Cycloaddition Reactions of 1-Phenylseleno-2-(*p*-toluenesulfonyl)ethyne

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1-Phenylseleno-2-(*p*-toluenesulfonyl)ethyne (**1**) is an effective dienophile and dipolarophile. It underwent facile Diels−Alder reactions with a variety of dienes to afford vicinal sulfone- and selenide-functionalized 1,4-cyclohexadienes. Unexpected regiochemistry that is the opposite of what is obtained with simple acetylenic sulfones was observed with several unsymmetrical dienes containing methyl or methoxy substituents at the 1- or 2-position. Acetylene **1** reacted with (trimethylsilyl)methyl azide, diazomethane, and 2,4,6-trimethylbenzonitrile *N*-oxide via 1,3-dipolar cycloadditions to afford the corresponding triazole, 1,2-diazole, and isoxazole products. It also underwent an ene reaction with *β*-pinene that showed anomalous regiochemistry compared to other acetylenic sulfones. The Diels−Alder cycloadducts obtained from the reaction of **1** with 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene were readily converted into the corresponding *β*-keto sulfones and ketones, thus rendering **1** as the synthetic equivalent of *p*-toluenesulfonylketene and ketene, respectively. Base-catalyzed elimination of TsOH from the Diels−Alder cycloadduct obtained with 2,3-dimethyl-1,3-butadiene afforded the corresponding aryl phenyl selenide, while the adduct from piperylene underwent oxidation to its selenoxide, followed by a Pummerer-type reaction to produce 2-(phenylseleno)-3-(*p*-toluenesulfonyl)toluene. The reaction of the bicyclic Diels−Alder product obtained from 1,3-cyclohexadiene with MeCu(SePh)Li resulted in substitution of the phenylseleno moiety by a methyl group, whereas similar treatment of the monocyclic adduct derived from piperylene effected elimination of PhSeH and aromatization.

Acetylenic and other types of unsaturated sulfones have many synthetic applications,[1] including their use as dienophiles in Diels−Alder reactions.[2] The electron-withdrawing sulfone group has the effect of both activating the dienophile and of controlling the regiochemistry of cycloadditions, as well as providing a useful functional group for further transformations. Removal of the sulfone moiety after the completion of the procedure by reductive desulfonylation provides access to sulfur-free products.[3] Acetylenic selenides are also known,[4] but their cycloaddition chemistry and the activating/directing abilities of their selenium substituents have, to our knowledge, not yet been investigated. We recently reported the preparation of the title compound **1**[5] (Scheme 1), and demonstrated that it undergoes conjugate addition reactions with organocopper reagents and various heteroatom nucleophiles. Of particular interest was the observation that hard nucleophiles, such as amines and alkoxides, attack **1** α to the sulfone group, leading to preferential or exclusive formation of the corresponding anti-Michael (with respect to the sulfone moiety) regioisomers. This suggests that the selenide substituent shows an unexpectedly powerful effect with respect to the regiocontrol of such additions. We now report that **1** also acts as an effective dienophile[6] and dipolarophile, affording cycloadducts containing sulfone and selenide functionalities that provide opportunities for further synthetic transformations. Moreover, we note that, as with the anti-Michael conjugate additions, the cycloadditions of **1** again display unexpected regiochemistry in several of the examples studied.

Results and Discussion

The Diels−Alder reactions of **1** with a series of dienes are shown in Table 1. Entries 1−5 are with symmetrical dienes and indicate that the cycloadditions proceed under mild conditions and in excellent yield, without the need

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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. (d) Simpkins, N. S. *Tetrahedron* **1990**, *46*, 6951. (e) 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) For examples, see ref 1a, Chapters 2 and 6. Also see: (a) De Lucchi, O.; Pasquato, L. *Tetrahedron* **1988**, *44*, 6755. (b) Paquette, L. A.; Williams, R. V. *Tetrahedron Lett.* **1981**, *22*, 4643. (c) Williams, R. V.; Chauhan, K.; Gadgil, V. R. *J. Chem. Soc., Chem. Commun.* **1994**, 1739. (d) Hickey, E. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1995**, *117*, 163. (e) Pasquato, L.; De Lucchi, O.; Krotz, L. *Tetrahedron Lett.* **1991**, *32*, 2177. (f) Corey, E. J.; Da Silva Jardine, P.; Mohri, T. *Tetrahedron Lett.* **1988**, *29*, 6409. (g) Kotian, P. L.; Carroll, F. I. *Synth. Commun.* **1995**, *25*, 63. (h) Davis, A. P.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1980**, 639. (i) Huang, D. F.; Shen, T. Y. *Tetrahedron Lett.* **1993**, *34*, 4477. (j) Jones, C. D.; Simpkins, N. S.; Giblin, G. M. P. *Tetrahedron Lett.* **1998**, *39*, 1021 and 1023. (k) Clasby, M. C.; Craig, D.; Marsh, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1444. (l) Virgili, M.; Belloch, J.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron Lett.* **1991**, *32*, 4583. (m) Djeghaba, Z.; Jousseaume, B.; Ratier, M.; Duboudin, J.-G. *J. Organomet. Chem.* **1986**, *304*, 115.

(3) Reference 1a, Chapter 9 and references therein.

(4) For a recent review, see: Stang, P. J.; Zhdankin, V. V. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Elsevier: Oxford, 1995; Vol. 2, Chapter 2.21.

(5) (a) Back, T. G.; Wehrli, D. *Tetrahedron Lett.* **1995**, *36*, 4737. (b) Back, T. G.; Bethell, R. J.; Parvez, M.; Wehrli, D. *J. Org. Chem.* **1998**, *63*, 7908. (c) Compound **1** was also recently reported as an intermediate in the reaction of tosylalkynyliodonium triflate with benzeneselenolate: Stang, P. J.; Murch, P. *Synthesis* **1997**, 1378.

(6) Preliminary communication: Back, T. G.; Wehrli, D. *Synlett* **1995**, 1123. This work is largely based on the Ph.D. Thesis of D. Wehrli (University of Calgary, 1997).

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Scheme 1

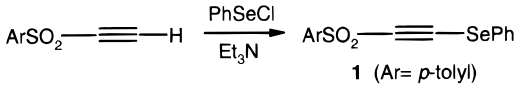
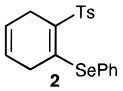
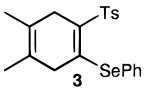
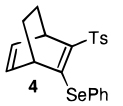
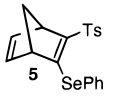
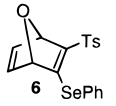
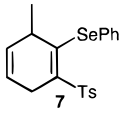
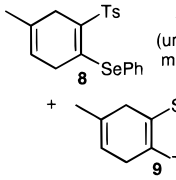
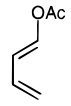
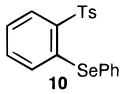
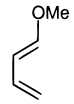
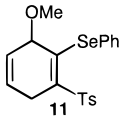
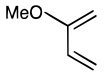
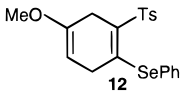
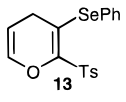


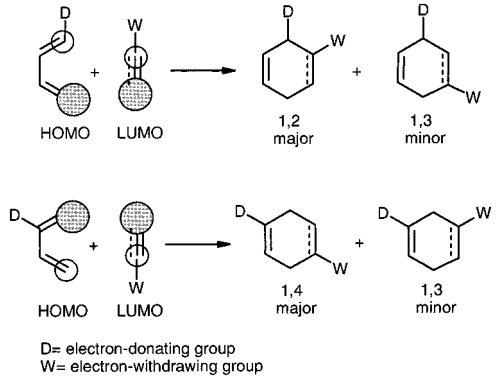
Table 1. Diels–Alder Cycloadditions of 1

