**4-Chloro-3,5-diphenyl-3-ethoxy-3*H*-pyrazole (17).** A mixture of 2.89 g (10 mmol) of **13** in 40 mL of ethanol (absolute) was treated with a solution of 1.7 g of silver nitrate in 1.5 mL of water and stirred at room temperature for 60 min. The AgCl was filtered off, and the filtrate was treated with 100 mL of ether, washed with four 50-mL portions of water and with 50 mL of saturated NaCl, and evaporated. The residue was treated with 50 mL of pentane and cooled, and 0.95 g of **18** was filtered off. The pentane filtrate was treated with 1 g of Norit A, heated on a steam bath, and filtered. Evaporation of the solvent gave 1.62 g of yellow oil which would not solidify on cooling and which decomposed upon attempted distillation: IR (neat) 1630 (w), 1493, 1470, 1450 $cm^{-1}$; UV-vis 405 nm (log $\epsilon$ 2.46), 320 (3.60), 242 (4.34); $^1H$ NMR $\delta$ 8.40 (m, 2 H), 7.25-7.65 (m, 8 H), 3.43 (q, 2 H), 1.31 (t, 3 H).

Anal. Calcd for $C_{17}H_{15}N_2OCl$: C, 68.34; H, 5.06; N, 9.37. Found: C, 68.69; H, 5.05; N, 9.17.

**4-Chloro-3,5-diphenyl-3-hydroxy-3*H*-pyrazole (18).** A solution of 2.89 g (10 mmol) of **13** in 40 mL of tetrahydrofuran was treated with a solution of 1.7 g of $AgNO_3$ in 10 mL of water and stirred at room temperature. After 75 min the AgCl was filtered off, and the filtrate was treated with 100 mL of ether. The ether solution was washed with two 50-mL portions of water and with 50 mL of saturated NaCl and evaporated under reduced pressure without heating. The pale yellow solid was recrystallized from $CH_2Cl_2$-pentane to give 2.58 g (95%) of **18**: mp 119-21 °C dec; IR (Nujol mull) 3230 (br d), 1630, 1490, 1455 $cm^{-1}$; UV-vis 385 nm (sh, log $\epsilon$ 2.54), 320 (3.56), 245 (4.30); $^1H$ NMR $\delta$ 8.22 (m, 2 H), 7.45 (m, 3 H), 7.35 (s, 5 H), 4.32 (br s, 1 H, exchanges with $D_2O$).

Anal. Calcd for $C_{15}H_{11}N_2OCl$: C, 66.55; H, 4.09; N, 10.35. Found: C, 66.33; H, 4.13; N, 10.36.

Reaction of **18** in benzene with acetyl chloride and pyridine gave the *O*-acetyl derivative, which was recrystallized as a yellow solid, mp 124-125 °C, from ether-pentane: IR (Nujol mull) 1760, 1625 (w), 1495, 1460 $cm^{-1}$; UV-vis 375 (sh, log $\epsilon$ 2.92), 325 (3.61), 245 (4.34); $^1H$ NMR $\delta$ 8.42 (m, 2 H), 7.35-7.80 (m, 8 H), 2.23 (s, 3 H).

**Acknowledgment.** This work was partially supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society. Y.I.K. wishes to acknowledge the support of Hong-Ik University and the Ministry of Education of the Republic of Korea during the course of this work.

**Registry No.** **1**, $R_1 = R_2$ = Ph, 59434-82-1; **1**, $R_1$ = Me, $R_2$ = Ph, 55026-66-9; **1**, $R_1 = R_2$ = Me, 71989-58-7; **2**, $R_1 = R_2$ = Ph, 59434-85-4; **2**, $R_1$ = Me, $R^2$ = Ph, 59434-84-3; **2**, $R_1 = R_2$ = Me, 71989-59-8; **3a**, 71989-60-1; **3b**, 71989-61-2; **3c**, 71989-62-3; **3d**, 71989-63-4; **3e**, 71989-64-5; **3f**, 71989-65-6; **3h**, 71989-66-7; **4a**, 71582-22-4; **4b**, 71989-67-8; **4c**, 71989-68-9; **4d**, 71549-27-4; **4e**, 71989-69-0; **4f**, 71989-70-3; **4g**, 71989-71-4; **4h**, 71989-72-5; **4i**, 71989-73-6; **6a**, 71989-74-7; **6b**, 71989-75-8; **6c**, 71989-76-9; **6d**, 71989-77-0; **6e**, 62925-70-6; **8a**, 71989-78-1; **8b**, 71989-79-2; **8c**, 71989-80-5; **9**, 2157-56-4; **10**, 1145-01-3; **11**, 71549-28-5; **12**, 71989-81-6; **13**, 71989-82-7; **16**, $R_1$ = Me, $R_2$ = Ph, 71989-83-8; **16**, $R_1 = R_2$ = Ph, 71989-84-9; **16**, $R_1 = R_2$ = Me, 71989-85-0; **17**, 71989-86-1; **18**, 71989-87-2; **18**, *O*-acetyl derivative, 71989-88-3; 3,5-dimethylisoxazole, 300-87-8.

# Substitution Reactions of Thallous Thiophenoxide and Thallous Phenylselenide with Halogen-Bearing Substrates

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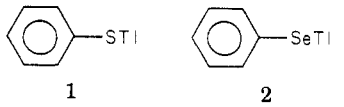
Thallous thiophenoxide (**1**) and thallous phenyl selenide (**2**) were prepared by the action of either thallous ethoxide or thallous phenoxide on thiophenol and benzeneselenol. The reagents **1** and **2** reacted readily with aroyl and acyl halides, imidoyl chlorides, $\alpha$-halo ketones, $\alpha$-halo esters, $\alpha$-halo lactones, $\alpha$-halo carboxylic acids, allyl halides, alkyl halides, chlorotrimethylsilane, chloroacetonitrile, and *N*-chlorosuccinimide to give substitution products and varying amounts of diphenyl disulfide and diphenyl diselenide. The reactions were run as heterogeneous mixtures in ether. The origin of the diphenyl disulfide and diphenyl diselenide was homolytic cleavage of the thallium-sulfur or thallium-selenium bond, on the basis of the products derived from the reactions of *N*-chlorosuccinimide with **1** and **2**.

The utility of thallium(I) salts of organic acids in synthesis was first reported by Taylor and McKillop in 1968.[1,2] They found that thallium(I) salts of $\beta$-dicarbonyl compounds were readily C-alkylated or C- or O-acylated[1] and that the thallous salts of phenols and carboxylic acids were excellent reagents for preparing phenyl esters and anhydrides, respectively, from acyl halides.[2] Since these initial papers, surprisingly little chemistry has been reported on thallium salts of other acidic groups. Recently, the reactions of thallous aliphatic sulfides with acyl halides and $\alpha$-halo ketones have been noted[3] as well as an isolated example of the reaction of a heteroaromatic thallous sulfide with an acyl halide.[4] We wish to report related work on the scope and limitations of substitution reactions of various halogen-containing compounds with thallous thiophenoxide (**1**) and thallous phenyl selenide (**2**).




1 2

## Results

The reagents **1** and **2** are prepared by the dropwise addition of thallous ethoxide to a solution of thiophenol or benzeneselenol, respectively, in hexane-ether. The thallous ethoxide should be clear and colorless to avoid side reactions. The thallous thiophenoxide (**1**) is isolated as a yellow solid, mp 260-265 °C (lit.[5] mp 258-260 °C), in nearly quantitative yield. Similarly, thallous phenyl sel-

(1) Taylor, E. C.; Hawks, G. H., III; McKillop, A. *J. Am. Chem. Soc.* **1968**, *90*, 2421.
(2) Taylor, E. C.; McLay, G. W.; McKillop, A. *J. Am. Chem. Soc.* **1968**, *90*, 2422.
(3) Nagao, Y.; Ochiai, M.; Kaneko, K.; Maeda, A.; Watanabe, K.; Fujita, E. *Tetrahedron Lett.* **1977**, 1345. Masamune, S.; Kamata, S; Schilling, W. *J. Am. Chem. Soc.* **1975**, *97*, 3515.
(4) Nagao, Y.; Kawabata, K.; Fujita, E. *J. Chem. Soc., Chem. Commun.* **1978**, 330.
(5) Gilman, H.; Abbott, R. K. *J. Am. Chem. Soc.* **1949**, *71*, 659.

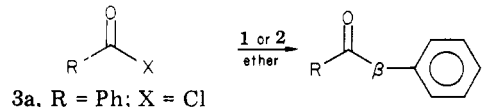
0022-3263/80/1945-0080$01.00/0 

enide is obtained as an orange solid, mp 228–234 °C, in quantitative yield.

The reagents may also be prepared by the heterogeneous reaction of thallous phenoxide[1] with either thiophenol or benzeneselenol in ether solution for 24 h. The salts **1** and **2** are isolated by filtration. The filtrates contain the theoretical amount of phenol.

Both **1** and **2** are air-insensitive, insoluble, high-melting solids that readily react with a variety of organic halides in ether. The progress of such reactions is easily monitored as the bright orange or yellow color of the reactant is replaced by the white or off-white of the thallous halide. The thallous halides are removed by filtration, leaving products of excellent purity contaminated by small amounts of diphenyl disulfide or diphenyl diselenide, which are removed by chromatography or recrystallization. Furthermore, the thallium salts can be stored indefinitely without oxidation to diphenyl disulfide and diphenyl diselenide, which plagues storage of the sodium or potassium salts.

