sodium borohydride (0.95 g, 25 mmol) at room temperature with stirring. The temperature was slowly raised to 70 °C, during which evolution of hydrogen was observed. The solution was kept at 70 °C for 12 h, cooled to room temperature, and acidified with 2 N HCl solution. The solution was extracted with diethyl ether (3 × 20 mL), and the organic solution was washed with water (3 × 20 mL) and dried (Na_2SO_4). Diethyl ether was distilled off at ambient pressure and hexadecane (**4a**) collected (90% yield) at 10 torr (149 °C) [lit.[13] bp 152 °C (15 torr)].

(B) Reduction of 1-[(*p*-Tolylsulfonyl)oxy]hexadecane (3j). To a mixture of 1-[(*p*-tolylsulfonyl)oxy]hexadecane (**3j**; 1.98 g, 5 mmol) in 25 mL of PEG was added sodium borohydride (0.57 g, 15 mmol) at room temperature with stirring. After 3 h at 70 °C the reaction was terminated by addition of 2 N HCl to an acidic pH. After the usual workup hexadecane (**4a**) was obtained (0.9 g, 80% yield) in >95% purity by GC.

(C) Reduction of Benzoyl Chloride (5c). A solution of sodium borohydride (0.57 g, 15 mmol) in PEG 400 (25 mL) was prepared at room temperature and then kept at 80 °C (2 h). After the mixture cooled to room temperature, **5c** (0.682 g, 5 mmol) was added and the temperature of the solution raised again to 80 °C. After 3 h the reaction was terminated and worked up as described previously. Benzyl alcohol (**2**) was obtained (0.42 g, 78%) in >95% purity by GC.

Preparation of $Na[(PEG)_2BH_2]$. The alkoxyborohydride, $Na[(PEG)_2BH_2]$, was prepared by addition of sodium borohydride (0.38 g, 10 mmol) to PEG 400 (8 g, 20 mmol) and the resulting solution kept at 80 °C for 5 h. During this time 2 molar equiv of hydrogen was evolved, and the freshly prepared alkoxyborohydride was used for the reduction of different substrates in tetrahydrofuran: IR ν_{max} 3300, 2850, 2250 cm^{-1}.

Reductions with $Na[(PEG)_2BH_2]$ in Tetrahydrofuran. Typical Procedure. (A) Reduction of 1-Bromohexadecane (3a). A solution of **3a** (1.22 g, 4 mmol) in tetrahydrofuran[11] (5 mL) was added to freshly prepared $Na[(PEG)_2BH_2]$ (4 mmol) and the temperature raised to 70 °C. During the time of reaction (4 h), the formation of a white solid was observed, which made the stirring difficult. After the mixture cooled to room temperature, 2 N HCl solution was added and the solvent removed under reduced pressure. Extractions with diethyl ether and the usual workup furnished hexadecane (**4a**) in 80% yield.

(B) Reduction of 1-[(*p*-Tolylsulfonyl)oxy]hexadecane (3j). A solution of **3j** (1.98 g, 5 mmol) in tetrahydrofuran (10 mL) was added to freshly prepared $Na[(PEG)_2BH_2]$ (5 mmol) at room temperature with stirring. After 1 h at 75 °C the reaction was quenched with 2 N HCl and the solvent removed under reduced pressure. After the usual workup hexadecane (**4a**) was obtained (0.81 g, 72% yield) in >95% purity by GC.

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Registry No. **1**, 93-58-3; **3a**, 112-82-3; **3b**, 112-29-8; **3c**, 1002-69-3; **3d**, 2050-77-3; **3e**, 544-77-4; **3f**, 100-39-0; **3g**, 100-11-8; **3h**, 2746-25-0; **3i**, 104-83-6; **3j**, 6068-28-6; **3k**, 5509-08-0; **3l**, 13187-99-0; **3m**, 86436-68-2; **5a**, 112-67-4; **5b**, 112-13-0; **5c**, 98-88-4; **5d**, 586-75-4; $NaBH_4$, 16940-66-2; PEG, 25322-68-3; $Na[(PEG)_2BH_2]$, 86436-69-3.

(13) "Handbook of Chemistry and Physics", 60th ed.; CRC Press: Cleveland, OH, 1980.

Selenosulfonation of Acetylenes: Preparation of Novel β-(Phenylseleno)vinyl Sulfones and Their Conversion to Acetylenic and β-Functionalized Sulfones[1a]

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The 1,2-additions of *Se*-phenyl *p*-tolueneselenosulfonate (**1**) to acetylenes under mild conditions afford β-(phenylseleno)vinyl sulfones **3**, generally in high yields. The reaction is highly regioselective (anti-Markovnikov) and stereoselective (anti) and proceeds via a free-radical chain mechanism initiated by the thermolysis of the selenosulfonate. The oxidation of β-(phenylseleno)vinyl sulfones with *m*-chloroperbenzoic acid generates the corresponding selenoxides **4**, which undergo syn or base-catalyzed elimination to furnish acetylenic sulfones **5**. Base-catalyzed alcoholyses of selenoxides **4** in methanol or ethylene glycol produce β-keto sulfone ketals **8** or **10**, respectively. Free β-keto sulfones **11** are formed by the acid-catalyzed hydrolysis of the corresponding β-(phenylseleno)vinyl sulfones **3**.

We recently reported[2] that *Se*-phenyl areneselenosulfonates (e.g., **1**) undergo electrophilic (eq 1a) or thermal free-radical additions (eq 1b) to olefins to afford, with complementary regiospecificity, the corresponding β-(phenylseleno)alkyl sulfones **2**. Gancarz and Kice[3a,b] have independently shown that the free-radical reactions can also be photoinitiated. The selenosulfonation of olefins, followed by oxidation and stereospecific selenoxide syn elimination, thus provides a regio- and stereocontrolled route to synthetically useful vinyl sulfones.

As an extension of these studies we,[4] and independently Miura and Kobayashi,[5] have observed that *Se*-phenyl *p*-tolueneselenosulfonate (**1**) also undergoes thermally induced 1,2-additions to acetylenes, producing novel β-

(1) (a) We thank the Natural Sciences and Engineering Research Council of Canada and the Research Corp. for financial support. (b) Recipient of an NSERC Postgraduate Scholarship and an Honorary Killam Scholarship. (c) Undergraduate summer research assistant.

(2) (a) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249. (b) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, *21*, 2215.

(3) (a) Gancarz, R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899. (b) Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett.* **1980**, *21*, 4155. (c) Gancarz, R. A.; Kice, J. L. *Ibid.* **1980**, *21*, 1697.

(4) Preliminary communication: Back, T. G.; Collins, S. *Tetrahedron Lett.* **1981**, *22*, 5111.

(5) Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438.

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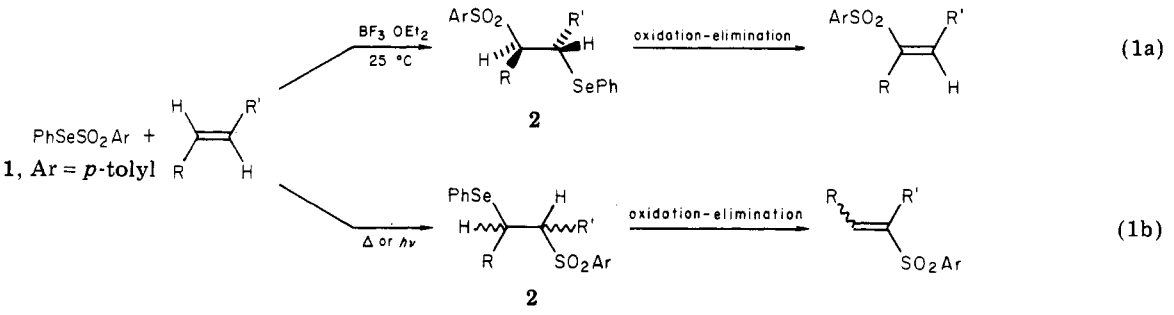
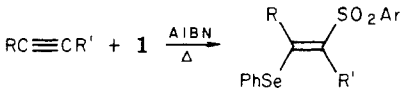


