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PHENYLSELENENYL CHLORIDE IN ACETONITRILE–WATER

A HIGHLY CONVENIENT REAGENT FOR HYDROXYSELENATION OF OLEFINS AND PREPARATION OF CYCLIC ETHERS FROM DIENES

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Abstract—The reaction of phenylselenenyl chloride with olefins in aqueous acetonitrile affords β-hydroxyalkyl phenyl selenides in excellent yields, providing the most convenient method for hydroxyselenation of olefins so far reported. When the reaction was applied to conjugated dienes, monohydroxyselenated products were obtained in good to excellent yields. From non-conjugated dienes, on the other hand, cyclic ethers containing two phenylseleno groups were produced in good to excellent yields, the first step of this reaction being the hydroxyselenation of one double bond.

β-Hydroxyalkyl aryl selenides are valuable intermediates in organic synthesis not only as precursors of allylic alcohols[1] but also in other transformations.[2,3] Recently they have been utilised in C—C[4] and C—N[5] bond formation reactions. Among several routes to the β-hydroxyselenides,[2,6] addition of both phenylseleno and hydroxy groups to double bonds (hydroxyselenation of olefins) belongs to the most simple methodologies. Several procedures have been reported for the hydroxyselenation of olefins.[7–16] Although they are very efficient, it is still necessary to use a catalyst such as a metal salt[7] or acid,[8] and/or to prepare effective organoselenium reagents from various selenium compounds.[7–15] Some are two-flask reactions because the hydrolysis of the organoselenium intermediates is carried out in another flask.[9,10,16] We now find that a one-pot reaction of commercially available phenylselenenyl chloride with olefins in aqueous acetonitrile at ambient temperature affords the β-hydroxyselenides in excellent yields.[17,18]

Much attention has been paid to the construction of cyclic ether frameworks from dienes accompanied by the introduction of two phenylseleno groups[8,19–21] because of the importance of oxygen heterocycles in biologically active compounds and the synthetic potential of the phenylseleno group.[2,6,22] Reported examples of this reaction required the preparation of organoselenium reagents such as N-phenylselenophthalimide,[8] 'phenylselenenic acid'[19] or phenylselenocyanate[21] from commercially available selenium compounds. We also find that 'phenylselenenyl chloride in acetonitrile–water' is a quite effective reagent for conversion of non-conjugated dienes to cyclic ethers containing two phenylseleno groups.[23]

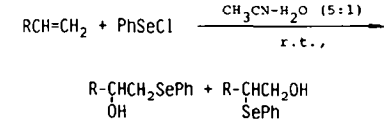
As far as we know, there is no precedent for the use of phenylselenenyl chloride in a solvent containing water. We describe here the utility and some limitations of the new reagent system, 'phenylselenenyl chloride in acetonitrile–water'.

RESULTS AND DISCUSSION

Hydroxyselenation of monoolefins

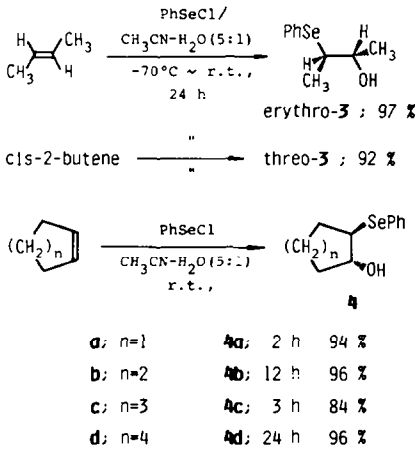
In a typical reaction, phenylselenenyl chloride (5 mmol) was added to 1-hexene (5 mmol) in acetonitrile containing water (15 + 3 ml) and the resulting solution was stirred at ambient temp for 24 hr to afford, after purification by column chromatography, a Markovnikov type hydroxyselenated product (**1a**) and an anti-Markovnikov type adduct (**2a**) in 74% and 9% yields, respectively (Scheme 1). The total yield and the isomer ratio of **1a** + **2a** were not affected by the reverse addition of the reactants. Even in the case where a solution of phenylselenenyl chloride in acetonitrile–water (5 : 1) was stirred for 2 hr prior to the addition of 1-hexene, a 9 : 1 mixture of **1a** + **2a** was produced in 81% total yield under the same conditions. This result indicates that phenylselenenyl chloride or a certain reagent derived from it can work as an electrophile to olefins in the presence of a large excess of water. When the reaction was applied to styrene, the hydroxyselenation reaction was much faster than that of 1-hexene and the Markovnikov type adduct (**1b**) was produced as a sole product in 97% yield (Scheme 1).

The stereochemical course of this reaction was disclosed to be *trans* from the hydroxyselenation of *trans*- and *cis*-2-butenes which afforded *erythro*- and *threo*-**3** respectively (Scheme 2). These reactions were carried out in the pressure bottles using excess butenes (approx 5 equiv) and the yields of *erythro*- and *threo*-**3** were based on the amount of phenylselenenyl chloride used. The products, *erythro*- and *threo*-**3**, were identical to authentic samples prepared from *trans*- and *cis*-2-butenes respectively by epoxidation and ring opening with sodium benzeneselenolate.[7b] From cyclic olefins of 5- to 8-membered rings, *trans* adducts possessing *threo*-



			1	2
a	R=Bu	24 h	74%	9%
b	R=Ph	2 h	97%	-

Scheme 1.