Acyl and aroyl halides **3a–d** reacted readily with **1** and **2** in ether to give the corresponding phenylthio or phenylseleno esters **4a–d** in >97% isolated yield. Reaction

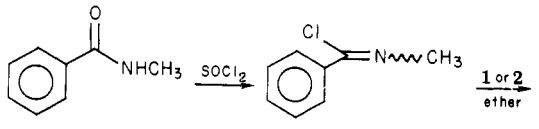


**3a**, R = Ph; X = Cl
**b**, R = Ph; X = Br
**c**, R = $CH_3$; X = Cl
**d**, R = $CH_3$; X = Br

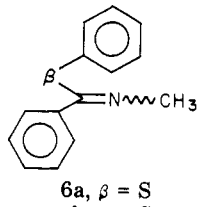
**4a**, R = Ph; β = S
**b**, R = Ph; β = Se
**c**, R = $CH_3$; β = S
**d**, R = $CH_3$; β = Se

conditions and physical and spectral properties of the products are given in Table I.

The imidoyl chloride **5** was prepared by treating *N*-methylbenzamide with thionyl chloride at 55 °C for 2 h.[6]



**5**

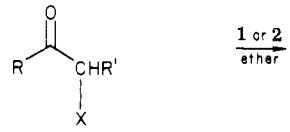


**6a**, β = S
**b**, β = Se

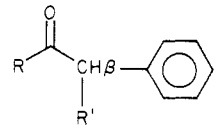
This colorless oil, isolated in 63% yield, rapidly hydrolyzed upon exposure to air to give *N*-methylbenzamide. The $^1H$ NMR spectrum of **5** indicated a mixture of the two isomers of **5** in nearly equal amounts.

The imidoyl chloride **5** reacted with either **1** or **2** within 5 min in ether to give **6a** in 91% yield or **6b** in 85% yield, respectively. Although both **6a** and **6b** can exist in two isomeric forms, only one isomer appears to be formed in each case, as indicated by the appearance of only one methyl signal for each compound in the $^1H$ NMR.

α-Halo ketones (**7a–c**), α-halo esters (**7d–e**), and α-bromo-γ-butyrolactone (**9**) reacted with **1** and **2** to give the corresponding phenylthio or phenylseleno derivatives (**8a–f**, **10a–b**) in 86 to 99% yield. Qualitatively, bromo compounds are more reactive than the corresponding chloro compounds with **1** and **2**. With an identical substrate, **1** appears to be somewhat more reactive than **2**.



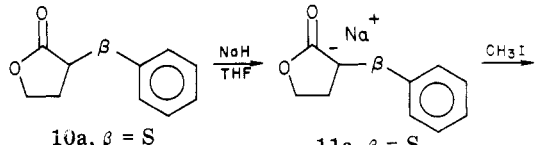
**7a**, R = Ph; R′ = H; X = Cl
**b**, R = Ph; R′ = H; X = Br
**c**, R = $CH_3$; R′ = $CH_3$; X = Br
**d**, R = $OC_2H_5$; R′ = H; X = Cl
**e**, R = $OC_2H_5$; R′ = H; X = Br



**8a**, R = Ph; R′ = H; β = S
**b**, R = Ph; R′ = H; β = Se
**c**, R = $CH_3$; R′ = $CH_3$; β = S
**d**, R = $CH_3$; R′ = $CH_3$; β = Se
**e**, R = $OC_2H_5$; R′ = H; β = S
**f**, R = $OC_2H_5$; R′ = H; β = Se

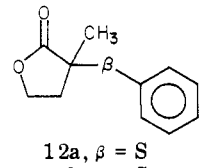
Trace amounts (<2%) of ethyl acetate and γ-butyrolactone were detected in the reaction mixtures from **7e** and **9**, respectively, as well as a small amount (3%) of 2-butanone from the reaction of **7c**.

The phenylthio- and phenylseleno-substituted lactones **10a** and **10b** were readily alkylated by treatment with



**10a**, β = S
**b**, β = Se

**11a**, β = S
**b**, β = Se

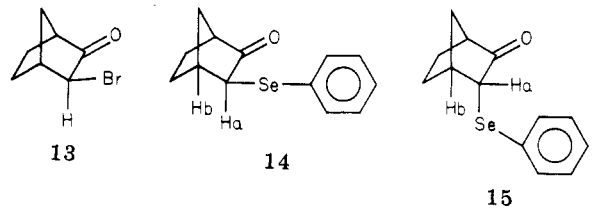


**12a**, β = S
**b**, β = Se

sodium hydride in tetrahydrofuran (THF) to give the sodium salts **11** followed by quenching with methyl iodide to give methylated derivatives **12**. Thus, **12a** was isolated in 91% yield from **10a**, and **12b** was isolated in 96% yield from **10b**.

Alkylation of the sodium salts of butyrolactones **10a** and **10b** offers an alternative route to molecules such as **12** that have been employed in the syntheses of furans or butenolides[7] and α-methylene lactones.[8] The overall yields of **12a** and **12b** make these routes competitive with others.

Surprisingly, *exo*-3-bromobicyclo[2.2.1]heptan-2-one (**13**)[9] showed no reaction with either **1** or **2** after 150 h.



**13** **14** **15**

Authentic samples of the phenylseleno derivatives **14** and **15** were prepared by treating **13** with sodium phenylselenide[10] and 18-crown-6 in THF. A 35:65 mixture of **14**

(6) Braun, H.; Pinkernelle, H. *Chem. Ber.* **1934**, *67*, 1218.

(7) Grieco, P. A.; Pogonowski, C. S.; Burke, S. *J. Org. Chem.* **1975**, *40*, 542.

(8) Grieco, P. A.; Miyashita, M. *J. Org. Chem.* **1974**, *39*, 120.

(9) Dalton, D. R.; Rodebaugh, R. K.; Jefford, C. W. *J. Org. Chem.* **1972**, *37*, 362.

Table I. Reaction Conditions and Physical and Spectral Properties of Products from Reactions of 1 and 2

