Mild Reductions of Oxides of the Group 6a Elements Sulfur, Selenium, and Tellurium with (Phenylseleno)trimethylsilane

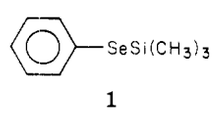
Michael R. Detty

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

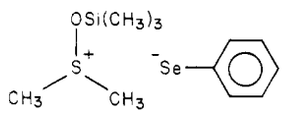
Received June 28, 1979

Sulfoxides, selenoxides, and telluroxides were reduced to the corresponding sulfides, selenides, and tellurides with 2 equiv of (phenylseleno)trimethylsilane in excellent yield and in the presence of a variety of functional groups. Evidence was found in support of onium intermediates, including an ylide rearrangement analogous to the Sommelet–Hauser rearrangement and olefinic capture of a phenylselenenyl species.

In recent years a number of methods have appeared for the reduction of sulfoxides to sulfides.[1] Some of the methods lack generality for other than simple systems, but the number of methods available allows most functional groups to be present in such reductions. We report our discovery of yet another reagent to accomplish this reduction—(phenylseleno)trimethylsilane (1)—which is also useful for reducing oxides of all the group 6a elements and which offers certain experimental advantages over other methods.



1

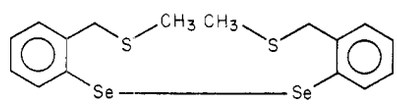


2

Results

When attempts to add 1 to certain ketones or to α,β-unsaturated carbonyl compounds with catalytic amounts of potassium fluoride,[2] potassium cyanide,[2] or even triphenylphosphine[3] did not meet with general success, we attempted to generate a complex such as 2 between 1 and dimethyl sulfoxide (Me_2SO). One hope for such a complex was that nucleophilic attack by the phenylselenide anion would be followed by silylation of an oxygen anion with the sulfonium species.

When 1 was added to Me_2SO, an immediate exothermic reaction occurred and dimethyl sulfide distilled from the reaction vessel. Diphenyl diselenide and hexamethyldisiloxane could be isolated from the reaction mixture. In chloroform, 2 equiv of 1 reacted with 1 equiv of Me_2SO to give dimethyl sulfide (98%), diphenyl diselenide (95% isolated), and hexamethyldisiloxane (90%). A fourth product was isolated in 2% yield and was assigned structure 3 based on spectral evidence. The ^1H NMR spectrum of 3 exhibited two singlets at δ 3.80 and 1.98 in a ratio of 2:3, respectively. The aromatic signals were two multiplets at δ 7.70 and 7.13 in a ratio of 1:3, respectively. The mass spectrum gave a parent ion of m/e 434 ($C_{16}H_{18}S_2Se_2$, M^+) containing two selenium atoms.



3

The reaction depicted in eq 1 is generally applicable to

$$R_2M{\rightarrow}O + 2PhSeSi(CH_3)_3 \rightarrow R_2M + PhSeSePh + (CH_3)_3SiOSi(CH_3)_3 \quad (1)$$

$$M = S, Se, Te$$

oxides of the group 6a elements sulfur, selenium, and tellurium. Two equivalents of 1 is required, and the reactions are rapid in many solvents including methylene chloride, chloroform, carbon tetrachloride, tetrahydrofuran, and benzene. If the oxide is soluble in the solvent, reaction is complete within 1 min. If the oxide is sparingly soluble, reaction is complete within 10 min. No aqueous workup is employed. The hexamethyldisiloxane is removed under reduced pressure, and the diphenyl diselenide is removed by chromatography or fractional crystallization. Although 1 is air sensitive, the rapid nature of the oxide reduction eliminates the need for an inert atmosphere and degassed solvents in the handling of 1.[2]

The method is compatible with a variety of functional groups, as shown by the examples in Table I. The reagent 1 failed to reduce the nitro group of nitrobenzene or the sulfone of sulfolane.

Butyl sulfoxide and phenyl sulfoxide were prepared from the corresponding sulfides with *m*-chloroperbenzoic acid in methylene chloride. Reduction of these two sulfoxides with 1 returned the sulfides in 96% yield in each case.