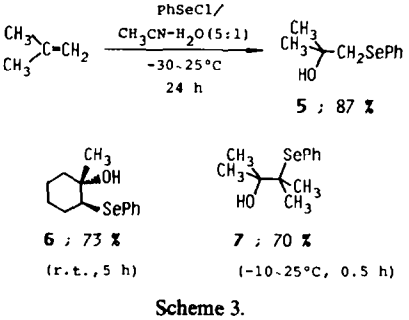


Scheme 2.

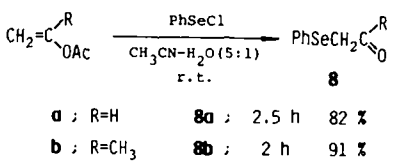
configuration (**4a–4d**) were obtained in excellent isolated yields. The reactions were monitored by TLC and continued until the increase of the products could no longer be observed. The hydroxyselenation reactions of cyclopentene and cycloheptene were found to be faster than those of cyclohexene and cyclooctene.

This reaction was also applied to 1,1-di-, tri-, and tetra-substituted olefins. From 2-methylpropene and 1-methylcyclohexene, the Markovnikov type hydroxyselenated products, **5** and **6**, were produced selectively (Scheme 3). When the hydroxyselenation of 2-methylpropene or 2,3-dimethyl-2-butene was carried out at ambient temp, the yield was unsatisfactory due to the formation of diphenyl diselenide. It was necessary to mix the reactants at low temp (−30 to −10°) and then to stir the solution at ambient temp to obtain **5** or **7** in a good yield. In the ^{1}H-NMR spectrum of **6**, the proton attached to the C atom bearing phenylseleno group appears as a doublet of doublets with coupling constants of 4.1 and 12.0 Hz, indicating that this proton is on an axial position. As the stereochemistry of the hydroxyselenation is *trans*, the stable conformation of **6** is such that the phenylseleno and hydroxy groups are on equatorial positions and the methyl group is on an axial one.

The hydroxyselenation of vinyl acetate affords (phenylseleno)acetaldehyde (**8a**) in 82% isolated yield by column chromatography (Scheme 4). The (phenylseleno)acetaldehyde is a valuable intermediate as a two carbon-atoms homologation reagent[24] or a synthetic equivalent of a vinyl carbonium ion.[25,26] Several efficient routes to **8a** have been reported using



Scheme 3.



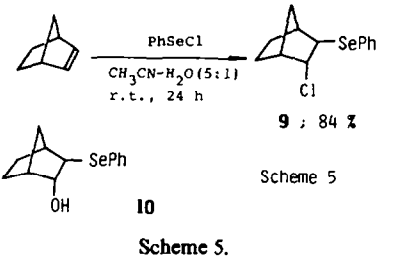
Scheme 4.

ethyl vinyl ether[24,25] or vinyl acetate[7b,17] as a starting material. The procedure described herein, however, seems to be the most attractive as it is a one-pot reaction and the use of excess vinylic compounds is not necessary. A similar procedure using isopropenyl acetate as an olefinic substrate afforded (phenylseleno)acetone (**8b**) in 91% isolated yield (Scheme 4).

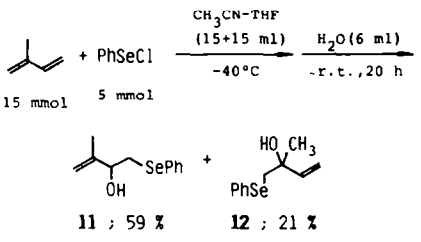
When the reaction was applied to norbornene, the phenylselenenyl chloride adduct (**9**)[27] was obtained in 84% isolated yield (Scheme 5). By stirring the solution of phenylselenenyl chloride in acetonitrile–water (5 : 1) for 2 hr prior to the addition of norbornene and subsequently heating the mixture under reflux for 24 hr, the yield of hydroxyselenated **10** was less than 20% and **9** was found to be the major product (66%). This result indicates that initial products in our reaction are the phenylselenenyl chloride adducts and the subsequent hydrolysis is extremely slow in the case of norbornene. The yield of **10** was not improved by the use of other selenium reagents such as N-phenylselenophthalimide under the reported condition[8] for hydroxyselenation of olefins.

