Oxidation of Olefins into α-Phenylseleno Carbonyl Compounds. Highly Regioselective *anti*-Markownikoff Type Oxidation of Allylic Alcohol Derivatives[1]

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By using $(C_6H_5Se)_2$–*t*-BuOOH or $(C_6H_5Se)_2$–$(C_6H_5SeO)_2O$ system, oxoselenenylation reactions of C=C bonds have been examined with allylic and homoallylic alcohol derivatives, and substituted cyclohexenes, and allyl *t*-butyldimethylsilyl ethers are found to undergo regioselective conversion into β-siloxy α-phenylseleno carbonyl compounds in high yields.

Regioselective introduction of various functional groups into the carbon atom adjacent to a carbonyl constitutes a major concern in synthetic organic chemistry. For this purpose, α-halo or α-phenylthio substituted carbonyl compounds offer one of the most promising methodologies to distinguish α from α′ carbons to a carbonyl group.

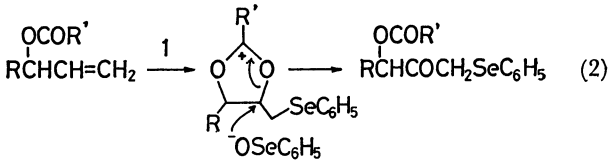
Recent developments in organoselenium chemistry[2] have realized that carbanions stabilized by arylseleno group are capable of attacking various electrophiles[3] and that arylseleno group is readily removed *via syn*-elimination reaction through selenoxides,[2] reduction with Raney nickel or trialkyltin hydride,[4] and so on.

Recently, several methods have been introduced by us[1,5] and others[6] for the direct preparation of α-phenylseleno carbonyl compounds from olefins. However, high regioselectivity in these oxidation reactions has only been achieved with terminal olefins to yield phenylselenomethyl ketones. We have examined steric and electronic effects of substituents for determining regiochemistry in the oxidation of olefins by using a system of diphenyl diselenide and *t*-butyl hydroperoxide, or diphenyl diselenide and benzeneseleninic anhydride.[1]

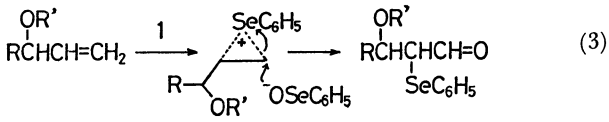
In this paper, we describe oxidation reactions of allylic and homoallylic alcohol derivatives, together with those of substituted cyclohexenes. Although a real reactive species in this reaction has not been confirmed yet,[7] it still appears to be reasonable for us to assume benzeneselenenic anhydride **1** as a plausible one as shown in the following equations.

$$\left.\begin{array}{l} (C_6H_5Se)_2 + t\text{-BuOOH} \longrightarrow \text{“}C_6H_5SeOSeC_6H_5\text{”} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \mathbf{1} \\ 2(C_6H_5Se)_2 + (C_6H_5SeO)_2O \\ \qquad\qquad\qquad \longrightarrow 3\text{“}C_6H_5SeOSeC_6H_5\text{”} \\ \qquad\qquad\qquad\qquad\qquad\quad \mathbf{1} \\ \qquad\qquad\qquad\qquad\quad OSeC_6H_5 \\ \qquad\qquad\qquad\qquad\quad | \\ R^1CH{=}CHR^2 \xrightarrow{\mathbf{1}} R^1CH\text{–}CHR \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad SeC_6H_5 \\ \qquad\qquad\qquad \longrightarrow R^1CH\text{–}CO\text{–}R^2 + C_6H_5SeH \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad SeC_6H_5 \end{array}\right\} \quad (1)$$

Oxidation of Allylic Alcohol Derivatives. Allylic alcohols are in general easily accessible *via* a number of standard procedures. Neighboring carbonyl group participation (Eq. 2) for allylic esters,[8] and steric



(2)



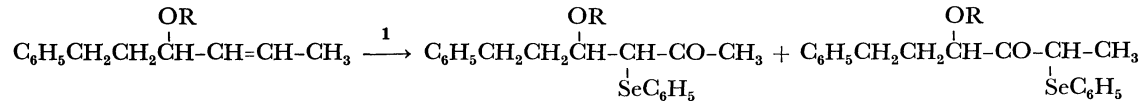
(3)

and electronic effects (Eq. 3) for allylic ethers are considered to play important roles which direct the site of introducing carbonyl functionality in the oxidation of carbon-carbon double bonds. Effects of substituents on oxygen atom were initially surveyed using 1-phenyl-4-hexen-3-ol derivatives. Thus, diphenyl diselenide was oxidized with an equimolar amount of *t*-butyl hydroperoxide in carbon tetrachloride, and *t*-butyl alcohol formed was removed together with the solvent *in vacuo*. The allylic alcohol derivatives were then treated with the resulting solid in refluxing benzene or toluene for an appropriate period and the corresponding oxoselenenylation products **2** and **3** were isolated. The results are listed in Table 1.

Comparison of these results implies that increasing steric conjestion around C=C bonds may enhance regioselectivity to introduce carbonyl functionality onto the remote carbon atoms of the double bonds. Trimethylsilyl ethers did not survive the reaction conditions to result in the formation of complex mixtures; a possible side-reaction may involve generation of the parent allylic alcohols which undergo oxidation under the present reaction conditions.[9] But, *t*-butyldimethylsilyl ether gave a remarkable result; only a single isomer was obtained in excellent yield. Satisfactory regioselectivity was also observed even with benzyl ether. In contrast, an effect based on neighboring group participation shown in Eq. 2 appeared to have little influence on the direction of this reaction.

Based on these results, similar oxidation was examined with a variety of allyl *t*-butyldimethylsilyl ethers. On treating with diphenyl diselenide and benzeneseleninic anhydride, they underwent regiospecific oxoselenenylation reaction to give the corresponding β-*t*-butyldimethylsiloxy α-phenylseleno carbonyl compounds **4**—**8** in excellent yields, without any contamination of their regio-isomers (see Table 2).

