Formation of Cyclopropanes and Epoxides from Vinylselenonium Salts

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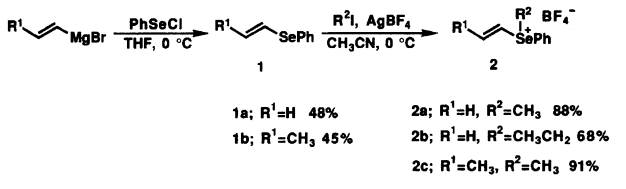
Treatment of vinyl- and (5-oxo-1-cyclopentenyl)selenonium tetrafluoroborates **2** and **4** with a variety of carbanions gives cyclopropane derivatives **3** and **5** in good yields. The reaction of vinylselenonium salt **2** with sodium alkoxides in the presence of aldehydes gives various kinds of glycidyl ethers **7** in excellent yields. The reaction of **2** with hydroxyacetone in the presence of K_2CO_3 affords cyclized products **8** and **9** together with the Michael addition product **10**.

Recent developments in organoselenium chemistry can be attributed to the specific properties of the arylseleno group which satisfy the requirements for the construction of hardly obtainable synthetic intermediates.[1] We have demonstrated several interesting reaction features of organoselenium compounds in the radical reaction,[2] in the selenation reaction,[3] and in the aldol reaction.[4] In the course of our study we have paid attention to the synthetic utility of vinylselenonium salts which could be efficient acceptors for the conjugate addition of nucleophiles to form selenonium ylides. In contrast to the studies on the synthetic utility of sulfonium salts and their ylides[5] for key steps such as cyclopropanations and epoxidations,[6] to our knowledge, little is known about the generation of selenonium ylides using the conjugate addition. We describe herein the convenient preparation of cyclopropanes and epoxides using selenonium ylides generated by the conjugate addition to vinyl selenonium salts.

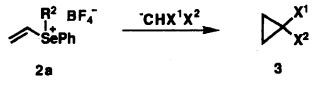
Results and Discussion

Methylphenylvinylselenonium tetrafluoroborate (**2a**) was prepared as follows. To a solution of phenyl vinyl selenide (**1a**)[7] (1 mmol) and methyl iodide (5 mmol) in acetonitrile (3 ml) was added silver tetrafluoroborate (1 mmol) portionwise at 0 °C. After 5 h silver iodide precipitated was removed by filtration and the solution was concentrated to give the crude vinyl selenonium salt which was recrystallized from CH_2Cl_2 to give the pure salt in 88% yield. Ethylphenylvinylselenonium salt (**2b**) and methylphenyl(1-propenyl)selenonium salt (**2c**) were prepared in a similar manner, but they were used without recrystallization for further transformation (Eq. 1).

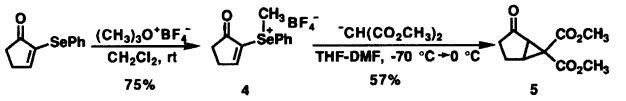


(1)

We first explored the cyclopropane formation reaction by treatment of the selenonium salt **2** with a variety of carbanions. The results are shown in Table 1. Methylphenylvinylselenonium salt (**2a**) was treated with an equimolar amount of sodium salt of dimethyl malonate in THF containing HMPA or DMF at −70 °C and then the reaction mixture was allowed to warm up to 0 °C over 2 h. After work-up dimethyl 1,1-cyclopropanedicarboxylate (**3a**) was obtained in 57% yield. Polar solvents such as HMPA or DMF which dissolve selenonium salts improved the yield of the cyclopropanation. The reaction of ethylphenylvinylselenonium salt (**2b**) also gave **3a** in 63% yield. Treatment of methylphenylvinylselenonium salt (**2a**) with carbanions derived from malononitrile, methylthiomethyl methyl sulfoxide, and 1,3-dithiane, provided the disubstituted cyclopropanes **3b**, **3c**, and **3d** in good yields. The reaction of **2a** with the lithium enolate derived from acetophenone gave the cyclopropyl ketone **3e** in 50% yield (Eq. 2 and Table 1). Methyl(5-oxo-1-cyclopentenyl)phenylselenonium tetrafluoroborate (**4**), easily obtainable by treatment of 2-phenylseleno-2-cyclopenten-1-one with trimethyloxonium tetrafluoroborate, afforded dimethyl 2-oxobicyclo[3.1.0]hexane-6,6-dicarboxylate (**5**) in 57% yield (Eq. 3).



