(S=S(O)) in the thermal rearrangement of **3c** to dibenzofuran (**4**) has been described.[11]

Sulfides **2a** and **3a** are minor products of the FVP of sulfoxide **2b** and **3b** (Table I). At least three sources of these sulfides can be considered: (i) oxygen extrusion from a sulfenate ester intermediate, (ii) direct deoxygenation of the sulfoxide, and (iii) combination of arylthiyl and aryl radicals (eq 7).

$$R\cdot + RS\cdot \rightarrow R\text{-}S\text{-}R \qquad (7)$$

Oxygen extrusion from a sulfenate ester (R–S–O–R) seems unlikely because, in addition to oxygen extrusion, sulfur extrusion would also be expected. Diphenyl ether (Ph–O–Ph) was not detected in the FVP of sulfoxide **2b** and dibenzofuran (**4**) is a minor product of the FVP of **3b**. Furthermore, an increase in temperature actually gave more sulfide in the case of **2b** but less for **3b** where the sulfenate ester (**6**) must be in greater concentration.

On the basis of available evidence one cannot readily distinguish between direct deoxygenation of the sulfoxide and combination of arylthiyl and aryl radicals (eq 6). However, it should be noted that as the FVP temperature increased from 700 to 900 °C for sulfoxide **2b** both the yield of sulfide (**2a**) and biphenyl increased suggesting deoxygenations of a sulfinyl (PhSO·) radical. Deoxygenation of sulfenic acids (RSOH) and sulfinyl radicals has been proposed.[3a,17] Furthermore, dibenzothiophene (**3a**) observed in the FVP of dibenzothiophene 5,5-dioxide (**3c**) occurs not from the sulfone (**3c**) but rather from the intermediate sultine.[11] Extrusion of molecular oxygen from the sultine, possibly from a thioperoxide intermediate (RS–O–O·), was suggested.

Summary and Conclusions

The initial or primary reaction of organosulfur **1–3** under pyrolytic conditions, is homolytic cleavage of the C–SO_n bond (eq 1). The order of reactivity was observed to be sulfoxide >> sulfone > sulfide as predicted on the basis of the relative stabilities of the radicals produced. These sulfur and carbon radicals combine regioselectivity to form new sulfur–sulfur and carbon–carbon bonds (eq 2 and 3, respectively).

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^{1}H spectra were measured on Varian A60-A and Joel FX 90Q NMR spectrometers. GS/MS data were obtained on a Finnigan 4000 GS/MS using a 6 ft × $^1/_4$ in., 3% OV-17 on Anakorm Q (90/100 mesh), glass column. Gas chromatographic analyses were performed on a Varian 3700 gas chromatograph (FID) with a 6 ft × $^1/_8$ in., 3 % OV-17 on Anakorm Q (90/100 mesh) column. The analyses were determined by comparison of peak areas with standard solutions of the reaction products. Analyses were performed at least twice and the results averaged. Solvents were commercial grade and used without additional purification. Compounds **1a–3a**, **1b**, **2b**, and **1c–3c** were purchased commercially (Aldrich & Parish Chem. Co.) and used unpurified. Dibenzothiophene 5-oxide (**3b**) was prepared by oxidation of **3a** using ceric ammonium nitrate and purified by flash chromatography on silica gel.[20]

General Flash Vacuum Pyrolysis (FVP) Procedure. FVP was carried out by vaporizing, at 80 °C, 100–150 mg samples of organo sulfur compounds **1–3** into a 1.5 × 20 cm quartz pyrolysis chamber at 10^{-2}–10^{-3} torr.[21] The pyrolyzate was collected on a cold finger cooled to −196 °C with liquid N_2. The temperature of the pyrolysis was monitored at the center of the pyrolysis chamber using a Barber-Coleman thermocouple, the accuracy of which is estimated to be ±10 °C. After completion of the FVP experiment the vacuum was disengaged and the system flushed with dry nitrogen gas. After warming to room temperature the products, which had collected on the cold finger, were washed into a receiver and separated by flash chromatography or preparative TLC. The products were analyzed by gas chromatography. The FVP experiments were performed at least twice and the results averaged (Table I).

1-Hydroxydibenzothiophene (5). FVP of dibenzothiophene 5-oxide (**3b**), 0.5 g (0.0025 mol), at 900 °C gave a dark solid on the cold finger condenser. After thawing the cold finger condenser, the deposited solid was dissolved in chloroform and treated once with decolorizing charcoal. After removing the solvent under vacuum the residue was purified by flash chromatography (Silica gel) eluting with 1:1 ether/*n*-pentane to give 0.28 g (55%) of a white solid, mp 141–142 °C (lit.[14] 142–143 °C), identified as **5** by comparison of its IR and NMR spectra with values recorded in the literature.[14]

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Registry No. **1a**, 831-91-4; **1b**, 833-82-9; **1c**, 3112-88-7; **2a**, 139-66-2; **2b**, 945-51-7; **2c**, 127-63-9; **3a**, 132-65-0; **3b**, 1013-23-6; **3c**, 1016-05-3.

(20) Tse-Lok, H.; Wong, C. M. *Synthesis* **1972**, 561.
(21) For a description of the flash vacuum pyrolysis apparatus see ref 3a and the references cited therein.

Reactions of 3-Hydroxyvinyl Selenones with Alkoxides. Oxetane Formation and Fragmentation Reactions[1,2]

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3-Hydroxyvinyl phenyl selenones are prepared and their behavior as conjugate addition acceptors has been investigated. As a result, a selenonyl group has been found to activate the C=C bond for conjugate addition of nucleophiles and further to behave as an excellent leaving group. According to such characteristic features, acyclic 3-hydroxyvinyl selenones undergo an addition reaction of alkoxides followed by an internal substitution reaction with a 3-hydroxy group to give the corresponding 3-alkoxyoxetanes. On the other hand, cyclic ones afford the corresponding ring-opened product, alkoxyethylenic or acetylenic ketones, via an addition–fragmentation or a direct fragmentation reaction. Application of this addition–fragmentation process to an intramolecular system has also been described.

From numerous reports[3] it is known that vinyl sulfones are more reactive than vinyl sulfoxides toward conjugate addition of nucleophiles. By analogy, vinyl selenones are expected to be more efficient acceptors of nucleophiles

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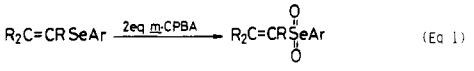
Table I. Preparation of 3-Methoxyoxetanes 3

run	Ar	olefin geometry	R—M	yield,[a] % (3)
1	C_6H_5	*E*	$C_6H_5CH_2CH_2MgCl$	80 (3a)
2	C_6H_5	*Z*	$C_6H_5CH_2CH_2MgCl$	78 (3a)
3	*p*-ClC_6H_4	*Z*	$C_6H_5CH_2CH_2MgCl$	69 (3a)
4	C_6H_5	*E*	$C_6H_{13}MgCl$	66 (3b)
5	*p*-ClC_6H_4	*Z*	C_6H_5MgCl	66 (3c)
6	C_6H_5	*E*	C_6H_5Li	80 (3c)
7	C_6H_5	*E*	$C_{10}H_{21}MgBr$	78 (3d)
8	C_6H_5	*Z*	$C_{10}H_{21}MgBr$	72 (3d)
9	C_6H_5	*E*	$C_4H_9CHLiCO_2$-*t*-Bu	81 (3e)

[a] Yields based on (*E*)- or (*Z*)-3-(phenylseleno)-2-propenal.

than the corresponding selenoxides. However, in strong contrast to sulfur analogues, oxidation of Se(IV) species to those of Se(VI) has been reported to be quite difficult,[4] and there are few examples in which such transformations have been described.[5]

We have found that oxidation of aryl vinyl selenides to the corresponding aryl vinyl selenones proceeds relatively easily and in high yields (eq 1). The vinyl selenones thus



(Eq 1)

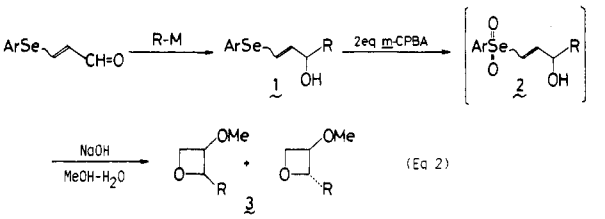
obtained exhibit several characteristic features in reactions with nucleophiles.[6] In this paper, we describe two types of reactions of 3-hydroxyvinyl selenones such as oxetane formation and fragmentation reactions.

Formation of 3-Alkoxyoxetanes

On addition of nucleophiles, vinyl selenoxides exhibit two roles characteristic of arylseleninyl group; as an electron-withdrawing activator of the carbon–carbon double bond and then as a good leaving group.[7] Similar effects are also expected for arylselenonyl group. The transformation of vinyl selenides to the corresponding vinyl selenoxides has been effected by the use of 1 equiv of *m*-CPBA or $NaIO_4$.[8] Further examination on the oxidation of vinyl selenides led us to a new finding that aryl vinyl selenones can be prepared easily by treating the corresponding selenides with 2–2.2 equiv of *m*-CPBA. As the reaction solvent, methanol or *tert*-butyl alcohol is preferable for complete conversion to the selenones within a reasonable period. When alcohols are replaced with methylene chloride, the oxidation of intermediary selenoxides to the selenones is sometimes too sluggish for practical synthetic purposes.

The vinyl selenones thus obtained are efficient acceptors of alkoxides. For example, treatment of 1-dodecenyl phenyl selenone with sodium hydroxide in methanol gave 1,2-dimethoxydodecane in 51% yield, which implied conjugate addition followed by substitution with methoxide. Many interesting results have arisen from the reaction of 3-(phenylselenonyl)-2-alken-1-ols **2** with methoxide. The starting materials, 3-(phenylseleno)-2-alken-1-ols **1**, were prepared by addition of appropriate nucleophiles to 3-(phenylseleno)-2-propenal, which was produced by oxidation of the corresponding alcohol with *tert*-butyl hydroperoxide and dimesityl diselenide.[9] Oxidation of the resulting **1** gave **2** almost quantitatively.

Treatment of the hydroxy vinyl selenone **2** (R = $CH_2CH_2C_6H_5$) thus prepared with sodium hydroxide in methanol afforded a mixture of *cis*- and *trans*-3-methoxy-2-(2-phenylethyl)oxetane (**3**, R = $CH_2CH_2C_6H_5$) in 80% yield (eq 2). In this case, the oxetane was the sole



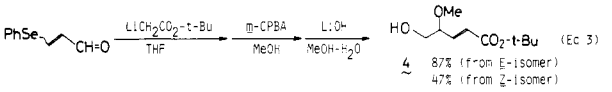
(Eq 2)

product, without side products arising from the intermolecular conjugate addition of alkoxy group or introduction of two methoxy groups on the vinyl linkage. A variety of methoxyoxetanes **3** can be prepared by the present procedures (see Table I).