The phenolic β-keto sulfoxide 4 was prepared by the procedure of Amick.[4] Reduction of 4 with 2 equiv of 1 in a methylene chloride slurry gave the sulfide 5 in 92% yield following chromatography on silica gel and distillation.

The diphenyl diselenide (95%) recovered from the reduction of 4 by chromatography displayed a spurious methyl signal in the ^1H NMR spectrum at δ 2.07. This signal could be intensified by concentrating the mother liquors from a recrystallization of the diphenyl diselenide in ligroin. The mass spectrum of the mother-liquor concentrate gave a peak corresponding to an ion of m/e 204 ($C_7H_8{}^{80}SeS$). This datum is consistent with 6 (eq 5) being present in the reaction mixture to the extent of 2–3%. We were not able to isolate 6 in analytically pure form, but integration of the ^1H NMR spectrum indicated a 90:10 mixture of 6 and diphenyl diselenide.

The selenoxides and telluroxides in Table I were prepared by oxidation of the corresponding selenides and tellurides with *tert*-butyl hypochlorite in methanolic methylene chloride followed by basic workup.[5] Reduction

(1) The following are representative examples: (a) T. H. Chan and A. Melnyk, *J. Am. Chem. Soc.*, **92**, 3718 (1970); (b) G. V. Kaiser, R. D. G. Cooper, R. E. Kochler, C. F. Murphy, J. A. Webber, I. G. Wright, and E. M. VanHeyningen, *J. Org. Chem.*, **35**, 2430 (1970); (c) D. W. Chasar, *ibid.*, **36**, 613 (1971); (d) C. R. Johnson, C. C. Bacon, and J. J. Rigau, *ibid.*, **37**, 919 (1972); (e) G. A. Olah, B. G. Gupta, and C. Narang, *ibid.*, **43**, 4503 (1978); (f) H. C. Brown and N. Ravindran, *Synthesis*, 42 (1973); (g) J. Drabowicz and M. Mikolajczyk, *ibid.*, 527 (1976); (h) G. A. Olah, G. K. S. Prakash, and F. L. Ho, *ibid.*, 810 (1976); (i) D. W. Chasar and T. M. Pratt, *ibid.*, 262 (1976); (j) J. Drabowicz and S. Oae, *ibid.*, 404 (1977); (k) I. W. J. Still, S. K. Hasan, and K. Turnbull, *ibid.*, 468 (1977); (l) G. A. Olah, B. G. B. Gupta, and S. C. Narang, *ibid.*, 583 (1977); (m) J. Drabowicz and M. Mikolajczyk, *ibid.*, 542 (1978); (n) G. A. Olah, S. C. Narang, B. G. B. Gupta, and R. Malhotra, *ibid.*, 60 (1979).

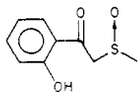
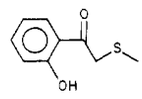
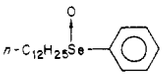
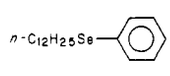
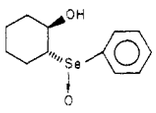
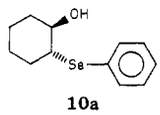
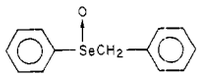
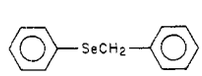
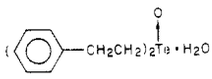
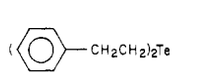
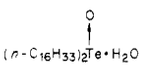
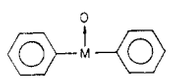
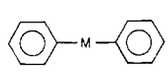
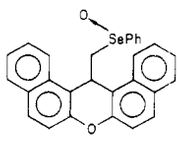
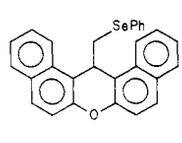
(2) M. R. Detty, *Tetrahedron Lett.*, 5087 (1978).

(3) D. C. Liotta, P. B. Paty, J. Johnston, and G. Zima, *Tetrahedron Lett.*, 5091 (1978).

(4) D. Amick, *J. Heterocycl. Chem.*, **12**, 1051 (1975).

