40140-16-7; **21c**, 76529-99-2; **22a**, 76530-00-2; **22c**, 76530-01-3; **23c**, 67509-39-1; **25**, 4835-90-9; **27**, 76530-02-4; **28**, 76530-03-5; **29**, 76530-04-6; **30**, 76530-05-7; **31**, 71404-95-0; **32**, 76530-06-8; **33**, 76530-07-9; **34**, 76530-08-0; *p*-methoxyphenylacetic acid, 104-01-8; *p*-methoxyphenylacetyl chloride, 4693-91-8; *p*-hydroxybenzaldehyde, 123-08-0; (*p*-hydroxyphenyl)acetic acid, 156-38-7; *O*-pivaloylhydroxylamine, 35657-34-2; *O*-*tert*-butylhydroxylamine HCl, 39684-28-1; *O*-tritylhydroxylamine, 31938-11-1; *O*-benzylhydroxylamine, 622-33-3.

Oxidation of Hydrazines with Benzeneseleninic Acid and Anhydride[1a]

Thomas G. Back,* Scott Collins,[1b] and Russell G. Kerr

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, T2N 1N4

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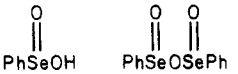
Benzeneseleninic acid (**1**) and anhydride (**2**) oxidize hydrazine or 1,2-disubstituted derivatives to the corresponding diazenes. Hydrazides afford selenoesters **4**, *N,N'*-diacyl- or -diaroylhydrazines **5**, and carboxylic acids. Benzeneselenenic acid (**7**) is a required intermediate in selenoester formation and may be generated independently by the reaction of triphenylphosphine with **1**. Selenoesters are efficiently prepared by the slow addition of a mixture of the hydrazide and triphenylphosphine to **1** in dichloromethane solution. Polar solvents are unsuitable. Inverse addition provides compounds **5** as the major products. Oxidation of hydrazides of structure HO-$(CH_2)_n$CONHNH$_2$ gives the corresponding selenoesters **14** and acids **16** when n = 11 or 14 and lactones **17** and **18** when n = 4 or 3. Arylhydrazines react with **1** or **2** to furnish arenes **23** and aryl phenyl selenides **24**.

Benzeneseleninic acid (**1**) and anhydride (**2**) are stable, readily available, odorless solids which serve as oxidants of diverse organic substrates. The latter include sulfur compounds,[2] nitrogenous species,[3] compounds containing hydroxyl[4] or carbonyl[3d,5] functions, and benzylic hydrocarbons.[5b] A number of synthetically useful transformations have resulted from these studies.

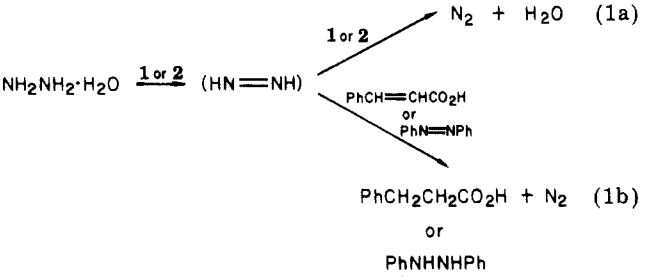


1 **2**

Recently, one of us observed that variously substituted hydrazines react vigorously with **1** or **2** at room temperature to produce diazenes or products derived from their fragmentation.[6] The dehydrogenation of hydrazo compounds to diazenes has been accomplished by numerous methods in the past.[7] However, limitations of scope and attendant side reactions frequently curtail their effectiveness. New methods for producing diazenes as products or as unstable intermediates (e.g., as in the case of monosubstituted derivatives) are therefore of continuing interest. In view of the rich and varied chemistry of species containing the -N=N- linkage, we performed the studies of hydrazine oxidations with **1** and **2** described herein.

Results and Discussion

Rheinboldt and Giesbrecht[8] observed that seleninic acids are reduced to selenenic acids (RSeOH) when treated with hydrazine hydrate, hydrochloride, or sulfate. We have found that an initial dehydrogenation produced diazene (diimide) when hydrazine hydrate was oxidized with **1** or **2**. Evidence for diazene formation derived from the in situ conversion of added azobenzene or cinnamic acid to *N,N'*-diphenylhydrazine or hydrocinnamic acid, respectively,[9] as shown in eq 1a,b. Since diazene may itself be easily



oxidized, its efficient generation requires the presence of excess hydrazine hydrate during the reaction. Under such conditions the oxidant reacts preferentially with the hydrazine. The oxidation of *N,N'*-diphenylhydrazine back to azobenzene (vide infra) is similarly avoided.

The reactions of two symmetrically disubstituted hydrazines with **1** or **2** were also studied. The oxidation of *N,N'*-diphenylhydrazine with **2** afforded azobenzene in 97% yield while *N,N'*-diisopropylhydrazine was converted to the corresponding diazene (azo compound) quantitatively by an equimolar amount of **1** or by 0.5 molar equiv of **2**. When 0.5 molar equiv of **1** were used in the oxidation, only a small amount (<10%) of the hydrazine remained

(1) (a) Financial support from the University of Calgary, the Natural Sciences and Engineering Research Council, and the Research Corp. is gratefully acknowledged. (b) Holder of an NSERC Postgraduate Scholarship.

(2) (a) H. Rheinboldt and E. Giesbrecht, *Chem. Ber.*, **88**, 1037 (1955); (b) J. L. Kice and T. W. S. Lee, *J. Am. Chem. Soc.*, **100**, 5094 (1978); (c) D. H. R. Barton, N. J. Cussans and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 751 (1977); (d) D. H. R. Barton, N. J. Cussans, and S. V. Ley, *ibid.*, 393 (1978); (e) L. G. Faehl and J. L. Kice, *J. Org. Chem.*, **44**, 2357 (1979); (f) R. A. Gancarz and J. L. Kice, *Tetrahedron Lett.*, **21**, 1697 (1980).

(3) (a) T. G. Back and N. Ibrahim, *Tetrahedron Lett.*, 4931 (1979); (b) D. H. R. Barton, D. J. Lester, and S. V. Ley, *J. Chem. Soc., Perkin Trans 1*, 1212 (1980); (c) D. H. R. Barton, D. J. Lester, and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 276 (1978); (d) T. G. Back, *ibid.*, 278 (1978); (e) M. R. Czarny, *ibid.*, 81 (1976).

(4) (a) D. H. R. Barton, A. G. Brewster, R. A. H. F. Hui, D. J. Lester, S. V. Ley, and T. G. Back, *J. Chem. Soc., Chem. Commun.*, 952 (1978); (b) D. H. R. Barton, S. V. Ley, P. D. Magnus, and M. N. Rosenfeld, *J. Chem. Soc., Perkin Trans 1*, 567 (1977); (c) T. Frejd and K. B. Sharpless, *Tetrahedron Lett.*, 2239 (1978).

(5) (a) D. H. R. Barton, D. J. Lester, and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 130 (1978); (b) D. H. R. Barton, R. A. H. F. Hui, D. J. Lester, and S. V. Ley, *Tetrahedron Lett.*, 3331 (1979).