In the cyclopropanation reaction of enolates with vinyl selenoxides,[7] electron-withdrawing substituents on the aryl selenoxides facilitated the reaction. In this oxetane formation, however, *p*-chlorophenyl derivatives were not very efficient conjugate-addition acceptors (runs 3 and 5).

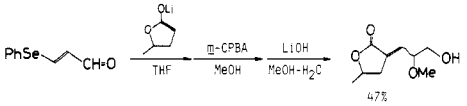
The selenones obtained from (*E*)-3-(phenylseleno)-2-propenal usually gave better results than those from its *Z* isomer (compare runs 1 and 7 to 2 and 8). The difference might be attributable to the higher lability of a *Z* isomer of a hydroxy vinyl selenone. For example, (*E*)-2-phenyl-4-(phenylseleno)-3-penten-2-ol gives the corresponding selenone almost quantitatively on treatment under standard oxidation conditions, whereas the *Z* isomer results in the formation of 2-phenyl-3-butyn-2-ol as the side product under similar reaction conditions.

The hydroxy selenone prepared by the addition of the lithium enolate of *tert*-butyl acetate to (*E*)-3-(phenylseleno)-2-propenal followed by oxidation underwent 1,3-hydroxy group transfer via the intermediacy of an oxetane: treatment of the addition product with 2 equiv of *m*-CPBA followed by lithium hydroxide in methanol gave rise to the (*E*)-α,β-unsaturated ester **4** exclusively in 87% yield (eq 3). In this reaction the *E* isomer has proved again to be



(Eq 3)

far superior to the *Z* isomer. A similar reaction was also observed with the γ-butyrolactone enolate. In these cases employment of lithium hydroxide in an appropriate amount (ca. 1.5 equiv) may prevent a retro-Reformatsky-type reaction[10] and keep this system free from side reactions (eq 4). It is likely that this reaction proceeds through

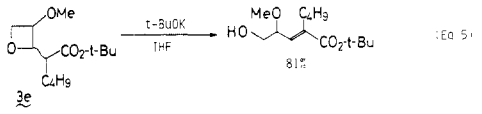


(Eq 4)

ring opening of the oxetane via its enolate anion. The

(1) Shimizu, M.; Kuwajima, I. *J. Org. Chem.* **1980**, *45*, 4063.
(2) Shimizu, M.; Ando, R.; Kuwajima, I. *J. Org. Chem.* **1981**, *46*, 5246.
(3) Posner, G. H.; Brunelle, D. J. *J. Org. Chem.* **1973**, *38*, 2747. Conrad P. C.; Fuchs, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 346. Barton, D. L.; Conrad, P. C.; Fuchs, P. L. *Tetrahedron Lett.* **1980**, *21*, 1811. Cory, R. M.; Rennebog, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 1081. Fatutta, S.; Risaliti, A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2387. Cardillo, G.; Savoia, D.; Umani-Ronchi, A. *Synthesis* **1975**, 453.
(4) Ayrey, G.; Barnard, D.; Woodbridge, D. T. *J. Chem. Soc.* **1962**, 2089.
(5) Paetzold, R.; Bochmann, G. *Z. Anorg. Chem.* **1968**, *360*, 293. Yagupol'ski, L. M.; Voloshchuk, V. G. *Zh. Obsch. Kim.* **1968**, *38*, 2509.
(6) Kuwajima, I.; Ando, R.; Sugawara, T. *Tetrahedron Lett.* **1983**, *24*, 4429.
(7) Shimizu, M.; Kuwajima, I. *J. Org. Chem.* **1980**, *45*, 2921.
(8) Sevrin, M.; Dumont, W.; Krief, A. *Tetrahedron Lett.* **1977**, 3835.
(9) Shimizu, M.; Urabe, H.; Kuwajima, I. *Tetrahedron Lett.* **1981**, *22*, 2183. Kuwajima, I.; Shimizu, M.; Urabe, H. *J. Org. Chem.* **1982**, *47*, 837.
(10) Yates, B. L.; Quijano, J. *J. Org. Chem.* **1969**, *34*, 2506.

following examples support this sequence. The oxetane **3e** could be isolated via a usual route and was stable under the conditions employed for the formation of oxetanes. The ring opening was performed under more forcing conditions, i.e., treatment with potassium *tert*-butoxide in tetrahydrofuran at 50 °C, and the ring-opened product was obtained in 81% yield (eq 5). However, the use of ketone

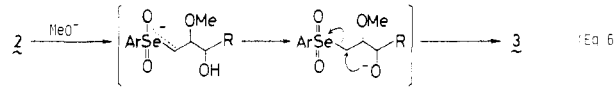


(Eq 5)

3e

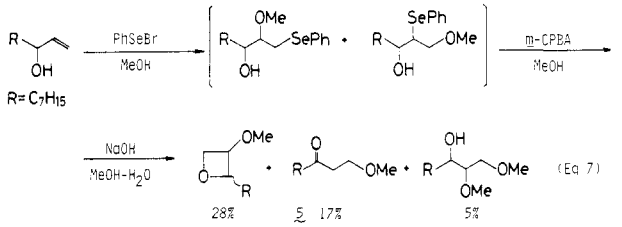
enolates as the initial nucleophiles failed to give the oxetane or its ring-opened products and resulted in the formation of complex mixtures.

The oxetane formation reaction proceeds most probably through a sequence of processes as shown in eq 6. The



(Eq 6)

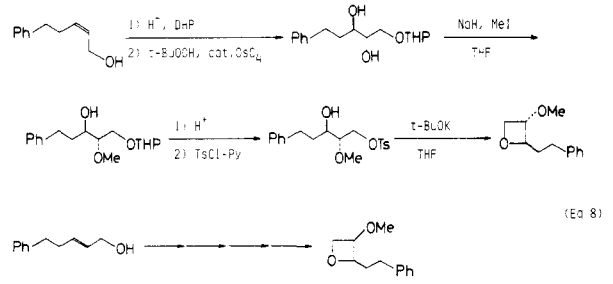
following reaction verifies the feasibility of the arylselenonyl moiety as the leaving group in the present reaction. A mixture of hydroxy selenides prepared via oxyselenenylation of an allylic alcohol[11] was oxidized with 2 equiv of *m*-CPBA (eq 7). Treatment of the resulting



(Eq 7)

reaction mixture with sodium hydroxide in methanol gave the methoxyoxetane along with the ketone **5**.[12] This observation supports the proposed conjugate addition of methoxide followed by ring closure through the elimination of an arylselenonyl group.[13] The efficiency of the arylselenonyl moiety as a leaving group is to be compared with sulfone analogues where arylsulfonyl groups are not always good leaving groups.[14]

Stereochemistry of the methoxyoxetane formation was also examined by comparison with authentic samples prepared according to eq 8.



(Eq 8)

(11) Reich, H. J. *J. Org. Chem.* **1974**, *39*, 428. Sharpless, K. B.; Lauer, R. F. *Ibid.* **1974**, 429. Toshimitsu, A.; Uemura, S.; Okano, M. *J. Chem. Soc., Chem. Commun.* **1977**, 166. Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1689. Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *Ibid.* **1978**, *43*, 1697. Laber, D.; Krief, A.; Hevesi, L. *Tetrahedron Lett.* **1978**, 3967. Nicolaou, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704.

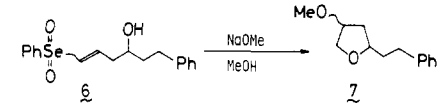
(12) Takahashi, T.; Nagashima, H.; Tsuji, J. *Tetrahedron Lett.* **1978**, 799. Reich, H. J.; Chow, F.; Shah, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 6638. Reich, H. J.; Shah, S. K.; Chow, F. *Ibid.* **1979**, *101*, 6648.

(13) Liotta reported the lactone formation from 5-(phenylseleno)valeric acid via oxidative elimination with hydrogen peroxide: Liotta, D.; Santiesteban, H. *Tetrahedron Lett.* **1977**, 4369.

(14) Curci, R.; DiFuria, F. *Tetrahedron Lett.* **1974**, 4085.

Close examination of the reaction mixture reveals that both (*E*)- and (*Z*)-3-(phenylselenonyl)-2-alken-1-ols produced *cis*-methoxyoxetane predominantly. For example, a 66:34 ratio for run 1 and 69:31 for run 2 were obtained. A similar ratio was obtained in every case (cis/trans = 2:1) in Table I.

In an analogous way to the oxetane-forming reaction, the vinyl selenone **6** bearing a hydroxy group at its homoallylic position underwent cyclization to give methoxytetrahydrofuran **7** in 68% yield (eq 9). This example



(Eq 9)

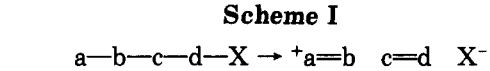
6 7

suggests the possible formation of other cyclic ethers by using vinyl selenones having a hydroxy group at suitable positions.

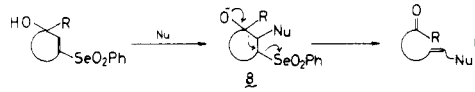
Fragmentation Reactions

The reactions involving selective carbon–carbon bond cleavage constitute important methodologies in synthetic organic chemistry, especially when they are applied to cyclic systems. Grob has organized fragmentation reactions and classified some of them as heterolytic fragmentations as depicted in Scheme I, where X and a=b are designated

Scheme I



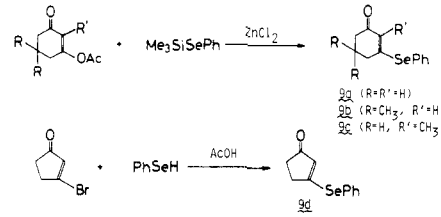
as a nucleofuge and an electrofuge, respectively.[15] The high efficacy of an arylselenonyl group as a leaving group described earlier has suggested that if X is displaced with an arylselenonyl group and a—b with an alkoxide (eq 10), this system **8** may undergo fragmentation to give a ring-opened product bearing carbonyl and olefinic moieties.



