NMR ($CDCl_3$) to determine the cycloadduct ratios.

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Supplementary Material Available: Crystallographic data for **33** and ^1H NMR and ^{13}C NMR spectra for **10a, 11, 12, 6, 5, 19a, 20, 23, 14, 13, 31a, 32, 28, 27, 26** (37 pages). Ordering information is given on any current masthead page.

Selenosulfonation of Conjugated Enynes and the Enyne Equivalent 1,4-Dichloro-2-butyne. Preparation of Sulfonyl-Substituted Allenic Alcohols and Dienes Using [2,3] Sigmatropic Rearrangements and Organocuprate Additions

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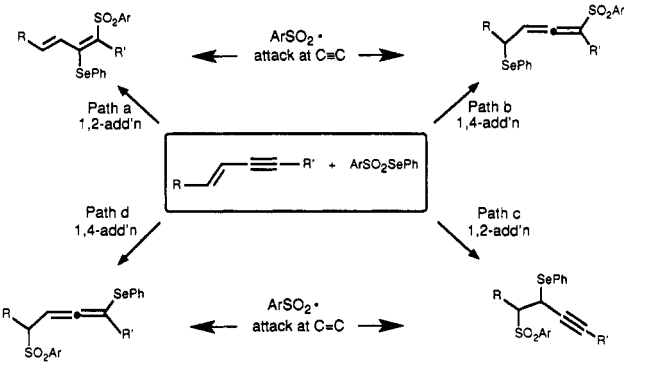
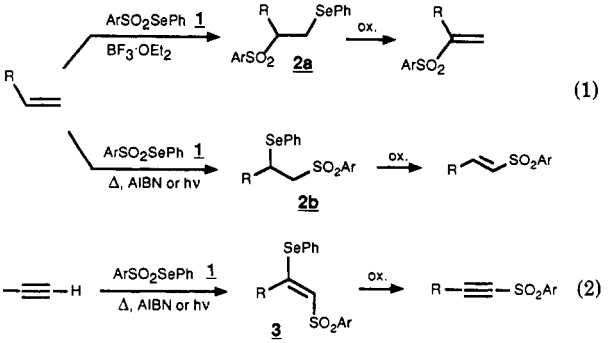
Conjugated enynes undergo free-radical selenosulfonation under either photochemical or thermal conditions with *Se*-phenyl *p*-tolueneselenosulfonate (**1**). Addition to the triple bond occurred preferentially with enynes having an acetylenic terminus (**6–8**) affording 1,2-adducts **10–12**, respectively, as well as the 1,4-adduct **13** from **8**. Enyne **9**, which has a terminal olefin and a disubstituted acetylene moiety, afforded 1,2- and 1,4-addition products to the double bond (**14** and **15**, respectively). [2,3] sigmatropic rearrangement of the selenoxides of the 1,2-adducts **10–12** produced the sulfonyl-substituted allenic alcohols **18–20**, respectively. The rearrangement was stereospecific, providing that excess oxidant was employed and the reaction promptly worked up. Otherwise, equilibration occurred and the products were obtained as mixtures of diastereomers. 1,4-Dichloro-2-butyne was converted to the sulfonyl-substituted allenic alcohol **23** by selenosulfonation, reductive dehalogenation, oxidation, and [2,3] sigmatropic rearrangement of the resulting selenoxide. The addition of organocuprates to **23**, followed by dehydration, afforded a series of 3-alkyl- or propenyl-substituted 2-sulfonyl-1,3-dienes **5a–e**. Alternatively, the treatment of **23** with acetic anhydride–triethylamine or thionyl chloride produced the 3-acetoxy- and 3-chloro-2-sulfonyl-1,3-dienes **5f** and **5g**, respectively. These methods therefore provide convenient access to a variety of synthetically useful sulfonyl-substituted allenic alcohols and dienes.

Unsaturated sulfones have numerous synthetic applications[1] that are stimulating interest in new methods for their preparation. The selenosulfonation reaction, where a selenosulfonate ($ArSO_2SePh$, **1**) undergoes electrophilic or free-radical addition to an unsaturated organic substrate, provides a convenient approach to this objective. In general, the resulting β-(phenylseleno)alkyl or β-(phenylseleno)vinyl sulfones (**2** and **3**, respectively) are subjected to selenoxide elimination, resulting in regeneration of the original unsaturated site, but with the newly appended sulfone group. The selenosulfonation of olefins[2] and acetylenes[3] thus provides convenient access to vinyl (eq 1) and acetylenic sulfones (eq 2), respectively. Variations of the latter process can be exploited for the preparation of allenic[4] and enamine[5] sulfones, while the selenosulfonation of allenes,[6] conjugated dienes,[2a,7] vinyl and acetylenic cyclopropanes,[8] and related compounds affords various other types of useful unsaturated sulfones. The selenosulfonates themselves are stable, crystalline, odorless solids that are easily handled and readily available.[9]

Scheme I





(1) For reviews, see: (a) *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Wiley: Chichester, 1988. (b) De Lucchi, O.; Pasquato, L. *Tetrahedron*, **1988**, *44*, 6755. (c) Trost, B. M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 107. (d) Block, E.; Aslam, M. *Tetrahedron* **1988**, *44*, 281. (e) Fuchs, P. L.; Braish, T. F. *Chem. Rev.* **1986**, *86*, 903. (f) Durst, T. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 3, Chapter 11.9. (g) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.

(2) (a) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249. (b) Gancarz, R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899. (c) Kang, Y.-H.; Kice, J. L. *J. Org. Chem.* **1984**, *49*, 1507.

(3) (a) Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077. (b) Back, T. G.; Collins, S.; Gokhale, U.; Law, K.-W. *J. Org. Chem.* **1983**, *48*, 4776. (c) Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438.

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

(5) Back, T. G.; Collins, S.; Law, K.-W. *Can. J. Chem.* **1985**, *63*, 2313.

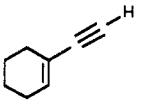
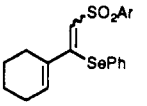
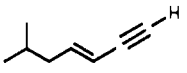
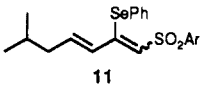
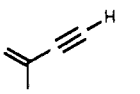
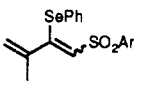
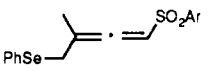
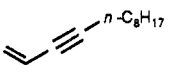
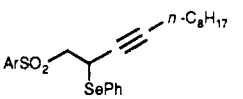
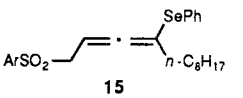
(6) Kice, J. L.; Kang, Y.-H. *Tetrahedron* **1985**, *41*, 4739.

(7) Bäckvall, J.-E.; Nåjera, C.; Yus, M. *Tetrahedron Lett.* **1988**, *29*, 1445.

(8) Back, T. G.; Muralidharan, K. R. *J. Org. Chem.* **1989**, *54*, 121.

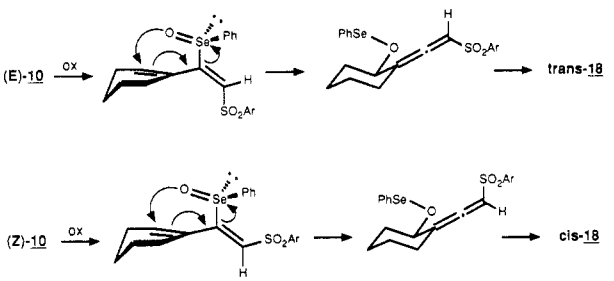
0022-3263/90/1955-4595$02.50/0

Table I. Selenosulfonation of Enynes

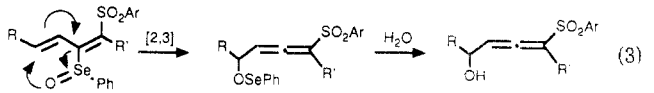
enyne	conditions	product(s)[a]	yield,[b] % (E:Z)[c]
 6	C_6H_6, $h\nu$	 10	83 (3.8:1)
 7	$CHCl_3$, AIBN, Δ	 11	92 (8:1)
 8	$CHCl_3$, AIBN, Δ	 12	22 (1.8:1)
		 13	53
 9	$CHCl_3$, $h\nu$	 14	37
		 15	10
9	C_6H_6, $h\nu$	14	32
		15	8

[a] Ar = *p*-tolyl. [b] Isolated yields are reported. [c] Determined by NMR integration.

