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ORGANOSELENIUM CHEMISTRY

A STUDY OF INTERMEDIATES IN THE FRAGMENTATION OF ALIPHATIC KETOSELENOXIDES. CHARACTERIZATION OF SELENOXIDES, SELENENAMIDES AND SELENOLSELENINATES BY ^{1}H-, ^{13}C- and ^{77}Se-NMR[1,2]

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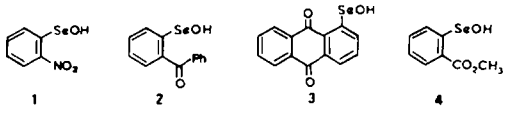
Abstract—A series of β-ketoselenenic acids was generated at low temperature (−20° to −50°) by selenoxide *syn* elimination of appropriate selenoxides (**13-ox**, **16-ox**, **35-ox**, **38-ox**, and **39-ox**). No evidence for the buildup of significant concentrations of selenenic acid was obtained. A selenolseleninate (**15**, 2,2' - diseleno - bis(1 - phenyl - 2 - methyl - 1 - propanone) - Se - oxide) was detected as an intermediate in the decomposition of **13-ox** and **16-ox**. This compound, which is stable in solution below −50° was characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{77}Se) and by its thermal decomposition and reactions with phosphite (reduction to diselenide **6**) and dialkylamines (formation of selenenamide **11**). Decomposition of **15** in the presence of dibenzylamine resulted in trapping of a selenenic acid-like species (RSeSeOH) to give $RSeSeN(CH_2Ph)_2$ (R = $PhC(O)C(CH_3)_2$). Although **15** could not be prepared by oxidation of diselenide **6**, it was possible to prepare a cyclic selenolseleninate (4,4-dimethyl-1,2-diselenolane monoxide, **20**) by oxidation of the related diselenide (**19**). Attempts to prepare more stable aliphatic selenenic acids by blocking the principal decomposition pathway of **15** were not successful. Thus 1 - benzoyl - 1 - cyclopropaneselenenic acid was generated from **35-ox** and **38-ox** and 1 - benzoyl - 2,2 - dimethylcyclopropaneselenenic from **39-ox**. The former underwent normal disproportionation (to **36** and **37**) even when prepared at −49°. The latter gave what appeared to be a selenolseleninate (**40**) which again disproportionated at −17°.

Selenenic acids and their derivatives play a key role in many areas of organoselenium chemistry. They are reactive intermediates during the oxidation of diselenides and selenols,[2b,3a] the reduction of seleninic acids,[2b,3,4] the hydrolysis of selenenyl halides[5] and they are formed during selenoxide *syn* eliminations[2b,2c,6] and [2,3]-sigmatropic rearrangements.[2d,2e,6b] In the form of their acid chlorides, mixed anhydrides,[3b,2f] amides,[2g] and imides[7] they are useful selenium electrophiles. Finally, there is the intriguing proposal that the oxidized form of the redox selenoenzyme glutathione peroxidase contains a selenenic acid in the form of a selenocysteine residue at the active site.[8] However, in spite of their central position in organoselenium chemistry, only three selenenic acids (e.g. **1**,[2c,4a,5b,9] **2**,[4b,9] **3**[5c]) have been isolated and characterized and a fourth **4**[2a] has been characterized in solution.[10] All are aromatic selenenic acids having electron-withdrawing groups at the ortho positions. Even these exceptionally stable selenenic acids share with their less stable aromatic and aliphatic



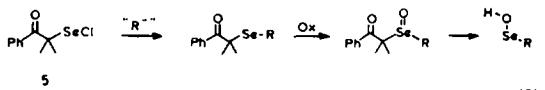
counterparts a tendency towards disproportionation Eq. (1).

$$3RSeOH \rightleftharpoons RSeSeR + RSeO_2H + H_2O. \quad (1)$$

We undertook a study of aliphatic selenenic acids to determine whether electronic or steric factors could be identified which would stabilize selenenic acids and help in understanding and eventually characterizing the selenium in glutathione peroxidase.[8]

RESULTS AND DISCUSSION

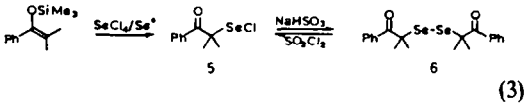
The technique we employed for the preparation of selenenic acids is the selenoxide *syn* elimination,[2a,2c,6] a reaction which, in suitable cases, can occur at temperatures below −50°.[2b] Several systems were chosen for study using the criteria that they be easily prepared, that selenoxide elimination be regioselective and that starting materials and products have informative NMR spectra for low temperature spectroscopic characterization. The overall strategy is illustrated in Eq. (2), in which the α-seleno isobutyrophenone group is a selenenic acid synthon.



(2)

Starting materials

Preparation of the precursor selenenyl chloride **5** proved most convenient by the reaction of "$SeCl_2$"[11] (prepared from the reaction of selenium tetrachloride and an equimolar amount of selenium) with the enol silyl ether of isobutyrophenone (Eq. (3)). It proved to be most effective to reduce **5** to the crystalline diselenide **6**, which could be purified and converted back to **5** as needed by treatment with sulfuryl chloride.



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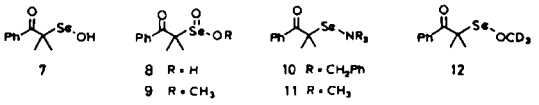
The first target chosen was the selenenic acid **7**. It was hoped that the combination of steric hindrance and a



7 8 R = H 9 R = CH_3 10 R = CH_2Ph 11 R = CH_3 12

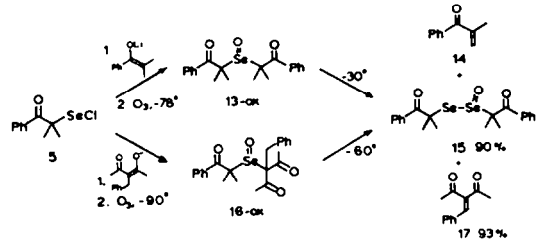
nearby polar group (as in the stable selenenic acids **1–4**) capable of interacting with the selenenic acid might stabilize **7** enough for observation. To set the stage for this work several additional selenium compounds were prepared in this series to aid the identification of products expected to be encountered during the study. The seleninic acid **8** was prepared by ozonolysis of diselenide **6** in the presence of a small amount of water. If the oxidation of **6** was carried out in deuteromethanol with NMR observation at low temperature, it was actually possible to observe first a material tentatively identified as the seleninic anhydride, then a ~1:1 mixture of acid **8** and ester **9**. The acid rapidly reacted with methanol so that after a few minutes at −20° only **9** was observed. It showed a characteristic pair of diastereotopic methyl resonances at δ 1.80 and 1.88. The ^{77}Se-NMR resonances of **8** and **9** (Table 1) are close to other seleninic acids which have been reported (e.g. $PhSeO_2H$: δ 1197; CH_3SeO_2H: δ 1216[12]).

The selenenamides **10** and **11** were prepared from selenenyl chloride **5** according to literature procedures.[2g,5b] They could not be isolated in pure form, but were identified spectroscopically in solution. Their ^{77}Se chemical shifts were in the same region as other selenenamides (e.g. $PhSeN(CH_3)_2$: δ 929).

A number of attempts were made to prepare the selenenate ester **12** from **5**. These attempts did not succeed, nor was **12** identified during experiments where **7** was generated in methanol solution.

In situ *generation of selenenic acid*

Two precursors to the selenenic acid **7** were prepared. The first was the selenoxide **13-ox**, easily obtained by selenation of isobutyrophenone enolate (selenation of enol silyl ether was unsuccessful)[2h] followed by low temperature oxidation with ozone (Eq. (4)). This selenoxide decomposed at −30° in deuterochloroform ($t_{1/2} \approx 20$ min) and at −20° in deuteromethanol ($t_{1/2} \approx 33$ min) to enone **14** and a product which was different from the expected disproportionation products diselenide **6** or seleninic acid **8**. The selenenic acid (**7**) structure could also be ruled out on the basis of the ^{1}H-NMR spectrum whose most characteristic feature was a 1:1:1:1 pattern of four methyl singlets (Fig. 1). We eventually assigned structure **15** to this compound. Since this selenolseleninate was the first of its kind,[13] a careful characterization was in order, but this proved difficult since **15** decomposed at temperatures comparable to those needed for its formation from **13-ox**.