Table I. Preparation of β-(Phenylseleno)vinyl Sulfones 3

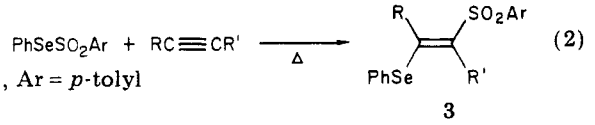


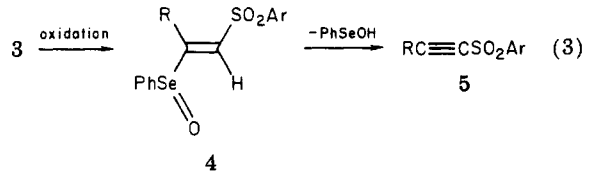
3

product	R	R'	solvent (temp, °C	time,[a] h	isolated yield,[a] %
3a	Ph	H	C_6H_6 (reflux)	4 (72)	93 (86)
3b	$Me(CH_2)_7$	H	C_6H_6 (reflux)	24 (84)	88 (82)
3c	$HOCH_2CH_2$	H	$CHCl_3$ (reflux)	24	88
3d	Me_3Si	H	C_6H_6 (80)[b]	96	94
3e	CO_2Me	H	$CHCl_3$ (reflux)	24 (96)	83 (82)
3f	H	H	CH_2Cl_2 (80)[c]	72 (72)	56 (45)
3g	Ph	Ph	C_6H_6 (reflux)	4 (72)	52 (52)
				4	92[d]
3h	Ph	Me	C_6H_6 (reflux)	20	92

[a] Reactions were performed in the presence of 5 mol % of AIBN. Reaction times and yields in the absence of AIBN are shown in parentheses for comparison. [b] The reaction was performed in a sealed glass tube. [c] The reaction was performed in a Parr high-pressure reaction vessel with excess acetylene; the yield is based on 1. [d] A twofold excess of diphenylacetylene was employed; the yield is based on 1.

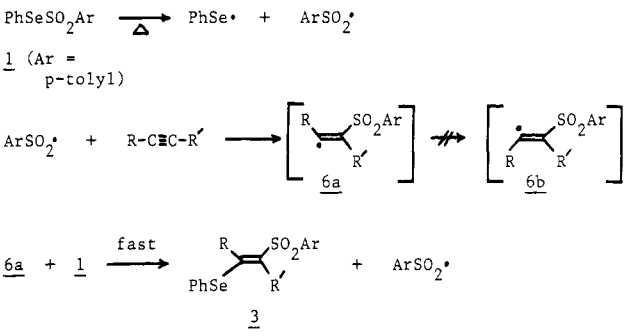
(phenylseleno)vinyl sulfones **3**, generally in high yield and under mild conditions (eq 2). We now report full details





of this work and include several new examples. In addition, we have found that adducts **3** are readily oxidized to selenoxides **4**, which smoothly undergo syn or base-catalyzed eliminations to afford acetylenic sulfones **5** (eq 3). Products **5** are of current interest as dienophiles in Diels–Alder cycloadditions,[6] as electrophiles in Michael additions,[7] and in other applications.[8] We also describe related reactions which permit the conversion of adducts **3** to synthetically useful β-keto sulfone derivatives.[9] These processes thus provide new methods for elaborating acetylenes to a number of useful types of products.

Scheme I



Results and Discussion

Selenosulfonate **1** is an odorless, easily handled solid which is readily available from the oxidation of *p*-toluenesulfonohydrazide[10] or its parent sulfinic acid[3a,c] with benzeneseleninic acid. The thermal additions of **1** to acetylenes were performed in solution at 60–80 °C and afforded the adducts **3a–h**, generally in excellent yield (Table I). The method is compatibile with unsubstituted acetylene, as well as with mono- and disubstituted derivatives, and tolerates functional groups such as esters and alcohols.

The reactions of **1** with terminal acetylenes proved highly regiospecific, favoring anti-Markovnikov adducts (where the sulfone moiety is bonded to the unsubstituted acetylenic carbon atom) to the exclusion of any significant amounts of their Markovnikov regioisomers. These results are consistent with a free-radical chain mechanism analogous to that observed in the selenosulfonation of olefins under similar conditions.[2a] In Scheme I, a sulfonyl radical is generated by the initial homolysis of the Se–SO_2 linkage

(6) For examples, see: (a) Kloek, J. A. *J. Org. Chem.* **1981**, *46*, 1951. (b) Shen, M.; Schultz, A.G. *Tetrahedron Lett.* **1981**, *22*, 3347. (c) Davis, A. P.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1980**, 639.

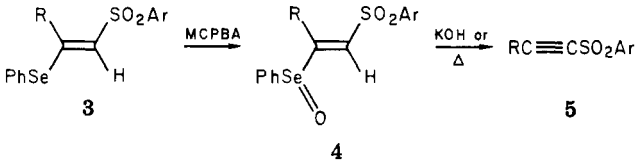
(7) (a) For a review, see: Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. For other examples, see: (b) Fiandanese, V.; Marchese, G.; Naso, F. *Tetrahedron Lett.* **1978**, 5131. (c) Truce, W. E.; Onken, D. W. *J. Org. Chem.* **1975**, *40*, 3200. (d) Sanders, J. A.; Hovius, K.; Engberts, J. B. F. N. *Ibid.* **1974**, *39*, 2641.

(8) For examples, see: (a) Paquette, L. A.; Williams, R. V. *Tetrahedron Lett.* 1981, *22*, 4643. (b) Snider, B. B.; Kirk, T. C.; Roush, D. M.; Gonzalez, D. *J. Org. Chem.* **1980**, *45*, 5015. (c) Smorada, R. L.; Truce, W. E. *Ibid.* **1979**, *44*, 3445.

(9) Anions derived from β-keto sulfones and their derivatives have wide applicability in synthesis. For examples, see ref 7a.

(10) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, *21*, 2213.

Table II. Preparation of Acetylenic Sulfones 5



3 4 5

starting material	R	selenoxide	product	method[a]	time, h	yield,[b] %
3a	Ph	4a	5a	A	15	89
				B	1	88
				C	0.5	91
3b	$Me(CH_2)_7$	4b	5b	B	2.5	87
				C	1.5	88[c]
3c	$HOCH_2CH_2$	4c	5c	B	3	58
3d	Me_3Si	4d	5d	A	2	100[d]
				A	3	39[e]
				A	3	88[f]

[a] A, CH_2Cl_2 or $CHCl_3$ at room temperature; B, $CHCl_3$ at reflux; C, THF/H_2O/KOH at room temperature. [b] Isolated yield unless otherwise noted. [c] Yield determined by GC. [d] Yield determined by NMR. [e] Isolated by preparative HPLC. [f] The product hydrolyzed during workup and was isolated as $HC{\equiv}CSO_2Ar$ (5f).

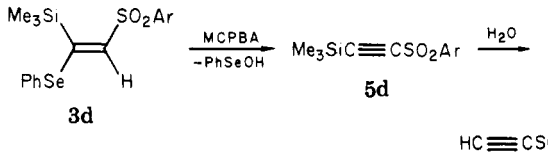
in 1 and then adds to the acetylene to form the more substituted β-sulfonylvinyl radical **6a**. Further reaction of **6a** with selenosulfonate 1 produces the product 3 and simultaneously regenerates the sulfonyl radical. Additional evidence for a free-radical chain mechanism derives from the often dramatic rate enhancements observed in the presence of small amounts (5 mol %) of the radical initiator azobis(isobutyronitrile) (AIBN).[11] Indeed, the routine use of AIBN is recommended in order to reduce reaction times and in some cases to improve yields (Table I).

The selenosulfonation of acetylenes is also highly stereoselective, providing the products of anti addition. Thus, the addition of 1 to acetylene produced only one stereoisomer **3f**, whose ^1H NMR spectrum clearly indicated the *E* configuration (J = 15.6 Hz for the vinylic protons). Anti additions were also implicated in the formation of products **3a–d**, since these compounds could be smoothly converted to acetylenic sulfones **5** by selenoxide syn elimination[12] (vide infra), which requires the phenylseleno group and the vinylic hydrogen atom to be cis oriented. In the remaining examples in Table I (**3e,g,h**) where direct evidence is unavailable, the stereochemistry has been tentatively inferred by analogy. No significant amounts of stereoisomers of the above products could be isolated.

