

## Rate Constants for Chalcogen Group Transfers in Bimolecular Substitution Reactions with Primary Alkyl Radicals

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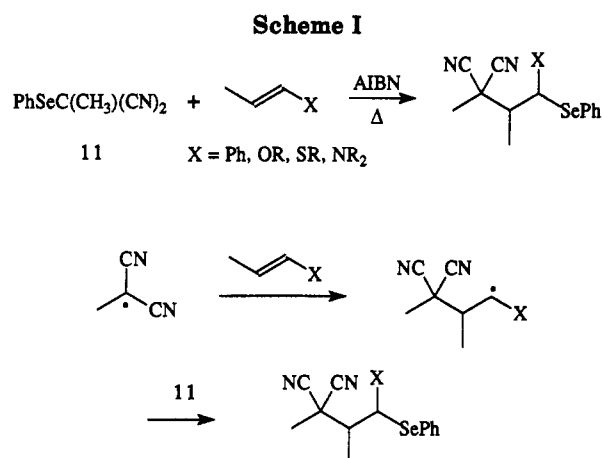
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Rate constants for group transfers of the MeS, PhS, PhSe, and PhTe groups from chalcogen-substituted acetate, acetonitrile, malonate, and malononitrile compounds, from *N*-(phenylthio)phthalimide and from Me<sub>2</sub>S<sub>2</sub> and Ph<sub>2</sub>S<sub>2</sub> to primary alkyl radicals, have been determined by competition kinetics using PTOC esters as the radical precursors and competing trapping agents. Thio group transfers from malononitrile derivatives are marginally faster than the corresponding group transfer from the symmetrical disulfide, and the rate constant for PhSe group transfer from PhSeSePh is greater than those from the derivatives studied here. Substituent effects suggest that the chalcogen transfer reactions may be concerted. For three cases in which direct comparisons can be made, the rate constants for reactions of phenylchalcogenides are approximately equal to those for halogen atom transfer when the chalcogen and halide are in the same row of the periodic table and the radical resulting from displacement is the same. The rate constants reported in this work will be useful for the rational design of synthetic schemes based on homolytic group transfer chemistry.

Group transfer reactions, or bimolecular homolytic substitutions, comprise one of the fundamental classes of radical chain propagation processes that are important in synthetic applications.<sup>2</sup> Transfers of substituted selenyl groups from their respective symmetrical diselenides have been employed to functionalize alkyl radicals in an oxidative manner,<sup>3</sup> and, recently, Barton *et al.* have expanded the potential of PTOC ester chemistry by employing group transfers from aryl tellurides as a method for generating complex radicals from a simple sacrificial PTOC ester.<sup>4</sup>

The recent incorporation of chalcogen group transfers into radical chain sequences involving carbon-carbon bond forming steps is a potentially powerful synthetic advance.<sup>5,6</sup> The sequence of reactions in this method involves addition of a stabilized radical to an alkene and subsequent group transfer from an activated chalcogen. A typical example of a phenylseleno group transfer reaction is shown in Scheme I. As with any radical chain propagation process, knowledge of the rate constants is important for the



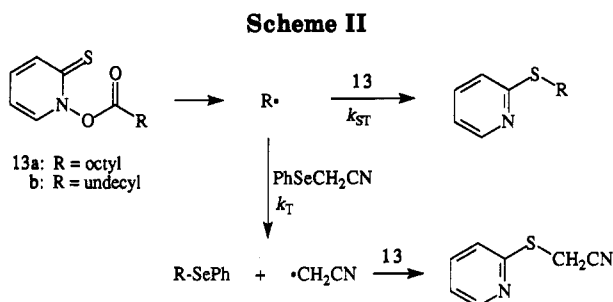
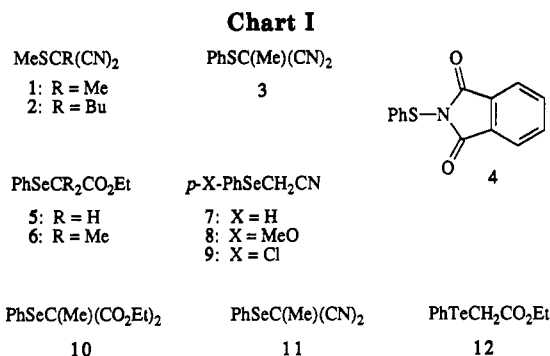
rational design of synthetic applications. In this work, we report rate constants for reactions of representative activated chalcogen compounds with primary alkyl radicals. From these rate constants, we draw conclusions about the mechanism of the chalcogen transfer and the synthetic utility of various classes of chalcogen reagents.

