mixture of diester nitrosofulvene 18 (0.33 g) and cinnamaldehyde (0.15 g) in acetonitrile was added tri-*n*-butylphosphine (0.40 g). An instantaneous exothermic reaction occurred, leading to a reddish brown solution. After the mixture was warmed 15 min on the steam bath, the solvent was evaporated under vacuum, and the residue was treated with methanol. The resulting vinylogous fulvene **26** was filtered. The residue from the filtrate was chromatographed (SiO_2/benzene–cyclohexane, 1:1) to yield more fulvene **26**. Crystallization yielded a total of 0.07 g (21%) of **26**, mp 125 °C (lit.[9] mp 124–125 °C).

Conversion of Diphenyl Nitrosofulvene 19 into the Vinylogous Fulvene 28. To a mixture of nitrosofulvene **19** (0.34 g) and cinnamaldehyde (0.13 mL) in dry acetonitrile (5 mL) at room temperature was added cautiously tri-*n*-butylphosphine (0.4 mL). After the initial exothermic reaction subsided, the reaction mixture was warmed on the steam bath. Cautious addition of methanol containing a trace of HCl afforded shiny glistening plates of **28**: 0.30 g; mp 206–212 °C. Recrystallization from acetonitrile afforded pure fulvene **28**: 0.27 g (80%); mp 215 °C; mass spectrum, *m/e* (relative intensity) 294 (M^+, 50), UV–vis λ_{max} 256 nm (log ϵ 4.393), 388 (4.461). Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79; S, 21.78. Found: C, 73.47; H, 4.87; S, 21.71.

Conversion of Diphenyl Nitrosofulvene 19 into Fulvene 27. Diphenyl nitrosofulvene **19** (0.30 g) was reacted with *p*-chlorobenzaldehyde (0.15 g) in acetonitrile (5 mL) with tri-*n*-butylphosphine (0.5 mL) at room temperature. A workup as described above led to the isolation of the (chlorophenyl)fulvene **27**: 0.27 g (55%); mp 239 °C. Recrystallization from BuOAc did not alter the melting point: mass spectrum, *m/e* (relative intensity) 303 (M^+, 50); UV–vis λ_{max} 244 nm (log ϵ 4.364), 285 (infl, 3.512), 358 (4.350). Anal. Calcd for $C_{16}H_{11}ClS_2$: C, 63.45; H, 3.66; S, 21.18. Found: C, 63.61; H, 3.70, S, 21.22.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE 76-83417 and CHE 79-25017).

Registry No. *cis*-**8**, 40753-17-1; *trans*-**8**, 40753-18-2; **12**, 51225-41-3; **13**, 77965-84-5; **17**, 77965-85-6; **18**, 77965-86-7; **19**, 77965-87-8; **21**, 77965-88-9; **22**, 26314-39-6; **26**, 74151-98-7; **27**, 51225-62-8; **28**, 51225-56-0; cinnamaldehyde, 104-55-2; *p*-chlorobenzaldehyde, 104-88-1.

Selenosulfonation: Boron Trifluoride Catalyzed or Thermal Addition of Selenosulfonates to Olefins. A Novel Regio- and Stereocontrolled Synthesis of Vinyl Sulfones[1a]

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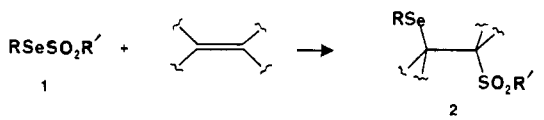
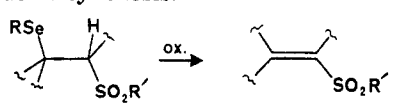
Received March 9, 1981

Se-Phenyl areneselenosulfonates **1** add to a variety of olefins to produce β-phenylseleno sulfones **2**. The reaction may be performed in the presence of boron trifluoride etherate to produce chiefly or exclusively Markovnikov products arising from a stereospecific anti addition. Alternatively, the addition may be thermally induced to afford anti-Markovnikov products generated by a nonstereospecific free-radical process. The two modes of addition achieve complementary regiospecificity. The β-phenylseleno sulfones are converted in high yield to vinyl sulfones by stereospecific oxidation–elimination with *m*-chloroperbenzoic acid.

The additions of selenenyl halides and pseudohalides to olefins have proven to be of both mechanistic interest and synthetic utility in the elaboration of simple unsaturated functionalities.[2] Although numerous selenenic species have been thoroughly investigated in these and other contexts,[3] the selenosulfonates **1** have seldom been studied.[4] It occurred to us that these compounds might also function as selenenylating agents as the sulfinate anion represents a reasonably effective leaving group. We envisaged that the addition of selenosulfonates to olefins would afford β-seleno sulfones **2**, thus providing a unique and convenient method for introducing the two synthetically versatile functionalities, sulfone and selenide, into a given unsaturated substrate in one step. Initial experiments revealed that such additions are feasible at room temperature in the presence of boron trifluoride etherate or at elevated temperatures in its absence.[5] We now report details of our attempts to extend the scope and to elucidate the mechanism of this novel process, which we have named "selenosulfonation". We also describe the facile oxidation–elimination[6] of β-seleno sulfones to provide a new, efficient route to vinyl sulfones, a class of compounds of proven value in synthesis.[7]





(1) (a) We gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada and the Research Corp. (b) Recipient of an NSERC Postgraduate Scholarship.

(2) For a review, see: Schmid, G. H.; Garratt, D. G. "The Chemistry of Double-bonded Functional Groups"; Patai, S., Ed., Wiley: London, 1977; Part 2, Chapter 9.

(3) See inter alia: (a) Garratt, D. G.; Kabo, A. *Can. J. Chem.* **1980**, *58*, 1030. (b) Garratt, D. G.; Ryan, M. D.; Ujjainwalla, M. *Ibid.* **1979**, *57*, 2145. (c) Garratt, D. G. *Ibid.* **1979**, *57*, 2180. (d) Clive, D. L. J.; Russell, C. G.; Chittattu, G.; Singh, A. *Tetrahedron* **1980**, *36*, 1399. (e) Toshimitsu, A.; Aoai, T.; Uemura, S.; Okano, M. *J. Org. Chem.* **1980**, *45*, 1953. (f) Nicloaou, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3884. (g) Shimizu, M.; Takeda, R.; Kuwajima, I. *Tetrahedron Lett.* **1979**, 3461. (h) Denis, J. N.; Vicens, J.; Krief, A. *Ibid.* **1979**, 2697. (i) Labar, D.; Krief, A.; Hevesi, L. *Ibid.* **1978**, 3967. (j) Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1689. (k) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *Ibid.* **1978**, *43*, 1697. (l) Barton, D. H. R.; Britten-Kelly, M. R.; Ferreira, D. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1090. (m) McManus, S. P.; Lam, D. H. *J. Org. Chem.* **1978**, *43*, 650. (n) Raucher, S.; Hansen, M. R.; Colter, M. A. *Ibid.* **1978**, *43*, 4885. (o) Takahashi, T.; Nagashima, H.; Tsuji, J. *Tetrahedron Lett.* **1978**, 799. (p) Liotta, D.; Zima, G. *Ibid.* **1978**, 4977.

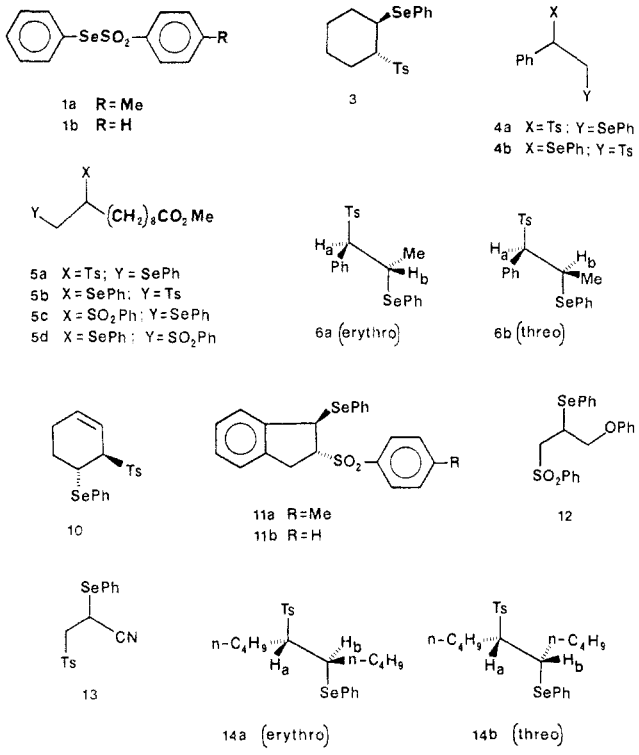
(4) (a) Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett.* **1980**, *21*, 1697. (b) Austad, T. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 479. (c) Foss, O. *J. Am. Chem. Soc.* **1947**, *69*, 2236.

