Varian CFT-20 spectrometer with Me_4Si as internal standard and are reported in parts per million. IR spectra were recorded on a Unicam SP-200 spectrophotometer. Mass spectra were taken on either an AEI-MS 9 or MS 12 spectrometer at 70 eV. Aluminium oxide for chromatography was Merck PF_{254} (type E) and Kieselgel was Merck (0.05–0.2 mesh).

Reduction of Bicyclo[2.2.2]octa-2,5-dione. The dione **1** (1.40 g, 10 mmol) was dissolved in ethanol (300 ml), the solution was stirred at room temperature, and sodium borohydride (2.85 g, 7.5 mmol) was added. After 3 h the clear solution was acidified with 20% HCl (100 ml) and then neutralized with Na_2CO_3. The solvent was removed by evaporation and the residual white solid was heated under reduced pressure whereupon a mixture of the diols (1.0 g) sublimed. The mixture was preadsorbed on Kieselgel (100 g), added to a column of Kieselgel (1000 g), and eluted with a mixture of $CHCl_3$–EtOH (9:1 v/v). Compound **2a** (100 mg) eluted first followed by a mixture of **3a** and **4a** (600 mg). The latter mixture was preadsorbed on alumina (15 g), added to a column of alumina (150 g), and eluted with $CHCl_3$–petroleum ether (9:1 v/v). Compound **3a** (300 mg) was eluted first followed by **4a** (150 mg).

Compound **2a:** mass spectrum *m/e* 142 (16%, M^+), 124 (66%, $M^+ - H_2O$); IR (KBr) 3320 (b), 2920, 2858, 1445, 1360 cm^{-1}; ^1H NMR δ 4.0 (m, 2 H), 2.2–1.0 (m, 12 H).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.60; H, 9.85. Found: C, 67.76; H, 9.79.

Compound **3a:** mass spectrum *m/e* 142 (20%, M^+), 124 (40%, $M^+ - H_2O$); IR (KBr) 3280 (b), 2920, 2858, 1440, 1362 cm^{-1}; ^1H NMR δ 4.0 (m, 2 H), 2.2–1.0 (m, 12 H).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.60; H, 9.85. Found: C, 67.70; H, 10.10.

Compound **4a:** mass spectrum *m/e* 142 (1%, M^+), 124 (100%, $M^+ - H_2O$); IR (KBr) 3280 (b), 2920, 2858, 1440, 1365 cm^{-1}.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.60; H, 9.85. Found: C, 67.45; H, 10.09.

A more efficient separation of the mixture of the three diols could be effected by high-pressure liquid–liquid chromatography on Porasil (4.0 ft × 0.375 in.) using MeOH–$CHCl_3$ (3:97 v/v) as eluent. Under these conditions 1.0 g of the mixture gave 100 mg of **2a,** 300 mg of **3a,** and 400 mg of **4a.**

Esterification of 2a, 3a and 4a. The diol (100 mg, 0.7 mmol) was dissolved in dry THF (10 ml) and butyryl chloride (80 mg, 0.74 mmol) was added. The solution was stirred for ca 2 h, the reaction being monitored by TLC (SiO_2) and worked up when the diester was detected (R_f ~0.9, Et_2O). The solvent was removed under reduced pressure and the residue was extracted with ether. Removal of the ether gave an oil which on preparative TLC (SiO_2, Et_2O) gave the monoester (ca. 125 mg, 80%).

Compound **2b:** mass spectrum *m/e* 212 (1%, M^+), 194 (55%, $M^+ - H_2O$); ^1H NMR δ 5.0 (m, 1 H), 4.0 (m, 1 H), 2.6–0.8 (m, 17 H).

Compound **3b:** mass spectrum *m/e* 212 (2%, M^+), 194 (100%, $M^+ - H_2O$); ^1H NMR δ 5.0 (m, 1 H), 4.0 (m, 1 H), 3.0–1.0 (m, 17 H).

Compound **4b,c:** These compounds were distinct on TLC but were not separated from each other. The mixture had mass spectrum *m/e* 212 (1%, M^+), 194 (100%, $M^+ - H_2O$); ^1H NMR δ 5.0 (m, 1 H), 4.0 (m, 1 H), 1.0–3.0 (m, 17 H).