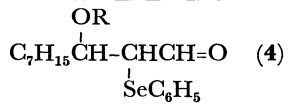
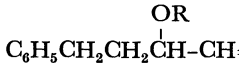
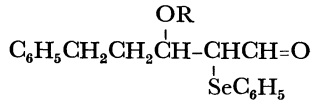
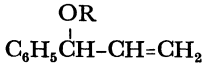
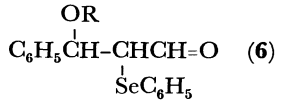
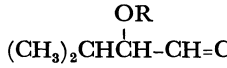
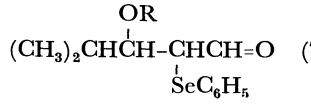
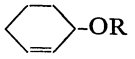
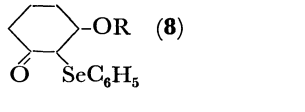
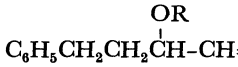
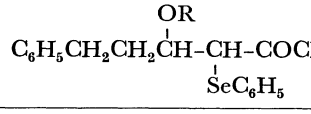
Table 1. Regioselectivity on the oxidation of 4-alkoxy-6-phenyl-2-hexene[a)]



R	Solvent	Period (h)	Ratio (**2**/**3**)	Yield/%
a) CH_3CO-	Toluene	3.0	67 : 33	71
b) $(CH_3)_3CCO$-	Toluene	10.0	75 : 25	60
c) $C_6H_5CH_2$-	Benzene	6.5	95 : 5	79
d) $(CH_3)_3CSi(CH_3)_2$-	Benzene	4.0	100 : 0	89

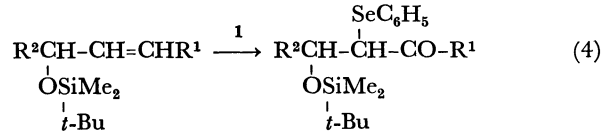
a) Reactions were carried out in a refluxing solvent with olefin: $(C_6H_5Se)_2$: *t*-BuOOH = 1.0 : 4.4 : 4.4.

Table 2. Oxidation of allyl *t*-butyldimethylsilyl ethers[a)]

Olefin	Product	Yield/%
	 (**4**)	87
	 (**5**)	81
	 (**6**)	79
	 (**7**)	74
	 (**8**)	76
	 (**2d**)	89

a) Reactions were carried out in reflxing toluene with olefin: $(C_6H_5Se)_2$:$(C_6H_5SeO)_2O$ = 1.0:1.4:0.7 for terminal olefins and 1.0:2.8:1.4 for internal olefin. b) R = $(CH_3)_3CSi(CH_3)_2$-.

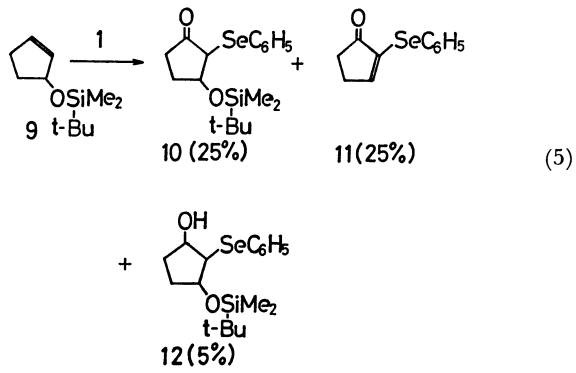
It should be remarkable that the ethers possessing a terminal olefin can be cleanly converted to the corresponding β-siloxy α-phenylseleno aldehydes exclusively, although such type of addition process appears to be disfavored electronically. β-Hydroxy or β-alkoxy aldehydes are usually quite unstable to undergo dehydration, but in these cases the products could be isolated without such kind of decomposition.



(4)

As the reaction solvent, benzene or toluene is preferable for this transformation. In other low-boiling solvents, a concomitant formation of β-hydroxy selenide was observed. The effect of *t*-butyldimethylsiloxy group was also prominent in the case with cyclohexene derivative, but the oxidation of 3-*t*-butyldimethylsiloxy-1-cyclopentene **9** afforded a mixture of 3-siloxy-2-phenylselenocyclopentanone **10**, 2-phenylseleno-2-cyclopentenone **11**, and 3-siloxy-2-phenylseleno-1-cyclopentanol **12**.

In addition to the bulky *t*-butyldimethylsiloxy group, substituents on the allylic position appear to have a marked influence on the regioselectivity; allyl *t*-butyldimethylsilyl ether derived from primary allylic alcohol did not show good regioselectivity to give a mixture of **13** and **14**.



(5)

$$C_3H_7CH{=}CHCH_2OSiMe_2(t\text{-Bu}) \xrightarrow{1} C_3H_7CO\text{-}CHCH_2OSiMe_2(C_6H_5Se,\ t\text{-Bu})\ (\mathbf{13}) + C_3H_7CH(C_6H_5Se)\text{-}COCH_2OSiMe_2(t\text{-Bu})\ (\mathbf{14}) \quad (6)$$

71% (**13**:**14**=77:23)

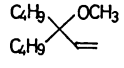
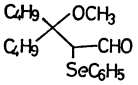
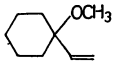
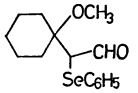
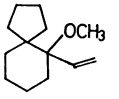
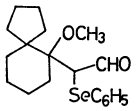
Addition of hypohalite to terminal olefins bearing tertiary carbon at their allylic position has been reported to proceed in a highly regioselective manner, and the *anti*-Markownikoff adducts were formed exclusively although the yields were low.[10] In a related system, *anti*-Markownikoff type oxidation was found to take place exclusively with methyl ethers of tertiary allylic alcohols in the present procedure. The results are shown in Table 3. However, in the case with a highly hindered olefin, the reaction did not proceed

$$R^1R^2C(OCH_3)\text{-}CH{=}CH_2 \xrightarrow{1} R^1R^2C(OCH_3)\text{-}CH(SeC_6H_5)\text{-}CH{=}O \quad (7)$$

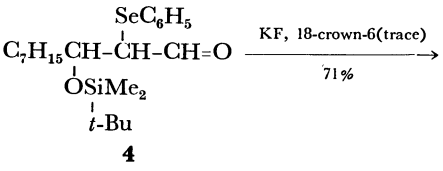
practically under the same conditions to recover the starting olefin.

The aldol type products obtained by the present procedure undergo a facile conversion to the corresponding α-phenylseleno enals on treatment with fluoride anion.[11] The use of other stronger bases such as lithium diisopropylamide (LDA), potassium *t*-butoxide, or tetrabutylammonium hydroxide led to formation of a mixture composed of several products. On the other hand, acidic treatment led to a mixture of α-phenylseleno enal and deselenenylated enal.[12] The products arising from the oxidation of allyl methyl ethers were more easily transformed into α-phenylseleno enals. They readily liberated methanol on treatment with silica gel.

Table 3. Oxidation of *t*-allyl methyl ethers[a]

Allyl methyl ether	Product		Yield/%
		**15**	93
		**16**	86
			trace[b]

a) Reactions were carried out in refluxing toluene with olefin: $(C_6H_5Se)_2$:$(C_6H_5SeO)_2O$=1.0:1.4:0.7. b) Most of the starting material was recovered.



