

tion, and for the optimum result about 10% of the catalyst was required.

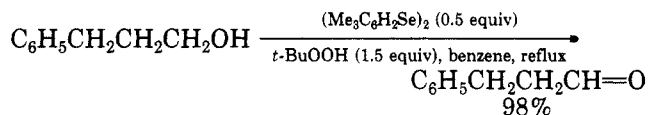
Oxidation of Allylic Alcohols. Allylic alcohols are, in general, more readily oxidized than their saturated analogues with a variety of oxidation reagents.¹¹ Oxidation of *trans*-2-hexen-1-ol was initially examined. During a series of experiments, bis(*p*-chlorophenyl) diselenide was found to work most efficiently as a catalyst.¹² In the selenoxide syn-elimination reaction an electron-withdrawing group on aryl selenoxides facilitates the reaction.¹³ In this oxidation, however, an *o*-nitro or *m*-trifluoromethyl substituent did not enhance the catalytic activity. Diselenides bearing an electron-donating group, e.g., bis(*o,p*-dimethoxyphenyl) or bis(*o*- or *p*-methoxyphenyl) diselenide did not find superiority. Because this oxidation system may produce areneseleonic acid which has a pK_a value of 4.70,⁹ the use of a proper buffer such as potassium dihydrogen phosphate may sometimes be preferable. For example, the yield of *trans*-2-hexenal was raised from 62% to 77% in the presence of buffer under the standard conditions (1.2 equiv of *t*-BuOOH, 15 mol % of $(C_6H_5Se)_2$, benzene, 80 °C).

Under similar reaction conditions cinnamyl alcohol was oxidized to cinnamaldehyde in 63% yield.

Geraniol has a trisubstituted double bond which is susceptible for the electrophilic additions. Recent examples demonstrate that electrophilic oxyselenenylation can be avoided by the use of secondary or tertiary amines.¹⁴ Oxidation of geraniol in the presence of 2,4,6-collidine or tetramethylammonium chloride affords the optimum result (71%) under the conditions cited above.

Oxidation of Saturated Aliphatic Alcohols. The extension of this catalytic system to the oxidation of saturated aliphatic alcohols was examined with respect to the effect of diaryl diselenide. In contrast to the allylic alcohol oxidation, diselenides possessing electron-donating substituents facilitate the reaction. However, several attempts did not lead to a sufficient catalytic oxidation system. The reaction after a prolonged period suffered from the dehydrogenation of the aldehyde formed to the enals. Close examination of the reaction reveals that overoxidation to carboxylic acid can be excluded and that decomposition via α,β -unsaturated aldehyde may be one of the undesired paths which destroy material balance.

Although we failed to find a wholly catalytic system, employment of 0.5 equiv of diaryl diselenide, namely, stoichiometric use of a selenium species, resulted in a remarkable improvement. As shown in the equation below,

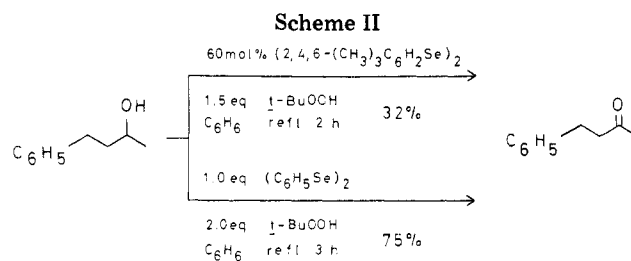


the use of bis(2,4,6-trimethylphenyl) diselenide gave an excellent result, whereas a less satisfactory result was obtained with diphenyl diselenide (64%). Bis(*o*-nitrophenyl) diselenide did not practically effect the oxidation (4%). A variety of alcohols were also cleanly oxidized to the

Table I. Oxidation of Alcohols with *t*-BuOOH and Bis(2,4,6-Trimethylphenyl) Diselenide^a

alcohol	period, h	product	yield, % ^b
cinnamyl alcohol	1	cinnamaldehyde	87 ^c
<i>trans</i> -2-hexen-1-ol	1	<i>trans</i> -2-hexenal	89 ^{c,d}
geraniol	1	geraniol	100 ^{c,e}
1-phenyl-4-hexen-3-ol	7	1-phenyl-4-hexen-3-one	90
3-phenyl-1-propanol	4	3-phenylpropanal	98 ^d
1-decanol	5	decanal	92 ^e
citronellol	1	citronellal	88 ^{d,f,g}
1-menthol	17	1-menthone	97
cyclododecanol	4	cyclododecanone	100
4-phenyl-2-butanol	3	4-phenyl-2-butanone	75 ^h

^a Reactions were performed in refluxing benzene with a reactant ratio of alcohol/diselenide/*t*-BuOOH of 1.0:0.5:1.5, unless otherwise noted. ^b Isolated yield. ^c *t*-BuOOH (1.1 equiv) was used. ^d Yield determined by GLC analysis using a calibrated internal standard. ^e The reaction was on a 100-mmol scale. ^f Alcohol/diselenide/*t*-BuOOH ratio of 1.0:0.75:1.25. ^g *N*-Isopropylcyclohexylamine (0.3 equiv) was used as an additive. ^h Diphenyl diselenide (1.0 equiv) and *t*-BuOOH (2.0 equiv) were used.



corresponding carbonyl compounds in excellent yields by the present system as shown in Table I.