Oxidation of the Diols to the Monoketones. The diol **4a** (100 mg, 0.07 mol) was dissolved in acetone (1.5 ml) and Jones reagent (0.01 N) was added dropwise, the reaction mixture being monitored by TLC (Al_2O_3; Et_2O–$CHCl_3$, 3:2 v/v) after each addition. After complete disappearance of the starting material the reaction mixture was separated by TLC, using the above conditions. TLC showed two compounds, the monoketones **5a** and **5b.** The mixture of **5a,b** had mass spectrum *m/e* 140 (M^+), 122 ($M^+ - H_2O$); IR ($CDCl_3$) 3600, 3400, 2900, and 1740 cm^{-1}. Oxidation of the mixture of monoketones with Jones reagent gave the diketone **1.** Similar oxidation of **2a** gave only the monoketone **5a** (TLC), and oxidation of **3a** gave only the monoketone **5b** (TLC). Both **5a** and **5b** were separately converted into **1** by further oxidation.

Reduction of the Keto Acids 6a and 6b. The keto acid (9.5 g, 52.2 mmol) was dissolved in ethanol (150 ml), the solution was made alkaline with 10% NaOH solution, sodium borohydride (6.0 g, 15.8 mmol) was added in several portions, and the mixture was refluxed for 3 h. The solution was neutralized with 10% HCl solution, the ethanol was removed under reduced pressure, and the residual mixture was extracted with chloroform. The chloroform solution was dried ($MgSo_4$) and the solvent removed by evaporation to give the corresponding alcohols (**6a** → **7a; 6b** → **7b** + **8b**).

Compound **7a:** 8.1 g, 85%; mp 143–144 °C (lit.[5] 143–144 °C); mass spectrum *m/e* 170.0951 ($C_9H_{14}O_3$ requires 170.0943); ^1H NMR δ 8.40 (s, 2 H, OH, CO_2H), 3.85 (m, 1 H, H-5), 2.8–1.6 (m, 11 H); ^{13}C NMR 180.04 (CO_2H), 68.46 (C-5), 41.47 (C-2), 33.68 (C-6), 31.16 (C-4), 28.55 (C-1), 25.01 (C-7), 22.80 (C-8), 21.28 ppm (C-3).

Compound **7b** (recrystallization from acetone): 66%; mp 167–168 °C; mass spectrum *m/e* 184.1087 ($C_{10}H_{16}O_3$ requires 184.1099), 93 (100%); IR ($CHCl_3$) 3500, 1710 cm^{-1}; ^1H NMR δ 6.50 (s, 2 H, OH, CO_2H), 3.85 (m, 1 H, H-5), 2.8–1.6 (m, 11 H), 1.30 (s, 3 H, CH_3); ^{13}C NMR 182.78 (CO_2H), 68.29 (C-5), 43.44 (C-2), 35.80 (C-6), 33.43, 32.53 (C-1, 4), 30.01 (C-3), 26.28 (Me), 22.76 (C-8), 20.07 ppm (C-7).

Compound **8b** (separated from **7b** by conversion of **7b** to the lactone **9b** (see below): 9%; mp 182–183 °C; mass spectrum *m/e* 184.1089 ($C_{10}H_{16}O_3$ requires 184.1099), 93 (100%); IR ($CHCl_3$) 3500, 1710 cm^{-1}; ^1H NMR δ 6.50 (s, 2 H, OH, CO_2H), 3.85 (m, 1 H, H-5), 2.8–1.6 (m, 11 H), 1.30 (s, 3 H, CH_3); ^{13}C NMR 181.80 (CO_2H), 68.00 (C-5), 42.76 (C-2), 35.53 (C-6), 34.31 (C-3), 33.11, 32.78 (C-1,4), 26.28 (Me), 20.91 (C-7), 17.61 ppm (C-8).

Lactonization of 7a and 7b. The alcohol (300 mg, 176 mmol) was dissolved in dry toluene (benzene for **7b**) (30 ml), a small amount of *p*-toluenesulfonic acid (ca. 10 mg) was added, and the mixture was heated to reflux under N_2 for 2 h. Ether (20 ml) was then added to the cooled solution, and the mixture was then extracted with 10% aqueous $NaHCO_3$ (2 × 5 ml), and then washed with water until the washings were neutral. The organic layer was dried ($MgSO_4$) and evaporation of the solvent gave the lactone.