Entry	Diene	Conditions[a]	Product(s)	Isolated Yield (%)
1		neat, RT 4 days	 **2**	81
2		neat Δ, 2 h	 **3**	97
3		toluene Δ, 6 h	 **4**	90
4		benzene RT, 4 h	 **5**	93
5		neat Δ, 6 h	 **6**	93
6		neat Δ, 12 h	 **7**	81
7		neat Δ, 12 h	 **8** + **9**	total 93 (unseparated mixture; 1:1)
8		toluene Δ, 15 h	 **10**	80
9		neat Δ, 12 h	 **11**	82
10		neat Δ, 12 h	 **12**	74
11		neat, Δ 3 days	 **13**	38

[a] RT = room temperature; Δ = 60–65 °C.

for Lewis acid catalysts. Entries 6–10 involve unsymmetrical dienes, resulting in the possible formation of two regioisomers. In general, dienes with an electron-donating substituent at the 1-position are expected to react with dienophiles containing an electron-withdrawing substituent to afford the corresponding 1,2-regioisomers preferentially. On the other hand, when the donor group is at the 2-position of the diene, the 1,4-regioisomer is favored (Scheme 2).[7] It is therefore interesting to note that the 1-methyl- and 1-methoxy-substituted dienes in

Scheme 2



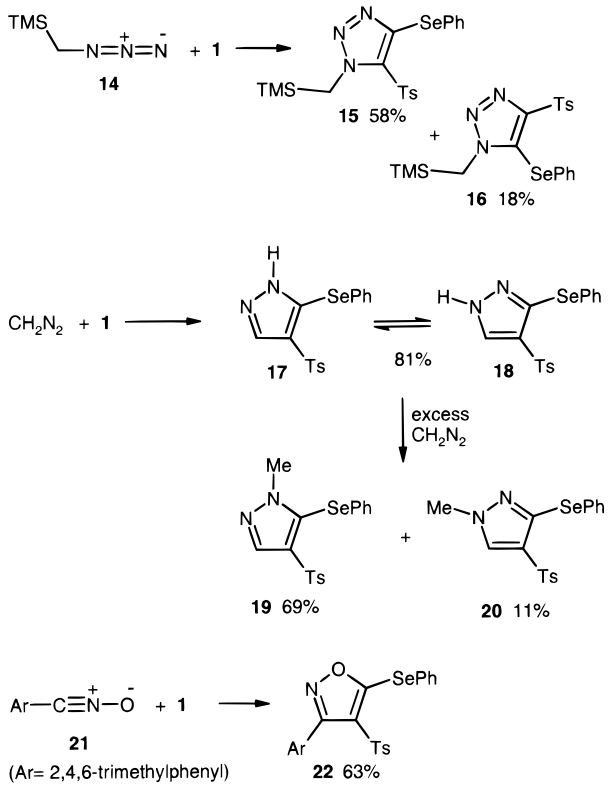
entries 6 and 9 preferentially afforded the regioisomers where the electron-withdrawing sulfone group is oriented 1,3 with respect to the diene substituent (**7** and **11**, respectively). Similarly, when the methyl or methoxy group was located in the 2-position of the diene, the corresponding 1,3-isomers **8** and **12** either were formed in an amount equal to that of the expected 1,4-regioisomer **9** (entry 7) or were the sole isolated product (entry 10). The cycloadduct obtained from 1-acetoxy-1,3-butadiene spontaneously eliminated acetic acid to produce **10** under the conditions of the experiment, thereby precluding determination of the regiochemistry. The assignment of regiochemistry to adducts **7** and **11** and **12** was made on the basis of NOE experiments (see the Experimental Section). That of **7** was confirmed by further chemical transformation (vide infra). Unequivocal assignment of regiochemistry could not be made for **8** and **9**, which were formed in equal amounts (NMR integration) and could not be separated. If one assumes that the above reactions are concerted and involve interaction of the diene HOMO with the LUMO of **1**, then the regiochemistry of these examples is anomalous, since the effect of the selenide group appears to outweigh that of the strongly electron-withdrawing sulfone moiety. While a clear explanation for these results is lacking, they are consistent with the observed regiochemistry in certain conjugate additions of **1**, as noted earlier.[8] It is also interesting to note that an acetylenic sulfone containing a β-silyl substituent has been reported to react with 1-methoxy-1,3-cyclohexadiene to afford the corresponding anomalous 1,3-cycloadduct (with respect to the sulfone and methoxy groups),[2c] whereas a related β-stannyl acetylenic sulfone afforded the normal 1,2-cycloadduct with 1-methoxy-1,3-butadiene.[2m] Finally, acrolein afforded the adduct **13** in modest yield (Table 1, entry 11) via a hetero-Diels–Alder reaction.[9,10]

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

(8) If **1** acts as the dienophile in a Diels–Alder cycloaddition with normal electron demand, then the frontier orbital interaction that determines the regiochemistry is between the LUMO of **1** and the HOMO of the diene. We noted earlier (ref 5b) that the LUMO of **1** is distributed roughly evenly over the two acetylenic carbon atoms, in contrast to what is expected in a simple acetylenic sulfone, where the β-carbon atom of the LUMO normally possesses the larger coefficient. Thus, it appears that the selenide substituent significantly affects the LUMO of **1** and therefore plays a major role in determining the regiochemistry of the cycloadditions and conjugate additons of **1**.

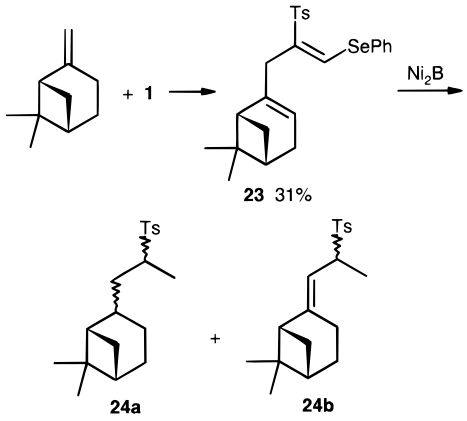
(9) It has been pointed out that hetero-Diels–Alder reactions between an α,β-unsaturated aldehyde and an electron-rich dienophile can proceed with inverse electron demand: (a) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1990; pp 40–45. (b) Desimoni, G.; Tacconi, G. *Chem. Rev.* **1975**, *75*, 651.

Scheme 3



Only a few reactions of acetylenic sulfones with 1,3-dipoles have been previously reported.[11] Although frontier molecular orbital interactions in 1,3-dipolar cycloadditions[12] have been previously investigated,[7,13,14] the regiochemistry of such processes with acetylenic dipolarophiles is generally more difficult to predict than that of the corresponding Diels−Alder reactions. The reactions of **1** with three representative dipoles were investigated, and the results are shown in Scheme 3. The azide **14**[15] produced cycloadducts **15** and **16** in yields of 58% and 18%, respectively. The assignment of the major isomer as **15** was established by means of an NOE experiment (Experimental Section). Azide **14** reacts with acetylenic esters and ketones to afford predominantly the regioisomers derived from attack of its terminal nitrogen atom α to the carbonyl group of the acetylene.[15b] On the other hand, in the principal regioisomer **15**, obtained from **1** and **14**, the terminal nitrogen atom is attached α to the selenide moiety, and not α to the more strongly electron-withdrawing sulfone group. When diazomethane[16] was used as the dipole, only one regioisomer **17** (or its tautomer **18**) was isolated in 81% yield when the reaction was performed rapidly. However, upon exposure to excess diazomethane for a longer period, the cycloaddition was followed by *N*-methylation and the two isomers **19** and **20** were isolated in yields of 69% and 11%, respectively. Both products were also obtained when pure **17** (or **18**) was treated with diazomethane, indicating that **20** is not derived from the unidentified minor regioisomer of **17** (or **18**) formed in the initial cycloaddition step. The nitrile *N*-oxide **21**[17] afforded the single isolable regioisomer **22**. The structures of the major isomer **19** from the diazomethane cycloaddition and that of **22** were established unequivocally by X-ray crystallography (see the Supporting Information).