(5) Preliminary communication: Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, 2215.

(6) The oxidation–elimination of selenoxides has been reviewed: (a) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22. (b) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. (c) Sharpless, K. B.; Gordon, K. M.; Lauer, R. F.; Patrick, D. W.; Singer, S. P.; Young, M. W. *Chem. Scr.* **1975**, *8A*, 9.

0022-3263/81/1946-3249$01.25/0

Chart I[a]



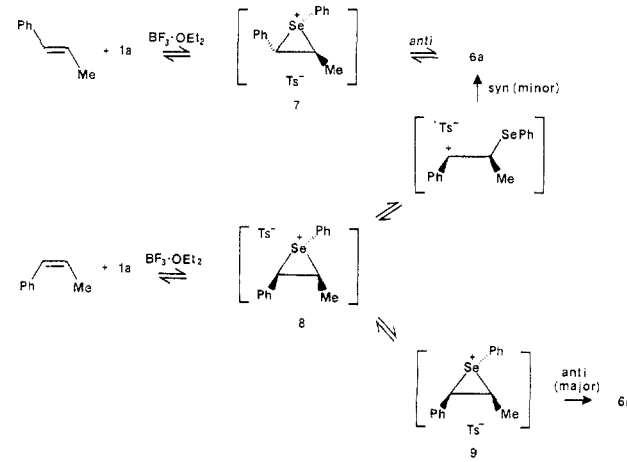
[a] Ts = $SO_2C_6H_4$-*p*-Me.

Results and Discussion

Se-Phenyl *p*-tolueneselenosulfonate (**1a**) and *Se*-phenyl benzeneselenosulfonate (**1b**) (Chart I) were obtained from the oxidation of the corresponding sulfonohydrazides with benzeneseleninic acid.[8] The reaction of **1a** with cyclohexene in dichloromethane solution at room temperature proved too sluggish to be of value. However, addition of boron trifluoride etherate to the reaction mixture produced 89% of *trans*-1-(phenylseleno)-2-(*p*-toluenesulfonyl)-cyclohexane (**3**) after 18 h; formation of the cis adduct was not observed. Catalysis with *p*-toluenesulfonic acid was less effective in this process. Similarly, adduct **4a** was obtained from the boron trifluoride catalyzed reaction of styrene with **1a** with complete exclusion of its regioisomer **4b**, while mixtures of **5a,b** or **5c,d** were produced in a ratio of ca. 2:1 from methyl 10-undecenoate and **1a** or **1b**, respectively. The selenosulfonation of unsymmetrical olefins performed under these conditions evidently results chiefly or exclusively in Markovnikov addition.

The unique formation of the trans adduct **3** from cyclohexene indicates that boron trifluoride catalyzed selenosulfonation is stereoselective. In order to ascertain whether it is also stereospecific,[9] we performed the addition of **1a** to (*E*)- and (*Z*)-1-phenylpropene. The two olefins each gave a different Markovnikov adduct, identified as **6a** (*erythro*) and **6b** (*threo*), respectively. The stereochemical assignment of the latter compounds was deduced from a comparison of their 200-MHz ^{1}H NMR spectra. Compounds **6a** and **6b** showed doublets at δ 1.92 and 1.69 respectively, assigned to the β-methyl protons. Decoupling experiments in which the latter signals were irradiated gave unambiguous values of 9.6 and 3.2 Hz for the vicinal methine proton coupling constants $^3J_{a,b}$. Previous NMR studies of a series of 1,2-disubstituted 1-arylpropanes revealed that the β-methyl protons are consistently found at lower field in the *erythro* than in the corresponding *threo* isomers[3c,10] and that the coupling constants $^3J_{a,b}$ are larger in the *erythro* series of other phenylseleno derivatives of 1-phenylpropane.[3c] The assignment of **6a** as the *erythro* and **6b** as the *threo* structure is consistent with these data and permits the following conclusion: selenosulfonation performed under these conditions is highly stereospecific and proceeds via anti addition.[11]

Scheme I



In order to gain further insight into the mechanism of boron trifluoride catalyzed selenosulfonation, we performed the reaction of **1a** with (*E*)- and (*Z*)-1-phenylpropene in deuteriochloroform and monitored it by ^{1}H NMR spectroscopy. The *E* isomer afforded solely adduct **6a** and starting material, formed in a ratio of 1.6:1 after 48 h which increased to 2.1:1 after 1 week. A mixture of identical composition was obtained by treating **6a** with boron trifluoride etherate under the same conditions for 3 h. These results indicate the reversible nature of this process. Different behavior was observed in the addition of **1a** to the *Z* olefin. After 50 min, the reaction had proceeded to ca. 50% completion, and formation of the *erythro* adduct **6a** was detected along with (*E*)-1-phenylpropene and the expected *threo* adduct **6b**. The ratio of **6b** to **6a** was 19.5:1, decreasing to 10.3:1 after 1 week. At this time, the ratio of product **6b** to (*E*)-1-phenylpropene was 13.8:1; no *Z* olefin remained, and the only other identifiable material present was a small amount of **1a**. A control experiment indicated that (*Z*)-1-phenylpropene in the presence of boron trifluoride etherate isomerizes too slowly to its *E* counterpart to account for the formation of significant amounts of the latter isomer in the previous reaction. Furthermore, adduct **6b** is itself stable under such conditions and so, once formed, does not contribute to the formation of other products. The departure from complete stereospecificity in the addition of **1a** to the *Z* olefin is therefore attributed to the rearrangements of intermediates along the reaction coordinate as shown in Scheme I.[12]

(7) For reviews see: (a) Truce, W. E.; Klingler, T. C.; Brand, W. W. In "Organic Chemistry of Sulfur"; Oae, S., Ed., Plenum Press: New York, 1977; Chapter 10; (b) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. For more recent examples see: (c) Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853; (d) Takaki, K.; Nakagawa, K.; Negoro, K. *J. Org. Chem.* **1980**, *45*, 4789; (e) Eisch, J. J.; Galle, J. E. *Ibid.* **1979**, *44*, 3279; (f) Little, R. D.; Myong, S. O. *Tetrahedron Lett.* **1980**, 3339; (g) Barton, D. L.; Conrad, P. C.; Fuchs, P. L. *Ibid.* **1980**, 1811; (h) Fabrissin, S.; Fatutta, S.; Malusá, N.; Risaliti, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 686.

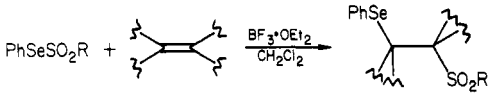
(8) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, 2213.

(9) The term "stereospecific" is used in the context defined by: Fleming, I. In "Selected Organic Syntheses"; Wiley: New York, 1973; p 11.

(10) Schmid, G. H. *Can. J. Chem.* **1968**, *46*, 3415.

(11) Electrophilic reactions of selenenyl halides and pseudohalides with olefins generally proceed via anti addition.[2,3a] This rule is not without exception, however.[3c]

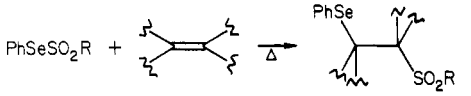
Table I. Boron Trifluoride Catalyzed Selenosulfonation of Olefins[a]



olefin (mmol)	selenosulfonate (mmol)	product	reaction time, h	isolated yield, %	mp,[b] °C
cyclohexene (0.5)	**1a** (0.5)	**3**	18	89	58-59
styrene (0.5)	**1a** (0.5)	**4a**	20	86	159
methyl 10-undecenoate (0.25)	**1a** (0.25)	**5a,b** (2:1)[c]	24	75	oil
methyl 10-undecenoate (1.38)	**1b** (1.50)	**5c,d** (2:1)[c]	24	72	oil
(*E*)-1-phenylpropene (1.0)	**1a** (1.0)	**6a**	27	62, 90[d]	138-140
(*Z*)-1-phenylpropene (0.5)	**1a** (0.5)	**6b**	24	70, 96[d]	oil
1,3-cyclohexadiene (0.5)	**1a** (0.5)	**10**	24	66, 86[d]	86-88

[a] For a typical procedure and for analytical and spectral data of the products, see the Experimental Section. [b] All solids were recrystallized from MeOH; product **6b** was homogeneous on TLC. [c] Ratio determined by NMR integration. [d] A two-fold excess of olefin was used; the yield is based on **1a**.

