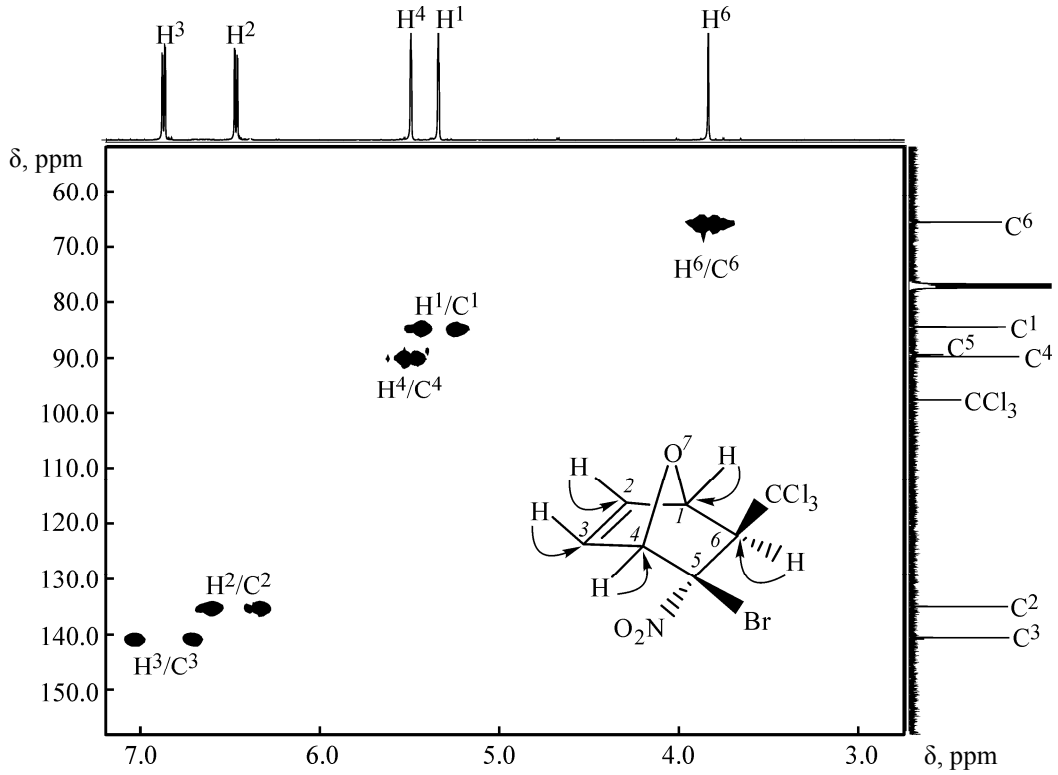


Fig. 3. $^{1}H–^{13}C$ HMQC spectrum ($CDCl_3$) of compound **IVa**.