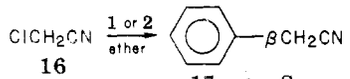
| substrate | reagent | product | reaction time, h | yield,[a] % | mp, °C (solvent) or bp, °C (torr) | lit. mp, °C or lit. bp, °C (torr) | formula (mol wt) | spectral properties[b] |
|---|---|---|---|---|---|---|---|---|
| 3a | 1 | 4a | 1.0 | 99 (<1) | 57-59 | 56[c] | $C_{13}H_{10}OS$ | $^1$H NMR 8.00 (m, 2 H), 7.46 (m, 8 H); IR |
| 3b | 1 | | 0.5 | 99 (<1) | (hexane) | | (214.3) | 3000, 1670, 1570, 1200, 900; *m/e* 214 |
| 3a | 2 | 4b | 2.5 | 98 (<1) | 130-135 | mp 40[d] | $C_{13}H_{10}OSe$ | $^1$H NMR 7.83 (m, 2 H), 7.40 (m, 8 H); IR |
| 3b | 2 | | 1.0 | 99 (<1) | (1.0) | | (261.2) | 3050, 1690, 1600, 1590, 1100, 880; *m/e* 262 |
| 3c | 1 | 4c | 0.5 | 99 (<1) | 94-95 | bp 228-230[e] | $C_8H_8OS$ | $^1$H NMR 7.37 (s, 5 H), 2.33 (s, 3 H); IR |
| 3d | 1 | | 1.0 | 98 (<1) | (4) | mp 76 | (152.2) | 3100, 1710, 1590, 1110, 745; *m/e* 152 |
| 3c | 2 | 4d | 1.0 | 98 (<1) | 112-116 | 115[c] | $C_8H_8OSe$ | $^1$H NMR 7.40 (m, 5 H), 2.37 (s, 2 H); IR |
| 3d | 2 | | 1.0 | 97 (<1) | (20) | (20) | (199.1) | 3050, 1740, 1600, 1100; *m/e* 200 |
| 5 | 1 | 6a | 0.1 | 91 (5) | 155-160 | | $C_{14}H_{13}NS$[f] | $^1$H NMR 7.50 (m, 2 H), 7.10 (m, 8 H), |
| | | | | | (3.0) | | (227.3) | 3.53 (s, 3 H); IR 1600, 1000, 766, 745; *m/e* 227 |
| 5 | 2 | 6b | 0.1 | 85 (7) | 180-182 | | $C_{14}H_{13}NSe$[g] | $^1$H NMR 7.43 (m, 2 H), 7.35-6.90 (m, 8 |
| | | | | | (3.5) | | (274.2) | H), 3.51 (s, 3 H); IR 1610, 1590, 988, 882; *m/e* 275 |
| 7a | 1 | 8a | 10 | 97 (1) | 50-53 | 52-53[h] | $C_{14}H_{12}OS$ | $^1$H NMR 7.87 (m, 2 H), 7.5-7.0 (m, 8 H), |
| 7b | 1 | | 4 | 93 (2) | | | (228.3) | 4.20 (s, 2 H); IR 3000, 1695, 1600, 1580; *m/e* 228 |
| 7a | 2 | 8b | 10 | 97 (1) | 162-164 | | $C_{14}H_{12}OSe$[i] | $^1$H NMR 7.77 (m, 2 H), 7.5-7.0 (m, 8 H), |
| 7b | 2 | | 1 | 96 (1) | (0.8) | | (275.2) | 4.09 (s, 2 H); IR 3050, 1680, 1600, 1590; *m/e* 276 |
| 7c | 1 | 8c | 24 | 90 (5) | 108-110 | 78-80[j] | $C_{10}H_{12}OS$ | $^1$H NMR 7.20 (m, 5 H), 3.67 (q, 1 H, $J$ = 7 Hz), 2.18 (s, 3 H), 1.32 (d, 3 H, $J$ = 7 |
| | | | | | (1.0) | (0.003) | (180.3) | Hz); IR 3000, 1720, 1600; *m/e* 180 |
| 7c | 2 | 8d | 24 | 91 (4) | 112-114 | | $C_{10}H_{12}OSe$[k] | $^1$H NMR 7.45 (m, 2 H), 7.18 (m, 3 H), |
| | | | | | (1.0) | | (227.2) | 3.71 (q, 1 H, $J$ = 7 Hz), 2.26 (s, 3 H), 1.40 (d, 3 H, $J$ = 7 Hz); IR 3000, 1705; *m/e* 228 |
| 7d | 1 | 8e | 24 | 98 (1) | 120-125 | 80[l] | $C_{10}H_{12}O_2S$ | $^1$H NMR 7.25 (m, 5 H), 4.10 (q, 2 H, $J$ = |
| 7e | 1 | | 2 | 90 (3) | (4) | (0.05) | (196.3) | 7 Hz), 3.60 (s, 2 H), 1.20 (t, 3 H, $J$ = 7 Hz); IR 3100, 1700, 1550, 1000, 740; *m/e* 196 |
| 7d | 2 | 8f | 24 | 95 (4) | 93-95 | 77-80[l] | $C_{10}H_{12}O_2Se$ | $^1$H NMR 7.51 (m, 2 H), 7.20 (m, 3 H), |
| 7e | 2 | | 5 | 86 (8) | (1.0) | (0.025) | (243.2) | 4.02 (q, 2 H, $J$ = 7 Hz), 3.44 (s, 2 H), 1.13 (t, 3 H, $J$ = 7 Hz); IR 3000, 1740, 1590, 740; *m/e* 244 |
| 9 | 1 | 10a | 16 | 91 (7) | 140-145 | | $C_{10}H_{10}O_2S$[m] | $^1$H NMR 7.25 (m, 2 H), 7.07 (m, 3 H), 3.93 |
| | | | | | (1.3) | | (194.3) | (t, 2 H, $J$ = 6 Hz), 3.59 (dd, 1 H, $J$ = 6, 7 Hz), 2.33 (m, 1 H), 1.97 (m, 1 H); IR 2900, 1770, 1560, 740; *m/e* 194 |
| 9 | 2 | 10b | 26 | 89 (11) | 152-155 | | $C_{10}H_{10}O_2Se$[n] | $^1$H NMR 7.55 (m, 2 H), 7.23 (m, 3 H), 4.25- |
| | | | | | (1.3) | | (241.1) | 3.70 (m, 3 H), 2.60 (m, 1 H), 2.16 (m, 1 H); IR 3000, 1770, 1580, 740; *m/e* 242 |
| 16 | 1 | 17a | 48 | 96 (2) | 100-104 | | $C_8H_7NS$[o] | $^1$H NMR 7.50 (m, 2 H), 7.35 (m, 3 H), 3.56 |
| | | | | | (1.5) | | (149.2) | (s, 2 H); IR 2270, 1490, 745, 658; *m/e* 149 |
| 16 | 2 | 17b | 120 | 20 (5) | 110-111 | 137-138[p] | $C_8H_7NSe$ | $^1$H NMR 7.61 (m, 2 H), 7.30 (m, 3 H), 3.48 |
| | | | | | (1.5) | (5) | (196.1) | (s, 2 H); *m/e* 197 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **26a** | 1 | **27a** | 24 | 95 (5) | 110–114 | 121–122[q] | $C_9H_{10}S$ | $^1$H NMR 7.22 (m, 5 H), 5.80 (m, 1 H), 5.05 |
| **26b** | 1 | | 1 | 90 (7) | (18) | (30) | | (m, 2 H), 3.51 (d, 2 H, $J$ = 6 Hz); IR |
| **26c** | 1 | | 2 | 93 (6) | | | (150.2) | 3050, 1595, 1495; *m/e* 150 |
| **26a** | 2 | **27b** | 24 | 95 (4) | 75–78 | 82–83[r] | $C_9H_{10}Se$ | $^1$H NMR 7.53 (m, 2 H), 7.30 (m, 3 H), 5.91 |
| **26b** | 2 | | 10 | 83 (9) | (1.3) | (3) | (197.1) | (m, 1 H), 5.03 (m, 1 H), 4.88 (m, 1 H), |
| **26c** | 2 | | 15 | 91 (5) | | | | 3.53 (dd, 2 H, $J$ = 1, 7 Hz); IR 3050, 1590, |
| | | | | | | | | 740; *m/e* 198 |
| **26d/** | 1 | **27c** | 48 | 90 (9) | 53–55 | 84[s] | $C_{11}H_{14}S$ | $^1$H NMR 7.15 (m, 5 H), 5.21 (triplet of sep- |
| **28** | | | | | (0.9) | (0.94) | (178.3) | tets, 1 H, $J$ = 6.1 Hz), 3.43 (d, 2 H, $J$ = 7 |
| | | | | | | | | Hz), 1.66 (s, 3 H), 1.53 (s, 3 H), IR 2900, |
| | | | | | | | | 1600, 735; *m/e* 178 |
| **26d/** | 2 | **27d** | 72 | 85 (10) | 65–67 | | $C_{11}H_{14}Se$[t] | $^1$H NMR 7.40 (m, 2 H), 7.17 (m, 3 H), 5.30 |
| **28** | | | | | (0.9) | | (225.2) | (triplet of septets, 1 H, $J$ = 7.1 Hz), 3.48 |
| | | | | | | | | (d, 2 H, $J$ = 7 Hz), 1.66 (s, 3 H); IR 2900, |
| | | | | | | | | 1590, 740; *m/e* 226 |
| **29** | 1 | **30a** | 18 | 98 (2) | 110 | 80–82[u] | $C_9H_{14}SSi$ | $^1$H NMR 7.20 (m, 5 H), 0.20 (s, 9 H); IR |
| | | | | | (16) | (1) | (182.4) | 3100, 1580; *m/e* 182 |
| **29** | 2 | **30b** | 24 | 93 (7) | 115–120 | 93–95[v] | $C_9H_{14}SeSi$ | $^1$H NMR 7.46 (m, 2 H), 7.10 (m, 3 H), 0.37 |
| | | | | | (18) | (9) | (229.3) | (s, 9 H); IR 3200, 3100, 1560; *m/e* 230 |
| **32a** | 1 | **33a** | 24 | 92 (1) | 62.5–63.5 | 61–62[w] | $C_8H_8O_2S$ | $^1$H NMR 11.42 (s, 1 H), 7.30 (m, 5 H), |
| **32b** | 1 | | 10 | 95 (1) | (hexane) | | (168.2) | 3.68 (s, 2 H); IR 3000, 1710, 1600, |
| | | | | | | | | 1200; *m/e* 168 |
| **32c** | 1 | | 16 | 93 (1) | | | | |
| **32a** | 2 | **33b** | 24 | 84 (3) | 33–36 | 40[x] | $C_8H_8O_2Se$ | $^1$H NMR 11.80 (s, 1 H), 7.52 (m, 2 H), 7.22 |
| **32b** | 2 | | 12 | 91 (2) | (hexane) | | (215.1) | (m, 3 H), 3.47 (s, 2 H); IR 3000, 1700, |
| **32c** | 2 | | 24 | 85 (3) | | | | 1580; *m/e* 216 |
| **32d** | 1 | **33c** | 4 | 97 (1) | 28–32 | oil[y] | $C_9H_{10}O_2S$ | $^1$H NMR 11.35 (s, 1 H), 7.50 (m, 2 H), 7.27 |
| | | | | | (hexane) | | (182.2) | (m, 3 H), 3.77 (q, 1 H, $J$ = 7 Hz), 1.50 (d, |
| | | | | | | | | 2 H, $J$ = 7 Hz); IR 3000, 1700, 1570, |
| | | | | | | | | 750; *m/e* 182 |
| **32d** | 2 | **33d** | 6 | 93 (2) | 50–53 | | $C_9H_{10}O_2Se$[z] | $^1$H NMR 11.27 (s, 1 H), 7.56 (m, 2 H), 7.23 |
| | | | | | (hexane) | | (229.1) | (m, 3 H), 3.67 (q, 1 H, $J$ = 7 Hz), 1.50 (d, |
| | | | | | | | | 2 H, $J$ = 7 Hz); IR 3000, 1700, 1580, 740; |
| | | | | | | | | *m/e* 230 |