(6) The oxidation of several hydrazines with **2** was reported simultaneously and independently by D. H. R. Barton and co-workers. For preliminary communications see ref 3c,d.

(7) B. T. Newbold in "The Chemistry of the Hydrazo, Azo and Azoxy Groups", S. Patai, Ed., Wiley, London, 1975, Part 1, Chapter 14.

(8) H. Rheinboldt and E. Giesbrecht, *Chem. Ber.*, **88**, 666 (1955).

(9) The hydrogenation of azo compounds and α,β-unsaturated carboxylic acids with diazene is well-known. (a) S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem., Int. Ed. Engl.*, **4**, 271 (1965); (b) H. O. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, London, 1972, Chapter 4.

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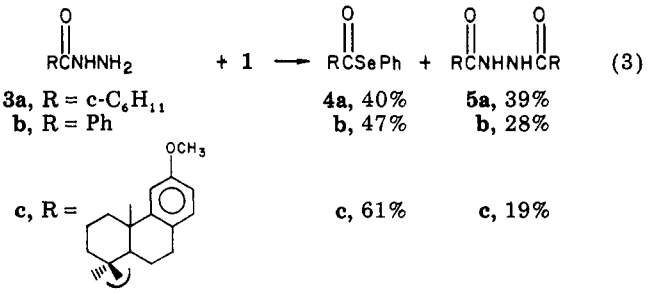
unreacted. Further oxidation of the product diazene to the azine or azoxy derivative did not occur in the presence of a threefold excess of **2**. A small amount of acetone (ca. 10%) was detected in the latter reaction after 18 h.[10] The process depicted in eq 2 thus provides a clean method of converting *N,N'*-dialkyl- or -diarylhydrazines to diazenes.[11]

$$\mathrm{RNHNHR} \xrightarrow{1 \text{ or } 2} \mathrm{RN{=}NR} \quad (\mathrm{R} = \mathrm{Ph} \text{ or } i\text{-}\mathrm{C_3H_7}) \qquad (2)$$

Admixture of benzeneseleninic acid (**1**) and acyl- or aroylhydrazines (hydrazides) **3** in chloroform or dichloromethane solution at room temperature affords selenoesters **4** and *N,N'*-diacyl- or *N,N'*-diaroylhydrazines (**5**, eq 3) as



(3)

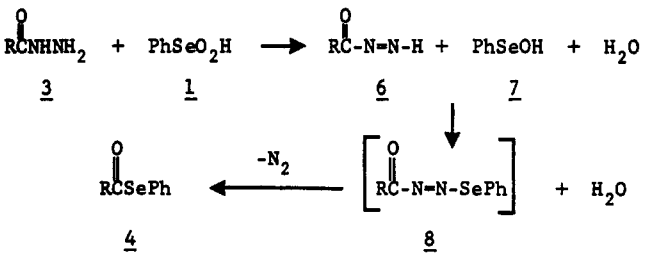
the principal isolated products. The latter compounds precipitate and so avoid further oxidation to diazenes. Products **4a–c** and **5a–c** were thus obtained.

The intriguing formation of these products warranted further study. Moreover, selenoesters are valuable acyl-transfer agents. They are relatively stable both thermally and hydrolytically but acylate a variety of nucleophiles when activated by species such as cuprous[12] or mercuric ion.[13] Existing procedures for selenoester synthesis generally employ air-sensitive or malodorous reagents.[12b,13,14] Such objections are circumvented by employing the reaction of readily available hydrazides with **1**. We therefore endeavored to optimize selenoester yields in the above process.

Since the formation of *N,N'*-diacyl- or *N,N'*-diaroylhydrazines (**5**) occurs at the expense of the desired selenoesters **4** and requires 2 mol of hydrazide, we reasoned that slow addition of hydrazides to the seleninic acid would suppress the production of compounds **5**. However, this expedient proved only partly successful in enhancing selenoester yields. Further improvements derived from mechanistic considerations.

By analogy to the reaction of hydrazine or its *N,N'*-disubstituted derivatives with **1**, the initial oxidation of a hydrazide is expected to generate the corresponding acyl- or aroyldiazene (**6**) and benzeneselenenic acid (**7**).[15,16] Further reaction of these species to produce the hypothetical intermediate **8**, followed by nitrogen extrusion,

Scheme I

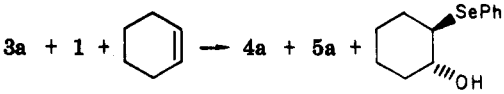


leads to selenoester formation via Scheme I. Alternatively, free acyl radicals generated by the homolytic fragmentation of diazenes **6**[17] could react with diphenyl diselenide by a radical substitution process[18] to produce selenoesters. The diselenide is an observed byproduct in the reaction. Its formation is expected from the known disproportionation of the selenenic acid[16] (eq 4). In principle, selenoesters

$$3\mathrm{PhSeOH} \rightleftharpoons \mathrm{PhSeO_2H} + \mathrm{PhSeSePh} + \mathrm{H_2O} \qquad (4)$$

could also be produced by the reaction of acyl anions derived from the base-catalyzed fragmentation of **6**[19] with selenenylating species. However, the absence of the required strong base permits the exclusion of this possibility.

If the mechanism depicted in Scheme I is correct, then removal of **7** from the reaction by means of a scavenger should impede selenoester formation. Conversely, generation of additional **7** during the reaction by a simultaneous and independent process should increase selenoester yields. The facile electrophilic addition of **7** to olefins is well documented,[16,20] and we chose cyclohexene for a scavenging experiment. When hydrazide **3a** was added slowly to seleninic acid **1** in a 1:1 mixture of dichloromethane and cyclohexene (eq 5), the yield of selenoester **4a** was only

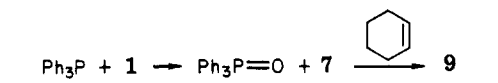


(5)

9

31%, compared to 62% in the absence of the olefin. The major byproducts were *N,N'*-diacylhydrazine **5a** and *trans*-2-(phenylseleno)cyclohexanol (**9**), obtained in yields of 11% and 47%, respectively.

We also sought a method for independently generating selenenic acid **7** in situ by reducing benzeneseleninic acid with a suitable reagent which could be added together with the hydrazide. A number of known candidates for this process[20,21] were unsuitable because of solubility or other problems. However, we observed that triphenylphosphine reacts readily with **1** to afford triphenylphosphine oxide and **7**,[22] confirmed by trapping the latter compound as its cyclohexene adduct **9** (eq 6). Slow addition of equimolar



(6)

amounts of the phosphine and hydrazide **3a** to 2 molar

(10) The presumably related regeneration of ketones from their hydrazones, oximes, and semicarbazones has been reported.[3b]

(11) Alternative oxidation methods have been reviewed.[7]

(12) (a) A. P. Kozikowski and A. Ames, *J. Am. Chem. Soc.*, **102**, 860 (1980). (b) S. Masamune, Y. Hayase, W. Schilling, W. K. Chan, and G. S. Bates, *ibid.*, **99** 6756 (1977).

(13) A. P. Kozikowski and A. Ames, *J. Org. Chem.*, **43**, 2735 (1978).