Table II. Thermal Selenosulfonation of Olefins[a]



olefin (mmol)	selenosulfonate (mmol)	product	method[b] (reaction time, h)	isolated yield, %	mp,[c] °C
styrene (0.5)	**1a** (0.5)	**4b**	A (24)	93	157-158
methyl 10-undecenoate (1.0)	**1a** (1.0)	**5b**	B (96)	76	46-48
indene (0.5)	**1a** (0.5)	**11a**[d]	A (72)	81	90-91
indene (0.5)	**1b** (0.5)	**11b**	A (48)	66	130-131
allyl phenyl ether (0.83)	**1b** (0.83)	**12**	B (67)	72	94-95
acrylonitrile (1.0)	**1a** (1.0)	**13**	A (96)	74	120-122
(*E*)-5-decene (0.86)	**1a** (1.0)	**14a,b** (1:4.5)[e]	C (21)	42	oil[f]
(*Z*)-5-decene (0.86)	**1a** (1.0)	**14a,b** (1:4.5)[e]	C (24)	45	oil[f]

[a] For a typical procedure and for analytical and spectral data of the products, see the Experimental Section. [b] Method A, performed in refluxing $CHCl_3$; method B, performed in refluxing C_6H_6; method C, reactants were heated neat in a sealed glass tube at 70-75 °C. [c] All solids were recrystallized from MeOH, except **5b** (from MeOH-H_2O) and **13** (from CH_2Cl_2-hexane). [d] This product was incorrectly identified in our preliminary communication.[5] [e] Ratio determined by NMR integration. GC analysis gave a different value of 1:9; the reason for the discrepancy is not clear. The NMR ratio corresponds closely to that of the derived vinyl sulfones (1:4.3; see Table III). [f] Product **14b** crystallized from MeOH; mp 79-80 °C.

Addition of **1a** to 1,3-cyclohexadiene produced the trans 1,2-adduct **10** in 66% yield; 1,4-addition was not observed.

The preparation of the above β-phenylseleno sulfones is summarized in Table I; the structures of the products are shown in Chart I.

In contrast to the selenosulfonations described above, thermal additions of **1a** or **1b** to olefins performed without boron trifluoride led to the highly regiospecific formation of anti-Markovnikov products. Thus, addition of **1a** to styrene in refluxing chloroform resulted in the exclusive formation of adduct **4b**, isolated in 93% yield. This result, together with the 86% yield of regioisomer **4a** obtained in the presence of boron trifluoride, *provides a clear example of the complementary regiospecificity of selenosulfonation under the two types of conditions.* The possibility of choosing either Markovnikov or anti-Markovnikov orientation by appropriate selection of the reaction conditions should prove a valuable feature in future synthetic applications.

Thermal selenosulfonation of methyl 10-undecenoate, indene, allyl phenyl ether, and acrylonitrile with **1a** or **1b** afforded the corresponding adducts **5b** and **11-13** in high yield. No significant amounts of Markovnikov products could be isolated. These results are summarized in Table II; the structures of the products are shown in Chart I.

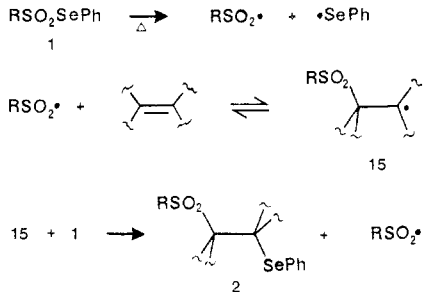
In order to probe the stereochemistry of the thermal addition process, we separately allowed (*E*)- and (*Z*)-5-decene to react with **1a**. The two olefins produced virtually the same mixture of stereoisomers **14a** (*erythro*) and **14b** (*threo*). Thermal selenosulfonation therefore lacks the stereospecificity of the boron trifluoride catalyzed reaction. The major isomer **14b** was obtained in a pure state by fractional crystallization. It was assigned the *threo* configuration on the basis of the following observations. First, its 200-MHz ^1H NMR spectrum showed two complex signals at δ 3.48 (H_a) and δ 3.19 (H_b), integrating as one proton each. The vicinal coupling constant $^3J_{a,b}$ was determined to be 1.6 Hz by means of decoupling experiments. The minor isomer **14a** could not be isolated in a pure state, but NMR analysis of the initial product mixture provided a value of 2.5 Hz for $^3J_{a,b}$. The smaller vicinal coupling in **14b** is more consistent with the *threo* structure.[13] Further confirmation of this assignment derived from the conversion of **14b** to its respective sulfone by stereospecific oxidation-elimination (vide infra).

The anti-Markovnikov orientation and the lack of stereospecificity in the thermal reactions are consistent with

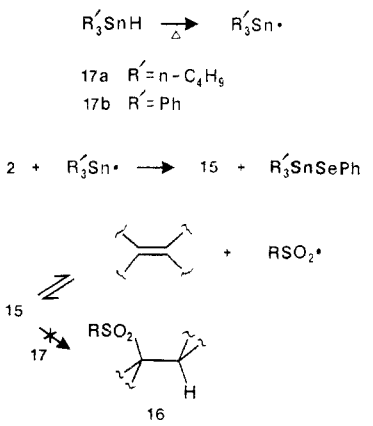
(12) We have arbitrarily shown intermediate **8** as an intimate ion pair and **7** and **9** as fully dissociated seleniranium ions. It has been postulated that selenenyl chloride additions to olefins proceed via a sequence of intermediates ranging from tetracoordinate selenium species (episelenuranes) through a series of ion pairs to fully dissociated ions.[2,3a] Similar considerations may apply to selenosulfonation, and precise assignment of structure to the intermediates awaits further study.

(13) Jackman, L. M.; Sternhell, S. In "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; p 291.

Scheme II



Scheme III



a free-radical mechanism initiated by homolysis of the selenosulfonate and proceeding via addition of the sulfonyl radical to the olefin to generate the radical intermediate **15**. Further reaction of **15** with **1** would result in product formation through the radical chain process displayed in Scheme II. Additional evidence for a radical chain mechanism was obtained by performing the thermal addition of **1a** to styrene in the presence of 20 mol % of the radical inhibitor 2,6-di-*tert*-butyl-*p*-cresol or 5 mol % of the initiator azobis(isobutyronitrile) (AIBN). As expected, a sharp reduction in the production of the expected adduct **4b** was observed in the former experiment while a dramatic increase in its formation occurred in the initial stages of the latter.

Subsequent to our preliminary communication on selenosulfonation,[5] Gancarz and Kice[14] demonstrated that the addition of selenosulfonates to olefins may also be photoinitiated. These authors proposed and substantiated a mechanism similar to that in Scheme II, except that initial cleavage of the Se–SO_2 linkage in **1** was effected by photolysis rather than thermolysis. They also raised the possibility that thermal additions[15] might actually be adventitiously initiated by the presence of ambient light. We note that the addition of **1a** to styrene proceeds in refluxing chloroform even in the dark, although reaction times may be somewhat reduced when the reaction is performed in the presence of normal fluorescent laboratory lights. We therefore conclude that the uncatalyzed additions may be either thermally initiated or photoinitiated and that they proceed via the same type of radical mechanism.

Attempts to perform selenosulfonations on more hindered olefins have so far been unsuccessful.

Scheme IV

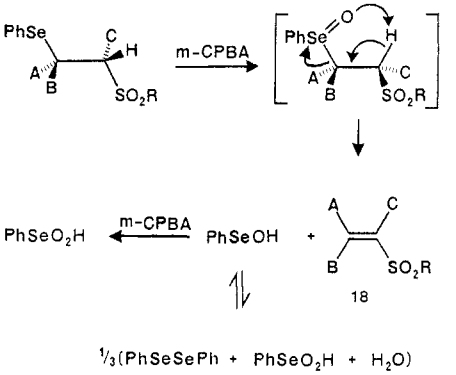
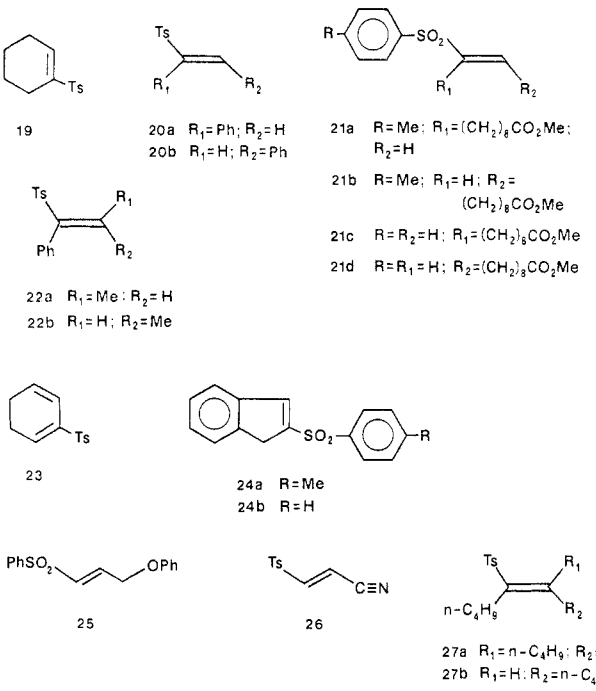


Chart II[a]



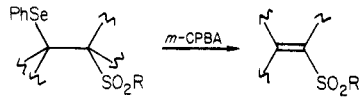
[a] Ts = $SO_2C_6H_4$-*p*-Me.