(2)

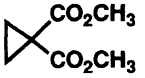
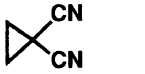
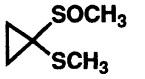
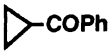


(3)

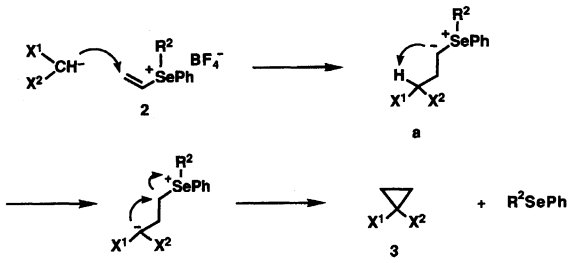
The success of the cyclopropanation reaction starting with vinylselenonium salts is apparently due to the characteristic features of the selenonium moiety; the electron-withdrawing selenonium not only activates the double bond for the conjugate addition but also facilitates the intramolecular substitution as a good leaving group. Thus the reaction rationally occurs through the pathway as outlined in Scheme 1. Conjugate addition of a nucleophile to the vinylselenonium salt **2** forms the selenonium ylide **a**, and the subsequent intramolecular proton transfer followed by the cyclopropane formation with removal of alkyl phenyl selenide gives the cyclopropane **3**.

Since the selenonium ylide **a** should be formed during the reaction according to this mechanism, we next

Table 1. Preparation of Cyclopropanes **3** by Treatment of Selenonium Salts **2** with Nucleophiles

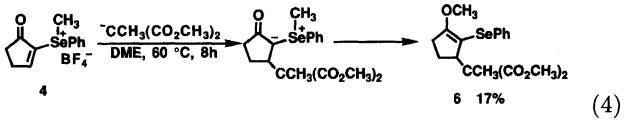
Nucleophile	Selenonium salt	Reaction conditions[a] Reaction temp	Reaction time/h	Product		Yield(%)
$^-CH(CO_2CH_3)_2$	**2a**	−50 °C	3[b]			55
	2a	−70 °C ⟶ 0 °C	2		**3a**	57
	2b	−70 °C ⟶ 0 °C	3			63
$^-CH(CN)_2$	**2a**	−70 °C ⟶ 0 °C	1.5		**3b**	47
$^-CH(SOCH_3)SCH_3$	**2a**	−70 °C ⟶ 0°C	2		**3c**	61
	**2a**	−70 °C ⟶ 0 °C	3		**3d**	40
$^-CH_2COPh$	**2a**	−70 °C ⟶ 0 °C	3		**3e**	50

a) THF–HMPA was used otherwise noted. b) THF–DMF was used.



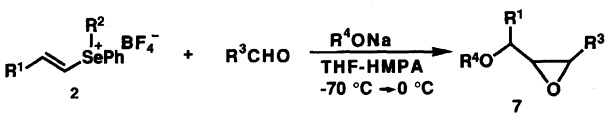
Scheme 1.

examined the trapping of the selenonium ylide with an aldehyde, expecting the formation of the oxirane. Sodium salt of dimethyl malonate was added to a solution of the methylphenylvinylselenonium salt (**2a**) in THF–HMPA in the presence of 3 equivalents of benzaldehyde at −70 °C, and the reaction mixture was gradually warmed to −30 °C. The compound which we could isolate from the reaction mixture, however, was only the cyclopropane dicarboxylate **3a**. We could not observe the formation of any detectable amount of the oxirane compound. This showed that the proton transfer from the acidic methine to the ylide predominated over the trapping of the ylide with the aldehyde. We therefore investigated the reaction with sodium salt of dimethyl methylmalonate which has no acidic protons. In this reaction sodium salt of dimethyl methylmalonate did not give the conjugate addition product with the selenonium salt **2a** in 1,2-dimethoxyethane (DME) in the presence of benzaldehyde but attacked the methyl group of **2a** to produce the parent vinyl selenide **1**. When methyl(5-oxo-1-cyclopentenyl)phenylselenonium salt (**4**) was treated with sodium salt of dimethyl methylmalonate at 60 °C, it gave a complex mixture of products from which compound **6** was isolated in 17% yield. Compound **6** is formed possibly via the methyl rearrangement from the methylselenonium salt to the enolate (Eq. 4).[8]



(4)

In light of difficulties with carbon anions we turned our attention to alkoxide anions which apparently have no acidic protons.[9] Thus to a solution of the methylphenylvinylselenonium salt (**2a**) in THF–HMPA was added a solution of sodium allyl oxide in THF at −70 °C. After confirming the disappearance of the salt **2a** by TLC, benzaldehyde was added and then the reaction mixture was gradually warmed to 0 °C over 6 h. In this manner allyl 2,3-epoxy-3-phenylpropyl ether (**7a**) was obtained in 27% yield. The yield was improved to 70% when sodium allyl oxide was added to a solution of the selenonium salt **2a** in the presence of 3-fold excess amount of benzaldehyde. Possible mechanism to afford the glycidyl ether is shown in Scheme 2. As shown in Table 2 other alkoxides such as benzyl, 2,2,2-trichloroethyl, cinnamyl, and 2-phenylethyl oxides also gave glycidyl ethers, **7b**, **7d**, **7e**, and **7f** in good yields (Eq. 5). From GLC analyses all these products were shown to be a ca. 1 : 1 mixture of *cis* and *trans* isomers. The reaction of the (1-propenyl)selenonium salt **2c** with sodium allyl oxide gave the glycidyl ether **7c** in 47% yield. When sodium phenoxide or methoxide was reacted with **2a**, it gave no adducts but led to the quantitative formation of the vinyl selenide **1a**.