Scheme II

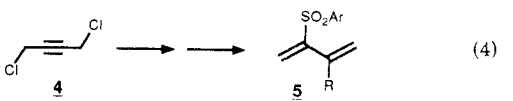


As part of our studies in this area, we investigated the free-radical selenosulfonation of several conjugated enynes. The corresponding additions to simple olefins and acetylenes can be effected by a radical-chain mechanism, in which initiation occurs by thermal or photochemical homolysis of the S–Se bond of the selenosulfonate, followed by addition of the sulfonyl radical ($ArSO_2^{\bullet}$) to the less substituted position of the double or triple bond, and finally chain-transfer between the selenosulfonate and the β-sulfonyl carbon-centered radical.[2,3] Therefore, in principle, a conjugated enyne could undergo attack by the sulfonyl radical upon either the acetylenic (paths a and b in Scheme I) or the olefinic terminus (paths c and d of Scheme I) of the conjugated system, via either 1,2- (paths a and c) or 1,4-addition (paths b and d). In order to determine which of these pathways is favored, we investigated the selenosulfonation of several differently substituted enynes. Furthermore, since the expected products are either allylic, allenic, or propargylic selenides, [2,3] sigmatropic rearrangements of the corresponding selenoxides[10] are expected to afford oxygenated products of further potential utility. We report that such processes can be employed for the preparation of sulfonyl-substituted allenic alcohols via eq 3. In general, allenic alcohols have a number of applications[11] and new methods for their preparation are in demand.[12]



(3)

We also investigated the selenosulfonation and further transformations of 1,4-dichloro-2-butyne (**4**).[13] Since reductive elimination of chlorine from derivatives of the latter can be used to introduce an additional unsaturated site, this readily available compound functions as an enyne equivalent. Furthermore, the internal position of the triple bond results in the incorporation of the sulfonyl group at the 2-position, rather than at the 1- or 4-position, as was the case in the selenosulfonation of enynes. This option therefore increases the diversity of the types of unsaturated sulfones that can be prepared. In particular, we describe a protocol that permits the convenient conversion of **4** to a series of 3-substituted 2-(arylsulfonyl)-1,3-dienes **5** (eq 4). Although several efficient methods for the preparation



(4)

(9) For the first preparation of these compounds, see: (a) Foss, O. *J. Am. Chem. Soc.* **1947**, *69*, 2236. For more convenient methods, see ref 2b and: (b) Back, T. G.; Collins, S.; Krishna, M. V. *Can. J. Chem.* **1987**, *65*, 38.

(10) For a review of [2,3] sigmatropic rearrangements of selenium compounds, see: Reich, H. J. In *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley: New York, 1987; Chapter 8.

(11) See inter alia: (a) Djahanbini, D.; Cazes, B.; Gore, J. *Tetrahedron* **1987**, *43*, 3441. (b) Kim, S. J.; Cha, J. K. *Tetrahedron Lett.* **1988**, *29*, 5613. (c) Crandall, J. K.; Batal, D. J. *Tetrahedron Lett.* **1988**, *29*, 4791. (d) Nikam, S. S.; Chu, K.-H.; Wang, K. K. *J. Org. Chem.* **1986**, *51*, 745.

(12) For other preparations of allenic alcohols, see: Hopf, H. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: Chichester, 1980; Part 2, pp 811–814.

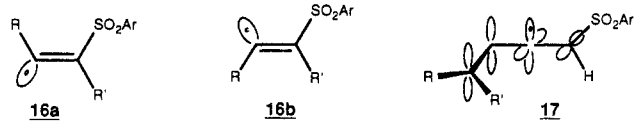
(13) Preliminary communication: Back, T. G.; Lai, E. K. Y.; Muralidharan, K. R. *Tetrahedron Lett.* **1989**, *30*, 6481.

of 2-(arylsulfonyl)-1,3-dienes have been reported,[2a,7,14] most afford products that contain substituents in only the 1- or 4-position. The present method is therefore a useful complement to the existing ones. The 2-(arylsulfonyl)-1,3-dienes are in turn of proven value in synthesis. For example, they display dual electron demand in [4+2] cycloadditions,[15] undergo nucleophilic addition and substitution reactions,[15a] and have other applications.[16]

Selenosulfonation of Enynes

The free-radical selenosulfonations of four differently substituted enynes **6–9** were investigated, and the results are summarized in Table I. The reactions were performed photochemically, or thermally in the presence of a small amount of the radical initiator azobis(isobutyronitrile) (AIBN). In the case of enynes containing a terminal acetylene moiety (i.e., **6–8**), addition of the sulfonyl radical to the unsubstituted acetylenic carbon atom occurred with high regioselectivity. Only the products of 1,2-addition (path a in Scheme I) were observed in the case of the alkynylcyclohexene **6** and the acyclic 4-substituted enyne **7**, which afforded high yields of **10** and **11**, respectively. The acyclic 3-substituted[17] enyne **8**, however, produced substantial quantities of both 1,2- and 1,4-adducts **12** and **13**, formed via paths a and b, respectively, in Scheme I. Enyne **9**, which contains a terminal olefin and a disubstituted acetylene moiety, afforded a complex reaction mixture, from which **14** and **15** were the only identifiable adducts. These are the products of 1,2- and 1,4-addition to the olefinic π-bond, via paths c and d, respectively, in Scheme I.

It is also interesting to note that adducts **10–12** were obtained as mixtures of *E* and *Z* isomers.[18] In contrast, simple acetylenes undergo highly stereospecific selenosulfonations, favoring the *E* isomers. The stereospecificity in the latter case has been attributed to the intermediacy of vinyl radicals **16a**, where the unpaired electron occupies



an sp^2-hybridized orbital and where chain transfer occurs more rapidly than inversion to **16b**.[3,8] In the case of enynes, it is possible that the unpaired electron in the corresponding intermediate **17** resides in a p orbital on an sp-hybridized carbon atom in order to permit conjugation with the olefinic π-bond.[19,20] Chain transfer to **17** can then occur from either the top or bottom of the conjugated π-system, resulting in syn or anti addition and producing the *Z* and *E* isomers, respectively. The latter are presumably favored because the approach to the top face of the conjugated π-system is hindered by the sulfone group. Although the pure *E* isomers of **10–12** were obtained by repeated recrystallization of the mixtures, homogeneous samples of their *Z* counterparts could not be isolated.

[2,3] Sigmatropic Rearrangements of Selenosulfonation Adducts

Equation 3 indicates that the 1,2-adducts **10–12** should produce allenic alcohols by [2,3] sigmatropic rearrangement of their corresponding selenoxides and hydrolysis of the initially formed selenenic esters.[21] The allene moiety of the resulting products **18–20** is in each case chiral. Furthermore, an additional chiral center is created during the formation of the secondary alcohols **18** and **19**, thereby leading to the possible formation of diastereomers. However, the stereospecific and concerted nature of such processes[22] leads to the expectation that each of the *E* and *Z* isomers of **10** and **11** should produce one diastereomer of the corresponding allenic alcohols exclusively. This is illustrated in Scheme II, where (*E*)-**10** and (*Z*)-**10** afford *trans*-**18** and *cis*-**18**, respectively.[23]

When pure (*E*)-**10** was oxidized with excess (3 equiv) *m*-chloroperbenzoic acid (MCPBA) for 5 min in chloroform, followed promptly by workup with aqueous potassium carbonate, the product **18** was nearly homogeneous (>90%) and was assumed to be the trans isomer, formed as shown in Scheme II. However, when the oxidation was repeated with smaller amounts of the peracid and longer reaction times, the formation of substantial amounts of both diastereomers of **18** occurred (ca. 1.8:1). Moreover, the similar treatment of the original 3.8:1 mixture of *E* and *Z* isomers of **10** afforded both diastereomers of **18** in the alterred ratio of 1.7:1. The presence of the two isomers was evident from the ^1H NMR spectrum of the product in C_6D_6, in which their separate signals could be distinguished (major isomer, δ 6.15 and 3.89; minor isomer, δ 6.11 and 3.75) and integrated. This was confirmed by the ^{13}C NMR spectrum, which showed duplicate signals for the carbon atoms. These results indicate that equilibration is possible during some stage of this reaction and suggest that the prompt removal of the initial selenenic ester product by further oxidation with MCPBA, or by hydrolysis, is necessary to maintain stereospecificity.[24]

(14) (a) Andell, O. S.; Bäckvall, J.-E. *Tetrahedron Lett.* **1985**, *26*, 4555. (b) Cuvigny, T.; Hervé du Penhoat, C.; Julia, M. *Tetrahedron* **1986**, *42*, 5329.

(15) (a) Bäckvall, J.-E.; Juntunen, S. K. *J. Am. Chem. Soc.* **1987**, *109*, 6396. (b) Bäckvall, J.-E.; Plobeck, N. A.; Juntunen, S. K. *Tetrahedron Lett.* **1989**, *30*, 2589. (c) Bäckvall, J.-E.; Rise, F. *Tetrahedron Lett.* **1989**, *30*, 5347. For other cycloaddition reactions of sulfonyl dienes, see ref 14b and: (d) Chou, T.; Hung, S.-C. *J. Org. Chem.* **1988**, *53*, 3020. (e) Padwa, A.; Harrison, B.; Murphree, S. S.; Yeske, P. E. *J. Org. Chem.* **1989**, *54*, 4232. (f) Padwa, A.; Harrison, B.; Norman, B. H. *Tetrahedron Lett.* **1989**, *30*, 3259. (g) Padwa, A.; Norman, B. H. *Tetrahedron Lett.* **1988**, *29*, 2417.

(16) (a) Bäckvall, J.-E.; Juntunen, S. K. *J. Org. Chem.* **1988**, *53*, 2398. (b) Hardinger, S. A.; Fuchs, P. L. *J. Org. Chem.* **1987**, *52*, 2739.

(17) (a) Strictly speaking, the methyl substituent of enyne **8** is at the 2-position as the olefin is assigned the lower number when both the double and triple bonds occur at the termini of the chain; see ref 17b. However, for the sake of consistency in discussions of compounds **6–8**, we will consider the acetylenic carbon atoms to have the numbers 1 and 2. (b) Pine, S. *Organic Chemistry*, 5th ed.; McGraw Hill: New York, 1987; pp 64–65.

(18) The assignment of the *E* and *Z* configurations was confirmed by their ^1H NMR α-sulfonyl olefinic hydrogen signals, which occur farther downfield in the *Z* isomers. This was also observed previously in the case of a selenosulfonate adduct where the *Z* isomer was obtained by the base-catalyzed isomerization of the original *E* isomer. See ref 4.

