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Reactions of Areneselenenamides with Alkenes in the Presence of Phosphorus(V) and Sulfur(IV) Oxyhalides. New Synthesis of β-Haloalkyl Selenides

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Abstract—A new procedure was proposed for activation of areneselenenamides with phosphorus(V) and sulfur(IV) oxyhalides. According to the ^{1}H, ^{13}C, and ^{31}P NMR data, areneselenenamide reacts with phosphorus oxyhalide to form intermediate adduct in which the phosphorus atom is coordinated at the selenium. Areneselenenamides activated by phosphorus(V) oxyhalides react with alkenes (norbornene and norbornadiene) with high *trans*-stereoselectivity. Their reactions with terminal olefins are regioselective, and they lead to preferential formation of the corresponding Markovnikov adducts.

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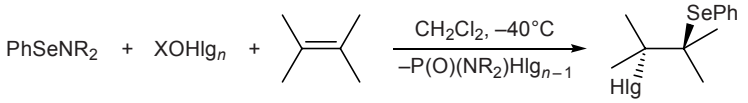
Arylselenenation of unsaturated compounds attracts considerable interest from the synthetic viewpoint. Successive selenenation–deselenenation provides a convenient method of synthesis of compounds having a functional substituent at double carbon–carbon bond. Selenium-containing fragments are commonly introduced into alkene and alkyne molecules via addition of the corresponding selenenyl halides [1–5], which leads to the formation of β-halo-substituted alkyl aryl selenides in 65–80% yield. These reactions are usually regio- and stereoselective, and the major products formed under thermodynamic control (MeCN, 25°C) are Markovnikov adducts, while the corresponding anti-Markovnikov adducts are obtained as minor products. The latter become the major products under conditions of kinetic control (THF, –78°C) [2].

From the practical viewpoint, an important problem is development of effective procedures for haloselenenation of olefins with the goal of improving the yield and regioselectivity in the addition of areneselenenyl halides. Over the past few years we developed a procedure for activation of weak sulfur-containing electrophiles (sulfenamides, sulfenates [6, 7], thio- and dithiobisamines [8, 9]) with phosphorus and sulfur halides and oxyhalides. The procedure is based on the transformation of weakly polar initial sulfur(II) compound into strongly polarized or ionic intermediate via reaction with appropriate Lewis acid. Phosphorus and sulfur oxyhalides were selected as Lewis acids, taking into account their mildness (according to Pearson), in contrast to traditionally used hard activators such as sulfuric anhydride and metal halides. Sulfur compound polarized in this way becomes capable of adding at a double C=C bond.

Selenenamides are milder Lewis bases than sulfenamides, and their reactions with phosphorus or sulfur oxyhalides may be expected to produce electrophilic complexes capable of adding to unsaturated compounds. In fact, we recently found that *N*,*N*-diethylbenzeneselenenamide reacts with alkenes in the presence

Scheme 1.



I, **II** **III–XV**

I, R = Et; **II**, R_2N = morpholino; $XOHlg_n$ = $POCl_3$, $POBr_3$, $SOCl_2$.

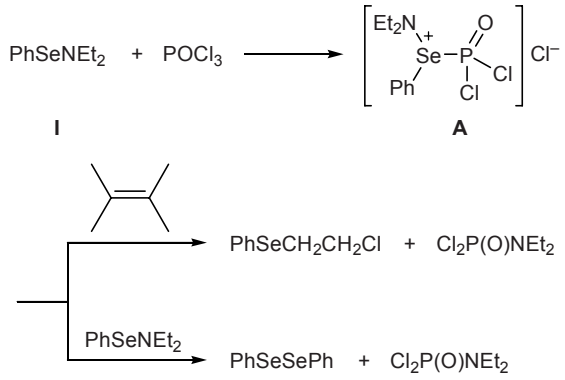
of $POCl_3$ or $SOCl_2$ to give the corresponding 1,2-haloselenenation products in high yield [10]. In the present article we report on the results of chloro- and bromoselenenation of a number of model cyclic and acyclic olefins having various substituents at the double C=C bond. Benzeneselenenamides **I** and **II** reacted with olefins in the presence of $POCl_3$, $POBr_3$, or $SOCl_2$ according to Scheme 1.