We attempted to convert β-phenylseleno sulfones **2** to saturated sulfones **16** by reduction with tri-*n*-butyl or triphenyltin hydride (**17a,b**).[16] However, when adduct **4a** was heated with tin hydride in toluene solution, we observed none of the expected sulfone **16** and instead detected the formation of styrene. Since such reductions of selenides are believed to proceed by radical pathways,[16] it is reasonable to assume that species **15** is an intermediate in the present case and that olefin formation ensues from its elimination (Scheme III). This in turn indicates that the addition of sulfonyl radicals to olefins (as in Scheme II) is reversible, in agreement with other studies.[17]

The above β-phenylseleno sulfones **2** may be converted in excellent yield to vinyl sulfones **18** by oxidation with *m*-chloroperbenzoic acid (*m*-CPBA), followed by spontaneous fragmentation of the initially formed selenoxides (Scheme IV). The formation of allylic sulfones is not detected. It is expedient to employ an excess of the peracid, as the byproduct diphenyl diselenide is then oxidized to benzeneseleninic acid. The latter compound is readily

(14) Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett.* **1980**, *21*, 4155.
(15) Several thermal additions of **1** to olefins were recently reported by Japanese workers. Their suggestion of seleniranium ion intermediates appears unlikely in view of the present results. Kobayashi, M.; Miura, T. Abstracts of the 9th International Symposium on Organic Sulfur Chemistry, Riga, USSR, June 1980, p 165.
(16) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438.
(17) The elimination of β-phenylsulfonyl radicals has been reported elsewhere. Boothe, T. E.; Greene, J. L., Jr.; Shevlin, P. B. *J. Org. Chem.* **1980**, *45*, 794 and references cited therein.

Table III. Preparation of Vinyl Sulfones[a]

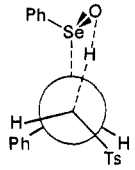


β-phenylseleno sulfone	vinyl sulfone	isolated yield,[b] %	mp,[c] °C
3	19	99	80-82[d]
4a	20a	81	oil
4b	20b	93	121-122[e]
5a,b[f] (2:1)	21a,b (1.8:1)[g]	96	oil[h]
5c,d[i] (2:1)	21c,d (1.8:1)[g]	93	oil
5b[j]	21b	90	38
6a	22a	90	81-83
6b	22b	100	82
10	23	100	99-100
11a	24a[k]	100	174
11b	24b	100	120-122[l]
12	25	87	89-100
13	26	77	132-134[m]
14a,b (1:4.5)	27a,b (1:4.3)[n]	100	oil
14b	27b	100	oil

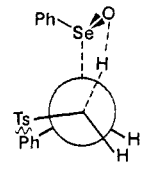
[a] For a typical procedure and for analytical and spectral data of the products, see the Experimental Section. [b] Yields of solid products are based on crystalline materials with melting points close to those of analytical samples or literature values; the homogeneity of oils **20a** and **27b** was confirmed by TLC and GC. [c] Analytical samples were obtained by recrystallization from the following solvents: **23**, MeOH; **22a,b**, hexane; **24a**, CH_2Cl_2-MeOH; **25**, CH_2Cl_2-hexane. [d] Lit.[19] mp 82-83 °C. [e] Lit.[20] mp 122-123 °C. [f] Obtained from the BF_3-catalyzed addition of **1a** to methyl 10-undecenoate. [g] Ratio determined by GC analysis. [h] Sulfone **21a** crystallized from ether-hexane; mp 36-38 °C. [i] Obtained from the BF_3-catalyzed addition of **1b** to methyl 10-undecenoate. [j] Obtained from the thermal addition of **1a** to methyl 10-undecenoate. [k] Previously reported;[21] no physical data were given. [l] Lit.[22] mp 121-122 °C. [m] Lit.[20] mp 131-133 °C. [n] Ratio determined by NMR integration and confirmed by GC analysis.

extracted into aqueous base, thereby avoiding the need for chromatographic separation of the desired sulfone from the diselenide. Selenoxides are known to fragment via a highly stereospecific syn elimination.[6] Each member of a regio- or diastereoisomeic pair of β-phenylseleno sulfones is therefore expected to generate a different vinyl sulfone. Consequently, the oxidation-elimination of **2** not only constitutes a convenient synthesis of vinyl sulfones but also serves to confirm the structures of the former compounds.

The preparation of vinyl sulfones **19**–**27** from the corresponding β-phenylseleno sulfones is summarized in Table III; the structures of the products are shown in Chart II. In particular, it is worth noting that oxidation of adduct **4b** could, in principle, produce both *E* and *Z* vinyl sulfones via the respective transition states **28** and **29**. The exclusive formation of the *E* isomer **20b** (J_{trans} = 15.6 Hz) is attributed to less crowding in transition state **28**. Similar considerations apply to β-phenylseleno sulfones **5b,d**, **12**, and **13**, where only one member of each diastereotopic pair of hydrogens undergoes elimination.



28



29

As expected, the diastereomeric adducts **6a** and **6b** each gave a different vinyl sulfone (**22a** and **22b**) upon oxidation. Furthermore, oxidation of the mixture of adducts **14a** and **14b** obtained from the addition of **1a** to either (*E*)- or (*Z*)-5-decene afforded a mixture of isomeric sulfones whose 200-MHz ^1H NMR spectrum showed two vinylic proton signals at δ 6.86 and 5.96, integrating in a ratio of 4.3:1. The former signal was a clean triplet (J = 7.6 Hz) while the latter exhibited long-range allylic coupling and was observed as a triplet of triplets (J = 7.5, 1.1 Hz). When the pure major isomer **14b** was oxidized separately, only the vinyl sulfone having the resonance at δ 6.86 was isolated. Since transoid allylic coupling constants are generally smaller than cisoid ones,[18] we assign the *E* configuration **27b** to the major sulfone and the *Z* configuration **27a** to the minor one. The identification of the latter compounds in turn supports the respective structural assignments of their β-phenylseleno sulfone precursors **14b** and **14a**. It is evident that selenosulfonation in conjunction with oxidation-elimination provides a powerful method for the regio- and stereocontrolled synthesis of vinyl sulfones from olefins.

Experimental Section

Melting points were obtained on an A. H. Thomas hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 467 spectrometer. Proton NMR spectra were obtained on a Hitachi Perkin-Elmer R24B instrument at 60 MHz or on a Varian XL-200 spectrometer at 200 MHz; ^{13}C NMR spectra were recorded on the latter instrument or on a Brüker WH-90 spectrometer. Only selected ^{13}C signals are reported. All NMR spectra were obtained in $CDCl_3$ solution and are reported in parts per million downfield from tetramethylsilane as internal standard. High- and low-resolution mass spectra were recorded on a Varian MAT CH5 spectrometer while gas chromatographic-mass spectral analyses were performed on a Hewlett-Packard 5990 A instrument. GC analyses were carried out on a Pye Unicam Series 104 chromatograph equipped with a flame-ionization detector and a Varian CDS 111-C electronic integrator. Glass columns (1.5 m × 0.64 cm) containing 5% SE-30 on Chromosorb G-HP were employed. Preparative TLC was performed on Analtech 20 × 20 cm glass plates (silica gel GF, 1000 μm). Elemental analyses were obtained by Mr. L. Malek (University of Calgary) or by Guelph Chemical Laboratories. Solvents were reagent grade and dried over molecular sieves. Methyl 10-undecenoate was prepared by the treatment of 1-undecenoic acid with diazomethane; *m*-CPBA (Aldrich Chemical Co.) was purified by treatment with a pH 7.5 phosphate buffer and was assumed to be 100% pure.[23] Selenosulfonates **1a,b** were obtained by a procedure described elsewhere.[8] All other reagents were purchased from commercial sources and purified as required by standard methods. All thermal selenosulfonations were performed under nitrogen; all reactions were carried out in the presence of ambient fluorescent laboratory lighting unless otherwise noted.