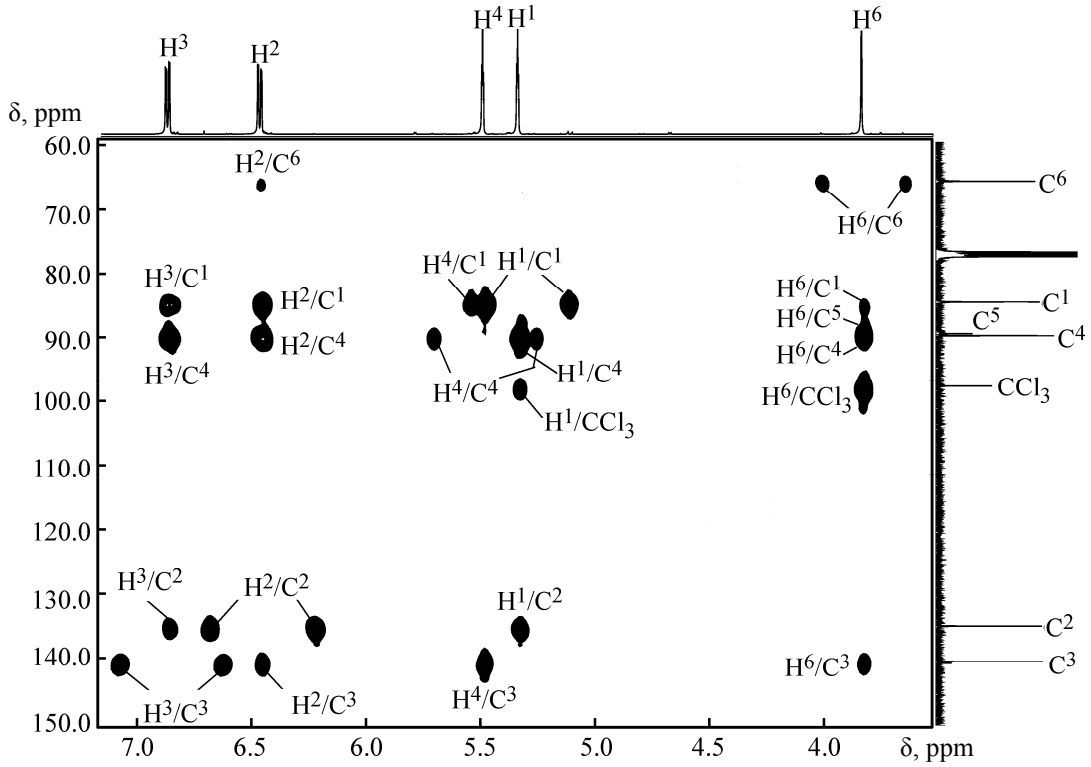


Fig. 4. $^{1}H–^{13}C$ HMBC spectrum ($CDCl_3$) of compound **IVa**.

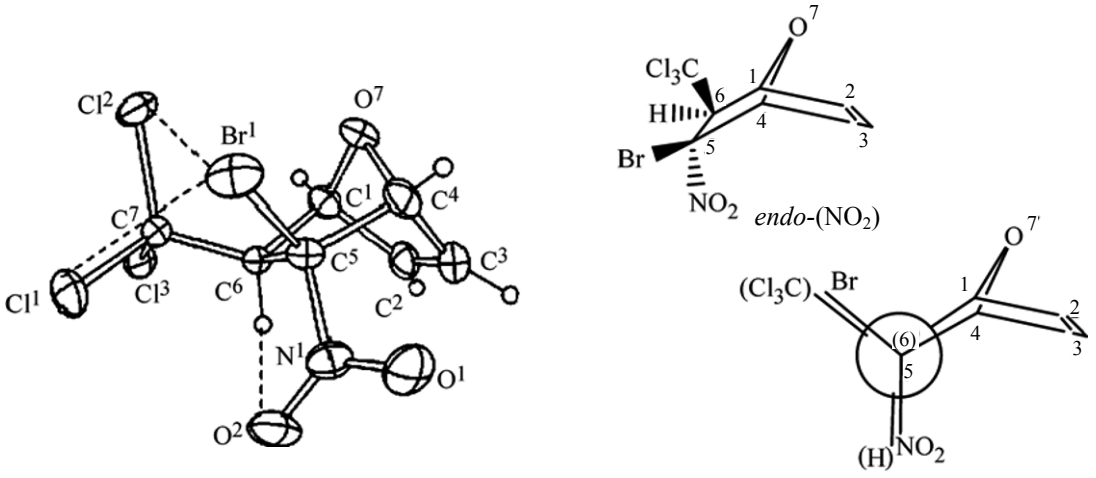


Fig. 5. Molecular geometry of compound **IVa** in srystal. Dashed lines show a weak H-bond like C–H···O and shortened sontacts like Br···Cl.

IVa is observed [$C^1C^2C^3C^4$ –0.9(3)°, $C^2=C^3$ 1.316(4) Å] The geometric parameters of the trichloromethyl and nitro substituents in the oxanorbornene ring are usual. The closest analog of compound **IVa** in the Cambridge Structural Database [29–31] is 1,4-dimethyl-5-*exo*-nitro-6-*endo*-(trichloromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (model compound) [19]. The largest difference between the model compound and compound **IVa** is observed in the $C^4–C^5$ and $C^3–C^4$, bond lengths: 1.554(4) and 1.505(4) Å in **IVa** and 1.589 and 1.472 Å in the model compound. Moreover, the trichloromethyl group in **IVa**, like in the model compound, is staggered with the respect to the $C^5–C^6$ bond, and the $C^5C^6C^7Cl^2$ torsion angle is 68.8(2)°. The orientation of the nitro group is determined by the $O^1N^1C^5C^4$ angle of 37.9(2)°.