Vinyl radicals are known to invert rapidly under normal circumstances.[13] The observed stereoselectivity in the above additions indicates that the rate of reaction of **6a** with 1 is much faster than its inversion to **6b** (Scheme I). The selenosulfonate therefore clearly functions as a highly efficient chain-transfer agent in this process.[14] A similarly rapid chain transfer involving 1 in the photoinitiated selenosulfonation of cyclohexene also accounts for the high stereoselectivity observed in that process, as pointed out by Gancarz and Kice.[3a]

By analogy to the synthesis of vinyl sulfones depicted in eq 1, we reasoned that similar syn eliminations of selenoxides derived from β-(phenylseleno)vinyl sulfones **3** should provide a convenient preparation of acetylenic sulfones **5**. Eliminations of other vinyl selenoxides have been previously studied by Reich and Willis.[15] Thus, compounds **3a–c** were oxidized with *m*-chloroperbenzoic acid (MCPBA) in chloroform or dichloromethane solution at room temperature. The rapid and complete disappearance of the starting material was evident from TLC analysis. Subsequent elimination of the corresponding selenoxides then occurred slowly at room temperature or rapidly in refluxing chloroform and afforded the acetylenic sulfones **5a–c** according to eq 3 (see Table II).

The similar oxidation of the β-(phenylseleno)-β-(trimethylsilyl)vinyl sulfone **3d** at room temperature produced the desilylated acetylenic sulfone **5f** in 88% yield after a workup with aqueous sodium bicarbonate, followed by chromatography on silica gel (eq 4). However, spectral



3d 5d 5f (4)

analysis of the reaction mixture prior to workup revealed that **5d** was the only acetylenic sulfone initially formed. The ^1H NMR spectrum of the reaction mixture displayed a signal at δ 0.19 (Me_3Si of **5d**) and no signal at δ 3.46 (acetylenic H of **5f**). Also, IR analysis indicated an absorption at 2120 cm^{-1} (C≡C of **5d**) and no absorptions at 2065 (C≡C of **5f**) or 3240 cm^{-1} (acetylenic H—C of **5f**). We therefore attribute the isolation of the desilylated product **5f** to the rapid hydrolysis of **5d** during workup.[16] The isolation of the silyl acetylene **5d** could be accomplished in poor yield by preparative HPLC (see Table II).

The byproduct of the elimination reaction in eq 3 is benzeneselenenic acid (PhSeOH), which is known to disproportionate according to eq 5.[17] Hence, the formation

$$3PhSeOH \rightleftharpoons PhSeO_2H + PhSeSePh + H_2O \quad (5)$$

(11) Radical trapping and ESR experiments corroborate this mechanism (see ref 5).

(12) For reviews of selenoxide eliminations, see: (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.

(13) Nonhebel, D. C.; Walton, J. C. In "Free-Radical Chemistry"; Cambridge Univeristy Press: Cambridge, 1974; pp 90–92.

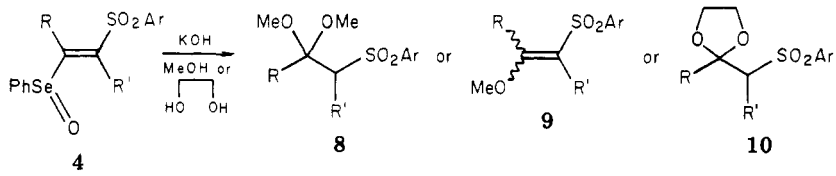
(14) Similar stereoselectivity has been observed in the additions of sulfonyl bromides and iodides to acetylenes. (a) Amiel, Y. *J. Org. Chem.* **1974**, *39*, 3867. (b) Truce, W. E.; Wolf, G. C. *Ibid.* **1971**, *36*, 1727.

(15) Reich, H. J.; Willis, W. W., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 5967.

(16) The facile hydrolysis of **5d** to **5f** has been previously observed: Bhattacharya, S. N.; Josiah, B. M.; Walton, D. R. M. *Organomet. Chem. Synth.* **1970/1971**, *1*, 145.

(17) (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.

Table III. Alcoholysis of Selenoxides 4[a]



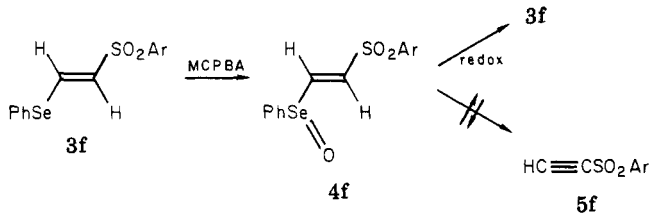
4 8 9 10

starting material	R	R'	alcohol	product(s)	time, h	isolated yield, %
4a	Ph	H	MeOH	8a	32	84
			$(CH_2OH)_2$	10a	24	82
4b	$Me(CH_2)_7$	H	MeOH	8b, 9b[b]	32	59, 22
			$(CH_2OH)_2$	10b	10	76
4f	H	H	MeOH	8f	1	91
			$(CH_2OH)_2$	10f	24	74
4g	Ph	Ph	MeOH	8g, 9g[b,c]	24	17, 65
			$(CH_2OH)_2$	10g	6	90

[a] All selenoxides were prepared in situ by oxidation of 3 with MCPBA; all reactions were performed at room temperature. [b] The unseparated mixture of 8 and 9 was isolated; their respective yields were determined by NMR. [c] Product 9g was obtained as a mixture of geometric isomers.

of diphenyl diselenide is observed unless excess MCPBA is employed to oxidize all selenium-containing byproducts to benzeneseleninic acid ($PhSeO_2H$). This is then readily extracted into aqueous base during the workup.

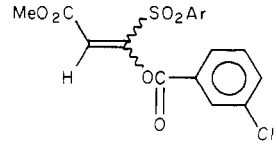
The oxidations of adducts **3e** and **3f** failed to produce the coresponding acetylenic sulfones. Compound **3f** was oxidized with MCPBA in the usual manner and afforded the expected selenoxide **4f**, which could be isolated in 97% yield. The latter product was stable for prolonged periods of time at room temperature in the solid state. However, when it was refluxed in chloroform, only traces of the expected acetylenic sulfone **5f** were detected. The major identifiable product was the selenide **3f** (51% yield), indicating that the unsubstituted selenoxide **4f** undergoes a redox reaction instead of elimination (eq 6). When the



(6)

selenoxide was pyrolyzed in the presence of 1,4-diazabicyclo[2.2.2]octane (Dabco), a reagent known to suppress redox processes in other vinyl selenoxides,[15] the formation of selenide **3f** was not observed. However, no significant amount of the acetylenic sulfone could be isolated from the resulting complex mixture. Other oxidants such as ozone and hydrogen peroxide also failed to convert **3f** to **5f**. Product **5f** is therefore most conveniently prepared by the oxidation, elimination, and hydrolysis of the silylated adduct **3d**, as described earlier.

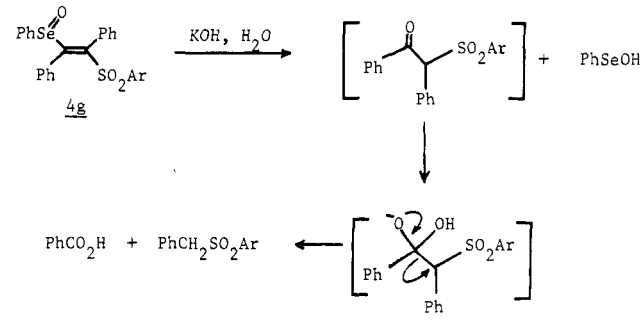
The oxidation of adduct **3e** with MCPBA under the usual conditions afforded some regenerated selenide and a product whose spectral characteristics were consistent with the enol ester **7**. Evidently, the byproduct *m*-



7

chlorobenzoic acid reacts further with the initially formed

Scheme II



highly reactive acetylenic sulfone via a Michael addition.[18]

Selenoxides **4a** and **4b**, formed in tetrahydrofuran solution from **3a** and **3b** in the usual manner, were treated with 1 M aqueous potassium hydroxide. A rapid reaction was indicated by the prompt appearance of the yellow color of diphenyl diselenide (from the disproportionation of PhSeOH). The acetylenic sulfones **5a** and **5b** were obtained in yields of 91% and 88% respectively (Table II). Since the selenoxides react more slowly in the absence of base, the elimination is evidently subject to base catalysis.

