Additions of Organocopper Reagents and Heteroatom Nucleophiles to 1-Phenylseleno-2-(*p*-toluenesulfonyl)ethyne. Preparation of Vinyl and Allenic Sulfones and Formation of Michael, Anti-Michael, and Rearrangement Products

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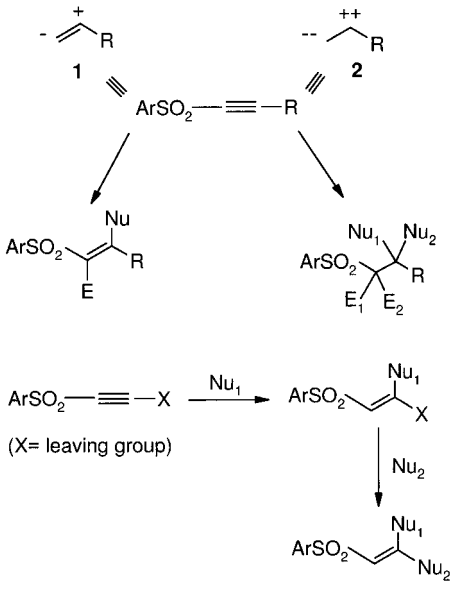
1-Phenylseleno-2-(*p*-toluenesulfonyl)ethyne (**4**) was produced nearly quantitatively from *p*-(toluenesulfonyl)ethyne and benzeneselenenyl chloride. It underwent stereo- and regioselective syn-additions of organocopper reagents RCu(CN)Li to the *β*-position of the sulfone moiety to afford adducts **5**. Further reaction of the products with reagents RCu(SePh)Li resulted in substitution of the phenylseleno group with retention of configuration. Control of *E*,*Z*-stereochemistry in the product *β*,*β*-disubstituted vinyl sulfones is therefore achieved by the order of addition of the reagents. Selenoxide syn-elimination of adducts **5** afforded the corresponding allenic sulfones. The additions of amines and alkoxides to **4** produced the corresponding anti-Michael regioisomers (where attack occurred α to the sulfone group) as the major or sole products. The additions were highly stereoselective, proceeding by anti-addition in the anti-Michael series and by syn-addition in the corresponding Michael regioisomers. The reactions of **4** with thiolates and selenolates were more complex, affording rearranged adducts and Michael adducts as the major and minor products, respectively. The formation of the rearranged products can be rationalized by a series of addition−elimination processes. Phenylselenoethyne (**43**) underwent conjugate additions of pyrrolidine, sodium methoxide, sodium ethanethiolate, and benzeneselenolate anion, affording the corresponding cis isomers via anti-addition. The experiments with heteroatom nucleophiles and acetylenes **4** and **43** show that the phenylseleno group has a surprisingly large activating effect upon conjugate additions.

Unsaturated sulfones have numerous uses in organic synthesis.[1] The sulfone group, like the carbonyl group, has an activating effect upon an adjacent carbon−carbon double or triple bond with respect to conjugate additions and cycloadditions. The resulting products are saturated or vinyl sulfones that can be further elaborated via reactions of the corresponding sulfone-stabilized α-carbanions with electrophiles. Furthermore, subsequent reductive desulfonylation permits the sulfone moiety to act as a temporary activating group. Thus, for example, acetylenic sulfones function as the synthetic equivalents of dipoles and "multipoles", such as **1** and **2** in Scheme 1.

In principle, further opportunities for synthetic transformations that can be used in conjunction with the above become possible if an appropriate nucleofuge is installed at the *β*-position of an acetylenic sulfone. This provides the site for the introduction of an additional nucleophile by substitution of the nucleofuge (Scheme 1) or for the regeneration of unsaturation by its elimination. It appeared to us that the phenylseleno group might be an appropriate *β*-substituent for this purpose, since certain *β*-selenovinyl sulfones are known to undergo substitution reactions of the selenium moiety with organocuprates[2] and other nucleophiles,[3,4] as well as syn-elimination reactions of their corresponding selenoxides.[5,6] We now report the preparation of the novel title compound **4** and its reactions with organocopper reagents and various heteroatom nucleophiles.[7]

Scheme 1



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(1) (a) Simpkins, N. S. *Sulphones in Organic Synthesis*, Pergamon Press: Oxford, 1993. (b) Fuchs, P. L.; Braish, T. F. *Chem. Rev.* **1986**, *86*, 903. (c) Trost, B. M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 107. (c) Simpkins, N. S. *Tetrahedron* **1990**, *46*, 6951. (d) Tanaka, K.; Kaji, A. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Wiley: Chichester, 1988; Chapter 15.

(2) Back, T. G.; Collins, S.; Krishna, M. V.; Law, K.-W. *J. Org. Chem.* **1987**, *52*, 4258.

(3) (a) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1987**, *52*, 4265. (b) Back, T. G.; Collins, S.; Law, K.-W. *Can. J. Chem.* **1985**, *63*, 2313.

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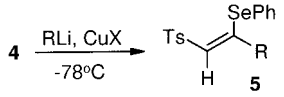
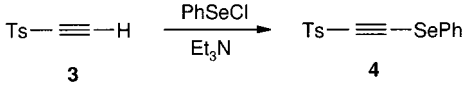
Table 1. Reactions of 4 with Organocopper Reagents



entry	CuX	RLi (equiv)	solvent[a]	product[b]	yield,[c] %
1	CuI	MeLi (1)	THF	**5a**	67
2	CuI	MeLi (2)	THF	**5a**	68
3	CuBr	MeLi (1)	THF, Me_2S	**5a**	53
4	CuSePh	MeLi (1)	THF	**5a**	71
5	CuSePh	MeLi (1)	THF, HMPA	**5a**	67
6	CuCN	MeLi (1)	THF	**5a**	64
7	CuCN	MeLi (2)	THF	**5a**	64
8	CuCN	MeLi (1)	Et_2O	**5a**	52
9	CuCN	MeLi (1)	THF, HMPA	**5a**	78
10	CuCN	*n*-BuLi (1)	THF, HMPA	**5b**	72
11	CuCN	PhLi (1)	THF, HMPA	**5c**	78

[a] Where Me_2S or HMPA was included, 5 equiv was used. [b] All products were pure (*Z*)-isomers. [c] Isolated yields are reported.

Scheme 2



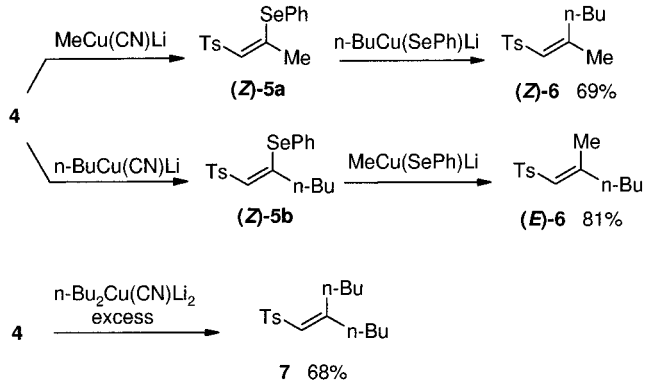
(Ts = p-toluenesulfonyl)

Results and Discussion

Reactions with Organocopper Reagents. Acetylenic sulfone **4** was conveniently prepared in nearly quantitative yield by the treatment of *p*-toluenesulfonylethyne (**3**)[8] with benzeneselenenyl chloride and triethylamine (Scheme 2). Since **3** is base-sensitive, it is necessary to premix the selenenyl chloride and triethylamine, and to add the acetylenic sulfone **3** last. The product **4** is a crystalline, odorless solid that can be stored in the freezer (−25 °C) for several months.

Since organocopper reagents undergo conjugate additions to acetylenic sulfones,[9] and effect substitutions of leaving groups in the β-position of vinyl sulfones,[10] we investigated the reactions of **4** with various organocopper species. The results are shown in Table 1. Typically, the reactions were performed in THF solution at −78 °C. Both organocopper reagents of the type RCuXLi and Gilman reagents (R_2CuLi) were successfully employed in this process, and a variety of Cu(I) salts proved effective. In the case of the methyl series **5a**, the best result was obtained with CuCN and 1 mol of MeLi in the presence of 5 equiv of HMPA (entry 9). Comparable results were obtained with R = *n*-Bu (**5b**) and R = Ph (**5c**) under these conditions (entries 10 and 11, respectively). The replacement of THF with ether gave a slightly lower yield (cf. entry 6 and entry 8). When HMPA was omitted from the reaction of **4** with the *n*-butylcopper reagent, partial isomerization of the product occurred to afford a mixture of the vinyl sulfone **5b** and its corresponding allylic sulfone isomer. The treatment of **4** with either methyllithium in the absence of a copper(I) salt or with methylmagnesium bromide in the presence or absence of catalytic amounts of copper(I) salts failed to produce the adduct **5a**. The β-(phenylseleno)vinyl sulfone products **5** were formed by a highly stereoselective syn-addition, affording the corresponding *Z*-isomers as the only significant products. The stereochemistry of **5a** and **5b** was confirmed by NOE experiments and by their further conversion to allenic sulfones (vide infra). That of **5c** was inferred by analogy.

Scheme 3



The substitutions of phenylseleno groups in (*E*)-β-(phenylseleno)vinyl sulfones by organocopper compounds of the type RCu(SePh)Li proceed stereospecifically with retention of configuration.[2] This reaction can be used in conjunction with the processes in Table 1 to permit the stereospecific preparation of either geometric isomer of β,β-disubstituted vinyl sulfones. This is illustrated in Scheme 3, where the order of addition of the two organocopper reagents determines the geometry of the complementary products (*E*)-**6** and (*Z*)-**6**. Moreover, treatment of **4** with an excess of the higher order[11] cuprate *n*-$Bu_2CuCNLi_2$ afforded **7**, the product of both formal conjugate addition and substitution.

In connection with another project, we required the β,β-disubstituted vinyl sulfone **8**, which, by analogy to Scheme 3, should be available from the treatment of **4** with an organocopper species derived from the homoallylic iodide **9**, followed by substitution of the phenylseleno group with an acyl anion equivalent. However, when iodide **9** was transmetalated with *tert*-butyllithium, followed by treatment with CuCN under the usual conditions (THF, HMPA), the unexpected conjugate addition product **10** was obtained instead (Scheme 4). The latter product was presumably formed by the known fragmentation of THF with *tert*-butyllithium to form

(4) Substitutions of the selenium moiety in other types of vinyl selenides with organometallic reagents and other nucleophiles are also known. For a review, see: (a) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *synthesis* **1997**, 373. For recent examples of coupling reactions of vinyl selenides with organometallic reagents, see: (b) Hevesi, L.; Hermans, B.; Allard, C. *Tetrahedron Lett.* **1994**, *35*, 6729. (c) Zhu, L.-S.; Huang, X. *Synth. Commun.* **1997**, *27*, 39.

(5) (a) Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077. (b) Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438.

(6) Simple vinyl selenoxides eliminate to afford acetylenes preferentially when an olefinic *cis*-hydrogen is available; otherwise allenes are obtained. See: Reich, H. J.; Willis, W. W., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 5967.

(7) Preliminary communication: Back, T. G.; Wehrli, D. *Tetrahedron Lett.* **1995**, *36*, 4737.

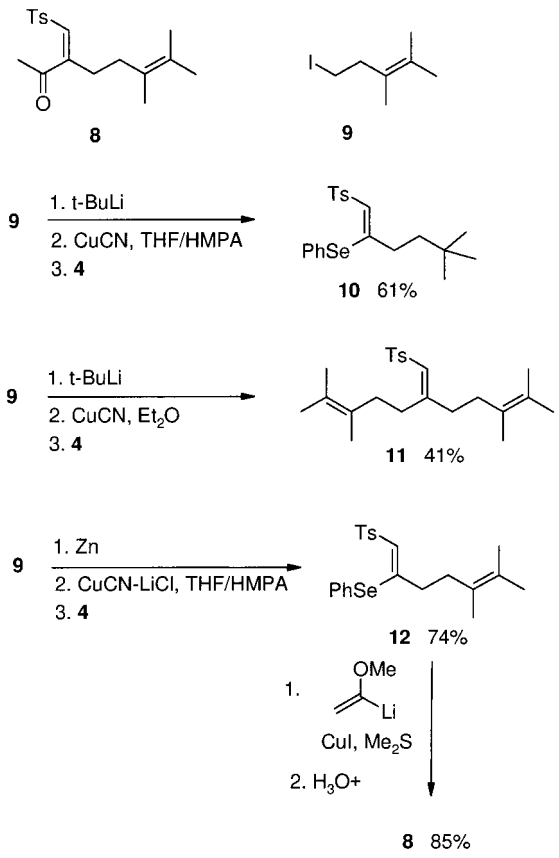
(8) Bhattacharya, S. N.; Josiah, B. M.; Walton, D. R. M. *Organomet. Chem. Synth.* **1970/1971**, *1*, 145.