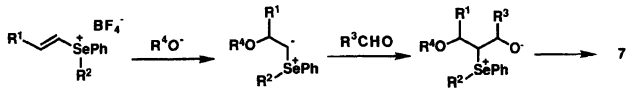


(5)

Table 2. Preparation of Glycidyl Ethers **7** by Treatment of Selenonium Salts **2** with Alkoxides and Aldehydes

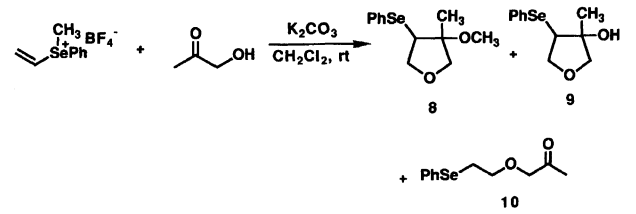
R^1	R^2	R^3	R^4	Reaction time (h)	Product	Yield(%)[a]	trans : cis [b]
H	CH_3	Ph	Allyl	4	**7a**	70	50.8 49.2
H	CH_3CH_2	Ph	Allyl	4	**7a**	88	51.1 48.9
H	CH_3CH_2	Ph	$PhCH_2$	3	**7b**	73	53.4 47.6
CH_3	CH_3	Ph	Allyl	5	**7c**	47	—[c]
H	CH_3CH_2	Ph	CCl_3CH_2	3	**7d**	63	51.9 48.1
H	CH_3CH_2	CH_3CH_2	$PhCH{=}CHCH_2$	5	**7e**	72	52.5 47.5
H	CH_3	$(CH_3)_2CH$	$PhCHCH_3$	5	**7f**	63	51.0 49.0

a) Isolated yield. b) Determined by GLC. c) Not determined.



Scheme 2.

The [2-(allyloxy)ethyl]selenonium salt, formed by the conjugate addition with allyl oxide, failed to react with ketones such as cyclohexanone, but it was found to react with a ketone carbonyl intramolecularly. When the selenonium salt **2a** was treated with hydroxyacetone in the presence of potassium carbonate at room temperature, the cyclized products **8** and **9** were obtained in 28 and 26% yields, respectively, together with the addition product **10** (24%) (Eq. 6).



(6)

The compounds **8** and **9** were apparently formed by the intramolecular cyclization of the ylide which was produced via the Michael addition of the alkoxide to the vinylselenonium salt. It should be noted that all these products are derived from the removal of methyl group of the selenonium salt instead of the loss of the selenonium moiety as a leaving group. The NOEDIF study of **8** and **9** showed the stereochemical disposition of the phenylseleno and hydroxyl or methoxyl groups. The NOEs were observed by the irradiation at the methyl protons of **8** (δ=1.22) at the C-4 methine proton (δ=3.41) attached to the phenylseleno group and by the irradiation at the methyl protons of **9** (δ=1.36) at C-4 methine proton (δ=3.50). These results suggest the *cis* configurations in both **8** and **9**, although uncertainty remains due to one of the diastereomers of **8** or **9** in hand. In summary, easily obtainable vinylselenonium tetrafluoroborates are shown to be good 2-carbon unit agents which provide convenient preparative methods for cyclopropyl compounds, glycidyl ethers, and tetrahydrofurans.

Experimental

General. Melting points are uncorrected. Infrared (IR) spectra were recorded on JASCO A-102 spectrometer; absorptions are given in reciprocal centimeter. Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a JEOL JNM-PMX-60si (60 MHz) or Varian XL-200 (200 MHz) or Gemini-200 (200 MHz) spectrometer, chemical shifts (δ) are expressed in per million downfield from internal tetramethylsilane. Mass spectra (eV) were determined on a Hitachi M-2000 spectrometer. Microanalyses were performed with a Perkin Elmer-240. Reactions involving air- or moisture-sensitive compounds were carried out in appropriate round-bottom flasks under nitrogen or argon. All reactions were monitored by thin-layer chromatography carried out on 0.25-mm Merck silica-gel plates (60-F254), with UV light and 7% phosphomolybdic acid in ethanol/heat as developing agent or acidic ethanol solution of 2,4-dinitrophenylhydrazine or *p*-anisaldehyde. Column chromatography was carried out with Fuji Devison Silica gel BW-200. Analysis of the products and the reagents were performed with a Shimazu Chromatopac C-R3A instrument attached to Hitachi 063 gas chromatography (column; OV-17, 3 mm×2 m) and Shimadzu GC-9A gas chromatography on a CBP 10 (25 m×0.25 mm) capirary column.