In some methods, e.g., Collins oxidation, the requirement for a large amount of solvent and reagent may prevent a large-scale operation. In the present system the choice of solvent is dependent only on the solubility of the substrate and the reaction temperature. For example, the oxidation of 1-decanol on a 100-mmol scale was performed in 200 mL of benzene by using bis(2,4,6-trimethylphenyl) diselenide (0.5 equiv) and *tert*-butyl hydroperoxide (1.5 equiv). Furthermore, after isolation of the product by direct distillation, the diselenide was recovered in more than 70% yield and could be used for another run.

Although in a related system we have demonstrated the oxoselenenylation of olefins,⁸ olefinic bonds usually survived the present oxidation conditions. For example, geraniol was converted to geraniol quantitatively. Even in the case of citronellol which is known to undergo oxidative cyclization,¹⁵ the oxidation could be performed effectively without affecting the double bond by using a small amount of *N*-isopropylcyclohexylamine whereas only a small amount of the desired product was obtained in the absence of amine.

The reaction rates are dependent on the structures of alcohols, i.e., faster for allylic and benzylic alcohols than for the saturated ones.

Because of its considerable selectivity, manganese dioxide occupies an important place in the oxidation of allylic alcohols.¹⁶ Hydroxy groups on allylic positions are usually

(11) Sharpless, K. B.; Akashi, A.; Oshima, K. *Tetrahedron Lett.* 1976, 2503.

(12) Sharpless et al. also examined on a catalytic efficiency of diselenides and found that bis[*o*-(*tert*-butoxycarbonyl)phenyl] diselenide acts as a good catalyst in a similar oxidation reaction: personal communication from Professor K. B. Sharpless.

(13) Sharpless, K. B.; Young, M. W. *J. Org. Chem.* 1975, 40, 47. Grieco, P. A.; Masaki, Y.; Boxler, D. *J. Am. Chem. Soc.* 1975, 97, 1597. Grieco, P. A.; Noguez, J. A.; Masaki, Y. *Tetrahedron Lett.* 1975, 4213. Reference 8.

(14) Brattesani, N. D.; Heathcock, C. H. *J. Org. Chem.* 1975, 40, 2165. Reference 8.

(15) Corey, E. J.; Boger, D. L. *Tetrahedron Lett.* 1978, 2461.

(16) Lee, D. G. In "Oxidation"; Augustine, R. L., Ed.; Marcel Dekker: New York, 1969; Vol. I, p 66-70.

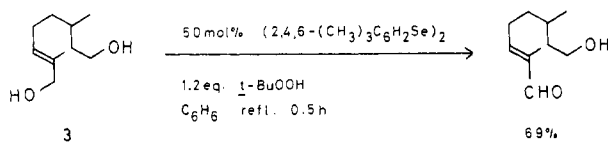
Table II. Oxidation of Alcohol 4^a

R ¹	R ²	n	X	reactn period, min	% yield of 5 ^b
(CH ₂) ₄		0	SeC ₆ H ₅	180	79
(CH ₂) ₆		0	SeC ₆ H ₅	15	91
(CH ₂) ₁₀		0	SeC ₆ H ₅	40	100
C ₄ H ₉	C ₄ H ₉	0	SeC ₆ H ₅	40	90
H	H	4	SeC ₆ H ₅	120	86
H	C ₄ H ₉	0	SeC ₆ H ₅	60	58
C ₁₀ H ₂₁	H	0	SeC ₆ H ₅	90	66
(CH ₂) ₁₀		0	SC ₆ H ₅	90	72

^a Reactions were carried out in refluxing benzene with an alcohol/*t*-BuOOH/((CH₃)₃C₆H₂Se)₂ ratio of 1.0:1.3–1.5:0.5–0.6. ^b Isolated yield.

oxidized selectively in the presence of saturated alcohols. However, the need for a large excess of manganese dioxide and for its activation appear to call for development of alternatives.

Careful oxidation of the diol 3 by the present procedure demonstrates a good alternative.



Oxidation of methylcarbinols by the present system appears to be problematic. Treatment of 4-phenyl-2-butanol under the usual conditions (0.5 equiv of the diselenide and 1.5 equiv of *t*-BuOOH, Scheme II) resulted in the substantial formation of 4-phenyl-1-[(2,4,6-trimethylphenyl)seleno]-2-butanone. After several trials, the optimum result was obtained when the reaction was performed in refluxing benzene for 3 h with 2.0 equiv of *tert*-butyl hydroperoxide in the presence of 1 equiv of diphenyl diselenide.