Boron Trifluoride Catalyzed Selenosulfonations (See Table I). Typical Procedure. *trans*-1-(Phenylseleno)-2-(*p*-toluenesulfonyl)cyclohexane (3). Selenosulfonate **1a** (156 mg, 0.50 mmol), cyclohexene (41 mg, 0.50 mmol), and 1 drop of boron trifluoride etherate were dissolved in 5 mL of dichloromethane. After 18 h at room temperature, the solution was concentrated and the residue separated by preparative TLC in benzene to afford 175 mg (89%) of **3**: mp 58–59 °C (from methanol); IR ($CHCl_3$) 1305, 1137 cm^{-1}; ^1H NMR (200 MHz) 7.64 (d, J = 8.4 Hz, 2 H), 7.40–7.12 (complex, 7 H), 3.92 (crude q, 1 H), 3.16 (crude q, 1 H), 2.65–2.40 (s at δ 2.44 superimposed on m, total 4 H), 2.36–2.10 (m, 2 H), 2.08–1.81 (m, 2 H), 1.74–1.52 (m, 3 H); ^{13}C NMR 64.0 (d, CSO_2Ar), 38.3 (d, CSePh); mass

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spectrum, m/e 394 (M^+, ^{80}Se), 392 (M^+, ^{78}Se). Anal. Calcd for $C_{19}H_{22}O_2SSe$: C, 58.01; H, 5.64; S, 8.15. Found: C, 57.56; H, 5.62; S, 8.49.

The following compounds were prepared in the same manner as **3**.

1-Phenyl-2-(phenylseleno)-1-(*p*-toluenesulfonyl)ethane (4a). The product was isolated by preparative TLC in benzene: IR ($CHCl_3$) 1304, 1145 cm^{-1}; ^1H NMR (60 MHz) 7.5–7.0 (complex, 14 H), 4.21 (dd, J = 12, 3 Hz, 1 H), 3.95–3.20 (m, 2 H), 2.36 (s, 3 H); ^{13}C NMR 71.6 (d, CSO_2Ar), 24.6 (t, CSePh); mass spectrum, m/e 416 (M^+, ^{80}Se), 414 (M^+, ^{78}Se). Anal. Calcd for $C_{21}H_{20}O_2SSe$: C, 60.72; H, 4.85; S, 7.72. Found: C, 60.42; H, 4.99; S, 8.12.

Methyl 11-(Phenylseleno)-10-(*p*-toluenesulfonyl)undecanoate (5a) and Methyl 10-(Phenylseleno)-11-(*p*-toluenesulfonyl)undecanoate (5b). The mixture of **5a** and **5b** was isolated by preparative TLC in 20% ethyl acetate–hexane and could not be further separated: IR (film) 1737, 1303, 1145 cm^{-1}; ^1H NMR (200 MHz) 7.68 and 7.62 (2 slightly superimposed d, J = 8 Hz, in a ratio of ca. 2:1, total 2 H), 7.44–7.14 (complex, 7 H), 3.66 (s, 3 H), 3.42–3.28 (dd, J = 12.4, 3.2 Hz, superimposed on m, total ca. 1.7 H), 3.05 (m, ca. 0.7 H), 2.82 (dd, J = 12.4, 8.8 Hz, ca. 0.7 H), 2.45 and 2.43 (2 s, total 3 H), 2.31 and 2.29 (2 overlapping t, total 2 H), 2.1–1.1 (complex, 14 H); ^{13}C NMR 174.1 (s, C=O), 64.5 (d, $CHSO_2Ar$), 61.7 (t, CH_2SO_2Ar), 51.3 (q, OCH_3), 37.4 (d, CHSePh), signal from CH_2SePh could not be distinguished from other CH_2 peaks; high-resolution mass spectrum calcd for $C_{25}H_{34}O_4S^{80}Se$ m/e 510.1342, found m/e 510.1292.

Methyl 10-(Benzenesulfonyl)-11-(phenylseleno)undecanoate (5c) and Methyl 11-(Benzenesulfonyl)-10-(phenylseleno)undecanoate (5d). The mixture of **5c** and **5d** was isolated by preparative TLC in 20% ethyl acetate–hexane and could not be further separated: IR (film) 1737, 1307, 1145 cm^{-1}; ^1H NMR (200 MHz) 7.79 and 7.72 (2 slightly superimposed d, J = 8 Hz, in a ratio of ca. 2:1, total 2 H), 7.70–7.44 (m. 3 H), 7.38–7.10, (m, 5 H), 3.64 (s, 3 H), 3.55–3.25 (m, ca. 1.5 H), 2.96 (m, ca. 0.7 H), 2.74 (dd, J = 12.4, 10.0 Hz, ca. 0.7 H), 2.25 (2 overlapping t, total 2 H), 2.0–1.1 (complex, 14 H); ^{13}C NMR 174.1 (s, C=O), 64.5 (d, $CHSO_2Ph$), 61.6 (t, CH_2SO_2Ph), 51.4 (q, OCH_3), 37.4 (d, CHSePh), signal from CH_2SePh could not be distinguished from other CH_2 peaks; high-resolution mass spectrum calcd for $C_{24}H_{32}O_4S^{80}Se$ m/e 496.1186, found m/e 496.1164.

***erythro*-1-Phenyl-2-(phenylseleno)-1-(*p*-toluenesulfonyl)propane (6a).** The product was isolated by preparative TLC in 25% chloroform–benzene: IR ($CHCl_3$) 1303, 1143 cm^{-1}; ^1H NMR (200 MHz) 7.39 (d, J = 8.0 Hz, 2 H), 7.30–7.00 (complex, 12 H), 4.34–4.16 (m, 2 H), 2.31 (s, 3 H), 1.92 (d, J = 6.4 Hz, 3 H); double irradiation at δ 1.92 gave an AB quartet centered at δ 4.21 (J = 9.6 Hz); ^{13}C NMR 76.0 (d, CSO_2Ar), 38.5 (d, CSePh); mass spectrum, m/e 430 (M^+, ^{80}Se), 428 (M^+, ^{78}Se). Anal. Calcd for $C_{22}H_{22}O_2SSe$: C, 61.53; H, 5.16; S, 7.47. Found: C, 61.57; H, 5.13; S. 7.22.

***threo*-1-Phenyl-2-(phenylseleno)-1-(*p*-toluenesulfonyl)propane (6b).** The product was isolated by preparative TLC in 25% chloroform–benzene: IR (film) 1303, 1145 cm^{-1}; ^1H NMR (200 MHz) 7.4–7.2 (complex, 12 H), 7.10 (d, J = 8.1 Hz, 2 H), 4.44 (dq, J = 7.2, 3.2 Hz, 1 H), 4.26 (d, J = 3.2 Hz, 1 H), 2.34 (s, 3 H), 1.69 (d, J = 7.2 Hz, 3 H); double irradiation at δ 1.69 gave δ 4.44 (d, J = 3.2 Hz); ^{13}C NMR 73.8 (d, CSO_2Ar), 36.4 (d, CSePh); high-resolution mass spectrum calcd for $C_{22}H_{22}O_2S^{80}Se$ m/e 430.0505, found m/e 430.0483.

***trans*-4-(Phenylseleno)-3-(*p*-toluenesulfonyl)cyclohexene (10).** The product was isolated by preparative TLC in 20% ether–hexane: IR ($CHCl_3$) 1647, 1302, 1143 cm^{-1}; ^1H NMR (200 MHz) 7.61 (d, J = 8.1 Hz, 2 H), 7.36–7.16 (complex, 7 H), 6.26 (crude d, 1 H), 5.68 (crude d, 1 H), 4.02 (br s, 1 H), 3.80 (br s, 1 H), 2.55–2.05 (s at δ 2.43 superimposed on m, total 6 H), 1.95–1.75 (m, 1 H); double irradiation at δ 1.8 gave δ 3.80 (dd, J = 4.0, 1.6 Hz); double irradiation at δ 2.2 gave δ 3.80 (d, J = 3.6 Hz), 5.68 (dd, J = 10.8, 5.2 Hz), 6.26 (d, J = 10.8 Hz); ^{13}C NMR 115.6 (d, vinylic C; other vinylic C could not be distinguished from aromatic carbons), 65.1 d, CSO_2Ar), 35.9 (d, CSePh) 23.3 (t), 21.8 (t), 21.6 (q); mass spectrum, m/e 392 (M^+, ^{80}Se); 390 (M^+, ^{78}Se). Anal. Calcd for $C_{19}H_{20}O_2SSe$: C, 58.31; H, 5.15; S, 8.19. Found: C, 58.26; H, 5.18; S, 8.55.

^1H NMR Studies of the Reaction of (*E*)- and (*Z*)-1-Phenylpropenes with 1a. The following reactions were performed at room temperature and were monitored by ^1H NMR (200 MHz) spectroscopy. Relative concentrations of adducts **6a** and **6b** and of selenosulfonate **1a** were obtained from integration of their respective aromatic methyl signals; those of the *E* and *Z* olefins were deduced from integration of the vinylic resonances.

(A) (*E*)-1-Phenylpropene (30 mg, 0.25 mmol), **1a** (78 mg, 0.25 mmol), and 1 drop of boron trifluoride etherate were dissolved in 1.0 mL of deuteriochloroform. The ratio of **6a** to either **1a** or the *E* olefin was 1.6:1 after 48 h and 2.1:1 after 1 week. Adduct **6b** was not detected.

