(FAB) calcd for $C_{23}H_{24}N_2O_4S$ $[M + H]^+$ 425.1535, found 425.1538.

3-Hydroxy-1-tosyl-1,2-dihydrobenz[*cd*]indoline (16). To a solution of 3-oxo-1-tosyl-1,3-dihydrobenz[*cd*]indoline (11) (0.100 g, 0.309 mmol) in 3 mL of benzene/methanol (1:1) at 0 °C was added sodium borohydride (0.023 g, 0.618 mmol). After 1 h, 10 drops of glacial acetic acid was added to the reaction. After 5 additional minutes of stirring, the reaction mixture was diluted with 30 mL of water and extracted with two 30-mL portions of ether. The combined organic extracts were washed with 20 mL each of saturated $NaHCO_3$ solution and saturated NaCl solution, dried over $MgSO_4$, and filtered, and solvent was removed under reduced pressure to give 0.105 g of crude yellow solid. Purification by silica gel flash chromatography (1:1 hexane/Et_2O, R_f = 0.41) yielded **16** (0.090 g, 90%) as a slightly yellow solid: mp 148-149 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3 H, $TsCH_3$), 5.18 (s, 2 H, CH_2), 5.20 (br s, 1 H, ArOH), 6.98 (d, 1 H, ArH, J = 8.6 Hz), 7.21 (d, 2 H, TsH, J = 8.2 Hz), 7.24-7.30 (m, 2 H, ArH), 7.43 (dd, 1 H, ArH, J = 2.4, 5.5 Hz), 7.51 (d, 1 H, ArH, J = 8.7 Hz), 7.78 (d, 2 H, TsH, J = 8.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, number of vicinal hydrogens assigned by DEPT) δ 21.48 (CH_3), 54.33 (CH_2), 107.03 (*C*H), 116.03 (C), 118.69 (*C*H), 119.76 (*C*H), 125.73 (*C*H), 126.38 (*C*H), 126.94 (C), 127.13 (*C*H), 129.85 (*C*H), 131.97 (C), 134.43 (C), 141.88 (C), 144.32 (C), 145.83 (C); UV (MeOH) λ_{max} 225 (ϵ 7500), 300, 342 nm. UV (MeOH + 1 drop concentrated aqueous NaOH) 211, 225, 302, 363 nm; IR (film) ν 3435 (OH), 2956, 2921, 2853, 1610, 1494, 1374, 1299, 1159, 1121, 1087 cm^{-1}; mass spectrum (EI) m/e 325 (parent). Anal. Calcd for $C_{18}H_{15}NO_3S$: C, 66.44; H, 4.65; N, 4.30. Found: C, 66.54; H, 4.84; N, 4.31.

3-Hydroxy-2-methyl-1-tosyl-1,2-dihydrobenz[*cd*]indoline (17). To a stirred suspension of copper bromide-dimethyl sulfide complex (0.127 g, 0.620 mmol) in 2.4 mL of dimethyl sulfide/diethyl ether (1:1 v/v) under argon at -45 °C was added methyllithium (0.87 mL of 1.4 M solution in ether, 0.620 mmol) dropwise via syringe. The suspension turned yellow immediately. After 3 h, a solution of tricyclic enone (11) (0.100 g, 0.310 mmol) in 2.5 mL of THF was added dropwise to the -45 °C suspension. After 3 h the mixture had warmed to -10 °C. The still cold mixture was diluted with 25 mL of 10% ammonium hydroxide in saturated ammonium chloride and extracted with three 25-mL portions of diethyl ether. Drying the combined organic extracts over $MgSO_4$, filtering, and removal of solvent under reduced pressure left a tan solid. Purification of the crude material by preparative TLC eluted with hexane/ethyl acetate (3:1) yielded indoline **17** (0.05 g, 0.155 mmol, 50%) as a slightly yellow solid: mp 117-120 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.89 (d, 3 H, CH_3, J = 6.4 Hz), 2.29 (s, 3 H, $TsCH_3$), 5.14 (br s, 1 H, ArOH), 5.51 (q, 1 H, CH, J = 6.4 Hz), 6.97 (d, 1 H, ArH, J = 8.6 Hz), 7.15 (d, 2 H, TsH, J = 8.3 Hz), 7.23-7.34 (m, 2 H, ArH), 7.42-7.52 (m, 2 H, ArH), 7.73 (d, 2 H, TsH, J = 8.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, number of hydrogens assigned by DEPT) δ 21.30 (CH_3), 21.44 (CH_3), 64.27 (*C*H), 108.49 (*C*H), 119.21 (*C*H), 119.99 (*C*H), 121.71 (C), 125.67 (*C*H), 126.38 (*C*H), 126.76 (C), 127.11 (*C*H), 129.67 (*C*H), 134.81 (C), 141.32 (C), 144.05 (C), 145.98 (C), 148.01 (C); IR (film) ν 3429 (OH), 3060, 2976, 2920, 1641, 1610, 1496, 1371, 1346, 1284, 1162 cm^{-1}; mass spectrum (EI) m/e 339 (parent). Anal. Calcd for $C_{19}H_{17}NO_3S$: C, 67.24; H, 5.05; N, 4.13. Found: C, 67.40; H, 5.20; N, 3.92.

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Preparation of Allenic Sulfones and Allenes from the Selenosulfonation of Acetylenes

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β-(Phenylseleno)vinyl sulfones **2** are readily obtained from the free-radical selenosulfonation of acetylenes. Compounds **2** isomerize to allyl sulfones **4** under base-catalyzed conditions in nearly quantitative yield, with high stereoselectivity favoring the *Z* configuration. Allyl sulfones **4** afford generally high yields of allenic sulfones **1** when subjected to oxidation with *m*-chloroperbenzoic acid or *tert*-butyl hydroperoxide, followed by selenoxide syn-elimination. The sulfone-stabilized anion intermediates in the isomerizations of **2** to **4** can be alkylated, deuterated, or silylated in the α-position prior to oxidation, providing allenic sulfones with an additional α-substituent. In some cases, spontaneous elimination of the phenylseleno group occurred, producing the allenic sulfone without the need for an oxidation step. Desulfonylation of allyl sulfones **4f**, **4c**, and **25** with sodium amalgam afforded vinyl selenides that were converted to allenes in moderate to good yields by oxidation-elimination. The copper-catalyzed coupling of allyl sulfones **4** with Grignard reagents comprises an alternative route to vinyl selenide precursors of allenes. These procedures permit the syntheis of various α- and γ-substituted allenic sulfones and allenes from acetylenes.

Allenic sulfones **1** are of increasing importance in organic synthesis, particularly as dienophiles[1] and dipolarophiles[2] in cycloadditions,[3] and in addition reactions with various nucleophiles.[4] They are typically prepared by the isomerization of propargyllic sulfones,[4f] from the oxidation of allenic sulfides or sulfoxides,[5] by the rearrangement of

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(2) (a) Padwa, A.; Kline, D. N.; Norman, B. H. *Tetrahedron Lett.* **1988**, *29*, 265. (b) Padwa, A.; Carter, S. P.; Chiacchio, U.; Kline, D. N.; Perumattam, J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2639. (c) Padwa, A.; Craig, S. P.; Chiacchio, U.; Kline, D. N. *J. Org. Chem.* **1988**, *53*, 2232. (d) Padwa, A.; Yeske, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 1617. (e) Padwa, A.; Kline, D. N.; Koehler, K. F.; Matzinger, M.; Venkatramanan, M. K. *J. Org. Chem.* **1987**, *52*, 3909. (f) Parpani, P.; Zecchi, G. *J. Org. Chem.* **1987**, *52*, 1417. (g) Bruché, L.; Gelmi, M. L.; Zecchi, G. *J. Org. Chem.* **1985**, *50*, 3206. (h) Veniard, L.; Pourcelot, G. *Bull. Soc. Chim. Fr.* **1973**, 2746.

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(4) (a) Denmark, S. E.; Harmata, M. A.; White, K. S. *J. Org. Chem.* **1987**, *52*, 4031, and references cited therein. (b) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1987**, *52*, 4265. (c) Back, T. G.; Brunner, K.; Krishna, M. V.; Lai, E. K. Y. *Can. J. Chem.*, in press. (d) Hayakawa, K.; Takewaki, M.; Fujimoto, I.; Kanematsu, K. *J. Org. Chem.* **1986**, *51*, 5100. (e) Fujii, I.; Ryu, K.; Hayakawa, K.; Kanematsu, K. *J. Chem. Soc., Chem. Commun.* **1984**, 844. (f) Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5856. (g) Thyagarajan, B. S.; Simon, J. A. *Phosphorus Sulfur* **1988**, *39*, 11.

(5) (a) Pourcelot, G.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, 3024. (b) Cinquini, M.; Colonna, S.; Cozzi, F.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2061.