Oxidation of Alcohols Bearing a Phenylthio or Phenylseleno Group. α -Phenylthio or α -phenylseleno carbonyl compounds are used extensively for regiospecific carbon-carbon bond formation and for the introduction of unsaturation.¹⁷ These compounds have usually been prepared by sulfonylation or selenenylation of the parent carbonyl compounds.¹⁸ On the other hand, β -hydroxy sulfides or selenides are readily accessible via a number of standard methods.¹⁹ However, no general method was reported for the oxidation of hydroxy groups in these substrates. Especially for α -hydroxy selenides, accompanying oxidation at selenium moieties causes a considerable decrease of the product yield.²⁰ The only reported selective oxidations involve the use of DDQ,²⁰ the Corey-Kim method,²⁰ aluminum surface oxidation,²¹ and organo-

(17) Grieco, P. A.; Nishizawa, M.; Oguri, T.; Burke, S. D.; Marinovic, N. *J. Am. Chem. Soc.* 1977, 99, 5773. Takahashi, T.; Nagashima, H.; Tsuji, *J. Tetrahedron Lett.* 1978, 799.

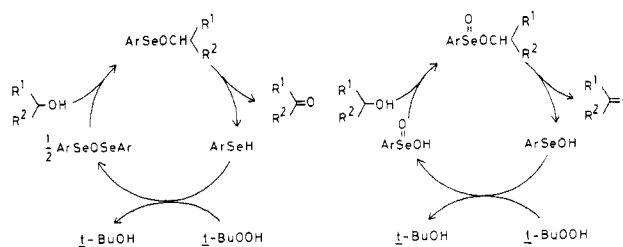
(18) (a) Clive, D. L. *J. J. Chem. Soc., Chem. Commun.* 1973, 695. (b) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* 1973, 95, 6137. Reference 8. For sulfonylation see: (c) Trost, B. M. *Chem. Rev.* 1978, 78, 363 and references cited therein.

(19) For oxy-selenenylation see: Reich, H. *J. Org. Chem.* 1974, 39, 428. Sharpless, K. B.; Lauer, R. F. *Ibid.* 1974, 39, 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. Labar, D.; Kreif, 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 and references cited therein. For oxy-sulfonylation see: Trost, B. M.; Ochiai, M.; McDorgal, P. G. *Ibid.* 1978, 100, 7103 and references cited therein.

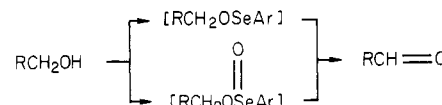
(20) Baudat, R.; Petrzilka, M. *Helv. Chim. Acta* 1979, 62, 1406.

(21) Posner, G. H.; Chapdelaine, M. *J. Tetrahedron Lett.* 1977, 3227.

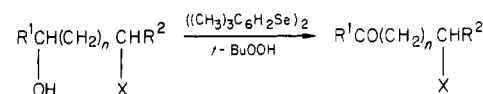
Scheme III



Scheme IV



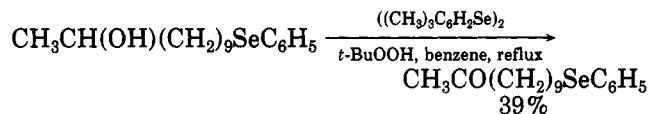
bismuth oxide.²² The present system has turned out to be very profitable for the selective oxidation of hydroxy groups in these bifunctional compounds 4. Table II summarizes the results.



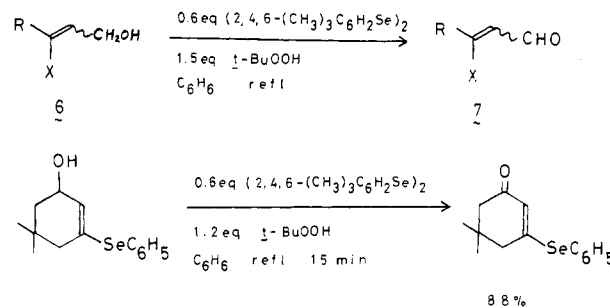
4, X = SC₆H₅; SeC₆H₅

5, X = SC₆H₅; SeC₆H₅

Similarly to the previously cited cases, when methyl ketones containing a phenylseleno moiety are formed as the oxidation products, some serious side reaction, i.e., most probably selenenylation of the oxidation products, occurs concomitantly with the desired reaction. In these instances where 2-hydroxyalkanes are oxidation substrates, careful operation and immediate quenching after completion of the reaction should be taken.



Oxidation of 3-(phenylthio)- or 3-(phenylseleno)-2-propen-1-ol or its homologues has not been easily attained by the methods reported so far.²³ Examination of the oxidation of alcohol 6 (R = H, X = SeC₆H₅) with pyridinium chlorochromate (PCC) afforded the crude aldehyde 7 (R = H, X = SeC₆H₅) in less than 50%. However, the



present procedure has cleanly transformed these compounds 6 to the corresponding α,β -unsaturated aldehydes 7 in good to excellent yields as shown in Table III.

These oxidation products are very versatile compounds for further useful organic transformations. For example,

(22) Barton, D. H. R.; Lester, D. J.; Motherwell, W. B.; Papoul, M. T. *B. J. Chem. Soc., Chem. Commun.* 1980, 246.