(4)

Compound **16-ox** was chosen as a more labile precursor, based on observations[2h] that β-dicarbonyl selenoxides were especially unstable. In fact, **16-ox** fragmented smoothly at −60° in CD_2Cl_2 ($t_{1/2} \approx 18$ min) and at −52° in CD_3OD ($t_{1/2} \approx 35$ min). Again, essentially the only products observed were the expected enedione **17** and compound **15**, which was stable for at least 1 hr under the conditions of its formation.

Spectroscopic characterization of selenolseleninate **15**

Typical "thermolyses" of **16-ox** were carried out at −50°, the samples were cooled to −91° and inserted into the probe of the NMR spectrometer precooled to

Table 1. NMR spectroscopic data for compounds in the isobutyrophenone series R = $PhC(O)C(CH_3)_2$

		^{1}H-NMR					^{77}Se-NMR[a]		
Compound	No.	Solvent	Temp (°)	δCH_3	($^3J_{SeH}$)	δ ortho-Ar	Solvent	Temp (°)	δ Se[b]
RSeR	**13**	$CDCl_3$	24	1.68	(12)	7.88	$CDCl_3$	24	608
RSe(O)R	**13-ox**	$CDCl_3$	−50	1.76		7.86			
				1.82					
RSeSeR	**6**	CD_2Cl_2	24	1.66	(12)	7.68	$CDCl_3$	24	561
							CD_2Cl_2	24	566
RSeCl	**5**	$CDCl_3$	24	2.09		7.89	$CDCl_3$	24	1145
$RSeNMe_2$	**11**	$CDCl_3$	24	1.69	(10)	7.95	$CDCl_3$	−56	994
$RSeN(CH_2Ph)_2$	**10**	$CDCl_3$	24	1.63	(12)	7.89	$CDCl_3$	0	948
RSe(O)OH	**8**	$CDCl_3$	24	1.82	(~8)	7.78	CD_3COCD_3	0	1240
$RSe(O)OCD_3$	**9**	CD_3OD	24	1.80		7.78	CD_3OD	0	1305
				1.88					
RSe(O)SeR	**15**	CD_2Cl_2	−56	1.80	(12)	7.72	CD_2Cl_2	−56	862
				1.84	(12)	7.86			540
				1.950	(~22)				
				1.956	(~22)				
$RSeSeN(CH_2Ph)_2$	**27**	CD_2Cl_2	24	1.80	(9.5)	8.05	CD_2Cl_2	−10	962
									566

[a] For previous studies of ^{77}Se shifts see W. McFarlane and R. J. Wood, *J. Chem. Soc. Dalton* 1397 (1972); J. D. Odom, W. H. Dawson and P. D. Ellis, *J. Am. Chem. Soc.* **101**, 5815 (1979) and references therein; G. Llabres, M. Baiwir, J.-L. Piette and L. Christiaens, *Org. Magn. Reson.* **15**, 152 (1981).

[b] Chemical shifts are downfield from external Me_2Se.

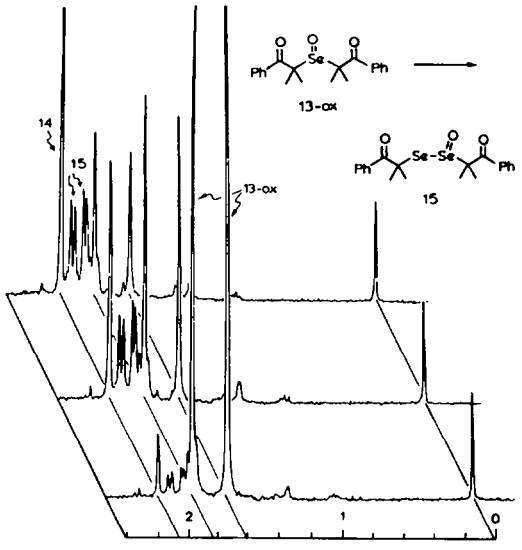


Fig. 1. Thermolysis of **13-ox** at −20° in CD_3OD. Formation of intermediate **15** at: (a) t = 6 min; (b) t = 21 min; (c) t = 33 min.

−80°. Complete characterization by ^1H-, ^{13}C- and ^{77}Se-NMR was now possible. Extensive use of the technique of spin polarization transfer (INEPT) as outlined by Ernst and Doddrell[14] was made to improve signal-to-noise, employing either one bond or long range ($^1J_{CH}$, $^2J_{CH}$, $^3J_{CH}$ or $^3J_{SeH}$) couplings. Simultaneous observation of both selenium resonances of **15** by this technique was almost impossible since, after much experimentation, it was discovered that the one at 540 ppm was coupled to the nearby methyl protons by J = 12 Hz, whereas the other at 862 ppm had a coupling of ~22 Hz. Thus when the INEPT parameters were optimized for the observation of one, the intensity of the other was essentially zero. These results show that the INEPT techniques must be used with proper care. Table 1 summarizes some of the spectral data obtained for **15** as well as several model systems. The observations of two sets of diastereotopic methyl groups in both ^1H and ^{13}C spectra, as well as two selenium signals, one close to the position expected for selenoxides (e.g. **18**), see Fig. 2, the other close to the resonance of **6**, are fully consistent with the assigned structure. The selenium resonances of **15** bear a similar relationship to each other and to those of diselenide **6** as

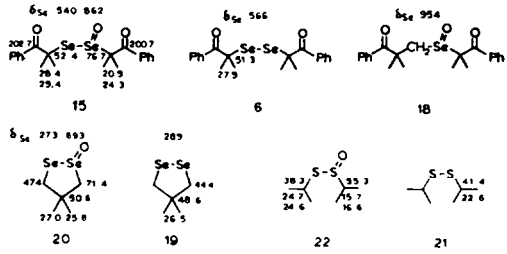


Fig. 2. ^{13}C- and ^{77}Se-NMR chemical shifts.

do those of the model compounds **19** and **20** (*vide infra*). Thus $\Delta\delta$ for **15** is 322 ppm, whereas $\Delta\delta$ for **20** is 420 ppm. Furthermore, the upfield resonance of **15** is 26 ppm upfield of **6**, whereas the upfield resonance of **20** is 16 ppm upfield of diselenide **19**.

Support for the structural assignment of **15** can also be found by comparison of the ^{13}C chemical shifts with those of **19**, **20** and some thiolsulfinates.[15] Thus the two α-carbons of **15** differ by 24.3 ppm, those of **20** by 24.0 ppm whereas those of the thiolsulfinate **22** differ by 17.0 ppm. Two of methyl groups of **15** also show an upfield shift compared to the other two, and compared to **6** (γ-effect of oxygen). This is also seen when **21** and **22** are compared.

Reactions of selenolseleninate **15**

Additional structural evidence was provided by chemical studies. When compound **15** was treated with trimethylphosphite[2f] at −91° the dark yellow color of the solution immediately lightened, and ^1H-NMR observation at −80° showed that diselenide **6** (74%) as well as other products (see Table 2, entry 2) from decomposition of the selenolseleninate were present. Approximately 1.2 equivalents of phosphite were needed to completely reduce a sample of **15**.