(Eq 10)

8

The cyclic compounds having hydroxy and phenylselenonyl groups at suitable positions have been prepared as shown in eq 11. Since the benzeneselenolate anion is a strong nucleophile,[16] it was expected that α,β-unsaturated ketones bearing leaving groups at their β-positions would react with the benzeneselenolate anion to produce β-(phenylseleno)-α,β-unsaturated ketones. Although the reaction of 3-acetoxy-5,5-dimethyl-2-cyclohexen-1-one with sodium benzeneselenolate in DMF gave the desired ketone in only 10% yield, a recently introduced reagent, trimethylsilyl phenyl selenide,[17] improved this addition process remarkably to afford the desired β-phenylseleno enones **9a** and **9b** in 89% and 83% yields, respectively (eq 11). Treatment of β-halo-α,β-unsaturated ketones with



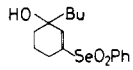
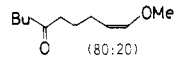
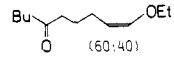
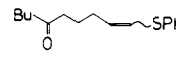
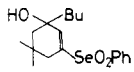
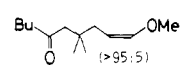
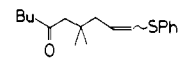
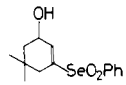
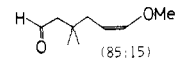
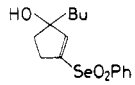
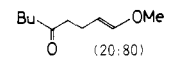
(Eq 11)

(15) Grob, C. A.; Schiess, P. W. *Angew. Chem.* **1967**, *79*, 1. Wakabayashi, T.; Watanabe, K. *J. Synth. Org. Chem. Jpn.* **1980**, *38*, 853.

(16) Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319. Barth, H.; Gosselck, J. *Z. Naturforsch., B: Anorg. Chem.; Org. Chem., Biochem., Biophys., Biol.*, **1961**, *166*, 280.

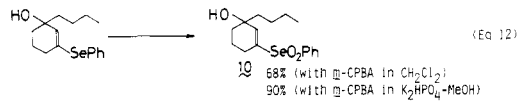
(17) Liotta, D.; Paty, P. D.; Johnston, J.; Zima, G. *Tetrahedron Lett.* **1978**, 5091. Miyoshi, N.; Ishii, H.; Kondo, K.; Murai, S.; Sonoda, N. *Synthesis* **1979**, 300.

Table II. Fragmentation Reactions of Type A

substrate	nucleophile	product (Z:E)	yield, %
	MeONa	 (80:20)	86
	EtONa	 (60:40)	84
	PhSNa		68
	MeONa	 (>95:5)	78
	PhSNa		63
	MeONa	 (85:15)	68
	MeONa	 (20:80)	68

benzeneselenol under acidic conditions also gave the corresponding β-seleno enones.[18]

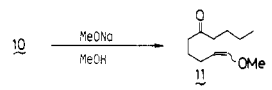
These compounds serve as good acceptors of nucleophiles to give the corresponding 1-alkyl-3-(phenylseleno)-2-cyclohexen-1-ols in good yields on treatment with the appropriate nucleophiles. However, the resulting tertiary allylic alcohols were very labile under acidic or even almost neutral conditions, and standing at room temperature leads to formation of complex mixtures. Owing to this lability, oxidation of 1-butyl-3-(phenylseleno)-2-cyclohexen-1-ol with *m*-CPBA in methanol or in methylene chloride gave the corresponding selenone in moderate or low yield (eq 12). However, these unstable alcohols could



(Eq 12)

be coverted to the desired selenones **10** in 80–100% yield by carrying out the oxidation in the presence of dipotassium hydrogen phosphate or sodium carbonate.

Treatment of the selenone **10** with sodium methoxide in methanol gave rise to product **11**, arising from the expected addition and fragmentation reactions (type A) in 86% yield (eq 13). Other cyclic hydroxy vinyl selenones



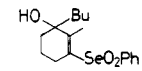
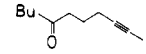
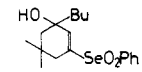
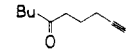
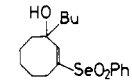
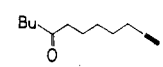
(Eq 13)

underwent similar fragmentations to give the corresponding acyclic ketones having vinyl ether moieties. Replacement of methoxide with ethoxide did not noticeably change the efficiency of this fragmentation system. Further, sodium benzenethiolate also effected a similar bond cleavage to afford the oxo vinyl sulfide (Table II).

Replacement of methoxide or ethoxide with bases of low nucleophilicity induces another type of fragmentation reaction. On treatment cyclic hydroxy vinyl selenones with sodium hydride, potassium *tert*-butoxide, or lithium di-

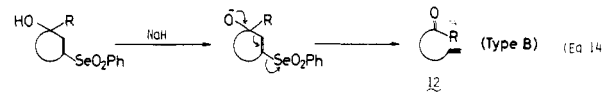
(18) Miyashita, M.; Yoshikoshi, A. *Synthesis* **1980**, 664.

Table III. Fragmentation Reactions of Type B

substrate	product	yield, %
		84 (40[a])
		59 (39[b]; 20[c])
		30 (28[a])

[a] The reaction was carried out with sodium methoxide in methanol. [b] The reaction was carried out with potassium *tert*-butoxide. [c] The reaction was carried out with LDA in THF.

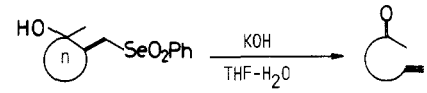
isopropylamide (LDA) in tetrahydrofuran, a direct fragmentation reaction (type B) takes place to give the corresponding acetylenic ketones **12** as shown in eq 14.



(Eq 14)

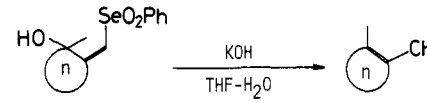
Among the several bases examined, sodium hydride has proved to be the most efficient for this transformation. Furthermore, in the case of vinyl selenones having tetrasubstituted olefins, the addition of alkoxide was quite slow, and type B fragmentation reactions predominated over the type A process (Table III).

Apparently, the trans relationship between an electron-donating oxido group and the leaving selenonyl group facilitates this fragmentation (type B). On treatment with potassium hydroxide in aqueous tetrahydrofuran, for example, *exo*-olefinic vinyl selenones **13** of E configuration underwent similar bond cleavage to give the corresponding acetylenic ketones **14** in good yield (eq 15). On the other, carbon–carbon bond cleavage did not take place so efficiently with the vinyl selenones **15** having the Z configuration, which gave the corresponding enal **16** under similar reaction conditions (eq 16).



(Eq 15)

13a (n=6) 14a 73%
13b (n=8) 14b 62%



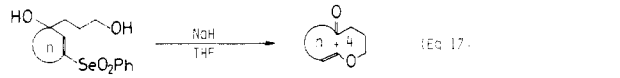
14 (Eq 16)

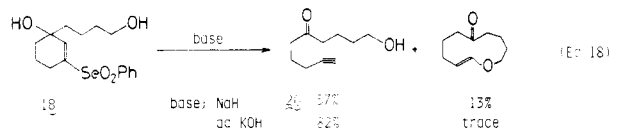
15a (n=6) 16a 30% 28% (14a)
15b (n=8) 16b 56% 0%

Application of this methodology to the substrates bearing a nucleophilic center seems to be quite useful because a medium-sized ring system having a vinyl ether moiety may be easily constructed. 3-(Phenylseleno)-2-cycloalken-1-ols **17** and **18** having the 3-hydroxypropyl or 4-hydroxybutyl group at their 1-positions were prepared by using appropriate Grignard reagents.[19,20] The former underwent the expected internal addition–fragmentation reaction (type A) cleanly to give the corresponding me-

(19) Fischli, A.; Branca, E.; Daly, J. *Helv. Chim. Acta* **1976**, *59*, 2443.
(20) Coke, J. L.; Williams, H. J.; Natarajan, S. *J. Org. Chem.* **1977**, *42*, 2380.

dium-sized cyclic product **19** in good yield on treatment with sodium hydride in tetrahydrofuran, whereas, under similar reaction conditions, the direct fragmentation process (Type B) predominated over the addition–fragmentation (type A) in the latter substrates (eq 18), probably because the addition involving formation of a seven-membered ring may be greatly disfavored.

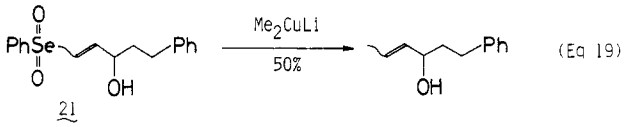




The ability of a selenonyl substituent as a leaving group in this fragmentation should be compared with those of others. Recently, a related fragmentation reaction has been applied to the synthesis of *d,l*-muscone where a tolylsulfonyl group was employed as the leaving group.[21] However, under the same conditions, 1-(2-phenylethyl)-3-(phenylsulfonyl)-1-cyclohexen-1-ol did not undergo fragmentation at all. Even with the successful muscone synthesis, rather forcing conditions were required for the C–C bond cleavage. By using chlorine as an electrofuge, a fragmentation reaction of 3-chloro-1-methyl-2-cyclohexen-1-ol similar to type B has also been described.[22] But in this case, a carbon–carbon bond cleavage was observed only at an elevated temperature, e.g., 200 °C, although the cationic species was different. In strong contrast, both fragmentation reactions type A and B usually proceed at about room temperature and give the corresponding ring-opened products in good yields, which clearly indicates an excellent tendency of selenonyl as a leaving group owing to weak carbon–selenium bonds.

Finally, it should be noted that nucleophilic reagents employed to vinyl selenones seem to be rather restricted to the ones having lower p*K*a values such as alcohols or thiols. In the reaction with dodecenyl phenyl selenone, lithium phenylacetylide works mainly as a base to afford 1-dodecyne in 63% yield.

Furthermore, treatment of the hydroxy vinyl selenone **21** with dimethylcuprate results in the displacements of the selenonyl group with a methyl substituent (eq 19).



Although anionic species of active methylene compounds add to acyclic vinyl selenones to yield the corresponding cyclopropanes,[6] they do not react with the cyclic hydroxy vinyl selenones described here, which has made it unfeasible to achieve a fragmentation reaction involving a new carbon–carbon bond formation.