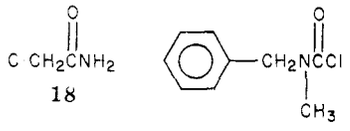
[a] The value in parentheses is the yield of PhSSPh or PhSeSePh. [b] $^1$H NMR data in units ($CDCl_3$ as solvent and $Me_4Si$ as standard); IR data in $cm^{-1}$ (solids as KBr pellet; oils as film on NaCl plates). [c] Wheeler, J.; Merriam, R. *J. Am. Chem. Soc.* **1901**, *23*, 294. [d] Renson, M.; Draquet, C. *Bull. Soc. Chim. Belg.* **1962**, *71*, 260. [e] *Beilstein* **1923**, *6*, 313. [f] Anal. Calcd: C, 74.0; H, 5.8; N, 6.2; S, 14.1. Found: C, 74.0; H, 6.1; N, 6.3; S, 14.2. [g] Anal. Calcd: C, 61.3; H, 4.8; N, 5.1; Se, 28.8. Found: C, 61.0; H, 4.7; N, 5.0; Se, 29.0. [h] Long, L. M. *J. Am. Chem. Soc.* **1946**, *68*, 2159. [i] Anal. Calcd: C, 61.1; H, 4.4; Se, 28.7. Found: C, 61.5; H, 4.7; Se, 28.3. [j] Harpp, D. N.; Mathiaparanam, P. *J. Org. Chem.* **1971**, *36*, 2540. [k] Anal. Calcd: C, 52.9; H, 5.3; Se, 34.8. Found: C, 53.3; H, 5.0; Se, 34.3. [l] Brockson, T. J.; Petragnani, N.; Rodriques, L. *J. Org. Chem.* **1974**, *39*, 2114. [m] Anal. Calcd: C, 61.8; H, 5.2; S, 16.5. Found: C, 61.5; H, 5.3; S, 16.3. [n] Anal. Calcd: C, 49.8; H, 4.2; Se, 32.7. Found: C, 49.7; H, 4.2; Se, 32.6. [o] Anal. Calcd: C, 64.4; H, 4.7; N, 9.4; S, 21.5. Found: C, 64.5; H, 5.0; N, 9.0; S, 21.7. [p] Makoto, Y.; Okawara, U. *Chem. Lett.* **1977**, 835. [q] Bogoslovski, N. V.; Lapkin, I. I. *Zh. Org. Khim.* **1968**, *4*, 805. [r] Kataev, E. G.; Kataev, L. M.; Chmotova, G. A. *Ibid.* **1968**, *4*, 805. [s] Julia, M.; Guy-Rouault, A. *Bull. Soc. Chim. Fr.* **1967**, 1411. [t] Anal. Calcd: C, 58.7; H, 6.3; Se, 35.1. Found: C, 58.6; H, 6.4; Se, 34.8. [u] Reference 11. [v] Reference 12. [w] Gabriel, B. *Chem. Ber.* **1879**, *12*, 1639. [x] Morgan, G. T.; Porritt, W. H. *J. Chem. Soc.* **1925**, *127*, 1755. [y] *Beilstein* **1933**, *6I*, 147. [z] Anal. Calcd: C, 47.2; H, 4.4; Se, 34.5. Found: C, 47.5; H, 4.6; Se, 34.5.

and **15** was obtained in 96% yield. The products were identified on the basis of $J_{HaHb}$. For **14**, $J_{HaHb}$ = 4.5 Hz, and for **15**, $J_{HaHb}$ = 3.1 Hz.[9]

Chloroacetonitrile (**16**) reacted with **1** in 48 h to give (phenylthio)acetonitrile (**17a**) in 96% yield and 2% of diphenyl disulfide. The reaction of **16** with **2** was more



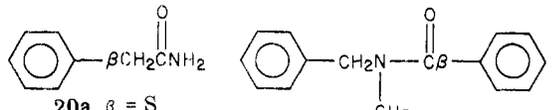
**16** **17a**, β = S; **b**, β = Se



**18** **19**

sluggish, giving only 20% of (phenylseleno)acetonitrile (**17b**) after 120 h. Unreacted **16** (75%) and diphenyl diselenide (5%) were isolated.

Chloroacetamide (**18**) and the carbamoyl chloride **19** were both unreactive toward **1** and **2**, whereas sodium thiophenoxide and sodium phenyl selenide in THF both reacted rapidly to give the expected substitution products **20** and **21**. The failure of the thallium salts to react with

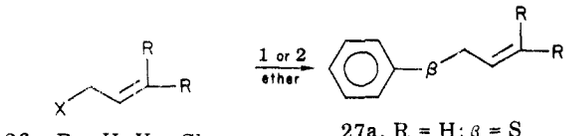


**20a**, β = S; **b**, β = Se **21a**, β = S; **b**, β = Se

these substrates as well as with α-bromo ketone **13** is significant and is considered in the Discussion section.

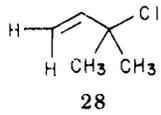
Iodomethane, iodoethane, bromoethane, chloroacetaldehyde dimethyl acetal, bromoacetaldehyde diethyl acetal, and *n*-hexyl iodide were unreactive with both **1** and **2** after 120 h when stoichiometric amounts of the reagents were used in ether. Reaction could be induced by using the alkyl halide in large excess as solvent warmed at reflux. Methyl phenyl sulfide (**23**) was obtained in 100% yield in this manner from **1** and methyl iodide after 24 h. Similarly, **2** and methyl iodide gave methyl phenyl selenide (**24**) in 98% yield after 24 h, and **2** and bromoethane gave ethyl phenyl sulfide (**25**) in 60% yield after 120 h.

The allyl halides **26a–d** reacted readily to give the allyl sulfides and allyl selenides **27a–d** in 83–95% yields. Allyl



**26a**, R = H; X = Cl; **b**, R = H; X = Br; **c**, R = H; X = I; **d**, R = $CH_3$; X = Cl

**27a**, R = H; β = S; **b**, R = H; β = Se; **c**, R = $CH_3$; β = S; **d**, R = $CH_3$; β = Se



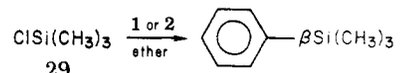
**28**

bromide (**26b**) was more reactive than allyl iodide (**26c**), which in turn was slightly more reactive than allyl chloride.

The commercially available 1-chloro-3-methyl-2-butene is actually an 87:13 mixture of **26d** and **28**. The regioselectivity of product formation of this mixture and **1** or **2** is such that **27c** and **27d** are formed exclusively.

The **26d**/**28** mixture of allyl chlorides, when treated with sodium thiophenoxide and 0.05 equiv of 18-crown-6 in ether (presumably a solution process), gave **27c** as the only detectable product. Similarly, this mixture gave only **27d** when treated with sodium phenyl selenide[10] and 18-crown-6 in ether.

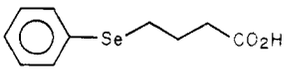
(Phenylthio)trimethylsilane (**30a**)[11] was isolated from the reaction of **1** with chlorotrimethylsilane (**29**). Similarly, (phenylseleno)trimethylsilane (**30b**)[12] was prepared from **2** and **29** in ether.



**29** **30a**, β = S; **b**, β = Se

Although distillation gives pure **30a** and **30b**, stock solutions of these air-sensitive reagents can be prepared in either THF or ether. Stock solutions of **30a** under argon at 0 °C are stable indefinitely, and stock solutions of **30b** under argon at 0 °C are stable for several weeks.

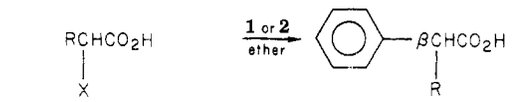
The utility of a stock solution of **30b** was demonstrated by the conversion of γ-butyrolactone to 4-(phenylseleno)butanoic acid, **31**. A solution of the lactone in the



**31**

stock solution of **30b** was treated with potassium fluoride and 18-crown-6, generating potassium phenyl selenide which opens the lactone.[10]

α-Halo carboxylic acids react directly with both **1** and **2** in ether to give the α-phenylthio or α-phenylseleno carboxylic acids in 84–97% yield. No evidence was found



**32a**, R = H; X = Cl; **b**, R = H; X = Br; **c**, R = H; X = I; **d**, R = $CH_3$; X = Br

**33a**, R = H; β = S; **b**, R = H; β = Se; **c**, R = $CH_3$; β = Se; **d**, R = $CH_3$; β = Se

for the formation of thiophenol or benzeneselenol, nor was evidence found for the thallous carboxylates. The bromo compounds were more reactive than chloroacetic or iodoacetic acid.

The benzylic bromo compound 3-bromo-3-phenylpropionic acid (**34**)[13] reacted within 12 h with either **1** or **2** to give product mixtures containing nearly equal amounts of **35a** or **35b** and *trans*-cinnamic acid (**36**). Attempts to separate the product mixtures by fractional crystallization or chromatography gave only **36** in a pure state. The products **35a** and **35b** were always contaminated with **36**, apparently due to product instability. Diphenyl disulfide and diphenyl diselenide were isolated in 20 and 25% yields, respectively, from the crude reaction mixtures.

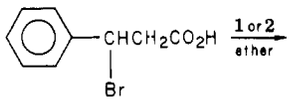
The direct reaction of the α- and β-halo carboxylic acids with the thallium salts to give substitution products without apparent acid–base exchange is contrary to the behavior expected for the sodium salts of thiophenol and

(10) Liotta, D. C.; Markiewicz, W.; Santiesteban, H. *Tetrahedron Lett.* **1977**, 4365.

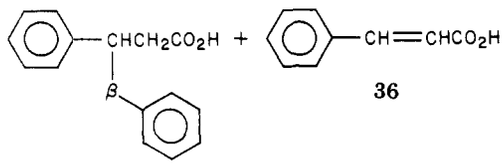
(11) Evans, D. A.; Grimm, K. G.; Truesdale, L. K. *J. Am. Chem. Soc.* **1975**, *97*, 3229.

(12) Derkach, N. Y.; Pasmurtseva, N. A.; Levchenko, E. S. *Zh. Org. Khim.* **1971**, *7*, 1543. Detty, M. R. *Tetrahedron Lett.* **1978**, 5087. Liotta, D. C.; Paty, P. B.; Johnson, J.; Zima, G. *Ibid.* **1978**, 5091.

(13) Sample donated by Dr. G. A. Reynolds (Eastman Kodak Co.). The compound was prepared by treating cinammic acid with HBr in acetic acid for 24 h; mp 130–131 °C.



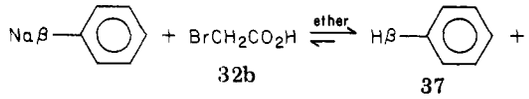
34



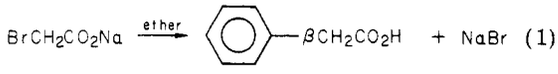
35a, $\beta$ = S
b, $\beta$ = Se

36

benzeneselenol. When $\alpha$-bromoacetic acid is treated with either sodium salt, a rapid acid–base exchange occurs to give thiophenol ($\beta$ = S) or benzeneselenol ($\beta$ = Se) and the sodium salt of bromoacetic acid (**37**). When the mixture is allowed to stand, the thiophenol or benzeneselenol reacts slowly with **37** to give **33a** or **33b** and sodium bromide.