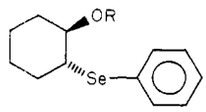
0022-3263/79/1944-4528$01.00/0

Table I. Reduction of Group 6a Oxides with (Phenylseleno)trimethylsilane (1)

oxide	product	solvent	% yield	bp (torr) or mp, °C
$(CH_3)_2S \rightarrow O$	$(CH_3)_2S$	$CHCl_3$	98	35-37 (760)
$(n\text{-}C_4H_9)_2S \rightarrow O$	$(n\text{-}C_4H_9)_2S$	CH_2Cl_2	96	60-63 (20)
 4	 5	CH_2Cl_2	92	100-102 (0.09)
		CH_2Cl_2	95	162-168 (1.4)
 8	 10a	CH_2Cl_2	96	135-136 (1.2)
		THF	92	
		CH_2Cl_2	91	33-36
		CH_2Cl_2	94	dec
	$(n\text{-}C_{16}H_{33})_2Te$	CH_2Cl_2	90	49-51
		CH_2Cl_2 (M = S)	96	165-168 (20)
		CH_2Cl_2 (M = Se)	94	168-171 (20)
		CH_2Cl_2 (M = Te)	95	183-185 (20)
 9		CH_2Cl_2	86	144-146
		C_6H_6	85	

of the selenoxides and telluroxides in Table I with 1 gave only the expected products. No others were detected. Phenyl selenoxide, benzyl phenyl selenoxide, dodecyl phenyl selenoxide, a 70:30 mixture of the diastereomeric selenoxides 8, and selenoxide 9 were reduced to the corresponding selenides with 1 in 94, 91, 95, 96, and 86% yields, respectively. Similarly, phenyl telluroxide, 2-phenylethyl telluroxide, and hexadecyl telluroxide gave the corresponding tellurides in 95, 94, and 90% yields, respectively.

A test of the compatibility of this method of reduction with olefinic substrates was made by reducing phenyl sulfoxide, phenyl selenoxide, and phenyl telluroxide as 0.5 M solutions in cyclohexene–methylene chloride (1:1 by volume). The (phenylseleno)trimethylsilane (1) was added dropwise over 0.5 h. Chromatographic separation of the product mixtures on silica gel (10% ether–hexane) gave the products of reduction and 2.5% or less of *trans*-2-(phenylseleno)cyclohexanol, **10a**.[6]



10a, R = H
b, R = $Si(CH_3)_3$

Discussion

Although a variety of methods exist for the reduction of sulfoxides to sulfides,[1] no extensions have been made to the reduction of selenoxides to selenides or telluroxides to tellurides. The reagent 1 reduces all three group 6a oxides with equal facility and in excellent yield. The method is compatible with a variety of functional groups including ketones, phenols, alcohols, sulfones, nitro compounds, and olefins.

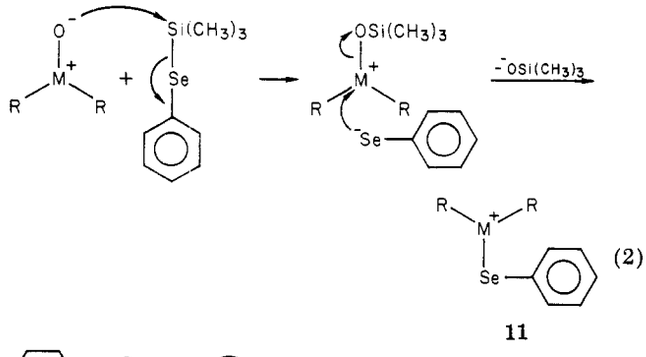
Mechanistically, the course of events outlined in Scheme I seems plausible. Initial attack by the oxide oxygen on 1 could give the onium species and phenylselenide anion. Attack by phenylselenide anion on the onium compound could lead to a net displacement of trimethylsilyl oxide giving the onium species 11, which can undergo a variety of reactions (eq 2). The trimethylsilyl oxide could attack a second equivalent of 1, giving hexamethyldisiloxane and phenylselenide anion (eq 3). The phenylselenide anion might then undergo nucleophilic attack on the selenium atom of onium species 11 to give the reduction product and diphenyl diselenide (eq 4).

