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Synthesis and Structure of Phosphorylated Nitronorbornenes

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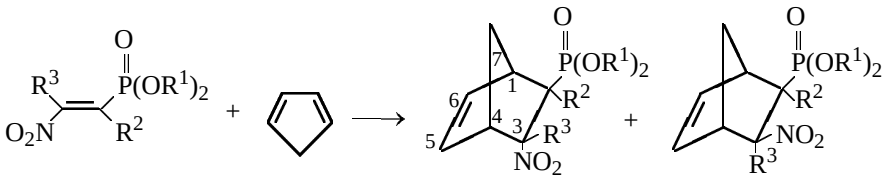
Abstract — A procedure was suggested for preparing previously unknown phosphorylated nitronorbornenes from nitroethenephosphonates and cyclopentadienes. The structures of the products were studied by IR and ^{1}H and ^{31}P NMR spectroscopy. A single crystal X-ray diffraction study of bis(2-chloroethyl) 3-bromo-3-nitrobicyclo[2.2.1]-5-heptene-2-phosphonate showed that the steric arrangement of the bicyclic fragment is typical of norbornenes. It is the *endo*-(NO_2) diastereomer in which Br and $P(O)(OC_2H_4Cl)_2$ substituents are eclipsed, and C^2–C^3 and C^3–NO_2 bonds are noticeably elongated.

Increased interest in functionalized norbornenes is due to a wide spectrum of their valuable properties, and also to their availability and high reactivity [1]. For example, norbornene derivatives are successfully used for preparing plastics [2], epoxy adhesives used in dentures [3], UV screeners, and dye binders for electronic printing [4]. Also, norbornene fragment is present in many native and synthetic biologically active compounds [5]. Among substances containing the pharmacophoric norbornene ring, there are compounds exhibiting the neurotropic and antiphlogistic action [6, 7, 8], and also the hypnotic [9] and tranquilizing [10] activity.

The presence of a nitro group in bicycloheptenes makes them interesting as synthetic intermediates, because of easy transformation of this substituent into other organic functions [11, 12] and the possibility of constructing nitrogen-containing heterocycles with its participation. Simultaneous presence of nitro and alkoxyphosphoryl groups in the bicycloheptene structure opens further synthetic prospects.

Highly reactive dialkyl 2-nitroethenephosphonates **I**–**III** are convenient precursors for preparing such compounds by the Diels–Alder reaction. However, there are virtually no data on the the behavior of nitroethenephosphonates, in contrast to vicinal alkoxycarbonyl- and cyano-substituted nitroethenes [13, 14], as dienophiles. Before our works, only one example of their participation in the diene synthesis was reported [15]. With the aim to reveal specific features of diene reactions with phosphorylated nitroethenes **I**–**III**, we studied their reactions with cyclopentadiene.

We found that, contrary to ethyl 3-nitroacrylate and 3-nitroacrylonitrile [13, 14] forming the diene adducts with cyclopentadiene at 0°C in ether in a quantitative yield, the nitroethenephosphonates under study react under more rigorous conditions: refluxing of a mixture of the starting reactants (molar ratio nitroethenephosphonate : cyclopentadiene 1 : 2) for 1 h in the case of **I** and **II** and for 6 h in the case of **III**. The reaction affords phosphorylated norbornenes, bis(2-chloroethyl) 3-nitrobicyclo[2.2.1]-5-heptene-2-phosphonates **IV**–**VI**, which were isolated by column chromatography on silica gel as viscous yellowish oils in 80–85% yields for **IVa**, **IVb**, and **Va** and in 34% yield for **VIa** and **VIb.**



I–**III** *endo*-**IVa**–**VIa** *exo*-**IVb**–**VIb**

R^1 = CH_2CH_2Cl, R^2 = R = H (**I, IVa, IVb**), R^2 = H, R^3 = Br (**II, Va**); R^1 = *i*-Pr, R^2 = CH_3, R^3 = H (**III, VIa, VIb**).