(14) (a) For a review of older methods see: K. A. Jensen in "Organic Selenium Compounds: Their Chemistry and Biology", D. L. Klayman and W. H. H. Günther, Eds., Wiley, London, 1973, Chapter 8; (b) P. A. Grieco, Y. Yokoyama, and E. Williams, *J. Org. Chem.*, **43**, 1283 (1978); (c) H.-J. Gais and T. Lied, *Angew. Chem., Int. Ed. Engl.*, **17**, 267 (1978); (d) H.-J. Gais, *ibid.*, **16**, 244 (1977); (e) G. S. Bates, J. Diakur, and S. Masamune, *Tetrahedron Lett.*, 4423 (1976).

(15) Reich[16a] and Sharpless[16b] have both pointed out that electrophilic reactions attributed to **7** may actually be perpetrated by other selenenylating species (e.g., PhSeOSePh or PhSe(O)OSePh) derived from **7**. Such considerations apply here as well.

(16) (a) H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, and D. F. Wendelborn, *J. Org. Chem.*, **43**, 1697 (1978); (b) T. Hori and K. B. Sharpless, *ibid.*, **43**, 1689 (1978).

(17) Benzoyl radicals are suspected intermediates in the oxidation of **3b** with silver oxide: D. Mackay, U. F. Marx, and W. A. Waters, *J. Chem. Soc.*, 4793 (1964).

(18) A similar reaction between ethyl radicals and diethyl diselenide has been reported: R. J. Cross and D. Millington, *J. Chem. Soc., Chem. Commun.*, 455 (1975).

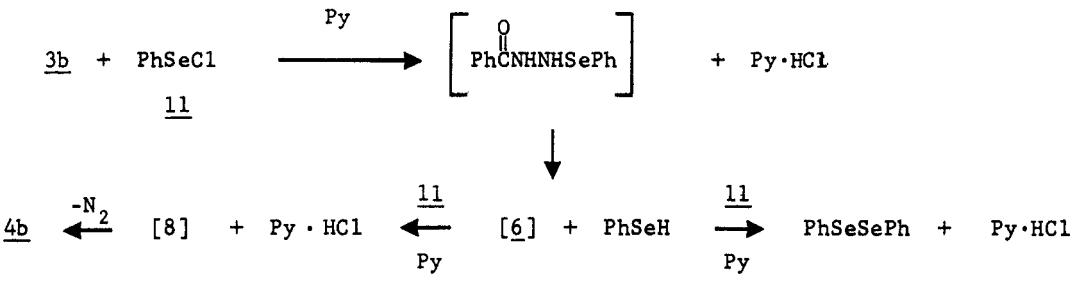
(19) J. S. McFadyen and T. S. Stevens, *J. Chem. Soc.*, 584 (1936).

(20) D. Labar, A. Krief, and L. Hevesi, *Tetrahedron Lett.*, 3967 (1978).

(21) D. L. Klayman, ref 14a, Chapter 4.

(22) An independent study by Faehl and Kice[2e] confirms this obeservation.

Scheme II[a]



[a] Py = pyridine.

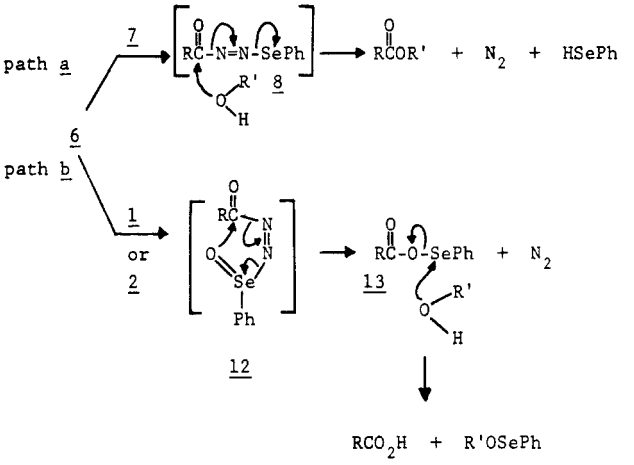
equiv of seleninic acid **1** in dichloromethane solution produced selenoester **4a** in 86% yield. This result and the observed suppression of selenoester formation by cyclohexene confirm that benzeneselenenic acid is a required intermediate in the formation of **4a**. Although this conclusion is entirely consistent with the process shown in Scheme I, other mechanisms, such as ones involving free radicals, cannot be entirely excluded. However, when **3a** and **3b** were oxidized with **1** in the presence of 20 mol % of 2,6-di-*tert*-butyl-*p*-cresol and 10 mol % of benzoquinone, respectively, only slightly lower yields of selenoesters were obtained. These inhibition experiments indicate that a mechanism involving free radicals is improbable, although the recombination of radicals formed by the extrusion of nitrogen from **8** within a solvent cage remains a possibility. Finally, the oxidation of **3a** with **1** in the presence of a stream of oxygen gave a sharp reduction in the yield of the selenoester to only 29%. This may be explained by assuming that diazene **6** is consumed by oxygen[23] and so is prevented from reacting with **7** in the usual manner.

A wide variety of hydrazides was oxidized with **1** in the presence of triphenylphosphine in dichloromethane. Excellent yields of alkyl, cycloalkyl, aryl, and heterocyclic selenoesters were generally obtained[24] (Table I). Highly hindered systems such as **4c** and **4d** presented no difficulty. The method is compatible with unsaturated substrates as shown by the high yield of product **4e**. Evidently under these conditions olefins do not react with benzeneselenenic acid to an appreciable extent unless they are present in large excess. Phenylacetaldehyde and benzyl phenyl selenide were coproducts of selenoester **4f**. Methyl carbazate gave *O*-methyl *Se*-phenyl selenocarbonate (**10**) in 67% yield. This method clearly provides a convenient, versatile, and efficient preparation of selenoesters.

We note that treatment of benzhydrazide (**3b**) with benzeneselenenyl chloride (**11**) and pyridine produced 47% of selenoester **4b**. This reaction is shown in Scheme II and may proceed by way of the same intermediates **6** and **8** as in Scheme I. It is inferior to the use of **1** and triphenylphosphine if a high selenoester yield is desired.

Certain hydrazides whose conversion to selenoesters is of special interest have low solubilities in dichloromethane. We therefore studied the feasibility of employing more polar solvents, using hydrazides **3a** and **3b** as standard substrates. When the former compound was oxidized with **1** in the presence of triphenylphosphine in a variety of polar solvents, consistently low yields of selenoester **4a** were obtained, in contrast to the 86% yield produced in dichloromethane (Table I). The product distributions resulting from the oxidation of both hydrazides with **1** in the absence of triphenylphosphine in acetonitrile, *N,N*-dimethylformamide (DMF), and methanol are shown in Table II. Results obtained in dichloromethane solution are included for comparison. Under these conditions the corresponding carboxylic acids were formed along with selenoesters and *N,N'*-diacylhydrazines. In methanol or 10% methanol–dichloromethane, methyl esters were also produced. These results indicate the presence of an acylating intermediate since the selenoesters themselves are hydrolytically inert under such conditions.[25] Although the putative intermediate **8** is expected to possess acylating powers (path a, Scheme III), the observation that carboxylic acid formation is significant (compared to that of the methyl ester) even in neat methanol suggests the coexistence of an alternative mechanism. Such a process is displayed in path b of Scheme III where the mixed carboxylic–selenenic anhydride **13** is formed by an intramolecular rearrangement of species **12** and reacts with methanol (or water) to form the corresponding carboxylic acid and selenenic ester (or acid). Analogous alcoholysis of a selenenyl acetate has been previously reported.[26] Path b may be favored in polar media as the result of a possible enhancement of the seleninylating ability of **1** and low selenenic acid concentrations ensuing from a shift in the disproportionation equilibrium. To verify that the carboxylic acid is not formed from adventitious hydrolysis of **8** (or **12**), we oxidized **3a** with benzeneseleninic anhydride (**2**) in dichloromethane in the presence of anhydrous magnesium sulfate. As expected, the more strongly seleninylating anhydride **2** afforded a slightly greater yield of cyclohexanecarboxylic acid (after workup) than when the oxidation was performed with **1** in the absence of magnesium sulfate. The failure of anhydrous conditions

