Radical Addition Reactions of 2-(Phenylseleno)propanedioates to Alkenes and Alkynes

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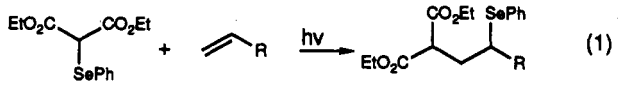
Sunlamp photolysis of methyl or ethyl 2-(phenylseleno)propanedioate with a variety of alkenes and alkynes in benzene yielded addition products in good to excellent yields. The proposed mechanism involves a radical chain process in which addition of a malonate ester radical is followed by phenylseleno transfer. Monosubstituted alkenes, 1,1- and 1,2-disubstituted alkenes, terminal alkynes, and internal alkynes were shown to undergo this reaction. Addition to diallyl ether led to substituted tetrahydrofurans, characteristic of a process involving initial addition, followed by cyclization prior to phenylseleno transfer. Vinyl arenes, conjugated dienes, and unsaturated carbonyl compounds proved unreactive.

Atom transfer reactions have recently provided some of the more interesting and potentially useful examples of radical-based synthetic methodology. Curran and others have demonstrated the utility of iodine and bromine transfer radical cyclizations.[1] Curran[2] has also demonstrated the addition of iodomalonates and iodomalononitriles to alkenes and alkynes, exemplifying intermolecular radical reactions which proceed with iodine transfer, while Giese[3] has demonstrated analogous reactions of bromomalonates. There have also been numerous examples of selenium-transfer radical additions involving addition of Se–heteroatom bonds.[4]

We recently reported what we believe to be the first examples of carbon–carbon bond-forming radical reactions proceeding with phenylseleno transfer (eq 1).[5] More

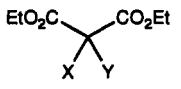


(1)

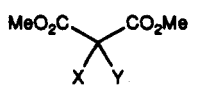
recently, Curran has demonstrated the use of (phenylseleno)malononitriles in radical additions.[2a] In this paper, we present the results of a more detailed study of the reactions of 2-(phenylseleno)propanedioate esters with a wide variety of alkenes and alkynes.

Results and Discussion

Our initial studies focused on the addition reactions of diethyl 2-(phenylseleno)propanedioate (**1a**) to simple alkenes. This reagent was obtained[6] by treating diethyl malonate with NaH and quenching the resulting anion with PhSeCl or PhSeBr. The efficient synthesis of this ethyl diester proved more difficult than first envisioned due to its tendency to react with 2 equiv of the phenylselenenyl halide under the reaction conditions, yielding a small, but observable amount of bis-phenylseleno ester **1b**. The formation of **1b** was suppressed, but not eliminated, by use of a 10-fold excess of the malonate anion. The purification of **1a** was further complicated by its thermal lability, which was first observed when vacuum distillation was attempted. Upon heating, **1a** would undergo disproportionation to generate **1b**, diethyl malonate, and a small amount of diphenyl diselenide. Thus, while the sample of **1a** obtained by removing the unreacted diethyl malonate by *Kugelrohr* distillation was pure enough for most synthetic uses, it was inevitably contaminated with about 5% **1b**. In situations where absolutely pure **1a** was desired, painstaking MPLC was required to separate diethyl malonate, **1a** and **1b**, which possessed virtually identical chromatographic mobility on silica gel with all solvent systems tried.



1a: X = PhSe, Y=H
1b: X = Y = PhSe



2a: X = PhSe, Y = H
2b: X = Y = PhSe

In our more recent studies, **2a**, the methyl analogue of **1a**, was used. Diester **2a** proved far easier to purify, as the more volatile unreacted dimethyl malonate could be removed by simply stirring the crude product at room temperature overnight under vacuum (<1 mm), thus eliminating the need for distillation at higher temperatures. This was followed by chromatography to remove the less polar PhSeSePh. Under these conditions, much less of the unwanted bis-phenylseleno diester **2b** was generated. We have observed no significant differences in the behavior of **1a** and **2a** in their subsequent addition reactions.

(1) (a) Curran, D. P.; Chen, M.-H.; Kim, D. *J. Am. Chem. Soc.* **1986**, *108*, 2489. (b) Curran, D. P.; Kim, D. *Tetrahedron Lett.* **1986**, *27*, 5821. (c) Curran, D. P.; Chen, M.-H. *J. Am. Chem. Soc.* **1987**, *109*, 6558. (d) Curran, D. P.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140. (e) Barth, F.; O-Yang, C. *Tetrahedron Lett.* **1990**, *31*, 1121. (f) Curran, D. P. *Synthesis* **1988**, 489. (g) Curran, D. P.; Chen, M.-H.; Spletzer, E.; Seong, C. M.; Chang, C.-T. *J. Am. Chem. Soc.* **1989**, *111*, 8872. (h) Curran, D. P.; Chen, M.-H; Kim, D. *J. Am. Chem. Soc.* **1989**, *111*, 6265. (i) Curran, D. P.; Chem, M.-H.; Kim, D. *J. Am. Chem. Soc.* **1989**, *111*, 6265.

(2) (a) Curran, D. P.; Thoma, G. *J. Am. Chem. Soc.* **1992**, *114*, 4436. (b) Curran, D. P.; Seong, C. M.; *Tetrahedron* **1992**, *48*, 2157. (c) Curran, D. P.; Seong, C. M.; *Tetrahedron* **1992**, *48*, 2175.

(3) Giese, B.; Horler, H.; Leising, M. *Chem. Ber.* **1986**, *119*, 444.

(4) Several examples with leading references: (a) Back, T. G.; Krishna, M. J. *J. Org. Chem.* **1988**, *53*, 2533. (b) Back, T. G.; Krishna, M. V.; Muralidharan, K. R. *Tetrahedron Lett.* **1987**, *28*, 1737. (c) Ogawa, A.; Takami, N.; Sekiguchi, M.; Yokoyama, H.; Kuniyasu, H.; Ryu, I.; Sonoda, N. *Chem. Lett.* **1991**, 2241. (d) Ogawa, A.; Yokoyama, H.; Yokoyama, K.; Masawaki, T.; Kambe, N.; Sonoda, M. *J. Org. Chem.* **1991**, *56*, 5721. (e) Toru, T.; Seko, T.; Maekawa, E.; Ueno, Y. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1927. (f) Ogawa, A.; Tanaka, H.; Yokoyama, H.; Obayashi, R.; Yokoyama, K.; Sonoda, N. *J. Org. Chem.* **1992**, *57*, 111. (g) Back, T. G.; Collins, S. J. *J. Org. Chem.* **1981**, *46*, 3249. (h) Gancarz, R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899. (i) Lin, H.-S.; Coghlan, M. J.; Paquette, L. A. *Org. Synth.* **1988**, *67*, 157.