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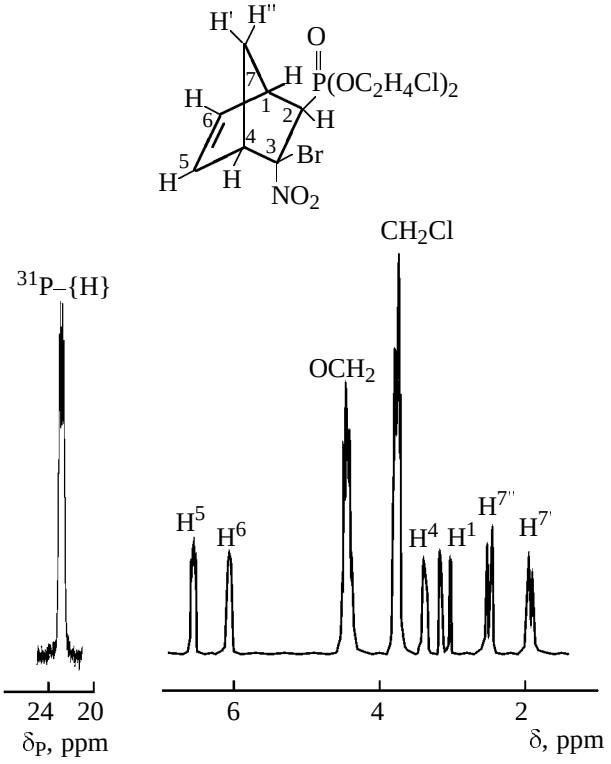


Fig. 1. Fragments of ^{31}P and ^{1}H NMR spectra of bis-(2-chloroethyl) *endo*-3-bromo-3-nitro-bicyclo[2.2.1]-5-heptene-2-phosphonate **Va**.

Note that shortening of the boiling time from 8 h (as in [15]) to 1 h in the case of **IV** leads to an increase in the total yield from 40 (data of [15]) to 80%. The decrease in the product yield in prolonged reactions may be due to the occurrence of the retro-Diels–Alder reaction [16]. At the same time, prolonged heating (6 h) is necessary with nitroethenephosphonate **III** with methyl radical in the geminal position to the phosphoryl group; with this compound, the yield of adduct **VI** is lower (34%) compared to **IV** and **V**. This is apparently due to the fact that the reaction center in **III** is more hindered sterically.

The structure of nitronorbornenephosphonates **IV**–**VI** was determined by IR and ^{1}H and ^{31}P NMR spectroscopy, and also by single crystal X-ray diffraction.

The signals of phosphorus nuclei in the ^{31}P NMR spectra of bicycloheptenes are located in the range 28.2–22.5 ppm, typical of organic phosphonates [17]. The ^{1}H and ^{31}P NMR spectra show (Fig. 1) that compound **Va** is sterically uniform and is the *endo*-(NO_2) diastereomer.

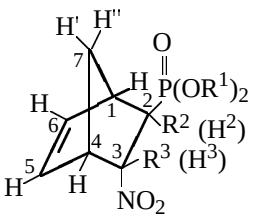
In contrast to the spectra of **V**, the ^{1}H and ^{31}P NMR spectra of **IV** and **VI** contain double sets of signals, suggesting their existence as mixtures of *endo* and *exo* diastereomers. The configurational assignment was based on the ^{1}H NMR spectra.

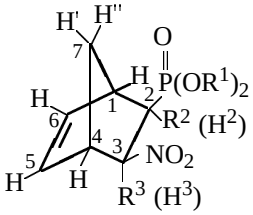
The criterion for the identification of isomers as *endo*-(NO_2) or *exo*-(NO_2) diastereomers was the chemical shift of C^3 protons, as accepted in the literature [7, 18] for structurally related compounds. The difference in the chemical shifts of these isomers arises from the magnetic anisotropy of the double bond and different steric arrangement of nitromethine protons relative to this bond [19]. Table 1) shows that, in the *endo* isomer, the H^3 proton having the *exo* orientation gives a signal shifted downfield relative to the respective proton in the *exo* isomer (*endo* orientation of C^3-H). For diastereomeric pairs **IVa** + **IVb** and **VIa** + **VIb**, the difference in the chemical shifts $\Delta\delta(H^3)$ is 0.68 and 0.30 ppm, respectively. Similar values were reported for related compounds, e.g., for 2-nitro-3-(phenylsulfo)bicyclo[2.2.1]-5-heptene [20]. The chemical shifts of protons at the bridging methylene group are also sensitive to the steric structure. In the case of *endo* isomers, the difference in the chemical shifts of these protons is usually larger than in the *exo* isomers [8]. For the spectra of **IV** and **VI**, this test also seems convincing. For example, $\Delta\delta$(H'H'') in the spectrum of **IVa** is 0.40 ppm, significantly exceeding the corresponding parameter for **IVb** (Table 1, 0.13 ppm). Thus, the first compound can be identified as the *endo* isomer, and the second compound, as the *exo* isomer. According to the integral intensities of signals in the ^{1}H and ^{31}P NMR spectra of **IV** and **VI**, the *endo*:*exo* ratio is 6:1 in **IV** and 3:1 in **VI**.