In the example where M = S and R = CH_3, the onium species would be 12. Proton abstraction by trimethylsilyl oxide anion would generate ylide 13, which could then undergo a rearrangement analogous to the classical Som-

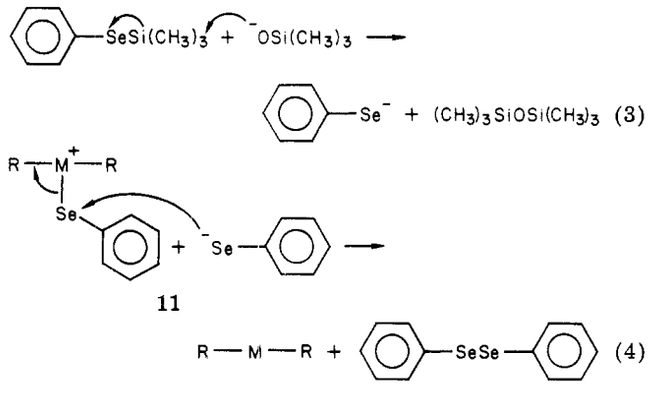
(5) M. R. Detty, *J. Org. Chem.*, accepted for publication.

(6) H. J. Reich, *J. Org. Chem.*, **39**, 428 (1974).

Scheme I



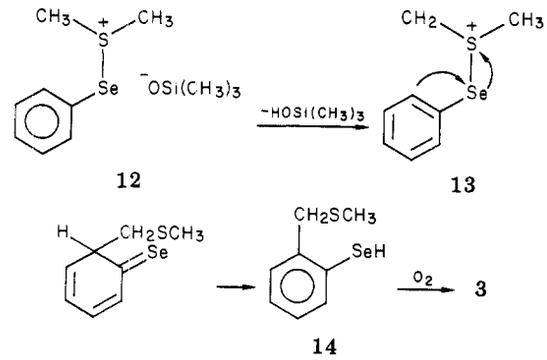
(2)



(3)

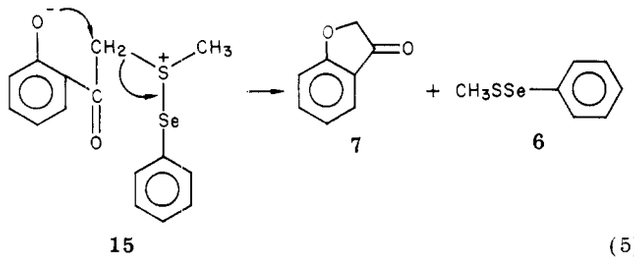
(4)

Scheme II



melet–Hauser rearrangement or the Gassman azasulfonium salt rearrangement.[7-9] Subsequent air oxidation of **14** or its anion would give **3** (Scheme II). Since this product is produced in only 2% yield, the process outlined in Scheme I must be dominant.

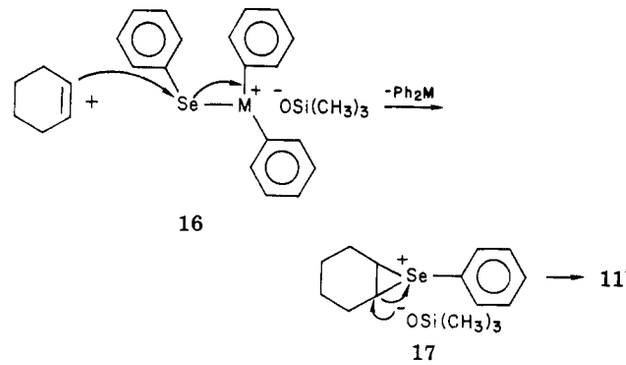
The phenolic β-keto sulfoxide **4** could lead to the sulfonium species **16**, which could then displace methylthio phenyl selenide **6** (eq 5). Unfortunately, **7** was not de-



(5)

tected in the reaction mixture to allow proof of the mechanism.