Experimental Section

General Methods. Boiling points and melting points are uncorrected. Infrared (IR) spectra were recorded on a Hitachi EPI-G3 spectrometer; absorptions are given in reciprocal centimeters. Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a Hitachi R-24B spectrometer; chemical shifts (δ) are expressed in parts per million downfield from internal tetramethylsilane. Analytical gas–liquid chromatography (GLC) was performed on a Hitachi 163 instrument with a flame-ionization detector and nitrogen carrier gas (1.0–1.3 kg/cm^2) by using a column of 20% PEG 20 M on Diasolid (3 mm × 2 m). Mass spectra (70 eV) were determined on a Hitachi RMU-6C or RMU-7M spectrometer. Microanalysis were performed with a Perkin-Elmer 240 spectrometer at the Microanalysis Laboratory, Tokyo Institute of Technology.

Reactions involving air- or moisture-sensitive compounds were carried out in appropriate round-bottomed flasks with magnetic stirring bars under nitrogen or argon. Bulb-to-bulb distillation was performed with a Büchi Kugelrohr apparatus.

Preparative thin-layer chromatography (TLC) was carried out on glass plates (20 × 20 cm) coated with Merck silica gel PF 254 (1 mm thick). Column chromatography was performed on Merck Kieselgel 60 or Wakogel C-200.

Ether, tetrahydrofuran, and dimethoxyethane were distilled from sodium benzophenone ketyl in a recycling still immediately before use. Methanol was distilled from sodium methoxide and stored over 3A molecular sieves. Ethanol was distilled from magnesium ethoxide in the presence of diethyl succinate and stored over 3A molecular sieves. *m*-Chloroperbenzoic acid (*m*-CBPA, 85% pure), purchased from Aldrich Chemical Co., was used directly without purification.

3-(Phenylseleno)-2-propenal was prepared by the procedure reported before.[9] 3-[(*p*-Chlorophenyl)seleno]-2-propenal was prepared from 3-[(*p*-chlorophenyl)seleno]-1-propene oxide in a similar manner. **(*E*)-3-[(*p*-Chlorophenyl)seleno]-2-propenal**: IR (neat) 1670, 1565; NMR (CCl_4) 6.07 (dd, J = 14.0 and 7.0 Hz, 1 H), 7.27–7.60 (m, 4 H), 7.92 (d, J = 14.0 Hz, 1 H), 9.28 (d, J = 7.0 Hz, 1 H). **(*Z*)-3-[(*p*-Chlorophenyl)seleno]-2-propenal**: IR (KBr) 1640, 1550; NMR (CCl_4) 6.80 (dd, J = 8.0 and 1.0 Hz, 1 H), 7.10–7.60 (m, 4 H), 7.78 (d, J = 8.0 Hz, 1 H), 9.73 (d, J = 1.0 Hz, 1 H).

1-Dodecenyl Phenyl Selenone. General Procedure for Oxidation of a Selenide to the Selenone. To a solution of *m*-CPBA (202 mg, 1.0 mmol) in 1 mL of methanol was added a solution of 1-dodecenyl phenyl selenide (162 mg, 0.5 mmol) in methanol (4 mL) and methylene chloride (1 mL) at −78 °C. After being allowed to stand at room temperature for 6 h, the reaction mixture was washed with saturated aqueous $NaHCO_3$, and the aqueous layer was extracted with methylene chloride. The combined extracts were dried over anhydrous $MgSO_4$. Removal of the solvent gave the title compound (176 mg, 99%) as a colorless oil. This compound decomposed to some extent on attempts at distillation or purification by TLC: IR (neat) 2890, 1610, 1465, 1445, 1075, 950, 895, 795, 770, 690; NMR (CCl_4) 0.60–1.80 (m, 19 H), 2.01–2.80 (m, 2 H), 6.40–6.73 (m, 1 H), 6.70–7.10 (m, 1 H), 7.33–7.70 (m, 3 H), 7.70–8.00 (m, 2 H); mass spectrum, *m/e* (relative intensity) 356 (M^+, 17), 340 (13), 314 (33), 191 (78), 174 (78), 157 (56), 145 (28), 109 (22), 95 (44), 81 (44), 77 (39), 70 (50), 69 (56), 57 (100), 55 (100).

Reaction of 1-Dodecenyl Phenyl Selenone with Methoxide. To a solution of 1-(phenylseleno)-1-decene (162 mg, 0.5 mmol) in 2 mL of methanol was added a solution of *m*-CPBA (345 mg, 2.0 mmol) in 3 mL of methanol at −78 °C, and the mixture was allowed to stand at room temperature for 3 h. Then, aqueous NaOH (2.5 mL of 1 M solution) was added to the reaction mixture, and the mixture was stirred for 12 h at room temperature. After addition of saturated aqueous NaCl followed by extraction of the aqueous layer with ether, the combined extracts were dried over anhydrous $MgSO_4$ and the solvent was removed to give an oil. Purification by TLC gave the title compound (59 mg, 51%) as a colorless oil: IR (neat) 2900, 1460, 1370, 1195, 1110, 850, 720; NMR (CCl_4) 0.80–1.75 (m, 21 H), 3.10–3.50 (m, 9 H, including two singlets at 3.30 and 3.33 each corresponding to 3 H); mass spectrum, *m/e* (relative intensity) 201 (M^+ − 29, 1), 177 (66), 118 (8), 101 (25), 98 (100), 83 (97), 71 (59), 69 (81), 55 (88). These spectra were identical with those of the authentic sample prepared in the following manner: osmium tetroxide catalyzed oxidation of 1-dodecene followed by methylation with methyl iodide in the presence of sodium hydride.

(21) Cahiez, G.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1978**, 3013.

(22) Eaton, P. E.; Cooper, G. E.; Johnson, R. C.; Mueller, R. H. *J. Org. Chem.* **1972**, *37*, 1947.

3-Methoxy-2-(2-phenylethyl)oxetane (3a). General Procedure for the Preparation of Methoxyoxetanes 3. To a solution of (*E*)-3-(phenylseleno)-2-propenal (106 mg, 0.5 mmol) in THF (5 mL) was added a THF solution of 2-phenylethylmagnesium chloride (0.77 mL of 0.78 M solution, 0.6 mmol) at 0 °C. After workup with saturated aqueous NH_4Cl followed by drying and concentration, the crude oil was treated with *m*-CPBA (206 mg, 1.0 mmol) in methanol (5 mL) at room temperature for 30 min. Then a 1 M aqueous solution of NaOH (2 mL) was added to the reaction mixture, and it was stirred for 18 h at room temperature. Workup with saturated aqueous NaCl followed by extraction with ether, drying, and removal of the solvent gave the crude product as an oil, which was purified by TLC to afford the title compound (77 mg, 80%) as a colorless oil: IR (neat) 2900, 1600, 1210, 1130, 970, 870, 750, 700; NMR (CCl_4) 1.73–2.33 (m, 2 H), 2.40–2.85 (m, 2 H), 3.20 (s, 3 H), 4.20–4.70 (m, 4 H), 7.43 (s, 5 H); mass spectrum, *m/e* (relative intensity) 162 ($M^+ - 30$, 7), 134 (83), 105 (30), 92 (90), 91 (100), 77 (33), 41 (88). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 75.08; H, 8.23. GLC analysis indicated that the product contained two isomers in a ratio of 63:32.

2-Hexyl-3-methoxyoxetane (3b): bp 60 °C (0.2 mmHg) (bath temp); IR (neat) 2910, 1460; NMR (CCl_4) 0.65–1.90 (m, 13 H), 3.20 (s, 3 H), 4.20–4.70 (m, 4 H); mass spectrum, *m/e* (relative intensity) 172 (M^+, 1), 142 (58), 141 (61), 110 (85), 85 (77), 71 (100); isomeric ratio 65:33. Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.86; H, 11.53.

2-Phenyl-3-methoxyoxetane (3c): IR (neat) 2890, 1660, 1585, 1125; NMR (CCl_4) 2.87 (s, 3 H), 4.30–4.75 (m, 3 H), 5.62 (d, J = 5.0 Hz, 1 H), 7.27 (br s, 5 H). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.19; H, 7.51.

2-Decyl-3-methoxyoxetane (3d): bp 85–93 °C (0.1 mmHg) (bath temp); IR (neat) 2870, 1450; NMR (CCl_4) 0.60–2.00 (m, 21 H), 3.20 (s, 3 H), 4.10–4.85 (m, 4 H); mass spectrum, *m/e* (relative intensity) 198 ($M^+ - 30$, 1), 85 (9), 72 (6), 71 (100), 58 (30), 57 (19), 43 (55); isomeric ratio 65:35. Anal. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 73.78; H, 12.51.

2-[(1-*tert*-Butoxycarbonyl)pentyl]-3-methoxyoxetane (3e): bp 90–100 °C (0.2 mmHg) (bath temp); IR (neat) 1710; NMR (CCl_4) 0.70–2.00 (m, 19 H, including singlet at 1.40 as 9 H), 3.20 (s, 3 H), 4.10–4.80 (m, 4 H). Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.08; H, 10.14. Found: C, 65.23; H, 10.02.

***tert*-Butyl 5-Hydroxy-4-methoxy-(*E*)-2-pentenoate (4).** To a solution of lithium cyclohexylisopropylamide (0.6 mmol) in 2 mL of THF was added a solution of *tert*-butyl acetate (64 mg, 0.55 mmol) in 3 mL of THF at −78 °C. After being stirred for 30 min at that temperature, the mixture was treated with (*E*)-3-(phenylseleno)-2-propenal (106 mg, 0.55 mmol) in THF (1 mL). Then the reaction mixture was stirred for 2 h at −78 to 0 °C. Usual workup of the reaction mixture gave an oil (180 mg), which was added to a solution of *m*-CPBA (203 mg, 1.0 mmol) in 5 mL of methanol at −78 °C. After being allowed to stand at room temperature for 1 h, the reaction mixture was treated with a 1 M solution of methanolic LiOH (2 mL, 2.0 mmol) at room temperature and was allowed to stand at room temperature for 12 h. Then it was washed with saturated aqueous $NaHCO_3$, and the aqueous layer was extracted with ethyl acetate. The combined extracts were dried and concentrated to give an oil (149 mg), which was purified by TLC to afford the title compound (88 mg, 87%) as a colorless oil: bp 85 °C (0.09 mmHg) (bath temp); IR (neat) 3360, 1700; NMR (CCl_4) 1.43 (s, 9 H), 2.90 (s, 1 H), 3.33 (s, 3 H), 3.20–3.90 (m, 3 H), 5.83 (d, J = 8.0 Hz, 1 H), 6.60 (dd, J = 8.0 and 6.0 Hz, 1 H). Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.58; H, 8.97.