The IR spectra of the compounds under study are complex. Along with the characteristic bands of the functional groups NO_2 (ν_{as} 1561–1546 cm^{-1}, ν_s 1346–1381 cm^{-1}), P=O (1232–1261 cm^{-1}), and P–O–C (1014–1084 cm^{-1}), they contain a series of bands characteristic of norbornene derivatives and differing from other cyclic systems containing a C=C bond. In particular, a $\nu_{C=C}$ band at 1550–1570 cm^{-1} in our case overlaps with the $\nu_s(NO_2)$ band, increasing its intensity. Unusual location of this band is due to the strain of the C=C bond in the norbornene core [21].

The absorption bands present at ~3030 cm^{-1} are evidently due to $\nu_{=CH}$, which, according to [22], distinguishes norbornenes from alkenes with a terminal C=C bond (3080 cm^{-1}) and also from cyclohexenes (3017 cm^{-1}) [22]. The presence of the absorption bands $\delta_{=CH}$ at 725–720 cm^{-1}, characteristic of norbornenes and depending on the substituent orientation [22], in the IR spectra of **IV**–**VI** points to the *endo* orientation of the nitro group. The related $\delta_{=CH}$ vibra-

Table 1. Parameters of ^{31}P and ^{1}H NMR spectra of phosphorylated nitronorbornenes **IVa, IVb, Va, VIa**, and **VIb** (δ, ppm; *J*, Hz) in deuterochloroform





Comp. no.	Yield, % (*endo*:*exo*)	H^1	R^2=H^2 (CH_3)	H^3	H^4	H^5	H^6	H^7		R^1		P^{31}
								H'	H''	CH_2Cl (OCH)	OCH_2 (CH_3)	
IVa	80[a] (6:1)	2.35 d.d.d (J_{H^1P} 15.7, ($J_{1,2}$ 2.5, $J_{1,6}$ 2.0)	3.65	5.10 d.d.d (J_{H^3P} 18.0, $J_{2,3}$ 4.5, $J_{3,4}$ 3.0)	3.15 d.d. ($J_{3,4}$ 3.0, $J_{4,5}$ 2.5)	6.44 d.d. ($J_{5,6}$ 5.6, $J_{4,5}$ 2.5)	5.87 d.d ($J_{5,6}$ 5.6, $J_{1,6}$ 2.0)	1.43	1.83 (J_{HH} 9.5)	3.65 m	4.29 m	28.5
IVb		3.00 d.d (J_{H^1P} 18.4, ($J_{1,2}$ 3.0, $J_{1,6}$ 2.0)	3.65	4.42 d.d.d. (J_{H^3P} 19.5, $J_{2,3}$ 0, $J_{3,4}$ 3.0)	3.32 d.d. ($J_{3,4}$ 3.0, $J_{4,5}$ 2.0)	6.27 d.d. ($J_{5,6}$ 5.5, $J_{4,5}$ 2.0)	6.05 d.d ($J_{5,6}$ 5.5, $J_{1,6}$ 2.0)	1.52	1.65 (J_{HH} 9.4)	3.65 m	4.29 m	27.8
Va	85 (1:0)	3.18 d.d.d (J_{H^1P} 13.7, ($J_{1,2}$ 3.0, $J_{1,6}$ 1.8)	3.75	–	3.37 d.d. ($J_{3,4}$ 3.0, $J_{4,5}$ 2.5)	6.56 d.d ($J_{5,6}$ 5.5, $J_{4,5}$ 2.5)	6.05 d.d ($J_{5,6}$ 5.5, $J_{1,6}$ 1.8)	1.90	2.50 (J_{HH} 9.2)	3.75 m	4.45 m	22.5
VIa	34[b] (3:1)	3.00 (J_{H^1P} 0, ($J_{1,6}$ 1.5)	(0.88) (J_{CH^3P} 17.0)	5.35 (J_{CH^3P} 20.5, $J_{2,3}$ 3.5, $J_{3,4}$ 0)	3.25 ($J_{3,4}$ 4.5, $J_{5,4}$ 0)	6.37 ($J_{5,6}$ 4.5, $J_{4,5}$ 0)	6.00 ($J_{5,6}$ 4.5, $J_{1,6}$ 1.5)	1.40	1.98 (J_{HH} 9.5)	(4.70 m)	(1.25 d.d)	29.0
VIb		2.68 (J_{H^1P} 0, ($J_{1,6}$ 2.0)	(1.35) (J_{CH^3P} 16.0)	5.05 (J_{CH^3P} 21.5, $J_{2,3}$ 3.0, $J_{3,4}$ 1.5)	3.18 ($J_{3,4}$ 1.5, $J_{5,4}$ 2.0)	6.30. ($J_{5,6}$ 4.7, $J_{5,4}$ 2.0)	6.00 ($J_{5,6}$ 4.7, $J_{1,6}$ 2.0)	1.65	2.00 (J_{HH} 9.5)	(4.70 m)	(1.25 d.d)	28.5