(19) Nonhebel, D. C.; Walton, J. C. *Free-radical Chemistry*; Cambridge University Press: Cambridge, 1974; pp 90–92.

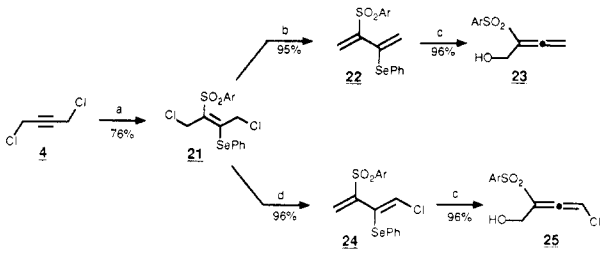
(20) It is surprising that the selenosulfonation of phenylacetylene (see ref 3a), where similar conjugation might be expected to stabilize the radical intermediate, is highly stereospecific (>97%) in favor of the *E* adduct.

(21) For the preparation of other allenic alcohols via [2,3] sigmatropic rearrangements of selenoxides, see: Lerouge, P.; Paulmier, C. *Tetrahedron Lett.* **1984**, *25*, 1987.

(22) For a review of the stereochemistry of [2,3] sigmatropic rearrangements, see: (a) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563. For a study of the kinetics and stereochemistry of the [2,3] sigmatropic rearrangements of selenoxides, see: (b) Reich, H. J.; Yelm, K. E.; Wollowitz, S. *J. Am. Chem. Soc.* **1983**, *105*, 2503.

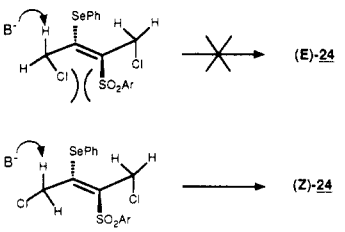
(23) An added complexity stems from the creation of a chiral center at the selenium atom when the achiral selenide is oxidized to the corresponding selenoxide. Although the present oxidation step produces a racemic selenoxide, we have arbitrarily shown only one enantiomer in Scheme II for simplicity. An asymmetric oxidation, followed by chirality transfer during the rearrangement, should result in the enantioselective formation of the allenic products. This possibility is under further investigation. For related work on chirality transfer during the [2,3] sigmatropic rearrangement of an allylic selenoxide, see: Davis, F. A.; Stringer, O. D.; McCauley, J. P., Jr. *Tetrahedron* **1985**, *41*, 4747.

Scheme III[a]

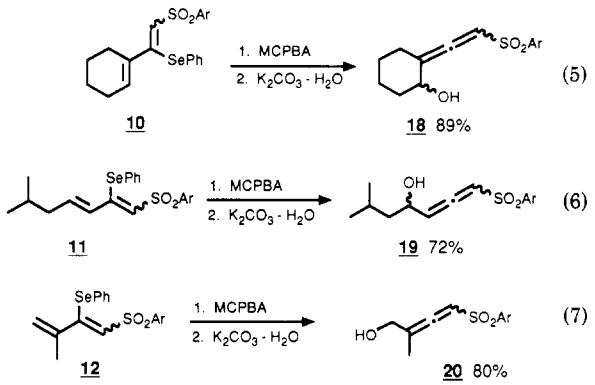


[a] Key: (a) $ArSO_2SePh$ (Ar = *p*-tolyl), C_6H_6, AIBN, Δ; (b) NaI, acetone, Δ; (c) MCPBA, $CHCl_3$, room temperature for 5 min and then $K_2CO_3 \cdot H_2O$; (d) Et_3N, $CHCl_3$, Δ.

Scheme IV



Similar behavior was observed in the oxidation and rearrangement of selenide **11** to **19**,[25] whereas selenide **12** afforded the homogeneous primary alcohol **20**. These results are shown in eqs 5–7.

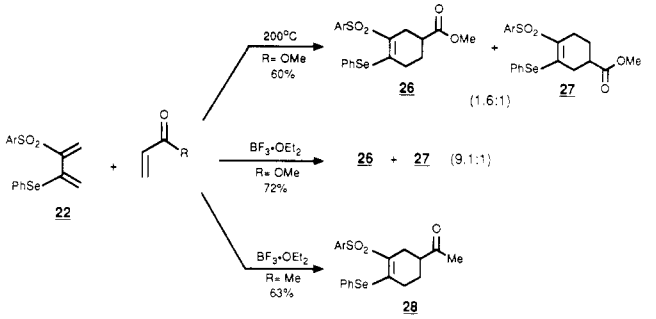


Preparation of Sulfonyl Dienes from 1,4-Dichloro-2-butyne

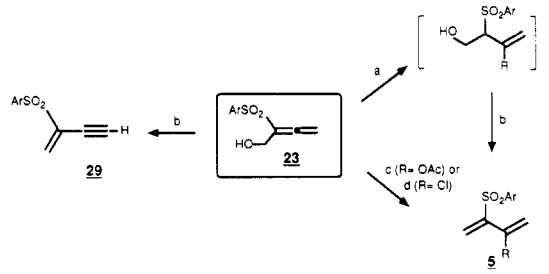
The free-radical selenosulfonation of 1,4-dichloro-2-butyne (**4**) afforded adduct **21** in the usual manner. Reductive elimination of chlorine from the latter gave **22**, which upon oxidation with MCPBA and [2,3] sigmatropic rearrangement of the resulting selenoxide, produced the sulfonyl-substituted allenic alcohol **23**, as shown in Scheme III. Alternatively, dehydrohalogenation of **21** afforded diene **24**, obtained as a single geometric isomer.[26] Presumably, this is the *Z* isomer, as the transition state leading to it is less hindered than the one required for the formation of the *E* isomer (Scheme IV). Similar observations have been made concerning the stereochemistry of the isomerization of certain β-(phenylseleno)vinyl sulfones to the corresponding allyl sulfones[4] and in the vinylogous Ramberg–Backlund rearrangement.[27] Oxidation and [2,3] sigmatropic rearrangement of **24** produced the corresponding sulfonyl-substituted allenic alcohol **25** (Scheme III).

The Diels–Alder reactions of dienes containing heteroatom substituents[26,28] are of considerable current interest. We therefore performed several experiments to determine whether the novel seleno- and sulfonyl-substituted diene **22** would undergo such cycloadditions. The reaction of **22** with methyl acrylate at 200 °C afforded a 1.6:1 mixture of the two regioisomers **26** and **27** in 60% yield (Scheme V). The yield and regioselectivity were improved by performing the reaction at room temperature in the presence of boron trifluoride etherate, thus affording **26** and **27** in the ratio 9.1:1 in 72% yield. Similarly, diene **22** and methyl vinyl ketone reacted in the presence of the

Scheme V



Scheme VI[a]



[a] Key: (a) $R_2CuLi \cdot SMe_2$ (R = alkyl, propenyl); (b) MsCl–Et_3N; (c) AcOAc–Et_3N; (d) $SOCl_2$.

Table II. Preparation of 2-Sulfonyl-1,3-dienes from Allenic Alcohol 23

product	R	reagent[a]	yield,[b] %
5a	Me	A	73
5b	*n*-Bu	A	72
5c	*s*-Bu	A	55
5d	*t*-Bu	A[c]	52
5e	CH=CHMe	A[d]	63
5f	OAc	B	57
5g	Cl	C	54

[a] Reagent A, $R_2CuLi \cdot SMe_2$ and then MsCl–Et_3N; reagent B, AcOAc–Et_3N; reagent C, $SOCl_2$. [b] Isolated yields are reported. [c] DBN was employed instead of Et_3N. [d] The product was a 10:1 mixture of *E* and *Z* isomers that could not be separated.

(24) The precise mechanism for the equilibration is not known, but we also observed that the isomerization of pure *trans*-**18** was promoted by the presence of benzeneseleninic acid ($PhSeO_2H$) and diphenyl diselenide (PhSeSePh), which are known to produce benzeneselenenic acid (PhSeOH) by comproportionation (see ref 24a,b). The latter compound, or its anhydride (see ref 24c,d), could presumably regenerate the selenenic ester from the allenic alcohol. (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. *J. Org. Chem.* **1978**, *43*, 1689. (c) Reich, H. J.; Willis, W. W., Jr.; Wollowitz, S. *Tetrahedron Lett.* **1982**, *23*, 3319. (d) Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *Tetrahedron Lett.* **1982**, *23*, 3323.

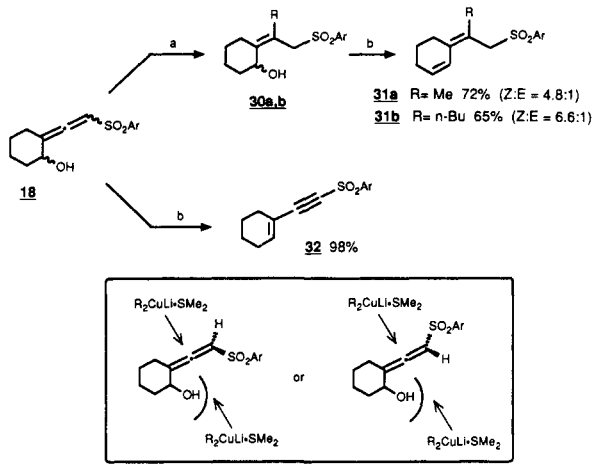
(25) The ^1H NMR signals of the two isomers were not sufficiently resolved to permit integration. However, the presence of two isomers was again confirmed by ^{13}C NMR spectroscopy.

