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One-step Oxidation of Olefins into α-Phenylseleno Carbonyl Compounds[1)]

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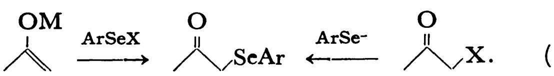
(Received April 14, 1981)

Oxidation of olefins has been examined with the following three types of reagents; (i) $(C_6H_5Se)_2$–Br_2–$(Bu_3Sn)_2O$, (ii) $(C_6H_5Se)_2$–*t*-BuOOH, and (iii) $(C_6H_5Se)_2$–$(C_6H_5SeO)_2O$, and the corresponding α-phenylseleno carbonyl compounds have been obtained directly from the olefins.

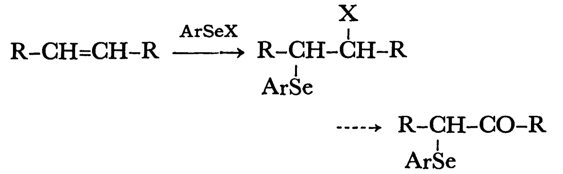
Recent developments in organoselenium chemistry[2)] have brought about a wide range of synthetic utilities of α-phenylseleno carbonyl compounds. They have been used for regioselective introduction of various functional groups, especially for that of unsaturation *via* well established *syn*-elimination process.[2)] For their preparation, both electrophilic and uncleophilic organoselenium reagents are usually available as shown below:[3)]



(1)

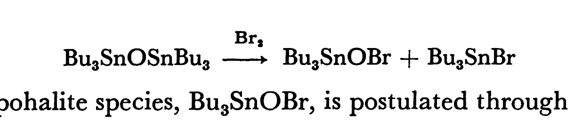
However, no simple and reliable route to α-phenylseleno carbonyl compounds from both internal and terminal olefins has been developed until now,[4)] although olefinic compounds are in general readily accessible *via* a number of established synthetic procedures.

Electrophilic 1,2-addition of PhSeX species constitutes a potential methodology for the introduction of double functionalities into carbon-carbon double bonds.[2)] It is expected that during this process if CH–X group is converted into a carbonyl simultaneously, α-phenylseleno carbonyl compounds may be produced directly from olefins (Eq. 2). In this paper, we describe an efficient approach for one-step oxoselenenylation reaction of olefins to afford α-phenylseleno carbonyl compounds.



$$\text{R-CH=CH-R} \xrightarrow{\text{ArSeX}} \underset{\text{ArSe}}{\text{R-CH}}\text{-}\overset{\text{X}}{\text{CH}}\text{-R} \dashrightarrow \text{R-}\underset{\text{ArSe}}{\text{CH}}\text{-CO-R} \quad (2)$$

Oxidation of Olefins with $(C_6H_5Se)_2$–Br_2–$(Bu_3Sn_2)O$. Trialkylstannyl ethers are well known to be transformed into carbonyl compounds on treatment with bromine or *N*-chlorosuccinimide (NCS)[5)] as shown in the following equation.

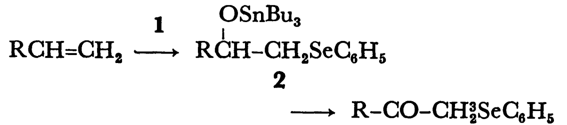


(3)

$$Bu_3SnOSnBu_3 \xrightarrow{Br_2} Bu_3SnOBr + Bu_3SnBr \quad (4)$$

In a related reaction, a formation of a hypohalite species, Bu_3SnOBr, is postulated through the reaction of hexabutyldistannoxane with bromine.[6)] In a similar way, a formation of "$C_6H_5SeOSnBu_3$" **1** is expected on treatment of hexabutyldistannoxane with benzeneselenenyl bromide. Like other electrophilic species such as ArSeCl, ArSeBr, ArSeOAc, *etc.*,[2)] **1** appears to behave as an electrophile to attack a C=C bond to form β-(phenylseleno)alkyl tributylstannyl ether **2** which may be converted to the corresponding α-phenylseleno carbonyl compounds **3** as usual with stannyl ethers.

$$Bu_3SnOSnBu_3 \xrightarrow{C_6H_5SeBr} \underset{\mathbf{1}}{Bu_3SnOSeC_6H_5} + Bu_3SnBr \quad (5)$$



$$RCH{=}CH_2 \xrightarrow{\mathbf{1}} \underset{\mathbf{2}}{R\overset{OSnBu_3}{CH}\text{-}CH_2SeC_6H_5} \longrightarrow \underset{\mathbf{3}}{R\text{-}CO\text{-}CH_2^3SeC_6H_5} \quad (6)$$