(B) Adduct **6a** (107 mg, 0.25 mmol) and 1 drop of boron trifluoride etherate were dissolved in 1.0 mL of deuteriochloroform. The ratio of **6a** to either **1a** or the *E* olefin was 2.5:1 after 30 min and 2.1:1 after 3 h.

(C) (*Z*)-1-Phenylpropene (30 mg, 0.25 mmol), **1a** (78 mg, 0.25 mmol), and 1 drop of boron trifluoride etherate were dissolved in 1.0 mL of deuteriochloroform. After 50 min, the ratio of **6b** to either **1a** or the *Z* olefin was 1.1:1. At this time the ratio of **6b** to **6a** was 19.5:1, and a small amount of the *E* olefin was also detected. After 1 week, the ratios of **6b**/**6a**, **6b**/**1a**, and **6b**/(*E*)-1-phenylpropene were 10.3:1, 4.9:1, and 13.8:1. No (*Z*)-1-phenylpropene was detected.

(D) Adduct **6b** (107 mg, 0.25 mmol) and 1 drop of boron trifluoride etherate were dissolved in 1.0 mL of deuteriochloroform. After 3 h, **6b** remained unreacted; neither **1a**, **6a**, nor (*E*)- or (*Z*)-1-phenylpropene could be detected. After 24 h, the latter four compounds were still not present, and only **6b** and a small amount of dark, unidentified material were observed.

(E) (*Z*)-1-Phenylpropene (30 mg, 0.25 mmol) and 1 drop of boron trifluoride etherate were dissolved in 1.0 mL of deuteriochloroform. No products were detected after 3 h. The *Z* olefin was still largely unchanged after 24 h, although a trace of the *E* olefin, along with a small amount of unidentified material, was observed at this time.

Thermal Selenosulfonations (See Table II). Typical Procedure. 1-Phenyl-1-(phenylseleno)-2-(*p*-toluenesulfonyl)ethane (4b). Styrene (52 mg, 0.50 mmol) and **1a** (156 mg, 0.50 mmol) were refluxed 24 h in 5 mL of chloroform. The solution was concentrated and separated by preparative TLC in benzene to afford 193 mg (93%) of **4b**: mp 157–158 °C (from methanol); IR ($CHCl_3$) 1303, 1139 cm^{-1}; ^1H NMR (60 MHz) 7.53–6.94 (complex, 14 H), 4.67 (dd, J = 10, 4 Hz, 1 H), 4.25–3.60 (m, 2 H), 2.31 (s, 3 H); ^{13}C NMR 61.2 (t, CSO_2Ar), 39.9 (d, CSePh); mass spectrum, m/e 416 (M^+, ^{80}Se), 414 (M^+, ^{78}Se). Anal. Calcd for $C_{21}H_{20}O_2SSe$: C, 60.72; H, 4.85; S, 7.72. Found: C, 60.21; H, 4.94; S, 7.81.

The above reaction was repeated in degassed chloroform in apparatus completely wrapped in aluminum foil to exclude light. After 24 h, 127 mg (61%) of adduct **4b** was isolated.

The following compounds were prepared in the same manner as **4b**.

Methyl 10-(Phenylseleno)-11-(*p*-toluenesulfonyl)undecanoate (5b). The product was isolated by preparative TLC in 25% ethyl acetate–hexane: IR (film) 1735, 1302, 1145 cm^{-1}; ^1H NMR (60 MHz) 7.62 (d, J = 8 Hz, 2 H), 7.40–7.05 (complex, 7 H), 3.66 (s, 3 H), 3.35 (m, 3 H), 2.43 (s, 3 H), 2.30 (t, J = 7 Hz, 2 H), 2.00–1.06 (complex, 14 H); ^{13}C NMR (200 MHz) 174.1 (s, C=O), 61.7 (t, CSO_2Ar), 51.3 (q, OCH_3), 37.4 (d, CHSePh); mass spectrum, m/e 510 (M^+, ^{80}Se), 508 (M^+, ^{78}Se). Anal. Calcd for $C_{25}H_{34}O_4SSe$: C, 58.93; H, 6.72; S, 6.29. Found: C, 58.92; H, 6.76; S, 6.35.

***trans*-1-(Phenylseleno)-2-(*p*-toluenesulfonyl)indan (11a).** The product was isolated by preparative TLC in 33% chloroform–benzene: IR ($CHCl_3$) 1304, 1147 cm^{-1}; ^1H NMR (60 MHz) 7.50 (d, J = 8 Hz, 2 H), 7.35–6.87 (complex, 11 H), 5.11 (d, J = 1.8 Hz, 1 H), 3.93 (ddd, J = 7.0, 3.4, 1.8 Hz, 1 H) 3.41–3.08 (m, 2 H), 2.35 (s, 3 H); ^{13}C NMR 70.7 (d, CSO_2Ar), 45.6 (d, CSePh), 31.9 (t, CH_2), 21.6 (q, CH_3); mass spectrum, m/e 428 (M^+, ^{80}Se), 426 (M^+, ^{78}Se). Anal. Calcd for $C_{22}H_{20}O_2SSe$: C, 61.82; H, 4.72; S, 7.50. Found: C, 62.06; H, 4.99; S, 7.82.

***trans*-2-(Benzenesulfonyl)-1-(phenylseleno)indan (11b).** The product was isolated by preparative TLC in 33% chloroform–benzene: IR ($CHCl_3$) 1308, 1146 cm^{-1}; ^1H NMR (60 MHz) 7.72–6.90 (complex, 14 H), 5.20 (d, J = 2.0 Hz, 1 H), 3.96 (ddd, J = 7.4, 3.0, 2.0 Hz, 1 H), 3.47–3.07 (m, 2 H); mass spectrum, m/e 414 (M^+, ^{80}Se), 412 (M^+, ^{78}Se). Anal. Calcd for $C_{21}H_{18}O_2SSe$: C,

61.02; H, 4.39; S, 7.76. Found: C, 60.62; H, 4.34; S, 7.43.

3-(Benzenesulfonyl)-2-(phenylseleno)propyl Phenyl Ether (12). The product was isolated by preparative TLC in 20% ethyl acetate–hexane: IR (Nujol) 1315, 1308, 1135 cm^{-1}; ^1H NMR (200 MHz) 7.8–6.5 (complex, 15 H), 4.43 (dd, J = 10.8, 4.1 Hz, 1 H), 4.27 (dd, J = 10.8, 4.2 Hz, 1 H), 3.82 (crude q superimposed on m, total 2 H), 3.45 (crude q, 1 H); double irradiation at δ 3.8 gave δ 4.43 (d, J = 10.8 Hz), 4.27 (d, J = 10.8 Hz), and 3.45 (crude s) while irradiation at δ 3.4 had no effect on signals at δ 4.43 and 4.27 but collapsed the signal at δ 3.82; ^{13}C NMR 68.7 (t, COPh), 57.8 (t, CSO_2Ph), 35.7 (d, CSePh); mass spectrum, m/e 432 (M^+, ^{80}Se), 430 (M^+, ^{78}Se). Anal. Calcd for $C_{21}H_{20}O_3SSe$: C, 58.44; H, 4.68; S, 7.44. Found: C, 58.64; H, 4.90; S, 7.67.

2-(Phenylseleno)-3-(*p*-toluenesulfonyl)propionitrile (13). The product was isolated by concentration of the reaction mixture and crystallization from dichloromethane–hexane: IR ($CHCl_3$) 2240, 1312, 1146 cm^{-1}; ^1H NMR (200 MHz) 7.76 (d, J = 8.3 Hz, 2 H), 7.65 (dd, J = 8.2, 1.7 Hz, 2 H), 7.50–7.27 (m, 5 H), 3.97 (dd, J = 8.8, 5.7 Hz, 1 H), 3.50–3.46 (m, 2 H), 2.44 (s, 3 H); ^{13}C NMR 58.5 (t, CSO_2Ar), 17.5 (d, CSePh); mass spectrum, m/e 365 (M^+, ^{80}Se), 363 (M^+, ^{78}Se). Anal. Calcd for $C_{16}H_{15}NO_2SSe$: C, 52.75; H, 4.15; N, 3.84; S, 8.80. Found: C, 53.11; H, 4.20; N, 3.85; S, 8.67.

