Organoselenium Chemistry. Conversion of Ketones to Enones by Selenoxide Syn Elimination

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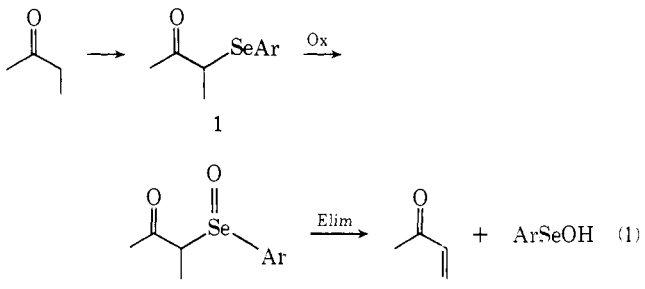
Abstract: The scope and limitation of the transformation of ketones to enones by selenenylation followed by selenoxide elimination have been examined. Several procedures for the preparation of α-phenylseleno ketones have been developed. The most useful are direct selenenylation of ketone enolates using PhSeBr and the reaction of enol acetates with electrophilic selenium species such as benzeneselenenyl trifluoroacetate. Several oxidants (ozone, hydrogen peroxide, sodium metaperiodate) and reaction conditions are described to allow optimization of the yield obtained in the transformation of α-phenylseleno ketones to enones. The reaction is quite general for acyclic carbonyl compounds and for tertiary selenides. Difficulties in achieving high yields may be anticipated when very strained double bonds are introduced, when the α-phenylseleno ketone is cyclic and has an α-hydrogen, or when the product is extremely reactive. Qualitative mechanistic studies have revealed two types of side reactions: (1) Pummerer-like transformations to give α-diketones and (2) reactions between the enolate or enol of α-phenylselenino ketones and selenenylating species formed during the disproportionation of benzeneselenenic acid. Reaction conditions which minimize these side reactions have been developed. The utility of benzeneseleninyl chloride as a seleninylating agent has been explored. One pot transformations of ketones to enones using this reagent can be achieved in satisfactory yield, but the procedure is prone to side reactions because of the sensitivity of the selenoxide function.

The many synthetic transformations originating from α,β-unsaturated carbonyl compounds have made their preparation a long standing important synthetic problem. The most straightforward method is the dehydrogenation of carbonyl compounds. There are a number of methods for performing this conversion,[1,2] the most important of which is the α-bromination-dehydrobromination method.[1] Orientational control is difficult to achieve in direct bromination of ketones, but Stotter and Hill[1d] have recently shown that bromination of cyclohexanone enolates can be carried out in high yield, and also that dehydrobromination can be performed without loss of regiospecificity. Isomerization of α-bromo ketones under conditions of the debrominations has been frequently reported,[1e] however, particularly for bromides of β-dicarbonyl compounds.[1f,g] The vigorous reaction conditions (frequently temperatures in excess of 120°) also severely limit this method because of the sensitivity of many enones.

Direct dehydrogenations can be performed by a number of reagents, including selenium dioxide,[2a,b] dichlorodicyanoquinone,[2c] periodic acid,[2d] oxygen in the presence of transition metal catalysts,[2e] and pyridine *N*-oxide-acetic anhydride.[2f] The first two methods have been studied in great detail, and some excellent procedures have been developed, but yields vary greatly, and effective control of regioselectivity is frequently a problem.

The discovery by Jones, Mundy, and Whitehouse[3] that selenoxides undergo clean syn elimination to form olefins at or below room temperature suggested that this reaction may offer a solution to the problem discussed above. We report here full details of our work[4a-c] on the conversion of ketones to enones using the selenoxide elimination (eq 1).



Sharpless and Lauer first used selenoxide eliminations synthetically in the conversion of epoxides to allyl alcohols.[5b,d] Several groups[4-8] have explored the reaction for the dehydrogenation of ketones,[4a,b,5c,6a] esters,[4a,5c] lactones,[5c,7a] and nitriles.[8] Selenium stabilized anions[9] have been used for formation of new carbon-carbon bonds, with subsequent selenoxide elimination to give α,β-unsaturated esters,[5c,10a] olefins,[4d,11] allyl alcohols,[4de,9bc] and dienes.[4d] Sulfoxide eliminations have also been explored for the introduction of unsaturation.[4f,7c,10]

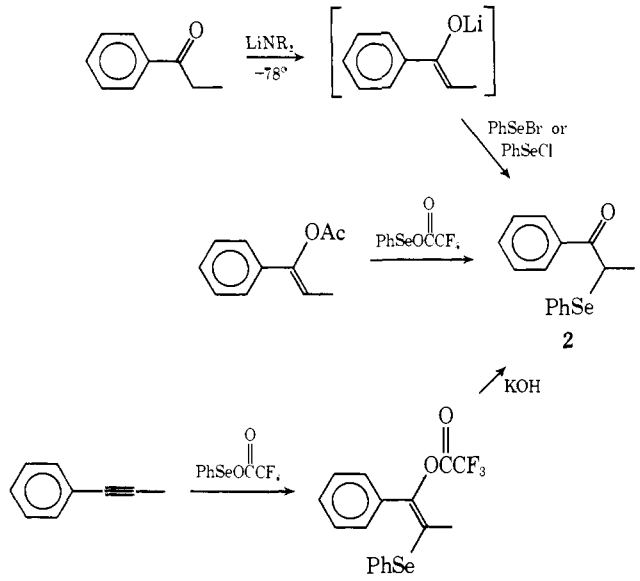
Preparation of α-Phenylseleno Ketones.[12] Literature methods for the preparation of the required α-arylseleno carbonyl compounds (**1**) were not suitable for the problem at hand. α-Arylseleno carboxylic esters have been prepared by nucleophilic displacements of α-halo esters by phenylselenolate anion.[5c,13] α-Bromo ketones also undergo displacements, provided the proper mode of addition (PhSeM to bromo ketone) is used under aprotic conditions, otherwise dehalogenation occurs.[14] This method may be useful in special cases.

Rheinboldt and Perrier[15] found that *o*-nitrobenzeneselenenyl thiocyanate (ArSeSCN) reacts with acetone to form α-arylseleno acetone. The reagent is not readily available, however, and the reaction has not been shown to be general. Although selenenyl bromides often brominate ketones, the chlorides behave as selenenylating agents.[5c,16] Sharpless, Lauer, and Teranishi discovered that benzeneselenenyl chloride converts aldehydes and ketones to their α-phenylseleno derivatives, and this represents an important route to compounds which are not accessible by other methods.[5c]

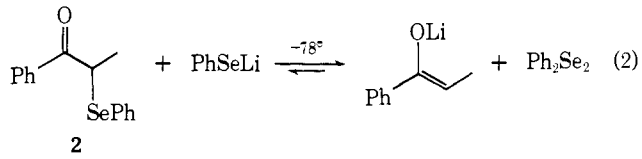
We have developed three routes to α-phenylseleno ketones, as shown for **2** in Scheme I. A number of specific examples are summarized in Table I. The most widely useful method is the reaction of ketone (and ester) enolates with benzeneselenenyl bromide or chloride (PhSeBr, PhSeCl). These reagents are prepared by cleavage of diphenyl diselenide (PhSeSePh) with bromine and chlorine (or sulfuryl chloride), respectively. Diphenyl diselenide does not react with lithium enolates of ketones but does react with ester enolates[5c,7] and more reactive carbanions.[8,12]

The failure of ketone enolates to react with diphenyl diselenide is apparently the result of an unfavorable equilibrium rather than of a kinetic barrier. Treatment of **2** with PhSeLi at −78° results in the rapid and almost quantitative

Scheme I



formation of diphenyl diselenide and, presumably, the enolate.[17]

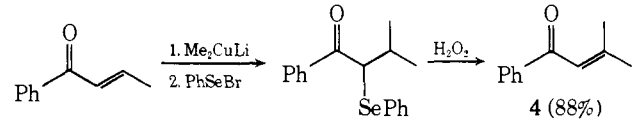


The selenenylation of ketones via the enolate is limited primarily by the availability of the enolate. Yields are frequently almost quantitative. The major by-product we have detected is starting ketone, usually present to the extent of 2-10% in the product. Where this is objectionable, the more volatile starting material can be removed by distillation or sublimation; or the selenides, which are frequently crystalline, can be purified by crystallization. In a few systems, we have tentatively identified traces of bis-selenenylated materials. Since reaction of enolate with selenenyl halide is very rapid at −78°, enolate equilibration is not normally a problem (runs 11, 13, 16, and 25). Brattesani and Heathcock[8] have recently reported that proton transfer during selenenylation of nitrile anions is unavoidable. Nitrile anions, perhaps because of their immunity to steric inhibition of resonance, frequently undergo disubstitution in competition with, or in preference to, monosubstitution.[18]

For most of the examples shown, we have prepared enolates by deprotonation of ketones using lithium diisopropylamide (LDA), but enolates prepared by cleavage of enol acetates with methyllithium (run 18), by conjugate addition of organocuprates, or by metalation of ketones with potassium hydride,[19] can also be converted to α-phenylseleno ketones.

It is important to use a quantity of selenenylating agent equal to or slightly in excess of the total strong base present since organocopper reagents, lithium amides, alkoxides, etc. may react with PhSeBr. The choice between PhSeBr and PhSeCl is dictated mainly by availability of the reagents; PhSeBr can conveniently be prepared in solution as needed, and we have used this method for most of the examples reported here. Care must be taken to avoid excess bromine and to ensure mixing of the solution during the reaction with PhSeSePh to prevent formation of $PhSeBr_3$, which is a brominating agent toward enolates.

The selenenylation of copper enolates prepared by conjugate addition of organocuprates to enones is complicated by the formation of small amounts of α-bromo and α-iodo ketones when pure PhSeBr is used.[4b] We have found that use of a mixture of PhSeBr and PhSeSePh solves this problem, although overall yields are not always high. A more satisfactory route may be to trap the enolate as the enol acetate with acetic anhydride. The purified enol acetate can then be converted to α-phenylseleno ketone in high yield.[4c,6a] (Stotter and Hill[1d] reported difficulty in the bromination of copper enolates; they found that clean bromination could be achieved through the enol acetate.) Thus, formation of selenide **3** and easy transformation to **4** represent a net β-alkylation of the enone.



3 (83%)

Even stabilized lithium and sodium enolates such as those formed from β-keto esters (runs 32-35), β-diketones (runs 36-40), β-keto sulfoxides (run 41), β-keto selenoxides,[4b] and phosphonoacetates[20] react cleanly and rapidly with PhSeBr and PhSeCl.

Enol acetates can be cleanly converted to seleno ketones via the enolates (run 18) or by direct reaction with electrophilic selenium reagents. The reagent we have found most useful for this reaction is benzeneselenenyl trifluoroacetate[4c,6] ($PhSeO_2CCF_3$) which is prepared by treatment of PhSeCl or PhSeBr with silver trifluoroacetate. The only enol acetate we have encountered which does not react with $PhSeO_2CCF_3$ is 1-acetoxy-2-phenylcyclohexene (run 18). By using enol acetates formed under acid catalyzed conditions,[21] it is often possible to achieve the preparation of α-phenylseleno ketones regioisomeric with those prepared from the kinetic enolate.[1d] We have in this way prepared isomeric enones from 2-phenylcyclohexanone (runs 16-18) and 2-benzylcyclopentanone (runs 11-12).

The conversion of acetylenes to α-phenylseleno ketones (Scheme I) has not been examined extensively as to generality and regioselectivity.[4c]

The Oxidation Reaction. With adequate methods for the preparation of keto selenides available, we can turn to the question of the oxidation reaction. The majority of the results described in Table I were obtained using the following oxidation methods, which are discussed in more detail below:

A. H_2O_2: one pot procedure.[4a]

B. H_2O_2: two phase (H_2O_2-dichloromethane) usually buffered with pyridine.[4b]

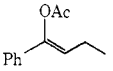
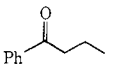
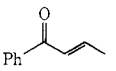
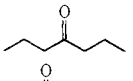
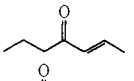
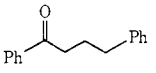
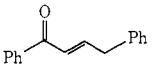
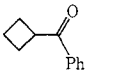
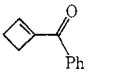
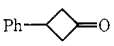
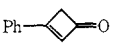
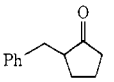
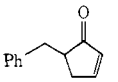
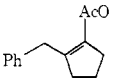
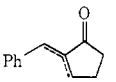
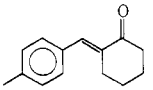
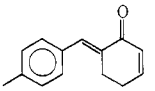
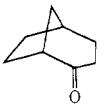
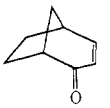
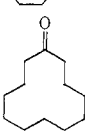
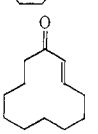
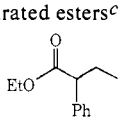
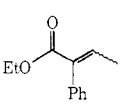
C. O_3: Ozonization at −78° in dichloromethane followed by warm up.

D. O_3: Ozonization at −78° in dichloromethane followed by addition to refluxing carbon tetrachloride in the presence of diisopropylamine.

E. Selenoxide prepared directly by reaction of enolate with benzeneseleninyl chloride.

Since all keto selenoxides we have worked with undergo the fragmentation reaction at or below room temperature, the oxidation must either be performed at low temperature, or the product enone must not itself be readily oxidized by the oxidizing agent chosen. We have explored sodium metaperiodate,[22a] ozone,[22b] hydrogen peroxide,[22c] and to a lesser extent *m*-chloroperbenzoic acid (*m*-CPBA) as oxidants. Because of its expense and the necessity of working in an aqueous methanolic medium, sodium metaperiodate is a reagent of last resort. Two selenides for which superior yields were obtained using this reagent are shown in runs 1 and 19 of Table I.