(5) (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) Byers, J. H.; Harper, B. C. *Tetrahedron Lett.* **1992**, *33*, 6953.

(6) Prior to our studies, the synthesis of **1a** from NaSePh and diethyl bromomalonate was described: (a) Stockel, R. F.; Dumas, E. U.S. Patent 4 536 571, 1985. (b) Stockel, R. F.; Dumas, E. U.S. Patent 4 617 189, 1986.

0022-3263/93/1958-3355$04.00/0

Reagents **1a** and **2a** were shown to add cleanly, and in synthetically useful yields, to a wide variety of alkenes. In most cases, the reaction proceeded to completion overnight upon photolysis of a benzene solution of the alkene and the selenide reagent with a 275-W sunlamp. The most satisfactory results were usually obtained when a 3:1 ratio of selenide/alkene was used. In a few cases, particularly when dealing with more volatile olefins, an excess of the alkene was preferable.

In all cases where a terminal alkene was was used, the only addition product obtained and identified was the isomer shown, arising from the attack of the malonate radical on the unsubstituted olefinic carbon. Analysis of the crude reaction products by GC/MS failed to indicate the presence of any other isomeric products.

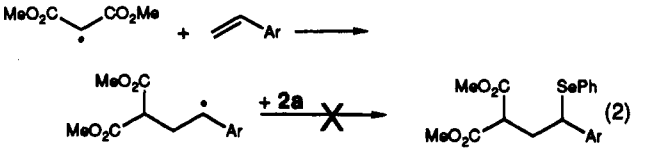
The addition of **2a** to disubstituted olefins also proved successful. The addition to isopropenyl acetate, a 1,1-disubstituted alkene, as well as the 1,2-disubstituted olefins, cyclohexene and norbornene, proceeded under the usual reaction conditions.

As expected, the addition to cyclohexene generated a mixture of *cis* and *trans* addition products, in this case in a 1.5:1 ratio, as measured by gas chromatography. In order to determine the stereochemistry of these isomeric products, we took advantage of the stereospecific syn elimination of selenoxides.[7] The *cis* isomer, upon oxidation with hydrogen peroxide, would be expected to eliminate to yield only one alkene, whereas the *trans* isomer should generate two isomeric alkenes. When a sample of the isolated major isomer was oxidized (H_2O_2, THF, 5 min at 0 °C), only one elimination product was generated, as monitored by GC/MS (*m/z* 212). When the minor isomer was subjected to the same conditions, two isomeric products (*m/z* 212) were obtained. These experiments indicate that *cis* product is the major isomer formed in this addition reaction. Interestingly, the stereochemical outcome of this addition is reversed from that observed in the addition of (phenylseleno)malononitrile[2a] to dihydropyran. While the source of this discrepancy is not clear, neither reaction demonstrates particularly noteworthy degrees of stereoselectivity.

The addition of **2a** to norbornene yielded only two of the four possible enantiomeric pairs of **9** in a 1.8:1 ratio. Both products arose from stereoselective attack of the malonyl radical at the *exo* face. The major isomer was isolated by preparative HPLC and was assigned to the *cis* stereochemistry based on the 8.1-Hz coupling constant between H_a and H_b. The minor isomer showed a smaller coupling constant (6.3 Hz) between these protons, as would be expected for the *trans* isomer.

Selenide **2a** demonstrated the ability for tandem addition–cyclization reactions, as would be expected in a radical addition. Photolysis of **2a** and diallyl ether generated a 1.8:1 ratio of the *cis* and *trans* isomers of substituted tetrahydrofuran **10**. We have assumed that the major stereoisomer formed in this reaction is the *cis* isomer based on literature precedent for 1,6-diene radical cyclizations,[8] which presumably proceed through the intermediacy of 1-substituted hexenyl radicals.[9] We were unable to identify any products arising from simple addition of **2a** to one or both of the alkene functionalities in this reaction. Thus, phenylseleno transfer from **2a** to an alkyl radical must be slower than the cyclization of the 3-oxahex-5-enyl radical, which has a rate constant of approximately 3×10^6 s^{-1}.[9b]

Unlike the apparently more reactive (phenylseleno)malononitrile,[2a] **2a** did not react with styrene derivatives such as 2-vinylnaphthalene, 1-methylstyrene, or triphenylethene. In these cases, the intermediate formed upon reaction with the alkene would generate a relatively unreactive benzylic radical, as shown in eq 2. This benzylic



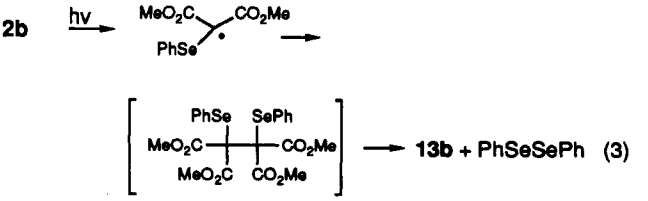
(2)

radical intermediate was unable to propagate the radical chain reaction by abstraction of PhSe from **2a**. The attempted addition to 1,3-hexadiene, which would proceed through the intermediacy of an allylic radical, also failed.

Neither **1a** nor **2a** would react with electron-deficient alkenes such as butyl vinyl ketone or 2-cyclohexenone to any significant degree. This lack of reactivity with electron-deficient alkenes is characteristic of electrophilic radicals.[10]

We have also shown that **2a** is capable of addition to alkynes. Addition of **2a** to 1-decyne yielded a 2:1 ratio of *E* and *Z* isomers. The *E* isomer was identified by the 1.1-Hz coupling constant between the olefinic and allylic protons. This coupling was not observed in the *Z* isomer. We obtained a similar (1.7:1) ratio of isomers in the addition to the internal alkyne, 5-decyne. We have assigned the *E* configuration to the major isomer based on Curran's observation[1h] that increased substitution on the initially formed radical increases the percentage of *E* alkenes formed during iodine-transfer additions to alkynes, as well as by analogy to our previous example.