(9) (a) Fiandanese, V.; Marchese, G.; Naso, F. *Tetrahedron Lett.* **1978**, 5131. (b) Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 14. In contrast to organocopper reagents, organolithium and Grignard reagents react with acetylenic sulfones by substitution of the sulfone moiety (alkyldesulfonylation): (c) Smorada, R. L.; Truce, W. E. *J. Org. Chem.* **1979**, *44*, 3444. (d) Eisch, J. J.; Behrooz, M.; Galle, J. E. *Tetrahedron Lett.* **1984**, *25*, 4851.

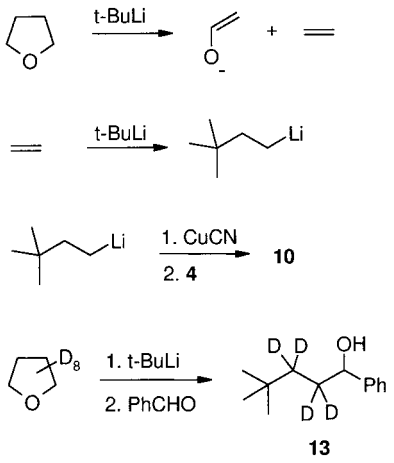
(10) (a) Truce, W. E.; Borel, A. W.; Marek, P. J. *J. Org. Chem.* **1976**, *41*, 401. (b) Giblin, G. M. P.; Simpkins, N. S. *J. Chem. Soc., Chem. Commun.*, **1987**, 207.

(11) (a) Lipshutz, B. H. *Synlett* **1990**, 119. (b) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005.

Scheme 4



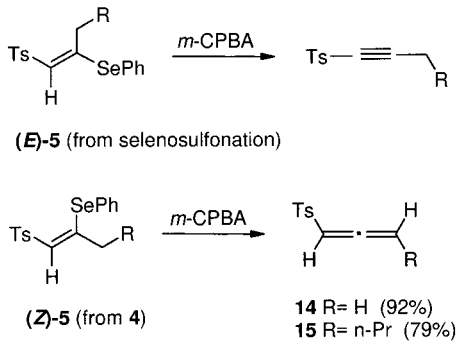
Scheme 5



ethylene,[12] followed by the addition of a second equivalent of *tert*-butyllithium to the latter, as shown in Scheme 5. This was confirmed by the formation of the tetradeuterated product **13** when the reagent generated from *tert*-butyllithium and **9** under similar conditions in perdeuterated THF was quenched with benzaldehyde. When ether was used instead of THF in the reaction with **4**, more complex reaction mixtures ensued, from which the bis-adduct **11** was the only homogeneous product that could be isolated (Scheme 4). Finally, the desired adduct **12** was obtained in good yield via prior formation of the corresponding organozinc derivative[13] from iodide **9**, followed by treatment with CuCN·2LiCl complex and then **4**. The conversion of **12** to the desired **8** was

(12) Jung, M. E.; Blum, R. B. *Tetrahedron Lett.* **1977**, 3791.

Scheme 6



achieved with the cuprate derived from α-methoxyvinyllithium and CuI·SMe_2 (Scheme 4).[14] These experiments show that a variety of β,β-disubstituted vinyl sulfones can be prepared stereoselectively from **4**. Since various β-substituted vinyl sulfones are themselves known to undergo conjugate additions of organocopper reagents,[15a] as well as α-deprotonation and reaction with electrophiles,[15b] these experiments also confirm that **4** can be employed as the synthetic equivalent of the hypothetical dipoles and multipoles **1** and **2**.

It is also noteworthy that the free-radical selenosulfonation of acetylenes[5] affords β-(phenylseleno)vinyl sulfones that have the opposite stereochemistry (i.e., where the PhSe and Ts groups are trans) compared to the products **5** in Table 1 (where the PhSe and Ts groups are cis). When the former products are subjected to selenoxide syn-elimination, they afford acetylenic sulfones exclusively.[5] On the other hand, since the olefinic hydrogen atoms in compounds **5** are trans to the selenium moiety, oxidation and syn-elimination lead exclusively to the corresponding allenic sulfone. The present protocol is therefore complementary to the earlier selenosulfonation-based methodology and permits the synthesis of allenic sulfones such as **14** and **15**, in lieu of acetylenic sulfones that are available from the previous method (Scheme 6).

Reactions with Heteroatom Nucleophiles. We next investigated the reactions of **4** with a series of heteroatom nucleophiles, including representative amines, alkoxides, thiolates, and selenolates. The expectation was that conjugate addition to the β-position of the sulfone moiety would occur,[16] possibly followed by addi-

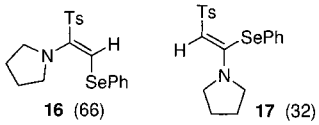
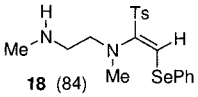
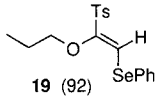
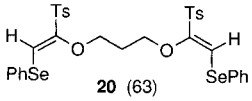
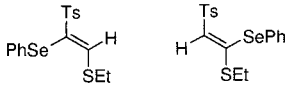
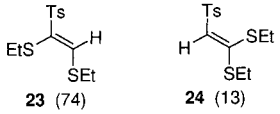
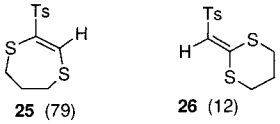
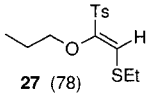
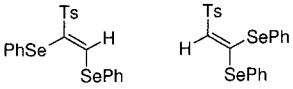
(13) The procedure was based on a similar copper-mediated conjugate addition of an organozinc reagent reported by Nakamura, E. In *Organocopper Reagents—A Practical Approach*; Taylor, R. J. K., Ed.; Oxford University Press: Oxford, 1994; pp 135–136.

(14) For the preparation of 1-methoxyvinyllithium, see: (a) Baldwin, J. E.; Höfle, G. A.; Lever, O. W., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 7125. For use of the corresponding cuprates, see: (b) Chavdarian, C. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1975**, *97*, 3822.

(15) (a) See ref 1a, pp 189–194 for examples. (b) See ref 1a, pp 138–142 for examples.

(16) For additions of amines, see: (a) Truce, W. E.; Brady, D. G. *J. Org. Chem.* **1966**, *31*, 3543. (b) Truce, W. E.; Markley, L. D. *J. Org. Chem.* **1970**, *35*, 3275. (c) Truce, W. E.; Onken, D. W. *J. Org. Chem.* **1975**, *40*, 3200. (d) Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5863. (e) Pink, R. C.; Spratt, R.; Stirling, C. J. M. *J. Chem. Soc.* **1965**, 5714. (f) McMullen, C. H. Stirling, C. J. M. *J. Chem. Soc. B* **1966**, 1217. (g) McDowell, S. T.; Stirling, C. J. M. *J. Chem. Soc. B* **1967**, 351. (h) Cossu, S.; De Lucchi, O.; Durr, R. *Synth. Commun.* **1996**, *26*, 4597. For additions of alkoxides see ref 16d. For additions of thiols and thiolates, see: (i) Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5856. (j) Truce, W. E.; Tichenor, G. J. W. *J. Org. Chem.* **1972**, *37*, 2391. (k) Selling, H. A. *Tetrahedron* **1975**, *31*, 2387. For double additions of nucleophiles, see: (l) Cinquini, M.; Cozzi, F.; Pelosi, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1430. (m) Cossu, S.; De Lucchi, O.; Fabris, F.; Ballini, R.; Bosica, G. *Synthesis* **1996**, 1481.

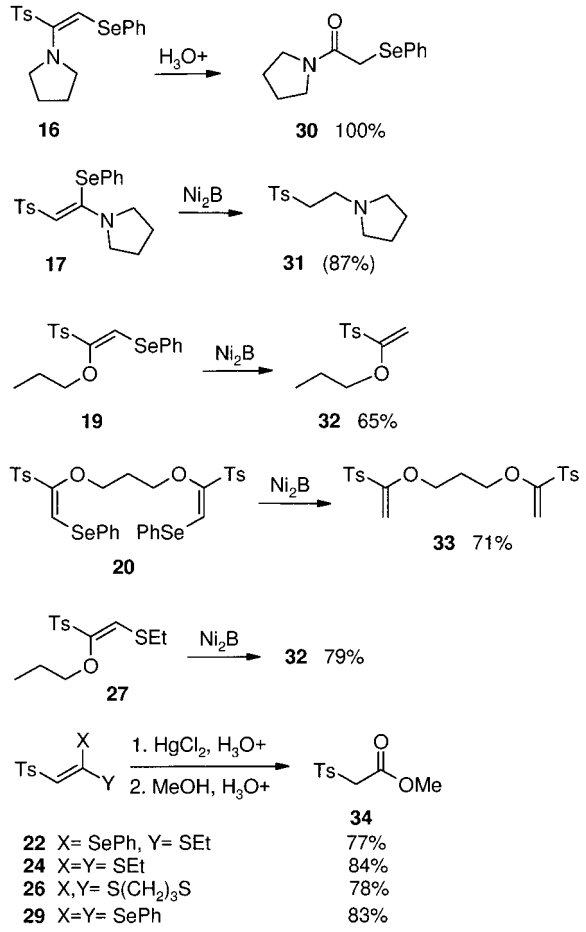
Table 2. Reactions of 4 with Heteroatom Nucleophiles

Entry	Nucleophile	Products (isolated yield, %)
1	pyrrolidine	 **16** (66) **17** (32)
2	$MeNHCH_2CH_2NHMe$	 **18** (84)
3	n-PrONa	 **19** (92)
4	$NaOCH_2CH_2CH_2ONa$	 **20** (63)
5	NaSEt	 **21** (81) **22** (16)
6	NaSEt (2 equiv)	 **23** (74) **24** (13)
7	$NaSCH_2CH_2CH_2SNa$	 **25** (79) **26** (12)
8	NaSEt (with **19**)	 **27** (78)
9	NaSePh	 **28** (62) **29** (32)

tion−elimination with a second mol of the nucleophile, resulting in overall substitution of the phenylseleno group (as in Scheme 1). The results are shown in Table 2.

The reaction of pyrrolidine with **4** afforded two isolable products **16** and **17** in high combined yield (entry 1). A similar reaction with *N*,*N*′-dimethylethylenediamine produced the less stable 1:1 adduct **18** (entry 2), while a primary amine, cyclohexylamine, formed complex mixtures of presumably polymeric materials. Sodium *n*-propoxide afforded the unique stereo- and regioisomer **19** in excellent yield (entry 3), while sodium 1,3-propanedialkoxide gave the 2:1 adduct **20** (entry 4), even under conditions of high dilution and slow addition of **4**. In each case, surprisingly, the principal or sole product was formed by an anti-Michael addition,[17] and each

Scheme 7



product was obtained as a unique geometric isomer. The regiochemistry of the products was determined by the relatively low-field chemical shifts of the olefinic protons in the anti-Michael adducts[18] and, unequivocally, by further chemical transformations of products **16**, **17**, **19**, and **20** as shown in Scheme 7. Thus, hydrolysis of **16** afforded the *β*-selenoamide **30**, while nickel boride-mediated deselenization[19] of **17**, **19**, and **20** produced the *β*-amino sulfone **31** and the α-alkoxyvinyl sulfones **32** and **33**, respectively. The indicated stereochemistry of **16**, **17**, **19**, and **20** was tentatively assigned on the basis of NOE experiments. The regio- and stereochemistry of the unstable product **18** was inferred by comparison of its NMR spectrum with those of **16** and **17**, respectively.

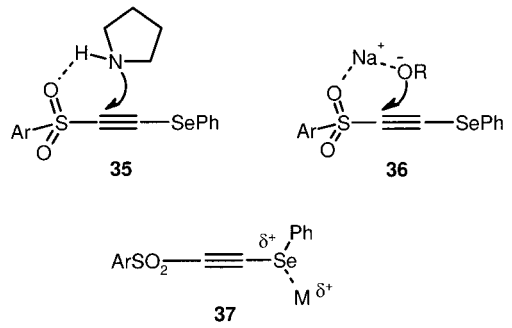
The predominantly anti-Michael regiochemistry in the additions of amines and alkoxides to **4** was unexpected, since conjugate additions of such nucleophiles to acetylenic sulfones are well known,[16a−h] while those to acetylenic selenides are, to our knowledge, unprecedented. Some examples of anti-Michael additions to other types of acceptors have been previously reported and attributed to SET reactions,[20] complexation effects,[21] intramolecular additions,[22] or the presence of electron-withdrawing *β*-substituents.[23] Anti-Michael regioisomers have also

(17) Strictly speaking, the term "Michael addition" has been defined as the addition of a carbanion to an unsaturated system conjugated with an activating group. See: Perlmutter, P. In *Conjugate Addition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1992; p 2. However, for convenience we will include heteroatom nucleophiles in the definition and refer to additions of nucleophiles to the *β*-position and α-position of the sulfone moiety of **4** as "Michael" and "anti-Michael", respectively.