Compound **9a** (purified by sublimation (13 mm), recrystallization from petroleum ether–benzene): 80 mg, 37%; mp 205–206 °C (lit.[5] 204.5–205.5 °C); mass spectrum *m/e* 152.0843 ($C_9H_{12}O_2$ requires 152.0837); IR ($CHCl_3$) 1760 cm^{-1}; ^1H NMR δ 4.5 (m, 1 H, H-5), 3.2–1.6 (m, 11 H); ^{13}C NMR 77.97 (C-2), 40.93 (C-5), 35.26 (C-3), 28.12 (C-6), 26.36 (C-4), 23.78 (C-1), 21.87, 21.52 ppm (C-7,8).

Compound **9b** (purified by sublimation): 195 mg, 71%; mp 124–125 °C; mass spectrum *m/e* 166.0994 ($C_{10}H_{14}O_2$ requires 166.0992); IR ($CHCl_3$) 1760 cm^{-1}; ^1H NMR δ 4.65 (m, 1 H, H-2), 3.2–1.6 (m, 11 H), 1.2 (s, 3 H, Me); ^{13}C NMR 76.67 (C-2), 43.00 (C-5), 35.39, 34.95 (C-3,6), 30.69 (C-4), 27.01 (C-1), 21.59 (C-8), 20.51 (C-7), 18.12 ppm (Me).

Acknowledgments. We thank the Science Research Council (U.K.) for support. One of us (D.D.) thanks the Pahlavi Foundation for a grant.

Registry No.—**1,** 57346-05-1; **2a,** 57378-53-7; **2b,** 60662-00-2; **3a,** 57378-52-6; **3b,** 60687-03-8; **4a,** 57346-04-0; **4b,** 60687-04-9; **4c,** 60687-05-0; **5a,** 60662-01-3; **5b,** 60687-06-1; **6a,** 49826-60-0; **6b,** 57346-07-3; **7a,** 41977-18-8; **7b,** 38347-91-0; **8b,** 57378-54-8; **9a,** 49826-59-7; **9b,** 38348-92-1; butyryl chloride, 141-75-3.

References and Notes

(1) P. C. Guha and C. Krishnamurthy, *Chem. Ber.*, **72,** 1374 (1939).
(2) B. J. Hunt and W. Rigby, *Chem. Ind. (London)*, 1868 (1967).
(3) P. J. Garratt and R. Riguera, *J. Org. Chem.*, **41,** 465 (1976).
(4) It is well known that $Eu(DPM)_3$ binds more readily to hydroxyl than to ester functions. See J. K. M. Sanders and D. H. Williams, *J. Am. Chem. Soc.*, **93,** 641 (1971); F. Bohlman and J. Jacob, *Chem. Ber.*, **108,** 2809 (1975).
(5) R. A. Lee, *Tetrahedron Lett.*, 3333 (1974).
(6) Each ketone group in **1** is flanked on one side by a two-carbon methylene bridge and on the other by a bridge consisting of a methylene group and a remote carbonyl group. The steric shielding provided by these bridges would appear to be very similar.
(7) See E. C. Ashby and S. A. Noding, *J. Am. Chem. Soc.*, **98,** 2010 (1976).
(8) However, compound **4a** can be obtained from either the monoketone **5a** or **5b** whereas **2a** can only arise from **5a,** so that without any steric preference twice as much of **4a** should be obtained as **2a** (or **3a**). That there is some direction of the second reduction is supported by the finding that with the more hindered reducing agent no **2a** was formed.

Oxidation of 1,3-Dihydrobenzo[*c*]selenaphene (2-Selenaindan) to 2,2′-Diformyldibenzyl Diselenide

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As part of the development of an alternate synthesis of selenobiotin (Figure 1),[1] we wished to explore the possibilities of α-alkylation of selenoxides lacking β hydrogen: whether they would be stable, and if they would react similarly to

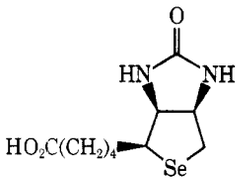
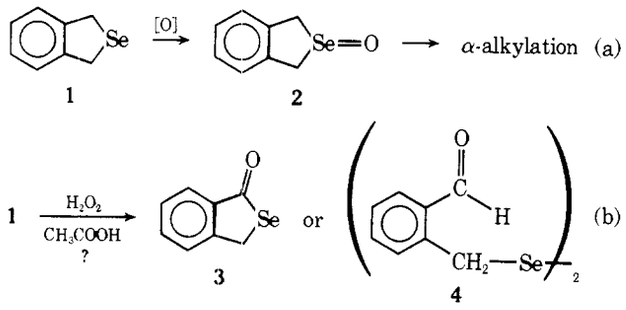