We had hoped that bis-phenylseleno ester **2b** would add to 2 equiv of an alkene upon photolysis to generate dialkylated products. However, when **2b** was photolyzed in the presence of a 10-fold excess of octene, no addition products were obtained. Instead, the only products formed were tetraester **13b** and PhSeSePh. A mechanistic rationale for this is outlined in eq 3. The α-phenylseleno



(3)

radical initially formed upon photolysis of **2b** appears to exhibit the behavior more characteristic of a capto-dative radical than the electrophilic radical formed upon C–Se bond homolysis of **1a** or **2a**. Capto-dative radicals are known to be generally unreactive toward alkenes[11] and instead simply dimerize. The dimer thus formed, which was never observed, simply suffers loss of PhSeSePh,

(7) (a) Liotta, D. *Organoselenium Chemistry*; John Wiley and Sons: New York, 1987. (b) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergammon Press: Oxford, 1986.

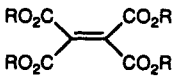
(8) Several examples, with leading references: Kuehne, M. E.; Damon, R. E. *J. Org. Chem.* **1977**, *42*, 1825.

(9) (a) Brace, N. O. *J. Org. Chem.* **1967**, *32*, 2711. (b) Beckwith, A. L. J.; Blair, I.; Phillipou, G. *J. Am. Chem. Soc.* **1974**, *96*, 1613.

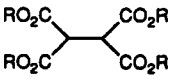
(10) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; *Pergamon*: Oxford, 1986.

(11) Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917.

presumably through a radical mechanism, to generate the observed products. This reaction proved so efficient that it could be used to further facilitate the purification of **2a**. When a benzene solution of crude **2a** was photolyzed for 2 h, the undesired diester **2b**, which possessed the same chromatographic mobility as **2a**, was efficiently converted to the much more polar **13b** and less polar diphenyl diselenide.



13a: R = Et
13b: R = Me

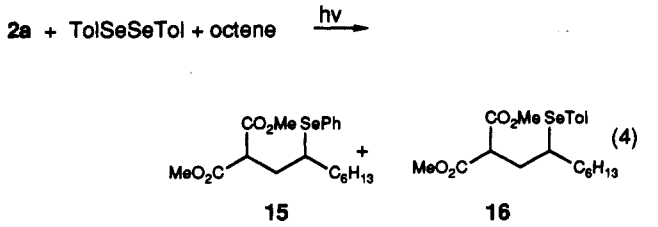


14a: R = Et
14b: R = Me

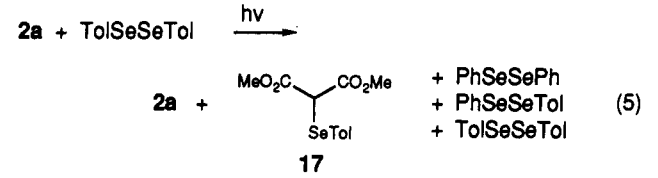
The facility with which this dimerization of **2b** occurred caused us to reexamine some of our earlier results and conclusions. Given that the coupling of malonate radicals had been previously observed when the reaction of an iodomalonate with a particularly unreactive alkene had been attempted,[1d] we had expected to see the products arising from the radical disproportionation of **1a** or **2a**, diphenyl diselenide, and tetraester **14a** or **14b**, respectively. We had detected and reported what we assumed to be **14a** as a frequent, but minor, byproduct in our earlier studies. However, more careful GC/MS analyses of our crude reaction mixtures have indicated that very little, if any, **14a** or **14b** was actually generated in the course of these reactions, indicating that the dimerization of the malonate radical is very slow relative to the other available reaction pathways. We were actually generating tetraester **13a** which was probably arising from the bisphenylseleno diester **1b** which was a contaminant in most of our samples of **1a** in our earlier studies. When scrupulously purified **2a** was photolyzed in the absence of an alkene, only **13b**, not **14b**, was generated! In this reaction, **2a** is probably undergoing thermal disproportionation to generate **2b** and dimethyl malonate and subsequently undergoing the aforementioned radical dimerization shown in eq 3.

Under the standard atom-transfer mechanism, the phenylseleno functionality is transferred from the addition reagent **1a** or **2a**. As these radical reactions proceed, a small concentration of PhSeSePh is invariably produced in the reaction mixture. This result led to our consideration of the possibility that a second mechanism, which differs slightly from the standard "atom-transfer" mechanism, might be involved in these reactions. The S_H2 reaction of the octyl radical with diphenyl diselenide leading to octyl phenyl selenide is quite fast (greater than 4.2×10^6 M^{-1} s^{-1} at 80 °C).[12] Thus, this PhSeSePh might be envisioned as the source of the "transferred" phenylseleno functionality.

When a mixture of **2a**, ditolyl diselenide,[13] and octene (in a 2:2:1 molar ratio) was photolyzed, a mixture of two products incorporating both a phenylseleno and a tolylseleno group were obtained, as shown in eq 4, suggesting that the ditolyl diselenide might be acting as a selenide-transfer reagent. However, when **2a** and ditolyl diselenide



15 **16**



17

were photolyzed in the absence of octene, an equimolar mixture of **2a** and **17**, in addition to a mixture of diaryl diselenides, was generated (eq 5). Thus, these experiments cannot determine with certainty whether the phenylseleno group is being transferred from the diesters **1a** or **2a** or from diphenyl diselenide. Perhaps more importantly, if phenylseleno transfer was occurring primarily from the diphenyl diselenide, one would expect that the additional diselenide would promote the reaction in some way, either in faster reaction rates, higher chemical yield, or both. The reaction outlined in eq 4 yielded only a 6% yield of phenylseleno adduct and a 12% yield of tolylseleno adduct after 36 h of photolysis. This is in contrast to the 95% yield after 12 h observed in the analogous reaction listed in Table I. Somewhat surprisingly, additional diselenide not only fails to promote the desired addition reaction, it actually appears to inhibit it! These data, in addition to the observation that the concentration of diphenyl diselenide generated in the reaction under normal conditions is much lower, clearly indicate that phenylseleno transfer from diphenyl diselenide is not a significant contributor to the overall reaction.