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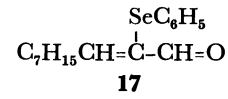

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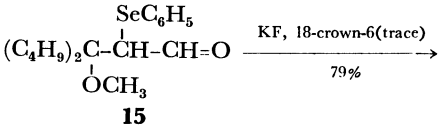

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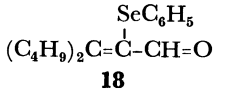

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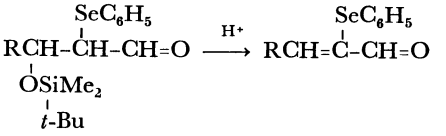
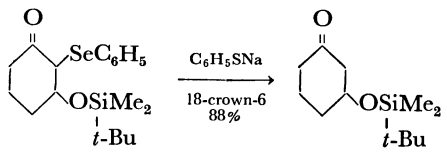


+ RCH=CH-CH=O (10)

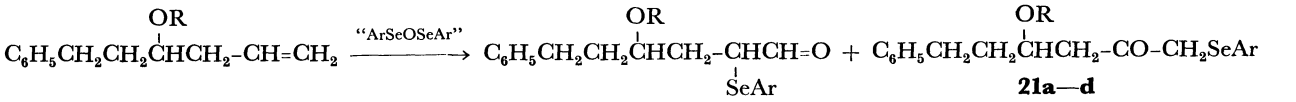
In addition, removal of phenylseleno group can also be readily performed. For example, treatment of 2-*t*-butyldimethylsiloxy-3-phenylselenocyclohexanone **8** with an excess amount of benzenethiolate anion in tetrahydrofuran afforded the deselenenylated ketone **19** in 88% yield.[13]



8 **19** (12)

Considering that the starting materials are easily accessible, this procedure may be employed as a useful alternative for the synthesis of aldols or α,β-unsaturated carbonyl compounds.

Table 4. Oxidation of 6-phenyl-3-trialkylsiloxy-1-hexene

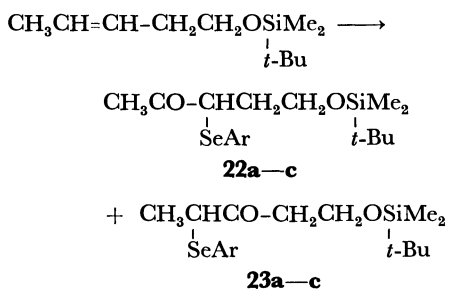


20a—d **21a—d**

	R	Ar	Ratio (**20**/**21**)	Yield/%
a)	$Si(CH_3)_2C(CH_3)_3$	C_6H_5	60 : 40	70[a]
b)	$Si(CH_3)_2C(CH_3)_3$	$2,4,6\text{-}(CH_3)_3C_6H_2$	75 : 25	74[b]
c)	$Si(C_6H_5)_3$	C_6H_5	73 : 27	72[a]
d)	$Si(C_6H_5)_3$	$2,4,6\text{-}(CH_3)_3C_6H_2$	77 : 23	71[b]

a) Reactions were carried out in refluxing benzene with olefin: $(C_6H_5Se)_2$:$(C_6H_5SeO)_2O$=1.0:1.4:0.7. b) Reactions were carried out in refluxing benzene with olefin: $(ArSe)_2$:*t*-BuOOH=1.0:2.0:2.0.

Table 5. Oxidation of 1-*t*-butyldimethylsiloxy-3-pentene[a]

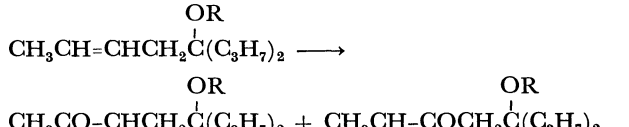


22a—c **23a—c**

	Ar	Ratio (**22**/**23**)	Yield/%
a)	C_6H_5	75 : 25	78
b)	$2,4,6\text{-}(CH_3)_3C_6H_2$	66 : 34	88
c)	$p\text{-}ClC_6H_4$	80 : 20	72

a) Reactions were carried out in refluxing benzene with olefin: $(ArSe)_2$:$(ArSeO)_2O$=1.0:2.8:1.4.

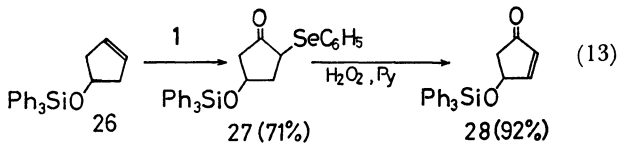
Table 6. Oxidation of 5-alkoxy-5-propyl-2-octene[a]



24a—b **25a—b**

	R	Ratio (**24**/**25**)	Yield/%
a)	CH_3	78 : 22	71
b)	$C_6H_5CH_2$	85 : 15	75

a) Reactions were carried out in refluxing benzene with olefin: $(C_6H_5Se)_2$:$(C_6H_5SeO)_2O$=1.0:2.8:1.4.



(13)

Oxidation of Homoallylic Alcohol Derivatives. As described above, the *t*-butyldimethylsilyl group has worked quite effectively on directing the site of introducing carbonyl functionality in the oxidation of allyl alcohol derivatives. Application of this procedure to homoallylic alcohol analogues has found relatively good regioselectivity.

As typical examples, we have examined the oxidation of 1-phenyl-5-hexen-3-ol, 3-penten-1-ol, and 4-propyl-6-octen-4-ol. The results are listed in Tables 4, 5, and 6.

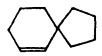
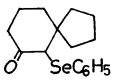
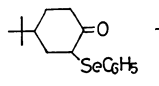
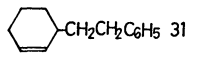
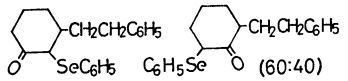
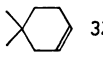
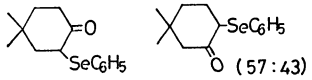
The results shown in the tables reveal that the effects of homoallylic substituents are not so sufficient to distinguish the remote sp^2 carbon from the other as those of allylic ones. In these cases, the highest ratio of γ-alkoxy α-phenylseleno ketones to their regioisomers is approximately 4:1. From a synthetic point of view, the present method is not so useful for this kind of transformation.

On the other hand, this system offers a convenient route to 4-siloxy-2-cyclopentenone **28**, a useful precursor for the synthesis of prostaglandin derivatives.[14] Thus, oxidation of 4-triphenylsiloxycyclopentene **26** by the present procedure followed by treatment with hydrogen peroxide afforded the cyclopentenone **28** in 65% overall yield.

Oxidation of Cyclohexene Derivatives. In the addition process to cyclohexene derivatives, two major interactions which may direct the site of introduction of anionic species, *e.g.*, $C_6H_5SeO^-$, appear to be involved; one is 1,3-diaxial interaction and the other is 1,2-interaction based on tortional strain. In the case with 3,3-disubstituted cyclohexene, if 1,3-diaxial interaction severely prevents the introduction of $C_6H_5SeO^-$ species to C-1 carbon, oxidation at C-2 may predominate, whereas the attack at C-1 will be a subject of tortional strain. Table 7 lists the results.