We previously showed that activation of arenesulfenamides with phosphorus oxyhalides involves coordination of the Lewis acid at the sulfur atom of sulfenamide [11]. In the reactions with selenenamides coordination of phosphorus- or sulfur-containing Lewis acid at both selenium and nitrogen atom of initial selenenamide may be presumed. Quantum-chemical calculations of donor–acceptor complexes formed from selenenamide **I** and $POBr_3$ (their geometric parameters were optimized using semiempirical SCF PM3 approximation) gave similar heats of formation of two possible structures (39.90 kcal/mol for the formation of P–N bond and 42.25 kcal/mol for the formation of P–Se bond).

The structure of the reactive intermediate was determined on the basis of the NMR data. The ^{31}P NMR spectrum of a mixture of phosphoryl chloride and *N*,*N*-diethylbenzeneselenenamide (**I**) in $CDCl_3$, prepared at –30°C, showed considerable decrease in the intensity of the $POCl_3$ signal at δ_P 8.6 ppm [12], and a new strong signal appeared at δ_P 17.0 ppm. The latter was assigned to $Et_2NP(O)Cl_2$ whose formation was proved by independent synthesis from $POCl_3$ and Et_2NH (see Experimental). In addition, the ^{31}P NMR spectrum contained a signal at δ_P 29.5 ppm, which is likely to belong to the selenium reagent. This signal was a singlet, indicating the absence of ^{31}P–^1H spin–spin coupling in the reagent. The same followed from the ^1H NMR data. The ^1H NMR spectrum of a $POCl_3$–$PhSeNEt_2$ mixture at –30°C contained only one multiplet due to coupling with ^{31}P, δ 3.30 ppm, which was assigned to $Cl_2P(O)NEt_2$; the corresponding protons in the electrophilic reagent resonated at δ 3.48 ppm. Apart from $Cl_2P(O)NEt_2$ and the reagent, the mixture contained 40% of initial selenenamide **I**. This means that the reaction of **I** with $POCl_3$ is reversible. The ^1H NMR spectrum of the same mixture, recorded at 20°C, contained no signal at δ 3.48 ppm, and only signals assignable to $Cl_2P(O)NEt_2$ and diphenyl diselenide were present.

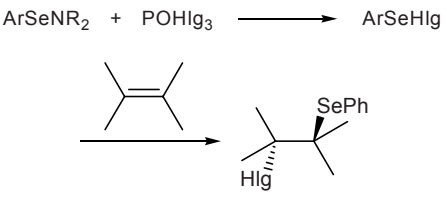
Likewise, in the ^{13}C NMR spectrum of $POCl_3$–$PhSeNEt_2$ we observed signals from ethyl carbon atoms in initial selenenamide **I** (δ_C 11.4, 42.9 ppm), $Cl_2P(O)NEt_2$ (δ_C 13.0 ppm, d, $J \approx 2.1$ Hz; 40.5 ppm, d, $J \approx 2.0$ Hz), and the electrophilic complex (δ_C 44.8, 13.0 ppm). Thus the NMR data indicate coordination of phosphorus-containing Lewis acid at the selenium atom of initial selenenamide **I** with formation of structure **A** (Scheme 2) in which the selenium atom has a positive charge and should be strongly electrophilic. Complex **A** is capable of adding at olefinic C=C bond to give β-halo-substituted alkyl phenyl selenide. If the reaction mixture contains no olefinic substrate, the second molecule of initial areneselenenamide (which is always present in the reaction mixture) can act as nucleophile. In this case, the final products are $Cl_2P(O)NEt_2$ and the corresponding diaryl diselenide, which are formed in nearly quantitative yield.

Scheme 2.