Figure 1. selenobiotin

sulfoxides in α-alkylation reaction.[2] A simplified model compound on which to try this reaction appeared to be 2-selenaindan (1), and so we attempted the first step of Scheme Ia. Since even oxidation at low temperatures with ozone failed

Scheme I



to result in anything but intractable yellow oils with IR and NMR spectra indicating that we had obtained a product or products not including the one in which we were interested at the time, we directed our experimental efforts into other areas.

Our interest was renewed in this reaction when a report appeared[3] that oxidation of 1 with H_2O_2/CH_3CO_2H yielded 2-selenaphthalide (3), Scheme Ib. Physical and spectral properties were attributed to 3, however, which were different from those attributed to 3 synthesized by nonoxidative routes.[4] Furthermore, the controlled oxidation of 1 with a stoichiometric amount of cold H_2O_2 led to a solution of 2 (which is not stable enough to be isolated), which was then converted to benzo[3]selenophene.[5] It was of interest to us to identify the solid reported by Magdesieva and Vdovin as the major product of a nonstoichiometric oxidation of 1.

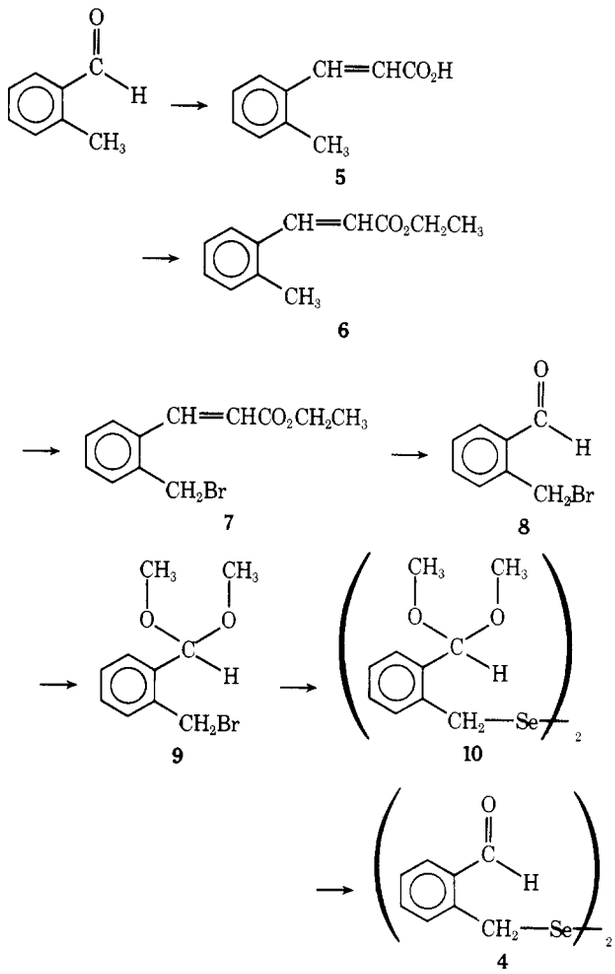
We repeated the oxidation of 1, using the reported[3] H_2O_2/CH_3COOH reagent, and continued to obtain as the major product a viscous yellow oil which did not crystallize, and which presented the same spectroscopic appearance and difficulty in purification which we had previously encountered with ozone oxidation. During all stages of purification, this oil slowly deposited elemental selenium, which has been reported to be characteristic of benzyl diselenides.[6] Spectral and TLC evidence indicated that while the oil was readily purified to better than 90% one component, a purity of greater than 98% was inaccessible by the methods we attempted [the high-purity, highly viscous light-yellow oils (which were used for all recorded spectra determinations) did not crystallize under a vacuum, protected from light]. NMR measurements gave the same two peaks (δ 4.28, singlet, CH_2; δ 7.50, multiplet, aromatic CH) reported by Magdesieva and Vdovin,[3] in the ratio of 4:2. Also, however, there is observed an additional peak at δ 10.1, singlet, relative intensity 1, characteristic of aromatic aldehydes.[7] The infrared spectrum of our oil, and the product reported by Magdesieva and Vdovin, possesses a peak at 1695 cm^{-1}, characteristic of an aromatic aldehyde.[8a] Additional absorptions not reported by Magdesieva and Vdovin, of 2835 and 2740 cm^{-1}, also characteristic of aldehydes,[8b] were found in the IR spectrum of our oil.