Scheme III[a]

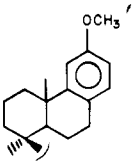


[a] R' = CH_3 or H.

(23) This reaction has precedent; phenyldiazene is known to react readily with oxygen. E. M. Kosower, *Acc. Chem. Res.*, 4, 193 (1971).
(24) Preliminary paper: T. G. Back and S. Collins, *Tetrahedron Lett.*, 2661 (1979).
(25) Even under more forcing conditions (50% acetic acid–water, 6 days), selenoester **4b** remained largely unchanged.
(26) W. Jenny, *Helv. Chim. Acta*, **35**, 1429 (1952).

Table I. Preparation of Selenoesters[a]

$$RC(O)NHNH_2 + PhSeO_2H \xrightarrow{Ph_3P} RC(O)SePh$$
3 1 4

product	R	solvent	isolated yield, %	$\nu_{C=O}$,[b] cm^{-1}	mp, °C
4a	c-C_6H_{11}	CH_2Cl_2	86	1723	oil[c]
		DMF	20		
		CH_3OH	21		
		CH_3CN	32		
		dioxane	20		
		pyridine	30		
4b	Ph	CH_2Cl_2	77	1690[d]	35-37[e]
		1% CH_3OH-CH_2Cl_2	88		
4c		CH_2Cl_2	84	1710	133-134
4d	t-C_4H_9[g]	CH_2Cl_2	83	1724	oil
4e	CH_2=CH $(CH_2)_8$[h]	CH_2Cl_2	81	1720	oil
4f	$PhCH_2$[i,j]	CH_2Cl_2	73	1710	41-43
4g	CH_3	CH_2Cl_2	94	1720[k]	oil
4h	c-C_3H_5[l]	CH_2Cl_2	89	1710	oil
4i	 [m]	CH_2Cl_2	89	1676	63-64
4j	 [n]	CH_2Cl_2	23	1692	39-41
10	CH_3O[o]	CH_2Cl_2	67	1720	oil

[a] See the Experimental Section for a typical procedure. All products had satisfactory ^1H NMR and mass spectra. [b] Spectra of oils were recorded as thin films; spectra of solids were recorded in $CHCl_3$ solution. [c] Boiling point (bulb to bulb) 100 °C (0.01 mm) [lit.[14b] bp 118–123 °C (0.12 mm)]. [d] Lit.[33] 1686 cm^{-1}. [e] Lit.[33] mp 40 °C. [f] $[\alpha]_D$ +43° (c 0.2, $CHCl_3$). Anal. Calcd for $C_{24}H_{28}O_2Se$: C, 67.44; H, 6.60. Found: C, 67.50; H, 6.72. [g] Previously reported by Gais.[14d] [h] Anal. Calcd for $C_{17}H_{24}OSe$: C, 63.13; H, 7.49. Found: C, 62.80; H, 7.62. [i] Previously reported;[34] no physical data given. Anal. Calcd for $C_{14}H_{12}OSe$: C, 61.08; H, 4.40. Found: C, 61.19; H, 4.44. [j] GC analysis detected 19% of phenylacetaldehyde in the reaction mixture. In refluxing CH_2Cl_2, benzyl phenyl selenide was isolated (preparative TLC) in 22% yield. [k] Lit.[33] 1723 cm^{-1}. [l] Anal. Calcd for $C_{10}H_{10}OSe$: C, 53.32; H, 4.48. Found: C, 53.59; H, 4.62. [m] Anal. Calcd for $C_{11}H_8OSSe$: C, 49.42; H, 3.02; S, 12.01. Found: C, 49.54; H, 3.05; S, 12.14. [n] Anal. Calcd for $C_{12}H_9NOSe$: C, 54.95; H, 3.46; N, 5.34. Found: C, 55.09; H, 3.77; N, 4.93. [o] Anal. Calcd for $C_8H_8O_2Se$: C, 44.65; H, 3.75. Found: C, 44.30; H, 3.72.

Table II. Oxidation of Hydrazides 3 with 1 in Polar Solvents[a]

entry	substrate	solvent	molar ratio of 3/1	yield, % 4[b]	5[c]	RCO_2H[d]	RCO_2CH_3[b]
1	3a	CH_2Cl_2	1:1	62[c]	10	15	
2	3a	CH_3CN	1:1	42	16	26	
3	3a	DMF	1:1	17	22	34	
4	3a	10% CH_3OH-CH_2Cl_2	1:2	34		16	14
5	3a	CH_3OH	1:2	10		44[c]	13
6	3b	CH_2Cl_2	1:2	55	11	28	
7	3b	CH_3CN	1:2	39	13	37	
8	3b	DMF	1:2	11	15	46	
9	3b	10% CH_3OH-CH_2Cl_2	1:2	58		26	16
10	3b	CH_3OH	1:2	16		18	56

[a] See the Experimental Section for the general procedure. [b] GC yield reported unless otherwise noted. [c] Isolated yield. [d] GC yield of corresponding methyl ester reported after treatment with CH_2N_2.

to block carboxylic acid formation thus lends credence to path b. Similarly, the reaction of oxygen with diazenes **6** could account for the genesis of carboxylic acids. However, their continued formation under oxygen-free conditions again supports an alternative mechanism as in path b.