Treatment of styrene with diphenyl diselenide (0.55 equiv.), bromine (0.50 equiv.), and hexabutyldistannoxane (1.0 equiv.) indeed afforded α-(phenylseleno)acetophenone in 38% yield. An optimum result was obtained when the reaction was performed with 2.2 equiv. of diphenyl diselenide, 2.1 equiv. of bromine, and 2.2 equiv. of hexabutyldistannoxane in refluxing chloroform for 2 h.

$$C_6H_5CH{=}CH_2 \xrightarrow{(C_6H_5Se)_2,\ Br_2,\ (Bu_3Sn)_2O} C_6H_5CO\text{-}CH_2SeC_6H_5 \quad (7)$$

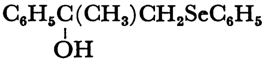
Various olefins were also converted to the corresponding α-phenylseleno carbonyl compounds **3** in good yields by this procedure. The results are shown in Table 1.

Styrene gave a single regioisomer, whereas other terminal olefins usually afforded a mixture of α-phenylseleno ketones and α-phenylseleno aldehydes. Their ratios are dependent on the reaction conditions, especially on the solvent. Electron-deficient olefins such as vinyl bromide or α,β-unsaturated esters are almost inert to this oxidation reaction. The major drawbacks of this procedure are relatively troublesome work-up for removal of organotin moieties and lack of regioselectivity. To eliminate these disadvantages, other methods were investigated, especially for improvement of regioselectivity in the oxoselenenylation reactions.

Oxidation of Olefins with $(C_6H_5Se)_2$–t*-BuOOH or* $(C_6H_5Se)_2$–$(C_6H_5SeO)_2O$. It has been described that allylic alcohols are oxidized with benzeneselenenyl bromide and silver acetate to give α,β-unsaturated carbonyl compounds.[7)] More recently, oxidation of aldehyde hydrazones with benzeneseleninic anhydride was reported,[8)] which proceeded presumably *via* an intermediacy of selenenate esters. These examples indicate that alkyl selenenates appear to undergo fragmentation readily to afford carbonyl compounds and selenols.[9)]

Benzeneselenenic anhydride "$C_6H_5SeOSeC_6H_5$" **4**, a rare class of compound, is expected to add to olefins to form alkyl selenenates **5** in a similar manner with other kinds of electrophilic organoselenium species,[2)] and the resulting selenenate esters **5** may decompose to

TABLE 1. OXIDATION OF OLEFINS WITH $(C_6H_5Se)_2$–Br_2–$(Bu_3Sn)_2O$[a]

Olefin	Solvent	Period/h	Product (ratio)	Yield/%[b]
1-Decene	CCl_4	7	$C_8H_{17}COCH_2SeC_6H_5$, $C_8H_{17}CH(SeC_6H_5)CH=O$ (68 : 32)	68
	CCl_4	10	(67 : 33)	54
	CCl_4	12	(72 : 28)	48
	THF	8.5	(58 : 42)	60
	C_6H_6	9	(80 : 20)	56
Ethyl 10-undecenoate	CCl_4	6.5	$C_2H_5O_2C(CH_2)_8COCH_2SeC_6H_5$, $C_2H_5O_2C(CH_2)_8CH(SeC_6H_5)CH=O$ (77 : 23)	60
Cyclooctene[c]	$C_6H_5CH_3$	7	2-Phenylselenocyclooctanone	72
Cyclododecene[c]	C_6H_6	8	2-Phenylselenocyclododecanone	52[d]
Cinnamyl acetate	$C_6H_5CH_3$	6.5	$C_6H_5COCH(SeC_6H_5)CH_2OAc$	73
α-Methylstyrene	CCl_4	2	 $C_6H_5\underset{OH}{C}(CH_3)CH_2SeC_6H_5$	62
β-Bromostyrene	CCl_4	12	No reaction	0
Ethyl cinnamate	CCl_4	6	No reaction	0

a) Reactions were performed on a 1 mmol scale with olefin : $(C_6H_5Se)_2$: Br_2 : $(Bu_3Sn)_2O$ = 1.0 : 2.0 : 2.0 : 2.0. b) Isolated yield. c) Olefin: $(C_6H_5Se)_2$: Br_2 : $(Bu_3Sn)_2O$ = 1.0 : 4.0 : 4.0 : 4.0. d) 2-Cyclododecenone was also formed in 20% yield.

give α-phenylseleno carbonyl compounds.