In addition, we repeated one of the reported syntheses of 3,[4b] and verified that the IR and NMR features obtained for 2-selenaphthalide are different from those for the yellow oil, and those reported by Magdesieva and Vdovin[3] (Table I).

[It is interesting to note that only the relative electronegativities of O, S, and Se (last column of Table I) need to be invoked to explain the relative chemical shifts of both the aliphatic and aromatic protons in the authentic 2-X-phthalides. It would not be possible to accommodate the reported relative chemical shift of the Magdesieva and Vdovin[2] compound on an electronegativity argument alone.]

On the basis of the spectral data reported in Table I, which are identical except for the aldehyde hydrogen peak in the NMR (δ 10.1), we postulated that oxidation of 1 yields 4, not 3. The reported elemental analysis[3] supports equally well structure 3 or 4 (compound 3, C_8H_6OSe, requires 48.75 C and 3.07 H; compound 4, $C_{16}H_{14}O_2Se_2$, requires 48.26 C and 3.54 H; Magdesieva and Vdovin report 48.6 C and 3.5 H[3]). We have confirmed that 2,2′-diformyldibenzyl diselenide (4) is indeed a product of nonstoichiometric oxidation of 1 by the synthesis indicated in Scheme II.

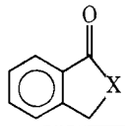
Scheme II



Several alternate mechanisms can account for these results on the basis of limited extrapolations of well-documented reactions of selenium and sulfur compounds. Scheme III represents a possible route via a seleno-Pummerer rearrangement.[5,12] Scheme IV invokes a selenoxide–selenenate rearrangement analogous to similar rearrangements of sulfoxides in solution,[13] in thermal reactions,[14] and in the mass spectrometer.[15] Corresponding rearrangements have been suggested for reactions of selenoxides in solution,[16] and observed in mass spectrometry.[17]

The absence of aliphatic hydrogens β to the selenoxide, and

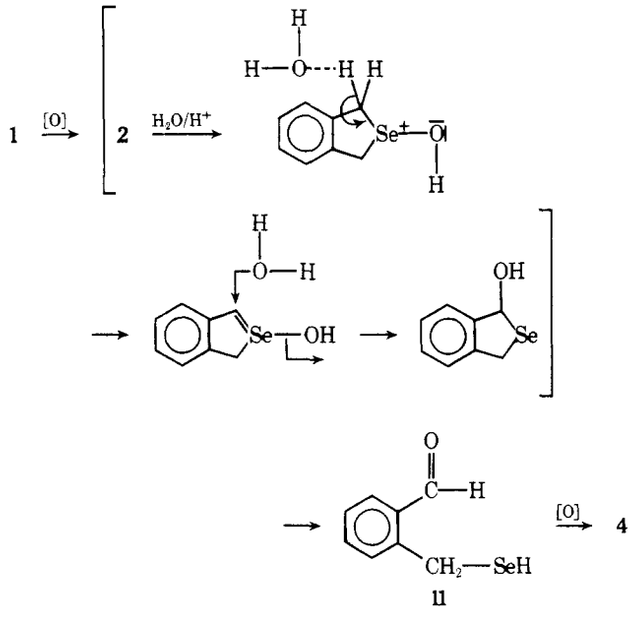
Table I



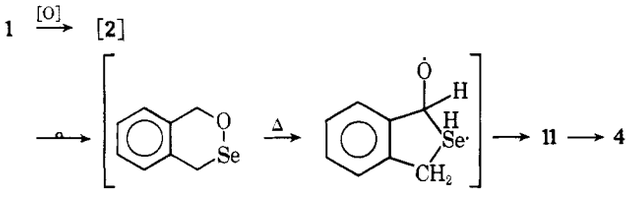
Registry no.	X	δ_{CH_2}	δ_{ArH} (center of multiplet)	δ –C(=O)H	$\nu_{C=O}$, cm^{-1}	Electronegativity of X[a]
87-41-2	O	5.27 (s) [5.32 (s)][c]	7.70 (m) [7.65 (m)][c]	*f*	1761[b]	3.50
1194-57-6	S	4.33	7.45 (m)	*f*	1686[b]	2.44
4938-13-0	Se	4.55 (s)	7.58 (m)	*f*	1668	2.48
	Magdesieva and Vdovin compd	4.28 (s)[d]	7.50 (m)[d]		1695[d]	
	Yellow oil; compd 4	4.28 (s)[e]	7.50 (m)[e]	10.1 (s)[e]	1695[e]	