When a solution of **15** in deuterodichloromethane was warmed above −20° it decomposed, giving, after warmup to room temperature, a complex mixture of products as shown in Table 2, entry 1. Apparently the normal disproportionation is only a minor pathway; the major reaction appears to be a cycloelimination of the selenolseleninate **15** to enone **14**, accompanied by additional redox reactions leading eventually to **6** and the tri- and tetraselenides **23** and **24** (R_2Se_3 and R_2Se_4, R = $PhC(O)C(CH_3)_2$). The picture is further confused by the fact that seleninic acid **8** itself

Table 2. Yields of reaction products from **16-ox** and selenolseleninate **15**

Entry	Reaction	Observed at T(°)	**17**	**14**	**6**[a]	**23**[a,b],**24**[a,b]	Other
1	**16-ox**, −50° to 25°	25	100	57	22	28	**8**(8)
2	**15**, $P(OCH_3)_3$, −91°	−80	86	4	74	9	
3	**15**, $HN(CH_2Ph)_2$, −50°	−30	98	50	15		**76**(27),[a] 6[c]
4	**15**, $HNMe_2$, −50°	−30		35	25	14	**23**(11), 14[c]
5	**16-ox**, $HN(CH_2Ph)_2$, −91°	−55	67				**70**(15),[a] 27(**10**), 37,[d] 6[c]
6	**16-ox**, $HN(CH_2Ph)_2$, −91°; −55°, 10 min; 25°, 5 min	25	67	42	14		27(**10**), 37,[d] 6[c] **52**(27)

[a] Yields for diselenide **6**, tri- and tetraselenides **23** and **24**, selenolseleninate **15**, and diselenoamide **27** were calculated on the basis that a maximum of 0.5 mmol could form from 1.0 mmol of **16-ox**.

[b] Compound **23**: $R(Se)_3R$; compound **24**: $R(Se)_4R$, R = $PhC(O)C(CH_3)_2$. Yields of **23** and **24** are combined in the table.

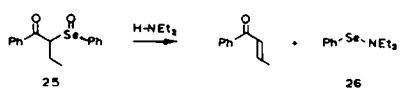
[c] Isobutyrophenone.

[d] 3-Benzyl-2,4-pentanedione.

decomposes to **14**, **6** and **23**, although this occurs only slowly at room temperature. More details of the decomposition pathway were obtained from the reactions with secondary amines outlined below.

Reactions with secondary amines

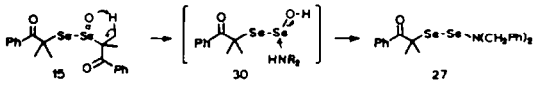
A characteristic reaction of selenenic acids is the reaction with amines to form selenenamides. For example, when selenoxide **25** was allowed to



25 **26**

decompose in the presence of diethylamine, the selenenamide **26** was observed as a product.[2h,2g] We therefore undertook a series of experiments in which the decomposition of **13-ox** and **16-ox** as well as **15** were carried out in the presence of dibenzylamine and dimethylamine.

Selenoxide elimination of **13-ox** at $-20°$ in the presence of dibenzylamine gave the expected selenenamide **10** and diselenide **6** in a 4:1 ratio, in addition to enone **14** (see also Table 2, entry 5). The preformed selenolseleninate **15**, however, is stable in the presence of dibenzylamine at $-50°$. A reaction occurred when the temperature was raised above $-35°$, although no selenenamide **10** was formed, but rather a compound very similar to it (Table 2, entry 3). We have assigned structure **27** to this product on the basis of its spectral



15 **30** **27**

(5)

properties and method of formation. A key observation was that **27** appeared to be formed at the same rate as enone **14**, and was therefore not a result of a direct reaction between **15** and dibenzylamine, but a product of its decomposition. Compound **27** had a proton methyl resonance at δ 1.80, a $PhCH_2N$ resonance at 3.77 (which showed selenium satellites, $^3J_{SeH} = 13$ Hz) and a characteristic ortho-aryl proton resonance at 8.05 δ. The compound also showed two selenium resonances at 566 and 962 ppm, which are quite close to the resonances of diselenide **6**, 561 ppm and selenenamide **10**, 994 ppm. The compound was stable in solution up to room temperature, but decomposed upon attempted chromatographic purification.

When **16-ox** was decomposed in the presence of dibenzylamine a complex mixture was obtained, including selenenamide **10** (27%) (Table 2, entry 5). Thus dibenzylamine reacts with **16-ox** directly (giving 3-benzyl-2,4-pentanedione), with the presumed intermediate selenenic acid (giving **10**) as well as with the selenolseleninate **15** (giving **27**).

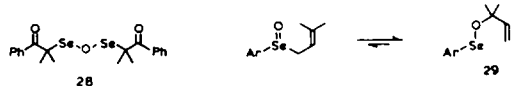
Reactions with dimethylamine were also complex, but differed from those with dibenzylamine in one significant fashion: selenolseleninate **15** did give selenenamide **11** in addition to an array of other products (Table 2, entry 4). Thus **15** shows selenenic acid-like reactivity, as expected from known reactions of thiolsulfinates.[16] The difference in the behaviour of dimethylamine and dibenzylamine can be rationalized in terms of the greater nucleophilicity of the former. Dibenzylamine does not react with **15** before it decomposes, whereas dimethylamine does.

Scheme 1 summarizes the results obtained during our attempts to detect selenenic acid **7**. Two new selenium functional groups (**15** and **27**) were detected and characterized. The formation of **15** is probably

7 **15**

entirely analogous to that of sulfur analogues,[17] involving bimolecular dehydration of two molecules of the selenenic acid. The equilibrium between **7** and **15** must lie very far on the right, since the reactions described with dibenzylamine show that the decomposition is faster than reversal to selenenic acid (selenenamide **10** should have been formed in the reaction of **15** with dibenzylamine if dissociation to **7** occurred). Furthermore, even in methanol solution neither the selenenic acid nor the selenolseleninate appear to undergo solvolysis.

One species which was not observed even though numerous attempts were made to prepare it was the selenenic anhydride **28**. This substance should be more



28 **29**

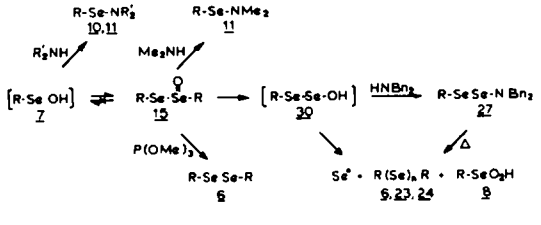
stable than the isomeric selenolseleninate **15**, on the basis that the allyl selenenate **29** is more stable than the selenoxide by ~ 11 kcal mol^{-1}.[2e] In addition, dehydration of *o*-nitrobenzeneselenenic acid **1** gives only the symmetric anhydride form, and no selenolseleninate.[2c,9] We assume that **15** is the kinetic product of the dehydration, and it decomposes under all conditions tried to isomerize it to its (presumably) more stable isomer **28**.

The formation of compound **27** is explained by trapping of the intermediate selenenic acid-like species **30** which is the expected primary product of the *syn*-eliminations of **15**[18] Eq. (5).

The results obtained during the reaction of dibenzylamine with **16-ox** and **15** demonstrate that the selenenic acid **7** is a substantially more potent selenenylating (RSe^+) agent than is the selenolseleninate **15**, since the former reacts with dibenzylamine to form selenenamide whereas the latter does not.

Oxidation of diselenides as a route to selenolseleninates

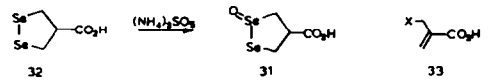
There are many reports in the literature on the successful preparation of thiolsulfinates by oxidation of disulfides.[15,16b,18] We made a number of attempts to prepare **15** by the oxidation of **6** with *m*-chloro-



Scheme 1. Reactions of the selenenic acid **7**.

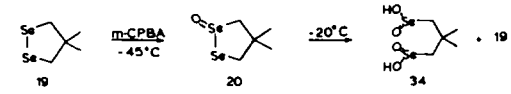
perbenzoic acid or ozone, but at most traces of the desired product were obtained.

There is one literature report of an unstable selenolseleninate (**31**) prepared by oxidation of diselenide **32**.[19] We could not duplicate Bergson's work



exactly (ammonium persulfate did not possess solubility levels suitable for NMR), so H_2O_2 in CD_3OD was substituted for ammonium persulfate in aqueous ethanol. Under these conditions oxidation of **32** led to immediate formation of a substituted methacrylic acid species **33**, which slowly solvolyzed to a second similar species. These products were not securely identified.