Woodbridge reported that the oxidation of diphenyl diselenide with ozone afforded benzeneseleninic anhydride,[10] presumably *via* an intermediate of benzeneselenenic anhydride **4**. We have examined the olefin oxidation under the expectation that the oxidation of diphenyl diselenide with *t*-butyl hydroperoxide may produce benzeneselenenic anhydride **4**.

$$(C_6H_5Se)_2 + t\text{-BuOOH} \longrightarrow \underset{\mathbf{4}}{\text{“}C_6H_5SeOSeC_6H_5\text{”}} + t\text{-BuOH} \quad (8)$$

Treatment of styrene with diphenyl diselenide (1.5 equiv.) and *t*-butyl hydroperoxide (2.0 equiv.) gave rise to α-(phenylseleno)acetophenone (48%) with 1-*t*-butoxy-1-phenyl-2-(phenylseleno)ethane (38%). The latter product was certainly produced *via* oxyselenenylation with $C_6H_5Se^+$ species and *t*-butyl alcohol formed from *t*-butyl hydroperoxide during the oxidation. The incorporation of *t*-butyl alcohol could be avoided by the removal of *t*-butyl alcohol after the oxidation of the diselenide with the peroxide followed by the addition of an olefin to the resulting solution. The optimum conditions were examined about the reaction of styrene.

$$C_6H_5CH=CH_2 \xrightarrow{\mathbf{4}} C_6H_5CO\text{-}CH_2SeC_6H_5 \quad (9)$$

The results shown in Table 2 indicate that the use of *ca.* 2 equiv. of reagents leads to the optimum yield and a slightly higher reaction temperature is required for the completion of the reaction when compared with the previous system.

Displacement of *t*-butyl hydroperoxide to other oxidants did not lead to the satisfactory result. Oxidation of diphenyl diselenide with pyridinium chlorochromate (PCC), active manganese dioxide, or Jones reagent followed by the addition of styrene to the oxidation product gave only a trace amount of α-(phenylseleno)acetophenone.[11]

A remarkable result was obtained when styrene was treated with diphenyl diselenide (1.4 equiv.) and benzeneseleninic anhydride (0.7 equiv.) as oxidant in refluxing carbon tetrachloride. By this system, α-(phenylseleno)acetophenone was obtained in 77% yield. Generation of benzeneselenenic anhydride **4** may occur *via* disproportionation reaction of diphenyl diselenide and benzeneseleninic anhydride, and it seems to be this species which acts as an electrophile toward olefins to form selenenate ester intermediates.

TABLE 2. OXIDATION OF STYRENE WITH $(CH_5Se)_2$–*t*-BuOOH. COMPARISON OF REACTION CONDITIONS[a]

t-BuOOH (equiv.)	$(C_6H_5Se)_2$ (equiv.)	Period/h	Yield % of α-(phenylseleno)-acetophenone
2.0	1.5	2	53
1.7	2.2	2	71
1.7	2.2	1	79
1.7	2.2	0.75	74
2.0	2.0	1	87[b]
2.1	2.1	1	80

a) Reactions were perormed in refluxing carbon tetrachloride. Yields were determined by NMR using a calibrated internal standard. b) Isolated yield.

$$2(C_6H_5Se)_2 + (C_6H_5SeO)_2O \longrightarrow 3\underset{\mathbf{4}}{\text{“}C_6H_5SeOSeC_6H_5\text{”}}$$

$$\xrightarrow{C_6H_5CH=CH_2} C_6H_5CO\text{-}CH_2SeC_6H_5 \quad (10)$$

Oxidation of Terminal Olefins. Oxidation of terminal olefins with $(C_6H_5Se)_2$–Br_2–$(Bu_3Sn)_2O$ system usually produces a mixture of α-phenylseleno ketones and aldehydes. The regioselectivity on the oxidation of terminal olefins with **4** was proved to be highly dependent on the reaction solvent. Predominant formation of α-phenylseleno ketones was observed in DMSO solvent, whereas the ratio of α-phenylseleno aldehydes increased in toluene, acetonitrile, sulfolane, and nitromethane. This tendency is explained in terms of the stabilization of the seleniranium intermediate which has often been involved in the addition process of ArSeX to olefins.[12]

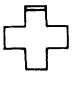
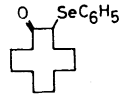
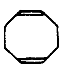
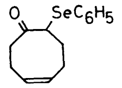
Raucher has examined the addition of benzeneselenen-

TABLE 3. OXIDATION OF TERMINAL OLEFINS[a)]

