Regio- and Stereoselectivity in Phenylselenoetherification of (*Z*)- and (*E*)-Hex-4-en-1-ols

Vera M. Divac, Zorica M. Bugarčić*[1]

University of Kragujevac, Faculty of Science, Department of Chemistry, Radoja Domanovića 12, P.O. Box 60, 34 000 Kragujevac, Serbia
Fax +381(34)335040; E-mail: zoricab@kg.ac.rs

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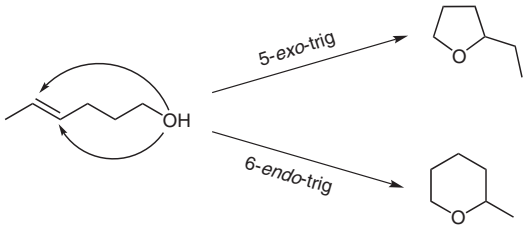
Abstract: Δ^4-Primary alkenols (*Z*)- and (*E*)-hex-4-en-1-ols underwent facile cyclization to the corresponding phenyl selenoethers using PhSeX (X = Cl, Br) in high yields and in good to excellent selectivities in the presence of some catalysts (Lewis acids and bases). The reaction succeeded in complete control of stereo- and regioselectivity. The best results were obtained with triethylamine and tin(II) chloride. Triethylamine as an additive in the reaction with (*Z*)-hex-4-en-1-ol gives only *erythro*-2-[1-(phenylseleno)ethyl]tetrahydrofuran, while the *E*-isomer gives *cis*-2-methyl-3-(phenylseleno)tetrahydropyran in large excess. Tin(II) chloride as an additive in the reaction with (*Z*)-hex-4-en-1-ol gives *threo*-2-[1-(phenylseleno)ethyl]tetrahydrofuran and with the *E*-isomer gives *trans*-2-methyl-3-(phenylseleno)tetrahydropyran. The reactions were performed under very mild experimental conditions, and the obtained yields were almost quantitative.

Key words: alcohol, cyclization, heterocycles, regioselectivity, Lewis acids

Cyclization of unsaturated alcohols leading to cyclic ethers, are well documented in the literature as convenient pathways in the synthesis of natural products and related compounds.[1] Organoselenium-induced cyclization of unsaturated alcohols has been widely explored in organic synthesis over the last decade and depending on the nature of the substrate, a variety of five- and six-membered ring heterocycles can be prepared.[2–6] It must be emphasized that different regio- and stereoisomers can be produced in some cases by simply choosing conditions favorable to kinetic or thermodynamic control. Selenium-induced cyclization has the advantage that the introduction of the heteroatom, the manipulation of the obtained product, and the removal of the function are facilitated by the simple and mild conditions required, such as oxidation–*syn*-selenoxide elimination, hydrogenolytic removal, or nucleophilic substitution of the corresponding selenones.[5–9] In past years we have investigated the influence of different types of additives on yields and selectivity of phenylselenium-induced cyclization of alkenols bearing a hydroxy group as an internal nucleophile.[10–14] In this work we report the regio- and stereocontrolled cyclization of two Δ^4-geometric isomers, (*Z*)- and (*E*)-hex-4-en-1-ols [(*Z*)- and (*E*)-**1**].

In cyclization reaction of Δ^4-alkenols, two regioisomeric products can be obtained. If ring-closure reaction is by 5-*exo*-trig attack of the hydroxy group (Scheme 1), the tetrahydrofuran-type of ring will be produced. On the other hand, if ring-closure is by 6-*endo*-trig attack then the tetrahydropyran-type of ring will be retrieved (Scheme 1).



Scheme 1

By using various reagents in the cyclization reaction of Δ^4-alkenols, such as H_2SO_4, $Hg(OAc)_2$, $Pb(OAc)_4$, NBS, peracid, $BF_3{\cdot}OEt_2$, $AlCl_3$, $SnCl_4$, etc., a mixture of tetrahydrofuran- and tetrahydropyran-type ring products are produced in various ratios.[1] Benzeneselenenyl halides are very good electrophilic reagents in organic synthesis and in reactions with olefin bonds they often produce regioselective products, which is also the case for (*Z*)- and (*E*)-hex-4-en-1-ols [(*Z*)-**1** and (*E*)-**1**] (Scheme 2). Reaction of benzeneselenenyl halides and (*Z*)-**1** and (*E*)-**1** affords a seleniranium intermediate **A** and **C**, respectively (Scheme 2), which can be trapped by an external (halide ion from reagent) or internal nucleophile (hydroxy group from alcohol) to give two diastereoisomeric addition products **4** and **5** or cyclization products **2** or **3**, respectively.

