Oxidation of Alcohols with *tert*-Butyl Hydroperoxide and Diaryl Diselenide¹

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Treatment of alcohols with *tert*-butyl hydroperoxide in the presence of diaryl diselenide in refluxing benzene gives the corresponding aldehydes or ketones. Although some allylic alcohols undergo oxidation in the presence of 10-15 mol % of bis(*p*-chlorophenyl) diselenide, use of 0.5 equiv of bis(2,4,6-trimethylphenyl) diselenide gives satisfactory results in almost all cases. The procedure can be used for selective oxidation of alcohols bearing a phenylthio or phenylseleno group, which usually survives the reaction conditions to give the corresponding carbonyl compounds.

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For past 7 years organoselenium chemistry has found considerable applications in synthetic organic chemistry.² Among them the selenoxide syn elimination has received the most attention² because it is one of the most reliable methods for the formation of olefins at around room temperature.

Scheme I is not limited for dehydrogenation of alkanes and alkenes (X = C). White found that this type of dehydrogenation in the case with seleninates (X = O) produced carbonyl compounds.³ The chemistry based on benzeneseleninic anhydride has recently been developed extensively.^{4,5} In one of their reports, Barton et al.⁵ⁱ described the oxidation of alcohols with benzeneseleninic anhydride, where the fragmentation of alkyl aryl seleninates has been postulated.

In addition to seleninic derivatives, alkyl selenenates also appear to undergo a similar fragmentation to yield the corresponding carbonyl compounds. For example, benzyl phenyl selenoxide, on being heated, undergoes rearrangement to benzyl selenenic ester which yields benzaldehyde and benzeneselenol via β elimination.⁶ Similarly, the involvement of alkyl arylselenenates appears to account for the facile introduction of carbonyl functionalities described in the following examples: the oxidation of aldehyde hydrazones with benzeneseleninic anhydride,^{5c} the reaction of allylic alcohols with benzeneselenenyl bromide and silver acetate,⁷ and the conversion of olefins into α phenylseleno carbonyl compounds by diphenyl diselenide and benzeneseleninic anhydride.⁸

$$ArSe_{X}^{O} \stackrel{H}{\underset{R}} \stackrel{R}{\longrightarrow} \stackrel{R}{\underset{R}} C=X + ArSeOH$$

In regard to the observations cited above, either alkyl selenenates 1 or alkyl seleninates 2 are capable of under-

$$\begin{array}{c} \mathrm{RCH}_{2}\mathrm{OSeAr} \rightarrow \mathrm{RCH}{=\!\!\!\!=}\mathrm{O} + \mathrm{ArSeH} \\ 1 \\ \mathrm{RCH}_{2}\mathrm{OSe}(\mathrm{O})\mathrm{Ar} \rightarrow \mathrm{RCH}{=\!\!\!\!=}\mathrm{O} + \mathrm{ArSeOH} \\ 2 \end{array}$$

going fragmentation to produce carbonyl compounds along with areneselenol or areneselenenic acid (known to undergo disproportionation to diaryl diselenide and areneseleninic acid).⁹ Furthermore, areneselenol and diaryl diselenide can be oxidized or subjected to disproportionation to give

areneselenenic acid, areneseleninic acid, or their anhydrides which may further react with alcohols to form selenenate or seleninate esters. Thus, it is expected that a catalytic use of diaryl diselenide and some stoichiometric oxidizing agent will constitute a new oxidation method for alcohols.

Results and Discussion

It has been reported that the reaction of diaryl diselenide with ozone or *tert*-butyl hydroperoxide produced areneseleninic anhydride.¹⁰ The involvement of areneselenenic anhydride as well as areneseleninic anhydride was postulated in this transformation, which indicates that the $(ArSe)_2$ -t-BuOOH system holds some promise as an oxidation method for alcohols.

Indeed, benzyl alcohol and benzhydrol could be quantitatively oxidized to benzaldehyde and benzophenone, respectively, on being heated with t-BuOOH (1.1–1.2 equiv) in the presence of diphenyl diselenide (10 mol %) in carbon tetrachloride.

Thus, a catalytic activity of diphenyl diselenide has been confirmed. However, the use of a lesser amount of the diselenide did not meet with the completion of the reac-

⁽¹⁾ Preliminary reports have appeared; Shimizu, M.; Kuwajima, I. Tetrahedron Lett. 1979, 2801. Shimizu, M.; Urabe, H.; Kuwajima, I. Ibid. 1981, 2381.