Table 3. Bond lengths (Å) in compound **IVa**

Bond	*d*	Bond	*d*	Bond	*d*
Br^1–C^5	1.934(2)	C^2–C^3	1.316(4)	C^6–H^6	0.98
O^1–N^1	1.217(3)	C^4–H^4	0.98	C^2–H^2	0.93
N^1–C^5	1.524(3)	C^3–H^3	0.93	Cl^2–C^7	1.773(2)
C^6–C^1	1.571(3)	Cl^1–C^7	1.760(2)	O^7–C^4	1.424(4)
Cl^3–C^7	1.785(2)	O^2–N(1)	1.201(3)	C^4–C^3	1.504(4)
O^7–C^1	1.437(3)	C^4–C^5	1.554(4)	C^1–C^2	1.509(3)
C^5–C^6	1.550(3)	C^6–C^7	1.530(3)	C^1–H^1	0.98

Table 4. Bond angles (deg) in compound **IVa**

Angle	ω	Angle	ω	Angle	ω
$C^1O^7C^4$	96.58(18)	$O^1N^1O^2$	125.0(2)	$O^1N^1C^5$	115.6(2)
$O^2N^1C^5$	119.4(2)	$O^7C^4C^5$	98.0(2)	$O^7C^4C^3$	102.6(2)
$C^5C^4C^3$	108.0(2)	$Br^1C^5N^1$	104.74(15)	$Br^1C^5C^4$	108.68(15)
$Br^1C^5C^6$	118.39(16)	$N^1C^5C^4$	110.7(2)	$N^1C^5C^6$	112.01(16)
$C^4C^5C^6$	102.32(18)	$C^5C^6C^1$	99.07(16)	$C^5C^6C^7$	121.75(18)
$C^1C^6C^7$	112.90(17)	$O^7C^1C^6$	101.50(17)	$O^7C^1C^2$	102.16(19)
$C^6C^1C^2$	105.16(18)	$C^1C^2C^3$	105.5(2)	$C^4C^3C^2$	106.1(2)
$Cl^1C^7Cl^2$	109.77(12)	$Cl^1C^7Cl^3$	107.01(12)	$Cl^1C^7C^6$	112.59(15)
$Cl^2C^7Cl^3$	106.67(12)	$Cl^2C^7C^6$	113.83(15)	$Cl^3C^7C^6$	106.52(15)
$O^7C^4H^4$	115	$C^5C^4H^4$	115	$C^3C^4H^4$	115
$C^5C^6H^6$	107	$C^1C^6H^6$	107	$C^7C^6H^6$	107
$O^7C^1H^1$	115	$C^6C^1H^1$	115	$C^2C^1H^1$	115
$C^1C^2H^2$	127	$C^3C^2H^2$	127	$C^4C^3H^3$	127
$C^2C^3H^2$	127				

The molecular structure of compound **IVa** is characterized by a $C^6H\cdots O^2N^1O^1$ intramolecular H-bond [H···O 2.38 and C···O 2.795(3) Å, CHO 105°] and shortened contacts between the bromine atom and the trichloromethyl $Cl^1$and Cl^2 atoms [$Br^1\cdots Cl^1$ 3.396 (1) Å and $Br^1\cdots Cl^2$ 3.417(1) Å; the sum of the Cl and Br van der Waals radii is 3.63 Å].

The oxanorbornene **IVa** molecules form chains (along the *a* axis) due to H-bonding between the methine hydrogen atom at C^1 of one molecule and an oxygen atom of the nitro group of another molecule $C^1H\cdots O^1$ [H··O 2.53 Å , C···O 3.312(3) Å, CHO 137°] (Fig. 6).