(23) For example, oxidation of 3-(phenylthio)-2-propen-1-ol with an excess of active manganese dioxide gave the corresponding aldehyde in moderate yield: personal communication from Professor H. Takei of this institute.

solved s, 7 H), 5.00 (m, 1 H), 5.73 (d, $J = 7.4$ Hz, 1 H), 9.79 (d, $J = 7.4$ Hz, 1 H).

Decanal. Large-Scale Preparation. To a refluxing solution of bis(2,4,6-trimethylphenyl) diselenide (19.8 g, 50 mmol) and 1-decanol (15.8 g, 100 mmol) in 150 mL of benzene was added a benzene (50 mL) solution of 70% *t*-BuOOH (18.2 g, 150 mmol) during 30 min. After being stirred for 5 h under refluxing, the reaction mixture was washed with saturated Na_2CO_3 and brine. Separation and removal of the solvent gave an orange-colored oil, which was distilled to afford the title compound: 14.4 g (92%); IR (neat) 2900, 1720 (vs), 1465, 795, 770; NMR (CCl_4) 0.67–1.73 (m, 17 H), 2.33 (t, $J = 6.0$ Hz, 2 H), 9.80 (t, $J = 6.0$ Hz, 1 H).

1-Phenyl-4-hexen-3-one: bp 90–92 °C (bath temperature; 0.1 mmHg) IR (neat) 2910, 1695 (vs), 1675 (vs), 1630, 1605, 980, 790, 760, 710; NMR (CCl_4) 1.80 (d, $J = 6.0$ Hz, 3 H), 2.03–3.03 (m, 4 H), 5.73–6.17 (m, 1 H), 6.33–7.33 (m, 6 H including singlet at 7.03). These spectra were identical with those of the authentic sample prepared by the oxidation of 1-phenyl-4-hexen-3-ol with Collins reagent.

Cinnamaldehyde, *trans*-2-hexenal, 3-phenylpropanal, menthone, and cyclododecanone exhibited spectroscopic data identical with those obtained from the authentic samples.

2,6-Dimethyl-8-hydroxy-2-octenal. Oxidation of 2,6-dimethyl-2-octene-1,8-diol with 0.5 equiv of bis(2,4,6-trimethylphenyl) diselenide and 70% *t*-BuOOH (1.2 equiv) in refluxing benzene for 30 min afforded the title compound: 69% yield; IR (neat) 3340, 2880, 1670 (vs), 1060; NMR (CCl_4) 1.10–1.70 (m, 5 H), 1.63 (d, $J = 6.0$ Hz, 3 H), 1.70 (s, 3 H), 2.10–2.60 (unresolved dt, 2 H), 2.93 (br s, 1 H), 3.56 (t, $J = 6.0$ Hz, 2 H), 6.40 (t, $J = 8.0$ Hz, 1 H), 9.26 (s, 1 H). Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_2$: C, 70.55; H, 10.66. Found: C, 70.38, H, 10.36.

Oxidation of Citronellol with *t*-BuOOH in the Presence of Bis(2,4,6-trimethylphenyl) Diselenide and an Amine. To a solution of bis(2,4,6-trimethylphenyl) diselenide (149 mg, 0.375 mmol) and *N*-isopropylcyclohexylamine (21 mg, 0.15 mmol) in 5 mL of carbon tetrachloride were added solutions of 70% *t*-BuOOH (144 mg, 1.125 mmol) in 2 mL of carbon tetrachloride and citronellol (78 mg, 0.5 mmol) in 3 mL of carbon tetrachloride. After the mixture was stirred under refluxing for 1 h, tridecane (51 mg, an internal standard) was added to the mixture. GLC analysis (column B, 100–150 °C) indicated the formation of citronellal in 88% yield. Typical retention times are as follows: tridecane, 1.15 min; citronellal, 2.44 min; citronellol, 5.13 min.

4-Phenyl-2-butanone. 4-Phenyl-2-butanol (1 mmol) was oxidized with diphenyl diselenide (1 mmol) and 70% *t*-BuOOH (2.0 mmol) in refluxing benzene for 3 h, and the title compound was obtained in 75% yield. The spectroscopic properties were identical with those of the authentic sample.

Preparation of β -Hydroxy Selenides. They were prepared according to the procedure reported by Sharpless et al.¹⁹

2-(Phenylseleno)-1-cyclohexanol: bp 155–160 °C (bath temperature; 0.18 mmHg); IR (neat) 3340, 2980, 2810, 1465, 1435, 1425, 1060, 740, 690; NMR (CCl_4) 0.90–2.40 (m, 8 H), 2.85 (br s, 1 H), 2.60–3.54 (m, 2 H, CHOH, centered at 3.24, CHSe at 2.84), 7.07–7.70 (m, 5 H). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{OSe}$: C, 56.47; H, 6.32. Found: C, 56.67; H, 6.37.

2-(Phenylseleno)-1-cyclooctanol: IR (neat) 3370, 2880, 2810, 1465, 1450, 1435, 1040, 740, 690; NMR (CCl_4) 1.19–2.19 (m, 12 H), 2.59 (s, 1 H), 3.02–3.82 (m, 2 H), 7.09–7.72 (m, 5 H).