As expected, selenoxide **4g** was inert toward base under similar conditions (elimination of PhSeOH is not possible). When heated, however, benzyl *p*-tolyl sulfone was formed in 95% yield, along with a substantial amount of benzoic acid. Scheme II provides a reasonable mechanism for this process, where hydrolysis of the selenoxide produces a β-keto sulfone intermediate, which undergoes base-catalyzed cleavage to the products.[19]

When the base-catalyzed eliminations of selenoxides **4** were performed in alcoholic media, further reactions with the solvent were observed. Thus, selenides **3a** and **3f** were oxidized with MCPBA in THF and then treated with methanolic potassium hydroxide at room temperature to afford the dimethyl ketal **8a** and the dimethyl acetal **8f** in yields of 84% and 91%, respectively (Table III). The competing addition of ^-OH was not observed under these conditions. The extension of this reaction to substrate **3b** produced an inseparable mixture of the ketal **8b** and the methyl enol ether **9b**, formed in the ratio of 2.7:1 and in

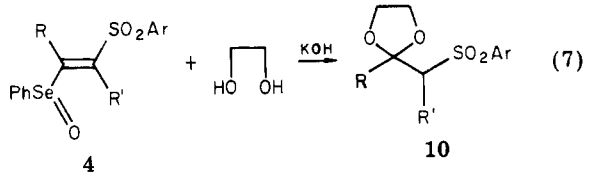
(18) It is also possible that the Michael addition occurs to the vinyl selenoxide and precedes elimination.

(19) A similar cleavage of β-keto sulfones by amine bases has been observed. Looker, J. J. *J. Org. Chem.* **1966**, *31*, 2714.

a combined yield of 81%. Neither longer reaction times nor the use of methanolic sodium methoxide instead of potassium hydroxide increased the proportion of the ketal. These experiments suggest that the acetylenic sulfones **5** are first produced from selenoxides **4** by the usual base-catalyzed elimination of PhSeOH and that they then undergo two successive Michael additions of methanol to form the enol ethers **9** and subsequently the ketals (or acetals) **8** (path a, Scheme III). The last addition is apparently reversible, although the equilibrium lies strongly in favor of the ketal (or acetal) in the case of **8a** and **8f**. The treatment of authentic sulfone **5a** with methanolic potassium hydroxide under similar conditions also produced the ketal **8a** as the chief product. This confirms that the acetylenic sulfones **5** are capable of functioning as the Michael acceptors in the above reactions.

Selenide **3g** was also subjected to oxidation with MCPBA and subsequent treatment with methanolic potassium hydroxide. A mixture of ketal **8g** and enol ether **9g** rapidly formed in a ratio of 1:3.7 and a combined yield of 82%. Since direct elimination of PhSeOH is not possible in this system, the selenoxide **4g** must be the species which functions as the Michael acceptor in this case[20] (path b, Scheme III). When the reaction mixture containing **8g** and **9g** was heated, the appearance of benzyl *p*-tolyl sulfone was detected, indicating a cleavage reaction similar to the one shown in Scheme II.

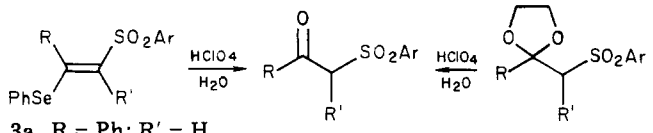
The use of ethylene glycol instead of methanol was also investigated with the expectation that the intermediate enol ethers would be more susceptible to a second, intramolecular Michael addition to provide the corresponding ethylene ketals **10** (eq 7). As shown in Table III, good to



4 10 (7)

excellent yields of ketals **10a,b,f,g** were obtained, even in those cases which led to the formation of equilibrium mixtures with methanol.

We also note that β-(phenylseleno)vinyl sulfones **3a** and **3b** were converted to the unprotected β-keto sulfones **11a** and **11b** in yields of 79% and 60%, respectively, by perchloric acid catalyzed hydrolysis[21] (eq 8). The more highly



3a, R = Ph; R′ = H
b, R = $(CH_2)_7Me$; R′ = H

11a, 79%
b, 60%
g, 98%

10g, R = R′ = Ph

(8)

substituted selenide **3g** proved unreactive under these conditions. The corresponding free β-keto sulfone **11g** could, however, be obtained in nearly quantitative yield by the perchloric acid catalyzed hydrolysis of ketal **10g** under standard conditions.[22]

It is clear that the selenosulfonation of acetylenes provides a convenient, novel route to various acetylenic and β-functionalized sulfones. Further studies of Michael additions to β-(phenylseleno)vinyl sulfones **3** and their selenoxides **4** are in progress in this laboratory.

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. NMR spectra were obtained on a Hitachi Perkin-Elmer R24B instrument at 60 MHz or on a Varian XL-200 spectrometer at 200 MHz. All NMR spectra were obtained in $CDCl_3$ solution unless otherwise noted and are reported in parts per million downfield from tetramethylsilane as an internal standard. High- and low-resolution mass spectra were recorded on a Varian MAT CH5 spectrometer, while gas chromatography/mass spectra were obtained on a Hewlett-Packard 5990 A instrument. GC analyses were carried out on a Varian 3700 chromatograph equipped with a Varian CDS 111C electronic integrator. Stainless steel columns (2 m × 0.3 cm) packed with 3% OV-17 on Chromosorb W-HP were employed. Preparative HPLC was performed with a Varian 5060-Vista 401 system on a 30 cm × 8 mm column containing a C_5 alkyl nitrile bonded phase on silica gel (10 μm). Preparative TLC was carried out on Analtech 20 × 20 cm glass plates coated with silica gel GF (1000 μm). Elemental analyses were obtained by L. Malek and Dr. W.S. Lin (University of Calgary). Solvents were reagent grade and dried over molecular sieves. *m*-Chloroperbenzoic acid (Aldrich Chemical Co.) was purified by treatment with a pH 7.5 phosphate buffer and was assumed to be 100% pure.[23] Selenosulfonate **1** was prepared from the oxidation of *p*-toluenesulfonohydrazide with benzeneseleninic acid.[10] All other reagents were purchased from commercial sources and purified as required by standard methods.

Preparation of β-(Phenylseleno)vinyl Sulfones 3. The following preparations were performed under nitrogen and were monitored for the disappearance of the starting materials by TLC, except in the case of **3d** (sealed-tube reaction). In several cases the following reactions were scaled up ca. fivefold and gave comparable yields. Reactions without AIBN were performed and worked up in the same manner as those below; the results are listed in Table I for comparison.

(*E*)-1-Phenyl-1-(phenylseleno)-2-(*p*-tolylsulfonyl)ethene (3a). Selenosulfonate **1** (156 mg, 0.50 mmol), phenylacetylene (51 mg, 0.50 mmol), and AIBN (4 mg, 0.025 mmol) were refluxed 4 h in 10 mL of benzene. The solution was then evaporated under reduced pressure, and the residue was crystallized from dichloromethane–hexane to afford 192 mg (93%) of **3a**: mp 152 °C; IR (KBr) 1604, 1592, 1324, 1140 cm^{-1}; NMR (60 MHz) 7.62–6.95 (complex, 14 H), 6.15 (s, 1 H), 2.42 (s, 3 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, 60.90; H, 4.35; S, 7.68.

(*E*)-2-(Phenylseleno)-1-(*p*-tolylsulfonyl)-1-decene (3b). Selenosulfonate **1** (311 mg, 1.00 mmol), 1-decyne (138 mg, 1.00 mmol), and AIBN (8 mg, 0.05 mmol) were refluxed 24 h in 10 mL of benzene. The solution was concentrated and purified by preparative TLC (hexane–ethyl acetate, 5:1) to provide **3b** as a homogeneous (TLC, GC), pale yellow oil in a yield of 394 mg (88%). Bulb-to-bulb distillation at 140–145 °C (0.025 mm) afforded an analytical sample: IR (film) 1599, 1303, 1146 cm^{-1}; NMR (60 MHz) 7.62 (d, J = 8 Hz, 2 H), 7.5–7.1 (complex, 7 H), 6.70 (s, 1 H), 2.81 (br t, 2 H), 2.33 (s, 3 H), 1.2 (complex, 12 H), 0.85 (br t, 3 H); mass spectrum, *m/e* 450 (M^+, ^{80}Se), 448 (M^+, ^{78}Se). Anal. Calcd for $C_{23}H_{30}O_2SSe$: C, 61.46; H, 6.73; S, 7.13. Found: C, 61.82; H, 6.83; S, 7.48.