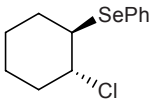
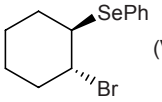
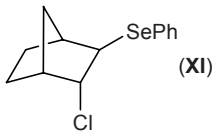
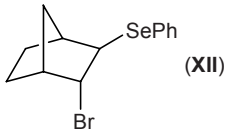
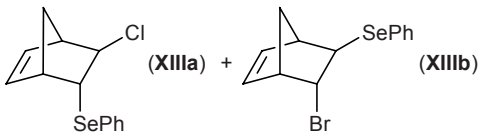
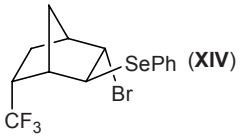
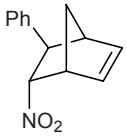
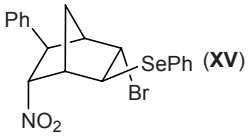
The results of reactions of benzeneselenenamides with phosphorus oxyhalides and alkenes also suggest an alternative mechanism involving preliminary formation of benzeneselenenyl halide which then adds to olefinic substrate (Scheme 3).

Scheme 3.



However, TLC analysis of the reaction mixture containing areneselenenamide and phosphorus oxyhalide showed the absence of a compound with R_f 0.26 (petroleum ether–ethyl acetate, 3 : 1), typical of benzeneselenenyl halide. The fact that areneselenenyl halide is not formed during the process is additionally supported by the observed regioselectivity in the reac-

Reactions of benzeneselenenamides **I** and **II** with alkenes in the presence of phosphorus(V) and sulfur(IV) oxyhalides

Alkene	$ArSeNR_2$	$XOHlg_3$	Product	Yield, % (ratio **a**:**b**)
Hex-1-ene	**I**	$POCl_3$	$C_4H_9CH(Cl)CH_2SePh$ (**IIIa**) + $C_4H_9CH(SePh)CH_2Cl$ (**IIIb**)	84 (9:1)
Hex-1-ene	**I**	$POBr_3$	$C_4H_9CH(Br)CH_2SePh$ (**IVa**) + $C_4H_9CH(SePh)CH_2Br$ (**IVb**)	93 (8.5:1)
Hex-1-ene	**I**	$SOCl_2$	**IIIa** + **IIIb**	98 (9:1)
Hex-1-ene	**II**	$POCl_3$	**IIIa** + **IIIb**	95 (9:1)
Hex-1-ene	**II**	$POBr_3$	**IVa** + **IVb**	98 (8:1)
Cyclohexene	**I**	$POCl_3$	 (**V**)	73
Cyclohexene	**I**	$SOCl_2$	**V**	98
Cyclohexene	**I**	$POBr_3$	 (**VI**)	97
Cyclohexene	**II**	$POCl_3$	**V**	91
Cyclohexene	**II**	$POBr_3$	**VI**	97
Styrene	**I**	$POCl_3$	$PhCH(Cl)CH_2SePh$ (**VIIa**) + $PhCH(SePh)CH_2Cl$ (**VIIb**)	74 (1:1)
Styrene	**I**	$POBr_3$	$PhCH(Br)CH_2SePh$ (**VIIIa**) + $PhCH(SePh)CH_2Br$ (**VIIIb**)	86 (1:1)
Styrene	**II**	$POCl_3$	**VIIa** + **VIIb**	75 (1:1)
Allyl chloride	**I**	$POCl_3$	$ClCH_2CH(SePh)CH_2Cl$ (**IX**)	79
Allyl chloride	**I**	$POBr_3$	$ClCH_2CH(SePh)CH_2Br$ (**X**)	80
Allyl chloride	**II**	$POCl_3$	**IX**	78
Allyl chloride	**II**	$POBr_3$	**X**	83
Norbornene	**I**	$POCl_3$	 (**XI**)	82
Norbornene	**I**	$POBr_3$	 (**XII**)	91
Norbornene	**II**	$POCl_3$	**XI**	81
Norbornene	**II**	$POBr_3$	**XII**	90
Norbornadiene	**I**	$POCl_3$	 (**XIIIa**) + (**XIIIb**)	75 (1:5)
	**I**	$POBr_3$	 (**XIV**)	59
	**I**	$POBr_3$	 (**XV**)	52

tions of areneselenenamide–phosphorus oxyhalide with terminal alkenes. In our case, the addition direction is opposite to that reported for the addition of selenenyl halides (see below). The results of reactions of selenenamides **I** and **II** with olefins are summarized in table. These data allowed us to formulate some general relations holding therein.