4-Methyl-2-(3-hydroxy-2-methoxy-1-propylidene)-γ-butyrolactone: bp 110 °C (0.03 mmHg) (bath temp); IR (neat) 3350, 1730; NMR (CCl_4) 1.40 (d, J = 6.0 Hz, 3 H), 2.50–2.80 (m, 1 H), 2.90–3.20 (m, 1 H), 2.70 (s, 1 H), 3.30 (s, 3 H), 3.60 (d, J = 6.0 Hz, 2 H), 3.90–4.20 (m, 1 H), 4.70 (dd, J = 10.0 and 6.0 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 156 ($M^+ - 30$, 4), 155 ($M^+ - 31$, 6), 119 (1), 111 (3), 61 (14), 45 (22), 43 (100), 41 (4), 29 (22), 28 (10), 27 (14).

***tert*-Butyl 2-Butyl-5-hydroxy-4-methoxy-2-pentenoate.** A solution of 2-[1-(*tert*-butoxycarbonyl)-1-pentyl]-3-methoxyoxetane (88 mg, 0.34 mmol) in 10 mL of THF was added to *t*-BuOK (38 mg, 0.34 mmol) at room temperature, and the mixture was stirred at 50–60 °C for 3 h. After usual workup and purification by TLC, the title compound (71 mg, 81%) was obtained: bp 80 °C (0.03 mmHg) (bath temp); IR (neat) 3320, 1695; NMR (CCl_4), 0.70–1.70 (m, 18 H, including a singlet at 1.47 as 9 H), 2.10–2.50 (m, 3 H), 3.30 (s, 3 H), 3.58 (d, J = 6.0 Hz, 2 H), 3.40–4.20 (m, 1 H), 6.20 (d, J = 9.0 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 227 ($M^+ - 31$, 55), 185 (7), 171 (100), 157 (17), 139 (34), 111 (34), 93 (34), 83 (28), 57 (100).

Cyclization Reaction of 3-Hydroxy-2-methoxy-1-(phenylseleno)decane. To a solution of benzeneselenenyl bromide (6.1 mmol) in 5 mL of methanol was added a solution of 3-hydroxy-1-decene (954 mg, 6.1 mmol) in 5 mL of methanol at room temperature. After being stirred for 2 h at room temperature, the reaction mixture was washed with saturated aqueous NaCl, extracted with ether, dried, and concentrated to give an oil. Purification by silica gel column chromatography gave a mixture of 3-hydroxy-2-methoxy-1-(phenylseleno)decane and 3-hydroxy-1-methoxy-2-(phenylseleno)decane (1.3 g, 62%). A mixture of selenides prepared above (172 mg) was dissolved in 4 mL of methanol, and a solution of *m*-CPBA (203 mg, 1.0 mmol) in 1 mL of methanol was added at −78 °C. After being allowed to stand at room temperature for 2 h, the mixture was treated with aqueous NaOH (0.7 mL of 3 M solution, 2.0 mmol), and it was stirred for 3 h at room temperature. Aqueous workup followed by purification by TLC gave a mixture of 2-heptyl-3-methoxyoxetane, 1-methoxy-3-decanone (5) (42 mg), and 1,2-dimethoxy-3-decanol (13 mg). **2-Heptyl-3-methoxyoxetane:** IR (neat) 2990, 1450, 1130, 960, 790; NMR (CCl_4) 0.60–2.00 (m, 15 H), 3.20 (s, 3 H), 3.67–4.60 (m, 4 H).

***cis*-2-(2-Phenylethyl)-3-methoxyoxetane.** To a solution of lithium dicyclohexylamide (33 mmol) in 45 mL of THF was added dropwise a solution of ethyl (trimethylsilyl)acetate (5.28 g, 33 mmol) in 5 mL of THF at −78 °C. After the mixture was stirred at that temperature for 40 min, a solution of 3-phenylpropanal (4.2 g, 30 mmol) in 10 mL of THF was added to it. After stirring at that temperature for 1 h and then at room temperature for 1 h, usual workup with saturated aqueous NH_4Cl followed by filtration of the precipitate gave the crude product. It was separated by silica gel column chromatography to afford ethyl 5-phenyl-(*E*)-2-pentenoate (848 mg, 52%) and its *Z* isomer (531 mg, 33%). The *E* isomer (848 mg, 4.16 mmol) was reduced with lithium aluminum hydride (79 mg, 2.09 mmol) in 17 mL of ether to give 5-phenyl-(*E*)-2-penten-1-ol (190 mg). It was treated with DHP (197 mg, 2.34 mmol) and a catalytic amount of *p*-TsOH in THF at room temperature for 4 h, and the tetrahdropyranyl ether (287 mg) was obtained. A mixture of the ether (287 mg) thus prepared, tetrabutylammonium hydroxide (0.117 mmol), *t*-BuOOH (240 mg of 70% solution, 1.87 mmol), and OsO_4 (0.03 mL of a 12.7 M aqueous solution, 0.0023 mmol) in 5 mL of *t*-BuOH was stirred at 0 °C for 18 h. Then the mixture was treated with $NaHSO_3$ and extracted with ethyl acetate to give triol monotetrahydropyranyl ether (322 mg), which was purified by silica gel column chromatography. The pure sample (104 mg) was treated with sodium hydride (0.48 mmol) and methyl iodide (0.03 mL, 0.48 mmol) in THF for 2 h at room temperature under stirring. Workup with saturated aqueous NaCl gave a methylated product (95 mg). The protecting pyranyl moiety was removed by treatment with 1 N HCl at room temperature for 14 h to give 2-methoxy-5-phenyl-1,3-pentanediol (66 mg). It was treated with *p*-TsCl (66 mg, 0.34 mmol) in 3 mL of pyridine at 0 °C for 24 h. Workup with saturated aqueous $NaHCO_3$ followed by removal of pyridine in vacuo gave the tosylated product (83 mg). Cyclization to methoxyoxetane was effected by treating with *t*-BuOK (46 mg, 0.23 mmol) in 2 mL of THF at room temperature for 4 h to afford the title compound (51 mg). Further purification by bulb-to-bulb distillation gave a pure sample [bp 80 °C (0.1 mmHg) (bath temp); IR (neat) 2920, 1600, 1490, 1450, 1380, 970, 750, 700; NMR (CCl_4) 1.70–2.37 (m, 2 H), 2.37–2.93 (m, 2 H), 3.20 (s, 3 H), 4.17–4.87 (m, 4 H), 7.13 (s, 5 H)], which was identical with the major product obtained from 5-phenyl-1-(phenylselenonyl)-1-penten-3-ol by comparison with GLC (retension time, 4.29 min at 190 °C).

***trans*-2-(2-Phenylethyl)-3-methoxyoxetane.** It was prepared from ethyl 5-phenyl-(*Z*)-2-pentenoate in the same manner as the the cis isomer [bp 80 °C (0.1 mmHg) (bath temp); IR (neat) 2920, 1600, 1490, 1450, 1360, 1190, 1175, 965, 750, 700; NMR (CCl_4)

1.70–2.20 (m, 2 H), 2.40–2.90 (m, 2 H), 3.23 (s, 3 H), 3.80–4.15 (m, 1 H), 4.20–4.75 (m, 3 H), 7.20 (s, 5 H)], which was identical with the minor product obtained from 5-phenyl-1-(phenylselenonyl)-1-penten-3-ol by comparison with GLC (retension time, 3.91 min at 190 °C).

2-(2-Phenylethyl)-4-methoxytetrahydrofuran (7). 6-Phenyl-1-(phenylseleno)-1-hexen-4-ol (**6**, 66 mg, 0.2 mmol) was oxidized with *m*-CPBA (89 mg, 0.44 mmol) in 2 mL of methanol. The reaction mixture was then treated with aqueous sodium hydroxide (0.74 mL of a 1 M solution, 0.74 mmol) for 18 h at room temperature. The usual workup followed by purification by silica gel column chromatography afforded the title compound as a colorless oil (28 mg, 68%): IR (neat) 2920, 1600, 1495; NMR (CCl_4) 1.33–2.10 (m, 4 H), 2.67 (dt, J = 8.0 and 2.0 Hz, 2 H), 3.20 (s, 3 H), 3.40–4.00 (m, 3 H), 7.07 (s, 5 H).

3-(Phenylseleno)-2-cyclohexen-1-one (9a). General Procedure for Preparation of 3-(Phenylseleno)-2-cycloalkan-1-ones. To a solution of 3-acetoxy-2-cyclohexen-1-one (2.31 g, 15 mmol) in 10 mL of benzene was added a solution of phenyl trimethylsilyl selenide (3.81 g, 16.6 mmol) in 5 mL of benzene and a catalytic amount of zinc iodide, and it was stirred for 2.5 h at room temperature. The reaction mixture was treated with saturated aqueous $NaHCO_3$, and the aqueous layer was extracted with ethyl acetate. Drying the combined extracts followed by removal of the solvent and purification by column chromatography afforded the title compound (3.35 g, 89%): bp 90 °C (0.08 mmHg) (bath temp); IR (neat) 1655; NMR (CCl_4) 1.73–2.65 (m, 6 H), 5.61 (t, J = 2.0 Hz, 1 H), 7.18–7.65 (m, 5 H). Anal. Calcd for $C_{12}H_{12}OSe$: C, 57.38; H, 4.82. Found: C, 57.21; H, 4.72.

5,5-Dimethyl-3-(phenylseleno)-2-cyclohexen-1-one (9b): yield 83%; bp 124 °C (0.15 mmHg) (bath temp); IR (neat) 1655; NMR (CCl_4) 1.03 (s, 6 H), 2.08 (s, 2 H), 2.33 (s, 2 H), 5.60 (t, J = 1.3 Hz, 1 H), 7.16–7.60 (m, 5 H). Anal. Calcd for $C_{14}H_{16}OSe$: C, 60.22; H, 5.77. Found: C, 59.95, H, 5.89.

2-Methyl-3-(phenylseleno)-2-cyclohexen-1-one (9c): yield 69%; mp 99.5–100.0 °C; IR (KBr) 1635; NMR (CCl_4) 1.6–2.5 (m, 9 H), 7.2–7.7 (m, 5 H). Anal. Calcd for $C_{13}H_{14}OSe$: C, 58.87; H, 5.32. Found: C, 58.95, H, 5.28.