Preparation of Vinyl Selenides. Phenyl Vinyl Selenide (1a).[10] To a THF solution of vinylmagnesium bromide (commercially available from Tokyo Kasei Co) (1.0 M solution, 30 ml, 30 mmol) was added a solution of benzeneselenenyl chloride (5.74 g, 30.0 mmol) in dry THF (10 ml) dropwise at 0 °C over 1 h (1 M=1 mol dm^{-3}). After having been stirred for an additional 1 h the reaction mixture was warmed to room temperature and stirred for 3 h. Then the reaction mixture was diluted with aqueous NH_4Cl and extracted with ether (3×50 ml). The etheral solution was dried over Na_2SO_4 and evaporated under reduced pressure. Purification by column chromatography (SiO_2, 50 g, hexane) gave the vinyl selenide **1a** (2.63 g, 48%). R_f=0.70 (hexane); ^{1}H NMR (CCl_4) δ=5.40 (1H, d, J=16 Hz), 5.67 (1H, d, J=10 Hz), 6.70 (1H, dd, J=16 and 10 Hz), and 6.97—7.50 (5H, m); IR (neat) 3050, 1570, 1470, 1430, 1365, 1245, 1060, 1020, 995, 950, 880, and 730 cm^{-1}.

Phenyl 1-Propenyl Selenide (1b).[11] Diphenyl diselenide (6.00 g, 19.22 mmol), was added portionwise to an ice-cooled solution of 1-propenylmagnesium bromide, prepared from magnesium (1.00 g, 41.14 mmol) and 1-bromo-

1-propene (3.7 ml, 43.21 mmol) in THF (40 ml). After having been stirred for 1 h the reaction mixture was allowed to warm to room temperature and stirred for an additional 3 h. Usual work-up and column chromatography (SiO_2, 100 g, hexane) gave **1b** (3.64 g, 45%). R_f=0.68 (hexane); ^{1}H NMR (CCl_4) δ=1.77 (3H, d, J=6 Hz), 5.77—6.50 (2H, m), and 7.10—7.53 (5H, m); IR (neat) 3050, 3000, 2900, 1605, 1570, 1470, 1430, 1370, 1305, 1210, 1065, 1020, 930, and 730 cm^{-1}.

Preparation of the Selenonium Salt. Methylphenylvinylselenonium Tetrafluoroborate (2a). To an ice-cooled solution of phenyl vinyl selenide (2.02 g, 11.00 mmol) and methyl iodide (5 ml, 80.32 mmol) in acetonitrile (5 ml) was added silver tetrafluoroborate (2.50 g, 12.20 mmol). The mixture was stirred for 5 h during which time silver iodide was precipitated. The precipitate was filtered and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure to leave a white solid, which was recrystallized from CH_2Cl_2–hexane to give **2a** (2.77 g, 88%). Mp 83—83.5 °C; ^{1}H NMR ($(CD_3)_2SO$) δ=3.12 (3H, s), 6.30 (1H, dd, J=16 and 2 Hz), 6.42 (1H, dd, J=8 and 2 Hz), 7.05 (1H, dd, J=16 and 8 Hz), and 7.48—7.88 (5H, m); IR (KBr) 3150, 3050, 1590, 1480, 1445, 1295, 1275, 1240, 1110, 1065, 1035, 975, 945, and 760 cm^{-1}. Anal. Found: C, 37.90; H, 3.90%. Calcd for $C_9H_{11}BF_4Se$; C, 37.93; H, 3.89%.

Ethylphenylvinylselenonium Tetrafluoroborate (2b). To a mixture of **1a** (0.492 g, 2.687 mmol) and ethyl iodide (0.6 ml, 7.50 mmol) in acetonitrile (3 ml) was added silver tetrafluoroborate (0.61 g, 3.13 mmol) portionwise at 0 °C and the mixture was stirred overnight at room temperature. Precipitated silver iodide was filtered and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure to give the residue which was purified by column chromatography (SiO_2, CH_2Cl_2–CH_3OH 95:5) to give **2b** as yellow oil (546 mg, 68%). ^{1}H NMR ($(CD_3)_2SO$) δ=1.45 (1.5H, t, J=7.0 Hz), 1.50 (1.5H, t, J=7.0 Hz), 3.50—4.07 (2H, m), 6.40 (0.5H, d, J=17 Hz), 6.45 (0.5H, d, J=17 Hz), 6.57 (0.5H, d, J=8.0 Hz), 6.61 (0.5H, d, J=8.0 Hz), 7.17 (1H, dd, J=17 and 8.0 Hz), and 7.60—8.00 (5H, m); IR (neat) 3050, 2950, 1575, 1480, 1440, 1380, 1230, 1050, and 740 cm^{-1}.