(*E*)-3-(Phenylseleno)-4-(*p*-tolylsulfonyl)-3-buten-1-ol (3c). Selenosulfonate **1** (311 mg, 1.00 mmol), 3-butyn-1-ol (70 mg, 1.00 mmol), and AIBN (8 mg, 0.05 mmol) were refluxed 24 h in 10 mL of chloroform. Preparative TLC (benzene–ether, 3:1) of the concentrated solution afforded 334 mg (88%) of **3c**: mp 92.5–93.5 °C (from ether–hexane); IR (film) 3600–3200 (br), 1592, 1570, 1300, 1142, 1082 cm^{-1}; NMR (60 MHz) 7.60 (d, J = 8 Hz, 2 H), 7.4–7.0

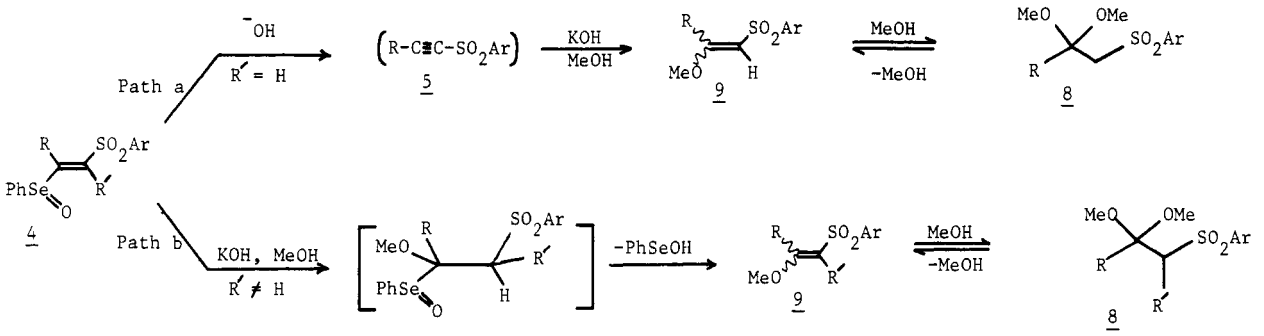
(20) We cannot rule out the possibility that selenoxides **4a,b,f** also act as Michael acceptors in competition with the corresponding acetylenic sulfones.

(21) The perchloric acid catalyzed hydrolysis of other vinyl selenides has been investigated. Hevesi, L; Piquard, J. L.; Wautier, H. *J. Am. Chem. Soc.* **1981**, *103*, 870.

(22) Greene, T. W. In "Protective Groups in Organic Synthesis"; Wiley-Interscience: New York, 1981; Chapter 4, pp 126, 127.

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

Scheme III



(complex, 7 H), 5.90 (s, 1 H), 3.79 (br t, J = 7 Hz, 2 H), 3.07 (t, J = 7 Hz, 2 H), 2.5 (br s, exchanged with D_2O, 1 H), 2.34 (s, 3 H); mass spectrum, m/e 382 (M^+, ^{80}Se), 380 (M^+, ^{78}Se). Anal. Calcd for $C_{17}H_{18}O_3SSe$: C, 53.54; H, 4.76; S, 8.41. Found: C, 53.52; H, 4.86; S, 8.15.

(*E*)-1-(Phenylseleno)-1-(trimethylsilyl)-2-(*p*-tolylsulfonyl)ethene (3d). Selenosulfonate 1 (311 mg, 1.00 mmol), (trimethylsilyl)ethyne (98 mg, 1.00 mmol), and AIBN (8 mg, 0.05 mmol) were heated in 1 mL of benzene in a sealed glass tube at an oil-bath temperature of 80 °C. After 4 days, the tube was cooled to −78 °C and opened. The contents were separated by preparative TLC (hexane–ethyl acetate, 4:1) to furnish 387 mg (94%) of **3d**: mp, 101–102 °C (from ether–hexane); IR (KBr) 1588, 1305, 1145 cm^{-1}; NMR (200 MHz) 7.55 (d, J = 8.4 Hz, 2 H), 7.42–7.23 (m, 5 H), 7.23 (d, J = 8.4 Hz, 2 H), 6.04 (s, 1 H), 2.38 (s, 3 H), 0.49 (s, 9 H); mass spectrum, m/e 410 (M^+, ^{80}Se), 408 (M^+, ^{78}Se). Anal. Calcd for $C_{18}H_{22}O_2SSeSi$: C, 52.80; H, 5.41. Found: C, 52.81; H, 5.45.

Methyl (*E*)-2-(Phenylseleno)-3-(*p*-tolylsulfonyl)-2-propenoate (3e). Selenosulfonate 1 (311 mg, 1.00 mmol), methyl 2-propynoate (84 mg, 1.00 mmol), and AIBN (8 mg, 0.05 mmol) were refluxed 24 h in 10 mL of chloroform. Preparative TLC (hexane–ethyl acetate, 3:1) of the concentrated solution provided 327 mg (83%) of **3e**: mp 90–92 °C (from hexane–ether); IR ($CHCl_3$) 1730, 1598, 1305, 1146 cm^{-1}; NMR (60 MHz) 7.63 (d, J = 8 Hz, 2 H), 7.6–7.2 (complex, 7 H), 6.02 (s, 1 H), 3.65 (s, 3 H), 2.38 (s, 3 H); mass spectrum, m/e 396 (M^+, ^{80}Se), 394 (M^+, ^{78}Se). Anal. Calcd for $C_{17}H_{16}O_4SSe$: C, 51.65; H, 4.08; S, 8.11. Found: C, 51.81; H, 4.12; S, 7.94.

(*E*)-1-(Phenylseleno)-2-(*p*-tolylsulfonyl)ethene (3f). Selenosulfonate 1 (6.224 g, 20.00 mmol) and AIBN (0.164 g, 1.00 mmol) were dissolved in 40 mL of dichloromethane in a glass-lined Parr high-pressure reaction vessel. The vessel was cooled to −78 °C, purged with nitrogen, and charged with acetylene to a pressure of 12.5 psi. The apparatus was slowly heated to 80 °C and recharged with acetylene as required to maintain a constant pressure. After 3 days, the vessel was cooled to −78 °C and opened. Addition of hexane to the contents effected the crystallization of 3.749 g (56%) of **3f**: mp 107–109 °C (from dichloromethane–hexane); IR ($CHCl_3$) 1595, 1550, 1300, 1138 cm^{-1}; NMR (60 MHz) 8.12 (d, J = 15.6 Hz, 1 H), 7.65 (d, J = 8 Hz, 2 H), 7.5–7.1 (complex, 7 H), 6.15 (d, J = 15.6 Hz, 1 H), 2.39 (s, 3 H); mass spectrum, m/e 338 (M^+, ^{80}Se), 336 (M^+, ^{78}Se). Anal. Calcd for $C_{15}H_{14}O_2SSe$: C, 53.42; H, 4.18; S, 9.50. Found: C, 53.82; H, 4.21; S, 9.71.

(*E*)-1,2-Diphenyl-1-(phenylseleno)-2-(*p*-tolylsulfonyl)ethene (3g). Selenosulfonate 1 (156 mg, 0.50 mmol), diphenylacetylene (89 mg, 0.50 mmol), and AIBN (4 mg, 0.025 mmol) were refluxed 4 h in 10 mL of benzene. Preparative TLC (benzene–chloroform, 3:2) of the concentrated solution afforded 127 mg (52%) of **3g**: mp 176–178 °C (from dichloromethane–hexane); IR (KBr) 1608, 1597, 1580, 1318, 1146 cm^{-1}; NMR (60 MHz) 7.3–6.8 (complex, 19 H), 2.32 (s, 3 H); mass spectrum, m/e 490 (M^+, ^{80}Se), 488 (M^+, ^{78}Se). Anal. Calcd for $C_{27}H_{22}O_2SSe$: C, 66.25; H, 4.53; S, 6.55. Found: C, 66.30; H, 4.44; S, 6.50. Although TLC had indicated the presence of starting material in the above reaction, separate experiments revealed that the yield of the title compound could not be improved either by a longer reaction time (24 h) or by the addition of further portions of AIBN during the course of the reaction. When a twofold excess of diphenylacetylene was employed, **3g** was isolated in 92% yield (based on 1) after 4 h in refluxing benzene.