3-(Phenylseleno)-2-cyclopenten-1-one (9d). Diphenyl diselenide (1.7 g, 5.4 mmol) was treated with sodium borohydride (410 mg, 10.8 mmol) in ethanol (20 mL) at room temperature. To the resulting solution of sodium benzeneselenolate was added acetic acid (2 mL) and then a solution of 3-bromo-2-cyclopenten-1-one (1.8 g, 11.2 mmol) in ethanol (5 mL) at 0 °C. After stirring overnight at room temperature, the solvent was removed and the residue was treated with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ethyl acetate, and the combined extracts were washed with saturated aqueous NaCl solution. Drying followed by removal of the solvent afforded an oil, which was purified by column chromatography to give the title compound (2.25 g, 85%); mp 51.0–52.0 °C; bp 88 °C (0.02 mmHg) (bath temp); IR (neat) 1685; NMR (CCl_4) 2.13–2.43 (m, 2 H), 2.50–2.80 (m, 2 H), 5.68 (t, J = 1.5 Hz, 1 H), 7.10–7.70 (m, 5 H). Anal. Calcd for $C_{11}H_{10}OSe$: C, 55.71; H, 4.25. Found: C, 55.44; H, 4.26.

3-(Phenylseleno)-2-cycloocten-1-one (9e): yield 73%; bp 110 °C (0.01 mmHg) (bath temp); IR (neat) 1625; NMR (CCl_4) 1.40–2.00 (m, 6 H), 2.40–3.07 (m, 4 H), 5.83 (s, 1 H), 7.16–7.70 (m, 5 H). Anal. Calcd for $C_{14}H_{16}OSe$: C, 60.22; H, 5.77. Found: C, 59.98; H, 5.82.

5,5-Dimethyl-3-(phenylseleno)-2-cyclohexen-1-ol. To a solution of 5,5-dimethyl-3-(phenylseleno)-2-cyclohexen-1-one (562 mg, 2.01 mmol) in 5 mL of methanol were added $CeCl_3 \cdot 6H_2O$ (714 mg, 2.01 mmol) and sodium borohydride (76.5 mg, 2.01 mmol) at 0 °C. After it was stirred for 15 min at 0 °C, the reaction mixture was quenched with 1 N HCl and was extracted with ether. The combined extracts were washed with saturated aqueous NaCl and were dried over anhydrous $MgSO_4$. Removal of the solvent followed by purification by column chromatography gave the title compound (485 mg, 86%): bp 100 °C, (0.08 mmHg) (bath temp); IR (neat) 3350; NMR (CCl_4) 0.88 (s, 3 H), 0.95 (s, 3 H), 1.05–2.10 (m, 4 H), 3.05 (s, 1 H), 3.87–4.35 (m, 1 H), 5.70–5.98 (m, 1 H), 6.90–7.50 (m, 5 H). Anal. Calcd for $C_{14}H_{18}OSe$: C, 59.79; H, 6.45. Found: C, 59.81; H, 6.36.

1-Butyl-3-(phenylselenonyl)-2-cyclohexen-1-ol (10). General Procedure for the Preparation of 3-(Phenylselenonyl)-2-cycloalken-1-ols. To a solution of 3-(phenylseleno)-2-cyclohexen-1-one (198 mg, 0.79 mmol) in ether (3 mL) was added BuLi (0.43 mL of 2.02 M hexane solution, 0.87 mmol) at −78 °C. After being stirred for 20 min at −78 °C and then for 10 min at 0 °C, the reaction mixture was quenched with saturated aqueous NaCl and the aqueous layer was extracted with ether. Drying the combined extracts followed by removal of the solvent afforded the crude 1-butyl-3-(phenylseleno)-2-cyclohexen-1-ol in 73% yield. To a solution of *m*-CPBA (478 mg, 2.37 mmol) and K_2HPO_4 (824 mg, 4.73 mmol) in methanol (4 mL) was added the above crude oil in methanol (2 mL) at 0 °C. After it was stirred for 2 h at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and was extracted with chloroform. Washing the combined extracts with saturated aqueous NaCl followed by drying and removal of the solvent afforded the almost pure title compound (90% yield): IR (neat) 3420, 933, 875; NMR ($CDCl_3$) 0.70–2.62 (m, 15 H), 2.85 (s, 1 H), 6.97 (s, 1 H), 7.50–8.18 (m, 5 H).

1-Butyl-5,5-dimethyl-3-(phenylseleno)-2-cyclohexen-1-ol: IR (Nujol) 3430, 930, 877; NMR ($CDCl_3$) 0.60–2.30 (m, 19 H), 3.50 (s, 1 H), 6.93 (s, 1 H), 7.33–8.06 (m, 5 H). Anal. Calcd for $C_{18}H_{26}O_3Se$: C, 58.53; H, 7.09 Found: C, 58.38; H, 7.05.

5,5-Dimethyl-3-(phenylselenonyl)-2-cyclohexen-1-ol: IR (neat) 3380, 927, 873; NMR ($CDCl_3$) 0.90 (s, 3 H), 1.05 (s, 3 H), 1.18–2.30 (m, 4 H), 4.23–4.77 (m, 1 H), 5.26 (s, 1 H), 6.90–7.17 (m, 1 H), 7.47–8.07 (m, 5 H).

1-Butyl-3-(phenylselenonyl)-2-cyclopenten-1-ol: IR (neat) 3370, 933, 880; NMR ($CDCl_3$) 0.57–2.93 (m, 13 H), 3.70 (s, 1 H), 6.63 (s, 1 H), 7.27–7.93 (m, 5 H).

1-Butyl-2-methyl-3-(phenylselenonyl)-2-cyclohexen-1-ol: IR (neat) 3360, 925, 873; NMR ($CDCl_3$) 0.50–2.77 (m, 18 H), 6.43 (s, 1 H), 7.0–8.2 (m, 5 H).

1-Butyl-3-(phenylselenonyl)-2-cycloocten-1-ol: IR (Nujol) 3350, 920, 870; NMR ($CDCl_3$) 0.67–2.10 (m, 19 H), 3.50 (s, 1 H), 7.03 (s, 1 H), 7.33–8.06 (m, 5 H).

10-Methoxy-9-decen-5-one (11). General Procedure for the Fragmentation Reaction of Type A. A solution of 1-butyl-3-(phenylselenonyl)-2-cyclohexen-1-ol (0.52 mmol) in THF (3 mL) was added to methanol (3 mL) and aqueous NaOH (1.2 mL of 1 M solution, 1.2 mmol), and it was stirred overnight at room temperature and then for 3 h at 45 °C. The reaction mixture was washed with aqueous NaCl, and the aqueous layer was extracted with ether. After drying and removal of the solvent, bulb-to-bulb distillation gave the title compound (82 mg, 86%): bp 95–98 °C (30 mmHg) (bath temp); IR (neat) 1715, 1668; NMR (CCl_4) 0.70–2.50 (m, 15 H), 3.43 (s, 0.8 H), 3.53 (s, 2.2 H), 4.00–4.40 (m, 1 H), 5.78 (d, J = 7.0 Hz, 0.8 H), 6.18 (d, J = 12.0 Hz, 0.2 H). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.42; H, 10.76.

10-Ethoxy-9-decen-5-one: bp 95–97 °C (28 mmHg) (bath temp); IR (neat) 1705, 1659; NMR (CCl_4) 0.50–2.51 (m, 18 H), 3.40–3.90 (m, 2 H), 4.02–4.60 (m, 1 H), 5.83 (ddd, J = 6.0, 1.0, and 1.0 Hz, 0.6 H), 6.31 (ddd, J = 13.0, 1.0, and 1.0 Hz, 0.4 H). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.95; H, 11.06.

10-Methoxy-7,7-dimethyl-9-decen-5-one: bp 122–123 °C (28 mmHg) (bath temp); IR (neat) 1705, 1658; NMR (CCl_4) 0.60–2.40 (m, 19 H), 3.51 (s, 3 H), 4.03–4.47 (m, 1 H), 5.35 (dt, J = 6.0 and 1.3 Hz, 1 H). Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.67; H, 11.13.

6-Methoxy-3,3-dimethyl-5-hexenal: bp 75 °C (9.5 mmHg) (bath temp); IR (neat) 1720, 1666; NMR (CCl_4) 1.02 (s, 6 H), 1.90–2.26 (m, 4 H), 3.46 (s, 0.4 H), 3.53 (s, 2.6 H), 4.07–4.50 (m, 1 H), 5.90 (d, J = 6.0 Hz, 0.86 H), 6.17 (d, J = 12.0 Hz, 0.14 H), 9.67 (t, J = 3.0 Hz, 1 H). Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.14; H, 10.45.

9-Methoxy-8-nonen-5-one: bp 85 °C (6.8 mmHg) (bath temp); IR (neat) 1705, 1650; NMR (CCl_4) 0.7–2.5 (m, 13 H), 3.41 (s, 3 H), 4.20–4.80 (m, 1 H), 5.75 (m, 0.2 H), 6.23 (d, J = 13.0 Hz, 0.8 H). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.52; H, 10.70.

10-(Phenylthio)-9-decen-5-one. A solution of 1-butyl-3-(phenylselenonyl)-2-cyclohexen-1-ol (0.18 mmol) in THF (1.5 mL) was added to sodium benzenethiolate (0.36 mmol) in THF (1.5 mL) and it was kept stirring overnight at room temperature. Then saturated aqueous NaCl was added and the aqueous layer was extracted with ether. The combined extracts were washed with

saturated aqueous NaCl and were dried. Removal of the solvent followed by purification with column chromatography afforded the title compound (32 mg, 68%): bp 88–105 °C (1.2 mmHg) (bath temp); IR (neat) 1704; NMR (CCl_4) 0.50–2.60 (m, 15 H), 5.50–6.30 (m, 2 H), 6.90–7.45 (m, 5 H). Anal. Calcd for $C_{16}H_{22}OS$: C, 73.34; H, 8.45. Found: C, 73.50; H, 8.54.

6,6-Dimethyl-10-(phenylthio)-9-decen-5-one: bp 124–125 °C (1.4 mmHg) (bath temp); IR (neat) 1700; NMR (CCl_4) 0.67–2.55 (m, 19 H), 5.33–6.37 (m, 2 H), 6.90–7.50 (m, 5 H). Anal. Calcd for $C_{18}H_{26}OS$: C, 74.43; H, 9.02; S, 11.04. Found: C, 74.60; H, 9.31; S, 11.07.