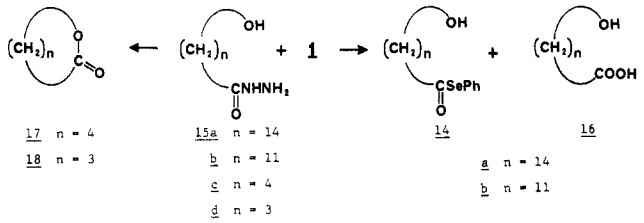
Inverse addition of benzeneseleninic acid (1) to hydrazides produces *N,N'*-diacylhydrazines (**5**) as the chief products. Thus, slow addition of **1** to hydrazides **3a** and **3f** in dichloromethane or chloroform afforded the corresponding *N,N'*-diacyl compounds **5a** and **5f** in yields of 60% and 80%, respectively (eq 7). A similar conversion of hydrazides to *N,N'*-diacylhydrazines has also been accomplished with diphenyl selenoxide.[27]

$$\underset{\text{3a, R = c-C}_6\text{H}_{11}\text{; f, R = PhCH}_2}{RCNHNH_2} + 1 \xrightarrow{\text{inverse addition}} \underset{\text{5}}{RCNHNHCR} \quad (7)$$

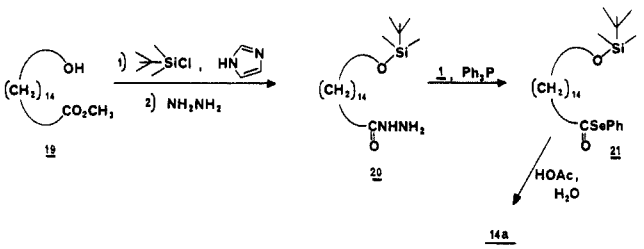
Thioesters of ω-hydroxycarboxylic acids undergo intra-

(27) K. Balenovic, R. Lazič, V. Polak, and P. Stern, *Bull. Sci., Sect. A (Zagreb)*, 17, 147 (1972); *Chem. Abstr.*, 77, 139499 (1972).

Scheme IV



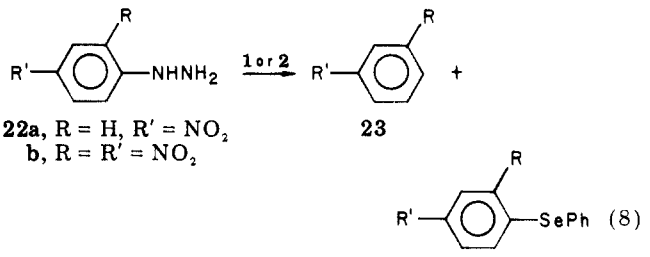
Scheme V



molecular acylation under suitable activating conditions. This makes them of considerable value as precursors of macrocyclic lactones (macrolides).[28] The possibility of exploiting analogous selenoesters in a similar manner has been but briefly explored,[12b] and their potential utility makes their preparation of interest. We therefore attempted to synthesize ω-hydroxy selenoesters **14** from the corresponding hydrazides by oxidation with **1**. Unfortunately, these hydrazides are highly insoluble in dichloromethane or other relatively nonpolar solvents, thereby precluding our usual methodology. When hydrazides **15a** and **15b** were stirred with **1** in dichloromethane, gradual dissolution was observed, and selenoesters **14a** and **14b** were obtained in modest yields of 34% and 40% along with the parent carboxylic acids **16a** and **16b** (38% and 41%, respectively). Similar treatment of hydrazides **15c** and **15d** furnished δ-valerolactone (**17**) and γ-butyrolactone (**18**) as the principal products.[29] No significant lactone formation was detected in the case of **15a** and **15b**. It therefore appears that lactonization is only observed when the product has a favored ring size. It may take place via intramolecular acylation in an intermediate such as **8** or, alternately, through spontaneous cyclization of an initially formed ω-hydroxy carboxylic acid (Scheme IV).

The low yields of the long-chain ω-hydroxy selenoesters **14a** and **14b** prompted us to seek a more efficient route to such compounds. Methyl 15-hydroxypentadecanoate (**19**) was treated sequentially with *tert*-butyldimethylsilyl chloride–imidazole[30] and hydrazine to provide hydrazide **20** in 88% yield. The solubility of the later compound in dichloromethane permitted its oxidation with **1** under our standard conditions in the presence of triphenylphosphine. The silylated selenoester **21**, obtained in 81% yield, was then converted quantitatively to the free hydroxy derivative **14a**, by acid hydrolysis (Scheme V). The latter approach, though more circuitous than direct oxidation, is the method of choice when high selenoester yields are required.

Oxidation of arylhydrazines **22a** and **22b** with **1** or **2** afforded the corresponding arenes **23a** and **23b** and aryl phenyl selenides **24a** and **24b** (eq 8). Product formation



may result from the collapse of an *N*-aryl-*N'*-(benzeneseleno)diazene (**25**, analogous to **8**), or via homolytic decomposition of diazene **26**.[31]

ArN=NSePh (**25**) ArN=NH (**26**)

Finally, we note that the oxidation of sulfonhydrazides with **1** has been reported elsewhere.[32]

Experimental Section

Melting points were obtained on an A. H. Thomas hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 467 spectrometer. NMR spectra were taken on a Hitachi Perkin-Elmer R24B instrument at 60 MHz with tetramethylsilane as an internal standard in $CDCl_3$ solution. A Varian MAT CH5 spectrometer was used to record mass spectra. GC analyses were performed on a Pye-Unicam Series 104 chromatograph equipped with a flame-ionization detector and a Varian CDS 111C electronic integrator. Glass columns (5 ft) containing 5% SE-30 on Chromosorb G-HP were employed. Internal standards were used in all analyses. Preparative TLC was carried out on Analtech 20 × 20 cm glass plates (silica gel GF, 1000 μm). Slow additions were performed with a Sage Instruments Model 355 syringe pump. Elemental analyses were obtained by Mr. H. Séguin (National Research Council of Canada), Ms. B. Gibson (University of Calgary), or Guelph Chemical Laboratories. Solvents were reagent grade and dried over molecular sieves. Pyridine was distilled from KOH prior to use. Oxidation reactions employing slow additions were performed under nitrogen. Hydrazides were obtained by hydrazinolysis of carboxylic esters or chlorides under standard conditions or from commercial sources unless otherwise noted. Benzeneseleninic acid and anhydride were either purchased (Aldrich Chemical Co.) or prepared by a literature method.[4b] All other reagents were commercially available and were purified by crystallization or distillation as required. Physical, spectral, and analytical data for selenoesters **4** are presented in Table I. Diphenyl diselenide was detected (TLC) in all hydrazide oxidations but was only isolated in a few representative examples.

Caution: Selenium compounds are toxic and should be handled with care. Hydrazine derivatives react very vigorously with **1** or **2** in the absence of solvent. Even a solid mixture of benzhydrazide and **1** was observed to decompose violently after an induction period of several minutes.

Diazene Reduction of Azobenzene. A solution of benzeneseleninic anhydride (**2**; 456 mg, 1.27 mmol) in 3 mL of DMF was added over 15 min to a solution of hydrazine hydrate (232 mg, 4.66 mmol) and azobenzene (91 mg, 0.50 mmol) in 5 mL of DMF. After 5 min, the solvent was removed in vacuo. Preparative TLC in carbon tetrachloride provided 94 mg (102%) of *N,N'*-diphenylhydrazine, identified by comparison with an authentic sample (melting point, IR).

Diazene Reduction of Cinnamic Acid. Benzeneseleninic acid (**1**; 95 mg, 0.50 mmol) in 2 mL of pyridine was added over

(28) For reviews of macrolide synthesis see: (a) K. C. Nicolaou, *Tetrahedron*, **33**, 683 (1977); (b) T. G. Back, *ibid.*, **33**, 3041 (1977); (c) S. Masamune, G. S. Bates, and J. W. Corcoran, *Angew. Chem., Int. Ed. Engl.*, **16**, 585 (1977).

(29) Similar formation of another δ-lactone has recently been reported: D. L. J. Clive, C. G. Russell, G. Chittattu, and A. Singh, *Tetrahedron*, **36**, 1399 (1980).