Scheme III



Conclusions

The group 6a oxides are readily deoxygenated by treatment with 2 equiv of (phenylseleno)trimethylsilane (**1**). The method is useful with a variety of functional groups and appears to involve the intermediacy of onium species as detected by rearrangement products and olefinic capture of a phenylselenenyl species.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. Boiling points are uncorrected. ^{1}H NMR spectra were run on a Varian EM 390 instrument. IR spectra were run on a Perkin-Elmer 137 spectrophotometer. Mass spectra were recorded on a Du Pont 21-491 instrument. Microanalyses were performed on a Perkin-Elmer 240 C, H, and N analyzer. The preparation of the oxides has been described.[5]

Preparation of (Phenylseleno)trimethylsilane (1). Diphenyl diselenide (15.6 g, 0.0500 mol) in 250 mL of dry tetrahydrofuran was added to freshly prepared sodium sand (2.5 g, 0.11 g-atom).[10] The resulting mixture was warmed at reflux for 3 h. Chlorotrimethylsilane (12 g, 0.11 mol) was added and reflux was maintained for 1 h. The reaction mixture was filtered through a pad of Super Celite and concentrated in vacuo. Distillation gave 15.6 g (68%) of **1** as a colorless oil, bp 63–65 °C (0.9 torr). The reagent should be stored under nitrogen at 0 °C. IR (film) 3210, 3080, 3010, 1555, 1450, 1410, 1233, 1230, 835, 695, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.45 (m, 2 H), 7.15 (m, 3 H), 0.37 (s, 9 H).

Reduction of Dimethyl Sulfoxide. Dimethyl sulfoxide (1.17 g, 0.0150 mol) in 50 mL of chloroform was cooled to 0 °C. (Phenylseleno)trimethylsilane (6.87 g, 0.0300 mol) was added dropwise over 1 min. Distillation of the reaction mixture through a 10-cm Vigreux column gave 0.91 g (98%) of dimethyl sulfide, bp 35–37 °C [^{1}H NMR($CDCl_3$) δ 2.10 (s)]. The pot residue was concentrated and separated by chromatography on silica gel (20% ether–hexane) to give 4.47 g (95%) of diphenyl diselenide (mp 61–62 °C) and 0.046 g (2%) of **3** as a yellow oil. For **3**: ^{1}H NMR ($CDCl_3$) δ 7.70 (m, 2 H), 7.13 (m, 6 H), 3.80 (s, 4 H), 1.98 (s, 6 H); IR (film) 3020 (m), 2890, 1585, 1455, 1433, 1060, 762, 733, 685 cm^{-1}; *m/e* 434, (M^+) 217 (100).

Reduction of Butyl Sulfoxide. General Procedure for Oxide Reductions with 1. Butyl sulfoxide (1.62 g, 0.0100 mol, mp 33–35 °C) was dissolved in 20 mL of methylene chloride.

(7) M. Sommelet, *C. R. Hebd. Seances Acad. Sci.*, **205**, 56 (1937).
(8) G. C. Jones and C. R. Hauser, *J. Org. Chem.*, **27**, 3592 (1962).
(9) P. G. Gassman and G. D. Gruetzmacker, *J. Am. Chem. Soc.*, **96**, 5487 (1974); *ibid.*, **95**, 588 (1973).

(10) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 1023.

Dropwise addition of 1 (4.58 g, 0.0200 mol) produced an immediate exothermic reaction. One minute after addition was complete, the reaction mixture was concentrated. The diphenyl diselenide (3.01 g, 96%) was removed by crystallization from ligroin. Distillation of the concentrated mother liquors gave 1.40 g (96%) of butyl sulfide, bp 60–63 °C (20 torr).

Reduction of Keto Sulfoxide 4. The sulfoxide 4 (1.00 g, 4.81 mmol) and 1 (2.20 g, 9.62 mmol) were treated as described. The sulfoxide was insoluble and complete reaction required 5 min. The reaction mixture was concentrated and separated by chromatography on silica gel (10% ether–hexane) to give 1.45 g (96%) of diphenyl diselenide containing 2–3% of **6** (*m/e* 204 (M^+); ^1H NMR ($CDCl_3$) δ 2.07) and a product fraction containing the sulfide **5**. Distillation of this fraction gave 0.85 g (92%) of the sulfide as a colorless oil, bp 100–102 °C (0.09 torr). For **5**: ^1H NMR ($CDCl_3$) δ 12.1 (s, 1 H), 7.78 (m, 1 H), 7.51 (m, 1 H), 6.99 (m, 2 H), 3.80 (s, 2 H), 2.26 (s, 3 H); IR (film) 3000 (br), 2850, 1620, 1250, 1225, 750 cm^{-1}; *m/e* 182 (M^+). Anal. Calcd for $C_9H_{10}O_2S$: C, 59.3; H, 5.5; S, 17.6. Found: C, 59.2; H, 5.5; S, 17.9.