### Results

The thio and seleno compounds shown in Chart I and the disulfides Me<sub>2</sub>S<sub>2</sub> and Ph<sub>2</sub>S<sub>2</sub> were studied. The substituted malonate 10 and malononitriles 1-3 and 11 were available from chalcogenations of the appropriate malonate or malononitrile anion with a sulfonyl chloride (MeSCl or PhSCl) or with phenylselenenyl bromide. Similarly, the tertiary selenium compound 6 was prepared by reaction of the lithium enolate of ethyl isobutyrate with PhSeBr, and *N*-(phenylthio)phthalimide (4) was prepared by reaction of benzenesulfonyl chloride with phthalimide in the presence of Et<sub>3</sub>N. The simple acetate 5, acetonitrile derivatives 7-9, and the telluride 12 were prepared by nucleophilic substitutions on ethyl bromoacetate and chloroacetonitrile with the appropriate chalcogen anion.

The kinetics of chalcogen group transfers were measured

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(2) Ingold, K. U.; Roberts, B. P. *Free-Radical Substitution Reactions; Bimolecular Homolytic Substitutions (SH<sub>2</sub> Reactions) at Saturated Multivalent Atoms*; Wiley: New York, 1971.  
(3) For examples, see the following: Barton, D. H. R.; Bridon, D.; Zard, S. Z. *Tetrahedron Lett.* 1984, 25, 5777. Newcomb, M.; Marquardt, D. J.; Kumar, M. U. *Tetrahedron* 1990, 46, 2252. Barton, D. H. R.; Bridon, D.; Herve, Y.; Potier, P.; Thierry, J.; Zard, S. Z. *Tetrahedron* 1986, 42, 4983.  
(4) Barton, D. H. R.; Camara, J.; Cheng, X.; Géro, S. D.; Jaszberenyi, J. C.; Quiclet-Sire, B. *Tetrahedron* 1992, 48, 9261. Barton, D. H. R.; Ramesh, M. J. *Am. Chem. Soc.* 1990, 112, 891. Barton, D. H. R.; Ozbalik, N.; Sarma, J. C.; *Tetrahedron Lett.* 1988, 29, 6581.  
(5) For examples of chalcogen group transfers, see: (a) Byers, J. H.; Lane, G. C. *Tetrahedron Lett.* 1990, 31, 5697. (b) Byers, J. H.; Gleason, T. G.; Knight, K. S. *J. Chem. Soc., Chem. Commun.* 1991, 354. (c) Curran, D. P.; Thoma, G. *J. Am. Chem. Soc.* 1992, 114, 4436. (d) Byers, J. H.; Harper, B. C. *Tetrahedron Lett.* 1992, 33, 6953. (e) Chen, C.; Crich, D.; Papadatos, A. J. *Am. Chem. Soc.* 1992, 114, 8313. (f) Han, L. E.; Ishihara, K. I.; Kambe, N.; Ogawa, A.; Ryu, I. H.; Sonoda, N. *J. Am. Chem. Soc.* 1992, 114, 7591-7592.  
(6) For examples of related halogen atom transfer sequences, see: (a) Curran, D. P.; Chen, M. H.; Kim, D. *J. Am. Chem. Soc.* 1989, 111, 6265. (b) Curran, D. P.; Chang, C. T. *J. Org. Chem.* 1989, 54, 3140. (c) Curran, D. P.; Tamine, J. *J. Org. Chem.* 1991, 56, 2746. (d) Curran, D. P.; Kim, D. *Tetrahedron* 1991, 47, 6171. (e) Curran, D. P.; Kim, D.; Ziegler, C. *Tetrahedron* 1991, 47, 6189. (f) Curran, D. P.; Thoma, G. *Tetrahedron Lett.* 1991, 32, 6307. (g) Curran, D. P.; Seong, C. M. *Tetrahedron* 1992, 48, 2157. (h) Curran, D. P.; Seong, C. M. *Tetrahedron* 1992, 48, 2175.



by a kinetic adaptation of Barton's PTOC ester chemistry<sup>7</sup> which is illustrated in Scheme II for trapping by PhSeCH<sub>2</sub>CN. Octyl and undecyl radicals were formed in radical chain reactions of their PTOC ester precursors 13. The primary alkyl radicals reacted with the PTOC ester precursors (self-trapping) to give, ultimately, alkyl 2-pyridyl sulfides in competition with chalcogen group transfer reactions. The product radicals from the group transfer step also reacted with the PTOC esters in a chain propagation step that gave, ultimately, (2-pyridylthio)-substituted products. Ratios of self-trapped products to group transfer trapped products were determined by GC or by NMR analysis of the reaction mixtures; in the case of NMR analyses, the ratios of the two (2-pyridylthio) products also were measured. The combined yields of chalcogen transfer trapped and self-trapped products generally were >75% as determined by GC comparison to an internal standard or by NMR integration.

