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# Oxidation of Selenides and Tellurides with Positive Halogenating Species

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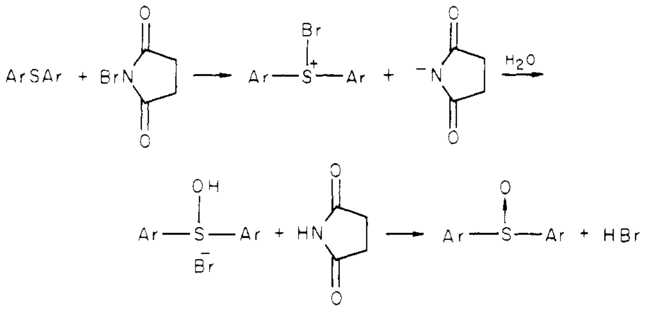
Treatment of diaryl or alkyl aryl selenides and diaryl or dialkyl tellurides first with a positive halogen source (*N*-chlorosuccinimide, *tert*-butyl hypochlorite) followed by alkaline hydrolysis (10% sodium hydroxide, saturated sodium bicarbonate) gave the corresponding selenoxides or telluroxides (or hydrates) in good yield. The method is tolerant of a variety of functional groups including esters, olefins, alcohols, ethers, and ketones. The formal oxidation step is believed to be the formation of a chloroselenonium or chlorotelluronium species followed by hydrolysis. $^1$H NMR evidence is given for a benzylphenylselenonium species. Selenoxide fragmentation reactions during the hydrolysis step were observed.

The organic chemistry of the group 6A elements selenium and tellurium has been actively investigated in recent years.[1,2] Of particular interest has been the chemistry of selenoxides which are synthetically useful owing to, among other reasons, their thermal instability (fragmentation with olefin formation)[3] and their ability to stabilize adjacent anionic centers.[4] The chemistry of telluroxides has been little explored, perhaps owing in part to the difficulty of oxidizing tellurides to telluroxides directly without overoxidation. Although selenides are oxidized to selenoxides with a variety of reagents, including ozone,[3b,c,5] peroxides,[3a,b,6] peracids,[3a,b,4a,7] sodium metaperiodate,[8] and iodobenzene dichloride,[8a] the clean oxidation of tellurides to telluroxides is unknown. Tellurides have been oxidized to telluroxides in only modest yield with additional overoxidation products by oxygen,[9] potassium permanganate,[10] and chloramine-T.[11] The common overoxidation products are tellurinic acids and adducts of tellurinic acids with telluroxides.[12]

We desired a mild oxidation procedure that would give both telluroxides from tellurides and selenoxides from selenides without giving products of overoxidation. A possible method was suggested by the oxidation of diaryl sulfides[13] and aryl fluoromethyl sulfides[14] to the corresponding sulfoxides without contamination by sulfones with *N*-bromosuccinimide (NBS) in moist solvents. Presumably, these oxidations occur through hydrolysis of an intermediate bromosulfonium compound, as shown in Scheme I, to give the sulfoxide and 1 equiv each of succinimide and hydrobromic acid. The use of positive halogenating species with selenides and tellurides to give hydrolyzable onium compounds might circumvent the problem of overoxidation associated with other methods of oxidation of tellurides and also be a mild method of selenide oxidation. The reaction of selenium compounds with *tert*-butyl hypochlorite to give selenonium species has been reported.[15]

Scheme I



I report here my results on the oxidation of selenides to selenoxides and tellurides to telluroxides by the initial action of a positive halogenating agent (NBS, *N*-chlorosuccinimide (NCS), or *tert*-butyl hypochlorite) under nonaqueous conditions followed by a basic hydrolytic workup.

## Results and Discussion

**Synthetic Considerations.** Methylene chloride solutions of diphenyl selenide (**1**) and diphenyl telluride (**3**) were treated with 1.05 equiv of NBS for 8 h at room temperature. The dark red reaction mixtures were treated with 10% sodium hydroxide to effect hydrolysis and to remove succinimide. Selenoxide **2** was isolated in 44% yield, and telluroxide **4** was isolated in 45% yield. Much better results were obtained with NCS under identical conditions. These reaction mixtures were pale yellow, and hydrolysis gave **2** in 66% yield and **4** in 81% yield.

The yields of the NCS oxidations were improved, and the reaction times were shortened by using a more polar solvent mixture, 1/1 (v/v) methylene chloride and methanol, and by lowering the reaction temperature to 0 °C. Under these conditions, the reaction mixtures were colorless. Hydrolysis with 10% sodium hydroxide gave **2** in 79% yield and **4** in 91% yield. The reaction time for consumption of starting material was reduced to 30 min.

The use of highly basic solutions during hydrolysis was necessary to remove the succinimide that was produced.

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(1) For an excellent review of organoselenium chemistry, see: Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049.

(2) For reviews of organotellurium chemistry, see: (a) Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach: New York, 1978. (b) Irgolic, K. J. *J. Organomet. Chem.* **1978**, *158*, 235. (c) Irgolic, K. J. *Ibid.* **1978**, *158*, 267.

(3) (a) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137. (b) Reich, H. J.; Renga, J. M.; Reich, I. L. *Ibid.* **1975**, *97*, 5434. (c) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Org. Chem.* **1974**, *39*, 2133.

(4) (a) Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 3250. (b) Reich, H. J.; Chow, F. *J. Chem. Soc., Chem. Commun.* **1975**, 790.

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(6) Sharpless, K. B.; Young, M. W.; Lauer, R. F. *Tetrahedron Lett.* **1973**, 1979.

(7) Reich, H. J.; Renga, J. M. *J. Org. Chem.* **1975**, *40*, 3313.

(8) (a) Cinquini, M.; Colonna, S.; Giovini, R. *Chem. Ind. (London)* **1969**, 1737. (b) Reich, H. J.; Reich, I. L.; Renga, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 5813.

(9) Reichel, L.; Kirschbaum, E. *Justus Liebigs Ann. Chem.* **1936**, *523*, 211.

(10) Campbell, I. B. M.; Turner, E. E. *J. Chem. Soc.* **1938**, 37.

(11) Hellwinkel, D.; Fahrbach, G. *Justus Liebigs Ann. Chem.* **1968**, *712*, 1.

(12) (a) Balfe, M. P.; Chaplin, C. A.; Phillips, H. *J. Chem. Soc.* **1938**, 341. (b) Balfe, M. P.; Nandi, K. N. *Ibid.* **1941**, 70.