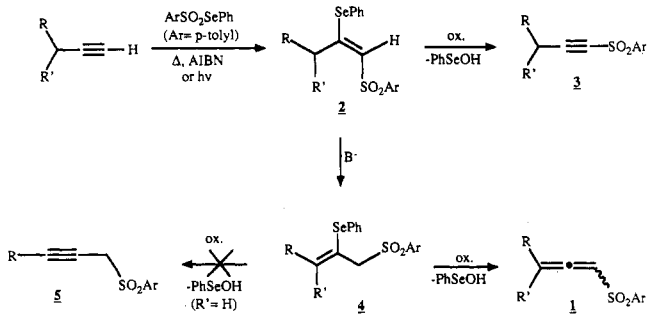
0022-3263/89/1954-4146$01.50/0

Table I. Preparation of γ-Substituted Allenic Sulfones[a]

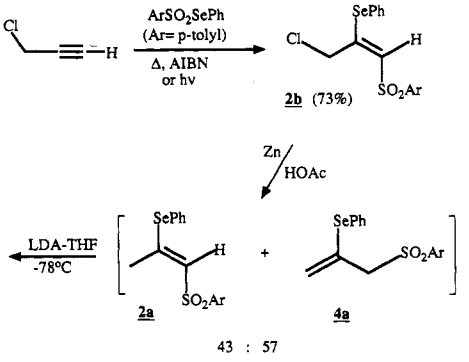
starting material 2 no.	R	R′	base[b]	Z:E ratio of 4	oxidant	product 1 no.	yield,[c] %
2a[d]	H	H	A	–	MCPBA	**1a**	92
2b	Cl	H	B	6:1	MCPBA	**1b**	98
2c	n-C_7H_{15}	H	C	>20:1	MCPBA	**1c**	82[e]
					t-BuOOH	**1c**	73[f]
2d	n-C_3H_7	H	C	10:1	MCPBA	**1d**	81[g]
2e	$CH_2OC(=O)Ph$	H	B	>20:1	MCPBA	**1e**	93
2f	$-(CH_2)_5-$		A	–	MCPBA/DABCO	**1f**	50
2g	n-C_7H_{15}	n-C_8H_{17}	A	*h*	MCPBA/DABCO	**1g**	84
2h	$O(C=O)Ph$	H	B	>20:1[i]	–		
2i	OSi-t-$BuMe_2$	H	A	>20:1[j]	–		

[a] Ar = *p*-tolyl. [b] Conditions were as follows: (A) LDA–THF, −78 °C; (B) Et_3N–$CHCl_3$, Δ; (C) t-BuOK–THF, −78 °C. [c] Isolated overall yields from **2** are reported. [d] The starting material was a 43:57 mixture (NMR integration) of **2a** and **4a**. [e] The product was isolated as a 86:14 mixture (NMR integration) of **1c** and **5c** in 95% yield. [f] The product was isolated as a 78:22 mixture (NMR integration) of **1c** and **5c** in 93% yield. [g] The product was isolated as a 94:6 mixture (NMR integration) of **1d** and **5d** in 86% yield. [h] Isomerization with base afforded the *Z* isomer of **2g**. [i] Isolated in 90% yield. [j] Isolated in 73% yield.

Scheme I



Scheme II



sulfinate esters of propargyllic alcohols,[4a,6] or via Horner–Wittig reactions of (sulfonylmethyl)phosphonates with ketenes.[7] These methods often work effectively, but are only useful in those cases where the required precursor is itself readily available. We now report a novel, general preparation of allenic sulfones **1**, employing common acetylenes as the starting materials.[8]

Numerous procedures exist for the preparation of allenes from various types of starting materials.[9] There are relatively few methods, however, for converting simple, unfunctionalized acetylenes into allenes.[10] We report that allenes can be produced by a variation of the procedure employed for the preparation of allenic sulfones by including an additional desulfonylation step prior to formation of the final product.

Results and Discussion

The free-radical additions of selenosulfonates ($ArSO_2SePh$) to acetylenes provide β-(phenylseleno)vinyl sulfones **2**,[11] generally in excellent yield and with high regio- and stereoselectivity, as indicated in Scheme I. The anti orientation of the phenylseleno moiety and the sulfone group in **2** places the vinylic hydrogen atom cis to the selenium substituent. Consequently, adducts **2** undergo facile oxidation and selenoxide syn-elimination to afford the corresponding acetylenic sulfones **3**.[11] Unactivated vinyl selenoxides containing cis hydrogens normally produce acetylenes preferentially (vs allenes),[12] and the regioselectivity is no doubt enhanced in the present case by the activating effect of the sulfone moiety. This method thus provides an exceptionally convenient preparation of acetylenic sulfones. However, in order to extend the utility of selenosulfonation, we sought to develop a complementary protocol that would make possible the selective formation of the allenic sulfones **1**.

Preparation of γ-Substituted Allenic Sulfones. The required β-(phenylseleno)vinyl sulfones **2b–i** were obtained by the selenosulfonation of the corresponding terminal acetylenes.[11] Sulfone **2a** was more conveniently prepared by an indirect route to avoid employing volatile propyne as the starting material. Thus, adduct **2b**, obtained from 3-chloropropyne in the usual manner, was reduced with

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(7) Fillion, H.; Hseine, A.; Pera, M.-H.; Dufaud, V.; Refouvelet, B. *Synthesis* **1987**, 708.
(8) Preliminary communication: Back, T. G.; Krishna, M. V.; Muralidharan, K. R. *Tetrahedron Lett.* **1987**, *28*, 1737.
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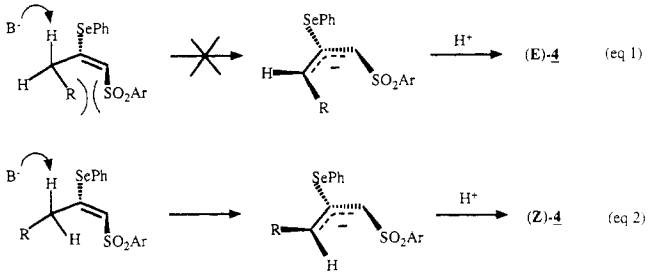
(10) For an example, see: Meisters, A.; Swan, J. M. *Aust. J. Chem.* **1965**, *18*, 155.
(11) (a) Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077. (b) Back, T. G.; Collins, S.; Gokhale, U.; Law, K.-W. *J. Org. Chem.* **1983**, *48*, 4776. (c) Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438. For lead references to the selenosulfonation of other unsaturated substrates, see: (d) Gancarz, R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899. (e) Kang, Y.-H.; Kice, J. L. *J. Org. Chem.* **1984**, *49*, 1507. (f) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249. (g) Kice, J. L.; Kang, Y.-H. *Tetrahedron* **1985**, *41*, 4739.
(12) Reich, H. J.; Willis, W. W., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 5967.

zinc dust in acetic acid to afford a 43:57 mixture of **2a** and its allyl sulfone isomer **4a** (Scheme II). This mixture was converted to pure **4a** by treatment with base, as described below.

The base-catalyzed isomerizations of various vinyl sulfones to allyl sulfones have been previously reported.[13] If similar isomerizations of β-(phenylseleno)vinyl sulfones **2** were carried out prior to selenoxide elimination, then elimination would again be expected to occur regioselectively toward the sulfone-activated hydrogen atom, but this time producing the desired allenic sulfone **1**, as shown in Scheme I.

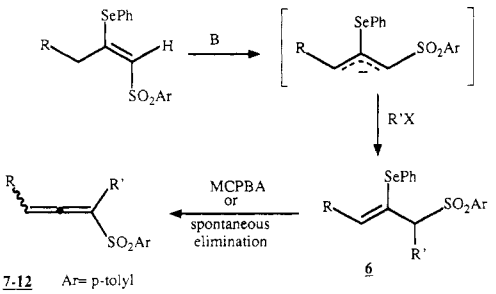
We have found that in general, vinyl sulfones **2** isomerize readily and quantitatively to their allylic counterparts **4** when treated with bases varying in strength from triethylamine to lithium diisopropylamide (LDA). The results are summarized in Table I. The products were formed as nearly pure geometric isomers, and only in the case of **4b** and **4d** were significant quantities of both *E* and *Z* isomers observed. The *Z* configuration was assigned to the major products of **4b** and **4d**, and to the sole observed isomers of **4e** and **4h**, on the basis of NOE experiments. The configurations of **4c** and **4i** were assumed to be *Z* by analogy. Block and Aslam[13a] invoked the "syn effect" to rationalize the stereoselectivity of the vinylogous Ramberg–Backlund reaction, which also involves γ-deprotonation of a vinyl sulfone. In the present case, the "syn effect" would be expected to favor the preferential formation of the *E* isomer of **4**. However, Block and Aslam also pointed out that steric interactions between a γ-substituent and a cis-sulfone group can preclude a conformation capable of stabilization by means of the "syn effect", and a similar argument can be applied to the isomerization of **2** to (*Z*)-**4**, providing that kinetic control is assumed (eq 1 and 2).



In one exceptional case, the vinyl sulfone (*E*)-**2g** did not afford the corresponding allyl sulfone **4g** when treated with base, but underwent essentially quantitative isomerization to (*Z*)-**2g**.

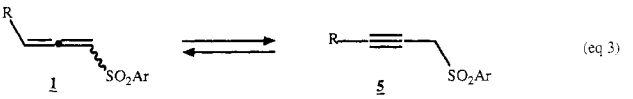
Products **4** were typically oxidized to the corresponding selenoxides with *m*-chloroperbenzoic acid (MCPBA), followed by syn-elimination to afford the desired allenic sulfones **1** in good to excellent yield (Table I). In some cases the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) improved the yields substantially.[12] Although each of the allylic sulfones **4** could be isolated and was fully characterized, these compounds were more conveniently produced in situ and oxidized without prior purification for the purpose of preparing allenes **1**. An exception was

Scheme III



observed with **2f**, where isomerization of **4f** proceeded in only 62% yield. In this case, it proved more expedient to purify the latter prior to oxidation.

