***trans*-3,6-Dimethyl-1,2,4,5-tetroxane (5b).** The diperoxidic character was determined by the reaction with triphenylphosphine. The reaction was done in a degassed, sealed tube. It was found that one tetroxane reacted with two Ph_3P to form two Ph_3PO and two acetaldehydes: ^1H NMR ($CDCl_3$) δ 5.99 (q, J = 5.5 Hz, 2 H, H-3), 1.28 (d, J = 5.5 Hz, 6 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 105.5 (dq, $J_{C[H]}$ = 179, 5 Hz), 15.0 (q, $J_{C[H]}$ = 130 Hz).

***cis*-3,6-Dimethyl-1,2,4,5-tetroxane (5a):** ^1H NMR ($CDCl_3$) δ 6.03 (q, J = 5.5 Hz, 1 H, H-3), 5.69 (d, J = 5.5 Hz, 1 H, H-6), 1.73 (d, J = 5.5 Hz, 3 H, CH_3 (C-6)), 1.06 (d, J = 5.5 Hz, 3 H, CH_3 (C-3)).

1-Methoxyethyl Hydroperoxide (6). Ten millimoles of alkene was ozonized in 20 mL of methanol at −78 °C. The solvent was stripped off, and the hydroperoxide was isolated without further purification in 75% yield. Its ^{1}NMR spectrum was slightly different from that reported in the literature:[17] ^{1}NMR ($CDCl_3$) δ 9.60 (s, 1 H), 4.96 (q, J = 5.6 Hz, 1 H), 3.50 (s, 3 H), 1.35 (d, J = 5.6 Hz, 3 H).

Trapping Experiments. Between 0.5 and 3 mmol of alkene and 0.5–1 mmol of aldehyde were ozonized in 5 mL of pentane. The resulting trioxolanes were isolated and weighed. They were identified by their ^{1}H NMR data in comparison to literature values.[18]

Computer Simulation. The program was written in FORTRAN-77 for a PDP-11/23 system and used numerical methods to approximate the kinetic reactions in Figure 3.[15] This scheme consists of unimolecular and bimolecular processes. Input to the calculation consisted of the initial concentration of the alkenes (and any added acetaldehyde or methanol) and relative values for the various rate constants. The product yields were then slowly changed for each iteration (typically < 0.1%). The algorithm contained several nested loops so that a systematic variation of reactant concentrations and rate constants could be explored. A flow diagram and listing of the program are available as supplementary material.

Acknowledgment. We are grateful to Professor Arthur Ashe for help in purification problems, Dr. H.-S. Choi for assistance in ozonolysis procedures, and Dr. K. W. Hillig II for advice on the computer programming.

Supplementary Material Available: Flow diagram and listing for the FORTRAN program called Rates, calculating the product yields (14 pages). Ordering information is given on any current masthead page.

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(18) Murray, R. W.; Youssefyeh, R. D.; Story, P. R. *J. Am. Chem. Soc.* **1967**, *89*, 2429.

Free-Radical Selenosulfonation of Vinylcyclopropanes, a Cyclopropylidene, and Cyclopropylacetylene. Relative Rates of Chain-Transfer, Ring-Opening, and Inversion in Radical Intermediates

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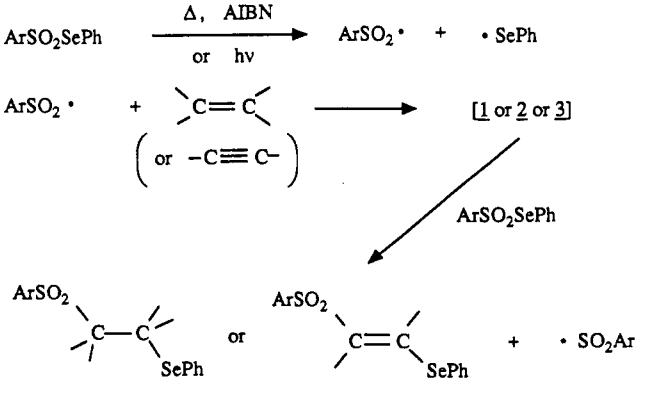
The free-radical selenosulfonation of vinylcyclopropanes **4a–e** and cyclopropylidene **9** was accompanied by ring-opening to afford 1,5- and 1,3-adducts **7a–e** and **11**, respectively, whereas cyclopropylacetylene (**13**) gave predominantly 1,2-addition to afford **15**. The relative rates of ring-opening, chain-transfer, and β-sulfonylvinyl radical inversion were inferred from the nature of the products. Selenoxide elimination of the products provided access to synthetically useful unsaturated sulfones. Thus, high yields of the dienyl sulfones **8a–e** and **12** and of the cyclopropylacetylenic sulfone **17** were obtained.

Selenosulfonates ($ArSO_2SePh$) undergo free-radical 1,2-additions to olefins,[1] acetylenes,[2] and allenes.[3] These processes[4] are synthetically useful[5] and proceed via the β-sulfonylalkyl, -vinyl, and -allyl radical intermediates **1–3**, respectively, which then react with a second molecule of the selenosulfonate in a chain-transfer step to afford the corresponding 1,2-adduct (Scheme I).