Scheme 4



Acetylenic sulfones are also known to undergo Lewis acid-catalyzed ene reactions.[2m,18] We observed that the treatment of β-pinene with **1** afforded the ene reaction product **23** in the absence of a Lewis acid, as shown in Scheme 4. Only the one regioisomer, tentatively identified by NOE experiments and by the chemical shift of the olefinic proton of the β-(phenylseleno)vinyl sulfone moiety,[19] was isolated. Furthermore, deselenization of the product with nickel boride[20] afforded a mixture of saturated and partly unsaturated and isomerized products **24a** and **24b** in the ratio of 57:43, each formed as a mixture of epimers. The regiochemistry of the ene reaction was confirmed by decoupling experiments involving the TsCH−CH_3 moiety of the reduced products (see the Experimental Section). Attempts to improve the yield with various Lewis acids were unsuccessful because of the decomposition of **1** in their presence. The regiochemistry of this reaction is again anomalous compared to ene reactions with other acetylenic sulfones.[2m,18]

Some further transformations of the Diels−Alder cycloadducts were then studied. First of all, we investigated

(10) It is possible that **1** is capable of cycloadditions with either normal or inverse electron demand, depending upon whether the other reactant is electron-rich or electron-poor. It is interesting to note that 2-sulfonyl-1,3-dienes also display dual electron demand in cycloadditions and thus react with both electron-rich and electron-deficient alkenes: Bäckvall, J.-E.; Juntunen, S. K. *J. Am. Chem. Soc.* **1987**, *109*, 6393.

(11) Croce, P. D.; La Rosa, C.; Zecchi, G. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2621.

(12) For a general review of 1,3-dipolar cycloadditions, see: *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vols. 1 and 2.

(13) See ref 9a, Chapter 6.

(14) Rauk, A. *Orbital Interaction Theory of Organic Chemistry*; Wiley: New York, 1994; pp 194−197.

(15) For 1,3-dipolar cycloadditions of azides, see: (a) Sheradsky, T. In *The Chemistry of the Azido Group*; Patai, S., Ed.; Wiley: London, 1971; Chapter 6. For other 1,3-dipolar cycloadditions of **14**, see: (b) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem Lett.* **1983**, 1131.

(16) For 1,3-dipolar cycloadditions of diazo compounds, see: Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: Chichester, 1978; Part 2, Chapter 18.

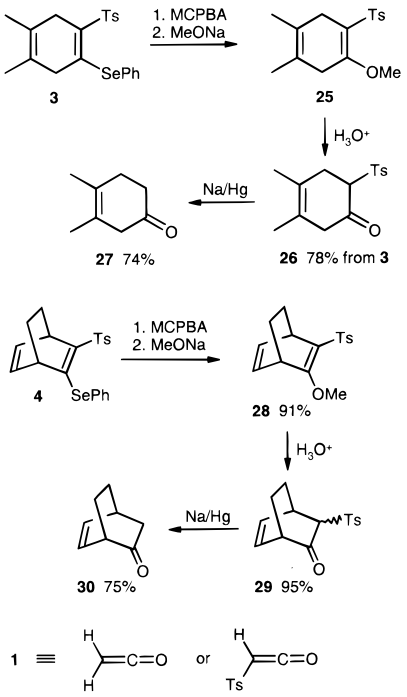
(17) For 1,3-dipolar cycloadditions of nitrile oxides, see: Torsell, K. B. G. *Nitrile Oxides, Nitrones and Nitronates in Organic Synthesis*; VCH: Weinheim, 1988.

(18) Snider, B. B.; Kirk, T. C.; Roush, D. M.; Gonzalez, D. *J. Org. Chem.* **1980**, *45*, 5015.

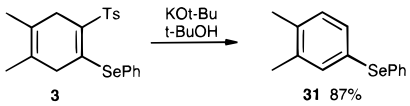
(19) Numerous β-(phenylseleno)vinyl sulfones of regiochemistry opposite that of product **24** [i.e., R(PhSe)C=CHTs] have been prepared by the selenosulfonation of terminal acetylenes. The olefinic protons of these compounds have NMR signals at significantly higher field (ca. δ 6 ppm) than **24** (δ 7.20 ppm), thereby supporting the structure assignment of the latter product. See: Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077.

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

Scheme 5



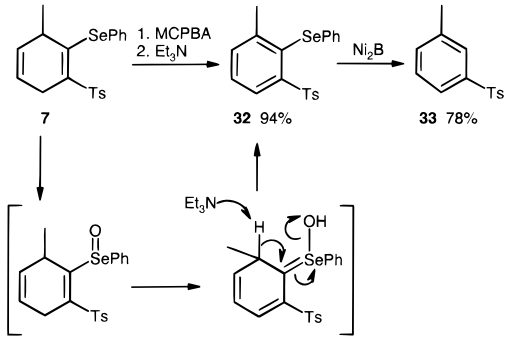
Scheme 6



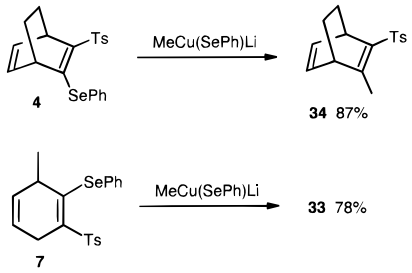
the possibility that **1** could be employed as a ketene equivalent in Diels−Alder reactions, as shown by the two representative examples in Scheme 5. The instability of ketenes, as well their tendency to undergo [2+2] instead of [4+2] cycloadditions,[21] has prompted efforts to design suitable synthetic equivalents for use in the latter reactions.[22,23] Both the monocyclic and bicyclic adducts **3** and **4** were converted into the enol ethers **25** and **28**, respectively, by oxidation and addition−elimination with sodium methoxide. Hydrolysis of the latter products to **26** and **29**, followed by reductive desulfonylation, then afforded the corresponding ketones **27** and **30**, respectively. Direct hydrolysis of the intermediate selenoxides was less effective in producing the desired ketones. Thus, **1** acts as the synthetic equivalent of ketene or *p*-(toluenesulfonyl)ketene in these transformations.

Three other types of transformations of representative cycloadducts were also investigated. First, the treatment of cycloadduct **3** with potassium *tert*-butoxide without prior oxidation resulted in elimination of *p*-toluenesulfinic acid to produce the corresponding aryl phenyl selenide **31** (Scheme 6). Second, adduct **7** was oxidized to its selenoxide and then treated with triethylamine, a milder

Scheme 7



Scheme 8



base than sodium methoxide. The aromatized product **32** was isolated in excellent yield, and was presumably formed via a Pummerer-type mechanism, as shown in Scheme 7. Deselenization of **32** with nickel boride[20] afforded only *m*-tolyl *p*-tolyl sulfone **33**, and not the *o*-tolyl *p*-tolyl isomer. This confirms the indicated regiochemistry of both **32** and the original cycloadduct **7**. Finally, *β*-(phenylseleno)vinyl sulfones are known to undergo substitution of the selenide moiety by organocopper reagents of general structure RCu(SePh)Li.[5b,24] A similar substitution was observed with the bicyclic compound **4**, whereas elimination of the selenol moiety, with accompanying aromatization, occurred in the case of the monocyclic adduct **7** (Scheme 8).

These experiments indicate that the acetylene **1** is an efficient dienophile and dipolarophile. It therefore provides access to 1,4-cyclohexadienes and various heterocycles (namely, 1,2,3-triazoles, 1,2-diazoles, and isoxazoles) containing the useful sulfone and selenide functionalities. Further transformations of the cyloadducts indicate that **1** can be used as a ketene equivalent and in certain elimination and substitution reactions. The unexpected regiochemistry of cycloadditions of **1** with unsymmetrical dienes is under further study.