However, the presence of the nucleophilic halide anions is sometimes responsible for some undesirable processes such as addition of the halide ion to give **4** or **5** (which gives a low yield of the cyclic ether product) and decrease in stereoselectivity especially in the case of bromide as the anion (Table 3, without additive). In order to decrease the side reaction and to increase the yields of cyclic products, we performed experiments with two different sets of additives: Lewis acids ($SnCl_2$, $CoCl_2$, $AlCl_3$) and Lewis bases (Et_3N, pyridine, quinoline, 2,2′-bipyridine). Results of these investigations are given in the Tables 1 and 2 and shows that all reactions proceed with good yields and with good to excellent stereoselectivites. From data in Table 1 (with Lewis acids as additives) it can be seen that (*Z*)-**1** gives *threo*-**2** as the main product, and in the case of (*E*)-**1** the predominate product is *trans*-**3**. Best results with both (*Z*)-**1** and (*E*)-**1** and both reagents (PhSeCl and

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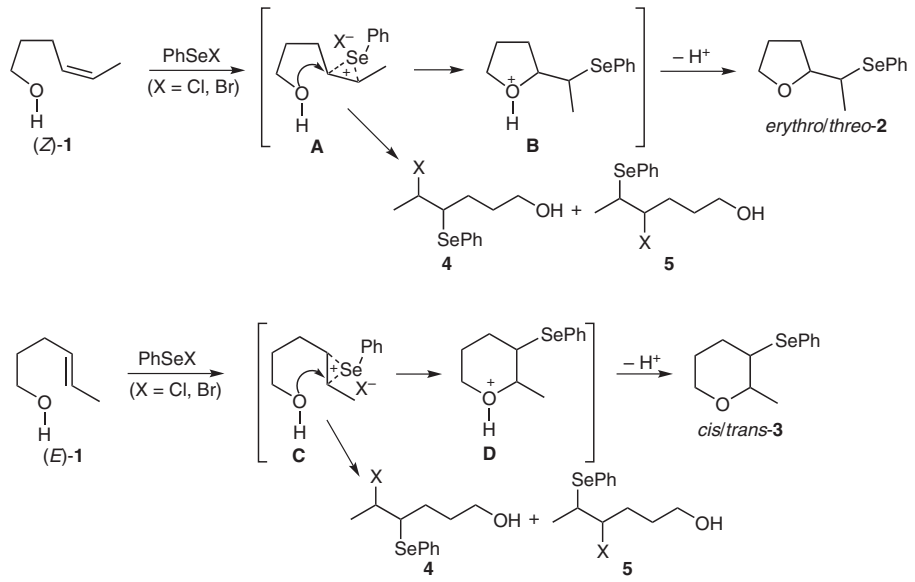


Scheme 2

PhSeBr) were obtained by using tin(II) chloride as an additive (Table 1); cyclic ethers were obtained as the product in almost quantitative yields and (*Z*)-**1** gave *threo*-**2** in large excess, while (*E*)-**1** gave *trans*-**3** as the main product. Cobalt(II) chloride as the additive (Table 1) also gave cyclic ether products in high yields, but in the reaction with (*Z*)-**1** the stereoselectivity was lower than with tin(II) chloride as an additive. Not so good results were obtained in the reactions with aluminum(III) chloride, which is a strong Lewis acid (Table 1). This could be explained by the high affinity of the additive for attack at the double bond of hex-4-en-1-ol when it forms a mixture of various products that are difficult to separate. From data in Table 2 (with Lewis bases as additives), the opposite results were noted. The main product of the cyclization of (*Z*)-**1** was *erythro*-**2** and (*E*)-**1** gives *cis*-**3** in excess. The best results were obtained in the presence of triethylamine. If the reaction of (*Z*)-**1** is performed in the presence of triethylamine a single *erythro*-stereoisomer, *erythro*-**2**, is obtained (Table 2), while in the case of other bases *erythro*-**2** is obtained in excess (Table 2). With (*E*)-**1** the unexpected product, *cis*-**3**, was indeed obtained in good yield, but this was accompanied by considerable amounts of *trans*-**3**.