(13) Tagaki, W.; Kikukawa, K.; Ando, K.; Oae, S. *Chem. Ind. (London)* **1964**, 1624.

(14) More, K. M.; Wemple, J. *Synthesis* **1977**, 791.

(15) (a) Derkach, N. Y.; Lyapina, T. V. *Zh. Org. Khim.* **1974**, *10*, 1991. (b) Derkach, N. Y.; Tischchenko, N. P.; Levchenko, E. S. *Ibid.* **1977**, *13*, 100.

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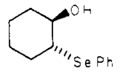
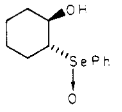
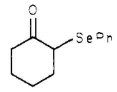
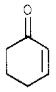
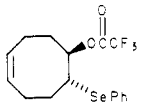
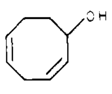
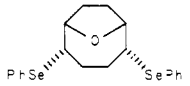
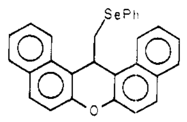
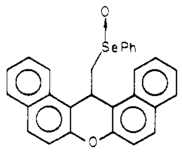
Table I. Oxidation of Selenides and Tellurides with NCS and *t*-BuOCl

| substrate | product | oxidant | reaction time, min[a] | yield, % | mp, °C | lit. mp, °C |
|---|---|---|---|---|---|---|
| $(C_6H_5)_2Se$<br>1 | $(C_6H_5)_2Se(O)$<br>2 | NCS<br>*t*-BuOCl | 30 (5)<br>5 (5) | 79<br>81 | 111-113 | 110.2-111.5[b] |
| $(C_6H_5)_2Te$<br>3 | $(C_6H_5)_2Te(O)$<br>4 | NCS<br>*t*-BuOCl | 30 (5)<br>5 (5) | 91<br>98 | 186-190 dec | 185-187[c] dec |
| $C_6H_5SeCH_2C_6H_5$<br>5 | $C_6H_5Se(O)CH_2C_6H_5$<br>6 | NCS<br>*t*-BuOCl | 30 (5)<br>5 (5) | 80<br>80 | 132-135 | 135-136[d] |
| $n$-$C_{12}H_{25}SeC_6H_5$<br>7 | $n$-$C_{12}H_{25}Se(O)C_6H_5$<br>8 | NCS<br>*t*-BuOCl | 30 (5)<br>5 (5) | 91<br>90 | 60-62 | |
| $(n$-$C_{16}H_{33})_2Te$<br>10 | $(n$-$C_{16}H_{33})_2Te(O)\cdot H_2O$<br>13a | *t*-BuOCl | 1 (5) | 96 | 92-95 | |
| $(C_6H_5CH_2CH_2)_2Te$<br>11 | $(C_6H_5CH_2CH_2)Te(O)\cdot H_2O$<br>13b | *t*-BuOCl | 1 (5) | 95 | 140 dec | |
| <br>14 | <br>15 | NCS<br>*t*-BuOCl | 30 (5)<br>5 (5) | 71[e]<br>71[e] | 116-120 dec | |
| <br>16 |  | NCS<br>*t*-BuOCl | 30 (30)<br>5 (30) | 74<br>76 | | |
| <br>17 |  | *t*-BuOCl | 5 (120) | 40 | | |
| <br>18 | <br>21 | *t*-BuOCl | 5 (60) | 55 | 29-32 | |
| <br>22 | <br>24 | NCS<br>*t*-BuOCl | 30 (5)<br>5 (5) | 82<br>90 | 120 dec | |

[a] Value in parentheses is the time of stirring with aqueous base. [b] Reference 8a. [c] Reference 15. [d] Reference 18. [e] 70:30 mixture of diastereomers.

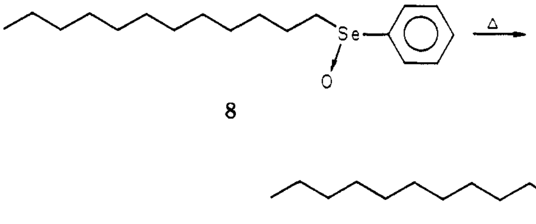
Sodium bicarbonate or sodium carbonate solutions could be substituted for the sodium hydroxide solution without affecting yield, but separation of succinimide from product was more tedious.

The use of *tert*-butyl hypochlorite (*t*-BuOCl) as a positive chlorine source eliminated the problem of byproduct separation. The *tert*-butyl alcohol formed during hydrolysis is easily removed under reduced pressure.

When **1** and **3** were treated with 1.05 equiv of *t*-BuOCl in methanol–methylene chloride at 0 °C, colorless solutions resulted within seconds. After 5 min for **1** and 1 min for **3**, the reaction mixtures were hydrolyzed with saturated sodium bicarbonate solution. Selenoxide **2** was isolated in 81% yield, and telluroxide **4** was isolated in 98% yield. The conditions and results of both NCS and *t*-BuOCl oxidations of **1**, **3**, and other substrates are contained in Table I.

Benzyl phenyl selenide (**5**) was prepared by treating benzyl bromide with thallous phenylselenide in ether.[16] The selenide was obtained as a low-melting (33–36 °C), white, crystalline solid. NCS or *t*-BuOCl oxidation of **5** as described gave mostly benzyl phenyl selenoxide (**6**)[17] and some benzyl chloride.

Dodecyl phenyl selenide (**7**) was prepared from sodium phenylselenide and dodecyl iodide in methanol. NCS or *t*-BuOCl oxidation of **7** gave dodecyl phenyl selenoxide (**8**) as a white solid. The selenoxide decomposed slowly at room temperature, or more rapidly on heating in refluxing benzene, to give 1-dodecene (**9**) in about 55% yield.



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9

Dihexadecyl telluride (**10**)[18] and bis(2-phenylethyl) telluride (**11**)[18] were both readily oxidized with *t*-BuOCl in methanol–methylene chloride followed by hydrolysis with sodium bicarbonate solution. The oxidation product

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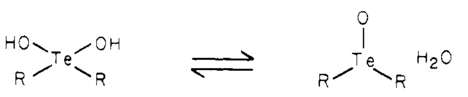
(16) Detty, M. R. *J. Org. Chem.*, in press.

(17) Oki, M.; Iwamura, H. *Tetrahedron Lett.* **1966**, 2917.