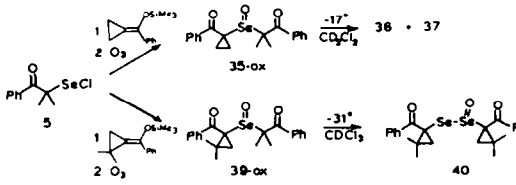
A simpler system in which this decomposition is blocked was investigated. Oxidation of the diselenide **19** with ozone or *m*-chloroperbenzoic acid at $-45°$ gave a species whose spectral properties (Experimental) identified it as the selenolseleninate **20**. Compound **20** decomposed at $-20°$ to give a mixture of **19** and the insoluble bis-seleninic acid **34** (δ Se of dimethyl ester in deuteromethanol: 1314 ppm).



Search for more stable selenenic acids or selenolseleninates

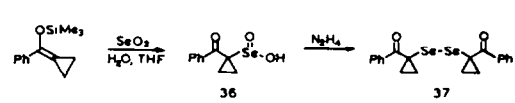
The results described above have shown clearly that intermediates more stable than **15** can only be prepared if the *syn* elimination of the selenolseleninate is prevented. An effective way of doing this should be to replace the gem-dimethyl group by cyclopropyl, since cyclopropyl selenoxides fragment only at elevated temperatures.[20] Hence two additional systems were studied, although not as thoroughly as in the previous case.

The first (**35-ox**) was prepared as before by use of the isobutyrophenonyl selenenyl chloride **5** as shown in Eq. (6). In this case, the enol silyl ether of phenyl cyclopropyl



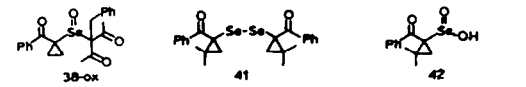
(6)

ketone reacted cleanly with selenenyl chloride. Authentic samples of seleninic acid and diselenide were prepared as shown in Eq. (7).



(7)

The fragmentation of **35-ox** proceeded at a substantially slower rate ($t_{1/2} \approx 35$ min at $-17°$) than did the gem-dimethyl analog **13-ox** ($t_{1/2} \approx 20$ min at $-30°$). The only products observed were the seleninic acid **36** and the diselenide **37**, the bulk of which precipitated. The same results were obtained when the more labile selenoxide **38-ox** ($t_{1/2} \approx 35$ min at $-49°$) was allowed to decompose.



The final system examined (**39-ox**) was prepared as in Eq. (6). Decomposition occurred rapidly at $-31°$ in deuterochloroform ($t_{1/2} < 5$ min). The ^{1}H-NMR spectrum of the product was complex, showing a pattern of seven methyl singlets (a maximum of 16 is expected for the four possible diastereomers of the selenolseleninate **40**). The ^{77}Se-NMR spectrum (CD_2Cl_2, $-52°$) showed resonances at 845 and 484 ppm, consistent with structure **40**. The intermediate was stable up to about $-17°$, at which point the corresponding diselenide (**41**) (δ Se 484, 499 for two diastereomers) and seleninic acid (**42**) appeared. Thus all three known selenolseleninates (**15**, **20**, **40**) decompose below $-10°$. The selenolseleninate **40** can also be cleanly reduced to diselenide with trimethylphosphite.

Summary—Attempts to generate several ketoselenenic acids have been unsuccessful although in three cases selenolseleninates were characterized spectroscopically and chemically. Their detection provides support for the idea that they are intermediates in the disproportionation as well as comproportionation[2b] of diselenides and seleninic acids. A second new selenium species of type $RSeSeNR'_2$ was obtained by interception of a reactive intermediate (RSeSeOH) with dibenzylamine.

EXPERIMENTAL

General. ^{1}H-NMR spectra were obtained on either a JEOL MH-100 (100 MHz), IBM WP-200SY (200 MHz), or Bruker WH-270 (270 MHz) spectrometer; ^{13}C-NMR spectra were obtained on either a JEOL FX-60 (15 MHz) or JEOL FX-200 (50.10 MHz) spectrometer; and ^{77}Se-NMR spectra were obtained on a JEOL FX-200 (38.00 MHz) spectrometer. IR spectra were obtained on a Beckman Acculab 7 spectrophotometer and MS on an AEI MS-902 spectrometer. Unless otherwise specified, NMR and CMR spectra were measured in $CDCl_3$ with TMS as an internal standard ($\delta = 0.00$); in cases of Si containing compounds, CH_2Cl_2 ($\delta = 5.32$) was used. Se shifts are referenced externally with respect to dilute solns of Me_2Se ($\delta = 0.00$) in the appropriate solvent. IR spectra were of the neat liquid between salt plates. M.ps and b.ps are uncorrected; all reaction temps were measured externally.

Starting materials were commercially available except for selenium tetrachloride,[21] 1 - benzoyl - 2,2 - dimethylcyclopropane,[22a] and 3 - benzyl - 2,4 - pentanedione[22b] which were prepared according to lit. procedures. THF was freshly distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2 and stored in an amber bottle over 4 Å molecular sieves. All reactions reported herein were carried out under an atmosphere of dry N_2, unless otherwise noted. Apparatus for anhyd reactions were dried in a 110° oven for at least 1.5 hr. Preparative TLC was carried out using Merck PF-254 (UV active) silica gel and dry column chromatography on MC silica gel. "Chromatotron" refers to Harrison Research's preparative, centrifugally accelerated, radial thin layer chromatograph. Using 9½ in diameter rotors coated with a 2 mm thick layer of Merck 69PF-254 (UV active) silica gel, with a solvent flow rate of 4.5 ml min^{-1}, bands are reported in the order they elute off the rotor. "Kugelrohr" refers to the Aldrich Chemical Co.'s apparatus for bulb-to-bulb distillation, and

temperatures reported indicate the highest bath temperature attained. In the work-up procedures, Na_2SO_4 was used as a drying agent and solvents were removed using a rotary evaporator.

Isobutyrophenone enol silyl ether. In a 100 ml round bottom flask at 0°, 3.4 g (4.4 ml, 21 mmol) of hexamethyldisilazane in 20 ml of THF was allowed to react with 13.3 ml (1.5 M, 20 mmol) of n-BuLi for 5 min. At this time, 2.96 g (3 ml, 20 mmol) of isobutyrophenone was added to the lithium hexamethyldisilazide (LiHMDS) sol, and allowed to warm to 22° over the course of 5 min. Chlorotrimethylsilane (TMSCl) (3 g, 3.6 ml, 28 mmol) was added and stirred for 10 min. Workup was effected by pouring into 30 ml of 7% $NaHCO_3$, extracting with 20 ml of 50% ether–pentane, washing with 15 ml of 1.2 M HCl, 15 ml of 7% $NaHCO_3$, and 15 ml of brine. The organic layer was filtered through a cone of Na_2SO_4 and concentrated. Residue was distilled (Kugelrohr, 60°, 0.5 mmHg) to yield 4.75 g of the enol silyl ether as a clear liquid (17 mmol, 85% yield); NMR (100 MHz): δ 1.67 (s, 3H), 1.76 (s, 3H), 7.28 (s, 5H); IR: 2960, 1605, 1495, 1260, 1162, 930, 852 cm^{-1}; MS: M^+ 220.1283 (calc for $C_{13}H_{20}OSi$, 220.1283).