In the Table 3 and Scheme 3 the results with additives that gave the best stereoselectivity in the reactions of (*Z*)-**1** and (*E*)-**1** are given and compared with reactions where no additive was present.

The role of Lewis acids in these reactions is to increase the electrophilicity of the reagent (PhSeX) and to decrease the possibility of the addition of halides by removing the anion from the reagent and, in this way, to improve yields of

Table 1 Phenylselenoetherification of (*Z*)- and (*E*)-Hex-4-en-1-ols in the Presence of Lewis Acids

Substrate	Product	Yield (%) [ratio *erythro*/*threo* or *cis*/*trans*]					
		PhSeCl[a]			PhSeBr[a]		
		$SnCl_2$	$CoCl_2$	$AlCl_3$	$SnCl_2$	$CoCl_2$	$AlCl_3$
(*Z*)-**1**	*erythro*/*threo*-**2**	100 [3:97]	98.5 [10:90]	91.7 [20:80]	99 [16:84]	95 [16:84]	83.7 [21:79]
(*E*)-**1**	*cis*/*trans*-**3**	96 [3:97]	97 [3:97]	73 [16:84]	100 [3:97]	98 [3:97]	79.6 [11:89]

[a] Additive as indicated.

Table 2 Phenylselenoetherification of (*Z*)- and (*E*)-Hex-4-en-1-ols in the Presence of Lewis Bases

Substrate	Product	Yield (%) [ratio *erythro*/*threo* or *cis*/*trans*]							
		PhSeCl[a]				PhSeBr[a]			
		Et_3N	Bipy	Py	Quinoline	Et_3N	Bipy	Py	Quinoline
(*Z*)-**1**	*erythro*/*threo*-**2**	100 [100:0]	97.9 [99:1]	97.5 [99:1]	97.4 [98:2]	100 [100:0]	98.3 [99:1]	95.8 [98:2]	98 [96:4]
(*E*)-**1**	*cis*/*trans*-**3**	100 [81:19]	99.3 [80:20]	96 [80:20]	98.4 [79:21]	100 [85:15]	99.7 [85:15]	99.5 [82:18]	99.6 [80:20]

[a] Additive as indicated.

Table 3 Phenylselenoetherification of (*Z*)- and (*E*)-Hex-4-en-1-ols in the Presence of Et_3N and $SnCl_2$

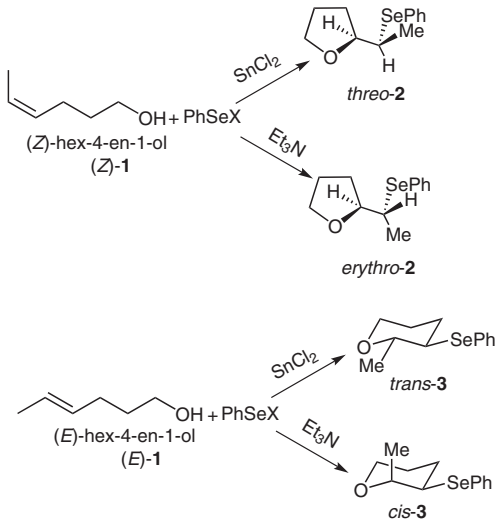
Substrate	Product	Yield (%) [ratio *erythro*/*threo* or *cis*/*trans*]					
		PhSeCl[a]			PhSeBr[a]		
		without	$SnCl_2$	Et_3N	without	$SnCl_2$	Et_3N
(*Z*)-**1**	*erythro*/*threo*-**2**	72 [30:70]	100 [3:97]	100 [100:0]	75 [70:30]	99 [16:84]	100 [100:0]
(*E*)-**1**	*cis*/*trans*-**3**	81 [31:69]	96 [3:97]	100 [81:19]	65 [35:65]	100 [3:97]	100 [85:15]

[a] Additive as indicated.