(*E*)-1-Phenyl-1-(phenylseleno)-2-(*p*-tolylsulfonyl)-1-propene (3h). Selenosulfonate 1 (311 mg, 1.00 mmol), 1-phenylpropyne (116 mg, 1.00 mmol), and AIBN (8 mg, 0.05 mmol) were refluxed 20 h in 10 mL of benzene. Crystallization of the concentrated residue from ether–hexane afforded 393 mg (92%) of **3h**: mp 99–100 °C; IR (KBr) 1598, 1585, 1575, 1299, 1157 cm^{-1}; NMR (60 MHz) 7.18 (d, J = 8 Hz, 2 H), 7.0–6.4 (complex, 12 H), 2.25 (s, 3 H), 2.22 (s, 3 H); 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, 61.75; H, 4.65; S, 7.47.

Preparation of Acetylenic Sulfones 5 (See Table II). 1-Phenyl-2-(*p*-tolylsulfonyl)ethyne (5a). *m*-Chloroperbenzoic acid (187 mg, 1.08 mmol) was added to a solution of **3a** (234 mg, 0.57 mmol) in 10 mL of chloroform at room temperature. TLC analysis indicated the complete consumption of starting material within 5 min. After 15 h the reaction mixture was extracted twice with 5% aqueous K_2CO_3 solution, washed with saturated brine, dried with anhydrous $MgSO_4$, and concentrated in vacuo. Preparative TLC (hexane–ethyl acetate, 3:1) afforded 129 mg (89%) of **5a**: mp 83–84 °C (lit.[14b] mp 83–84° C); IR (KBr) 2181, 1302, 1156 cm^{-1}.

When the above reaction was performed at reflux for 1 h, the yield of the title compound was 88% and the melting point 82–84 °C.

The peracid (52 mg, 0.30 mmol) was added to a solution of **3a** (103 mg, 0.25 mml) in 10 mL of THF. After 10 min, 5 mL of 1 M aqueous KOH solution was added with vigorous stirring. The THF layer gradually turned yellow. After 30 min, the mixture was diluted with ether, and the organic layer was washed with saturated brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. Preparative TLC as above provided 31 mg of diphenyl diselenide, identical with an authentic sample (TLC), and 58 mg (91%) of **5a**, mp 82–84 °C.

1-(*p*-Tolylsulfonyl)-1-decyne (5b). A solution of MCPBA (116 mg, 0.66 mmol) and **3b** (151 mg, 0.33 mmol) in 10 mL of chloroform was refluxed 2.5 h and worked up as in the case of **5a**. Preparative TLC (hexane–ethyl acetate, 5:1) of the crude product afforded 86 mg (87%) of **5b** as a homogeneous (TLC, GC) oil: IR (film) 2195, 1596, 1330, 1160 cm^{-1}; NMR (60 MHz) 7.82 (d, J = 8 Hz, 2 H), 7.28 (d, J = 8 Hz, 2 H), 2.42 (s, 3 H) superimposed on 2.31 (br t, J = 6 Hz, 2 H), 1.7–1.05 (br s, 12 H), 0.89 (br t, J = 6 Hz, 3 H); high-resolution mass spectrum, calcd for $C_{17}H_{24}O_2S$ m/e 292.149 69, found m/e 292.1491.

The peracid (65 mg, 0.38 mmol) and **3b** (142 mg, 0.31 mmol) were allowed to stand for 10 min in 10 mL of THF. The reaction mixture was then treated with KOH solution as in the case of **5a**. After 1.5 h, GC analysis with diphenylacetylene as the internal standard indicated the presence of 81 mg (88%) of the title compound.

4-(*p*-Tolylsulfonyl)-3-butyn-1-ol (5c). *m*-Chloroperbenzoic acid (104 mg, 0.60 mmol) was dissolved in 2 mL of dichloromethane and then diluted to 15 mL with hexane. Selenide **3c** (191 mg, 0.50 mmol) was added in portions with stirring. After 10 min, a white precipitated had formed (presumed to be the crude selenoxide **4c**) and was filtered, washed with ether, and suspended in chloroform. The chloroform suspension was refluxed for 3 h, concentrated, and separated by preparative TLC (benzene–THF, 3:1) to furnish 65 mg (58%) of **5c** as a homogeneous (TLC) oil: IR (film) 3600–3100 (br), 2210, 1590, 1325, 1160 cm^{-1}; NMR (60 MHz) 7.61 (d, J = 8 Hz, 2 H), 7.17 (d, J = 8 Hz, 2 H), 3.62 (br t, J = 6 Hz, 2 H, sharpens on addition of D_2O), 2.50 (t, J = 6 Hz,

2 H), 2.33 (s, 3 H), 2.13 (br s, exchanged with D_2O, 1 H); high-resolution mass spectrum, calcd for $C_{11}H_{12}O_3S$ m/e 224.050 70, found m/e 224.0521.

1-(*p*-Tolylsulfonyl)-2-(trimethylsilyl)ethyne (5d) and 1-(*p*-Tolylsulfonyl)ethyne (5f). *m*-Chloroperbenzoic acid (52 mg, 0.30 mmol) and selenide **3d** (102 mg, 0.25 mmol) were allowed to react in 1.5 mL of deuteriochloroform, and the reaction was monitored by NMR spectroscopy. After 2 h at room temperature, the only signals observed, apart from aromatic ones, were attributed to **5d** (δ 2.38 and 0.19, vide infra) and to the starting material **3d**. The integrated intensities indicated a conversion of 85%. IR spectroscopy of the mixture showed absorptions at 2120, 1335, and 1169 cm^{-1}, corroborating the presence of the title compound **5d** (vide infra). When 2.00 mmol of MCPBA was employed, the formation of **5d** was quantitative.

The above reaction was repeated with 183 mg (0.45 mmol) of selenide **3d** and 93 mg (0.54 mmol of MCPBA in 10 mL of dichloromethane. After 3 h, the product was isolated by preparative HPLC (hexane, dichloromethane, acetonitrile; solvent gradient from 80:19:1 to 60:39:1): 39% yield; mp 80–82 °C (lit.[16] mp 81–82 °C); IR (KBr) 2120, 1586, 1335, 1169 cm^{-1}; NMR (60 MHz) 7.78 (d, J = 8 Hz, 2 H), 7.24 (d, J = 8 Hz, 2 H), 2.38 (s, 3 H), 0.19 (s, 9 H); mass spectrum, m/e 252 (M^+).

The same reaction was repeated with 236 mg (0.58 mmol) of selenide **3d** and 109 mg (0.63 mmol) of MCPBA in 10 mL of dichloromethane. After 3 h, the reaction mixture was worked up as in the case of product **5a**. Preparative TLC (hexane–ethyl acetate, 4:1) of the crude product afforded 49 mg of diphenyl diselenide and 92 mg (88%) of the desilylated acetylenic sulfone **5f**: mp 72–75 °C (lit.[24a] mp 74–75 °C); IR (KBr) 3240, 2065, 1590, 1328, 1153 cm^{-1}; NMR (60 MHz) 7.79 (d, J = 8 Hz, 2 H), 7.27 (d, J = 8 Hz, 2 H), 3.46 (s, 1 H), 2.38 (s, 3 H); mass spectrum, m/e 180 (M^+).

Oxidation of Selenide 3e. Selenide **3e** (99 mg, 0.25 mmol) was treated with MCPBA (43 mg, 0.25 mmol) in 5 mL of chloroform. After standing for 10 min at room temperature, the solution of the resulting selenoxide **4e** was refluxed for 1 h. The mixture was then diluted with ether, extracted twice with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and evaporated in vacuo. An IR spectrum of the product indicated no acetylenic absorptions in the range 2300–2000 cm^{-1}. The product was separated by preparative TLC (hexane–ethyl acetate, 4:1) to afford 38 mg (39%) of enol ester **7** as an oil: IR (film) 1771, 1734, 1330, 1162 cm^{-1}; NMR (60 MHz) 7.85–7.15 (complex, 8 H), 6.87 (s, 1 H), 3.60 (s, 3 H), 2.39 (s, 3 H); mass spectrum, m/e 396 (M^+, ^{37}Cl), 394 (M^+, ^{35}Cl). A more polar band provided 29 mg (30%) of regenerated selenide **3e**.