2-(Phenylseleno)-1-cyclododecanol: bp 180–185 °C (bath temperature; 0.06 mmHg); IR (neat) 3350, 2880, 2820, 1460, 1425, 1020, 740, 690; NMR (CCl_4) 0.80–2.00 (m, 20 H), 2.10 (br s, 1 H), 3.20–3.80 (m, 2 H), 7.10–7.63 (m, 5 H). Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{OSe}$: C, 63.70; H, 8.32. Found: C, 63.64; H, 8.31.

1-(Phenylseleno)-2-dodecanol. This was prepared by the reaction of 1-dodecene oxide with benzeneselenenyl anion:²⁷ bp 175–178 °C (bath temperature; 0.08 mmHg); IR (neat) 3360, 1460, 1430, 1090, 730, 720, 685; NMR (CCl_4) 0.80–1.50 (m, 21 H), 2.50 (br s, 1 H), 2.97 (d, $J = 4.0$ Hz, 2 H), 3.30–3.70 (m, 1 H), 7.00–7.50 (m, 5 H). Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{OSe}$: C, 63.33; H, 8.86. Found: C, 63.58; H, 8.98.

6-(Phenylseleno)-5-decanol: IR (neat) 3340, 2910, 2880, 2820, 1465, 1425, 1020, 740, 690; NMR (CCl_4) 0.67–1.08 (m, 18 H), 2.07

(s, 1 H), 2.80–3.17 (m, 1 H), 3.17–3.60 (m, 1 H), 7.00–7.60 (m, 5 H).

6-(Phenylseleno)-1-hexanol. This was prepared by the ring opening reaction of ϵ -caprolactone with phenyl trimethylsilyl selenide in the presence of zinc iodide²⁸ followed by reduction with lithium aluminum hydride: bp 126–130 °C (bath temperature; 0.06 mmHg); IR (neat) 3270, 2880, 2810, 1470, 1430, 1075, 840, 695; NMR (CCl_4) 1.00–1.86 (m, 8 H), 2.83 (t, $J = 7.0$ Hz, 2 H), 3.17 (s, 1 H), 3.38–3.56 (m, 2 H), 7.00–7.48 (m, 5 H). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{OSe}$: C, 56.03; H, 7.05. Found: C, 56.26; H, 7.23.

2-(Phenylseleno)-1-hexanol. It was prepared by the reduction of 2-(phenylseleno)-1-hexanal^{18b} with sodium borohydride in ethanol: bp 115–120 °C (bath temperature; 0.15 mmHg); IR (neat) 3300, 3000, 2900, 2880, 2810, 1465, 1425, 1020, 740, 690; NMR (CCl_4) 0.67–1.67 (m, 9 H), 2.35 (s, 1 H), 3.00–3.33 (m, 1 H), 3.50 (d, $J = 6.0$ Hz, 2 H), 7.10–7.56 (m, 5 H). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{OSe}$: C, 56.03; H, 7.05. Found: C, 56.09; H, 7.19.

11-(Phenylseleno)-2-undecanol. It was prepared by selective tosylation of 2,11-dodecanediol followed by phenylselenenylation: IR (neat) 3250, 2860, 2800, 1450, 1425, 1130, 1075, 1020, 730, 690; NMR (CCl_4) 0.97–1.93 (m, 19 H), 2.55 (s, 1 H), 2.83 (t, $J = 6.5$ Hz, 2 H), 3.30–3.90 (m, 1 H), 7.00–7.50 (m, 5 H). Anal. Calcd for $\text{C}_{15}\text{H}_{26}\text{OSe}$: C, 62.37; H, 8.62. Found: C, 62.09; H, 8.49.

3-(Phenylseleno)-2-propen-1-ol. To a suspension of NaH (1.1 g, 25 mmol, washed twice with hexane) in 10 mL of THF was added a solution of 3-(phenylseleno)-1-propene oxide (4.26 g, 20 mmol) in 20 mL of THF at room temperature. After being refluxed for 30 min, the reaction mixture was worked up by washing with saturated aqueous NH_4Cl . The crude oil obtained after concentration was distilled to give the title compound: 3.0 g (70%); an oil; bp 135 °C (0.2 mmHg); IR (neat) 3300; NMR (CCl_4) 3.50 (br s, 1 H), 3.90–4.30 (m, 2 H), 5.70–6.85 (m, 2 H), 7.05–7.60 (m, 5 H). Anal. Calcd for $\text{C}_9\text{H}_{10}\text{OSe}$: C, 50.72; H, 4.73. Found: C, 50.54; H, 4.86.

3-(Phenylthio)-2-propen-1-ol. This was prepared according to the reported procedure.²⁹ This compound exhibited the following spectra: IR (neat) 3300; NMR (CCl_4) 3.73–4.40 (m, 3 H); these signals were changed on D_2O exchange as follows: 4.00, d, $J = 6.0$ Hz, and 4.18, $J = 6.0$ Hz, 2 H), 5.57–6.53 (m, 2 H), 6.93–7.50 (m, 5 H).