(18) The tellurides were generously provided by Dr. Henry Gysling (Eastman Kodak Co.). They were prepared by treating tellurium metal with potassium borohydride to give dipotassium telluride, which was then treated with an excess of alkyl iodide in ethanol.

of **10** (96%) was a white, crystalline solid, mp 92–95 °C, and the oxidation product of **11** (95%) was a white powder that decomposed at 140 °C. These solids gave elemental analyses consistent with the expected telluroxides plus 1 equiv of water. This equivalent of water might be in the form of a water of hydration as represented by **13a** and **13b**, or the actual oxidized species may be the dihydroxy



**12a**, R = $n$-$C_{16}H_{33}$ **13a**, R = $n$-$C_{16}H_{33}$

**b**, R = $C_6H_5CH_2CH_2$ **b**, R = $C_6H_5CH_2CH_2$

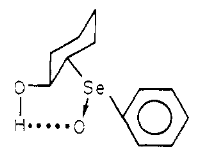
tellurides **12a** and **12b**. Attempted dehydration with heat under vacuum led to decomposition.

The IR spectra of both oxidation products show broad absorptions of medium intensity centered at 3500 cm$^{-1}$. The $^1$H NMR spectra are rather interesting. The $^1$H NMR spectrum of the oxidation product of **10** displays a broadened two-proton singlet at $\delta$ 3.44 and a broadened, two-humped mass of four protons at $\delta$ 2.3–3.0. The spectrum of telluride **10** displays a sharp, four-proton triplet ($J$ = 7 Hz) at $\delta$ 2.60. The $^1$H NMR spectrum of the oxidation product of **11** displays a broadened ten-proton singlet at $\delta$ 7.17 and a broadened ten-proton multiplet at $\delta$ 2.6–3.7, whereas the spectrum of **11** displays a well-defined aromatic multiplet of ten protons at $\delta$ 7.20 and a well-defined eight-proton multiplet at $\delta$ 2.90. The dihydroxy tellurides **12** ought to be highly symmetrical molecules, whereas the telluroxides should exhibit diastereotropic protons adjacent to the prochiral telluroxide center. The broadening observed in the $^1$H NMR spectra of the oxidation products is most likely due to rapid inversion (perhaps water aided)[17] about the telluroxide center in **13** or due to an equilibrium interconversion of **12** and **13** in solution.

Further support for **13** or an equilibrium including **13** is found in the fact that both oxidation products are cleanly reduced to **10** and **11** with (phenylseleno)trimethylsilane.[19] If the oxidation products existed only in form **12**, the reduction with the silane reagent is not easily explained mechanistically.

The NCS and $t$-BuOCl methods of oxidation were also examined with a few other selenides containing different functional groups.

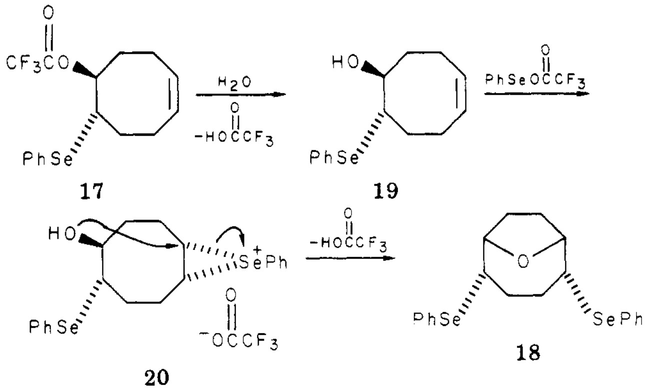
*trans*-2-(Phenylseleno)cyclohexanol (**14**) was prepared according to the procedure of Reich.[20] Oxidation with either NCS or $t$-BuOCl gave a 71% yield of a 70:30 mixture of two selenoxides **15**. The $^1$H NMR spectrum of the mixture displays a five-proton aromatic multiplet at $\delta$ 7.85–7.20, one-proton multiplets at $\delta$ 3.85 and 2.90, and eight protons in three multiplets at $\delta$ 2.30–0.80. Two sharp doublets in a ratio of 70:30 appear at $\delta$ 6.61 ($J$ = 4.1 Hz) and 6.10 ($J$ = 3.6 Hz). When $D_2O$ was added to the $^1$H NMR sample, the downfield doublets disappeared, and the multiplet at $\delta$ 3.85 simplified to approximately an eight-line pattern. These data indicate a diastereomeric mixture of selenoxides[21] with considerable hydrogen bonding between



**15**

the hydroxyl proton and the selenoxide oxygen, allowing the vicinal **H–C–O–H** coupling to be observed.

Scheme II



The strength of the hydrogen bonds in selenoxides **15** can be qualitatively approximated by comparison of the IR spectra of **15** and cyclohexanol. The IR spectrum of the selenoxide mixture **15** (0.0010 M, $CH_2Cl_2$) shows an OH stretching frequency of 3232 cm$^{-1}$. If one assumes that the hydroxyl (3605 cm$^{-1}$, $CH_2Cl_2$) of cyclohexanol (0.0010 M) is a good model for a "free" hydroxyl in **15**, then intramolecular hydrogen bonding has lowered the frequency of OH stretching by 373 cm$^{-1}$.

2-(Phenylseleno)cyclohexanone (**16**) was prepared according to the procedure of Sharpless and Michaelson.[22] When **16** was treated with either NCS or $t$-BuOCl as described and then stirred with aqueous base for 30 min, cyclohexenone was isolated in 74% yield from the NCS reaction and in 86% yield from the $t$-BuOCl reaction. This method of oxidation–elimination of **16** compares quite well to others in the literature for **16** and other 2-(phenylseleno)cyclohexanones.[3a,b,23]

When 1,5-cyclooctadiene was treated with 2 equiv of benzeneselenenyl trifluoroacetate in moist benzene followed by ethanolic hydroxide,[20] two products were isolated in 32 and 37% yields. The major product was identified as **17** on the basis of IR, $^1$H NMR, and mass spectra, and the minor component was assigned structure **18** on the basis of IR, $^1$H NMR, and mass spectra as well as elemental analysis.

When **17** was treated with $t$-BuOCl as described and the resulting reaction mixture was stirred for 2 h at room temperature, cycloocta-2,5-dienol[24] was obtained in modest yield (40%).