[a] Reference 9. [b] Reference 10. [c] Reference 11. [d] Reference 3. [e] Measured in same solvents and at same concentrations reported by Magdesieva and Vdovin.[3] [f] No NMR absorption in the region δ 9–11.

Scheme III



Scheme IV



the geometrical restrictions of the phthalide molecules, make unlikely an elimination of the kind so elegantly exploited synthetically by Sharpless,[18] and result in a reactivity apparently unique to this ring system.[5] The similar compound, dibenzyl selenoxide, is stable even when heated to its melting point.[19]

Experimental Section

All temperature readings were uncorrected. IR spectra were determined on a Perkin-Elmer Model 457 spectrophotometer on dilute solutions in KBr pellets. NMR spectra were recorded on a Varian A-60 or HA-100D spectrophotometer in 8% w/w solutions in CCl_4, unless otherwise specified. Mass spectra were determined on a Du Pont 24-491B mass spectrometer. Sodium selenide was purchased from Alfa Inorganics, Inc., Beverly, Mass. Those melting points taken in sealed evacuated capillaries are designated (sec).

2-Selenaindan (1) was prepared from α,α'-dibromo-*o*-xylene (Aldrich Chemical Co.) by the method of Magdesieva and Vdovin.[3] Yields ranged from 34 to 73%, mp 33.5–34.0 °C (sec).

Oxidation of 2-Selenaindan. A stirred solution of **1** (10.0 g, 0.055 mol) in glacial acetic acid (100 ml) at 0–5 °C was treated with a 22% solution of hydrogen peroxide (11.5 ml, 0.08 mol) in the course of 0.5 h. Removal of solvent under reduced pressure at 35 °C followed by steam distillation recovered 1.5 g of unreacted **1**. The residual oil was dried azeotropically with benzene to leave 8.3 g of a yellow-orange oil after solvent removal; the oil lightened to a bright yellow on cooling (such thermochromic behavior has previously been noted for diselenides).[20] TLC (Chromar 500, Mallinckrodt, Inc.) with benzene eluent and iodine development gave R_f 1.00 (**1**), 0.47 (visibly yellow), 0.05 (minor; Se?); in addition, a reddish streak (amorphous Se allotrope) developed on short standing, R_f 0.47–0.23, indicative of decomposition. Column chromatography on a 2-in. diameter column using 400 g of neutral alumina, Brockman activity 1 (Fischer Scientific Co., Inc.) with benzene eluent separated 2.3 g of **1**, followed by 3.9 g (58%) of diselenide **4**. Column wash with methanol gave 1.6 g of brown tar which displayed no absorptions in the carbonyl region; this material was not further investigated. The upper portion of the column was gray-black at this point, probably owing to precipitated elemental selenium.

Solution of **4** in alcohol and treatment with sodium borohydride completely discharged the yellow coloration, which was re-formed on air oxidation.

Repeat of TLC with the yellow oil, under the same conditions as described above, gave a lone R_f 0.46, with slight streaking of red selenium. After 24 h in the dark, TLC gave a single spot, R_f 0.47, with considerable streaking attributable to selenium. The oil as obtained by column chromatography gave $\nu_{C=O}$ 1695 cm^{-1} in the IR (film between NaCl plates), and the NMR signals noted in the discussion section. The aromatic region of the NMR spectrum of **4** greatly resembles the same region of the NMR spectrum of *o*-tolualdehyde.[21] Attempts to crystallize the oil, with or without a variety of solvents and solvent mixtures, failed. Solvents tried included ether, which reportedly allows recovery of 2-selenophthalide,[3] and alcohols, which notably precipitated amorphous selenium.