Preparation and Decomposition of (*E*)-1-(Phenylseleno)-2-(*p*-tolylsulfonyl)ethene *Se*-Oxide (4f). *m*-Chloroperbenzoic acid (104 mg, 0.60 mmol) was dissolved in 2 mL of dichloromethane and diluted to 15 mL with hexane. Selenide **3f** (169 mg, 0.50 mmol) was added, and a precipitate formed immediately. After 10 min at room temperature, the mixture was filtered, and the solid was washed with ether and dried in vacuo to afford 171 mg (97%) of the title selenoxide: mp 118–120 °C dec; IR (KBr) 1592, 1307, 1156, 826 cm^{-1}; NMR (200 MHz, Me_2SO-d_6) 8.25 (d, J = 14 Hz, 1 H), 7.8–7.5 (complex, 7 H), 7.48 (d, J = 8 Hz, 2 H), 7.33 (d, J = 14 Hz, 1 H), 2.42 (s, 3 H); mass spectrum, m/e 354 (M^+, ^{80}Se, weak), 352 (M^+, ^{78}Se, weak), 338 (M^+ – O, ^{80}Se), 336 (M^+ – O, ^{78}Se). Attempted recrystallization of the product from methanol resulted in partial decomposition. A satisfactory elemental analysis could not be obtained.

Selenoxide **4f** (250 mg, 0.71 mmol) was prepared by the above procedure and was suspended in a mixture of 6.7 mL of benzene and 3.3 mL of chloroform. The mixture was refluxed, and the selenoxide dissolved. After 5 h, the solvent was removed under reduced pressure. An IR spectrum of the crude mixture showed only very weak absorptions at 3240 and 2065 cm^{-1} (attributed to **5f**). Preparative TLC (hexane–ethyl acetate, 3:1) afforded 122 mg (51%) of selenide **5f**. The complex mixture of other products was not further investigated.

Oxidation and Hydrolysis of Selenide 3g. *m*-Chloroperbenzoic acid (62 mg, 0.36 mmol) was added to selenide **3g** (147 mg, 0.30 mmol) in 10 mL of THF. After several minutes, 5 mL of 1 M aqueous KOH solution was added, and the mixture was refluxed for 18 h. The solution was diluted with ether, and the organic layer was washed twice with saturated brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Preparative TLC (hexane–ethyl acetate, 4:1) afforded 21 mg of diphenyl diselenide and 70 mg (95%) of benzyl *p*-tolyl sulfone [mp 142–145 °C (lit.[25] mp 144–145 °C)], identified by its IR and NMR spectra. The aqueous layer and extracts were combined, acidified with 1 M HCl solution, and extracted three times with ether. The ether extracts were dried over anhydrous Na_2SO_4 and concentrated to 5 mL. The presence of a large amount of benzoic acid was indicated by GC analysis.

Preparation of β-Keto Sulfone Ketals 8 and 10 (See Table III). In each of the following procedures, the selenoxide precursors were generated in situ by the addition of a 20% excess of MCPBA to solutions of the selenides **3**. The oxidations were shown to be complete after 5–10 min at room temperature by TLC analysis.

1-Phenyl-1,1-dimethoxy-2-(*p*-tolylsulfonyl)ethane (8a). Selenoxide **4a** (0.50 mmol) in 10 mL of THF was treated with 5 mL of 3 M methanolic KOH (containing a small amount of water to aid dissolution of KOH). The mixture was stirred for 32 h at room temperature. It was then diluted with ether, washed three times with concentrated brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Preparative TLC (hexane–ethyl acetate, 3:1) provided 134 mg (84%) of the ketal **8a**: mp 109–110 °C (from ether–hexane); IR (KBr) 1589, 1302, 1143, 1078, 1041 cm^{-1}; NMR (60 MHz) 7.29 (d, J = 8 Hz, 2 H), 7.18–6.81 (complex, 7 H), 3.72 (s, 2 H), 2.97 (s, 6 H), 2.24 (s, 3 H); mass spectrum, m/e 320 (M^+, extremely weak), 151 (base peak, $M^+ - CH_2Ts$). Anal. Calcd for $C_{17}H_{20}O_4S$: C, 63.73; H, 6.29. Found: C, 63.72; H, 6.31.

In a separate experiment, 1-phenyl-2-(*p*-tolylsulfonyl)ethyne (**5a**; 26 mg, 0.10 mmol) was treated with methanolic KOH for 32 h as described above. The usual workup provided 26 mg (80%) of **8a**, mp 107–109 °C.

1-Phenyl-2-(*p*-tolylsulfonyl)ethanone Ethylene Ketal (10a). A solution of 0.84 g of KOH (15 mmol) in 1 mL of water was added dropwise to selenoxide **4a** (0.48 mmol) in 2 mL of THF and 13 mL of ethylene glycol. After 24 h at room temperature, the mixture was diluted with 30 mL of ether and washed with water (2 × 20 mL). The aqueous extracts were saturated with NaCl and extracted with ether (2 × 20 mL). The combined ether layers were dried with anhydrous $MgSO_4$ and concentrated in vacuo. Preparative TLC (hexane–ethyl acetate, 3:1) afforded 125 mg (82%) of ketal **10a**: mp 105–107 °C (from dichloromethane–hexane); IR ($CHCl_3$) 1599, 1303, 1144, 1087 cm^{-1}; NMR (60 MHz) 7.58 (d, J = 8 Hz, 2 H), 7.25–7.0 (complex, 7 H), 4.05–3.50 (s at δ 3.62 superimposed on m, total 6 H), 2.31 (s, 3 H); mass spectrum, m/e 318 (M^+, extremely weak), 149 (base peak, $M^+ - HC_2Ts$). Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 64.34; H, 5.73.

2,2-Dimethoxy-1-(*p*-tolylsulfonyl)decane (8b) and 2-Methoxy-1-(*p*-tolylsulfonyl)-1-decene (9b). Selenoxide **4b** (0.55 mmol) in 10 mL of THF was treated with methanolic KOH for 32 h and then worked up as in the case of **8a**. Preparative TLC (hexane–ethyl acetate, 5:1) afforded 155 mg of an oil which could not be further separated. Gas chromatographic/mass spectral analysis indicated the presence of a major product with m/e 356 (M^+ of **8b**) and a minor product with m/e 324 (M^+ of **9b**). A 60-MHz NMR spectrum of the mixture showed signals at δ 3.27 (s, CH_2Ts of **8b**), 2.88 (s, OMe of **8b**), 5.36 (s, vinylic H of **9b**), and 3.44 (s, OMe of **9b**) as well as other expected aliphatic and aromatic signals. The integrated intensities of the signals at δ 2.88 and 3.44 indicated that the molar ratio of **8b**/**9b** was 2.7:1. Separate experiments monitored by GC showed that this ratio was not significantly changed after 48 h at room temperature and that the employment of 1 M methanolic sodium methoxide instead of KOH failed to increase the proportion of **8b** in the reaction mixture.

1-(*p*-Tolylsulfonyl)-2-decanone Ethylene Ketal (10b). Selenoxide **4b** (0.35 mmol) was treated with KOH and ethylene glycol for 10 h and then worked up as in the case of **10a**. Preparative TLC (hexane–ethyl acetate, 4:1) afforded 94 mg (76%)

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of **10b** as a homogeneous (TLC, GC) oil. Bulb-to-bulb distillation at 80 °C (0.05 mm) gave an analytical sample: IR (film) 1600, 1306, 1155, 1082 cm^{-1}; NMR (60 MHz) 7.71 (d, J = 8 Hz, 2 H), 7.23 (d, J = 8 Hz, 2 H), 3.74 (br s, 4 H), 3.34 (s, 2 H), 2.36 (s, 3 H), 2.0–1.5 (m, 2 H) 1.5–1.0 (m, 12 H), 0.90 (br t, 3 H); mass spectrum, m/e 241 (base peak, $M^+ - n\text{-}C_8H_{17}$), 185 ($M^+ - CH_2Ts$). Anal. Calcd for $C_{19}H_{30}O_4S$: C, 64.37; H, 8.53. Found: C, 64.12; H, 8.73.

