A New Method of Generation of α-Selenocarbenium Ions from *Se,O*-Heteroacetals and Their Reactions

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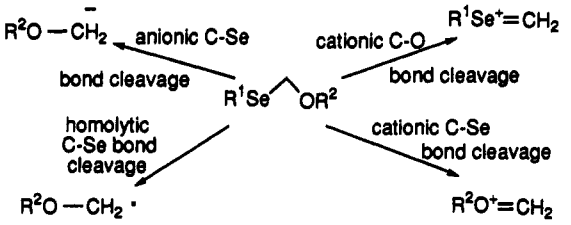
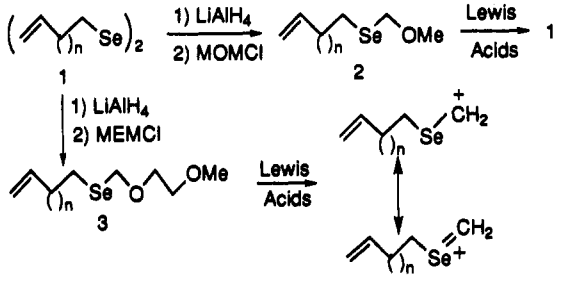
Various *Se,O*-heteroacetals were prepared by the $LiAlH_4$ reduction of diselenides 1 followed by alkylation with methoxymethyl chloride or (2-methoxyethoxy)methyl (MEM) chloride. Olefinic and acetylenic α-seleno carbenium ions were generated by the selective C–O bond cleavage of *O*-(2-methoxyethyl)-*Se,O*-heteroacetals with titanium(IV) chloride and cyclized to give the seleno heterocyclic compounds. Olefinic MEM-selenides **3a,b,d–f,h** underwent the endo-mode cyclization to afford 4-chloroselenacycloalkanes **4a,b,d–f,h** in good yields, whereas acetylenic MEM-selenides **12b–e,g–j** underwent the exo-mode cyclization to give 3-(1-chloroalkylidene)selenacycloalkanes **13b–e,g–j**. This new utilization of α-seleno carbenium ions was also applied to the intramolecular and intermolecular Friedel–Crafts reactions.

Se,O-Heteroacetals are versatile tools for generation of α-alkoxymethyl radicals, α-selenocarbenium ions, α-alkoxycarbenium ions, and α-alkoxymethanide ion by homolysis and heterolysis of the C–Se or the C–O bonds as shown in Scheme 1. The carbon-centered radicals arising from homolytic C–Se bond cleavage of *Se,O*-heteroacetals were used for syntheses of the tetrahydrofuran and pyran rings.[1] In general, the C–Se bond heterolytically cleaves easier than the C–O bond and it seems very difficult to cleave selectively the C–O bond of *Se,O*-heteroacetals. To our knowledge, generation of α-seleno- and α-alkoxycarbenium ions from *Se,O*-heteroacetals has not been reported. Although sulfur-stabilized carbenium ions can be generated by the Pummerer reaction of sulfoxides[2] or the reaction of α-chlorosulfides with Lewis acids,[3] the similar methodology cannot be used for formation of the selenium-stabilized carbenium ions. The Pummerer reaction is restricted to the selenoxides without β-hydrogen, because selenoxides bearing a β-hydrogen undergo the smooth β-elimination.[4] The halogenation of selenium compounds does not give the α-halo selenides but gives dihaloselenuranes.[5] There has been known only one method for the generation of α-selenocarbenium ions, *i.e.* the reaction of diselenoacetals with tin(IV) tetrachloride,[5] and this method has been applied to the C–C bond formation using trimethylsilyl enol ethers and the Friedel–Crafts reactions.[6] We previously reported the intramolecular cyclization reactions of selenium-stabilized carbenium ions generated from the enediselenoacetals[7] or ene-*Se,O*-heteroacetals[8] and Lewis acids. Now we report synthesis of seleno heterocyclic compounds by the intramolecular cyclization reactions of olefinic and acetylenic α-selenocarbenium ions, and Friedel–Crafts reactions of the α-selenocarbenium ions.

Scheme 1



Scheme 2



First, we prepared the methoxymethyl selenides (MOM-selenides) **2** by the reaction of olefinic selenolates with MOM chloride and examined their reactions with various Lewis acids. However, cyclized products were not obtained and the products were only diselenides **1**. Therefore, we selected (2-methoxyethoxy)methyl selenides (MEM-selenides) with expectation of the selective C–O bond cleavage by the chelation effect between the two oxygen atoms and a metal. The MEM-selenides **3** were prepared in high yields by the reduction of diselenides **1** with $LiAlH_4$ in THF–HMPA followed by the treatment of MEM chloride (Scheme 2). Then we examined some reactions of the olefinic MEM-selenides **3a–h** with some Lewis acids

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(1) Burke, S. D.; Rancourt, J. *J. Am. Chem. Soc.* **1991**, *113*, 2335. Lolkema, L. D. M.; Hiemstra, H.; Ghouch, A. A. A.; Speckamp, W. N. *Tetrahedron Lett.* **1991**, *32*, 1491.

(2) Oae, S.; Numata, T. *Tetrahedron* **1974**, *30*, 2641. Oae, S.; Numata, T. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: New York, 1980; Vol. 5, Chapter 2. Oae, S.; Numata, T. In *The Chemistry of the Sulfonium Group*; Stirling, J. M., Patai, S., Eds.; John Wiley & Sons: New York, 1981. De Lucchi, O.; Miotti, U.; Modena, G. In *Organic Reactions*; Paquette, L. A., Ed.; John Wiley and Sons: New York, 1991; Vol. 40, Chapter 3.

(3) Ishibashi, H.; Ikeda, M. In *Reviews on Heteroatom Chemistry*; Oae, S., Ed.; Myu: Tokyo, 1992; Vol. 7, p 191.

(4) Paulmier, C. In *The Selenium Reagent and Intermediate in Organic Synthesis*; Baldwin, J. E., Ed.; Pergamon Books Ltd.: New York, 1986; Chapter V.

(5) Hevesi, L.; Desauvage, S.; Georges, B.; Evard, G.; Blanpain, P.; Michael, A.; Harkema, S.; van Hummel, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 3786.

(6) Nsunda, K. M.; Hevesi, L. *Tetrahedron Lett.* **1984**, *25*, 4441. Hermans, B.; Hevesi, L. *Ibid.* **1990**, *30*, 4363. Silveira, C. C.; Lenardao, M. J. *Ibid.* **1991**, *32*, 5741.

(7) Kataoka, T.; Yoshimatsu, M.; Shimizu, H.; Hori, M. *Tetrahedron Lett.* **1991**, *32*, 105.

(8) Yoshimatsu, M.; Fujimoto, M.; Shimizu, H.; Hori, M.; Kataoka, T. *Chem. Pharm. Bull.* **1993**, *41*, 1160.

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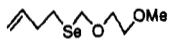
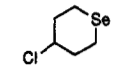
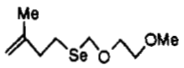
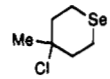
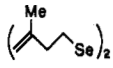
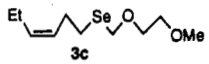
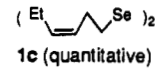
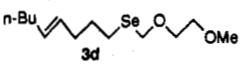
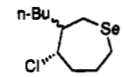
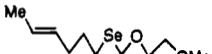
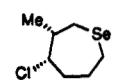
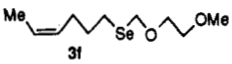
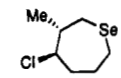
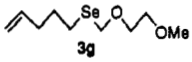
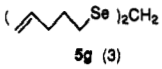
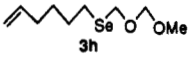
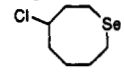
Table 1. Cyclization of Olefinic *Se,O*-Heteroacetals

entry no.	acetals	Lewis acids (molar ratio)	products (% yields)
1	 **3a**	$TiCl_4$ (2)	 **4a** (89)
2	 **3b**	$TiCl_4$ (2)	 **4b** (87)
3	**3b**	$SnCl_4$ (2)	 **1b** (4)
4	 **3c**	$SnCl_4$ (2)	 **1c** (quantitative)
5	 **3d**	$TiCl_4$ (2)	 **4d** (9)[a]
6	 **3e**	$TiCl_4$ (2)	 **4e** (49), **4f** (12)
7	 **3f**	$TiCl_4$ (2)	 **4e** (5), **4f** (23)
8	 **3g**	$TiCl_4$ (2)	 **5g** (3)
9		Et_2AlCl (2)	**5g** (20)
10	 **3h**	$TiCl_4$ (2)	 **4h** (15)

[a] A 1:1 mixture of *cis*- and *trans*-**4d**.

such as $FeCl_3$, $AlCl_3$ and $EtAlCl_2$ or reactions at 0 °C to cleave the C–O bond selectively. However, three reactions gave products in low yields or the unidentified complex mixture. Tin(IV) chloride cleaved the C–Se bond of *Se,O*-heteroacetals **3b,c** and the diselenides **1b** and **1c** were obtained (Table 1, entries 3 and 4). Therefore, olefinic MEM-selenides **3a,b** were treated with titanium(IV) chloride at −40 °C and gave 4-chloroselenacyclohexanes **4a,b** via endo-mode cyclization in satisfactory yields. Titanium(IV) chloride was very suitable for the selective C–O bond cleavage of the *Se,O*-heteroacetals. The results are shown in Table 1.