Repetitive (three times) preparative TLC (Chromar 1000) of 0.5 g of the oil with benzene eluent gave continuous deposition of red selenium and progressive weight loss of yellow component; a new component appeared near the solvent front which did not develop with iodine (UV visualization: blue) but which had a definite strong odor similar to that of benzaldehyde. A similar odor was observed with a sample left exposed to light for 1 week, or heated on the steam bath for several hours (accompanied by irreversible darkening of the oil).

Preparation of *trans*-*o*-Methylcinnamic Acid (5). The Doebner condensation product of *o*-tolualdehyde and malonic acid, **5**, was synthesized in 90% yield:[22] mp 175–176 °C (lit.[22] mp 176.6–177.2 °C); IR (Nujol) 3000–2800 (broad), 2700–2500 (broad), 1685, 1625 cm^{-1}; NMR (D_2O, NaOD) δ 2.38 (s, 3 H, CH_3), 6.39 (d, 1 H, C=H) (J = 16 Hz), 7.13 (m, 4 H, aromatic), 7.7 (d, 1 H, C=CH) (J = 16 Hz).

Preparation of *trans*-*o*-Methylethyl Cinnamate (6) The ethyl ester of **17** was prepared via Fischer esterification[23] in 95% yield: bp 114–117 °C (2.2 mm) [lit.[24] bp 148 °C (1.2 mm)]; IR (neat) 2995, 1715, 1638 cm^{-1}; NMR (CCl_4) δ 1.32 (t, 3 H, CH_3), 2.4 (s, 3 H, CH_3), 4.2 (q, 2 H, CH_2), 6.22 (d, 1 H, C=C=H) (J = 16 Hz), 7.22 (m, 4 H, aromatic), 7.85 (d, 1 H, C=C=H) (J = 16 Hz).

Preparation of *trans-o*-(Bromomethyl)ethyl Cinnamate (7). Wohl–Ziegler bromination[25] of **6** yielded **7**. A mixture of **6** (10.0 g, 53 mmol), *N*-bromosuccinimide (9.7 g, 55 mol) (Aldrich), dibenzoyl peroxide (0.8 g), and carbon tetrachloride (200 ml) was heated under reflux until formation of succinimide was complete (3 h). The mixture was cooled and the succinimide filtered and washed with carbon tetrachloride. A preliminary vacuum distillation (short path) afforded two fractions: bp 100–130 °C (0.4 mm) (2.5 g) and bp 130–154 °C (0.4 mm) (10.24 g). The higher boiling fraction was crystallized from methanol (75 ml) at −65 °C to give a 65% yield (9.3 g) of **7**: mp 33.0–33.5 °C; IR (CCl_4) 2995, 1720, 1640 cm^{-1}; NMR (CCl_4) δ 1.31 (t, 3 H, CH_3), 4.22 (q, 2 H, CH_2), 4.5 (s, 2 H, CH_2), 6.30 (d, 1 H, C=CH) (J = 16 Hz), 7.28 (m, 4 H, aromatic), 7.90 (d, 1 H, C=CH) (J = 16 Hz).

Preparation of *o*-Formylbenzyl Bromide (8). A solution of **7** (5.38 g, 20 mmol), methanol (80 ml), and methylene chloride (20 ml) was ozonolyzed at −63 °C. The blue color from the presence of excess ozone indicated that ozonolysis was complete after 0.25 h. After reduction with dimethyl sulfide (10 ml) was complete (0.5 h) (in a preparative reaction, this methanol solution ordinarily was used without further purification), the solution was diluted with benzene (25 ml). The organic phase was washed with water (25 ml) and concentrated to give 1.02 g of clear, yellow liquid. Crude **8** was distilled (bulb to bulb) to give a 10% yield (0.4 g) of brown liquid: bp 70–75 °C (0.4 mm); IR (neat) 2840, 2770, 1700 cm^{-1}; NMR (CCl_4) δ 4.9 (s, 2 H, CH_2), 7.55 (m, 4 H aromatic), 10.1 (s, 1 H, CHO).

Preparation of 2,2-Diformyldibenzyl Diselenide Dimethyl Acetal (10). A solution of **7** (4.0 g, 14.8 mmol) and methanol (100 ml) was ozonolyzed at −60 °C. The blue color from the presence of excess ozone indicates that ozonolysis was complete after 20 min. Reduction with dimethyl sulfide (10 ml) was complete in 0.5 h.