Transannular reactions of 1,5-cyclooctadiene to give 9-oxa(or 9-aza)bicyclo[3.3.1]nonane structures are well precedented.[25] In the present example, cyclooctadiene most likely adds 1 equiv of benzeneselenenyl trifluoroacetate to give **17**. Moisture present in the reaction mixture might then hydrolyze the trifluoroacetate to give alcohol **19** (Scheme II). A second equivalent of benzeneselenenyl trifluoroacetate could give episelenonium species **20** which would then undergo intramolecular nucleophilic attack by the hydroxyl oxygen to give **18** with loss of

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(19) Detty, M. R. *J. Org. Chem.*, in press.

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

(21) For another example of diastereomeric selenoxides, see: Jones, D. N.; Mundy, D.; Whitehouse, R. D. *J. Chem. Soc., Chem. Commun.* **1970**, 86.

(22) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6137.

(23) Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1973**, 695.

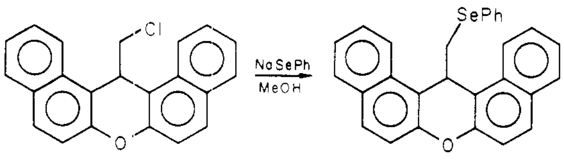
(24) Moon, S.; Ganz, C. R. *J. Org. Chem.* **1970**, *35*, 1241.

(25) (a) Stetter, H.; Meissner, H.-J. *Tetrahedron Lett.* **1966**, 4599. (b) Stetter, H.; Meissner, H.-J.; Last, W. D. *Chem. Ber.* **1968**, *101*, 2889. (c) Stetter, H.; Heckel, K. *Ibid.* **1973**, *106*, 339. (d) Averina, N. V.; Zefirov, S.; Kadzyauskas, P.; Rogozina, S. V.; Sadovsya, N. K.; Sotdatov, N. M. *Zh. Org. Khim.* **1974**, *10*, 1442.

trifluoroacetic acid. When a sample of **17** was treated with 1 equiv of benzeneselenenyl trifluoroacetate in moist benzene, **18** was produced in modest yield (35%) without benefit of a hydroxide workup. When 1,5-cyclooctadiene was treated with 2 equiv of benzeneselenenyl trifluoroacetate under rigorously anhydrous conditions, no **18** was detected, even after hydrolytic workup.

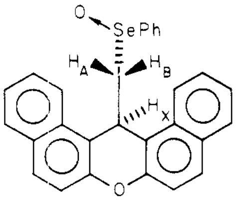
When **18** was treated with 2.2 equiv of *t*-BuOCl in methanol–methylene chloride at 0 °C and the resulting solution was stirred at room temperature with saturated sodium bicarbonate for 1 h, 9-oxabicyclo[4.2.1]nona-2,4-diene (**21**) was isolated in 55% yield as a low-melting solid, mp 29–32 °C.[26]

Selenide **22** was prepared by treating chloride **23** (prepared by the procedure of Delephine)[27] with sodium phenylselenide in methanol. Oxidation with NCS gave selenoxide **24** in 82% yield, and oxidation with *t*-BuOCl gave **24** in 90% yield.



23 22

The $^1$H NMR spectrum of **22** is that of a symmetrical molecule. The $^1$H NMR spectrum of **24** is that of an unsymmetrical molecule with the asymmetry being introduced by the asymmetric selenoxide center. The simple triplet and doublet of the nonaromatic protons of **22** are replaced with an ABX pattern.



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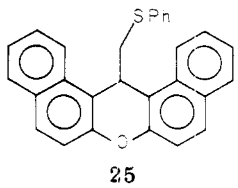
**Mechanistic Considerations.** As the results described above have shown, NCS or *t*-BuOCl oxidation of selenides and tellurides is highly competitive with other methods of oxidation. Interestingly, dialkyl and alkyl aryl selenides and tellurides are oxidized without significant (if any) formation of $\alpha$-chloro selenides and tellurides. Such products are commonly observed from the reactions of dialkyl or alkyl aryl sulfides, and these reactions have been used synthetically.[28] As a case in point, sulfide **25** (prepared from **23** and sodium thiophenoxide) when treated with NCS at 0 °C as described gave chloride **26** in more than 85% yield and trace amounts (<5%) of sulfoxide **27**. Similarly, *t*-BuOCl oxidation of **25** at 0 °C gave **26** and **27** in about 45% yield for each.



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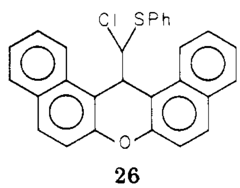

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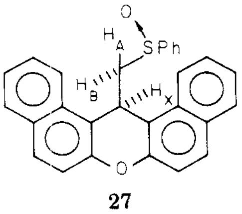

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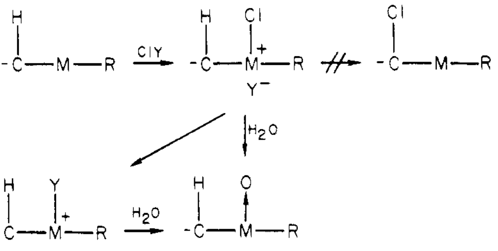
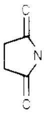
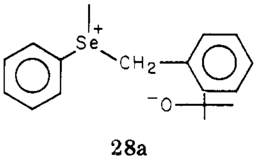
Scheme III$^a$



$^a$ M = Se or Te and Y = +O or 

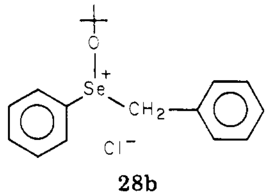
The reaction of sulfide **25** with NCS or *t*-BuOCl is markedly different from the reaction of the corresponding selenide with the same reagents. Perhaps this difference can be explained by an increased basicity of selenium and tellurium relative to sulfur for the Lewis acid Cl$^+$. Such an increased basicity should stabilize the intermediate onium compounds, minimizing the tendency to rearrange to the $\alpha$-chloroselenide or -telluride. Hydrolysis of the onium species then gives the desired oxidized product. Alternatively, the initially formed chloro onium species might undergo nucleophilic displacement by the counterion (perhaps via a tetravalent intermediate) with loss of chloride and formation of a more stable onium intermediate.[15] Scheme III summarizes such mechanistic considerations.

Attempts to isolate selenonium or telluronium salts from these reactions gave oils that quickly decomposed. However, direct evidence of the formation of selenonium compound **28** was found by following the reaction of benzyl phenyl selenide (**5**) with *t*-BuOCl.