Methylphenyl(1-propenyl)selenonium Tetrafluoroborate (2c). To a mixture of **1b** (1.23 g, 6.24 mmol) and methyl iodide (2 ml) in acetonitrile (7 ml) was added silver tetrafluoroborate (1.48 g, 7.45 mmol) portionwise at 0 °C and the mixture was stirred for 3 h. Precipitated silver iodide was filtered and the filtrate was concentrated under reduced pressure. The residue was washed with a mixed solvent (hexane–ethyl acetate=9:1) three times and dried over P_2O_5 under reduced pressure to give **2c** (1.70 g, 91%). ^{1}H NMR ($(CD_3)_2SO$) δ=2.13 (3H, d, J=6 Hz), 3.25 (3H, s), 6.40—7.03 (2H, m), and 7.45—7.90 (5H, m); IR (neat) 3050, 1620, 1575, 1480, 1440, 1380, 1310, 1280, 1080, 1050, 940, and 740 cm^{-1}.

Dimethyl 1,1-Cyclopropanedicarboxylate[12] (3a). To a suspension of sodium hydride (18.6 mg, 0.775 mmol) in THF (2 ml) was added dimethyl malonate (93 mg, 0.704 mmol) at 0 °C. After having been stirred for 10 min, the reaction mixture was cooled to −70 °C and a solution of methylphenylvinylselenonium tetrafluoroborate (200 mg, 0.702 mmol) in a mixed solvent (THF:HMPA=9:1, 1 ml) was added. The mixture was stirred for 1.5 h at that temperature and then the cooling bath was removed. After having been stirred for an additional 2 h, the mixture was quenched with water and the aqueous layer was extracted with ether (3×20 ml). The combined organic layers were washed with saturated NaCl, dried over anhydrous $MgSO_4$, and then concentrated to give a crude oil, which was purified by column chromatography (SiO_2, hexane:AcOEt=8:2) to afford **3a** (61 mg, 55%). R_f=0.32 (hexane:AcOEt=8:2); ^{1}H NMR (CCl_4) δ=1.30 (4H, s) and 3.67 (6H, s); IR (neat) 3010, 2960, 1720, 1435, 1310, 1205, 1125, 990, 940, 880, and 750 cm^{-1}; MS m/z 157 (M^+).

1,1-Dicyanocyclopropane[13] (3b). The reaction was carried out as described above using **2a** (265 mg, 0.930 mmol) and sodiomalononitrile prepared from malononitrile (62 mg, 0.939 mmol) and sodium hydride (23 mg, 0.958 mmol). Purification by column chromatography (SiO_2, hexane:AcOEt=1:1) afforded **3b** (40 mg, 47%). R_f=0.21 (hexane:AcOEt=1:1); ^{1}H NMR ($CDCl_3$) δ=1.81 (4H, s); IR (neat) 2950, 2300, and 1460 cm^{-1}; MS m/z 92 (M^+).

1-Methylsulfinyl-1-(methylthio)cyclopropane[14] (3c). The reaction was carried out as described above using **2a** (285 mg, 1.00 mmol) and sodio derivative of FAMSO (methyl methyltiomethyl sulfoxide) prepared from FAMSO (124 mg, 0.998 mmol) and sodium hydride (24 mg, 1.00 mmol). Purification by column chromatography (SiO_2, hexane:AcOEt=7:3) afforded **3c** (91 mg, 61%). R_f=0.10 (hexane:AcOEt=1:1); ^{1}H NMR ($CDCl_3$) δ=0.88—1.60 (4H, m), 2.25 (3H, s), and 2.56 (3H, s); IR (neat) 2980, 2900, 1420, and 1050 cm^{-1}; MS m/z 150 (M^+).

4,8-Dithiaspiro[2.5]octane[15] (3d). To a solution of 1,3-dithiane (62 mg, 0.500 mmol) in dry THF (1.8 ml) was added n-BuLi (1.53 M hexane solution, 0.36 ml, 0.551 mmol) at −70 °C and the mixture was stirred for 1 h. A solution of **2a** (125 mg, 0.439 mmol) in dry DMF (0.2 ml) was then added and the mixture was allowed to react for 3 h at −70 °C. Purification by column chromatography (SiO_2, hexane:AcOEt=8:2) afforded **3d** (29 mg, 40%). R_f=0.35 (hexane:AcOEt=8:2); ^{1}H NMR ($CDCl_3$) δ=1.20 (1H, d, J=6.0 Hz), 1.45 (1H, d, J=6.0 Hz), 1.85—2.22 (2H, m), and 2.70—2.90 (4H, m); IR (neat) 2920, 2850, 1575, 1460, and 1095 cm^{-1}; MS m/z 146 (M^+).