Bis-(2-benzoyl-2-propyl) diselenide (**6**). In a 25 ml flask equipped with a magnetic stirrer was placed 0.56 g (2.5 mmol) of $SeCl_4$[21] and 0.21 g (2.6 mmol) of grey powdered Se in 8 ml of THF. This was stirred at 22° for 15 min, then cooled to 16° (cold H_2O bath) and 1.1 g (1.57 ml, 5 mmol) of isobutyrophenone enol silyl ether was added and the resulting soln allowed to stir 5 min. After stirring for 5 min (the soln had solidified into a light yellow mass) 25 ml of H_2O containing approx. 3 g (29 mmol) of $NaHSO_3$ was added and then allowed to stir for 20 min. Workup was effected by extraction with CH_2Cl_2, washing with 10% HCl, washing with brine, and drying over Na_2SO_4. After filtration, the CH_2Cl_2 was stripped off to yield a yellow oil. Chromatography through a silica gel column (6 × 2 cm, 5% ether–pentane) and collection of the yellow band, followed by solvent removal yielded a yellow solid (1.1 g, 2.4 mmol, 97% yield) which was recrystallized from pentane to give **6**, m.p. 60–61°; ^{1}H-NMR (100 MHz): δ 1.62 (s, $^3J_{(Se-H)}$ = 12 Hz, 12H), 7.02–7.28 and 7.6–7.75 (m, 10H); ^{13}C-NMR (50.10 MHz): δ 27.94, 51.13, 128.01, 129.15, 131.40, 137.09, 200.72; ^{77}Se-NMR ($CDCl_3$): δ 561; IR: 2962, 1669, 1601, 1582, 988, 711 cm^{-1}; MS: M^+ 453.9940 (calc for $C_{20}H_{22}O_2Se_2$, 453.9949). (Found: C, 53.04; H, 5.08. Calc: C, 52.86; H, 4.88%.)

1 - *Phenyl* - 2 - (*chloroseleno*) - 2 - *methylpropanone* (**5**). In a 5 ml Erlenmeyer flask containing 1 ml of CCl_4 was placed 0.2 g (0.44 mmol) of **6**. To this was added 0.059 g (0.035 ml, 0.44 mmol) of SO_2Cl_2 and the mixture was swirled for 5 min. Removal of solvent yielded a dark orange oil (0.23 g, 0.88 mmol, 100% yield), shown to be pure **5** by NMR; ^{1}H-NMR (100 MHz): δ 2.09 (s, 6H), 7.24–7.92 (m, 5H); ^{13}C-NMR (50.10 MHz): δ 26.98, 64.81, 128.86, 129.33, 132.97, 134.20, 206.60; ^{77}Se-NMR ($CDCl_3$): δ 1145; IR: 2988, 1631, 1599, 1579, 1121, 980 cm^{-1}. (Found: C, 45.88; H, 4.3. Calc for $C_{10}H_{11}ClOSe$: C, 45.81; H, 4.23%.)

2 - *Benzoyl* - 2 - *propaneseleninic acid* (**8**). In a 10 ml Erlenmeyer flask containing 0.02 ml of H_2O in 5 ml of diethyl ether was placed 0.12 g (0.26 mmol) of diselenide **6**. This soln was cooled to −78° and ozonized until blue. During the ozonization a white ppt formed. N_2 gas was then bubbled through the soln to disperse excess O_3 after which 5 ml of distilled pentane was added. The soln was filtered to yield 0.133 g (0.051 mmol, 98% yield) of a white solid, m.p. 74–77°. This was stored in the freezer where it keeps indefinitely; ^{1}H-NMR (acetone-d_6, 270 MHz): δ 1.82 (s, 6H), 7.26–7.86 (m, 5H); ^{77}Se-NMR (acetone-d_6): δ 1240; MS: M^+ 259.9951 (calc for $C_{10}H_{12}O_3Se$, 259.9951). (Found: C, 46.27; H, 4.61. Calc: C, 46.34; H, 4.66%.)

Methyl-d_3 2-benzoyl-2-propaneseleninate (**9**). This was prepared by placing the seleninic acid into CD_3OD at room temp; however, it is not stable enough to be isolated; ^{1}H-NMR (CD_3OD, 270 MHz): δ 1.80 (s, 3H), 1.88 (s, 3H), 7.26–7.86 (m, 5H).

N,N - *Dimethyl* 2 - *benzoyl* - 2 - *propane selenenamide* (**11**). In an 8 mm NMR tube containing 1.5 ml of $CDCl_3$ was placed 0.14 g (0.54 mmol) of freshly prepared selenenyl chloride **5**. The soln was cooled to 0° and 0.05 g (0.073 ml, 1.1 mmol) of dimethylamine was added via a cold syringe. The soln went from dark orange to colorless. Spectral measurements were made on this sample directly, as it is too unstable to isolate; ^{1}H-NMR (270 MHz): δ 1.69 (s, $^3J_{Se-H}$ = 10.29 Hz, 6H), 2.99 (s, $^3J_{Se-H}$ = 8.82 Hz, 6H), 7.28–7.50 (m) and 7.91–8.00 (d, *o*-H's) total 5 H; ^{13}C-NMR (50.10 MHz): δ 24.67, 35.56, 52.67, 127.92, 128.88, 131.28, 137.24, 202.44; ^{77}Se-NMR ($CDCl_3$, −56°): δ 994.

N,N - *Dibenzyl* 2 - *benzoyl* - 2 - *propane selenamide* (**10**). This was prepared exactly as described for **11**; thus, 0.025 g (0.096 mmol) of selenenyl chloride **5** and 0.038 g (0.037 ml, 0.19 mmol) of dibenzylamine were allowed to react to form dibenzylselenenamide **10**; ^{1}H-NMR (270 MHz): δ 1.63 (s, $^3J_{Se-H}$ = 12.13 Hz, 6H), 4.148 (bs, 4H), 7.19–7.70 (m) and 7.95–7.83 (*o-aryl*) total 15H; ^{13}C-NMR (50.10 MHz, partial): δ 24.99, 54.28, 62.75, 201.59; ^{77}Se-NMR ($CDCl_3$): δ 948.

Bis - 2 - *benzoyl* - 2 - *propyl selenide* (**13**). In a 25 ml round bottom flask equipped with a stirring bar and N_2 inlet at 0°, 0.186 g of hexamethyldisilazane (0.244 ml, 1.15 mmol) in 10 ml of THF was allowed to react with 0.77 ml of n-BuLi (1.43 M, 1.1 mmol) for 5 min. Isobutyrophenone (0.163 g, 0.165 ml, 1.1 mmol) was added to the lithium hexamethyldisilazide (LiHMDS) soln, and allowed to warm to 22° over the course of 5 min. The anion soln was cooled to −78° and 0.278 g (1.06 mmol) of freshly prepared **5** was added rapidly via cannula. The cold reaction was then poured into cold 1.2 N HCl and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and solvent stripped off to yield 0.421 g (1.04 mmol, 98% yield) of **13** which was recrystallized from pentane to give white needles, m.p. 83–84°; ^{1}H-NMR (100 MHz): δ 1.68 (s, 12H), 7.02–7.28 and 7.82–7.96 (m, total 10H); ^{77}Se-NMR ($CDCl_3$): δ 608; IR (KBr): 1660, 1590, 1570, 1250, 701 cm^{-1}; MS: M^+ 374.0785 (calc for $C_{20}H_{22}O_2Se$, 374.0785). (Found: C, 64.28; H, 5.93. Calc: C, 64.16; H, 5.93%.)

3 - *Benzyl* - 2,4 - *dioxo* - 3 - *pentyl* 2 - *benzoyl* - 2 - *propyl selenide* (**16**)

In a 25 ml round bottom flask equipped with a stirring bar and N_2 inlet was placed 0.055 g of a 50% NaH–mineral oil dispersion (0.028 g of NaH, 1.15 mmol). This was washed with two 5 ml portions of pentane, after which 8 ml of THF was added. This was cooled to 0° and 0.22 g (1.39 ml, 0.77 mmol) of 3 - benzyl - 2,4 - pentanedione[22b] in 2 ml of THF was added over the course of 5 min. At this time, 0.20 g (0.76 mmol) of freshly prepared selenenyl chloride **5** in 1 ml of THF was added rapidly via cannula to the stirring anion. The soln was poured into a cold acidic (HCl) brine–50% ether–pentane mixture and the organic layer dried and concentrated to yield a yellowish powder. This was recrystallized from hot pentane to yield 0.253 g (0.61 mmol, 80%) of **16** as white needles, m.p. 91–92°; ^{1}H-NMR (100 MHz): δ 1.74 (s, 6H), 2.20 (s, 6H), 3.60 (s, 2H), 7.15 (s, 5H), 7.17–8.12 (m, 5H); IR (KBr): 2960, 1690, 1660, 1500, 1260 cm^{-1}; MS: M^+ 416.0889 (calc 416.0890). (Found: C, 63.49; H, 5.82. Calc for $C_{22}H_{24}O_3Se$: C, 63.45; H, 5.81%.)