The structure of selenacyclohexane **4a** was assigned by ^1H and ^{13}C NMR and mass spectral data. The ^1H NMR spectrum exhibited a multiplet at δ 4.12–4.20 due to the 4-methine proton. ^{13}C NMR spectrum showed two methylene carbons at δ 15.96 and 36.55 as a triplet, respectively, and 4-C bound to a chlorine atom at δ 59.18 as a doublet. The mass spectrum showed the molecular ion peak at *m/z* 184 indicating a molecular formula of C_5H_9ClSe corresponding to **4a**. The structure of selenacyclohexane **4b** was similarly determined. *Se*-4- or 5-Alkenyl-*Se,O*-heteroacetals underwent the 7- and 8-endo-mode cyclization reactions. The reaction of (*E*)-hex-4-enyl-MEM-selenide **3e** and (*Z*)-isomer **3f** with titanium(IV) chloride proceeded in a fashion of the stereospecific 7-endo cyclization to afford *cis*-4-chloro-3-methylselenacycloheptane (**4e**) and *trans*-isomer **4f**, respectively (entries 6 and 7). However, the stereospecificity was moderate. *Se*-Non-3-enyl-*Se,O*-heteroacetal (**3d**) did not undergo the stereospecific cyclization and gave a 1:1 diastereomeric mixture of *cis*- and *trans*-3-(*n*-butyl)-4-chloroselenacycloheptanes (**4d**) (entry 5). Selenacycloheptane structures of **4e** and **4f** were determined by the decoupling technique. If **4e** and **4f** were the diastereomers of 3-(1-chloroethyl)selenacyclohexane, a methine proton of the chloroethyl group should appear as a doublet by irradiation of the methyl group. However, the methine proton adjacent to the methyl group was not observed as a doublet but observed still as a multiplet. The stereochemical assignment of both *cis*-**4e** and *trans*-isomer **4f** was made on the basis of the ^1H NOE enhancement between the 3-Me hydrogens and the 4-methine hydrogen (6% for **4e** and 17% for **4f**). The acetal **3g** bearing no substituent at the olefinic terminus produced no cyclized product but diselenoacetal **5g** in contrast with the acetals **3e,f** described above. These results are consistent with the report that addition of carbenium ions to alkenes is accelerated by 6–50 times by methyl groups at the attacked vinylic position and by approximately 10^4 times by methyl groups at the new carbenium center.[9]

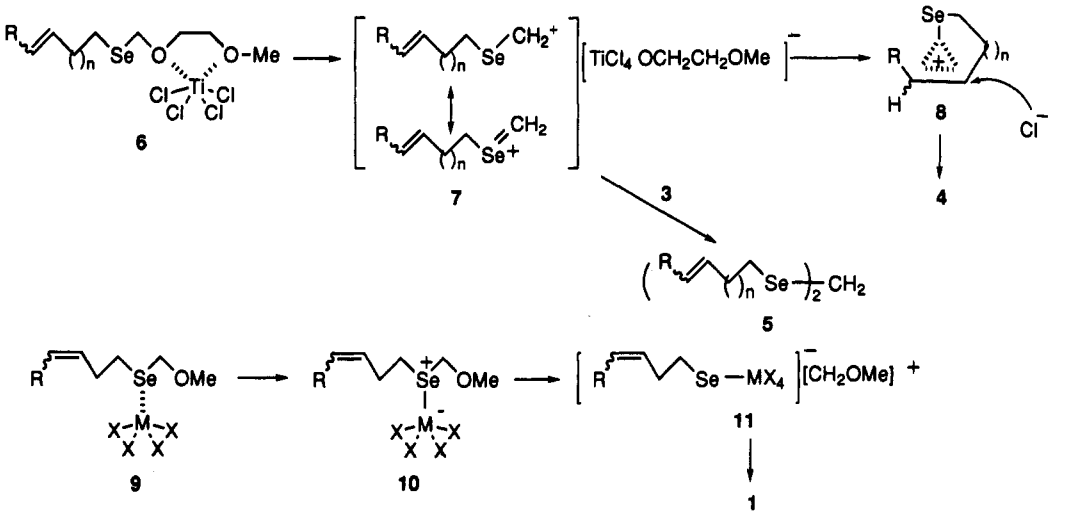
The mechanism for formation of the products **1c**, **4**, and **5g** is shown in Scheme 3. Since tin is a metal which has a strong affinity for a selenium atom, tin(IV) chloride combines with the selenium atom and the C–Se bond cleaves. Reactions of MOM- and MEM-selenides with tin(IV) chloride produced only diselenides. Titanium(IV) chloride would chelate with two oxygens of MEM-selenides **3**, and intermediates **6** are formed. Then the acetal C–O bond of the intermediates **6** cleaves and α-selenocarbenium ions **7** are generated.[10] The carbenium ion intermediates **7** cyclize to the selenacycloalkanes *via* the π-complexes **8** because the reactions of **3e,f** proceed stereospecifically (entries 6 and 7). A chloride ion attacks at the less-hindered side of the π-complex **8**, so that (*E*)-olefinic *Se,O*-heteroacetal **3e** and (*Z*)-isomer **3f** afford *cis*-4-chloro-3-methylselenacycloheptane derivative **4e** and *trans*-isomer **4f**, respectively. The stereochemical sequences of the reactions of **3e,f** can also be considered by a dissociative pathway involving the formation of separated ion pairs **7** followed by a rapid attack by the nucleophiles, an alkenyl group, and a chloride ion.[10] Diselenoacetal **5g** would be formed by an electrophilic attack of the α-selenocarbenium ion **7** at the selenium atom of *Se,O*-heteroacetal **3g**. In the case of *O*-methyl-*Se,O*-heteroacetals, a Lewis acid coordinates with a selenium or an oxygen atom depending upon the character of the Lewis acid. Even if the Lewis acid combines with the oxygen atom, the metal-coordinated oxygen atom interacts with the selenium atom because of proximity of these heteroatoms. Consequently the weaker C–Se bond of the complex **10** cleaves and the methoxycarbenium ion and the selenolate–Lewis acid complex **11** are formed. The selenolate–Lewis acid complex **11** decomposes to give a diselenide **1**.

Next, we attempted the intramolecular cyclization of acetylenic *Se,O*-heteroacetals and the results are shown in Table 2. *Se,O*-Heteroacetals without a substituent at the acetylenic terminus, **12a,f**, afforded no cyclized product but rather diselenides **14a** and/or diselenoacetals **15a**, **15f**

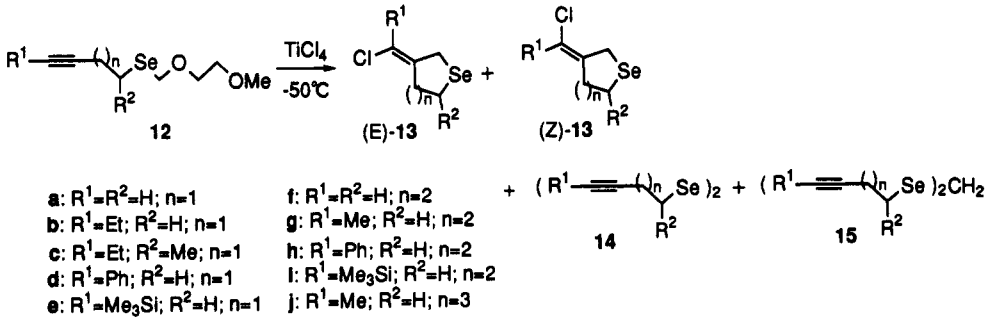
(9) Mayr, H.; Pock, R. *Chem. Ber.* **1986**, *119*, 2473. *Idem. Tetrahedron Lett.* **1983**, *24*, 2155.

(10) A similar dissociative mechanism has been demonstrated for reactions of dioxane acetals with allyltrimethylsilane: Denmark, S. E.; Willson, T. M. *J. Am. Chem. Soc.* **1989**, *111*, 3475. Denmark, S. E.; Almstead, N. G. *Ibid.* **1991**, *113*, 8089.

Scheme 3



Scheme 4



a: $R^1=R^2=H$; n=1
b: $R^1=Et$; $R^2=H$; n=1
c: $R^1=Et$; $R^2=Me$; n=1
d: $R^1=Ph$; $R^2=H$; n=1
e: $R^1=Me_3Si$; $R^2=H$; n=1
f: $R^1=R^2=H$; n=2
g: $R^1=Me$; $R^2=H$; n=2
h: $R^1=Ph$; $R^2=H$; n=2
i: $R^1=Me_3Si$; $R^2=H$; n=2
j: $R^1=Me$; $R^2=H$; n=3

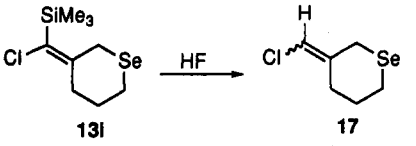
Table 2. Cyclization Reactions of Acetylenic *Se,O*-Heteroacetals

entry	*Se,O*-acetal	products (% yields)
1	**12a**	**14a** (17); **15a** (34)
2	**12b**	(*E*)-**13b** (48); (*Z*)-**13b** (24)[a]
3	**12c**	(*E*)-**13c** (49); (*Z*)-**13c** (27)[a]
4	**12d**	(*E*)-**13d** (27); (*Z*)-**13d** (27)[a]
5	**12e**	(*E*)-**13e** (55); (*Z*)-**13e** (18)[a]
6	**12f**	**15f** (33)
7	**12g**	(*E*)-**13g** (46); (*Z*)-**13g** (32)[b]
8	**12h**	(*E*)-**13h** (37); (*Z*)-**13h** (15); **14h** (3)[b]
9	**12i**	(*E*)-**13i** (32); (*Z*)-**13i** (28); **14i** (36)[b]
10	**12j**	(*E*)-**13j** (15)

[a] The product was obtained as a mixture of (*E*)- and (*Z*)-isomers and the ratios of (*E*)- and (*Z*)-isomers were determined by the intensities of 2-H in the ^{1}H NMR spectra. [b] The (*E*)- and (*Z*)-isomers were isolated.

(entries 1 and 6). However, the heteroacetals with a substituent at the acetylenic terminus, **12b–e,g–j**, underwent the exo-mode cyclization to give the stereoisomers of five-, six- and seven-membered selenacycloalkanes **13b–e,g–j** in good yields, respectively. These results are in marked contrast to those that cyclizations of acetylenic iminium ions that proceeded in the endo-mode.[11] If the cyclization had proceeded *via* the endo-mode, the products should have been only 4-chloroselenacycloalk-3-enes and the isomeric products should not have been formed. Structures of the *exo*-methyleneselenacyclopentanes **13b–e** were estimated by their ^{1}H NMR spectra, of which patterns were different from those of the 6-endo products, 3,6-dihydro-2*H*-selenopyrans.[12] Furthermore, 2-[1-chloro-1-(trimethylsilyl)methylene]selenacyclohexane (**13i**) was

Scheme 5



desilylated with a boiling hydrofluoric acid to give 1-chloromethylene derivative **17** (Scheme 5), of which the ^{1}H NMR spectrum showed two broad singlets at δ 5.86 and 6.03 due to the vinyl protons of the *E*- and *Z*-isomers, respectively. This indicates that **13i** is an *exo*-methyleneselenacyclohexane but not a selenacycloheptene derivative. The stereostructures of the isomers (*E*)-**13g** and (*Z*)-**13g** were determined as *E*- and *Z*-isomers, respectively, by their ^{1}H NMR spectra exhibiting the 2-methylene protons of (*Z*)-**13g** at δ 3.51, lower than those of (*E*)-**13g** at δ 3.35, because of the deshielding effect of the chlorine atom. This was more clearly shown by the ^{1}H NMR spectra of the selenonium salts **16g–h** derived from the selenacyclohexanes **13g–h**. The methylene protons at 2-position appeared at δ 4.06 as a broad singlet for (*E*)-**16g** and at δ 4.03 and 4.29 as a pair of doublets (J = 13 Hz) for (*Z*)-**16g**, and consequently the stereochemistry of (*E*)-**16g** and (*Z*)-**16g** was assigned as the *E*- and *Z*-configuration, respectively. The similar low-field shift was observed at δ 4.43 in the ^{1}H NMR spectrum of *Z*-isomer (*Z*)-**16h**, and no low-field shift in that of *E*-isomer (*E*)-**16h**.