2-(Phenylthio)-1-cyclododecanol. This was prepared by the reduction of 2-(phenylthio)cyclododecanone³⁰ with sodium borohydride: IR (neat) 3400, 1460, 1430, 1065, 1020, 750, 690; NMR (CCl_4) 1.00–1.90 (m, 20 H), 2.33 (br s, 1 H), 3.00–3.40 (m, 1 H), 3.40–3.80 (m, 1 H), 7.00–7.20 (m, 5 H).

Other hydroxy vinyl selenides and sulfides were prepared by the reduction of the corresponding ethyl 3-(phenylseleno)- or 3-(phenylthio)-2-alkenoates with lithium aluminum hydride.

Oxidation of 3-(Phenylseleno)-2-propen-1-ol. General Procedure for the Oxidation of Phenylseleno Alcohols in a Large-Scale Preparation. To a refluxing solution of bis(2,4,6-trimethylphenyl) diselenide (2.8 mmol) and 3-(phenylseleno)-2-propen-1-ol (3.0 g, 14 mmol) in 20 mL of benzene was added a solution of 70% *t*-BuOOH (2.7 g, 21 mmol) in 5 mL of benzene during 10 min. After being refluxed for 45 min, the reaction mixture was treated with a small amount of $\text{Na}_2\text{S}_2\text{O}_3$ for 10 min and then washed with saturated aqueous NaCl. Drying and concentration of the combined extracts gave an oil, which was purified by silica gel column chromatography to give a mixture of (*E*)-3-(phenylseleno)-2-propenal and its *Z* isomer (2.657 g, 90%) and the recovered diselenide (2.8 g, 100%). The isomeric ratio was determined to be 72:28 (*E/Z*) by NMR. However, this ratio was time dependent. If the reaction was carried out for a prolonged period, the formation of *E* isomer increased. Further purification by flash column chromatography afforded analytically pure samples.

(*Z*)-3-(Phenylseleno)-2-propenal: IR (neat) 1670 (vs), 1665 (vs); NMR (CCl_4) 6.76 (dd, $J = 10.0, 2.0$ Hz, 1 H), 7.17–7.67 (m,

(28) Miyoshi, N.; Ishii, H.; Murai, S.; Sonoda, N. *Chem. Lett.* 1979, 873.

(29) Wada, M.; Nakamura, H.; Taguchi, T.; Takei, H. *Chem. Lett.* 1977, 345.

(30) Trost, B. M.; Salzman, T. N.; Hiroi, K. *J. Am. Chem. Soc.* 1976, 98, 4887.

5 H), 7.73 (d, $J = 10.0$ Hz, 1 H), 9.63 (d, $J = 2.0$ Hz, 1 H). Anal. Calcd for C_9H_8OSe : C, 51.20; H, 3.82. Found: C, 50.90; H, 3.77.

(E)-3-(Phenylseleno)-2-propenal: bp 92 °C (bath temperature; 0.07 mmHg); IR (neat) 1660 (vs); NMR (CCl_4) 6.10 (dd, $J = 14.0, 7.0$ Hz, 1 H), 7.00–7.65 (m, 5 H), 7.97 (d, $J = 14.0$ Hz, 1 H), 9.30 (d, $J = 7.0$ Hz, 1 H). Anal. Calcd for C_9H_8OSe : C, 51.20; H, 3.82. Found: C, 51.27; H, 3.82.

3-(Phenylthio)-2-propenal. **General Procedure for the Oxidation of Phenylseleno or Phenylthio Alcohols in a Small-Scale Preparation.** A benzene (8 mL) solution of 70% *t*-BuOOH (230 mg, 1.8 mmol) was added to a benzene (1 mL) solution of bis(2,4,6-trimethylphenyl) diselenide (357 mg, 0.9 mmol), and the mixture was heated to refluxing for 10 min. A benzene (12 mL) solution of 3-(phenylthio)-2-propen-1-ol (248 mg, 1.5 mmol) was added to the resulting orange solution which was heated at reflux for 45 min. Then, the reaction mixture was washed with saturated aqueous NaCl, and the aqueous layer was extracted with ether. Drying and concentration of the combined extracts followed by purification by silica gel column chromatography gave the title compound as a mixture of *E* and *Z* isomers (246 mg, 100%) and the recovered diselenide: 322 mg (93%); bp 80–83 °C (bath temperature; 0.03 mmHg). Anal. Calcd for C_9H_8OS : C, 65.83; H, 4.91. Found: C, 65.82; H, 4.99. Further purification by silica gel column chromatography afforded the pure samples. (*Z*)-3-(Phenylthio)-2-propenal: IR (neat) 1650 (vs); NMR (CCl_4) 6.18 (dd, $J = 10.0, 4.0$ Hz, 1 H), 7.10–7.67 (m, 6 H), 9.77 (d, $J = 4.0$ Hz, 1 H). (*E*)-3-(Phenylthio)-2-propenal: IR (neat) 1655 (vs); NMR (CCl_4) 5.90 (dd, $J = 16.0, 7.0$ Hz, 1 H), 7.40 (s, 5 H), 7.54 (d, $J = 16.0$ Hz, 1 H), 9.33 (d, $J = 7.0$ Hz, 1 H).