From the ratios of products and the concentrations of trapping agent and PTOC ester, ratios of rate constants for trapping by the chalcogen transfer agent ( $k_T$ ) to self-trapping by the PTOC ester ( $k_{ST}$ ) were calculated from eq 1 where  $[PTOC]_m$  is the average concentration of PTOC ester over the course of the reaction,  $[Trap]_m$  is the average concentration of chalcogen transfer agent, and  $([R-trap]/[R-Spyr])$  is the observed ratio of chalcogen transfer trapped products to self-trapped products. Eq 1 is strictly correct only when pseudo-first order conditions are maintained for both trapping agents which is not the case

$$k_T/k_{ST} = ([R-trap]/[R-Spyr])([PTOC]_m/[Trap]_m) \quad (1)$$

in these studies where the PTOC ester was largely or completely depleted at the end of the reaction. However, the errors introduced by use of eq 1 were smaller than the

range of measured values in most cases.<sup>8</sup> Ratios of rate constants averaged for several runs are given in Table I.

Although knowledge of the relative rate constants for competing reactions is sufficient for many synthetic applications, crude absolute rate constants for the chalcogen transfer reactions can be calculated when the rate constants for alkyl radical self-trapping are available. Rate constants for self-trapping of both the octyl radical and the undecyl radical by their respective PTOC esters in benzene solvent have been reported;<sup>7b,9</sup> these kinetic values differ slightly although one might expect that they should be the same. For the purposes of estimating absolute rate constants for the chalcogen transfer reactions, we have used the average Arrhenius function for these two primary alkyl radical self-trapping reactions (eq 2) to calculate the

$$\log(k_{ST}Ms) = 9.4 - 4.7/2.3RT \quad (2)$$

value of  $k_{ST}$ . Calculated values of  $k_T$  for reactions conducted in benzene are given in the final column of Table I. Because of the apparent solvent effects (see below), we have not calculated absolute rate constants for reactions in other solvents.

The internal consistency of the two methods employed in this study was judged to be good on the basis of the results for two of the trapping agents. Phenylthio transfer from PhSC(Me)(CN)<sub>2</sub> (3) at 50 °C in benzene gave ratios of rate constants of 0.27 by the GC method (undecyl radical) and 0.34 by the NMR method (octyl radical). Similarly, phenylselenenyl transfer from PhSeCH<sub>2</sub>CN (7) in benzene gave a ratio of rate constants of 0.11 at 25 °C by the GC method and a ratio of 0.13 at 50 °C by the NMR method. We conclude that the two methods produced equivalent results.

A check on the accuracy of the absolute rate constants determined in this work is also possible. A rate constant for reaction of PhSSPh with the 5-hexenyl radical can be calculated from the results reported by Russell *et al.*<sup>10</sup> By using the now accepted value for the rate constant for cyclization of the 5-hexenyl radical,<sup>11</sup> we calculate a rate constant for reaction with PhSSPh of  $k = 1.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C. The value obtained in this work,  $k = 2.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C, is in excellent agreement.

## Discussion

Inspection of the results in Table I suggests that there was a solvent effect on one or both of the trapping reactions.

(8) Trapping agents were used in excess, and the trapping reactions can be treated as pseudo-first-order processes. For a pseudo-first-order reaction competing with a second-order process (e.g. the self-trapping reaction) in which the PTOC precursor is completely depleted, the exact kinetic expression<sup>12</sup> is given in eq i

$$(k_T[Trap]/k_{ST})\{\ln([PTOC]_i + k_T[Trap]/k_{ST}) - \ln(k_T[Trap]/k_{ST})\} = [PTOC]_i([Trapped]/[Self-trapped])(1 + ([Trapped]/[Self-Trapped]))^{-1} \quad (i)$$

where  $k_T$  and  $k_{ST}$  are the rate constants for trapping and self-trapping, respectively,  $[Trap]$  is the concentration of trapping agent,  $[PTOC]_i$  is the initial concentration of PTOC ester, and  $[Trapped]/[Self-Trapped]$  is the ratio of products obtained. Eq i, which is solved by iteration, is cumbersome. For some representative reactions we studied, the use of the approximate eq 1 rather than eq i introduced errors that ranged from 1 to 15%. These errors are smaller than the deviation of the extreme values from the mean (which ranged up to 50%) and the difference between the averaged rate constant for PTOC self-trapping (used in this work to calculate crude absolute rate constants for trapping) and the measured values.