Table I. Conversion of Carbonyl Compounds to α,β-Unsaturated Carbonyl Compounds

Starting material	Olefin	Run no.	Oxidation method[a]	Yields[b] Selenide	Yields[b] Olefin
α,β-Unsaturated ketones[c]					
		1	$NaIO_4$	88	89
		2	B		56[d]
		3		83	
		4	B	83	92
		5	E		80
		6	B		72
		7	D		80
		8[e]	A		84
		9	B	87	83
		10	C[f]	50	53
		11	B		66
		12	B	96	95
	endo/exo: 56/44				
		13	A		36
		14	C[f]	89	48
		15	D		73
		16	B		60
		17	D		62, 58[g]
		18	B	86	94
		19	$NaIO_4$	68	74
		20	B	80	72
		21	B or $NaIO_4$		<10
		22	D		50
		23	D		55[g]
		24	D	85	85
		25	B	81	61
		26	A		72
α,β-Unsaturated esters[c]					
		27	A		79
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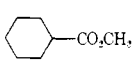	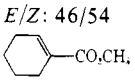	28	A		96

Table I (*Continued*)

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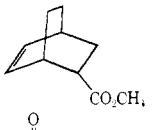
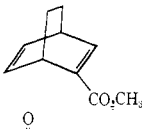
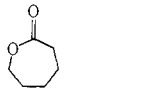
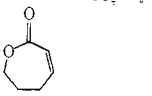
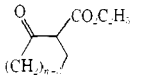
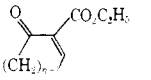
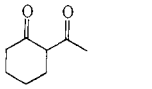
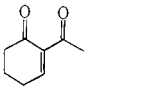
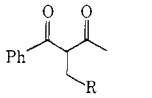
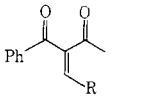
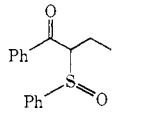
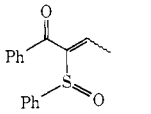
			29	A		79
			30	E		68
			31	C	70	66
β-Dicarbonyl enones[h]						
		(n = 8)	32	B	96	93
		(n = 7)	33	B	90	93
		(n = 6)	34	B[i]		89
		(n = 5)	35	B[i]		81
			36	C[f]		84
			37	B[i]		84
			38	*m*-CPBA		85
		(R = H)	39	B	93	80
		(R = *n*-Pr)	40	B	96	93
α-Phenylsulfino enone[h]						
			41	B	78	71

[a] See text for a description of the oxidation procedures. [b] Olefin yields are overall unless yields of selenide are given. [c] Selenides were prepared from the lithium enolate, except for runs 3 and 12. [d] α-Diketone (6%) was also formed. [e] See ref 4a for experimental details. [f] Pyridine was added during selenoxide elimination. [g] Diethylamine rather than diisopropylamine was used during selenoxide elimination (method D). [h] Selenide prepared by reaction of sodium enolate (NaH) with PhSeBr or PhSeCl. [i] No pyridine was added during H_2O_2 oxidation.

Ozonization of selenides[22b] at −78° stops cleanly at the selenoxide stage so that, in the absence of other readily ozonized functionalities or solvents (such as THF), one can simply add excess ozone. We have used ozonization when an aqueous work-up is undesirable because of substrate reactivity or water solubility (run 31), when the enone product is sensitive to excess hydrogen peroxide (as in runs 10, 36), when further transformations of the selenoxide are to be carried out,[4b,d] or when oxidation and elimination are best carried out in separate steps (method D). The enone can sometimes be distilled directly out of the ozonization mixture provided that the volatility of the PhSeSePh [bp 202-203° (11 mm)] formed is not near that of the product.

m-Chloroperbenzoic acid cleanly oxidizes selenides to selenoxides, usually at temperatures (−30 to 0°) where elimination is slow. This oxidant can thus often be used in situations similar to those described above for ozone with the added advantage that selective oxidation of selenides or Ph_2Se_2 in the presence of double bonds can be more readily carried out.[4d]

Hydrogen peroxide is the oxidant of choice under aqueous conditions. We have developed a one-pot procedure (method A) in which the oxidation is done directly without isolation of the selenide. It requires the least manipulation, and is ideal when contamination by small amounts of starting carbonyl compound is not objectionable, and when the elimination is uncomplicated by side reactions (see below). A second procedure (method B) is a two phase method (dichloromethane-aqueous hydrogen peroxide) which is convenient, requires only a small excess of hydrogen peroxide, is easy to control for larger scale oxidations, and gives superior yields to other methods using hydrogen peroxide that we have examined. For some keto selenides, it is advantageous to add pyridine as buffer, and we routinely do this. Important exceptions are some of the β-dicarbonyl enones which are sensitive to base catalyzed epoxidation by hydrogen peroxide. If the amount of H_2O_2 is carefully controlled (2 equiv), even the very sensitive 2-carbethoxycyclopentenone (run 35) can be prepared. The selenoxide elimination is the only satisfactory procedure in the literature for the preparation of this compound[2b] and the related 2-acetyl- and 2-carbethoxycyclohexenones (runs 34, 36-38).[1f,g]

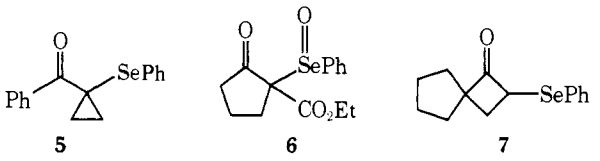
The fate of the selenium depends on the oxidation conditions. When 1 equiv of oxidant is used, the benzeneselenenic acid (PhSeOH) disproportionates to a 1:1 ratio of benzeneseleninic acid ($PhSeO_2H$) and Ph_2Se_2. With excess oxidant, $PhSeO_2H$ (pK_a 4.70[23]) is the only product. When weakly acidic conditions are undesirable, the reaction mixture can be buffered with pyridine to ensure near neutral conditions.

$$3PhSeOH \longrightarrow PhSeSePh + PhSeO_2H + H_2O$$

The seleninic acid is nonvolatile and is removed during aqueous work-up by base extraction. The diselenide can on occasion cause separation problems. It is nonpolar and can be separated chromatographically where this is feasible. The benzeneseleninic acid can easily be reduced to PhSeSePh[5d] (see Experimental Section), which can be recovered in high yield.

The Elimination Reaction. The selenoxide elimination is not uniformly successful in all systems, but the following generalizations may be helpful. Assuming that the selenide can be formed in satisfactory yield, acyclic ketones can be converted to enones in high yield, practically without exception. Cyclic α-phenylseleno ketones fully substituted at the carbon bearing selenium can almost invariably be converted to enones in excellent yield. The only exception we have encountered is **5**. The high reactivity of the expected product may be at least in part responsible for the failure to isolate enone in detectable yield for this example.

Little information is available on the rates of selenoxide eliminations, but we have made the qualitative observation



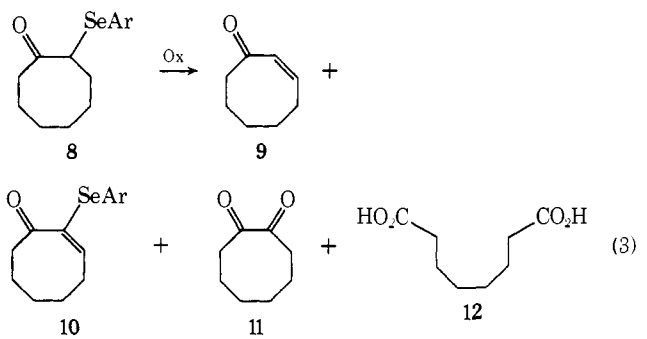
5 6 7

that the carbonyl group significantly accelerates the elimination compared with simple alkyl selenoxides. We have similarly observed that the ethylene ketals of keto selenoxides (see below) undergo significantly slower elimination than the keto selenoxides themselves. The accelerating effect is even more pronounced for selenoxides derived from β-dicarbonyl compounds. Here the elimination is rapid well below 0° and for **6** appears to occur even at −78°. Similar trends are clearly present in sulfoxide eliminations.[10]

Cyclic systems where the carbon bearing selenium also bears a hydrogen are subject to side reactions which lower the yield to varying extent depending on reaction conditions and subtle conformational and other factors in the substrate. Apparently the cyclic transition state[3,5a] for the syn elimination conflicts to a greater or lesser extent with conformational preferences of the cyclic ketone.

A four-membered cyclic system in which the selenide is tertiary (run 9) gives cyclobutene in good yield. The reaction is still feasible for the preparation of 3-phenylcyclobutenone (run 10), but compound **7**[24] gives no detectable cyclobutenone on oxidation. It is not clear whether no product is formed or whether that which is formed is destroyed subsequent to elimination. 2-Benzylcyclopentanone can be converted to 5-benzylcyclopent-2-enone in fair yield (run 11). Note that an almost quantitative yield of the isomeric enones is formed from the tertiary selenide (run 12). The yields of cyclohexenones vary from fair to good depending on substituents and reaction conditions. Cycloheptenone and cyclooctenone are formed in very low yield when oxidation of the respective selenides with hydrogen peroxide at room temperature (method A or B), ozonization followed by slow warm-up to 25° (method C), or oxidation with sodium metaperiodate is employed. The conversion of 2-cycloheptenone to cyclohepta-2,6-dienone, however, proceeds without complication, possibly because the ring is flattened by the two additional sp^2 carbons in the ring. This could make the cycloelimination occur more readily. A similar effect may be responsible for the somewhat higher yield obtained for 2-*p*-tolyidenecyclohexanone (run 19) when compared with those of the other cyclohexanones.

We have attempted to improve yields for the cyclic enones by determining the nature of the side reactions which are occurring. This information should then be of use in modifying substituents or reaction conditions to eliminate by-products. Most of these studies were carried out using 2-arylselenocyclooctanones (**8**), although cycloheptanone



8 **9** **10** **11** **12** (3)

a, Ar = C_6H_5
b, Ar = *m*-$CF_3C_6H_4$

Table II. Product Yields from the Oxidation of 2-Arylselenocyclooctanone (**8**)

Oxidizing conditions	Yields[a] 9	10	11	12
Aryl = phenyl (**8a**)				
$NaIO_4$–$NaHCO_3$	14	48	*b*	*b*
Method B	16	2	13	39
Method C[c]	39	8	43	*b*
Method D, HN-*i*-Pr_2[d]	67	14	<2	*b*
Method D, $HNEt_2$	74	<2	<2	*b*
Aryl = 3-$CF_3C_6H_4$ (**8b**)				
Method B	27	0	5	44
Method C[c]	39	14	32	*b*
Method D, HN-*i*-Pr_2	69	22	<2	*b*

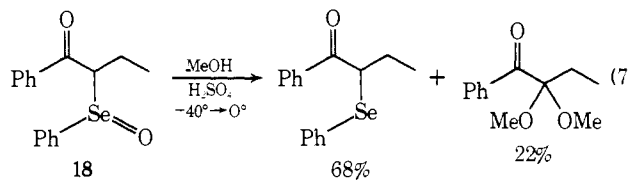
[a] Absolute yields. [b] The yield was not determined for these products. [c] No pyridine was added during selenoxide elimination; 2–5% of **8** was recovered during these runs. [d] Preparative scale reaction gave 56% yield of **9**.

and 2-methylcyclohexanone were also used. We have isolated and characterized two major types of by-products[4b] formed in cyclic systems: α-arylseleno enones (**10**) and α-diketones (**11**). When hydrogen peroxide is used, acyclic dicarboxylic acids (**12**) are also formed, probably by further oxidation of the diketone.[25] The replacement of phenylseleno by benzylseleno in **8** does not improve the ratio of elimination to side reactions. However, the use of more strongly electron-withdrawing groups (**8b**) increases the rate of syn elimination[26] and gives some improvement in yield of enone with hydrogen peroxide as oxidant (Table II), although still not to synthetically useful levels for cycloheptenone or cyclooctenone. Attempts to improve yields by changing pH during sodium metaperiodate oxidation also failed.

A procedure which sacrifices some of the mildness of the usual conditions but dramatically improves the reaction in some cases, was the following: the selenide was ozonized at −78° and then added while cold to refluxing carbon tetrachloride containing diisopropylamine (method D, see runs 21 and 22, Table I; Table II). Unfortunately, this procedure is not the whole answer. Yields are still less than quantitative for the more troublesome systems, and no improvement was obtained for 2-phenylcyclohexanone (runs 16 and 17).

Small amounts of α-phenylseleno enones are still formed using method D, but less than 2% of α-diketone is present (see Table II). This lends support to our postulate[4b] that Pummerer-like reactions are responsible for α-diketone formations. The base prevents protonation of the selenoxide (**13**, Scheme II).