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 W.; Singer, S. P.; Young, M. W. Chem. Scr. 1975, 8A, 9. Clive, D. L. J.
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 43. Reich, H. J. Acc. Chem. Res. 1979, 12, 22.

⁽³⁾ White, J. W. Ph.D. Thesis, University of Arizona, 1967; Diss. Abstr. B 1967, 28, 853.

⁽⁴⁾ Czarny, M. R. J. Chem. Soc., Chem. Commun. 1976, 81.

^{(5) (}a) Barton, D. H. R.; Brewster, A. G.; Ley, S. V.; Rosenfeld, M. N. J. Chem. Soc., Chem. Commun. 1976, 985. (b) Ibid. 1977, 147. (c) Barton, D. H. R.; Lester, D. J.; Ley, S. V. Ibid. 1977, 445. (d) Barton, D. H. R.; Cussans, N. J.; Ley, S. V. Ibid. 1977, 751. (e) Barton, D. H. R.; Lester, D. J.; Ley, S. V. Ibid. 1977, 751. (e) Barton, D. H. R.; Lester, D. J.; Ley, S. V. Ibid. 1978, 393. (h) Barton, D. H. R.; Ley, S. V.; Magnus, P. D.; Rosenfeld, M. N. J. Chem. Soc., Perkin Trans. 1 1977, 567. (i) Barton, D. H. R.; Brewster, A. G.; Hui, R. A. H. F.; Lester, D. J.; Ley, S. V. J. Chem. Soc., Chem. Commun. 1978, 952. (j) Barton, D. H. R.; Hui, R. A. H. F.; Lester, D. J.; Ley, S. V. J. Chem. Soc., Chem. Commun. 1978, 952. (j) Barton, D. H. R.; Hui, R. A. H. F.; Lester, D. J.; Ley, S. V.; Barton, D. H. R.; Dey, S. V.; Barton, D. H. R. J. Chem. Soc., Perkin Trans. 1 1979, 3331. (k) Cussans, N. J.; Ley, S. V.; Barton, D. H. R. J. Chem. Soc., Perkin Trans. 1 1980, 1650, 1654.

⁽⁶⁾ Entwhistle, I. D.; Johnstone, R. A. W.; Varley, J. H. J. Chem. Soc., Chem Commun. 1976, 61.
(7) Sharpless, K. B.; Lauer, R. F. J. Am. Chem. Soc. 1972, 84, 7145.

⁽⁷⁾ Sharpless, K. B.; Lauer, R. F. J. Am. Chem. Soc. 1972, 84, 7145.
(8) Shimizu, M.; Takeda, R.; Kuwajima, I. Tetrahedron Lett. 1979, 419, 3461; Shimizu, M.; Takeda, R.; Kuwajima, I. Bull. Chem. Soc. Jpn. 1981, 54, 3510.

⁽⁹⁾ Reich, H. J.; Renga, J. M.; Reich, I. L. J. Am. Chem. Soc. 1975, 97, 5434.

⁽¹⁰⁾ Ayrey, G.; Barnard, D.; Woodbridge, D. T. J. Chem. Soc. 1962, 2089.

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 are neseleninic 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 extention 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 wholely 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,

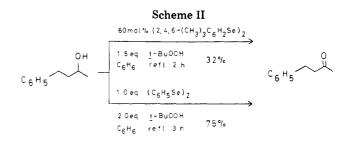
 $C_{6}H_{5}CH_{2}CH_{2}CH_{2}OH \xrightarrow{(Me_{3}C_{6}H_{2}Se)_{2} (0.5 \text{ equiv})}{t-BuOOH (1.5 \text{ equiv}), \text{ benzene, reflux}} C_{6}H_{5}CH_{2}CH_{2}CH \xrightarrow{\bullet} O$

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°
trans-2-hexen-1-ol	1	trans-2-hexenal	89c,d
geraniol	1	geranial	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	88d,f,g
1-menthol	17	1-menthone	97
cyclododecanol	4	cyclododecanone	100
4-phenyl-2-	3	4-phenyl-2-	75^{h}
butanol		butanone	

^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 geranial 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.

<sup>munication from Professor K. B. Sharpless.
(13) Sharples, 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.</sup>

⁽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.