Experimental Section

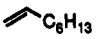
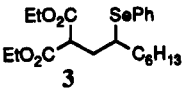
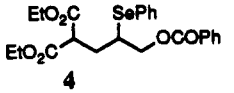
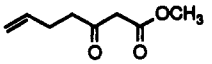
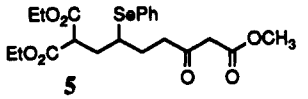
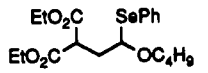
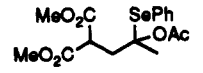
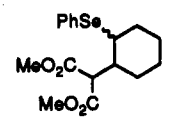
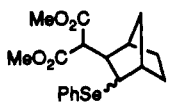
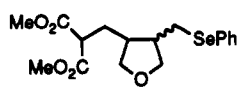
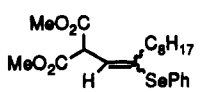
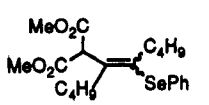
General. Melting points were obtained on a Hoover-Thomas melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 1600 FT-IR. ^1H and ^{13}C NMR were obtained in $CDCl_3$ on a General Electric GN-300 Omega spectrometer. Gas chromatographic analysis and mass spectroscopy (GC/MS) were carried out on a Hewlett-Packard 5890 gas chromatograph with a 25-m HP-1 methyl silicone capillary column interfaced to a Hewlett-Packard 5970 mass selective detector (EI, 70 eV). Preparative HPLC separations were performed on a Hewlett-Packard 1090 LC equipped with an analytical silica gel column. Elemental analyses were performed by Atlantic Microlab of Norcross, GA. Photolyses were carried out in standard Pyrex glassware with a 275-W General Electric sunlamp. Flash chromatography and medium-pressure liquid chromatography (MPLC) were caried out on EM Science silica gel 60 (230–400 mesh). Benzene and tetrahydrofuran (THF) were freshly disilled from K/benzophenone under Ar. Reagent-grade hexane and ethyl acetate were distilled prior to use. Phenylselenenyl chloride was recrystallized from hexane. Liquid olefins which were purchased with radical inhibitors were eluted through a pad of basic alumina immediately prior to use. All other reagents were used as obtained. Yields are reported for isolated products which were pure by NMR and TLC, except where noted.

Diethyl 2-(Phenylseleno)propanedioate (1a). A 0.80-g (20-mmol) portion of NaH (60% by wt in mineral oil) was suspended in 40 mL of dry THF under Ar and cooled to 0 °C. Diethyl malonate (3.2 g, 20 mmol) was added via syringe. After evolution of H_2 had ceased, the mixture was cooled to −25 °C. PhSeCl (0.96 g, 5 mmol) was added in one portion. The mixture was

(12) Barton has shown that diphenyl diselenide efficiently traps radicals in competition with "self-trapping" by a *N*-hydroxypyridine-2-thione ester: Barton, D. H. R.; Brindon, D.; Zard, S. Z. *Tetrahedron Lett.* **1984**, *25*, 5777. Newcomb has reported that the rate constant for *N*-hydroxypyridine-2-thione ester self-trapping by simple alkyl radicals is approximately 4.2×10^6 M^{-1} s^{-1} at 80 °C: Newcomb, M.; Kaplan, J. *Tetrahedron Lett.* **1987**, *28*, 1615.

(13) Pappalardo, G. C.; Ingolic, K. J.; Grigsby, R. A. *J. Organomet. Chem.* **1977**, *133*, 311.

Table I. Addition of 2-(Phenylseleno)propanedioates 1a and 2a

selenide	olefin	product	yield	time (h)
1a		 **3**	95%	12
1a		 **4**	88%	12
1a		 **5**	74%	12
1a		 **6**	65%	12
2a		 **7**	64%	16
2a		 **8a** *(cis)*, **8b** *(trans)*	54% 1.5:1, **a:b**	12
2a		 **9a** *(cis)*, **9b** *(trans)*	66% 1.4:1, **a:b**	12
2a		 **10a** *(cis)*, **10b** *(trans)*	86% 1.8:1, **a:b**	14
2a		 **11a** *(E)*, **11b** *(Z)*	79% 1.9:1, **a:b**	16
2a		 **12a** *(E)*, **12b** *(Z)*	61% 1.7:1, **a:b**	12

stirred overnight, gradually warming to room temperature. Ether (100 mL) was added, and the resulting mixture was washed successively with 100 mL of 0.5 M HCl, water, and brine. The resulting organic phase was dried over anhydrous $MgSO_4$ and filtered, and solvents were removed by rotary evaporation. Excess diethyl malonate was removed by Kugelrohr distillaton (80 °C, approximately 1 mm), and the remaining undistilled oil was further purified by MPLC (hexane, followed by 5% EtOAc, 95% hexane, v/v) to give 0.85 g of **1a** as a clear, colorless oil: ^{1}H NMR δ 7.80–7.20 (m, 5H), 4.50 (s, 1H), 4.18 (q, 4H), 1.22 (t, 6H).

Dimethyl 2-(Phenylseleno)propanedioate (2a). A 3.30-g (82.5-mmol) portion of NaH (60% by wt in mineral oil) was suspended in 150 mL of dry THF under Ar or N_2 and cooled to 0 °C. Dimethyl malonate (10.9 g, 82.5 mmol) was slowly added via syringe. After evolution of H_2 had ceased, the mixture was cooled to −25 °C. A 2.38-g (10.1-mmol) portion of PhSeBr was added, and the mixture was stirred overnight, gradually warming to room temperature. Ether (300 mL) was added, and the resulting mixture was washed successively with 150-mL portions of 1.0 M HCl, brine, and three portions of water. The organic layer was dried over anhydrous $MgSO_4$ and filtered, and solvents were removed by rotary evaporation. In order to remove the small quantities of **2b** that had formed, the resulting crude yellow oil was dissolved in 100 mL of benzene, the flask was equipped with a stir bar and condenser, and traces of oxygen were displaced by bubbling N_2 through the solution for 20 min. The solution was photolyzed for 2 h, during which time it heated to reflux. The solution was allowed to cool to room temperature, and the solvent was removed by rotary evaporation. The resulting crude yellow oil was evacuated (<1 mm) overnight with stirring to remove excess dimethyl malonate. Subsequent purification by flash chromatography (hexane, followed by 15% EtOAc, 85% hexane, v/v) gave pure **2a** (2.23 g, 77%): ^{1}H NMR δ 7.65 (m, 2H), 7.35 (m, 3H), 4.50 (s, 1H), 3.70 (s, 6H); ^{13}C NMR δ 167.6, 135.7, 129.2, 129.1, 127.3, 53.1, 45.7; IR (neat 1736 cm^{-1}; MS (EI) *m/z* 288 (M^+), 197, 169, 157, 121, 77. Anal. Calcd for $C_{11}H_{12}O_4Se$: C, 46.01; H, 4.21; found: C, 46.03; H, 4.20.