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(7) (a) Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* 1989, 111, 275. (b) Curran, D. P.; Bosch, E.; Kaplan, J.; Newcomb, M. *J. Org. Chem.* 1989, 54, 1826. (c) For a brief introduction to competition kinetics in radical reactions, see Newcomb, M. *Tetrahedron* 1993, 49, 1151.

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Table I. Results of Chalcogen Transfer Trapping Reactions

chalcogen	method <sup>a</sup>	solvent	temp, <sup>b</sup> °C	runs <sup>c</sup>	( <i>k<sub>T</sub></i> / <i>k<sub>ST</sub></i> ) <sup>d</sup>	<i>k<sub>T</sub></i> (M <sup>-1</sup> s <sup>-1</sup> ) <sup>e</sup>
MeSSMe	A	benzene	25	6	0.064	6 × 10 <sup>4</sup>
PhSSPh	A	benzene	25	3	0.21	2.0 × 10 <sup>5</sup>
MeSC(Me)(CN) <sub>2</sub> (1)	A	benzene	25	4	0.082	8 × 10 <sup>4</sup>
MeSC(Bu)(CN) <sub>2</sub> (2)	A	CH <sub>2</sub> Cl <sub>2</sub>	25	4	0.17	
	A	benzene	25	4	0.077	7 × 10 <sup>4</sup>
	A	toluene	25	4	0.071	
PhSC(Me)(CN) <sub>2</sub> (3)	A	CH <sub>2</sub> Cl <sub>2</sub>	25	4	0.15	
	A	benzene	25	5	0.24	2.3 × 10 <sup>5</sup>
	A	benzene	50	2	0.27	5 × 10 <sup>5</sup>
	B	benzene	50	3	0.34	6 × 10 <sup>5</sup>
	A	toluene	-78	2	0.033	
	A	toluene	25	2	0.10	
	A	toluene	50	2	0.14	
	A	THF	-78	2	0.081	
	A	THF	25	2	0.17	
	A	CH <sub>2</sub> Cl <sub>2</sub>	0	1	0.39	
PhS-phthalimide (4)	A	PhH/CH <sub>2</sub> Cl <sub>2</sub>	25	4	0.011	
PhSeSePh	<i>f</i>		25			2.6 × 10 <sup>7</sup>
PhSeCH <sub>2</sub> CO <sub>2</sub> Et (5)	B	benzene	50	3	0.056	1.0 × 10 <sup>5</sup>
PhSeCMe <sub>2</sub> CO <sub>2</sub> Et (6)	B	benzene	50	3	0.13	2.3 × 10 <sup>5</sup>
PhSeCH <sub>2</sub> CN (7)	A	benzene	25	4	0.11	1.1 × 10 <sup>5</sup>
	B	benzene	50	3	0.13	2.3 × 10 <sup>5</sup>
<i>p</i> -MeOPhSeCH <sub>2</sub> CN (8)	B	benzene	50	3	0.13	2.3 × 10 <sup>5</sup>
<i>p</i> -ClPhSeCH <sub>2</sub> CN (9)	B	benzene	50	3	0.17	3.0 × 10 <sup>5</sup>
PhSeCMe(CO <sub>2</sub> Et) <sub>2</sub> (10)	B	benzene	50	3	0.44	8 × 10 <sup>5</sup>
PhSeCMe(CN) <sub>2</sub> (11)	B	benzene	50	3	4.4	8 × 10 <sup>6</sup>
PhTeTePh	<i>f</i>		25			1.1 × 10 <sup>6</sup>
PhTeCH <sub>2</sub> CO <sub>2</sub> Et (12)	B	benzene	50	3	13	2.3 × 10 <sup>7</sup>

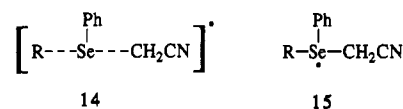
<sup>a</sup> Method A: undecyl radical, GC analysis. Method B: octyl radical, NMR analysis. <sup>b</sup> ±2 °C. <sup>c</sup> Number of experiments. <sup>d</sup> Average ratio of chalcogen transfer to self-trapping rate constants. <sup>e</sup> Absolute rate constant from ratio of rate constants and eq 2. *f* References 7c and 10.