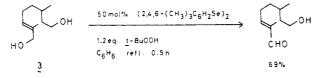
Table II. Oxidation of Alcohol 4^a

R ¹	R²	n	x	reactn period, min	% yield of 5 ^b
(CH ₂),	0	SeC ₆ H ₅	180	79
(CH ₂).	0	SeC ₆ H	15	91
(CH ₂),,	0	SeC̃́H₅́	40	100
C₄H,	[°] C₄H,	0	SeC ₆ H,	40	90
н̈́	н	4	SeC ₆ H ₅	120	86
н	C₄H,	0	Se C ₆ H ₅	60	58
$C_{10}H_{21}$	H	0	SeC ₆ H ₅	90	66
ŰĈH,)10	0	SC, Ĭ,	90	72

^a Reactions were carried out in refluxing benzene with an alcohol/t-BuOOH/($(CH_3)_3C_6H_2Se)_2$ ratio of 1.0:1.3-1.5: 0.5-0.6. ^b Isolated yield.

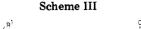
oxidized selectively in the presence of saturated alcohols. However, the need for a large excess of manganese dioxide and for its activation appear to call for development of alternatives.

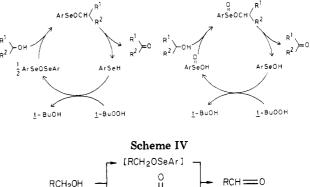
Careful oxidation of the diol 3 by the present procedure demonstrates a good alternative.



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 sulfenylation 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-





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.

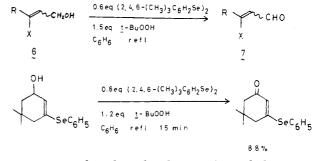
$$\begin{array}{c|c} R^{1}CH(CH_{2})_{n} CHR^{2} & \frac{((CH_{3})_{3}C_{6}H_{2}S_{6})_{2}}{PBUOOH} \\ & & \\ OH & X \\ X = SC_{6}H_{5}; SeC_{6}H_{5} \\ \end{array} \qquad \begin{array}{c} R^{1}CO(CH_{2})_{n} CHR^{2} \\ & & \\ R^{1}CO(CH_{2})_{n} CHR^{2} \\ & & \\ X \\ X \end{array}$$

4,

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.

$$CH_{3}CH(OH)(CH_{2})_{9}SeC_{6}H_{5} \xrightarrow{((CH_{3})_{3}C_{6}H_{2}Se)_{2}}{t-BuOOH, \text{ benzene, reflux}} CH_{3}CO(CH_{2})_{9}SeC_{6}H_{5}$$

Oxidation of 3-(phenylthio)- or 3-(phenylseleno)-2propen-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 = SeC_6H_5) with pyridinium chlorochromate (PCC) afforded the crude aldehyde 7 (R = H, X = SeC_6H_5) 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,

⁽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 sulfenylation see: (c) Trost, B. M. Chem. Rev.
 1978, 78, 363 and references cited therein.

⁽¹⁹⁾ For oxyselenenylation see: Reich, H. J. 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 oxysulfenylation 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.

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

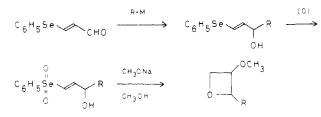
⁽²³⁾ For example, oxidation of 3-(phenylthio)-2-propen-1-ol with a excess of active manganese dioxide gave the corresponding aldehyde in moderate yield: personal communication from Professor H. Takei of this institute.

Table III. Oxidation of Alcohol 6^a

R	х	reactn period, min	% yield of 7 ^b
Н	SC ₆ H ₅	45	100
Н	SeČ₄H₅	45	90
CH ₃	SC₄H₅	45	55°
$C_6 \tilde{H_{13}}$	$SC_{6}H_{5}$	10	78^d

^{*a*} Reactions were performed in refluxing benzene with a reactant ratio of alcohol/*t*-BuOOH/((CH_3)₃C₆H₂Se)₂ of 1.0:1.5:0.6. ^{*b*} Isolated yield. ^{*c*} Yield determined by NMR based on an internal standard. ^{*d*} The reaction was carried out in isopropyl acetate in the presence of KH₂PO₄ (2.4 equiv).

3-(phenylseleno)-2-propenal can be used for the construction of the oxetane ring as shown in the following equation.²⁴



Oxidation Mechanism. Although we have found no evidence for the generation of selenenate or seleninate esters, there appear to be two possible routes for the formation of the carbonyl compounds (Scheme III).