Scheme I



It has been reported that the additions to acyclic olefins are not stereospecific,[1a] whereas those to cyclohexene[1b] or

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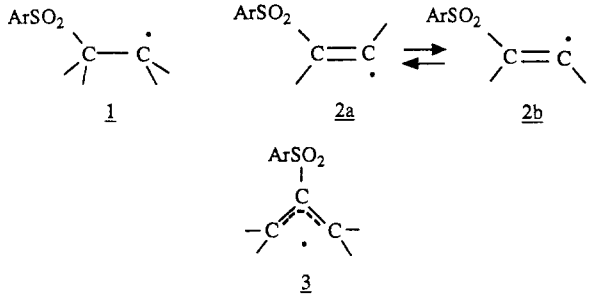


1 2a 2b 3

to acetylenes[2a] afford exclusively the products of anti addition. A plausible explanation for the stereospecificity in the latter two instances is that chain-transfer is faster than either cyclohexane ring-flipping[1b] or equilibration of **2a** ⇌ **2b**.[2a,6] An alternative explanation, that the additions display high stereoselectivity reflecting the greater thermodynamic stabilities of the observed products, is less compelling in view of the virtually complete absence of the corresponding stereoisomers from both cyclohexene and acetylenes, regardless of the nature of the substituents in the latter.[7] The possibility that bridged radical intermediates[8] are responsible for the stereospecificity of selenosulfonation was ruled out by Gancarz and Kice[1b] in the case of cyclohexene. These authors pointed out that the formation of bridged intermediates would result in the stereospecific selenosulfonation of both cyclic and acyclic olefins, in contrast to the previous observation that *E,Z* pairs of acyclic olefins produce identical mixtures of erythro and threo adducts.[1a] Although the extrapolation of this conclusion from olefinic to acetylenic substrates cannot be made unequivocally, it appears that bridging is at least not a general phenomenon in free-radical selenosulfonations.

The efficiency of selenosulfonates as chain-transfer agents is an important consideration in such arguments, as well as in the devising of new synthetic applications, where the accurate prediction of stereochemistry is often crucial. To date, reaction rates of selenosulfonates with certain other alkyl radicals have been reported by Gancarz and Kice[1b] and by Russell and Tashtoush.[9]

Several years ago, Ingold et al.[10] determined that the rate constant for the ring-opening of the cyclopropylcarbinyl radical to the isomeric allylcarbinyl radical at 25 °C was 1.3×10^8 s^{-1}. This process provides a convenient "free-radical clock" against which the relative rates of other radical reactions can be measured.[11] In an effort to gain further information concerning the chain-transfer efficiency of selenosulfonates with both alkyl and vinyl radicals, we investigated the free-radical selenosulfonation of several types of unsaturated cyclopropanes in which the expected intermediates would be cyclopropylcarbinyl or cyclopropylvinyl radicals. Moreover, we anticipated that such processes would provide access to various synthetically useful unsaturated sulfones[12] via selenoxide elimination of the resulting adducts.[13]

Results and Discussion

Photolysis of *Se*-phenyl *p*-tolueneselenosulfonate with UV light or pyrolysis with the radical initiator azobisisobutyronitrile (AIBN) in the presence of vinylcyclopropanes **4a–e** in chloroform or benzene afforded the 1,5-adducts **7a–e** in high yield (Table I). NMR analysis of the crude reaction mixtures showed no significant amounts of the corresponding 1,2-adducts **6**. This indicates that the intermediate cyclopropylcarbinyl radicals **5** undergo ring-opening considerably faster than chain-transfer (Scheme II). Oxidation of the products **7** with *m*-chloroperbenzoic acid (MCPBA) smoothly effected selenoxide elimination to furnish the corresponding allylic dienyl sulfones **8a–e** (Table I).

The selenosulfonation of cyclopropylidene **9** was performed similarly. The formation of the 1,3-adduct **11** and the absence of any significant quantity of the 1,2-isomer revealed that again ring-opening of the intermediate **10** had occurred far more rapidly than reaction with the selenosulfonate (Scheme III). As expected, selenoxide elimination produced the corresponding dienyl sulfone **12** nearly quantitatively.

In contrast to the above results, cyclopropylacetylene (**13**) afforded the 1,2-adduct **15** in 46% yield and the ring-opened 1,5-adduct **16** in only 24% yield (Scheme IV). Evidently, chain-transfer in the case of the cyclopropylvinyl radical **14** competes effectively with ring-opening. Indeed, enhanced yields of **15** of up to 76% were obtained when an excess of the selenosulfonate was employed in the reaction, as this facilitates the bimolecular chain-transfer step at the expense of the unimolecular ring-opening. The addition of diphenyl diselenide to the reaction mixture also resulted in a marked increase in the yield of the 1,2-adduct. This demonstrates that the diselenide is also an efficient chain-transfer agent.[14] Failure to detect the *Z* isomer of **15** is again consistent with a relatively slow rate of inversion in intermediate **14** (analogous to **2a** ⇌ **2b**), compared to the rate of chain-transfer. Oxidation of **15** produced the interesting acetylenic sulfone **17** in 86% yield. Furthermore, the facile selenoxide syn elimination of **15** confirms that the PhSe moiety and the vinylic H atom are cis-oriented and that the formation of **15** must have occurred by anti addition, as in the selenosulfonation of other acetylenic substrates.