(30) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972).

(31) The formation of arenes from aryldiazenes has been reported.[23]

(32) T. G. Back and S. Collins, *Tetrahedron Lett.*, **21**, 2213 (1980).

(33) M. Renson and C. Draguet, *Bull. Soc. Chim. Belg.*, **71**, 260 (1962).

(34) W. Clauss and D. Menz, German Offen., 1 926 100, Dec 3, 1970; *Chem. Abstr.*, **74**, 44886 (1971).

30 min to a solution of hydrazine hydrate (120 mg, 2.4 mmol) and cinnamic acid (37 mg, 0.25 mmol) in 1 mL of pyridine. After 5 min, pyridine was removed in vacuo, and the residue was treated with excess ethereal diazomethane. Preparative TLC in benzene afforded 37 mg (90%) of methyl hydrocinnamate, identified by comparison (NMR, no signals between δ 5.0 and 7.0) with an authentic sample.

Oxidation of 1,2-Diphenylhydrazine with 2. The hydrazine (30 mg, 0.16 mmol) and **2** (72 mg, 0.20 mmol) were stirred 30 min in 5 mL of dichloromethane. Preparative TLC in 50% carbon tetrachloride–hexane gave 29 mg (97%) of *trans*-azobenzene, identified by comparison (melting point, IR, TLC) with an authentic sample.

Oxidation of 1,2-Diisopropylhydrazine with 1 or 2. 1,2-Diisopropylhydrazine hydrochloride[35] (30 mg, 0.20 mmol) was dissolved in 2 mL of $CDCl_3$ and shaken with 5% K_2CO_3 solution. The organic layer was removed by pipet and filtered through anhydrous $MgSO_4$. Anhydride **2** (36 mg, 0.10 mmol) was added, and an NMR analysis performed after 15 min showed quantitative conversion to *N,N'*-diisopropyldiazene. Additional **2** (72 mg, 0.20 mmol) was added, and the mixture was shaken periodically for 18 h. Appearance of a new signal at δ 2.1 indicated the presence of acetone (10% by NMR integration). In a separate experiment performed in carbon tetrachloride, volatile material was distilled at 20 mm into a cooled (−78 °C) receiver. The presence of the diazene was confirmed by its UV spectrum.

The oxidation was repeated with seleninic acid **1** (38 mg, 0.20 mmol). NMR analysis showed quantitative conversion to the azo compound. With 19 mg (0.10 mmol) of **1**, the conversion was >90% complete (NMR integration).

Oxidation of Cyclohexanecarboxylic Acid Hydrazide (3a) with 1 and 2. (a) The hydrazide (43 mg, 0.30 mmol) was added in one portion to **1** (63 mg, 0.33 mmol) in 3 mL of dichloromethane. After the mixture was stirred for 10 min, 15 mg (39%) of *N,N'*-bis(cyclohexylcarbonyl)hydrazine (**5a**) was filtered off: mp 275 °C (sublimes) (lit.[36] mp 281 °C); IR identical with that of an authentic sample. Preparative TLC of the filtrate in 20% benzene–hexane gave 27 mg (0.087 mmol) of diphenyl diselenide, identical with an authentic sample (melting point, TLC), and 32 mg (40%) of *Se*-phenyl cyclohexanecarboselenoate (**4a**).

(b) By Slow Addition. The hydrazide (71 mg, 0.50 mmol) in 10 mL of dichloromethane was added over 30 min to **1** (95 mg, 0.50 mmol) in 10 mL of dichloromethane. The solution was concentrated to ca. 3 mL and worked up as in the preceding experiment to furnish 83 mg (62%) of **4a** and 6 mg (10%) of **5a**. In a separate experiment, the reaction mixture was treated with excess ethereal diazomethane. GC analysis showed the presence of 11 mg (15%) of methyl cyclohexanecarboxylate.

(c) In the Presence of Radical Inhibitors. The preceding reaction was repeated in the presence of 2,6-di-*tert*-butyl-*p*-cresol (22 mg, 0.10 mmol) to afford 72 mg (54%) of **4a**. In a control experiment the *p*-cresol derivative (22 mg, 0.10 mmol) remained almost completly unreacted when treated with **1** (47 mg, 0.25 mmol) in $CDCl_3$ for 1 h (NMR analysis). Procedure b was repeated while a slow stream of oxygen was passed through the reaction mixture. The yield of **4a** was 38 mg (29%).

(d) In the Presence of Cyclohexene. The hydrazide (71 mg, 0.50 mmol) in 10 mL of dichloromethane was added over 30 min to **1** (95 mg, 0.50 mmol) in 10 mL of 50% cyclohexane–dichloromethane. The usual workup afforded 7 mg (11%) of **5a** and 41 mg (31%) of **4a**. The base-line component from the TLC of **4a** was rechromatographed in 50% ether–hexane to give 60 mg (47%) of *trans*-2-(phenylseleno)cyclohexanol (**9**),[37] identified by its IR, NMR, and mass spectra. A complex mixture of unidentified byproducts was detected by GC analysis prior to workup.

(e) By Inverse Addition. The seleninic acid **1** (95 mg, 0.50 mmol) in 10 mL of dichloromethane was added over 1 h to the hydrazide (71 mg, 0.50 mmol) in 10 mL of dichloromethane. The solution was concentrated in vacuo and hexane was added to precipitate 38 mg (60%) of **5a**.

(f) Under Anhydrous Conditions. The hydrazide (71 mg, 0.50 mmol) in 10 mL of dichloromethane was added over 1 h to **2** (180 mg, 0.50 mmol) in 10 mL of dichloromethane containing 0.5 g of anhydrous $MgSO_4$ in oven-dried glass apparatus. The mixture was filtered, concentrated, and separated by preparative TLC to afford 83 mg (62%) of **4a**. The base-line component was removed with methanol, evaporated to dryness, and triturated with ether. The ether was filtered, washed twice with water, dried over anhydrous $MgSO_4$ and evaporated in vacuo to furnish 15 mg (23%) of cyclohexanecarboxylic acid, identified by comparison with an authentic sample (IR, NMR, GC).

Oxidation of Benzhydrazide (3b) with 1. (a) The hydrazide (68 mg, 0.50 mmol) was added in one portion to **1** (104 mg, 0.55 mmol) in 1 mL of chloroform. After 5 min, the solution was filtered to provide 17 mg (28%) of *N,N'*-dibenzoylhydrazine (**5b**): mp 232–234 °C (lit.[38] mp 241 °C); IR identical with that of an authentic sample. Preparative TLC of the filtrate in 20% benzene–hexane gave 61 mg (47%) of *Se*-phenyl selenobenzoate (**4b**).

(b) By Slow Addition. The reaction was performed with 0.50 mmol of **3b** and 1.00 mmol of **1** as described for **3a** to give the products shown in Table II.

(c) In the Presence of Benzoquinone. The preceding reaction was repeated with 1.00 mmol of **3b** and 1.00 mmol of **1** in the presence of benzoquinone (11 mg, 0.10 mmol) to afford 130 mg (50%) of **4b**.