Dimethyl 2,2-(Diphenylseleno)propanedioate (2b). A 510-mg (12.8-mmol) portion of NaH (60% by wt in mineral oil) was suspended in 150 mL of dry THF under Ar or N_2 and cooled to

0 °C. Dimethyl malonate (1.32 g, 10.0 mmol) was slowly added via syringe. After evolution of H_2 had ceased, a 2.42-g (10.1-mmol) porton of PhSeBr was added, and the mixture was stirred overnight, gradually warming to room temperature. The solution was recooled to 0 °C, and 510 mg (12.8 mmol) of NaH was added. After evolution of H_2 had ceased, 2.48 g of PhSeBr (10.5 mmol) was added, and the mixture was stirred overnight, gradually warming to room temperature. Ether (300 mL) was added, and the resulting mixture was washed successively with 150 mL portions of 1.0 M HCl, brine, and three portions of water. The organic layer was dried over anhydrous $MgSO_4$ and filtered, and solvents were removed by rotary evaporation. The crude oil crystallized upon evacuation overnight. The crystals were washed once with cold hexane and further purified by flash chromatography (20% EtOAc, 80% hexane, v/v) to give **2b** (2.87 g, 65%) as white crystals: mp 98.5–100.0 °C; ^{1}H NMR δ 7.75 (m, 4H), 7.5–7.3 (m, 6H), 3.56 (s, 6H); ^{13}C NMR δ 167.1, 137.4, 130.0, 128.8, 127.5, 57.7, 53.3; IR (KBr) 1732 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_4Se_2$: C, 46.17; H, 3.65; found: C, 46.20; H, 3.62.

General Procedure for Addition Reactions of 1a or 2a. Diester **1a** or **2a** and the desired alkene or alkyne were dissolved in 2 mL of benzene in a 5-mL flask equipped with a reflux condenser. The resulting solution was degassed with bubbling Ar or N_2 for 15–20 min prior to photolysis by a sunlamp placed 6–8 in. from the solution.

Ethyl 2-(Ethoxycarbonyl)-4-(phenylseleno)decanoate (3). A mixture of **1a** (316 mg, 1.00 mmol) and octene (41 mg, 0.37 mmol) was photolyzed for 12 h. MPLC (hexane, followed by 10% EtOAc, 90% hexane, v/v) gave **3** as a clear oil (151 mg, 95%): ^{1}H NMR δ 7.55 (m, 2H), 7.30 (m, 3H), 4.20 (m, 4H), 3.92 (dd, J = 5.0, 9.4 Hz, 1H), 3.00 (m, 1H), 2.30 (ddd, J = 5.0, 10.0, 14.4 Hz, 1H), 2.00 (ddd, J = 5.0, 10.0, 14.4 Hz, 1H), 1.65–1.40 (m, 10H), 1.25 (t, J = 6.8 Hz, 3H), 1.22 (t, J = 7.3 Hz, 3H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR δ 169.4, 169.1, 135.5, 128.8, 128.1, 127.7, 61.4, 61.3, 50.6, 44.7, 36.1, 34.6, 31.6, 28.8, 27.5, 22.5, 14.0 (2 peaks); IR (neat) 1731 cm^{-1}; MS (EI) m/z 428 (M$^+$), 383 (M – OEt)$^+$, 337, 271 (M – PhSe)$^+$, 179, 151, 123, 77. Anal. Calcd for $C_{21}H_{32}O_4Se$: C, 59.01; H, 7.55. Found: C, 59.09; H, 7.58.

Ethyl 5-(Benzoyloxy)-2-(ethoxycarbonyl)-4-(phenylseleno)pentanoate (4). A mixture of **1a** (316 mg, 1.00 mmol) and allyl benzoate (54 mg, 0.33 mmol) was photolyzed for 12 h. Flash chromatography (hexane, followed by 10% EtOAc, 90% hexane, v/v) gave **4** as a clear oil (138 mg, 88%): ^{1}H NMR δ 8.00 (m, 2H), 7.57 (m, 3H), 7.45 (m, 2H), 7.40 (m, 3H), 4.62 (dd, J = 5.2, 11.3 Hz, 1H), 4.36 (dd, J = 7.9, 11.3 Hz, 1H), 4.20 (m, 4H), 3.98 (dd, J = 4.8, 10.0 Hz, 1H), 3.40 (m, 1H), 2.53 (ddd, J – 4.5, 5.5, 14.7 Hz, 1H), 2.09 (ddd, J = 4.8, 5.6, 14.7 Hz, 1H), 1.26 (t, J = 6.9 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 169.1, 168.8, 166.1, 135.6, 133.0, 129.8, 129.6, 129.2, 128.3 (2 peaks), 127.0, 67.7, 61.6, 61.5, 50.4, 41.4, 31.1, 14.0; IR (neat) 1747, 1726 cm^{-1}; MS (EI) m/z 478 (M$^+$), 356 (M – PhCO$_2$)$^+$, 321 (M – PhSe)$^+$, 199, 105, 77. Anal. Calcd for $C_{23}H_{26}O_6Se$: C, 57.86; H, 5.49. Found: C, 58.08; H, 5.53.

1-Ethyl 9-Methyl 2-(Ethoxycarbonyl)-7-oxo-4-(phenylseleno)nonanedioate (5). A mixture of **1a** (315 mg, 1.00 mmol) and methyl 3-oxo-6-heptenoate (62 mg, 0.39 mmol) was photolyzed for 12 h. MPLC (hexane, followed by 20% EtOAc, 80% hexane, v/v) gave pure **5** as a clear oil (137 mg, 74%): ^{1}H NMR δ 7.55 (m, 2H), 7.30 (m, 3H), 4.20 (m, 4H), 3.91 (dd, J = 5.0, 9.6 Hz, 1H), 3.75 (s, 3H), 3.40 (s, 2H), 3.00 (m, 1H), 2.80 (m, 2H), 2.20 (m, 1H), 2.00 (m, 3H), 1.25 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 201.7, 169.2, 169.0, 167.5, 135.6, 129.1, 128.1, 127.2, 61.5 (two peaks), 52.3, 50.5, 49.0, 43.6, 41.1, 34.5, 29.4, 14.0; IR (neat) 1746, 1727 cm^{-1}; MS (EI) m/z 472 (M$^+$), 315 (M – PhSe)$^+$, 283, 237, 191, 101, 77. Anal. Calcd for $C_{21}H_{28}O_7Se$: C, 53.51; H, 5.90. Found: C, 53.89; H, 6.18.

