1-Phenyl-*c*-2-methylcyclohexan-*r*-1-ol (36a): distillation bp 86–89 °C (0.2 mmHg); ^{1}H NMR δ 0.60 (d, 3 H, J = 7.0 Hz), 1.20–2.15 (m, 9 H), 3.20 (s, 1 H), 7.31 (m, 5 H); IR (CCl_4) 3610, 3500, 3080, 3055, 3020, 2925, 2850, 1640, 1490, 1450, 1370, 1025, 750, 710, 695 cm^{-1}.

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Registry No. 1, 626-87-9; 2, 25118-28-9; 3, 42474-23-7; 4, 70690-24-3; 5, 109-94-4; 6, 141-78-6; 7, 105-37-3; 8, 5452-75-5; 9, 3289-28-9; 10, 93-89-0; 11, 94-08-6; 12, 7335-27-5; 13, 94-30-4; 14a, 16467-04-2; 14b, 16467-13-3; 15a, 22865-14-1; 15b, 22865-01-6; 16a, 22865-01-6; 16b, 109433-88-7; 17a, 109433-94-5; 17b, 109433-95-6; 18a, 109433-89-8; 18b, 109433-90-1; 19a, 109466-71-9; 19b, 109433-91-2; 20a, 109433-92-3; 20b, 109433-93-4; 21a, 25144-05-2; 21b, 25144-04-1; 22a, 16467-06-4; 22b, 16467-12-2; 23a, 101934-19-4; 23b, 101934-20-7; 24a, 22865-13-0; 24b, 22862-81-3; 25a, 75968-43-3; 25b, 101934-21-8; 26a, 75968-45-5; 26b, 101934-22-9; 27a, 75968-44-4; 27b, 101934-23-0; 33, 627-96-3; 34a, 7443-70-1; 34b, 7443-52-9; 35a, 19879-11-9; 35b, 19879-12-0; 36a, 30689-79-3; 36b, 30689-80-6.

Studies on the Addition of Allyl Oxides to Sulfonylallenes. Preparation of Highly Substituted Allyl Vinyl Ethers for Carbanionic Claisen Rearrangements

Scott E. Denmark,*[1a] Michael A. Harmata,[1b,c] and Kathleen S. White[†]

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801

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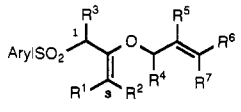
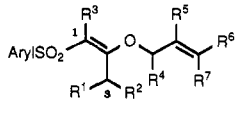
Thirty-five allyl vinyl ethers bearing an arylsulfonyl anion-stabilizing group have been prepared by addition of allylic alkoxides to (arylsulfonyl)allenes. The allyl vinyl ethers are produced as either β,γ-unsaturated or α,β-unsaturated sulfones depending upon the substitution pattern of the allene and the reaction conditions. A wide variety of substitution patterns are available by using this method. Factors that control the position and stereochemistry of the vinyl ether double bond are discussed.

Introduction

In preliminary papers[2] we have reported the carbanion-accelerated Claisen rearrangements (Scheme I) of allyl vinyl ethers with arylsulfonyl-stabilized anions. To investigate the scope of this reaction and its suitability as a general synthetic method we needed an efficient preparation of a variety of allyl vinyl ethers of the type 1 (β,γ-unsaturated) and type 2 (α,β-unsaturated). The



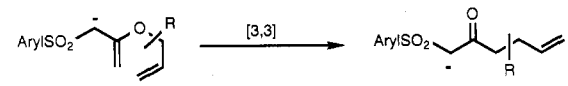
1



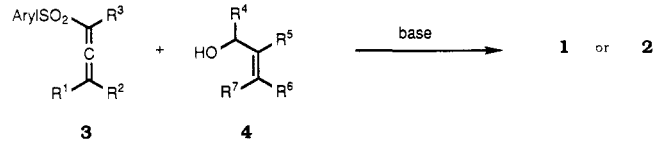
2

disconnection we selected which allowed for good versatility in assembling different substitution patterns involves the combination of (arylsulfonyl)allenes 3 with allylic alcohols 4 activated as their alkoxide salts (Scheme II).[3] The addition of oxygen,[7] nitrogen,[7a,8] and sulfur[7c,9] nucleophiles to sulfonylallenes is well documented.[10] Of particular interest to us were the classic studies by Stirling[7a] who first demonstrated the formation of vinyl ethers by base-catalyzed addition of methanol to (phenylsulfonyl)propadiene. Unfortunately in this and subsequent papers by Stirling et al. the alcohols are inexpensive, expendable, and often used as solvents. For the carbanionic Claisen rearrangement to be of value in more complex syntheses we need to construct the precursors from stoichiometric reagents in good yields. Therefore, the purpose of this study was to develop a reliable protocol for the preparation of 1 and 2 which met the criteria of (1) high yield, (2) versatility, (3) control of double bond position and configuration, and (4) use of minimal amounts of alcohols 4.