4,4-*Dimethyl* - 1,2 - *diselenolane* (**19**). To a soln of 6.16 g (40 mmol) of Rongalite and 4.8 g of NaOH in 300 ml of DMF was added 6.32 g (80 mmol) of selenium powder in small portions. The soln was heated to 70° with stirring under N_2 for 2 hr. Then 7.24 g (40 mmol) of 2,2-dimethyl-1,3-propanediol dimesylate (prepared by lit. procedure[23]) was slowly added. After heating 2 days at 70°, the soln was filtered, diluted with 300 ml of ether–pentane and washed with four 300 ml portions of water, then NaOH, and saturated salt solns. Solvent removal and Kugelrohr distillation (0.5 mm, 60°) gave 3.51 g (38% yield) of **19** (m.p. 33.5–34.5°). ^{1}H-NMR (270 MHz, CD_3OD): δ 1.27 (s, 6H), 3.11 (s, J_{Se-H} = 15 Hz, 4H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 26.5 (q), 44.4 (t/satellites, J_{Se-C} = 67 Hz), 48.6 (s, J_{Se-C} = 24 Hz). ^{77}Se-NMR (38.1 MHz, $CDCl_3$): δ 289. MS: M^+ 229.9112 (calc 229.9113).

Bis(deuteromethyl) 2,2-dimethy-1,3-propanediseleninate: (dimethyl ester of **34**)

Compound **19** was dissolved in $CHCl_3$ (0.2 M and cooled to −40°. A stream of O_3 was passed through the sample until the

characteristic blue color persisted. The sample was flushed with dry N_2 and the solvent was removed. The product was insoluble in $CDCl_3$ and CD_2Cl_2. The spectrum in CD_3OD showed diastereotopic methylenes indicative of the asymmetry at selenium. The product proved unstable and decomposed overnight on the bench. ^{1}H-NMR (270 MHz, CD_3OD): δ 1.36 (s, 6H), 3.12 (d, J = 13 Hz, 2H), 3.34 (d, J = 13 Hz, 2H). ^{13}C-NMR (50 MHz, CD_3OD): δ 34.92 (q), 40.3 (s), 73.96 (t, J_{Se-C} = 100 Hz). ^{77}Se-NMR(38 MHz, CD_3OD): δ 1314.

Selenolseleninate **20**. A soln of 0.011 g (0.05 mmol) of **19** in 1 ml of CD_2Cl_2 was cooled to −45° and a soln of 0.01 g (0.05 mmol) of 85% *m*-CPBA in 1 ml of CD_2Cl_2 was added via a precooled pipette. After 10 min, the soln was transferred to an NMR tube at −45°, and observed via 270 MHz NMR at −44°. A mixture of a diselenide (25%) and a new compound (75%) was observed. At −20°, the new compound slowly reverted to diselenide. However, by integration, one third of **20** was converted to an insoluble material, presumably the bisseleninic acid **34**. Compound **20** could also be prepared by first titrating a stream of O_3 with an equimolar amount of PhSeSePh. Compound **19** was then exposed to the O_3 for 1/3 the time required for complete oxidation of the diselenide to seleninic anhydride. The ozonizations were carried out in CD_2Cl_2 at −78°. ^{1}H-NMR (270 MHz, CD_2Cl_2, −50°): δ 1.24 (s, 3H), 1.45 (s, 1H), 3.18 (d, J = 11.8 Hz, 1H), 3.56 (d, J = 10.3 Hz, 1H), 3.65 (d, J = 11.8 Hz, 1H), 3.90 (d, J = 10.3 Hz, 1H). ^{13}C-NMR (50 MHz, CD_2Cl_2, −56°): δ 25.8 (q), 27.0 (q), 47.4 (t), 50.6 (s), 71.4 (t) ppm. ^{77}Se-NMR (38 MHz, CD_2Cl_2, −56°): δ 693, 273 ppm.

TMS enol ether of phenyl cyclopropyl ketone. In a 50 ml flask equipped with a stirring bar and N_2 inlet cooled to 0° was placed 2.12 g (2.52 ml, 15 mmol) of 2,2,6,6-tetramethylpiperidine in 51 ml of THF and allowed to react with 9.8 ml (1.53 M, 15 mmol) of n-BuLi for 5 min. To the LiTMP soln thus formed was added 2.19 g (2.10 ml, 15 mmol) of phenyl cyclopropyl ketone and the soln was left to stir at 0° for 15 min. Chlorotrimethylsilane (2.03 g, 18.5 mmol, 2.3 ml) was added, the reaction was allowed to warm to 22° over the course of 30 min, Et_3N (2 ml was added to the reaction, and this mixture was poured into a cold, stirring 7% $NaHCO_3$ (50 ml)/50% ether–pentane (20 ml) soln. The organic layer was washed with brine, dried over K_2CO_3 and the solvent removed to give a cloudy oil. This was distilled (Kugelrohr, 79°, 0.1 mmHg) to yield 2.54 g of enol silyl ether as a clear liquid (11.65 mmol, 78% yield); ^{1}H-NMR (200 MHz): δ 0.36 (s, 9H), 1.30–1.41 (dd, J = 9, 7.5 Hz, 2H), 1.60–1.70 (dd, J = 9, 7.5 Hz, 2H), 7.25–7.5 and 7.80–7.90 (m, 5H); ^{13}C-NMR (50.10 MHz): δ 139.91, 138.36, 127.92, 127.16, 125.11, 98.82, 5.71, 3.53, 0.77; IR: 3040, 2970, 1753, 1600, 1500, 1450, 1200, 1081 cm^{-1}; MS: M$^+$ 218.1126 (calc for $C_{13}H_{18}OSi$: 218.11266).

1 - *Benzoyl* - 1 - *cyclopropaneseleninic acid* (**36**). In an open 25 ml flask fitted with a stirring bar was placed 0.55 g (4.9 mmol) of SeO_2 in 12 ml of dry THF at 22°. Water was added until the SeO_2 was dissolved (approx. 0.3 ml of H_2O required). To this was added silyl enol ether of phenyl cyclopropyl ketone (1.08 g, 4.9 mmol) and the resulting mixture was stirred at 22° for 30 min. The seleninic acid could be obtained by diluting the reaction with 10–20 ml of pentane, until a white solid precipitated. Filtration and recrystallization from acetone (done by dissolving the seleninic acid in acetone at 22°, cooling to 0°, and collecting the white crystals formed) yielded **36** as white needles, m.p. 110–112° (decomp.); ^{1}H-NMR (d_6–acetone, 200 MHz): δ 1.48–1.72 (m, 4H), 3.51 (bs), 7.52–7.74 (m) and 7.91–7.99 (d, *o*-proton) total 5H; ^{13}C-NMR (d_6–acetone, 50.10 MHz): δ 198.69, 137.19, 133.81, 129.54, 128.61, 54.21, 11.17; ^{77}Se-NMR (d_6–acetone): δ 1210; IR (KBr): 2870, 2410, 1680, 1600, 1585, 1455, 1001, 850 cm^{-1}; MS: M$^+$ 257.9794 (calc for $C_{10}H_{10}O_3Se$: 257.9795). Yields of seleninic acid **36** could be obtained in the range of 100%; however, the seleninic acid was usually not isolated but taken directly on to diselenide **37**.