(18) The related analogues where the PhSe moiety of the products in Table 2 is replaced by RS have a consistently lower calculated chemical shift for the olefinic protons in the anti-Michael vs the Michael series of products. See: Jackman, L. M.; Sternhell, S. In *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon Press: Oxford, 1969; pp 184−185.

(19) Back, T. G.; Birss, V. I.; Edwards, M.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 3815.

Scheme 8



been observed, among other products, in the additions of thiols to 2-arylalkynyl sulfones, particularly where the aryl group contained electron-withdrawing substituents.[16k] In an attempt to provide further insight into the surprising regiochemistry observed with **4**, we performed several additional experiments.

First, we separately subjected each of the pure regioisomers **16** and **17** to the identical reaction conditions under which they were formed. No equilibration was observed, and each product was recovered intact. This rules out the possibility that the expected Michael adduct **17** is formed initially from pyrrolidine and **4** under kinetic conditions but subsequently equilibrates to the 67:33 mixture of isomers **16** and **17** observed in entry 1 of Table 2.

Second, we considered that preorganization of the reactants via hydrogen bonding with the sulfone oxygen atoms in the case of amines (i.e., as in **35**) or via coordination with the metal counterion in the case of alkoxides (i.e., as in **36**) could promote a preferential 5-*exo*-*dig* addition,[24] resulting in the observed anti-Michael regiochemistry (Scheme 8). When the addition of pyrrolidine to **4** was repeated in ethanol, a protic solvent that might be expected to disrupt hydrogen bonding between the reactants, the ratio of **16**:**17** was very similar (73:27) to that observed in aprotic THF (67:33). An explanation based on hydrogen bonding is therefore tenuous. Interestingly, the inclusion of various metal salts in the reaction mixture of pyrrolidine and **4** in THF resulted in strong enhancement of anti-Michael regioselectivity. Thus, when 5 molar equiv of LiCl was added, the ratio of **16**:**17** was 86:14, while with 1 mol of CsCl, $NiCl_2$, or $HgCl_2$, the ratio increased to 92:8, 92:8, and >95:5, respectively. This could be the result of coordination of the metal with the selenium atom of **4**, as in **37**, which would increase the positive character of the selenium substituent, thereby promoting anti-Michael regiochemistry (Scheme 8). Such coordination is expected to be strongest with soft, selenophilic metal cations such as mercury(II). The less regioselective, but still predominantly anti-Michael addition observed in the absence of added metal ions, however, is not explained by the above experiments.

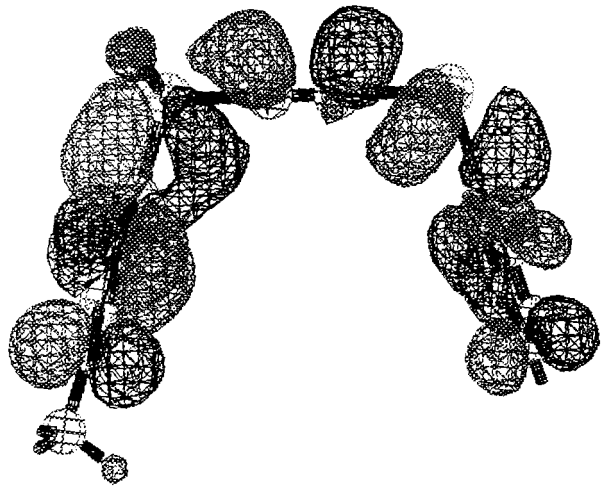


Figure 1. LUMO of **4**. The structure is shown with the acetylenic moiety horizontal, the Ts substituent on the left, and the SePh group on the right. The indicated conformation may represent a local energy minimum and not necessarily the global minimum.

Ab initio calculations were performed on **4** (Spartan Version 4.1, Hartree−Fock method using the 3-21G* basis set). The LUMO of **4**, which is the frontier orbital expected to interact with a nucleophile,[25] is shown in Figure 1. The nearly even distribution of the MO over the two acetylenic carbon atoms indicates that the effects of the sulfone and selenide substituents are remarkably similar. This is consistent with competitive Michael and anti-Michael additions to **4** under kinetic control but does not explain the strongly favored or exclusive formation of anti-Michael products in entries 1−4.

We next investigated the reactions of **4** with thiolate and selenolate nucleophiles. When an equimolar amount of sodium ethanethiolate was used, two products were obtained in excellent combined yield (entry 5, Table 2). The minor product proved to be the Michael adduct **22**, while the major product **21** was formed by rearrangement, resulting in geminal selenide and sulfone groups. When 2 mol of the thiolate was added to **4**, products **23** and **24** were obtained, probably from the addition−elimination of the second mole of thiolate to the initially formed monoadducts **21** and **22** (entry 6). As in entry 6, but in contrast to the more weakly nucleophilic dialkoxide in entry 4, disodium 1,3-propanedithiolate produced the 1:1 adducts **25** and **26** (entry 7), while adduct **19** reacted with ethanethiolate to afford the substitution product **27** (entry 8). Finally, benzeneselenolate anion[26] reacted with **4** to give the Michael adduct **29** as the minor product and **28** as the major product (entry 9). Since its two selenium substituents are identical, the structure of **28** does not

(20) (a) Holm, T.; Crossland, I.; Madsen, J. O. *Acta Chem. Scand. B* **1978**, *32*, 754. (b) For an example where radical intermediates were considered but could not be detected, see: Gerold, A.; Krause, N. *Chem. Ber.* **1994**, *127*, 1547.

(21) (a) Klumpp, G. W.; Mierop, A. J. C.; Vrielink, J. J.; Brugman, A.; Schakel, M. *J. Am. Chem. Soc.* **1985**, *107*, 6740. (d) For a related review, see: Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356.

(22) Rudorf, W.-D.; Schwarz, R. *Synlett* **1993**, 369.

(23) (a) Bumgardner, C. L.; Bunch, J. E.; Whangbo, M.-H. *J. Org. Chem.* **1986**, *51*, 4082. (b) Martin, V.; Molines, H.; Wakselman, C. *J. Org. Chem.* **1992**, *57*, 5530. (c) Ponticello, G. S.; Freedman, M. B.; Habecker, C. N.; Holloway, M. K.; Amato, J. S.; Conn, R. S.; Baldwin, J. J. *J. Org. Chem.* **1988**, *53*, 9.

(24) According to Baldwin's rules, both 5-*exo*-*dig* and 6-*endo*-*dig* closures are favored: Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734. However, for a precedent where an intramolecular conjugate addition to another acetylenic Michael acceptor proceeded preferentially by 5-*exo*-*dig* closure, resulting in anti-Michael regiochemistry, see ref 22.

(25) Fleming, I. In *Frontier Orbitals and Organic Chemical Reactions*; Wiley: Chichester, 1976.

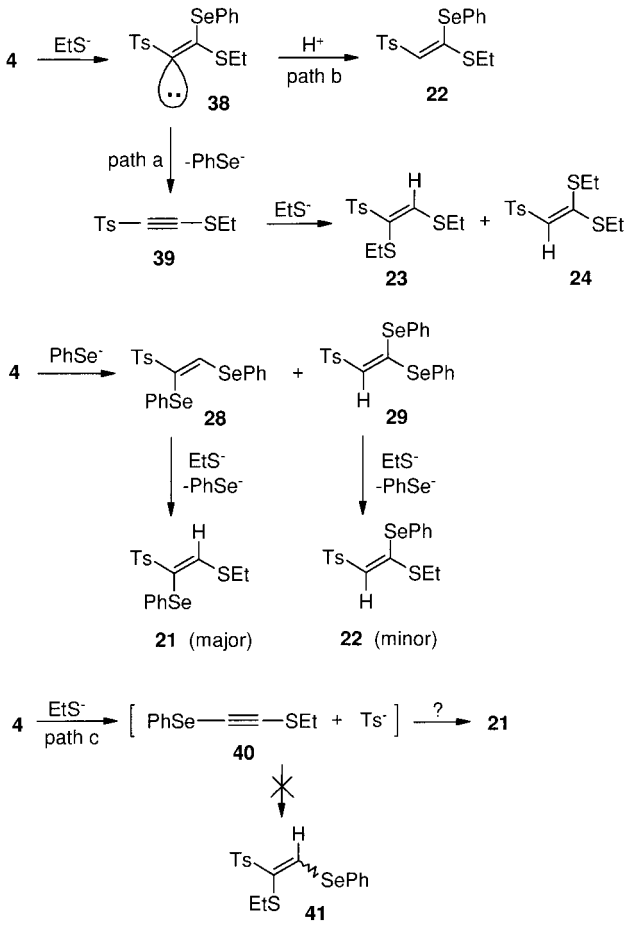
(26) When generated in this manner, the selenolate is actually formed as a borane complex rather than as a sodium selenolate. See: Monahan, R.; Brown, D.; Waykole, L.; Liotta, D. In *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley: New York, 1987; Chapter 4.

reveal whether it is formed by an anti-Michael addition to **4** or by a rearrangement analogous to the formation of **21**.

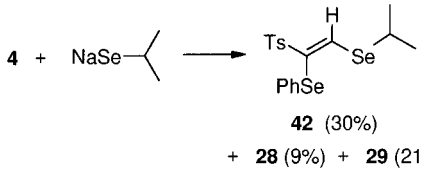
The structures of the products in entries 5−9 in Table 2 were determined by standard spectroscopic methods as well as by the following additional experiments. Hydrolysis of the mixed ketene selenothioacetal **22**, the ketene dithioacetals **24** and **26**, and the ketene diselenoacetal **29**, followed by esterification in methanol, afforded the same product **34** in each case (Scheme 7), thus confirming their regiochemistry, and therefore also that of their regioisomers **21**, **23**, **25**, and **28**, respectively. The regiochemistry of **27** was ascertained by its desulfurization with nickel boride[27] to afford the same product **32** obtained previously from the deselenization of **19** (Scheme 7). The geometry of **21** and **28** was shown to be *Z* by means of X-ray crystal structures,[28] while that of **22**, **23**, and **27** was tentatively indicated to be *Z*, *E*, and *E*, respectively, by NOE experiments.

A plausible mechanism for the formation of the rearranged product **21** in entry 5 of Table 2 is shown in Scheme 9. The elimination of selenolate anion from the initially formed intermediate **38** produces the acetylene **39** (path a). The selenolate is a powerful nucleophile that competes with the original thiolate and adds to **4** to generate the regioisomers **28** and **29**. These undergo further addition−elimination with the thiolate to afford the major and minor products **21** and **22**. Although the intermediate **39** could not be isolated from this reaction, several considerations and additional observations support the mechanism in Scheme 9. First, it is worth noting that the quantitative formation of the acetylene **39** is not necessary in the scheme, since the required selenolate anion that is simultaneously formed plays a catalytic role and is regenerated in the final step leading to **21** and **22**. Second, careful NMR analysis of the crude reaction mixture revealed small amounts (<5%) of the postulated intermediates **28** and **29**, as well as **23** and **24**, the expected products of thiolate addition to the acetylene **39**. Third, control experiments were performed with authentic **28** and **29** (obtained from entry 9 in Table 2), in which they were separately treated with sodium ethanethiolate, affording **21** and **22**, respectively, as required by the mechanism in Scheme 9. There was no crossover between the two systems and each product was formed stereospecifically. Finally, when the reaction was repeated with ethanethiol and triethylamine instead of sodium ethanethiolate, the yield of the previously minor product **22** increased from 16% to 64% at the expense of the previously major product **21**. This is consistent with the presence of triethylammonium ion in the reaction mixture, which can act as a proton donor to **38**, thereby facilitating reaction via path b in Scheme 9. We also considered the possibility that the rearrangement occurs via the elimination of *p*-toluenesulfinate anion, followed

Scheme 9



Scheme 10



by its readdition to the acetylene **40** (path c). While this possibility cannot be entirely ruled out, the failure to observe any significant amounts of the regioisomer **41**, which would be expected to accompany **21** during the reaction of **40** with the sulfinate anion, makes path c less likely. Further experiments are still required to establish the mechanism of the rearrangement unequivocally.