Benzoylcyclopropane[16] (3e). To a solution of the lithium enolate, prepared from (30 μl, 0.257 mmol) of acetophenone and 1 equivalent of LDA, was added **2a** (65 mg, 0.228 mmol) and allowed to react for 3 h. Purification by column chromatography (SiO_2, hexane:AcOEt=95:5) afforded **3e** (16.7 mg, 50%). R_f=0.45 (hexane:AcOEt=9:1); ^{1}H NMR (CCl_4) δ=0.72—1.25 (4H, m), 2.25—2.75 (1H, m), 7.30—7.50 (3H, m), and 7.80—8.05 (2H, m); IR (neat) 2980, 2900, and 1660 cm^{-1}.

Methyl(5-oxo-1-cyclopentenyl)phenylselenonium Tetrafluoroborate (4). To a solution of 2-phenylseleno-2-cyclopenten-1-one[17] (0.163 mg, 0.682 mmol) in dry CH_2Cl_2 (2 ml) trimethyloxonium tetrafluoroborate (131 mg, 0.887 mmol) was added portionwise at 0 °C, and the mixture was stirred for 3 h. Then the solvent was evaporated to leave a crude oil which was washed with ether 3 times giving **4** (0.237 mg, 92%). ^{1}H NMR (CD_3OD) δ=2.50—2.77 (2H, m), 2.90—3.09 (2H, m), 3.35 (3H, s), 7.51—7.93 (5H, m), and 8.53 (1H, t, J=3.0 Hz); IR (neat) 1050 and 1700 cm^{-1}.

Dimethyl 2-Oxobicyclo[3.1.0]hexane-6,6-dicarboxylate (5). To a solution of sodium salt of dimethyl malonate in THF–DMF (10:1, 0.9 ml), prepared from di-

methyl malonate (42.3 mg, 0.320 mmol) and sodium hydride (12.8 mg, 0.320 mmol), was added **4** (108 mg, 0.320 mmol) in DMF (0.1 ml) at −70 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h. Then sat. NH_4Cl (5 ml) and water (5 ml) were added and aqueous layer was extracted with ether (3×10 ml). The combined organic solutions were washed, dried over $MgSO_4$, and evaporated under reduced pressure to give an oil which was purified by column chromatography (SiO_2, hexane : AcOEt=9 : 1) giving **5** (38.8 mg, 57%). ^1H NMR (CCl_4) δ=1.71—2.75 (6H, m) and 3.76 (6H, m); IR (neat) 1730, 1718, and 1230 cm^{-1}; MS m/z 212 (M^+). Anal. Found: C, 56.82; H, 5.90%. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70%.

The Reaction of the Selenonium Salt 4 with Sodium Salt of Dimethyl Methylmalonate. To an ice-cooled solution of the selenonium salt **4** (0.166 g, 0.490 mmol) and benzaldehyde (156 mg, 1.47 mmol) in DME (1 ml) was added a solution of sodium salt of dimethyl methylmalonate in DME (1 ml), prepared from dimethyl methylmalonate (166 mg, 0.490 mmol) and sodium hydride (11.8 mg, 0.490 mmol), and then the mixture was heated at 60 °C for 5 h. To the cooled mixture was added sat. NH_4Cl (5 ml) and water (5 ml) and the aqueous layer was extracted with ether (3×10 ml). The combined organic layers were washed, dried over $MgSO_4$, and evaporated under reduced pressure. Purification by column chromatography (SiO_2, hexane : AcOEt=9 : 1 and then 8 : 2) afforded dimethyl 2-[3-methoxy-2-(phenylseleno)-2-cyclopentenyl]-2-methylpropanedioate **6** (33.2 mg, 17%). ^1H NMR (CCl_4) δ=1.45 (3H, s), 1.57—2.69 (5H, m), 3.68 (6H, s), 3.85—4.33 (3H, m), and 7.93—8.35 (5H, m); IR (neat) 1680 and 1700 cm^{-1}; MS m/z 398 (M^+ for ^{79}Se) and 396 (M^+ for ^{77}Se). Anal. Found: C, 54.67; H, 5.72%. Calcd for $C_{18}H_{22}O_5Se$: C, 54.41; H, 5.58%.