The reactions performed in the presence of $POBr_3$ usually provide higher yields than those in analogous reactions promoted by $POCl_3$. Thionyl chloride ensured better results as compared to phosphoryl chloride. Finally, *N*,*N*-diethylamide **I** is more reactive than morpholide **II**. Obviously, the presence of additional donor centers in the initial selenenamide molecule is undesirable because of concurrent coordination of Lewis acid at those centers.

As follows from the results of reactions with norbornene and norbornadiene, the addition is strictly *trans*-stereoselective. *trans* Orientation of the chlorine atom and phenylselanyl group in adducts **XI**–**XIII** unambiguously follows from the coupling constant for the corresponding protons (J = 3.7 Hz). The fact that no rearrangement products were detected in the reactions with norbornene and norbornadiene suggests low effective electrophilicity of reactive complex **A**.

The regioselectivity in the reactions under study depends on the substitution pattern at the double carbon–carbon bond in initial olefin. As a rule, electron-withdrawing substituents at the double bond in terminal olefin favor formation of the corresponding anti-Markovnikov adducts (see table). For example, the isomer ratio in the reaction with hex-1-ene is 9:1. It should be noted that the addition of benzeneselenenyl halide is characterized by the reverse selectivity (15:85) [2]. The addition to styrene was not selective, while the reaction with allyl chloride gave only the corresponding anti-Markovnikov adduct.

Thus the proposed procedure for selenenation of alkenes using the system areneselenenamide–phosphorus(V) [or sulfur(IV)] oxyhalide is convenient for the preparation of β-halo-substituted alkyl aryl selenides. The procedure ensures higher yields of the target products, as compared to traditionally used addition of areneselenenyl halides, and in some cases makes it possible to vary ratio of isomeric products.

EXPERIMENTAL

The NMR spectra were recorded on Bruker Avance 400 and Varian VXR-400 spectrometers (400 MHz for ^1H and 100 MHz for ^{13}C) using $CDCl_3$ as solvent. The products were analyzed by GC–MS on a Finnigan MAT SSQ-7000 instrument [electron impact, 70 eV; OV-1 quartz capillary column, 25 m; oven temperature programming from 70°C (2 min) to 280°C (10 min) at a rate of 20 deg/min].

Quantum-chemical calculations were performed in terms of the semiempirical SCF PM3 approximation [13] using HyperChem software package (HyperCube Inc., FL, USA); geometric parameters were optimized with a convergence gradient of ≤10 cal $Å^{-1}$ mol^{-1}.

Addition of *N*,*N*-diethylbenzeneselenenamide (I) to olefins in the presence of phosphorus(V) and sulfur(IV) oxyhalides (*general procedure***).** A solution of 2.5 mmol of selenenamide **I** in 10 ml of anhydrous methylene chloride was cooled to –30°C, a solution of 2.5 mmol of phosphoryl chloride or bromide or thionyl chloride in 10 ml of anhydrous methylene chloride was added under stirring, the mixture was stirred for 5 min, and a solution of 2.5 mmol of the corresponding olefin in 10 ml of the same solvent was added. The mixture was allowed to warm up to room temperature and filtered through a column charged with silica gel (5 cm in height). Removal of the solvent from the filtrate gave a yellow oily substance.

2-Chloro-1-phenylselanylhexane (IIIa). ^1H NMR spectrum, δ, ppm: 0.86 t (3H, CH_3, J 7.3 Hz), 1.3 m (4H, CH_2), 1.7 m (1H, 3-H), 2.0 m (1H, 3-H), 3.17 d.d (1-H, J = 8.5, 12.4 Hz), 3.26 d.d (1-H, J = 5.2, 12.4 Hz), 4.0 m (1H, 2-H), 7.4 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 15.25, 22.85, 29.10, 35.95, 38.50 (CSe), 63.40 (CCl), 127.36, 129.25, 136.65.

1-Chloro-2-phenylselanylhexane (IIIb). ^1H NMR spectrum, δ, ppm: 0.84 t (3H, CH_3, J = 7.3 Hz), 1.34 m (4H, CH_2), 1.74 m (1H, 3-H), 2.05 m (1H, 3-H), 3.2 d.d (1-H, J = 8.5, 12.4 Hz), 3.28 d.d (1-H, J = 5.2, 12.4 Hz), 4.06 m (1H, 2-H), 7.4 m (5H, H_{arom}). Mass spectrum (**IIIa/IIIb**), m/z (I_{rel}, %): 276 (45) $[M]^+$, 278 (13) $[M + 2]^+$.