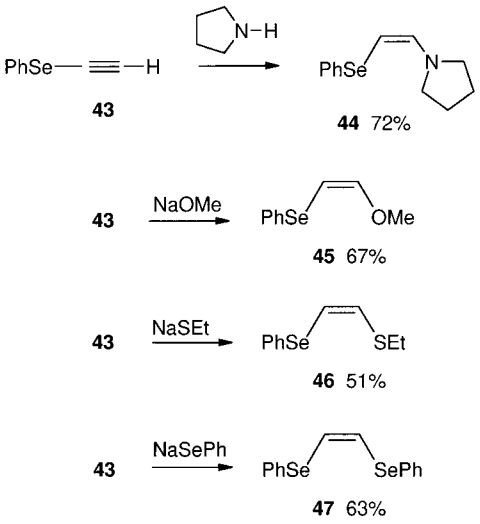
The minor adduct **29** in entry 9 of Table 2 is consistent with a Michael addition of the selenolate to **4**. However, it is not possible to differentiate between an anti-Michael addition or a rearrangement similar to the one in Scheme 9 to account for the major product **28**, because of the identical phenylseleno substituents. When a different selenolate (isopropyl instead of phenyl) was used, the formation of the major product **42** in addition to smaller amounts of **28** and **29** (Scheme 10) confirmed the rearrangement pathway. The structure of product **42** was confirmed by NOE experiments.

The stereoselectivity of the reactions in Table 2 is also noteworthy. The conjugate additions of secondary amines to acetylenic sulfones typically proceed via an initial anti addition (where N and H are trans), followed by equilibration to their thermodynamically more stable geometric isomers (where N and H are cis).[16a−d,f] Similarly, meth-

(27) Nickel boride readily cleaves sulfide and sulfoxide functions but not sulfones: (a) Back, T. G.; Yang, K.; Krouse, H. R. *J. Org. Chem.* **1992**, *57*, 1986. (b) Back, T. G.; Baron, D.; Yang, K. *J. Org. Chem.* **1993**, *58*, 2407.

(28) (a) The structure of **21** was tentatively shown as the anti-Michael adduct in our preliminary communication (ref 7), based on NMR data. Its X-ray crystal structure clearly indicates that it is the rearranged product shown here. (b) Very recently, **28** of unspecified geometry was also obtained from the reaction of a *p*-toluenesulfonylalkynyliodonium triflate with benzeneselenolate anion, presumably via the formation of **4** as an intermediate: Stang, P. J.; Murch, P. *Synthesis* **1997**, 1378.

Scheme 11



oxide ion has been reported to add kinetically by anti-addition, but the product isomerizes readily to the corresponding *trans*-β-methoxyvinyl sulfone (product of syn-addition).[16d] Presumably, dipole repulsions between the sulfone and amino or methoxy groups drive the equilibrium toward the syn-adducts. On the other hand, thiolates generally undergo anti-addition to acetylenic sulfones, although exceptions are known.[16j] Thus, the *Z* geometry of the Michael adduct **17** (product of syn addition) is consistent with equilibration to minimize dipole repulsions. On the other hand, the anti-Michael adducts in Table 2 (**16**, **18**, **19**, and **20**) appear to be formed under kinetic control (anti-addition), since the absence of strong dipole repulsions between cis-oriented substituents provides less driving force for equilibration. The Michael adduct **22** appears to be the product of syn-addition, which is unusual for a thiolate nucleophile. The other products in the table that are capable of geometric isomerism (**21**, **23**, **27**, and **28**) are formed by more complex reaction pathways, making firm conclusions concerning the stereochemistry of their formation difficult.

The predominantly anti-Michael regiochemistry in entries 1−4 in Table 2 suggests that the phenylseleno group can be remarkably effective as an activating group in conjugate additions, competing effectively with the *p*-toluenesulfonyl group in some cases.[29] We therefore wished to determine whether a simple acetylenic selenide such as **43** would undergo similar conjugate additions as **4**. Although cuprate additions to **43** have been reported,[30] additions of simple heteroatom nucleophiles, to our knowledge, have not. Scheme 11 shows the results of the additions of pyrrolidine, sodium methoxide, and ethanethiolate and benzeneselenolate anion to the acetylenic selenide **43**. In each case, more forcing conditions were required than with similar additions to **4**, but the corresponding adducts **44**−**47** were obtained in reasonably high yield. Only the cis isomer was isolated in each case.[31]

(29) We have also noted that cycloadditions of **4** often show the opposite regiochemistry from that expected of normal acetylenic sulfones, again pointing to a strong directing effect of the selenium moiety. Back, T. G.; Wehrli, D. *Synlett* **1995**, 1123.

(30) Braga, A. L.; Reckziegel, A.; Silveira, C. C.; Comasseto, J. V. *Synth. Commun.* **1994**, *24*, 1165.

Conclusions

The novel title compound **4** is easily prepared from *p*-toluenesulfonylethyne and benzeneselenenyl chloride. It can be used in carbon−carbon bond-forming reactions with organocopper reagents by undergoing highly regioselective conjugate additions (Michael with respect to the sulfone substituent) with the first equivalent of reagent and substitution of the phenylseleno moiety with a second equivalent. The two steps proceed stereoselectively by syn-addition and with retention of configuration, respectively. The *E*,*Z*-stereochemistry of the resulting β,β-disubstituted vinyl sulfones is therefore determined by the order of addition of the copper reagents. These reactions, in conjunction with known transformations of the products (further conjugate additions, α-alkylations, desulfonylations) render **4** the synthetic equivalent of dipole and multipole species **1** and **2**. Moreover, selenoxide syn-elimination of the initial adducts **5** affords the corresponding allenic sulfones in a manner complementary to the previously described synthesis of acetylenic sulfones from the selenoxide elimination of the geometrical isomers of **5** that are available from the selenosulfonation of acetylenes.

The reactions of **4** with hard and soft heteroatom nucleophiles afford different types of products. The additions of hard nucleophiles (amines, alkoxides) produce the corresponding anti-Michael regioisomers as the major or sole products. The unexpected regiochemistry indicates that the selenium substituent is remarkably effective in activating the triple bond toward conjugate additions, outweighing the effects of the sulfone group. The additions are also highly stereoselective, proceeding by anti-addition in the anti-Michael series and by syn-addition in the corresponding Michael regioisomers.

The reactions of **4** with soft nucleophiles (thiolates and selenolates) are more complex, affording rearranged adducts and Michael adducts as the major and minor products, respectively. The formation of the rearranged products can be rationalized by a series of addition−elimination processes.

Phenylselenoethyne undergoes conjugate additions of both hard and soft nucleophiles, thereby confirming the ability of the selenide moiety to act as an activating group in the absence of other substituents. These reactions afforded the corresponding cis isomers via anti-addition.

Experimental Section

The following compounds were prepared by literature methods: **3**,[8] **43**,[30] 5-bromo-2,3-dimethyl-2-pentene,[32] copper(I) selenolate,[2] and diisopropyl diselenide.[33] Alkyllithiums were titrated[34] prior to use. *m*-CPBA was purified by washing with a phosphate buffer.[35] All other products were purchased

(31) The cis geometry of **45** and **46** was confirmed by typical cis coupling constants (J = 5.1 and 8.5 Hz, respectively) while *cis*-**47** is a known compound that also had appropriate J_{Se-H} couplings (see Experimental Section). The assignment of the cis geometry to adduct **44** is tentative and based largely on analogy with **45**−**47**. Neither the olefinic coupling constant (J = 12.9 Hz) nor NOE experiments gave conclusive evidence of cis−trans configuration. A referee has suggested that this may be due to rapid equilibration between cis and trans isomers in the case of **44**.

(32) De Silva, A. N.; Francis, C. L.; Ward, A. D. *Aust. J. Chem.* **1993**, *46*, 1657.

(33) The following general procedure was used: Strecker, W.; Willing, A. *Ber.* **1915**, *48*, 196.

(34) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87.

(35) Schwartz, N. N.; Blumbergs, J. H. *J. Org. Chem.* **1964**, *29*, 1976.

from commercial sources and purified by standard procedures as required. THF and ether were dried by distillation from lithium aluminum hydride.

1-Phenylseleno-2-(*p*-toluenesulfonyl)ethyne (4). Triethylamine (140 μL, 1.00 mmol) was added to a solution of benzeneselenenyl chloride (192 mg, 1.00 mmol) in diethyl ether (10 mL), and the solution was stirred for 5 min. A solution of *p*-toluenesulfonylethyne (**3**, 180 mg, 1.00 mmol) in diethyl ether (2 mL) was then added. After an additional 45 min of stirring at room temperature, the reaction was quenched with an NH_4Cl solution (10 mL). The separated organic phase was washed three times with an NH_4Cl solution, dried ($MgSO_4$), and evaporated in vacuo to leave a yellow oil, which was purified by rapid flash chromatography over silica gel (10% ether−hexanes) to afford **1** (325 mg, 97%) as white crystals: mp 72−75 °C (dec, from methanol−ether): IR (KBr) 2104, 1335, 1159 cm^{-1} ; ^1H NMR (200 MHz) δ 7.90 (d, J = 8.4 Hz, 2 H), 7.48 (dd, J = 7.0, 2.6 Hz, 2 H), 7.40−7.34 (m, 5 H), 2.47 (s, 3 H); ^{13}C NMR (50 MHz) δ 145.3, 138.9, 130.9, 130.1, 130.0, 128.7, 127.4, 125.0, 98.9, 82.9, 21.7; ^{77}Se NMR (276 MHz) δ 285.8 (relative to dimethyl selenide); mass spectrum, *m*/*z* (relative intensity, %) 336 (34, M^+), 280 (47), 192 (90), 91 (91), 77 (100). Anal. Calcd for $C_{15}H_{12}O_2SSe$: C, 53.74; H, 3.61. Found C, 53.43; H, 3.42.

(*Z*)-2-Phenylseleno-1-(*p*-toluenesulfonyl)-1-propene (5a) (Entry 9, Table 1). Methyllithium (714 μL, 1.40 M, 1.00 mmol) was added to a stirred suspension of copper(I) cyanide (90 mg, 1.0 mmol) in THF (4 mL) under argon at 0 °C. After 15 min, the solution was cooled to −78 °C and acetylene **4** (335 mg, 1.00 mmol) in THF (4 mL) was added, followed by HMPA (870 μL, 5.00 mmol). The solution was stirred at −78 °C for 2.5 h. The reaction mixture was then quenched with an NH_4Cl solution and warmed to room temperature. The reaction mixture was poured into ether (20 mL), extracted with an NH_4Cl solution (5 × 10 mL), and dried ($MgSO_4$). Evaporation of the solvent afforded a yellow oil that was flash chromatographed over silica gel (elution with 10% ethyl acetate−hexanes) to provide **5a** (274 mg, 78%) as white crystals: mp 78−80 °C (from hexanes): IR (CH_2Cl_2) 1560, 1311, 1144 cm^{-1}; ^1H NMR (200 MHz) δ 7.95 (d, J = 8.3 Hz, 2 H), δ 7.61 (dd, J = 8.1, 1.2 Hz, 2 H), 7.45−7.31 (m, 5 H), 6.52 (q, J = 1.2 Hz, 1 H), 2.47 (s, 3 H), 1.86 (d, J = 1.2 Hz, 3 H); NOE was observed between signals at δ 6.52 and 1.86; mass spectrum, *m*/*z* (relative intensity, %) 352 (53, M^+), 259 (7), 246 (14), 197 (37), 155 (60), 116 (82), 91 (100). Anal. Calcd for $C_{16}H_{16}O_2SSe$: C, 54.70; H, 4.59. Found C, 54.53; H, 4.47.

The same product **5a** was obtained in the yields indicated in entries 1−8 of Table 1 by similar procedures, with the variations indicated in the table.

(*Z*)-2-Phenylseleno-1-(*p*-toluenesulfonyl)-1-hexene (5b) (Entry 10, Table 1). *n*-Butyllithium (457 μL, 2.19 M, 1.00 mmol) was added to a stirred suspension of copper(I) cyanide (89 mg, 1.0 mmol) in THF (3 mL) under argon at −78 °C. The mixture was warmed to 0 °C until a clear solution was formed (15 min). The solution was cooled to −78 °C, and acetylene **4** (335 mg, 1.00 mmol) in THF (2 mL) was added, followed by HMPA (870 μL, 5.00 mmol). The mixture was stirred at −78 °C for 2 h and then worked up as in the preceding procedure to afford a yellow oil which was chromatographed over silica gel (elution with 10% ethyl acetate−hexanes) to afford **5b** (283 mg, 72%) as white crystals: mp 67−68 °C (from hexanes): IR (CH_2Cl_2) 1577, 1304, 1146 cm^{-1}; ^1H NMR (200 MHz) δ 7.90 (d, J = 8.3 Hz, 2 H), 7.63−7.58 (m, 2 H), 7.38−7.34 (m, 5 H), 7.23 (s, 1 H), 2.46 (s, 3 H), 2.25 (t, J = 7.8 Hz, 2 H), 1.57−1.18 (m, 4 H), 0.82 (t, J = 7.0 Hz, 3 H); NOE was observed between signals at δ 7.23 and 2.25; ^{13}C NMR (50 MHz) 147.4, 144.9, 133.7, 129.6, 129.3, 128.9, 127.5, 117.1, 110.6, 110.5, 59.9, 32.4, 22.0, 21.7, 13.7; mass spectrum, *m*/*z* (relative intensity, %) 394 (46, M^+), 248 (25), 238 (26), 157 (34), 91 (73), 81 (78), 69 (100); exact mass calcd for $C_{19}H_{22}O_2SSe$ 394.0508, found 394.0509.