Along with these intra- and intermolecular interactions, in the crystal of compound **IV** double shortened contacts are observed between the bromine atom of one chain and one of the trichloromethyl chlorine atoms of another chain [$Br^1\cdots Cl^2$ 3.454(1) Å] to form dimers (Fig. 6).

The H-bonded dimer chains form a 3D parquet-pattern packing due to weak H-bonding between the methine proton on C^6 and the bridging O^7 atom $C^6H\cdots O^7$ [H···O 2.36 Å, C···O 3.295(3) Å, CHO 160°].

The structure of 2,5-disubstituted furans **VI**, **VIIIa**, and **VIIIb** was analyzed using their structural analogs as model compounds [16–18]. The ^{1}H NMR spectra of compounds **VI**, **VIIIa**, and **VIIIb** (Table 6) show furan ring proton signals at 5.99–6.52 ppm ($^3J_{H^3H^4}$ 3.20–3.36 Hz) as narrow doublets, as well splitted signals of the methine and methylene protons of the saturated part of the molecule.

The methine (H_A) and methylene protons in compound **VI** ($H_{B'}$ and $H_{B''}$) are magnetically non-equivalent and form a three-spin system; the H_A signal (4.72 ppm) is split due to coupling with $H_{B'}$ and $H_{B''}$ (5.07 and 5.20 ppm, respectively), $^3J(H_AH_{B'})$ 9.69 Hz and $^3J(H_AH_{B''})$ 3.79 Hz (Fig. 7).

Table 5. Torsion angles (τ) in compound **IVa**

Angle	τ	Angle	τ	Angle	τ
$C^1O^7C^4C^5$	–62.5(2)	$C^1O^7C^4C^3$	48.1(2)	$C^4O^7C^1C^6$	59.9(2)
$C^4O^7C^1C^2$	–48.5(2)	$O^1N^1C^5Br^1$	–79.1(2)	$O^1N^1C^5C^4$	37.9(3)
$O^1N^1C^5C^6$	151.4(2)	$O^2N^1C^5Br^1$	99.6(2)	$O^2N^1C^5C^4$	–143.4(2)
$O^2N^1C^5C^6$	–29.9(3)	$O^7C^4C^5Br^1$	–84.4(19)	$O^7C^4C^5N^1$	161.1(18)
$O^7C^4C^5C^6$	41.6(2)	$C^3C^4C^5Br^1$	169.45(18)	$C^3C^4C^5N^1$	55.0(3)
$C^3C^4C^5C^6$	–64.6(2)	$O^7C^4C^3C^2$	–30.5(3)	$C^5C^4C^3C^2$	72.4(3)
$Br^1C^5C^6C^1$	113.53(16)	$Br^1C^5C^6C^7$	–10.7(3)	$N^1C^5C^6C^1$	124.44(19)
$N^1C^5C^6C^7$	111.4(2)	$C^4C^5C^6C^1$	–5.9(2)	$C^4C^5C^6C^7$	–130.1(2)
$C^5C^6C^1O^7$	–31.38(19)	$C^5C^6C^1C^2$	74.8(2)	$C^7C^6C^1O^7$	98.9(2)
$C^7C^6C^1C^2$	–155.03(19)	$C^5C^6C^7Cl^1$	–56.9(2)	$C^5C^6C^7Cl^2$	68.8(2)
$C^5C^6C^7Cl^3$	–173.93(15)	$C^1C^6C^7Cl^1$	–174.49(14)	$C^1C^6C^7Cl^2$	48.7(2)
$C^1C^6C^7Cl^3$	68.52(18)	$O^7C^1C^2C^3$	31.7(3)	$C^6C^1C^2C^3$	–74.0(3)
$C^1C^2C^3C^4$	–0.9(3)	$C^4O^7C^1H^1$	–175	$H^4C^4C^5Br^1$	39
$C^1O^7C^4H^4$	174	$H^4C^1C^5C^6$	165	$O^7C^4C^3H^3$	149
$H^4C^4C^5N^1$	–76	$H^4C^4C^3C^2$	–157	$H^4C^4C^3H^3$	23
$C^5C^4C^3H^3$	–108	$N^1C^5C^6H^6$	–13	$C^4C^5C^6H^6$	106
$Br^1C^5C^6H^6$	–135	$C^7C^6C^1H^1$	–27	$H^6C^6C^1O^7$	–143
$C^5C^6C^1H^1$	–157	$H^6C^6C^1H^1$	92	$H^6C^6C^7Cl^1$	67
$H^6C^6C^1C^2$	–37	$H^6C^6C^7Cl^3$	–50	$O^7C^1C^2H^2$	–148
$H^6C^6C^7Cl^2$	–167	$H^1C^1C^2C^3$	158	$H^1C^1C^2H^2$	–22
$C^6C^1C^2H^2$	106	$H^2C^2C^3C^4$	179	$H^2C^2C^3H^3$	–1
$C^1C^2C^3H^3$	179				