This especially appeared to be true when CH<sub>2</sub>Cl<sub>2</sub> was employed as solvent; the chalcogen transfer reactions of MeSCR(CN)<sub>2</sub> and PhSC(Me)(CN)<sub>2</sub> appeared to compete more efficiently with self-trapping in CH<sub>2</sub>Cl<sub>2</sub> than when aromatic solvents or THF were employed. Minor solvent effects might be present in both the chalcogen transfer and self-trapping reactions, both of which are expected to have slightly polarized transition states, but we believe that the rate constants for self-trapping in CH<sub>2</sub>Cl<sub>2</sub> probably are not significantly greater than those in aromatic solvents. We concluded this because the absolute yields of chalcogen transfer products from reactions in CH<sub>2</sub>Cl<sub>2</sub> were similar to those obtained in aromatic solvents when the concentrations of trapping agents were similar, but the yields of self-trapped products (and, thus, also the total yields) were reduced when CH<sub>2</sub>Cl<sub>2</sub> was the solvent. Therefore, a decrease in the yield of self-trapped product seemed to be the major reason for the increase in the calculated ratio *k<sub>T</sub>*/*k<sub>ST</sub>* for reactions run in CH<sub>2</sub>Cl<sub>2</sub>. Other radical reaction products in the CH<sub>2</sub>Cl<sub>2</sub> reactions were not identified, although we did observe that hydrocarbon products from reduction of the alkyl radical by hydrogen atom transfer from the solvent or from disproportionation were not formed to any great extent in these reactions.

The rate constants for reactions of the various chalcogens studied follow some predictable patterns. In the selenyl transfer series, increasing the stability of the product radical from an acetate radical to a malonate radical or from an acetonitrile radical to a malonitrile radical increases the rate constant for group transfer by about 1 order of magnitude. The members of the nitrile series are somewhat more reactive than the corresponding members in the ester series. Both trends were previously observed in rate constants for iodine atom transfers.<sup>7b</sup>

The chalcogen group transfer processes could occur by direct displacement with a transition state such as 14 or by formation of a hypervalent, chalcogen-centered radical

intermediate (e.g. 15) that subsequently fragments.<sup>12</sup> If hypervalent intermediates are involved, it is unlikely that addition of the primary alkyl radicals we employed was reversible given the stability of the ester and nitrile-substituted radical products ultimately formed in the displacement. Therefore, our relative rate constants most likely are a measure of the competition between the self-trapping reaction and the actual alkyl radical attack on the chalcogen. The pronounced leaving group effects we observed would appear to be most consistent with direct displacement processes because it would seem to be unlikely that a high degree of radical character would develop on the carbon of the leaving group in the transition state leading to intermediate 15. Similarly, the apparent lack of a kinetic effect in reactions of the *para*-substituted



phenyl selenides 8 and 9, species that might relay some portion of the radical stabilizing effects of the heteroatoms to the radical center in a hypervalent radical intermediate 15, suggests that direct displacements occur. Recent calculations have also suggested that direct displacements are favored over hypervalent intermediates.<sup>12d,e</sup>

In regard to potential for radical functionalizations via chalcogen group transfers, the results in Table I show that rate constants for RS group transfer from activated thio derivatives are only marginally greater than those for the disulfides. Given these modest rate constants, radical

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based thiolations will be limited to cases where reactive radicalophiles are not present and the concentrations of radicals are kept low to avoid radical-radical reactions. The rate constants for PhSe group transfer from the series of donors studied here approach but do not equal that from PhSeSePh (Table I), and the diselenide would usually be the preferred reagent for installation of a PhSe group in a radical-based construction.