(*Z*)-1-Phenyl-1-phenylseleno-2-(*p*-toluenesulfonyl)ethene (5c) (Entry 11, Table 1). Phenyllithium (555 μL, 1.80 M, 1.00 mmol) was added to a stirred suspension of copper(I) cyanide (89 mg, 1.0 mmol) in THF (3 mL) under argon at −78 °C. The suspension was warmed to 0 °C until a clear solution was formed (15 min). The solution was cooled to −78 °C, and acetylene **4** (335 mg, 1.00 mmol) in THF (2 mL) was added, followed by HMPA (870 μL, 5.00 mmol). The reaction mixture was stirred for an additional 2 h and quenched with NH_4Cl solution. The mixture was poured into ether (10 mL) and washed with an NH_4Cl solution (5 × 10 mL) until the washings remained colorless. The organic phase was then dried ($MgSO_4$) and filtered, and the solvent was evaporated in vacuo to yield a yellow oil which was chromatographed over silica gel (elution with 10% ethyl acetate−hexanes) to afford **5c** (322 mg, 78%) as white crystals: mp 115−117 °C (from ethanol); IR (CH_2Cl_2) 1555, 1302, 1142 cm^{-1}; ^1H NMR (200 MHz) δ 7.71−7.67 (m, 4 H), 7.59 (s, 1 H), 7.40−7.37 (m, 3 H), 7.31−7.25 (m, 7 H), 2.44 (s, 3 H); ^{13}C NMR (50 MHz) δ 144.4, 143.2, 138.2, 137.2, 135.0, 133.5, 132.5, 129.6, 129.5, 129.4, 128.7, 128.5, 128.2, 127.7, 21.6; mass spectrum, *m*/*z* (relative intensity, %) 414 (45, M^+), 259 (72), 178 (100), 157 (53), 91 (40), 77 (45); exact mass calcd for $C_{21}H_{18}O_2SSe$ 414.0197, found 414.0157.

(*Z*)-2-Methyl-1-(*p*-toluenesulfonyl)-1-hexene (*Z*-6).[10b] *n*-Butyllithium (227 μL, 2.21 M, 0.500 mmol) was added to a stirred suspension of copper(I) benzeneselenolate (110 mg, 0.500 mmol) in THF (2 mL) under argon at 0 °C. After 15 min, the solution was cooled to −78 °C and **5a** (176 mg, 0.500 mmol) in THF (1 mL) was added. The solution was warmed to 0 °C and stirred for 2 h. The reaction was quenched by adding an NH_4Cl solution. The heterogeneous mixture was poured into ether and washed with an NH_4Cl solution (5 × 10 mL). The organic phase was dried ($MgSO_4$), and the solvent was evaporated in vacuo to yield a yellow oil that was chromatographed over silica gel (elution with hexanes, then 7% ethyl acetate−hexanes) to afford ***Z*-6** (87 mg, 69%) as a colorless oil.[36]

(*E*)-2-Methyl-1-(*p*-toluenesulfonyl)-1-hexene (*E*-6).[10b] Methyllithium (217 μL, 1.19 M, 0.258 mmol) was added to a stirred suspension of copper(I) benzeneselenolate (57 mg, 0.26 mmol) in THF (1 mL) under argon at 0 °C. After 15 min, the solution was cooled to −78 °C and **5b** (103 mg, 0.262 mmol) in THF was added. The solution was warmed to 0 °C and stirred for 2 h. The reaction was worked up as in the preceding procedure to provide a yellow oil that was chromatographed over silica gel (elution with hexanes, then 7% ethyl acetate−hexanes) to afford ***E*-6** (53 mg, 81%) as a colorless oil.[36]

2-*n*-Butyl-1-(*p*-toluenesulfonyl)-1-hexene (7).[10a] *n*-Butyllithium (1.70 mL, 2.35 M, 4.00 mmol) was added to a suspension of copper(I) cyanide (179 mg, 2.00 mmol) in THF (1 mL) at −78 °C under argon. The mixture was allowed to warm to 0 °C and was kept there for 10 min. The resulting clear solution was cooled to −78 °C, and **4** (338 mg, 1.01 mmol) in THF (1 mL) was added. The mixture was stirred for 90 min at −78 °C, and then the reaction was quenched with a 10% aqueous solution of NH_4OH in saturated NH_4Cl (2 mL). The suspension was warmed to room temperature and stirred for an additional 30 min. The reaction mixture was poured into ether (10 mL) and extracted with the NH_4OH−NH_4Cl solution until the aqueous phase was colorless. The organic layer was dried ($MgSO_4$), filtered, and added to alumina (500 mg). The solvent was evaporated, and the alumina was loaded onto alumina in a flash chromatography column. Elution with 10% ether−hexanes afforded **7** (201 mg, 68%) as a colorless oil.

5-Iodo-2,3-dimethyl-2-pentene (9). 5-Bromo-2,3-dimethyl-2-pentene (5.00 g, 28.2 mmol) was dissolved in acetone (400 mL), and NaI (4.66 g, 31.1 mmol) was added. The solution was refluxed for 4 h, during which a precipitate formed. The suspension was filtered and the filtrate was poured into ether (500 mL). The solution was washed with water (5 × 200 mL) and carefully with an ice-cold Na_2SO_3 solution (3 × 100 mL). The organic phase was dried ($MgSO_4$), and the solvent was evaporated to give a brown oil. Vacuum distillation (bp 70−

(36) NMR analysis of the crude reaction mixture indicated signals that could be due to the presence of small amounts (ca. 10% relative to the major isomer) of the other geometric isomer, indicating that the substitution reaction is not completely stereospecific under these conditions.

73 °C, 10 Torr) afforded **9** (6.03 g, 95%) as a colorless liquid: IR (neat) 2917, 2862, 1657 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.14 (t, J = 8.1 Hz, 2 H), 2.63 (t, J = 8.2 Hz, 2 H), 1.66 (s, 6 H), 1.64 (s, 3 H); ^{13}C NMR (50 MHz) δ 127.4, 126.8, 39.3, 20.7, 20.3, 17.9, 4.1; mass spectrum, *m/z* (relative intensity, %) 224 (5, M^+), 127 (20), 97 (100), 69 (21), 55 (69), 41 (46); exact mass calcd for $C_7H_{13}I$ 224.0058, found 224.0061.

5,5-Dimethyl-2-phenylseleno-1-(*p*-toluenesulfonyl)-1-hexene (10). *tert*-Butyllithium (479 μL, 1.51 M, 0.723 mmol) was added to a solution of iodide **9** (78 mg, 0.36 mmol) in THF (2 mL) under argon at −78 °C. The yellow solution was stirred for 1 h, during which the color disappeared. The solution was then added to a suspension of copper(I) cyanide (32 mg, 0.36 mmol) in THF at −78 °C under argon via cannula. The resulting suspension was warmed to 0 °C and was stirred for 30 min, during which a clear solution formed. The reaction mixture was then cooled to −78 °C and **4** (121 mg, 0.361 mmol) in THF (1 mL) was added, followed by HMPA (313 μL). After being stirred for 2 h at −78 °C, the reaction mixture was quenched with an NH_4Cl solution, poured into ether (10 mL), and washed with an NH_4Cl solution (3 × 10 mL). The organic phase was dried ($MgSO_4$), and the solvent was evaporated in vacuo to yield a yellow oil which was chromatographed over silica gel (elution with 10% ethyl acetate−hexanes) to give **10** (93 mg, 61%) as a colorless oil: IR (CH_2Cl_2) 1595, 1554, 1309, 1141 cm^{-1}; ^1H NMR (200 MHz) δ 7.97 (d, J = 8.3 Hz, 2 H), 7.58 (dd, J = 7.7 Hz, 1.4 Hz, 2 H), 7.41−7.33 (m, 5 H), 6.53 (s, 1 H), 2.47 (s, 3 H), 2.08 (m, 2 H), 1.33 (m, 2 H), 0.55 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 159.2, 144.1, 138.8, 137.5, 129.6, 129.5, 129.3, 127.4, 126.4, 124.1, 43.6, 33.9, 30.1, 28.8, 21.6; mass spectrum, *m/z* (relative intensity, %) 422 (7, M^+), 266 (14), 208 (31), 157 (43), 139 (35), 91 (51), 77 (32), 57 (100); exact mass calcd for $C_{21}H_{26}O_2SSe$ 422.0812, found 422.0807.

5,6-Dimethyl-2-(3,4-dimethyl-3-pentenyl)-1-(*p*-toluenesulfonyl)-1,5-heptadiene (11). *tert*-Butyllithium (665 μL, 1.26 M, 0.837 mmol) was added to a solution of **9** (94 mg, 0.42 mmol) in ether (2 mL) under argon at −78 °C. The solution was stirred for 1 h and was then added to a suspension of copper(I) cyanide (38 mg, 0.42 mmol) in ether at −78 °C under argon via a cannula. The suspension was warmed to 0 °C and was stirred for 30 min, during which a clear solution formed. The reaction mixture was then cooled to −78 °C, and **4** (141 mg, 0.421 mmol) in ether (3 mL) was added. The solution was stirred for 2 h at −78 °C, and the reaction was then quenched with an NH_4Cl solution. The mixture was poured into ether (10 mL) and washed with an NH_4Cl solution (3 × 10 mL). The organic phase was dried ($MgSO_4$), and the solvent was evaporated in vacuo to yield a yellow oil that was chromatographed over silica gel (elution with 10% ethyl acetate−hexanes) to give **11** (65 mg, 41%) as a colorless oil and recovered **4** (52 mg, 37%) as white crystals. Compound **11**: IR (CH_2Cl_2) 1592, 1311, 1153 cm^{-1}; ^1H NMR (200 MHz) δ 7.80 (d, J = 8.1 Hz, 2 H), 7.34 (dd, J = 8.1 Hz, 2 H), 6.23 (s, 1 H), 2.46 (s, 3 H), 2.40−2.31 (m, 4 H), 2.05−1.87 (m, 4 H), 1.54 (s, 3 H), 1.49 (s, 6 H), 1.41 (s, 3 H), 1.32 (s, 6 H); mass spectrum, *m/z* (relative intensity, %) 374 (11, M^+), 219 (47), 177 (23), 135 (39), 91 (100), 77 (85). Anal. Calcd for $C_{23}H_{34}O_2S$: C, 73.75; H, 9.15. Found C, 73.49; H, 8.98.

(*Z*)-5,6-Dimethyl-2-phenylseleno-1-(*p*-toluenesulfonyl)-1,5-heptadiene (12). Lithium chloride (254 mg, 5.99 mmol) and copper(I) cyanide (269 mg, 3.00 mmol) were placed in a flame-dried 10 mL flask. The flask was repeatedly evacuated and flushed with argon until it reached room temperature. THF (3 mL) was added with stirring under argon. The suspension turned clear within 10 min. Stirring was continued for 3 h, and the solution of the copper(I) cyanide−lithium chloride complex was allowed to stand undisturbed for 12 h under argon.

Zinc dust (216 mg, 3.30 mmol) was placed in a similarly flame-dried 25 mL flask fitted with a condenser and a septum under argon. THF (3.3 mL) was added, followed by dibromoethane (13 μL, 0.15 mmol), and the mixture was refluxed for 5 min. After the suspension had cooled to room temperature, chlorotrimethylsilane (19 μL, 0.15 mmol) was added and the suspension was stirred for 5 min at room temperature. Iodide **9** (672 mg, 3.00 mmol) was added, and the mixture was refluxed for 5 h, during which the zinc dissolved completely to give a clear, colorless solution. The organozinc reagent solution was then cooled to −10 °C and used immediately.