The oxidation of **4c** produced varying quantities of the desired allenic sulfone **1c** and the isomeric propargyllic sulfone **5c**, whose ratio depended upon the precise conditions. The highest yield of **1c** (**1c**:**5c** = 86:14; total 95%) was obtained by oxidation of the selenide with MCPBA, followed by rapid extraction of the byproduct *m*-chlorobenzoic acid with aqueous $NaHCO_3$ and pyrolysis of the selenoxide under essentially neutral conditions. The use of *tert*-butyl hydroperoxide[14] in chloroform also gave satisfactory results (**1c**:**5c** = 78:22; total 93%). Lower yields of **1c** were observed when *m*-chlorobenzoic acid was not removed after the initial oxidation step, and only **5c** was formed when an amine was included during the selenoxide elimination step.[15] Control experiments demonstrated that **1c** isomerizes rapidly to the propargyllic sulfone **5c** under base-catalyzed conditions. For example, exposure of the mixture of **1c** and **5c** to ethyldiisopropylamine, triethylamine, or DABCO in chloroform for 12 h at room temperature resulted in its quantitative conversion to pure **5c**. This indicates that the allenic sulfone is the chief or exclusive kinetic product of selenoxide elimination, and that the propargyllic isomer ensues from its subsequent isomerization (eq 3). Moreover, the



direct formation of **5c** from the syn-elimination of the selenoxide of **4c** is precluded by the trans orientation of the vinylic hydrogen atom and the selenoxide moiety. It is interesting that the isomerization of **1c** to **5c** contrasts with the behavior **1a** and **5a**, where the allenic sulfone **1a** was previously reported to be the thermodynamically favored product.[4f]

A small amount of the propargyllic sulfone **5d** also accompanied the formation of the allenic sulfone **1d** (**1d**:**5d** = 94:6), but no significant amounts of propargyllic sulfones **5a**, **5b**, or **5e** were observed during the preparation of the corresponding allenic sulfones **1a**, **1b**, and **1e**. Attempts to convert **4h** and **4i** to the allenes **1h** and **1i**, respectively, using a variety of oxidation procedures proved unsuccessful. In each case complex mixtures of products were formed and spectroscopic analysis indicated degradation of the ester and silyl ether groups. Oxidation of (*Z*)-**2g** afforded the desired allenic sulfone **1g** in 84% overall yield.

Preparation of α,γ-Disubstituted Allenic Sulfones. Allyl sulfones can be deprotonated, and the resulting anions can be alkylated regioselectively in the α-position.[16]

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(14) Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1689.

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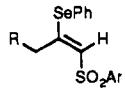
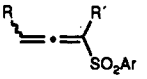
Table II. Preparation of α,γ-Disubstituted Allenic Sulfones[a]

starting material			allenic sulfone product		
					
no.	R	electrophile	no.	R′	yield,[b] %
2a	H	MeI	**7**	Me[c]	56
2b	Cl	D_2O	**8**	D[c]	85
2c	n-C_7H_{15}	MeI	**9**	Me[c]	80
2c		EtI	**10**	Et[d]	51
2c		CH_2=$CHCH_2I$	**11**	CH_2=$CHCH_2$[d]	59
2c		Me_3SiCl	**12**	Me_3Si[c]	82

[a] Ar = *p*-tolyl. [b] Isolated overall yields from **2** are reported. [c] Oxidation–elimination of the alkylated intermediate was effected with MCPBA. [d] Elimination of the PhSe group occurred spontaneously in situ.

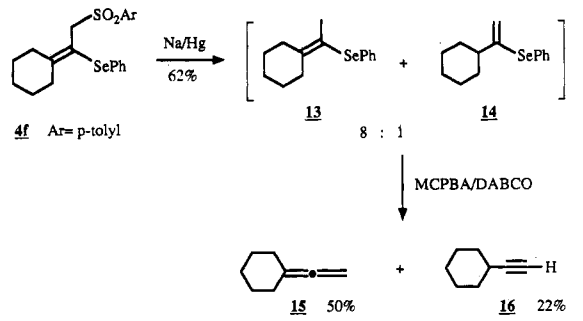
Since similar anions are intermediates in the base-catalyzed isomerization of **2** to **4**, the possibility exists of introducing an additional substituent into the α-position of the product allenic sulfone by alkylation prior to oxidation and selenoxide elimination (Scheme III). In general, adducts **2** were treated with LDA at −78 °C, followed by the desired electrophile. Only fairly reactive electrophiles could be employed as otherwise elimination of the phenylseleno group from the anion intermediate occurred at a rate competitive to that of alkylation, resulting in complex product mixtures. In some cases, spontaneous elimination occurred cleanly from the alkylated sulfones **6** in situ, affording the product allenic sulfones **10** and **11** without the need for a subsequent oxidation step. In the remaining cases **7–9** and **12**, the alkylated products **6** were treated with MCPBA in the usual manner. These results are summarized in Table II.

The conversion of **2b** to **8** illustrates that the method can also be employed for the preparation of α-deuterated allenic sulfones.[17] This was accomplished by simultaneous exchange and isomerization of **2b** in the presence of triethylamine and D_2O in refluxing chloroform, followed by selenoxide elimination with MCPBA.

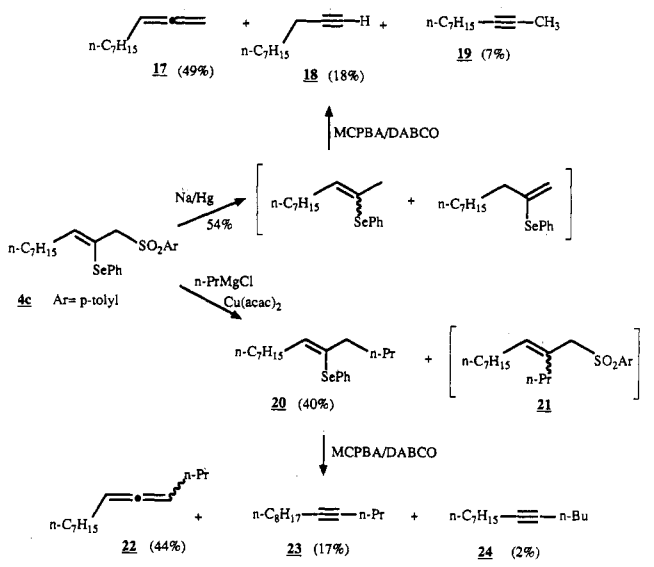
These results indicate that the selenosulfonation of acetylenes provides a convenient and efficient method for the synthesis of γ-substituted and α,γ-disubstituted allenic sulfones.

Preparation of Allenes. The desulfonylation of allenic sulfones **1** would permit the synthetically useful overall synthesis of allenes from acetylenes. Unfortunately, a variety of reagents commonly employed for desulfonylation[18] either failed to react with **1** or resulted in overreduction of the allene moiety. However, desulfonylation of allyl sulfones **4** prior to selenoxide syn-elimination comprises an alternative route to allenes, particularly if the competing formation of acetylene regioisomers is precluded by the absence of a cis vinylic hydrogen atom in the resulting vinyl selenide.

Scheme IV



Scheme V



When **4f** was desulfonylated with sodium amalgam,[18a-e] the corresponding unseparated vinyl selenides **13** and **14** were produced in 62% yield in the ratio of 8:1 (Scheme IV). Apparently, some isomerization of the double bond occurred, probably via the corresponding allyl radical or anion intermediates. Oxidation–elimination of this mixture produced the allene **15** and acetylene **16** in yields of 50% and 22%, respectively. Since selenoxide syn-elimination of **13** cannot produce the acetylene **16** directly, the source of the latter is assumed to be the selenoxide elimination of **14**,[19] and the isomerization of **15**. Some selenide **13** was regenerated during the elimination of the selen-

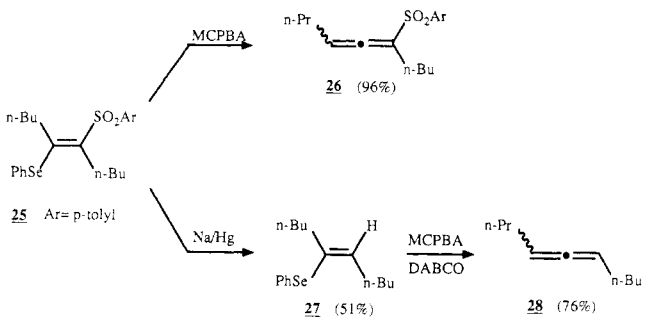
(16) The following reviews contain recent examples: (a) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. (b) Durst, T. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 3, Chapter 11.9. (c) Trost, B. M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 107.

(17) For a review of isotopically labeled allenes, see: Schiavelli, M. D. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: Chichester, 1980; Vol. 1, Chapter 11.