Ethyl 4-Butoxy-2-(ethoxycarbonyl)-4-(phenylseleno)-butanoate (6). A mixture of **1a** (316 mg, 1.00 mmol) and butyl vinyl ether (500 mg, 5 mmol) was photolyzed for 12 h. MPLC (hexane, followed by 5% EtOAc, 95% hexane, v/v) gave **6** as a clear oil (269 mg, 65%): ^{H} NMR δ 7.60 (m, 2H), 7.30 (m, 3H), 4.95 (dd, J = 5.1, 8.7 Hz, 1H), 4.20 (m, 4H), 3.91 (dt, J = 6.3, 9.3 Hz, 1H), 3.66 (dd, J = 6.1, 7.8 Hz, 1H), 3.30 (dt, J = 6.3, 9.3 Hz, 1H), 2.50 (m, 2H), 1.55 (m, 2H), 1.38 (m, 2H), 1.23 (t, J = 7.2 Hz, 6H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 169.0, 168.9, 135.7, 130.2, 129.0, 127.4, 84.8, 69.9, 61.4, 49.6, 36.7, 31.1, 30.9, 19.4, 14.0 (2 peaks), 13.8; IR (neat) 1732 cm^{-1}; MS (EI) m/z 259 (M – PhSe)$^+$, 185, 157, 129. Anal. Calcd for $C_{19}H_{28}O_5Se$: C, 54.94; H, 6.79. Found: C, 55.32; H, 6.97.

Methyl 4-Acetoxy-4-(phenylseleno)-2-(methoxycarbonyl)pentanoate (7). A mixture of **2a** (295 mg, 1.02 mmol) and isopropenyl acetate (506 mg, 5.06 mmol) was photolyzed for 15.5 h. MPLC (hexane, followed by 20% EtOAc, 80% hexane, v/v) gave unreacted **2a** (26 mg) and pure **7** as a clear oil (217 mg, 56%, 64% based on consumed **2a**): ^{1}H NMR δ 7.65 (m, 2H), 7.35 (m, 3H), 3.75 (s, 3H), 3.7 (m, 1H), 3.70 (s, 3H), 2.75–2.55 (m, 2H), 2.0 (s, 3H), 1.8 (s, 3H); ^{13}C NMR δ 169.5, 169.2, 169.0, 137.8, 129.1, 129.0, 127.3, 85.4, 52.8, 52.7, 48.6, 40.7, 27.2, 21.9; IR (neat) 1740 cm^{-1}; MS (EI) m/z 328 (M – CO$_2$Me)$^+$, 265, 196, 171 (M – SePh)$^+$, 139, 111, 77. Anal. Calcd for $C_{16}H_{20}O_6Se$: C, 49.61; H, 5.21. Found: C, 49.68; H, 5.22.

Addition of 2a to Cyclohexene. A mixture of **2a** (287 mg, 1.00 mmol) and cyclohexene (411 mg, 5.00 mmol) was photolyzed for 12 h. The solution was subjected to MPLC (hexane, followed by 5% EtOAc, 95% hexane, v/v) to give a mixture of stereoisomers **8a** and **8b** as a clear oil (199 mg, 54%) in a 1.3:1.0 ratio by GC. Sufficient quantities of spectroscopically pure **8a** and **8b** were isolated upon further purification by MPLC.

***cis*-Dimethyl 2-[[2-(phenylseleno)cyclohexyl]]propanedioate (8a):** ^{1}H NMR δ 7.5 (m, 2H), 7.25 (m, 3H), 3.80 (d, J = 11.1 Hz, 1H), 3.75 (s, 3H), 3.40 (s, 3H), 2.4 (m, 1H), 2.2 (m, 1H), 1.95 (m, 1H), 1.75 (m, 1H), 1.6 (m, 3H), 1.55–1.25 (m, 3H); ^{13}C NMR δ 169.2, 168.4, 134.1, 130.7, 129.0, 127.2, 57.1, 52.5, 52.2, 51.0, 42.5, 34.1, 26.7, 25.6, 22.0; IR (neat) 1737 cm^{-1}; MS (EI) m/z 370 (M$^+$), 339, 307, 213 (M – SePh)$^+$, 181, 153, 121, 81, 77. Anal. Calcd for $C_{17}H_{22}O_4Se$: C, 55.29; H, 6.00. Found: C, 55.44; H, 6.09.

***trans*-Dimethyl 2-[2-(phenylseleno)cyclohexyl]propanedioate (8b):** ^{1}H NMR δ 7.5 (m, 2H), 7.25 (m, 3H), 4.40 (d, J = 4.2 Hz, 1H), 3.75 (s, 3H), 3.65 (s, 3h), 3.2 (m, 1H), 2.2 (m, 2H), 1.9 (m, 1H), 1.7–1.2 (m, 6H); ^{13}C NMR δ 169.9, 168.9, 135.5, 128.9, 128.3, 127.8, 54.5, 52.4, 52.0, 47.6, 43.1, 35.4, 28.5, 27.0, 25.3; IR (neat) 1736 cm^{-1}; MS (EI) m/z 370 (M$^+$), 339, 307, 213 (M – SePh)$^+$, 181, 153, 121, 81, 77. Anal. Calcd for $C_{17}H_{22}O_4Se$: C, 55.29; H, 6.00. Found: C, 55.53; H, 6.04.

Oxidative Selenoxide Elimination of 8a and 8b. A sample of the major isomer (**8a**, 51 mg, 0.14 mmol, pure by GC/MS) was dissolved in THF (5 mL) and cooled to 0 °C. Three drops of 30% H_2O_2 were added. Analysis of the reaction mixture by GC/MS after 5 min showed only one peak, corresponding to a product with m/z 212, characteristic of one elimination product, as would be expected for **8a**. A sample of the minor isomer (**8b**, 23 mg, 0.062 mmol, pure by GC/MS) was dissolved in THF (5 mL) and cooled to 0 °C. Three drops of 30% H_2O_2 were added. Analysis of the reaction mixture by GC/MS after 5 min showed two peaks, corresponding to a product with m/z 212, characteristic of two elimination products, as would be expected for **8b**.