Bis-1-*benzoyl*-1-*cyclopropyl diselenide* (**37**). To 1.26 g of seleninic acid **36** (4.9 mmol, obtained from the preceding reaction) in 12 ml of wet THF was added 0.85 g (6.5 mmol) of hydrazine sulfate in 5 ml of H_2O over the course of 5 min at 22°. After stirring at 22° for 1 h, the yellow reaction mixture was extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. Solvent evaporation, followed by recrystallization from pentane yielded 0.90 g of diselenide **37** (2 mmol, 82% yield) as a yellow powder, m.p. 82–84°; ^{1}H-NMR (200 MHz): δ 1.33–1.44 (m, 4H), 1.57–1.69 (m, 4H), 7.35–7.60 (m, 6H), 7.90–8.00 (*o*-proton doublet, 4H); ^{13}C-NMR (50.10 MHz): δ 196.60, 135.72, 132.62, 129.24, 128.19, 27.80, 17.64; ^{77}Se-NMR ($CDCl_3$): δ 555; IR (KBr): 1661, 1600, 1582, 1455, 1437, 990 cm^{-1}; MS: M$^+$ 449.9638 (calc for $C_{20}H_{18}O_2Se$: 449.963).

1 - (1 - *Benzoylcyclopropyl*) 2 - *benzoyl* - 2 - *propyl selenide* (**35**). A 25 ml flask fitted with stirring bar, N_2 inlet and cooled to 0° was charged with 0.47 g (2.1 mmol) of the silyl enol ether of phenyl cyclopropyl ketone in 5 ml THF. To this was added 0.28 g of freshly prepared selenenyl chloride **5** and the resulting soln allowed to stir at 0° for 5 min. Workup was effected by pouring the mixture into a cold acidic (HCl) brine–CH_2Cl_2 mixture. Separation, drying (Na_2SO_4), and concentration of the organic layer yielded a light yellow oil. Recrystallization from hot pentane gave 0.48 g of **35** (1.3 mmol, 63% yield) as white needles, m.p. 78.5–79.5°; ^{1}H-NMR (200 MHz, CD_2Cl_2): δ 1.3–1.39 (m, 2H), 1.61 (s) and 1.61–1.71 (m, total 8H), 7.19–7.50 (m, 6H), 7.61–7.72 (*o*-proton d, 2H), 7.79–7.90 (*o*-proton d, 2H); ^{13}C-NMR (50.10 MHz): δ 200.51, 197.79, 137.06, 136.05, 132.07, 131.12, 129.31, 129.03, 127.83, 127.70, 50.94, 27.47, 25.22, 15.01; ^{77}Se-NMR ($CDCl_3$): δ 564; IR: 3050, 2962, 1665, 1600, 1584, 1361, 1350, 982 cm^{-1}; MS: M$^+$ 372.0628 (calc for $C_{20}H_{20}O_2Se$: 372.0628).

1 - *Benzoyl* - 1 - *cyclopropaneselenenyl chloride*. This compound was prepared exactly as previously described for selenenyl chloride **5**: thus, 0.066 g (0.15 mmol) of diselenide **37** and SO_2Cl_2 (0.02 g, 0.012 ml, 0.15 mmol) reacted to form 0.078 g (0.3 mmol) of selenenyl chloride as an orange oil; ^{1}H-NMR (200 MHz): δ 1.76–2.10 (m, 4H), 7.41–7.66 and 7.84–7.99 (m, 5H); ^{13}C-NMR (50.10 MHz): δ 19.33, 34.02, 128.36, 128.86, 133.00, 135.43; ^{77}Se-NMR ($CDCl_3$): δ 1151. The selenenyl chloride was used without further purification.

1 - (1 - *Benzoylcyclopropyl*) 3 - *benzyl* - 2,4 - *dioxo* - 3 - *pentyl selenide* (**38**). In a 25 ml round bottom flask equipped with a stirring bar and N_2 inlet was placed 0.022 g of a 50% NaH–mineral oil dispersion (0.011 g of NaH, 0.45 mmol). This was washed with two 5 ml portions of pentane, after which 10 ml of THF was added. After cooling to 0° for 30 min, 0.055 g (0.054 ml, 0.3 mmol) of 3-benzyl-2,4-pentanedione in 1 ml of THF was added over the course of 3 min. After allowing the anion to stir at 0° for 30 min, 0.078 g (0.3 mmol) of freshly prepared 1-benzoyl-1-cyclopropane selenenyl chloride was added rapidly via cannula. The soln was then allowed to stir at 0° for 3 min and then poured into a cold acidic (HCl) brine–CH_2Cl_2 mixture. Separation, drying (Na_2SO_4), and concentration of the organic layer, followed by recrystallization from hot pentane gave 0.043 g (0.10 mmol, 34% yield) of **38** as white needles, m.p. 149–150°; ^{1}H-NMR (200 MHz): δ 1.19–1.28 (m, 2H), 1.60–1.69 (m, 2H), 1.94 (s, 6H), 3.61 (s, 2H), 7.15 (s, 5H), 7.35–7.60 (m) and 7.85–7.95 (m, total 5H); ^{13}C-NMR (50.10 MHz): δ 201.14, 196.46, 135.83, 135.29, 132.45, 129.47, 129.19, 128.33, 127.95, 126.78, 74.47, 36.64, 26.90, 23.36, 14.41; ^{77}Se-NMR ($CDCl_3$): δ 499; IR: 1695, 1680, 1545, 1360, 1000 cm^{-1}; MS: M$^+$ 414.0733 (calc for $C_{28}H_{22}O_3Se$: 414.0734).

1 - (1 - *Benzoyl* - 2,2 - *dimethylcyclopropyl*) 2 - *benzoyl* - 2 - *propyl selenide* (**39**). In a 25 ml flask equipped with a stirring bar and N_2 inlet cooled to 0° was placed 0.24 g (0.28 ml, 1.69 mmol) of 2,2,6,6-tetramethylpiperidine in 8 ml of THF and allowed to react with 1.3 ml n-BuLi (1.49 M, 1.69 mmol) for 15 min. To the LiTMP soln thus formed was added 0.28 g (1.61 mmol) of 1-benzoyl-2,2-dimethylcyclopropane[22a] in 2 ml of THF and left to stir at 22° for 1.5 hr. The soln was then cooled to −78° and 0.42 g (1.6 mmol) of freshly prepared selenenyl chloride **5** in 2 ml of THF was added rapidly via cannula. The cold mixture was then poured into 20 ml of cold 1.2 N HCl and 20 ml of 50% ether–pentane. Separation of the organic layer, followed by a brine wash, drying (Na_2SO_4), and solvent removal yielded a yellow oil, which could be recrystallized from hot pentane (note: some of it decomposes via enolene rearrangement[22]) to

yield 0.29 g of **39** (0.73 mmol, 45%) as white crystals, m.p. 90–92°; ^{1}H-NMR (200 MHz): δ 1.0 (s, 3H), 1.20 (d, J = 5.5 Hz, 1H), 1.52 (s, 3H), 1.60 (s, 3H), 1.62 (s, 3H), 2.0 (d, J = 5.5 Hz, 1H), 7.20–7.50 (m), 7.68–7.76 (*o*-doublet), 7.76–7.84 (*o*-doublet) total 10H; ^{13}C-NMR (50.10 MHz): δ 200.34, 196.89, 136.97, 136.68, 132.07, 131.13, 129.21, 127.98, 127.69, 50.60, 50.49, 38.69, 27.53, 27.42, 26.43, 25.43, 24.03, 23.92, 21.82; ^{77}Se-NMR ($CDCl_3$): δ 495; IR (KBr): 2980, 2960, 1667, 1600, 1581, 1450, 1000 cm^{-1}; MS: M$^+$ 400.0940 (calc for $C_{22}H_{24}O_2Se$: 400.09412).

1 - *Benzoyl* - 2,2 - *dimethyl* - 1 - *cyclopropaneseleninic acid* (**42**). This compound was prepared exactly as described for **36**; 69% yield, white needles, m.p. 110–112°; ^{1}H-NMR (200 MHz): δ 1.08 (s, 3H), 1.48 (s, 3H), 1.69 (d, J = 6.5 Hz, 1H), 1.95 (d, J = 6.5 Hz, 1H), 7.46–7.70 (m) and 7.81–7.93 (*o*-proton, total 5H); IR (KBr): 3180, 2980, 1668, 1600, 1585, 1459, 1252, 860 cm^{-1}. The seleninic acid was typically taken directly to the diselenide.