Olefin	Solvent	Temp/°C	Product (ratio)	Yield/%[b)]
1-Decene	$C_6H_5CH_3$	110	$C_8H_{17}COCH_2SeC_6H_5$, $C_8H_{17}CH(SeC_6H_5)CH{=}O$ (66 : 34)	81
	CH_3CN	82	(55 : 45)	75
	$C_6H_5CH_3$[c)]	110	(58 : 42)	85
	CH_3CN[c)]	82	(54 : 46)	72
	CH_3NO_2[c)]	80	(55 : 45)	66
	Sulfolane	110	(59 : 41)	79
	DMSO	110	(91 : 9)	70
	(1 : 1)DMSO-$C_6H_5CH_3$[c)]	110	(81 : 19)	86
Ethyl 10-undecenoate	DMSO[d)]	110	$C_2H_5O_2C(CH_2)_8COCH_2SeC_6H_5$, $C_2H_5O_2C(CH_2)_8CH(SeC_6H_5)CH{=}O$ (94 : 6)	70
1-Dodecene	DMSO[d)]	110	$C_{10}H_{21}COCH_2SeC_6H_5$, $C_{10}H_{21}CH(SeC_6H_5)CH{=}O$ (93 : 7)	71

a) Reactions were performed with olefin : $(C_6H_5Se)_2$: *t*-BuOOH=1.0 : 2.0 : 2.0. b) Isolated yield. c) Olefin : $(C_6H_5Se)_2$: $(C_6H_5SeO)_2O$=1.0 : 1.4 : 0.7. d) Olefin : $(C_6H_5Se)_2$: *t*-BuOOH=1.0 : 4.4 : 4.4.

TABLE 4. OXIDATION OF INETRNAL OLEFINS[a)]

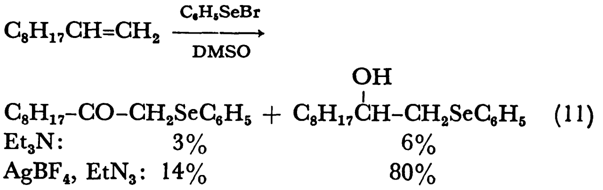
Olefin	Product	Yield/%
$C_6H_5CH\overset{t}{=}CHCH_2OAc$	$C_6H_5\text{-CO-}\underset{SeC_6H_5}{CH}CH_2OAc$	83
$C_6H_5CH_2OCH_2CH\overset{t}{=}CHCH_2OCH_2C_6H_5$	$C_6H_5CH_2OCH_2\text{-CO-}\underset{SeC_6H_5}{CH}CH_2OCH_2C_6H_5$	81
		67[b)]
		56[c)]

a) Reactions were performed in refluxing benzene with olefin: $(C_6H_5Se)_2$: *t*-BuOOH=1.0 : 4.4 : 4.4 or olefin: $(C_6H_5Se)_2$: $(C_6H_5SeO)_2O$=1.0 : 2.8 : 1.4. b) Cyclododecenone was formed in 15% yield. c) Reported by Smith III, Nicolaou *et al.*, see Ref. 18.

yl bromide to terminal olefins and has observed the following regioselectivity: under thermodynamically controlled conditions, olefin-PhSeX adducts undergo equilibration to form Markownikoff type adducts predominantly, while under kinetically controlled conditions, the formation of *anti*-Markownikoff adducts are favored.[13)] In this regard, in DMSO, oxygen atom on sulfoxide appears to associate with the seleniranium ion and stabilize it, which results in the equilibration of this intermediate to afford the Markownikoff adduct predominantly.

One disadvantage of this oxidation lies in the insolubility of olefins in this solvent, and for reproducible results the use of an excess reagent is required. DMSO–toluene solvent system has found a complemental use for insoluble olefins, although regioselectivity has been somewhat decreased.

We may exclude a possibility for the role of DMSO as oxidant by the following observations. It is well known that olefin–PhSeX adducts are very susceptible to solvolysis.[14)] The reaction of these adducts with DMSO,

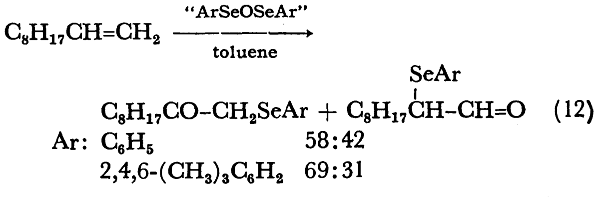


$$C_8H_{17}CH{=}CH_2 \xrightarrow[\text{DMSO}]{C_6H_5SeBr} C_8H_{17}\text{-CO-}CH_2SeC_6H_5 + C_8H_{17}\overset{OH}{C}H\text{-}CH_2SeC_6H_5 \quad (11)$$

Et_3N:	3%	6%
$AgBF_4$, EtN_3:	14%	80%

however, did not practically proceed. Even in the presence of silver tetrafluoroborate, a phenylseleno ketone was obtained in only low yield. These strongly suggest inefficiency of DMSO as an oxidant in the present system.