(26) For the preparation of some other sulfur- and selenium-containing dienes by electrophilic addition to **4**, followed by elimination, see: Bridges, A. J.; Fischer, J. W. *J. Org. Chem.* **1984**, *49*, 2954.

(27) Block, E.; Aslam, M. *J. Am. Chem. Soc.* **1983**, *105*, 6164.

(28) For a review, see: Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753.

Scheme VII[a]



[a] Key: (a) $R_2CuLi{\cdot}SMe_2$; (b) MsCl–Et_3N.

Lewis acid, producing cycloadduct **28** as an essentially homogeneous regioisomer in 63% yield. Comparable results were recently reported with the phenylthio analogue[29] of diene **22**. The indicated regiochemistry of the cycloaddition is consistent with that previously reported for the phenylthio derivative and was confirmed by ^1H NMR decoupling experiments in the 400-MHz spectrum of **28** in C_6D_6. The electron-withdrawing sulfonyl substituent of diene **22** should also enable it to participate in Diels–Alder reactions with inverse electron demand.[15] However, attempts to react diene **22** with ethyl vinyl ether have so far failed to produce synthetically useful results.

The sulfonyl-substituted allenic alcohol **23** reacted with organocuprates to furnish the corresponding crude addition products, which underwent elimination when treated with methanesulfonyl chloride and triethylamine to afford the desired 3-alkyl-substituted 2-(*p*-toluenesulfonyl)-1,3-dienes **5a–e**. Alternatively, the acetoxy and chloro derivatives **5f** and **5g** were obtained by the reaction of **23** with acetic anhydride and triethylamine or with thionyl chloride, respectively. The results are illustrated in Scheme VI and summarized in Table II and demonstrate that the readily available allenic alcohol **23** provides convenient access to various 3-substituted 2-(*p*-toluenesulfonyl)-1,3-dienes **5**. Elimination of the allenic alcohol itself, without prior cuprate addition, produced the relatively unstable enyne sulfone **29** (Scheme VI).

Organocuprate additions were also performed with the allenic alcohol **18** (cis–trans mixture). The principal products were the allyl sulfones **30a** and **30b** (Scheme VII), which could be isolated or subjected to elimination with methanesulfonyl chloride and triethylamine to afford **31a** and **31b**, respectively.[30] The *Z* isomers of the products, which were distinguished from their *E* counterparts by NOE experiments, were formed preferentially, as this permitted approach of the organocuprate from the less hindered side of the allenic π-system, as shown in Scheme VII. The direct elimination of **18**, as in the case of **23**, afforded the enyne sulfone **32** nearly quantitatively.

Conclusions

The selenosulfonation of conjugated enynes containing terminal acetylene groups results in the incorporation of the sulfone moiety exclusively at the acetylenic terminus and proceeds via either 1,2- or 1,4-addition, depending on the location of substituents. The 1,2-additions are much less stereospecific than those to isolated acetylenes, producing *E–Z* mixtures. Enynes with terminal olefin groups afford complex mixtures, including the products of 1,2- and 1,4-addition to the double bond. The 1,2-adducts to acetylenes undergo oxidation and facile [2,3] sigmatropic rearrangement of the corresponding selenoxides to produce sulfonyl-substituted allenic alcohols. These processes are stereospecific, but equilibration of diastereomeric products under the conditions of the reaction is possible unless a prompt workup is performed. 1,4-Dichloro-2-butyne acts as an enyne equivalent that can be readily converted to synthetically useful 3-substituted 2-sulfonyl-1,3-dienes by selenosulfonation, reductive dehalogenation, oxidation and [2,3] sigmatropic rearrangement, and treatment with organocuprates. 3-Phenylseleno, 3-chloro, and 3-acetoxy derivatives are also available by variations of these procedures.

Experimental Section

Melting points were obtained on an A. H. Thomas hot-stage apparatus and are uncorrected. IR spectra were recorded on a Nicolet 5DX FT instrument. Routine ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker ACE or Varian XL200 spectrometer at 200 MHz. NOE difference spectroscopy[31] was performed on a Bruker AM400 spectrometer at 400 MHz. Deuteriochloroform was employed as the solvent and internal TMS as the standard unless otherwise noted. Mass spectra were recorded on a Kratos MS80 or a VG 7070 instrument. Elemental analyses were obtained by Dr. W. S. Lin (University of Calgary) or from Guelph Chemical Laboratories. Preparative TLC was carried out on Analtech 20 × 20 cm glass plates coated with 1 mm of silica gel GF. Flash chromatography was performed essentially by the method of Still.[32] Photolyses were conducted in a Rayonet RMR-500 reactor equipped with four 254-nm UV lamps.

Se-Phenyl *p*-tolueneselenosulfonate[9b] and 1-dodecen-3-yne[33] were prepared as reported previously. Enyne **7** was obtained by a variation of a literature method[34] via the dehydration of 6-methyl-1-heptyn-4-ol. All other starting materials and reagents were purchased from commercial sources and purified by standard methods as required.

Selenosulfonation of Enynes. 1-Ethynylcyclohexene. The enyne (60 μL, 0.50 mmol) and *Se*-phenyl *p*-tolueneselenosulfonate (156 mg, 0.500 mmol) were dissolved in 3 mL of benzene, and the resultant mixture was irradiated with UV light for 18 h. The crude product was separated by preparative TLC in 20% ethyl acetate–hexane to afford 176 mg (83%) of a mixture of the corresponding (*E*)- and (*Z*)-1-(1-cyclohexenyl)-1-(phenylseleno)-2-(*p*-toluenesulfonyl)ethene (**10**) as a pale yellow oil with R_f 0.45. The *E:Z* ratio was determined to be 3.8:1 by NMR integration of the respective vinylic signals. Repeated recrystallization from chloroform–hexane afforded the pure *E* isomer: mp 89–90 °C; IR (film) 1650, 1596, 1567, 1317, 1302, 1146, 1085 cm^{-1}; ^1H NMR δ 7.65 (d, J = 8.3 Hz, 2 H), 7.54–7.21 (complex, 7 H), 6.06 (s, 1 H), 5.47 (m, 1 H), 2.40 (s, 3 H), 2.04 (m, 2 H), 1.92 (m, 2 H), 1.44 (m, 4 H); mass spectrum, *m/e* (relative intensity, %) 418 (4, M^+), 261 (5, M^+ – PhSe$^\cdot$), 155 (22, $ArSO_2^+$), 105 (51), 91 (80), 83 (82), 43 (98), 41 (100). Additional NMR signals assigned to the *Z* isomer were observed at δ 6.61 (s), 5.56 (m) and 2.44 (s). Anal. Calcd for $C_{21}H_{22}O_2SSe$: C, 60.42; H, 5.31. Found: C, 59.99; H, 5.41.

6-Methyl-3-hepten-1-yne. The enyne (54 mg, 0.50 mmol), *Se*-phenyl *p*-tolueneselenosulfonate (156 mg, 0.500 mmol), and

(29) Chou, S.-S. P.; Sun, D.-J. *J. Chem. Soc., Chem. Commun.* **1988**, 1176.

(30) A similar addition was recently used in the synthesis of a steroid side chain: Back, T. G.; Brunner, K.; Krishna, M. V.; Lai, E. K. Y. *Can. J. Chem.* **1989**, *67*, 1032.

(31) Derome, A. E. In *Modern NMR Techniques for Chemistry Research*; Pergamon Press: Oxford, 1987; Chapter 5.

(32) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(33) Koshino, J.; Sugawara, T.; Suzuki, A. *Synth. Commun.* **1984**, *14*, 245.

(34) Casaderall, E.; Jallageas, J.-C.; Mior, L.; Mior, M.; Moreau, P. *C. R. Acad. Sci., Ser. C* **1967**, *265*, 839.

AIBN (10 mg, 0.06 mmol) were refluxed in 5 mL of chloroform for 24 h. The crude product was separated by preparative TLC in 20% ethyl acetate–hexane to afford 192 mg (92%) of a mixture of the corresponding (*E*)- and (*Z*)-6-methyl-2-(phenylseleno)-1-(*p*-toluenesulfonyl)-1,3-heptadiene (**11**) as a pale yellow oil with R_f 0.53. The *E*:*Z* ratio was determined to be 8:1 by NMR integration of the respective vinylic signals. Recrystallization from chloroform–hexane afforded the pure *E* isomer: mp 83–84 °C; IR (film) 1629, 1596, 1328, 1299, 1284, 1144, 1086 cm^{-1}; ^1H NMR δ 7.66 (d, J = 8.2 Hz, 2 H), 7.55–7.23 (complex, 8 H), 6.42 (dt, J = 15.4, 7.4 Hz, 1 H), 5.82 (s, 1 H), 2.42 (s, 3 H), 2.12 (ddd, J = 7.4, 7.1, 1.3 Hz, 2 H), 1.68 (m, 1 H), 0.88 (d, J = 6.6 Hz, 6 H); mass spectrum, m/e (relative intensity, %) 420 (37, M^+), 262 (100, M^+ – PhSeH), 157 (78, $PhSe^+$), 155 (74, $ArSO_2^+$), 91 (95, $C_7H_7^+$). Additional NMR signals assigned to the *Z* isomer were observed at δ 6.25 (m), 5.88 (d, J = 2.3 Hz), 1.89 (m), and 0.87 (d, J = 6.6 Hz). Anal. Calcd for $C_{21}H_{24}O_2SSe$: C, 60.13; H, 5.77. Found: C, 60.42; H, 5.79.