2-Bromo-1-phenylselanylhexane (IVa). ^1H NMR spectrum, δ, ppm: 0.80 t (3H, CH_3, J = 7.3 Hz), 1.25 m (4H, CH_2), 1.65 m (1H, 3-H), 2.10 m (1H, 3-H), 3.20 d.d (1-H, J = 8.5, 12.4 Hz), 3.30 d.d (1-H, J = 5.2, 12.4 Hz), 3.80 m (1H, 2-H), 7.4 m (5H, H_{arom}).

1-Bromo-2-phenylselanylhexane (IVb). ^1H NMR spectrum, δ, ppm: 0.83 t (3H, CH_3, J = 7.3 Hz), 1.32 m (4H, CH_2), 1.72 m (1H, 3-H), 2.12 m (1H, 3-H), 3.23 d.d (1-H, J = 8.5, 12.4 Hz), 3.35 d.d (1-H, J = 5.2, 12.4 Hz), 3.87 m (1H, 2-H), 7.4 m (5H, H_{arom}). Mass spectrum (**IVa/IVb**), m/z (I_{rel}, %): 319 (43) $[M]^+$, 321 (39) $[M + 2]^+$.

***trans*-1-Chloro-2-phenylselanylcyclohexane (V).** ^{1}H NMR spectrum, δ, ppm: 1.40 m (2H, 4-H), 1.60 m (2H, 5-H), 1.7 m (2H, 3-H), 2.30 d.d.t (2H, 6-H), 3.50 d.d (1H, 2-H, J = 6, 10.1 Hz), 4.15 d.d (1H, 1-H, J = 7, 10.1 Hz), 7.40 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 22.95, 25.30, 32.67, 34.15, 50.32 (CSe), 64.10 (CCl), 127.85, 129.78, 136.30. Mass spectrum, m/z (I_{rel}, %): 274 (35) $[M]^+$, 276 (32) $[M + 2]^+$.

***trans*-1-Bromo-2-phenylselanylcyclohexane (VI).** ^{1}H NMR spectrum, δ, ppm: 1.32 m (2H, 4-H), 1.58 m (2H, 5-H), 1.67 m (2H, 3-H), 2.35 d.d.t (2H, 6-H), 3.41 d.d (1H, 2-H, J = 6, 10.1 Hz), 3.84 d.d (1H, 1-H, J = 7, 10.1 Hz), 7.4 m (5H, H_{arom}). Mass spectrum, m/z (I_{rel}, %): 317 (40) $[M]^+$, 319 (14) $[M + 2]^+$.

1-Chloro-1-phenyl-2-phenylselanylethane (VIIa). ^{1}H NMR spectrum, δ, ppm: 3.50 d.d (1H, 2-H, J = 9.4, 12.6 Hz), 3.52 d.d (1H, 2-H, J = 6.1, 12.6), 4.98 d.d (1H, 1-H, J = 6.1, 9.4 Hz), 7.10–7.55 m (10H, H_{arom}).

2-Chloro-1-phenyl-1-phenylselanylethane (VIIb). ^{1}H NMR spectrum, δ, ppm: 3.49 d.d (1H, 2-H, J = 9.4, 12.6 Hz), 3.62 d.d (1H, 2-H, J = 6.1, 12.6 Hz), 4.57 d.d (1H, 1-H, J = 6.1, 9.4 Hz), 7.30–7.68 m (10H, H_{arom}). Mass spectrum (**VIIa/VIIb**), m/z (I_{rel}, %): 295 (33) $[M]^+$, 297 (35) $[M + 2]^+$.

1-Bromo-1-phenyl-2-phenylselanylethane (VIIIa). ^{1}H NMR spectrum, δ, ppm: 3.38 d.d (1H, 2-H, J = 9.5, 12.6 Hz). 3.44 d.d (1H, 2-H, J = 6.8, 12.8 Hz), 4.65 d.d (1H, 1-H, J = 6.8, 9.4 Hz), 7.05–7.45 m (10H, H_{arom}).