Experimental Section

The following compounds were prepared by literature methods: acetylene **1**,[5a,b] 2-methoxy-1,3-butadiene,[25] (trimethylsilyl)methyl azide (**14**),[26] 2,4,6-trimethylbenzonitrile *N*-oxide,[27] and cuprous benzeneselenolate.[24] Dienes were distilled prior to use. Chromatography refers to flash chromatography performed on silica gel (230−400 mesh), unless otherwise indicated. NMR spectra were recorded in deuteriochloroform with TMS or residual chloroform as the internal standard.

(21) See: (a) Reference 9a, Chapter 7. (b) Tidwell, T. T. *Ketenes*; Wiley: New York, 1995; Chapter 5. (c) Brady, W. T. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: Chichester, 1980; Part 1, Chapter 8.

(22) For a review of ketene equivalents, see: Ranganathan, S.; Ranganathan, D.; Mehrotra, A. K. *Synthesis* **1977**, 289.

(23) For some previous examples of synthetic equivalents of ketene, see: (a) Corey, E. J.; Ravindranathan, T.; Terashima, S. *J. Am. Chem. Soc.* **1971**, *93*, 4326. (b) Trost, B. M.; Tamaru, Y. *J. Am. Chem. Soc.* **1975**, *97*, 3528. (c) Evans, D. A.; Scott, W. L.; Truesdale, L. K. *Tetrahedron Lett.* **1972**, 121. (d) Bartlett, P. A.; Green, F. R., III; Webb, T. R. *Tetrahedron Lett.* **1977**, 331.

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

(25) Dolby, L. J.; Marshall, K. S. *Org. Prep. Proced. Int.* **1969**, *1*, 229.

(26) Nishiyama, K.; Tanaka, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1322.

(27) Grundmann, C.; Richter, R. *J. Org. Chem.* **1968**, *33*, 476.

Diels−Alder Cycloadditions of 1-Phenylseleno-2-(*p*-toluenesulfonyl)ethyne (1). Typical Procedure (Entry 1, Table 1). A 1 mL thick-walled reaction vial with a Teflon-lined cap containing acetylene **1** (210 mg, 0.626 mmol) was cooled to −78 °C, and excess 1,3-butadiene was condensed into the vial from a lecture bottle. The sealed vial was warmed to room temperature, and stirring was continued for 4 days. The excess butadiene was then allowed to evaporate, and the oily residue was chromatographed (elution with 5% ethyl acetate−hexanes) to afford 199 mg (81%) of 1-phenylseleno-2-(*p*-toluenesulfonyl)-1,4-cyclohexadiene (**2**) as a colorless oil; IR (neat) 1300, 1148 cm^{-1}; ^1H NMR (200 MHz) δ 8.00 (d, J = 8.3 Hz, 2 H), 7.60 (dd, J = 8.0 Hz, 1.5 Hz, 2 H), 7.46−7.28 (m, 5 H), 5.66 (m, 1 H), 5.36 (m, 1 H), 3.06 (m, 2 H), 2.63 (m, 2 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz) δ 144.4, 143.2, 137.7, 137.3, 129.8, 129.6, 129.4, 129.1, 127.7, 127.2, 122.4, 122.2, 35.3, 29.0, 21.6; MS *m*/*z* (relative intensity, %) 390 (44, M^+), 233 (33), 157 (54), 91 (100); exact mass calcd for $C_{19}H_{18}O_2SSe$ 390.0196, found 390.0194.

The other products listed in Table 1 were prepared similarly, by heating the diene with **1** in a sealed vial under the conditions indicated in Table 1. In general, a 5−10-fold excess of the diene was employed, and the yields in Table 1 are based on the acetylene **1**.

4,5-Dimethyl-1-phenylseleno-2-(*p*-toluenesulfonyl)-1,4-cyclohexadiene (3) (Entry 2): mp 180−182 °C (from chloroform−ethanol); IR (CH_2Cl_2) 1310, 1157 cm^{-1}; ^1H NMR (200 MHz) δ 8.00 (d, J = 8.1 Hz, 2 H), 7.58 (dd, J = 6.5, 0.5 Hz, 2 H), 7.41−7.28 (m, 5 H), 2.97 (t, J = 7.2 Hz, 2 H),[28] 2.53 (t, J = 7.1 Hz, 2 H),[28] 2.46 (s, 3 H), 1.58 (s, 3 H), 1.35 (s, 3 H); ^{13}C NMR (50 MHz) δ 144.3, 143.0, 137.53, 137.50, 130.4, 129.6, 129.3, 129.1, 127.6, 127.3, 121.9, 121.7, 41.7, 35.3, 21.6, 17.7, 17.3; MS *m*/*z* (relative intensity, %) 418 (7, M^+), 182 (23), 105 (27), 91 (100); exact mass calcd for $C_{21}H_{22}O_2SSe$ 418.0505, found 418.0533.

2-Phenylseleno-3-(*p*-toluenesulfonyl)-2,5-bicyclo[2.2.2]-octadiene (4) (Entry 3): mp 128−130 °C (from ethanol); IR (CH_2Cl_2) 1318, 1299, 1147, 1088 cm^{-1}; ^1H NMR (400 MHz) δ 7.86 (d, J = 8.3 Hz, 2 H), 7.55 (dd, J = 8.0, 1.2 Hz, 2 H), 7.45−7.32 (m, 5 H), 6.24 (ddd, J = 6.2, 6.0, 1.2 Hz, 1 H), 6.00 (ddd, J = 6.3, 6.1, 1.2 Hz, 1 H), 4.10−4.07 (m, 1 H), 3.51−3.48 (m, 1 H), 2.44 (s, 3 H); 1.37−1.20 (m, 4 H); MS *m*/*z* (relative intensity, %) 416 (45, M^+), 388 (87), 323 (100). Anal. Calcd for $C_{21}H_{20}O_2SSe$: C, 60.72; H, 4.85. Found: C, 60.27; H, 4.88.

2-Phenylseleno-3-(*p*-toluenesulfonyl)-2,5-bicyclo[2.2.1]-heptadiene (5) (Entry 4): mp 137−138.5 °C (from hexanes); IR (CH_2Cl_2) 1310, 1299, 1138 cm^{-1}; ^1H NMR (400 MHz) δ 7.79 (d, J = 8.3 Hz, 2 H), 7.61 (dd, J = 8.3, 1.3 Hz, 2 H), 7.47−7.36 (m, 3 H), 7.33 (d, J = 8.1 Hz, 2 H), 6.46 (dd, J = 5.0, 2.9 Hz, 1 H), 6.35 (dd, J = 5.0, 3.3 Hz, 1 H), 3.81 (m, 1 H), 3.32 (m, 1 H), 2.45 (s, 3 H), 2.12 (ddd, J = 6.7, 1.5, 1.5 Hz, 1 H), 1.83 (ddd, J = 6.8, 1.6, 1.6 Hz, 1 H); MS *m*/*z* (relative intensity, %) 402 (90, M^+), 245 (43), 165 (100). Anal. Calcd for $C_{20}H_{18}O_2SSe$: C, 59.85; H, 4.52. Found: C, 59.58; H, 4.50.