[a] Total yield of **IVa** and **IVb**. [b] Total yield of **VIa** and **VIb**.

tions in the *exo* isomers are usually observed in the range 710–700 cm^{-1}.

More complete information about the fine structure of phosphorylated nitronorbornenes was furnished by a single crystal X-ray diffraction study of one of the representatives of this series, **Va**. The steric structure of **Va** is shown in Fig. 2; the atomic coordinates and geometric parameters of the molecule are given in Tables 2–5. The geometry of the bicyclic fragment is usual for the norbornene group. Its five-membered rings have the conformation of C^7 *envelope*, and the six-membered ring has the *boat* conformation, The bulky bis(chloroethoxy)phosphoryl substituent at C^2 and the bromine atom at C^3 are equatorial, whereas the nitro group at C^3 is axial. The C^5–C^6 double bond in **Va** is not twisted, the torsion $C^1C^6C^5C^4$ angle is 0(1)°, and C^5=C^6 bond has the usual length, 1.32(1) Å. The eclipsed conformation takes place along the C^2–C^3 bond [$P^2C^2C^3Br^1$ torsion angle –9.0(1)°], which leads to certain elongation of the C^2–C^3 bond to 1.56(2)Å. The axial N^3–C^3 bond is also noticeably elongated [1.56(1) Å]. The geometric parameters of the phosphonate group and norbornene fragments are usual.

The crystal structure of **Va** is determined by weak van der Waals contacts and weak hydrogen bonds (Fig. 3) formed by chloroethoxy group and bromine atoms. The bond parameters are as follows: C^{10}–

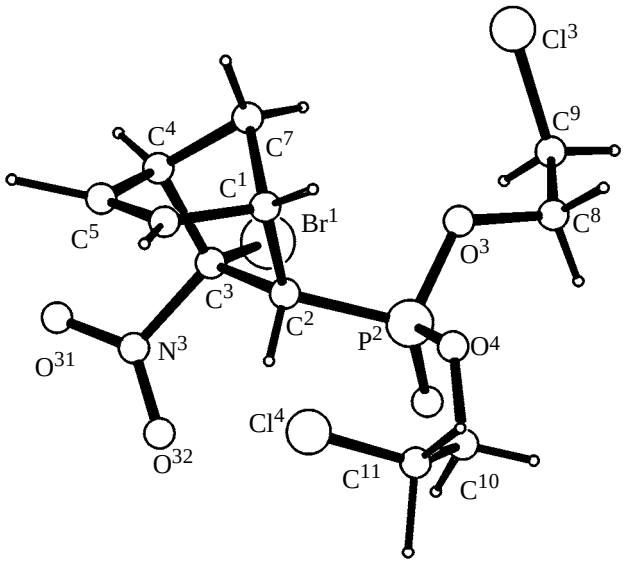


Fig. 2. Geometry of a molecule of **Va** in the crystal.