Hydroxyselenation of conjugated dienes

'Phenylselenenyl chloride in acetonitrile–water' is also feasible for the monohydroxyselenation of conjugated dienes. The yields of hydroxyselenated products, however, were unsatisfactory under the standard reaction conditions described in the previous section. In the case of isoprene, the best result was obtained by adding a solution of phenylselenenyl chloride (5 mmol) in acetonitrile (15 ml) to a solution of isoprene (15 mmol) in tetrahydrofuran (THF) (15 ml) at −40° followed by the addition of water (6 ml) and then by stirring the resulting solution at ambient temp for 20 hr (Scheme 6). The products were found to be a 3 : 1 (by GLC) mixture of 3,4-adduct **11** and 1,2-adduct **12** in 80% total yield. In the methoxyselenation of isoprene using phenylselenenyl chloride in methanol,[28] the formation of the 1,2-adduct is kinetically favoured and that of 3,4-adduct is thermodynamically favoured. In contrast to this, in the present case the ratio of **11** and **12** was not affected by the change of reaction conditions, the reason being as yet unknown.



Scheme 5.



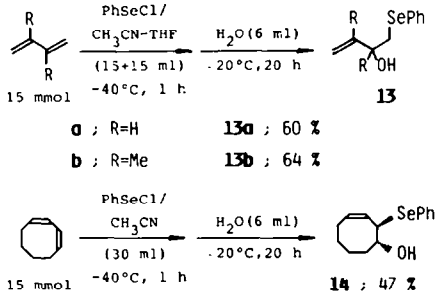
Scheme 6.

The results of the application to symmetrical conjugated dienes are summarised in Scheme 7. Markovnikov type 1,2-adducts were obtained in moderate to good yields under the conditions shown in Scheme 7. The formation of 1,4-adducts was not observed in any of the cases, which is one of the characteristic features of our reagent.

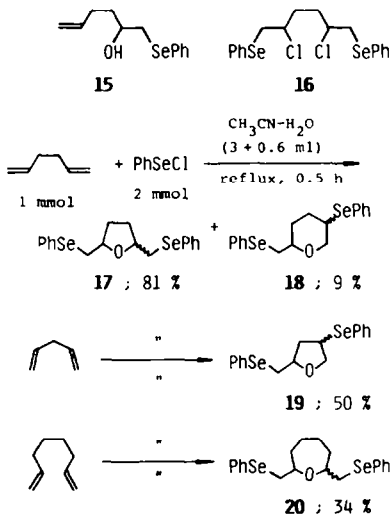
Preparation of cyclic ethers from non-conjugated dienes

By the reaction of 1,5-hexadiene with 2 equiv of phenylselenyl chloride in acetonitrile–water (5:1) under reflux for 5 hr, cyclic ethers containing two phenylseleno groups, **17** and **18**, were produced in 90% total yield (Scheme 8). The isomer ratio was determined by HPLC analysis, the major isomer being a tetrahydrofuran derivative (**17**). When the reaction was applied to 1,4-pentadiene and 1,7-octadiene, 5-membered (**19**) and 7-membered (**20**) cyclic ethers were produced, respectively. Although we could not isolate the monohydroxyselenated compounds such as **15** under the present reaction conditions, **15** is expected to cyclise to **17** and **18** by the reaction with phenylselenenyl chloride from extensive works of selenium-induced etherification of olefinic alcohols.[8,29] Initial formation of the bis-adduct of phenylselenenyl chloride (**16**) can not be ruled out, as we confirmed separately that a 90:10 mixture of **17** and **18** was formed in 98% total yield by heating **16** in acetonitrile–water (5:1) under reflux for 5 hr. The formation of a bis-hydroxyselenated compound was not observed in any case, indicating that an intramolecular oxyselenation is much faster than an intermolecular hydroxyselenation.

When diallyl ether and diallyl sulfide were used as dienes, 1,4-dioxane and 1,4-oxathiane derivatives, **21a** and **21b**, were produced respectively in good yields (Scheme 9). The yields were not improved by the change of the ratio of acetonitrile to water or the change of concentration of the reactants. Each of the cyclic ethers



Scheme 7.



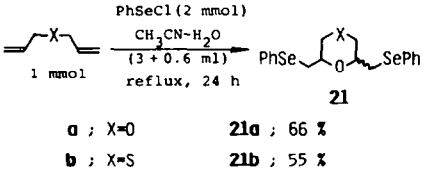
Scheme 8.

(**17**–**21**), thus prepared, was found to be a mixture of nearly equal amounts of stereoisomers (*cis* and *trans* with respect to two phenylseleno and/or (phenylseleno)methyl substituents) by ^{13}C-NMR spectrum.

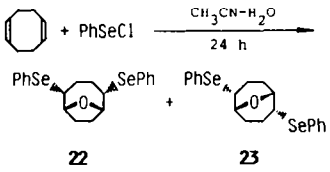
By the reaction of 1,5-cyclooctadiene with 'phenylselenenyl chloride in acetonitrile–water' at ambient temp, 2,5-bis-(phenylseleno)-9-oxabicyclo[4.2.1]nonane (**22**) was produced as a major product accompanied with a small amount of its [3.3.1]-isomer (**23**). When this reaction was carried out at reflux temp, **23** was produced almost exclusively by the isomerisation of **22** to **23** (Scheme 10).[30] As expected from the *trans*-stereospecificity of this hydroxyselenation reaction, both phenylseleno groups were found to be in the *endo* position.[21] The oxidative elimination of the phenylseleno group from **22**[19,20] and the reductive elimination from **22**[19,21c] and **23**[21c] have already been reported to afford unsaturated and saturated bicyclic ethers.