(18) (a) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477. (b) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 3435. (c) Julia, M.; Uguen, D. *Bull. Soc. Chim. Fr.* **1976**, 513. (d) Posner, G. H.; Brunelle, D. J. *J. Org. Chem.* **1973**, *38*, 2747. (e) Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4976. (f) Pascali, V.; Umani-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1973**, 351. (g) Bremner, J.; Julia, M.; Launay, M.; Stacino, J.-P. *Tetrahedron Lett.* **1982**, *23*, 3265. (h) Fabre, J.-L.; Julia, M. *Tetrahedron Lett.* **1983**, *24*, 4311. (i) Cuvigny, T.; Herve du Penhoat, C.; Julia, M. *Tetrahedron* **1987**, *43*, 859. (j) Mohri, M.; Kinoshita, H.; Inomata, K.; Kotake, H. *Chem. Lett.* **1985**, 451. (k) Inomata, K.; Igarashi, S.; Mohri, M.; Yamamoto, T.; Kinoshita, H.; Kotake, H. *Chem. Lett.* **1987**, 707. (l) Brown, A. C.; Carpino, L. A. *J. Org. Chem.* **1985**, *50*, 1749.

(19) Vinyl selenoxides that have both vinylic and allylic hydrogens available for syn-elimination afford chiefly the acetylene product (ref 12) in the absence of activating groups or overriding conformational factors. Thus, acetylene **16** is expected to be the major product from **14**.

Scheme VI



oxide, even in the presence of DABCO,[12] and accounts in part for the relatively low yield of the allene.

Allyl sulfone **4c** also afforded a mixture of unseparated vinyl selenide products when similarly desulfonylated. Oxidation–elimination of the mixture produced the allene **17** as the principal product (49%), along with the isomeric 1- and 2-acetylenes **18** and **19** (18% and 7%, respectively) (Scheme V).

The copper-catalyzed coupling of allyl sulfones with Grignard reagents reported by Julia[20] was investigated as an alternative to reductive desulfonylation. This variation permits the introduction of an additional substituent derived from the Grignard reagent into the product allene. Thus, **4c** afforded a modest yield of the corresponding coupled product **20** when treated with *n*-propylmagnesium chloride and a catalytic amount of copper(II) acetylacetonate [$Cu(acac)_2$]. A substantial quantity of a byproduct tentatively identified as **21** was also formed (Scheme V). Allyl sulfone **21** may arise from the base-catalyzed elimination of benzeneselenol from **4c** to produce the allenic sulfone **1c**, followed by Michael addition of the Grignard reagent[21] to the latter. Oxidation of vinyl selenide **20** again furnished the corresponding allene **22** as the principal product, along with smaller amounts of the acetylenes **23** and **24**.

The possibility of producing allenes from internal acetylenes was also investigated. The β-(phenylseleno)vinyl sulfone **25**, obtained from the selenosulfonation of 5-decyne, is known[11b] to afford the corresponding allenic sulfone **26** in excellent yield upon selenoxide elimination. We now report that prior desulfonylation of **25** produced the vinyl selenide **27** in 51% yield, which in turn cleanly afforded the desired allene **28** upon oxidation. Only traces (ca. 1%) of acetylenic byproducts were detected (Scheme VI).

Thus, the selenosulfonation of acetylenes provides a new route for the synthesis of allenes. Acetylenic byproducts are also formed in those cases where the isomeric vinyl selenide intermediates are able to equilibrate during desulfonylation.

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 or a Nicolet 5DX instrument as thin films for oils and as Nujol mulls for solids unless otherwise noted. ^1H NMR spectra were obtained on either a Hitachi Perkin-Elmer R24B spectrometer at 60 MHz, a Varian XL200 or a Bruker ACE spectrometer at 200 MHz, or a Bruker AM400 spectrometer at 400 MHz. NOE difference spectroscopy[22] was performed on the latter instrument. Deuteriochloroform was employed as the solvent and internal TMS as the standard unless otherwise noted. Mass spectra were recorded on a Kratos MS80 or a VG 7070 instrument. Elemental analyses were obtained by Dr. W. S. Lin (University of Calgary). Preparative TLC was carried out on Analtech 20 × 20 cm glass plates coated with 1 mm of silica gel GF. GC analyses were performed on a Varian 3700 chromatograph equipped with a Varian CDS111C integrator, a flame ionization detector, and a 15-m Megabore DB17 column, or a 30-m DB5 column (J and W Scientific Co.). Flash chromatography was performed by a variation of the method of Still.[23] Photolyses were conducted in a Rayonet RMR-500 reactor equipped with four 254-nm UV lamps.

Se-Phenyl *p*-tolueneselenosulfonate was prepared by a procedure described earlier.[24] 3-Heptyl-1-undecyne was prepared from 1-decyne and 1-bromooctane by the general method of Quillinan and Scheinmann.[25] 3-Butynyl benzoate and 2-propynyl benzoate were obtained by benzoylation of 3-butyn-1-ol and 2-propyn-1-ol, respectively, with benzoyl chloride in pyridine in the presence of a catalytic amount of 4-(*N*,*N*-dimethylamino)-pyridine.[26] All other acetylenes, as well as other starting materials and reagents, were purchased from commercial sources. MCPBA was purified by washing with a pH 7.5 buffer prior to use.[27]

Preparation of β-(Phenylseleno)vinyl Sulfones 2 and 25. Adducts **2c**,[11a] **2d**,[4b] **2i**,[4b] and **25**[11b] were prepared as described previously.

Adducts 2a and 2b. 3-Chloropropyne (1.86 g, 25.0 mmol) and *Se*-phenyl *p*-tolueneselenosulfonate (6.22 g, 20.0 mmol) were refluxed for 30 h in 30 mL of chloroform. Small portions (5–10 mg) of azobis(isobutyronitrile) (AIBN) were added periodically. The product was then concentrated in vacuo, and the residue was recrystallized from chloroform–hexane to afford 5.61 g (73%) of **2b**: mp 74–75 °C; IR 1597, 1326, 1145, 1084 cm^{-1}; ^1H NMR (200 MHz) δ 7.72–7.29 (complex, 9 H), 5.95 (s, 1 H), 4.90 (s, 2 H), 2.44 (s, 3 H); mass spectrum, *m/e* (relative intensity, %) 386 (M^+, 16), 229 (31), 195 (41), 157 (100), 155 (80). Anal. Calcd for $C_{16}H_{15}ClO_2SSe$: C, 49.81; H, 3.92; S, 8.31. Found: C, 49.85; H, 3.92; S, 8.30. A similar yield of **2b** was obtained when the reaction mixture was photolyzed for 23 h in carbon tetrachloride without AIBN.

Adduct **2b** (3.41 g, 8.84 mmol) and zinc dust (7.0 g) were stirred for 1 h in 25 mL of acetic acid. The mixture was filtered through Celite, and the filtrate was slowly added to 100 mL of 20% aqueous NaOH at 0 °C. The product was extracted three times with dichloromethane, dried ($MgSO_4$), and evaporated in vacuo to afford 3.13 g (100%) of a 43:57 mixture of **2a** and **4a**, identified by comparison of its NMR spectrum with that of pure **4a** (vide infra). The signal attributed to the vinylic H of **2a** was observed at δ 5.95.

Adduct 2e. 3-Butynyl benzoate (0.87 g, 5.0 mmol) and *Se*-phenyl *p*-tolueneselenosulfonate (1.56 g, 5.0 mmol) were refluxed for 24 h in 10 mL of benzene in the presence of ca. 10 mg of AIBN. The solvent was evaporated, and the residue was recrystallized from chloroform–hexane to afford 2.04 g (84%) of **2e**: mp 111–112 °C; IR 1715, 1600, 1585, 1311, 1296, 1273, 1255, 1140, 1115 cm^{-1}; ^1H NMR (60 MHz) δ 8.0–7.0 (complex, 14 H), 5.80 (s, 1 H), 4.40 (t, J = 6.5 Hz, 2 H), 3.27 (t, J = 6.5 Hz, 2 H), 2.25 (s, 3 H); mass spectrum, *m/e* (relative intensity, %) 329 (M^+ – PhSe, 18), 105 (100), 91 (76). Anal. Calcd for $C_{24}H_{22}O_4SSe$: C, 59.38; H, 4.57; S, 6.61. Found: C, 59.15; H, 4.48; S, 6.24.

Adduct 2f. Cyclohexylacetylene (0.325 g, 3.00 mmol) and *Se*-phenyl *p*-tolueneselenosulfonate (0.936 g, 3.00 mmol) were photolyzed in 30 mL of benzene for 20 h. Flash chromatography (elution with 15% ethyl acetate–hexane) afforded 1.101 g (88%) of **2f**: mp 128–129 °C (from chloroform–hexane); IR 1596, 1563, 1288, 1261, 1143, 1135, 1083 cm^{-1}; ^1H NMR δ 7.68–7.20 (complex, 9 H), 5.72 (s, 1 H), 3.65 (m, 1 H), 2.41 (s, 3 H), 1.79–1.15 (complex, 10 H); mass spectrum, *m/e* (relative intensity, %) 420 (M^+, 8), 263 (17), 157 (98), 139 (75), 91 (100). Anal. Calcd for $C_{21}H_{24}O_2SSe$:

(20) (a) Julia, M.; Righini-Tapie, A.; Verpeaux, J.-N. *Tetrahedron* **1983**, *39*, 3283. (b) Julia, M.; Verpeaux, J.-N. *Tetrahedron* **1983**, *39*, 3289.
(21) The selenoxides of adducts **2** also react with various nucleophiles by elimination–addition mechanisms; see ref 4b.
(22) Derome, A. E. In *Modern NMR Techniques for Chemistry Research*; Pergamon Press: Oxford, 1987; Chapter 5.
(23) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(24) Back, T. G.; Collins, S.; Krishna, M. V. *Can. J. Chem.* **1987**, *65*, 38.
(25) Quillinan, A. J.; Scheinmann, F. *Org. Synth.* **1978**, *58*, 1.
(26) Scriven, E. F. V. *Chem. Soc. Rev.* **1983**, *12*, 129.
(27) Schwartz, N. N.; Blumbergs, J. H. *J. Org. Chem.* **1964**, *29*, 1976.