$H^{102}\cdots Br^{1'}$ [*x*, 1/2 – *y*, 1/2 + *z*], C^{10}–H^{102} 0.99, $H^{102}\cdots Br^{1'}$ 2.9, $C^{10}\cdots Br^{1'}$ 3.88(1)Å, C^{10}–$H^{102}\cdots Br^{1'}$ angle 171°; C^{11}–$H^{111}\cdots Br^{1''}$ [*x*, *y*, 1 + *z*], C^{11}–H^{111} 1.22, $H^{111}\cdots Br^{1''}$ 2.72, $C^{11}\cdots Br^{1''}$ 3.84(2) Å, C^{11}–$H^{111}\cdots Br^{1''}$ angle 152°. Due to this interaction, the infinite chains along the *z*-axis (Fig. 3) are formed. Along with these interactions, there are short intramolecular contacts of bromine with the oxygen aton of the phosphoryl group: $Br^{1}\cdots O^{2'}$ [*x*, 1/2 – *y*, *z* – 1/2] = 2.878 Å, which is 0.5 Å shorter than the sum of the van der Waals radii of these atoms.

EXPERIMENTAL

The IR spectra were taken on an Infralyum FT02 spectrometer from 0.1–0.001 M chloroform solutions. The ^1H and ^{31}P NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz) in $CDCl_3$. The chemical shifts (δ) were measured against external HMDS with an accuracy of ±0.5 Hz. The ^{31}P NMR spectra were recorded against external 85% phosphoric acid.

The crystals of **Va** are monoclinic, mp 85–86°C. At 20°C, *a* 8.8826(8), *b* 21.2324(2), *c* 9.5216(9) Å, β 116.5831(7)°, *V* 1605.9(4) $Å^3$, *Z* 4, d_{calc} 1.74 g/cm^3, space group $P2_1/c$. The unit cell parameters and intensities of 3122 reflections, including 1131 relfections were with $I \geq 3\sigma$, were measured on an Enraf–Nonius CAD-4 automatic four-circle diffractometer at 20°C (MoK_α irradiation, graphite monochromator, ω/2θ scanning, $\theta \leq 27°$). No decrease in the intensity of three check reflections was observed in the course of the experiment. The absorption was taken into account empirically (μMo 29.8 cm^{-1}).

Table 2. Atomic coordinates of the structure of **V**, equivalent isotropic temperature factors of non-hydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i, j)$ ($Å^2$), and isotropic temperature factors of hydrogen atom B_{iso} ($Å^2$)

Atom	*x*	*y*	*z*	*B* or B_{iso}
Br^1	0.7039(2)	0.19653(6)	–0.1246(1)	3.96(3)
Cl^3	0.2202(4)	0.1016(2)	–0.4195(4)	6.4(1)
Cl^4	0.7382(6)	0.0695(2)	0.5293(5)	12.3(2)
P^2	0.5135(3)	0.1567(1)	0.0960(3)	2.69(7)
O^2	0.5112(8)	0.2249(3)	0.1088(7)	3.2(2)
O^3	0.3908(8)	0.1293(3)	–0.0687(7)	3.4(2)
O^4	0.4578(8)	0.1204(3)	0.2109(8)	3.9(2)
O^{41}	1.0851(8)	0.1781(4)	0.1207(9)	5.8(2)
O^{42}	0.9653(9)	0.2091(4)	0.2701(8)	5.3(2)
N^4	0.9727(9)	0.1794(4)	0.1628(9)	3.5(2)
C^1	0.712(1)	0.0480(5)	0.120(1)	2.9(3)
C^2	0.709(1)	0.1207(4)	0.140(1)	2.6(3)
C^3	0.814(1)	0.1406(4)	0.052(1)	2.5(3)
C^4	0.865(1)	0.0780(5)	0.001(1)	3.2(3)
C^5	0.976(1)	0.0448(5)	0.148(1)	3.8(3)
C^6	0.886(1)	0.0270(5)	0.219(1)	3.7(3)
C^7	0.701(1)	0.0405(4)	–0.044(1)	2.7(3)
C^8	0.230(1)	0.1555(6)	–0.159(1)	5.8(4)
C^9	0.204(2)	0.1707(6)	–0.322(2)	6.2(4)
C^{10}	0.482(1)	0.1445(6)	0.360(1)	4.7(3)
C^{11}	0.573(2)	0.109(1)	0.485(2)	15.9(7)
H^1	0.6293	0.0198	0.1325	3
H^2	0.7628	0.1370	0.2480	3
H^3	0.9139	0.0826	–0.0724	4
H^5	1.1161	0.0269	0.1673	6
H^6	0.9308	0.0033	0.3190	4
H^{71}	0.6030	0.0680	–0.1372	6
H^{72}	0.7180	–0.0084	–0.0525	6
H^{81}	0.2142	0.1949	–0.1118	6
H^{82}	0.1395	0.1284	–0.1695	6
H^{91}	0.0969	0.1913	–0.3828	7
H^{92}	0.2898	0.2012	–0.3151	7
H^{101}	0.3725	0.1560	0.3523	6
H^{102}	0.5424	0.1852	0.3766	6
H^{111}	0.6195	0.1505	0.5820	6
H^{112}	0.4881	0.0752	0.4738	19

The structure was solved by the direct method using the SIR program [23]. The structure was refined first in isotropic and then in anisotropic approximation. After that, all the hydrogen atoms were revealed from the differential electron density series, and their contribution to the structure amplitude was considered with the fixed positional and isotropic temperature parameters in the final stage. The final divergence

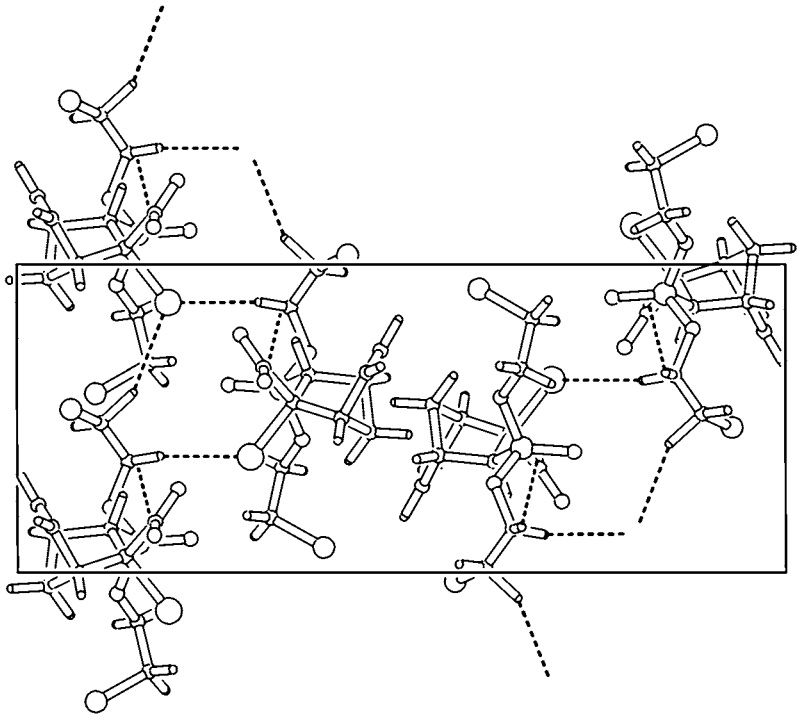


Fig. 3. Molecular packing in the crystal of **Va**. Projection along 0*x* axis. Hydrogen bonds are shown by dotted lines.

factors are R 0.049, R_W 0.047 for 1005 unique reflections with $F^2 > 3\sigma$. All the calculations were carried out on an AlphaStation 200 computer with the MOLEN program package [24]. PLATON program was used to plot the figures and analyze the intermolecular contacts in the crystal [25].