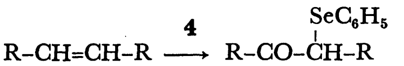
Displacement of diphenyl diselenide did not noticeably improve product distribution.



$$C_8H_{17}CH{=}CH_2 \xrightarrow[\text{toluene}]{\text{"ArSeOSeAr"}} C_8H_{17}CO\text{-}CH_2SeAr + C_8H_{17}\overset{SeAr}{C}H\text{-}CH{=}O \quad (12)$$

Ar: C_6H_5	58:42
2,4,6-$(CH_3)_3C_6H_2$	69:31

Oxidation of Internal Olefins. By the procedures reported so far, oxidation of internal olefins to α-phenylseleno ketones appears to be quite difficult. For example, treatment of (*E*)-3-hexene and (*E*)-6-dodecene with PhSeBr–AgPF$_6$–DMSO–Et$_3$N produced the corresponding β-hydroxy selenides in *ca.* 60% yield,[4b] whiles terminal olefins gave phenylselenomethyl ketones. The procedure developed by Tsuji *et al.*[4a] does not appear to be applicable to internal olefins due to a facile *syn*-elimination of the resulting selenoxides, although this point has not been tested. By the present method, internal olefins were smoothly oxidized to α-phenylseleno ketones in good yields. The results are listed in Table 4.

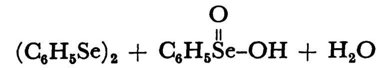


$$\mathrm{R\text{-}CH{=}CH\text{-}R} \xrightarrow{\mathbf{4}} \mathrm{R\text{-}CO\text{-}\overset{SeC_6H_5}{\overset{|}{C}}H\text{-}R} \tag{13}$$

In general, however, internal olefins are less reactive than terminal ones even under the present oxidation conditions, and good conversion of the starting olefins calls for the use of *ca.* 4.4 equiv. of the reagent.

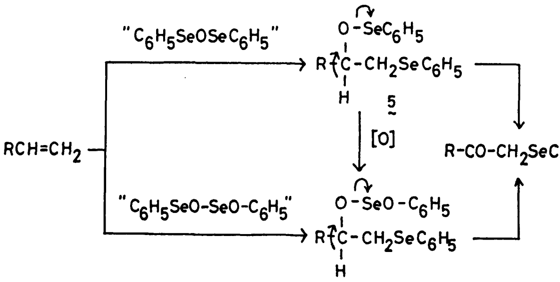
The difference of the reactivity of C=C bonds in a polyene has been studied by van Tamelen and Sharpless using addition reaction of a hypohalite.[15] More recently, Krief *et al.*[16] examined the reactivity of dienes bearing an internal and a terminal C=C bonds toward methane- and benzeneselenenyl bromide, and they observed selective addition to the terminal olefin. In the present oxidation, a terminal olefin was selectively oxidized to the corresponding α-phenylseleno ketone. For example, when an equimolar mixture of ethyl 10-undecenoate and cyclododecene was treated with diphenyl diselenide (2.8 equiv.) and benzeneseleninic anhydride (1.4 equiv.) in DMSO at 110 °C for 30 min, a mixture of ethyl 10-oxo-11-phenylselenoundecanoate and ethyl 11-oxo-10-phenylselenoundecanoate (92 : 8) was obtained in 64% yield with the recovered cyclododecene (90%). It is expected that the present system will find applications in selective oxidation of polyenes.

Reaction Mechanism. Sharpless and Reich have suggested a "Conproportionation" reaction between diphenyl diselenide and benzeneseleninic acid to yield benzeneselenenic acid as a reactive species to olefinic bonds.[17] Smith III and Nicolaou have also described a cyclization reaction of dienes using this kind of species.[18]



$$(\mathrm{C_6H_5Se})_2 + \mathrm{C_6H_5\overset{O}{\overset{\|}{Se}}\text{-}OH} + \mathrm{H_2O} \longrightarrow 3\text{“}\mathrm{C_6H_5SeOH}\text{”} \tag{14}$$

We propose here a generation of benzeneselenenic anhydride **4** from both of the systems, which acts as a reactive species. However, it is not very clear whether the introduction of carbonyl proceeds *via* a selenenate ester or not. One possible alternative seems to be the involvement of the fragmentation of a seleninate ester *via* addition of "C$_6$H$_5$SeOSe(=O)C$_6$H$_5$" species or oxidation of a selenenate ester intermediate. In regard to the reports dealing with fragmentation of seleninate esters proposed by Barton *et al.*,[19] we can not exclude the possibility of seleninates as the intermediates in this oxidation process.



(15)

Experimental

All reactions involving air- or moisture-sensitive compounds 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- G3 or 260-10 spectrometer, and mass spectra on a Hitachi RMU-7M or RMU-6C spectrometer at 70 eV ionizing irradiation. Analytical gas liquid chromatography was performed on a Hitachi 063 or 163 instrument. Microanalyses were performed on a Perkin Elmer 240 instrument. Melting points which were taken in open capillaries and 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 and Reich.[3c,17] Benzeneseleninic anhydride was prepared according to the procedure of Woodbridge,[10] and was stored over P$_2$O$_5$.