C, 60.13; H, 5.77. Found: C, 59.71; H, 5.83.

Adduct 2g. 3-Heptyl-1-undecyne (375 mg, 1.50 mmol of crude material[28]) and *Se*-phenyl *p*-tolueneselenosulfonate (311 mg, 1.00 mmol) were photolyzed for 14 h in 10 mL of benzene. Flash chromatography (elution with 5% ethyl acetate–hexane) afforded 471 mg (84%) of **2g**: mp 53–54.5 °C (from hexane); IR (KBr) 1596, 1578, 1303, 1148, 1087 cm^{-1}; ^1H NMR (200 MHz) δ 7.65–7.24 (complex, 9 H), 5.86 (s, 1 H), 3.69 (m, 1 H), 2.41 (s, 3 H), 1.58–1.23 (complex, 26 H), 0.90 (m, 6 H); mass spectrum, *m/e* (relative intensity, %) 562 (M^+, 1.3), 157 (72), 91 (71), 55 (86), 43 (100). Anal. Calcd for $C_{31}H_{46}O_2SSe$: C, 66.27; H, 8.27. Found: C, 66.50; H, 8.47.

Adduct 2h. 2-Propynyl benzoate (1.60 g, 10.0 mmol) and *Se*-phenyl *p*-tolueneselenosulfonate (3.11 g, 10.0 mmol) were refluxed for 25 h in 20 mL of benzene in the presence of ca. 10 mg of AIBN. The reaction mixture was then evaporated in vacuo and recrystallized from ethanol to afford 3.79 g (80%) of **2h**: mp 129–131 °C; IR 1723, 1597, 1567, 1320, 1270, 1145, 1118, 1087 cm^{-1}; ^1H NMR (200 MHz) δ 8.12–7.30 (complex, 14 H), 5.78 (t, *J* = 1.7 Hz, 1 H), 5.74 (d, *J* = 1.7 Hz, 2 H), 2.42 (s, 3 H); mass spectrum, *m/e* (relative intensity, %) 472 (M^+, 0.2), 315 (21), 105 (100). Anal. Calcd for $C_{23}H_{20}O_4SSe$: C, 58.60; H, 4.28; S, 6.80. Found: C, 58.74; H, 4.11; S, 6.99.

Preparation of Allenic Sulfones 1 and Allyl Sulfones 4 (See Table I). In general, allyl sulfones **4** were produced from adducts **2** in situ and converted directly to the allenes **1**. The yields given in Table I are overall yields based on **2**. Samples of **4** were prepared in separate experiments for the purpose of characterization.

Allyl Sulfone 4a. The 43:27 mixture of **2a** and **4a** described above (100 mg, 0.285 mmol) was treated with LDA (0.285 mmol) in 2 mL of THF at −78 °C for 5 min. The reaction was quenched with aqueous NH_4Cl solution, diluted with ether, washed three times with aqueous NaCl, dried ($MgSO_4$), and evaporated in vacuo. NMR analysis showed quantitative conversion to **4a**. The product was recrystallized from chloroform–hexane: mp 83–84.5 °C; IR ($CHCl_3$) 1600, 1321, 1305, 1150, 1143 cm^{-1}; ^1H NMR (200 MHz) δ 7.78–7.25 (complex, 9 H), 5.71 (s, 1 H), 5.41 (s, 1 H), 3.97 (s, 2 H), 2.47 (s, 3 H); mass spectrum, *m/e* (relative intensity, %) 352 (M^+, 9), 197 (25), 157 (46), 116 (100), 91 (82). Anal. Calcd for $C_{16}H_{16}O_2SSe$: C, 54.70; H, 4.59; S, 9.13. Found: C, 54.79; H, 4.68; S, 8.95.

Allenic Sulfone 1a. Allyl sulfone **4a**, prepared as described above, was stirred for 5 min with a 20% molar excess of MCPBA in 5 mL of chloroform. The solution was washed three times with aqueous K_2CO_3 to remove the byproduct *m*-chlorobenzoic acid, dried ($MgSO_4$), and allowed to stand for 3 h at room temperature to complete the elimination of the selenoxide. The allenic sulfone **1a** was isolated by preparative TLC in 20% ethyl acetate–hexane, R_f 0.29. It crystallized on standing, mp 83–86 °C (lit.[29] mp 85–87 °C). Its structure was confirmed by its IR and NMR spectra.

Allyl Sulfones (*Z*)-4b and (*E*)-4b. Adduct **2b** (0.73 g, 1.89 mmol) and triethylamine (0.5 mL) were refluxed in 15 mL of chloroform for 3 h. Volatile material was removed in vacuo, and the residue contained a 6:1 mixture of (*Z*)-**4b** and (*E*)-**4b** (NMR integration). Flash chromatography (elution with 5% ethyl acetate–hexane) afforded 0.11 g of the less polar *E* isomer, ca. 0.1 g of a mixture containing both isomers, and 0.56 g of the more polar *Z* isomer. The less polar isomer had mp 87–88 °C (from ethanol): IR 1595, 1315, 1139, 1087, 904 cm^{-1}; ^1H NMR (400 MHz) δ 7.83–7.31 (complex, 9 H), 6.50 (s, 1 H), 4.23 (s, 2 H), 2.46 (s, 3 H); neither irradiation of the vinylic signal at δ 6.50, nor of the methylene signal at δ 4.23 produced any noticeable NOE in the other signal: mass spectrum, *m/e* (relative intensity, %) 386 (M^+, 15), 247 (24), 195 (84), 157 (65), 115 (48), 91 (100). Anal. Calcd for $C_{16}H_{15}ClO_2SSe$: C, 49.81; H, 3.92; S, 8.31. Found: C, 49.85; H, 3.81; S, 8.49. The more polar isomer had mp 92–93 °C (from chloroform–hexane): IR 1593, 1322, 1140, 915 cm^{-1}; ^1H NMR (400 MHz) δ 7.64–7.29 (complex, 9 H), 6.51 (t, *J* = 0.8 Hz, 1 H), 3.75 (d, *J* = 0.8 Hz, 2 H), 2.48 (s, 3 H); irradiation of either the vinylic signal at δ 6.51 or the methylene signal at δ 3.75 caused substantial NOE enhancement of the other signal; mass spectrum, *m/e* (relative intensity, %) 386 (M^+, 20), 247 (41), 195 (90), 157 (80), 115 (75), 91 (100). Anal. Calcd for $C_{16}H_{15}ClO_2SSe$: C, 49.81; H, 3.92; S, 8.31. Found: C, 49.68; H, 3.83; S, 8.17.

Allenic Sulfone 1b. A mixture of *Z* and *E* isomers of **4b**, prepared as described above, was oxidized with a 50% molar excess of MCPBA as in the case of **1a**, except that the resulting selenoxide was refluxed for 1 h in chloroform to effect elimination. The allenic sulfone **1b** was isolated by flash chromatography (elution with 10% ethyl acetate–hexane) as a pale yellow oil: IR 1963, 1596, 1332, 1303, 1150, 1083 cm^{-1}; ^1H NMR (200 MHz) δ 7.82 (d, *J* = 8 Hz, 2 H), 7.38 (d, *J* = 8 Hz, 2 H), 6.57 (d, *J* = 5.5 Hz, 1 H), 6.52 (d, *J* = 5.5 Hz, 1 H), 2.47 (s, 3 H); mass spectrum, *m/e* (relative intensity, %) 228 (M^+, 0.2), 180 (30), 155 (84), 91 (100). Anal. Calcd for $C_{10}H_9ClO_2S$: C, 52.52; H, 3.97; S, 14.02. Found: C, 52.02; H, 4.23; S, 14.14.

Allyl Sulfone 4c. Adduct **2c** (449 mg, 1.00 mmol) and potassium *tert*-butoxide (168 mg, 1.00 mmol) were stirred in 3 mL of THF at −78 °C for 1.5 h. The reaction mixture was diluted with ether, washed with aqueous NaCl solution, and dried ($MgSO_4$) to afford 442 mg (98%) of the allyl sulfone **4c** as a pale yellow oil: bp (short-path) 165–170 °C (0.4 Torr); IR 1597, 1577, 1320, 1146, 1087 cm^{-1}; ^1H NMR (200 MHz) δ 7.69–7.20 (complex, 9 H), 6.07 (t, *J* = 7.2 Hz, 1 H), 3.90 (s, 2 H), 2.45 (s, 3 H), 2.42–2.23 (m, 2 H), 1.25 (complex, 10 H), 0.87 (crude t, *J* = 6.5 Hz, 3 H); mass spectrum, *m/e* (relative intensity, %) 450 (M^+, 8), 294 (58), 157 (72), 91 (91), 43 (100). Anal. Calcd for $C_{23}H_{30}O_2SSe$: C, 61.44; H, 6.74. Found: C, 61.24; H, 6.77.