Oxidation of *O*-Methylpodocarpic Acid Hydrazide (3c) with 1. The hydrazide[39] (64 mg, 0.21 mmol) was added in one portion to **1** (44 mg, 0.23 mmol) in 2 mL of dichloromethane. After 5 min, preparative TLC in 5% methanol–chloroform afforded 12 mg (19%) of *N,N'*-bis(*O*-methylpodocarpoyl)hydrazine (**5c**): mp 108–110 °C; $[\alpha]_D$ +128° (*c* 0.1, $CHCl_3$); IR (Nujol) 3290, 1665 cm^{-1}. Anal. Calcd for $C_{36}H_{48}N_2O_4$: C, 75.47; H, 8.45; N, 4.90. Found: C, 75.11; H, 8.62; N, 4.78. More mobile material was removed and rechromatographed in benzene to furnish 55 mg (61%) of *Se*-phenyl *O*-methylselenopodocarpoate (**4c**).

Preparation of Selenoesters 4a–j and Selenocarbonate 10 (See Table I). Typical Procedure. Hydrazide **3a** (71 mg, 0.50 mmol) and triphenylphosphine (131 mg, 0.50 mmol) in 10 mL of dichloromethane were added over 0.5 h to a stirred suspension of seleninic acid **1** (189 mg, 1.00 mmol) in 10 mL of dichloromethane. The clear, yellow solution was concentrated in vacuo, and the residue was separated by preparative TLC in 30% benzene–hexane to afford 62 mg (0.20 mmol) of diphenyl diselenide (R_f 0.8), identified by comparison (melting point, TLC) with an authentic sample, and selenoester **4a**: 115 mg (86%); R_f 0.5; NMR δ 7.6–7.1 (complex, 5 H), 2.6 (m, 1 H), 2.3–1.0 (complex, 10 H); mass spectrum, *m/e* 268 (M^+, ^{80}Se), 266 (M^+, ^{78}Se); for IR and boiling point data, see Table I. The base-line component was removed and rechromatographed in 20% ether–chloroform to give 136 mg (98%) of triphenylphosphine oxide (R_f 0.5), identified by comparison (melting point, TLC, IR) with an authentic sample.

Oxidation of Hydrazide 3a with 1 in Polar Solvents (See Table II). General Procedure. The hydrazide (0.50 mmol) in 10 mL of the solvent was added over 1 h to **1** (95 mg, 0.50 mmol, or 1.89 mg, 1.00 mmol) in 10 mL of the solvent. The yields of **4a** and methyl cyclohexanecarboxylate were obtained by GC analysis. Cyclohexanecarboxaldehyde was not detected in significant amounts. The reaction mixture was concentrated, and addition of hexane precipitated **5a**. In a separate experiment the reaction mixture was treated with excess ethereal diazomethane, and the yield of cyclohexanecarboxylic acid was determined by GC analysis of the resulting methyl ester. In entry 4, the yield of the acid was determined by difference between analyses before and after addition of diazomethane. The isolation of the acid in entry 5 was performed as described previously.

Oxidation of Hydrazide 3b with 1 in Polar Solvents (See Table II). The general procedure for hydrazide **3a** was employed.

Reaction of Hydrazide 3b with Benzeneselenenyl Chloride (11). The hydrazide (41 mg, 0.30 mmol) in 5 mL of dichloromethane was added over 30 min to **11** (191 mg, 1.00 mmol) in 10% pyridine–dichloromethane. The solvent was removed in vacuo,

(35) H. L. Lochte, J. R. Bailey, and W. A. Noyes, *J. Am. Chem. Soc.*, **43**, 2597 (1921).
(36) S. Olsen and E. M. Enkemeyer, *Chem. Ber.*, **81**, 359 (1948).
(37) (a) H. J. Reich, *J. Org. Chem.*, **39**, 428 (1974); (b) K. B. Sharpless and R. F. Lauer, *ibid.*, **39**, 429 (1974).
(38) J. R. A. Pollock and R. Stevens, Eds., "Dictionary of Organic Compounds", Eyre and Spottiswoode, London, 1965.
(39) J. W. ApSimon and O. E. Edwards, *Can. J. Chem.*, **40**, 896 (1962).

and preparative TLC afforded 37 mg (47%) of selenoester **4b**.

Reaction of Phenylacethydrazide (3f) with 1 by Inverse Addition. Seleninic acid **1** (189 mg, 1.00 mmol) in 10 mL of chloroform was added over 1 h to **3f** (150 mg, 1.00 mmol) in 10 mL of chloroform. The solution was concentrated to ca. 4 mL, and hexane was added to precipitate 107 mg (80%) of **5f**: mp 235–236 °C (lit.[40] mp 243 °C); IR identical with that of an authentic sample.

***Se*-Phenyl 15-Hydroxypentadecanecarboselenoate (14a). (a) By Direct Oxidation with 1.** 15-Hydroxypentadecanoic acid hydrazide[41] (**15a**; 68 mg, 0.25 mmol) and seleninic acid **1** (95 mg, 0.50 mmol) were stirred in 20 mL of dichloromethane. The hydrazide slowly dissolved, and after 24 h preparative TLC (50% ether–benzene) gave 34 mg (34%) of the title compound: mp 50–52 °C (from hexane); IR (Nujol) 3430, 3370, 1720 cm^{-1}. Anal. Calcd for $C_{21}H_{34}O_2Se$; C, 63.44; H, 8.63. Found: C, 63.21; H, 8.80. In a separate experiment, treatment of the reaction mixture with excess ethereal diazomethane followed by GC analysis indicated the presence of 26 mg (38%) of methyl 15-hydroxypentadecanoate (**19**).

(b) Via Silyl Ether 21. Methyl 15-hydroxypentadecanoate[41] (**19**; 0.41 g, 1.5 mmol), *tert*-butyldimethylsilyl chloride (0.30 g, 2.0 mmol), and imidazole (0.20 g, 3.0 mmol) were stirred 31 h in 3 mL of DMF. The solvent was removed in vacuo, and the residue was triturated with chloroform, washed thoroughly with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting crude silyl ether was refluxed 1 h in 3 mL of ethanol containing 0.5 mL of hydrazine. The ethanol was evaporated, and the product was taken up in chloroform, washed, dried as before, filtered through Celite, and evaporated to near dryness. Addition of hexane precipitated the silyl ether hydrazide **20** as a waxy semisolid (0.51 g, 88%) of sufficient purity for further use: IR (Nujol) 3320, 3180, 1630 cm^{-1}.

Compound **20** (74 mg, 0.19 mmol) and triphenylphosphine (52 mg, 0.20 mmol) in 7 mL of dichloromethane were added over 40 min to **1** (85 mg, 0.45 mmol) in 5 mL of dichloromethane. Preparative TLC in 40% benzene–hexane gave 79 mg (81%) of **21** as a pale yellow oil, IR (film) 1728 cm^{-1}. The latter compound (41 mg, 0.080 mmol) was treated with 2 mL of 50% acetic acid–water containing sufficient acetone to effect dissolution. After 24 h, the solution was diluted with water and extracted three times with chloroform. The organic extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. Preparative TLC as in procedure a provided 33 mg (100%) of selenoester **14a**: mp 49–51 °C; IR identical with that of an analytical sample.