One involves the intermediate seleninate ester which is analogous to the one proposed in the syn elimination of alkyl selenoxides. Barton et al. have postulated this intermediate for their oxidation method with benzeneseleninic anhydride⁵ⁱ (Scheme IV).

The selenenate ester is another plausible intermediate. This type of intermediate, selenenate esters, has been proposed in several oxidation reactions to form carbonyl groups. $5^{5c,6-8}$

To test further the possibility of selenenate ester to undergo fragmentation to carbonyl compounds, we treated benzhydrol with benzeneselenenyl chloride and triethylamine in refluxing benzene, and benzophenone was obtained along with diphenyl diselenide.

$$(C_6H_5)_2CHOH + 2C_6H_5SeCl \xrightarrow{Et_3N} (C_6H_5)_2C=O + (C_6H_5)_2CHOH + (C_6H_5Se)_2 \\ 61\% \qquad 34\% \qquad 89\%$$

The result above clearly suggests the possibility for the decomposition of the selenenate ester to the carbonyl compound and benzeneselenol. However, a recent report has described an equimolar reaction of bis(p-fluorophenyl) diselenide with *tert*-butyl hydroperoxide, which affords a mixture of the diselenide and the seleninic anhydride without formation of the selenenic anhydride in a detectable concentration.²⁵ In our reaction conditions, 2–3-fold excess amounts of the peroxide to those of the diselenide are usually employed, which may further favor the formation of the seleninic anhydride and exclude the possibility of selenenate ester intermediates.

Experimental Section

General Methods. Infrared spectra were recorded on a Hitachi EPI-G3 or 260-10 spectrometer and are given in reciprocal centimeters. Proton magnetic resonance spectra (NMR) were taken on a Hitachi R-24B, and the 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 as the carrier gas. Columns A and B refer to 20% PEG 20M on Diasolid L (3 mm × 2 m) and 20% PEG 20M on Diasolid L (3 mm × 1 m), respectively. Microanalyses were performed on a Perkin-Elmer 240 instrument. Analytical thin-layer chromatography was carried out by using Merk precoated, glassbacked, Kieselgel 60 F₂₅₄ plates. Column chromatography was performed on Merk Kieselgel 60 or Wakogel C-200. Melting points which were taken in open glass capillaries, and boiling points were uncorrected.

Preparation of Diaryl Diselenides. Bis[m-(trifluoromethyl)phenyl] diselenide, bis(o-methoxyphenyl) diselenide, and bis(o-nitrophenyl) diselenide were prepared according to the described procedures.^{9,19} Other diselenides were prepared by the addition of selenium metal to arylmagnesium bromides followed by hydrolysis²⁶ and air oxidation. The preparation of bis(2,4,6trimethylphenyl)diselenide represents a typical procedure.

Bis(2,4,6-trimethylphenyl) Diselenide. Arylmagnesium bromide was prepared from 1-bromo-2,4,6-trimethylbenzene (199 g, 1 mol) and magnesium (26 g, 1.1 mol) in 1 L of ether. To the resulting solution was added selenium powder (79 g, 1 mol), and the mixture was heated under stirring for 2 h. Then the reaction mixture was treated with dilute HCl, and the aqueous layer was extracted with ether. The combined extracts were concentrated, and the residual oil was dissolved in ethanol. Air was bubbled to the solution until no more precipitate was formed. Deposited precipitate was filtered and was recrystallized from ethanol to give the title diselenide (94 g, 47%) as a yellow crystal: mp 113-114.5 °C; IR (KBr) 3010, 2900, 1590, 1450, 1430, 1290, 1025, 855, 845, 700; NMR (CCl₄) 2.26 (s, 12 H), 2.29 (s, 6 H), 6.73 (s, 4 H). Anal. Calcd for $C_{18}H_{22}Se_2$: C, 54.55; H, 6.00. Found: C, 54.52; H, 5.77.

Bis(*p***-chlorophenyl) Diselenide.** This was prepared in 73% yield by a similar procedure: mp 85–86 °C (ethanol); IR (KBr) 3050, 1460, 1380, 1080, 1000, 810, 720; NMR (CCl₄) 7.10–7.70 (m). Anal. Calcd for $C_{12}H_8Cl_2Se_2$: C, 37.83; H, 2.12. Found: C, 37.76; H, 2.16.