Bis - 1 - (1 - *benzoyl* - 2,2 - *dimethylcyclopropane*) *diselenide* (**41**). This compound was prepared exactly as described for **37**; yellow oil; ^{1}H-NMR (200 MHz) mixture of diasteromers: δ 1.05 (s), 1.06 (s), 1.10 (d, J = 6 Hz), 1.12 (d, J = 6 Hz), 1.51 (s), 1.57 (s), 1.60 (s), 1.75 (d, J = 6 Hz) total 16H, and 7.39–7.90 (m, 10H); ^{77}Se-NMR (CD_2Cl_2): δ 484, 499; IR: 3029, 2972, 1670, 1599, 1580, 1390, 1378, 992 cm^{-1}; MS: M$^+$ 506.0264 (calc for $C_{24}H_{26}O_2Se_2$: 506.02627).

General procedure for the oxidation of selenides and diselenides

Oxidation of **16**. Selenide **16** (0.02 g, 0.048 mmol) was weighed into a 5 mm o.d., thin walled, precision NMR tube and dissolved in 0.50 ml of CD_2Cl_2. Tetramethylsilane was added as an internal reference. When yields were to be obtained, 0.01 ml (0.083 mmol) of pentachloroethane (δ6.14) was added as an integration standard. A capillary pipet (drawn out from a Pasteur pipet so that it was long enough to reach the bottom of the NMR tube and beveled at the narrow end) was placed in the NMR tube containing the CD_2Cl_2 soln of **16** and the tube and pipet cooled to −91° (n-heptane/LN_2). A stream of ozone was passed through the soln via the pipet until the characteristic blue color appeared. The O_3 stream was disconnected from the top of the pipet, and a N_2 line connected in its place. The soln (still at −91°) was purged with a slow stream of N_2 until the blue color was dispersed. The sample of **16-ox** was then subjected to thermolysis as described below.

To obtain a ^{77}Se or ^{13}C spectrum of **15** (or other low temperature intermediates), 0.15 g (0.36 mmol) of **16** in 1.5 ml CD_2Cl_2 was ozonized as above in an 8 mm NMR tube, subjected to thermolysis at −50° and observed on the FX-200.

Thermolysis of selenoxide **16-ox**

General procedure. Compound **16-ox** (prepared as described above) was thermolyzed in one of two ways: (1) if the *syn* elimination was to be observed directly, the NMR tube containing the cold (−91°) CD_2Cl_2 soln of the selenoxide was placed directly into the precooled (−50°) probe of the WH-270 and spectra taken every *ca* 5 min; (2) if observation of the *syn* elimination was not of interest, the selenolseleninate **15** could be formed by placing the NMR tube containing the cold (−91°) CD_2Cl_2 soln of **16-ox** into a thermostatically controlled cold bath (operating at −50°) for 17 min. The sample was then cooled back down to −91° and placed into the probe of the spectrometer (either the WH-270 or FX-200) already operating at the desired temp.

Low temperature quench of selenolseleninate **15** *with dibenzylamine*

Formation of **27**. *General procedure for low temperature quenches*[24] (Table 2, entry 3). A soln of selenolseleninate **15** in CD_2Cl_2 was prepared by ozonization (see General procedure) of 0.097 mmol of selenide **16** at −91°, followed by thermolysis of the subsequently formed selenoxide **16-ox**. This soln was cooled to −91° and 19 mg (0.02 ml, 0.097 mmol) of dibenzylamine in 0.1 ml of cold (−78°) CD_2Cl_2 was added via a cooled (−78°) microliter syringe. The sample was quickly agitated, and placed in a thermostatically controlled cold-bath operating at −30° for 25 min. The sample was then placed in the precooled (−30°) probe of the WH-270 and yields of products determined (integration vs C_2HCl_5 standard). Beginning with 0.097 mmol of selenide **16**, was obtained 0.095 mmol of enedione **17** (98%), 0.05 mmol of enone **14** (50%), 0.036 mmol of **27** (76%), and 0.007 mmol of diselenide **6** (15%). Compound **27** was stable indefinitely at −78° but slowly decomposed at 22° to give (for the entire reaction) 0.071 mmol of enone **14** (73%) and 0.03 mmol of a mixture of diselenide **6** and its corresponding triselenide (60%). Spectral data for **27**: partial ^{1}H-NMR (270 MHz, CD_2Cl_2, −30°): δ 1.80 (s, 6H, J_{Se-H} = 9.5 Hz), 3.77 (s, 4H, J_{Se-H} = 13 Hz), 8.05 (*o*-aryl, doublet); ^{77}Se-NMR (38 MHz, CD_2Cl_2, −30°): δ 566 and 962 ppm.

Low temperature quench of selenolseleninate **15** *with dimethylamine*[24] (Table 2, entry 4)

To a freshly generated soln of **15** in CD_2Cl_2 at −91° (from 0.04 mmol of **16**; see above for procedure) was added 0.01 ml (0.15 mmol) of dimethylamine in 0.1 ml of cold CD_2Cl_2 in the same fashion described in the general procedure for low-temperature quenches (see above). After 30 min at −30°, proton observation indicates the presence of dimethyl selenenamide **11** (23%), diselenide **6** (25%) and enone **14** (35%), along with a number of other decomposition products.

Low temperature quench of **15** *with* $P(OMe)_3$[24] (Table 2, entry 2)

To a cold (−91°) freshly prepared CD_2Cl_2 soln of **15** (from 0.063 mmol of selenide **16** by the general procedure described above) was added 0.009 ml (9.7 mg, 0.076 mmol) of neat trimethyl phosphite. An immediate lightening of the soln was noted. NMR analysis (270 MHz, −80°) indicated the complete disappearance of **15**, with diselenide **6** being the major selenium containing species. Starting with 0.063 mmol of **16**, one obtains 0.054 mmol of enedione **17** (86%); 0.023 mmol of diselenide **6** (74%); 0.003 mmol of the tetraselenide **24** (9%) and 0.003 mmol of enone **14** (4.3%). In addition, 0.014 mmol of the $P(OMe)_3$ added was not consumed in the reaction.

Thermolysis of selenoxide **16-ox** *in the presence of dibenzylamine*[24] (Table 2, entry 5)

Selenide **16** (0.051 g, 0.12 mmol) was ozonized as previously described. To this cold (−91°) selenoxide soln was added 25.7 mg (0.026 ml, 0.12 mmol) of dibenzylamine in 0.1 ml of cold (−78°) CD_2Cl_2 The sample was then placed in the precooled (−55°) probe of the WH-270 and the reaction monitored. One obtains upon disappearance of **16-ox** the following products: 0.083 mmol of enedione **17** (67%), 0.034 mmol of selenenamide **10** (27%), 0.007 mmol of isobutyrophenone (6%), 0.046 mmol of 3-benzyl-2,4-pentanedione (37%), and 0.04 mmol of selenolseleninate **15** (70%). Upon warming of this reaction to −30° (Table 2, entry 6), **15** disappears to give, in addition to the products previously listed, 0.05 mmol of enone **14** (42%), 0.008 mmol of diselenide **6** (12%), and 0.032 mmol of **27** (52%).

Decomposition of selenolseleninate **15**[24] (Table 2, entry 1)

A freshly generated soln of selenolseleninate **15** at −91° (from 0.175 mmol of selenide **16**; prepared as described above) was allowed to warm to room temperature over the course of 5 min. NMR analysis (room temperature) showed the following products (yields based on starting selenide): 0.10 mmol of enone **14** (57%), 0.014 mmol of seleninic acid **8** (8%), 0.016 mmol of diselenide **6** (22%) and 0.026 mmol of tri- and tetraselenides **23** and **4** (28%). After 6 hr at room temperature there was 62% of **14**, 14% of **6** and 34% of **23** and **24**.

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[24] See footnote a, Table 2 for a definition of percent yield in cases where two molecules of starting material form one molecule of product (e.g. **6**, **15**, **23**, **24**, **27**).