2-Methyl-1-buten-3-yne. The enyne (94 μL, 1.00 mmol), *Se*-phenyl *p*-toluenesulfonate (156 mg, 0.500 mmol), and AIBN (10 mg, 0.06 mmol) were refluxed in 5 mL of chloroform for 14 h. The crude product was separated by preparative TLC in 10% ethyl acetate–hexane to afford 100 mg (53%) of 3-methyl-4-(phenylseleno)-1-(*p*-toluenesulfonyl)-1,2-butadiene (**13**) as a pale yellow oil: R_f 0.31; IR (film) 1955, 1596, 1579, 1321, 1303, 1147, 1085 cm^{-1}; ^1H NMR δ 7.76 (d, J = 8.3 Hz, 2 H), 7.38–7.24 (complex, 7 H), 5.71 (m, 1 H), 3.64 (m, 2 H), 2.42 (s, 3 H), 1.84 (d, J = 2.8 Hz, 3 H); mass spectrum, m/e (relative intensity, %) 378 (4, M^+), 157 (80, $PhSe^+$), 155 (88, $ArSO_2^+$), 91 (92, $C_7H_7^+$), 69 (90), 41 (100); exact mass for $C_{18}H_{18}O_2SSe$, calcd 377.9493, found 377.9487. A less polar band afforded 40 mg (22%) of 3-methyl-2-(phenylseleno)-1-(*p*-toluenesulfonyl)-1,3-butadiene (**12**) as a mixture of *E* and *Z* isomers with R_f 0.47. The *E*:*Z* ratio was determined to be 1.8:1 by NMR integration of the respective vinylic signals. Repeated recrystallization from chloroform–hexane afforded the pure *E* isomer: mp 92–93 °C; IR (film) 1635, 1597, 1574, 1322, 1303, 1289, 1146, 1085 cm^{-1}; ^1H NMR δ 7.66 (d, J = 8.3 Hz, 2 H), 7.57–7.25 (complex, 7 H), 5.86 (s, 1 H), 5.07 (crude s, 1 H), 4.84 (crude s, 1 H), 2.42 (s, 3 H), 2.01 (dd, J = 1.3, 0.9 Hz, 3 H); mass spectrum, m/e (relative intensity, %) 378 (10, M^+), 223 (17, $M^+ - ArSO_2^{\bullet}$), 157 (44, $PhSe^+$), 155 (48, $ArSO_2^+$), 142 (67), 91 (100, $C_7H_7^+$). Additional NMR signals assigned to the *Z* isomer were observed at δ 7.97 (d, J = 8.3 Hz), 6.71 (s), 4.91 (crude s), 4.78 (crude s), 2.45 (s), and 1.56 (s). Anal. Calcd for $C_{18}H_{18}O_2SSe$: C, 57.29; H, 4.81. Found: C, 57.41; H, 4.84.

1-Dodecen-3-yne. The enyne (82 mg, 0.50 mmol) and *Se*-phenyl *p*-toluenesulfonate (156 mg, 0.500 mmol) were dissolved in chloroform, and the resultant mixture was irradiated with UV light for 24 h. The crude product was separated by preparative TLC in 20% ethyl acetate–hexane to afford 88 mg (37%) of 2-(phenylseleno)-1-(*p*-toluenesulfonyl)-3-dodecyne (**14**) as a pale yellow oil: R_f 0.62; IR (film) 2231, 1597, 1578, 1323, 1303, 1138, 1087 cm^{-1}; ^1H NMR δ 7.75 (d, J = 8.3 Hz, 2 H), 7.56–7.24 (complex, 7 H), 4.19–4.12 (m, 1 H), 3.60–3.36 (m, 2 H), 2.43 (s, 3 H), 1.87 (m, 2 H), 1.23 (complex, 12 H), 0.89 (t, J = 6.6 Hz, 3 H); mass spectrum, m/e (relative intensity, %) 476 (8, M^+), 418 (21), 157 (92, $PhSe^+$), 155 (82, $ArSO_2^+$), 139 (82), 91 (99, $C_7H_7^+$), 79 (97), 55 (100); exact mass for $C_{25}H_{32}O_2SSe$, calcd 476.1288, found 476.1291. A more polar band afforded 24 mg (10%) of 4-(phenylseleno)-1-(*p*-toluenesulfonyl)-2,3-dodecadiene (**15**) as a pale yellow oil: R_f 0.35; IR (film) 1961, 1597, 1321, 1303, 1151, 1086 cm^{-1}; ^1H NMR δ 7.79 (d, J = 8.3 Hz, 2 H), 7.68 (d, J = 8.3 Hz, 2 H), 7.39–7.27 (complex, 5 H), 5.70 (m, 1 H), 3.76 (m, 2 H), 2.45 (s, 3 H), 2.10 (m, 2 H), 1.21 (complex, 12 H), 0.88 (t, J = 6.5 Hz, 3 H); mass spectrum, m/e (relative intensity, %) 476 (0.3, M^+), 223 (32), 157 (59, $PhSe^+$), 155 (71, $ArSO_2^+$), 139 (75), 91 (83, $C_7H_7^+$), 43 (100); exact mass for $C_{25}H_{32}O_2SSe$, calcd 476.1288, found 476.1246.

Allenic Alcohol 18. The selenosulfonate adduct **10** (417 mg, 1.00 mmol; 3.8:1 mixture of *E* and *Z* isomers) and MCPBA (345 mg of ca. 85% purity, ca. 1.7 mmol) were stirred in 20 mL of chloroform for 15 min. The reaction mixture was then washed three times with aqueous K_2CO_3 and once with aqueous NaCl and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography (elution with 30% ethyl acetate–hexane) afforded 248 mg (89%) of the allenic alcohol **18** as a 1.7:1 mixture of isomers, as determined by NMR integration: IR (film) 3350 (br), 1960, 1594, 1313, 1302, 1146, 1083 cm^{-1}; ^1H NMR δ 7.78 (m, 2 H), 7.33 (m, 2 H), 6.28 (m, 1 H), 4.23–4.12 (m, 1 H), 2.44 (s, 3 H), 2.48–1.32 (complex, 9 H); ^1H NMR (C_6D_6) (major isomer) δ 7.89 (d, J = 8.3 Hz), 6.15 (m), 3.89 (m), 1.86 (s), (minor isomer) δ 7.90 (d, J = 8.3 Hz), 6.11 (m), 3.75 (m), 1.85 (s); ^{13}C NMR (major isomer) δ 199.4, 118.5, 102.8, 69.05, (minor isomer) δ 199.1, 118.5, 103.0, 69.1; mass spectrum, m/e (relative intensity, %) 278 (8, M^+), 260 (7, $M^+ - H_2O$), 139 (68), 123 (92), 105 (80), 91 (100, $C_7H_7^+$); exact mass for $C_{15}H_{18}O_3S$, calcd 278.0976, found 278.0975. The above procedure was repeated with the pure *E* isomer of **10** to afford an 1.8:1 mixture of stereoisomers of **18**. When the oxidation was performed with 3 mol equiv of MCPBA for only 5 min and the workup carried out as rapidly as possible, the ratio of diastereomers was 9.4:1.

Allenic Alcohol 19. The pure *E* isomer of **11** was oxidized with ca. 1.7 mol equiv of MCPBA for 15 min as in the above procedure. Flash chromatography (elution with 25% ethyl acetate–hexane) afforded 72% of the allenic alcohol **19** as a mixture of diastereomers:[25] IR (film) 3480, 1956, 1598, 1319, 1303, 1147, 1085 cm^{-1}; ^1H NMR δ 7.79 (m, 2 H), 7.34 (m, 2 H), 6.32 (m, 1 H), 5.91 (m, 1 H), 4.35 (m, 1 H), 2.44 (s, 3 H), 1.76 (m, 1 H), 1.61–1.45 (m, 1 H), 1.38–1.25 (m, 1 H), 0.94–0.89 (m, 6 H); ^{13}C NMR (major isomer) δ 204.2, 105.5, 103.3, 67.4 (minor isomer) δ 204.3, 105.4, 103.0, 67.6; mass spectrum, m/e (relative intensity, %) 280 (1, M^+), 156 (97, $ArSO_2H^{\bullet+}$), 155 (63, $ArSO_2^+$), 139 (98), 91 (100, $C_7H_7^+$); exact mass for $C_{15}H_{20}O_3S$, calcd 280.1133, found 280.1123. When the oxidation was performed with 3 mol equiv of MCPBA for only 5 min and the workup carried out as rapidly as possible, the major diastereomer was produced in a high state of purity.

Allenic Alcohol 20. The pure E isomer of **12** was oxidized with MCPBA as in the preceding procedure. Flash chromatography (elution with 25% ethyl acetate–hexane) afforded 80% of the allenic alcohol **20**: IR (film) 3477, 1962, 1597, 1315, 1303, 1143, 1085 cm^{-1}; ^1H NMR δ 7.78 (d, J = 8.4 Hz, 2 H), 7.33 (d, J = 8.4 Hz, 2 H), 6.24 (m, 1 H), 4.15 (m, 2 H), 2.45 (s, 3 H), 2.12 (crude t, J = 6.7 Hz, 1 H), 1.82 (d, J = 2.7 Hz, 3 H); mass spectrum, m/e (relative intensity, %) 238 (0.2, M^+), 208 (15, $M^+ - CH_2O$), 156 (25, $ArSO_2H^{\bullet+}$), 139 (39), 92 (100), 91 (94); exact mass for $C_{12}H_{14}O_3S$, calcd 238.0664, found 238.0660.