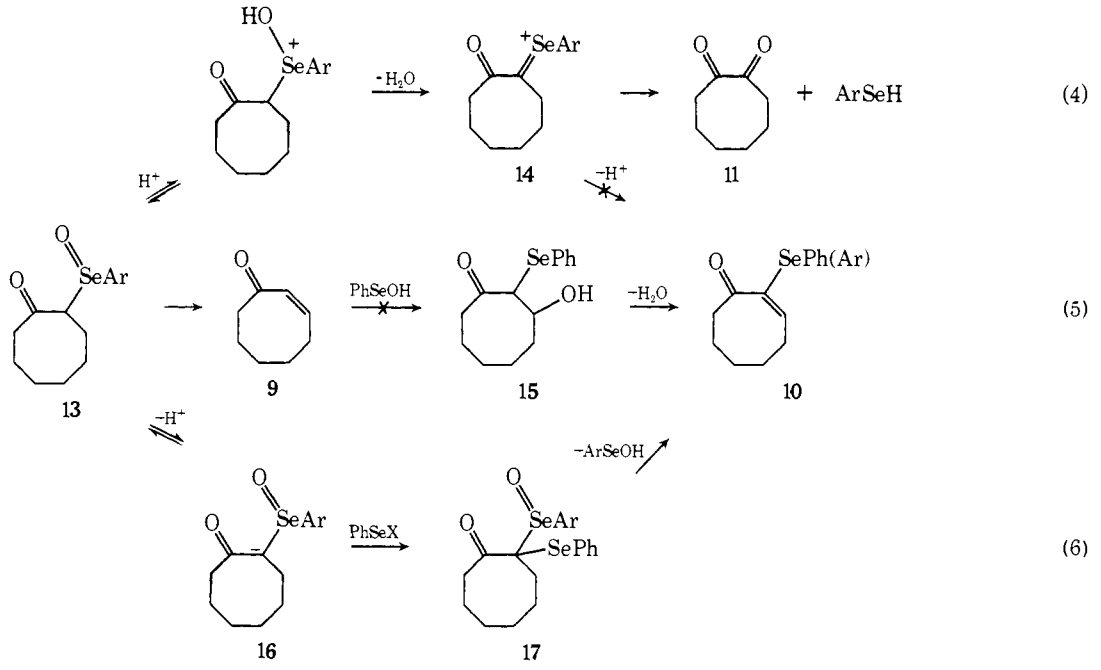
Under highly acidic conditions, the Pummerer reaction is the only pathway observed. No enone is formed (eq 7 gives



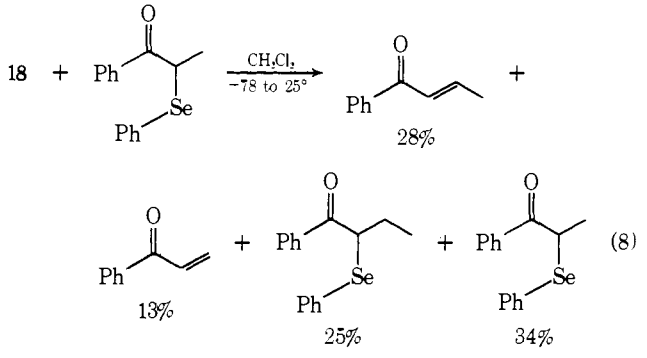
18 68% 22% (7)

an example). This reaction also illustrates another problem that arises under acidic conditions—the occurrence of redox reactions. The hydrolysis of the presumed Pummerer intermediate (e.g., **14**) gives benzeneselenol, which reduces selenoxides to selenides. Small amounts of reduction were observed for method C (Table II). Under these conditions, the $PhSeO_2H$ formed makes the reaction mixture slightly acidic. Redox reactions are also illustrated in eq 8, again under the conditions of method C. Such redox reactions are com-

Scheme II



pletely suppressed under mildly basic conditions (pyridine or diisopropylamine).



The formation of 2-phenylseleno-2-cycloocten-1-one (**10a**) could conceivably occur by three mechanisms (eq 4, 5, and 6, in Scheme II). The first involves deprotonation of the Pummerer intermediate (**14**); the second involves addition of selenenic acid to enone, followed by dehydration (eq 5). This mechanism seemed unlikely (conditions were sufficiently mild that the hydroxyl compound **15** should have been isolated) and could be ruled out by generating PhSeOH (by elimination of **18**) in the presence of cyclooctenone (**9**); no **10a** was formed.[27] The third plausible mechanism (eq 6) involves reaction of the stabilized enolate **16** (or the enol) with some selenenylating agent, most probably PhSeO-SePh produced during the disproportionation of PhSeOH (PhSO-SPh is formed during the disproportionation of PhSOH; it behaves as a sulfenylating reagent[28]). The intermediate **17** would then undergo selenoxide elimination. Oxygen scrambling between the two arylseleno groups is unlikely, at least under basic conditions.

A straightforward test for the above mechanism is based on the fact that the arylseleno group in **10,** formed according to eq 6, would not be the same one originally present in **13** whereas, in eq 4, the carbon-selenium bond is never broken. We thus carried out the elimination reaction on a mixture of two different arylselenino ketones. The acyclic selenoxide **18** undergoes high-yield elimination under most conditions. It was used as an in situ source of PhSeOH.

Table III. Cross Over Experiments

$$13b + 18 \xrightarrow{\Delta} 9 + 10$$

Ratio 13b:18	Relative yields[a] 9	10b	10a
1:0[b]	76	24	
1:1[b]	43	15	42
1:4[b]	25	7	68
1:0[c]	74	26	
1:1[c]	43	17	40
1:4[c]	45	9	46

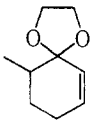
[a] Relative yields (NMR integration) of products 9 and 10 only are shown. [b] Elimination by method D (HN-*i*-Pr_2). [c] Elimination by method C. The absolute yields are considerably lower (see Table II) than for method D.

Some results of crossover experiments are summarized in Table III. Reversing the aryl groups gave similar results. The formation of the crossover product **10a** from **13b** is fully consistent with the mechanism of eq 6, even to the extent of a pronounced decrease in the relative yield of enone **9** when more PhSeX is present to react with enolate **16.** Clearly, the formation of **10** according to eq 6 could be prevented by the presence of a nucleophile which reacts more rapidly with PhSeO-SePh than does **16.** In fact, if the selenoxide elimination is carried out in the presence of diethylamine (rather than diisopropylamine) using method D, the formation of **10** is completely suppressed (Table II). Only moderate increases in yields of enones are obtained, however (runs 22 and 23). The selenenamide ($PhSeNEt_2$) is formed in high yield under these conditions. The reaction in the presence of HN-*i*-Pr_2 also gives the selenenamide (PhSeN-*i*-Pr_2), but formation of **10** is not prevented. Apparently diisopropylamine is of lower or comparable reactivity toward PhSeO-SePh than **16,** whereas diethylamine is much more reactive than **16.**

Thus in the presence of an unhindered secondary or primary amine, the formation of by-product α-diketones and α-phenylseleno enones can be prevented, although at some cost in the mildness of the reaction conditions; i.e., with reactive enones, products resulting from Michael addition of the amine (and of selenenamide) may be formed. We have not been able to find a trapping agent for PhSeX which

does not have the potential of participating in Michael additions.

Our conclusion that the activating effect of the carbonyl function is required for the formation of by-products is supported by the observation that the ketals **19** and **20** are formed in good yield by selenoxide elimination,[4b,29] whereas the α-phenylseleno ketones themselves do not undergo clean elimination under comparable conditions. By similar reasoning, esters should be less prone toward these side reactions than ketones, because of the lower acidity of the α-hydrogen. In fact, an ε-lactone (run 31) can be successfully dehydrogenated (compare run 21).



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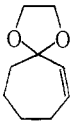

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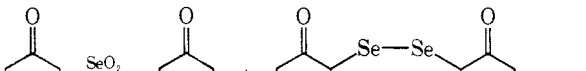
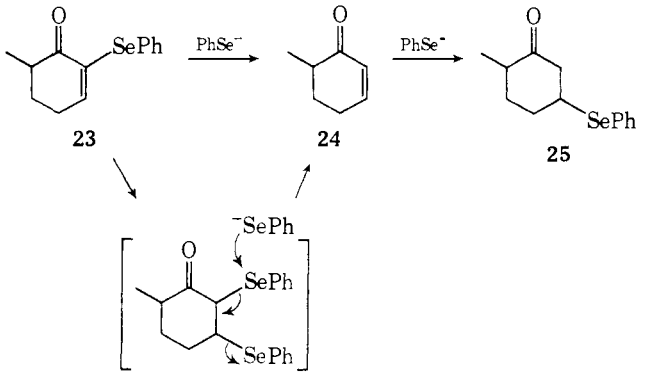
In summary, given the successful preparation of an α-phenylseleno carbonyl compound, the following is suggested: if products are stable to hydrogen peroxide, use method A or preferably method B; if not, try method C (pyridine) or D (diisopropylamine). If seleno enone formation is a problem, try method D with diethylamine. If above methods fail, or if selective ozonization is difficult, try sodium metaperiodate in aqueous methanol, with or without sodium bicarbonate. Other potentially useful oxidizing agents which we have not explored in detail are *tert*-butyl hydroperoxide, peracetic acid,[5c] and MoO_5·Py·HMPA.[30]

We have briefly explored the deselenation of α-phenylseleno enones as an approach to improving the yields of enones. Selenium dioxide dehydrogenation of ketones[2] often gives selenium containing by-products. Kocor and Tuszy-Maczka[31a] found that these by-products could be removed and yields improved by treatment of the oxidation products with ammonium sulfide. The structure of these by-products has not been often determined, but Marx and Norman[31b] recently reported the isolation of **21** in 14% yield. If one assumes that by-products like **21** are usually formed during SeO_2 oxidations, then the ammonium sulfide purification results imply that analogs of **21** were deselenated to enones by this reagent. Accordingly, we have treated the α-phenylseleno enone **23** with $(NH_4)_2S$ as well as PhSeLi and find



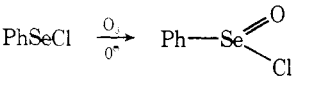
22 21



that both reagents do result in the conversion to enone (**24**). Apparently, Michael reaction subsequently leads to **25** since **24** disappears at a rate comparable to its rate of formation from **23.** Oxidation of the reaction mixture gives back enone **24** by selenoxide elimination of **25.** We postulate that this deselenation proceeds as shown (see eq 2).

The product **21** isolated by Marx and Norman is quite analogous to the by-products we have found in the selenoxide elimination and may actually be formed by a similar mechanism.

Reaction of Benzeneseleninyl Chloride (26) with Enolates. Difficulties with the oxidation in several systems led us to explore the utility of benzeneseleninyl chloride (**26**) as a



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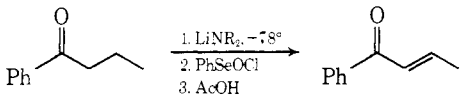

seleninylating agent. This compound is prepared by ozonization of PhSeCl[22b] and was conveniently isolated by crystallization. The reagent is very hygroscopic and, to avoid hydrolysis, contact with moist air must be avoided. This is a major disadvantage of this reagent; crystalline PhSeBr or PhSeCl can be handled in air with no special precautions.

Ketone and other enolates undergo C-seleninylation with **26,** and satisfactory yield of enone can be obtained in some cases (Method E, Table I, runs 5 and 30). Yields are rather variable, however, and frequently lower than obtained by the two-step procedure. Major by-products which are formed are starting ketone and α-phenylseleno ketone. The use of amine-free solutions of sodium or potassium enolates (from the reaction of carbonyl compounds with NaH or KH) did not improve matters significantly. The use of benzeneseleninyl chloride is recommended only when the normal selenide oxidation procedure fails because of competing or preferential oxidation elsewhere in the molecule.

Conclusion

The methods described here, together with related published procedures employing the selenoxide elimination,[4-8] provide techniques for the preparation of α,β-unsaturated carbonyl compounds and nitriles under uniquely mild conditions. A wide range of carbonyl compounds can be dehydrogenated, and good control of positional selectivity in unsymmetric ketones can often be achieved.

The power of the method is shown in the conversion of β-dicarbonyl compounds to sensitive β-dicarbonyl enones (runs 32 to 40), for which the dehydrobromination often fails completely.[1f,g] The procedure described here effects this conversion in excellent yield for most systems, with the further advantage that products are not detectably converted to the often more stable enol forms.[1f,g]

We have tried to explore in some detail the limitations of the methods described here. There are systems where the reaction fails to give high yields, and the results reported here should permit anticipation of systems where difficulties may be encountered and lead to quick selection of appropriate procedures to optimize yields.

The closely related sulfoxide elimination procedure developed by Trost and Salzmann[10] does not suffer from the necessity of working with toxic compounds and appears to be somewhat less prone to side reactions. The advantages of the selenoxide route, however, include the almost ideal stoichiometry of the selenenylation reaction (which compensates for the somewhat higher expense of the reagent), the

mildness of the selenenylation reaction, and, of course, the extreme mildness of the olefin forming step (Jones, Mundy, and Whitehouse[3] have reported that the selenoxide elimination proceeds at ca. 80–100° lower temperatures than the sulfoxide elimination). This point is illustrated in run 41, where an α-phenylsulfino-α-phenylselenino ketone undergoes selenoxide elimination to give a vinyl sulfoxide. A further advantage of the selenoxide route is the great reluctance of selenoxides to undergo further oxidation to selenones so that a wide range of oxidants is available, and these may be used in excess.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a Varian A-60A, Joel MH-100, or Brucker WH270 spectrometer. Infrared spectra were obtained on a Beckman IR-8 or Perkin-Elmer IR-267 spectrophotometer and mass spectra on an AEI MS-902 spectrometer. Unless specified otherwise, NMR and ir spectra were measured in CCl_4 solution.

Starting materials were commercially available or prepared according to the literature references cited. *n*-Butyllithium in hexane was purchased from Foote Mineral Co. or Alfa. Tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride; diisopropylamine was distilled from potassium hydroxide and stored over 4A molecular sieves. All reactions involving ketone or ester enolates were run under an atmosphere of dry nitrogen.

Preparative thin layer chromatography (preparative TLC) was carried out using Merck PF-254 silica gel, with 10% ether–pentane as eluent unless indicated otherwise.

Elemental analyses were performed according to the procedure of Gould[32] (Se) or by Spang Microanalytical Laboratories (C, H).

The normal work-up procedure involved addition of the reaction mixture to 30 ml of 50% ether–pentane and 30 ml of saturated $NaHCO_3$ solution. The aqueous layer was separated and washed with ether, and the combined organic portions were washed with 10% HCl if amine is present and with saturated NaCl solution and dried by filtering through a cone of Na_2SO_4. Solvent was removed on a rotary evaporator.

CAUTION. Selenium containing compounds are toxic and should be handled with due care. Most of the selenium containing compounds described here are sufficiently high boiling that volatility does not pose a severe toxicity or odor problem. PhSeCl and PhSeBr, however, are volatile enough to have pronounced odors.