It is evident from these studies that bimolecular chain-transfer between selenosulfonates and cyclopropylcarbinyl radicals **5** and **10** occurs substantially more slowly than the unimolecular ring-opening under these conditions. On the

(6) ESR studies at −180 °C have shown that the barrier to inversion in the unsubstituted vinyl radical is only 2 kcal mol^{-1}, and its lifetime is between 3×10^{-10} and 3×10^{-8} s. See: (a) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147. However, substituted vinyl radicals exhibit a decreased rate of inversion. For a general discussion, see: (b) Nonhebel, D. C.; Walton, J. C. In *Free-Radical Chemistry*; Cambridge University: Cambridge, 1974; pp 90–92. (c) Simamura, O. In *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Wiley: New York, 1969; Vol. 4, pp 1–37.

(7) Free-radical additions to acetylenes usually afford mixtures of cis and trans isomers; see: (a) Abell, P. I. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 13, pp 82–83 and 100–101. Exceptions have been observed with other addends which are particularly efficient chain-transfer agents. These also react via anti addition, e.g., HBr: (b) Skell, P. S.; Allen, R. G. *J. Am. Chem. Soc.* **1958**, *80*, 5997. (c) Skell, P. S.; Allen, R. G. *Ibid.* **1964**, *86*, 1559. Sulfonyl iodides: Truce, W. E.; Wolf, G. C. *J. Org. Chem.* **1971**, *36*, 1727.

(8) Skell, P. S.; Shea, K. J. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 26.

(9) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398.

(10) (a) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024. (b) For a lead reference to subsequent revisions of this value determined at higher temperatures, see: Mathew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981.

(11) For a review of "free-radical clocks", see: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(12) For reviews of sulfone chemistry, see: (a) Durst, T. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: New York, 1979; Vol. 3, Chapters 11.8 and 11.9. (b) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. (c) Fuchs, P. L.; Braish, T. F. *Chem. Rev.* **1986**, *86*, 903. (d) Trost, B. M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 107.

(13) (a) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *J. Org. Chem.* **1978**, *43*, 1697. (b) Hori, T.; Sharpless, K. B. *Ibid.* **1978**, *43*, 1689.

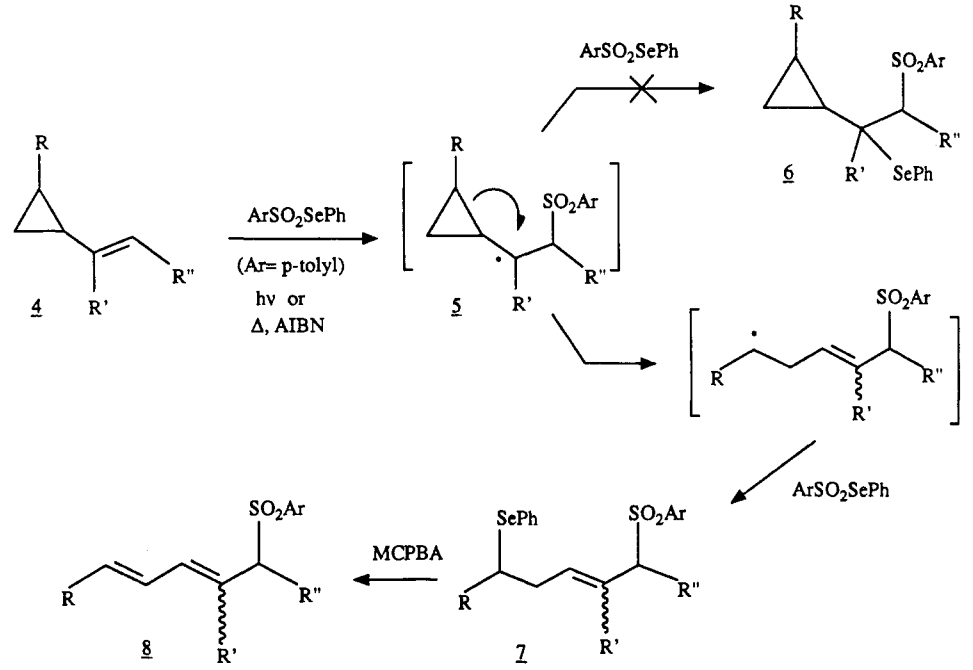
(14) The free-radical additions of diselenides to dimethyl acetylenedicarboxylate and methyl propiolate result in the formation of substantial amounts of both *E* and *Z* isomers: Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 2533.

Table I. Selenosulfonation of Vinylcyclopropanes[a-d]

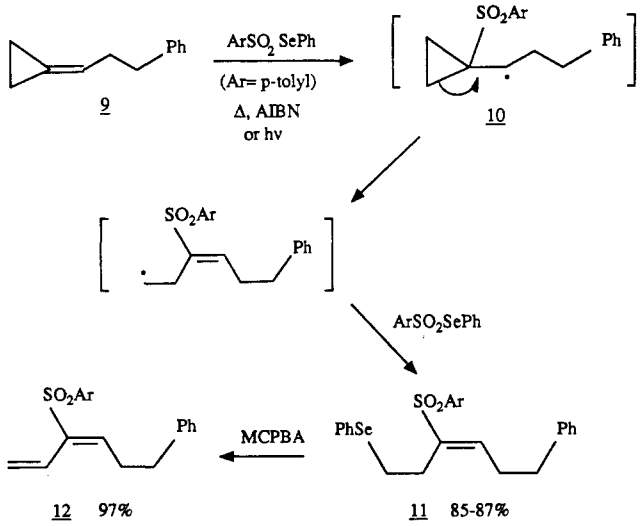
vinylcyclopropane				1,5-adduct			elimination product	
no.	R	R′	R″	No.	yield, % (*E*:*Z* ratio)	method	no.	yield, %
4a	H	H	H	**7a**	92 (4:1)[e]	A	**8a**	98
4b	H	Me	H	**7b**	97 (8:1)[f]	A	**8b**	98
					71 (1.5:1)	B		
4c	H	Cl	H	**7c**	92 (1:10)[f]	B	**8c**	97
4d	H	H	Et	**7d**	95 (4:1)[e]	A	**8d**	95
4e	CO_2Et	H	H[g]	**7e**	80 (5:1)[e]	C	**8e**	75