7,7-Dimethyl-9-decyn-5-one (12a). General Procedure for the Fragmentation of Type B. A solution of 1-butyl-5,5-dimethyl-3-(phenylselenonyl)-2-cyclohexen-1-ol (67.9 mg, 0.18 mmol) in THF (1.5 mL) was added to a solution of NaH (0.18 mmol) in THF (0.5 mL) and it was stirred overnight at room temperature. Then, saturated aqueous NaCl was added and the aqueous layer was extracted with ether. After washing with saturated aqueous NaCl and drying, removal of the solvent from the combined extracts followed by purification with column chromatography afforded the title compound (19.5 mg, 59%): bp 75 °C (18 mmHg) (bath temp); IR (neat) 3280, 2110, 1705; NMR (CCl_4) 0.68–1.68 (m, 13 H), 1.79 (t, J = 3.0 Hz, 1 H), 2.11–2.48 (m, 6 H). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. C, 79.84; H, 11.10.

9-Undecyn-5-one (12b): bp 87 °C (6.6 mmHg) (bath temp); IR (neat) 1695; NMR (CCl_4) 0.65–2.60 (m, 18 H). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.16; H, 10.98.

11-Dodecyn-5-one (12c): bp 89 °C (6.4 mmHg) (bath temp); IR (neat) 3245, 2100, 1695; NMR (CCl_4) 0.67–1.67 (m, 13 H), 1.73 (t, J = 2.5 Hz, 1 H), 1.97–2.50 (m, 6 H). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.21; H, 11.17.

(*E*)- and (*Z*)-2-[(Phenylseleno)methylidene]-1-cyclohexanone. Method A. To a solution of 2-(acetoxymethylidene)-1-cyclohexanone (1.13 g, 6.7 mmol) in 5 mL of benzene were added a solution of phenyl trimethylsilyl selenide (1.88 g, 8.2 mmol) in 5 mL of benzene and a catalytic amount of zinc iodide, and it was stirred for 1.5 h at room temperature. Usual workup with saturated aqueous NaCl followed by extraction with ethyl acetate, drying, and removal of the solvent gave an oil, which was purified by column chromatography to give the *E* isomer (457 mg, 26%) and the *Z* isomer (883 mg, 50%). ***E* isomer 13a**: bp 106 °C (0.09 mmHg) (bath temp); IR (neat) 1667; NMR (CCl_4) 1.50–2.65 (m, 8 H), 7.05–7.65 (m, 5 H), 7.77 (t, J = 2.0 Hz, 1 H). Anal. Calcd for $C_{13}H_{14}OSe$: C, 58.87; H, 5.32. Found: C, 58.99; H, 5.15. ***Z* isomer 15a**: mp 65.0–66.0 °C; IR (KBr) 1633; NMR (CCl_4) 1.50–2.65 (m, 8 H), 7.05–7.65 (m, 6 H). Anal. Found: C, 58.95; H, 5.37.

Method B. Diphenyl diselenide (333 mg, 1.07 mmol) was treated with sodium borohydride (81 mg, 2.13 mmol) in ethanol (6 mL) at room temperature, and then acetic acid (0.5 mL) was added at 0 °C. Then, a solution of 2-(acetoxymethylidene)-1-cyclohexanone (421 mg, 2.5 mmol) in ethanol (2 mL) was added, and it was stirred for 3 h at room temperature. After the solvent was removed in vacuo, saturated aqueous NaCl was added and was extracted with ethyl acetate. After drying and removal of the solvent, purification by column chromatography gave *E* (278 mg, 42%) and *Z* isomers (247 mg, 37%).

(*E*)- and (*Z*)-2-[(Phenylseleno)methylidene]-1-cyclooctanone. They were prepared in a similar manner with method B above. 2-(Acetoxymethylidene)-1-cyclooctanone (1.45 g, 7.41 mmol) gave the *E* isomer (1.04 g, 51%) and the *Z* isomer (0.70 g, 35%). ***E* isomer 13b**: bp 120 °C (0.07 mmHg) (bath temp); IR (neat) 1630; NMR (CCl_4) 1.30–2.00 (m, 8 H), 2.35–2.85 (m, 4 H), 7.05–7.60 (m, 5 H), 7.66 (s, 1 H). Anal. Calcd for $C_{15}H_{18}OSe$: C, 61.43; H, 6.19. Found: 61.43; H, 5.98. ***Z* isomer 15b**: bp 118 °C (0.02 mmHg) (bath temp); IR (neat) 1630; NMR (CCl_4) 1.30–2.00 (m, 8 H), 2.45–2.80 (m, 4 H), 7.05–7.60 (m, 6 H). Anal. Found: C, 61.33; H, 6.18.

7-Octyn-2-one (14a). A 5 M aqueous KOH solution (0.38 mL, 1.89 mmol) was added to a THF (3.5 mL) solution of (*E*)-1-methyl-2-[(phenylselenonyl)methylidene]-1-cyclohexen-1-ol (**15**, 197 mg, 0.63 mmol), which was prepared in a similar manner as described earlier. After the reaction mixture was stirred ovrnight at room temperature, 1 N HCl was added and was extracted with ether. After washing the combined extracts with saturated aqueous NaCl and drying, removal of the solvent followed by column chromatography afforded the title compound (57.2 mg, 73%): bp 90 °C (67 mmHg) (bath temp); IR (neat) 3170, 2110, 1705; NMR (CCl_4) 1.05–1.70 (m, 4 H), 1.77 (t, J = 2.5 Hz, 1 H), 2.03 (s, 3 H), 1.97–2.53 (m, 4 H).

9-Decyn-2-one (14b): IR (neat) 3260, 2110, 1700; NMR (CCl_4) 0.80–2.60 (m, 13 H), 2.05 (s, 3 H).

1-(3-Hydroxypropyl)-3-(phenylselenonyl)-2-cyclohexen-1-ol (17b). General Procedure for the Preparation of Dihydroxy Vinyl Selenones. Method A. Chloromagnesium 3-(chloromagnesio)propoxide (6.5 mL of a 0.198 M THF solution, 1.29 mmol) was added to a THF (3 mL) solution of 3-(phenylseleno)-2-cyclohexen-1-one (295 mg, 1.18 mmol) and it was stirred for 20 min at 0 °C. Then, the reaction mixture was quenched with water and the aqueous layer was extracted with ether. The combined extracts were washed with saturated aqueous NaCl and were dried over anhydrous $MgSO_4$. Removal of the solvent gave the crude product, which was treated with *m*-CPBA (950 mg, 4.7 mmol) and K_2HPO_4 (1.64 g, 9.4 mmol) in methanol (10 mL, overnight at room temperature. To the reaction was added saturated aqueous $NaHCO_3$, and it was extracted with chloroform. The combined extracts were washed with saturated aqueous NaCl and were dried. Removal of the solvent followed by purification with column chromatography afforded the title compound (187 mg, 46%): IR (neat) 3360, 933, 875; NMR ($CDCl_3$) 1.40–2.50 (m, 10 H), 3.33–3.83 (m, 4 H), 6.88 (s, 1 H), 7.40–8.07 (m, 5 H).

Method B. 1-Ethoxyethyl 3-lithiopropyl ether (1.90 mL of a 0.27 M ether solution, 0.52 mmol) was added to an ether (1 mL) solution of 3-(phenylseleno)-2-cyclohexen-1-one (118 mg, 0.47 mmol) at −78 °C, and it was stirred for 40 min at that temperature. Then the reaction mixture was quenched with water and was extracted with ether. The combined extracts were treated in a similar manner as above and the resulting residual oil was oxidized by a similar procedure. The resulting selenone was treated with 0.5 N HCl in THF for 15 min at room temperature and then neutralized with aqueous $NaHCO_3$. Usual workup of the reaction mixture followed by purification by column chromatography afforded the title compound (88.3 mg, 55%).

1-(3-Hydroxypropyl)-3-(phenylselenonyl)-2-cyclopenten-1-ol (17a): IR (neat) 3360, 933, 878; NMR ($CDCl_3$) 1.10–2.95 (m, 8 H), 3.23–3.93 (m, 2 H), 4.60 (s, 2 H), 6.78 (s, 1 H), 7.47–8.13 (m, 5 H).

1-(3-Hydroxypropyl)-3-(phenylselenonyl)-2-cycloocten-1-ol (17c): IR (neat) 3370, 933, 875; NMR ($CDCl_3$) 1.28–2.17 (m, 14 H), 3.51–3.83 (m, 2 H), 4.23 (s, 2 H), 6.93 (s, 1 H), 7.37–8.02 (m, 5 H).

1-(4-Hydroxybutyl)-3-(phenylselenonyl)-2-cyclohexen-1-ol (18): IR (neat) 3360, 927, 873; NMR ($CDCl_3$) 1.13–2.47 (m, 12 H), 3.20–3.80 (m, 4 H), 6.85 (s, 1 H), 7.37–8.07 (m, 5 H).

1-Oxa-9-cyclodecen-5-one (19b). General Procedure for the Preparation of Cyclic Keto Vinyl Ether. 1-(3-Hydroxypropyl)-3-(phenylselenonyl)-2-cyclohexen-1-ol (187 mg, 0.54 mmol) was treated with sodium hydride (0.57 mmol) in THF (2.5 mL) overnight at room temperature. Usual workup of the reaction mixture followed by purification with column chromatography afforded the title compound (61.8 mg, 74%): bp 92 °C (3.8 mmHg) (bath temp); IR (neat) 1700, 1645; NMR (CCl_4) 1.30–2.70 (m, 10 H), 3.57–4.05 (m, 2 H), 4.17–4.83 (m, 1 H), 5.81 (d, J = 6.0 Hz, 0.8 H), 5.93 (d, J = 13.0 Hz, 0.2 H). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.28; H, 9.14.

(*E*)-1-Oxa-8-cyclononen-5-one (19a): IR (neat) 1700, 1635; NMR (CCl_4) 1.60–2.90 (m, 8 H), 3.60–4.36 (m, 2 H), 4.37–5.50 (m, 1 H), 5.98 (d, J = 13.0 Hz, 1 H); mass spectrum, m/e (relative intensity) 140 (M^+, 16), 112 (21), 97 (33), 84 (32), 71 (24), 70 (33), 69 (20), 57 (16), 56 (26), 55 (27), 43 (30), 42 (100).

(*E*)-1-Oxa-11-cyclododecen-5-one (19c): bp 120–121 °C (5.8 mmHg) (bath temp); IR (neat) 1698, 1655; NMR (CCl_4) 1.05–2.80 (m, 14 H), 3.80 (t, J = 6.0 Hz, 2 H), 4.60 (dt, J = 12.0 and 6.0 Hz, 1 H), 5.75 (d, J = 12.0 Hz, 1 H). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.52; H, 9.96.