As for the yields of cyclic ethers (**17**–**25**) (Schemes 8–11), the procedure described herein gave better than or comparable results to the reported procedures.[8,19–21] Accompanied with other merits such as the simplicity of the experimental procedure and the use of commercially available selenium reagent, it makes our procedure the most attractive one for the conversion of diene to cyclic ethers containing two phenylseleno groups.

Application to diethyl diallylmalonate resulted in almost quantitative formation of two types of products; namely, tetrahydropyran derivatives (**26**) and spiro-bislactone derivatives (**27**) (Scheme 11). It was revealed by ^{13}C-NMR spectra that **26** and **27**



Scheme 9.



22 23

temp.	$CH_3CN:H_2O$	Yield(%)	(22:23)
25°C	10:1	77	(92: 8)
25°C	5:1	92	(88:12)
reflux	5:1	94	(3:97)

Scheme 10.

consisted of two (*ca* 3:1) and three (*ca* 5:3:2) stereoisomers respectively. In the case of **26**, they are *cis* and *trans* isomers with respect to two (phenylseleno)methyl groups as in the cases of **17–21**. The predominant isomer seems to be the *cis* isomer, as the *trans* isomer is expected to be less stable due to the 1,3-diaxial interaction of one of the (phenylseleno)methyl groups with the ethoxycarbonyl group. Molecular asymmetry is contained in **27** in addition to two asymmetric carbons. Thus, three pairs of enantiomers are possible as shown in Scheme 11 (**27a–c**; one of the mirror images is depicted). The major isomer was assigned as **27a** on the statistical base. The ratio of **27** to **26** increased slightly by the change of reaction temp from 25° to refluxing temp. We have observed separately that an 84:16 mixture of **26** and **27** was formed from pure **26** by heating it in acetonitrile–water (5:1) under reflux for 24 hr in the presence of hydrogen chloride. This isomerisation is so slow that another route to **27** such as the direct lactonisation of the olefinic ester should be present. Although organoselenium-induced lactonisation of olefinic carboxylic acid has been extensively studied,[8,31] the present result seems to be the first example for such phenylselenolactonisation from the carboxylic ester.[32] The scheme where the hydrolysis of the ester gives a free carboxylic acid which then suffers lactonisation can be ruled out, since the hydrolysed compound of **26** (mono- or di-carboxylic acid of **26**) was not detected in the products.

EXPERIMENTAL

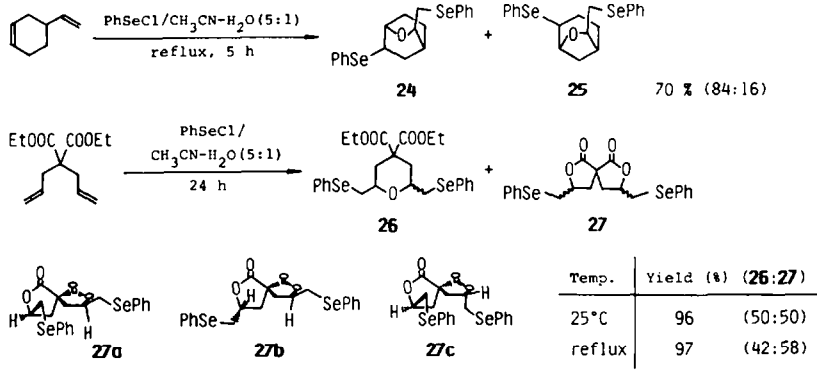
IR spectra were recorded with Hitachi EPI-S2 and JASCO IR-810 spectrometers. ^{1}H- and ^{13}C-NMR spectra were obtained with Varian EM-360 (60 MHz), JEOLCO JNM-FX-100 (100 MHz), and JEOLCO-GX-400 (400 MHz) instruments on solns in $CDCl_3$ with Me_4Si as an internal standard. GLC analyses were carried out with a Shimadzu 4CMPF apparatus by using EGSS-X (15%)-Chromosorb W (1 m) column (N_2 as carrier gas). M.ps were determined with Shimadzu MM-2 micro m.p. apparatus and were uncorrected. Liquid chromatographic analyses were carried out with a Waters HPLC system equipped with a 6000A solvent delivery system, a Model 440 absorbance detector (at 254 nm), and a μ-Porasil (3.9 mm × 0.3 m) column.