The ^{1}H NMR spectrum of compound **VIII** contains a double set of proton signals of all molecular fragments, implying that this compound is present as two diastereomers **VIIIa** and **VIIIb** in a 1 : 1 ratio; however, this ratio changes after chromatography on silica gel. The methine protons H_A and H_B form a two-spin system and appear in the ^{1}H NMR spectrum as doublets; the H_A signals are at 5.02 and 4.73 ppm, and the H_B signals are shifted downfield to 6.69 and 6.61 ppm under the action of the nitro and bromine (J_{AB} 7.63 and 6.71 Hz [32]).

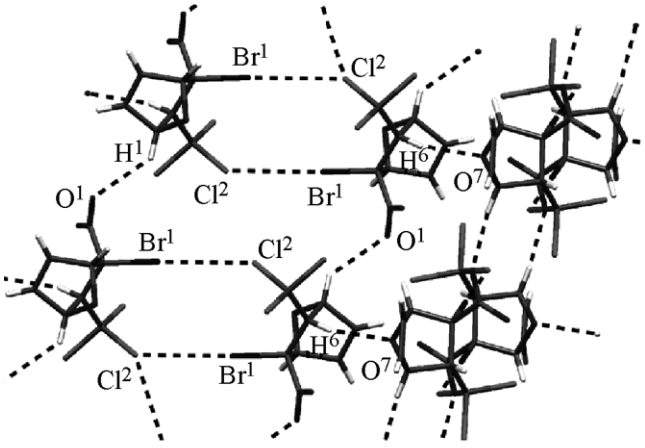
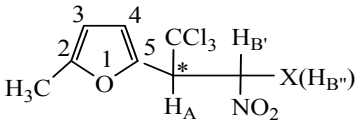


Fig. 6. Fragment of the srystal packing of compound **IVa**. Dashed lines show intermolecular H-bonds like $C^1H\cdots O^1NO$ and $C^6H\cdots O^7$ and intermolecular sontacts like $Br^1\cdots Cl^2$.

EXPERIMENTAL

The ^{1}H, ^{13}C–{^{1}H} ^{1}H–^{13}C HMQC, and ^{1}H–^{13}C HMBC spectra were run on a Jeol ECX400A spectrometer at 100.52 (^{13}C) and 399.78 MHz (^{1}H) in $CDCl_3$ against the residual of nondeuterated solvent signal as reference. The IR spectra were run on a Shimadzu IR Prestige-21 Fourier spectrometer in chloroform. The ^{1}H, ^{13}C–{^{1}H} ^{1}H–^{13}C HMQC, ^{1}H–^{13}C HMBC, and IR spectra were measured in the Center for Collective Use, Spectral Analytical Center, Gertsen Russian State Pedagogical University.