(11) Overman, L. E.; Sharp, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 612 and 5934.

(12) Kirby, G. W.; Trethewey, A. N. *J. Chem. Soc. Perkin Trans. 1* **1988**, 1913. Meinke, P. T.; Krafft, G. A. *J. Am. Chem. Soc.* **1988**, *110*, 8671 and 8679.

Scheme 6

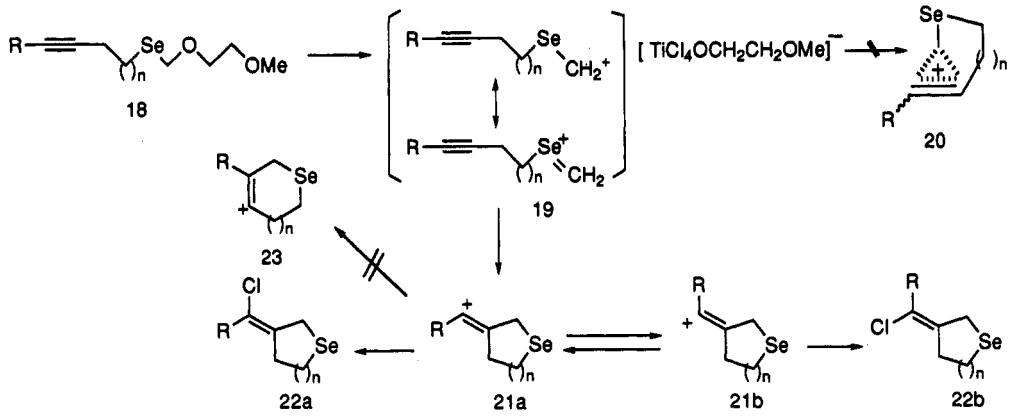
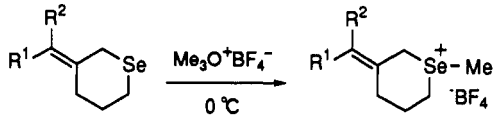


Table 3. Alkylation Reactions of Selenacyclohexanes 13 with Meerwein Reagent



entry	selenacyclohexane 13	selenonium salt 16 (%)
1	(*E*)-**13g**: R^1 = Cl; R^2 = Me	(*E*)-**16g** (quantitative)
2	(*Z*)-**13g**: R^1 = Me; R^2 = Cl	(*Z*)-**16g** (94)
3	(*E*)-**13h**: R^1 = Cl; R^2 = Ph	(*E*)-**16h** (quantitative)
4	(*Z*)-**13h**: R^1 = Ph; R^2 = Cl	(*Z*)-**16h** (quantitative)

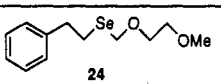
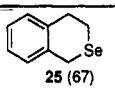
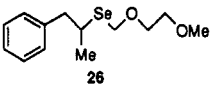
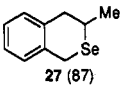
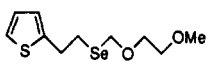
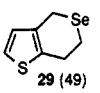
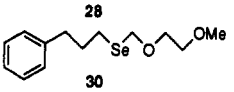
The mechanism for cyclization reactions of acetylenic *Se,O*-heteroacetals is shown in Scheme 6. The reaction intermediate would not be a π-complex **20** but classical cation species **21a** and **21b**, because the chloride ion was not introduced stereoselectively different from anti stereoselectivity in the alkyne–iminium ion cyclization.[11] The vinyl cation **21** produces vinyl chloride **22a** or **22b** by the preferential attack of the chloride ion from the sterically less-hindered side.[13] It has been reported that *exo*-methylenecyclopentane vinyl cations rearrange to cyclohexene vinyl cations in biomimetic polyene cyclizations.[14] However, since the endo-mode cyclization products were not obtained in our cases, rearrangement of *exo*-vinyl cation **21a** to *endo*-vinyl cation **23** should be excluded.

This methodology utilizing α-seleno carbenium ions was applied to Friedel–Crafts reactions. The intramolecular Friedel–Crafts reaction smoothly proceeded using titanium(IV) chloride as a Lewis acid to afford dihydro-2-benzoselenins **25**, **27**, and thieno derivative **29** in satisfactory yields. However, benzoselenacycloheptane was not obtained from *Se,O*-heteroacetal **30**.

The intermolecular Friedel–Crafts reactions of the α-seleno carbenium ions with aromatic hydrocarbons were investigated, and the results are shown in Table 5. Mixtures of ortho and para isomers **33**, **34** were obtained in moderate yields. Diselenides **35** and diselenoacetals **36** were produced as byproducts, *via* the similar pathways as for olefinic derivatives **1** and **5**, respectively.

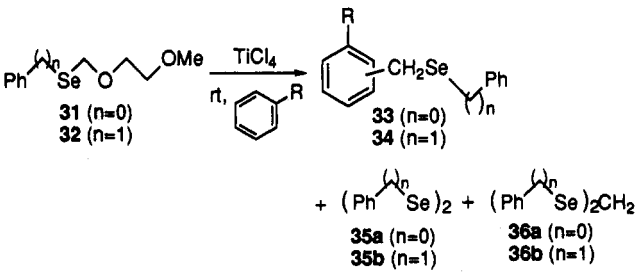
In summary, α-selenocarbenium ions are very reactive with alkenes and alkynes and useful for the organic syntheses.

Table 4. Intramolecular Friedel–Crafts Reactions of *Se,O*-Heteroacetals

entry	*Se,O*-heteroacetals[a]	product (% yield)
1	 **24**	 **25** (67)
2	 **26**	 **27** (87)
3	 **28**	 **29** (49)
4	 **30**	complex mixture

[a] The *Se,O*-heteroacetals were treated with $TiCl_4$ (2 equiv) at −40 °C.

Table 5. Intermolecular Friedel–Crafts Reactions of *Se,O*-Heteroacetals



entry	selenoacetals	aromatics (molar ratio)	products (% yields)
1	**31**	benzene	**33a** (47); **36a** (41)
2	**31**	toluene (5)	**33b** (86)[a]
3	**31**	furan (5)	**35a** (27); complex mixture
4	**31**	anisole (5)	**33d** (31); **36a** (8); **35a** (43)
5	**32**	benzene (5)	**34a** (10); **36b** (39)
6	**32**	toluene (5)	**34b** (82);[a] **36b** (10)

[a] The compounds **33b** and **34b** were obtained as a mixture of ortho and para isomers and their ortho/para ratios were 1:1 for **33b** and for **34b**.

Experimental Section

Melting points were determined by using a Yanagimoto micro-melting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. ^1H and ^{13}C NMR spectra were determined with a JEOL GX-270 (270 MHz) spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to tetramethylsilane as an internal standard. Splitting

(13) Marcuzzi, F.; Melloni, G. *J. Am. Chem. Soc.* **1976**, *98*, 3295. Mayr, H.; Klein, H. *J. Org. Chem.* **1981**, *46*, 4097.
(14) Johnson, W. S.; Ward, C. E.; Boots, S. G.; Gravestock, M. B.; Markezich, R. L.; McCarry, B. E.; Okorie, D. A.; Parry, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 88.

patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet. IR spectra were determined on a JASCO IR A-100 infrared spectrometer and are expressed in reciprocal centimeters. EI Mass spectra (MS) were obtained using a JMS-D300 spectrometer with a direct-insertion probe at an ionization voltage of 70 eV. High-resolution mass determination was conducted on the JMA 2000 on-line system. Analytical and preparative TLC were performed by using E. M. Merck silica gel 60PF-254. The known compounds were prepared by the procedures in the literature: 1-iodo-4-phenyl-3-butyne,[15] 1-iodo-4-(trimethylsilyl)-3-butyne,[16] 1-iodo-5-(trimethylsilyl)-4-pentyne,[16] 2-(methoxy)-ethoxymethyl phenyl selenide (**31**),[8] benzyl (2-methoxyethoxy)-methyl selenide (**32**).[8]

Preparation of Diselenides. General Procedure. EtOH (50 mL) was added dropwise to a mixture of selenium powder (0.62 g, 7.8 mmol) and $NaBH_4$ (0.21 g, 5.5 mmol) at 0 °C. The reaction mixture was refluxed for 1.5 h and then cooled to 0 °C. Alkyl halide (7.8 mmol) was added dropwise to it. The whole was stirred overnight and then poured into water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane–CH_2Cl_2 (10:1) to give a diselenide as a yellow oil.

Di-3-butenyl diselenide: IR (film, cm^{-1}) 3100, 3000, 2830, 1830, 1640, 1440, 1420, 1300, 1260, 1180, 1060, 1000, 920, 760, 660; ^1H NMR (60 MHz) ($CDCl_3$) δ 2.40–2.65 (4H, m), 2.98 (4H, brt, J = 8 Hz), 4.88–5.25 (4H, m), 5.50–6.18 (2H, m); EI MS m/z 270 (small M^+), 135 ($M^+/2$).

Bis(3-methylbut-3-enyl) diselenide: IR (film, cm^{-1}) 3100, 3000–2800, 1650, 1450, 1380, 1300, 1240, 1180, 900; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.75 (6H, s), 2.30–2.63 (4H, m), 3.00 (4H, t, J = 8 Hz), 4.80 (4H, br s); high-resolution mass calcd for $C_{10}H_{18}Se_2$ m/z 297.9737, found m/z 297.9716.

Di-(*E*)-non-3-enyl diselenide: IR (film, cm^{-1}) 2950–2850, 1450, 1380, 1220, 1180, 960, 730, 660; ^1H NMR (270 MHz) ($CDCl_3$) δ 0.89 (6H, t, J = 7 Hz), 1.28–1.32 (8H, m), 1.75–1.87 (4H, m), 1.97–1.99 (4H, m), 2.06–2.10 (4H, m), 2.90 (4H, t, J = 7 Hz), 5.34–5.48 (4H, m); EI MS m/z 205 ($M^+/2$).

Di-(*Z*)-hex-3-enyl diselenide: IR (film, cm^{-1}) 3000–2900, 1460, 1300, 1260, 1180, 1070, 870, 800, 720; ^1H NMR (60 MHz) ($CDCl_3$) δ 0.95 (6H, t, J = 8 Hz), 1.83–2.18 (4H, m), 2.80–3.13 (4H, m), 5.33–5.50 (4H, m); EI MS m/z 163 ($M^+/2$).