The result of the oxidation of spiro compound **29** indicates that 1,2-interaction predominates over 1,3-interaction. Apparently, this interaction was not so prominent for 3-monosubstituted cyclohexene, and the selectivity was greatly decreased with the substrate **31**. Other cases, *e.g.*, 4,4-disubstituted derivatives did not show any preference for regioselectivity of 1,2-electrophilic addition, probably because the steric congestions are almost same for both olefinic carbons and because there is little difference of electronic

Table 7. Oxidation of substituted cyclohexenes[a)]

Substrate	Product (ratio)	Yield/%
 29		72
 30	 (55:45)	70
 31	 (60:40)	67
 32	 (57:43)	68

a) Reactions were carried out in refluxing benzene with olefin: $(C_6H_5Se)_2$:*t*-BuOOH = 1.0:4.4:4.4.

effects.

Experimental

All reactions were performed under either argon or ultra grade nitrogen atmosphere. NMR spectra were taken on a Hitachi R-24B spectrometer and chemical shifts are recorded in parts per million downfield from internal tetramethylsilane. IR spectra were taken on a Hitachi EPI G-3 or 260-10 spectrometer, and mass spectra on a Hitachi RMU-7M or RMU-6C spectrometer at 70 eV ionizing irradiation. Boiling points were uncorrected.

Diphenyl diselenide, bis(*p*-chlorophenyl) diselenide, and bis(2,4,6-trimethylphenyl) diselenide were prepared by the procedure reported by Sharpless[15)] or Reich.[16)] Benzeneseleninic anhydride was prepared according to the procedure of Woodbridge,[17)] and was stored over P_2O_5.

Oxidation of 4-Alkoxy-6-phenyl-2-hexene with $(C_6H_5Se)_2$–t-BuOOH. Examination of Regioselectivity (General Procedure). To a solution of diphenyl diselenide (1.382 g, 4.4 mmol) in 10 ml of carbon tetrachloride were added molecular sieves 3A (4 g) and a solution of 70% *t*-butyl hydroperoxide (563 mg, 4.4 mmol) in 10 ml of carbon tetrachloride, and the mixture was heated to refluxing for 1 h. Then, *t*-butyl alcohol formed as well as the solvent was removed *in vacuo*, and a solution of 4-alkoxy-6-phenyl-2-hexene (1 mmol) in 5 ml of benzene or toluene was added to the resulting solution. After heated to refluxing for the period indicated in Table 1 followed by usual work-up, the ratio of the regio-isomers was determined on the bases of chromatographycally pure samples.

*4-Acetoxy-6-phenyl-3-phenylseleno-2-hexanone (**2a**).* IR (neat): 1730, 1710 cm^{-1}; NMR (CCl_4): δ 1.80—2.41 (m, 2H), 2.21 (s, 3H), 2.30 (s, 3H), 2.42—3.00 (m, 2H), 3.43—4.00 (m, 1H), 5.01—5.32 (m, 1H), 7.00—7.52 (m, 10H); Found: C, 61.91; H, 5.50%. Calcd for $C_{20}H_{22}O_3Se$: C, 61.71; H, 5.69%.

*4-Acetoxy-6-phenyl-2-phenylseleno-3-hexanone (**3a**).* IR (neat): 1730, 1710 cm^{-1}; NMR (CCl_4): δ 1.83—2.10 (m, 2H), 1.91 (d, J=4.0 Hz, 3H), 2.20 (s, 3H), 2.51—3.00 (m, 2H), 3.35 (q, J=6.0 Hz, 1H), 5.06—5.32 (m, 1H), 7.00—7.52 (m, 10H); Found: C, 61.82; H, 5.63%. Calcd for $C_{20}H_{22}O_3Se$: C, 61.71; H, 5.69%.

*4-Pivaloyloxy-6-phenyl-3-phenylseleno-2-hexanone (**2b**).* IR (neat): 1725, 1710 cm^{-1}; NMR (CCl_4): δ 1.20 (s, 9H), 2.10—2.42 (m, 2H), 2.31 (s, 3H), 2.35—2.62 (m, 2H), 3.60—4.02 (m, 1H), 4.91—5.42 (m, 1H), 6.98—7.62 (m, 10H); Found: C, 64.23; H, 6.50%. Calcd for $C_{23}H_{28}O_3Se$: C, 64.04; H, 6.54%.

*4-Pivaloyloxy-6-phenyl-2-phenylseleno-3-hexanone (**3b**).* IR (neat): 1725, 1705 cm^{-1}; NMR (CCl_4): δ 1.10 (d, J=4.5 Hz, 2H), 1.21 (s, 9H), 1.93—2.42 (m, 2H), 2.43—3.01 (m, 2H), 4.00—4.20 (m, 1H), 4.92—5.45 (m, 1H), 6.88—7.71 (m, 10H); Found: C, 63.90; H, 6.41%. Calcd for $C_{23}H_{28}O_3Se$: C, 64.04; H, 6.54%.

*4-Benzyloxy-6-phenyl-3-phenylseleno-2-hexanone (**2c**).* IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 1.80—2.33 (m, 2H), 2.12 (s, 3H), 2.47—2.83 (m, 2H), 3.57—4.08 (m, 2H), 4.50 (s, 2H), 6.85—7.53 (m, 15H); Found: C, 68.35; H, 6.09%. Calcd for $C_{25}H_{26}O_2Se$: C, 68.64; H, 5.99%.

*3-Benzyloxy-6-phenyl-2-phenylseleno-3-hexanone (**3c**).* IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 1.30 (d, J=6.5 Hz, 3H), 1.76—2.30 (m, 2H), 2.37—2.80 (m, 2H), 4.00—4.37 (m, 2H), 4.50 (s, 2H), 6.90—7.50 (m, 15H). These spectra were identical with those of the authentic samples prepared in the following manner: addition of sodium benzeneselenolate to 4-benzyloxy-6-phenyl-2-hexene oxide followed by oxidation with benzeneseleninic anhydride and diphenyl diselenide.[9)]

*4-t-Butyldimethylsiloxy-6-phenyl-3-phenylseleno-2-hexanone (**2d**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.92 (s, 9H), 2.00—2.60 (m, 2H), 2.30 (s, 3H), 2.70—3.00 (m, 2H), 4.00 (d, J=6.0 Hz, 1H), 4.10—4.42 (m, 1H), 7.00—7.81 (m, 10H); Found: C, 62.25; H, 7.39%. Calcd for $C_{24}H_{34}O_2SeSi$: C, 62.45; H, 7.42%.

Preparation of Allyl t-Butyldimethylsilyl Ethers. Silyl ethers were prepared by silylation of the corresponding alcohols.[18)] They exhibit the following spectroscopic properties.

3-t-Butyldimethylsiloxy-1-decene. IR (neat): 1640, 1460, 1255, 1080, 1010, 995, 925, 840, 780 cm^{-1}; NMR (CCl_4): δ 0.00 (s, 6H), 0.73—1.80 (m, 24H including singlet at 0.82 (9H, *t*-Bu)), 3.73—4.17 (m, 1H), 4.90 (dd, J=8.0 and 3.0 Hz, 1H), 5.00 (dd, J=16 and 3.0 Hz, 1H), 5.70 (ddd, J=16.0, 8.0, and 6.0 Hz, 1H).