7-Oxa-2-phenylseleno-3-(*p*-toluenesulfonyl)-2,5-bicyclo[2.2.1]heptadiene (6) (Entry 5): mp 135−138 °C (from ethanol); IR (CH_2Cl_2) 1312, 1302, 1270, 1149 cm^{-1}; ^1H NMR (400 MHz) δ 7.83 (d, J = 8.3 Hz, 2 H), 7.65 (dd, J = 8.3, 1.4 Hz, 2 H), 7.51−7.36 (m, 5 H), 6.91 (dd, J = 5.3, 1.7 Hz, 1 H), 6.79 (dd, J = 5.3, 1.9 Hz, 1 H), 5.46 (dd, J = 1.5, 1.5 Hz, 1 H), 4.90 (dd, J = 1.6, 1.6 Hz, 1 H), 2.47 (s, 3 H); MS *m*/*z* (relative intensity, %) 404 (20, M^+), 336 (100). Anal. Calcd for $C_{19}H_{16}O_3SSe$: C, 56.58; H, 4.00. Found: C, 56.55; H, 4.14.

3-Methyl-2-phenylseleno-1-(*p*-toluenesulfonyl)-1,4-cyclohexadiene (7) (Entry 6): mp 125−130 °C (from ethanol); IR (CH_2Cl_2) 1301, 1150 cm^{-1}; ^1H NMR (400 MHz) δ 8.03 (d, J = 8.2 Hz, 2 H), 7.49 (dd, J = 8.1, 1.0 Hz, 2 H), 7.40−7.28 (m, 5 H), 5.68−5.64 (m, 1 H), 5.49−5.45 (m, 1 H), 3.18 (ddt, J = 22.1, 2.7, 0.4 Hz, 1 H), 3.05 (ddt, J = 22.1, 4.4, 0.9 Hz, 1 H), 2.74 (m, 1 H), 2.46 (s, 3 H), 1.08 (d, J = 6.8 Hz, 3 H); an NOE was observed for δ 7.49 (*ortho*-protons of PhSe) when δ 2.74 (H-3) was irradiated and vice versa; MS *m*/*z* (relative intensity, %) 404 (20, M^+), 155 (28), 91 (100). Anal. Calcd for $C_{20}H_{20}O_2SSe$: C, 59.55; H, 5.00. Found: C, 59.60; H, 4.69.

4-Methyl-1-phenylseleno-2-(*p*-toluenesulfonyl)-1,4-cyclohexadiene (8) and 4-Methyl-2-phenylseleno-1-(*p*-toluenesulfonyl)-1,4-cyclohexadiene (9) (Entry 7). The unseparated mixture, containing equal amounts of **8** and **9**, was obtained as a colorless oil: IR (CH_2Cl_2) 1311, 1302, 1146, 1085 cm^{-1}; ^1H NMR (200 MHz) δ 8.00 (two superimposed d, total 4 H, both isomers), 7.6 (two superimposed dd, total 4 H, both isomers), 7.41−7.28 (m, total 10 H, both isomers), 5.35 (m, 1 H, one isomer), δ 5.05 (m, 1 H, one isomer; the reported ratio is based on the integration of this signal and that at δ 5.35), 3.10 (m, 2 H, one isomer), 2.91 (t, J = 7.6 Hz, 2 H, one isomer),[28] 2.64 (m, 2 H, one isomer), 2.51 (t, J = 7.7 Hz, 2 H, one isomer),[28] 2.47 (s, total 6 H, both isomers), 1.62 (d, J = 0.8 Hz, 3 H, one isomer), δ 1.41 (d, J = 0.9 Hz, 3 H, one isomer); MS *m*/*z* (relative intensity, %) 404 (35, M^+), 168 (60), 91 (100). Anal. Calcd for $C_{20}H_{20}O_2SSe$: C, 59.55; H, 5.00. Found: C, 59.47; H, 4.51.

1-Phenylseleno-2-(*p*-toluenesulfonyl)benzene (10) (Entry 8): mp 141−144 °C (from ethanol); IR (CH_2Cl_2) 1315, 1304, 1154 cm^{-1}; ^1H NMR (200 MHz) δ 8.18 (dd, J = 7.7, 1.7 Hz, 1 H), 7.99 (d, J = 8.4 Hz, 2 H), 7.49−7.17 (m, 9 H), 6.99 (dd, J = 7.5, 1.7 Hz, 1 H), 2.43 (s, 3 H); MS *m*/*z* (relative intensity, %) 388 (100, M^+), 323 (84), 91 (31). Anal. Calcd for $C_{19}H_{16}O_2SSe$: C, 58.91; H, 4.16. Found: C, 58.89; H, 3.94.

3-Methoxy-2-phenylseleno-1-(*p*-toluenesulfonyl)-1,4-cyclohexadiene (11) (Entry 9): colorless oil; IR (CH_2Cl_2) 1304, 1150 cm^{-1}; ^1H NMR (400 MHz) δ 8.04 (d, J = 8.3 Hz, 2 H), 7.59 (dd, J = 6.9, 1.4 Hz, 2 H), 7.38−7.28 (m, 5 H), 6.08 (dt, J = 9.9, 3.5 Hz, 1 H), 5.55 (m, 1 H) 4.29 (dd, J = 9.5, 4.7 Hz, 1 H), 3.26 (d of quintets, J = 23.6, 2.7 Hz, 1 H), 3.06 (dm, J = 23.6 Hz, 1 H), 2.93 (s, 3 H), 2.47 (s, 3 H); an NOE was observed for δ 7.59 (*ortho*-protons of PhSe) when δ 4.29 (H-3) was irradiated and vice versa; ^{13}C NMR (100 MHz) δ 144.8, 143.6, 137.5, 137.1, 136.7, 129.7, 129.2, 128.9, 128.2, 127.9, 127.2, 122.7, 70.8, 50.9, 30.4, 21.7; MS *m*/*z* (relative intensity, %) 420 (15, M^+), 388 (100); exact mass calcd for $C_{20}H_{20}O_3SSe$ 420.0338, found 420.0343.

4-Methoxy-1-phenylseleno-2-(*p*-toluenesulfonyl)-1,4-cyclohexadiene (12) (Entry 10). Chromatography was performed on alumina: colorless oil; IR (CH_2Cl_2) 1301, 1147 cm^{-1}; ^1H NMR (400 MHz) δ 7.99 (d, J = 8.2 Hz, 2 H), 7.62 (dd, J = 8.0, 1.0 Hz, 2 H), 7.38−7.28 (m, 5 H), 4.30 (br t, J = 3.6 Hz, 1 H), 3.44 (s, 3 H), 3.06 (dt, J = 7.3, 0.7 Hz, 2 H),[28] 2.75 (dt, J = 7.3, 3.6 Hz, 2 H),[28] 2.47 (s, 3 H); an NOE was observed for δ 7.99 (*ortho*-protons of Ts) when δ 3.06 (H-3) was irradiated and vice versa; when δ 3.06 was irradiated, the signal at δ 3.44 (OMe) was also enhanced; ^{13}C NMR (100 MHz) δ 151.4, 144.5, 143.5, 137.8, 137.1, 136.3, 129.7, 129.4, 129.1, 127.7, 127.3, 89.3, 54.2, 35.8, 30.9, 21.7; MS *m*/*z* (relative intensity, %) 420 (25, M^+), 157 (55), 91 (100); exact mass calcd for $C_{20}H_{20}O_3SSe$ 420.0338, found 420.0302.

1-Oxa-3-phenylseleno-2-(*p*-toluenesulfonyl)-2,5-cyclohexadiene (13) (Entry 11). Chromatography was performed on alumina: colorless oil; IR (CH_2Cl_2) 1303, 1139 cm^{-1}; ^1H NMR (200 MHz) δ 7.94 (d, J = 8.3 Hz, 2 H), 7.58 (dd, J = 8.1, 1.5 Hz, 2 H), 7.39−7.23 (m, 5 H), 5.98 (dt, J = 6.0, 1.9 Hz, 1 H), 4.96 (dt, J = 6.0, 3.6 Hz, 1 H), 2.95 (m, 2 H), 2.47 (s, 3 H); an NOE was observed for δ 7.58 (*ortho*-protons of PhSe) when δ 2.95 (H-4) was irradiated and vice versa; ^{13}C NMR (50 MHz) δ 144.4, 139.9, 136.8, 136.5, 130.4, 129.7, 129.0, 128.8, 127.9, 127.4, 110.9, 102.7, 29.7, 21.7; MS *m*/*z* (relative intensity, %) 392 (6, M^+), 91 (48), 57 (100); exact mass calcd for $C_{18}H_{16}O_3SSe$ 391.9888, found 391.9990.