the desired products. The possible role of Lewis bases is to remove a proton from the oxonium ions **B** and **D** (Scheme 1) and alleviate the formation of the final cyclic product. That the specific distribution of cyclic ethers *erythro*/*threo*-**2** and *cis*/*trans*-**3** depends of the additive used can be explained by the nature of the additive itself.

trans-Isomer *trans*-**3** is formed in excess in the reactions of (*E*)-hex-4-en-1-ol [(*E*)-**1**] with PhSeX in the presence of Lewis acids due to the greater stability of the *trans*-isomer over the *cis*-isomer (thermodynamically controlled product). Unexpected formation of *cis*-**3** in the reactions with Lewis bases present (Table 2) can be explained by steric hindrance during the ring-closure process by these additives in the cyclization step. Since, the base forms a hydrogen bond with the proton from the hydroxy group, in this way they are bonded together, hence, they make the approach of oxygen in the ring-closure reaction difficult and the attack of the hydroxy group occurs from the opposite side from that expected (Figure 1).

That the stereoselectivity for *erythro*- or *threo*-isomers **2** from (*Z*)-**1** depends on the additive present was harder to explain. Nevertheless, it was noticed that, if the reaction mixture (when reactions were performed without additive) was left without purification for a few days, the ratio of isomers *erythro*/*threo*-**2** changed, that is, isomerization occurred (which did not happen with additive present). This observation may be ascribed to the role of the additives. It appears that the presence of some additives is beneficial to the isomerization process and this is most likely due to their elimination of the possibility of forming an acidic medium which is responsible for ring opening and isomerization.



Scheme 3

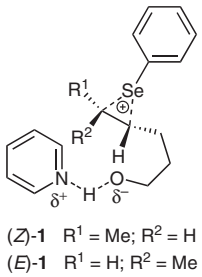


Figure 1

Reactions with benzeneselenenyl chloride as a reagent were faster than with benzeneselenenyl bromide. All reactions were faster with an additive than without, but there were some differences with different reagents. When benzeneselenenyl chloride was used as a reagent, in the presence of additives, the reaction went to completion in only a few minutes, while when benzeneselenenyl bromide was used the reaction could took up to 30 minutes.

^{1}H NMR spectroscopy was used to investigate the process of conversion of (*E*)-**1** and (*Z*)-**1** to cyclic ether products **2** and **3**. Due to the high rate of these reactions only the reactions with benzeneselenenyl bromide and no additive present were of experimental relevance in the NMR study i.e. they were slow enough for this method. In all other cases by the time when the first spectrum was taken isomerization reaction was already in progress or at the end. The useful signals were the doublets from methyl groups in ether products marked as I and II in Figure 2. The equimolar concentrations of (*Z*)-**1** and benzeneselenenyl bromide were mixed in an NMR tube and first spectrum was taken after 15 minutes. Only the doublet at $\delta = 1.41$ from the methyl group of *erythro*-**2** appeared (Figure 2, spectrum A). The second spectrum was taken after one hour and pairs of two doublets at $\delta = 1.41$ and $\delta = 1.33$ showed that the isomerization process had occurred. The doublet from *erythro*-**2** decrease in size while the doublet from *threo*-**2** began to appear. During this process of isomerization some peaks from the addition products begin to appear (Figure 2, spectrum B). The third spectrum, which was taken after 24 hour from the start of the reaction, showed that the isomerization process was