3-t-Butyldimethylsiloxy-5-phenyl-1-pentene. IR (neat): 1640, 1600, 1460, 1255, 1090, 1010, 995, 925, 845, 780, 750, 700 cm^{-1}; NMR (CCl_4): δ 0.00 (s, 6H), 0.90 (s, 9H), 1.50—2.00 (m, 2H), 2.43—2.80 (m, 2H), 4.10 (dt, J=5.5 and 5.5 Hz, 1H), 5.00 (dd, J=8.5 and 2.0 Hz, 1H), 5.12 (dd, J=16.0 and 2.0 Hz, 1H), 5.80 (ddd, J=16.0, 8.5, and 5.5 Hz, 1H), 7.07 (s, 5H).

3-t-Butyldimethylsiloxy-3-phenyl-1-propene. IR (neat): 1640, 1600, 1460, 1255, 1130, 1090, 1070, 1010, 990, 940, 925, 870, 840, 780, 700 cm^{-1}; NMR (CCl_4): δ −0.03 (s, 3H), 0.67 (s, 3H), 0.90 (s, 9H), 4.90—5.40 (m, 3H), 5.90 (ddd, J=16.0, 10.0, and 4.0 Hz, 1H), 7.22 (s, 6H).

3-t-Butyldimethylsiloxy-4-methyl-1-pentene. IR (neat): 1690, 1470, 1255, 1080, 1010, 995, 925, 865, 845, 780 cm^{-1}; NMR (CCl_4): δ 0.00 (s, 6H), 0.80 (d, J=6.0 Hz, 6H), 0.83 (s, 9H), 1.65 (ses, J=6.0 Hz, 1H), 3.80 (dd, J=5.0 and 5.0 Hz, 1H), 5.00 (dd, J=8.0 and 2.0 Hz, 1H), 5.03 (dd, J=16.0 and 2.0 Hz, 1H), 5.73 (ddd, J=16.0, 8.0, and 5.0 Hz, 1H).

3-t-Butyldimethylsiloxy-1-cyclohexene. IR (neat): 1250, 1080 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.98 (s, 9H), 1.64—2.21 (m, 6H), 4.08—4.36 (m, 1H), 6.15—6.80 (m, 2H).

4-t-Butyldimethylsiloxy-6-phenyl-2-hexene. IR (neat): 3010, 1250, 1100 cm^{-1}; NMR (CCl_4): δ 0.12 (s, 6H), 0.97 (s, 9H), 1.61—2.10 (m, 3H), 1.89 (d, J=5.0 Hz, 2H), 2.50—2.86 (m, 2H), 3.84—4.30 (m, 1H), 5.43—5.63 (m, 2H), 7.17 (s, 5H).

*3-t-Butyldimethylsiloxy-2-phenylselenodecanal (**4**) (General Pro-*

cedure for the Oxidation of Allyl t-*Butyldimethylsiloxy Ethers).* To a solution of diphenyl diselenide (874 mg, 2.8 mmol) and benzeneseleninic anhydride (504 mg, 1.4 mmol) in 5 ml of toluene was added a solution of 3-*t*-butyldimethylsiloxy-1-decene (540 mg, 2.0 mmol) in 15 ml of toluene. After stirring for 30 min under refluxing, the reaction mixture was washed with satd aq NaCl and the aqueous layer was extracted with ether. Drying and concentration of the combined extracts followed by purification by silica gel column chromatography afforded the title compound (764 mg, 87%) as an oil and diphenyl diselenide (1.03 g). IR (neat): 1710 cm^{-1}; NMR (CCl_4): δ 0.03 (s, 6H), 0.80—2.00 (m, 15H), 0.83 (s, 9H), 3.23—3.70 (m, 1H), 3.90—4.30 (m, 1H), 6.90—7.77 (m, 5H), 9.23 (d, J=6.0 Hz, C<u>H</u>=O), 9.43 (d, J=4.0 Hz, C<u>H</u>=O); Found: C, 60.11; H, 8.90%. Calcd for $C_{22}H_{38}O_2SeSi$: C, 59.84; H, 8.67%.

3-t-Butyldimethylsiloxy-5-phenyl-2-phenylselenopentanal (5). Bp 110 °C/0.25 mmHg;[19] IR (neat): 1710 cm^{-1}; NMR (CCl_4): δ 0.03 (s, 6H), 0.87 (s, 9H), 1.73—2.33 (m, 2H), 2.33—2.90 (m, 2H), 3.30—3.83 (m, 1H), 3.93—4.40 (m, 1H), 6.70—7.80 (m, 10H), 9.36 (d, J=5.0 Hz, C<u>H</u>=O), 9.43 (d, J=3.0 Hz, C<u>H</u>=O); MS:[20] *m/e* (%) 311 (M^+ −137, 2), 262 (2), 216 (7), 157 (4), 132 (22), 129 (17), 117 (9), 115 (9), 104 (9), 91 (78), 77 (57), 76 (100); Found: C, 62.17; H, 7.37%. Calcd for $C_{23}H_{32}O_2SeSi$: C, 61.73; H, 7.21%.

3-t-Butyldimethylsiloxy-3-phenyl-2-phenylselenopropanal (6). Bp 115—120 °C/0.02 mmHg;[19] IR (neat): 1710 cm^{-1}; NMR (CCl_4): δ −0.02, −0.015, and 0.08 (s, 6H), 0.90 (s, 9H), 3.56—3.83 (m, 1H), 5.07 (d, J=7.0 Hz, C<u>H</u>OSi), 5.22 (d, J=4.0 Hz, C<u>H</u>OSi), 7.00—7.50 (m, 10H), 9.43 (d, J=4.0 Hz, C<u>H</u>=O), 9.50 (d, J=8.0 Hz, C<u>H</u>=O); MS:[20] *m/e* (%) 283 (M^+ −137, 9), 264 (2), 258 (3), 218 (4), 205 (4), 177 (6), 176 (6), 157 (7), 137 (20), 131 (18), 117 (6), 115 (5), 105 (10), 103 (12), 77 (62), 76 (100); Found: C, 60.06; H, 6.57%. Calcd for $C_{21}H_{28}O_2SeSi$: C, 60.13; H, 6.73%.

3-t-Butyldimethylsiloxy-4-methyl-2-phenylselenopentanal (7). Bp 100—105 °C/0.025 mmHg;[19] IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 0.18 (s, 6H), 0.85—1.20 (m, 1H), 1.10 (d, J=2.0 Hz, 6H), 1.00 (s, 9H), 3.57—3.87 (m, 1H), 3.87—4.13 (m, 1H), 6.70—7.53 (m, 5H), 9.30 (d, J=4.0 Hz, C<u>H</u>=O), 9.33 (d, J=4.0 Hz, C<u>H</u>=O); MS:[20] *m/e* (%) 303 (M^+ −83, 8), 249 (M^+ −137, 33), 182 (23), 170 (27), 167 (47), 155 (40), 142 (20), 130 (18), 127 (33), 113 (7), 95 (33), 77 (17), 76 (70), 75 (100); Found: C, 56.39; H, 7.88%. Calcd for $C_{18}H_{30}O_2SeSi$: C, 56.09; H, 7.84%.