Oxidation of Styrene with $(C_6H_5Se)_2$–Br_2–$(Bu_3Sn)_2O$. To a solution of diphenyl diselenide (686 mg, 2.2 mmol) and hexabutyldistannoxane (1.31 g, 2.2 mmol) in 3 ml of chloroform were added a carbon tetrachloride solution of bromine (1.55 ml of 1.35 M (1 M=1 mol dm^{-3}) solution, 2.10 mmol) and then a solution of styrene (104 mg, 1.0 mmol) in 2 ml of chloroform. After stirring for 2 h under refluxing, the brown colored mixture was washed with 5% aq NaOH, and satd aq NaCl. The organic layer was dried over MgSO$_4$, concentrated, and purified by silica gel column chromatography followed by bulb-to-bulb distillation to afford α-(phenylseleno)acetophenone (204 mg, 74%). Bp 150—160 °C/0.15 mmHg;[20] IR (neat): 1665 cm^{-1}; NMR (CDCl$_3$): δ 4.13 (s, 2H), 7.13—7.63 (m, 8H), 7.73—7.97 (m, 2H); MS:[21] *m/e* (%) 276 (M$^+$, 16), 105 (100), 77 (20), 52 (13); Found: C, 61.37; H, 4.62%. Calcd for C$_{14}$H$_{12}$OSe: C, 61.10; H, 4.40%.

Oxidation of 1-Decene with $(C_6H_5Se)_2$–Br_2–$(Bu_3Sn)_2O$. To a solution of diphenyl diselenide (686 mg, 2.2 mmol) and hexabutyldistannoxane (1.31 g, 2.2 mmol) in 5 ml of carbon tetrachloride in the presence of molecular sieves 3A (1 g) were added a carbon tetrachloride solution of bromine (1.3 ml of 1.64 M solution, 2.1 mmol) and then a solution of 1-decene (140 mg, 1.0 mmol) in 5 ml of carbon tetrachloride, and the mixture was heated to refluxing for 7 h. After a usual work-up, the crude oil was purified by silica gel column chromatography to give diphenyl diselenide (437 mg), 1-phenylseleno-2-decanone (143 mg, 46%), and 2-p henylselenodecanal(68 mg, 22%). *1-Phenylseleno-2-decanone*, Bp 168 °C/0.3 mmHg;[20] Mp 39—40 °C (hexane); IR (KBr): 1692 cm^{-1}; NMR (CCl$_4$): δ 0.60—1.90 (m, 15H), 2.50 (t, J=7.0 Hz, 2H), 3.47 (s, 2H), 6.70—7.60 (m, 5H); MS[21] *m/e* (%) 321 (M$^+$, 5), 155 (6), 141 (6), 77 (20), 57 (69), 43 (100); Found: C, 61.66; H, 7.68%. Calcd for C$_{16}$H$_{24}$OSe: C, 61.73; H, 7.77%. *2-Phenylselenodecanal*, Bp 142—143 °C/0.06 mmHg;[20] IR(neat): 1705 cm^{-1}; NMR (CCl$_4$): δ 0.70—2.20 (m, 17H), 3.20—3.90 (m, 1H), 7.10—7.70 (m, 5H), 9.40 (d, J=4.0 Hz, 1H); MS:[21] *m/e* (%) 312 (M$^+$, 18), 283 (18), 155 (19), 57 (75), 43 (100), 29 (59).

Ethyl 10-Oxo-11-phenylselenoundecanoate. Mp 37—38 °C (hexane); IR (KBr): 1730, 1695 cm^{-1}; NMR (CCl$_4$): δ 1.00—2.00 (m, 17H), 2.23 (t, J=8.0 Hz, 2H), 2.50 (t, J=7.0 Hz, 2H), 3.47 (s, 2H), 4.10 (q, J=5.0 Hz, 2H), 7.10—7.60 (m, 5H); MS:21) *m/e* (%) 384 (M$^+$, 30), 339 (13), 213 (65), 171 (54), 157 (41), 97 (65), 83 (28), 77 (33), 69 (70), 46 (100); Found: C, 59.67; H, 7.42%. Calcd for $C_{19}H_{28}O_3Se$: C, 59.52; H, 7.36%.