Materials

An authentic sample of **8a** was prepared by the hydrolysis of the corresponding acetal according to the reported procedure.[7b] Authentic samples of 2-methyl-3-methoxy-4-(phenylseleno)-1-butene and 3-methyl-3-methoxy-4-(phenylseleno)-1-butene were prepared by methoxyselenation of isoprene under thermodynamically and kinetically controlled conditions respectively[28] and were purified by flash-chromatography (silica gel (Wakogel C-200), hexane–EtOAc (15:1) as eluent).[33] 2-Methyl-3-methoxy-4-(phenylseleno)-1-butene: NMR (100 MHz) δ 1.68 (t, 3H, J = 1 Hz), 3.01 (dd, 1H, J = 12.5, 6 Hz), 3.19 (dd, 1H, J = 12.5, 7.5 Hz), 3.24 (s, 3H), 3.79 (dd, 1H, J = 7.5, 6 Hz), 5.02 (q, 2H, J = 1 Hz), 7.2–7.35 (m, 2H), 7.45–7.6 (m, 2H). (Calc for $C_{12}H_{16}OSe$: C, 56.45; H, 6.3. Found: C, 56.45; H, 6.3%.) 3-Methyl-3-methoxy-4-(phenylseleno)-1-butene: NMR (100 MHz) δ 1.40 (s, 3H), 3.12 (d, 1H, J = 12 Hz), 3.19 (s, 3H), 3.24 (d, 1H, J = 12 Hz), 5.24 (dd, 1H, J = 18, 1.5 Hz), 5.26 (dd, 1H, J = 10, 1.5 Hz), 5.89 (dd, 1H, J = 18, 10 Hz), 7.2–7.35 (m, 3H), 7.45–7.6 (m, 2H). (Found: C, 56.6; H, 6.2%.) Compound **16** was prepared by the reaction of 1,5-hexadiene with 2 equiv of phenylselenenyl chloride in dry acetonitrile at ambient temp for 6 hr and isolated by column chromatography (silica gel, hexane–EtOAc (10:1) as eluent) in 73% yield: NMR (60 MHz) δ 1.4–2.6 (m, 4H), 2.8–3.4 (m, 4H), 3.6–4.3 (m, 2H), 7.0–7.3 (m, 6H), 7.3–7.6 (m, 4H). (Calc for $C_{18}H_{20}Cl_2Se_2$: C, 46.5; H, 4.35. Found: C, 46.65; H, 4.45%.) Authentic samples of **17**, **18**, **21a**, **21b**, **22**, **23**, and a mixture of **24** and **25** were also prepared by the reported procedure.[21c] All other organic and inorganic materials were commercial products and were used without purification.

Hydroxyselenation of 1-*hexene.*

General procedure for hydroxyselenation of monoolefins. Phenylselenenyl chloride (5 mmol, 0.96 g) was added to a soln of 1-hexene (5 mmol, 0.42 g) in acetonitrile (15 ml) and water (3 ml), and the resulting pale yellow soln was stirred at ambient temp for 24 hr. The soln was added to $NaHCO_3$ aq (50 ml) and the products were extracted with CH_2Cl_2 (20 ml × 3). The organic layer was washed with brine (20 ml), dried ($MgSO_4$), and evaporated *in vacuo* to leave yellow oil. Column chromatography (flash-chromatography[33] using silica gel (Wakogel C-200), hexane–EtOAc (20:1–5:1) as eluent) of this residual oil afforded diphenyl diselenide (0.33 g, 0.41 mmol;



Temp.	Yield (%)	(26:27)
25°C	96	(50:50)
reflux	97	(42:58)

Scheme 11.

16%), **1a** (0.95 g, 3.7 mmol; 74%) and **2a** (0.12 g, 0.46 mmol; 9%). **1a**; IR (film) 3410 cm^{-1}; NMR (400 MHz) δ 0.88 (t, 3H, J = 7.1 Hz), 1.24–1.35 (m, 2H), 1.37–1.45 (m, 2H), 1.53 (br q, 2H, J = 6.5 Hz), 2.39 (br s, 1H), 2.88 (dd, 1H, J = 8.8, 12.7 Hz), 3.14 (dd, 1H, J = 3.9, 12.7 Hz), 3.63–3.69 (m, 1H), 7.23–7.29 (m, 3H), 7.50–7.55 (m, 2H). (Calc for $C_{12}H_{18}OSe$: C, 56.0; H, 7.05. Found: C, 56.0; H, 6.9%.) **2a**: IR (film) 3400 cm^{-1}; NMR (400 MHz) δ 0.90 (t, 3H, J = 7.3 Hz), 1.26–1.38 (m, 2H), 1.39–1.49 (m, 2H), 1.50–1.72 (m, 2H), 2.41 (s, 1H), 3.18–3.25 (m, 1H), 3.53 (dd, 1H, J = 6.8, 11.7 Hz), 3.61 (dd, 1H, J = 5.4, 11.7 Hz), 7.22–7.31 (m, 3H), 7.55–7.57 (m, 2H). (Found: C, 56.25; H, 6.9%.)

Spectral and combustion analytical data of other hydroxyselenated compounds of monoolefins are as follows.