Reduction of *n*-Dodecyl Phenyl Selenoxide. The selenoxide (1.71 g, 5.00 mmol, mp 60–62 °C) and 1 (2.29 g, 10.0 mmol) were treated as described. The diphenyl diselenide was removed by fractional crystallization from ligroin. Distillation of the concentrated mother liquors gave 1.54 g of a pale yellow oil: bp 162–168 °C (1.4 torr); ^1H NMR ($CDCl_3$) δ 7.39 (m, 2 H), 7.10 (m, 3 H), 3.49 (t, 2 H, J = 7 Hz), 1.65 (m, 2 H), 1.23 (m, 18 H), 0.86 (m, 3 H); IR (film) 2850, 1585, 1460, 730, 680 cm^{-1}; *m/e* 326 (M^+).

Reduction of the Selenoxides 8. A 70:30 mixture of the diastereomers of selenoxides **9** (0.27 g, 1.0 mmol) and **1** (0.46 g, 2.0 mmol) were treated in 5 mL of methylene chloride as described. Preparative thin-layer chromatography (silica gel, 50% ether–hexane) gave 0.25 g (96%) of the selenide **10a**: bp 135–136 °C (1.2 torr); ^1H NMR ($CDCl_3$) δ 7.50 (m, 2 H), 7.i23 (m, 3 H), 3.27 (m, 1 H), 2.87 (s, 1 H), 2.85 (m, 1 H), 2.10 (m, 2 H), 1.8–1.0 (m, 6 H); IR (film) 3400 (br), 2890, 1585, 1440, 1120, 736, 688 cm^{-1}; *m/e* 256 (M^+).

Reduction of Benzyl Phenyl Selenoxide. The selenoxide (0.66 g, 2.5 mmol, mp 132–135 °C) and 1 (1.20 g, 5.1 mmol) were treated in 10 mL of methylene chloride as described. The diphenyl diselenide (0.75 g, 94%) was recovered by fractional crystallization from ligroin. Recrystallization of the concentrated mother liquors from methanol gave 0.56 g (91%) of benzyl phenyl selenide: mp 33–36 °C; ^1H NMR ($CDCl_3$) δ 7.37 (m, 2 H), 7.17 (m, 8 H), 4.03 (s, 2 H); IR (KBr) 3000, 1605 (m), 1585, 1500, 1480, 1450, 1440, 732, 680 cm^{-1}; *m/e* 248 (M^+).

Reduction of 2-Phenylethyl Telluroxide. The telluroxide (1.86 g, 5.00 mmol) and 1 (2.29 g, 10.0 mmol) were treated as described. The diphenyl diselenide was removed by fractional crystallization from ligroin. Chromatographic separation of the remainder of the reaction mixture gave 1.59 g (94%) of a pale yellow oil that decomposed on distillation. ^1H NMR ($CDCl_3$) δ 7.20 (m, 10 H), 3.15–2.65 (m, 8 H); IR (film) 3010, 2900, 1610, 1500, 1460, 748, 694 cm^{-1}. Anal. Calcd for $C_{16}H_{18}Te$: C, 56.9; H, 5.4. Found: C, 56.8; H, 5.3.

Reduction of Hexadecyl Telluroxide. The telluroxide (0.30 g, 0.52 mmol, mp 92–95 °C) and 1 (0.24 g, 1.0 mmol) were treated in 10 mL of methylene chloride as described. After 3 min, 10 mL of methanol was added to the reaction mixture, precipitating 0.27 g (94%) of the telluride as a white solid: mp 49–51 °C [lit.[11] mp 43–45 °C]; ^1H NMR ($CDCl_3$) δ 2.60 (t, 4 H, J = 7 Hz), 1.67 (m, 4 H), 1.30 (m, 52 H), 0.87 (m, 6 H); IR (KBr) 2900, 1475, 718, 700 cm^{-1}. Anal. Calcd for $C_{32}H_{66}Te$: C, 66.4; H, 11.5. Found: C, 66.3; H, 11.5.