Di-(*Z*)-hex-4-enyl diselenide: IR (film, cm^{-1}) 3050, 2950, 2850, 1660, 1440, 1240, 1180, 970, 700; ^1H NMR δ 1.68 (6H, d, J = 5 Hz), 1.75–2.30 (8H, m), 2.93 (4H, t, J = 8 Hz), 5.3–5.50 (4H, m); EI MS m/z 326 (small M^+), 163 ($M^+/2$).

Di-(*E*)-hex-4-enyl diselenide: IR (film, cm^{-1}) 3000–2850, 1440, 1380, 1230, 1180, 960, 660; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.66 (6H, dd, J = 7 Hz), 1.75–1.84 (4H, m), 2.06–2.11 (4H, m), 2.90 (4H, t, J = 7 Hz), 5.40–5.50 (4H, m); EI MS m/z 326 (small M^+), 163 ($M^+/2$).

Dipent-4-enyl diselenide: IR (film, cm^{-1}) 3100, 3000–2850, 1640, 1450, 1240, 1180, 1000, 920; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.80–1.96 (4H, m), 2.14–2.20 (4H, m), 2.92 (4H, t, J = 7 Hz), 4.98–5.08 (4H, m), 5.75–5.85 (2H, m); EI MS m/z 298 (small M^+), 149 ($M^+/2$).

Dihex-5-enyl diselenide: IR (film, cm^{-1}) 3100, 2950, 2850, 1640, 1440, 1230, 1180, 1000, 920; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.25–2.25 (12H, m), 3.18 (4H, t, J = 8 Hz), 4.85–5.20 (4H, m), 5.50–6.15 (2H, m); high-resolution mass calcd for $C_{12}H_{22}Se_2$ m/z 326.0051, found m/z 326.0077.

Dibut-3-ynyl diselenide: IR (film, cm^{-1}) 3300, 2950, 2100, 1560, 1420, 1320, 1260, 1180, 1140, 1020, 940, 800, 650; ^1H NMR (270 MHz) ($CDCl_3$) δ 2.07 (2H, t, J = 2 Hz), 2.68 (4H, dt, J = 2 and 7 Hz), 3.03 (4H, t, J = 7 Hz); high-resolution mass calcd for $C_8H_{10}Se_2$ m/z 265.9113, found m/z 265.9118.

Dihex-3-ynyl diselenide: IR (film, cm^{-1}) 3000–2850, 1460, 1440, 1380, 1320, 1260, 1200, 1140, 1070, 940, 840, 790, 740; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.13 (6H, t, J = 8 Hz), 1.98–2.25 (4H, m), 2.50–2.75 (4H, m), 3.00 (4H, t, J = 7 Hz); high-resolution mass calcd for $C_{12}H_{18}Se_2$ m/z 321.9738, found m/z 321.9753.

Dihept-4-yn-2-yl diselenide: IR (film, cm^{-1}) 3000–2850, 1450, 1370, 1320, 1240, 1160, 1100, 1070, 1000, 900, 780, 660; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.10 (6H, t, J = 8 Hz), 1.43 (6H, d, J = 8 Hz), 1.93–2.25 (4H, m), 2.38–2.68 (4H, m), 2.88–3.45 (2H, m); high-resolution mass calcd for $C_{14}H_{22}Se_2$ m/z 350.0051, found m/z 350.0072.

Bis(4-phenylbut-3-ynyl) diselenide: IR (film, cm^{-1}) 3150, 2930, 1600, 1480, 1440, 1320, 1250, 1180, 1060, 910, 750, 680; ^1H NMR (60 MHz) ($CDCl_3$) δ 2.80–3.40 (8H, m), 7.10–7.60 (10H, m); high-resolution mass calcd for $C_{20}H_{18}Se_2$ m/z 417.9737, found m/z 417.9719.

Bis[4-(trimethylsilyl)but-3-ynyl] diselenide: IR (film, cm^{-1}) 3000–2860, 2200, 1460, 1250, 1030, 850; ^1H NMR (270 MHz) ($CDCl_3$) δ 0.16 (18H, s), 2.69 (4H, t, J = 8 Hz), 3.02 (4H, t, J = 8 Hz); high-resolution mass calcd for $C_{14}H_{26}Se_2Si_2$ m/z 409.9902, found m/z 409.9920.

Dipent-4-ynyl diselenide: IR (film, cm^{-1}) 3300, 2950, 2850, 2120, 1430, 1340, 1260, 1240, 1160, 940, 820, 660; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.82–1.92 (4H, m), 1.97 (2H, t, J = 2 Hz), 2.31–2.35 (4H, m), 3.01 (4H, t, J = 7 Hz), high-resolution mass calcd for $C_{10}H_{14}Se_2$ m/z 293.9424, found m/z 293.9407.

Dihex-4-ynyl diselenide: IR (film, cm^{-1}) 2920, 2850, 1440, 1340, 1240, 1180; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.75 (6H, t, J = 2 Hz), 1.88–2.40 (8H, m), 3.00 (4H, t, J = 7 Hz); high-resolution mass calcd for $C_{12}H_{18}Se_2$ m/z 321.9738, found m/z 321.9753.

Bis(5-phenylpent-4-ynyl) diselenide: IR (film, cm^{-1}) 3060, 2950 (alkyl), 2250 (acetylene), 1600, 1500, 1450, 1340, 1240, 920, 760, 700; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.98–2.70 (4H, m), 2.52 (4H, t, J = 7 Hz), 3.09 (4H, t, J = 7 Hz), 7.23–7.27 (6H, m), 7.37–7.41 (4H, m); high-resolution mass calcd for $C_{22}H_{22}Se_2$ m/z 446.0050, found m/z 446.0024.

Bis[5-(trimethylsilyl)pent-4-ynyl] diselenide: IR (film, cm^{-1}) 2950, 2180, 1420, 1340, 1250, 1120, 900, 760; ^1H NMR (60 MHz) ($CDCl_3$) δ 0.13 (18H, s), 1.83–2.15 (4H, m), 2.25–2.50 (4H, m), 3.00 (4H, t, J = 8 Hz); high-resolution mass calcd for $C_{16}H_{30}Se_2Si_2$ m/z 438.0212, found m/z 438.0182.

Dihept-5-ynyl diselenide: IR (film, cm^{-1}) 3300, 2950, 2850, 1440, 1320, 1280, 1220, 1170, 1110, 720; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.75 (6H, t, J = 2 Hz), 1.23–1.70 (12H, m), 2.90 (4H, t, J = 8 Hz), high-resolution mass calcd for $C_{14}H_{22}Se_2$ m/z 350.0051, found m/z 350.0079.

Bis(2-phenylethyl) diselenide: IR (film, cm^{-1}) 3060, 3030, 2930, 1600, 1495, 1450, 1245, 1180, 1030, 750, 695, 650; ^1H NMR (60 MHz) ($CDCl_3$) δ 2.98–3.20 (8H, m), 7.10–7.30 (10H, m); high-resolution mass calcd for $C_{16}H_{18}Se_2$ m/z 369.9737, found m/z 369.9717.

Bis(3-phenylprop-2-yl) diselenide: IR (film, cm^{-1}) 3190, 3070, 3020, 2930, 1600, 1495, 1450, 1245, 1180, 1030, 750, 695, 650; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.38 (6H, d, J = 7 Hz), 2.63–3.53 (6H, m), 7.03–7.40 (10H, m); high-resolution mass calcd for $C_{18}H_{22}Se_2$ m/z 398.0051, found m/z 398.0066.

Bis[2-(2-thienyl)ethyl] diselenide: IR (film, cm^{-1}) 3110, 3075, 2975, 2930, 2840, 1440, 1260, 1230, 1180, 850, 820, 690; ^1H NMR (60 MHz) ($CDCl_3$) δ 3.13–3.43 (8H, m), 6.75–7.03 (4H, m), 7.13 (2H, dd, J = 2 and 5 Hz); high-resolution mass calcd for $C_{12}H_{14}S_2Se_2$ m/z 381.8866, found m/z 381.8851.

Bis(3-phenylpropyl) diselenide: IR (film, cm^{-1}) 3100–2850, 1600, 1500, 1460, 1350, 1280, 1240, 1180, 1080, 1040, 920, 750, 700; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.80–2.20 (4H, m), 2.63 (4H, t, J = 8 Hz), 2.83 (4H, t, J = 8 Hz), 7.10 (10H, br s); high-resolution mass calcd for $C_{18}H_{22}Se_2$ m/z 398.0052, found m/z 298.0064.

Preparation of *Se,O*-Heteroacetals 3, 12, 24, 26, 28, 30–32. General Procedure. A solution of diselenide (5.37 mmol) in THF (10 mL) was added dropwise to a THF (20 mL) suspension of $LiAlH_4$ (0.12 g, 3.06 mmol) at −78 °C under an Ar atmosphere. The reaction mixture was stirred for 30 min and then MEM chloride (2.01 g, 16.10 mmol) was added to it. The whole was warmed to room temperature and poured into a saturated NH_4Cl solution (100 mL). The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane–AcOEt (5:1). MEM-selenide was obtained as a pale yellow oil.

(15) Bengtsson, M.; Liljefors, T. *Synth. Commun.* **1987**, 250.
(16) MacInnes, I.; Walton, J. C. *J. Chem. Soc. Perkin Trans. 2* **1987**, 1077.

But-3-enyl (2-methoxyethoxy)methyl selenide (3a): yield 83%; IR (film, cm^{-1}) 2800–3000 (alkyl), 1450, 1260, 1080, 920, 840; ^1H NMR (60 MHz) ($CDCl_3$) δ 2.40–2.88 (2H, m), 2.73 (2H, t, J = 6 Hz), 3.38 (3H, s), 3.50–3.78 (4H, m), 4.88–5.18 (2H, m), 5.00 (2H, s), 5.50–6.18 (1H, m); MS m/z 224 (small M^+). Anal. Calcd for $C_8H_{16}O_2Se$: C, 43.06; H, 7.23. Found: C, 43.08; H, 7.13.

3-Methyl-3-butenyl (2-methoxyethoxy)methyl selenide (3b): yield 91%; IR (film, cm^{-1}) 3000–2800 (alkyl), 1440, 1240, 1200, 1080, 880; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.70 (3H, br s), 2.25–2.93 (4H, m), 3.35 (3H, s), 3.43–3.73 (4H, m), 4.65–4.80 (2H, m), 5.00 (2H, s); high-resolution mass calcd for $C_9H_{18}O_2Se$ m/z 238.0471, found m/z 238.0484.