***erythro*- and *threo*-5-(Phenylseleno)-6-(*p*-toluenesulfonyl)decanes (14a,b).** The product from the reaction of (*E*)-5-decene with **1a** was isolated by preparative TLC in 20% ethyl acetate–hexane. The mixture had the following: IR (film) 1302, 1147 cm^{-1}. ^1H NMR (200 MHz) showed two products in a ratio of 4.5:1. The major product **14b** had signals at δ 7.48 (d, J = 8.0 Hz, 2 H), 7.40–7.10 (complex, 7 H), 3.48 (crude d, 1 H), 3.19 (ddd, J = 7.5, 5.2, 1.6 Hz, 1 H), 2.43 (s, 3 H), 2.20–1.20 (complex, 12 H), and 1.0–0.8 (2 overlapping t, J = 7.0 Hz, total 6 H); double irradiation at δ 3.5 gave δ 3.19 (dd, J = 7.5, 5.2 Hz) while irradiation at δ 3.2 gave δ 3.48 (dd, J = 8.4, 2.4 Hz). The minor product **14a** had signals at δ 7.76 (d, J = 8.2 Hz), 3.59 (br dd, J = 7.2, 2.5, <1 Hz), and 3.36 (br dd, J = 6.5, 2.5, <1 Hz) as well as other aromatic and aliphatic resonances superimposed on those of **14b**; double irradiation at δ 3.36 gave δ 3.59 (br d, J = 7.2, <1 Hz) while irradiation at δ 3.6 gave δ 3.36 (crude t, $J \simeq$ 6 Hz). For the mixture: ^{13}C NMR 69.2 (d, CSO_2Ar, minor product), 68.4 (d, CSO_2Ar, major product), 44.6 (br d, CSePh, both products superimposed); GC/MS analysis showed both components with m/e 452 (M^+, ^{80}Se) and 450 (M^+, ^{78}Se). Crystallization of the mixture from methanol afforded pure **14b** with ^1H NMR signals at δ 3.48 and 3.19 and a ^{13}C NMR signal at δ 68.4 as described above. Anal. Calcd for $C_{23}H_{32}O_2SSe$: C, 61.16; H, 7.15; S, 7.11. Found: C, 60.83; H, 7.47; S, 7.15.

The mixture of products obtained from the reaction of (*Z*)-5-decene with **1a** under similar conditions was identical in all respects with that obtained above.

Reaction of Styrene with 1a in the Presence of 2,6-Di-*tert*-butyl-*p*-cresol or AIBN. (A) Styrene (26 mg, 0.25 mmol), **1a** (78 mg, 0.25 mmol), and the *p*-cresol derivative (11 mg, 0.05 mmol) were refluxed 20 h in 10 mL of degassed chloroform. Preparative TLC in benzene provided 51 mg (65%) of recovered **1a** and 34 mg (33%) of adduct **4b**. A control experiment without the *p*-cresol was performed simultaneously under the same conditions and afforded 30 mg (38%) of **1a** and 61 mg (59%) of **4b**. Other control experiments revealed that the *p*-cresol derivative does not react appreciably with either **1a** or **4b** under these conditions.

(B) Styrene (52 mg, 0.50 mmol), **1a** (156 mg, 0.50 mmol), and AIBN (4 mg, 0.025 mmol) were refluxed 1 h in 10 mL of degassed benzene. Workup as in part A gave 37 mg (24%) of recovered **1a** and 139 mg (67%) of **4b**. A control experiment without AIBN was performed simultaneously under the same conditions to afford 120 mg (77%) of recovered **1a** and 42 mg (20%) of **4b**. A separate reaction and control were worked up after 7 h; the former provided 24 mg (15%) of **1a** and 177 mg (85%) of **4b** while the latter furnished 48 mg (30%) of **1a** and 150 mg (72%) of **4b**.

Reaction of Adduct 4a with Tin Hydrides 17a,b. Adduct **4a** (104 mg, 0.25 mmol) and tri-*n*-butyltin hydride (**17a**; 194 mg, 0.83 mmol) were dissolved in 10 mL of toluene under nitrogen in a flask fitted with a serum stopper. The solution was heated at 80–85 °C (oil bath temperature), and the reaction was monitored by GC analysis. After 5.5 h, 18 mg (69%) of styrene was produced. When triphenyltin hydride (**17b**) was used instead of **17a**, the yield of styrene was 52% after 2.5 h at reflux.

Preparation of Vinyl Sulfones (see Table III). Typical Procedure. 1-(*p*-Toluenesulfonyl)cyclohexene (19). A solution of *m*-CPBA (107 mg, 0.62 mmol) in 10 mL of dichloromethane was added over 5 min to adduct **3** (98 mg, 0.25 mmol) in 2 mL of dichloromethane. An initial yellow color appeared and was discharged with further addition of the peracid. The mixture was washed with several portions (5 mL) of 5% Na_2CO_3 solution, dried over anhydrous $MgSO_4$, and evaporated to dryness *in vacuo* to afford 58 mg (99%) of **19**: mp 80–82 °C (lit.[19] mp 82–83 °C); IR (Nujol) 1641, 1302, 1148 cm^{-1}; ^1H NMR (60 MHz) 7.75 (d, J = 8 Hz, 2 H), 7.30 (d, J = 2 Hz, 2 H), 7.03 (m, 1 H), 2.43 (s, 3 H), 2.40–2.00 (m, 4 H), 1.80–1.44 (m, 4 H); mass spectrum, m/e 236 (M^+).

The following compounds were prepared in the same manner as **19**.

1-Phenyl-1-(*p*-toluenesulfonyl)ethene (20a): IR (film) 1646, 1307, 1150 cm^{-1}; ^1H NMR (60 MHz) 7.43 (d, J = 8 Hz, 2 H), 7.21 (m, 5 H), 7.06 (d, J = 8 Hz, 2 H), 6.46 (s, 1 H), 5.76 (s, 1 H), 2.34 (s, 3 H); high-resolution mass spectrum calcd for $C_{15}H_{14}O_2S$ m/e 258.0714, found m/e 258.0712.

(*E*)-1-Phenyl-2-(*p*-toluenesulfonyl)ethene (20b). The product had IR and ^1H NMR spectra as reported in the literature;[20] mass spectrum, m/e 258 (M^+).

Methyl 10-(*p*-Toluenesulfonyl)-10-undecenoate (21a). Oxidation of **5a** and **5b** (2:1, obtained by the boron trifluoride catalyzed addition of **1a** to methyl 10-undecenoate) in the usual manner gave a 1.8:1 mixture (GC) of sulfones **21a** and **21b**, confirmed by comparison of the ^1H NMR spectrum of each pure sulfone (*vide infra*) to that of the mixture. Repeated recrystallization from ether–hexane afforded the pure major isomer: IR (film of melted product) 1738, 1304, 1142 cm^{-1}; ^1H NMR (60 MHz) 7.73 (d, J = 8 Hz, 2 H), 7.28 (d, J = 8 Hz, 2 H), 6.29 (s, 1 H), 5.66 (t, J = 1 Hz, 1 H), 3.65 (s, 3 H), 2.43 (s superimposed on m, total 7 H), 1.95–1.10 (complex, 12 H); mass spectrum, m/e 352 (M^+). Anal. Calcd for $C_{19}H_{28}O_4S$: C, 64.74; H, 8.00; S, 9.10. Found: C, 64.70; H, 8.06; S, 9.26.

Methyl (*E*)-11-(*p*-Toluenesulfonyl)-10-undecenoate (21b). Oxidation of **5b** (obtained from the thermal addition of **1a** to methyl 10-undecenoate) in the usual manner gave **21b**: IR (film of melted product) 1731, 1631, 1308, 1148 cm^{-1}; ^1H NMR (60 MHz) 7.72 (d, J = 8 Hz, 2 H), 7.30 (d, J = 8 Hz, 2 H), 6.96 (dt, J = 16, 6 Hz, 1 H), 6.25 (d, J = 16 Hz, 1 H), 3.60 (s, 3 H), 2.39 (s superimposed on m, total 7 H), 1.90–1.05 (complex, 12 H); mass spectrum, m/e 352 (M^+). Anal. Calcd for $C_{19}H_{28}O_4S$: C, 64.74; H, 8.00; S, 9.10. Found: C, 64.57; H, 8.07; S, 8.80.

Methyl 10-(Benzenesulfonyl)-10-undecenoate (21c) and Methyl (*E*)-11-(Benzenesulfonyl)-10-undecenoate (21d). Oxidation of **5c** and **5d** (2:1, obtained by the boron trifluoride catalyzed addition of **1a** to methyl undecenoate) in the usual manner gave a 1.8:1 mixture (GC) of sulfones **21c** and **21d**: IR (film) 1737, 1626, 1307, 1147 cm^{-1}; ^1H NMR (60 MHz) 7.98–7.45 (m, 5 H), 6.98 (dt, J = 16, 7 Hz, ca. 0.3 H), 6.35 (s) superimposed on 6.31 (d, J = 16 Hz, total ca. 1 H), 5.72 (br s, ca. 0.7 H), 3.65 (s, 3 H), 2.45–2.05 (m, 4 H), 1.70–1.05 (complex, 12 H). Anal. Calcd for $C_{18}H_{26}O_4S$: C, 63.87; H, 7.74; S, 9.48. Found: C, 63.91; H, 7.86; S, 9.53.