To the stirred reaction mixture, trimethyl orthoformate (28 ml) and *p*-toluenesulfonic acid (0.8 g) were added at room temperature. After stirring for 48 h, the crude product was neutralized with solid potassium carbonate and methanol (80 ml) was distilled off at atmospheric pressure.

The crude acetal in methanol (21 ml) was added dropwise to a freshly prepared solution of bismethoxymagnesium diselenide[26] (50 mmol) at room temperature. After the resulting dark solution was stirred at room temperature for 18 h, water (1 l.) was added to the reaction mixture and the crude product was extracted with diethyl ether (4 × 125 ml). The combined, yellow ether extracts were washed with saturated sodium bicarbonate solution (75 ml) and saturated sodium chloride solution (75 ml), and dried ($MgSO_4$). Concentration of the filtered ether extracts afforded a 26% yield (0.94 g) of crude **10**, which was applied to a hexane-packed column (17 × 9.3 cm) of basic II alumina (Woelm) and eluted with hexane/benzene (30:70). A 10.8% yield (0.39 g) of **10** was obtained as an oil: IR (neat) 2840, 1200, 1110, 1080, 1060 cm^{-1}; NMR ($CDCl_3$) δ 3.22 (s, 12 H, OCH_3), 4.11 (s, 4 H, CH_2), 5.54 (s, 2 H, CH), 7.34 (m, 8 H, aromatic); mass spectrum *m/e* (rel intensity) 490 (39, M^+), 245 (22), 165 (100), 134 (39), 119 (26), 105 (79).

Preparation of 2,2′-Diformyldibenzyl Diselenide (4). A solution of **10** (40 mg) and deuterium oxide (2 drops) in deuterioacetone (360 mg) was added to an NMR tube. Hydrolysis was effected with trifluorodeuterioacetic acid (1 drop) after approximately 2 h at room temperature (a brown, uncharacterized sediment which settled out of the tube at this time was removed from the reaction mixture). The resultant solution was used directly for determining the NMR spectrum. This solution was then concentrated, diluted with anhydrous diethyl ether (2 ml), and dryed over $MgSO_4$. The filtered ether solution crystallized in the freezer and yielded yellow-tan crystals, mp 50–64 °C. Two recrystallizations from anhydrous diethyl ether afforded yellow-tan crystals of **4**: mp 72.5–73.5 °C; IR (neat) 2750, 1695 cm^{-1}; NMR ($CLCl_3$) δ 4.30 (s, 4 H, CH_2), 7.50 (m, 8 H, aromatic), 10.1 (s, 2 H, CHO); mass spectrum *m/e* (rel intensity) 398 (6, M^+), 199 (0.3), 119 (100), 91 (42), 65 (6) (mp of Magdasieva and Vdovin product,[3] 71–72 °C).

2-Selenaphthalide was synthesized from phthalide (Aldrich Chemical Co.) by the method of Gunther.[4b] Samples recrystallized from petroleum ether were used for IR and NMR spectral determinations.

2-Thiaphthalide was synthesized from phthalide (Aldrich Chemical Co.) by the method of Prey.[10] Samples purified by benzene elution from alumina columns gave mp 55.5–56.5 °C (reported 55–60 and 60 °C).[27]

Registry No.—**1**, 35951-68-9; **2**, 58534-05-7; **4**, 60633-89-8; **5**, 939-57-1; **6**, 24393-48-4; **7**, 60633-90-1; **8**, 60633-91-2; **10**, 60633-92-3.

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Homogeneous Catalytic Cyclization and Oxidation of Diols

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The 1,4-diketone unit is an important synthon for a variety of synthetic quests. Such diones are difficult to prepare directly via oxidation of 1,4-diols because other products are actually favored.[2] Hence, several indirect approaches have been developed.[3] These routes are stoichiometric and often involve several steps. We sought an alternative procedure, one that would be catalytic; palladium chloride oxidation of diols was chosen because Pd(II) is a mild oxidizing agent that can be made catalytic in an oxygen environment by the addition of copper chloride. Also, unlike many other oxidizing agents, palladium is not known to effect cleavage of the carbon skeleton in 1,2-diols, so it was considered that Pd(II) might be useful for preparing a variety of diones of differing structural relationships.

The oxidation of simple alcohols with palladium salts has been reported by Lloyd.[4] He found that primary and secon-