Oxidation Procedures. Typical experimental procedures for the oxidations are given below: method A (run 28 and ref 4a), method B (runs 4, 6, 9, 34, and 35), method C (runs 10, 31, and 37), method D (run 15), method E (run 5), $NaIO_4$ (run 1), *m*-chloroperbenzoic acid (run 38).

The oxidation of divalent selenium compounds using hydrogen peroxide is highly exothermic and appears to be autocatalytic (i.e., $PhSeO_2H$ is a catalyst, either because of its acidity or through the formation of $PhSeO_3H$). Under no conditions should oxidations of amounts greater than 5 mmol be carried out by adding the full amount of H_2O_2 before oxidation has commenced (see runs 4 and 6 for larger scale oxidations).

Lithium Diisopropylamide. Solutions of LDA in THF were usually prepared as needed (see run 1). For small scale experiments, preformed solution was convenient, prepared as follows: a dry septum-capped flask was flushed with nitrogen and cooled to −78°. THF (8 ml) and diisopropylamine (7.9 ml) were added, followed by 40 ml of 1.40 M *n*-butyllithium in hexane. The 1 *M* LDA solution was warmed to 0° and stored at that temperature. It keeps indefinitely if air and moisture are carefully excluded.

Diphenyl Diselenide. This procedure is based on the organic synthesis preparation of benzeneselenol.[33a] We have used the air oxidation of benzeneselenol developed by Sharpless and Young,[5b,e] or the alternative procedure below, which is essentially odorless since it avoids the necessity for acid work-up of the Grignard reaction, during which hydrogen selenide and benzeneselenol are liberated.

To a 2-l. three-neck flask purged with nitrogen (condenser, mechanical stirrer, 250-ml addition funnel) were added 24.0 g (1 mol) of Mg turnings, 50 ml of anhydrous ether, and 30 ml of a solution of 160 g (1.02 mol) of bromobenzene in 100 ml of ether. When the Grignard reaction had started, 400 ml of ether was added; the remainder of the bromobenzene solution was added over a period of 30 min. The solution was refluxed for an additional 30 min after completion of the addition. The addition funnel was replaced by a Y adapter, and 74 g (0.94 mol) of grey powdered selenium was added during 15 min in small portions through one arm of the Y tube, while nitrogen purge was continued through the other. The reaction was again refluxed for 30 min after completion of the selenium addition.

The flask was placed in an ice bath, and 23.5 ml (70 g, 0.435 mol) of bromine was added dropwise at a rate such that the solution did not reflux. A solution of 53.5 g (1 mol) of NH_4Cl in 150 ml of water was then slowly added, while vigorous stirring was continued. The ether layer was decanted from the precipitated magnesium salts and gravity filtered, the salts were washed with three 50-ml portions of ether, and the ether was evaporated on the steam bath. After most of the ether had evaporated, air was blown through the hot solution for 10 min, 500 ml of hexane was added, and the solution was again filtered if necessary and allowed to crystallize overnight at 5°. If the crystallized diphenyl diselenide was red (due to the presence of small amounts of amorphous selenium), it was redissolved by swirling and warming *gently*, filtered, and again allowed to crystallize. Filtration gave 82 g (56% yield) of yellow diphenyl diselenide, mp 60–62° (lit.[33b] mp 63.5°). A second crop (14 g) can be obtained by concentration of the mother liquor to 200 ml, for a total yield of 66%. Material prepared in this way contains a small amount of selenium (probably as diphenyl triselenide) but is adequate for most purposes.

Diphenyl diselenide can be recovered in high yield from applications such as those described below. A procedure for reduction of the $PhSeO_2H$ and recovery of Ph_2Se_2 is given in the Experimental Section following run 6.

Benzeneselenenyl Chloride. Chlorine gas was passed into a magnetically stirred solution of 25.0 g (80 mmol) of Ph_2Se_2 in 190 ml of hexane until the weight had increased by 5.4 g. The white precipitate of $PhSeCl_3$ which forms at the entrance point of the chlorine does not redissolve when the end point is passed—this can be used to determine the correct amount of chlorine (if excess chlorine was added, the $PhSeCl_3$ can be removed by addition of a further small quantity of Ph_2Se_2). The solution was heated to dissolve any crystallized PhSeCl (if the solution is cloudy at this point, it should be filtered) and allowed to crystallize (0°), giving 27.3 g (89%) of PhSeCl as large orange crystals, mp 62–64° (lit.[33c] mp 64–65°). If the starting Ph_2Se_2 was pure, a second crop can be obtained, giving an almost quantitative yield.

Benzeneselenenyl Bromide.[33d] This compound was usually prepared in situ and used directly. A typical procedure for 12 mmol of PhSeBr is as follows: 1.88 g (6 mmol) of Ph_2Se_2 were dissolved in 5 ml of THF, and 0.324 ml (0.96 g, 6 mmol) of Br_2 were added dropwise with stirring. The reaction is essentially instantaneous, and the solution can be used directly. Larger scale preparations require cooling (10°), because the reaction is slightly exothermic.

Benzeneseleninyl Chloride (26). A solution of 5.0 g (26 mmol) of PhSeCl in 25 ml of dichloromethane was ozonized through a $CaSO_4$ drying tube at −5° until the color has faded to a light yellow. The solution was warmed to 25°, and the drying tube was replaced by a septum in a dry bag. Care must be taken to avoid moisture since the chloride is extremely hygroscopic. After crystallization at −24° overnight, the mother liquor was transferred by cannula to a flask equipped with a septum. The pale white crystals were washed with 5 ml of cold dichloromethane, which was added to the mother liquor. After drying in vacuo for 2 hr, 2.81 g of nearly white crystals were obtained, mp 56–64° (lit.[22b] mp 75°). A second crop (2.12 g) was obtained by adding 10 ml of cold hexane to the mother liquor and cooling overnight at −24° for a combined yield of 92%.

Anal. Calcd for C_6H_5ClOSe: Se, 38.07, Found: Se, 37.82.

3,3′-Bis(trifluoromethyl)diphenyl Diselenide. A 1-l. three-neck round-bottomed flask was fitted with a reflux condenser, a mechanical stirrer, a dropping funnel, and a nitrogen inlet tube. The exit tube is attached to an NaOH bubbler. *m*-Trifluoromethylphenylmagnesium bromide was prepared using 28.1 g (0.125 mol) of *m*-bromobenzotrifluoride, 3.0 g (0.125 mol) of magnesium turnings, and 250 ml of dry ether. The dropping funnel was removed, and 9.5 g (0.12 mol) of powdered black selenium was added gradually over a 10-min period through the side arm. It is important to

avoid the introduction of oxygen during this operation. After stirring for an additional 20 min, 100 g of ice were slowly added to the flask followed by 20 ml of concentrated HCl. The reaction mixture was worked up (water wash), 100 ml of methanol was added to the yellow solution, and air was bubbled through overnight. Distillation of the residue gave 23.2 g (88%) of diselenide, an orange liquid, bp 121–123° (0.25 mm).

Anal. Calcd for $C_{14}H_8F_6Se_2$: Se, 35.24. Found: Se, 35.10.

4,4′-Bis(trifluoromethyl)diphenyl Diselenide. Following the procedure outlined to prepare the 3,3′ isomer, 5.62 g (25 mmol) of bromide gave 2.52 g (45%) of the yellow diselenide after recrystallization from methanol (mp 53–55°).

Anal. Calcd for $C_{14}H_8F_6Se_2$: Se, 35.24. Found: Se, 34.90.

3-Trifluoromethylbenzeneselenenyl Chloride. To a solution of 4.48 g (10 mmol) of diselenide in 10 ml of dichloromethane at 25° under nitrogen was added, dropwise, a solution of 1.35 g (10 mmol) of SO_2Cl_2 in 1 ml of dichloromethane with stirring over a 15-min period. Solvent was removed under vacuum, and distillation gave 4.62 g (89%) of chloride, a dark orange liquid, bp 54–55° (0.25 mm).

Anal. Calcd for $C_7H_4ClF_3Se$: Se, 30.42. Found: Se, 30.07.

***(Z)*-1-Acetoxy-1-phenylpropene.** This compound was prepared by treatment of the lithium enolate of propiophenone with acetic anhydride and purified by distillation and recrystallization from pentane: mp 29–30.5°; NMR δ 1.63 (d, J = 7.2 Hz, 3 H), 2.13 (s, 3 H), 5.73 (q, J = 7.2 Hz, 1 H), 7.1–7.5 (m, 5 H); ir 1762, 1207 cm^{-1}.

1-Phenyl-2-phenylseleno-1-propanone (2). A. Run 1. The following serves as a typical procedure for the preparation of an α-phenylseleno ketone via the lithium enolate. Into a 50-ml two-neck round-bottomed flask (magnetic stirrer, septum, 10-ml addition funnel) was distilled 20 ml of THF under nitrogen. The flask was cooled to −78°, and 0.92 ml (6.0 mmol) of diisopropylamine were added, followed by 2.94 ml of 2.05 *M* *n*-BuLi in hexane. A solution of propiophenone (0.67 g, 5 mmol) in 2 ml of THF was added dropwise, and the solution was stirred for 15 min. Into the addition funnel was placed 0.94 g (3.0 mmol) of Ph_2Se_2, and this was dissolved in 2 ml of THF. Bromine (0.162 ml, 0.48 g, 3.0 mmol) was added dropwise to the solution, which was agitated briefly to dissolve any $PhSeBr_3$ formed. The PhSeBr solution was added rapidly to the enolate solution (immediate decolorization), and the cold reaction mixture was poured into 50 ml of 0.5 *N* HCl and 40 ml of 50% ether–pentane. The organic layer was washed with water, saturated $NaHCO_3$ solution, and saturated NaCl solution and dried by filtering through a cone of anhydrous Na_2SO_4. Solvent was removed, and the crude product was crystallized from ether–pentane at −20° (0.87 g, mp 36.5–37°). Chromatography of the mother liquor gave a further 0.40 g, isolated by crystallization (total yield 1.27 g, 87%): NMR δ 1.60 (d, J = 7.0 Hz, 3 H), 4.58 (q, J = 7.0 Hz, 1 H), 7.1–7.6 (m, 8 H), 7.88 (m, 2 H); ir 1680, 1598, 1582 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}OSe$: C, 62.29; H, 4.88. Found: C, 62.23; H, 4.95.

To a solution of 1.00 g (3.46 mmol) of 1-phenyl-2-phenylseleno-1-propanone (**2**) in 60 ml of methanol was added 10 ml of H_2O, 0.35 g (4 mmol) of $NaHCO_3$, and 1.72 g (8 mmol) of $NaIO_4$ with vigorous stirring. After 90 min at 25°, the reaction mixture was poured into 40 ml of 15% ether–pentane and 40 ml of saturated $NaHCO_3$ solution. The organic layer was washed with H_2O and NaCl solution. A few crystals of hydroquinone were added, solvent was removed, and the residue was distilled (0.2 mm, receiver at −20°), giving 404 mg (89% yield) of **1-phenyl-2-propen-1-one,**[34] with no detectable impurities by NMR: δ 5.84 (dd, J = 2.2, 10.7 Hz, 1 H), 6.39 (dd, J = 2.2, 17.3 Hz, 1 H), 7.16 (dd, J = 10.7, 17.3 Hz, 1 H), 7.4–7.6 (m, 3 H), 7.92 (dd, J = 2, 8 Hz, 2 H); ir 1672, 1664, 1610, 1597 cm^{-1}.

B. Run 3. The following serves as a typical procedure for the conversion of enol acetates to α-phenylseleno ketones. To a stirred solution of 243 mg (1.1 mmol) silver trifluoroacetate[33e] in 5 ml of benzene at 25° under nitrogen was added a solution of 176 mg (1 mmol) of (*Z*)-1-acetoxy-1-phenylpropene in 0.5 ml of benzene followed by 1.1 mmol of PhSeBr. After stirring the reaction mixture for 1 min, 2 drops of saturated NaCl solution was added along with 124 mg (1 mmol) of $Na_2CO_3 \cdot H_2O$ in 0.4 ml of water. After filtering the reaction mixture through Celite and Na_2SO_4, solvent removal followed by preparative TLC gave 240 mg (83%) of 1-phenyl-2-phenylseleno-1-propanone (**2**).

C. From 1-Phenylpropyne. Silver trifluoroacetate (112 mg, 0.5 mmol) was stirred with 2 ml of dry dichloromethane, and 97 mg (0.5 mmol) of PhSeCl was added. When the PhSeCl had dissolved (2 min), the pale yellow suspension was added with stirring to 62 mg (0.53 mmol) of 1-phenyl-1-propyne in 2 ml of dichloromethane. After 10 min, this suspension was added to 0.75 mmol of KOH and one drop of saturated aqueous NaCl solution in 5 ml of ethanol. After stirring for 5 min, 20 ml of 50% ether–pentane and 20 ml of water were added, and the mixture was filtered through Celite. The organic layer was washed with $NaHCO_3$ solution and dried. Solvent was removed, and the product was purified by preparative TLC, giving 95 mg (66%) of 1-phenyl-2-phenylseleno-1-propanone (**2**).

***trans*-1-Phenyl-2-buten-1-one. A. Run 4.** Following the selenide preparation outlined in run 1, 2.96 g (0.02 mmol) of *n*-butyrophenone gave 5.00 g (82%) of 1-phenyl-2-phenylseleno-1-butanone after slow crystallization at −24° from 25 ml of 50% ether–pentane: mp 50.5–52.5°; NMR δ 1.01 (t, J = 6.9 Hz, 3 H), 1.6–2.2 (m, 2 H), 4.30 (*t*, J = 7.2 Hz, 1 H), 7.0–7.5 (m, 8 H), 7.77 (m, 2 H); ir 1678, 1599, 1581 cm^{-1}.

Anal. Calcd for $C_{16}H_{16}OSe$: C, 63.37; H, 5.32; Se, 26.04. Found: C, 63.45; H, 5.28; Se, 25.86.