Reduction of Selenoxide 9. The selenoxide (0.38 g, 0.83 mmol, mp 120 °C dec) and 1 (0.38 g, 1.7 mmol) were treated in 5 mL of methylene chloride as described. The reaction mixture was concentrated and the product obtained by crystallization from 1:1 benzene–ethanol to give 0.32 g of selenide (86%): mp 144–146 °C; ^1H NMR ($CDCl_3$) δ 8.13 (d, 2 H, J = 8 Hz), 7.90–7.10 (m, 10 H), 6.80 (m, 5 H), 5.81 (t, 1 H, J = 5 Hz), 3.59 (d, 2 H, J = 5 Hz); IR (KBr) 3020 (m), 1630, 1600, 1260, 1250, 815, 740 cm^{-1}; *m/e* 452 (M^+). Anal. Calcd for $C_{28}H_{20}OSe$: C, 74.5; H, 4.5; Se, 17.5. Found: C, 74.6; H, 4.7; Se, 17.2.

Reduction of Phenyl Sulfoxide. A. Phenyl sulfoxide (2.02 g, 10.0 mmol) and 1 (4.58 g, 20.0 mmol) were treated as described in 40 mL of methylene chloride. The diphenyl diselenide was removed by crystallization from ligroin. Distillation of the concentrated mother liquors gave 1.89 g (96%) of phenyl sulfide, bp 165–168 °C (20 torr).

B. Phenyl sulfoxide (2.02 g, 10.0 mmol) and 1 (4.58 g, 20.0 mmol) were treated as described in 10 mL of methylene chloride and 10 mL of cyclohexene. The product mixture was separated by chromatography on silica gel (30% ether–hexane) to give 0.060 g of **10a** and 1.88 g of phenyl sulfide.

Reduction of Phenyl Selenoxide. A. The selenoxide (1.25 g, 5.00 mmol, mp 111–113 °C) and 1 (2.29 g, 10.0 mmol) were treated as described. The diphenyl diselenide was removed by crystallization from ligroin. Distillation gave 1.10 g (94%) of phenyl selenide as a yellow oil, bp 168–171 °C (20 torr).

B. The reaction was the same as in A except that the solvent was a mixture of 5 mL of methylene chloride and 5 mL of cyclohexene. Chromatographic separation of the reaction mixture gave 0.038 g (2.5%) of **10a** and 1.12 g of phenyl selenide.

Reduction of Phenyl Telluroxide. A. The telluroxide (1.48 g, 5.00 mmol, mp 186–190 °C) and 1 (2.29 g, 10.0 mmol) were treated as described. The diphenyl diselenide was removed by crystallization from ligroin. Distillation gave 1.34 g of phenyl telluride, bp 183–185 °C (20 torr).

B. The reaction was the same as in A except that the solvent was a mixture of 5 mL of methylene chloride and 5 mL of cyclohexene. Chromatographic separation of the reaction mixture gave 0.020 g (1.3%) of **10a** and 1.34 g of phenyl telluride.

Registry No. 1, 33861-17-5; **3**, 71766-34-2; **4**, 16697-77-1; **5**, 56986-82-4; **6**, 37826-16-7; **8** isomer 1, 71766-35-3; **8** isomer 2, 71806-57-0; **9**, 71766-36-4; **9** selenide, 71766-37-5; **10a**, 35446-84-5; diphenyl diselenide, 1666-13-3; chlorotrimethylsilane, 75-77-4; dimethyl sulfoxide, 67-68-5; dimethyl sulfide, 75-18-3; butyl sulfoxide, 2168-93-6; butyl sulfide, 544-40-1; dodecyl phenyl selenoxide, 71766-38-6; dodecyl phenyl selenide, 42066-69-3; benzyl phenyl selenoxide, 13154-11-5; benzyl phenyl selenide, 18255-05-5; 1-phenylethyl telluroxide, 71766-39-7; 2-phenylethyl telluride, 71766-40-0; hexadecyl telluroxide, 71766-41-1; hexadecyl telluride, 71766-42-2; phenyl sulfoxide, 945-51-7; phenyl sulfide, 139-66-2; phenyl selenoxide, 7304-91-8; phenyl selenide, 1132-39-4; phenyl telluroxide, 51786-98-2; phenyl telluride, 1202-36-4.

(11) U.S. Patent 2 398 414; *Chem. Abstr.*, **40**, 3598 (1945).