28a

or



28b

A $^1$H NMR sample of selenide **5** in dry deuteriochloroform was cooled to 0 °C, and 1.05 equiv of *t*-BuOCl was added. The $^1$H NMR spectrum of the resulting solution is quite revealing. The aromatic protons appear as two two-proton multiplets at $\delta$ 8.40 and 7.83 and two three-proton multiplets at $\delta$ 7.57 and 7.41. The methylene protons appear as an AB pattern at $\delta$ 5.81 and 4.66 with $J_{AB}$ = 10.5 Hz. The *tert*-butoxy protons appear as a singlet at $\delta$ 1.13. Small amounts of unreacted starting material and benzyl chloride are also apparent. The downfield shift of all of the proton signals relative to those in selenide **5** indicates an onium species. Furthermore, the diastereotopic nature of the benzylic protons in the resulting species indicates the formation of onium compound **28**.[29]

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(26) Scarborough, R. M.; Smith, A. B., III; Barnette, W. E.; Nicolau, K. C. *J. Org. Chem.* **1979**, *44*, 1742.

(27) Delephine, M. *Ann. Chim. Phys.* **1925**, *77*, 490.

(28) Paquette, L. A.; Snow, R. A.; Klobucar, W. D. *Synth. Commun.* **1976**, *6*, 575.

(29) One of the reviewers suggested that **28a** is initially formed followed by rapid rearrangement to **28b** through a tetracovalent selenium intermediate. The actual species observed in solution is most likely **28b**.

Addition of deuterium oxide to the NMR sample resulted in some rather dramatic changes in the spectrum. *tert*-Butyl alcohol-*O-d* appears as a sharp singlet at δ 1.33. The aromatic protons appear as a series of broadened multiplets at δ 8.1–6.8, and the methylene protons appear as two broadened signals at δ 5.50 and 4.33. However, addition of sufficient sodium deuterioxide to neutralize any DCl present led to the appearance of the signals for benzyl phenyl selenoxide (**6**). Apparently, alkaline conditions are necessary during hydrolysis to obtain the selenoxide.

## Conclusions

Oxidation of selenides and tellurides by treatment with positive halogenating species followed by alkaline hydrolysis gives very good yields of the corresponding selenoxides (or fragmentation products) and telluroxides (or hydrates). The method is compatible with a variety of functional groups and should be generally applicable in synthetic transformations. The oxidation appears to involve the intermediacy of chloroselenonium and chlorotelluronium species. These compounds do not show a tendency to rearrange, unlike their chlorosulfonium counterparts.

## Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. Boiling points are uncorrected. $^1H$ 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. Solvents were used as received from Eastman Organic Chemicals. *N*-Chlorosuccinimide was obtained from Eastman Organic Chemicals and was recrystallized prior to use. *tert*-Butyl hypochlorite was obtained from J. T. Baker Co. and was distilled prior to use.

**Oxidation of Diphenyl Selenide (1). A. General Procedure for NCS Oxidation.** The selenide 1 (2.33 g, 10.0 mmol) was dissolved in 20 mL of 1/1 (v/v) methanol/methylene chloride, and the solution was cooled to 0 °C. NCS (1.41 g, 10.5 mmol) was added, and the resulting solution was stirred for 30 min at 0 °C. The reaction mixture was diluted with 20 mL of methylene chloride, and 30 mL of a 10% sodium hydroxide solution was added. After the mixture was stirred for 5 min, the organic phase was separated, dried over sodium sulfate, and concentrated to give a pink solid. Recrystallization from 4/1 hexane/methylene chloride gave 1.97 g (79%) of **2** as a white, crystalline solid, mp 111–113 °C.

**B. General Procedure for *t*-BuOCl Oxidation.** The selenide 1 (2.33 g, 10.0 mmol) was dissolved in 20 mL of 1/1 (v/v) methanol/methylene chloride and was cooled to 0 °C. *t*-BuOCl (1.15 g, 10.5 mmol) was added, and the resulting solution was stirred for 5 min at 0 °C. The reaction mixture was diluted with 20 mL of methylene chloride, and 20 mL of a saturated sodium bicarbonate solution was then added. After the mixture was stirred for 5 min, the organic phase was separated, dried over sodium sulfate, and concentrated to give an off-white solid. Recrystallization from 4/1 hexane/methylene chloride gave 2.08 g (81%) of **2** as a white solid: mp 111.5–113 °C; $^1H$ NMR ($CDCl_3$) δ 7.70 (m, 4 H), 7.47 (m, 6 H); IR (KBr) 2990, 1570, 1470, 1440, 820, 745, 730, 685 $cm^{-1}$.

Anal. Calcd for $C_{12}H_{10}OSe$: C, 57.8; H, 4.0; Se, 31.7. Found: C, 57.7; H, 3.9; Se, 31.6.

**Oxidation of Diphenyl Telluride (3). A.** Telluride 3 (1.41 g, 5.00 mmol) was treated with NCS (0.74 g, 5.3 mmol) as described to give a yellow oil. Precipitation from 4/1 hexane/methylene chloride gave 1.35 g (91%) of **4** as a white solid, mp 186–190 °C dec.

**B.** Diphenyl telluride (3; 1.41 g, 5.00 mmol) was treated with *t*-BuOCl (0.60 g, 5.5 mmol) as described to give a pale yellow oil which crystallized in 4/1 hexane/methylene chloride to give 1.45 g (98%) of **4** as a white, crystalline solid: mp 186–189 °C dec; $^1H$ NMR ($CDCl_3$) δ 7.65 (m, 4 H), 7.45 (m, 6 H); IR (KBr) 2990, 1570, 1470, 1430, 728, 718, 682 $cm^{-1}$.

Anal. Calcd for $C_{12}H_{10}Te$: C, 48.4; H, 3.4; Te, 42.8. Found: C, 48.5; H, 3.7; Te, 42.7

**Preparation of Benzyl Phenyl Selenide (5).** Benzyl bromide (5.5 g, 0.032 mol) was added to a slurry of thallous phenylselenide[17] (11.5 g, 0.032 mol) in 100 mL of ether, and the resulting mixture was stirred for 2.0 h at room temperature. The reaction mixture was filtered through Celite, and the filtrate was concentrated to give a yellow solid. Recrystallization from methanol gave 7.1 g (90%) of **5** as white needles: mp 33–36 °C; $^1H$ NMR ($CDCl_3$) δ 7.33 (m, 2 H), 7.17 (m, 8 H), 4.03 (s, 2 H); IR (KBr) 3000, 1580, 755, 731, 688 $cm^{-1}$; mass spectrum *m/e* 248 ($C_{13}H_{12}{}^{80}Se$).