Table 6. [1]H and [13]C NMR spectra of 2,5-dialkylfurans **VI**, **VIIIa**, and **VIIIb**[a]



Comp. no.	X	[1]H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz)					[13]C NMR spectrum ($CDCl_3$), δ_C, ppm							
		H^4	H^3	H_A	$H_{B'}$, $H_{B''}$	CH_3	C^2	C^3	C^4	C^5	$\underline{C}H_A$	$\underline{C}H_B$	$\underline{C}H_3$	$\underline{C}Cl_3$
VI	H	6.43 d	5.99 d	4.72 d. d	5.07 d. d, 5.20 d. d	2.28 s	144.11	107.12	113.20	153.89	57.09	75.11	13.71	98.23
				J($H_AH_{B'}$) 9.69	*J*($H_{B'}H_A$) 9.69, *J*($H_{B''}H_A$)									
				J($H_AH_{B''}$) 3.79	3.79									
					J($H_{B'}H_{B''}$) 13.86									
		$J_{H^3H^4}$ 3.20												
VIIIa	Br	6.52 d	6.02 d	5.02 d	6.69 d	2.31 s	144.04	106.92	114.32	153.71	62.29	78.95	13.72	96.41
				J(H_AH_B) 7.63	*J*(H_BH_A) 7.63									
		$J_{H^3H^4}$ 3.36												
VIIIb	Br	6.45 d	5.99 d	4.73 d	6.61 d	2.29 s	142.47	107.34	113.83	154.32	62.88	76.55	13.72	96.79
				J(H_AH_B) 6.71	*J*(H_BH_A) 6.71									
		$J_{H^3H^4}$ 3.36												

[a] **VIIIa** : **VIIIb** 1 : 1.

Individual *endo* and *exo* isomers were isolated by column chromatography on a Chemapol 100/200 silica by the procedure described in [33]. Thin-layer chromatography was performed on Silufol-254 plates in a hexane–acetone mixture (3 : 2), development in UV light. The *endo/exo* ratio was determined by [1]H NMR spectroscopy before column chromatography.

X-ray diffraction analysis of a single crystale of compound **IVa** was performed at Department of X-ray

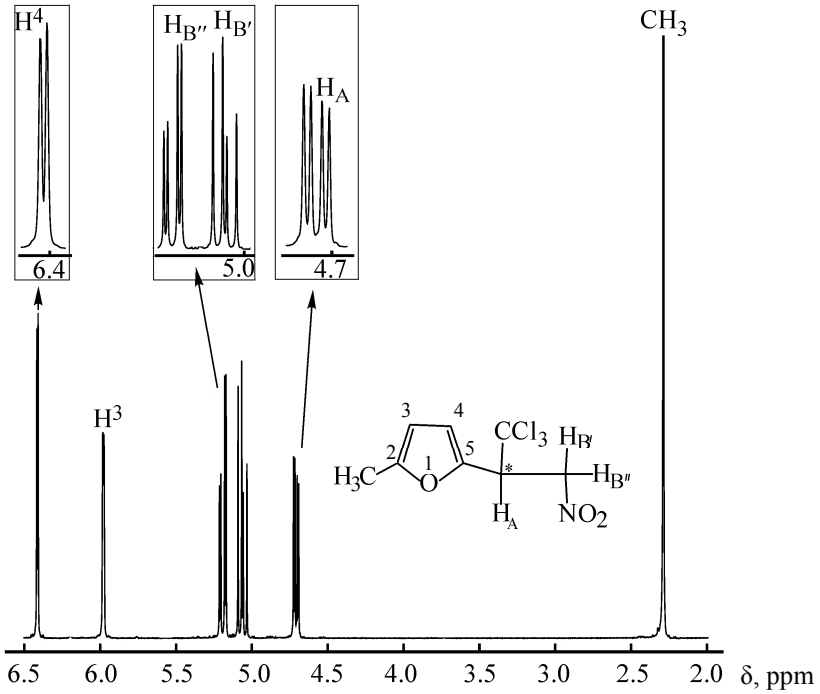


Fig. 7. [1]H NMR spectrum of 2-methyl-5-[2-nitro-1-(trichloromethyl)ethyl. furan (**VI**) in $CDCl_3$.

diffraction studies, Center for Collective Use, Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences.