Into a 250-ml three-necked round-bottomed flask equipped with a dropping funnel, condenser, and thermometer was added a solution of 4.55 g (0.015 mol) of selenide (prepared as above) in 50 ml of dichloromethane containing 2.42 ml (0.03 mol) of pyridine. To the stirred solution was gradually added 0.04 mol of H_2O_2 (4.53 g of 30% H_2O_2 in 4 ml of water), with cooling by an ice–salt bath to keep the temperature between 30 and 35° (CAUTION).[35] The reaction mixture was stirred vigorously at 25° for an additional 15 min after removing the bath and then was added to 25 ml of dichloromethane and 30 ml of 7% $NaHCO_3$ solution. The aqueous layer was washed with 25 ml of dichloromethane, and the combined organic layers were washed with 30 ml of 10% HCl solution and 30 ml of saturated NaCl and dried (Na_2SO_4). After solvent removal, distillation gave 2.02 g (92%) of *trans*-enone: bp 84–85° (0.5 mm) [lit.[36] bp of cis,trans mixture 120–122° (7 mm)]; NMR δ 1.89 (d, J = 5.2 Hz, 3 H), 6.72–7.15 (m, 2 H), 7.4 (m, 3 H), 7.84 (m, 2 H).

B. Run 5. To a magnetically stirred solution of 1.2 mmol of LDA in 5 ml of freshly distilled THF under nitrogen at −78° was added a solution of 148 mg (1 mmol) of *n*-butyrophenone in 0.5 ml of THF. After stirring the reaction mixture for 10 min, a solution of 374 mg (1.8 mmol, weighed in a dry bag) of benzeneseleninyl chloride (**26**) in 1 ml of THF was added, followed immediately by a solution of 72 mg (1.2 mmol) of acetic acid in 0.5 ml of THF. The reaction mixture was warmed to 25° over a 15 min period. Normal work-up and purification by preparative TLC gave 117 mg (80% yield) of *trans*-1-phenyl-2-buten-1-one.

***trans*-2-Hepten-4-one (Run 6).** The selenide preparation in run 1 was followed using 0.105 mol of LDA in 50 ml of THF, a solution of 11.42 g (0.1 mol) of 4-heptanone in 10 ml of THF, and a solution of 0.11 mol of PhSeBr in 30 ml of THF. The reaction mixture was added to 100 ml of 10% HCl solution and 100 ml of 50% ether–pentane. The aqueous layer was washed with 50 ml of ether–pentane, and the combined organic layers were washed with 50 ml of 7% $NaHCO_3$ solution, 50 ml of saturated NaCl solution, and dried (Na_2SO_4). After solvent removal, remaining 4-heptanone (~5%) was removed under vacuum with a Dry Ice trap, leaving crude 3-phenylseleno-4-heptanone: NMR δ 0.7–1.1 (m, 6 H), 1.3–2.0 (m, 4 H), 2.1–2.8 (m, 2 H), 3.51 (t, J = 7 Hz, 1 H), 7.0–7.7 (m, 5 H).

The oxidation procedure outlined in run 4 was followed by slowly (CAUTION[35]), adding 0.3 mol of H_2O_2 (34.1 g of 30% H_2O_2 in 30 ml of water) to a solution of the crude selenide in 150 ml of dichloromethane containing 17 ml (0.2 mol) of pyridine, cooled by an ice–salt bath, to keep the temperature between 30 and 35°. The reaction was worked up by washing with a solution of 15.5 g (0.125 mol) of $Na_2CO_3 \cdot H_2O$ in 50 ml of water (save), twice with 100 ml of 10% HCl solution, and 50 ml of saturated NaCl solution and drying (Na_2SO_4). Distillation gave 8.07 g (72% yield, 76% based on recovered 4-heptanone) of *trans*-enone: bp 53–54° (15 mm) [lit.[36] bp of cis,trans mixture 78–80° (50 mm)]; NMR δ 0.89 (t, J = 7.2 Hz, 3 H), 1.58 (sextet, J = 7.2 Hz, 2 H), 1.87 (dd, J = 2, 6.8 Hz, 3 H), 2.44 (t, J = 7.2 Hz, 2 H), 6.04 (dd, J = 2, 15.8 Hz,

1 H), 6.76 (dq, J = 15.8, 6.8 Hz, 1 H).

Recovery of Diphenyl Diselenide. The aqueous sodium carbonate wash from the oxidation procedure outlined in run 7 was neutralized with concentrated HCl and kept acidic by further additions of acid, while 48.2 g (0.306 mol) of sodium thiosulfate was added gradually over a 30-min period. After stirring the solution for 2 hr, an additional 7.9 g (0.05 mol) of sodium thiosulfate was added, and the solution was stirred for 18 hr as Ph_2Se_2 precipitated. The crude Ph_2Se_2 was isolated by filtration (15.26 g, 89%) and was recrystallized from ethanol to give 12.0 g (70%, two crops), mp 59–60°.

1-Cyclobutenylphenyl Ketone (Run 9). Following the selenide preparation outlined in run 1, 400 mg (2.5 mmol) of cyclobutylphenyl ketone gave 679 mg (87%) of 1-phenylseleno-1-cyclobutylphenyl ketone, after preparative TLC: NMR δ 1.7–3.0 (m, 6 H), 7.0–7.5 (m, 8 H), 7.87 (m, 2 H); ir (neat) 1665, 1595, 1580, 968 cm^{-1}.

To a stirred solution of 315 mg (1 mmol) of selenide in 5 ml of dichloromethane containing 0.2 ml (2.4 mmol) of pyridine was added 8.8 mmol of H_2O_2 (1 ml of 30% H_2O_2 in 1 ml of water), and the reaction mixture was stirred at 25° for 30 min. Normal work-up gave 131 mg (83%) of enone, after preparative TLC: NMR δ 2.50 (m, 2 H), 2.82 (m, 2 H), 6.60 (m, 1 H), 7.40 (m, 3 H), 7.85 (m, 2 H); ir (neat) 1643, 1600, 1585 cm^{-1}; *m/e* (calcd for $C_{11}H_{10}O$, 158.07312) 158.07310.

3-Phenyl-2-cyclobutenone (Run 10). Following the selenide preparation outlined in run 1, except with enolate formation and rapid quench at −100°, 146 mg (1 mmol) of 3-phenylcyclobutanone[37] gave, after preparative TLC, 230 mg (65% pure, ca. 50% yield) of a mixture containing predominantly one isomer: NMR δ 2.8–3.8 (m, 4 H), 4.42 (d, J = 7.3 Hz, 1 H), 7.0–7.4 (br s, 8 H), 7.55 (m, 2 H).

A solution of 151 mg (0.5 mmol) of impure selenide prepared above in 4 ml of dichloromethane was ozonized at −78°. After the addition of 0.1 ml (1.2 mmol) of pyridine, the reaction mixture was warmed to 25° and was worked up as usual. Preparative TLC (50% ether–pentane) gave 30 mg of enone (83% pure, ca. 53% yield from pure selenide): NMR[37] δ 3.44 (s, 2 H), 6.32 (s, 1 H), 7.5 (m, 5 H); ir 1767, 1609, 1585, 1566 cm^{-1}.

2-Benzylcyclopentanone. This compound was prepared by the procedure of Forward and Whiting:[38] NMR δ 1.2–2.7 (m, 8 H), 3.06 (dd, J = 13.5, 3.5 Hz, 1 H), 7.0–7.4 (m, 5 H). These authors incorrectly reported the resonance at δ 3.06 as a two proton doublet.

5-Benzyl-2-cyclopenten-1-one (Run 11). Following the selenide preparation outlined in run 1 and the oxidation procedure in run 9, 174 mg (1 mmol) of 2-benzylcyclopentanone gave 113 mg (66%) of enone, after preparative TLC (50% ether–pentane): NMR δ 2.15–2.85 (m, 4 H), 2.9–3.3 (m, 1 H), 6.11 (dt m, J = 5.5, 2, <1 Hz, 1 H), 7.2 (br s, 5 H), 7.54 (dt m, J = 5.5, 2.5, <1 Hz, 1 H); ir (neat) 1698, 1638, 1600, 1588 cm^{-1}; *m/e* (calcd for $C_{12}H_{12}O$, 172.08878) 172.08873.

1-Acetoxy-2-benzylcyclopentene. Using the method of House, Gall, and Olmstead,[21] a solution of 552 mg (3 mmol) of 2-benzylcyclopentanone in 3 ml of CCl_4 containing 0.75 ml of acetic anhydride and 10 μl of 60% $HClO_4$ was stirred at 25°, under nitrogen, for 1.5 hr and worked up. Preparative TLC gave 484 mg (78% yield) of enol acetate: NMR δ 1.7–2.3 (m, 4 H), 2.07 (s, 3 H), 2.5 (m, 2 H), 3.27 (br s, 2 H), 7.16 (m, 5 H); ir 1755, 1696(w), 1210 cm^{-1}; *m/e* (calcd for $C_{14}H_{16}O_2$, 216.11496) 216.11419.

2-Benzylidinecyclopentanone and 2-Benzyl-2-cyclopenten-1-one (Run 12). Following the selenide preparation outlined in run 3, 432 mg (2 mmol) of 1-acetoxy-2-benzylcyclopentene gave 603 mg (96%) of 2-benzyl-2-phenylselenocyclopentanone, after preparative TLC: mp 52–54° (recrystallized from ether–pentane); NMR δ 1.6–2.5 (m, 6 H), 2.99 and 3.25 (AB q, J = 13.8 Hz, 2 H), 6.9–7.6 (m, 10 H); ir 1727, 1601 (w), 1580 (w) cm^{-1}.

Anal. Calcd for $C_{18}H_{18}OSe$: Se, 23.98. Found: Se, 23.58.

Oxidation of 329 mg (1 mmol) of selenide using the procedure described for run 9 gave a mixture of the exo- and endocyclic enones. The mixture was separated by using preparative TLC (50% ether–pentane) to give 72 mg (42%) of 2-benzylidenecyclopentanone [mp 69–71° (lit.[39a] mp 70–71°); NMR[39b] δ 1.7–2.5 (m, 4 H), 2.90 (td, J = 7, 2.4 Hz, 2 H), 7.2–7.6 (m, 6 H, =CH and ArH)] and 92 mg (53%) of 2-benzyl-2-cyclopenten-1-one [NMR[39b] δ 2.14–2.63 (m, 4 H), 3.40 (m, 2 H), 7.01 (m, 1 H), 7.17 (br s, 5 H)].

6-Methyl-2-cyclohexen-1-one (Run 15). Following the selenide preparation outlined in run 1, 0.022 mol of LDA, 0.022 mol of PhSeBr, and 0.02 mol (2.24 g) of 2-methylcyclohexanone gave crude 6-methyl-2-phenylselenocyclohexanone. Remaining starting material (5%) was removed by sublimation at 40–45° (Dry Ice cold finger, 0.2 mm). The selenide was a mixture of *cis,trans*-2-methyl-6-phenylselenocyclohexanones in a 1:1 ratio which could be separated by preparative TLC: NMR *cis*-selenide δ 1.06 (d, J = 5.8 Hz, 3 H), 1.6–2.6 (m, 7 H), 4.01 (dd, J = 11, 5 Hz, 1 H, H_6), 7.2–7.7 (m, 5 H); *trans*-selenide, δ 1.01 (d, J = 5.6 Hz, 3 H), 1.6–2.5 (m, 6 H), 3.12 (sextet, J = 6.4 Hz, 1 H, H_2), 3.82 (br t, J = 4 Hz, 1 H, H_6), 7.2–7.7 (m, 5 H).

A solution of the crude selenide in 20 ml of dichloromethane was cooled to −78° and ozonized until green. Nitrogen was bubbled in until excess ozone had been removed and 2.8 ml (20 mmol) of cold diisopropylamine were added. The cold solution was transferred by cannula to a refluxing CCl_4 solution (100 ml) containing 1.4 ml (10 mmol) of diisopropylamine. The solution was cooled to 25°, was washed with 30 ml of 10% HCl solution, 30 ml of 7% $NaHCO_3$ solution, 30 ml of saturated NaCl solution, and dried (Na_2SO_4). After solvent removal, distillation gave 1.39 g (63% yield) of enone, bp 76–78° (15 mm) [lit.[40] bp 74–75° (24 mm)]. An additional 0.21 g was isolated by preparative TLC (20% ether–pentane) of the pot residue, total yield: 73%; NMR δ 1.10 (d, J = 6.8 Hz, 3 H), 1.45–2.55 (m, 5 H), 5.91 (dt, J = 10, 2 Hz, 1 H), 6.88 (dt m, J = 10, 4, ~2 Hz, 1 H).

Preparative TLC of the distillation pot residue also gave 0.595 g (11%) of 2-phenylseleno-2-cyclohexen-1-one: mp 42–43° (recrystallized from ether–pentane); NMR δ 1.22 (d, J = 6.7 Hz, 3 H), 1.6–2.7 (m, 5 H), 6.23 (t, J = 4 Hz, 1 H), 7.2–7.7 (m, 5 H); ir 1675, 1597, 1580 cm^{-1}

Anal. Calcd for $C_{13}H_{14}OSe$: C, 58.87; H, 5.32. Found: C, 58.75; H, 5.37.

Ethylene Ketal of 6-Methyl-2-cyclohexen-1-one (19). A solution of 0.41 g (1.53 mmol) of 2-methyl-6-phenylselenocyclohexanone in 35 ml of benzene containing 5 ml of ethylene glycol and 58 mg *p*-TsOH·H_2O was refluxed for 2.5 hr with water removal. Normal work-up (four water washes) followed by preparative TLC gave the ketal selenide: yield 0.389 g (81%); mixture of cis and trans isomers; NMR δ 1.06, 1.14 (d, J = 6.6, 6.4 Hz, 3 H), 1.2–2.3 (m, 7 H), 3.20, 3.44 (dd, J = 13.4, 4.5, 6.0, 4.5 Hz, 1 H, H_6), 3.7–4.4 (m, 4 H), 7.0–7.7 (m, 5 H).