**Oxidation of Benzyl Phenyl Selenide (5). A.** Selenide **5** (2.47 g, 10.0 mmol) was treated with NCS (1.41 g, 10.5 mmol) as described to give a white solid. Recrystallization from 4/1 hexane/methylene chloride gave 2.10 g (80%) of selenoxide **6** as a white solid, mp 132–135 °C. Concentration of the mother liquors and preparative TLC (silica gel, hexane) of the residue gave 0.060 g of benzyl chloride.

**B.** Selenide **5** (1.24 g, 5.00 mmol) was treated with *t*-BuOCl (0.60 g, 5.5 mmol) as described to give a white solid. Recrystallization from 4/1 hexane/methylene chloride gave 1.06 g (80%) of **6** as a white solid, mp 132–135 °C. Concentration of the mother liquors and preparative TLC (silica gel, hexane) gave 0.084 g of benzyl chloride.

For **6**: $^1H$ NMR ($CDCl_3$) δ 7.43 (m, 5 H), 7.22 (m, 3 H), 6.90 (m, 2 H), 4.15 (d, 1 H, *J* = 11 Hz), 3.90 (d, 1 H, *J* = 11 Hz); IR (KBr) 3000, 2900, 1430, 815, 755, 736, 688 $cm^{-1}$.

**Preparation of Dodecyl Phenyl Selenide (7).** Sodium methoxide (1.6 g, 0.030 mol) was added to a solution of benzeneselenol (3.14 g, 0.0200 mol) in 25 mL of methanol. The resulting solution was stirred for 0.5 h at room temperature. Dodecyl iodide (5.92 g, 0.0200 mol) was added. The resulting solution was stirred for 2.0 h at reflux. The reaction mixture was concentrated in vacuo. The residue was taken up in 100 mL of methylene chloride and 50 mL of saturated sodium bicarbonate. The organic phase was dried over sodium sulfate and concentrated. Distillation of the residue yielded 5.21 g (80%) of a pale yellow oil: bp 162–168 °C (1.4 torr); $^1H$ NMR ($CDCl_3$) δ 7.38 (m, 2 H), 7.11 (m, 3 H), 2.83 (t, 2 H, *J* = 7 Hz), 1.67 (m, 2 H), 1.23 (br s, 18 H), 0.85 (t, 3 H, *J* = 6 Hz); IR (film) 3000, 2850, 2800, 1580, 1460, 730, 684 $cm^{-1}$; mass spectrum *m/e* 326 ($C_{18}H_{30}{}^{80}Se$).

Anal. Calcd for $C_{18}H_{30}Se$: C, 66.4; H, 9.3; Se, 24.3. Found: C, 66.3; H, 9.2; Se, 24.6.

**Oxidation of Dodecyl Phenyl Selenide (7).** Selenide **7** (1.63 g, 5.00 mmol) was treated with NCS (0.71 g, 5.3 mmol) as described to give a pale yellow oil that solidified upon standing. Recrystallization from ligroin gave 1.55 g (91%) of **8** as white platelets: mp 60–62 °C; $^1H$ NMR ($CDCl_3$) δ 7.69 (m, 2 H), 7.48 (m, 3 H), 2.87 (dd, 1 H, *J* = 2, 8 Hz), 2.78 (dd, 1 H, *J* = 0.5, 8 Hz), 1.70 (m, 2 H), 1.23 (br s, 18 H), 0.85 (t, 3 H, *J* = 6 Hz); IR (KBr) 3000, 2850, 2800, 815, 731, 688 $cm^{-1}$.

**Oxidation of Dihexadecyl Telluride (10).** Telluride **10** (0.50 g, 0.87 mmol) was treated with *t*-BuOCl (0.11 g, 1.0 mmol) as described to give a white powder which was recrystallized from 1/1 hexane/ethanol to give 0.49 g (96%) of **13a**: mp 92–95 °C; $^1H$ NMR ($CDCl_3$) δ 3.44 (s, 2 H), 2.3–3.0 (m, 4 H), 1.65 (m, 4 H), 1.27 (m, 52 H), 0.85 (m, 6 H); IR (KBr) 3400, 2850, 2800, 1470, 715 $cm^{-1}$.

Anal. Calcd for $C_{32}H_{66}TeO \cdot H_2O$: C, 62.8; H, 11.2; Te, 20.8. Found: C, 62.4; H, 11.1; Te, 21.2.

**Oxidation of Bis(2-phenylethyl) Telluride (11).** Telluride **11** (1.50 g, 4.44 mmol) was treated with *t*-BuOCl (0.55 g, 5.0 mmol) as described to give 1.57 g of an off-white solid: mp 140 °C dec; $^1H$ NMR ($CDCl_3$) δ 7.17 (br s, 10 H), 2.6–3.7 (m, 10 H); IR (KBr) 3400, 2990, 2890, 745, 692 $cm^{-1}$.

Anal. Calcd for $C_{16}H_{18}OTe \cdot H_2O$: C, 51.7; H, 5.4; Te, 34.3. Found: C, 51.2; H, 5.1; Te, 34.7.

**Preparation of *trans*-2-(Phenylseleno)cyclohexanol (14).** Benzeneselenenyl chloride (5.73 g, 0.0300 mol) was added to a stirred suspension of silver trifluoroacetate (6.63 g, 0.0300 mol) in 150 mL of benzene. Cyclohexene (3.0 g, 0.037 mol) was added, resulting in an instantaneous reaction which gave a colorless solution. The silver salts were removed via filtration, and 50 mL of 10% sodium hydroxide in aqueous ethanol (1/1) was added. The resulting mixture was stirred for 1.0 h. The benzene solution was washed with water, dried over sodium sulfate, and concentrated. Distillation of the residue gave 6.12 g (81%) of a yellow oil: bp 135–136 °C (1.2 torr); $^1$H NMR (CDCl$_3$) δ 7.51 (m, 2 H), 7.23 (m, 3 H), 3.27 (m, 1 H), 2.89 (s, 1 H), 2.89 (m, 1 H), 2.10 (m, 2 H), 1.8–1.0 (m, 6 H); IR (film) 3400, 3000, 2860, 2800, 1580, 735, 688 cm$^{-1}$; mass spectrum *m/e* 256 ($C_{12}H_{16}O^{80}Se$).