(*Z*)-3-Hexenyl (2-methoxyethoxy)methyl selenide (3c): yield 97%; IR (film, cm^{-1}) 3000–2830 (alkyl), 1450, 1250, 1140–1020; ^1H NMR (60 MHz) ($CDCl_3$) δ 0.95 (3H, t, J = 7 Hz), 1.80–2.60 (4H, m), 2.68 (2H, t, J = 6 Hz), 3.38 (3H, s), 3.43–3.80 (4H, m), 5.03 (2H, s), 5.20–5.50 (2H, m). The EI MS of **3c** did not show the M^+ (m/z 252) but showed $(M - OCH_2CH_2OMe)^+$ at m/z 163. Anal. Calcd for $C_{10}H_{20}O_2Se$: C, 47.81; H, 8.02. Found: C, 47.44; H, 8.00.

4-Nonenyl (2-methoxyethoxy)methyl selenide (3d): yield 36%; IR (film, cm^{-1}) 3050–2800, 1460, 1360, 1300–1240, 1200, 1140, 1080, 1030, 970, 860, 840; ^1H NMR (60 MHz) ($CDCl_3$) δ 0.88 (3H, br t, J = 8 Hz), 1.18–2.25 (10H, m), 2.68 (2H, t, J = 8 Hz), 3.38 (3H, s), 3.50–3.75 (4H, m), 5.00 (2H, s), 5.30–5.50 (2H, m). Anal. Calcd for $C_{13}H_{26}O_2Se$: C, 53.23; H, 8.93. Found: C, 53.04; H, 8.96.

(*E*)-4-Hexenyl (2-methoxyethoxy)methyl selenide (3e): yield 64%; IR (film, cm^{-1}) 2950 (alkyl), 1450, 1240, 1080, 960, 850; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.50–2.25 (4H, m), 1.63 (3H, dd, J = 5 and 2 Hz), 2.65 (2H, t, J = 6 Hz), 3.38 (3H, s), 3.43–3.78 (4H, m), 5.00 (2H, s), 5.30–5.50 (2H, m). The EI MS of **3e** did not show M^+ (m/z 252) but showed $(M^+ - OCH_2CH_2OMe)$ at m/z 163. Anal. Calcd for $C_{10}H_{20}O_2Se$: C, 47.81; H, 8.02. Found: C, 47.48; H, 7.99.

(*Z*)-4-Hexenyl (2-methoxyethoxy)methyl selenide (3f): yield 77%; IR (film, cm^{-1}) 2950 (alkyl), 1080; ^1H NMR (60 MHz)-($CDCl_3$) δ 1.45–2.25 (4H, m), 1.60 (3H, d, J = 5 Hz), 2.68 (2H, t, J = 8 Hz), 3.35 (3H, s), 3.43–3.73 (4H, m), 5.00 (2H, s), 5.25–5.45 (2H, m). The EI MS of **3f** did not show M^+ (m/z 252) but showed $(M^+ - OCH_2CH_2OMe)$ at m/z 163. Anal. Calcd for $C_{10}H_{20}O_2Se$: C, 47.81; H, 8.02. Found: C, 47.37; H, 7.95.

4-Pentenyl (2-methoxyethoxy)methyl selenide (3g): yield 80%; IR (film, cm^{-1}) 2950 (alkyl), 1090; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.58–2.25 (4H, m), 2.68 (2H, t, J = 6 Hz), 3.38 (3H, s), 3.50–3.78 (4H, m), 4.80–4.93 (1H, m), 5.00 (2H, s), 5.08–5.20 (1H, m), 5.48–6.10 (1H, m); EI MS m/z 149 $(M^+ - OCH_2CH_2OMe)$. Anal. Calcd for $C_9H_{18}O_2Se$: C, 45.57; H, 7.65. Found: C, 45.55; H, 7.60.

5-Hexenyl (2-methoxyethoxy)methyl selenide (3h): yield 48%; IR (film, cm^{-1}) 2950 (alkyl), 1450, 1240, 1080, 960, 850; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.46–1.54 (2H, m), 1.66–1.75 (2H, m), 2.03–2.11 (2H, m), 2.67 (2H, t, J = 7 Hz), 3.39 (3H, s), 3.55–3.58 (2H, m), 3.66–3.69 (2H, m), 4.93–4.99 (2H, m), 5.03 (2H, s), 5.72–5.84 (1H, m); EI MS m/z 252 (small M^+). Anal. Calcd for $C_{10}H_{20}O_2Se$: C, 47.81; H, 8.02. Found: C, 47.30; H, 7.92.

3-Butynyl (2-methoxyethoxy)methyl selenide (12a): yield 87%; IR (film, cm^{-1}) 3300 (acetylene), 3000–2850 (alkyl), 1450, 1260, 1200, 1080, 850; ^1H NMR (60 MHz) ($CDCl_3$) δ 2.00 (1H, t, J = 2 Hz), 2.58–2.73 (2H, m), 2.80 (2H, t, J = 6 Hz), 3.35 (3H, s), 3.45–3.78 (4H, m), 5.05 (2H, s); high-resolution mass calcd for $C_8H_{14}O_2Se$ m/z 222.0159, found m/z 222.0208.

3-Hexynyl (2-methoxyethoxy)methyl selenide (12b): yield 63%; IR (film, cm^{-1}) 3000–2800 (alkyl), 1450, 1260, 1200, 1080, 850; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.11 (3H, t, J = 8 Hz), 2.11–2.21 (2H, m), 2.55–2.61 (2H, m), 2.76 (2H, t, J = 6 Hz), 3.39 (3H, s), 3.55–3.58 (2H, m), 3.67–3.70 (2H, m), 5.08 (2H, s); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 12.27 (t), 14.02 (q), 21.07 (t), 22.41 (t), 58.85 (q), 67.89 (t), 68.74 (t), 71.26 (t), 78.28 (s), 82.55 (s); high-resolution mass calcd for $C_{10}H_{18}O_2Se$ m/z 250.0472, found m/z 250.0490.

Hept-4-yn-2-yl (2-methoxyethoxy)methyl selenide (12c): yield 86%; IR (film, cm^{-1}) 3000–2800 (alkyl), 1450, 1250, 1080, 1010, 840; ^1H NMR (60 MHz)($CDCl_3$) δ 1.10 (3H, t, J = 8 Hz), 1.50 (3H, d, J = 6 Hz), 1.98–2.25 (2H, m), 2.43–2.65 (2H, m), 2.93–3.30 (1H, m), 3.35 (3H, s), 3.45–3.78 (4H, m), 5.08 (2H, s); high-resolution mass calcd for $C_{11}H_{20}O_2Se$ m/z 264.0627, found m/z 264.0623.

4-Phenylbut-3-ynyl (2-methoxyethoxy)methyl selenide (12d): yield quantitative; IR (film, cm^{-1}) 3000–2800 (alkyl), 2240 (acetylene), 1600, 1490, 1440, 1250, 1200, 1080, 1020, 840, 760, 680; ^1H NMR (60 MHz)($CDCl_3$) δ 2.53–3.00 (4H, m), 3.33 (3H, s), 3.43–3.73 (4H, m), 5.00 (2H, s), 7.07–7.37 (5H, m); high-resolution mass calcd for $C_{14}H_{18}O_2Se$ m/z 298.0470, found m/z 298.0445.

4-(Trimethylsilyl)but-3-ynyl (2-methoxyethoxy)methyl selenide (12e): yield quantitative; IR (film, cm^{-1}) 3000–2800 (alkyl), 2180 (acetylene), 1450, 1240, 1200, 1080, 840, 760; ^1H NMR (60 MHz) ($CDCl_3$) δ 0.13 (9H, s), 2.63–2.80 (4H, m), 3.38 (3H, s), 3.43–3.75 (4H, m), 5.05 (2H, s), high-resolution mass calcd for $C_{11}H_{22}O_2SeSi$ m/z 294.0553, found m/z 294.0531.

4-Pentynyl (2-methoxyethoxy)methyl selenide (12f): yield 74%; IR (film, cm^{-1}) 3300 (CH), 2950 (alkyl), 2120 (acetylene), 1450, 1240, 1200, 1080, 850; ^1H NMR (270 MHz)($CDCl_3$) δ 1.85–1.94 (2H, m), 1.97 (1H, t, J = 2 Hz), 2.33 (2H, dt, J = 2 and 7 Hz), 2.78 (2H, t, J = 5 Hz), 3.39 (3H, s), 3.55–3.58 (2H, m), 3.66–3.69 (2H, m), 5.04 (2H, s); MS m/z 236 (small M^+). The M^+ peak was too small to determine the molecular formula by high-resolution mass spectroscopy.

4-Hexynyl (2-methoxyethoxy)methyl selenide (12g): yield quantitative; IR (film, cm^{-1}) 2875 (alkyl), 1450, 1080; ^1H NMR (60 MHz)($CDCl_3$) δ 1.78 (3H, t, J = 2 Hz), 1.88–2.45 (4H, m), 2.78 (2H, t, J = 8 Hz), 3.38 (3H, s), 3.50–3.75 (4H, m), 5.00 (2H, s); MS m/z 250 (small M^+). Anal. Calcd for $C_{10}H_{18}O_2Se$: C, 48.20; H, 7.28. Found: C, 47.92; H, 7.21.

5-Phenylpent-4-ynyl (2-methoxyethoxy)methyl selenide (12h): yield 77%; IR (film, cm^{-1}) δ 2950–2850 (alkyl), 2230 (acetylene), 1500, 1450, 1250, 1080, 1020, 850, 760, 700; ^1H NMR (270 MHz)($CDCl_3$) δ 1.95–2.07 (2H, m), 2.52 (2H, t, J = 7 Hz), 2.84 (2H, t, J = 7 Hz), 3.32 (3H, s), 3.55–3.58 (2H, m), 3.68–3.71 (2H, m), 5.03 (2H, s), 7.26–7.28 (3H, m), 7.36–7.40 (2H, m); high-resolution mass calcd for $C_{15}H_{20}O_2Se$ m/z 312.0628, found m/z 312.0600.

5-(Trimethylsilyl)pent-4-ynyl (2-methoxyethoxy)methyl selenide (12i): yield 84%; IR (film, cm^{-1}) 2950–2800 (alkyl), 2180 (acetylene), 1450, 1240, 1080, 1020, 840, 760; ^1H NMR (60 MHz)($CDCl_3$) δ 0.13 (9H, s), 1.65–2.05 (2H, m), 2.18–2.43 (2H, m), 2.70 (2H, t, J = 8 Hz), 3.30 (3H, s), 3.43–3.70 (4H, m), 5.00 (2H, s); high-resolution mass calcd for $C_{12}H_{24}O_2SeSi$ m/z 308.0710, found m/z 308.0726.

5-Heptynyl (2-methoxyethoxy)methyl selenide (12j): yield quantitative; IR (film, cm^{-1}) 2950–2850 (alkyl), 1450, 1080, 1040, 850; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.40–1.85 (4H, m), 1.75 (3H, t, J = 2 Hz), 2.00–2.28 (2H, m), 2.70 (2H, t, J = 6 Hz), 3.38 (3H, s), 3.50–3.80 (4H, m), 5.00 (2H, s); MS m/z 175 $(M^+ - CH_2OCH_2CH_2OMe)$. The EI MS did not show a molecular ion peak (M^+) at m/z 264. Anal. Calcd for $C_{11}H_{20}O_2Se$: C, 50.19; H, 7.66. Found: C, 50.45; H, 7.71.