Ethyl 11-Oxo-10-phenylselenoundecanoate. IR (neat): 1720, 1700 cm^{-1}; NMR (CCl_4): δ 0.85—1.90 (m, 19H), 2.13 (t, J=6.0 Hz, 2H), 3.20—3.60 (m, 1H), 3.97 (q, J=5.0 Hz, 2H), 7.00—7.50 (m, 5H), 11.5 (d, J=3.0 Hz, 1H); MS:21) *m/e* (%) 384 (M$^+$, 5), 354 (2), 226 (5), 77 (8), 73 (92), 45 (12), 29 (100); Found: C, 59.34; H, 7.56%. Calcd for $C_{19}H_{28}O_3Se$: C, 59.52; H, 7.36%.

2-Phenylselenocyclododecanone. The reaction was carried out with cyclododecene (84 mg, 0.5 mmol) using diphenyl diselenide (2.2 equiv.), bromine (2.1 equiv.), and hexabutyldistannoxane (2.2 equiv.) in refluxing benzene for 8 h. Purification of the reaction mixture by silica gel column chromatography gave 2-cyclododecenone (18 mg, 20%) and the title compound (87 mg, 52%). Bp 148—152 °C/0.06 mmHg;20) IR (neat): 1685 cm^{-1}; NMR (CCl_4): δ 0.70—2.35 (m, 18H), 2.53 (unresolved dd, J=10.0 and 6.0 Hz, 2H), 3.90 (dd, J= 5.0 and 8.0 Hz, 1H), 7.10—7.60 (m, 5H); MS:21) *m/e* (%) 338 (M$^+$, 2), 181 (6), 157 (28), 83 (61), 55 (100).

3-Oxo-3-phenyl-2-phenylselenopropyl Acetate. IR (neat): 1740, 1680 cm^{-1}; NMR (CCl_4): δ 1.90 (s, 3H), 4.40—4.90 (m, 3H), 7.10—7.55 (m, 8H), 7.75—8.00 (m, 2H); MS:21) *m/e* (%) 348 (M$^+$, 8), 289 (90), 271 (7), 191 (40), 105 (100), 77 (45), 59 (88), 43 (40).

1-Phenylseleno-2-phenyl-2-propanol. Bp 127—130 °C/0.4 mmHg;20) IR (neat): 3440 cm^{-1}; NMR (CCl_4): δ 1.57 (s, 3H), 2.80 (brs, 1H, disappeared on D_2O exchange), 3.38 (d, J= 6.0 Hz, 1H), 3.40 (d, J=6.0 Hz, 2H), 7.00—7.50 (m, 12H); MS:21) *m/e* (%) 274 (M$^+$ − 18, 5), 172 (18), 117 (70), 115 (100), 77 (80).

Oxidation of Styrene with $(C_6H_5Se)_2$*-t-BuOOH (General Procedure).* To a solution of diphenyl diselenide (628 mg, 2 mmol) in 5 ml of carbon tetrachloride were added molecular sieves 3A (2 g) and a solution of 70% *t*-butyl hydroperoxide (256 mg, 2.0 mmol) in 5 ml of carbon tetrachloride, and the mixture was heated to refluxing for 1 h. Then all the solvent as well as *t*-butyl alcohol was removed *in vacuo*, and a solution of styrene (104 mg, 1.0 mmol) in 5 ml of carbon tetrachloride was added to the resulting pale yellow solid. After stirring for 1 h under refluxing, the reaction mixture was washed with satd aq NaCl and dried over $MgSO_4$. Removal of the solvent gave a brown oil, which was purified by silica gel column chromatography to give α-(phenylseleno)acetophenone (238 mg, 87%) and diphenyl diselenide (414 mg).

Oxidation with $(C_6H_5Se)_2$*-*$(C_6H_5SeO)_2O$ *(General Procedure).* To a solution of diphenyl diselenide (437 mg, 1.4 mmol) and benzeneseleninic anhydride (252 mg, 0.7 mmol) in 5 ml of the solvent were added an olefin (1 mmol) in 5 ml of solvent and molecular sieves 3A (2 g), and the mixture was stirred under refluxing until the starting olefin was all consumed. The resulting reaction mixture was worked up and purified as described above.

Oxidation of 1-Decene. 1-Decene (70 mg, 0.5 mmol) was oxidized with diphenyl diselenide (686 mg, 2.2 mmol) and *t*-butyl hydroperoxide (282 mg of 70% solution, 2.2 mmol) in DMSO at 110 °C for 1 h. A mixture (108 mg, 70%) of 2-phenylselenodecanal and 1-phenylseleno-2-decanone was obtained. The isomeric ratio was determined to be 9 : 91 by NMR analysis. Further purification gave both samples which exhibit similar spectroscopic properties to ones prepared previously.