Scheme I

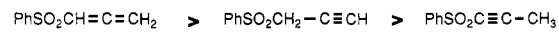


Scheme II



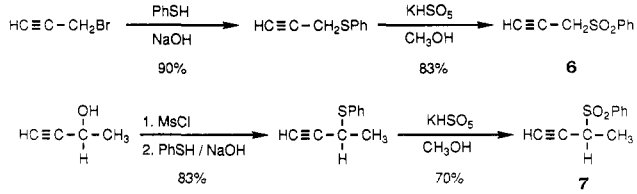
3 4

Scheme III

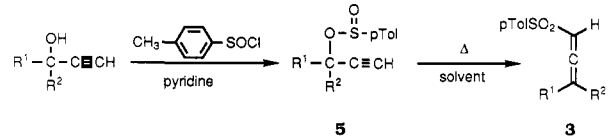


3a 6 6'

Scheme IV



Scheme V



5 3

[†] In part.

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Table I. Preparation of Aryl Sulfinates and (Arylsulfonyl)allenes 3

entry	R^1	R^2	ester	yield, %	solvent[a]	time, h	allene	yield, %
1	Me	H	**5b**	86	PhCl	2.5	**3b**	59
2	Me	Me	**5c**	65	CCl_4	24	**3c**	96
3	Et	Et	**5d**	84	CCl_4	13.5	**3d**	98
4	*i*-Pr	*i*-Pr	**5e**	73	CCl_4	3	**3e**	89
5	$(CH_2)_5$		**5f**	82	CCl_4	31	**3f**	67
6	$(CH_2CH_2CH(t\text{-}Bu)CH_2CH_2)$		**5g**	68	CH_3CN	21	**3g**	70
7	Ph	H	**5h**	93	CH_3CN[b]	5.25	**3h**	43

[a] All reactions were run at reflux. [b] $NaHCO_3$ added as buffer.

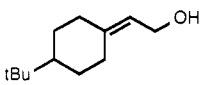
Results

1. Preparation of (Arylsulfonyl)allenes 3. The parent, unsubstituted allene **3a** ($R^1 = R^2 = R^3 = H$) and the 2-methylallene **3i** ($R^1 = R^2 = H$, $R^3 = CH_3$) did not have to be prepared directly. Stirling has shown that among the three possible acetylenic and allenic tautomers of **3a** (Scheme III) the allene is the thermodynamically most stable and kinetically most reactive toward nucleophilic addition.[7a] Thus, treatment of any tautomer with a basic reagent led first to isomerization to the allene followed by addition. If desired, **3a** could be obtained from [2-propynylsulfonyl]benzene (**6**) by filtration through a column of basic alumina. The preparations of **6** and **7** (the precursor to **3i**) were straightforward as outlined in Scheme IV.

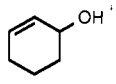
The remainder of the allenes **3** were prepared by thermal [2,3]-rearrangement[11] of the arenesulfinate esters **5** of the corresponding acetylenic carbinols (Scheme V). The results for the preparation of both substances are collected in Table I. Esterification of the carbinols proceeded in good yield with *p*-toluenesulfinyl chloride in pyridine to provide the sulfinate esters **5b–h** as stable, characterizable compounds. Thermolysis of these esters was carried out in CCl_4, CH_3CN or C_6H_5Cl at reflux to afford the crystalline allenes **3b–h**. The higher temperature was necessary only for **3b**.[12] The yields were high and the reactions were clean in general except for **2b** and **2h** for which competing, heterolytic processes are likely in the rearrangement step.