[a] Ar = *p*-tolyl. [b] Isolated yields are reported. [c] An excess (ca. 10–50 mol %) of the vinylcyclopropane was employed with **4a–4d**; an equimolar amount of **4e** was used. [d] Method A: photolysis in $CHCl_3$ for 20–24 h. Method B: reflux in $CHCl_3$ with 5 mol % of AIBN for 24 h. Method C: photolysis in C_6H_6 for 24 h. [e] Geometric isomers were identified on the basis of their ^1H NMR vinylic coupling constants J_{cis} and J_{trans}. Their relative proportions were determined by integration. [f] ^1H NMR signals of *E* and *Z* isomers were identified by NOE difference spectroscopy, and their relative proportions were determined by integration. [g] The starting material was a mixture of cis and trans isomers.

Scheme II



Scheme III



other hand, chain-transfer competes effectively with ring-opening in the cyclopropylvinyl radical **14**. To the best of our knowledge, the rate of ring-opening of the latter species has not been measured. However, if it is assumed that the rates of ring-opening are at least roughly comparable for cyclopropylvinyl radicals **14** and cyclopropylcarbinyl radicals such as **5** and **10** (ca. 10^8 s^{-1}), then it follows that selenosulfonates are substantially more reactive toward species **14** than toward **5** or **10**.[15] Furthermore, only the *E* isomer of **15** was produced from cyclopropylacetylene within the limits of detection by NMR analysis (ca. 2%) under conditions where chain-transfer and ring-opening proceeded at comparable rates. It can therefore be concluded that the rates of inversion of β-sulfonylvinyl radicals **14** (i.e., **2a** ⇌ **2b**) must be ≤2 × 10^6 s^{-1}.[16]

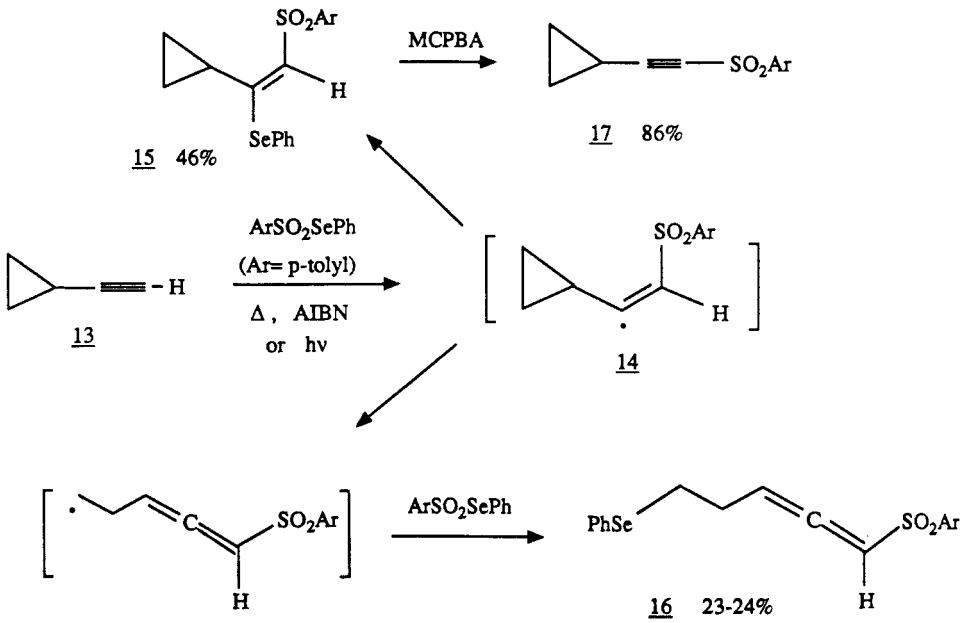
Experimental Section

Melting points were obtained on an A. H. Thomas hot-stage apparatus and are uncorrected. IR spectra were recorded on a

(15) This assumption is tentative as the degree of overlap between the orbitals of the radical center and the cyclopropyl moiety in **14** compared to **5** or **10** may be substantially different, resulting in different rates of ring-opening for these species. Firm kinetic data for the ring-opening of **14** is required for an unequivocal conclusion on this point.

(16) This is comparable to the value of $k \leq 2 \times 10^6$ s^{-1} reported for the inversion of the bromopropenyl radical by Skell and Allen.[7c]

Scheme IV



Nicolet 5DX instrument as thin films for oils and as Nujol mulls for solids. ^{1}H NMR spectra were obtained on either a Varian XL200 or a Bruker AC-E spectrometer at 200 MHz, or on a Bruker AM400 spectrometer at 400 MHz. NOE difference spectroscopy[17] was performed on the latter instrument. Deuteriochloroform was employed as the solvent and internal TMS as the standard unless otherwise noted. Mass spectra were recorded on a Kratos MS80 or a VG 7070 instrument. Elemental analyses were obtained by Dr. W. S. Lin (University of Calgary). Photolyses were performed in a Rayonet RMR-500 reactor equipped with four 254-nm UV lamps.