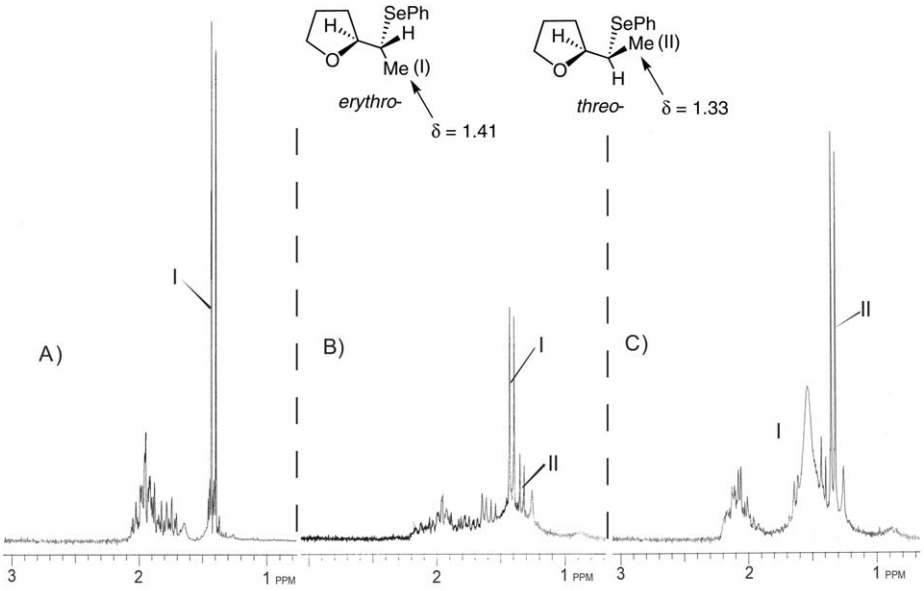


Figure 2

finished and *threo*-**2** was present in excess (Figure 2, spectrum C). From this experiment it can be concluded that *erythro*-**2** is the kinetically controlled product, and *threo*-**2** is the thermodynamically controlled product. The same experiment was repeated with (*E*)-**1** and the tetrahydropyran products **3** were formed in a ratio *trans*/*cis* of 70:30; during the 24 hour experiment no isomerization was noticed.

In this work we have demonstrated a practical, fast, inexpensive, and efficient process for the preparation of cyclic ethers under mild reaction condition. The additives used not only provide selectivity, they also increase the yields to almost quantitative. The correct choice of alkenol **1** and catalysts (Lewis acid or base) enables formation of the desired regio- or stereocontrolled product. The process can be extended to other compounds with a hydroxy group and double bond. The methodology should be easily applicable to the synthesis of a large number of biologically active compounds containing an oxacyclic moiety. These units can be found in monocyclic or polycyclic compounds, fused with other cyclic ethers or forming spiro systems.[15] The presence of molecules with oxygenated heterocycles in nature receives considerable attention due to their capacity to modify of the transport of Na^+, K^+, and Ca^{2+} cations through lipid membranes.[16–19] This activity is responsible for their antibiotic,[16] neurotoxic,[20,21] antiviral,[22] and cytotoxic action[23,24] and as growth regulators[16,25,26] or inhibitors of the level of cholesterol in blood.[27]

GM analysis were obtained with an Agilent Technologies instrument, model 6890 N with HP-5NS columns (5% phenyl-, 95% methyl-polysiloxane). ^{1}H and ^{13}C NMR spectra were run in $CDCl_3$ on Varian Gemini 200 MHz and Bruker WH 400 MHz NMR spectrometers. IR spectra were obtained with Perkin-Elmer Model 137B and Nicolet 7000 FT spectrophotometers. Microanalyses were performed by Dornis and Colbe and found to be in good agreement with the calculated values. TLC was carried out on 0.25 mm E. Merck precoated silica gel plates (60F-254) using UV light for visualization. Column chromatography used E. Merck silica gel (60, particle size 0.063–0.200 mm). Olefinic alcohols used as substrates are commercially available. Reagents (PhSeCl and PhSeBr) were used as supplied by Aldrich. CH_2Cl_2 was distilled from CaH_2.

Phenylselenoetherification of (*E*)- and (*Z*)-Hex-4-enols; General Procedure

All reactions were carried out on a 1-mmol scale. To a magnetically stirred soln of alkenol **1** (0.1 g, 1 mmol) and Et_3N (0.101 g, 1 mmol) [or $SnCl_2$ (0.19 g, 1 mmol), 2,2′-bipyridine (0.156 g, 1 mmol), pyridine (0.079 g, 1 mmol), quinoline (0.129 g, 1 mmol), $AlCl_3$ (0.133 g, 1 mmol), or $CoCl_2$ (0.065 g, 0.5 mmol)] in anhyd CH_2Cl_2 (5 mL) was added solid PhSeCl (0.212 g, 1.1 mmol) or PhSeBr (0.260 g, 1.1 mmol) at r.t. until the solid dissolved. The reaction went to completion virtually instantaneously. The pale yellow soln was washed with 2 M HCl (only when the additive was a base), then sat. aq $NaHCO_3$ soln, and brine. The organic layer was dried (Na_2SO_4), concentrated, and chromatographed. TLC and GM analysis as well as NMR spectra showed complete conversion of starting alkenol into cyclic ether products. The products were obtained after the elution of the traces of $(PhSe)_2$ on a column (silica gel, CH_2Cl_2). All products were characterized and identified on the basis of their spectral data. Cyclic ether products were known compounds and their spectral data have been presented previously.[10]