1,4-Dichloro-2-(phenylseleno)-3-(*p*-toluenesulfonyl)-2-butene (21). 1,4-Dichloro-2-butyne (1.85 g, 15.0 mmol), *Se*-phenyl *p*-toluenesulfonate (4.67 g, 15.0 mmol), and AIBN (0.12 g, 0.75 mmol) were refluxed in 20 mL of benzene for 30 h. The reaction mixture was then concentrated under reduced pressure, and the residue was recrystallized from chloroform–hexane to afford 4.91 g (76%) of **21**: mp 138 °C; IR (Nujol) 1565, 1313, 1304, 1146, 710, 687 cm^{-1}; ^1H NMR δ 7.92 (d, J = 8.3 Hz, 2 H), 7.71–7.35 (complex, 7 H), 4.77 (s, 2 H), 4.65 (s, 2 H), 2.45 (s, 3 H); mass spectrum, m/e (relative intensity) 364 (7, $M^+ - Cl_2$), 157 (27, $PhSe^+$), 128 (100), 91 (81). Anal. Calcd for $C_{17}H_{16}O_2SSeCl_2$: C, 47.02; H, 3.72; S, 7.38. Found: C, 47.29; H, 3.58; S, 7.19.

2-(Phenylseleno)-3-(*p*-toluenesulfonyl)-1,3-butadiene (22). The dichloro compound **21** (434 mg, 1.00 mmol) and NaI (2.98 g, 20.0 mmol) were refluxed in 15 mL of acetone for 24 h. The solution was evaporated in vacuo, and the residue was triturated with ether and washed three times with aqueous sodium thiosulfate and once with aqueous NaCl. The ether was dried (anhydrous $MgSO_4$) and evaporated, and the resulting oil was purified by flash chromatography (elution with benzene) to afford 343 mg (95%) of **22**. Short-path distillation produced an analytical sample: bp 130 °C (0.05 Torr); IR (film) 1596, 1576, 1314, 1303, 1146, 1075, 742, 719 cm^{-1}; ^1H NMR δ 7.69 (d, J = 8.3 Hz, 2 H), 7.33–7.19 (complex, 7 H), 6.57 (s, 1 H), 6.26 (s, 1 H), 6.19 (s, 1 H), 5.59 (s, 1 H), 2.46 (s, 3 H); mass spectrum, m/e (relative intensity) 364 (2, M^+), 158 (63), 128 (46), 91 (50), 43 (100). Anal. Calcd for $C_{17}H_{16}O_2SSe$: C, 56.20; H, 4.44; S, 8.83. Found: C, 56.03; H, 4.51; S, 8.78.

The same product **22** was obtained in 83% yield when the dichloro compound was treated with zinc dust in acetic acid for 1 h.

2-(*p*-Toluenesulfonyl)-2,3-butadien-1-ol (23). The diene **22** (288 mg, 0.80 mmol) and MCPBA (273 mg, 1.6 mmol) were stirred for 5 min in 2 mL of chloroform. The mixture was then washed three times with aqueous K_2CO_3 and once with aqueous NaCl, dried (anhydrous $MgSO_4$), evaporated in vacuo, and re-

crystallized from chloroform–petroleum ether to afford 172 mg (96%) of **23**: mp 65–66 °C; IR (film) 3500, 1968, 1597, 1316, 1303, 1148 cm^{-1}; ^1H NMR δ 7.81 (d, J = 8.4 Hz, 2 H), 7.36 (d, J = 8.4 Hz, 2 H), 5.45 (t, J = 1.8 Hz, 2 H), 4.36 (t, J = 1.8 Hz, 2 H), 2.57 (br s, 1 H), 2.45 (s, 3 H); mass spectrum, m/e (relative intensity) 224 (0.7, M^+), 194 (4, $M^+ - CH_2O$), 155 (40), 91 (100). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.40; S, 14.30. Found: C, 58.93; H, 5.43; S, 14.13. In general, this compound was prepared on a ca. 15 mmol scale from 1,4-dichloro-2-butyne with only partial purification of the intermediates, in only slightly lower overall yield.

1-Chloro-2-(phenylseleno)-3-(*p*-toluenesulfonyl)-1,3-butadiene (24). The dichloro compound **21** (434 mg, 1.00 mmol) and triethylamine (0.3 mL) were refluxed in 10 mL of chloroform for 3 h. The mixture was washed with aqueous NaCl, dried (anhydrous $MgSO_4$), and evaporated in vacuo. Preparative TLC (20% ethyl acetate–hexane) afforded 382 mg (96%) of **24**: R_f 0.56; mp 71–72 °C (from chloroform–hexane); IR (film) 1596, 1576, 1318, 1143, 1084, 726 cm^{-1}; ^1H NMR δ 7.62 (d, J = 8.2 Hz, 2 H), 7.34–7.13 (complex, 7 H), 6.85 (s, 1 H), 6.34 (s, 1 H), 5.72 (s, 1 H), 2.48 (s, 3 H); mass spectrum, m/e (relative intensity) 398 (19, M^+), 208 (39), 157 (61), 91 (100). Anal. Calcd for $C_{17}H_{15}O_2SSeCl$: C, 51.33; H, 3.80; S, 8.06. Found: C, 51.36; H, 3.76; S, 8.17.

4-Chloro-2-(*p*-toluenesulfonyl)-2,3-butadien-1-ol (25). The procedure for the preparation of 2-(*p*-toluenesulfonyl)-2,3-butadien-1-ol (**23**) was employed. The product **25** was isolated by preparative TLC (50% ethyl acetate–hexane) as an oil in 96% yield: R_f 0.70; IR (film) 3500, 1970, 1596, 1326, 1303, 1150, 1088, 815, 716 cm^{-1}; ^1H NMR δ 7.80 (d, J = 8.3 Hz, 2 H), 7.38 (d, J = 8.2 Hz, 2 H), 6.59 (t, J = 1.8 Hz, 1 H), 4.45 (m, 2 H), 2.80 (br s, 1 H), 2.46 (s, 3 H); mass spectrum, m/e (relative intensity) 258 (0.5, M^+), 155 (21, $ArSO_2^+$), 139 (38), 91 (100, $C_7H_7^+$); exact mass for $C_{11}H_{11}O_3SCl$, calcd 258.0117, found 258.0095.

Diels–Alder Reactions of Diene 22. With Methyl Acrylate. The diene **22** (129 mg, 0.356 mmol), methyl acrylate (0.2 mL), and boron trifluoride etherate (0.02 mL) were stirred for 3 days. Additional portions of the Lewis acid were added every 24 h. Volatile material was removed in vacuo, and the product was purified by preparative TLC (30% ethyl acetate–hexane) to afford 114.5 mg (72%) of a 9.1:1 mixture of cycloadducts **26** and **27** as a solid foam: R_f 0.36; IR (CCl_4) 1740, 1596, 1577, 1317, 1304, 1153 cm^{-1}; ^1H NMR δ 7.94 (m, 2 H), 7.55 (m, 2 H), 7.48–7.22 (complex, 5 H), 3.60 and 3.54 (two s with ratio of integrated intensities of 9.1:1, total 3 H), 2.77 (m, 1 H), 2.6–1.4 (s at δ 2.46 superimposed upon m, total 9 H); mass spectrum, m/e (relative intensity) 450 (13 M^+), 293 (22), 233 (52), 155 (100), 139 (40), 91 (89); exact mass for $C_{21}H_{22}O_4SSe$, calcd 450.0404, found 450.0401.

In a separate experiment, the diene (54 mg, 0.15 mmol) and methyl acrylate (15 mg, 0.17 mmol) were heated in 0.5 mL of *p*-xylene in a sealed glass tube at 200 °C for 9 h. Preparative TLC of the reaction mixture (20% ethyl acetate–hexane) afforded 40 mg (60%) of a 1.6:1 mixture of **26** and **27**.

With Methyl Vinyl Ketone. The diene **22** (148 mg, 0.408 mmol) and 2 drops of boron trifluoride etherate were dissolved in 1 mL of freshly distilled methyl vinyl ketone, and the mixture was allowed to stand at room temperature for 3 days. The mixture was then evaporated in vacuo, triturated with 50% ethyl acetate–hexane, filtered through silica gel to remove polymeric material, and purified by preparative TLC (30% ethyl acetate–hexane) to afford 12 mg (63%) of cycloadduct **28**: R_f 0.25; mp 126–127 °C (from chloroform–hexane); IR (KBr) 1702, 1593, 1585, 1577, 1310, 1302, 1148, 745 cm^{-1}; ^1H NMR (400 MHz, C_6D_6)[35] δ 8.14 (d, J = 8.2 Hz, 2 H), 7.41 (d, J = 8.1 Hz, 2 H), 6.99–6.90 (m, 3 H), 6.82 (d, J = 8.0 Hz, 2 H), 2.78 (dd, J = 17.2, 5.3 Hz, 1 H), 2.58 (dd, J = 17.2, 9.2 Hz, 1 H), 1.92 (m, 1 H), 1.85 (s, 3 H), 1.75–1.65 (m, 2 H), 1.47 (s, 3 H), 0.99 (m, 1 H), 0.85 (m, 1 H); mass spectrum, m/e (relative intensity) 434 (5, M^+), 235 (58), 91 (25), 77 (26), 43 (100). Double irradiation of the NMR signal at δ 2.78 collapsed the signal at δ 2.58 to d (J = 9.2 Hz); double irradiation at δ 2.58 collapsed the signal at δ 2.78 to d (J = 8.2 Hz); double irradiation at δ 1.7 collapsed the signals at δ 2.78 and 2.58 to d (each with J = 17.2 Hz); double irradiation at δ 0.99 collapsed the signal at δ 1.92 to dd (J = 17 Hz, 4.8 Hz). Anal. Calcd for $C_{21}H_{22}O_3SSe$: C, 58.19; H, 5.12. Found: C, 57.92; H, 5.11.