12-Hydroxydodecanoic Acid Hydrazide (15b). Dodecanolide[42] (1.98 g, 10 mmol) was refluxed 5 h in 4 mL of ethanol containing 2 mL of hydrazine. An additional 5 mL of ethanol was added, and 1.31 g (57%) of the title compound crystallized on cooling; mp 141–142 °C, after recrystallization from methanol. Anal. Calcd for $C_{12}H_{26}N_2O_2$: C, 62.55; H, 11.38; N, 12.16. Found: C, 62.22; H, 11.36; N, 11.93.

***Se*-Phenyl 12-Hydroxydodecanecarboselenoate (14b).** Hydrazide **15b** (58 mg, 0.25 mmol) and **1** (95 mg, 0.50 mmol) were stirred 6 h in 20 mL of dichloromethane. The title compound was isolated as for **14a** as a pale yellow oil [36 mg (40%); IR (thin film) 3440, 1720 cm^{-1}] which gave a crystalline *N*-phenylurethane with phenyl isocyanate; mp 73–75 °C. Anal. Calcd for $C_{25}H_{33}NO_3Se$: C, 63.28; H, 7.01; N, 2.95. Found: C, 63.81; H, 6.87; N, 3.11. GC analysis as for **16a** indicated the presence of 41% of **16b**.

Oxidation of 5-Hydroxypentanoic Acid Hydrazide (15c) with 1. The hydrazide (66 mg, 0.50 mmol) was added in small portions over 45 min to **1** (189 mg, 1.00 mmol) in 40 mL of dichloromethane. After the mixture was stirred for 1 h, GC analysis indicated the presence of 50 mg (100%) of δ-valerolactone (**17**).

Oxidation of 4-Hydroxybutanoic Acid Hydrazide (15d) with 1. The hydrazide (30 mg, 0.25 mmol) and **1** (95 mg 0.50 mmol) were allowed to react as in the preceding experiment. GC analysis indicated the presence of 21 mg (96%) of γ-butyrolactone. The experiment was repeated with 5 mmol of **15d** and 10 mmol of **1**. The reaction mixture was distilled to provide 0.39 g (91%) of the lactone: bp 83–84 °C (15 mm) [lit.[38] bp 89 °C (12 mm)]; identical with an authentic sample (IR, GC).

Oxidation of *p*-Nitrophenylhydrazine (22a) with 2. The hydrazine (77 mg, 0.50 mmol) was added in one portion to **2** (200 mg, 0.56 mmol) in 5 mL of dichloromethane. After 5 min the reaction mixture was separated by preparative TLC in 20% benzene–carbon tetrachloride to afford *p*-nitrophenyl phenyl selenide [**24a**; 83 mg (60%); mp 56–58 °C (from methanol) (lit.[43] mp 58 °C)] and nitrobenzene (**23a**; 12 mg, 20%), identified by comparison with an authentic sample (IR, NMR, TLC).

Oxidation of 2,4-Dinitrophenylhydrazine (22b) with 1 or 2. The title hydrazine was oxidized as in the previous experiment. Preparative TLC in benzene afforded 92 mg (56%) of 2,4-dinitrophenyl phenyl selenide (**24b**):[44] mp 129–130 °C (from methanol); NMR δ 9.19 (d, J = 2 Hz, 1 H), 8.17 (dd, J = 9, 2 Hz, 1 H), 8.0–7.4 (m, 5 H), 7.26 (d, J = 9 Hz, 1 H). Anal. Calcd for $C_{12}H_8N_2O_4Se$: C, 44.58; H, 2.50; N, 8.67. Found: C, 44.52; H, 2.55; N, 8.68. A band of greater polarity provided 25 mg (29%) of *m*-dinitrobenzene [**23b**, mp 81–85 °C (lit.[38] mp 89.57 °C)] identified by its IR, NMR, and mass spectra.

The hydrazine (50 mg, 0.25 mmol) was oxidized with **1** (50 mg, 0.26 mmol) as in the previous procedure to afford 58% of **24b** and 24% of **23b**.

Registry No. **1**, 6996-92-5; **2**, 17697-12-0; **3a**, 38941-47-8; **3b**, 613-94-5; **3c**, 76582-30-4; **3d**, 42826-42-6; **3e**, 5458-77-5; **3f**, 937-39-3; **3g**, 1068-57-1; **3h**, 6952-93-8; **3i**, 2361-27-5; **3j**, 54-85-3; **4a**, 60718-41-4; **4b**, 38447-68-6; **4c**, 76582-31-5; **4d**, 60718-40-3; **4e**, 73335-20-3; **4f**, 30876-65-4; **4g**, 1068-57-1; **4h**, 73335-19-0; **4i**, 76529-36-7; **4j**, 76529-37-8; **5a**, 5814-04-0; **5b**, 787-84-8; **5c**, 76529-38-9; **5f**, 793-25-9; **9**, 35446-84-5; **10**, 76529-39-0; **11**, 5707-04-0; **14a**, 73335-23-6; **14b**, 76529-40-3; **15a**, 18270-60-5; **15b**, 76529-41-4; **15c**, 2034-25-5; **15d**, 3879-08-1; **16a**, 4617-33-8; **16b**, 505-95-3; **17**, 542-28-9; **18**, 96-48-0; **19**, 76529-42-5; **20**, 73335-17-8; **21**, 73335-21-4; **22a**, 100-16-3; **22b**, 119-26-6; **23a**, 98-95-3; **23b**, 99-65-0; **24a**, 6343-83-5; **24b**, 67516-66-9; hydrazine, 302-01-2; azobenzene, 103-33-3; *N,N'*-diphenylhydrazine, 122-66-7; cinnamic acid, 621-82-9; methyl hydrocinnamate, 103-25-3; **14b** (*N*-phenylurethane derivative), 76529-43-6; benzyl phenyl selenide, 18255-05-5; 1,2-diisopropylhydrazine hydrochloride, 76529-44-7; *N,N'*-diisopropyldiazene, 3880-49-7; diphenyl diselenide, 1666-13-3; phenylacetaldehyde, 122-78-1; 2,6-di-*tert*-butyl-*p*-cresol, 128-37-0; dodecanolide, 947-05-7; triphenylphosphine oxide, 791-28-6; phenyl isocyanate, 103-71-9; *tert*-butyldimethylsilyl chloride, 18162-48-6; imidazole, 288-32-4; *trans*-azobenzene, 17082-12-1; (c-C_6H_{11})CO_2H, 98-89-5; (c-C_6H_{11})CO_2CH_3, 4630-82-4; $PhCO_2H$, 65-85-0; $PhCO_2CH_3$, 93-58-3.

(40) A. Kreutzberger, *J. Org. Chem.*, **22**, 679 (1957).
(41) R. U. Lemieux, *Can. J. Chem.*, **31**, 396 (1953).
(42) K. Kosswig, W. Stumpf, and W. Kirchhof, *Justus Liebigs Ann. Chem.*, **681**, 28 (1965).
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(44) Previously reported: no melting point given. L. Bartolotti and R. Passerini, *Ric. Sci.*, **25**, 1095 (1955); *Chem. Abstr.*, **50**, 224e (1956).