1,1-Dimethoxy-2-(*p*-tolylsulfonyl)ethane (8f). Selenoxide **4f** (0.37 mmol) in 10 mL of THF was treated with methanolic KOH for 1 h and then worked up as in the case of **8a**. Preparative TLC (hexane–ethyl acetate, 4:1) gave 83 mg (91%) of **8f** as a homogeneous (TLC, GC) oil that solidified on standing: mp 50–52 °C (lit.[24b] mp 50–51 °C); IR (film) 1592, 1303, 1149, 1120, 1082, 1068 cm^{-1}; NMR (60 MHz) 7.74 (d, J = 8 Hz, 2 H), 7.19 (d, J = 8 Hz, 2 H), 4.72 (t, J = 6 Hz, 1 H), 3.30 (d, J = 6 Hz, 2 H), 3.10 (s, 6 H), 2.33 (s, 3 H); mass spectrum, m/e 244 (M^+, weak), 75 (base peak, $M^+ - CH_2Ts$).

2-(*p*-Tolylsulfonyl)ethanal Ethylene Ketal (10f). Selenoxide **4f** (0.50 mmol) was treated with KOH and ethylene glycol for 24 h and then worked up as in the case of **10a**. Preparative TLC (benzene–dichloromethane, 5:1) provided 90 mg (74%) of **10f**: mp 86.5–87.5 °C (from dichloromethane–hexane); IR (KBr) 1598, 1302, 1145, 1087 cm^{-1}; NMR (60 MHz) 7.66 (d, J = 8 Hz, 2 H), 7.18 (d, J = 8 Hz, 2 H), 5.15 (t, J = 4 Hz, 1 H), 3.73 (s, 4 H), 3.30 (d, J = 4 Hz, 2 H), 2.34 (s, 3 H); mass spectrum, m/e 242 (M^+, weak), 73 ($M^+ - CH_2Ts$). Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82; S, 13.23. Found: C, 54.68; H, 6.06; S, 13.20.

1,1-Dimethoxy-1,2-diphenyl-2-(*p*-tolylsulfonyl)ethane (8g) and 1-Methoxy-1,2-diphenyl-2-(*p*-tolylsulfonyl)ethene (9g). Selenoxide **4g** (0.30 mmol) in 10 mL of THF was treated with methanolic KOH for 24 h and then worked up as in the case of **8a**. Preparative TLC (hexane–ethyl acetate, 3:1) afforded 92 mg of a solid which could not be further separated. NMR (60 MHz) signals were observed at δ 4.60 (s, methine H of **8g**), 3.29 (s, OMe of **8g**), and 3.07 and 3.02 (s, OMe of the two geometric isomers of **9g**) as well as aromatic and aryl methyl signals. The molar ratio of **8g**/**9g** was determined to be 1:3.7 from the integrated intensities of the peaks at δ 3.29 vs. those at δ 3.07 and 3.02. Further reaction at room temperature did not lead to significant change in the ratios of the products.

When the above reaction was repeated for 10 h at reflux, the usual workup provided a mixture containing a substantial amount of benzyl *p*-tolyl sulfone (ca. 17% yield) as well as **8g** and **9g** (NMR analysis).

1,2-Diphenyl-2-(*p*-tolylsulfonyl)ethanone Ethylene Ketal (10g). Selenoxide **4g** (0.24 mmol) was treated with KOH and ethylene glycol[26] for 6 h and then worked up as in the case of **10a**. Preparative TLC (hexane–ethyl acetate, 3:1) furnished 85 mg (90%) of **10g**: mp 124–125 °C (from dichloromethane–hexane); IR (KBr) 1590, 1301, 1160, 1140, 1080 cm^{-1}; NMR (60 MHz) 7.30 (d, J = 8 Hz, 2 H), 7.1–6.8 (complex, 12 H), 4.54 (s, 1 H), 4.13–3.07 (m, 4 h), 2.21 (s, 3 H); mass spectrum, m/e 239 (M^+ – Ts), 149 (base beak, M^+ – PhCHTs). Further proof of the structure derives from the hydrolysis of the product to the known β-keto sulfone **11g** (vide infra).

Preparation of β-Keto Sulfones 11. α-(*p*-Tolylsulfonyl)acetophenone (11a). A solution of selenide **3a** (103 mg, 0.25 mmol) in 10 mL of dioxane and 2 mL of 6 M aqueous $HClO_4$ was heated at 50 °C (oil-bath temperature). After 4 h, the mixture was cooled, diluted with ether, and washed twice with 5% aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Preparative TLC (hexane–ethyl acetate, 3:1) provided 32 mg (83%) of diphenyl diselenide and 54 mg (79%) of **11a** [mp 105–107 °C (lit.[27] mp 105.5–106.5 °C)], identified by its IR, NMR, and mass spectra.

1-(*p*-Tolylsulfonyl)-2-decanone (11b). Selenide **3b** (231 mg, 0.51 mmol) was hydrolyzed with $HClO_4$ for 7 h at 50 °C as in the preceding procedure. Preparative TLC (hexane–ethyl acetate, 4:1) furnished 96 mg (60%) of **11b**: mp 40–41.5 °C (from hexane); IR (film) 1715, 1595, 1301, 1152 cm^{-1}; NMR (60 MHz) 7.60 (d, J = 8 Hz, 2 H), 7.18 (d, J = 8 Hz, 2 H), 4.00 (s, 2 h), 2.59 (br t, J = 7 Hz, 2 H), 2.34 (s, 3 h), 1.85–1.10 (br s, 12 H), 0.86 (br t, 3 H); mass spectrum, m/e 310 (M^+). Anal. Calcd for $C_{17}H_{26}O_3S$: C, 65.77; H, 8.44. Found: C, 65.76; H, 8.59.

α-Phenyl-α-(*p*-tolylsulfonyl)acetophenone (11g). Ketal **10g** (76 mg, 0.19 mmol) was dissolved in 2 mL of dioxane and 1 mL of water. Perchloric acid (70%) was added (0.3 mL), and the solution was heated for 22 h at an oil-bath temperature of 85 °C. The solution was then poured into 10 mL of water and extracted three times with chloroform. The combined chloroform extracts were washed with water, dried over anhydrous $MgSO_4$, and evaporated in vacuo to provide 66 mg (98%) of the title compound [mp 151–154 °C (lit.[28] mp 153–154 °C)], identified by its IR and NMR spectra.

Registry No. **1**, 68819-94-3; **3a**, 81763-73-7; **3b**, 86409-85-0; **3c**, 86409-86-1; **3d**, 86409-87-2; **3e**, 86409-88-3; **3f**, 86409-89-4; **3g**, 81763-76-0; **3h**, 86409-90-7; **4a**, 82721-83-3; **4b**, 86409-98-5; **4e**, 86409-93-0; **4f**, 86409-95-2; **4g**, 86410-04-0; **5a**, 28995-88-2; **5b**, 86409-91-8; **5c**, 86409-92-9; **5d**, 34452-56-7; **5f**, 13894-21-8; **7**, 86409-94-1; **8a**, 86409-96-3; **8b**, 86409-99-6; **8f**, 86410-02-8; **8g**, 86410-05-1; **9b**, 86410-00-6; (*E*)-**9g**, 86410-06-2; (*Z*)-**9g**, 86410-07-3; **10a**, 86409-97-4; **10b**, 86410-01-7; **10f**, 86410-03-9; **10g**, 86410-08-4; **11a**, 31378-03-7; **11b**, 86410-09-5; **11g**, 28925-53-3; phenylacetylene, 536-74-3; 1-decyne, 764-93-2; 3-butyn-1-ol, 927-74-2; (trimethylsilyl)ethyne, 1066-54-2; methyl 2-propynoate, 922-67-8; acetylene, 74-86-2; diphenylacetylene, 501-65-5; 1-phenylpropyne, 673-32-5; benzyl *p*-tolyl sulfone, 5395-20-0; ethylene glycol, 107-21-1.

(26) Selenoxide **4g** is only slightly soluble in this solvent. Gentle heating is recommended until it is completely dissolved. Otherwise, the reaction fails to go to completion.

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