The major impetus for studying chalcogen group transfer rate constants, however, was the development of carbon-carbon bond forming sequences involving PhSe group transfer from substituted malonic esters, malononitriles, and related reagents (i.e. Scheme I).<sup>5</sup> Related halogen atom transfer sequences, especially with iodine atom transfer, are more common,<sup>6</sup> and an interesting comparison can be made between the rate constants for halogen atom transfers and those for chalcogen group transfers. Specifically, the rate constants for phenyl-substituted chalcogen group transfer to a primary radical appear to be quite similar to those for transfer of a halogen atom in the same row of the periodic table as long as the displaced radical is the same in both cases. For reactions in benzene at 50 °C, PhSeCH<sub>2</sub>CO<sub>2</sub>Et and BrCH<sub>2</sub>CO<sub>2</sub>Et react with rate constants of 1.0 and  $0.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , PhSeCMe(CO<sub>2</sub>Et)<sub>2</sub> and BrCMe(CO<sub>2</sub>Et)<sub>2</sub> react with rate constants of 8 and  $10 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , and PhTeCH<sub>2</sub>CO<sub>2</sub>Et and ICH<sub>2</sub>CO<sub>2</sub>Et react with rate constants of 2.3 and  $2.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>13</sup> This suggests that successful synthetic sequences that employ iodine atom transfer reactions<sup>6</sup> could also be accomplished with the corresponding phenyl telluride<sup>5e,f</sup> and that sequences that employ phenylselenyl group transfers<sup>5</sup> could be accomplished with the corresponding bromide.

## Experimental Section

**General.** All reactions were performed under an atmosphere of nitrogen in flame-dried glassware with dry solvents. Unless noted, reagents were obtained from Aldrich Chemical Co. and used as obtained. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. NMR spectra of CDCl<sub>3</sub> solutions containing internal TMS were obtained on GE GN-300 and QE-300 spectrometers or on Bruker AF-300 or WH-300 spectrometers. Gas chromatographic analyses were performed on a Varian 3400 chromatograph equipped with a flame ionization detector; a 15-m wide bore capillary column (SE-54, Alltech) was employed. GC-mass spectral analyses were performed with an HP 5890 chromatograph interfaced to an HP 5971 mass-selective detector; a 30-m capillary column (SE-54) was used.

*N*-(Phenylthio)phthalimide (4),<sup>14</sup> ethyl 2-methyl-2-(phenylseleno)propionate (6),<sup>15</sup> ethyl phenyltelluroacetate (12),<sup>16</sup> 1-(1-oxononyl)-2(1*H*)-pyridinethione (13a),<sup>17</sup> and 1-(1-oxododecoyl)-2(1*H*)-pyridinethione (13b)<sup>17</sup> were prepared as described previously. PTOC ester 13b had mp 45–50 °C (lit.<sup>18</sup> mp 52–54 °C).

**2-Methyl-2-(methylthio)malononitrile (1)** was prepared by the procedure described below for 3 from 2.06 g of methylma-

lononitrile<sup>19</sup> (25 mmol). Deprotonation of the malononitrile was followed by addition of a solution of methylsulfonyl chloride<sup>20</sup> in CCl<sub>4</sub> until the yellow-orange color of MeSCl persisted. Chromatography (silica gel, hexanes-ethyl acetate, 3:2) gave 3.2 g (71%) of 1 as a colorless oil. The product was sealed in a glass ampule and stored at 3 °C. To insure purity, samples of compound 1 were distilled (bulb to bulb, 100 °C bath, 15 Torr) immediately before use: <sup>1</sup>H NMR δ 2.05 (s, 3H), 2.55 (s, 3H); <sup>13</sup>C NMR δ 15.95, 24.45, 32.35, 114.11; exact mass, calcd for C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>S 126.0252, found 126.0248.

**2-Butyl-2-(methylthio)malononitrile (2).** Butylmalononitrile was prepared by the reported procedure for the preparation of methylmalononitrile.<sup>19</sup> Compound 2 was prepared by the procedure described below for 3 from 1.00 g (8.2 mmol) of butylmalononitrile. Column chromatography (silica gel, hexanes-ethyl acetate, 15:1) gave 0.86 g (62%) of 2 as a slightly yellow oil. Samples of 2 used in trapping studies were distilled immediately before use (bulb to bulb, 95 °C bath, 15 Torr): <sup>1</sup>H NMR 0.96 (t, *J* = 7.2 Hz, 3 H), 1.44 (sextet, *J* = 7.2 Hz, 2 H), 1.69 (m, 2 H), 2.12 (m, 2 H), 2.55 (s, 3 H); <sup>13</sup>C NMR 13.55, 21.84, 27.90, 36.99, 37.87, 113.45. Compound 2 was not further analyzed.