A solution of 556 mg (1.79 mmol) of the ethylene ketal of 2-methyl-6-phenylselenocyclohexanone and 0.32 ml of pyridine in 15 ml of dichloromethane was stirred with 4 ml of 15% H_2O_2 for 1.5 hr. Normal work-up gave the selenoxide, which was refluxed for 5 min in 5 ml of CCl_4 containing 0.32 ml of pyridine to cause elimination. Purification by preparative TLC gave 0.221 g (80% yield) of **19**: NMR δ 0.89 (d, J = 6.0 Hz, 3 H), 1.5–2.2 (m, 5 H), 3.6–4.0 (m, 4 H), 5.45 (dt, J = 9.6, 1.8 Hz, 1 H), 5.74 (dt, J = 9.6, 3.6 Hz, 1 H); *m/e* (calcd for $C_9H_{14}O_2$, 154.09938) 154.09939.

6-Phenyl-2-cyclohexen-1-one (Run 16). The selenide was prepared as in run 1, using 174 mg (1.0 mmol) of 2-phenylcyclohexanone, 1.1 mmol of LDA, and 213 mg (1.1 mmol) of PhSeCl. The mixture of cis,trans isomers of 6-phenyl-2-phenylselenocyclohexanone was oxidized as in run 9 (stirred for 5 min with H_2O_2). The crude product was purified by preparative TLC, giving 103 mg of enone (60% yield): mp 65–67° (lit.[1e] mp 68–69°); NMR δ 1.9–2.4 (m, 4 H), 3.43 (br t, J = 7.2 Hz, 1 H), 5.96 (dt, J = 10.1, 1.8 Hz, 1 H), 6.81 (dt, J = 10.1, 3.5 Hz, 1 H), 6.9–7.3 (m, 5 H); ir 1675, 1618, 1603 cm^{-1}.

Additional runs as above, except that method D (run 15) was used for the oxidation–elimination, gave 62% of enone with diisopropylamine as base and 58% yield when pyrolysis was carried out in the presence of diethylamine.

1-Acetoxy-2-phenylcyclohexene. Using the method of House, Gall, and Olmstead,[21] a solution of 2.12 g of 2-phenylcyclohexanone in 12 ml of CCl_4 containing 5 ml of acetic anhydride and 2 drops of 60% $HClO_4$ (25 mg) was stirred at 25° for 3 hr, and worked up. Distillation gave 2.11 g of enol acetate[41] (80% yield); NMR and gas chromatographic analysis (300-ft capillary column, Carbowax, 180°) showed the presence of 10% of the isomeric enol acetate (1-acetoxy-6-phenylcyclohexanone, relative retention time 1.1): NMR δ 1.78 (s + m, 7 H), 2.0–2.4 (m, 4 H), 7.1 (m, 5 H).

1-Acetoxy-6-phenylcyclohexene. The lithium enolate of 2-phen-

ylcyclohexanone was quenched with acetic anhydride, and the product was analyzed by GLC as above, showing a 99/1 ratio of 6-phenyl to 2-phenyl compounds: NMR δ 1.5–2.4 (m, 6 H), 1.73 (s, 3 H), 3.7 (m, 1 H), 5.50 (td, J = 3.7, 1.2 Hz, 1 H), 7.1 (m, 5 H).

2-Phenyl-2-cyclohexen-1-one (Run 18). A solution of 1.6 ml of 1.55 M methyllithium (2.5 mmol) in 2 ml of THF was cooled to −20° under nitrogen. To the stirred solution was added a solution of 0.216 g (1.0 mmol) of 1-acetoxy-2-phenylcyclohexene in THF. The mixture was warmed to 0°, stirred for 10 min, and cooled to −78°, and a solution of 2.75 mmol of PhSeBr in 3 ml of THF was added rapidly dropwise. The contents of the flask was added to 0.5 N HCl and 50% ether–pentane. Normal work-up and preparative TLC purification (chloroform–hexane) gave 0.302 g (87% yield) of 2-phenyl-2-phenylselenocyclohexanone. Crystallization from ether–pentane gave selenide with mp 116–117°: NMR δ 1.5–2.1 (m, 4 H), 2.1–2.9 (m, 4 H), 6.9–7.4 (m, 10 H); ir ($CHCl_3$) 1718 cm^{-1}.

Oxidation of 0.404 g (1.2 mmol) of the above selenide as in run 9 followed by preparative TLC (chloroform–hexane) gave 0.202 g (94% yield) of enone: mp 92–94° (lit.[1e] mp 94–95°); NMR δ 1.97 (quint, 2 H), 2.4 (m, 4 H), 6.88 (t, J = 5 Hz, 1 H), 7.22 (br s, 5 H); ir 1686 cm^{-1}.

6-(*p*-Tolylidene)-2-cyclohexen-1-one (Run 19). To a solution of 6 mmol of LDA (from 0.92 ml of HN-i-Pr_2 and 2.94 ml of 2.05 M n-BuLi) in 10 ml of THF at −78° was added 1.2 ml of hexamethylphosphoric triamide. A solution of 2-(*p*-tolylidene)cyclohexanone[42] (1.0 g, 5 mmol) in 3 ml of THF was added dropwise, followed after 10 min by a solution of 6 mmol of PhSeBr (from 0.94 g Ph_2Se_2 and 0.162 ml of Br_2) in 3 ml of THF. The reaction mixture was worked up as usual. Crystallization from methanol (−20°) gave 1.10 g, mp 70.5–72°. The mother liquor was purified by preparative TLC and recrystallized from methanol for a total yield of 1.20 g (68%): NMR δ 1.6–3.1 (m, 6 H), 2.38 (s, 3 H), 4.01 (br t, J = 5 Hz, 1 H), 7.1–7.4 (m, 8 H), 7.58 (m, 2 H); ir 1676, 1600 (br) cm^{-1}.

Anal. Calcd for $C_{20}H_{20}OSe$: C, 67.60; H, 5.67. Found: C, 67.49; H, 5.56.

To a solution of 320 mg (0.9 mmol) of the above selenide in 50 ml of warm methanol was added 15 ml of water. The resulting suspension was cooled to 10°, and 430 mg (2.0 mmol) of $NaIO_4$ was added. The mixture was stirred at room temperature for 3 hr, then worked up by pouring into 40 ml of 50% ether–pentane and 40 ml of saturated $NaHCO_3$ solution. The crude product was purified by preparative TLC (20% ether–pentane) and crystallized from pentane to give 133 mg (74%) of dienone: mp 63–65°; NMR δ 2.34 (s + m, 5 H, CH_3 + H_4), 2.97 (dt, $J_{5,4}$ = 6, $J_{5,7}$ = 1.9 Hz, H_5), 6.08 (dt, $J_{2,3}$ = 10, $J_{2,4}$ = 2.0 Hz, H_2), 6.88 (dt, $J_{3,2}$ = 10, $J_{3,4}$ = 4.0 Hz, H_3), 7.13 (AB q, J = 7 Hz, 4 H, ArH), 7.41 (br s, H_7); ir 1672, 1610 cm^{-1}; m/e (calcd for $C_{14}H_{14}O$, 198.10446) 198.10186.

2-Cyclohepten-1-one (Run 22). Following the procedure outlined in run 15, 20 mmol (2.24 g) of cycloheptanone gave, by distillation, 1.10 g (50%) of enone: bp 26–38° (0.3 mm) [lit.[1c] 52–52.5° (2.4 mm)]; NMR δ 1.6–2.0 (m, 4 H), 2.2–2.6 (m, 4 H), 5.81 (br d, J = 11.8 Hz, 1 H), 6.42 (dt, J = 11.8, 5.2 Hz, 1 H). Preparative TLC of the distillation pot residue (20% ether–pentane) gave 0.96 g (18%) of 2-phenylseleno-2-cyclohepten-1-one: mp 43–45°; NMR δ 1.5–2.1 (m, 4 H), 2.1–2.7 (m, 4 H), 6.24 (t, J = 6 Hz, 1 H), 7.1–7.7 (m, 5 H); ir 1667, 1594, 1580 cm^{-1}; m/e (calcd for $C_{13}H_{14}OSe$, 266.02098) 266.02033.

Run 23. An identical run with the one above using diethylamine instead of diisopropylamine during the selenoxide pyrolysis gave 55% of enone and no 2-phenylseleno-2-cyclohepten-1-one.

Ethylene Ketal of 2-Phenylselenocycloheptanone. Following the selenide preparation outlined in run 1, 280 mg (2.5 mmol) of cycloheptanone gave 641 mg (84% pure, ca. 81% yield) of 2-phenylselenocycloheptanone after preparative TLC: NMR δ 1.1–2.5 (m, 9 H), 1.5–2.9 (m, 2 H), 3.70 (dd, J = 11, 5.5 Hz, 1 H), 7.1–7.7 (m, 5 H).

A solution of the selenide prepared above in 65 ml of benzene containing 10 ml of ethylene glycol and 120 mg of p-TsOH·H_2O was refluxed for 2.5 hr with water removal. After work-up as described for the preparation of the ethylene ketal of 2-methyl-6-phenylselenocyclohexanone, preparative TLC gave 570 mg (90% yield from pure selenide): mp 40–42°; NMR δ 1.1–2.2 (m, 10 H), 3.48 (dd, J = 8.2, 4 Hz, 1 H), 3.7–4.2 (m, 4 H), 7.19 (m, 3 H), 7.56 (m, 2 H); ir 1580 cm^{-1}.

Anal. Calcd for $C_{15}H_{20}O_2Se$: Se, 25.37. Found: Se, 25.15.

Ethylene Ketal of 2-Cyclohepten-1-one (20). Following the oxidation procedure outlines in run 9 (stirred for 2 hr with H_2O_2), 157 mg (0.5 mmol) of the ethylene ketal of 2-phenylselenocycloheptanone gave 67 mg (87%) of **20**[1c] after preparative TLC: NMR δ 1.5–1.9 (m, 6 H), 2.2 (m, 2 H), 3.86 (s, 4 H), 5.59 (d, J = 12 Hz, 1 H), 5.78 (dt, J = 12, 5.5 Hz, 1 H).

Spiro[2.6]non-5-en-4-one (Run 24). Following the selenide preparation outlined in run 1, 138 mg (1 mmol) of spiro[2.6]nonan-4-one[43] gave 249 mg (85% yield) of 5-phenylselenospiro[2.6]nonan-4-one after preparative TLC: mp 50–52° (recrystallized from ether–pentane); NMR δ 0.64 (m, 2 H), 1.24 (m, 2 H), 1.4–2.2 (m, 8 H), 4.23 (dd, J = 6.6, 4.2 Hz, 1 H), 7.1–7.7 (m, 5 H); ir 3080, 3065, 1673, 1582, 1480, 1452, 1440 cm^{-1}.

Anal. Calcd for $C_{15}H_{18}OSe$: C, 61.43; H, 6.19. Found: C, 61.48; H, 6.04.

Following the oxidation procedure outlined in run 15, 293 mg (1 mmol) of selenide gave 116 mg (85%) of enone after preparative TLC: NMR δ 0.65 and 1.22 (AA′BB′, 4 H), 1.5–2.1 (m, 4 H), 2.45 (m, 2 H), 5.87 (dt, J = 12.2, 1.7 Hz, 1 H), 6.28 (dt, J = 12.2, 4.5 Hz, 1 H); ir (neat) 3095, 1660 (sh), 1645, 1453, 1440 cm^{-1}; m/e (calcd for $C_9H_{12}O$, 136.08876) 136.08891.

Methyl 1-Cyclohexenecarboxylate (Run 28). To a stirred solution of 6 mmol of LDA in 20 ml of THF under nitrogen at −78° was added dropwise a solution of 0.71 g (5 mmol) of methyl cyclohexanecarboxylate in 2 ml of THF over 5 min. After stirring for an additional 10 min, a solution of 6 mmol of PhSeBr in 2 ml of THF was added rapidly. Upon warming the reaction to 0° (ice water bath), water (3 ml) and acetic acid (0.6 ml, 10 mmol) were added, followed by the slow addition of 2.8 g of 30% H_2O_2, keeping the temperature below 25°. After stirring for 30 min at 25°, the reaction was worked up as usual. Distillation gave 0.675 g (96%) of methyl 1-cyclohexenecarboxylate: bp 75–76° (15 mm) [lit.[44] bp 47–50° (2 mm)]; NMR δ 1.45–1.85 (m, 4 H), 2.0–2.4 (m, 4 H), 3.67 (s, 3 H), 6.90 (m, 1 H).

Methyl 1-cyclohexane-1-phenylselenocarboxylate can be isolated by work-up prior to oxidation: mp 46–47° (crystallized from pentane); NMR δ 1.1–1.9 (m, 8 H), 1.9–2.3 (m, 2 H), 3.60 (s, 3 H), 7.2–7.7 (m, 5 H); ir 1726, 1578 (w) cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O_2Se$: Se, 26.56. Found: Se, 25.90.

6-Hydroxy-2-hexenoic Acid ε-Lactone (Run 31). Following the selenide preparation outlined in run 1, 0.572 g (5 mmol) of ε-caprolactone gave 0.935 g (70%) of 2-phenylseleno-6-hydroxyhexanoic acid ε-lactone by slow crystallization from pentane at −24°: mp 73–75°; NMR δ ($CDCl_3$) 1.5–2.2 (m, 6 H), 4.28 (m, 2 H), 4.55 (ddd, J = 13, 5.5, 3.5 Hz, 1 H), 7.28 (m, 3 H), 7.55 (m, 2 H), ir ($CHCl_3$) 1716 (br), 1581 (w) cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_2Se$: C, 53.54; H, 5.24. Found: C, 53.50; H, 5.18.