3-t-Butyldimethylsiloxy-2-phenylselenocyclohexanone (8). IR (neat): 1710 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.92 (s, 9H), 1.22—2.90 (m, 6H), 3.31—4.50 (m, 2H), 6.98—7.61 (m, 5H); Found: C, 56.09; H, 7.42%. Calcd for $C_{18}H_{28}O_2SeSi$: C, 56.39; H, 7.36%.

Oxidation of 3-t-Butyldimethylsiloxy-1-cyclopentene (9). Diphenyl diselenide (312 mg, 1.0 mmol) was oxidized with 70% *t*-butyl hydroperoxide (141 mg, 1.0 mmol) in refluxing carbon tetrachloride (5 ml) for 1 h. Then all the solvent as well as *t*-butyl alcohol was removed from the reaction mixture, to which was added a solution of 3-*t*-butyldimethylsiloxy-1-cyclopentene (100 mg, 0.5 mmol) in 12 ml of benzene. After heating to refluxing for 2 h, the mixture was washed with satd aq NaCl and the aqueous layer was extracted with ethyl acetate. The combined extracts were dried and concentrated to give an oil, which was purified by preparative TLC to afford 3-*t*-butyldimethylsiloxy-2-phenylselenocyclopentanone **10** (46 mg, 25%), 2-phenylseleno-2-cyclopentenone **11** (30 mg, 25%), and 3-*t*-butyldimethylsiloxy-2-phenylseleno-1-cyclopentanol **12** (9 mg, 5%).

3-t-Butyldimethylsiloxy-2-phenylselenocyclopentanone (10). IR (neat): 1730 cm^{-1}; NMR (CCl_4): δ 0.12 (s, 6H), 0.91 (s, 9H), 1.67—2.30 (m, 4H), 3.42—3.65 (m, 1H), 3.71—4.05 (m, 1H), 7.10—7.71 (m, 5H).

2-Phenylseleno-2-cyclopentenone (11). IR (neat): 1690 cm^{-1}; NMR (CCl_4): δ 2.41—2.87 (m, 4H), 7.01 (t, J=3.0 Hz, 1H), 7.20—7.70 (m, 5H).

3-t-Butyldimethylsiloxy-2-phenylseleno-1-cyclopentanol (12). IR (neat): 3350 cm^{-1}; NMR (CCl_4): δ 0.12 (s, 6H), 0.92 (s, 9H), 2.12—2.70 (m, 5H), 3.10—3.40 (m, 1H), 3.43—3.76 (m, 2H), 7.12—7.62 (m, 5H).

1-t-Butyldimethylsiloxy-2-phenylseleno-3-hexanone (13). IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.92 (s, 9H), 1.05—1.82 (m, 5H), 2.34—2.72 (m, 2H), 3.54—4.05 (m, 3H), 7.01—7.52 (m, 5H); Found: C, 56.22; H, 8.01%. Calcd for $C_{18}H_{30}O_2SeSi$: C, 56.08; H, 7.84%.

1-t-Butyldimethylsiloxy-3-phenylseleno-2-hexanone (14). IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 0.19 (s, 6H), 0.93 (s, 9H), 1.05—1.81 (m, 7H), 3.66—3.90 (m, 1H), 4.20 (d, J=7.0 Hz, 2H), 7.00—7.51 (m, 5H); Found: C, 56.18; H, 7.96%. Calcd for $C_{18}H_{30}O_2SeSi$: C, 56.08; H, 7.84%.

3-Butyl-3-methoxy-2-phenylselenoheptanal (15) (General Procedure). To a solution of diphenyl diselenide (874 mg, 2.8 mmol) and benzeneseleninic anhydride (504 mg, 1.4 mmol) in 2 ml of toluene was added a solution of 3-butyl-3-methoxy-1-heptene (368 mg, 2 mmol) in 3 ml of toluene. After stirring for 30 min at refluxing temperature, the reaction mixture was washed with satd aq NaCl and the aqueous layer was extracted with ether. Drying and concentration of the combined extracts followed by purification by silica gel column chromatography (SiO_2 deactivated with 20% of water was used) afforded the title compound (649 mg, 91%) and diphenyl diselenide (960 mg). IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 0.67—2.00 (m, 18H), 3.20 (s, 3H), 3.50 (d, J=7.0 Hz, 1H), 7.00—7.60 (m, 5H), 9.77 (d, J=7.0 Hz, 1H); Found: C, 61.03; H, 7.98%. Calcd for $C_{18}H_{28}O_2Se$: C, 60.84; H, 7.94%.

2-(1-Methoxycyclohexyl)-2-phenylselenoacetaldehyde (16). Bp 110—115 °C/0.02 mmHg;[19] IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 1.00—2.20 (m, 10H), 3.17 (s, 3H), 3.62 (d, J=7.0 Hz, 1H), 7.00—7.67 (m, 5H), 9.42 (d, J=7.0 Hz, 1H); MS:[20] *m/e* (%) 312 (M^+, 13), 277 (7), 230 (7), 197 (8), 157 (40), 123 (73), 113 (60), 95 (60), 81 (60), 77 (100), 67 (60); Found: C, 57.87; H, 6.39%. Calcd for $C_{15}H_{20}O_2Se$: C, 57.88; H, 6.48%.

2-Phenylseleno-2-decenal (17). To a suspension of potassium fluoride (102 mg, 1.77 mmol) in 1 ml of benzene were added a solution of 3-*t*-butyldimethylsiloxy-2-phenylselenodecanal (78 mg, 0.177 mmol) in 2 ml of benzene and 18-crown-6 (4.7 mg, 0.018 mmol) in 1 ml of benzene. After stirring for 12 h at room temperature, the reaction mixture was washed with satd aq NaCl and the aqueous layer was extracted with ether. Drying and concentration of the combined extracts followed by purification by silica gel column chromatography (SiO_2 deactivated with 20% water) afforded the title compound (38 mg, 71%) as an oil. Bp 115—118 °C/0.37 mmHg;[19] IR (neat): 1685 cm^{-1}; NMR (CCl_4): δ 0.67—1.80 (m, 13H), 2.26—2.83 (m, 2H), 6.83—7.50 (m, 6H), 9.20 (s, 1H); MS:[20] 310 (M^+, 5), 187 (5), 157 (20), 115 (23), 91 (28), 81 (45), 78 (50), 77 (60), 67 (65), 55 (100).