2-Methyl-3-(*p*-toluenesulfonyl)-1,3-butadiene (5a).[36] A solution of methyllithium in ether (1.74 mmol) was added by syringe to $CuBr{\cdot}SMe_2$ (179 mg, 0.87 mmol) in 3 mL of THF at −78 °C. After 15 min, the allenic sulfone (130 mg, 0.58 mmol) in 2 mL of THF was added. Stirring was continued at −78 °C for 0.5 h, and the reaction was quenched with aqueous NH_4Cl solution. The mixture was then diluted with ether, washed three times with aqueous NaCl, dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was stirred for 2 h with 1 mL of triethylamine and 0.20 mL of mesyl chloride in 5 mL of benzene at room temperature. The mixture was evaporated in vacuo, triturated with ether, washed three times with aqueous NaCl, dried ($MgSO_4$), and evaporated to dryness. Flash chromatography (elution with 15% ethyl acetate–hexane) afforded 94 mg (73%) of **5a** as an oil: IR (film) 1597, 1312, 1302, 1158, 1127, 1081, 756, 717 cm^{-1}; ^1H NMR δ 7.73 (d, J = 8.3 Hz, 2 H), 7.30 (d, J = 8.3 Hz, 2 H), 6.45 (s, 1 H), 5.90 (s, 1 H), 5.33 (s, 1 H), 5.13 (s, 1 H), 2.43 (s, 3 H), 1.88 (s, 3 H); mass spectrum, m/e (relative intensity) 222 (5, M^+), 158 (17), 143 (55), 139 (90), 91 (60), 41 (100); exact mass for $C_{12}H_{14}O_2S$, calcd 222.0715, found 222.0703.

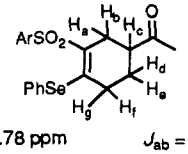
2-*n*-Butyl-3-(*p*-toluenesulfonyl)-1,3-butadiene (5b). The procedure for the preparation of **5a** was employed with *n*-butyllithium to afford 72% of **5b** as an oil after flash chromatography (elution with 15% ethyl acetate–hexane): IR (film) 1597, 1314, 1303, 1157, 1128, 1081, 814, 720 cm^{-1}; ^1H NMR δ 7.72 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 2 H), 6.45 (s, 1 H), 5.82 (s, 1 H), 5.16 (s, 1 H), 5.06 (s, 1 H), 2.43 (s, 3 H), 2.19 (t, J = 6.8 Hz, 2 H), 1.60–1.11 (m, 4 H), 0.80 (t, J = 7.0 Hz, 3 H); mass spectrum, m/e (relative intensity) 264 (1.6, M^+), 222 (18), 157 (19), 139 (81), 91 (49), 67 (100); exact mass for $C_{15}H_{20}O_2S$, calcd 264.1184, found 264.1175.

2-*sec*-Butyl-3-(*p*-toluenesulfonyl)-1,3-butadiene (5c). The procedure for the preparation of **5a** was employed with *sec*-butyllithium to afford 55% of **5c** as an oil after preparative TLC (18% ethyl acetate–hexane): R_f 0.62; IR (film) 1597, 1314, 1303, 1164, 1146, 1080, 815, 721 cm^{-1}; ^1H NMR δ 7.70 (d, J = 8.4 Hz, 2 H), 7.29 (d, J = 8.4 Hz, 2 H), 6.42 (s, 1 H), 5.77 (s, 1 H), 5.06 (br s, 1 H), 5.02 (br s, 1 H), 2.42 (s, 3 H), 2.40 (m, 1 H), 1.45–1.15 (m, 2 H), 0.92 (d, J = 6.9 Hz, 3 H), 0.76 (t, J = 7.3 Hz, 3 H); mass spectrum, m/e (relative intensity) 264 (2.9 M^+), 157 (13), 139 (72), 91 (65), 67 (87), 41 (100); exact mass for $C_{15}H_{20}O_2S$, calcd 264.1184, found 264.1171.

2-*tert*-Butyl-3-(*p*-toluenesulfonyl)-1,3-butadiene (5d). The procedure for the preparation of **5a** was employed with *tert*-butyllithium, except that DBN was employed for the elimination of the mesylate. The title compound **5d** was obtained in 52% yield as an oil after preparative TLC (20% ethyl acetate–hexane): R_f 0.62; IR (film) 1597, 1314, 1303, 1141, 1079, 815, 752 cm^{-1}; ^1H NMR δ 7.72 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 2 H), 6.44 (s, 1 H), 5.70 (s, 1 H), 5.22 (s, 1 H), 4.65 (s, 1 H), 2.44 (s, 3 H), 1.06 (s, 9 H); mass spectrum, m/e (relative intensity) 264 (2.6, M^+), 157 (12), 139 (47), 91 (33), 67 (40), 57 (100). Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.63. Found: C, 68.23; H, 7.68.

3-Methylidene-2-(*p*-toluenesulfonyl)-1,4-hexadiene (5e). Propenyllithium in ether (1.8 mmol) was added with a syringe to $CuBr{\cdot}SMe_2$ (185 mg, 0.90 mmol) in 5 mL of THF at −78 °C. After 15 min, the allenic alcohol **23** (135 mg, 0.603 mmol) was added in 2 mL of THF. The reaction mixture was stirred at −78 °C for 1 h and was then quenched with NH_4Cl, diluted with ether, filtered through Celite, washed three times with aqueous NaCl,

(35) The NMR assignments are summarized as follows:



δ H_a 2.78 ppm	J_{ab} = 17.2 Hz
δ H_b 2.58 ppm	J_{ac} = 8.2 Hz
δ H_c and H_f 1.7 ppm	J_{bc} = 9.2 Hz
δ H_d 0.99 ppm	J_{eg} = 4.8 Hz
δ H_e 0.85 ppm	J_{fg} = 17.0 Hz
δ H_g 1.92 ppm	

(36) Padwa, A.; Wannamaker, M. W.; Dyszlewski, A. D. *J. Org. Chem.* **1987**, *52*, 4760.

dried ($MgSO_4$), and evaporated in vacuo. The crude alcohol was purified by flash chromatography (elution with 30% ethyl acetate–hexane). It was then stirred for 1 h with 3 mL of triethylamine and 0.20 mL of mesyl chloride in 3 mL of chloroform at room temperature. The product was concentrated, diluted with ether, washed three times with aqueous NaCl, dried ($MgSO_4$), and evaporated in vacuo to afford 94 mg (63%) of **5e** as an oil. Attempts at further chromatographic purification resulted in decomposition: IR (film) 1597, 1314, 1303, 1152, 1080, 814 cm^{-1}; ^1H NMR δ 7.72 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 2 H), 6.48 (s, 1 H), 5.91 (s, 1 H), 5.79–5.61 (m, 3 H), 5.17 (s, 1 H), 2.43 (s, 3 H), 1.62 (d, J = 5.2 Hz, 3 H) (the minor isomer had a singlet at δ 6.58 integrating as 0.1 H); mass spectrum, m/e (relative intensity) 248 (1.3, M^+), 169 (41), 139 (51), 91 (100); exact mass for $C_{14}H_{16}O_2S$, calcd 248.0871, found 248.0867.

2-Acetoxy-3-(*p*-toluenesulfonyl)-1,3-butadiene (5f). The allenic alcohol **23** (107 mg, 0.478 mmol) was dissolved in 2 mL of dichloromethane at −78 °C. Triethylamine (0.35 mL) and then acetic anhydride (0.12 mL) were added dropwise. The reaction mixture was stirred at 4 °C for 24 h. The mixture was washed with water and aqueous NaCl, dried ($MgSO_4$), and evaporated under reduced pressure. Flash chromatography (elution with 20% ethyl acetate–hexane) afforded 72 mg (57%) of **5f** as an oil: IR (film) 1767, 1637, 1596, 1313, 1304, 1197, 1155, 1080, 729 cm^{-1}; ^1H NMR δ 7.76 (d, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H), 6.58 (s, 1 H), 6.13 (s, 1 H), 5.56 (d, J = 2 Hz, 1 H), 5.08 (d, J = 2 Hz, 1 H), 2.44 (s, 3 H), 2.07 (s, 3 H); mass spectrum, m/e (relative intensity) 266 (12, M^+), 224 (31), 160 (53), 145 (61), 139 (64), 117 (62), 91 (78), 43 (100); exact mass for $C_{13}H_{14}O_4S$, calcd 266.0613, found 266.0636.

2-Chloro-3-(*p*-toluenesulfonyl)-1,3-butadiene (5g). The allenic alcohol **23** (115 mg, 0.51 mmol) and 0.12 mL (1.65 mmol) of thionyl chloride were refluxed 6 h in 3 mL of benzene. Volatile material was then removed in vacuo, and the reaction mixture was washed with aqueous NaCl, dried ($MgSO_4$), and evaporated in vacuo. Flash chromatography (elution with 20% ethyl acetate–hexane) afforded 67 mg (54%) of **5g** as an oil that solidified on standing: mp 31–35 °C; IR (film) 1596, 1316, 1305, 1149, 1072, 814, 726 cm^{-1}; ^1H NMR δ 7.74 (d, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H), 6.73 (s, 1 H), 6.44 (s, 1 H), 6.12 (d, J = 2.3 Hz, 1 H), 5.64 (crude s, 1 H), 2.44 (s, 3 H); mass spectrum, m/e (relative intensity) 242 (2.3, M^+), 143 (96), 139 (71), 91 (100); exact mass for $C_{11}H_{11}O_2ClS$, calcd 242.0168, found 242.0164.