Allenic Sulfone 1c. The crude allyl sulfone **4c**, prepared as described above, was dissolved in chloroform and treated with 1.5 molar equiv of MCPBA. After 10 min, the reaction mixture was rapidly washed with aqueous $NaHCO_3$, water, and dried ($MgSO_4$). The chloroform solution of the resulting selenoxide was refluxed for 2 h, and the reaction mixture was worked up in the same way. NMR analysis of the residue indicated the presence of **1c** and the propargyllic sulfone **5c** in the ratio of 86:14. Preparative TLC (15% ethyl acetate–hexane) afforded a mixture of the unseparated isomers **1c** and **5c**, R_f 0.48, with the following properties: IR 2236 (weak), 1954, 1597, 1321, 1148, 1086 cm^{-1}; ^1H NMR (200 MHz) δ 6.18 (m, allenic H of **1c**), 5.84 (m, allenic H of **1c**), as well as signals attributed to **5c** (vide infra).

Conversion of Allenic Sulfone 1c to Propargyllic Sulfone 5c. The mixture of **1c** and **5c** (33 mg, 0.11 mmol), prepared as described above, was dissolved in 1 mL of chloroform containing 10 mg of ethyldiisopropylamine. After 12 h, the mixture was washed with aqueous solutions of HCl, K_2CO_3, and NaCl, dried ($MgSO_4$), and evaporated in vacuo. NMR analysis showed complete conversion to **5c**: pale yellow oil; bp (short path) 136–138 °C (0.25 Torr); IR 2236, 1598, 1325, 1167, 1151, 1135, 1087 cm^{-1}; ^1H NMR (200 MHz) δ 7.85 (d, *J* = 8 Hz, 2 H), 7.37 (d, *J* = 8 Hz, 2 H), 3.92 (t, *J* = 2.5 Hz, 2 H), 2.47 (s, 3 H), 2.16–2.11 (m, 2 H), 1.42–1.26 (complex, 10 H), 0.89 (crude t, *J* = 6 Hz, 3 H); mass spectrum, *m/e* (relative intensity, %) 292 (M^+, 0.3), 157 (36), 139 (73), 95 (97), 91 (100). Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.80; H, 8.28. Found: C, 69.84; H, 8.28. Similar results were obtained with triethylamine or DABCO instead of ethyldiisopropylamine.

Allyl Sulfone 4d. The adduct **2d** (393 mg, 1.00 mmol) and potassium *tert*-butoxide (168 mg, 1.5 mmol) were stirred in 10 mL of THF at −78 °C for 2 h. The reaction was worked up as in the case of **4c**, and the product was purified by flash chromatography (elution with 10% ethyl acetate–hexane) to afford 377 mg (96%) of **4d** as a 10:1 mixture of *Z* and *E* isomers, which showed all of the NMR signals of the pure *Z* isomer (vide infra), as well as ones at δ 6.27 (t, *J* = 7.5 Hz) and 4.06 (s) attributed to the vinylic H and the sulfone-substituted methylene group, respectively, of the *E* isomer. Recrystallization of the mixture from chloroform–hexane afforded the pure *Z* isomer: mp 55–56 °C; IR 1595, 1303, 1143, 1087 cm^{-1}; ^1H NMR (400 MHz) δ 7.69–7.22 (9 H), 6.09 (t, *J* = 7.2 Hz, 1 H), 3.91 (s, 2 H), 2.46 (s, 3 H), 2.25 (dt, *J* = 7.3, 7.3 Hz, 2 H), 1.38 (tq, *J* = 7.3, 7.3 Hz, 2 H), 0.89 (t, *J* = 7.3 Hz, 3 H); irradiation of either the vinylic signal at δ 6.09 or the methylene signal at δ 3.91 caused substantial NOE enhancement of the other signal; mass spectrum, *m/e* (relative intensity, %) 394 (M^+, 4), 238 (20), 157 (38), 91 (90), 81 (100).

(28) The crude acetylene was employed in excess to compensate for the presence of several unidentified impurities. This was found to be more convenient than the use of a stoichiometric amount of the pure acetylene. The reported yield is based on the amount of the selenosulfonate used.

(29) McDowell, S. T.; Stirling, C. J. M. *J. Chem. Soc. B* **1967**, 351.

Anal. Calcd for $C_{19}H_{22}O_2SSe$: C, 58.01; H, 5.64. Found: C, 57.62; H, 5.68.

Allenic Sulfone 1d. The mixture of *Z* and *E* isomers of **4d**, prepared as described above, was subjected to the same oxidation and elimination procedure as employed for **1b**. The product was purified by preparative TLC (20% ethyl acetate–hexane) to afford an unseparated 94:6 mixture of **1d**[5b] and the propargyllic sulfone **5d**: R_f 0.47; IR 1954, 1597, 1321, 1148, 1085 cm^{-1}; ^1H NMR (200 MHz) signals attributed to allene **1d** δ 7.78 (d, J = 8.3 Hz, 2 H), 7.33 (d, J = 8.3 Hz, 2 H), 6.18 (dt, J = 6.0, 3.0 Hz, 1 H), 5.83 (dt, J = 7.0, 6.0 Hz, 1 H), 2.44 (s, 3 H), 2.12 (m, 2 H), 1.45 (m, 2 H), 0.93 (t, J = 7.3, 3 H). An additional signal at δ 3.92 (t, J = 2.4 Hz) was assigned to **5d**.

Allyl Sulfone 4e. Adduct **2e** (485 mg, 1.00 mmol) and 2 mL of triethylamine were refluxed 5 h in 15 mL of chloroform. Volatile material was evaporated in vacuo, and the residue crystallized spontaneously to afford **4e** quantitatively: mp 94–95 °C (from ethanol); IR 1716, 1315, 1262, 1151, 1086 cm^{-1}; ^1H NMR (400 MHz) δ 8.08–7.24 (complex, 14 H), 6.28 (t, J = 6.2 Hz, 1 H), 4.99 (d, J = 6.2 Hz, 2 H), 3.93 (s, 2 H), 2.40 (s, 3 H); irradiation of the vinylic H at δ 6.28 resulted in substantial NOE enhancement of both of the methylene signals at δ 4.99 and δ 3.93, and irradiation of the methylene protons at δ 3.93 enhanced the vinylic signal at δ 6.28; mass spectrum, m/e (relative intensity, %) 364 (M^+ – $PhCO_2H$, 18), 157 (47), 155 (50), 128 (88), 122 (87), 105 (98), 91 (97), 77 (100). Anal. Calcd for $C_{24}H_{22}O_4SSe$: C, 59.38; H, 4.57; S, 6.61. Found: C, 59.57; H, 4.45; S, 6.89.

Allenic Sulfone 1e. Allyl sulfone **4e**, prepared as described above, was suspended in 5 mL of ether, and 3 molar equiv of MCPBA was added in portions. The selenide first dissolved, and a new precipitate (selenoxide) formed after a few minutes. After 5 min, the latter was filtered, dried, and refluxed 1 h in 5 mL of chloroform. The solvent was removed under reduced pressure, and the product **1e** was isolated by flash chromatography (elution with 20% ethyl acetate–hexane): mp 104–105 °C (from ethanol); IR 1966, 1721, 1597, 1314, 1268, 1144, 1118, 1083 cm^{-1}; ^1H NMR (200 MHz) δ 8.02–7.24 (complex, 9 H), 6.41 (dt, J = 6.0, 2.9 Hz, 1 H), 6.08 (dt, J = 6.0, 5.9 Hz, 1 H), 4.90 (dd, J = 5.9, 2.9 Hz, 2 H), 2.38 (s, 3 H); mass spectrum, m/e (relative intensity, %) 173 (M^+ – $ArSO_2$, 45), 122 (35), 105 (100), 91 (60), 77 (62). Anal. Calcd for $C_{18}H_{16}O_4S$: C, 65.83; H, 4.91; S, 9.77. Found: C, 65.77; H, 4.87; S, 10.04.

Allyl Sulfone 4f. The adduct **2f** (148 mg, 0.35 mmol) and LDA (0.53 mmol) were stirred for 2 h in 3 mL of THF at –78 °C. The reaction was worked up as in the case of **4a**. NMR analysis of the crude product showed a 62% conversion of **4f**, along with some unreacted **2f**. Product **4f** was isolated by preparative TLC (20% ethyl acetate–hexane): R_f 0.45; mp 116–117 °C (from chloroform–hexane); IR 1596, 1564, 1314, 1300, 1289, 1261, 1143, 1083, 1064 cm^{-1}; ^1H NMR (200 MHz) δ 7.74–7.20 (complex, 9 H), 4.24 (s, 2 H), 2.57 (m, 2 H), 2.46 (s, 3 H), 2.34 (m, 2 H), 1.56 (complex, 6 H); mass spectrum, m/e (relative intensity, %) 420 (M^+, 2), 264 (31), 107 (100), 91 (67), 79 (62). Anal. Calcd for $C_{21}H_{24}O_2SSe$: C, 60.13; H, 5.77. Found: C, 60.16; H, 5.99.