Se-Phenyl *p*-tolueneselenosulfonate was prepared by a literature procedure.[18] Vinylcyclopropanes **4a**, **4b**, and **4d** and cyclopropylidene **9** were obtained by the Wittig reactions of cyclopropanecarbaldehyde, cyclopropyl methyl ketone, propanal, and 3-phenylpropanal, respectively, with the appropriate phosphoranes under standard conditions. Compound **4e** was prepared by the method of Kirmse et al.[19] Vinylcyclopropane **4c** and cyclopropylacetylene (**13**) were prepared by the mono- or didehydrochlorination of (1,1-dichloroethyl)cyclopropane, respectively, by a modification of the procedure of Hanack et al.[20]

Selenosulfonation of Vinylcyclopropanes 4a–d. Typical Procedure: Preparation of Adduct 7a. *Se*-Phenyl *p*-tolueneselenosulfonate (156 mg, 0.50 mmol) and vinylcyclopropane (**4a**) (ca. 0.6 mmol) were photolyzed in 3 mL of chloroform in a Pyrex vessel for 24 h. Flash chromatography over silica gel (elution with 20% ethyl acetate–hexane) afforded 174 mg (92%) of the 1,5-adduct **7a** as a 4:1 mixture of *E* and *Z* isomers: IR 1597, 1579, 1318, 1146, 1087, 739 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.74 (d, J = 8 Hz, 2 H), 7.5–7.2 (complex, 7 H), 5.55–5.46 (complex, 2 H), 3.73 (2 overlapping d with J = 6 Hz, 2 H), 2.81 (t, J = 7.3 Hz, *E* isomer) and 2.64 (t, J = 7.4 Hz, *Z* isomer, total 2 H), 2.44 and 2.42 (2 s superimposed upon m, total 5 H). At 400 MHz in C_6D_6, the vinylic region showed δ 5.36 (m, both vinylic hydrogens of the *Z* isomer), 5.25 (dt, J = 15.4, 7.4 Hz, *E* isomer, 1 H), and 5.05 (dt, J = 15.4, 6.8 Hz, *E* isomer, 1 H). Mass spectrum: m/e (relative intensity) 380 (M^+, 7), 225 ($M^+ - SO_2Ar$, 32), 91 ($C_7H_7^+$, 100). Exact mass calcd for $C_{18}H_{20}O_2SSe$: 380.0349. Found: 380.0355.

Adducts **7b–e** were prepared similarly with the minor variations indicated in Table I. Their properties are as follows.

Adduct 7b. Crystallization from chloroform–hexane afforded the pure *E* isomer: mp 82–83 °C; IR 1597, 1579, 1317, 1146, 759 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.72 (d, J = 8 Hz, 2 H), 7.5–7.2 (complex, 7 H), 5.10 (t, J = 7.2 Hz, 1 H), 3.69 (s, 2 H), 2.71 (t, J = 7.2 Hz, 2 H), 2.43 (s, 3 H), 2.33 (m, 2 H), 1.71 (d, J < 1 Hz, 3 H). Additional signals attributable to the *Z* isomer were observed in the original mixture at δ 5.48 (t, J = 6.7 Hz) and 3.73 (s). Mass spectrum: m/e (relative intensity) 394 (M^+, 23), 239 ($M^+ - SO_2Ar$, 59), 91 ($C_7H_7^+$, 89), 81 (100). Anal. Calcd for $C_{19}H_{22}O_2SSe$: C, 58.01; H, 5.64; S, 8.15. Found: C, 57.72; H, 5.83; S, 8.03.

Adduct 7c. Crystallization from chloroform–hexane afforded the pure *Z* isomer: mp 67–68 °C; IR 1615, 1597, 1579, 1321, 1153, 742 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.78 (d, J = 8 Hz, 2 H), 7.5–7.2 (complex, 7 H), 5.72 (t, J = 7.0 Hz, 1 H), 3.99 (s, 2 H), 2.82 (t, J = 7.2 Hz, 2 H), 2.54 (m, 2 H), 2.45 (s, 3 H). Additional signals attributable to the *E* isomer were observed in the original mixture at δ 6.12 (t, J = 7 Hz) and 3.94 (s). Mass spectrum: m/e (relative intensity) 414 (M^+, 0.3), 259 ($M^+ - ArSO_2$, 3), 91 ($C_7H_7^+$, 100). Exact mass calcd for $C_{18}H_{19}ClO_2SSe$: 413.99595. Found: 413.9971.

Adduct 7d. The product was obtained as an unseparated 4:1 mixture of *E* and *Z* isomers: IR 1597, 1576, 1314, 1144, 739 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.69 (d, J = 8 Hz, 2 H), 7.5–7.2 (complex, 7 H), 5.72 (m, both vinylic hydrogens of the *Z* isomer), 5.46 (dt, J = 15.5, 6.4 Hz, *E* isomer, 1 H), 5.26 (crude dd, J = 15.5, 8.8 Hz, *E* isomer, 1 H), 3.63 (m, *Z* isomer) and 3.33 (m, *E* isomer, total 1 H), 2.77 (m, *E* isomer) and 2.55 (m, *Z* isomer, total 2 H), 2.42 (s superimposed on m, total 5 H), 2.10 (m, 1 H), 1.63 (m, 1 H), 0.93 (t, J = 7.5 Hz, 3 H); mass spectrum, m/e (relative intensity) 408 (M^+, <1), 253 ($M^+ - ArSO_2$, 12), 95 (100). Exact mass calcd for $C_{20}H_{24}O_2SSe$: 408.0662. Found: 408.0664.