Cycloaddition of Acetylene 1 with (Trimethylsilyl)-methyl Azide (14). Acetylene **1** (85 mg, 0.25 mmol) and 300 μL of (trimethylsilyl)methyl azide were stirred in 5 mL of ether for 2 days at room temperature. Volatile material was then evaporated in vacuo, and the crude mixture was separated by chromatography (elution with hexanes−ethyl acetate, 5:1) to afford 68 mg (58%) of **15** and 21 mg (18%) of **16**.

(28) The large coupling constant of ca. J = 7 Hz is assigned to the 5-bond coupling of the methylene protons at the 3-position with those at the 6-position. Similar large couplings have been reported for other 1,4-cyclohexadienes: Durham, L. J.; Studebaker, J.; Perkins, M. J. *J. Chem. Soc., Chem. Commun.* **1965**, 456.

Compound 15: R_f 0.38; mp 103−108 °C; IR (film) 1335, 1304, 1293, 1162, 1151 cm^{-1}; ^1H NMR (200 MHz) δ 7.92 (d, J = 8.4 Hz, 2 H), 7.65−7.59 (m, 2 H), 7.39−7.30 (m, 5 H), 4.01 (s, 2 H), 2.45 (s, 3 H), 0.13 (s, 9 H); an NOE was observed for δ 7.92 (*ortho*-protons of Ts) when δ 4.01 (CH_2Si) was irradiated and vice versa; ^{13}C NMR (50 MHz) δ 145.9, 137.3, 134.9, 130.1, 129.3, 129.1, 128.8, 128.6, 127.4, 126.5, 41.8, 21.7, −2.0; MS *m*/*z* (relative intensity, %) 465 (19, M^+), 73 (100); exact mass calcd for $C_{19}H_{23}N_3O_2SSeSi$ 465.0455, found 465.0431.

Compound 16: R_f 0.24; oil; IR (film) 1335, 1157 cm^{-1}; ^1H NMR (200 MHz) δ 7.95 (d, J = 8.4 Hz, 2 H), 7.28−7.18 (m, 7 H), 3.70 (s, 2 H), 2.40 (s, 3 H), 0.04 (s, 9 H); ^{13}C NMR (50 MHz) δ 144.8, 137.5, 131.9, 129.9, 129.7, 129.6, 128.9, 128.4, 128.3, 127.6, 41.0, 21.6, −2.2; MS *m*/*z* (relative intensity, %) 465 (11, M^+), 91 (73), 73 (100); exact mass calcd for $C_{19}H_{23}N_3O_2SSeSi$ 465.0455, found 465.0495.

Cycloaddition of Acetylene 1 with Diazomethane. Acetylene **1** (37 mg, 0.11 mmol) was dissolved in 5 mL of ether, and diazomethane was added dropwise until a yellow color persisted. After 5 min, volatile material was evaporated and the residue was purified by chromatography (elution with 33% ethyl acetate−hexane) to afford 34 mg (81%) of homogeneous cycloadduct **17** (or **18**): mp 112−116 °C; IR (film) 3259, 3135, 1316, 1302, 1148 cm^{-1}; ^1H NMR (200 MHz) δ 7.95−7.86 (m, 3 H), 7.54−7.49 (m, 2 H), 7.40−7.28 (m, 5 H), 2.41 (s, 3 H); ^{13}C NMR (50 MHz) δ 144.1, 138.9, 137.8, 134.5, 129.8, 129.64, 129.55, 129.47, 129.0, 127.2, 125.9, 21.5; MS *m*/*z* (relative intensity, %) 378 (100, M^+), 91 (64); exact mass calcd for $C_{16}H_{14}N_2O_2SSe$ 377.9944, found 377.9914.

When the reaction was repeated with excess diazomethane for 3 h at room temperature, chromatography (elution with 33% ethyl acetate-hexane) afforded 69% of the major *N*-methylated regioisomer **19** and 11% of the minor regioisomer **20**.

Major Isomer 19: R_f 0.37; mp 104−107 °C; IR (film) 1316, 1302, 1168, 1148 cm^{-1}; ^1H NMR (400 MHz) δ 8.07 (s, 1 H), 7.90 (d, J = 8.3 Hz, 2 H), 7.21−7.19 (m, 3 H), 7.14−7.10 (m, 2 H), 6.95 (d, J = 7.7 Hz, 2 H), 3.76 (s, 3 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz) δ 144.0, 140.3, 139.1, 131.0, 129.7, 129.5, 129.3, 128.4, 128.3, 127.8, 127.7, 38.7, 21.5; MS *m*/*z* (relative intensity, %) 392 (95, M^+), 91 (75), 84 (100); exact mass calcd for $C_{17}H_{16}N_2O_2SSe$ 392.0102, found 392.0058. For the X-ray crystal structure of **19**, see the Supporting Information.

Minor Isomer 20: R_f 0.13; mp 116−119 °C; IR (film) 1348, 1314, 1302, 1153 cm^{-1}; ^1H NMR (200 MHz) δ 7.95 (s, 1 H), 7.86 (d, J = 8.2 Hz, 2 H), 7.35−7.15 (m, 7 H), 3.89 (s, 3 H), 2.37 (s, 3 H); an NOE was observed for δ 7.95 (diazole ring CH) when δ 3.89 (NMe) was irradiated and vice versa; ^{13}C NMR (50 MHz) δ 143.9, 138.8, 134.7, 132.8, 132.7, 129.4, 129.0, 128.9, 128.8, 127.6, 127.4, 39.8, 21.5; MS *m*/*z* (relative intensity, %) 392 (100, M^+), 157 (47), 91 (35); exact mass calcd for $C_{17}H_{16}N_2O_2SSe$ 392.0102, found 392.0057.

Cycloaddition of Acetylene 1 with 2,4,6-Trimethylbenzonitrile *N*-Oxide (21). Acetylene **1** (275 mg, 0.820 mmol) and *N*-oxide **21** (132 mg, 0.820 mmol) were stirred in 25 mL of ether at room temperature for 24 h. The mixture was concentrated in vacuo, and the crude product was separated by chromatography (elution with hexanes−ethyl acetate, 5:1) to afford 254 mg (63%) of the corresponding cycloadduct **22**,[29] which was recrystallized from ethyl acetate−hexane: R_f 0.48; mp 120−124 °C; IR (film) 1323, 1304, 1159, 1135 cm^{-1}; ^1H NMR (200 MHz) δ 7.83 (dd, J = 7.8, 1.8 Hz, 2 H), 7.48−7.40 (m, 3 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.16 (d, J = 8.6 Hz, 2 H), 6.83 (s, 2 H), 2.42 (s, 3 H), 2.34 (s, 3 H), 1.72 (s, 6 H); ^{13}C NMR (50 MHz) δ 168.1, 160.3, 144.8, 139.8, 138.0, 137.7, 136.8, 130.1, 129.7, 129.4, 128.0, 127.6, 122.4, 122.2, 119.1, 21.6, 21.3, 19.6; MS *m*/*z* (relative intensity, %) 340 (64, M^+ − PhSe), 157 (98), 155 (91), 91 (100), 77 (99); exact mass calcd for $C_{19}H_{18}NO_3S$ (M^+ − PhSe) 340.1007, found 340.1005. For the X-ray crystal structure of **22**, see the Supporting Information.