Allenic Sulfone 1f. The allyl sulfone **4f**, prepared as described above, was oxidized with a 50% molar excess of MCPBA in chloroform. After 15 min, the reaction mixture was washed three times with aqueous K_2CO_3 solution and dried ($MgSO_4$). DABCO (3 molar equiv) was added, and the solution was refluxed for 24 h, washed with 5% HCl and aqueous NaCl, and dried ($MgSO_4$). The product **1f** was isolated by preparative TLC (20% ethyl acetate–hexane), R_f 0.55, with IR and NMR spectra in accord with those reported in the literature.[4a]

Isomerization of (*E*)-2g to (*Z*)-2g: The adduct (*E*)-**2g** (156 mg, 0.28 mmol) and LDA (0.28 mmol) were stirred for 12 min in 3 mL of THF at –78 °C, and worked up as in the case of **4a**, to afford a quantitative yield of (*Z*)-**2g**: mp 48.5–50 °C (from hexane); IR (KBr) 1597, 1550, 1311, 1302, 1141, 1084 cm^{-1}; ^1H NMR (200 MHz) δ 7.97–7.27 (complex, 9 H), 6.47 (s, 1 H), 2.46 (s, 3 H), 2.10 (m, 1 H), 1.27–0.84 (complex, 32 H); mass spectrum, m/e (relative intensity, %) 562 (M^+, 0.6), 194 (16), 157 (30), 91 (27), 55 (54), 43 (100). Anal. Calcd for $C_{31}H_{46}O_2SSe$: C, 66.27; H, 8.27. Found: C, 66.31; H, 8.49.

Allenic Sulfone 1g. The isomerized adduct (*Z*)-**2g**, prepared as described above, was subjected to oxidation and elimination as in the preparation of **1f**, except that heating with DABCO was performed for 2.5 h at 100 °C in benzene (sealed vessel). The product **1g** was isolated by preparative TLC (benzene) as a pale yellow gum (GC purity >96%): R_f 0.47; IR 1954, 1597, 1322, 1146, 1085 cm^{-1}; ^1H NMR (200 MHz) δ 7.77 (d, J = 8.3 Hz, 2 H), 7.31 (d, J = 8.3 Hz, 2 H), 6.16 (m, 1 H), 2.43 (s, 3 H), 2.07–1.99 (m, 4 H), 1.24 (complex, 22 H), 0.88 (crude t, 6 H); mass spectrum, m/e (relative intensity, %) 404 (M^+, 0.4), 249 (6), 109 (32), 95 (77), 91 (64), 81 (84), 67 (63), 55 (84), 43 (100); exact mass calcd for $C_{25}H_{40}O_2S$ 404.2749, found 404.2735.

Allyl Sulfone 4h. The adduct **2h** (0.86 g, 1.83 mmol) was refluxed in 20 mL of chloroform containing 3 mL of triethylamine for 3 h. Volatile material was removed in vacuo, and NMR analysis of the residue indicated quantitative isomerization to **4h**. Recrystallization from ethanol afforded 0.77 g (90%) of **4h**: mp 122–124 °C; IR 1732, 1633, 1598, 1313, 1261, 1138, 1083 cm^{-1}; ^1H NMR (200 MHz) δ 8.01–7.24 (complex, 15 H), 3.94 (d, J = 1.8 Hz, 2 H), 2.46 (s, 3 H); irradiation at δ 7.72 (vinylic H) caused substantial NOE enhancement of the signal at δ 3.94 (CH_2) and its collapse to a singlet; irradiation of the signal at δ 3.94 caused substantial NOE enhancement of the signal at δ 7.72; mass spectrum, m/e (relative intensity, %) 472 (M^+, 1.2) 212 (16), 105 (100). Anal. Calcd for $C_{23}H_{20}O_4SSe$: C, 58.60; H, 4.28; S, 6.80. Found: C, 58.49; H, 4.05; S, 6.76.

Allyl Sulfone 4i. The adduct **2i** (722 mg, 1.50 mmol) and LDA (2.00 mmol) were stirred for 15 min in 12 mL of THF at –78 °C. The reaction was worked up as in the case of **4a**, and the crude product was purified by flash chromatography (elution with 10% ethyl acetate–hexane) to afford 528 mg (73%) of **4i**: mp 90–92 °C (from hexane); IR 1622, 1597, 1311, 1289, 1247, 1147, 1084 cm^{-1}; ^1H NMR (200 MHz) δ 7.71–7.17 (complex, 9 H), 6.66 (s, 1 H), 3.88 (s, 2 H), 2.45 (s, 3 H), 0.85 (s, 9 H), 0.09 (s, 6 H); mass spectrum, m/e (relative intensity, %) 482 (M^+, <0.1), 213 (56), 183 (28), 149 (100). Anal. Calcd for $C_{22}H_{30}O_3SSeSi$: C, 54.86; H, 6.28; S, 6.66. Found: C, 54.92; H, 6.28; S, 7.06.

Preparation of α,γ-Disubstituted Allenic Sulfones 7–12 (See Table II). Allenic Sulfone 7. The 43:27 mixture of **2a** and **4a** described earlier (480 mg, 1.37 mmol) and LDA (1.50 mmol) were stirred for 10 min in 10 mL of THF at –78 °C. Iodomethane (0.19 mL, 3.0 mmol) was added, and the mixture was slowly warmed to 0 °C, quenched with water, diluted with ether, washed three times with aqueous NaCl, dried ($MgSO_4$), and evaporated in vacuo. Flash chromatography (elution with 10% ethyl acetate–hexane) afforded 466 mg (93%) of the methylated intermediate **6** (R = H; R′ = Me). A portion of this material (241 mg, 0.660 mmol) was stirred with MCPBA (1 mmol) in 3 mL of chloroform for 5 min. The solution was washed three times with aqueous $NaHCO_3$, dried ($MgSO_4$), and refluxed for 1 h. The products were separated by preparative TLC (20% ethyl acetate–hexane) to afford 30 mg of recovered **6** (R = H; R′ = Me), R_f 0.44, and 72 mg of allene **7** (60% based on recovered **6**; overall yield from the mixture of **2a** and **4a**: 56%), R_f 0.35; mp 63–66 °C (lit.[5b] mp 64–65 °C).

Allenic Sulfone 8. The adduct **2b** (188 mg, 0.487 mmol) was isomerized to the allylic sulfone *E,Z*-**4b** as described earlier, except that the solvent was a 10:1 mixture of THF–D_2O instead of chloroform. The NMR spectrum of the product showed complete exchange of the methylene signals at δ 4.23 and 3.75, and no exchange of the vinylic signals at δ 6.5. This product was stirred in 4 mL of chloroform containing 0.2 mL of D_2O.[30] MCPBA (0.55 mmol) was added, and the solution was refluxed for 0.5 h. The mixture was cooled to room temperature, and enough MCPBA was added to discharge the yellow color of the diphenyl diselenide byproduct. The solution was washed three times with aqueous $NaHCO_3$ solution, dried ($MgSO_4$), concentrated, and purified by flash chromatography (elution with 10% ethyl acetate–hexane) to afford 94 mg (85%) of the deuterated allene **8**. The ^1H NMR spectrum (200 MHz) showed only one allenic proton at δ 6.57 (broad s, 1 H), and only traces (<5%) of the signals from the protio derivative **1b**.

Allenic Sulfone 9. The adduct **2c** (295 mg, 0.66 mmol) and LDA (1.1 mmol) were stirred in 3 mL of THF at –78 °C. After 10 min, iodomethane (0.15 mL, 2.4 mmol) was added, and the

(30) When D_2O was omitted from this step, substantial formation of the protio derivative **1b** was observed, indicating that further exchange can take place during the selenoxide elimination.

mixture was stirred for an additional 15 min at −78 °C. The reaction was quenched with water, the mixture was diluted with ether, washed three times with aqueous NaCl, dried ($MgSO_4$), and evaporated in vacuo. The product was oxidized to the selenoxide, as in the procedure for the preparation of **7**, and the selenoxide was pyrolyzed in refluxing chloroform for 2 h. The allene **9** (160 mg, 80%) was isolated by preparative TLC (20% ethyl acetate–hexane) as a pale yellow oil, R_f 0.52; bp (short path) 120–125 °C (0.05 Torr); IR 1960, 1597, 1318, 1154, 1076 cm^{-1}; ^1H NMR (200 MHz) δ 7.77 (d, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H), 5.69 (m, 1 H), 2.44 (s, 3 H), 2.07 (m, 2 H), 1.94 (d, J = 2.9 Hz, 3 H), 1.2 (complex, 10 H), 0.88 (crude t, 3 H); mass spectrum, m/e (relative intensity, %) 306 (M^+, 1.3), 157 (38), 109 (57), 95 (100), 91 (88). Anal. Calcd for $C_{18}H_{26}O_2S$: C, 70.54; H, 8.55; S, 10.46. Found: C, 70.56; H, 8.73; S, 10.43.

Allenic Sulfone 10. The adduct **2c** (149 mg, 0.330 mmol) was treated with LDA in THF at −78 °C as in the preceding procedure. Excess ethyl iodide was added, and stirring at −78 °C was continued for 30 min. The reaction mixture was quenched with water, diluted with ether, washed three times with aqueous $NaHCO_3$ solution, dried ($MgSO_4$), concentrated, and separated by preparative TLC (20% ethyl acetate–hexane) to afford 54 mg (51%) of **10** as a homogeneous (TLC) pale yellow oil: R_f 0.55; IR 1959, 1597, 1316, 1150, 1084 cm^{-1}; ^1H NMR (200 MHz) δ 7.76 (d, J = 8 Hz, 2 H), 7.31 (d, J = 8 Hz, 2 H), 5.78 (tt, J = 6.8, 3.5 Hz, 1 H), 2.44 (s, 3 H), 2.27 (dq, J = 7.4, 3.5 Hz, 2 H), 2.07 (m, 2 H), 1.2 (complex, 10 H), 1.01 (t, J = 7.4 Hz, 3 H), 0.88 (crude t, 3 H); mass spectrum, m/e (relative intensity, %) 320 (M^+, 0.4), 157 (21), 109 (74), 95 (73), 91 (70), 81 (77), 67 (72), 55 (93), 41 (100); exact mass calcd for $C_{19}H_{28}O_2S$ 320.1810, found 320.1829.