Adduct 7e. The product was obtained as an unseparated 5:1 mixture of *E* and *Z* isomers: IR 1725, 1597, 1575, 1318, 1149, 744 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.72 (d, J = 8 Hz, 2 H), 7.6–7.2 (complex, 7 H), 5.75 (dt, J = 10.8, 7.4 Hz, *Z* isomer, 1 H), 5.51 (m, both vinylic hydrogens of *E* isomer and other vinylic hydrogen of *Z* isomer), 4.05 (m, 2 H), 3.9–3.2 (complex, 3 H), 2.43 (s superimposed on m, total 5 H), 1.15 (t, J = 7.1 Hz, 3 H). At 400 MHz in C_6D_6 with double irradiation of the CH_2SO_2 signal, the vinylic resonances of the *E* isomer were discerned: δ 5.34 (d, J = 15.4 Hz, 1 H), 5.17 (dt, J = 15.4, 6.2 Hz, 1 H). Mass spectrum: m/e (relative intensity) 452 (M^+, 2), 297 ($M^+ - ArSO_2$, 11), 155 ($ArSO_2^+$, 28), 139 (58), 91 ($C_7H_7^+$, 95), 67 (100). Exact mass calcd for $C_{21}H_{24}O_4SSe$: 452.0560. Found: 452.0565.

Selenoxide Elimination of Adducts 7a–e. Typical Procedure: Preparation of 5-(*p*-Tolylsulfonyl)-1,3-pentadiene (8a). MCPBA (ca. 0.84 mmol) was added to a solution of the 4:1 mixture of *E* and *Z* isomers of adduct **7a** (160 mg, 0.40 mmol) in 6 mL of chloroform. After 30 min, the reaction mixture was washed 3× with aqueous K_2CO_3 and then with aqueous NaCl and

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(18) Back, T. G.; Collins, S.; Krishna, M. V. *Can. J. Chem.* **1987**, *65*, 38.
(19) Kirmse, W.; Chiem, P. v.; Henning, P.-G. *Tetrahedron* **1985**, *41*, 1441.
(20) Hanack, M.; Bassler, T. *J. Am. Chem. Soc.* **1969**, *91*, 2117.

dried over anhydrous $MgSO_4$. The resulting chloroform solution was refluxed for 1 h and then evaporated to dryness. Flash chromatography over silica gel (elution with 22% ethyl acetate–hexane) afforded 91.3 mg (98%) of a 4:1 mixture of *E* and *Z* isomers of the title compound:[21] IR 1598, 1319, 1148, 1087, 749 cm^{-1}; ^1H NMR (200 MHz) δ 7.74 (d, J = 8 Hz, 2 H), 7.35 (d, J = 8 Hz), 6.4–6.0 (m, 2 H), 5.64 (m, 1 H), 5.20 (m, 2 H), 3.95 (d, J = 7.9 Hz, CH_2SO_2 of *Z* isomer), 3.81 (d, J = 7.6 Hz, CH_2SO_2 of *E* isomer, total 2 H), 2.45 (s, 3 H). Double irradiation of the signal at δ 3.81 resulted in the collapse of the signal at δ 5.64 to d, J = 15.1 Hz. Mass spectrum: m/e (relative intensity) 222 (M^+, 2), 157 (15), 91 ($C_7H_7^+$, 73), 67 (100).

The selenoxide elimination of adducts **7b–e** was effected similarly to afford the following products in the yields given in Table I.

Sulfonyl diene 8b: from pure (*E*) **7b**; pale yellow oil; IR 1598, 1315, 1216, 1146, 759 cm^{-1}; ^1H NMR (200 MHz) δ 7.72 (d, J = 8 Hz, 2 H), 7.32 (d, J = 8 Hz), 6.47 (dt, J = 16.7, 10.6 Hz, 1 H), 5.67 (d, J = 10.8 Hz, 1 H), 5.12 (d, J = 10.3 Hz, 1 H), 5.08 (d, J = 16.6 Hz, 1 H), 3.75 (s, 2 H), 2.44 (s, 3 H), 1.86 (d, J = 1.3 Hz, 3 H); mass spectrum, m/e (relative intensity) 236 (M^+, 2), 139 (16), 91 ($C_7H_7^+$, 28), 81 (100). Exact mass calcd for $C_{13}H_{16}O_2S$: 236.0871. Found: 236.0869.

Sulfonyl diene 8c: from pure (*E*) **7c**; pale yellow oil; IR 1638, 1597, 1581, 1317, 1146, 1087, 737 cm^{-1}; ^1H NMR (200 MHz) δ 7.77 (d, J = 8 Hz, 2 H), 7.35 (d, J = 8 Hz, 2 H), 6.57 (dt, J = 16.8, 10.4 Hz, 1 H), 6.21 (d, J = 10.3 Hz, 1 H), 5.36 (d, J = 16.7 Hz, 1 H), 5.34 (d, J = 10.5 Hz, 1 H), 4.06 (s, 2 H), 2.46 (s, 3 H); mass spectrum, m/e (relative intensity) 256 (M^+, 45), 220 (M^+ – Cl, 8), 155 ($ArSO_2^+$, 61), 101 (M^+ – $ArSO_2$, 97), 91 ($C_7H_7^+$, 90), 65 (100). Exact mass calcd for $C_{12}H_{13}ClO_2S$: 256.0325. Found: 256.0329.