1-*Phenyl*-2-(*phenylseleno*)*ethanol* (**1b**). IR (film) 3470 cm^{-1}; NMR (60 MHz) δ 3.0 (br s, 1H), 3.14 (d, 1H, J = 8 Hz), 3.17 (d, 1H, J = 5 Hz), 4.71 (dd, 1H, J = 8, 5 Hz), 7.1–7.5 (m, 10H). (Calc for $C_{14}H_{14}OSe$: C, 60.65; H, 5.1. Found: C, 60.75; H, 5.2%.)

erythro-3-(*Phenylseleno*)-2-*butanol* (erythro-**3**). IR (film) 3470 cm^{-1}; NMR (60 MHz) δ 1.20 (d, 3H, J = 6 Hz), 1.40 (d, 3H, J = 7 Hz), 2.30 (br s, 1H), 3.37 (dq, 1H, J = 3.5, 7 Hz), 3.80 (dq, 1H, J = 3.5, 6 Hz), 7.2–7.4 (m, 3H), 7.4–7.7 (m, 2H). (Calc for $C_{10}H_{14}OSe$: C, 52.4; H, 6.15. Found: C, 52.35; H, 6.5%.)

threo-3-(*Phenylseleno*)-2-*butanol* (threo-**3**). IR (film) 3470 cm^{-1}; NMR (60 MHz) δ 1.29 (d, 3H, J = 6 Hz), 1.39 (d, 3H, J = 7 Hz), 2.60 (br s, 1H), 3.11 (quint, 1H, J = 7 Hz), 3.62 (quint, 1H, J = 6 Hz), 7.1–7.4 (m, 3H), 7.4–7.7 (m, 2H). (Found: C, 52.35; H, 6.45%.)

trans-2-(*Phenylseleno*)*cyclopentanol* (**4a**). IR (film) 3360 cm^{-1}; NMR (100 MHz) δ 1.4–2.6 (m, 6H), 1.93 (s, 1H), 3.3–3.5 (m, 1H), 4.0–4.2 (m, 1H), 7.1–7.3 (m, 3H), 7.4–7.6 (m, 2H). (Calc for $C_{11}H_{14}OSe$: C, 54.75; H, 5.85. Found: C, 54.55; H, 5.65%.)

trans-2-(*Phenylseleno*)*cyclohexanol* (**4b**). IR (film) 3480 cm^{-1}; NMR (400 MHz) δ 1.15–1.47 (m, 4H), 1.60–1.76 (m, 2H), 2.11–2.22 (m, 2H), 2.90 (ddd, 1H, J = 12.2, 10.3, 3.9 Hz), 2.92 (s, 1H), 3.33 (dt, 1H, J = 3.9, 10.3 Hz), 7.26–7.35 (m, 3H), 7.58–7.62 (m, 2H). (Calc for $C_{12}H_{16}OSe$: C, 56.45; H, 6.3. Found: C, 56.2; H, 6.45%.)

trans-2-(*Phenylseleno*)*cycloheptanol* (**4c**). IR (film) 3440 cm^{-1}; NMR (400 MHz) δ 1.35–1.73 (m, 8H), 1.95–2.04 (m, 1H), 2.18–2.25 (m, 1H), 2.77 (br s, 1H), 3.11 (ddd, 1H, J = 10.3, 9.3, 3.4 Hz), 3.59 (ddd, 1H, J = 9.3, 7.8, 3.9 Hz), 7.25–7.34 (m, 3H), 7.57–7.61 (m, 2H). (Calc for $C_{13}H_{18}OSe$: C, 58.0; H, 6.75. Found: C, 58.0; H, 6.7%.)

trans-2-(*Phenylseleno*)*cyclooctanol* (**4d**). IR (film) 3450 cm^{-1}; NMR (100 MHz) δ 1.1–2.4 (m, 12H), 2.88 (br s, 1H), 3.31 (ddd, 1H, J = 10.0, 8.1, 2.8 Hz), 3.70 (dt, 1H, J = 10.0, 4.3 Hz), 7.1–7.35 (m, 3H), 7.5–7.65 (m, 2H). (Calc for $C_{14}H_{20}OSe$: C, 59.35; H, 7.1. Found: C, 59.2; H, 7.0%.)

1-(*Phenylseleno*)-2-*methyl*-2-*propanol* (**5**). IR (film) 3410 cm^{-1}; NMR (60 MHz) δ 1.28 (s, 6H), 2.39 (br s, 1H), 3.09 (s, 2H), 7.05–7.35 (m, 3H), 7.35–7.65 (m, 2H). (Calc for $C_{10}H_{14}OSe$: C, 52.4; H, 6.15. Found: C, 52.15; H, 6.2%.)

1-*Methyl*-2-(*phenylseleno*)*cyclohexanol* (**6**). IR (film) 3490 cm^{-1}; NMR (60 MHz) δ 1.30 (s, 3H), 1.1–2.4 (m, 8H), 2.58 (br s, 1H), 3.16 (dd, 1H, J = 10, 4 Hz), 7.1–7.4 (m, 3H), 7.5–7.7 (m, 2H). (Calc for $C_{13}H_{18}OSe$: C, 58.0; H, 6.75. Found: C, 57.55; H, 7.0%.)