Addition of 2a to Norbornene. A mixture of **2a** (297 mg, 1.03 mmol) and norbornene (480 mg, 5.10 mmol) was photolyzed for 12 h. The solution was subjected to MPLC (hexane, followed by 10% EtOAc, 90% hexane, v/v) to give a mixture of stereoisomers **9a** and **9b** as a clear oil (261 mg, 66%) in a 1.4:1.0 ratio by GC. Anal. Calcd for $C_{18}H_{22}O_4Se$: C, 56.70; H, 5.81. Found: C, 56.71; H, 5.89. Preparative HPLC (0.3% EtOAc, 99.7% hexane, v/v, 200 × 4.6 mm Hypersil column, 5-μm packing, equipped with a guard column, 150 bar, 40 °C, detection at 275 nm) was used to give spectroscopically pure **9a** and **9b**.

***exo*-2-(Phenylseleno)-*exo*-3-[bis(methoxycarbonyl)methyl]bicyclo[2.2.1]heptane (9a):** ^{1}H NMR δ 7.5 (m, 2H), 7.3 (m, 3H), 3.80 (s, 3H), 3.75 (s, 3H), 3.50 (d, J = 12.5 Hz, 1H), 3.45 (dd, J = 8.1 Hz, ^4J = 2.2 Hz, 1H), 2.75 (m, J = 12.5, 8.1 Hz, ^4J = 1.1 Hz, 1H), 2.50 (d, J = 2.9 Hz, 1H), 1.95 (d, J = 1.8 Hz, 1H), 1.65–1.45 (m, 2H), 1.4–1.2 (m, 4H); ^{13}C NMR δ 169.5, 168.8, 133.2, 131.2, 129.0, 127.1, 56.5, 54.3, 52.8, 52.7, 47.2, 46.6, 39.8, 34.9, 30.3, 28.5; IR (neat) 1754, 1732 cm^{-1}; MS (EI) m/z 382 (M$^+$), 351, 319, 225 (M – SePh)$^+$, 193, 165, 133, 105, 77.

***endo*-2-(Phenylseleno)-*exo*-3-[bis(methoxycarbonyl)methyl]bicyclo[2.2.1]heptane (9b):** ^{1}H NMR δ 7.5 (m, 2H), 7.3 (m, 3H), 3.75 (s, 3H), 3.75 (s, eH), 3.35 (m, J = 6.3 Hz, 1H), 3.20 (d, J = 10.7 Hz, 1H), 2.2 (s, 1H), 2.1 (d, J = 4.0 Hz, 1H), 1.95 (dd, J = 10.7, 6.3 Hz, 1H), 1.6–1.2 (m, 6H); ^{13}C NMR δ 168.9, 168.2, 133.8, 128.9, 127.2, 56.1, 52.7, 52.5, 49.4, 48.0, 41.6, 41.3,

35.3, 29.7, 23.9; IR (neat) 1750, 1731 cm^{-1}; MS (EI) m/z 382 (M$^+$), 319, 225 (M – SePh)$^+$, 193, 165, 133, 105, 77.

Addition of 2a to Diallyl Ether. A mixture of **2a** (292 mg, 1.02 mmol) and diallyl ether (491 mg, 5.00 mmol) was photolyzed for 14 h. Purification of the reaction mixture by MPLC (hexane, followed by 10% EtOAc, 90% hexane, v/v) gave mixture of stereoisomers **10a** and **10b** as a clear oil (339 mg, 86%) in a 1.8:1.0 ratio by GC/MS. The mixture of isomers was resubjected to MPLC (10% EtOAc, 90% hexane, v/v) to give pure **10a** and **10b** in sufficient quantities for spectroscopic characterization.

***Cis*-cyclized product 10a:** ^{1}H NMR δ 7.5 (m, 2H), 7.3 (m, 3H), 3.90 (m, 2H), 3.75 (m, 1H), 3.75 (s, 3H), 3.75 (s, 3H), 3.55 (m, 1H), 3.30 (m, 1H), 3.05 (dd, J = 11.7, 4.8 Hz, 1H), 2.75 (m, 1H), 2.50 (m, 1H), 2.3–2.1 (m, 2H), 1.95–1.80 (m, 1H); ^{13}C NMR δ 169.4, 169.3, 133.1, 129.5, 129.2, 127.3, 72.7, 71.5, 52.7 (two peaks), 50.4, 42.1, 40.4, 26.6, 26.3; IR (neat) 1735 cm^{-1}; MS (EI) m/z 386 (M$^+$), 355, 197, 157, 137, 97. Anal. Calcd for $C_{17}H_{22}O_5Se$: C, 52.99; H, 5.76. Found: C, 53.39; H, 5.81.

***Trans*-cyclized product 10b:** ^{1}H NMR δ 7.5 (m, 2H), 7.3 (m, 3H), 4.0–3.9 (m, J = 11.9, 9.0, 8.7, 7.1, 6.7, 4.8, 4.5 Hz, 2H), 3.75 (s, 3H), 3.75 (s, 3H), 3.55 (dd, J = 9.0, 5.8 Hz, 1H), 3.40 (dd, J = 8.7, 6.4 Hz, 1H), 3.30 (m, J = 8.3, 8.0, 7.1, 6.7 Hz, 1H), 3.10 (m, J = 12.2, 11.9, 6.1, 5.8 Hz, 1H), 2.85 (dd, J = 12.2, 9.0 Hz, 1H); ^{13}C NMR δ 169.4, 169.3, 132.9, 129.6, 129.2, 127.2, 73.4, 73.2, 52.7, 50.4, 45.7, 43.7, 32.1, 31.0; IR (neat) 1733 cm^{-1}; MS (EI) m/z 386 (M$^+$), 355, 197, 157, 137, 97.

Addition of 2a to 1-Decyne. A mixture of **2a** (332 mg, 1.15 mmol) and 1-decyne (51.7 mg, 0.374 mmol) was photolyzed for 16 h. The solution was subjected to MPLC (hexane, followed by 5% EtOAc, 95% hexane, v/v) to give a mixture of stereoisomers **11a** and **11b** as a clear oil (126 mg, 79%) in a 1.9:1.0 ratio by ^{1}H NMR. Anal. Calcd for $C_{21}H_{30}O_4Se$: C, 59.29; H, 7.11. Found: C, 59.33; H, 7.16. Further MPLC separation (1% EtOAc, 99% hexane, v/v) gave pure **11a** and **11b** in sufficient quantities for spectroscopic characterization.