The copper(I) cyanide−lithium chloride solution was added via cannula to the organozinc reagent at −10 °C. The mixture was stirred at −10 °C for 1 h. A solution of acetylene **4** (1.01 g, 3.01 mmol) in THF (3 mL) was added, followed by HMPA (2.61 mL, 15.0 mmol). The yellow mixture was stirred at −10 °C for 2 h. The reaction was quenched with an NH_4Cl solution (5 mL), and the mixture was poured into ether (50 mL), filtered through Celite, and washed with an NH_4Cl solution (3 × 20 mL) and water (3 × 20 mL). The organic layer was dried ($MgSO_4$), and the solvent was evaporated in vacuo to give a yellow oil. Chromatography over silica gel (elution with 7% ethyl acetate−hexanes) afforded **12** (962 mg, 74%) as white crystals: mp 111−113 °C (from ethanol); IR (CH_2Cl_2) 1595, 1552, 1310, 1141 cm^{-1}; ^1H NMR (200 MHz) δ 7.97 (d, J = 8.3 Hz, 2 H), 7.59 (m, 2 H), δ 7.45−7.29 (m, 5 H), 6.51 (s, 1 H), 2.47 (s, 3 H), 2.21−2.12 (m, 2 H), 2.05−1.96 (m, 2 H), 1.50 (s, 3 H), 1.40 (s, 3 H), 1.24 (s, 3 H); ^{13}C NMR (50 MHz) δ 157.7, 144.2, 138.8, 137.3, 129.6, 129.41, 129.39, 127.5, 126.6, 126.3, 125.0, 124.9, 36.5, 34.6, 21.6, 20.5, 20.1, 17.9; mass spectrum, *m/z* (relative intensity, %) 434 (0.9, M^+), 279 (40), 237 (33), 195 (36), 121 (64), 91 (100); exact mass calcd for $C_{22}H_{26}O_2SSe$ 434.0823, found 434.0806.

(*Z*)-6,7-Dimethyl-3-[(*p*-toluenesulfonyl)methylidene]-6-octen-2-one (8). *tert*-Butyllithium (1.90 mL, 1.37 M, 2.60 mmol) was added to a solution of methoxyethene (ca. 0.5 mL) in THF (5 mL) under argon at −78 °C. The yellow solution was warmed to 0 °C and was stirred until a colorless, clear solution formed (5 min). It was then added to a solution of copper(I) iodide (179 mg, 0.940 mmol) and dimethyl sulfide (346 μL, 4.71 mmol) in THF (5 mL) at −78 °C, resulting in a dark red suspension. The mixture was stirred at −30 °C for 1 h, during which it turned clear yellow. The solution was cooled to −78 °C, and the vinyl sulfone **12** (314 mg, 0.724 mmol) in THF (1 mL) was added, causing the reaction mixture to turn red. After 2 h, a 10% HCl solution was added and the reaction mixture was stirred at room temperature for 1 h. It was poured into ether and was washed with brine. The organic phase was dried ($MgSO_4$), and the solvent was evaporated in vacuo to give a yellow oil which was subjected to column chromatography over silica gel (elution with 7% ethyl acetate−hexanes) to afford **8** (197 mg, 85%) as a colorless oil: IR (neat) 1690, 1597, 1311, 1148 cm^{-1}; ^1H NMR (200 MHz) δ 7.84 (d, J = 8.3 Hz, 2 H), 7.38 (d, J = 8.6 Hz, 2 H), 6.88 (s, 1 H), 2.92−2.84 (m, 2 H), 2.47 (s, 3 H), 2.30 (s, 3 H), 2.20−2.12 (m, 2 H), 1.70 (s, 6 H), 1.63 (s, 3 H); ^{13}C NMR (50 MHz) δ 197.9, 152.1, 145.1, 137.9, 136.0, 130.1, 127.6, 126.4, 125.9, 33.9, 26.5, 25.1, 21.6, 20.5, 20.2, 18.1; mass spectrum, *m/z* (relative intensity, %) 320 (2.6, M^+), 238 (37), 165 (60), 91 (62), 83 (93), 55 (80), 43 (100); exact mass calcd for $C_{18}H_{24}O_3S$ 320.1446, found 320.1426.

4,4-Dimethyl-1-phenyl-2,2,3,3-tetradeuterio-1-pentanol (13). *tert*-Butyllithium (389 μL, 1.36 M, 0.529 mmol) was added to THF-d_8 (500 μL) under argon at −78 °C. After 1 h, benzaldehyde (55 μL, 0.54 mmol) was added and the solution was stirred for an additional 2 h. The mixture was quenched with an NH_4Cl solution, poured into ether (10 mL), and washed with an NH_4Cl solution (3 × 5 mL). The organic phase was dried ($MgSO_4$) and the solvent was evaporated in vacuo. The resulting oil was purified by preparative GC to afford **13** (37 mg, 69%) as a colorless oil: ^1H NMR (200 MHz) δ 7.33−7.31 (m, 5 H), 4.41 (m, 1 H), 1.85 (d, J = 2.8 Hz, 1 H, D_2O exchangeable), 0.91 (s, 9 H); mass spectrum, *m/z* (relative intensity, %) 196 (2, M^+), 177 (3), 91 (75), 77 (100).

1-(*p*-Toluenesulfonyl)-1,2-propadiene (14). Vinyl sulfone **5a** (351 mg, 1.00 mmol) was dissolved in chloroform (20 mL) and treated with *m*-CPBA (207 mg, 1.20 mmol). After 10 min, the solution was washed three times with aqueous K_2CO_3 solution, dried, and refluxed for 25 h. The solvent was evaporated, and the resulting oil was chromatographed over silica gel (elution with 10% ethyl acetate−hexanes) to afford 179 mg (92%) of **14** as white crystals: mp 83−86 °C (from ethyl

acetate−hexanes) (lit.[37] mp 83−86 °C), with spectra identical to those of an authentic sample.

1-(*p*-Toluenesulfonyl)-1,2-hexadiene (15). Vinyl sulfone **5b** (393 mg, 1.00 mmol) was treated with *m*-CPBA as in the preceding procedure to afford **15** (187 mg, 79%) as a colorless oil, with spectra identical to those of an authentic sample.[37]

(*E*)-2-Phenylseleno-1-(*N*-pyrrolidinyl)-1-(*p*-toluenesulfonyl)ethene (16) and (*Z*)-1-Phenylseleno-1-(*N*-pyrrolidinyl)-2-(*p*-toluenesulfonyl)ethene (17) (Entry 1, Table 2). Pyrrolidine (84 μL, 1.0 mmol) was added dropwise to a solution of **4** (335 mg, 1.00 mmol) in THF (1 mL) under argon. The solution was stirred at room temperature for 2 h. Alumina (400 mg) was added, and the solvent was evaporated. The residue was loaded onto alumina in a chromatographic column and eluted with 5% ethyl acetate−hexanes and then 15% ethyl acetate−hexanes to give 268 mg (66%) of **16** as white crystals and 130 mg (32%) of **17** as pale yellow crystals.

Compound 16: mp 72−75 °C (dec, from ethyl acetate−hexanes): IR (KBr) 1573, 1349, 1144 cm^{-1}; ^1H NMR (200 MHz) δ 7.76 (d, J = 8.2 Hz, 2 H), 7.64 (s, 1 H), 7.60−7.57 (m, 2 H), 7.37−7.30 (m, 5 H), 3.06−3.02 (m, 4 H), 2.44 (s, 3 H), 1.72−1.68 (m, 4 H); mass spectrum, *m*/*z* (relative intensity, %) 407 (5, M^+), 252 (38), 157 (78), 77 (100). Anal. Calcd for $C_{19}H_{21}NO_2SSe$: C, 56.15; H, 5.21; N, 3.44. Found: C, 55.68; H, 5.23; N, 3.41.

Compound 17: mp 152−155 °C (from methanol): IR (KBr) 1596, 1360, 1132 cm^{-1}; ^1H NMR (200 MHz) 7.92 (d, J = 8.2 Hz, 2 H), 7.19−6.99 (m, 7 H), 5.66 (s, 1 H), 3.26−3.19 (m, 4 H), 2.34 (s, 3 H), 1.81−1.74 (m, 4 H); mass spectrum, *m*/*z* (relative intensity, %) 407 (3, M^+), 250 (61), 186 (21), 123 (100), 98 (77), 55 (51). Anal. Calcd for $C_{19}H_{21}NO_2SSe$: C, 56.15; H, 5.21; N, 3.44. Found: C, 55.81; H, 5.01; N, 3.38.

(*E*)-3,6-Diaza-3-methyl-1-phenylseleno-2-(*p*-toluenesulfonyl)-1-heptene (18) (Entry 2, Table 2). *N*,*N*′-Dimethylethylenediamine (106 μL, 1.00 mmol) was added dropwise to a solution of **4** (335 mg, 1.00 mmol) in THF (1 mL) under argon. The solution was stirred at room temperature for 2 h. The solvent was evaporated in vacuo, and the resulting oil was rapidly chromatographed over alumina (elution with 5% ethyl acetate−hexanes) to afford 355 mg (84%) of **18** as a colorless oil: IR (neat) 3213, 1549, 1370, 1138 cm^{-1}; ^1H NMR (200 MHz) δ 7.90 (s, 1 H), 7.78 (d, J = 8.3 Hz, 2 H), 7.61−7.56 (m, 2 H), 7.38−7.31 (m, 5 H), 3.05 (t, J = 5.9 Hz, 2 H), 2.55 (t, J = 5.9 Hz, 2 H), 2.54 (s, 3 H), 2.43 (s, 3 H), 2.36 (s, 3 H), 2.39−2.34 (br s, 1 H). Further characterization of **18** was precluded by its instability (decomposition within a few hours even at −20 °C).

(*E*)-2-Phenylseleno-1-propoxy-1-(*p*-toluenesulfonyl)-ethene (19) (Entry 3, Table 2). 1-Propanol (748 μL, 10.0 mmol) was added dropwise to sodium hydride (480 mg, 10.0 mmol, 50% suspension in oil) and THF (4 mL) in a 10 mL volumetric flask. After hydrogen evolution had ceased, the flask was filled to the mark with THF. One milliliter of this solution (1.00 mmol) was then added slowly to a solution of **4** (335 mg, 1.00 mmol) in THF (1 mL) under argon. The mixture was stirred at room temperature for 2 h. Alumina (400 mg) was added, the solvent was evaporated, and the residue was chromatographed over alumina (elution with 20% ether−hexanes) to give 364 mg (92%) of **19** as white crystals, mp 59−63 °C (from hexanes): IR (KBr) 1597, 1318, 1152, 1092 cm^{-1}; ^1H NMR (200 MHz) δ 7.79 (d, J = 8.3 Hz, 2 H), 7.59−7.54 (m, 2 H), 7.53 (s, 1 H), 7.34−7.31 (m, 5 H), 4.11 (t, J = 6.6 Hz, 2 H), 2.44 (s, 3 H), 1.72 (tq, J = 7.4 Hz, 6.8 Hz, 2 H), 0.97 (t, J = 7.4 Hz, 3 H); mass spectrum, *m*/*z* (relative intensity, %) 396 (26, M^+), 198 (100), 170 (72), 91 (51), 43 (59). Anal. Calcd for $C_{18}H_{20}O_3SSe$: C, 54.68; H, 5.10. Found: C, 54.66; H, 5.03.

(*E*,*E*)-1,9-Di(phenylseleno)-2,8-di(*p*-toluenesulfonyl)-3,7-dioxa-1,8-nonadiene (20) (Entry 4, Table 2). 1,3-Propanediol (72 μL, 1.0 mmol) was added to sodium hydride (96 mg, 2.0 mmol, 50% suspension in oil) in THF (2 mL) under argon at room temperature. After 30 min, **4** (337 mg, 1.00 mmol) in THF (4 mL) was added via a syringe pump over a period of 2 h. The mixture was stirred for 4 h, then quenched with an NH_4Cl solution, and poured into ether. The organic phase was washed with water, dried ($MgSO_4$), and evaporated. Chromatography over alumina (elution with 30% ethyl acetate−hexanes) afforded **20** (236 mg, 63%) as pale yellow crystals: mp 103−105 °C (from hexanes); IR (CH_2Cl_2) 1596, 1317, 1151, 1049 cm^{-1}; ^1H NMR (200 MHz) δ 7.79 (d, J = 8.2 Hz, 4 H), 7.58−7.53 (m, 4 H), 7.54 (s, 2 H), 7.37−7.30 (m, 10 H), 4.28 (t, J = 6.3 Hz, 4 H), 2.41 (s, 6 H), 2.11 (quintet, J = 6.3 Hz, 2 H); mass spectrum, *m*/*z* (relative intensity, %) 748 (1.4, M^+), 395 (16), 200 (26), 170 (34), 124 (100). Anal. Calcd for $C_{33}H_{32}O_6S_2Se_2$: C, 53.08; H, 4.32. Found: C, 53.02; H, 4.16.