**2-Methyl-2-(phenylthio)malononitrile (3).** To a stirred suspension of NaH (0.22 g, 5.50 mmol) in 30 mL of dry THF was added dropwise a solution of methylmalononitrile (0.40 g, 5.0 mmol) in 10 mL of THF. The suspension was stirred until the evolution of H<sub>2</sub> ceased (ca. 3 h). A solution of benzenesulfonyl chloride<sup>21</sup> (0.79 g, 5.5 mmol) in 10 mL of THF was added dropwise until the point at which the yellow color of the sulfonyl chloride persisted in solution. The mixture was stirred at room temperature for 12 h. The solvent was removed at reduced pressure, and the residue was taken up in ether. The ethereal solution was filtered and concentrated under reduced pressure. The residue was purified by radial chromatography (silica gel, hexanes-ethyl acetate, 15:1) to give 0.78 g (83%) of 3 which crystallized on standing: mp 44–46 °C; <sup>1</sup>H NMR 2.10 (s, 3 H), 7.30 (m, 3 H), 7.80 (m, 2 H); <sup>13</sup>C NMR 24.61, 36.50, 114.26, 127.37, 129.98, 132.19, 137.02; exact mass, calcd for C<sub>10</sub>H<sub>9</sub>N<sub>2</sub>S 188.0408, found 188.0411.

**Ethyl (Phenylseleno)acetate (5).** To a solution of diphenyl diselenide (0.50 g, 1.60 mmol) in EtOH (10 mL) was added NaBH<sub>4</sub> (0.13 g, 3.45 mmol) with ice-cooling. A solution of ethyl bromoacetate (0.36 mL, 3.25 mmol) in EtOH (5 mL) was added dropwise. The mixture was stirred at 0 °C for 1 h and warmed to room temperature. Water (20 mL) and diethyl ether (50 mL) were added. The organic layer was separated, washed with saturated aqueous NaCl solution, and dried over anhydrous MgSO<sub>4</sub>. After evaporation, the residue was purified by flash chromatography (silica gel, hexane-ethyl acetate, 5:1) to give 0.64 g (82%) of known<sup>15</sup> compound 5: <sup>1</sup>H NMR δ 1.18 (t, *J* = 7.1 Hz, 3 H), 3.49 (s, 2 H), 4.10 (q, *J* = 7.1 Hz, 2 H), 7.27 (m, 3 H), 7.57 (m, 2 H); <sup>13</sup>C NMR δ 13.81, 27.28, 60.97, 127.53, 128.91, 129.01, 133.09, 170.52.

**(Phenylseleno)acetonitrile (7)** was prepared by the procedure described above for 5 from chloroacetonitrile and was isolated as a colorless oil (99%): <sup>1</sup>H NMR δ 3.38 (s, 2 H), 7.39 (m, 3 H), 7.70 (m, 2 H); <sup>13</sup>C NMR δ 7.90, 117.43, 126.94, 129.09, 129.53, 134.57; exact mass, calcd for C<sub>6</sub>H<sub>7</sub>N<sup>80</sup>Se 196.9744, found 196.9780.

**[(*p*-Methoxyphenyl)seleno]acetonitrile (8)** was prepared by the procedure described above for 5. Reduction of bis(*p*-methoxyphenyl) diselenide (0.13 g, 0.34 mmol) with NaBH<sub>4</sub> was followed by the addition of chloroacetonitrile (60 mg, 0.8 mmol). Chromatography (silica gel, hexane-ethyl acetate, 5:1) gave 92 mg (61%) of 8 as an oil: <sup>1</sup>H NMR δ 3.28 (s, 2H), 3.83 (s, 3H), 6.89 (d, 2 H, *J* = 8.8 Hz), 7.65 (d, *J* = 8.8 Hz, 4 H); <sup>13</sup>C NMR: δ 8.06, 55.28, 115.22, 117.04, 117.59, 137.42, 160.97; exact mass, calcd for C<sub>9</sub>H<sub>9</sub>NO<sup>80</sup>Se 226.9849, found 226.9858.

**[(*p*-Chlorophenyl)seleno]acetonitrile (9)** was obtained as a white solid by the procedure described above for 8 (99%): mp 53 °C; <sup>1</sup>H NMR δ 3.36 (s, 2 H), 7.34 (d, *J* = 8.4 Hz), 7.63 (d, *J*

(13) (a) Rate constants for halogen atom transfer reactions are from ref 7b. (b) Abstractions of Cl and SPh or Br and SePh by tin radicals also occur at roughly comparable rates, see: Beckwith, A. L. J.; Pigou, P. E. *Aust. J. Chem.* 1986, 39, 1151. (c) Vinyl radicals abstract TePh faster than I: see ref 5f.