A solution of 135 mg (0.5 mmol) of the above selenide in 2 ml of dichloromethane was ozonized at −78° and then warmed to room temperature with stirring (10 min). Solvent was removed, and the residue was immediately sublimed at 50° (Dry Ice cold finger, 0.2 mm) to give 60 mg of material [80% α,β-unsaturated lactone (ca. 66% yield), 6% Ph_2Se_2, 14% unknown]: NMR δ 1.8–2.3 (m, 2 H), 2.3–2.7 (m, 2 H), 4.17 (m, 2 H), 5.91 (dt, J = 12.5, 1.7 Hz, 1 H), 6.25 (dt, J = 12.5, 4.4 Hz, 1 H); ir 1709 (br), 1640 (sh) cm^{-1}; m/e (calcd for $C_6H_8O_2$, 112.05240) 112.05231.

2-Carbethoxy-2-cyclohexen-1-one (Run 34). To a stirred suspension of 0.63 g (15 mmol) of NaH (57% dispersion in mineral oil; washed free of oil with 3 × 25 ml of pentane) in 30 ml of THF under nitrogen at 0° was added dropwise a solution of 1.86 g (10 mmol) of 2-carbethoxycyclohexanone in 2 ml of THF over a 15-min period. A solution of 2.11 g (11 mmol) of benzeneselenenyl chloride in 5 ml of THF was added rapidly, and the reaction mixture was slowly added with stirring to 50 ml of 50% ether–pentane, 25 ml of saturated $NaHCO_3$ solution, and some ice. The aqueous layer was washed with 50 ml of 50% ether–pentane. The combined organic layers were washed with 25 ml of saturated NaCl solution and dried (Na_2SO_4). 2-Carbethoxy-2-phenylselenocyclohexanone had: NMR δ 1.18 (t, J = 7 Hz, 3 H), 1.3–2.6 (m, 8 H), 4.08 (q, J = 7 Hz, 2 H), 7.24 (m, 3 H), 7.48 (m, 2 H); ir 1712 cm^{-1}.

Into a 100-ml three-necked round-bottomed flask equipped with a dropping funnel, condenser, and thermometer was added the crude selenide in 30 ml of CH_2Cl_2. To the magnetically stirred so-

lution was gradually added 25 mmol of H_2O_2 (2.83 g of 30% H_2O_2 in 2.5 ml of water) over a 10-min period with occasional cooling in an ice bath to keep the temperature between 20 and 30° (CAUTION:[35] do not add more than 10% of the H_2O_2 solution until oxidation has begun). After stirring for an additional 10 min at 25°, the reaction mixture was poured into 25 ml of CH_2Cl_2 and 10 ml of 10% Na_2CO_3 with stirring. The aqueous layer was washed with 25 ml of CH_2Cl_2. The combined organic layers were washed with 25 ml of saturated NaCl solution and dried (Na_2SO_4). Solvent removal gave 1.88 g of 2-carbethoxy-2-cyclohexen-1-one.[1g] Distillation [Kugelrohr, 70° (0.08 mm)] gave 1.63 g (89%) of a 92:8 mixture of keto:enol forms of the cyclohexenone (to minimize enolization the glassware used during the distillation was cleaned with CrO_3·H_2SO_4 and soaked in NH_4OH): NMR δ 1.29 (t, J = 7 Hz, 3 H), 2.06 (m, 2 H), 2.46 (m, 4 H), 4.19 (q, J = 7 Hz, 2 H), 7.49 (t, J = 4 Hz, 1 H); ir 1736, 1712, 1695, 1621 cm^{-1}; *m/e* (calcd for $C_9H_{12}O_4$, 184.07349) 184.07319.

2-Carbethoxy-2-cyclopenten-1-one (Run 35). The commercially available 2:1 mixture of 2-carbethoxy- and 2-carbomethoxycyclopentanones (0.76 g, 5 mmol) was converted to selenide using the procedure for run 34: NMR δ 1.21 (t, J = 7 Hz, 3 H), 1.6–2.6 (m, 6 H), 4.08 (q, J = 7 Hz, 2 H), 7.0–7.4 (m, 3 H), 7.4–7.6 (m, 2 H).

The crude 2-carbethoxy-2-phenylselenocyclopentanone in 15 ml of CH_2Cl_2 was oxidized as in run 34, using 2.15 ml of 15% H_2O_2 solution (9.5 mmol).[35] It is essential to avoid excess H_2O_2. After completion of the oxidation, the organic layer was washed twice with 10 ml of H_2O, and each aqueous portion was back extracted with two 2-ml portions of CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and evaporated. To the residue was added 10 ml of ether to precipitate the benzeneseleninic acid, which was filtered (removal of $PhSeO_2H$ by $NaHCO_3$ extraction appears to cause a small amount of decomposition of the base-sensitive enone). The filtrate was evaporated and distilled [Kugelrohr, 60–65° (0.05 mm)], to yield 0.605 g (81%) of enone[2b] (2:1 mixture of ethyl and methyl esters) which was ~90% pure by NMR: δ 1.32 (t, J = 7 Hz, 3 H), 2.4 (m, 2 H), 2.7 (m, 2 H), 4.18 (q, J = 7 Hz, 2 H), 8.29 (t, J = 2.6 Hz, 1 H); ir 1761, 1729, 1626, 1550 cm^{-1}.

2-Acetyl-2-cyclohexen-1-one. 2-Acetylcyclohexanone[46a] (1.40 g, 10 mmol) was converted to selenide using the procedure of run 34. Pure 2-acetyl-2-phenylselenocyclohexanone can be isolated by preparative TLC of a sample of crude selenide: mp 72–73° (crystallized from ether–pentane); NMR δ 1.3–2.3 (m, 7 H), 2.30 (s, 3 H), 2.5–2.8 (m, 1 H), 7.28 (m, 5 H); ir 1693, 1579 (w) cm^{-1}.

Anal. Calcd for $C_{14}H_{16}O_2Se$: C, 56.96; H, 5.46. Found: C, 57.12; h, 5.48.

Run 36. The crude selenide prepared above was dissolved in 30 ml of dichloromethane and ozonized at −78°. To the reaction mixture was added 2.0 ml (24 mmol) of pyridine, and it was warmed to 25° while stirring. After work-up as described for run 15, sublimation at 35–40° (Dry Ice cold finger, 0.2 mm) gave 1.157 g of enone (84% yield <1% enolized): NMR δ 1.9–2.2 (m, 2 H), 2.35 (s, 3 H), 2.3–2.7 (m, 4 H), 7.56 (t, J = 4.3 Hz, 1 H); ir 1694, 1602 cm^{-1}; *m/e* (calcd for $C_8H_{10}O_2$, 138.06808) 138.06819.

Run 37. Following the oxidation procedure outlined in run 34 (using 10 mmol of H_2O_2), 1.5 g (5 mmol) of crude selenide prepared as above gave 0.68 g of enone (ca. 91% pure, <1% enolized). Distillation using a Kugelrohr [40° (0.07 mm)] gave 582 mg (84% yield) of a 85:15 mixture of keto:enol forms of 2-acetyl-2-cyclohexen-1-one.

Run 38. To a magnetically stirred solution of 1.5 g (5 mmol) of selenide in 30 ml of CH_2Cl_2 was added in small portions 2.03 g (10 mmol) of *m*-chloroperoxybenzoic acid (tech, 85%) in small portions, keeping the temperature between 20 and 30°. Work-up as for run 34 followed by Kugelrohr distillation gave 586 mg (85% yield) of 60:40 mixture of keto and enol forms of enone. The crude material was less than 2% enolized and is sufficiently pure for most purposes.

1-Phenyl-2-phenylthio-1-butanone. The lithium enolate of 1.48 g (10 mmol) of *n*-butyrophenone was prepared at −78° as in run 1, warmed to 25°, and added to 2.62 g (12 mmol) of diphenyl disulfide.[10b] After stirring for 20 min under nitrogen at 25°, the reaction mixture was worked up as usual with the substitution of a 2 *N* NaOH wash for $NaHCO_3$. Preparative TLC followed by crystallization from pentane gave 1.17 g (46%) of sulfide: mp 40–42°; NMR δ 1.02 (t, J = 7.7 Hz, 3 H), 1.5–2.2 (m, 2 H), 4.27 (t, J = 7.4 Hz, 1 H), 7.1–7.6 (m, 8 H), 7.88 (m, 2 H); ir 1682, 1600, 1583 cm^{-1}; *m/e* (calcd for $C_{16}H_{16}OS$, 256.09219) 256.09399.

1-Phenyl-2-phenylsulfino-1-butanone. A mixture of 0.768 g (3 mmol) of 1-phenyl-2-phenylthio-1-butanone and 1.28 g (6 mmol) of $NaIO_4$ in 10 ml of 80% aqueous methanol was stirred at 25° under nitrogen for 24 hr. After filtration and solvent removal, the crude reaction mixture was added to 20 ml of chloroform and was washed with 5 ml of 7% $NaHCO_3$ solution and 10 ml of saturated NaCl solution and dried ($MgSO_4$). Solvent removal, followed by preparative TLC, eluting first with 10% ether–pentane and then 5% methanol–ether gave 0.695 g (85%) of an equal mixture of diastereomers separable by crystallization from ether–pentane, mp 107.5–108.5° [NMR δ ($CDCl_3$) 0.93 (t, J = 7.3 Hz, 3 H), 1.92 (quintet, J = 7.2 Hz, 2 H), 4.64 (t, J = 7.1 Hz, 1 H), 7.2–7.7 (m, 8 H), 7.91 (m, 2 H); ir ($CHCl_3$) 1677, 1598, 1580, 1048 cm^{-1}] and mp 67–68° [NMR δ ($CDCl_3$) 1.03 (t, J = 7.8 Hz, 3 H), 2.33 (m, 2 H), 4.56 (dd, J = 7.8, 6 Hz, 1 H), 7.1–7.9 (m, 10 H); ir ($CHCl_3$) 1670, 1598, 1580, 1042 cm^{-1}].

1-Phenyl-2-phenylsulfino-2-buten-1-one (Run 41). Following the selenide preparation outlined in run 37, 544 mg (2 mmol) of 1-phenyl-2-phenylsulfino-1-butanone (mixture of diastereomers) gave 668 mg (78%) of a viscous mixture of the diastereomers of 1-phenyl-2-phenylseleno-2-phenylsulfino-1-butanone after preparative TLC (50% ether–pentane). Two crystallizations from ether–pentane gave one diastereomer pure, which decomposed above 100°: NMR δ ($CDCl_3$) 0.78 (t, J = 7 Hz, 3 H), 1.5–1.9 (m, 1 H), 2.55–2.95 (m, 1 H), 7.0–8.2 (m, 15 H); ir ($CDCl_3$) 1655, 1598, 1580, 1228, 1075, 1040 cm^{-1}.

Anal. Calcd for $C_{22}H_{20}O_2SSe$: C, 61.82; H, 4.72. Found: C, 61.79; H, 4.74.

Following the oxidation procedure outlined in run 9 (stirring with 1.5 mmol of H_2O_2 for 20 min), 214 mg (0.5 mmol) of sulfinyl selenide (mixture of diastereomers) gave 96 mg (71% yield, >93% one isomer) of sulfinyl enone after preparative TLC (50% ether–pentane). The material was crystallized twice from ether–pentane: mp 72–74°; NMR δ ($CDCl_3$) 1.77 (d J = 7.2 Hz, 3 H), 6.94 (q, J = 7.2 Hz, 1 H), 7.2–7.7 (m, 10 H); ir ($CHCl_3$) 1655 (br), 1598, 1582, 1225 (br), 1078, 1042 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.09; H, 5.22. Found: C, 71.19; H, 5.16.

Additional Spectral Data. Spectral properties of selenides and α,β-unsaturated carbonyl compounds not discussed in detail above are given below.

Run 20. 3-Phenylselenobicyclo[3.2.1]octan-2-one (major isomer, mp 94–96°): NMR δ ($CDCl_3$) 1.5–2.3 (m, 8 H), 2.38 (br s, 1 H), 2.92 (br s, 1 H), 4.13 (dd, J = 8.5, 11.6 Hz, 1 H), 7.24 (m, 3 H), 7.52 (m, 2 H); ir ($CHCl_3$) 1709, 1581 cm^{-1}.

Anal. Calcd for $C_{14}H_{16}OSe$: Se, 28.28. Found: Se, 28.10.

Bicyclo[3.2.1]oct-3-en-2-one:[46b] NMR δ 1.2–2.4 (m, 6 H), 2.7–3.1 (m, 2 H), 5.67 (dd, J = 9.7, 1.5 Hz, 1 H), 7.13 (ddd, J = 9.7, 7.0, 1.5 Hz, 1 H); ir 1705, 1675 cm^{-1}; *m/e* (calcd for $C_8H_{10}O$, 122.07314) 122.07300.

Run 25. 7-Phenylseleno-2-cycloheptен-1-one: NMR δ 1.5–2.6 (m, 6 H), 3.99 (dd, J = 8, 5 Hz, 1 H), 5.95 (dt, J = 12.5, ~1.5 Hz, 1 H), 6.26 (dt, J = 12.5, 4.8 Hz, 1 H), 7.0–7.7 (m, 5 H); ir 1659, 1580 cm^{-1}. **2,6-Cycloheptadien-1-one:** NMR[1c] δ 2.47 (m, 4 H), 5.98 (br d, J = 12 Hz, 1 H), 6.62 (dm, J = 12 Hz, 1 H); ir 1651, 1616 cm^{-1}.

Run 26. *trans*-2-Cyclododecen-1-one: NMR δ 1.1–1.9 (m, 14 H), 2.1–2.6 (m, 4 H), 6.28 (d, J = 16.0 Hz, 1 H), 6.73 (dt, J = 16.0, 6.9 Hz, 1 H); ir[46c] 1692, 1661, 1626 cm^{-1}.