Oxidation of Benzyl Alcohol with t-BuOOH in the Presence of Diphenyl Diselenide. To a solution of diphenyl diselenide (63 mg, 0.2 mmol) and benzyl alcohol (216 mg, 2 mmol) in 3 mL of carbon tetrachloride was added a solution of 70% t-BuOOH (307 mg, 2.4 mmol) in 4 mL of carbon tetrachloride, and the mixture was heated to reflux for 1 h. Then, nitromethane (41 mg, an internal standard) was added to the resulting mixture, which was analyzed by NMR. Examination of the relative intensity of the aldehyde proton and those of nitromethane indicates the formation of benzaldehyde in 100% yield.

Oxidation of Benzhydrol with t-BuOOH in the Presence of Diphenyl Diselenide. To a solution of diphenyl diselenide (31 mg, 0.1 mmol) in 5 mL of carbon tetrachloride were added a solution of 70% t-BuOOH (141 mg, 1.1 mmol) and benzhydrol (184 mg, 1.0 mmol) in 3 mL of carbon tetrachloride and 3A molecular sieves (2 g). The mixture was heated to refluxing under stirring for 2 h. Then, 0.1 mmol of t-BuOOH was added to the mixture, and it was stirred for 15 min under refluxng. Filtration of the molecular sieves and concentration of the filtrate gave an oil, which was purified by TLC to give benzophenone, 182 mg (100%).

Oxidation of Alcohols with t-BuOOH and Bis(2,4,6-trimethylphenyl) Diselenide. General Procedure. Oxidation of geraniol represents a typical procedure. To a benzene (2 mL) solution of bis(2,4,6-trimethylphenyl) diselenide (198 mg, 0.5 mmol) were added successively solutions of 70% t-BuOOH (141 mg, 1.1 mmol) in 3 mL of benzene and geraniol (154 mg, 1.0 mmol) in 2 mL of benzene. After the mixture was stirred for 1 h under refluxing, the solvent was removed in vacuo, and the remaining oil was purified by silica gel column chromatography to afford the diselenide (161 mg, 81% recovery) and geranial (151 mg, 100%). GLC analysis (column B) indicated that geranial (98%) and neral (2%) were formed: IR (neat) 2740, 1660 (vs), 1430, 1370, 1190, 1120; NMR (CCl₄) 1.60 (s, 3 H), 1.67 (s, 3 H), 2.13 (unre-

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

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 (CCl₄) 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 C₁₂H₁₈OSe: C, 56.03; H, 7.05. Found: C, 56.26; H, 7.23.

of 2-(phenylseleno)-1-hexanal^{18b} with sodium borohydride in

ethanol: bp 115-120 °C (bath temperature; 0.15 mmHg); IR (neat)

(d, J = 6.0 Hz, 2 H), 7.10–7.56 (m, 5 H). Anal. Calcd for

2-(Phenylseleno)-1-hexanol. It was prepared by the reduction

6-(Phenylseleno)-1-hexanol. This was prepared by the ring

H).

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 Na₂CO₃ 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 (CCl₄) 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 (CCl₄) 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 (CCl₄) 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 C₁₀H₁₈O₂: 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 (CCl₄) 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 $C_{12}H_{16}OSe:$ 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 (CCl₄) 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).

 $\begin{array}{l} \textbf{2-(Phenylseleno)-1-cyclododecanol: bp 180-185 °C (bath temperature; 0.06 mmHg); IR (neat) 3350, 2880, 2820, 1460, 1425, 1020, 740, 690; NMR (CCl_4) 0.80-2.00 (m, 20 H), 2.10 (br s, 1 H), 3.20-3.80 (m, 2 H), 7.10-7.63 (m, 5 H). Anal. Calcd for C_{18}H_{28}OSe: C, 63.70; H, 8.32. Found: C, 63.64; H, 8.31. \end{array}$

1-(Phenylseleno)-2-dodecanol. This was prepared by the reaction of 1-dodecene oxide with benzeneselenenate anion:²⁷ bp 175–178 °C (bath temperature; 0.08 mmHg); IR (neat) 3360, 1460, 1430, 1090, 730, 720, 685; NMR (CCl₄) 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 C₁₈H₃₀OSe: 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 (CCl₄) 0.67-1.08 (m, 18 H), 2.07

3300, 3000, 2900, 2880, 2810, 1465, 1425, 1020, 740, 690; NMR (CCl₄) 0.67-1.67 (m, 9 H), 2.35 (s, 1 H), 3.00-3.33 (m, 1 H), 3.50