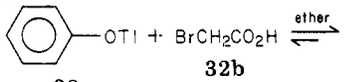
32b 37



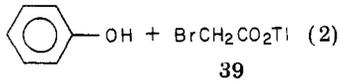
(1)

33a, $\beta$ = S
b, $\beta$ = Se

With these results, the behavior of the thallium salt of a harder nucleophile became of interest.[14] Thallous phenoxide (**38**) and bromoacetic acid (**32b**) reacted rapidly



38 32b

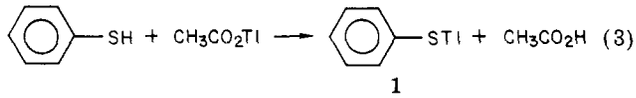


(2)

39

in ether to give phenol in 98% isolated yield and the thallium(I) salt of bromoacetic acid in 97% isolated yield. This reaction mixture showed no further changes after standing for 120 h.

When thallous acetate and thiophenol were stirred together in ether, complete metal exchange occurred to give **1** and acetic acid after 1.5 h (eq 3). The progress of the



(3)

1

exchange was followed by VPC analysis on aliquots of the reaction mixture at 0.5 h intervals. The analyses were unchanging after 1.5 h. No thiophenol could be detected at this point, with an upper limit of detectability of 0.5%.

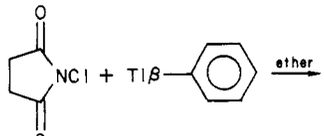
One rationalization for the observed results can be found in the principle of hard and soft acids and bases.[14] The soft acid thallium(I) prefers to be coordinated to the soft bases thiophenoxide and phenyl selenide rather than the hard carboxylate anion, even though these anions are stronger bases than carboxylate. With the sodium salts, the rapid exchange of hard sodium and proton simply reflects $pK_a$ differences, thus forming the sodium carboxylate. With thallous phenoxide, where thallium must be coordinated to oxygen, rapid acid–base exchange is observed to give phenol and thallous carboxylate as shown in eq 2. The preference of thallium(I) for sulfur rather than oxygen as a ligand is amplified by eq 3. Even though the thallous acetate was preformed, exchange occurred with thiophenol to give thallous thiophenoxide and acetic acid. No thiophenol could be detected.

The origin of the diphenyl disulfide and diphenyl diselenide observed in most of the product mixtures as well as the isolation of apparent products of reduction from $\alpha$-bromoethyl acetate (ethyl acetate), $\alpha$-bromobutyrolactone ($\gamma$-butyrolactone), and 3-bromo-2-butanone (**7c**) (2-butanone) was next investigated. We felt that two pathways should be considered: (1) that dissolved oxygen might initiate the observed redox chemistry or (2) that a homolytic cleavage pathway of the thallium–sulfur or thallium–selenium bond might be responsible.

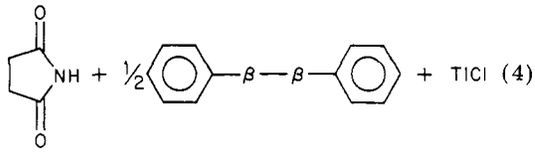
The reagents **1** and **2** were stirred for 48 h both in degassed ether under argon and in ether exposed to air. No diphenyl disulfide or diphenyl diselenide was detected in either case by thin-layer chromatography.

Anhydrous ether and 3-bromo-2-butanone (**7c**) were carefully degassed under argon by bubbling a slow stream of the gas through the solution for 45 min. Either **1** or **2** was then added. After reaction was complete, the quantities of diphenyl disulfide and diphenyl diselenide were unchanged, and 2-butanone was still detectable.

The viability of a homolytic cleavage pathway would be easily demonstrated by conducting a reaction in which such a pathway was the only reasonable one available. The direct reaction of *N*-chlorosuccinimide (NCS, **40**) with



40



(4)

either thallium salt to give thallous chloride by an ionic mechanism should be precluded, since such a reaction would necessitate the formation of a succinimidyl cation or thallium anion. Homolytic cleavage to give phenylthio or phenylseleno radicals, succinimidyl radicals, and thallous chloride should occur.

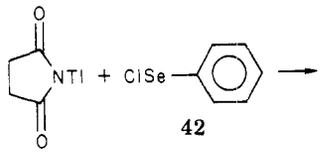
When equivalent amounts of NCS (**40**) and **1** or **2** were allowed to react in ether for 1.0 min, thallous chloride, succinimide, and diphenyl disulfide or diphenyl diselenide were isolated in yields greater than 95% (eq 4).

The thallium(I) salt of succinimide (**41**) was prepared by adding thallous ethoxide to a hot ethanolic solution of succinimide. The thallous succinimide did not react with either diphenyl disulfide or diphenyl diselenide in ether or in ether with thallous chloride. Interestingly, **41** reacted with phenylselenenyl chloride (**42**) to give succinimide, diphenyl diselenide, and thallous chloride (eq 5) over a period of 3 h. When **41** was treated with thiophenol or benzeneselenol in ether, **1** or **2** was precipitated over a 3-h period. The disappearance of thiophenol or benzeneselenol was followed by VPC. No thiophenol or benzeneselenol could be detected at the completion of reaction. Succinimide was recovered (100%).

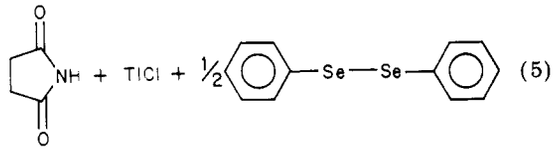
Phenylselenenyl chloride reacted with **2** in 0.5 min to give diphenyl diselenide and thallous chloride in 100% yields.

To test the possibility that free-radical chains might be involved, we treated the substrates **5** and **26b** with **1** or **2** in the presence of 2,5-di-*tert*-butyl-1,4-dihydroquinone.

(14) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827.



41 42



(5)

Reaction occurred at essentially unchanged rates to give product mixtures containing nearly identical amounts of **6a**, **6b**, **27a**, and **27b** as well as diphenyl disulfide and diphenyl diselenide. **6a** was isolated in 85% yield with 6% diphenyl disulfide, and **6b** was isolated in 85% yield with 7% diphenyl diselenide. Phenyl allyl sulfide was isolated in 90% yield with 8% diphenyl disulfide, and phenyl allyl selenide (**27b**) was isolated in 85% yield with 11% diphenyl diselenide. Side-by-side runs were made with and without inhibitor, with the color change of the insoluble salts indicating completion of reaction.

## Discussion

Arylthio- and arylseleno-substituted[15] molecules have become important synthetic intermediates because of their versatility in forming new C–C bonds[16,17] and the ease of removal of sulfur and selenium from the carbon framework.[18,19] Substitution reactions of activated organic halides with the thallium salts of thiophenol and benzeneselenol represent a very mild method for introducing sulfur and selenium.

Organic thallium(I) compounds in which oxygen, nitrogen, and sulfur are bound to the metal appear to have a more covalent bond to the metal than the bond to alkali metal ions in similar compounds.[20] Furthermore, thallium(I) compounds of this type tend to be aggregates or polymeric, with thallium being four-coordinate or higher.[21] Such compounds are generally insoluble. One would expect the properties of thallous thiophenoxide (**1**) and thallous phenyl selenide (**2**) to be similar. A covalent metal–heteroatom bond might impart some unusual characteristics to substitution reactions.

The general insolubility of **1** and **2** in all solvents and the heterogeneous nature of the reactions of **1** and **2** with halogen substrates suggest that reaction does not occur through a solution process. Presumably, the reactions of bromonorcamphor **13**, carbamoyl chloride **19**, and α-chloroamide **18** with sodium phenylselenide and 18-crown-6 are homogeneous processes.[10] The reactivity of the sodium phenylselenide is in sharp contrast to the unreactive nature of the thallium salts **1** and **2** toward **13**, **18**, and **19**. This contrast in reactivity is perhaps explained as the difference in steric demands between a solution process (sodium phenyl selenide/18-crown-6) and a heterogeneous process, involving aggregates of $(Ph\beta Tl)_n$ or reactions on the surface of polymeric $(Ph\beta Tl)_s$. A monomeric sodium phenyl selenide is easily approached by **13**, **18**, and **19** but the aggregate or surface states are not, indicating strikingly different steric demands for the reagents.

Other reactions of thallium(I) salts have been thought to be ionic,[1,2] and from the substitution products observed, one might assume that **1** and **2** react in simple nucleophilic fashion. Obtaining identical product mixtures from the **26d**/**28** allylic chlorides with **1** and sodium thiophenoxide/18-crown-6 or **2** and sodium phenyl selenide/18-crown-6 indicates that similar intermediates are involved. However, the detection of 2-butanone, ethyl acetate, and γ-butyrolactone from the reactions of **7c**, **7d**, and **9**, respectively, and the presence of diphenyl disulfide or diphenyl diselenide in all the reaction mixtures are not readily accommodated by an ionic mechanism.

The possibility that the disulfide and diselenide might arise from decomposition of **1** and **2** or that dissolved oxygen might be responsible for the unexpected products was eliminated by the blank runs of **1** and **2** in argon-degassed ether and in ether exposed to air. Furthermore, the reactions with 3-bromo-2-butanone (**7c**) in degassed ether displayed no changes in product mixtures. Thus, the reduced products and diphenyl disulfide or diphenyl diselenide probably arise from direct reaction of **1** or **2** with substrate.