The X-ray diffraction experiment was performed at 296(2) K on a Bruker Kappa APEX **II** diffractometer (MoK_α radiation, graphite monochromator, CCD detector, maximum 2θ angle 58.9°). Single crystals of compound **IVa** were grown from acetone, monoclinic: *a* 7.2649(3), *b* 9.9098(4), *c* 15.2604(6) Å, β 90.506(2)°, *V* 1098.61(8) Å^3, space group $P2_1/n$, *Z* 4, $C_7H_5BrCl_3NO_3$, d_{calc} 2.040 g/cm^3, μ 4.45 mm^{-1}, sample size 0.52×0.32×0.26 mm. The intensities of 3231 unique reflections were measured. Absorption correction was applied using SADABS (transmission 0.2054–0.3905). The structure was decoded by a direct method (SHELXS-97) and refined anisotropically for nonhydrogen atoms (SHELXL-97). Hydrogen atoms were placed at their geometrically calculated positions and refined isotropically by the rider model. Final refinement parameters: wR_2 0.0946, *S* 1.041, 136 refinement parameters (*R* 0.0483 for 2560 $F > 4$). Atomic coordinates and bond lengths and angles were deposited in the Cambridge Structural Database [29] (CCDC 874994).

The starting nitroalkene **I** and *hem*-bromonitroalkene **II** was prepared by the procedures described in [34, 35] and [36, 37], respectively.

5-Nitro-6-(trichloromethyl)-7-oxabicyclo[2.2.1]-hept-2-enes (IIIa, IIIb). *a.* A mixture of 3.00 g (0.016 mol) of 3,3,3-trichloro-1-nitropropene (**I**) and 1.31 g (1.4 mL, 0.02 mol) of furan was allowed to stand at 16–18°C for 19 days, after which it was subjected to chromatography on silica gel to isolate 0.24 g (8%) of nitroalkene **I** from the hexane fraction and 3.58 g (88%) of oxanorbornenes **IIIa** and **IIIb** (1 : 1) from the CCl_4 fraction (100 mL). Repeated chromatography of the **IIIa**/**IIIb** mixture from the first fraction (100 mL) gave oxanorbornene **IIIa**, mp 62–64°C {mp 64–64.5°C (pentane:ether 20 : 1) [19]}. From the fraction eluted by the second portion of CCl_4 (50 mL), a mixture of oxanorbornenes **IIIa** and **IIIb** was obtained. Oxanorbornene **IIIb** was isolated from the third fraction (100 mL), mp 70–71°C {mp 69–71°C (pentane:ether 20 : 1) [19]}. Found, %: C 32.44, 32.47; H 2.28, 2.31; N 5.40, 5.44. $C_7H_6Cl_3NO_3$. Calculated, %: C 32.50; H 2.32; N 5.42.

b. Furan, 1.31 g (1.4 mL, 0.02 mol) was added to a solution of 3.00 g (0.016 mol) of nitroalkene **I** in 10 mL of absolute benzene. The reaction mixture was heated under reflux for 1 h. The solvent was removed on a rotary evaporator, and the oil residue was subjected to chromatography on silica gel. From the hexane fraction, 2.4 g (80%) of the starting nitroalkene **I** was isolated. Oxanorbornenes **IIIa** and **IIIb** (1 : 1), 0.45 g (11%), was isolated from CCl_4 fraction.

5-Bromo-5-nitro-6-(trichloromethyl)-7-oxabicyclo[2.2.1]hept-2-enes IVa and IVb. *a*. A mixture of 3.50 g (0.013 mol) of 1-bromo-3,3,3-trichloro-1-nitropropene (**II**) and 1.06 g (1.1 mL, 0.016 mol) of furan was allowed to stand at 16–18°C for 19 days, after which the reaction mixture was subjected to chromatography on silica gel. Nitroalkenea **II**, 0.32 g (9%), was isolated from the first fraction (hexane, 100 mL) Oxanorbornene **IVa**, 2.63 g (60%), mp 94–96°C, was isolated from the second fraction (hexane, 100 mL). From the CCl_4 fraction (100 mL), a mixture of *exo*- and *endo*-oxanorbornenes **IVa** and **IVb** (4 : 1), 1.14 g (26%), was isolated. Found, %: C 24.86, 24.80; H 1.44, 1.48; N 4.14, 4.17. $C_7H_5Cl_3BrNO_3$. Calculated, %: C 24.89; H 1.48; N 4.15.