(*Z*)-2-Ethylthio-1-phenylseleno-1-(*p*-toluenesulfonyl)-ethene (21) and (*Z*)-1-Ethylthio-1-phenylseleno-2-(*p*-toluenesulfonyl)ethene (22) (Entry 5, Table 2). Ethanethiol (741 μL, 10.0 mmol) was added dropwise to sodium hydride (480 mg, 10.0 mmol, 50% suspension in oil) and THF (4 mL) in a 10 mL volumetric flask. After hydrogen evolution had ceased, the flask was filled to the mark with THF. One milliliter of this solution (1.00 mmol) was added slowly to a solution of **4** (335 mg, 1.00 mmol) in THF (1 mL) under argon at 0 °C. After the solution had warmed to room temperature, stirring was continued for 2 h. Alumina (400 mg) was added, the solvent was evaporated, and the residue was chromatographed over alumina (elution with 20% ether−hexanes) to give 322 mg (81%) of **21** and 64.4 mg (16%) of **22**, both as white crystals.

Compound 21: mp 97−98 °C (from ethyl acetate−hexanes): IR (CH_2Cl_2) 1592, 1301, 1146 cm^{-1}; ^1H NMR (200 MHz) δ 8.58 (s, 1 H), 7.78 (d, J = 8.3 Hz, 2 H), 7.23−7.10 (m, 7 H), 2.93 (q, J = 7.5 Hz, 2 H), 2.39 (s, 3 H), 1.39 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz) 157.2, 144.0, 136.2, 131.3, 129.4, 129.0, 128.8, 127.3, 123.6, 28.7, 21.5, 15.7; mass spectrum, *m*/*z* (relative intensity, %) 398 (82, M^+), 243 (85), 182 (100), 134 (86), 91 (63); exact mass calcd for $C_{17}H_{18}O_2S_2Se$ 397.9915, found 397.9890. The structure was confirmed by X-ray crystallography (Supporting Information).

Compound 22: mp 94−97 °C (from ethyl acetate−hexanes); IR (CH_2Cl_2) 1597, 1312, 1142 cm^{-1}; ^1H NMR (200 MHz) δ 7.79 (d, J = 8.3 Hz, 2 H), 7.55−7.30 (m, 7 H), 6.15 (s, 1 H), 2.99 (q, J = 7.4 Hz, 2 H), 2.43 (s, 3 H), 1.21 (t, J = 7.3 Hz, 3 H); NOE observed between signals at δ 6.15 and 7.79, 6.15 and 2.99; mass spectrum, *m*/*z* (relative intensity, %) 398 (6, M^+), 242 (18), 155 (39), 139 (80), 91 (100). Anal. Calcd for $C_{17}H_{18}O_2S_2Se$: C, 51.38; H, 4.57. Found: C, 51.09; H, 4.50.

(*E*)-1,2-Di(ethylthio)-1-(*p*-toluenesulfonyl)ethene (23) and 1,1-Di(ethylthio)-2-(*p*-toluenesulfonyl)ethene (24) (Entry 6, Table 2). Two milliliters of the solution of sodium ethanethiolate in THF (2.00 mmol) prepared in the preceding procedure was added slowly to a solution of **4** (335 mg, 1.00 mmol) in THF (1 mL) under argon. After 5 h, the mixture was quenched with an NH_4Cl solution, poured into ether, and washed with an NH_4Cl solution. The organic phase was dried ($MgSO_4$), evaporated, and chromatographed over silica gel (elution with 10% ethyl acetate−hexanes) to afford **23** (225 mg, 74%) and **24** (40 mg, 13%), both as white crystals.

Compound 23: mp 65−67 °C (from hexanes); IR (CH_2Cl_2) 1596, 1312, 1146 cm^{-1}; ^1H NMR (200 MHz) δ 8.36 (s, 1 H), 7.80 (d, J = 8.2 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 2.93 (q, J = 7.4 Hz, 2 H), 2.80 (q, J = 7.4 Hz, 2 H), 2.42 (s, 3 H), 1.40 (t, J = 7.4 Hz, 3 H), 1.19 (t, J = 7.4 Hz, 3 H); mass spectrum, *m*/*z* (relative intensity, %) 302 (61, M^+), 147 (100), 118 (38), 103 (36), 91 (40), 87 (65). Anal. Calcd for $C_{13}H_{18}O_2S_3$: C, 51.62; H, 6.00. Found: C, 51.54; H, 5.74.

Compound 24: mp 68−70 °C (from hexanes): IR (CH_2Cl_2) 1597, 1312, 1142 cm^{-1}; ^1H NMR (200 MHz) δ 7.90 (d, J = 8.3 Hz, 2 H), 7.31 (d, J = 8.4 Hz, 2 H), 6.19 (s, 1 H), 2.94 (q, J = 7.4 Hz, 2 H), 2.84 (q, J = 7.4 Hz, 2 H), 2.44 (s, 3 H), 1.32 (t, J = 7.4 Hz, 3 H), 1.17 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (50 MHz) δ 156.4, 143.7, 139.5, 129.3, 127.8, 120.2, 28.1, 27.3, 21.6, 14.4, 12.7; mass spectrum, *m*/*z* (relative intensity, %) 302 (12, M^+), 210 (70), 155 (21), 152 (36), 147 (55), 139 (36), 119 (39), 105 (32), 91 (100); exact mass calcd for $C_{13}H_{18}O_2S_3$ 302.0469, found 302.0454.

(37) Back, T. G.; Krishna, M. V.; Muralidharan, K. R. *J. Org. Chem.* **1989**, *54*, 4146.

2-(*p*-Toluenesulfonyl)-1,4-dithiacyclohept-2-ene (25) and 2-[(*p*-Toluenesulfonyl)methylidene]-1,3-dithiane (26) (Entry 7, Table 2). 1,3-Propanedithiol (100 μL, 1.00 mmol) was added to sodium hydride (96 mg, 2.0 mmol, 50% suspension in oil) in THF (1 mL) under argon at room temperature. After hydrogen evolution had ceased, **4** (335 mg, 1.00 mmol) in THF (1 mL) was added. The mixture was stirred for 4 h, quenched with an NH_4Cl solution, and worked up as in the preceding procedure. Chromatography over silica gel (elution with 10% ethyl acetate−hexanes) afforded **25** (227 mg, 79%) and **26** (34.5 mg, 12%), both as white crystals.

Compound 25: mp 127−131 °C (from hexanes); IR (CH_2Cl_2) 1596, 1317, 1302, 1140 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.78 (d, J = 8.3 Hz, 2 H), 7.45 (s, 1 H), 7.31 (d, J = 8.1 Hz, 2 H), 3.59 (t, J = 5.9 Hz, 2 H), 3.26 (t, J = 6.3 Hz, 2 H), 2.44 (s, 3 H), 2.19 (tt, J = 6.3 Hz, 6.0 Hz, 2 H); mass spectrum, *m*/*z* (relative intensity, %) 286 (100, M$^+$), 131 (54), 89 (52,), 45 (34). Anal. Calcd for $C_{12}H_{14}O_2S_3$: C, 50.32; H, 4.93. Found: C, 49.86; H, 4.78.

Compound 26: mp 106−109 °C (from hexanes); IR (CH_2Cl_2) 1596, 1312, 1142 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.87 (d, J = 8.3 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 6.51 (s, 1 H), 3.02−2.89 (m, 4 H), 2.44 (s, 3 H), 2.17 (tt, J = 6.3 Hz, 6.0 Hz, 2 H); mass spectrum, *m*/*z* (relative intensity, %) 286 (94, M$^+$), 222 (40), 175 (17), 147 (61), 132 (46), 91 (100), 65 (62), 45 (78). Anal. Calcd for $C_{12}H_{14}O_2S_3$: C, 50.32; H, 4.93. Found: C, 50.26; H, 4.76.

(*E*)-2-Ethylthio-1-propoxy-1-(*p*-toluenesulfonyl)ethene (27) (Entry 8, Table 1). A solution of sodium ethanethiolate was prepared as in entry 5. An aliquot (900 μL, 0.900 mmol) of this solution was added slowly to a solution of **19** (355 mg, 0.899 mmol) in THF (1 mL) under argon. The mixture was stirred at room temperature for 5 h, alumina (400 mg) was added, and the solvent was evaporated. The residue was placed onto alumina in a chromatographic column and was eluted with 10% ethyl acetate−hexanes to give **27** (212 mg, 78%) as a colorless oil: IR (film) 1596, 1317, 1149 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.78 (d, J = 7.7 Hz, 2 H), 7.32 (d, J = 7.9 Hz, 2 H), 7.12 (s, 1 H), 4.01 (t, J = 6.6 Hz, 2 H), 2.83 (q, J = 7.4 Hz, 2 H), 2.43 (s, 3 H), 1.68 (m, 2 H), 1.37 (t, J = 7.4 Hz, 3 H), 0.94 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (50 MHz) δ 147.9, 144.3, 136.2, 129.6, 128.2, 125.8, 75.7, 28.3, 23.2, 21.6, 15.5, 10.2; mass spectrum, *m*/*z* (relative intensity, %) 300 (M$^+$, 14), 199 (4), 157 (17), 139 (13), 119 (74), 102 (100), 91 (20), 74 (18); exact mass calcd for $C_{14}H_{20}O_3S_2$ 300.0854, found 300.0856.

(*Z*)-1,2-Di(phenylseleno)-1-(*p*-toluenesulfonyl)ethene (28) and 1,1-Di(phenylseleno)-2-(*p*-toluenesulfonyl)ethene (29) (Entry 9, Table 2). Diphenyl diselenide (141 mg, 0.450 mmol) was added in portions to a solution of sodium borohydride (34 mg, 0.90 mmol) in aqueous sodium hydroxide (450 μL, 2 M) and ethanol (450 μL). The mixture was refluxed for 30 min, cooled to 0 °C, and added to a solution of **4** (335 mg, 1.00 mmol) in THF (1 mL) at 0 °C over 10 min via cannula. The solution was stirred at 0 °C for 10 min and then at room temperature for an additional 20 min. The mixture was poured into ether (10 mL), and the organic layer was separated, washed with water (5 mL), and dried ($MgSO_4$). The solvent was evaporated, and the resulting yellow oil was chromatographed over silica gel (elution with 10% ether−hexanes) to afford **28** (275 mg, 62%) as pale yellow crystals and **29** (142 mg, 32%) as white crystals.

Compound 28: mp 103−105 °C (from hexanes): IR (CH_2Cl_2) 1575, 1310, 1147 cm^{-1}; ^{1}H NMR (200 MHz) δ 9.09 (s, 1 H), 7.78 (d, J = 8.2 Hz, 2 H), 7.61−7.56 (m, 2 H), 7.40−7.36 (m, 3 H), 7.26−7.13 (m, 7 H), 2.38 (s, 3 H); mass spectrum, *m*/*z* (relative intensity, %) 494 (43, M$^+$), 337 (6), 261 (27), 237 (26), 183 (100), 102 (88), 77 (82), 51 (35). Anal. Calcd for $C_{21}H_{18}O_2SSe_2$: C, 51.23; H, 3.69. Found: C, 50.91; H, 3.85. The structure was confirmed by X-ray crystallography (Supporting Information).

For 29: mp 125−129 °C (from hexanes): IR (CH_2Cl_2) 1597, 1312, 1146 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.83 (d, J = 8.3 Hz, 2 H), 7.75 (d, J = 7.0 Hz, 2 H), 7.41−7.31 (m, 10 H), 6.10 (s, 1 H), 2.38 (s, 3 H); mass spectrum, *m*/*z* (relative intensity, %) 494 (17, M$^+$), 338 (36), 273 (13), 234 (25), 182 (173), 155 (61), 120 (84), 91 (100). Anal. Calcd for $C_{21}H_{18}O_2SSe_2$: C, 51.23; H, 3.69. Found: C, 50.84; H, 3.98.

Hydrolysis of Adduct 16. The enamine **16** (102 mg, 0.251 mmol) was stirred in THF (0.5 mL) and 20% aqueous NH_4Cl solution (1 mL) at room temperature for 30 min. It was then poured into ether (10 mL) and washed three times with water. The organic phase was dried ($MgSO_4$) and evaporated to give *N*-(phenylselenoacetyl)pyrrolidine (**30**) (67 mg, 100%) as yellow crystals: mp 57−62 °C (from methanol); IR (CH_2Cl_2) 1635, 1610 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.64−7.60 (m, 2 H), 7.29−7.14 (m, 3 H), 3.60 (s, 2 H), 3.44 (t, J = 6.7 Hz, 2 H), 3.33 (t, J = 6.6 Hz, 2 H), 1.91−1.78 (m, 4 H); mass spectrum, *m*/*z* (relative intensity, %) 269 (31, M$^+$), 188 (89), 157 (11), 112 (26), 98 (100), 91 (21), 55 (84). Anal. Calcd for $C_{12}H_{15}NOSe$: C, 53.74; H, 5.64, N, 5.22. Found: C, 53.25; H, 5.80, N, 5.58.