Sulfonyl diene 8d: from 4:1 mixture of *E* and *Z* isomers of **7d**, pale yellow oil; IR 1598, 1314, 1145, 1086, 759 cm^{-1}; ^1H NMR (200 MHz) signals attributed to the *E* isomer were observed at δ 7.68 (d, J = 8 Hz, 2 H), 7.31 (d, J = 8 Hz, 2 H), 6.28 (m, 1 H), 5.97 (dd, J = 15.2, 10.4 Hz, 1 H), 5.41 (dd, J = 15.2, 9.4 Hz, 1 H), 5.14 and 5.13 (2 overlapping d, J = 15.9 and 11.1 Hz, total 2 H), 3.4 (m, 1 H), 2.44 (s, 3 H), 2.14 (m, 1 H), 1.62 (m, 1 H), 0.93 (t, J = 7.4 Hz, 3 H); separate signals attributed to the *Z* isomer were observed at δ 3.85 (m) and 2.42 (s); mass spectrum, m/e (relative intensity) 250 (M^+, 2), 157 (32), 139 (31), 95 (100). Exact mass calcd for $C_{14}H_{18}O_2S$: 250.10275. Found: 250.1015.

Sulfonyl diene 8e: from 5:1 mixture of *E* and *Z* isomers of **7e**; crystallization from chloroform–hexane afforded the pure *E* isomer of **8e**, mp 90–91 °C; IR 1714, 1641, 1613, 1300, 1253, 1164, 1142, 1020, 745 cm^{-1}; ^1H NMR (200 MHz) δ 7.72 (d, J = 8 Hz, 2 H), 7.35 (d, J = 8 Hz, 2 H), 7.19 (dd, J = 15.4, 10.6 Hz, 1 H), 6.19 (dd, J = 15.3, 10.6 Hz, 1 H), 5.94 (dt, J = 15.3, 7.6 Hz, 1 H), 5.84 (d, J = 15.4 Hz, 1 H), 4.21 (q, J = 7 Hz, 2 H), 3.88 (d, J = 7.4 Hz, 2 H), 2.45 (s, 3 H), 1.29 (t, J = 7 Hz, 3 H); additional signals attributed to the *Z* isomer were observed in the original mixture at δ 7.00 (dd, J = 15.2, 11.6 Hz), 6.34 (crude t), 5.83 (d, J = 15.2 Hz), 4.05 (d, J = 8.3 Hz); mass spectrum, m/e (relative intensity) 294 (M^+, 1), 249 (M^+ – OEt, 12), 155 (18), 139 (90), 111 (63), 91 ($C_7H_7^+$, 80), 67 (100). Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16. Found: C, 61.14; H, 6.22.

Selenosulfonation and Selenoxide Elimination of Cyclopropylidene 9. *Se*-Phenyl *p*-tolueneselenosulfonate (228 mg, 0.733 mmol), cyclopropylidene **9** (116 mg, 0.733 mmol), and AIBN (6 mg, 0.04 mmol) were refluxed in 5 mL of benzene for 35 h. Flash chromatography of the resulting mixture over silica gel (elution with 10% ethyl acetate–hexane) afforded 300 mg (87%) of adduct **11** as a pure geometrical isomer: mp 85–86 °C (from chloroform–hexane); IR 1642, 1597, 1579, 1300, 1138, 1085, 742 cm^{-1}; ^1H NMR (200 MHz) δ 7.53 (d, J = 8 Hz, 2 H), 7.5–7.1 (complex, 12 H), 6.93 (t, J = 7.6 Hz, 1 H), 2.8–2.65 (m, 4 H), 2.41 (s superimposed on m, total 7 H). The four methylene signals were resolved at 400 MHz in C_6D_6, and the *E* configuration was established by NOE difference spectroscopy whereby double irradiation of each vinylic CH_2 signal resulted in enhanced intensity of the other signal, indicating their cis relationship. Mass spectrum: m/e (relative intensity) 470 (M^+, 2.5), 313 (M^+ – PhSe, 22), 157 ($PhSe^+$, 20), 91 ($C_7H_7^+$, 100). Exact mass calcd for $C_{25}H_{26}O_2SSe$: 470.0819. Found: 470.0806.

When the reaction was repeated by irradiation with UV light in the absence of AIBN in benzene for 20 h, the yield of **11** was 85%.

Selenoxide elimination of **11** was performed as in the preparation of **8a–e** to afford 6-phenyl-3-(*p*-tolylsulfonyl)-1,3-hexadiene (**12**) (97%): mp 83–84 °C (from chloroform–hexane); IR 1598, 1302, 1216, 1147, 757 cm^{-1}; ^1H NMR (200 MHz) δ 7.62 (d, J = 8 Hz, 2 H), 7.3–7.1 (complex, 7 H), 7.01 (t, J = 7.5 Hz, 1 H), 6.17 (m, 1 H), 5.38 (m, 2 H), 2.83 (t, J = 7 Hz, 2 H), 2.65 (m, 2 H), 2.42 (s, 3 H); mass spectrum, m/e (relative intensity) 312 (M^+, 3), 221 (M^+ – C_7H_7, 8), 156 (75), 91 ($C_7H_7^+$, 100). Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45; S, 10.26. Found: C, 73.26; H, 6.37; S, 10.47.