2-Phenylethyl (2-methoxyethoxy)methyl selenide (24): yield 90%; IR (film, cm^{-1}) 2800–3000, 1450, 1125, 1080, 980, 745, 695, 650; ^1H NMR (60 MHz)($CDCl_3$) δ 2.88–3.10 (4H, m), 3.35 (3H, s), 3.53–3.78 (4H, m), 4.99 (2H, s), 7.20–7.30 (5H, m); high-resolution mass calcd for $C_{12}H_{18}O_2Se$ m/z 274.0470, found m/z 274.0453.

3-Phenylprop-2-yl (2-methoxyethoxy)methyl selenide (26): yield 55%; IR (film, cm^{-1}) 3025–2800, 1495, 1455, 1130, 1120–1060, 1025, 745, 700, 655; ^1H NMR (60 MHz)($CDCl_3$) δ 1.43 (3H, d, J = 7 Hz), 3.01 (2H, d, J = 6 Hz), 3.15–3.85 (5H, m), 3.35 (3H, s), 5.03 (2H, s), 7.18–7.38 (5H, m); high-resolution mass calcd for $C_{13}H_{20}O_2Se$ m/z 288.0628, found m/z 288.0635.

2-(2-Thienyl)ethyl (2-methoxyethoxy)methyl selenide (28): yield 99%; IR (film, cm^{-1}) 3110, 3075, 3000–2800, 1440, 1360, 1320–1230, 1195, 1140–1060, 1025, 850–820, 690; ^1H NMR (60 MHz) ($CDCl_3$) δ 2.78–3.23 (4H, m), 3.33 (3H, s), 3.43–3.80 (4H, m), 4.99 (2H, s), 6.73–6.99 (2H, m), 7.10 (1H, dd, J = 2 and 5 Hz); high-resolution mass calcd for $C_{10}H_{16}O_2SSe$ m/z 280.0035, found m/z 280.0024.

3-Phenylpropyl (2-methoxyethoxy)methyl selenide (30): yield quantitative; IR (film, cm^{-1}) 3040, 3000–2800, 1740, 1600, 1500, 1455, 1270, 1240, 1200, 1130, 1080, 1030, 980, 850, 745, 700; ^1H NMR (60 MHz) ($CDCl_3$) δ 1.70–2.38 (2H, m), 2.65 (2H, t, J

= 5 Hz), 2.69 (2H, t, J = 7 Hz), 3.33 (3H, s), 3.43–3.73 (4H, m), 5.00 (2H, s), 6.93–7.40 (5H, m); EI MS m/z 288 (small M^+), 89 (OCH_2CH_2OMe), 59 (CH_2CH_2OMe). Anal. Calcd for $C_{13}H_{20}O_2Se$: C, 54.35; H, 7.02. Found: C, 54.21; H, 7.05.

(2-Methoxyethoxy)methyl phenyl selenide (31): yield 45%; IR (film, cm^{-1}) 3060, 2990, 2930–2875, 2825, 1740, 1580, 1480, 1440, 1270–1240, 1200, 1080, 1070, 1020, 835, 690, 665; ^1H NMR (60 MHz) ($CDCl_3$) δ 3.33 (3H, s), 3.40–3.83 (4H, m), 5.28 (2H, s), 7.10–7.38 (3H, m), 7.38–7.73 (2H, m); high-resolution mass calcd for $C_{10}H_{14}O_2Se$ m/z 246.0159, found m/z 246.0163.

Benzyl (2-methoxyethoxy)methyl selenide (32): yield 85%; IR (film, cm^{-1}) 3000–2850, 1600, 1500, 1460, 1280, 1250, 1200, 1080, 1030, 840, 760, 700; ^1H NMR (60 MHz)($CDCl_3$) δ 3.35 (3H, s), 3.43–3.75 (4H, m), 3.83 (2H, s), 4.93 (2H, s), 7.25 (5H, s); high-resolution mass calcd for $C_{11}H_{16}O_2Se$ m/z 260.0315, found m/z 260.0322.

Cyclization Reactions of Olefinic *Se,O*-Heteroacetals 3. General Procedure. A solution of *Se,O*-heteroacetal **3** (1.0 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a CH_2Cl_2 (3 mL) solution of $TiCl_4$ (0.38 g, 2.0 mmol) at −40 °C under an Ar atmosphere. After 10 min stirring, the reaction mixture was poured into a saturated $NaHCO_3$ solution (200 mL). The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with hexane. Cyclic selenium compounds **4** were obtained as colorless oils. The results are shown in Table 1.

4-Chloroselenacyclohexane (4a): IR (film, cm^{-1}) 2940 (alkyl), 1420, 1250, 920; ^1H NMR (270 MHz)($CDCl_3$) δ 2.15–2.37 (2H, m), 2.35–2.46 (2H, m), 2.53–2.62 (2H, m), 2.94–3.05 (2H, m), 4.12–4.20 (1H, m); ^{13}C NMR (67.5 MHz)($CDCl_3$) δ 15.96 (t), 36.55 (t), 59.18 (d); MS m/z 184 (M^+), 149 (M^+ − Cl); high-resolution mass was not measured because **4a** was contaminated with bis(butenylseleno)methane.

4-Chloro-4-methylselenacyclohexane (4b): IR (film, cm^{-1}) 2900–2980 (alkyl); ^1H NMR (270 MHz)($CDCl_3$) δ 1.53 (3H, s), 1.92–2.03 (2H, m), 2.27–2.35 (2H, m), 2.43–2.50 (2H, m), 3.12–3.22 (2H, m); ^{13}C NMR (67.5 MHz)($CDCl_3$) δ 15.53 (t), 34.47 (q), 41.98 (t), 70.62 (s); high-resolution mass calcd for $C_6H_{11}ClSe$ m/z 197.9696, found m/z 197.9705.

3-*n*-Butyl-4-chloroselenacycloheptane (4d): IR (film, cm^{-1}) 3000–2850, 1450; ^1H NMR (270 MHz)($CDCl_3$) δ 0.93 (t, J = 7 Hz), 1.02 (t, J = 7 Hz), 1.25–1.58 (m), 1.60–1.84 (m), 2.08–2.18 (m), 2.51–2.67 (m), 3.79–3.83 (m), 4.00–4.05 (m); high-resolution mass calcd for $C_{10}H_{19}ClSe$ m/z 254.0340, found m/z 254.0346.

***cis*-4-Chloro-3-methylselenacycloheptane (4e)**: IR (film, cm^{-1}) 2850–3000 (alkyl); ^1H NMR (270 MHz)($CDCl_3$) δ 1.19–1.34 (1H, m), 1.48 (3H, d, J = 7 Hz), 1.76–2.09 (3H, m), 2.24–2.36 (1H, m), 2.49–2.75 (4H, m), 3.63–4.08 (1H, m); ^{13}C NMR (67.5 MHz)-($CDCl_3$) δ 19.57 (t), 20.77 (t), 21.60 (q), 28.31 (t), 29.10 (t), 45.72 (d), 63.11 (d); high-resolution mass calcd for $C_7H_{13}ClSe$ m/z 211.9871, found m/z 211.9880.

***trans*-4-Chloro-3-methylselenacycloheptane (4f)**: IR (film, cm^{-1}) 2850–3000 (alkyl); ^1H NMR (270 MHz)($CDCl_3$) δ 1.25–1.42 (1H, m), 1.51 (3H, d, J = 7 Hz), 1.81–2.05 (3H, m), 2.23–2.31 (1H, m), 2.51–2.75 (4H, m), 3.98–4.08 (1H, m); ^{13}C NMR (67.5 MHz)-($CDCl_3$) δ 19.56 (t), 19.99 (t), 22.16 (q), 28.30 (t), 30.62 (t), 45.64 (d), 63.27 (d); high-resolution mass calcd for $C_7H_{13}ClSe$ m/z 211.9871, found m/z 211.9882.

Bis(4-pentenylseleno)methane (5g): IR (film, cm^{-1}) 2850–3000 (alkyl), 1640, 1440, 1130, 1000, 920. ^1H NMR (270 MHz)-($CDCl_3$) δ 1.73–1.83 (4H, m), 2.13–2.21 (4H, m), 2.69 (4H, t, J = 7 Hz), 3.65 (2H, s), 4.98–5.08 (4H, m), 5.73–5.88 (2H, m); high-resolution mass calcd for $C_{11}H_{20}Se_2$ m/z 311.9895, found m/z 311.9912.

4-Chloroselenacyclooctane (4h): IR (film, cm^{-1}) 2950 (alkyl), 1440, 1130, 990, 910; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.65–1.89 (2H, m), 1.96–2.22 (4H, m), 2.33–2.58 (2H, m), 2.64–2.94 (4H, m), 4.30–4.40 (1H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 18.56 (t), 23.13 (t × 2), 29.08 (t), 33.91 (t), 37.76 (t), 61.48 (d); MS m/z 212 (small M^+). Because the selenide **4h** was contaminated with a small amount of bis(5-hexenyl) diselenide at δ 340 (M^+), the molecular formula was not determined by high resolution mass spectroscopy.

Cyclization Reactions of Acetylenic *Se,O*-Heteroacetals 12a–j were performed by the same procedure as for olefinic *Se,O*-heteroacetals **3**. The results were shown in Table 2.

Bis(but-3-ynylseleno)methane (15a): IR (film, cm^{-1}) 3300 (acetylene), 2950 (alkyl), 2120 (acetylene), 1430, 1260, 1200, 1140, 940; ^1H NMR (60 MHz)($CDCl_3$) δ 2.00 (2H, t, J = 2 Hz), 2.68 (4H, dt, J = 2 and 6 Hz), 2.80 (4H, t, J = 6 Hz), 3.75 (2H, s); high-resolution mass calcd for $C_9H_{12}Se_2$ m/z 279.9269, found m/z 279.9283.

(*E*)- and (*Z*)-3-(1-Chloropropylidene)selenacyclopentane (13b): colorless oil; IR (film, cm^{-1}) 3000–2900 (alkyl), 1650, 1460–1420, 1250, 1220, 1180, 1100, 920, 850; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.15 (t, J = 7 Hz), 1.16 (t, J = 8 Hz), 2.45 (brq, J = 7 Hz), 2.89–3.06 (m), 3.57 (brs), 3.66 (br s); ^{13}C NMR (67.5 MHz)($CDCl_3$) δ 12.16 (q), 12.51 (q), 22.00 (t), 22.90 (t), 24.21 (t), 26.49 (t), 29.79 (t), 30.45 (t), 35.79 (t), 37.80 (t), 128.49 (s), 129.24 (s), 136.54 (s), 136.56. The compound **13b** was contaminated with a trace amount of other complex compounds and its molecular formula was not measured by the high-resolution mass spectroscopy.