(*E*)-Methyl 2-(methoxycarbonyl)-4-(phenylseleno)-3-dodecenoate (11a): ^{1}H NMR δ 7.45 (m, 2H), 7.25 (m, 3H), 6.10 (dd, J = 9.3 Hz, ^4J = 1.1 Hz, 1H), 4.85 (d, J = 9.3 Hz, 1H), 3.75 (s, 6H), 2.25 (m, ^4J = 1.1 Hz, 2H), 1.55–1.15 (m, 12H), 0.85 (t, J = 7.1, 6.4 Hz, 3H); ^{13}C NMR δ 168.4, 141.1, 133.1, 129.2, 129.1, 129.1, 127.3, 125.2, 54.9, 52.8, 38.9, 31.8, 29.2 (two peaks), 28.6 (two peaks), 22.6, 14.1; IR (neat) 1740, 1578 cm^{-1}; MS (EI) m/z 426 (M$^+$), 328, 269 (M – SePh)$^+$, 205, 171, 149, 111, 81.

(*Z*)-Methyl 2-(methoxycarbonyl)-4-(phenylseleno)-3-dodecenoate (11b): ^{1}H NMR δ 7.5 (m, 2H), 7.3 (m, 3H), 6.0 (d, J = 10.0 Hz, 1H), 4.35 (d, J = 10.0 Hz, 1H), 3.75 (s, 6H), 2.25 (dd, 2H), 1.55–1.15 (m, 12H), 0.85 (t, 3H); ^{13}C NMR δ 167.9, 140.2, 134.0, 129.2 (2 peaks), 127.7, 123.7, 52.8, 51.9, 33.1, 31.8, 29.3, 29.2, 29.1, 28.8, 22.6, 14.1; IR (neat) 1738, 1579 cm^{-1}; MS (EI) m/z 426 (M$^+$), 328, 269 (M – SePh)$^+$, 171, 157, 95, 81.

Addition of 2a to 5-Decyne. A mixture of **2a** (917 mg, 3.18 mmol) and 5-decyne (155 mg, 1.12 mmol) was photolyzed for 12 h. Flash chromatography (hexane, followed by 15% EtOAc, 85% hexane, v/v) of the solution gave a mixture of stereoisomers **12a** and **12b** as a clear oil (260.4 mg, 61%) in a 1.7:1.0 ratio by ^{1}H NMR. Anal. Calcd for $C_{21}H_{30}O_4Se$: C, 59.29; H, 7.11. Found: C, 59.18; H, 7.09. A small sample (100 mg) of the mix of isomers was subjected to preparative TLC until two separate bands were visible (six passes, 5% EtOAc, 95% hexane, v/v, UV detection). Based on spectral data (*vide infra*), the higher R_f band was identified as **12a** and the lower R_f band was identified as **12b**.

(*E*)-5-(Phenylseleno)-6-[1,3-bis(methoxycarbonyl)-2-propyl]-5-decene (12a): ^{1}H NMR δ 7.35 (m, 2H), 7.25 (m, 3H), 5.29 (s, 1H), 3.70 (s, 6H), 2.3 (m, 4H), 1.6–1.2 (m, 8H), 0.90 (t, 3H), 0.85 (t, 3H); ^{13}C NMR δ 168.9, 138.7, 136.6, 131.6, 131.1, 129.0, 126.6, 59.4, 52.5, 34.8, 31.5 (two peaks), 23.1, 22.3, 14.0, 13.8; IR (neat) 1738, 1578 cm^{-1}; MS (EI) m/z 368 (M$^+$), 211 (M – SePh)$^+$, 179, 151, 137, 95.

(*Z*)-5-(Phenylseleno)-6-[1,3-bis(methoxycarbonyl)-2-propyl]-5-decene (12b): ^{1}H NMR δ 7.45 (m, 2H), 7.25 (m, 3H), 4.60 (s, 1H), 3.78 (s, 6H), 2.5 (m, 2H), 2.2 (m, 2H), 1.5–1.1 (m, 8H), 0.90 (t, 3H), 0.80 (t, 3H); ^{13}C NMR δ 168.5, 136.2, 135.1, 132.7, 130.7, 129.1, 126.9, 54.2, 52.6, 35.3, 34.6, 31.7, 31.5, 23.0, 22.2, 13.9; IR (neat) 1740, 1579 cm^{-1}; MS (EI) m/z 368 (M$^+$), 309, 211 (M – SePh)$^+$, 179, 157, 137, 95.

Attempted Addition of 2b to Octene. A mixture of 450 mg (1.0 mmol) of **2b** and 1.11 g (9.9 mmol) of octene was photolyzed for 17 h. Analysis of the crude reaction mixture by GC/MS showed the formation of PhSeSePh (m/z 314) and **13b** (m/z 260), accompanied by the absence of unreacted **2b**. The mixture was eluted through a column of Florisil to remove PhSeSePh and unreacted octene. Subsequent elution with ether gave a solution which yielded 80.6 mg (61%) of **13b** after removal of solvents by rotary evaporation: mp 119.5–120 °C (lit.[14] mp 121 °C); ^{1}H NMR δ 3.90 (s).

Photolysis of Ditolyl Diselenide, 2a, and Octene. A mixture of 46.9 mg (0.42 mmol) octene, 247 mg (0.86 mmol) of **2a**, and 301 mg (0.88 mmol) ditolyl diselenide was dissolved in 2 mmol of benzene and photolyzed for 36 h. Analysis of the crude reaction mixture by GC/MS showed addition products **15** (m/z 400) and **16** (m/z 414) in a 1:2 ratio. A mixture consisting of **15** and **16** was isolated from the crude reaction mixture by MPLC to give 35 mg of material corresponding to a 6% yield of **15** and a 12% yield of **16**.

Photolysis of Ditolyl Diselenide and 2a. A mixture of 340 mg (1 mmol) of ditolyl diselenide and 288 mg (1 mmol) of **2a** in 3 mL of benzene were photolyzed for 18 h. Analysis of the crude reaction mixture by GC/MS showed the presence of **17** (m/z 302) and unreacted **2a** (m/z 288 (M$^+$)) in a 1:1 ratio, in addition to PhSeSePh (m/z 314 (M$^+$)), PhSeSeTol (m/z 328 (M$^+$)), and TolSeSeTol (m/z 342 (M$^+$)).

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