3-Allyloxy-1,2-epoxy-1-phenylpropane (7a). a) To a suspension of **2a** (86 mg, 0.302 mmol) and benzaldehyde (92 μl, 0.902 mmol) in THF–HMPA (10 : 1, 0.7 ml) was added dropwise at −50 °C sodium allyl oxide, prepared from allyl alcohol (61 μl, 0.897 mmol) and sodium hydride (22 mg, 0.917 mmol) in THF–HMPA (10 : 1, 0.5 ml). The reaction mixture was stirred for 2 h at −50 °C and for an additional 2 h at 0 °C. Usual work-up and purification by column chromatography (SiO_2, hexane : AcOEt=9 : 1) afforded **7a** (40 mg, 70%). R_f=0.52 (hexane : AcOEt=9 : 1); ^1H NMR (CCl_4) δ=2.87—3.40 (2H, m), 3.50—4.07 (4H, m), 4.63—6.15 (3H, m), 7.20 (2.5H, s), and 7.25 (2.5H, s); IR (neat) 3000, 2850, 1640, 1600, 1490, 1450, 1240, 1090, 985, 920, and 875 cm^{-1}. Anal. Found: C, 75.58; H, 7.38%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%. b) The reaction of **2b** (55 mg, 0.184 mmol), benzaldehyde (50 μl, 0.551 mmol), and sodium allyl oxide prepared from allyl alcohol (35 μl, 0.515 mmol) and sodium hydride (12.6 mg, 0.525 mmol) afforded **7a** (31 mg, 88%).

3-Benzyloxy-1,2-epoxyl-1-phenylpropane (7b). The reaction of **2b** (61 mg, 0.204 mmol), benzaldehyde (62 μl, 0.608 mmol), and sodium benzyl oxide prepared from benzyl alcohol (63 μl, 0.609 mmol) and sodium hydride (15 mg, 0.625 mmol) afforded, after purification by column chromatography (SiO_2, hexane : AcOEt=97 : 3), **7b** (36 mg, 73%). R_f=0.43 (hexane : AcOEt=9 : 1); ^1H NMR (CCl_4) δ=3.13—4.20 (4H, m), 4.43 (1H, s), 4.63 (1H, s), 7.20 (5H, s), and 7.30 (5H, s); IR (neat) 3040, 3000, 2860, 1605, 1500, 1450, 1360, 1205, 1025, 995, 880, and 740 cm^{-1}. Anal. Found: C, 79.61; H, 6.81%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

3-Allyloxy-1,2-epoxy-1-phenylbutane (7c). A mixture of **2c** (103 mg, 0.345 mmol), benzaldehyde (105 μl, 1.03 mmol) and sodium allyl oxide prepared from allyl alcohol (70 μl, 1.03 mmol) and sodium hydride (24 mg, 1.00 mmol) was allowed to react for 5 h. Purification by column chromatography (SiO_2, hexane : AcOEt=95 : 5) afforded **7c** (33 mg, 47%). R_f=0.5 (hexane : AcOEt=9 : 1); ^1H NMR (CCl_4) δ=1.22 (3H, d, J=6 Hz), 2.70—3.23 (2H, m), 3.40—3.72 (1H, m), 3.80—4.10 (2H, m), 4.87—6.10 (3H, m), 7.10 (2.5H, s) and 7.20 (2.5H, s); IR (neat) 3040, 2950, 2860, 1605, 1500, 1360, 1200, 1030, 990, 880, and 740 cm^{-1}. Anal. Found: C, 76.15; H, 7.85%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%.

1,2-Epoxy-1-phenyl-3-(2,2,2-trichloroethoxy)propane (7d). A mixture of **2b** (95 mg, 0.333 mmol), benzaldehyde (102 μl, 1.00 mmol), and sodium 2,2,2-trichloroethoxide, prepared from 2,2,2-trichloroethanol (96 μl, 1.00 mmol) and sodium hydride (24 mg, 1.00 mmol) was allowed to react for 3 h. Purification by column chromatography (SiO_2, hexane : benzene=1 : 1) afforded **7d** (59 mg, 63%). R_f=0.5 (hexane : AcOEt=9 : 1); ^1H NMR (CCl_4) δ=2.98—4.22 (6H, m), 7.15 (2.5H, s), and 7.20 (2.5H, s); IR (neat) 3050, 2980, 2870, 1590, 1500, 1450, 1370, 1200, 1030, 900, 880, and 760 cm^{-1}. Anal. Found: C, 46.73; H, 3.95%. Calcd for $C_{11}H_{11}Cl_3O_2$: C, 46.92; H, 3.94%.