NMR Measurements

All reactions were carried out in NMR tubes and $CDCl_3$ was used as the solvent. ^{1}H NMR chemical shifts, δ, were calibrated to TMS as standard. The ^{1}H NMR spectra were recorded every 15 min, at the beginning of the reactions, and later every 30 min, 1 h, 2 h, and 4 h. The reaction began with mixing alkenol (1.50 mg) with PhSeBr (3.54 mg, 1 equiv) in $CDCl_3$ (3 mL). The real concentration of the reagents was 5×10^{-3} M.

***threo*-2-[1-(Phenylseleno)ethyl]tetrahydrofuran (*threo*-2)**

^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 7 Hz, 3 H, CH_3), 2.00–2.20 (m, 4 H, H3, H4), 3.37 (m, *J* = 7 Hz, 1 H, H2), 3.51 (dt, *J* = 3, 12 Hz, 1 H, $H5_{cis}$ to H2), 3.66 (dq, *J* = 7, 1.5 Hz, 1 H, CHSe), 4.00 (br d, *J* = 12 Hz, 1 H, $H5_{trans}$ to H2), 7.22–7.30 (m, 3 H, H_{Ph}), 7.52–7.60 (m, 2 H, H_{Ph}).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 18.6, 26.0, 30.1, 44.0, 68.2, 82.6, 127.2, 128.7, 130.7, 134.9.

***erythro*-2-[1-(Phenylseleno)ethyl]tetrahydrofuran (*erythro*-2)**

^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.41 (d, *J* = 7 Hz, 3 H, CH_3), 1.68–2.07 (m, 4 H, H3, H4), 3.41 (quint, *J* = 7 Hz, 1 H, CHSe), 3.77 (q, *J* = 7 Hz, 1 H, $H5_{cis}$ to H2), 3.90 and 3.95 (2 q, *J* = 7 Hz, 2 H, $H5_{trans}$ to H2 and H2), 7.22–7.30 (m, 3 H, H_{Ph}), 7.55–7.62 (m, 2 H, H_{Ph}).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 18.3, 26.1, 29.0, 43.9, 68.5, 82.2, 127.2, 128.7, 129.1, 134.6.

***trans*-2-Methyl-3-(phenylseleno)tetrahydropyran (*trans*-3)**

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 6.1 Hz, 3 H, CH_3), 1.65–2.20 (m, 4 H, H4, H5), 2.95 (sym. m, 1 H, CHSe), 3.30–3.50 (m, 2 H, H2 and H_{ax} of CH_2O), 3.92 (d, *J* = 11.3 Hz, 1 H, H_{eq} of CH_2O), 7.27 (m, 3 H, H_{Ph}), 7.56 (m, 2 H, H_{Ph}).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 21.0, 27.9, 32.2, 46.9, 67.9, 78.1, 127.6, 127.9, 128.8, 135.3.

***cis*-2-Methyl-3-(phenylseleno)tetrahydropyran (*cis*-3)**

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.43 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.65–2.20 (m, 4 H, H4, 5-H5), 3.32 (quint, *J* = 6.9 Hz, 1 H, H2), 3.60–4.05 (m, 3 H, H3, H6), 7.27 (m, 3 H, H_{Ph}), 7.56 (m, 2 H, H_{Ph}).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 21.0, 22.2, 30.8, 50.5, 68.2, 76.0, 126.9, 128.9, 130.5, 133.8.