2-(*p*-Toluenesulfonyl)-1-buten-3-yne (29). The allenic alcohol **23** (38 mg, 0.17 mmol) was dissolved in 1 mL of dichloromethane at −78 °C. Triethylamine (0.07 mL) and mesyl chloride (0.02 mL, 0.26 mmol) were added, and stirring was continued for 40 min. The reaction was quenched with water, diluted with ether, washed with aqueous NaCl, and dried ($MgSO_4$). Evaporation in vacuo produced the crude enyne that decomposed when further purification was attempted by various chromatographic methods. The crude product showed the following: IR (CCl_4) 3310, 1595, 1335, 1145 cm^{-1}; ^1H NMR δ 7.83 (d, J = 8.3 Hz, 2 H), 7.35 (d, J = 8.6 Hz, 2 H), 6.76 (s, 1 H), 6.24 (s, 1 H), 3.26 (s, 1 H), 2.46 (s, 3 H). Additional signals from **5g** were also observed.

Reaction of Allenic Alcohol 18 with Me_2CuLi·SMe_2. Methyllithium (1.5 mmol) in ether was added by syringe to $CuBr$·SMe_2 (154 mg, 0.75 mmol) in THF at −78 °C. After 15 min, the allenic alcohol **18** (140 mg, 0.50 mmol) in 2 mL of THF was injected. Stirring was continued for 1 h at −78 °C and then for 3 h at room temperature. The reaction was quenched with aqueous NH_4Cl, the mixture was diluted with ether, washed three times with aqueous NaCl solution, dried ($MgSO_4$), and evaporated in vacuo. The crude product was dissolved in 3 mL of chloroform, and 1 mL of triethylamine was added, followed by the dropwise addition of 0.4 mL of methanesulfonyl chloride. After 16 h, volatile material was removed under reduced pressure and the residue was taken up in ether, washed three times with aqueous NaCl solution, dried ($MgSO_4$), and evaporated in vacuo. Preparative TLC in 20% ethyl acetate–hexane afforded 99 mg (72%) of a 4.8:1 mixture of Z and E isomers of **31a**, as determined by NMR integration: R_f 0.35; IR (film) 1673, 1631, 1598, 1314, 1302, 1146, 1134, 1086 cm^{-1}; ^1H NMR (Z isomer) δ 7.72 (d, J = 8.3 Hz, 2 H), 7.29 (d, J = 8.6 Hz, 2 H), 5.92 (dt, J = 10.2, 1.9 Hz, 1 H), 5.61 (dt, J = 10.2, 4.1 Hz, 1 H), 3.95 (s, 2 H), 2.42 (s, 3 H), 2.27 (m, 2 H), 1.99 (m, 2 H), 1.82 (s, 3 H), 1.59 (m, 2 H), (E isomer) δ 6.37 (dt, J = 10.2, 1.9 Hz), 4.04 (s), 1.86 (s);[37] mass spectrum, m/e (relative intensity, %) 276 (10, M^+), 121 (100, $M^+ - ArSO_2^{\bullet}$), 105 (39), 93 (86), 91 (65, $C_7H_7^+$), 79 (83); exact mass for $C_{16}H_{20}O_2S$ calcd 276.1184, found 276.1182. Double irradiation of the NMR signal at δ 1.82 (olefinic Me group of the Z isomer) resulted in enhancement of the CH_2SO_2 signal at δ 3.95, but not of the olefinic signals of the cyclohexene moiety. Double irradiation at δ 3.95 resulted in enhancement of the olefinic signal at δ 5.92 and that of the olefinic Me group at δ 1.82.

Reaction of Allenic Alcohol 18 with n-Bu_2CuLi·SMe_2. The preceding procedure was repeated with use of n-butyllithium instead of methyllithium to afford 65% of a 6.6:1 mixture of Z and E isomers of **31b**, as determined by NMR integration: R_f 0.55; IR (film) 1668, 1598, 1315, 1302, 1146, 1135, 1086 cm^{-1}; ^1H NMR (Z isomer) δ 7.71 (d, J = 8.3 Hz, 2 H), 7.39–7.26 (m, 2 H), 5.90 (dt, J = 10.2, 2.0 Hz, 1 H), 5.59 (dt, J = 10.2, 4.1 Hz, 1 H), 3.93 (s, 2 H), 2.42 (s, 3 H), 2.33–2.17 (m, 4 H), 2.05–1.25 (complex, 8 H), 0.88 (m, 3 H), (E isomer) δ 6.35 (dt, J = 10.2, 2.0 Hz), 4.13 (s); mass spectrum, m/e (relative intensity, %) 318 (6, M^+), 162 (53, $M^+ - ArSO_2H$), 139 (55), 91 (97, $C_7H_7^+$), 43 (100); exact mass for $C_{19}H_{26}O_2S$, calcd 318.1654, found 318.1655. When the elimination step with triethylamine and methanesulfonyl chloride was omitted, the corresponding alcohol **30b** was isolated as the pure Z isomer by repeated recrystallization of the crude product from methanol–hexane: mp 85–86 °C; IR (Nujol) 3380, 1594, 1309, 1286, 1145, 1081 cm^{-1}; ^1H NMR δ 7.78 (d, J = 8.4 Hz, 2 H), 7.36 (d, J = 8.4 Hz, 2 H), 4.59 (m, 1 H), 4.19 (d, J = 13.8 Hz, 1 H), 3.70 (d, J = 13.8 Hz, 1 H), 2.68 (m, 1 H), 2.46 (s, 3 H), 2.44–1.15 (m, 14 H), 0.86 (crude t, 3 H); mass spectrum, m/e (relative intensity, %) 336 (0.3, M^+), 318 (10, $M^+ - H_2O$), 162 (65), 139 (63), 120 (80), 91 (100, $C_7H_7^+$). Anal. Calcd for $C_{19}H_{28}O_3S$: C, 67.82; H, 8.39. Found: C, 67.71; H, 8.37.

1-(1-Cyclohexenyl)-2-(*p*-toluenesulfonyl)ethyne (32). The allenic alcohol **18** (140 mg, 0.500 mmol) was dissolved in 5 mL of chloroform containing 3 mL of triethylamine. Methanesulfonyl chloride (0.8 mL) was added, and the solution was stirred at room temperature for 1 h. Volatile material was removed in vacuo, and the residue was dissolved in ether, washed three times with aqueous NaCl solution, dried ($MgSO_4$), and evaporated. Flash chromatography (elution with 15% ethyl acetate–hexane) afforded 127 mg (98%) of the enyne: mp 79–80 °C (from chloroform–hexane); IR (Nujol) 2163, 1619, 1592, 1330, 1160, 1083 cm^{-1}; ^1H NMR δ 7.89 (d, J = 8.4 Hz, 2 H), 7.36 (d, J = 8.4 Hz, 2 H), 6.45 (m, 1 H), 2.46 (s, 3 H), 2.11 (m, 4 H), 1.61 (m, 4 H); mass spectrum, m/e (relative intensity, %) 260 (75, M^+), 139 (100), 105 (57), 91 (86, $C_7H_7^+$); exact mass for $C_{15}H_{16}O_2S$, calcd 260.0871, found 260.0862.

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Registry No. **5a**, 110355-44-7; **5b**, 127381-22-0; **5c**, 127381-23-1; **5d**, 127381-24-2; (*E*)-**5e**, 127381-25-3; (*Z*)-**5e**, 127381-26-4; **5f**, 127381-27-5; **5g**, 127381-28-6; **6**, 931-49-7; **7**, 127381-29-7; **8**, 78-80-8; **9**, 74744-36-8; (*E*)-**10**, 127381-30-0; (*Z*)-**10**, 127381-31-1; (*E*)-**11**, 127381-32-2; (*Z*)-**11**, 127381-33-3; (*E*)-**12**, 127381-34-4; (*Z*)-**12**, 127381-35-5; **13**, 127381-36-6; **14**, 127381-37-7; **15**, 127381-38-8; **18** (isomer 1), 127420-39-7; **18** (isomer 2), 127381-39-9; **19** (isomer 1), 127381-40-2; **19** (isomer 2), 127381-41-3; **20**, 127381-42-4; **21**, 127381-43-5; **22**, 127381-44-6; **23**, 127381-45-7; **24**, 127381-46-8; **25**, 127381-47-9; **26**, 127381-48-0; **27**, 127381-49-1; **28**, 127381-50-4; **29**, 127381-51-5; **30b**, 127381-52-6; (*Z*)-**31a**, 127381-53-7; (*E*)-**31a**, 127381-54-8; (*Z*)-**31b**, 127381-55-9; (*E*)-**31b**, 127381-56-0; **32**, 127381-57-1; *Se*-phenyl *p*-tolueneselenosulfonate, 68819-94-3; 1,4-dichloro-2-butyne, 821-10-3; methyl acrylate, 96-33-3; methyl vinyl ketone, 78-94-4.

(37) Additional ^1H NMR signals at δ 5.25 (s), 4.98 (s), and 3.92 (s) suggest the presence of the following compound in the crude reaction mixture: