Electrophilic addition to norbornene derivatives containing CF_3 and NO_2 groups

N. V. Zyk, E. K. Beloglazkina, S. E. Sosonyuk, M. N. Bulanov, and R. L. Antipin★

Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119992 Moscow, Russian Federation. Fax: + 7 (095) 939 0290. E-mail: antipin@org.chem.msu.ru

Electrophilic sulfenylation, selenenation, and halogenation of bicyclo[2.2.1]heptenes containing CF_3 or NO_2 group in position *endo*-5 were studied. The sulfenylation and selenenation were accomplished by arylsulfene- and arylselenenamides activated by $POHal_3$ (Hal = Br, Cl), and iodination was performed by $KICl_2$. The reactions are regiospecific and involve an *exo*-attack of the electrophilic fragment (arylthio or arylseleno group or iodine) on the C=C bond atom located closer to the CF_3 or NO_2 group.

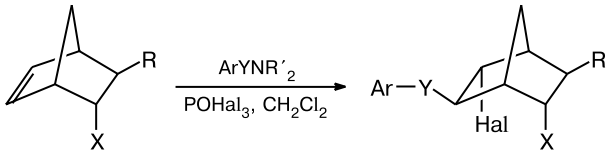
Key words: sulfenamides, selenenamides, phosphorus(v) oxychloride, phosphorus(v) oxybromide, activating reagents, electrophilic addition, potassium dichloroiodate(i), bicyclo[2.2.1]heptenes.

Electrophilic halochalcogenation and mixed halogenation of olefins are convenient reactions for the introduction of two functional groups of different chemical nature into unsaturated molecules. Previously, we demonstrated the possibility of chloro- and bromosulfenylation of alkenes with arylsulfenamides in the presence of phosphorus oxyhalides,[1,2] chloroselenenation with arylselenenamides activated by sulfur(iv) and phosphorus(v) oxychlorides,[3] and iodination of the C=C bonds on treatment with potassium dichloroiodate(i).[4] However, only alkenes containing electron-donor substituents have been studied as substrates in the above reactions.

The purpose of the present work is to study the electrophilic addition to bicyclo[2.2.1]heptenes containing an electron-withdrawing group at the C(5) atom. For these substrates, one can expect predominant (or exclusive) formation of 1,2-addition products, as the Wagner—Meerwein rearrangement, usual for norbornene systems, is less probable in this case. In addition, for the NO_2-containing substrate, there is a probability of precoordination of an electrophilic species to the nitro-group oxygen,[5] which may result in products with unusual stereochemistry.

It has been shown previously[2] that the sulfenylation of unsubstituted norbornene in the presence of phosphorus oxyhalides affords nonrearranged addition products. Similarly, the corresponding *trans*-1,2-chloroselenides have been isolated upon the selenenation of alkenes with selenenamides activated with sulfur(iv) and phosphorus(v) oxychlorides.[3] The sulfenylation and selenenation of norbornene with the electron-withdrawing CF_3 group gave no Wagner—Meerwein rearrangement products either. The corresponding bromosulfide **1** and bromoselenide **2** were obtained in 80—90%* yields (Scheme 1).

Scheme 1



1—9

Compound	X	R	Ar	Hal	NR_2'	Y	Yield (%)
1	CF_3	H	4-$O_2NC_6H_4$	Br	$N(CH_2CH_2)_2O$	S	91
2	CF_3	H	Ph	Br	NEt_2	Se	81
3	NO_2	H	4-$O_2NC_6H_4$	Cl	$N(CH_2CH_2)_2O$	S	58
4	NO_2	H	4-$O_2NC_6H_4$	Br	$N(CH_2CH_2)_2O$	S	51
5	NO_2	H	Ph	Br	$N(CH_2CH_2)_2O$	S	43
6	NO_2	Ph	4-$O_2NC_6H_4$	Br	$N(CH_2CH_2)_2O$	S	42
7	NO_2	Ph	Ph	Br	$N(CH_2CH_2)_2O$	S	42
8	NO_2	Ph	2-$O_2NC_6H_4$	Br	$N(CH_2CH_2)_2O$	S	28
9	NO_2	Ph	Ph	Br	NEt_2	Se	83

The high regio- and stereoselectivities of the reaction may be attributed to the fact that the *endo*-CF_3 group increases the probability of the *exo*-attack by the electrophile and exerts a steric (and possibly electronic) influence on the direction of the nucleophile attack on position 2 of the norbornene cage, which is most remote from the CF_3 group.

* The starting 5-trifluoromethylnorbornene is a mixture of *endo*- and *exo*-isomers in 3 : 1 ratio. The yield is given in relation to pure *endo*-isomer. No products of reaction with the *exo*-isomer were detected in the reaction mixture.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1445—1448, June, 2005.

1066-5285/05/5406-1488

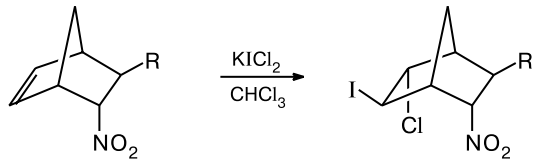
Sulfenylation of 5-*endo*-nitronorbornene and 5-*endo*-nitro-6-*exo*-phenylnorbornene with arylsulfenamides in the presence of phosphorus oxyhalides was also studied. As in the case of trifluoromethylnorbornene, the reaction gives nonrearranged 2,3-*trans*-substituted products **3—9** in 28—58% yields (see Scheme 1).

The product structure was determined by ^{1}H NMR spectroscopy using the NOE experiment taking compound **4** an the example. The irradiation of the H(1) proton induces a NOE equal to 6.1% on the H(2) proton, which confirms the *exo*-orientation of the latter. In addition, a somewhat less pronounced effect (4.4%) was found on the H(6) proton, while the NOE for the proton at the nitro group is not manifested. This approves the 2,5-arrangement of the nitro group and bromine.

In addition, the *exo*-orientation of the proton of the HCBr fragment is confirmed by the presence of two coupling constants J = 4.6 Hz and one w-coupling constant with the *exo*-H(6) proton (J = 2.2 Hz). Conversely, the proton of the HCS fragment has only two spin—spin coupling constants: J = 4.6 Hz corresponding to the H(2)—H(3) *trans*-interaction and J = 2.9 Hz (w-coupling) with the *anti*-H(7) proton, which proves its *endo*-orientation. The ^{1}H NMR spectra of compounds **3—9** exhibit a similar set of signals; therefore, the same configuration of substituents was ascribed to them. As in the case of product **4**, the arylthio group in compounds **3—9** occurs in the 3-*exo*-position.

A similar result has been obtained on iodochlorination of 5-*endo*-nitronorbornene and 5-*endo*-nitro-6-*exo*-phenylnorbornene (Scheme 2). The electrophilic species (the I atom) also attacks the carbon atom of the C=C bond located most closely to the nitro group.

Scheme 2



10: R = H (48%)
11: R = Ph (53%)

The structure of products **10** and **11** was determined using ^{1}H NMR spectroscopy with the NOE effect and ^{13}C—{^{1}H} selective double resonance. For compound **10**, irradiation at the $HCNO_2$ proton frequency (δ 4.85) produced the NOE on the H(1) (5.3%), *exo*-H(6) (3.8%), and *anti*-H(7) (2.4%) protons. The presence of the effect on the last-mentioned proton attests to an *endo*-orientation of the nitro group, *i.e.*, the Wagner—Meerwein rearrangement does not take place. In addition, the chemical shift of the bridgehead proton adjacent to the nitro group was identified (δ 3.2). The chemical shifts of the protons of the HCHal fragment in compound **10** are 4.63 and 3.86 ppm. The irradiation at the frequency of the proton at δ 4.63 induces the NOE for the second proton of the HCHal fragment (2.4%) and the H(4) (5.2%) and *syn*-H(7) protons (2.8%), which indicates the *endo*-orientation of the HCHal proton located most closely to the nitro group.

An experiment with selective ^{13}C—{^{1}H} double resonance clearly shows the spin-spin coupling between the proton with δ 4.63 and the carbon atom with δ 69.4 and the lack of coupling with the carbon atom at δ 38.9. Conversely, for a proton with δ 3.86, spin-spin coupling with only the carbon atom with δ 38.9 is observed. This proves that the signal with δ 4.63 corresponds to the proton of the HCCl fragment, while signal with δ 3.86 is due to the proton of the HCI fragment. These results provide unambiguous regio- and stereochemical assignment for compounds **10** and **11**.

Thus, irrespective of the nature of the electrophilic species (ArS^+, $ArSe^+$, I^+), the addition to norbornene derivatives containing a strong electron-withdrawing substituent in the 5-*endo*-position is regio- and stereospecific. The *exo*-attack by the electrophile is determined by the properties of the norbornene system, while the pattern of the subsequent *endo*-addition of the nucleophilic fragment is due to the steric effect of the trifluoromethyl or nitro group. This specificity of the addition is apparently due to the fact that the reaction proceeds through a cyclic three-membered intermediate by analogy with sulfenylation processes.[2]

Experimental

NMR spectra were recorded on a Varian VXR-400 spectrometer (400 (^{1}H) and 100 MHz (^{13}C)) in $CDCl_3$. Mass spectra were run in a JMS-D300 GC/MS spectrometer with a JMA-2000 computer and a HP-5890 chromatograph (temperature of the ion source 150 °C, energy of the ionizing electrons 70 eV, accelerating voltage 3 kV, mass numbers 40—400 amu). IR spectra were recorded on a UR-20 instrument. Sulfenamides[6] and selenenamides[7] were synthesized according to the literature.

Sulfenylation of norbornenes with sulfenamides in the presence of phosphorus oxyhalides (general procedure). A solution of phosphorus oxyhalide (2.5 mmol) in anhydrous CH_2Cl_2 (10 mL) and, 15 min later, a solution of sulfenamide (2.5 mmol) in CH_2Cl_2 (10 mL) were added at –40 °C with stirring to a solution of norbornene derivative (1.2 mmol) in anhydrous CH_2Cl_2 (20 mL). The reaction mixture was stirred for 24 h. After completion of the reaction, the solvent was evaporated *in vacuo*, and the residue was chromatographed on a silica gel-packed column (10 cm, petroleum ether—ethyl acetate, 3 : 1, as the eluent).

2-*endo*-Bromo-3-*exo*-(4-nitrophenylthio)-5-*endo*-(trifluoromethyl)bicyclo[2.2.1]heptane (1). Yield 0.47 g (91%), m.p. 64—66 °C, R_f 0.40. ^{1}H NMR, δ: 8.13, 7.37 (both d, 2 H each, H arom., J = 9.0 Hz); 4.09 (dt, 1 H, H(2), $J_{H(2),H(3)}$ = 4.2, $J_{H(2),H(1)}$ = 4.2 Hz, $J_{H(2),exo\text{-}H(6)}$ = 1.9 Hz); 3.89 (dd, 1 H, H(3), $J_{H(3),H(2)}$ = 4.2 Hz, $J_{H(3),anti\text{-}H(7)}$ = 3.0 Hz); 2.70 (dddq, 1 H, H(5), $J_{H(5),exo\text{-}H(6)}$ = 12.0 Hz, $J_{H(5),F}$ = 10.3 Hz, $J_{H(5),endo\text{-}H(6)}$ =

6.4 Hz, $J_{H(5),H(4)}$ = 3.8 Hz); 2.66 (m, 1 H, H(4)); 2.53 (br.s, 1 H, H(1)); 2.21 (ddd, 1 H, *endo*-H(6), $J_{endo\text{-}H(6),exo\text{-}H(6)}$ = 13.7 Hz, $J_{endo\text{-}H(6),H(5)}$ = 6.4 Hz, $J_{endo\text{-}H(6),syn\text{-}H(7)}$ = 2.6 Hz); 2.00 (ddt, 1 H, *syn*-H(7), $J_{syn\text{-}H(7),anti\text{-}H(7)}$ = 11.2 Hz, $J_{syn\text{-}H(7),endo\text{-}H(6)}$ = 2.6 Hz, $J_{syn\text{-}H(7),H(1)}$ = 1.0 Hz, $J_{syn\text{-}H(7),H(4)}$ = 1.0 Hz); 1.91 (dddd, 1 H, *exo*-H(6), $J_{exo\text{-}H(6),endo\text{-}H(6)}$ = 13.7 Hz, $J_{exo\text{-}H(6),H(5)}$ = 12.0 Hz, $J_{exo\text{-}H(6),H(1)}$ = 4.9 Hz, $J_{exo\text{-}H(6),H(2)}$ = 1.9 Hz); 1.63 (ddt, 1 H, *anti*-H(7), $J_{anti\text{-}H(7),syn\text{-}H(7)}$ = 11.2 Hz, $J_{anti\text{-}H(7),H(3)}$ = 3.0 Hz, $J_{anti\text{-}H(7),H(1)}$ = 1.7 Hz, $J_{anti\text{-}H(7),H(4)}$ = 1.7 Hz). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 396 $[M]^+$ (53.6), 398 $[M + 2]^+$ (56.8), 316 $[M - Br]^+$ (13.6), 242 $[M - ArS]^+$ (20.0), 244 $[M + 2 - ArS]^+$ (20.0), 161 $[M - ArS - HBr]^+$ (100.0).

5-*endo*-Nitro-3-*exo*-(4-nitrophenylthio)-2-*endo*-chlorobicyclo[2.2.1]heptane (3). Yield 0.95 g (58%), R_f 0.59. Found (%): C, 47.97; H, 3.84; N, 8.84. $C_{13}H_{13}ClN_2O_4S$. Calculated (%): C, 47.49; H, 3.99; N, 8.52. ^{1}H NMR, δ: 8.15, 7.41 (both d, 2 H each, H arom., *J* = 8.8 Hz); 4.93 (dt, 1 H, H(5), $J_{H(5),exo\text{-}H(6)}$ = 11.3 Hz, $J_{H(5),H(4)}$ = 4.6 Hz, $J_{H(5),endo\text{-}H(6)}$ = 4.6 Hz); 4.09 (dt, 1 H, H(2), $J_{H(2),H(3)}$ = 4.3 Hz, $J_{H(2),H(1)}$ = 4.3 Hz, $J_{H(2),exo\text{-}H(6)}$ = 1.8 Hz); 3.38 (dd, 1 H, H(3), $J_{H(3),H(2)}$ = 4.3 Hz, $J_{H(3),anti\text{-}H(7)}$ = 3.3 Hz); 3.00 (dq, 1 H, H(4), $J_{H(4),H(5)}$ = 4.6 Hz, $J_{H(4),syn\text{-}H(7)}$ = 1.2 Hz, $J_{H(4),anti\text{-}H(7)}$ = 1.2 Hz, $J_{H(4),H(1)}$ = 1.2 Hz); 2.91 (ddd, 1 H, *endo*-H(6), $J_{endo\text{-}H(6),exo\text{-}H(6)}$ = 14.8 Hz, $J_{endo\text{-}H(6),H(5)}$ = 4.6 Hz, $J_{endo\text{-}H(6),syn\text{-}H(7)}$ = 3.7 Hz); 2.67 (tq, 1 H, H(1), $J_{H(1),H(2)}$ = 4.3 Hz, $J_{H(1),exo\text{-}H(6)}$ = 4.3 Hz, $J_{H(1),syn\text{-}H(7)}$ = 1.2 Hz, $J_{H(1),anti\text{-}H(7)}$ = 1.2 Hz, $J_{H(1),H(4)}$ = 1.2 Hz); 2.13 (dddd, 1 H, *exo*-H(6), $J_{exo\text{-}H(6),endo\text{-}H(6)}$ = 14.8 Hz, $J_{exo\text{-}H(6),H(5)}$ = 11.3 Hz, $J_{exo\text{-}H(6),exo\text{-}H(1)}$ = 4.3 Hz, $J_{exo\text{-}H(6),H(2)}$ = 1.8 Hz); 2.06 (ddt, 1 H, *syn*-H(7), $J_{syn\text{-}H(7),anti\text{-}H(7)}$ = 11.5 Hz, $J_{syn\text{-}H(7),endo\text{-}H(6)}$ = 3.7 Hz, $J_{syn\text{-}H(7),H(1)}$ = 1.2 Hz, $J_{syn\text{-}H(7),H(4)}$ = 1.2 Hz); 1.76 (ddt, 1 H, *anti*-H(7), $J_{anti\text{-}H(7),syn\text{-}H(7)}$ = 11.5 Hz, $J_{anti\text{-}H(7),H(3)}$ = 3.3 Hz, $J_{anti\text{-}H(7),H(1)}$ = 1.2 Hz, $J_{anti\text{-}H(7),H(4)}$ = 1.2 Hz).

2-*endo*-Bromo-5-*endo*-nitro-3-*exo*-(4-nitrophenylthio)bicyclo[2.2.1]heptane (4). Yield 0.53 g (51%), R_f 0.47. Found (%): C, 41.25; H, 3.74; N, 7.49. $C_{13}H_{13}BrN_2O_4S$. Calculated (%): C, 41.84; H, 3.51; N, 7.51. ^{1}H NMR, δ: 8.15, 7.41 (both d, 2 H each, H arom., *J* = 8.8 Hz); 4.90 (dt, 1 H, H(5), $J_{H(5),exo\text{-}H(6)}$ = 11.3 Hz, $J_{H(5),H(4)}$ = 4.6 Hz, $J_{H(5),endo\text{-}H(6)}$ = 4.6 Hz); 4.08 (dt, 1 H, H(2), $J_{H(2),H(3)}$ = 4.5 Hz, $J_{H(2),H(1)}$ = 4.5 Hz, $J_{H(2),exo\text{-}H(6)}$ = 2.0 Hz); 3.46 (dd, 1 H, H(3), $J_{H(3),H(2)}$ = 4.5 Hz, $J_{H(3),anti\text{-}H(7)}$ = 2.8 Hz); 2.96 (dq, 1 H, H(4), $J_{H(4),H(5)}$ = 4.6 Hz, $J_{H(4),syn\text{-}H(7)}$ = 1.2 Hz, $J_{H(4),anti\text{-}H(7)}$ = 1.2 Hz, $J_{H(4),H(1)}$ = 1.2 Hz); 2.91 (ddd, 1 H, *endo*-H(6), $J_{endo\text{-}H(6),exo\text{-}H(6)}$ = 14.8 Hz, $J_{endo\text{-}H(6),H(5)}$ = 4.6 Hz, $J_{endo\text{-}H(6),syn\text{-}H(7)}$ = 3.4 Hz); 2.68 (tq, 1 H, H(1), $J_{H(1),H(2)}$ = 4.5 Hz, $J_{H(1),exo\text{-}H(6)}$ = 4.5 Hz, $J_{H(1),syn\text{-}H(7)}$ = 1.2 Hz, $J_{H(1),anti\text{-}H(7)}$ = 1.2 Hz, $J_{H(1),H(4)}$ = 1.2 Hz); 2.19 (dddd, 1 H, *exo*-H(6), $J_{exo\text{-}H(6),endo\text{-}H(6)}$ = 14.8 Hz, $J_{exo\text{-}H(6),H(5)}$ = 11.3 Hz, $J_{exo\text{-}H(6),H(1)}$ = 4.5 Hz, $J_{exo\text{-}H(6),H(2)}$ = 2.0 Hz); 2.06 (ddt, 1 H, *syn*-H(7), $J_{syn\text{-}H(7),anti\text{-}H(7)}$ = 11.4 Hz, $J_{syn\text{-}H(7),endo\text{-}H(6)}$ = 3.4 Hz, $J_{syn\text{-}H(7),H(1)}$ = 1.2 Hz, $J_{syn\text{-}H(7),H(4)}$ = 1.2 Hz); 1.74 (ddt, 1 H, *anti*-H(7), $J_{anti\text{-}H(7),syn\text{-}H(7)}$ = 11.4 Hz, $J_{anti\text{-}H(7),H(3)}$ = 2.8 Hz, $J_{anti\text{-}H(7),H(1)}$ = 1.2 Hz, $J_{anti\text{-}H(7),H(4)}$ = 1.2 Hz).

2-*endo*-Bromo-5-*endo*-nitro-3-*exo*-(phenylthio)bicyclo[2.2.1]heptane (5). Yield 0.72 g (43%), R_f 0.65. Found (%): C, 47.35; H, 4.21; N, 4.43. $C_{13}H_{14}BrNO_2S$. Calculated (%): C, 47.57; H, 4.30; N, 4.27. ^{1}H NMR, δ: 7.20—7.50 (m, 5 H, H arom.); 4.81 (dt, 1 H, H(5), $J_{H(5),exo\text{-}H(6)}$ = 11.3 Hz, $J_{H(5),H(4)}$ = 4.6 Hz, $J_{H(5),endo\text{-}H(6)}$ = 4.6 Hz); 4.07 (dt, 1 H, H(2), $J_{H(2),H(3)}$ = 4.6 Hz, $J_{H(2),H(1)}$ = 4.6 Hz, $J_{H(2),exo\text{-}H(6)}$ = 2.2 Hz); 3.28 (dd, 1 H, H(3), $J_{H(3),H(2)}$ = 4.6 Hz, $J_{H(3),anti\text{-}H(7)}$ = 2.9 Hz); 2.90 (dq, 1 H, H(4), $J_{H(4),H(5)}$ = 4.6 Hz, $J_{H(4),syn\text{-}H(7)}$ = 1.4 Hz, $J_{H(4),anti\text{-}H(7)}$ = 1.4 Hz, $J_{H(4),H(1)}$ = 1.4 Hz); 2.86 (ddd, 1 H, *endo*-H(6), $J_{endo\text{-}H(6),exo\text{-}H(6)}$ = 14.7 Hz, $J_{endo\text{-}H(6),H(5)}$ = 4.6 Hz, $J_{endo\text{-}H(6),syn\text{-}H(7)}$ = 3.6 Hz); 2.61 (tq, 1 H, H(1), $J_{H(1),H(2)}$ = 4.6 Hz, $J_{H(1),exo\text{-}H(6)}$ = 4.6 Hz, $J_{H(1),syn\text{-}H(7)}$ = 1.4 Hz, $J_{H(1),anti\text{-}H(7)}$ = 1.4 Hz, $J_{H(1),H(4)}$ = 1.4 Hz); 2.09 (dddd, 1 H, *exo*-H(6), $J_{exo\text{-}H(6),endo\text{-}H(6)}$ = 14.7 Hz, $J_{exo\text{-}H(6),H(5)}$ = 11.3 Hz, $J_{exo\text{-}H(6),H(1)}$ = 4.6 Hz, $J_{exo\text{-}H(6),H(2)}$ = 2.2 Hz); 2.05 (ddt, 1 H, *syn*-H(7), $J_{syn\text{-}H(7),anti\text{-}H(7)}$ = 11.3 Hz, $J_{syn\text{-}H(7),endo\text{-}H(6)}$ = 3.6 Hz, $J_{syn\text{-}H(7),H(1)}$ = 1.4 Hz, $J_{syn\text{-}H(7),H(4)}$ = 1.4 Hz); 1.64 (ddt, 1 H, *anti*-H(7), $J_{anti\text{-}H(7),syn\text{-}H(7)}$ = 11.3 Hz, $J_{anti\text{-}H(7),H(3)}$ = 2.9 Hz, $J_{anti\text{-}H(7),H(1)}$ = 1.4 Hz, $J_{anti\text{-}H(7),H(4)}$ = 1.4 Hz).

2-*endo*-Bromo-5-*endo*-nitro-3-*exo*-(4-nitrophenylthio)-6-*exo*-phenylbicyclo[2.2.1]heptane (6). Yield 0.43 g (42%), R_f 0.47. Found (%): C, 50.24; H, 3.77; N, 6.45. $C_{19}H_{17}BrN_2O_4S$. Calculated (%): C, 50.79; H, 3.81; N, 6.24. ^{1}H NMR, δ: 8.17, 7.43 (both d, 2 H each, H arom., *J* = 9.0 Hz); 4.97 (dd, 1 H, H(5), $J_{H(5),H(6)}$ = 5.5 Hz, $J_{H(5),H(4)}$ = 4.4 Hz); 4.42 (dd, 1 H, H(6), $J_{H(6),H(5)}$ = 5.5 Hz, $J_{H(6),syn\text{-}H(7)}$ = 2.3 Hz); 4.18 (t, 1 H, H(2), $J_{H(2),H(3)}$ = 4.5 Hz, $J_{H(2),H(1)}$ = 4.5 Hz); 3.57 (dd, 1 H, H(3), $J_{H(3),H(2)}$ = 4.5 Hz, $J_{H(3),anti\text{-}H(7)}$ = 2.6 Hz); 3.06 (dq, 1 H, H(4), $J_{H(4),H(5)}$ = 4.4 Hz, $J_{H(4),syn\text{-}H(7)}$ = 1.3 Hz, $J_{H(4),anti\text{-}H(7)}$ = 1.3 Hz, $J_{H(4),H(1)}$ = 1.3 Hz); 2.85 (dq, 1 H, H(1), $J_{H(1),H(2)}$ = 4.5 Hz, $J_{H(1),syn\text{-}H(7)}$ = 1.3 Hz, $J_{H(1),anti\text{-}H(7)}$ = 1.3 Hz, $J_{H(1),H(4)}$ = 1.3 Hz); 2.12 (ddt, 1 H, *syn*-H(7), $J_{syn\text{-}H(7),anti\text{-}H(7)}$ = 11.8 Hz, $J_{syn\text{-}H(7),H(6)}$ = 2.3 Hz, $J_{syn\text{-}H(7),H(1)}$ = 1.3 Hz, $J_{syn\text{-}H(7),H(4)}$ = 1.3 Hz); 2.06 (ddt, 1 H, *anti*-H(7), $J_{anti\text{-}H(7),syn\text{-}H(7)}$ = 11.8 Hz, $J_{anti\text{-}H(7),H(3)}$ = 2.6 Hz, $J_{anti\text{-}H(7),H(1)}$ = 1.3 Hz, $J_{anti\text{-}H(7),H(4)}$ = 1.3 Hz).

2-*endo*-Bromo-5-*endo*-nitro-6-*exo*-phenyl-3-*exo*-(phenylthio)bicyclo[2.2.1]heptane (7). Yield 0.39 g (42%), R_f 0.69. Found (%): C, 56.20; H, 4.57; N, 3.57. $C_{19}H_{18}BrNO_2S$. Calculated (%): C, 56.44; H, 4.49; N, 3.46. ^{1}H NMR, δ: 7.26—7.49 (m, 5 H, H arom.); 4.97 (dd, 1 H, H(5), $J_{H(5),H(6)}$ = 5.5 Hz, $J_{H(5),H(4)}$ = 4.7 Hz); 4.41 (dd, 1 H, H(6), $J_{H(6),H(5)}$ = 5.5 Hz, $J_{H(6),syn\text{-}H(7)}$ = 2.4 Hz); 4.18 (t, 1 H, H(2), $J_{H(2),H(3)}$ = 4.5 Hz, $J_{H(2),H(1)}$ = 4.5 Hz); 3.56 (dd, 1 H, H(3), $J_{H(3),H(2)}$ = 4.5 Hz, $J_{H(3),anti\text{-}H(7)}$ = 2.7 Hz); 3.05 (dq, 1 H, H(4), $J_{H(4),H(5)}$ = 4.7 Hz, $J_{H(4),syn\text{-}H(7)}$ = 1.4 Hz, $J_{H(4),anti\text{-}H(7)}$ = 1.4 Hz, $J_{H(4),H(1)}$ = 1.4 Hz); 2.85 (dq, 1 H, H(1), $J_{H(1),H(2)}$ = 4.5 Hz, $J_{H(1),syn\text{-}H(7)}$ = 1.4 Hz, $J_{H(1),anti\text{-}H(7)}$ = 1.4 Hz, $J_{H(1),H(4)}$ = 1.4 Hz); 2.11 (ddt, 1 H, *syn*-H(7), $J_{syn\text{-}H(7),anti\text{-}H(7)}$ = 11.8 Hz, $J_{syn\text{-}H(7),H(6)}$ = 2.4 Hz, $J_{syn\text{-}H(7),H(1)}$ = 1.4 Hz, $J_{syn\text{-}H(7),H(4)}$ = 1.4 Hz); 2.06 (ddt, 1 H, *anti*-H(7), $J_{anti\text{-}H(7),syn\text{-}H(7)}$ = 11.8 Hz, $J_{anti\text{-}H(7),H(3)}$ = 2.7 Hz, $J_{anti\text{-}H(7),H(1)}$ = 1.4 Hz, $J_{anti\text{-}H(7),H(4)}$ = 1.4 Hz).

2-*endo*-Bromo-5-*endo*-nitro-3-*exo*-(2-nitrophenylthio)-6-*exo*-phenylbicyclo[2.2.1]heptane (8). Yield 0.29 g (28%), R_f 0.42. Found (%): C, 50.43; H, 3.72; N, 6.49. $C_{19}H_{17}BrN_2O_4S$. Calculated (%): C, 50.79; H, 3.81; N, 6.24. ^{1}H NMR, δ: 7.28—7.52 (m, 4 H, H arom.); 4.99 (dd, 1 H, H(5), $J_{H(5),H(6)}$ = 5.7 Hz, $J_{H(5),H(4)}$ = 4.6 Hz); 4.47 (dd, 1 H, H(6), $J_{H(6),H(5)}$ = 5.7 Hz, $J_{H(6),syn\text{-}H(7)}$ = 2.5 Hz); 4.27 (t, 1 H, H(2), $J_{H(2),H(3)}$ = 4.6 Hz, $J_{H(2),H(1)}$ = 4.6 Hz); 3.55 (dd, 1 H, H(3), $J_{H(3),H(2)}$ = 4.6 Hz, $J_{H(3),anti\text{-}H(7)}$ = 2.8 Hz); 3.07 (dq, 1 H, H(4), $J_{H(4),H(5)}$ = 4.6 Hz, $J_{H(4),syn\text{-}H(7)}$ = 1.5 Hz, $J_{H(4),anti\text{-}H(7)}$ = 1.5 Hz, $J_{H(4),H(1)}$ = 1.5 Hz); 2.87 (dq, 1 H, H(1), $J_{H(1),H(2)}$ = 4.6 Hz, $J_{H(1),syn\text{-}H(7)}$ = 1.5 Hz, $J_{H(1),anti\text{-}H(7)}$ = 1.5 Hz, $J_{H(1),H(4)}$ = 1.5 Hz); 2.16 (ddt, 1 H, *syn*-H(7), $J_{syn\text{-}H(7),anti\text{-}H(7)}$ = 11.8 Hz, $J_{syn\text{-}H(7),H(6)}$ = 2.5 Hz, $J_{syn\text{-}H(7),H(1)}$ = 1.5 Hz, $J_{syn\text{-}H(7),H(4)}$ = 1.5 Hz); 2.04 (ddt, 1 H, *anti*-H(7), $J_{anti\text{-}H(7),syn\text{-}H(7)}$ = 11.8 Hz, $J_{anti\text{-}H(7),H(3)}$ = 2.8 Hz, $J_{anti\text{-}H(7),H(1)}$ = 1.5 Hz, $J_{anti\text{-}H(7),H(4)}$ = 1.5 Hz). IR (mineral oil), ν/cm^{-1}: 1340, 1520 (NO_2).

Selenenation of alkenes with selenenamides in the presence of phosphorus oxyhalides (general procedure). A solution of phosphorus oxyhalide (2.5 mmol) in anhydrous CH_2Cl_2 (10 mL) and, 15 min later, a solution of selenenamide (2.5 mmol) in anhydrous CH_2Cl_2 (10 mL) were added at –40 °C with stirring to a solution of olefin (1.2 mmol) in anhydrous CH_2Cl_2 (20 mL). The reaction mixture was stirred for 24 h. After completion of the reaction, the solvent was removed *in vacuo*, and the residue was chromatographed on a silica gel-packed column (10 cm, petroleum ether—ethyl acetate, 3 : 1, as the eluent).

2-*endo*-Bromo-3-*exo*-phenylselenenyl-5-*endo*-(trifluoromethyl)bicyclo[2.2.1]heptane (2). Yield 0.74 g (81%), R_f 0.33. ^{1}H NMR, δ: 7.37 (m, 5 H, H arom.); 4.12 (dt, 1 H, H(2), $J_{H(2),H(3)}$ = 4.1 Hz, $J_{H(2),H(1)}$ = 4.1 Hz, $J_{H(2),exo\text{-}H(6)}$ = 1.9 Hz); 3.78 (dd, 1 H, H(3), $J_{H(3),H(2)}$ = 4.3 Hz, $J_{H(3),anti\text{-}H(7)}$ = 2.8 Hz); 2.58 (dddq, 1 H, H(5), $J_{H(5),exo\text{-}H(6)}$ = 11.9 Hz, $J_{H(5),F}$ = 10.3 Hz, $J_{H(5),endo\text{-}H(6)}$ = 6.5 Hz, $J_{H(5),H(4)}$ = 3.6 Hz); 2.58 (m, 1 H, H(4)); 2.55 (br.s, 1 H, H(1)); 2.24 (ddd, 1 H, *endo*-H(6), $J_{endo\text{-}H(6),exo\text{-}H(6)}$ = 13.4 Hz, $J_{endo\text{-}H(6),H(5)}$ = 6.7 Hz, $J_{endo\text{-}H(6),syn\text{-}H(7)}$ = 2.6 Hz); 2.09 (ddt, 1 H, *syn*-H(7), $J_{syn\text{-}H(7),anti\text{-}H(7)}$ = 10.9 Hz, $J_{syn\text{-}H(7),endo\text{-}H(6)}$ = 2.7 Hz, $J_{syn\text{-}H(7),H(1)}$ = 1.1 Hz, $J_{syn\text{-}H(7),H(4)}$ = 1.1 Hz); 1.93 (dddd, 1 H, *exo*-H(6), $J_{exo\text{-}H(6),endo\text{-}H(6)}$ = 13.4 Hz, $J_{exo\text{-}H(6),H(5)}$ = 11.9 Hz, $J_{exo\text{-}H(6),H(1)}$ = 5.1 Hz, $J_{exo\text{-}H(6),H(2)}$ = 1.9 Hz); 1.69 (ddt, 1 H, *anti*-H(7), $J_{anti\text{-}H(7),syn\text{-}H(7)}$ = 11.1 Hz, $J_{anti\text{-}H(7),H(3)}$ = 3.1 Hz, $J_{anti\text{-}H(7),H(1)}$ = 1.6 Hz, $J_{anti\text{-}H(7),H(4)}$ = 1.6 Hz).

2-*endo*-Bromo-5-*endo*-nitro-3-*exo*-phenylselenenyl-6-*exo*-phenylbicyclo[2.2.1]heptane (9). Yield 0.85 g (83%), R_f 0.39. ^{1}H NMR, δ: 7.18—7.47 (m, 5 H, H arom.); 4.89 (dd, 1 H, H(5), $J_{H(5),H(6)}$ = 5.2 Hz, $J_{H(5),H(4)}$ = 4.8 Hz); 4.27 (dd, 1 H, H(6), $J_{H(6),H(5)}$ = 5.3 Hz, $J_{H(6),syn\text{-}H(7)}$ = 2.7 Hz); 4.23 (t, 1 H, H(2), $J_{H(2),H(3)}$ = 4.4 Hz, $J_{H(2),H(1)}$ = 4.4 Hz); 3.39 (dd, 1 H, H(3), $J_{H(3),H(2)}$ = 4.4 Hz, $J_{H(3),anti\text{-}H(7)}$ = 2.6 Hz); 3.12 (dq, 1 H, H(4), $J_{H(4),H(5)}$ = 4.5 Hz, $J_{H(4),syn\text{-}H(7)}$ = 1.7 Hz, $J_{H(4),anti\text{-}H(7)}$ = 1.6 Hz, $J_{H(4),H(1)}$ = 1.6 Hz); 2.91 (dq, 1 H, H(1), $J_{H(1),H(2)}$ = 4.6 Hz, $J_{H(1),syn\text{-}H(7)}$ = 1.7 Hz, $J_{H(1),anti\text{-}H(7)}$ = 1.7 Hz, $J_{H(1),H(4)}$ = 1.7 Hz); 2.28 (ddt, 1 H, *syn*-H(7), $J_{syn\text{-}H(7),anti\text{-}H(7)}$ = 12.1 Hz, $J_{syn\text{-}H(7),H(6)}$ = 2.5 Hz, $J_{syn\text{-}H(7),H(1)}$ = 1.7 Hz, $J_{syn\text{-}H(7),H(4)}$ = 1.7 Hz); 2.12 (ddt, 1 H, *anti*-H(7), $J_{anti\text{-}H(7),syn\text{-}H(7)}$ = 12.1 Hz, $J_{anti\text{-}H(7),H(3)}$ = 2.7 Hz, $J_{anti\text{-}H(7),H(1)}$ = 1.7 Hz, $J_{anti\text{-}H(7),H(4)}$ = 1.7 Hz).

Iodination of alkenes with potassium dichloroiodate(I) (general procedure). Potassium dichloroiodate(I) (5.2 mmol) in chloroform was added in portions with stirring and ice-cooling to a solution of the specified norbornene (5 mmol) in chloroform (10 mL). The reaction mixture was stirred for 0.5 h, and an aqueous solution of sodium sulfite (10 mL) was added. The organic phase was separated and the aqueous phase was extracted with chloroform (3×5 mL). The combined organic fractions were dried with anhydrous sodium sulfate. Solvent evaporation *in vacuo* gave a yellow oil, which was chromatographed on a silica gel column (10 cm, petroleum ether—ethyl acetate, 10 : 1, as the eluent).

3-*endo*-Chloro-2-*exo*-iodo-6-*endo*-nitrobicyclo[2.2.1]heptane (10). Yield 0.98 g (48%), R_f 0.51. ^{1}H NMR, δ: 4.85 (dt, 1 H, H(5), $J_{H(5),exo\text{-}H(6)}$ = 11.3 Hz, $J_{H(5),H(4)}$ = 4.6 Hz, $J_{H(5),endo\text{-}H(6)}$ = 4.6 Hz); 4.63 (dt, 1 H, H(3), $J_{H(2),H(3)}$ = 4.1 Hz, $J_{H(2),H(1)}$ = 4.1 Hz, $J_{H(2),exo\text{-}H(6)}$ = 1.8 Hz); 3.86 (dd, 1 H, H(2), $J_{H(3),H(2)}$ = 4.1 Hz, $J_{H(3),anti\text{-}H(7)}$ = 3.4 Hz); 3.24 (dq, 1 H, H(4), $J_{H(4),H(5)}$ = 4.6 Hz, $J_{H(4),syn\text{-}H(7)}$ = 1.2 Hz, $J_{H(4),anti\text{-}H(7)}$ = 1.2 Hz, $J_{H(4),H(1)}$ = 1.2 Hz); 2.81 (ddd, 1 H, *endo*-H(6), $J_{endo\text{-}H(6),exo\text{-}H(6)}$ = 14.7 Hz, $J_{endo\text{-}H(6),H(5)}$ = 4.6 Hz, $J_{endo\text{-}H(6),syn\text{-}H(7)}$ = 3.6 Hz); 2.52 (tq, 1 H, H(1), $J_{H(1),H(2)}$ = 4.1 Hz, $J_{H(1),exo\text{-}H(6)}$ = 4.1 Hz, $J_{H(1),syn\text{-}H(7)}$ = 1.2 Hz, $J_{H(1),anti\text{-}H(7)}$ = 1.2 Hz, $J_{H(1),H(4)}$ = 1.2 Hz); 2.28 (ddt, 1 H, *syn*-H(7), $J_{syn\text{-}H(7),anti\text{-}H(7)}$ = 11.5 Hz, $J_{syn\text{-}H(7),endo\text{-}H(6)}$ = 3.6 Hz, $J_{syn\text{-}H(7),H(1)}$ = 1.2 Hz, $J_{syn\text{-}H(7),H(4)}$ = 1.2 Hz); 2.02 (dddd, 1 H, *exo*-H(6), $J_{exo\text{-}H(6),endo\text{-}H(6)}$ = 14.7 Hz, $J_{exo\text{-}H(6),H(5)}$ = 11.3 Hz, $J_{exo\text{-}H(6),H(1)}$ = 4.1 Hz, $J_{exo\text{-}H(6),H(2)}$ = 1.8 Hz); 1.85 (ddt, 1 H, *anti*-H(7), $J_{anti\text{-}H(7),syn\text{-}H(7)}$ = 11.5 Hz, $J_{anti\text{-}H(7),H(3)}$ = 3.4 Hz, $J_{anti\text{-}H(7),H(1)}$ = 1.2 Hz, $J_{anti\text{-}H(7),H(4)}$ = 1.2 Hz).

3-*endo*-Chloro-2-*exo*-iodo-6-*endo*-nitro-5-*exo*-phenylbicyclo[2.2.1]heptane (11). Yield 0.42 g (54%), R_f 0.63. Found (%): C, 40.98; H, 3.62; N, 3.66. $C_{13}H_{13}ClINO_2$. Calculated (%): C, 41.35; H, 3.47; N, 3.71. ^{1}H NMR, δ: 7.22—7.35 (m, 5 H, H arom.); 4.88 (dd, 1 H, H(5), $J_{H(5),H(6)}$ = 5.6 Hz, $J_{H(5),H(4)}$ = 4.6 Hz); 4.68 (t, 1 H, H(3), $J_{H(2),H(3)}$ = 4.3 Hz, $J_{H(2),H(1)}$ = 4.3 Hz); 4.29 (dd, 1 H, H(6), $J_{H(6),H(5)}$ = 5.6 Hz, $J_{H(6),syn\text{-}H(7)}$ = 2.5 Hz); 3.94 (dd, 1 H, H(2), $J_{H(3),H(2)}$ = 4.3 Hz, $J_{H(3),anti\text{-}H(7)}$ = 3.1 Hz); 3.31 (dq, 1 H, H(4), $J_{H(4),H(5)}$ = 4.6 Hz, $J_{H(4),syn\text{-}H(7)}$ = 1.6 Hz, $J_{H(4),anti\text{-}H(7)}$ = 1.6 Hz, $J_{H(4),H(1)}$ = 1.6 Hz); 2.66 (dq, 1 H, H(1), $J_{H(1),H(2)}$ = 4.3 Hz, $J_{H(1),syn\text{-}H(7)}$ = 1.6, $J_{H(1),anti\text{-}H(7)}$ = 1.6 Hz, $J_{H(1),H(4)}$ = 1.6 Hz); 2.29 (ddt, 1 H, *syn*-H(7), $J_{syn\text{-}H(7),anti\text{-}H(7)}$ = 11.8 Hz, $J_{syn\text{-}H(7),H(6)}$ = 2.5 Hz, $J_{syn\text{-}H(7),H(1)}$ = 1.6 Hz, $J_{syn\text{-}H(7),H(4)}$ = 1.6 Hz); 2.14 (ddt, 1 H, *anti*-H(7) Hz, $J_{anti\text{-}H(7),syn\text{-}H(7)}$ = 11.8 Hz, $J_{anti\text{-}H(7),H(3)}$ = 3.1 Hz, $J_{anti\text{-}H(7),H(1)}$ = 1.6 Hz, $J_{anti\text{-}H(7),H(4)}$ = 1.6 Hz). ^{13}C NMR, δ: 15.25, 22.85, 29.10, 35.95, 38.90 (CI), 69.40 (CCl), 127.36, 129.25, 136.65.

This work was financially supported by the Russian Foundation for Basic Research (Project 02-03-33347), the Foundation "Universities of Russia" (Grant 05.03.046), and the Presidium of the Russian Academy of Sciences (the program "Theoretical and Experimental Studies of the Nature of Chemical Bond and the Mechanisms of Chemical Reactions and Processes").

References

1. E. K. Beloglazkina, N. V. Zyk, V. S. Tyurin, I. D. Titanyuk, and N. S. Zefirov, *Dokl. Akad. Nauk SSSR*, 1995, **344**, 487 [*Dokl. Chem.*, 1995 (Engl. Transl.)].
2. N. V. Zyk, E. K. Beloglazkina, R. A. Gazzaeva, V. S. Tyurin, and I. D. Titanyuk, *Phosphorus, Sulfur, Silicon*, 1999, **155**, 33.
3. N. V. Zyk, E. K. Beloglazkina, and R. L. Antipin, *Izv. Akad. Nauk. Ser. Khim.*, 2004, 2250 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2352].
4. N. V. Zyk, G. A. Sereda, S. E. Sosonyuk, and N. S. Zefirov, *Izv. Akad. Nauk. Ser. Khim.*, 1997, 877 [*Russ. Chem. Bull.*, 1997, **46**, 843 (Engl. Transl.)].
5. J. A. Creighton and K. M. Thomas, *J. Mol. Struct.*, 1971, **7**, 173; R. Weiss, M. Rechingen, F. Hampel, and A. Wolski, *Angew. Chem.*, 1995, **107**, 483.
6. J. H. Billman and E. J. O´Mahony, *J. Am. Chem. Soc.*, 1939, **61**, 2340.
7. N. V. Zyk, I. V. Alabugin, A. G. Kutateladze, J. L. Cais, and N. S. Zefirov, *Dokl. Akad. Nauk SSSR*, 1994, **337**, 208 [*Dokl. Chem.*, 1994 (Engl. Transl.)].

Received January 12, 2005;
in revised form April 26, 2005