Ene Reaction of Acetylene 1 with *β*-Pinene. Acetylene **1** (156 mg, 0.465 mmol) was dissolved in (1*S*)-*β*-pinene (1.0 mL, 6.3 mmol) in a sealed 5 mL reaction vial fitted with a Teflon-lined cap. The solution was heated at 60 °C for 4 days. The excess pinene was then evaporated in vacuo to yield a brown oil which was chromatographed (elution with 5% ethyl acetate−hexanes) to afford **23** (68.5 mg, 31%) as a colorless oil along with recovered **1** (72 mg, 46%).

Compound 23: IR (neat) 1306, 1141 cm^{-1}; ^1H NMR (200 MHz) δ 7.88 (d, J = 8.3 Hz, 2 H), 7.58 (dd, J = 7.3, 2.1 Hz, 2 H), 7.38−7.32 (m, 5 H), 7.20 (s, 1 H), 5.22 (m, 1 H), 2.92 (m, 2 H), 2.47 (s, 3 H), 2.25 (m, 1 H), 2.13 (m, 2 H), 1.99 (m, 2 H), 1.71 (m, 1 H), 1.16 (s, 3 H), 0.67 (s, 3 H); an NOE was observed for δ 2.92 (bisallylic CH_2) and δ 7.58 (*ortho*-protons of PhSe) when the signal at δ 7.88 (*ortho*-protons of Ts) was irradiated; irradiation of δ 7.20 (vinylic H *gem* to PhSe) produced an NOE at δ 2.92 and 7.58; no NOE was observed between signals at δ 7.58 and 2.92; ^{13}C NMR (50 MHz) δ 144.6, 143.1, 140.2, 137.2, 134.4, 133.4, 132.4, 129.7, 129.3, 128.3, 127.6, 121.0, 44.9, 40.3, 39.4, 37.8, 31.8, 31.3, 26.0, 21.6, 20.8; MS *m*/*z* (relative intensity, %) 472 (2, M^+), 91 (56), 41 (100); exact mass calcd for $C_{25}H_{28}O_2SSe$ 472.0979, found 472.0974.

Deselenization of Cycloadduct 23. Compound **23** (131 mg, 0.28 mmol) and $NiCl_2 \cdot 6H_2O$ (198 mg, 0.83 mmol) were stirred in 7 mL of methanol−THF (85:15) and cooled to 0 °C. Sodium borohydride (150 mg, 3.97 mmol) was added in portions over 5 min. (*Caution*: vigorous reaction with evolution of hydrogen!) After 15 min the black suspension was filtered through Celite, which was washed repeatedly with ether. The combined ether fractions were washed with water and dried ($MgSO_4$), and the solvent was evaporated. Chromatography of the residue (elution with hexanes−ethyl acetate, 20:1) afforded 65 mg of the crude mixture of deselenized products **24a** and **24b**, produced in the ratio of 57:43, showing ^1H NMR signals attributed to **24a** [δ 3.01 (m, CHTs) and 1.25 (d, J = 6.7 Hz, CH_3CHTs)] and **24b** [δ 4.99 (d, J = 10.3 Hz, C=CH; major stereoisomer) and 4.83 (d, J = 10.2 Hz, C=CH; minor stereoisomer), 3.82 (m, CHTs) and 1.42 (d, J = 6.8 Hz, CH_3-CHTs)]. Double irradiation at δ 3.01 collapsed the doublet at δ 1.25 to a singlet; irradiation at δ 1.25 collapsed the multiplet at δ 3.01 to a crude triplet. Double irradiation at δ 3.82 collapsed the doublets at δ 4.99, 4.83 and 1.42 to singlets; irradiation at δ 1.42 collapsed the multiplet at δ 3.82 to two doublets at δ 3.86 and 3.81 (minor and major stereoisomers, respectively, each with J = 10.3 Hz).

Preparation of 3,4-Dimethyl-3-cyclohexenone (27). Cycloadduct **3** (967 mg, 2.32 mmol) was dissolved in chloroform (3 mL), *m*-CPBA (406 mg, 2.35 mmol) was added, and the solution was stirred at room temperature for 20 min. The reaction mixture was washed with K_2CO_3 and dried ($MgSO_4$), and the solvent was evaporated to give a colorless oil (997 mg), which was suspended in methanol (2 mL). Sodium methoxide in methanol (2.3 mL, 1 M) was added. The mixture was stored at −20 °C for 24 h, and the resulting mixture containing **25** was poured into ether (10 mL), extracted with 10% hydrochloric acid, and washed with water. The organic layer was dried ($MgSO_4$), the solvent was evaporated, and the resulting yellow oil was chromatographed (elution with hexanes and then 10% ethyl acetate−hexanes) to give **26** (499 mg, 78%) as a colorless oil that was used directly in the next step.

Compound **26** (472 mg, 1.70 mmol) was desulfonylated with 5% sodium amalgam (2.35 g, 5.11 mmol of Na) in the presence of Na_2HPO_4 (965 mg, 6.80 mmol) in dry methanol−THF (7 mL, 1:1) by the procedure of Trost et al.[30] to afford the known[23a] compound **27** (156 mg, 74%) as an oil.

Preparation of 5-Bicyclo[2.2.2]octen-2-one (30). Cycloadduct **4** (208 mg, 0.501 mmol) was dissolved in chloroform (1 mL), and *m*-CPBA (104 mg, 0.603 mmol) was added. The solution was stirred at room temperature for 20 min. The reaction mixture was washed with K_2CO_3 solution and dried ($MgSO_4$), and the solvent was evaporated to give the corre-

(29) The mother liquor contained a minor product that could not be isolated in pure form, but that may be the other regioisomer: ^1H NMR (200 MHz) δ 8.08 (d, J = 8.4 Hz), 6.71 (s), 2.49 (s), 2.26 (s), 1.72 (s).

(30) (a) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4743. (b) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

sponding selenoxide (216 mg, 100%) as a mixture of diastereomers, obtained as white crystals. The latter product was suspended in methanol (0.5 mL), and a solution of sodium methoxide in methanol (500 μL, 1 M) was added. The mixture was then refluxed for 30 min, poured into ether (10 mL), and washed with water. The organic layer was dried ($MgSO_4$), and the solvent was evaporated in vacuo. The residual oil was chromatographed (elution with 10% ethyl acetate−hexanes) to afford **28** (132 mg, 91%) as white crystals: mp 125−127 °C (from ethanol); IR (CH_2Cl_2) 1299, 1141 cm^{-1}; ^1H NMR (200 MHz) 7.75 (d, J = 8.3 Hz, 2 H), 7.25 (d, J = 8.4 Hz, 2 H), 6.46 (ddd, J = 7.3, 6.1, 1.2 Hz, 1 H), 6.17 (ddd, J = 7.4, 6.0, 1.6 Hz, 1 H), 4.17 (m, 1 H), 3.89 (m, 1 H), 3.78 (s, 3 H), 2.41 (s, 3 H), 1.51−1.36 (m, 4 H); ^{13}C NMR (50 MHz) δ 169.2, 142.9, 140.7, 137.2, 130.9, 129.4, 129.2, 126.8, 56.8, 37.3, 37.2, 25.5, 24.6, 21.5; MS *m*/*z* (relative intensity, %) 290 (51, M^+), 262 (85), 105 (100), 91 (74); exact mass calcd for $C_{16}H_{18}O_3S$ 290.0977, found 290.0995.

Compound **28** (160 mg, 0.551 mmol) was dissolved in THF (1 mL), and 10% hydrochloric acid (1 mL) was added. The mixture was stirred at room temperature for 1 h and was then neutralized (Na_2CO_3), poured into ether (10 mL), and washed with water and brine. The organic phase was dried ($MgSO_4$) and evaporated to give **29** (145 mg, 95%) as white crystals consisting of a 1.4:1 mixture of diastereomers (NMR integration). The product was used in the next step without further purification or attempts at separating the two diastereomers.