3-Butyl-2-phenylseleno-2-heptenal (18). To a suspension of silica gel (2 g) in 10 ml of carbon tetrachloride was added a solution of 3-butyl-3-methoxy-2-phenylselenoheptanal (196 mg, 0.55 mmol) in 2 ml of carbon tetrachloride. After stirring for 2 h under refluxing, the reaction mixture was filtered. Concentration followed by purification by silica gel column chromatography (SiO_2 deactivated with 20%

water) gave the title compound (150 mg, 84%). Bp 95—100 °C/0.01 mmHg;[19] IR (neat): 1680 cm^{-1}; NMR (CCl_4): δ 0.50—1.90 (m, 14H), 2.30—2.90 (m, 4H), 7.00—7.33 (m, 5H), 9.53 (s, 1H); MS:[20] *m/e* (%) 324 (M^+, 4), 314 (8), 234 (4), 167 (10), 166 (10), 157 (19), 139 (17), 132 (56), 123 (13), 111 (40), 97 (25), 95 (77), 91 (13), 83 (33), 81 (40), 77 (40), 69 (33), 55 (100); Found: C, 60.56; H, 7.81%. Calcd for $C_{17}H_{24}OSe$: C, 60.84; H, 7.94%.

*3-t-Butyldimethylsiloxycyclohexanone (**19**).* To a solution of sodium hydride (55% in mineral oil, 18 mg, washed twice with hexane) in 1 ml of THF was added a solution of benzenethiol (90 mg, 0.8 mmol) in 1 ml of THF at room temperature, and the mixture was stirred for 5 min. Then a solution of 3-*t*-butyldimethylsiloxy-2-phenylselenocyclohexanone (76 mg, 0.2 mmol) and a trace amount of 18-crown-6 in 2 ml of THF was added to the resulting solution. After allowed to stand for 6 h at room temperature, the mixture was washed with satd aq NaCl, and the aqueous layer was extracted with ether. The combined extracts were dried and concentrated to give an oil, which was purified by silica gel column chromatography to afford the title compound **19** (41 mg, 88%). IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.92 (s, 9H), 1.22—2.41 (m, 8H), 3.91—4.20 (m, 1H); Found: C, 63.24; H, 10.37%. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59%.

1-Phenyl-5-hexen-3-ol was prepared by the reaction of 3-phenylpropanal with allylmagnesium bromide. 3-Penten-1-ol was prepared by treating 1-bromo-3-pentene with aq sodium acetate and then with aq sodium hydroxide. 4-Propyl-6-octen-4-ol was preapared by treating ethyl 3-pentenoate with 2.2 eq of propylmagnesium bromide in ether.

*4-t-Butyldimethylsiloxy-6-phenyl-2-phenylselenohexanal (**20a**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.98 (s, 9H), 1.46—2.33 (m, 4H), 2.51—2.88 (m, 2H), 3.30—3.61 (m, 1H), 4.08—4.30 (m, 1H), 7.02—7.48 (m, 10H), 8.30 (d, J=2.0 Hz, C<u>H</u>=O), 8.80 (d, J=2.0 Hz, C<u>H</u>=O); Found: C, 62.71; H, 7.58%. Calcd for $C_{24}H_{34}O_2SeSi$: C, 62.45; H, 7.42%.

*4-t-Butyldimethylsiloxy-6-phenyl-1-phenylseleno-2-hexanone (**21a**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 0.12 (s, 6H), 0.97 (s, 9H), 1.41—2.31 (m, 4H), 2.31—2.85 (m, 2H), 3.17 (s, 2H), 3.72—4.01 (m, 1H), 7.01—7.55 (m, 10H); Found: C, 62.57; H, 7.63%. Calcd for $C_{24}H_{34}O_2SeSi$: C, 62.45; H, 7.42%.

*4-t-Butyldimethylsiloxy-6-phenyl-2-mesitylselenohexanal (**20b**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 0.12 (s, 6H), 0.92 (s, 9H), 1.44—1.78 (m, 4H), 2.00—2.75 (m, 2H), 2.28 (s, 3H), 2.45 (s, 6H), 3.31—3.52 (m, 1H), 4.05—4.31 (m, 1H), 6.86 (s, 2H), 7.00—7.40 (m, 5H), 8.31 (d, J=3.0 Hz, C<u>H</u>=O), 8.78 (d, J=3.0 Hz, C<u>H</u>=O); Found: C, 64.51; H, 8.19%. Calcd for $C_{27}H_{40}O_2SeSi$: C, 64.39; H, 8.01%.

*4-t-Butyldimethylsiloxy-6-phenyl-1-mesitylseleno-2-hexanone (**21b**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 0.13 (s, 6H), 0.92 (s, 9H), 1.42—1.75 (m, 4H), 2.00—2.85 (m, 2H), 2.27 (s, 3H), 2.43 (s, 6H), 2.98 (s, 2H), 4.01—4.30 (m, 1H), 6.83 (s, 2H), 7.00—7.40 (m, 5H); Found: C, 64.60; H, 8.23%. Calcd for $C_{27}H_{40}O_2SeSi$: C, 64.39; H, 8.01%.

*6-Phenyl-4-triphenylsiloxy-2-phenylselenohexanal (**20c**).* IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 1.62—2.38 (m, 4H), 2.42—2.83 (m, 2H), 3.41—3.73 (m, 1H), 4.08—4.31 (m, 1H), 6.67—7.74 (m, 25H), 8.53 (d, J=3.0 Hz, C<u>H</u>=O), 8.80 (d, J=3.0 Hz, C<u>H</u>=O); Found: C, 71.52; H, 5.80%. Calcd for $C_{36}H_{34}O_2SeSi$: C, 71.38; H, 5.66%.

*6-Phenyl-4-triphenylsiloxy-1-phenylseleno-2-hexanone (**21c**).* IR (neat): 1710 cm^{-1}; NMR (CCl_4): δ 1.50—2.35 (m, 4H), 2.41—2.80 (m, 2H), 3.19 (s, 2H), 4.01—4.32 (m, 1H), 6.62—7.75 (m, 25H); Found: C, 71.59; H, 5.76%. Calcd for $C_{36}H_{34}O_2SeSi$: C, 71.38; H, 5.66%.

*2-Mesitylseleno-6-phenyl-4-triphenylsiloxyhexanal (**20d**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 1.53—2.15 (m, 4H), 2.17—2.70 (m, 2H), 2.27 (s, 3H), 2.47 (s, 6H), 3.41—3.62 (m, 1H), 4.07—4.30 (m, 1H), 6.67—7.64 (m, 20H), 6.85 (s, 2H), 8.56 (d, J=3.0 Hz, C<u>H</u>=O), 8.83 (d. J=3.0 Hz, C<u>H</u>=O); Found: C, 72.53; H, 6.47%. Calcd for $C_{39}H_{40}O_2SeSi$: C, 72.31; H, 6.22%.