The starting nitroethenephosphonates **I**–**III** were prepared by the procedures described in [26, 27]. The individual *endo* isomers were isolated by column chromatography on Chemapol 100/200 silica gel using the series of solvents similar to [28]. TLC was carried out on Silufol-254 plates using 3:2 hexane–

Table 3. Bond lengths (*d*, Å) in the molecule of **Va**

Bond	*d*	Bond	*d*
Br^1–C^3	1.933(9)	N^3–C^3	1.56(1)
Cl^3–C^9	1.77(1)	C^1–C^2	1.56(1)
Cl^4–C^{11}	1.57(2)	C^1–C^6	1.47(1)
P^2–O^2	1.452(7)	C^1–C^7	1.53(2)
P^2–O^3	1.566(6)	C^2–C^3	1.56(2)
P^2–O^4	1.589(9)	C^3–C^4	1.55(1)
P^2–C^2	1.77(1)	C^4–C^5	1.48(1)
O^3–C^8	1.41(1)	C^4–C^7	1.54(1)
O^4–C^{10}	1.43(1)	C^5–C^6	1.32(2)
O^{31}–N^3	1.23(1)	C^8–C^9	1.50(2)
O^{32}–N^3	1.23(1)	C^{10}–C^{11}	1.34(2)

Table 4. Bond angles (ω, deg) in the molecule of **Va**

Angle	ω	Angle	ω
$O^2P^2O^3$	115.0(4)	$Br^1C^3N^3$	102.4(6)
$O^2P^2O^4$	114.1(5)	$Br^1C^3C^2$	116.3(6)
$O^2P^2C^2$	117.3(4)	$Br^1C^3C^4$	111.1(7)
$O^3P^2O^4$	102.5(4)	$N^3C^3C^2$	110.9(8)
$O^3P^2C^2$	104.3(4)	$N^3C^3C^4$	111.0(7)
$O^4P^2C^2$	101.7(4)	$C^2C^3C^4$	105.3(8)
$P^2O^3C^8$	121.9(7)	$C^3C^4C^5$	106.2(8)
$P^2O^4C^{10}$	123.6(7)	$C^3C^4C^7$	99.0(8)
$O^{31}N^3O^{32}$	129.4(8)	$C^5C^4C^7$	99.4(8)
$O^{31}N^3C^3$	112.9(8)	$C^4C^5C^6$	108.7(9)
$O^{32}N^3C^3$	117.5(8)	$C^1C^6C^5$	106.9(9)
$C^2C^1C^6$	106.9(7)	$C^1C^7C^4$	92.5(7)
$C^2C^1C^7$	102.9(8)	$O^3C^8C^9$	112.0(1)
$C^6C^1C^7$	100.9(9)	$Cl^3C^9C^8$	110.4(9)
$P^2C^2C^1$	117.7(7)	$O^4C^{10}C^{11}$	116.0(1)
$P^2C^2C^3$	121.0(6)	$Cl^4C^{11}C^{10}$	131.0(2)
$C^1C^2C^3$	99.3(9)		