(*E*)- and (*Z*)-3-(1-Chloropropylidene)-5-methylselenacyclopentane (13c): IR (film, cm^{-1}) 3000–2850 (alkyl), 1650, 1450, 1370, 1240, 1180, 1100, 900, 860; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.12 (t, J = 7 Hz), 1.45 (d, J = 7 Hz), 1.46 (d, J = 7 Hz), 2.41 (q, J = 7 Hz), 2.51 (dd, J = 7 and 15 Hz), 2.65 (dd, J = 7 and 15 Hz), 2.64–2.82 (m), 2.95 (dd, J = 6 and 14 Hz), 3.13 (dd, J = 6 and 14 Hz), 3.60–3.80 (m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 12.19 (q), 12.56 (q), 22.80 (q), 22.85 (q), 24.83 (t), 27.11 (t), 29.45 (t), 30.01 (t), 35.52 (d), 36.08 (d), 44.39 (t), 46.26 (t), 128.33 (s), 129.70 (s), 132.73 (s), 135.89 (s); high-resolution mass calcd for C_8H_{13} ClSe m/z 223.9870, found m/z 223.9851.

(*E*)- and (*Z*)-3-(1-Chloro-1-phenylmethylidene)selenacyclopentane (13d): IR (film, cm^{-1}) 3050, 2950 (alkyl), 1490, 1440, 1230, 1180, 900, 850, 760, 700; ^1H NMR (270 MHz) ($CDCl_3$) δ 2.81 (br s), 2.94–3.01 (m), 3.13–3.19 (m), 3.50 (br s), 3.85 (br s), 7.27–7.41 (m); ^{13}C NMR (67.5 MHz)($CDCl_3$) δ 21.32 (t), 22.79 (t), 26.13 (t), 26.68 (t), 37.64 (t), 38.00 (t), 124.02 (s), 124.83 (s), 128.08 (d), 128.13 (d), 128.32 (d), 128.37 (d), 128.66 (d), 128.75 (d), 138.48 (s), 138.95 (s), 140.02 (s), 140.20 (s); high-resolution mass calcd for $C_{11}H_{11}ClSe$ m/z 257.9674, found m/z 257.9694.

(*E*)- and (*Z*)-3-[1-Chloro-1-(trimethylsilyl)methylidene]selenacyclopentane (13e): IR (film, cm^{-1}) 2950–2900 (alkyl), 1600, 1400, 1240, 1090, 1010, 930, 840, 750; ^1H NMR (270 MHz) ($CDCl_3$) δ 0.23 (s), 0.25 (s), 2.75–2.84 (m), 2.91–2.95 (m), 3.09–3.11 (m), 3.29 (br s), 3.58 (br s); ^{13}C NMR (67.5 MHz)($CDCl_3$) δ −0.44 (q), −0.31 (q), 17.77 (t), 20.52 (t), 21.22 (t), 26.01 (t), 36.58 (t), 38.67 (t), 131.93 (s), 143.37 (s), 152.99 (s); high-resolution mass calcd for $C_8H_{15}ClSiSe$ m/z 253.9783, found m/z 253.9789.

Bis(pent-4-ynylseleno)methane (15f) was contaminated by other unknown products, but detected by the ^1H NMR spectrum: ^1H NMR (60 MHz) ($CDCl_3$) δ 1.99 (2H, t, J = 2 Hz), 2.20–2.45 (4H, m), 2.55–2.90 (4H, m), 3.10 (4H, t, J = 6 Hz), 3.63 (2H, s).

(*E*)-3-(1-Chloroethylidene)selenacyclohexane ((*E*)-13g): IR (film, cm^{-1}) 3000–2850 (alkyl), 1640, 1430, 1380, 1260, 1160, 1090, 1070, 940, 880, 820; ^1H NMR (270 MHz) ($CDCl_3$) δ 2.13 (3H, s), 2.15–2.19 (2H, m), 2.41–2.46 (2H, m), 2.81–2.85 (2H, m), 3.35 (2H, br s); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 20.98 (t), 22.16 (q), 30.48 (t), 32.61 (t), 121.90 (s), 131.38 (s); high-resolution mass calcd for $C_7H_{11}ClSe$ m/z 209.9712, found m/z 209.9697.

(*Z*)-3-(1-Chloroethylidene)selenacyclohexane ((*Z*)-13g): IR (film, cm^{-1}) 3000–2850 (alkyl), 1650, 1420, 1380, 1250, 1160, 1090, 1070, 940, 780, 760, 660; ^1H NMR (270 MHz) ($CDCl_3$) δ 2.13 (3H, s), 2.13–2.20 (2H, m), 2.27–2.32 (2H, m), 2.81–2.84 (2H, m), 3.51 (2H, br s); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 20.56 (t), 22.09 (q), 22.34 (t), 31.26 (t), 31.81 (t), 121.14 (s), 131.61 (s); high-resolution mass calcd for $C_7H_{11}ClSe$ m/z 209.9712, found m/z 209.9702.

(*E*)-3-(1-Chloro-1-phenylmethylidene)selenacyclohexane ((*E*)-13h): IR (film, cm^{-1}) 2980–2850 (alkyl), 1480, 1440, 1240, 1140, 900, 830, 760, 700; ^1H NMR (270 MHz)($CDCl_3$) δ 2.11–2.23 (4H, m), 2.82–2.85 (2H, m), 3.66 (2H, br s), 7.31–7.39 (5H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 20.81 (t), 22.60 (t), 32.34 (t), 32.75 (t), 122.97 (s), 128.14 (t), 128.23 (t), 128.84 (t), 134.49 (s), 138.60 (s); high-resolution mass calcd for $C_{12}H_{13}ClSe$ m/z 271.9871, found m/z 271.9890.

(*Z*)-3-(1-Chloro-1-phenylmethylidene)selenacyclohexane ((*Z*)-13h): 2950–2900 (alkyl), 1480, 1440, 1260, 1150, 940, 900, 760, 700; ^{1}H NMR (270 MHz) ($CDCl_3$) δ 2.25–2.33 (2H, m), 2.57–2.62 (2H, m), 2.57–2.62 (2H, m), 3.30 (2H, s), 7.25–7.44 (5H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 21.07 (t), 22.35 (t), 30.88 (t), 32.99 (t), 123.65 (s), 128.22 (d), 128.35 (d), 128.70 (d), 134.46 (s), 138.61 (s); high-resolution mass calcd for $C_{12}H_{13}ClSe$ *m/z* 271.9870, found *m/z* 271.9849.

(*E*)-3-[1-Chloro-1-(trimethylsilyl)methylidene]selenacyclohexane ((*E*)-13i): IR (film, cm^{-1}) 3000–2850 (alkyl), 1590, 1450–1400, 1250, 1150, 920, 840, 760; ^{1}H NMR (270 MHz) ($CDCl_3$) δ 0.25 (9H, s), 2.14–2.23 (2H, m), 2.48–2.53 (2H, m), 2.82–2.86 (2H, m), 3.40 (2H, br s); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 0.06 (q), 21.06 (t), 23.10 (t), 30.74 (t), 33.28 (t), 128.38 (s), 147.77 (s); high-resolution mass calcd for $C_9H_{17}ClSeSi$ *m/z* 267.9953, found *m/z* 267.9957.

(*Z*)-3-[1-Chloro-1-(trimethylsilyl)methylidene]selenacyclohexane ((*Z*)-13i): IR (film, cm^{-1}) 2950–2850 (alkyl), 1590, 1420, 1240, 920, 840, 760; ^{1}H NMR (270 MHz)($CDCl_3$) δ 1.26 (9H, s), 2.21–2.23 (2H, m), 2.33–2.37 (2H, m), 2.81–2.89 (2H, m), 3.58 (2H, br s); ^{13}C NMR (67.5 MHz)($CDCl_3$) δ 0.31 (q), 20.59 (t), 22.41 (t), 33.10 (t), 34.50 (t), 127.04 (s), 147.88 (s); high-resolution mass calcd for $C_9H_{17}ClSeSi$ *m/z* 267.9953, found *m/z* 267.9965.

(*E*)- and (*Z*)-3-(1-Chloroethylidene)selenacycloheptane (13j): IR (film, cm^{-1}) 3000–2850 (alkyl), 1640, 1440, 1380, 1240, 1180, 880, 780, 750; ^{1}H NMR (270 MHz) ($CDCl_3$) δ 1.64–1.73 (2H, m), 2.02–2.10 (2H, m), 2.17 (3H, s), 2.34–2.39 (2H, m), 2.62–2.66 (2H, m), 3.59–3.62 (2H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 22.17 (t), 22.39 (q), 24.36 (t), 26.55 (t), 32.29 (t), 32.56 (t), 126.56 (s), 132.76 (s); EI MS *m/z* 224 (small M$^+$). The M$^+$ peak was too small to determine the molecular formula by high-resolution mass.

Methylation of (*E*)- and (*Z*)-3-(1-Chloromethylene)selenacyclohexane 13g,h with the Meerwein Reagent. General Procedure. Trimethyloxonium tetrafluoroborate (0.26 g, 1.73 mmol) was added to a CH_2Cl_2 (3 mL) solution of selenacyclohexane 13 (0.33 g, 1.57 mmol). The reaction mixture was stirred overnight. The solvent was removed under reduced pressure. The resulting powder was washed with ether. Recrystallization from acetonitrile–hexane afforded 1-methylselenacyclohexanium tetrafluoroborate as colorless needles. The results are shown in Table 3. **(*E*)-3-(1-Chloroethylidene)-1-methylselenacyclohexanium tetrafluoroborate ((*E*)-16g)** (mp 82–84 °C): IR (KBr, cm^{-1}) 3000–2900 (alkyl), 1640, 1450, 1280, 1150–1000 (BF_4), ^{1}H NMR (270 MHz)($CDCl_3$) δ 2.17 (3H, s), 2.48 (3H, s), 2.88–2.94 (2H, m), 3.12–3.18 (2H, m), 3.39–3.52 (2H, m), 4.06 (2H, br s); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 13.41 (q), 20.63 (t), 21.33 (q), 28.73 (t), 32.06 (t), 34.19 (t), 121.15 (s), 131.65 (s). Anal. Calcd for $C_8H_{14}BClF_4Se$: C, 30.86; H, 4.53. Found: C, 30.68; H, 4.44.