1-Hydroxy-9-decyn-5-one (20). A THF (2 mL) solution of 1-(4-hydroxybutyl)-3-(phenylselenonyl)-2-cyclohexen-1-ol (96.5 mg, 0.27 mmol) was treated with a 5 N KOH solution (0.16 mL, 0.80 mmol) overnight at room temperature. Usual workup of the reaction mixture followed by purification with column chromatography afforded the title compound (37.1 mg, 82%): bp 108 °C (3.6 mmHg) (bath temp); IR (neat) 3390, 3260, 2100, 1700;

NMR (CCl_4) 1.00–2.68 (m, 13 H), 3.57 (t, J = 5.0 Hz, 2 H), 4.01 (s, 1 H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.20; H, 9.56.

Reaction of 5-Phenyl-1-(phenylselenonyl)-1-penten-3-ol (21) with Lithium Dimethylcuprate. To a suspension of cuprous iodide (953 mg, 5.0 mmol) in 4 mL of ether was added an ethereal solution of methyllithium (16 mL of 0.63 M solution, 10 mmol) at 0 °C. Then, a solution of 5-phenyl-1-(phenylselenonyl)-1-penten-3-ol (**23**, 153 mg) in 5 mL of THF was added to the ice-cooled mixture, which was allowed to stand overnight at room temperature. Usual workup of the reaction mixture followed by separation with TLC afforded 1-phenyl-4-hexen-3-ol (**24**, 44 mg, 50%) as an oil: IR (neat) 3300, 970; NMR (CCl_4) 1.40–2.30 (m, 6 H), 2.63 (t, J = 8.0 Hz, 2 H), 3.74–4.10 (m, 1 H), 5.37–5.60 (m, 2 H), 7.07 (s, 5 H); mass spectrum, m/e (relative intensity) 176 (M^+, 19), 158 (19), 143 (19), 129 (23), 105 (31), 91 (100), 77 (19), 71 (100).

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Registry No. (*E*)-1 (Ar = Ph; R = $(CH_2)_2Ph$), 74824-73-0; (*E*)-1 (Ar = Ph; R = CH_2CO_2Bu-*t*), 88842-03-9; *cis*-**3a**, 74824-84-3; *trans*-**3a**, 74824-85-4; *cis*-**3b**, 74824-88-7; *trans*-**3b**, 74824-89-8; *cis*-**3c**, 74824-90-1; *trans*-**3c**, 74824-91-2; *cis*-**3d**, 74824-86-5; *trans*-**3d**, 74824-87-6; **3e**, 74824-99-0; (*E*)-**4**, 74824-93-4; (*Z*)-**4**, 88842-02-8; **5**, 74835-33-9; **6**, 88842-07-3; **7**, 88841-82-1; **9a**, 88841-83-2; **9b**, 78998-88-6; **9c**, 88841-84-3; **9d**, 88841-85-4; **9e**, 88841-86-5; **10**, 79681-30-4; **12a**, 61882-83-5; **12b**, 79681-48-4; **12c**, 79681-49-5; **13a**, 88841-89-8; **13b**, 88841-91-2; **14a**, 16737-04-5; **14b**, 88842-08-4; **15a**, 88841-90-1; **15b**, 88841-92-3; **16a**, 54625-15-9; **16b**, 88842-09-5; **17a**, 88841-94-5; **17b**, 88841-93-4; **17c**, 88841-95-6; **18**, 88841-96-7; *trans*-**19a**, 88841-98-9; *cis*-**19b**, 88841-97-8; *trans*-**19b**, 88842-10-8; *trans*-**19c**, 88841-99-0; **20**, 88842-00-6; **21**, 88842-01-7; $CH_3(CH_2)_6CH(OH)CH(OCH_3)CH_2SePh$, 74824-96-7; $CH_3(CH_2)_6CH(OH)CH(SePh)CH_2OCH_3$, 74824-97-8; (*Z*)-$CH_3(CH_2)_3C(O)(CH_2)_3CH{=}CHOCH_3$, 79681-32-6; (*E*)-$CH_3(CH_2)_3C(O)(CH_2)_3CH{=}CHOCH_3$, 79681-31-5; (*Z*)-$CH_3(CH_2)_3C(O)(CH_2)_3CH{=}CHOCH_2CH_3$, 79681-37-1; (*E*)-$CH_3(CH_2)_3C(O)(CH_2)_3CH{=}CHOCH_2CH_3$, 79681-36-0; $CH_3(CH_2)_3C(O)(CH_2)_3CH{=}CHSPh$, 79681-38-2; (*Z*)-$CH_3(CH_2)_3C(O)CH_2C(CH_3)_2CH_2CH{=}CHOCH_3$, 79681-40-6; (*E*)-$CH_3(CH_2)_3C(O)CH_2C(CH_3)_2CH_2CH{=}CHOCH_3$, 79681-39-3; $CH_3(CH_2)_3C(O)CH_2C(CH_3)_2CH_2CH{=}CHSPh$, 79681-41-7; (*Z*)-$CH(O)CH_2C(CH_3)_2CH_2CH{=}CHOCH_3$, 79681-43-9; (*E*)-$CH(O)CH_2C(CH_3)_2CH_2CH{=}CHOCH_3$, 79681-42-8; (*Z*)-$CH_3(CH_2)_3C(O)(CH_2)_2CH{=}CHOCH_3$, 79681-45-1; (*E*)-$CH_3(CH_2)_3C(O)(CH_2)_2CH{=}CHOCH_3$, 79681-44-0; (*R**,*S**)-$Ph(CH_2)_2CH(OH)CH(OH)CH(OCH_3)CH_2OTHP$, 88853-99-0; (*R**,*S**)-$Ph(CH_2)_2CH(OH)CH(OCH_3)CH_2OTs$, 88842-06-2; (*Z*)-$PhSeCH{=}CHCHO$, 74824-71-8; (*Z*)-Cl-*p*-$C_6H_4SeCH{=}CHCHO$, 74824-72-9; $CH_3(CH_2)_3CHLiC(O)OBu$-*t*, 88842-12-0; MeONa, 124-41-4; (*R**,*S**)-$Ph(CH_2)_2CH(OH)CH(OH)CH_2OTHP$, 88842-14-2; 1-dodecenyl phenyl selenone, 88841-79-6; 1-dodecenyl phenyl selenide, 88841-80-9; 4-methyl-2-(3-hydroxy-2-methoxy-1-propylidene)-γ-butyrolactone, 74824-94-5; *tert*-butyl 2-butyl-5-hydroxy-4-methoxy-2-pentenoate, 88841-81-0; 2-heptyl-3-methoxyoxetane, 74824-98-9; 5,5-dimethyl-3-(phenylseleno)-2-cyclohexen-1-ol, 78998-82-0; 1-butyl-5,5-dimethyl-3-(phenylseleno)-2-cyclohexen-1-ol, 88841-87-6; 5,5-dimethyl-3-(phenylselenonyl)-2-cyclohexen-1-ol, 79681-34-8; 1-butyl-3-(phenylselenonyl)-2-cyclopenten-1-ol, 79681-35-9; 1-butyl-2-methyl-3-(phenylselenonyl)-2-cyclohexen-1-ol, 79681-46-2; 1-butyl-3-(phenylselenonyl)-2-cycloocten-1-ol, 79681-47-3; 10-(phenylthio)-9-decen-5-one, 79681-38-2; 6,6-dimethyl-10-(phenylthio)-9-decen-5-one, 88841-88-7; 2-hydroxy-5-methyl-4,5-dihydrofuran lithium salt, 88853-98-9; 1,2-dimethoxy-3-decanol, 88842-04-0; ethyl 5-phenyl-2(*E*)-pentenoate, 55282-95-6; ethyl 5-phenyl-2(*Z*)-pentenoate, 88842-13-1; (*E*)-5-phenyl-2-penten-1-ol, 75553-23-0; (*R**,*S**)-2-methoxy-5-phenyl-1,3-pentanediol, 88842-05-1; 1-(phenylseleno)-1-decene, 88842-11-9; (*E*)-3-(phenylseleno)-2-propenal, 74824-70-7; benzeneselenenyl bromide, 34837-55-3; 3-acetoxy-2-cyclohexen-1-one, 57918-73-7; 2-(acetoxymethylidene)-1-cyclohexanone, 15839-56-2; chloromagnesium 3-(chloromagnesio)-propoxide, 68236-10-2; 1-ethoxyethyl 3-lithiopropyl ether, 88842-15-3; benzenethiol sodium salt, 930-69-8; phenethyl chloride, 622-24-2; hexyl chloride, 544-10-5; phenyl chloride, 108-90-7; dodecyl bromide, 143-15-7; phenyllithium, 591-51-5; 3-hydroxy-1-decene, 51100-54-0; ethyl (trimethylsilyl)acetate, 4071-88-9; 3-phenylpropenal, 104-55-2; phenyl trimethylsilyl selenide, 33861-17-5; diphenyl diselenide, 1666-13-3; sodium benzeneselenolate, 23974-72-3; 3-bromo-2-cyclopenten-1-one, 51865-32-8; sodium ethoxide, 141-52-6.

Silicon-Mediated Synthesis of Bibenzyl Systems: Synthesis of Ring and Side-Chain Functionalized Hexestrol Derivatives

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Derivatives of hexestrol [(3*R**,4*S**)-3,4-bis(4-hydroxyphenyl)hexane], a non-steroidal estrogen, bearing photochemically reactive functional groups or γ-emitting radionuclides, are useful as affinity labeling agents for the estrogen receptor or as imaging agents for receptor positive breast tumors, respectively. We have developed convenient synthetic routes to two side chain functionalized and aromatic ring functionalized hexestrol derivatives, based on a direct benzylic coupling reaction mediated by allylsilanes or silyl ketene acetals. 1-Dehydrohexestrol and various aromatic ring substituted 1-dehydrohexestrol derivatives can be prepared by coupling 3-(trimethylsilyl)-1-(4-methoxyphenyl)propene with various reactive benzylic derivatives, and pentestrol derivatives are prepared by the coupling of the silyl ketene acetal derivative of *p*-methoxyphenyl acetic ester with benzylic derivatives. The *R**,*S** (erythro) and *R**,*R** (threo) diastereomers formed in each case can be separated readily by chromatography and recrystallization. This silicon-mediated approach to functionalized hexestrol derivatives provides a convenient route to many compounds of interest as biochemical probes and receptor-based diagnostic reagents.

Introduction

The estrogen receptor is an intracellular protein thought to play a key role in mediating the effects of estrogens on target tissue cells. We have been interested in developing probes for the estrogen receptor that are designed to label the receptor covalently (affinity labeling reagents)[1,2] or to

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