β-Keto sulfone **29** (207 mg, 0.749 mmol) was desulfonylated as in the case of **26** to afford 69 mg (75%) of the known[23b] compound **30** as an oil.

1,2-Dimethyl-4-(phenylseleno)benzene (31). Cycloadduct **3** (156 mg, 0.374 mmol) and potassium *tert*-butoxide (46 mg, 0.41 mmol) were refluxed for 4 h in 5 mL of *tert*-butyl alcohol. The mixture was poured into ether (20 mL) and washed with water, and the organic phase was dried ($MgSO_4$) and evaporated in vacuo. The brown residue was chromatographed (elution with hexanes) to afford 84 mg (87%) of **31** as a colorless oil: IR (CH_2Cl_2) 1576, 812, 746 cm^{-1}; ^1H NMR (200 MHz) δ 7.35−7.31 (m, 2 H), 7.25 (d, J = 1.0 Hz, 1 H), 7.19−7.13 (m, 4 H), 6.98 (d, J = 7.8 Hz, 1 H), 2.17 (s, 3 H), 2.15 (s, 3 H); ^{13}C NMR (50 MHz) δ 137.9, 136.4, 135.1, 132.3, 131.9, 131.6, 130.6, 129.2, 126.8, 126.7, 19.6, 19.5; MS *m*/*z* (relative intensity, %) 262 (71, M^+), 182 (100); exact mass calcd for $C_{14}H_{14}Se$ 262.0261, found 262.0243.

Preparation and Deselenization of 2-Phenylseleno-3-(*p*-toluenesulfonyl)toluene (32). Cycloadduct **7** (202 mg, 0.501 mmol) was dissolved in chloroform (1 mL), and *m*-CPBA (104 mg, 0.603 mmol) was added. The solution was stirred at room temperature for 20 min and was then washed with K_2CO_3 solution and dried ($MgSO_4$), and the solvent was evaporated to give a white residue. It was dissolved in THF (1 mL) containing triethylamine (70 μL, 0.50 mmol) and refluxed for 12 h. The solution was poured into ether (20 mL), washed with water, and dried ($MgSO_4$), and the solvent was evaporated. Chromatography (elution with 5% ethyl acetate−hexanes) afforded 189 mg (94%) of **32**: IR (CH_2Cl_2) 1312, 1303, 1151 cm^{-1}; ^1H NMR (200 MHz) δ 8.37 (m, 1 H), 7.84 (d, J = 8.3 Hz, 2 H), 7.53−7.49 (m, 2 H), 7.10 (d, J = 8.4 Hz, 2 H), 7.05−6.93 (m, 3 H), 6.62 (dd, J = 8.0, 1.5 Hz, 2 H), 2.27 (s, 6 H); ^{13}C NMR (50 MHz) δ 146.5, 145.8, 143.5, 137.7, 135.5, 132.3, 129.5, 129.0, 128.94, 128.90, 128.9, 128.8, 128.2, 126.1, 23.6, 21.4; MS *m*/*z* (relative intensity, %) 402 (27, M^+), 165 (100), 91 (94); exact mass calcd for $C_{20}H_{18}O_2SSe$ 402.0196, found 402.0204.

Compound **32** (100 mg, 0.249 mmol) and $NiCl_2 \cdot 6H_2O$ (416 mg, 1.75 mmol) were dissolved in 2.5 mL of methanol and THF (85:15) and cooled to 0 °C. Sodium borohydride (199 mg, 5.25 mmol) was added in portions over 5 min. (*Caution*: vigorous reaction with evolution of hydrogen!) After 15 min the black suspension was filtered through Celite, which was washed repeatedly with ether. The combined ether fractions were washed with water and dried ($MgSO_4$), and the solvent was evaporated. Chromatography of the residue (elution with 10% ether−hexanes) afforded 47 mg (78%) of *m*-tolyl *p*-tolyl sulfone (**33**) as white crystals: mp 114−115 °C (from ethanol) (lit.[31] mp 116 °C); IR (CH_2Cl_2) 1301, 1150, 1103 cm^{-1}; ^1H NMR (200 MHz) δ 7.83 (d, J = 8.4 Hz, 2 H), 7.75−7.72 (m, 2 H), δ 7.38−7.28 (m, 4 H), δ 2.40 (s, 6 H); MS *m*/*z* (relative intensity, %) 246 (20, M^+), 139 (100), 91 (32).

2-Methyl-3-(*p*-toluenesulfonyl)-2,5-bicyclo[2.2.2]-octadiene (34). MeLi (357 μL, 1.38 M, 0.493 mmol) was added to a suspension of cuprous benzeneselenolate (110 mg, 0.501 mmol) in dry THF (2 mL) at 0 °C under argon, and the solution was stirred for 20 min at 0 °C. The mixture was cooled to −78 °C, and a solution of **4** (208 mg, 0.501 mmol) in dry THF (1 mL) was added dropwise over a period of 5 min. The mixture was warmed to 0 °C and stirred for 2.5 h. The reaction was quenched with 2 mL of NH_4Cl solution and was stirred for an additional 30 min. The suspension was poured into ether (15 mL), washed with NH_4Cl solution, dried ($MgSO_4$), and evaporated. Chromatography of the residue (elution with 10% ethyl acetate−hexanes) afforded 119 mg (87%) of **34** as a yellow oil: IR (neat) 1292, 1147 cm^{-1}; ^1H NMR (200 MHz) δ 7.70 (d, J = 8.3 Hz, 2 H), 7.25 (d, J = 8.4 Hz, 2 H), 6.25−6.21 (m, 2 H), 3.95−3.90 (m, 1 H), 3.51−3.47 (m, 1 H), 2.41 (s, 3 H), 2.32 (s, 3 H), 1.39−1.21 (m, 4 H); ^{13}C NMR (200 MHz) δ 156.4, 143.5, 139.0, 136.7, 134.4, 132.5, 129.6, 126.9, 46.8, 38.6, 25.8, 23.8, 21.5, 17.7; MS *m*/*z* (relative intensity, %) 274 (5, M^+), 246 (72), 91 (100); exact mass calcd for $C_{16}H_{18}O_2S$ 274.1028, found 274.1026.

Reaction of 7 with MeCu(SePh)Li. MeLi (214 μL, 1.38 M, 0.295 mmol) was added to a suspension of cuprous benzeneselenolate (65 mg, 0.30 mmol) in dry THF (2 mL) at 0 °C under argon, and the solution was stirred for 20 min. The mixture was cooled to −78 °C, and a solution of **7** (121 mg, 0.300 mmol) in dry THF (1 mL) was added dropwise over a period of 5 min. The mixture was warmed to 0 °C and stirred for 2.5 h. The reaction was worked up as in the preceding experiment to give a yellow oil, which was chromatographed (elution with 10% ethyl acetate−hexanes) to afford 56 mg (78%) of **33** as white crystals with mp 112−114.5 °C (from ethanol) (lit.[31] mp 116 °C), identical (TLC and IR and ^1H NMR spectra) with the sample prepared from the deselenization of **32**.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of new compounds not having combustion analyses, ORTEP diagrams of compounds **19** and **22**, and tables of crystal data, bond lengths and angles, atomic coordinates, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) *Dictionary of Organic Compounds*, 6th ed.; Cadogan, J. I. G., Ley, S. V., Pattenden, G., Raphael, R. A., Rees, C. W., Eds.; Chapman and Hall: London, 1996; Vol. 3, entry D-0-09403. The mp of the *o*-tolyl *p*-tolyl sulfone isomer of **33** is 60 °C and therefore considerably lower; see entry D-0-0941.