(*Z*)-1-Phenyl-1-(*p*-toluenesulfonyl)propene (22a): IR ($CHCl_3$) 1630, 1305, 1150 cm^{-1}; ^1H NMR (200 MHz) 7.53 (d, J = 8.4 Hz, 2 H), 7.40–7.16 (complex, 7 H), 6.26 (q, J = 7.5 Hz, 1 H), 2.36 (s, 3 H), 2.34 (d, J = 7.5 Hz, 3 H); mass spectrum, m/e 272 (M^+). Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; S, 11.77. Found: C, 70.60; H, 5.96; S, 11.61.

(*E*)-1-Phenyl-1-(*p*-toluenesulfonyl)propene (22b): IR ($CHCl_3$) 1645, 1303, 1147 cm^{-1}; ^1H NMR (60 MHz) 7.56–6.77 (complex, 10 H), 2.33 (s, 3 H), 1.68 (d, J = 7 Hz, 3 H); double irradiation at δ 7.1 gave δ 1.68 (s); mass spectrum, m/e 272 (M^+). Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; S, 11.77. Found: C, 70.97; H, 6.04; S, 11.52.

2-(*p*-Toluenesulfonyl)-1,3-cyclohexadiene (23): IR ($CHCl_3$) 1630, 1300, 1149 cm^{-1}; ^1H NMR (200 MHz) 7.74 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 6.90 (crude t, J = 4.4 Hz, 1 H), 6.07 (crude dd, J = 10.4, 2.0 Hz, 1 H) 5.93 (dt, J = 10.4, 4.0 Hz, 1 H), 2.44–2.34 (s at δ 2.41 superimposed on m, total 5 H), 2.16 (crude t, J = 9.6 Hz, 2 H); double irradiation at δ 2.2 collapsed

the multiplet at δ 2.4, gave δ 5.93 (d, J = 10.4 Hz), and sharpened the dd at δ 6.07; mass spectrum, m/e 234 (M^+). Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02; S, 13.68. Found: C, 66.46; H, 6.08; S, 13.86.

2-(*p*-Toluenesulfonyl)indene (24a): IR ($CHCl_3$) 1303, 1147 cm^{-1}; ^1H NMR (60 MHz) 7.87 (d, J = 8 Hz, 2 H), 7.65 (t, J = 2 Hz, 1 H), 7.55–7.20 (m, 6 H), 3.62 (d, J = 2 Hz, 2 H), 2.40 (s, 3 H); mass spectrum, m/e 270 (M^+). Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22; S, 11.86. Found: C, 71.05; H, 5.44; S, 11.82.

2-(Benzenesulfonyl)indene (24b): IR ($CHCl_3$) 1308, 1151 cm^{-1}; ^1H NMR as reported in the literature;[22] mass spectrum, m/e 256 (M^+).

(*E*)-3-(Benzenesulfonyl)-2-propenyl Phenyl Ether (25): IR (Nujol) 1640, 1308, 1147 cm^{-1}; ^1H NMR (200 MHz) 7.89 (dt, J = 6.6, 1.4 Hz, 2 H), 7.70–7.50 (m, 3 H), 7.30–7.22 (m, 2 H), 7.12 (dt, J = 15.0, 3.3 Hz, 1 H), 6.97 (t, J = 7.5 Hz, 1 H), 6.86 (dd, J = 7.8, 1.2 Hz, 2 H), 6.76 (dt, J = 15.0, 2.2 Hz, 1 H), 4.72 (dd, J = 3.3, 2.2 Hz, 2 H); double irradiation at δ 4.7 gave δ 7.12 (d, J = 15.0 Hz), 6.76 (d, J = 15.0 Hz); mass spectrum, m/e 274 (M^+). Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.66;, H, 5.15; S, 11.70. Found: C, 65.69; H, 5.07; S, 11.49.

(*E*)-1-Cyano-2-(*p*-toluenesulfonyl)ethene (26). The product had IR and ^1H NMR spectra as reported in the literature;[20] mass spectrum, m/e 207 (M^+).

(*Z*)- and (*E*)-5-(*p*-Toluenesulfonyl)-5-decenes (27a,b). Oxidation of **14a** and **14b** (1:4.5, obtained by the thermal addition of **1a** to 5-decene) in the usual manner gave a mixture of sulfones **27a** and **27b**: ^1H NMR (200 MHz) showed signals at δ 6.86 (t, J = 7.6 Hz, E sulfone) and 5.96 (tt, J = 7.5, 1.1 Hz, Z sulfone) in a ratio of 4.3:1; GC/MS analysis showed both components with m/e 294 (M^+).

Oxidation of pure **14b** gave only the E sulfone **27b**: IR (film) 1640, 1301, 1138, cm^{-1}; ^1H NMR (60 MHz) 7.65 (d, J = 8 Hz, 2 H), 7.20 (d, J = 8 Hz, 2 H), 6.86 (t, J = 7.6 Hz, 1 H), 2.40 (s, 3 H), 2.40–2.00 (m, 4 H), 1.70–0.70 (complex, 14 H); high-resolution mass spectrum calcd for $C_{17}H_{26}O_2S$ m/e 294.1655, found m/e 294.1644.

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Registry No. 1a, 68819-94-3; **1b**, 60805-71-2; **3**, 76649-90-6; **4a**, 76649-84-8; **4b**, 76649-85-9; **5a**, 76649-86-0; **5b**, 76649-87-1; **5c**, 76649-88-2; **5d**, 76649-89-3; **6a**, 77825-67-3; **6b**, 77825-68-4; **10**, 77825-69-5; **11a**, 77825-70-8; **11b**, 77825-71-9; **12**, 76649-92-8; **13**, 77825-72-0; **14a**, 77825-73-1; **14b**, 77882-25-8; **19**, 67963-03-5; **20a**, 77825-74-2; **20b**, 16212-08-1; **21a**, 77825-75-3; **21b**, 77825-76-4; **21c**, 77825-77-5; **21d**, 77825-78-6; **22a**, 77825-79-7; **22b**, 77825-80-0; **23**, 77825-81-1; **24a**, 77825-82-2; **24b**, 26189-65-1; **25**, 77825-83-3; **26**, 19542-67-7; **27a**, 77825-84-4; **27b**, 77825-85-5; boron trifluoride, 7637-07-2; cyclohexene, 110-83-8; styrene, 100-42-5; methyl 10-undecenoate, 111-81-9; (*E*)-1-phenylpropene, 873-66-5; (*Z*)-1-phenylpropene, 766-90-5; 1,3-cyclohexadiene, 592-57-4; indene, 95-13-6; allyl phenyl ether, 1746-13-0; acrylonitrile, 107-13-1; (*E*)-5-decene, 7433-56-9; (*Z*)-5-decene, 7433-78-5.

Investigation of the Synthesis of Benzoxazole via Aryne Reaction[1a]

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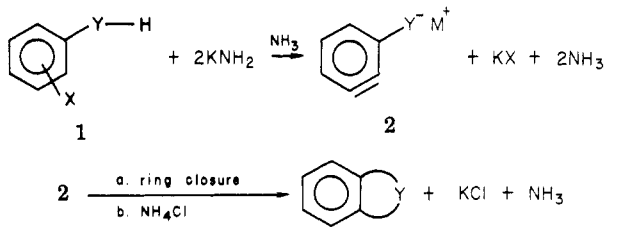
The reaction of *o*- and *m*-halobenzamides under aryne-forming conditions yielded the corresponding *o*-hydroxyphenyl amidines instead of the expected benzoxazole derivatives. The amidines, however, were converted to the corresponding benzoxazole either by sublimation or acidic hydrolysis. Evidence is presented that benzoxazoles are initially formed in these reactions but are readily aminated to the corresponding hydroxyphenyl amidines under the highly basic reaction conditions used in these aryne-forming reactions.

Bunnett[2,3] and Huisgen[4-7] have shown that aryne intermediates, **2**, which possess a strong nucleophile located suitably in a side chain undergo intramolecular nucleophilic addition to yield the corresponding ring-closure products. Arynes, **2**, are prepared by treating either ortho- or meta-substituted haloaromatics with a strong base, generally potassium amide in liquid ammonia or phenyllithium in ether. Several heterocyclic systems,[8] such as benzoxazoles, benzothiazoles, indoles, phenothiazine, etc., have been prepared in this manner, generally in good to excellent yields.



Heterocyclic ring systems which contain a C=N bond are susceptible to covalent solvation by nucleophilic solvents.[9] Of particular interest to us was the report[3] that 2-phenylbenzoxazole was prepared in 70% yield from the aryne reaction of 2-chlorobenzanilide and potassium amide in liquid ammonia. Many of these solvated heterocyclics undergo ring opening in the presence of strong bases; the

(1) (a) Supported in part by Grant N-118 of the Robert A. Welch Foundation, Houston, TX. (b) Robert A. Welch postdoctoral fellow. (c) Robert A. Welch predoctoral fellow.
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