(*Z*)-3-(1-Chloroethylidene)-1-methylselenacyclohexanium tetrafluoroborate ((*Z*)-16g) (mp 81–82 °C): colorless needles; IR (KBr, cm^{-1}) 3000, 2930 (alkyl), 1640, 1450, 1280, 1200, 1140–1000 (BF_4); ^{1}H NMR (270 MHz)($CDCl_3$) δ 2.25 (3H, s), 2.53 (3H, s), 2.70–2.75 (2H, m), 3.14–3.26 (2H, m), 3.42–3.52 (2H, m), 4.03 (1H, d, *J* = 13 Hz), 4.29 (1H, d, *J* = 13 Hz); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 12.92 (q), 21.24 (t), 21.28 (q), 27.70 (t), 32.07 (t), 34.73 (t), 121.20 (s), 131.57. Anal. Calcd for $C_8H_{14}BClF_4Se$: C, 30.86; H, 4.53. Found: C, 30.67; H, 4.44.

(*E*)-3-(1-Chloro-1-phenylmethylene)-1-methylselenacyclohexanium tetrafluoroborate ((*E*)-16h) (mp 187–188 °C): IR (KBr, cm^{-1}) 3000, 2900 (alkyl), 1440, 1420, 1250, 1100–1000 (BF_4), 900, 840, 760, 700; ^{1}H NMR (270 MHz) ($CDCl_3$) δ 1.93–2.25 (3H, m), 2.43–2.62 (1H, m), 2.67 (3H, s), 3.18–3.27 (1H, m), 3.43–3.54 (1H, m), 4.20 (1H, br d, *J* = 13 Hz), 4.43 (1H, d, *J* = 13 Hz), 7.38–7.50 (5H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 13.34 (q), 22.36 (t), 29.29 (t), 32.41 (t), 34.92 (t), 125.05 (s), 128.19 (d), 128.46 (d), 129.08 (d), 132.96 (s), 136.77 (s). Anal. Calcd for $C_{13}H_{16}BClF_4Se$: C, 41.81; H, 4.32. Found: C, 41.79; H, 4.32.

(*Z*)-3-(1-Chloro-1-phenylmethylene)-1-methylselenacyclohexanium tetrafluoroborate ((*Z*)-16h) (mp 171–172 °C): IR (film, cm^{-1}) 3050–2850 (alkyl), 1440, 1420, 1280, 1260, 1150–1020 (BF_4), 950, 760, 700; ^{1}H NMR (270 MHz) ($CDCl_3$) δ 2.17–2.27 (3H, m), 2.43 (3H, s), 2.96–3.04 (1H, m), 3.14–3.22 (1H, m), 3.46–3.54 (1H, m), 3.80 (1H, d, *J* = 13 Hz), 4.08 (1H, d, *J* = 13 Hz), 7.33–7.36 (2H, m), 7.43–7.49 (3H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 14.38 (q), 20.16 (t), 29.16 (t), 33.14 (t), 35.09 (t), 124.72 (s), 128.65 (d), 128.73 (d), 129.09 (d), 133.40 (s), 136.39 (s). Anal. Calcd for $C_{13}H_{16}BClF_4Se$: C, 41.81; H, 4.32. Found: C, 41.61; H, 4.28.

Desilylation of 3-[1-Chloro-1-(trimethylsilyl)methylene]selenacyclohexane (13i) with Hydrogen Fluoride. Selenacyclohexane 13i (70 mg, 0.26 mmol) was added to a 46% solution of HF (5 mL). The reaction mixture was refluxed for 1 h and poured into water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with hexane. A mixture of (*E*)- and (*Z*)-3-chloromethyleneselenacyclohexane (17) (42 mg, 58%) was obtained as a colorless oil: IR (film, cm^{-1}) 2950–2900, 1620, 1440–1420, 1320, 1260, 1160, 1000, 940, 900, 860, 820–760, 740; ^{1}H NMR (270 MHz) ($CDCl_3$) δ 2.12–2.27 (m), 2.38–2.42 (m), 2.79–2.86 (m), 3.29 (br s), 3.44 (br s), 5.56 (br s), 6.03 (br s); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 18.64 (t), 20.69 (t), 20.98 (t), 23.63 (t), 29.31 (t), 30.14 (t), 32.09 (t), 34.94 (t), 109.11 (s), 110.52 (s) 138.39 (s), 138.74 (s); MS *m/z* 196 (M$^+$).

Intramolecular Friedel–Crafts Cyclization Reactions of *Se,O*-Heteroacetals 24, 26, 28, and 30. Friedel–Crafts reactions were performed by the same methods as olefinic *Se,O*-heteroacetals 3. The results are shown in Table 4. Dihydro-2-benzoselenin (25) was identical with an authentic sample in all respects.[17]

3-Methylselenoisochroman (27): yellow oil; IR (film, cm^{-1}) 3030, 2960, 2930, 2870, 1485, 1450, 1245, 765, 750, 740, 655; ^{1}H NMR (270 MHz) ($CDCl_3$) δ 1.45 (3H, t, *J* = 7 Hz), 2.77 (1H, dd, *J* = 9 and 14 Hz), 3.05 (1H, dd, *J* = 4 and 9 Hz), 3.44–3.55 (1H, m), 3.69 (1H, d, *J* = 12 Hz), 3.84 (1H, d, *J* = 12 Hz), 7.18–7.29 (4H, m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 20.40 (t), 23.98 (q), 33.13 (d), 40.20 (t), 126.30 (d), 126.74 (d), 126.77 (d), 128.99 (d), 137.33 (s), 138.30 (s); high-resolution mass calcd for $C_{10}H_{12}Se$ *m/z* 212.0103, found *m/z* 212.0085.

6,7-Dihydrothieno[2,3-*c*]selenacyclohexane (29): yellow oil; IR (film, cm^{-1}) 3100, 2930, 2900, 2825, 1420, 1265, 1240, 980, 700, 650; ^{1}H NMR (270 MHz) ($CDCl_3$) δ 2.92 (2H, m), 3.14 (2H, m), 3.74 (2H, brs), 6.78 (1H, d, *J* = 5 Hz), 7.00 (1H, d, *J* = 5 Hz); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 15.73 (t), 18.11 (t), 27.21 (t), 120.29 (d), 127.66 (d), 130.53 (s), 136.57 (s); high-resolution mass calcd for C_7H_8SSe: *m/z* 203.9511, found *m/z* 203.9503.

Intermolecular Friedel–Crafts Reactions of 31 and 32 with Aromatic Hydrocarbons. General Procedure. A solution of *Se,O*-heteroacetal 31 or 32 (0.25 g, 1.0 mmol) in benzene (1 mL) was added dropwise to a benzene (2 mL) solution of $TiCl_4$ (0.38 g, 2.0 mol) at 0 °C under an Ar atmosphere. After stirring for 1.5 h, the reaction mixture was poured into a saturated $NaHCO_3$ solution (200 mL). The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with hexane. Products and their yields are listed in Table 5.

Benzyl phenyl selenide (33a): IR (film, cm^{-1}) 1575, 1490, 1475, 1450, 1435, 1175, 1060, 1020, 760, 730, 695; ^{1}H NMR (60 MHz) ($CDCl_3$) δ 4.08 (2H, s), 7.10–7.55 (10H, m); high-resolution mass calcd for $C_{13}H_{12}Se$ *m/z* 248.0104, found *m/z* 248.0124.

Bis(phenylseleno)methane (36a): yield 41%. This compound was identical with an authentic sample.[18]

A mixture of *o*- and *p*-[(phenylseleno)methyl]toluenes (33b): IR (film, cm^{-1}) 3060, 3025, 2950–2925, 2860, 1580, 1510, 1475, 1435, 1175, 1070, 1020, 760, 735, 685, 660; ^{1}H NMR (270 MHz)($CDCl_3$) δ 2.26 (s), 2.32 (s), 4.04 (s), 4.06 (s), 7.00–7.20 (m), 7.41–7.49 (m); high-resolution mass calcd for $C_{14}H_{14}Se$: *m/z* 262.0259, found *m/z* 262.0247.

***o*- and *p*-[(Phenylseleno)methyl]anisole (33d)**: IR (film, cm^{-1}) 3050, 3000, 2950, 2840, 1600, 1580, 1490, 1460, 1440, 1245, 1175, 1045, 1025, 735, 690, 660; ^{1}H NMR (270 MHz) ($CDCl_3$) δ 3.76 (s), 4.11 (s), 6.76–6.84 (m), 7.02 (br d, *J* = 7 Hz), 7.15 (dd, *J* = 8 and 2 Hz), 7.44–7.48 (m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 26.83 (t), 55.29 (q), 110.50 (d), 120.23 (d), 127.01 (d), 127.30 (s), 128.21 (d), 128.74 (d), 130.07 (d), 130.98 (s), 133.68 (d), 157.05 (s);

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high-resolution mass calcd for $C_{14}H_{14}OSe$: *m/z* 278.0210, found *m/z* 278.0215.

Dibenzyl selenide (34a): IR (film, cm^{-1}) 3070, 3030, 2930, 1600, 1490, 1450, 1065, 1030, 760, 695, 660; ^1H NMR (270 MHz) ($CDCl_3$) δ 3.71 (4H, s), 7.20–7.32 (10H, m); high-resolution mass calcd for $C_{14}H_{14}Se$: *m/z* 262.0261, found *m/z* 262.0272. This compound was identical with an authentic sample in all respects.[19]

Bis(benzylseleno)methane (36b): IR (film, cm^{-1}) 1490, 1450, 1415, 1140, 1065, 755, 695; ^1H NMR (60 MHz) ($CDCl_3$) δ 3.38 (2H, s), 3.83 (4H, s), 7.15–7.35 (10H, m); high-resolution mass calcd for $C_{15}H_{16}Se$ *m/z* 355.9581, found *m/z* 355.9562.

A mixture of *o*- and *p*-[(benzylseleno)methyl]toluene (34b): IR (film, cm^{-1}) 3030, 2930, 1600, 1510, 1490, 1450, 1175, 1060, 1025, 810, 755, 695, 650; ^1H NMR (270 MHz) ($CDCl_3$) δ 2.25 (s), 2.29 (s), 3.65 (s), 3.67 (brs), 3.71 (s), 7.04–7.30 (m); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 19.03 (q), 21.03 (q), 25.59 (t), 27.21 (t), 27.40 (t), 27.74 (t), 125.79 (d), 126.55 (d), 126.60 (d), 126.96 (d), 128.37 (d), 128.77 (d), 128.89 (d), 129.08 (d), 129.45 (d), 130.53 (d), 135.95 (s), 136.16 (s), 136.34 (s), 136.65 (s), 139.11 (s), 139.20 (s); high-resolution mass calcd for $C_{15}H_{16}Se$ *m/z* 276.0417, found *m/z* 276.0425.

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Supplementary Material Available: NMR data, complete with peak assignments (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.