2-Bromo-1-phenyl-1-phenylselanylethane (VIIIb). ^{1}H NMR spectrum, δ, ppm: 3.58 d.d (1H, 2-H, J = 9.5, 12.6 Hz). 3.69 d.d (1H, 2-H, J = 6.8, 12.8 Hz), 4.69 d.d (1H, 1-H, J = 6.8, 9.4 Hz), 7.36–7.57 m (10H, H_{arom}). Mass spectrum (**VIIIa/VIIIb**), m/z (I_{rel}, %): 340 (44) $[M]^+$, 342 (39) $[M + 2]^+$.

1,3-Dichloro-2-phenylselanylpropane (IX). ^{1}H NMR spectrum, δ, ppm: 3.52 q (1H, 2-H, J = 5.7 Hz), 3.87 d (4H, 1-H, 3-H, J = 5.7 Hz), 7.18–7.47 m (5H, H_{arom}). Mass spectrum, m/z (I_{rel}, %): 267 (35) $[M]^+$, 269 (14) $[M + 2]^+$.

1-Bromo-3-chloro-2-phenylselanylpropane (X). ^{1}H NMR spectrum, δ, ppm: 3.36 d.d (1H, 2-H, J = 5.6, 6.4 Hz), 3.66 d (2H, 3-H, J = 6.4 Hz), 3.84 d (2H, 1-H, J = 5.6 Hz), 7.07–7.35 m (5H, H_{arom}). Mass spectrum, m/z (I_{rel}, %): 312 (33) $[M]^+$, 314 30 $[M + 2]^+$.

***endo*-2-Chloro-*exo*-3-phenylselanylbicyclo[2.2.1]-heptane (XI).** ^{1}H NMR spectrum, δ, ppm: 1.75 d.t (1H, 7-H, J = 10.3 Hz), 1.98 m (2H, 5-H), 2.45 t (1H, 1-H, J = 3.7 Hz), 2.30 d (1H, 4-H, J = 3.7 Hz), 3.11 d.d (1H, 3-H, J = 3.2, 3.7 Hz), 4.18 d.t (1H, 2-H, J = 1.7, 3.7 Hz), 7.21–7.51 m (5H, H_{arom}). Mass spectrum, m/z (I_{rel}, %): 285 (43) $[M]^+$, 287 (39) $[M + 2]^+$.

***endo*-2-Bromo-*exo*-3-phenylselanylbicyclo[2.2.1]-heptane (XII).** ^{1}H NMR spectrum, δ, ppm: 1.69 d.t (1H, 7-H, J = 10.3 Hz), 1.85 m (2H, 5-H), 2.15 d (1H, 4-H, J = 3.5 Hz), 2.25 t (1H, 1-H, J = 3.5 Hz), 3.05 d.d (1H, 3-H, J = 3.2, 3.5 Hz), 3,21 d.t (1H, 2-H, J = 1.6, 3.5 Hz), 7.20–7.56 m (5H, H_{arom}). Mass spectrum, m/z (I_{rel}, %): 329 (35) $[M]^+$, 331 (19) $[M + 2]^+$.

***exo*-2-Chloro-*endo*-3-phenylselanylbicyclo[2.2.1]-hept-2-ene (XIIIa).** ^{1}H NMR spectrum, δ, ppm: 1.87 d.t (1H, 7-H, J = 1.6, 9.5 Hz), 2.14 d (1H, 7-H, J = 9.5 Hz), 3.16 br.s (2H, 1-H, 4-H), 3.66 t (1H, 2-H, J = 2.4 Hz), 3.97 t (1H, 3-H, J = 2.4 Hz), 6.22 d.d (1H, 6-H, J = 3.4, 5.6 Hz), 6.28 d.d (1H, 5-H, J = 2.7, 5.6 Hz), 7.20–7.55 m (5H, H_{arom}).