Table 5. Torsion angles (τ, deg) in the molecule of **Va**

Angle	ω	Angle	ω
$O^2P^2O^3C^8$	–37.0(1)	$C^2C^1C^6C^5$	–73.0(1)
$O^4P^2O^3C^8$	87.2(9)	$C^7C^1C^6C^5$	34.0(1)
$C^2P^2O^3C^8$	–167.1(8)	$C^2C^1C^7C^4$	59.6(9)
$O^2P^2O^4C^{10}$	–29.4(9)	$C^6C^1C^7C^4$	–50.8(9)
$O^3P^2O^4C^{10}$	–154.4(8)	$P^2C^2C^3Br^1$	–9.0(1)
$C^2P^2O^4C^{10}$	97.9(8)	$P^2C^2C^3N^3$	107.7(8)
$O^2P^2C^2C^1$	–177.7(6)	$P^2C^2C^3C^4$	–132.2(7)
$O^2P^2C^2C^3$	–55.7(9)	$C^1C^2C^3Br^1$	121.7(7)
$O^3P^2C^2C^1$	–49.2(8)	$C^1C^2C^3N^3$	–121.9(8)
$O^3P^2C^2C^3$	72.7(8)	$C^1C^2C^3C^4$	–1.8(9)
$O^4P^2C^2C^1$	57.1(8)	$Br^1C^3C^4C^5$	169.1(7)
$O^4P^2C^2C^3$	179.1(7)	$Br^1C^3C^4C^7$	–88.4(8)
$P^2O^3C^8C^9$	127.2(9)	$N^3C^3C^4C^5$	56.0(1)
$P^2O^4C^{10}C^{11}$	–122.0(1)	$N^3C^3C^4C^7$	158.6(7)
$O^{31}N^3C^3Br^1$	–78.0(8)	$C^2C^3C^4C^5$	–64.0(1)
$O^{31}N^3C^3C^2$	157.3(8)	$C^2C^3C^4C^7$	38.5(9)
$O^{31}N^3C^3C^4$	40.0(1)	$C^3C^4C^5C^6$	68.0(1)
$O^{32}N^3C^3Br^1$	97.8(8)	$C^7C^4C^5C^6$	–34.0(1)
$O^{32}N^3C^3C^2$	–27.0(1)	$C^3C^4C^7C^1$	–58.2(8)
$O^{32}N^3C^3C^4$	–143.7(8)	$C^5C^4C^7C^1$	50.0(9)
$C^6C^1C^2P^2$	–157.9(7)	$C^4C^5C^6C^1$	0.0(1)
$C^6C^1C^2C^3$	69.6(9)	$O^3C^8C^9Cl^3$	61.0(1)
$C^7C^1C^2P^2$	96.2(9)	$O^4C^{10}C^{11}Cl^4$	42.0(2)
$C^7C^1C^2C^3$	–36.2(9)		

acetone, development with a UV lamp. The ratio of *endo* and *exo* stereoisomers was determined by ^1H and ^{31}P spectroscopy after performing the column chromatography.

Bis(2-chloroethyl) 3-nitrobicyclo[2.2.1]-5-heptene-2-phosphonate IVa and IVb. To a solution of 1.2 g of bis(2-chloroethyl) 2-nitroethenephosphonate **I** in 5 ml of absolute benzene, 0.71 ml of 1,3-cyclopentadiene was added at room temperature, and the reaction mixture was refluxed with stirring for 1 h. Then the solvent was removed on a rotary evaporator, the residual oil was chromatographed on silicic acid, and from the fraction eluted with carbon tetrachloride 1.18 g (80%) of **IV** was isolated as a mixture of *endo* (**IVa**) and *exo* (**IVb**) isomes in 6:1 ratio. Repeated chromatography of the benzene fraction gave the individual *endo* isomer **IVa**, R_f 0.36. The analytical data are given in [29].

Bis(2-chloroethyl) 3-bromo-3-nitrobicyclo-[2.2.1]-5-heptene-2-phosphonate Va was prepared similarly to **IVa** and **IVb** from 1 g of bis(2-chloroethyl) 2-bromo-2-nitroethenephosphonate **II** and 0.5 ml of 1,3-cyclopentadiene. Adduct **V** was isolated from the fraction eluted with carbon tetrachloride as *endo* isomer **Va**; its yield was 1 g (85%). Compound **Va** is a yellow oil (R_f 0.42) crystallizing on standing (mp 85–86°C, from 5:1 hexane–benzene). The analytical data are given in [29].

Diisopropyl 2-methyl-3-nitrobicyclo[2.2.1]-5-heptene-2-phosphonate VIa and VIb. To a solution of 1 g of diisopropyl 1-methyl-2-nitroethenephosphonate **III** in 5 ml of absolute benzene, 0.7 ml of 1,3-cyclopentadiene was added at room temperature. The reaction mixture was refluxed with stirring for 6 h. After removing the solvent on a rotary evaporator, the residual oil was chromatographed on silica gel (elution with ether) to give 0.42 g (34%) of **VI** as an unseparable mixture of *endo* (**VIa**) and *exo* (**VIb**) isomers in 3:1 ratio with R_f 0.79. Found, %: C 53.03, 53.02; H 7.63, 7.60; N 4.49, 4.49; P 9.75; 9.81. $C_{14}H_{24}NO_5P$. Calculated, %: C 53.00; H 7.57; N 4.42; P 9.78.

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