**Oxidation of *trans*-2-(Phenylseleno)cyclohexanol (14). A.** Selenide 14 (1.28 g, 5.00 mmol) was treated with NCS (0.71 g, 5.3 mmol) as described to give an off-white solid. Recrystallization from 1/1 ether/hexane gave 0.96 g (71%) of **15** as a 70:30 mixture of two diastereomers, mp 116–120 °C dec.

**B.** Selenide 14 (1.28 g, 5.00 mmol) was treated with *t*-BuOCl (0.60 g, 5.5 mmol) as described to give 0.96 g (71%) of **15** as a 70:30 mixture of diastereomers: mp 116–120 °C dec; $^1$H NMR (CDCl$_3$), see text; IR (KBr) 2980 (br), 2890, 2800, 1440, 805, 795, 735, 658 cm$^{-1}$.

Anal. Calcd for $C_{12}H_{16}O_2Se$: C, 53.1; H, 5.9; Se, 29.1. Found: C, 53.2; H, 6.3; Se, 28.7.

**Preparation of 2-(Phenylseleno)cyclohexanone (16).** Benzeneselenenyl chloride (4.02 g, 0.0210 mol) was added to a solution of cyclohexanone (2.00 g, 0.0204 mol) in 100 mL of ethyl acetate. The resulting solution was stirred for 0.5 h at room temperature. The reaction mixture was washed with several portions of saturated sodium bicarbonate solution, dried over sodium sulfate, and concentrated. Distillation of the residue gave 3.96 g (80%) of an orange oil, bp 134–137 °C (1 torr), that crystallized on standing. Recrystallization from ligroin gave a white solid: mp 55–57 °C; $^1$H NMR (CDCl$_3$) δ 7.50 (m, 2 H), 7.28 (m, 3 H), 3.90 (m, 1 H), 2.90 (m, 1 H), 2.5–1.5 (m, 7 H); IR (KBr) 1700 cm$^{-1}$; mass spectrum *m/e* 254 ($C_{12}H_{14}O^{80}Se$).

Anal. Calcd for $C_{12}H_{14}OSe$: C, 56.9; H, 5.6; Se, 31.2. Found: C, 57.2; H, 5.5; Se, 31.0.

**Oxidation of 2-(Phenylseleno)cyclohexanone (16). A.** Selenide 16 (1.22 g, 5.00 mmol) was treated with NCS (0.77 g, 5.5 mmol) as described except that the reaction mixture was stirred with base for 30 min. The organic phase was separated, dried, and concentrated. Chromatography on silica gel (1/1 hexane/ether) gave 0.35 g (74%) of cyclohexenone.

**B.** Selenide 16 (1.22 g, 5.00 mmol) was treated with *t*-BuOCl (0.60 g, 5.5 mmol) as described to give 0.36 g (76%) of cyclohexenone.

**Reaction of Benzeneselenenyl Trifluoroacetate with 1,5-Cyclooctadiene.** Benzeneselenyl chloride (5.73 g, 0.0300 mol) was added to a suspension of silver trifluoroacetate (6.63 g, 0.0300 mol) in 100 mL of benzene. The pale yellow mixture was added to 1,5-cyclooctadiene (1.54 g, 0.015 mol) in 100 mL of benzene. The resulting mixture was filtered through Celite. Ethanolic sodium hydroxide was added to the filtrate. After being stirred for 0.5 h at room temperature, the reaction mixture was washed with water, dried over sodium sulfate, and concentrated. Chromatography of the residue on silica gel (1/1 hexane/ether) gave 1.94 g (37%) of **17** as a colorless oil and 2.09 g (32%) of **18** as a white solid, mp 100–102 °C.

For **17**: $^1$H NMR (CDCl$_3$) δ 7.50 (m, 2 H), 7.25 (m, 3 H), 5.65 (m, 2 H), 5.30 (m, 1 H), 3.68 (m, 1 H), 2.60–1.70 (m, 8 H); IR (film) 1780 cm$^{-1}$; mass spectrum *m/e* 378 ($C_{16}H_{17}F_3O_2{}^{80}Se$).

For **18**: $^1$H NMR (CDCl$_3$) δ 7.50 (m, 4 H), 7.22 (m, 6 H), 4.57 (m, 2 H), 3.62 (m, 2 H), 2.05 (m, 8 H); IR (KBr) 2900, 1575, 1470, 1430, 920, 735, 688 cm$^{-1}$; mass spectrum *m/e* 438 ($C_{20}H_{22}O^{80}Se_2$).

Anal. Calcd for $C_{20}H_{22}OSe_2$: C, 55.1; H, 5.1; Se, 36.2. Found: C, 55.0; H, 5.2; Se, 36.0.

**Oxidation of 17.** Selenide 17 (1.26 g, 0.033 mol) was treated with *t*-BuOCl (0.39 g, 0.035 mol) as described. The reaction mixture was stirred over saturated sodium bicarbonate for 2 h. Workup and chromatography on silica gel (1/1 hexane/ether) gave 0.16 g (40%) of cycloocta-2,5-dienol: $^1$H NMR (CDCl$_3$) δ 6.0–5.0 (m, 4 H), 4.70 (quin, 1 H, *J* = 5 Hz), 3.80 (s, 1 H), 2.78 (t, 2 H, *J* = 4 Hz), 3.0–1.0 (m, 4 H); IR (film) 3400 cm$^{-1}$; mass spectrum *m/e* 124 ($C_8H_{12}O$).

**Oxidation of 18.** Selenide 18 (1.50 g, 3.44 mmol) was treated with *t*-BuOCl (0.82 g, 7.6 mmol) as described. The reaction mixture was stirred over saturated sodium bicarbonate for 1 h. Workup and chromatography on silica gel (4/1 hexane/ether) gave 0.23 g (55%) of 9-oxabicyclo[4.2.1]nona-2,4-diene (**21**) as an oil that solidified on standing: mp 29–32 °C; $^1$H NMR (CDCl$_3$) δ 6.10 (m, 2 H), 5.75 (m, 2 H), 4.64 (m, 2 H), 2.15 (m, 4 H); IR (KBr) 2900, 1460, 1070, 920, 875 cm$^{-1}$; mass spectrum *m/e* 122 ($C_8H_{10}O$).