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= 8.4 Hz);  $^{13}\text{C}$  NMR  $\delta$  8.35, 117.20, 124.94, 129.92, 135.97, 136.39; exact mass, calcd for  $\text{C}_9\text{H}_6\text{ClN}^{80}\text{Se}$  230.9354, found 230.9338.

**Diethyl 2-Methyl-2-(phenylseleno)malonate (10)** was prepared by the procedure described above for **3** from diethyl methylmalonate (0.20 g, 1.15 mmol). Deprotonation of the malonate with oil free NaH was followed by the addition of a solution of phenylselenenyl bromide (0.33 g, 1.38 mmol) in THF at 0 °C. Column chromatography (silica gel, hexane-ethyl acetate, 10:1) gave 0.37 g (97%) of **10** as an oil:  $^1\text{H}$  NMR  $\delta$  1.27 (t,  $J = 7.1$  Hz, 6 H), 1.70 (s, 3 H), 4.25 (q,  $J = 7.1$  Hz, 4 H), 7.38 (m, 3 H), 7.63 (m, 2 H);  $^{13}\text{C}$  NMR  $\delta$  13.88, 22.48, 53.18, 62.05, 126.49, 128.79, 129.63, 138.10, 169.84; exact mass, calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_4^{80}\text{Se}$  330.0370, found 330.0315 (calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_4^{78}\text{Se}$  326.0398, found 326.0369).

**2-Methyl-2-(phenylseleno)malononitrile (11)** was prepared by the procedure described above for **10** from methylmalononitrile<sup>5c</sup> and was isolated as a pale yellow solid (77%): mp 71–72 °C;  $^1\text{H}$  NMR  $\delta$  2.06 (s, 3 H), 7.56 (m, 3 H), 7.88 (m, 2 H);  $^{13}\text{C}$  NMR  $\delta$  20.0, 24.3, 32.6, 114.9, 125.0, 129.9, 131.7, 137.6; exact mass, calcd for  $\text{C}_{10}\text{H}_8\text{N}_2^{78}\text{Se}$  233.9861, found 233.9861.

**Kinetic Measurements. Method A.** Under low-intensity light, the desired amounts of PTOC ester **13b** (0.02–0.06 mmol) and trapping agent were weighed into a 1-mL volumetric flask containing a small stir bar. The flask was sealed with a septum and flushed with nitrogen, and dry solvent was added to the mark. Solutions were degassed (three freeze-thaw cycles), equilibrated at the desired temperature in a thermostated bath, and then irradiated with a 150-W tungsten-filament lamp at a distance of 1 m. Reaction progress was monitored by TLC (silica gel). After the reaction was complete (ca. 12–20 h), a weighed amount of decane was added by syringe (internal standard), and the product mixture was analyzed by GC. Products were identified by GC coelution with authentic samples and by GC-mass spectral comparison to the mass spectra of the authentic samples. Yields were calculated using predetermined response factors; typically, the total yields from reactions run in aromatic

solvents were 70–100%, whereas the total yields from reactions run in  $\text{CH}_2\text{Cl}_2$  were 60–80%. Authentic samples of undecyl methyl sulfide, undecyl phenyl sulfide, and undecyl phenyl selenide were prepared by reaction of the the chalcogen anion (from reaction of the dichalcogenide with  $\text{NaBH}_4$ ) with 1-bromoundecane. An authentic sample of undecyl 2-pyridyl sulfide<sup>7b</sup> was prepared by allowing PTOC ester **13b** to react in the absence of other trapping agents.

**Method B.** Individual  $\text{C}_8\text{D}_8$  solutions of each of the trapping agents and the PTOC ester (**13a**) were placed in a 5.0-mm NMR tube.  $(\text{Me}_3\text{Si})_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$  were added as internal standards. The NMR tube was sealed, and the spectrum was recorded. The tube was then submerged in an Erlenmeyer flask filled with water at 50 °C. The reaction mixture was irradiated with a 275-W sunlamp from a distance of 15 cm. After the disappearance of the yellow color (3–4 min), an NMR spectrum was recorded, and the concentrations of each of the reactants and products were calculated relative to both of the internal standards. Authentic samples of octyl aryl selenides and octyl phenyl telluride were prepared by reaction of the appropriate chalcogen anion with 1-bromooctane.

**Purities of chalcogen transfer agents** were judged to be >95% and usually >98% on the basis of their  $^1\text{H}$  NMR spectra.

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**Supplementary Material Available:**  $^1\text{H}$  NMR spectra of all new compounds (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.