Allenic Sulfone 11. The adduct **2c** (197 mg, 0.500 mmol) was deprotonated with LDA, alkylated in situ with excess allyl iodide, and permitted to eliminate spontaneously, as in the preceding procedure. The product **11** was isolated (98 mg, 59%) by preparative TLC (benzene) as a pale yellow oil: R_f 0.60; IR 1959, 1641, 1597, 1321, 1150 cm^{-1}; ^1H NMR (200 MHz) δ 7.77 (d, J = 8 Hz, 2 H), 7.32 (d, J = 8 Hz, 2 H), 5.80–5.57 (m, 2 H), 5.22–5.01 (m, 2 H), 3.02 (m, 2 H), 2.44 (s, 3 H), 2.18–2.01 (m, 2 H), 1.26 (complex, 10 H), 0.89 (crude t, 3 H); mass spectrum, m/e (relative intensity, %) 332 (M^+, 0.3), 91 (100). Anal. Calcd for $C_{20}H_{28}O_2S$: C, 72.25; H, 8.49; S, 9.64. Found: C, 72.65; H, 8.59; S, 9.24. A minor impurity with ^1H NMR signals at δ 3.85 (m), 2.63 (m), and 2.46 (s) was tentatively identified as 4-(*p*-toluenesulfonyl)-1-tridecen-5-yne, the acetylene isomer of **11**.

Allenic Sulfone 12. The adduct **2c** (295 mg, 0.660 mmol) was deprotonated with LDA, silylated in situ with excess trimethylsilyl chloride, and subjected to oxidation–elimination as in the procedure for the preparation of **9**. The product **12** was isolated (197 mg, 82%) as a homogeneous (GC), pale yellow oil by Kugelrohr distillation: bp 110 °C (0.1 Torr); IR 1939, 1597, 1312, 1301, 1249, 1143, 1086 cm^{-1}; ^1H NMR (200 MHz) δ 7.73 (d, J = 8 Hz, 2 H), 7.26 (d, J = 8 Hz, 2 H), 5.29 (t, J = 7.0 Hz, 1 H), 2.41 (s, 3 H), 1.88 (m, 2 H), 1.20 (complex, 10 H), 0.87 (crude t, 3 H), 0.24 (s, 9 H); mass spectrum, m/e (relative intensity, %) 364 (M^+, 0.5), 149 (28), 91 (32), 73 (100). Anal. Calcd for $C_{20}H_{32}O_2SSi$: C, 65.89; H, 8.85; S, 8.79. Found: C, 65.42; H, 9.14; S, 8.31.

Preparation of Allenes. Ethenylidenecyclohexane (15). Allyl sulfone **4f** (42 mg, 0.10 mmol), 5% sodium amalgam (0.7 g, 1.5 mmol), and Na_2HPO_4 (60 mg, 0.50 mmol) were stirred for 6 h in 10 mL of methanol. The methanol was decanted and extracted three times with pentane. The pentane was washed with aqueous NaCl solution, dried ($MgSO_4$), and concentrated. Flash chromatography (elution with pentane) afforded 16.2 mg (62%) of an 8:1 mixture (NMR integration) of selenides **13** and **14**: ^1H NMR (200 MHz) signals attributed to **13** were observed at δ 7.57–7.18 (complex, 5 H), 2.56 (m, 2 H), 2.35 (m, 2 H), 2.08 (s, 3 H), 1.6–0.8 (complex, 6 H). Additional signals attributed to **14** were observed at δ 5.51 (d, J = 1.1 Hz) and δ 5.02 (s). This mixture was oxidized to the corresponding selenoxides with 0.09 mmol of MCPBA in chloroform. The solution was washed three times with aqueous K_2CO_3, dried ($MgSO_4$), and evaporated in vacuo. The residue was pyrolyzed in 0.8 mL of benzene containing 20 mg of DABCO at 90 °C for 20 h. GC analysis of the mixture using undecane as the internal standard indicated the formation of allene **15** and acetylene **16** in yields of 50% and 22%, respectively. The identity of **15** was confirmed by the presence of a strong peak at 1959 cm^{-1} (lit.[31] 1955 cm^{-1}) in the IR spectrum of the mixture and by its GC–mass spectrum, m/e (relative intensity, %) 108 (M^+, 93), 107 (10), 93 (98), 91 (48), 80 (36), 79 (100), 77 (70). The identity of **16** was confirmed by comparison of its GC–mass spectrum with that of an authentic sample.

1,2-Decadiene (17). Allyl sulfone **4c** (0.67 g, 1.5 mmol), 5% sodium amalgam (3.47 g, 7.50 mmol), and Na_2HPO_4 (1.29 g, 9.00 mmol) were stirred in 8 mL of methanol for 4 h. The supernatant liquid was decanted, concentrated in vacuo, and separated by flash chromatography (elution with hexane) to afford 241 mg (55%) of a mixture of isomeric vinyl selenides. Oxidation of this mixture with MCPBA was carried out as in the preceding procedure, followed by pyrolysis of the resulting selenoxides in the presence of DABCO in benzene at 95 °C (sealed vessel) for 24 h. The solution was washed with 5% aqueous HCl, and GC analysis of the product mixture, using decane as the internal standard, indicated the presence of allene **17** (49%), 1-decyne (**18**, 18%), and 2-decyne (**19**, 7%). The identities of **18** and **19** were confirmed by comparison of their GC–mass spectra with those of authentic samples. Allene **17** was identified by its GC–mass spectrum, m/e (relative intensity, %) 138 (M^+, 1) 110 (15), 95 (15), 81 (26), 67 (43), 55 (43), 54 (100), 53 (23). Careful concentration of the crude product afforded an oil with prominent IR and ^1H NMR signals matching those previously reported[32] for **17**. The pyrolysis of the selenoxide was repeated using C_6D_6 as the solvent, and the crude mixture displayed ^{13}C NMR signals at δ 209.5 (C-2 of **17**), 90.7 (C-3 of **17**), 85.0 (C-2 of **18**), 79.9 and 75.9 (C-2 and C-3 of **19**), 71.4 (C-1 of **17**), 69.8 (C-1 of **18**).

4,5-Tridecadiene (22). *n*-Propylmagnesium chloride (0.63 mmol) in THF was slowly added to a stirred solution of allyl sulfone **4c** (156 mg, 0.35 mmol) and copper(II) acetylacetonate (5 mg) in 5 mL of THF. After 6 h, the reaction mixture was washed with aqueous NH_4Cl and aqueous NaCl, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (elution with pentane) afforded 47 mg (40%) of selenide **20**: ^1H NMR (200 MHz) δ 7.28–7.21 (m, 5 H), 5.85 (t, J = 7.1 Hz, 1 H), 2.25 (m, 4 H), 1.3 (complex, 14 H), 0.89 (m, 6 H). This product was subjected to oxidation–elimination as described in the preceding procedure. GC analysis of the product mixture, using decane as the internal standard, indicated the formation of 44% of allene **22**, identified by its GC–mass spectrum, m/e (relative intensity, %) 180 (M^+, 8), 96 (96), 81 (95), 67 (97), 54 (100). Careful concentration of the crude product afforded an oil with prominent IR and ^1H NMR signals at 1961 cm^{-1} and δ 5.06 (m). Acetylenes **23** (17%) and **24** (2%) were also detected and identified by comparison of the GC–mass spectrum of the mixture with those of authentic samples.

4,5-Decadiene (28). The adduct **25** (896 mg, 2.00 mmol), 5% sodium amalgam (4.60 g, 10.0 mmol), and Na_2HPO_4 (1.70 g, 12.0 mmol) were stirred for 12 h in 10 mL of methanol and 2 mL of THF. The supernatant liquid was decanted and concentrated, and the residue was separated by flash chromatography (elution with hexane) to afford 300 mg (51%) of (*Z*)-5-(phenylseleno)-5-decene (**27**), a pale yellow oil with a ^1H NMR (200 MHz) signal assigned to the vinylic H at δ 5.84 (tt, J = 7.0, 1.1 Hz), [lit.[33] δ 5.80 (t, J = 7 Hz)]. This product was subjected to oxidation–elimination via the procedure used for the preparation of allene **17**. GC analysis of the product mixture, using decane as the internal standard, indicated the formation of 76% of allene **28**,[34] identified by its GC–mass spectrum, m/e (relative intensity, %) 138 (M^+, 8), 96 (97), 95 (90), 81 (96), 67 (100), 54 (97). Only traces (ca. 1 %) of 5-decyne were detected. Careful concentration of the crude product afforded an oil with a strong IR absorption at 1962 cm^{-1} and a ^1H NMR (200 MHz) signal assigned to the allenic hydrogens at δ 5.06 (m).

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