2,3-*Dimethyl*-3-(*phenylseleno*)-2-*butanol* (**7**). IR (film) 3520 cm^{-1}; NMR (60 MHz) δ 1.33 (s, 6H), 1.39 (s, 6H), 2.44 (br s, 1H), 7.1–7.4 (m, 3H), 7.5–7.8 (m, 2H). (Calc for $C_{12}H_{18}OSe$: C, 56.05; H, 7.05. Found: C, 55.6; H, 7.25%.)

(*Phenylseleno*)*acetone* (**8b**). IR (film) 1700 cm^{-1}; NMR (60 MHz) δ 2.24 (s, 3H), 3.55 (s, 2H), 7.1–7.4 (m, 3H), 7.5–7.7 (m, 2H). (Calc for $C_9H_{10}OSe$: C, 50.7; H, 4.75. Found: C, 51.1; H, 4.85%.)

trans-2-*Chloro*-3-(*phenylseleno*)*bicyclo*[2.2.1]*heptane* (**9**). NMR (400 MHz) δ 1.33–1.50 (m, 3H), 1.69 (tt, 1H, J = 3.9, 12.7 Hz), 1.80 (dddd, 1H, J = 1.5, 2.4, 3.9, 10.3 Hz), 1.99 (dddd, 1H, J = 2.4, 3.9, 8.8, 12.7 Hz), 2.34 (br d, 1H, J = 3.4 Hz), 2.46 (dt, 1H, J = 1.0, 3.9 Hz), 3.12 (dd, 1H, J = 2.9, 3.9 Hz), 4.18 (dt, 1H, J = 2.0, 3.9 Hz), 7.24–7.29 (m, 3H), 7.54–7.59 (m, 2H). (Calc for $C_{13}H_{15}ClSe$: C, 54.65; H, 5.3. Found: C, 54.6; H, 5.25%.)

3-(*Phenylseleno*)*bicyclo*[2.2.1]*heptan*-2-*ol* (**10**). IR (film) 3400 cm^{-1}; NMR (400 MHz) δ 1.10–1.21 (m, 2H), 1.49–1.61 (m, 2H), 1.88–1.96 (m, 2H), 2.39–2.45 (m, 2H), 2.7–2.8 (br s, 1H), 3.23 (br s, 1H), 3.81 (dt, 1H, J = 1.5, 4.4 Hz), 7.22–7.28 (m, 3H), 7.53–7.59 (m, 2H). (Calc for $C_{13}H_{16}OSe$: C, 58.45; H, 6.05. Found: C, 58.5; H, 6.05%.)

Hydroxyselenation of isoprene

Representative procedure for hydroxyselenation of conjugated dienes. To a cooled (−40°) soln of isoprene (15 mmol, 1.0 g) in THF (15 ml) was added dropwise a soln of phenylselenenyl chloride (5 mmol, 0.96 g) in acetonitrile (15 ml) and the resulting pale yellow mixture was stirred at the same temp for 1 hr. Water (6 ml) was added and the mixture was stirred at ambient temp for 20 hr. After the work-up as described above, column chromatography (Wakogel C-200, hexane/hexane–EtOAc (5:1) as eluent) afforded diphenyl diselenide (0.16 g, 0.5 mmol; 20%) and a mixture of **11** and **12** (0.96 g, 4.0 mmol; 80%). GLC analysis of this mixture revealed the isomer ratio of **11**:**12** to be 74:26. The mixture of **11** and **12** was methylated using NaH and MeI[34] and the products were confirmed to be identical to the authentic samples of 2-methyl-3-methoxy-4-(phenylseleno)-1-butene and 3-methyl-3-methoxy-4-(phenylseleno)-1-butene respectively.

Spectral and combustion analytical data of other hydroxyselenated compounds of conjugated diolefins are as follows.

4-(*Phenylseleno*)-1-*buten*-3-*ol* (**13a**). IR (film) 3400, 1643 cm^{-1}; NMR (60 MHz) δ 2.70 (br s, 1H), 2.94 (d, 1H, J = 8 Hz), 2.98 (d, 1H, J = 6 Hz), 4.12 (br q, 1H, J = 6 Hz), 5.01 (br dd, 1H, J = 10, 2 Hz), 5.15 (dd, 1H, J = 16, 2 Hz), 5.80 (ddd, 1H, J = 16, 10, 6 Hz), 7.1–7.3 (m, 3H), 7.3–7.6 (m, 2H). (Calc for $C_{10}H_{12}OSe$: C, 52.85; H, 5.3. Found: C, 52.4; H, 5.25%.)

2,3-*Dimethyl*-4-(*phenylseleno*)-1-*buten*-3-*ol* (**13b**). IR (film) 3460, 1643 cm^{-1}; NMR (60 MHz) δ 1.37 (s, 3H), 1.70 (d, 3H, J = 1 Hz), 2.58 (br s, 1H), 3.01 (d, 1H, J = 12 Hz), 3.34 (d, 1H, J = 12 Hz), 4.77 (q, 1H, J = 1 Hz), 5.00 (s, 1H), 7.0–7.3 (m, 3H), 7.3–7.6 (m, 2H). (Calc for $C_{12}H_{16}OSe$: C, 56.45; H, 6.35. Found: C, 56.5; H, 6.3%.)