**Preparation of Selenide 22.** Chloride 23 (6.14 g, 0.0186 mol) and 0.3 g of 18-crown-6 were added dropwise to a stirred mixture of benzeneselenol (3.01 g, 0.0182 mol) and sodium hydride (50% dispersion, 1.20 g, 0.025 mol) in 100 mL of dry tetrahydrofuran. The resulting mixture was warmed at reflux for 1 h. The reaction mixture was concentrated, and the residue was taken up in methylene chloride and water (100 mL each). The organic phase was dried over sodium sulfate and concentrated. Recrystallization from 1/1 (v/v) ethanol/benzene gave 6.54 g (78%) of **22** as white prisms: mp 145–147 °C; $^1$H 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, 1630, 1600, 1260, 1250, 740 cm$^{-1}$; mass spectrum *m/e* 452 ($C_{28}H_{20}O^{80}Se$).

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.

**Oxidation of 22. A.** Selenide 22 (0.60 g, 1.3 mmol) was treated with NCS (0.19 g, 1.4 mmol) as described to give an off-white crystalline solid. Recrystallization from 4/1 hexane/methylene chloride gave 0.51 g (82%) of **24**, mp 120 °C dec.

**B.** Selenide 22 (2.26 g, 5.00 mmol) was treated with *t*-BuOCl (0.60 g, 5.5 mmol) as described to give 2.10 g (90%) of selenoxide **24**: $^1$H NMR (CDCl$_3$) δ 8.63 (d, 1 H, *J* = 9 Hz), 8.39 (d, 1 H, *J* = 9 Hz), 7.27 (s, 5 H), 8.10–7.33 (m, 10 H), 6.10 (dd, 1 H, *J* = 4, 8 Hz), 3.55 (dd, 1 H, *J* = 8, 12 Hz), 3.35 (dd, 1 H, *J* = 4, 12 Hz); IR (KBr) 1630, 1600, 1249, 820, 740, 685 cm$^{-1}$.

Anal. Calcd for $C_{28}H_{20}O_2Se$: C, 71.9; H, 4.3; Se, 16.9. Found: C, 71.3; H, 4.5; Se, 16.6.

**Preparation of Sulfide 25.** Chloride 23 (6.60 g, 0.0200 mol), thiophenol (2.20 g, 0.0200 mol), sodium hydride (50% dispersion, 1.1 g, 0.023 mol), and 18-crown-6 (0.5 g) were treated as described for selenide **22**. The crude crystalline product was recrystallized from 2/1 ethanol/benzene to give 6.87 g (78%) of **25** as white prisms: mp 131–132 °C; $^1$H NMR (CDCl$_3$) δ 8.13 (d, 2 H, *J* = 9 Hz), 7.9–7.2 (m, 10 H), 7.13 (s, 5 H), 5.73 (t, 1 H, *J* = 4.5 Hz), 3.56 (d, 2 H, *J* = 4.5 Hz); IR (KBr) 3000, 1630, 1600, 1250, 815, 740, 688 cm$^{-1}$; mass spectrum *m/e* 404 ($C_{28}H_{20}OS$).

Anal. Calcd for $C_{28}H_{20}OS$: C, 83.1; H, 5.0; S, 7.9. Found: C, 83.3; H, 4.8; S, 7.6.

**Oxidation of 25. A.** Sulfide 25 (1.00 g, 2.49 mmol) was treated with NCS (0.35 g, 2.6 mmol) as described to give **26** as a glass (1.08 g, 85%) and 0.050 g of sulfoxide **27**. For **26**: $^1$H NMR (CDCl$_3$) δ 8.40 (d, 1 H, *J* = 8 Hz), 8.27 (d, 1 H, *J* = 8 Hz), 7.8–6.8 (m, 15 H), 6.13 (d, 1 H, *J* = 2 Hz), 5.62 (d, 1 H, *J* = 2 Hz); mass spectrum *m/e* 438 ($C_{28}H_{19}ClOS$).

**B.** Sulfide 25 (1.00 g, 2.48 mmol) was treated with *t*-BuOCl (0.30 g, 2.7 mmol) as described to give 0.47 g (45%) of **26** and 0.46 g (45%) of **27**: mp 120 °C dec; $^1$H NMR (CDCl$_3$) δ 9.68 (d, 1 H, *J* = 8 Hz), 8.35 (d, 1 H, *J* = 8 Hz), 8.0–7.0 (m, 15 H), 6.02 (dd, 1 H, *J* = 3, 10 Hz), 3.11 (dd, 1 H, *J* = 3, 14 Hz), 2.87 (dd, 1 H, *J* = 10, 14 Hz).

Anal. Calcd for $C_{28}H_{20}O_2S$: C, 80.0; H, 6.7; S, 7.6. Found: C, 79.9; H, 6.7; S, 7.9.

The products **26** and **27** were separated by chromatography on silica gel (ether).

**Registry No. 1**, 1132-39-4; **2**, 7304-91-8; **3**, 1202-36-4; **4**, 51786-98-2; **5**, 18255-05-5; **6**, 13154-11-5; **7**, 42066-69-3; **8**, 71766-38-6; **9**, 112-41-4; **10**, 71766-42-2; **11**, 71766-40-0; **13a**, 71766-41-1; **13b**, 71766-39-7; **14**, 35446-84-5; **15**, isomer 1, 71806-57-0; **15**, isomer 2, 71766-35-3; **16**, 50984-16-2; **17**, 72138-25-1; **18**, 71098-90-3; **21**, 19740-75-1; **22**, 71766-37-5; **23**, 72138-26-2; **24**, 71766-36-4; **25**, 72138-27-3; **26**, 72138-28-4; **27**, 72138-29-5; *N*-chlorosuccinimide, 128-09-6; *t*-BuOCl, 507-40-4; benzyl bromide, 100-39-0; thallous phenylselenide, 72017-00-6; benzeneselenol, 645-96-5; dodecyl iodide, 4292-19-7; benzeneselenenyl chloride, 5707-04-0; cyclohexene, 110-83-8; cyclohexanone, 108-94-1; cyclohex-2-enone, 930-68-7; 1,5-cyclooctadiene, 111-78-4; cycloocta-2,5-dienol, 10054-74-7; thiophenol, 108-98-5.