1-Cinnamyloxy-2,3-epoxypentane (7e). A mixture of **2a** (96 mg, 0.321 mmol), butanal (70 μl, 0.970 mmol), and sodium cinnamyl oxide prepared from cinnamyl alcohol (124 μl, 0.961 mmol) and sodium hydride (23 mg, 0.958 mmol) was allowed to react for 5 h. Purification by column chromatography (SiO_2, hexane : AcOEt=95 : 5) afforded **7e** (50.5 mg, 72%). R_f=0.40 (hexane : AcOEt=9 : 1); ^1H NMR (CCl_4) δ=1.35 (3H, d, J=6.6 Hz), 1.40—2.18 (2H, m), 3.47—4.85 (6H, m), 6.70—6.95 (2H, m), and 7.15 (5H, s); IR (neat) 3050, 3000, 2850, 1610, 1500, 1440, 1360, 1200, 1030, 990, 870, and 760 cm^{-1}. Anal. Found: C, 76.95; H, 8.40%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

4-Methyl-1-(1-phenylethoxy)-2,3-epoxypentane (7f). A mixture of **2a** (228 mg, 0.800 mmol), isobutylaldehyde (220 μl, 2.41 mmol), and lithium 1-phenylethyoxide prepared from 1-phenylethanol (116 μl, 0.964 mmol) and *n*-BuLi (1.53 M hexane solution, 0.70 ml, 1.07 mmol) was allowed to react for 5 h. Purification by column chromatography (SiO_2, hexane : AcOEt=9 : 1) afforded **7f** (111 mg, 63%). R_f=0.45 (benzene); ^1H NMR (CCl_4) δ=1.17—1.85 (6H, m), 1.33 (3H, d, J=6.6 Hz), 1.45—2.00 (1H, m), 2.73—3.40 (2H, m), 3.47—4.10 (2H, m), 4.67 (1H, q, J=6.6 Hz), and 7.28 (5H, brs); IR (neat) 3050, 2950, 2860, 1580, 1450, 1360, 1240, 1030, 990, and 740 cm^{-1}. Anal. Found: C, 76.35; H, 9.25%. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%.

Reaction of the Vinylselenonium Salt 2a and Hydroxyacetone. A mixture of **2a** (230 mg, 0.807 mmol), hydroxyacetone (170 μl, 2.48 mmol) and potassium carbonate (335 mg, 2.42 mmol) in CH_2Cl_2 (3 ml) was stirred for 12 h at room temperature. The reaction mixture was quenched with water, and extracted with ether (3×30 ml). The combined organic solutions were washed with saturated NaCl, dried over Na_2SO_4, and concentrated under reduced pressure. The residual oil was subjected to column chromatography (SiO_2, 7 g, hexane : AcOEt=9 : 1 and then 8 : 2) to give

3-methoxy-3-methyl-4-(phenylseleno)tetrahydrofuran **8** (60 mg, 28%), 3-methyl-4-(phenylseleno)tetrahydro-3-furanol **9** (56 mg, 26%), and 1-[2-(phenylseleno)ethoxy]-2-propanone **10** (48 mg, 24%).

8: R_f=0.23 (hexane : AcOEt=8 : 2); ^{1}H NMR (200 MHz) ($CDCl_3$) δ=1.22 (3H, s), 3.28 (3H, s), 3.41 (1H, dd, J=7.7 and 10.0 Hz), 3.53 (1H, d, J=10.0 Hz), 4.06 (1H, t, J=7.8 Hz), 4.11 (1H, d, J=10.0 Hz), 4.22 (1H, t, J=7.8 Hz), 7.20—7.30 (3H, m), and 7.46—7.58 (2H, m); IR (neat) 3050, 2920, 2850, 1575, 1470, 1430, 1360, 1240, 1160, 1110, 1070, and 1040 cm^{-1}. Anal. Found: C, 53.28; H, 6.01%. Calcd for $C_{12}H_{16}O_2Se$: C, 53.14; H, 5.95%.

9: R_f=0.06 (hexane : AcOEt=8 : 2); ^{1}H NMR (200 MHz) ($CDCl_3$) δ=1.36 (3H, s), 2.42 (1H, brs), 3.50 (1H, dd, J=8.6 and 10.0 Hz), 3.72 (1H, d, J=8.7 Hz), 3.86 (1H, d, J=8.7 Hz), 3.92 (1H, t, J=9.3 Hz), 4.32 (1H, t, J=11.6 Hz), 7.22—7.32 (3H, m), and 7.53—7.60 (2H, m); IR (KBr) 3360, 1575, 1460, 1430, 1405, 1375, 1245, 1145, 1065, 1020, 940, 895, and 735 cm^{-1}. Anal. Found: C, 51.29; H, 5.37%. Calcd for $C_{11}H_{14}O_2Se$: C, 51.37; H, 5.49%.

10: R_f=0.15 (hexane : AcOEt=8 : 2); ^{1}H NMR (200 MHz) ($CDCl_3$) δ=2.12 (3H, s), 3.10 (2H, t, J=6.8 Hz), 3.73 (2H, t, J=6.8 Hz), 4.02 (2H, s), 7.22—7.30 (3H, m), and 7.47—7.55 (2H, m); IR (neat) 2900, 2850, 1710, 1575, 1475, 1430, 1350, 1110, and 730 cm^{-1}. Anal. Found: C, 51.50; H, 5.62%. Calcd for $C_{11}H_{14}O_2Se$: C, 51.37; H, 5.49%.

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