Oxidation of Ethyl 10-Undecenoate. Ethyl 10-undecenoate (106 mg, 0.5 mmol) was oxidized with diphenyl diselenide (686 mg, 2.2 mmol) and 70% *t*-butyl hydroperoxide (282 mg, 2.2 mmol) in 10 ml of DMSO at 110 °C for 1.5 h. A mixture (134 mg, 70%) of ethyl 10-oxo-11-phenylselenoundecanoate and ethyl 11-oxo-10-phenylselenoundecanoate was obtained, and their ratio was determined to be 94 : 6 by NMR analysis. Separation of the mixture gave pure samples which exhibit similar spectroscopic properties to ones prepared previously.

Oxidation of 1-Dodecene. 1-Dodecene (84 mg, 0.5 mmol) was oxidized by the same procedure. A mixture of 1-phenylseleno-2-dodecanone and 2-phenylselenododecanal was obtained, and their ratio was determined to be 93 : 7 by NMR analysis. Separation of the mixture gave pure samples. *1-Phenylseleno-2-dodecanone,* IR (neat): 1705 cm^{-1}: NMR (CCl_4): δ 0.70—2.00 (m, 19H), 2.60 (t, J=7.0 Hz, 2H), 3.57 (s, 2H), 7.30—7.90 (m, 5H); MS:21) *m/e* (%) 340 (M$^+$, 71), 172 (89), 15; (32), 133 (29), 109 (54), 95 (39), 91 (57), 85 (54), 77 (25), 71 (57), 57 (100). *2-Phenylselenododecanal,* IR (neat): 1705 cm^{-1}; NMR (CCl_4): δ 0.70—2.00 (m, 21H), 3.3—3.9 (m, 1H), 7.40—7.90 (m, 5H), 9.50 (d, J=3.0 Hz, 1H).

3-Oxo-3-phenyl-2-phenylselenopropyl Acetate. Cinnamyl acetate (88 mg, 0.5 mmol) was oxidized by a similar procedure in benzene (5 ml) for 4 h, and the title compound (144 mg, 83%) was obtained as an oil. IR (neat): 1740, 1680 cm^{-1}; NMR (CCl_4): δ 1.90 (s, 3H), 4.40—4.90 (m, 3H), 7.10—7.55 (m, 8H), 7.75—8.00 (m, 2H); Found: C, 58.92; H, 4.78%. Calcd for $C_{17}H_{16}O_3Se$: C, 58.80; H, 4.64%.

2-Phenylselenocyclododecanone. Cyclododecene (91 mg, 0.5 mmol) was oxidized in a similar procedure in refluxing benzene for 3 h, and the title compound (118 mg, 67%) and 2-cyclododecenone (14 mg, 15%) were obtained.

1,4-Bis(benzyloxy)-3-phenylseleno-2-butanone. (*E*)-1,4-Bis(benzyloxy)-2-butene (120 mg, 0.5 mmol) was oxidized in a similar procedure in refluxing benzene for 4.5 h, and the title compound (166 mg, 81%) was obtained. IR (neat): 3100, 1710, 1100, 750 cm^{-1}; NMR (CCl_4): δ 3.90—4.17 (m, 3H), 4.37 (d, J=5.0 Hz, 4H), 7.00—7.53 (m, 5H). Further deselenenylation with benzenethiol (0.15 ml) and triethylamine (1.0 ml) gave analytically pure deselenenylated product, 1,4-bis(benzyloxy)-2-butanone. IR (neat): 3100, 1705 cm^{-1}; NMR (CCl_4): δ 2.71 (t, J=7.0 Hz, 2H), 3.60 (t, J=7.0 Hz, 2H), 3.90 (s, 2H), 4.07 (s, 2H), 4.74 (s, 2H), 7.20 (s, 10H); Found: C, 76.19; H, 7.14%. Calcd for $C_{18}H_{20}O_3$: C, 76.037; H, 7.09%.

Oxidation of Ethyl 10-Undecenoate in the Presence of Cyclododecene. To a mixture of diphenyl diselenide (437 mg, 1.4 mmol) and benzeneseleninic anhydride (252 mg, 0.7 mmol) were added a solution of cyclododecene (83 mg, 0.5 mmol) and ethyl 10-undecenoate (106 mg, 0.5 mmol) in DMSO (10 ml) and then molecular sieves 3A (2 g). After stirring for 30 min at 110 °C, the reaction mixture was washed with satd aq NaCl and was extracted with ether. Cyclododecanone (91 mg) was added to the reaction mixture as an internal standard, and the resulting solution was examined by GLPC to give an indication that cyclododecene was recovered in 90%. Purification of the mixture by silica gel column chromatography afforded a mixture of ethyl 10-oxo-11-phenylselenoundecanoate and ethyl 11-oxo-10-phenylselenoundecanoate (123 mg, 64%). The ratio of the seleno ketone *vs.* the seleno aldehyde was determined to be 92 : 8 by NMR analysis.

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