*1-Mesitylseleno-6-phenyl-4-triphenylsiloxy-2-hexanone (**21d**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 1.57—2.16 (m, 4H), 2.21—2.72 (m, 2H), 2.28 (s, 3H), 2.48 (s, 6H), 3.05 (s, 2H), 4.06—4.32 (m, 1H), 6.68—7.64 (m, 20H), 6.86 (s, 2H); Found: C, 72.18; H, 6.09%. Calcd for $C_{39}H_{40}O_2SeSi$: C, 72.31; H, 6.22%.

*5-t-Butyldimethylsiloxy-3-phenylseleno-2-pentanone (**22a**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.92 (s, 9H), 1.62—2.01 (m, 2H), 2.31 (s, 3H), 3.51—3.93 (m, 3H), 7.01—7.54 (m, 5H); Found: C, 54.91; H, 7.52%. Calcd for $C_{17}H_{28}O_2SeSi$: C, 54.97; H, 7.60%.

*5-t-Butyldimethylsiloxy-2-phenylseleno-3-pentanone (**23a**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.92 (s, 9H), 1.45 (d, J=8.0 Hz, 3H), 2.62 (t, J=8.0 Hz, 1H), 2.67 (t, J=6.0 Hz, 2H), 3.40—3.90 (m, 2H), 7.00—7.50 (m, 5H); Found: C, 54.85; H, 7.54%. Calcd for $C_{17}H_{28}O_2SeSi$: C, 54.97; H, 7.60%.

*5-t-Butyldimethylsiloxy-3-mesitylseleno-2-pentanone (**22b**).* IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.92 (s, 9H), 1.05—1.35 (m, 2H), 2.01 (s, 3H), 2.32 (s, 3H), 2.71 (s, 6H), 3.10—3.90 (m, 3H), 6.85 (s, 2H); Found: C, 58.21; H, 8.12%. Calcd for $C_{20}H_{34}O_2SeSi$: C, 58.09; H, 8.29%.

*5-t-Butyldimethylsiloxy-2-mesitylseleno-3-pentanone (**23b**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.92 (s, 9H), 1.38 (d, J=6.0 Hz, 3H), 2.21—2.41 (m, 2H), 2.25 (s, 3H), 2.50 (s, 6H), 3.42 (q, J=6.0 Hz, 1H), 3.51—3.87 (m, 2H), 6.85 (s, 2H); Found: C, 58.35; H, 8.08%. Calcd for $C_{20}H_{34}O_2SeSi$: C, 58.09; H, 8.08%.

*5-t-Butyldimethylsiloxy-3-(p-chlorophenylseleno)-2-pentanone (**22c**).* IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.92 (s, 9H), 1.74—2.03 (m, 2H), 2.28 (s, 3H), 3.52—4.03 (m, 3H), 7.01—7.45 (m, 4H); Found: C, 50.28; H, 6.79%. Calcd for $C_{17}H_{27}O_2ClSeSi$: C, 50.30; H, 6.70%.

*5-t-Butyldimethylsiloxy-2-(p-chlorophenylseleno)-3-pentanone (**23c**).* IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 0.11 (s, 6H), 0.92 (s, 9H), 1.31 (d, J=6.0 Hz, 3H), 2.72 (t, J=6.0 Hz, 2H), 3.53—4.05 (m, 3H), 7.00—7.30 (m, 4H); Found: C, 50.20; H, 6.69%. Calcd for $C_{17}H_{27}O_2ClSeSi$: C, 50.30; H, 6.70%.

*5-Methoxy-5-propyl-3-phenylseleno-2-octanone (**24a**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 0.70—1.61 (m, 16H), 2.13 (s, 3H), 2.92 (s, 3H), 3.57—3.90 (m, 1H), 7.00—7.61 (m, 5H); Found: C, 61.02; H, 8.06%. Calcd for $C_{18}H_{28}O_2Se$: C, 60.84; H, 7.94%.

*5-Methoxy-5-propyl-2-phenylseleno-3-octanone (**25a**).* IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 0.75—1.65 (m, 17H), 1.92 (s, 2H), 2.95 (s, 3H), 3.82—4.10 (m, 1H), 7.02—7.61 (m, 5H); Found: C, 61.13; H, 8.11%. Calcd for $C_{18}H_{28}O_2Se$: C, 60.84; H, 7.94%.

*5-Benzyloxy-3-phenylseleno-5-propyl-2-octanone (**24b**).* IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 0.73—1.68 (m, 16H), 2.15 (s, 3H), 3.72—4.01 (m, 1H), 4.31 (s, 2H), 7.01—7.58 (m, 10H); Found: C, 67.02; H, 7.68%. Calcd for $C_{24}H_{32}O_2Se$: C, 66.81; H, 7.48%.

*5-Benzyloxy-2-phenylseleno-5-propyl-3-octanone (**25b**).* IR (neat): 1700 cm^{-1}; NMR (CCl_4): δ 0.78—1.72 (m, 17H), 1.85 (s, 2H), 3.72—3.95 (m, 1H), 4.34 (s, 2H), 7.01—7.55 (m, 10H); Found; C, 66.95; H, 7.56%. Calcd for C_{24}-

$H_{32}O_2Se$: C, 66.81; H, 7.48%.

2-Phenylseleno-4-triphenylsiloxycyclopentanone (27). IR (neat): 1740 cm^{-1}; NMR (CCl_4): δ 2.39—2.53 (m, 4H), 3.29—3.60 (m, 1H), 4.54 (t, J=5.0 Hz, 1H), 7.07—7.62 (m, 20H).

4-Triphenylsiloxy-2-cyclopentenone (28). To a solution of 2-phenylseleno-4-triphenylsiloxycyclopentanone (155 mg, 0.3 mmol) and pyridine (0.07 ml, 0.72 mmol) in 1 ml of dichloromethane were added 30% hydrogen peroxide (0.28 ml, 2.6 mmol) and water (0.28 ml) at 0 °C. After stirring at 0 °C for 30 min, the reaction mixture was washed with 7% $NaHCO_3$ and then with 4% HCl. Drying and concentration of the extracts followed by purification with preparative TLC gave the title compound (99 mg, 92%) as an oil. IR (neat): 1680 cm^{-1}; NMR (CCl_4): δ 2.21—2.40 (m, 2H), 3.74—4.00 (m, 1H), 4.83—5.11 (m, 1H), 5.80—6.00 (m, 1H), 7.00—7.66 (m, 15H); Found: C, 77.32; H, 5.40%. Calcd for $C_{23}H_{20}SiO_2$: C, 77.49; H, 5.65%.

Oxidation of Substituted Cyclohexenes. Oxidation of these compounds was performed in a similar manner with that of 4-alkoxy-6-phenyl-2-hexene in refluxing benzene for 3—5 h. The reaction mixtures were treated with benzenethiolate anion as described above, and the resulting deselenenylated products were identified by comparison with the authentic samples. Ratios of the regio-isomers were also determined with the deselenenylated products by GLPC analyses.

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