 $\begin{array}{l} C_{12}H_{18} \text{OSe: C, } 56.03; \text{ H, } 7.05. \text{ Found: C, } 56.09; \text{ H, } 7.19. \\ \textbf{11-(Phenylseleno)-2-undecanol.} \text{ It was prepared by selective tosylation of 2,11-dodecanediol followed by phenylselenenylation: IR (neat) 3250, 2860, 2800, 1450, 1425, 1130, 1075, 1020, 730, 690; \\ \text{NMR (CCl}_4) 0.97-1.93 (m, 19 \text{ H}), 2.55 (s, 1 \text{ H}), 2.83 (t, J = 6.5 \\ \text{Hz, } 2 \text{ H}), 3.30-3.90 (m, 1 \text{ H}), 7.00-7.50 (m, 5 \text{ H}). \text{ Anal. Calcd for C}_{15}H_{28} \text{OSe: C, } 62.37; \text{ H, } 8.62. \text{ Found: C, } 62.09; \text{ H, } 8.49. \end{array}$

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 NH₄Cl. 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 (CCl₄) 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 C₉H₁₀OSe: 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 (CCl₄) 3.73-4.40 (m, 3 H; these signals were changed on D₂O 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 (CCl₄) 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 Na₂S₂O₃ 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 (CCl₄) 6.76 (dd, J = 10.0, 2.0 Hz, 1 H), 7.17-7.67 (m,

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5 H), 7.73 (d, J = 10.0 Hz, 1 H), 9.63 (d, J = 2.0 Hz, 1 H). Anal. Calcd for C₉H₈OSe: 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 (CCl₄) 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 C₉H₈OSe: 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 C₉H₈OS: 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 (CCl₄) 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 (CCl₄) 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 (CCl₄) 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 (CCl₄) 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 (CCl₄) 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 (CCl₄) 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 C₁₆H₂₄OSe: C, 61.73; H, 7.77. Found: C, 61.88; H, 7.91.

6-(Phenylseleno)hexanal: IR (neat) 1720 (vs); NMR (CCl₄) 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 (CCl₄) 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 (CCl₄) 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 (CCl₄) 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 (CCl₄) 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 (CCl₄) 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 (CCl₄) 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 C₁₅H₂₀OS: 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 (CCl₄) 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 (\mathbb{R}^1 , $\mathbb{R}^2 = (CH_2)_4$; n = 0; X = SeC_6H_5 , 73501-53-8; 4 (R¹, R² = (CH₂)₆; n = 0; X = SeC_6H_5), 78998-73-9; 4 (R¹, R² = (CH₂)₁₀; n = 0; X = SeC₆H₅), 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 ($\mathbf{R}^1 = C_{10}\mathbf{H}_{21}$; $\mathbf{R}^2 = \mathbf{H}$; n = 0, $\mathbf{X} = \mathbf{SeC}_6\mathbf{H}_5$), 60221-17-2; 4 (R¹, R² = (CH₂)₁₀; n = 0; X = SC₆H₅), 79082-23-8; 5 (R¹, R² = $(CH_2)_4$; n = 0; $X = SeC_6H_5$), 50984-16-2; 5 (R¹, R² = (CH₂)₆; n = 0; $X = SeC_6H_5$), 57205-24-0; 5 (R¹, R² = (CH₂)₁₀; n = 0; $X = SeC_6H_5$), 42858-37-7; 5 (R¹, R² = C₄H₉; n = 0; X = SeC₆H₅), 78998-77-3; 5 (R¹, $R^2 = H; n = 4; X = SeC_6H_5), 78998-78-4; 5 (R^1 = H, R^2 = C_4H_9; n$ = 0; X = SeC₆H₅), 78998-79-5; 5 (R¹ = C₁₀H₂₁, R² = H; n = 0; X = $SeC_{6}H_{5}$, 70677-95-1; 5 (R¹, R² = (CH₂)₁₀; n = 0; X = $SC_{6}H_{5}$), 52190-43-9; 6 (R = CH₃; X = SC₆H₅), 78998-80-8; 6 (R = C₆H₁₃; X = SC_6H_5 , 78998-81-9; bis[m-(trifluoromethyl)phenyl] diselenide, 53973-75-4; bis(o-methoxyphenyl) diselenide, 80227-68-5; bis(onitrophenyl) 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.