***endo*-2-Chloro-*exo*-3-phenylselanylbicyclo[2.2.1]-hept-2-ene (XIIIb).** ^{1}H NMR spectrum, δ, ppm: 1.69 d.t (1H, 7-H, J = 1.6, 10.3 Hz), 2.15 d (1H, 4-H, J = 3.5 Hz), 2.25 t (1H, 1-H, J = 3.5 Hz), 3.05 d.d (1H, 3-H, J = 3.2, 3.5 Hz), 3,21 d.t. (1H, 2-H, J = 1.6, 3.5 Hz), 6.18 t (1H, 5-H), 6.30 t (1H, 6-H, J = 3.2 Hz), 7.20–7.56 m (5H, H_{arom}). Mass spectrum (**XIIIa/XIIIb**), m/z (I_{rel}, %): 327 (34) $[M]^+$, 329 (32) $[M + 2]^+$.

***endo*-2-Bromo-*exo*-3-phenylselanyl-*endo*-5-trifluoromethylbicyclo[2.2.1]heptane (XIV).** ^{1}H NMR spectrum, δ, ppm: 1.69 d.d.t (1H, *anti*-7-H, ^2J = 11.1, $J_{7,3}$ = 3.1, $J_{7,1}$ = 1.6, $J_{7,4}$ = 1.6 Hz), 1.93 d.d.d.d (1H, *exo*-6-H, ^2J = 13.4, $J_{6,5}$ = 11.9, $J_{6,1}$ = 5.1, $J_{6,2}$ = 1.9 Hz), 2.09 d.d.t (1H, *syn*-7-H, ^2J = 10.9, $J_{7,endo\text{-}6}$ = 2.7, $J_{7,1} = J_{7,4}$ = 1.1 Hz), 2.24 d.d.d (1H, *endo*-6-H, ^2J = 13.4, $J_{6,5}$ 6.7, $J_{6,syn\text{-}7}$ = 2.6 Hz), 2.55 br.s (1H, 1-H), 2.57 m (1H, 4-H), 2.58 d.d.d.q (1H, 5-H, $J_{5,exo\text{-}6}$ = 11.9, J_{HF} = 10.3, $J_{5,endo\text{-}6}$ = 6.5, $J_{5,4}$ = 3.6 Hz), 3.78 d.d (1H, 3-H, $J_{3,2}$ = 4.3, $J_{3,anti\text{-}7}$ = 2.8 Hz), 4.12 d.t (1H, 2-H, $J_{2,3} = J_{2,1}$ = 4.1, $J_{2,exo\text{-}6}$ = 1.9 Hz), 7.37 m (5H, H_{arom}). Mass spectrum, m/z (I_{rel}, %): 347 (43) $[M]^+$, 349 (39) $[M + 2]^+$.

***endo*-2-Bromo-*endo*-5-nitro-*exo*-6-phenyl-*exo*-3-phenylselanylbicyclo[2.2.1]heptane (XV).** ^{1}H NMR spectrum, δ, ppm: 2.12 d.d.t (1H, *anti*-7-H, ^2J = 12.1, $J_{7,3}$ = 2.7, $J_{7,1} = J_{7,4}$ = 1.7 Hz), 2.28 d.d.t (1H, *syn*-7-H, ^2J = 12.1, $J_{7,6}$ = 2.5, $J_{7,1} = J_{7,4}$ = 1.7 Hz), 2.91 d.q (1H, 1-H, $J_{1,2}$ = 4.6, $J_{1,syn\text{-}7} = J_{1,anti\text{-}7} = J_{1,4}$ = 1.7 Hz), 3.12 d.q (1H, 4-H, $J_{4,5}$ = 4.5, $J_{4,syn\text{-}7}$ = 1.7, $J_{4,anti\text{-}7} = J_{4,1}$ = 1.6 Hz), 3.39 d.d (1H, 3-H, $J_{3,2}$ = 4.4, $J_{3,anti\text{-}7}$ = 2.6 Hz), 4.23 t (1H, 2-H, $J_{2,3} = J_{2,1}$ = 4.4 Hz), 4.27 d.d (1H, 6-H, $J_{6,5}$ = 5.3, $J_{6,syn\text{-}7}$ = 2.7 Hz), 4.89 d.d (1H, 5-H,

$J_{5,6}$ = 5.2, $J_{5,4}$ = 4.8 Hz), 7.18–7.47 m (5H, H_{arom}). Mass spectrum, m/z (I_{rel}, %): 406 (26) $[M]^+$, 408 (29) $[M + 2]^+$.

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