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References

(1) Bugarcic, Z.; Mojsilovic, B. *Cyclization of Alcohols*; Faculty of Science, Kragujevac: Serbia, **2006**.
(2) Recent advances in selenocyclofunctionalization reactions, see: Petragnani, N.; Stefani, H. A.; Valdugab, C. J. *Tetrahedron* **2001**, *57*, 1411.
(3) Tiecco, M.; Testaferri, L.; Marini, F.; Bagnoli, L.; Santi, C.; Temperini, A.; Sternativo, S.; Tomassini, C. *Phosphorus, Sulfur Silicon Relat. Elem.* **2005**, *180*, 729.
(4) Tiecco, M.; Testaferri, L.; Bagnoli, L.; Marini, F.; Temperini, A.; Tomassini, C.; Santi, C. *Tetrahedron Lett.* **2000**, *41*, 3241.
(5) (a) Paulimer, C. In *Selenium Reagents and Intermediates in Organic Synthesis*, Vol. 4; Baldwin, J. E., Ed.; Pergamon: New York, **1986**. (b) *The Chemistry of Organic Selenium and Tellurium Compounds*, Vol. 2; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, **1987**.
(6) Electrophilic selenium, selenocyclizations, see: Tiecco, M. *Top. Curr. Chem.* **2000**, *208*, 7.
(7) Nicolaou, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3884.
(8) Nikolaou, K. C. *Tetrahedron* **1981**, *37*, 4097.
(9) Schimdt, G. H.; Garratt, D. G. In *The Chemistry of Double Bonded Functional Groups: Supplement A*, Vol. 2; Patai, S., Ed.; Wiley: New York, **1977**.
(10) Konstantinovic, S.; Bugarcic, Z.; Milosavljevic, S.; Schroth, G.; Mihailovic, M. Lj. *Liebigs Ann. Chem.* **1992**, 261.
(11) Mojsilovic, B.; Bugarcic, Z. *Heteroat. Chem.* **2001**, *12*, 475.
(12) Bugarcic, Z.; Gavrilovic, M. *Monatsh. Chem.* **2003**, *134*, 1359.
(13) Bugarcic, Z.; Mojsilovic, B. *Heteroat. Chem.* **2004**, *15*, 146.
(14) (a) Bugarcic, Z.; Mojsilovic, B.; Divac, V. *J. Mol. Catal. A: Chem.* **2007**, *272*, 288. (b) Divac, V. M.; Rvovic, M. D.; Bugarcic, Z. M. *Monatsh. Chem.* **2008**, *139*, 1373.
(15) Faulkner, D. J. *Nat. Prod. Rep.* **1997**, *14*, 259.
(16) *Polyether Antibiotics Naturally Occurring Acid Ionophores*, Vols. 1 & 2; Wesley, J. W., Ed.; Dekker: New York, **1982**.
(17) Painter, G. R.; Presman, B. C. *Top. Curr. Chem.* **1982**, *101*, 83.
(18) Still, W. C.; Hauck, P.; Kempf, D. *Tetrahedron Lett.* **1987**, *28*, 2817.
(19) Smith, P. W.; Still, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 7917.
(20) Shimizu, Y. *Marine Natural Products: Chemical and Biological Perspectives*, Vol 1; Scheuer, P. J., Ed.; Academic: New York, **1978**, 1.
(21) Ellis, S. *Toxicon* **1985**, *23*, 469.
(22) Sakemi, S.; Higa, T.; Jefford, C. W.; Bernardinelli, G. *Tetrahedron Lett.* **1986**, *27*, 4287.
(23) Suzuki, T.; Suzuki, A.; Furusaki, T.; Matsumoto, A.; Kato, A.; Imanaka, Y.; Kurosawa, E. *Tetrahedron Lett.* **1985**, *26*, 1329.
(24) Corley, D. G.; Herb, R.; Moore, E.; Scheuer, P. J.; Paul, V. J. *J. Org. Chem.* **1988**, *53*, 3644.
(25) Cohran, V. M. *Physiology of Fungi*; Wiley: New York, **1958**.
(26) Schreiber, S. L.; Kelly, S. E.; Porco, J. A.; Sanmakia, T.; Suh, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 6210.
(27) Gonzalez, A. G.; Martin, J. D.; Martin, V. S.; Norte, M.; Perez, R.; Ruano, J. Z.; Drexler, S. A.; Clardy, J. *Tetrahedron* **1982**, *38*, 1009.