Run 27. Ethyl 2-Phenyl-2-phenylseleno-2-butanoate: NMR δ 1.00 (t, J = 7 Hz, 3 H), 1.16 (t, J = 7 Hz, 3 H), 2.08 (m, 2 H), 4.18 (q, J = 7 Hz, 2 H), 7.25 (m, 10 H). **(*E*)- and (*Z*)-Ethyl 2-Phenyl-2-butenoates**[46d] (54:46 mixture): NMR δ 1.28, 1.22 (t, J = 7.1 Hz, 3 H), 2.02, 1.72 (d, J = 7.2 Hz, 3 H), 4.22, 4.14 (q, J = 7.1 Hz, 2 H), 6.16, 7.06 (q, J = 7.2 Hz, 1 H), 7.0–7.4 (m, 5 H); ir 1717 cm^{-1}.

Run 29. Ethyl Bicyclo[2.2.2]octa-2,5-diene-2-carboxylate: NMR δ 1.30 (t, J = 7.1 Hz, 3 H), 1.33 (m, 4 H), 3.79 (m, 1 H), 4.19 (q + m, 3 H), 6.33, 6.45 (two td, J = 7, 1.7 Hz, 2 H), 7.27 (dd, J = 7.0, 2.0 Hz, 1 H); ir 1597, 1629, 1701 cm^{-1}.

Run 32. 2-Carbethoxy-2-phenylselenocyclooctanone: NMR δ 1.20 (t, J = 6.8 Hz, 3 H), 1.2–2.8 (m, 12 H), 4.10 (q, J = 6.8 Hz, 2 H), 7.2–7.7 (m, 5 H). **2-Carbethoxy-2-cycloocten-1-one:** NMR δ 1.25 (t, J = 6.8 Hz, 3 H), 1.5–2.0 (m, 6 H), 2.1–2.6 (m, 4 H), 4.12 (q, J = 6.8 Hz, 2 H), 7.04 (t, J = 5.2 Hz, 1 H); ir 1727, 1701,

1642 cm^{-1}; *m/e* (calcd for $C_{11}H_{16}O_3$, 196.10989) 196.11024.

Run 33. 2-Carbethoxy-2-phenylselenocycloheptanone: NMR δ 1.23 (t, J = 7 Hz, 3 H), 1.4–2.2 (m, 8 H), 2.52 (m, 2 H), 4.11 (q, J = 7 Hz, 2 H), 7.1–7.6 (m, 5 H); ir 1724 (sh), 1708, 1580 (w), 1224 cm^{-1}. **2-Carbethoxy-2-cyclohepten-1-one:**[46e] NMR δ 1.26 (t, J = 7.2 Hz, 3 H), 1.6–2.0 (m, 4 H), 2.3–2.7 (m, 4 H), 4.13 (q, J = 7.2 Hz, 2 H), 7.16 (t, J = 5.6 Hz, 1 H); ir 1725, 1700, 1638 cm^{-1}; *m/e* (calcd for $C_{10}H_{14}O_3$, 182.09424) 182.09430.

Run 39. 3-Methyl-1-phenyl-2-phenylseleno-1,3-butanedione: mp 119–121°; NMR δ ($CDCl_3$) 1.76 (s, 3 H), 2.32 (s, 3 H), 7.15–7.65 (m, 8 H), 7.88 (m, 2 H); ir 1705, 1672, 1598, 1581 cm^{-1}. **2-Methylene-1-phenyl-1,3-butanedione:**[46f] NMR δ 2.31 (s, 3 H), 5.86 (s, 1 H), 6.46 (s, 1 H), 7.3–7.7 (m, 3 H), 7.77 (m, 2 H); ir 1725, 1670 (br), 1597 cm^{-1}.

Run 40. 2-Butyl-1-phenyl-2-phenylseleno-1,3-butanedione: NMR δ 0.77 (t, J = 7 Hz, 3H), 1.0–2.2 (m, 6 H), 2.29 (s, 3 H), 7.1–7.5 (m, 8 H), 7.83 (dd, J = 8, 2 Hz, 2 H); ir 1698, 1669 cm^{-1} **2-(1-Butylidene)-1-phenyl-1,3-butanedione:** NMR δ 0.82 (t, J = 7 Hz, 3 H), 1.43 (sextet, J = 7 Hz, 2H), 1.99 (q, J = 7 Hz, 2 H), 2.18 (s, 3 H), 6.86 (t, J = 7.6 Hz, 1 H), 7.4 (m, 3 H), 7.76 (dd, J = 8, 2 Hz, 2 H); ir 1692, 1669, 1616, 1603 cm^{-1}; *m/e* (calcd for $C_{14}H_{16}O_2$, 216.11496) 216.11514.

3-Methyl-1-phenyl-2-phenylseleno-1-butanone (3). To a stirred suspension of 238 mg (1.25 mmol) of cuprous iodide in 10 ml of freshly distilled ether at −40° under nitrogen was added 1.52 ml (2.5 mmol) of 1.64 M ethereal methyllithium. After stirring the solution for 2 min, a solution of 146 mg (1.0 mmol) of 1-phenyl-2-buten-1-one in 1 ml of ether was added, followed by a solution of PhSeBr and Ph_2Se_2 [from 390 mg (1.25 mmol) of Ph_2Se_2 and 45 μl (0.85 mmol) of Br_2 in 2 ml of THF]. The reaction mixture was added to 20 ml of 50% ether–pentane and 10 ml of saturated NH_4Cl solution. Normal work-up followed by preparative TLC gave 264 mg (83%) of **3**: mp 43–44° (recrystallized from ether–pentane); NMR δ 0.96 (d, J = 6.8 Hz, 3 H), 1.26 (d, J = 6.8 Hz, 3 H), 2.1–2.5 (m, 1 H), 4.12 (d, J = 10 Hz, 1 H), 7.1–7.5 (m, 8 H), 7.77 (m, 2 H); ir 1678, 1596, 1582 cm^{-1}.

Anal. Calcd for $C_{17}H_{18}OSe$: C, 64.35; H, 5.72; Se, 24.89. Found: C, 64.31; H, 5.69; Se, 24.76.

3-Methyl-1-phenyl-2-buten-1-one (4). Oxidation of 159 mg (0.5 mmol) of **3** as in run 9 (stirring for 30 min with H_2O_2) followed by purification (preparative TLC) gave 70 mg (87.5% yield) of **4**: NMR[47] δ 1.98 (d, J = 1.3 Hz, 3 H), 2.17 (d, J = 1.3 Hz, 3 H), 6.62 (m, 1 H), 7.36 (m, 3 H), 7.79 (m, 2 H); ir 1665, 1616 cm^{-1}.

2-Phenylselenocyclooctanone (8a). Following the selenide preparation outlined in run 1 using 10.5 mmol of LDA and 11 mmol of PhSeBr, 1.26 g (10 mmol) of cyclooctanone gave 1.92 g (70% yield, >95% yield based on recovered cyclooctanone from sublimation of crude selenide) of **8a** after purification by dry column chromatography on silica gel (10% ether–pentane). The selenide was crystallized twice from pentane at −24°: mp 25.5–27°; NMR δ 0.9–2.3 (m, 11 H), 2.70 (td, J = 11, 4.5 Hz, 1 H), 3.58 (dd, $J \simeq 7$, 6 Hz, 1 H), 6.9–7.5 (m, 5 H); ir 1691, 1581 cm^{-1}. This material was used in the mechanistic and yield experiments involving **13a**.

Anal. Calcd for $C_{14}H_{18}OSe$: C, 59.79; H, 6.45. Found: C, 59.78; H, 6.51.

2-(*m*-Trifluoromethylphenylseleno)cyclooctanone (8b). Following the selenide preparation outlined above, using *m*-trifluoromethylbenzeneselenenyl chloride instead of PhSeBr, gave 2.27 g (65% yield) of **8b**. The selenide was crystallized twice from pentane at −24°: mp 36–38°; NMR δ 0.9–2.4 (m, 11 H), 2.75 (td, J = 11, 4.5 Hz, 1 H), 3.69 (dd, $J \simeq 7.5$, 6.5 Hz, 1 H), 7.1–7.9 (m, 4 H); ir 1692, 1600 (w), 1580 cm^{-1}. This material was used in the mechanistic and yield experiments involving **13b**.

Anal. Calcd for $C_{15}H_{17}F_3OSe$: C, 51.58; H, 4.91. Found: C, 51.52; H, 4.94.

Comparative Elimination Products of 13a and 13b (Table II). The following procedure for method B serves as a typical model for the isolation and characterization of the compounds listed in Table II. To a stirred solution of 281 mg (1 mmol) of **8a** in 2 ml of dichloromethane containing 0.2 ml (2.4 mmol) of pyridine was added 3 mmol of H_2O_2 (341 mg of 30% H_2O_2 in 0.3 ml of water), and the reaction mixture was stirred at 25° for 25 min. The reaction mixture was added to 10 ml of dichloromethane, was washed with 310 mg (2.5 mmol) of $Na_2CO_3 \cdot H_2O$ in 1 ml of water (save), 2 ml of 10% HCl solution, 2 ml of saturated NaCl, and dried (Na_2SO_4). After solvent removal, sublimation at 50–60° (Dry Ice cold finger, 0.3 mm) of the crude product gave 40 mg of a mixture of 2-cycloocten-1-one (**9**)[1c] and 1,2-cyclooctanedione (**11**).[48] These were separated, and relative yields were determined by GLC (20% Carbowax on Chrom W, 150°) and NMR integration. **9**: NMR δ 1.4–2.0 (m, 6 H), 2.3–2.7 (m, 4 H), 5.86 (br d, J = 12 Hz, 1 H), 6.31 (dt, J = 12, 6.7 Hz, 1 H); ir 1668 cm^{-1}. **11**: NMR δ 1.5–2.0 (8 H, m), 2.4–2.7 (m, 4 H); ir 1709 cm^{-1}. Quinoxaline derivative: mp 119–121° (lit.[48] mp 120.2–120.7°); *m/e* (calcd for $C_8H_{12}O_2$, 140.08373) 140.08441.

The yield of 2-phenylseleno-2-cycloocten-1-one (**10a**) (and recovered **8a** for method C) was obtained by preparative TLC of the pot residue (20% ether–pentane): NMR δ 1.4–2.0 (m, 6 H), 2.1–2.5 (m, 4 H), 6.27 (t, J = 5.8 Hz, 1 H), 7.2–7.7 (m, 5 H); ir 1688, 1658, 1590 (w), 1579 cm^{-1}; *m/e* (calcd for $C_{14}H_{16}OSe$, 280.03663) 280.03646.

The aqueous Na_2CO_3 layer was acidified, washed with 25 ml of ethyl acetate, and dried (Na_2SO_4) to give 118 mg of a 60:40 mixture of 1,8-octanedioic acid (**12**) and $PhSeO_2H$ by NMR analysis. Pure **12** was obtained by reducing the $PhSeO_2H$ to Ph_2Se_2 ($Na_2S_2O_3$), mp 140°, with authentic **12** mmp 140–142°.

For the other entries in Table II, the oxidation procedures of run 1 ($NaIO_4$–$NaHCO_3$), run 10 (method C, no pyridine added), and run 15 (method D) were done on 1-mmol samples of **8a** and **8b** as listed. The isolation and characterization techniques described above were used. With **8b**, 2-(*m*-trifluoromethylphenylseleno)-2-cycloocten-1-one (**10b**) was obtained: NMR δ 1.4–2.0 (m, 6 H), 2.2–2.6 (m, 4 H), 6.40 (t, J = 5.7 Hz, 1 H), 7.2–7.9 (m, 4 H); ir 1688, 1663, 1591 (w), 1580 (w) cm^{-1}.

Crossover Experiments (Table III). The oxidation procedures of run 10 (method C, no pyridine added) and run 15 (method D) were followed on mixtures of **8b** and 1-phenyl-2-phenylseleno-1-butanone as indicated in Table III. The relative yields of products **9**, **10a**, and **10b** were determined using the isolation and characterization techniques described in the Experimental Section for Table II.

Redox Studies. A. Selenoxide (18) plus Selenide (2) (Equation 8). A solution of 76 mg (0.25 mmol) of 1-phenyl-2-phenylseleno-1-butanone in 1 ml of dichloromethane was ozonized at −78°, and 72 mg (0.25 mmol) of **2** was added. The reaction mixture was warmed to 25° and worked up as usual. The relative yields of products as indicated in eq 8 were determined by NMR comparison with known compounds. The addition of 0.5 mmol of pyridine or diisopropylamine before warm-up gave only 1-phenyl-2-buten-1-one and recovered **2**.

B. Selenoxide (18) plus Selenol. The procedure above (A) was repeated with the substitution of 39 mg (0.25 mmol) of benzeneselenol for **2**. The NMR of crude product indicated >90% recovered 1-phenyl-2-phenylseleno-1-butanone and <10% 1-phenyl-2-buten-1-one.

C. Selenoxide plus H_2SO_4 (Equation 7). A solution of 152 mg (0.5 mmol) of 1-phenyl-2-phenylseleno-1-butanone in 4 ml of methanol was ozonized at −40°, and 0.11 ml of concentrated H_2SO_4 was added to give 0.5 M methanolic H_2SO_4. The reaction mixture was warmed to −5° with stirring for 4 hr and then left at 0° for an additional 64 hr. Normal work-up and preparative TLC gave 106 mg (68%) of recovered selenide and 28 mg (80% pure, ca. 22% yield) of 2,2-dimethoxy-1-phenyl-1-butanone: NMR δ 0.74 (t, J = 7.7 Hz, 3 H), 1.93 (q, J = 7.7 Hz, 2 H), 3.28 (s, 6 H), 7.4 (m, 3 H), 8.16 (m, 2 H); ir 1697, 1598, 1579 cm^{-1}. Quinoxaline derivative of 1-phenyl-1,2-butanedione gave suitable physical and spectral properties.[49]

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