Although the following mechanistic considerations are highly speculative, they are consistent with the experimental facts. A radical chain pathway is seemingly excluded by the observation that the radical inhibitor 2,5-di-*tert*-butyl-1,4-dihydroquinone shows no effect on the qualitative rates of reaction of **1** or **2** or on the product mixtures obtained. If one assumes that a homolytic pathway in the reactions of **1** and **2** leads to radicals or radicaloids that are bound on the surface or aggregate and not to free radicals in solution, then the following course of events becomes possible. Attack of the substrate RX on the surface $(Ph\beta Tl)_s$ leads to the formation of the thallous halide, as well as caged substrate radical, R·, and Phβ· on the surface or aggregate (eq 6). The substrate

$$RX + (Ph\beta Tl)_s \rightarrow R\cdot + [(Ph\beta)_s Tl_{s-1}]\cdot + TlX \quad (6)$$

$$R\cdot + [(Ph\beta)_s Tl_{s-1}]\cdot \rightarrow R\beta Ph + (Ph\beta Tl)_{s-1} \quad (7)$$

$$R\cdot + (Ph\beta Tl)_s \rightarrow R\beta Ph + (Ph\beta Tl)_{s-1} + Tl\cdot \quad (8)$$

$$R\cdot + HS \rightarrow RH + S\cdot \quad (9)$$

$$[(Ph\beta)_s Tl_{s-1}]\cdot \rightarrow {}^1/_2 Ph\beta\beta Ph + (Ph\beta Tl)_{s-1} \quad (10)$$

$$[(Ph\beta)_s Tl_{s-1}]\cdot \rightarrow Ph\beta\beta Ph + (Ph\beta Tl)_{s-2} + Tl\cdot \quad (11)$$

radical combines with the radical-bearing surface to give products (eq 7) or with a fresh surface to give products and a thallium atom (eq 8). It is possible that some of the substrate radicals occasionally escape the surface and abstract hydrogen from the solvent, leading to the reduction products (eq 9). Diphenyl disulfide and diphenyl diselenide might arise from disproportionation of the radical-bearing surface to give 0.5 equiv of Phββ Ph and a radical-free surface (eq 10) or by disproportionation to Phββ Ph, a radical-free surface, and thallium atoms (eq 11).

(15) For a recent review of organoselenium chemistry see: Clive, D. L. J. *Tetrahedron Lett.* **1978**, 1049.

(16) (a) Peterson, D. J. *J. Org. Chem.* **1967**, *32*, 1717. (b) Corey, E. J.; Seebach, D. *Ibid.* **1966**, *31*, 4097. (c) Corey, E. J.; Jautelct, M. *Tetrahedron Lett.* **1968**, 5787. (d) Lebar, D.; Dumont, W.; Hevesi, L.; Krief, A. *Ibid.* **1978**, 1145. (e) Takahashi, T.; Nagashima, H.; Tsuji, J. *Ibid.* **1978**, 799. (f) Sevrin, M.; Krief, A. *Ibid.* **1978**, 187.

(17) (a) Corey, E. J.; Chaykovski, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353. (b) Johnson, A. W.; Hruby, V. J.; Williams, J. L. *Ibid.* **1964**, *86*, 918. (c) Frost, B. M.; LaRochelle, R.; Bogdanowicz, M. J. *Tetrahedron Lett.* **1970**, 3449. (d) Dumont, W.; Bayet, P.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 274.

(18) (a) McGhie, J. F.; Ross, W. A.; Laney, D. H.; Barker, J. M. *J. Chem. Soc. C* **1968**, *1*. (b) Crossley, N. S.; Djerassi, C.; Kielczewski, M. A. *J. Chem. Soc.* **1965**, 6253. (c) Khazemova, L. A.; Allbitskaya, V. M. *J. Org. Chem. USSR (Engl. Transl.)* **1969**, *5*, 1873. *Ibid.* **1971**, *6*, 941. (d) Sevrin, M.; VanEnde, D.; Krief, A. *Tetrahedron Lett.* **1976**, 2643.

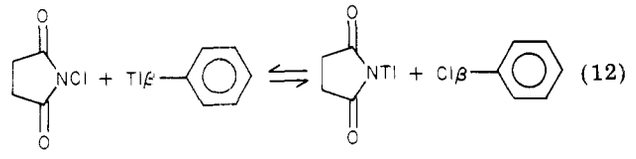
(19) (a) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434. (b) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Org. Chem.* **1974**, *39*, 2133. (c) Kingsbury, M.; Cram, D. *J. Am. Chem. Soc.* **1960**, *82*, 1810. (d) Walling, C.; Bollyky, M. *J. Org. Chem.* **1964**, *29*, 2699.

(20) Lee, A. G. *J. Chem. Soc. A* **1971**, 2007.

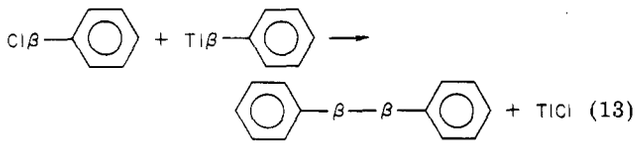
(21) Maroni, V. A.; Spiro, T. G. *Inorg. Chem.* 1968, *7*, 193.

The reactions of **1** and **2** with NCS (**40**) in ether (eq 4) are entirely consistent with a homolytic cleavage mechanism to give products. Hydrogen abstraction from solvent by the succinimidyl radical gives succinimide, and disproportionation of a radical-bearing surface or combination of radicals gives diphenyl disulfide and diphenyl diselenide.

An alternative explanation to the products from the NCS reaction is outlined in eq 12 and 13. Metal–halogen




**40** **41**




exchange could conceivably occur to give thallous succinimide and phenylsulfenyl chloride or phenylselenenyl chloride which could then attack **1** or **2** to give thallous chloride and diphenyl disulfide or diphenyl diselenide. The feasibility of such a reaction was demonstrated by the reaction of **2** with phenylselenenyl chloride (**42**) in ether to give diphenyl diselenide and thallous chloride within 0.5 min. However, the process described by eq 12 and 13 may be discounted when one considers that the reaction of **41** with phenylselenyl chloride is much slower than the reaction of phenylselenyl chloride with **2** (3 h vs. 0.5 min). Furthermore, thallous succinimide (**41**) is inert with thallous chloride, diphenyl disulfide, and diphenyl diselenide and is thermally stable under the conditions of reaction. Thallous succinimide also does not react with NCS after 24 h. In other words, if the reactions depicted in eq 12 and 13 were being followed, some thallous succinimide and NCS should be present. This is not the case; neither thallous succinimide nor NCS was detected.

Given the preference of thallium(I) for sulfur and selenium rather than nitrogen as indicated by the reaction of thiophenol and benzeneselenol with **41**, what may well take place in the reaction of **41** with phenylselenenyl chloride is slow establishment of the left-hand side of the equilibrium depicted in eq 12 followed by rapid reaction of **40** and **2**.

The qualitative rates observed for reactions of the salts **1** and **2** with the various halides were often contrary to those expected from simple nucleophilic substitution reactions. Thallous phenyl sulfide was more reactive than thallous phenyl selenide even though phenyl selenide anion is presumably a better nucleophile than thiophenoxide anion. The iodides examined in this study were similar in reactivity to the corresponding chlorides. However, the bromides were the most reactive substrates investigated, contrary to the expected order I > Br > Cl for nucleophilic displacement. Such discrepancies augur for a process that is not the standard nucleophilic substitution reaction.

## Conclusions

Substitution products from the reactions of **1** and **2** with halogen-containing substrates may arise by nucleophilic displacement reactions. However, the experimental evidence indicates that a homolytic pathway is being followed at least part of the time. When an ionic pathway is not available to the reagents (NCS reactions), the homolytic pathway proceeds rapidly to completion. Homolytic cleavages of thallium–sulfur and thallium–selenium bonds are novel observations in the chemistry of thallium(I) salts and may well be general phenomena for thallium(I) compounds.

Independent of the mechanistic considerations, the synthetic utility of thallous aryl sulfides and thallous aryl selenides is great in that the reagents are easily prepared, reactions are heterogeneous which makes the conditions mild and workup facile, and yields are excellent, exceeding yields obtained by other methods with the exception of alkyl halides. Synthetic applications of other thallium(I) salts are being investigated as well as the utility of homolytic cleavage pathways.

## Experimental Section

Thallium compounds are highly toxic and should be handled with care and disposed of properly. The specific toxicological properties of the thallium salts have not been determined.

$^1$H NMR spectra were recorded on a Varian EM-390 instrument. IR spectra were recorded on a Perkin-Elmer 137 spectrophotometer. Mass spectra were recorded on a Du Pont 21-491 instrument. Elemental analyses were performed on a Perkin-Elmer 240 C, H, and N analyzer. Melting points were determined on a Thomas-Hoover apparatus and are corrected. Boiling points are uncorrected. α-Bromo-γ-butyrolactone was purchased from Aldrich Chemicals. All other reagents whose preparation is not described were obtained from Eastman Organic Chemicals and were distilled prior to use.

**Preparation of Thallous Thiophenoxide (1). A.** To a stirred solution of thiophenol (11.0 g, 0.100 mol) in 100 mL of ether and 100 mL of hexane was added thallous ethoxide (25.0 g, 0.100 mol) dropwise via syringe. The yellow precipitate which formed immediately was isolated by filtration, washed with ether, and dried to give 34.2 g (98%) of a yellow solid, mp 260–265 °C. Anal. Calcd for $C_6H_5STl$: C, 23.0; H, 1.6; S, 10.2. Found: C, 23.1; H, 1.6; S, 10.1.

**B.** To a stirred solution of thiophenol (0.186 g, 1.70 mmol) in 25 mL of ether was added thallous phenoxide (0.50 g, 1.7 mmol). A yellow solid developed slowly with stirring. After 24 h, the solid was collected by filtration, washed with ether, and dried to give 0.59 g (100%) of **1**. The filtrate contained 0.15 g (94%) of phenol.