b. Furan, 1.06 g (1.1 mL, 0.016 mol) was added to a solution of 3.50 g (0.013 mol) of nitroalkene **II** in 10 mL of absolute benzene. The reaction mixture was heated under reflux for 1 h. The solvent was removed on a rotary evaporator, and the oil residue was subjected to chromatography on silica gel. From the hexane fraction, 2.10 g (60%) of nitroalkene **II** was isolated and from the CCl_4 fraction, 0.66 g (15%) of a mixture of *endo*- and *exo*-oxanorbornenes **IVa** and **IVb** (6 : 1).

1-Methyl-6-nitro-5-(trichloromethyl)-7-oxabicyclo[2.2.1]hept-2-enes (Va, Vb) and 2-methyl-5-[2-nitro-1-(trichloromethyl)ethyl]furan (VI). *a*. 2-Methylfuran, 1.57 g (0.019 mol, 1.7 mL), was added to 3.00 g (0.016 mol) of 3,3,3-trichloro-1-nitropropene (**I**), and the reaction mixture was allowed to stand at 16–18°C for 5 days. According to ^{1}H NMR data, the oily liquid than formed contained oxanorbornenes **Va** and **Vb** (1 : 2) and compound **VI**. It was subjected to chromatography on silica gel to obtain 3.09 g (72%) of compound **VI**, R_f 0.79, from the CCl_4 fraction. Found, %: C 35.25, 35.29; H 2.93, 2.97; N 5.15, 5.20. $C_8H_8Cl_3NO_3$. Calculated, %: C 35.23; H 2.94; N 5.14.

b. 2-Methylfuran, 1.57 g (1.7 mL, 0.019 mol), was added to a solution of 3.00 g (0.016 mol) of nitroalkene **I** in 10 mL of absolute benzene. The reaction mixture was heated for 5 h. The solvent was removed on a rotary evaporator. According to ^{1}H NMR data, the

residue contained oxanorbornenes **Va** and **Vb** (4 : 1), furan **VI**, and nitroalkene **I**. The oily residue was distilled in a vacuum (15–16 mm) to obtain 1.07 g (25%) of compound **VI**, R_f 0.79.

6-Bromo-1-methyl-6-nitro-5-(trichloromethyl)-7-oxabicyclo[2.2.1]hept-2-enes (VIIa, VIIb) and 2-methyl-5-[2-bromo-2-nitro-1-(trichloromethyl) ethyl]furans (VIIIa, VIIIb). *a*. 2-Methylfuran, 1.28 g (0.016 mol, 1.4 mL), was added to 3.50 g (0.013 mol) of 1-bromo-3,3,3-trichloro-1-nitropropene (**II**), and the reaction mixture was allowed to stand at 16–18°C for 5 days. According to ^{1}H NMR data, the reaction mixture contained oxanorbornenes **VIIa** and **VIIb** (10 : 1) and compounds **VIIIa** and **VIIIb** (1 : 1). The reaction mixture was subjected to chromatography on silica gel, and a mixture of isomers **VIIIa** and **VIIIb**, 3.10 g (68%), colorless liquid, R_f 0.74 and 0.55, was isolated from the CCl_4 fraction. Found, %: C 27.32, 27.38; H 2.03, 2.08; N 4.02; 4.06. $C_8H_7BrCl_3NO_3$. Calculated, %: C 27.31; H 1.99; N 3.98.

b. 2-Methylfuran, 1.28 g (1.4 mL, 0.016 mol), was added to a solution of 3.50 g (0.013 mol) of nitroalkene **II** in 10 mL of absolute benzene, and the reaction mixture was heated under reflux for 5 h. The solvent was removed on a rotary evaporator. According to ^{1}H NMR data, the oily residue contained 2,5-dialkylfuran **VIII** as a mixture of diastereomers **VIIIa** and **VIIIb** (1 : 1). The residue was subjected to chromatography on silica gel, and 3.88 g (85%) of the **VIIIa**/**VIIIb** mixture, R_f 0.74 and 0.55, was obtained from the hexane fraction.

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