4-(*Phenylseleno*)-1-*cycloocten*-3-*ol* (**14**). IR (film) 3240, 1640 cm^{-1}; NMR (60 MHz) δ 1.0–2.4 (m, 8H), 2.86 (br s, 1H), 2.95–3.35 (m, 1H), 4.44 (dd, 1H, J = 11, 6 Hz), 5.3–5.8 (m, 2H), 7.0–7.3 (m, 3H), 7.4–7.7 (m, 2H). (Calc for $C_{14}H_{18}OSe$: C, 59.8; H, 6.45. Found: C, 59.65; H, 6.35%.)

Preparation of 2-[(*phenylseleno*)*methyl*]-4-(*phenylseleno*)*oxolane* (**19**)

General procedure for the preparation of cyclic ethers from non-conjugated dienes. To a pale yellow soln of phenylselenenyl chloride (10 mmol, 1.9 g) in acetonitrile–water (15 + 3 ml) was added 1,4-pentadiene (5.0 mmol, 0.34 g) and the resulting soln was stirred under reflux for 5 hr. After the work-up as described above, column chromatography (Wakogel C-200, hexane/hexane–EtOAc (5:1) as eluant) afforded diphenyl diselenide (0.32 g, 1.0 mmol; 20%) and a mixture (*ca* 1:1) of *cis*- and *trans*-**19** (0.98 g, 2.5 mmol; 50%). **19**: IR (film) 1070, 1020 cm^{-1}; ^{1}H-NMR (60 MHz) δ 2.0–2.3 (m, 2H), 2.8–3.2 (m, 2H), 3.5–4.4 (m, 4H), 7.1–7.7 (m, 10H); ^{13}C-NMR δ 32.5 (t, two signals overlapped), 38.5 (d), 38.8 (d), 38.8 (t), 39.1 (t), 73.7 (t), 74.0 (t), 77.6 (d), 78.4 (d) and phenyl signals. (Calc for $C_{17}H_{18}OSe_2$: C, 51.55; H, 4.6. Found: C, 51.3; H, 4.55%.) Spectral as well as combustion analytical data of other cyclic ethers are as follows.

2,7-*Bis*[(*phenylseleno*)*methyl*]*oxepane* (**20**). IR (film) 1095 cm^{-1}; ^{1}H-NMR (60 MHz) δ 1.0–2.2 (m, 8H), 2.5–3.3 (m, 4H), 3.3–4.0 (m, 2H), 7.1–7.7 (m, 10H); ^{13}C-NMR δ 25.0 (t), 27.0 (t), 33.8 (t), 34.2 (t), 35.6 (t), 35.9 (t), 74.6 (d), 79.8 (d) and phenyl signals. (Calc for $C_{20}H_{24}OSe_2$: C, 54.8; H, 5.5. Found: C, 54.8; H, 5.65%.)

4,4-*Bis*(*ethoxycarbonyl*)-2,6-*bis*[(*phenylseleno*)*methyl*]*oxane* (**26**). IR (film) 1732 cm^{-1}; ^{1}H-NMR (60 MHz) δ 1.0–1.4 (m, 6H), 1.5–2.7 (m, 4H), 2.7–3.3 (m, 4H), 3.3–3.9 (m, 2H), 4.08 (q, 4H, J = 7 Hz), 7.1–7.7 (m, 10H); ^{13}C-NMR δ (*cis*-**26**) 13.9 (q), 32.8 (t), 35.4 (t), 53.4 (s), 61.4 (t), 73.7 (d), 169.9 (s), 171.0 (s) and phenyl signals; (*trans*-**26**) 13.9 (q), 31.5 (t), 33.0 (t), 50.8 (s), 61.6 (t), 68.9 (d), 169.9 (s), 170.5 (s) and phenyl signals. (Calc for $C_{25}H_{30}O_5Se_2$: C, 52.85; H, 5.3. Found: C, 52.5; H, 5.2%.)

2,7 - *Dioxa* - 4,8 - *bis*[(*phenylseleno*)*methyl*]*spiro*[4.4]*nona* - 1,6 - *dione* (**27**). IR (KBr disc) 1767, 1749 (sh) cm^{-1}; ^{1}H-NMR (60 MHz) δ 1.8–2.9 (m, 4H), 2.9–3.6 (m, 4H), 4.3–5.2 (m, 2H), 7.1–7.7 (m, 10H); ^{13}C-NMR δ (**27a**) 31.1 (t), 31.4 (t), 37.3 (t), 39.4 (t), 53.1 (s), 77.9 (d), 172.7 (s) and phenyl signals; (**27b**) 31.7 (t), 38.2 (t), 53.4 (s), 77.4 (d), 173.1 (s) and phenyl signals; (**27c**) 30.8 (t), 38.5 (t), 52.4 (s), 78.1 (d), 173.5 (s) and phenyl signals. (Calc for $C_{21}H_{20}O_4Se_2$: C, 51.05; H, 4.1. Found: C, 51.15; H, 4.15%.)

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