**Preparation of Thallous Phenyl Selenide (2). A.** To a stirred solution of benzeneselenol (3.14 g, 0.0200 mol) in 35 mL of ether and 35 mL of hexane was added 5.00 [illegible]201 mol) of thallous ethoxide via syringe. Ar [illegible]ite formed immediately. The solid was remov [illegible]ashed with ether, and dried to give 6.82 g (94[illegible]... orange powder, mp 228–234 °C. Anal. Calcd for $C_6H_5SeTl$: C, 20.0; H, 1.4; Se, 21.9. Found: C, 19.9; H, 1.5; Se, 21.4.

**B.** To a stirred solution of benzeneselenol (2.64 g, 0.0168 mol) in 50 mL of ether was added thallous phenoxide (5.0 g, 0.017 mol). After the mixture was stirred for 24 h at room temperature, the orange product was removed by filtration, washed with ether, and dried to give 5.99 g (99%) of **2**.

**General Procedure for Reactions of 1 and 2 with Halogen Compounds.** The substrate was dissolved in ether (5 mL/mmol). The thallous salt (1.0 equiv) was added in one portion. The mixture was stirred for the indicated time (Table I) and then filtered through a pad of Super Celite. The insoluble solids were washed with ether, and the combined filtrates were concentrated. Crystalline products were purified by recrystallization. Oils were purified by chromatography on silica gel (1/1 hexane/ether) followed by distillation. Reduction products were detected on a Packard 824 VPC with a flame-ionization detector (2 mm × 6 ft, 5% OV-25 on Chromosorb W) by retention time comparison with an authentic sample.

**Preparation of Imidoyl Chloride 5.** A solution of *N*-methylacetamide (25.0 g, 0.185 mol) in 27 mL of thionyl chloride was warmed at 55 °C for 2.0 h. The reaction mixture was concentrated in vacuo. The residue was distilled to give 18.0 g (63%) of a colorless oil: bp 80–85 °C (6 torr); $^1$H NMR ($CDCl_3$) δ 7.91 (m, 2 H), 7.26 (m, 3 H), 3.38, and 3.41 (s, 3 H); IR (film) 1660, 1235, 990, 880, 765 cm$^{-1}$; mass spectrum, *m/e* 163.

**Preparation of Carbamoyl Chloride 19.** A solution of *N*-methylbenzylamine (25.0 g, 0.21 mol) and triethylamine (43 mL,

0.31 mol) in 50 mL of THF was added dropwise to a mechanically stirred saturated solution of phosgene in 500 mL of THF at 0 °C. The reaction was exothermic and instantaneous. The triethylamine hydrochloride was removed by filtration, and the filtrate was concentrated under reduced pressure. Distillation of the residue gave 28.1 g (74%) of a colorless oil: bp 98–99 °C (0.15 torr); $^1$H NMR ($CDCl_3$) $\delta$ 7.32 (s, 5 H), 4.55 and 4.67 (s, 2 H), 2.97 and 3.03 (s, 3 H); IR (film) 1725 cm$^{-1}$; mass spectrum, $m/e$ 183. Anal. Calcd for $C_9H_{10}ClNO$: C, 58.9; H, 5.5; N, 7.6. Found: C, 59.1; H, 5.4; N, 7.2.

**Alkylation of 10a with Methyl Iodide. Preparation of α-Methyl-α-(phenylthio)-γ-butyrolactone (12a).** A 50% dispersion of sodium hydride in mineral oil (0.33 g, 6.8 mmol) was washed twice with hexane and dried under a stream of nitrogen. A solution of **10a** (1.20 g, 6.19 mmol) in 25 mL of dry THF was added dropwise. The resulting mixture was heated at reflux for 1.0 h. The reaction mixture was cooled to room temperature and methyl iodide (1.42 g, 10.0 mmol) was added. The resulting mixture was stirred for 1.0 h at room temperature. The reaction mixture was concentrated. The residue was taken up in 50 mL of methylene chloride and 50 mL of water. The organic phase was dried over sodium sulfate and concentrated. Distillation gave 1.18 g (91%) of a colorless oil: bp 153–158 °C (0.9 torr); $^1$H NMR ($CDCl_3$) $\delta$ 7.60–7.15 (m, 5 H), 4.13 (m, 2 H), 2.31 (m, 2 H), 1.49 (s, 3 H); IR (film) 1790 cm$^{-1}$; mass spectrum $m/e$ 208.

**Alkylation of 10b with Methyl Iodide. Preparation of α-Methyl-α-(phenylseleno)-γ-butyrolactone (12b).** A mixture of 50% sodium hydride (0.33 g, 6.8 mmol) and **10b** (1.50 g, 6.20 mmol) was treated in 25 mL of THF as described above. The reaction mixture was quenched with methyl iodide (1.42 g, 10.0 mmol), and workup as before gave 1.53 g (96%) of a pale yellow oil bp 160–162 °C (1.0 torr); $^1$H NMR ($CDCl_3$) $\delta$ 7.55 (m, 2 H), 7.21 (m, 3 H), 4.15 (m, 2 H), 2.35 (m, 2 H), 1.51 (s, 3 H); IR (film) 1785 cm$^{-1}$; mass spectrum, $m/e$ 256.

**Preparation of Methyl Phenyl Sulfide (23).** Thallous thiophenoxide (1; 0.94 g, 3.0 mmol) was added to 3 mL of methyl iodide. The resulting mixture was warmed at reflux for 24 h. The inorganic solids were removed via filtration. The filtrate was concentrated to give 0.37 g (100%) of a colorless oil, bp 180–185 °C (molecular still).

**Preparation of Methyl Phenyl Selenide (24).** Thallous phenyl selenide (2; 1.08 g, 3.00 mmol) was added to 3 mL of methyl iodide. The resulting mixture was warmed at reflux for 24 h. The organic solids were removed via filtration. The filtrate was concentrated to give 0.51 g (99%) of a pale yellow oil: bp 60–63 °C (18 torr); $^1$H NMR ($CDCl_3$) $\delta$ 7.40 (m, 2 H), 7.20 (m, 3 H), 2.31 (s, 3 H); mass spectrum, $m/e$ 172.

**Preparation of Ethyl Phenyl Selenide (25).** Thallous phenyl selenide (2; 1.08 g, 3.00 mmol) was added to 3 mL of ethyl bromide. The resulting solution was warmed at reflux for 120 h. The inorganic solids were removed via filtration. The filtrate was concentrated to give 0.35 g (63%) of a pale yellow oil: bp 65–67 °C (18 torr); $^1$H NMR ($CDCl_3$) $\delta$ 7.42 (m, 2 H), 7.18 (m, 3 H), 2.82 (q, 2 H, $J$ = 7.54 Hz), 1.40 (t, 3 H, $J$ = 7.5 Hz); mass spectrum, $m/e$ 186.

**Reaction of Sodium Thiophenoxide with the 26a/28 Mixture. Preparation of 4-(Phenylthio)-2-methyl-2-butene (27c).** A solution of thiophenol (1.10 g, 0.0100 mol) in 25 mL of ether was added slowly to 0.55 g (0.011 mol) of a 50% dispersion of sodium hydride in mineral oil that had been twice washed with ether. The butenyl chlorides **26a** and **28** (1.05 g, 0.0100 mol) and 0.13 g (0.5 mmol) of 18-crown-6 in 20 mL of ether were then added. The reaction mixture was stirred for 12 h at room temperature. The inorganic solids were dissolved in 50 mL of water. The organic phase was dried over sodium sulfate and concentrated. Distillation gave 1.67 g (94%) of a colorless oil, bp 53–55 °C (0.9 torr), that was pure **27c**.

**Reaction of Sodium Phenyl Selenide with the 26a/28 Mixture. Preparation of 4-(Phenylseleno)-2-methyl-2-butene (27d).** Benzeneselenol (1.57 g, 0.0100 mol) was treated with 50% sodium hydride (0.55 g, 0.011 mol) and the butenyl chloride mixture (1.05 g, 0.0100 mol) as described. Workup and distillation gave 1.99 g (88%) of a colorless oil: bp 65–67 °C (0.9 torr), that was pure **27d**.

**Preparation of a Stock Solution of (Phenylseleno)trimethylsilane (30b).** To a stirred solution of chlorotrimethylsilane (3.24 g, 0.0300 mol) in 60.0 mL of ether was added 10.8 g (0.0300 equiv) of **2**. The colorless solution was stirred in an inert atmosphere for 24 h and then decanted through glass wool into an argon-flushed bottle equipped with a rubber septum.

**Reaction of 30b with γ-Butyrolactone.** To a mixture of γ-butyrolactone (0.86 g, 0.010 mol), potassium fluoride (0.64 g, 0.011 mol), and 0.13 g (0.50 mmol) of 18-crown-6 in 20 mL of ether was added a 22-mL (0.011 mol) aliquot of the stock solution of **30b**. The resulting mixture was warmed at reflux under argon for 12 h. The reaction was cooled to room temperature, and 50 mL of saturated sodium bicarbonate was added. The aqueous phase was extracted twice with ether and was then acidified with 10% hydrochloric acid. The acidic solution was extracted with methylene chloride (2 × 25 mL). The combined organic extracts were dried over sodium sulfate and concentrated to give a brown solid. Recrystallization from 2/1 hexane/ether gave 1.94 g (80%) of **31** as an off-white solid: mp 60–62 °C; $^1$H NMR ($CDCl_3$) $\delta$ 10.2 (br s, 1 H), 7.39 (m, 2 H), 7.20 (m, 3 H), 2.90 (t, 2 H, $J$ = 7 Hz), 2.46 (t, 2 H, $J$ = 7 Hz), 1.94 (quintet, 2 H, $J$ = 7 Hz); IR (KBr) 3200 (br), 1695, 1560, 735, 690 cm$^{-1}$; mass spectrum, $m/e$ 244.