Nickel Boride Reduction of Adduct 17. The enamine **17** (130 mg, 0.320 mmol) and $NiCl_2 \cdot 6H_2O$ (532 mg, 2.24 mmol) were dissolved in a methanol−THF mixture (85:15, 3.5 mL) and cooled to 0 °C. Sodium borohydride (254 mg, 6.71 mmol) was added in portions over 5 min. After 15 min, the black suspension was filtered through Celite. The filtrate was poured into ether (10 mL), washed with water (3 × 5 mL, dried ($MgSO_4$), and evaporated. The crude product was chromatographed over silica gel (elution with chloroform) to give *N*-[2-(*p*-toluenesulfonyl)ethyl]pyrrolidine (**31**) (71 mg, 87%) as white crystals, mp 63−65 °C (from hexanes; lit.[38] mp 65.5−66 °C), identified by its IR and NMR spectra.

Nickel Boride Reduction of Adduct 19. Enol ether **19** (395 mg, 1.00 mmol) was treated with nickel boride as in the reduction of **17**. Chromatography over silica gel (elution with 20% ethyl acetate−hexanes) afforded 1-propoxy-1-(*p*-toluenesulfonyl)ethene (**32**) (156 mg, 65%) as a slightly yellow oil: IR (CH_2Cl_2) 1624, 1596, 1322, 1145, 1084 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.83 (d, J = 8.3 Hz, 2 H), 7.33 (d, J = 8.5 Hz, 2 H), 5.49 (d, J = 4.0 Hz, 1 H), 4.69 (d, J = 4.0 Hz, 1 H), 3.71 (t, J = 7.0 Hz, 2 H), 2.44 (s, 3 H), 1.66 (tq, J = 7.4 Hz, 7.1 Hz, 2 H), 0.86 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (50 MHz) δ 160.4, 144.6, 135.4, 129.5, 128.8, 91.2, 72.3, 21.8, 21.6, 10.1; mass spectrum, *m*/*z* (relative intensity, %) 240 (10, M$^+$), 156 (43), 139 (54), 92 (100), 65 (24), 43 (77); exact mass calcd for $C_{12}H_{16}O_3S$ 240.0820, found 240.0818.

Nickel Boride Reduction of Adduct 20. Enol ether **20** (75 mg, 0.10 mmol) was treated with nickel boride as in the reduction of **17**. Chromatography over alumina (elution with 5% ethyl acetate−hexanes) afforded 2,8-di(*p*-toluenesulfonyl)-3,7-dioxa-1,8-nonadiene (**33**) (31 mg, 71%) as a slightly yellow oil: IR (CH_2Cl_2) 1593, 1322, 1148, 1049 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.84 (d, J = 8.4 Hz, 4 H), 7.34 (d, J = 8.4 Hz, 4 H), 5.46 (d, J = 3.8 Hz, 2 H), 4.60 (d, J = 3.8 Hz, 2 H), 3.87 (t, J = 6.9 Hz, 4 H), 2.41 (s, 3 H), 2.05 (quintet, J = 6.9 Hz, 2 H); mass spectrum, *m*/*z* (relative intensity, %) 436 (6, M$^+$), 281 (14), 156 (32), 139 (62), 91 (100). Anal. Calcd for $C_{21}H_{24}O_6S_2$: C, 57.78; H, 5.54. Found: C, 58.01; H, 5.71.

Nickel Boride Reduction of Adduct 27. Enol ether **27** (104 mg, 0.347 mmol) was treated with nickel boride as in the reduction of **17**. Chromatography over silica gel (elution with 20% ethyl acetate−hexanes) afforded **32** (66 mg, 79%), identical to the sample prepared from the similar reduction of **19**.

Hydrolysis of Ketene Dichalcogenoacetals 22, 24, 26, and 29. Ketene selenothioacetal **22** (43 mg, 0.11 mmol) and $HgCl_2$ (60 mg, 0.22 mmol) were dissolved in THF (1 mL). Dilute hydrochloric acid (1 mL, 10%) was added, and the mixture was refluxed for 15 h. The solution was poured into ether (10 mL), and the organic phase was washed with water (3 × 5 mL), dried ($MgSO_4$), and evaporated in vacuo. The residue was refluxed in methanol (5 mL) and concentrated sulfuric acid (250 μL) for 12 h. The cooled solution was poured into ether (5 mL) and washed with water (3 × 5 mL) and an $NaHCO_3$ solution. The organic phase was dried ($MgSO_4$), evaporated in vacuo, and distilled (Kugelrohr) bp 147 °C (0.1

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Torr) [lit.[39] bp 145 °C (0.1 Torr)], to afford **34** as a clear oil (19 mg, 77%): IR (neat) 1749, 1336, 1153, 1087 cm^{-1}; ^1H NMR (200 MHz) δ 7.83 (d, J = 8.3 Hz, 2 H), 7.39 (d, J = 8.4 Hz, 2 H), 4.12 (s, 2 H), 3.73 (s, 3 H), 2.48 (s, 3 H).

Similarly, hydrolysis and esterification of **24**, **26**, and **29** afforded the same product **34** as obtained above.

Addition of Isopropylselenolate to 4. Diisopropyl diselenide (122 mg, 0.500 mmol) was added in portions to a solution of sodium borohydride (38 mg, 1.0 mmol) in aqueous sodium hydroxide (500 μL, 2 M) and ethanol (500 μL). The mixture was refluxed for 30 min and cooled to 0 °C with an ice bath. The resulting solution was added to a solution of **4** (335 mg, 1.00 mmol) in THF (1 mL) at 0 °C over 10 min via cannula. The mixture was stirred at 0 °C for 10 min and at room temperature for 20 min. It was poured into ether (10 mL), and the organic layer was quickly washed with water (5 mL), dried ($MgSO_4$), and evaporated. The resulting black oil was chromatographed over silica gel (10% ether−hexanes) to afford **28** (44 mg, 9%) as pale yellow crystals, mp 103−105 °C, **29** (103 mg, 21%) as white crystals, mp 125−129 °C, and **42** (138 mg, 30%) as a pale yellow oil. Compounds **28** and **29** were identical (TLC, IR, ^1H NMR spectra) with samples prepared via entry 9 in Table 2. Compound **42**: IR (CH_2Cl_2) 1516, 1310, 1141 cm^{-1}; ^1H NMR (200 MHz) δ 9.14 (s, 1 H), 7.77 (d, J = 8.3 Hz, 2 H), 7.22−7.09 (m, 7 H), 3.53 (septet, J = 6.9 Hz, 1 H), 2.38 (s, 3 H), 1.53 (d, J = 6.9 Hz, 6 H); irradiation of the olefinic signal at δ 9.14 resulted in a strong enhancement of the signals from the isopropyl methine proton and the *ortho* protons of the Ts group at δ 3.53 and 7.77, respectively, while irradiation at δ 3.53 strongly enhanced the signal at δ 9.14; ^{13}C NMR (50 MHz) δ 155.3, 144.1, 135.9, 131.3, 129.5, 129.0, 128.9, 128.6, 127.6, 127.3, 34.7, 24.7, 21.6; mass spectrum, *m*/*z* (relative intensity, %) 460 (37, M^+), 305 (10), 182 (94), 102 (94), 91 (65), 77 (53), 43 (100); exact mass calcd for $C_{18}H_{20}O_2SSe_2$ 459.9527, found 459.9554.

(*Z*)-1-Phenylseleno-2-(*N*-pyrrolidinyl)ethene (44). Pyrrolidine (125 μL, 1.50 mmol) and phenylselenoethyne (**43**) (272 mg, 1.50 mmol) were refluxed for 25 h in THF (5 mL). The solvent was evaporated in vacuo, and the residue was subjected to chromatography over alumina (elution with 5% ethyl acetate−hexanes) to yield **44** (272 mg, 72%) as a slightly yellow oil: IR (neat) 1586, 732, 685 cm^{-1}; ^1H NMR (200 MHz) δ 7.43 (dd, J = 8.5 Hz, 1.3 Hz, 2 H), 7.39−7.12 (m, 3 H), 6.95 (d, J = 12.9 Hz, 1 H), 4.75 (d, J = 12.9 Hz, 1 H), 3.24 (m, 4 H), 1.93 (m, 4 H); ^{13}C NMR (50 MHz) δ 148.9, 136.7, 128.6, 127.8, 124.9, 73.5, 48.6, 25.1; mass spectrum, *m*/*z* (relative intensity, %) 253 (63, M^+), 173 (100), 96 (87), 77 (71), 54 (51), 41 (54); exact mass calcd for $C_{12}H_{15}NSe$ 253.0374, found 253.0374.

(*Z*)-1-Methoxy-2-phenylselenoethene (45). Methanol (81 μL, 2.0 mmol) was added to sodium hydride (96 mg, 2.0 mmol, 50% suspension in oil) in THF (5 mL) under argon at room temperature. After gas evolution had ceased, **43** (362 mg, 2 mmol) in THF (2 mL) was added. The solution was refluxed for 36 h, the solvent was evaporated in vacuo, and the residue was chromatographed over alumina (elution with 5% ethyl acetate−hexanes) to give **45** (285 mg, 67%) as a yellow oil: IR (neat) 1577, 1100, 735, 688 cm^{-1}; ^1H NMR (200 MHz) δ 7.49 (dd, J = 7.9 Hz, 1.6 Hz, 2 H), 7.31−7.20 (m, 3 H), 6.52 (d, J = 5.1 Hz, 1 H), 5.39 (d, J = 5.2 Hz, 1 H), 3.76 (s, 3 H); ^{13}C NMR (50 MHz) δ 150.0, 131.4, 131.0, 129.0, 126.4, 92.6, 60.2; mass spectrum, *m*/*z* (relative intensity, %) 214 (38, M^+), 134 (100), 91 (70), 77 (65); exact mass calcd for $C_9H_{10}OSe$ 213.9897, found 213.9887.

(*Z*)-1-Ethylthio-2-phenylselenoethene (46). Ethanethiol (111 μL, 1.50 mmol) was added to sodium hydride (72 mg, 1.5 mmol, 50% suspension in oil) in THF (5 mL) under argon at room temperature. After gas evolution had ceased, **43** (272 mg, 1.50 mmol) in THF (2 mL) was added. The solution was refluxed for 36 h, the solvent was evaporated in vacuo, and the residue was chromatographed over alumina (elution with 5% ethyl acetate−hexanes) to give **46** (186 mg, 51%) as a yellow oil: IR (neat) 1572, 729, 682 cm^{-1}; ^1H NMR (200 MHz) δ 7.58−7.50 (m, 2 H), 7.38−7.28 (m, 3 H), 6.64 (d, J = 8.5 Hz, 1 H), 6.62 (d, J = 8.5 Hz, 1 H), 2.81 (q, J = 7.4 Hz, 2 H), 1.37 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (50 MHz) δ 132.0, 129.4, 129.2, 127.1, 119.2, 110.2, 28.2, 15.5; mass spectrum, *m*/*z* (relative intensity, %) 244 (52, M^+), 215 (2), 183 (35), 157 (20), 103 (50), 77 (48), 40 (100); exact mass calcd for $C_{10}H_{12}SSe$ 243.9825, found 243.9804.

(*Z*)-1,2-Di(phenylseleno)ethene (47).[40] Diphenyl diselenide (125 mg, 0.400 mmol) was added to a solution of sodium borohydride (30 mg, 0.79 mmol) in aqueous sodium hydroxide (400 μL, 2 M) and ethanol (400 μL). The mixture was refluxed for 30 min and then cooled to 0 °C with an ice bath. The resulting solution was added to **43** (145 mg, 0.800 mmol) in THF (2 mL) at 0 °C over 10 min via a cannula. The mixture was refluxed for 28 h and then poured into ether (10 mL), washed quickly with water (5 mL), dried ($MgSO_4$), and evaporated. Column chromatography of the residue over silica gel (elution with hexanes) afforded **47** (176 mg, 65%) as a yellow oil: ^1H NMR (200 MHz) δ 7.19 (lit.[40] δ 7.1), $J_{Se-Htrans}$ = 1.3 Hz, $J_{Se-Hgem}$ = 11.7 Hz.[41]

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Supporting Information Available: ORTEP diagrams, tables of atomic coordinates, bond angles and bond lengths for compounds **21** and **28**, and the ^1H and ^{13}C NMR spectra of new compounds not having combustion analyses (43 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.

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