2-(Phenylseleno)cyclohexanone: IR (neat) 1690 (vs); NMR (CCl_4) 1.28–2.58 (m, 7 H), 2.58–3.12 (m, 1 H), 3.62–3.95 (m, 1 H), 6.95–7.65 (m, 5 H).

2-(Phenylseleno)cyclooctanone: bp 142–143 °C (bath temperature; 0.25 mmHg); IR (neat) 1670 (vs); NMR (CCl_4) 0.67–3.00 (m, 12 H), 3.65 (dd, $J = 7.5, 6.5$ Hz, 1 H), 7.00–7.67 (m, 5 H).

2-(Phenylseleno)cyclododecanone: IR (neat) 1675 (vs); NMR (CCl_4) 1.08–1.81 (m, 18 H), 2.35–2.71 (m, 2 H), 3.81 (dd, $J = 12.0, 3.5$ Hz, 1 H), 7.05–7.48 (m, 5 H).

6-(Phenylseleno)-5-decanone: bp 130–132 °C (bath temperature; 0.08 mmHg); IR (neat) 1690 (vs); NMR (CCl_4) 0.78–1.60 (m, 16 H), 2.36–2.65 (m, 2 H), 3.51 (t, $J = 7.0$ Hz, 1 H), 7.08–7.50 (m, 5 H). Anal. Calcd for $C_{16}H_{24}OSe$: C, 61.73; H, 7.77. Found: C, 61.88; H, 7.91.

6-(Phenylseleno)hexanal: IR (neat) 1720 (vs); NMR (CCl_4) 1.23–1.79 (m, 6 H), 2.30 (m, 2 H), 2.82 (t, $J = 7.0$ Hz, 2 H), 7.03–7.47 (m, 5 H), 9.58 (t, $J = 1.6$ Hz, 1 H). Anal. Calcd for $C_{12}H_{16}OSe$: C, 56.47; H, 6.32. Found: C, 56.77; H, 6.36.

2-(Phenylseleno)hexanal: bp 103–105 °C (bath temperature; 0.04 mmHg); IR (neat) 1700 (vs); NMR (CCl_4) 0.67–2.00 (m, 9 H), 3.47 (dt, $J = 3.0, 7.0$ Hz, 1 H), 7.00–7.67 (m, 5 H), 9.28 (d, $J = 3.0$ Hz, 1 H). These spectra were identical with those of the authentic sample prepared by the procedure of Sharpless et al.^{18b}

1-(Phenylseleno)-2-dodecanone: IR (neat) 1675 (vs); NMR (CCl_4) 0.67–1.67 (m, 19 H), 2.47 (t, $J = 7.0$ Hz, 2 H), 3.43 (s, 2 H), 7.03–7.53 (m, 5 H). Anal. Calcd for $C_{18}H_{28}OSe$: C, 63.70; H, 8.32. Found: C, 63.83; H, 8.27.

2-(Phenylthio)cyclododecanone: IR (neat) 1700 (vs); NMR (CCl_4) 1.00–2.00 (m, 18 H), 2.20–2.80 (m, 2 H), 3.83 (dd, $J = 10.0, 4.0$ Hz, 1 H), 7.22 (s, 5 H).

11-(Phenylseleno)-2-undecanone: IR (neat) 1695 (vs); NMR (CCl_4) 1.00–1.80 (m, 14 H), 2.02 (s, 3 H), 2.30 (t, $J = 6.5$ Hz, 2 H), 2.83 (t, $J = 6.5$ Hz, 2 H), 7.06–7.46 (m, 5 H).

3-(Phenylthio)-2-butenal: IR (neat) 1645 (vs); NMR (CCl_4) 1.97 (s), 2.37 (s), 5.33 (d, $J = 7.0$ Hz), 5.98 (d, $J = 7.0$ Hz), 7.33 (s), 9.57 (d, $J = 7.0$ Hz, CH=O), 9.90 (d, $J = 7.0$ Hz, CH=O).

3-(Phenylthio)-2-nonenal: IR (neat) 1670 (vs); NMR (CCl_4) 1.00–1.60 (m, 12 H), 2.22 (t, $J = 7.0$ Hz, 2 H), 6.05 (d, $J = 6.5$ Hz, 1 H), 7.30 (m, 5 H), 10.00 (d, $J = 6.5$ Hz, 1 H). Anal. Calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.12. Found: C, 72.47; H, 7.98.

5,5-Dimethyl-3-(phenylseleno)-2-cyclohexen-1-one: bp 124 °C (bat temperature; 0.15 mmHg); IR (neat) 1655, 1580; NMR (CCl_4) 1.03 (s, 6 H), 2.08 (s, 2 H), 2.33 (s, 2 H), 5.60 (s, 1 H), 7.13–7.60 (m, 5 H). Anal. Calcd for $C_{12}H_{16}OSe$: C, 60.22; H, 5.77. Found: C, 59.95; H, 5.89.

Oxidation of Benzhydrol with Benzeneselenenyl Chloride in the Presence of Triethylamine. Benzhydrol (184 mg, 1 mmol) was treated with benzeneselenenyl chloride (278 mg, 2 mmol) and triethylamine (202 mg, 2 mmol) in refluxing benzene (5 mL) for 3 h. After the usual workup, benzophenone (112 mg, 61%) was isolated along with recovered benzhydrol (63 mg, 34%) and diphenyl diselenide (278 mg, 89%) by separation of the reaction mixture with TLC.