**Reaction of 3-Bromo-3-phenylpropionic Acid (34) with 1.** The reagent **1** (0.28 g, 0.89 mmol) was added to a stirred solution of **34** (0.192 g, 0.842 mmol) in 5 mL of degassed ether under nitrogen. The reaction mixture was stirred for 16 h, filtered through Super Celite, and concentrated to give 0.18 g of a 1:1 mixture of 3-(phenylthio)-3-phenylpropionic acid (**35a**) and cinnamic acid (**36**). The mixture was inseparable by recrystallization or chromatography. For **35a**: $^1$H NMR ($CDCl_3$) $\delta$ 10.5 (br s, 1 H), 7.8–7.15 (m, 10 H), 4.70 (t, 1 H, $J$ = 7.5 Hz), 3.06 (d, 2 H, $J$ = 7.5 Hz); mass spectrum, $m/e$ 258.

**Reaction of 3-Bromo-3-phenylpropionic Acid (34) with 2.** Thallous phenyl selenide (**2**; 0.36 g, 1.0 mmol) was added in one portion to 0.23 g of **34** (1.0 mmol) in 5 mL of degassed ether under nitrogen. The reaction mixture was stirred for 16 h, filtered through Super Celite, and concentrated to give 0.20 g of an inseparable 1:1 mixture of **35b** and **36**. For **35b**: $^1$H NMR ($CDCl_3$) $\delta$ 7.8–7.1 (m, 10 H), 4.73 (t, 1 H, $J$ = 7.5 Hz), 3.11 (d, 2 H, $J$ = 7.5 Hz); mass spectrum, $m/e$ 308.

**Reaction of *exo*-3-Bromobicyclo[2.2.1]heptan-2-one (13) with Sodium Phenyl Selenide.** Thiophenol (1.10 g, 0.0100 mol) in 10 mL of ether was added dropwise to a stirred slurry of 0.50 g of a 50% dispersion of sodium hydride in mineral oil (0.010 mol) in 50 mL of ether. (The sodium hydride had been washed twice with hexane and dried under a stream of nitrogen.) After 0.5 h, 1.89 g (0.0100 mol) of **13** in 10 mL of ether and 0.3 g of 18-crown-6 were added. After the mixture was stirred for 2.0 h, 5 mL of methanol was added followed by 20 mL of water. The ether layer was separated, dried over sodium sulfate, and concentrated to give 2.10 g (96%) of a 35:65 mixture of **14** and **15**, respectively. For **14**: $^1$H NMR ($CDCl_3$) $\delta$ 3.82 (d, 1 H, $J$ = 4.5 Hz), 2.60 (m, 2 H), 2.20–1.20 (m, 6 H); mass spectrum, $m/e$ 218. For **15**: $^1$H NMR $\delta$ 3.40 (d, 1 H, $J$ = 3.1 Hz), 2.60 (m, 2 H), 2.20–1.20 (m, 6 H); mass spectrum, $m/e$ 218.

**Reaction of Bromoacetic Acid with Sodium Thiophenoxide.** Sodium thiophenoxide was prepared from thiophenol (1.10 g, 0.0100 mol) and 50% sodium hydride (0.50 g, 0.010 mol) in 25 mL of ether as described. Bromoacetic acid (1.39 g, 0.0100 mol) was added. The reaction mixture was stirred for 1.0 h at room temperature, filtered through Super Celite, and concentrated to give 1.02 g (93%) of thiophenol.

The procedure above was repeated except that the reaction mixture was stirred for 48 h at room temperature before filtration. $^1$H NMR showed the filtrate contained about 2:1 (phenylthio)-acetic acid (**33a**) and thiophenol.

**Reaction of Bromoacetic Acid with Sodium Phenyl Selenide.** Sodium phenylselenide was prepared from benzeneselenol (1.58 g, 0.0100 mol) and 50% sodium hydride (0.50 g, 0.010 mol) in 25 mL of ether as described. Bromoacetic acid (1.39 g, 0.0100 mol) was added. The reaction mixture was stirred for 1.0 h at room temperature, filtered through Super Celite, and concentrated to give 1.45 g (92%) of benzeneselenol.

The procedure above was repeated except that the reaction mixture was stirred for 48 h at room temperature before filtration. $^1$H NMR showed the filtrate contained about 1:1 (phenylseleno)acetic acid (**33b**) and benzeneselenol.

**Reaction of Thallous Phenoxide with Bromoacetic Acid.** Thallous phenoxide (0.30 g, 1.0 mmol) was added to a stirred solution of bromoacetic acid (0.14 g, 1.0 mmol) in 5 mL of ether. The reaction mixture was stirred for 18 h at room temperature and then filtered through Super Celite. The filtrate was concentrated to give 0.092 g (98%) of phenol and 0.33 g of the thallous carboxylate (97%).

**Reaction of *N*-Chlorosuccinimide with 1.** Thallous thiophenoxide (**1**; 0.96 g, 3.0 mmol) was added to NCS (0.40 g, 3.0 mmol) in 15 mL of ether. After 5 min, the reaction mixture was filtered to give 0.68 g of thallous chloride (97%). The filtrate was concentrated and purified by chromatography on silica gel (1/1 ethyl acetate/hexane) to give 0.32 g of diphenyl disulfide (97%) and 0.28 g (94%) of succinimide.

**Reaction of *N*-Chlorosuccinimide with 2.** Thallous phenyl selenide (**2**; 1.00 g, 2.77 mmol) was added to 0.37 g (2.77 mmol) of NCS in 15 mL of ether. After 5 min, the reaction was worked up as described above to give 0.63 g (95%) of thallous chloride, 0.40 g (95%) of diphenyl diselenide, and 0.26 g (96%) of succinimide.

**Reaction of Phenylselenyl Chloride with 2.** Thallous phenyl selenide (**2**; 0.72 g, 2.0 mmol) was added to a stirred solution of phenylselenyl chloride (0.38 g, 2.0 mmol) in 10 mL of ether. The reaction mixture was stirred for 0.5 min at room temperature, filtered through Celite, and concentrated to give 0.63 g (100%) of diphenyl diselenide and 0.47 g (100%) of thallous chloride.

**Preparation of Thallous Succinimide (41).** To a hot ethanolic solution of 9.90 g (0.100 mol) of succinimide was added 25.0 g (0.100 mol) of thallous ethoxide dropwise via syringe. After a few minutes, a white precipitate began forming. After the mixture was cooled to room temperature, the precipitate was removed by filtration and dried to give 24.2 g (80%) of a white solid, mp 186–189 °C dec. Anal. Calcd for $C_4H_4NO_2Tl$: C, 15.9; H, 1.3; N, 4.6. Found: C,15.9; H, 1.2; N, 4.7.

**Reaction of Thallous Succinimide (41) with Phenylselenyl Chloride.** Thallous succinimide (0.60 g, 2.0 mmol) was added to a stirred solution of phenylselenyl chloride (0.38 g, 2.0 mmol) in 10 mL of ether. After 3.0 h, the reaction mixture was filtered through Celite. The filtrate was concentrated to give a red gum. Crystallization from hexane gave 0.16 g (80%) of succinimide. The mother liquors were concentrated to 5 mL and cooled to give 0.50 g (81%) of diphenyl diselenide as a yellow solid, mp 60–62 °C. Apparently, reaction was not complete.

**Attempted Reaction of *N*-Chlorosuccinimide with 41.** A mixture of NCS (0.26 g, 2.0 mmol) and **41** (0.60 g, 2.0 mmol) in 10 mL of ether was stirred at room temperature for 24 h. The reaction mixture was filtered and the filtrate concentrated to give only unreacted NCS and **41**.

**Blank Runs of 1 and 2.** Thallous thiophenoxide (**1**) and thallous phenyl selenide (**2**) were individually added to 5 mL of degassed ether (argon bubbling, 45 min) under argon and 5 mL of ether open to the air. The mixtures were stirred for 48 h. Thin-layer chromatography (silica gel, 1/1 hexane/ether) showed no evidence of diphenyl disulfide or diphenyl diselenide.

**Reactions of 1 and 2 with 5 in the Presence of 2,5-Di-*tert*-butyl-1,4-dihydroquinone.** The thallous salt alone (3.0 mmol) or the thallous salt (3.0 mmol) and dihydroquinone (0.67 g, 3.0 mmol) were added simultaneously to degassed solutions of **5** (0.46 g, 3.0 mmol) in 10 mL of ether. The reaction mixtures were stirred for 5 min and filtered through Super Celite. The filtrates were compared by VPC (2 mm × 6 ft, OV-25 on Chromosorb W, 200 °C). Product ratios agreed within ±2%. The products were isolated by chromatography on silica gel (4/1 (v/v) hexane/ether).

**Reactions of 1 and 2 with 26b in the Presence of 2,5-Di-*tert*-butyl-1,4-dihydroquinone.** The thallous salt (3.0 mmol) alone or the thallous salt (3.0 mmol) and 2,5-di-*tert*-butyl-1,4-dihydroquinone (0.67 g, 3.0 mmol) were added simultaneously to degassed solutions of allyl bromide (**26b**; 0.36 g, 3.0 mmol) in 10 mL of ether. The reaction mixtures were stirred for 1.0 h and filtered through Super Celite. The filtrates were compared by VPC (2 mm × 6 ft, OV-25 on Chromosorb W, 200 °C). The product ratios agreed within ±2%. The products were isolated by chromatography on silica gel (hexane).

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