Selenosulfonation of Cyclopropylacetylene (13). *Se*-Phenyl *p*-tolueneselenosulfonate (156 mg, 0.50 mmol) and cyclopropylacetylene (ca. 0.6 mmol) in 3 mL of benzene were irradiated with UV light for 20 h. The mixture was then separated by preparative TLC on silica gel (20% ethyl acetate–hexane) to afford 86 mg (46%) of the 1,2-adduct **15**: R_f 0.47; mp 113–114 °C (from chloroform–hexane); IR 1595, 1549, 1306, 1273, 1135, 1082, 750 cm^{-1}; ^1H NMR (200 MHz) δ 7.69 (d, J = 8 Hz, 2 H), 7.5–7.3 (complex, 7 H), 5.88 (s, 1 H), 2.89 (m, 1 H), 2.43 (s, 3 H), 0.96 (crude d, 4 H); mass spectrum, m/e (relative intensity) 378 (M^+, 10), 221 (M^+ – SePh, 12), 91 ($C_7H_7^+$, 100). Anal. Calcd for $C_{18}H_{18}O_2SSe$: C, 57.29; H, 4.81; S, 8.50. Found: C, 57.28; H, 4.97; S, 8.56.

A second band afforded 43 mg (23%) of the allene **16** as an oil: R_f 0.34; IR 1955, 1596, 1579, 1321, 1147, 1085, 739 cm^{-1}; ^1H NMR (200 MHz) δ 7.78 (d, J = 8 Hz, 2 H), 7.5–7.2 (complex, 7 H), 6.23 (m, 1 H), 5.90 (m, 1 H), 2.88 (t, J = 7.5 Hz, 2 H), 2.44 (s superimposed on m, total 5 H). Double irradiation at δ 2.5 collapsed the signals at δ 6.23 and 5.90 to doublets with J = 6.0 Hz. Mass spectrum: m/e 378 (M^+, <1), 91 ($C_7H_7^+$, 75), 83 (100). Anal. Calcd for $C_{18}H_{18}O_2SSe$: C, 57.29; H, 4.81; S, 8.50. Found: C, 57.42; H, 4.90; S, 8.25.

When the reaction was repeated by refluxing the same quantities of the reactants with 5 mol % of AIBN in chloroform for 24 h, the yields of **15** and **16** were 46% and 24%, respectively.

When either a 3-fold excess of the selenosulfonate or an equimolar amount of the selenosulfonate together with 2 molar equiv of diphenyl diselenide was employed, the 1,2-adduct **15** was produced in up to 76% yield and no significant amount of allene **16** was isolated.

Selenoxide Elimination of 1,2-Adduct 15. Selenoxide elimination of **15** was performed as in the case of the preparation of **8a–e** to afford 86% of 1-cyclopropyl-2-(*p*-tolylsulfonyl)ethyne (**17**) as an oil: IR 2197, 1596, 1325, 1158, 1087, 756 cm^{-1}; ^1H NMR (200 MHz) δ 7.86 (d, J = 8 Hz, 2 H), 7.36 (d, J = 8 Hz, 2 H), 2.46 (s, 3 H), 1.40 (m, 1 H), 0.94 (m, 4 H); mass spectrum, m/e (relative intensity) 220 (M^+, 62), 155 ($ArSO_2^+$, 22), 139 ($ArSO^+$, 100), 91 ($C_7H_7^+$, 60). Exact mass calcd for $C_{12}H_{12}O_2S$: 220.0558. Found: 220.0559.

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Registry No. **4a**, 693-86-7; **4b**, 4663-22-3; **4c**, 24154-06-1; **4d**, 694-46-2; *cis*-**4e**, 2183-89-3; *trans*-**4e**, 2183-90-6; (*E*)-**7a**, 117734-71-1; (*Z*)-**7a**, 117734-72-2; (*E*)-**7b**, 117734-73-3; (*Z*)-**7b**, 117734-74-4; (*E*)-**7c**, 117734-75-5; (*Z*)-**7c**, 117734-76-6; (*E*)-**7d**, 117734-77-7; (*Z*)-**7d**, 117734-78-8; (*E*)-**7e**, 117734-79-9; (*Z*)-**7e**, 117734-80-2; (*E*)-**8a**, 103084-17-9; (*Z*)-**8a**, 117734-85-7; (*E*)-**8b**, 117734-81-3; (*E*)-**8c**, 117734-82-4; (*E*)-**8d**, 117734-83-5; (*Z*)-**8d**, 117734-86-8; (*E*)-**8e**, 117734-84-6; (*Z*)-**8e**, 117734-87-9; **9**, 69485-62-7; **11**, 117754-20-8; **12**, 117734-88-0; **13**, 6746-94-7; **15**, 117734-89-1; **16**, 117734-90-4; **17**, 117734-91-5; *p*-$TolylSO_2SePH$, 68819-94-3.

(21) The *E* isomer has been previously reported: Kauffmann, T.; Gaydoul, K.-R. *Tetrahedron Lett.* **1985**, *26*, 4067.