Registry No. 3, 26489-18-9; 4 ($R^1, R^2 = (CH_2)_4$; $n = 0$; $X = SeC_6H_5$), 73501-53-8; 4 ($R^1, R^2 = (CH_2)_6$; $n = 0$; $X = SeC_6H_5$), 78998-73-9; 4 ($R^1, R^2 = (CH_2)_{10}$; $n = 0$; $X = SeC_6H_5$), 72474-91-0; 4 ($R^1, R^2 = C_4H_9$; $n = 0$; $X = SeC_6H_5$), 78998-74-0; 4 ($R^1, R^2 = H$; $n = 4$; $X = SeC_6H_5$), 78998-75-1; 4 ($R^1 = H, R^2 = C_4H_9$; $n = 0$; $X = SeH_5$), 78998-76-2; 4 ($R^1 = C_{10}H_{21}$; $R^2 = H$; $n = 0$; $X = SeC_6H_5$), 60221-17-2; 4 ($R^1, R^2 = (CH_2)_{10}$; $n = 0$; $X = SC_6H_5$), 79082-23-8; 5 ($R^1, R^2 = (CH_2)_4$; $n = 0$; $X = SeC_6H_5$), 50984-16-2; 5 ($R^1, R^2 = (CH_2)_6$; $n = 0$; $X = SeC_6H_5$), 57205-24-0; 5 ($R^1, R^2 = (CH_2)_{10}$; $n = 0$; $X = SeC_6H_5$), 42858-37-7; 5 ($R^1, R^2 = C_4H_9$; $n = 0$; $X = SeC_6H_5$), 78998-77-3; 5 ($R^1, R^2 = H$; $n = 4$; $X = SeC_6H_5$), 78998-78-4; 5 ($R^1 = H, R^2 = C_4H_9$; $n = 0$; $X = SeC_6H_5$), 78998-79-5; 5 ($R^1 = C_{10}H_{21}$; $R^2 = H$; $n = 0$; $X = SeC_6H_5$), 70677-95-1; 5 ($R^1, R^2 = (CH_2)_{10}$; $n = 0$; $X = SC_6H_5$), 52190-43-9; 6 ($R = CH_3$; $X = SC_6H_5$), 78998-80-8; 6 ($R = C_6H_{13}$; $X = SC_6H_5$), 78998-81-9; bis(*m*-(trifluoromethyl)phenyl) diselenide, 53973-75-4; bis(*o*-methoxyphenyl) diselenide, 80227-68-5; bis(*o*-nitrophenyl) diselenide, 35350-43-7; bis(2,4,6-trimethylphenyl) diselenide, 71518-92-8; bis(*p*-chlorophenyl) diselenide, 20541-49-5; benzyl alcohol, 100-51-6; benzaldehyde, 100-52-7; benzhydrol, 91-01-0; benzophenone, 119-61-9; geraniol, 106-24-1; geranial, 141-27-5; 1-decanol, 112-30-1; decanal, 112-31-2; 1-phenyl-4-hexen-3-one, 60550-53-0; 2,6-dimethyl-8-hydroxy-2-octenal, 26489-19-0; 2,6-dimethyl-2-octene-1,8-diol, 26489-18-9; citronellol, 106-22-9; citronellal, 106-23-0; 4-phenyl-2-butanone, 2550-26-7; 4-phenyl-2-butanol, 2344-70-9; 11-(phenylseleno)-2-undecanol, 80227-69-6; 3-(phenylseleno)-2-propen-1-ol, 78998-90-0; 3-(phenylthio)-2-propen-1-ol, 15286-68-7; (*E*)-3-(phenylseleno)-2-propenal, 74824-70-7; (*Z*)-3-(phenylseleno)-2-propenal, 74824-71-8; (*Z*)-3-(phenylthio)-2-propenal, 80227-70-9; (*E*)-3-(phenylthio)-2-propenal, 80227-71-0; 11-(phenylseleno)-2-undecanone, 80227-72-1; 3-(phenylthio)-2-butenal, 78998-85-3; 3-(phenylthio)-2-nonenal, 78998-87-5; 5,5-dimethyl-3-(phenylseleno)-2-cyclohexen-1-one, 78998-88-6; cinnamyl alcohol, 104-54-1; *trans*-2-hexen-1-ol, 928-95-0; 1-phenyl-4-hexen-3-ol, 80227-73-2; 3-phenyl-1-propanol, 122-97-4; 1-menthol, 1490-04-6; cyclododecanol, 1724-39-6; cinnamaldehyde, 104-55-2; *trans*-2-hexenal, 6728-26-3; 3-phenylpropanal, 104-53-0; 1-menthone, 89-80-5; cyclododecanone, 830-13-7; 5,5-dimethyl-3-(phenylseleno)-2-cyclohexen-1-ol, 78998-82-0; *t*-BuOOH, 75-91-2.