Table II. Allylic Alcohols 4 Used To Prepare 1 and 2

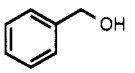
compd	R^4	R^5	R^6	R^7
4a	H	H	H	H
4b	H	H	CH_3	H
4c	H	H	H	CH_3
4d	H	CH_3	H	H
4e	CH_3	H	H	H
4f	Et	H	H	H
4g	*i*-Pr	H	H	H
4h	H	H	Ph	H
4i	H	H	Me_3Si	H
4j	H	H	CH_3	CH_3
4k	H	H	Et	Et
4l	H	H	*i*-Pr	*i*-Pr
4m	H	H	$(CH_2)_5$	
4n	H	$(CH_2)_5$		H



4o



4p



4q

4r

2. Preparation of Allyl Vinyl Ethers 1 and 2. Due to the large number of variables involved, the preparation of the allyl vinyl ethers required a great deal of experimentation. The most important factor that influences the addition is the substitution on the allene or allene precursor. Therefore the products have been separated into three classes; C(3) unsubstituted, C(3) or C(1) monosubstituted, and C(3) disubstituted, and will be discussed separately.[14] The allylic alcohols used in these preparations (Table II) have been obtained from commercial sources, from the literature procedures, or as described in the Experimental Section. Only those described herein warrant comment. *trans*- and *cis*-2-butenol were obtained by reduction of 2-butyn-1-ol with $LiAlH_4$ in DME[15a] and H_2/Lindlar, respectively. A reproducible and selective cis-hydrogenation method is lacking as this, as well as H_2/Ni_3B_2,[15b,c] were capricious in our hands.

2.1. C(3)-Unsubstituted Allyl Vinyl Ethers. This class of allyl vinyl ethers proved the most difficult to prepare in good yield due to the ready isomerization of **1**

(1) (a) Fellow of the Alfred P. Sloan Foundation (1985–1987), NSF Presidential Young Investigator (1985–1988). (b) Taken in part from: Harmata, M. A. Ph.D. Thesis, University of Illinois, Urbana, IL 1985. (c) Present Address: Department of Chemistry, University of Missouri—Columbia, Columbia, MO 65211.

(2) (a) Denmark, S. E.; Harmata, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 4972. (b) Denmark, S. E.; Harmata, M. A. *J. Org. Chem.* **1983**, *48*, 3369. (c) Denmark, S. E.; Harmata, M. A. *Tetrahedron Lett.* **1984**, *25*, 1543.

(3) This approach was also used with sulfinylallenes[4] and phosphorylallenes[5] to prepare allyl vinyl ethers for Claisen rearrangements. Subsequently, Blechert has reported the addition of aryl hydroxylamines and nitrones to a variety of activated allenes to set up aryl aza-Claisen rearrangements.[7]

(4) Cookson, R. C.; Gopalan, R. *J. Chem. Soc., Chem. Commun.* **1978**, 608.

(5) Cooper, D.; Trippett, S. *J. Chem. Soc., Perkin Trans. 1*, **1981**, 2127.

(6) (a) Blechert, S. *Tetrahedron Lett.* **1984**, *25*, 1547. (b) Blechert, S. *Helv. Chim. Acta* **1985**, *68*, 1835. (c) Blechert, S. *Liebigs Ann. Chem.* **1985**, 673.

(7) (a) Stirling, C. J. M. *J. Chem. Soc. C* **1964**, 5863. (b) Appleyard, G. D.; Stirling, C. J. M. *Ibid.* **1967**, 2686. (c) Horner, L.; Lindel, H. *Phosphorus Sulfur* **1984**, *20*, 165.

(8) (a) McMullen, C. H.; Stirling, C. J. M. *J. Chem. Soc. B* **1966**, 1217, 1221. (b) McDowell, S. T.; Stirling, C. J. M. *Ibid.* **1967**, 351. (c) Mikhailova, V. N.; Yurevich, V. P.; Bulat, A. D. *J. Org. Chem. USSR (Engl. Transl.)* **1978**, *14*, 200. (d) Cinquini, M.; Colonna, S.; Cozzi, F. *J. Chem. Soc., Perkin Trans. 1*, **1978**, 247. (e) Cinquini, M.; Cozzi, F.; Pelosi, M. *Ibid.* **1979**, 1430. (f) Bruche, L.; Zecchi, G. *J. Heterocycl. Chem.* **1983**, *20*, 1705. (g) Fujii, I.; Ryu, K.; Hayakawa, K.; Kanematsu, K. *J. Chem. Soc., Chem. Commun.* **1984**, 844 and references cited therein.

(9) (a) Stirling, C. J. M. *J. Chem. Soc. C* **1964**, 5856. (b) Thyagarajan, B. S.; Wood, B. F. *Phosphorus Sulfur* **1984**, *20*, 165. (c) Thyagarajan, B. S.; Wood, B. F.; Glowienka, J. A.; Delgado, P. *Ibid.* **1985**, *25*, 1.

(10) Review: Landor, S. R. In *The Chemistry of Allenes*; Landor, S. R., Ed.; Academic: New York, 1982; Vol. 2, pp 361–397.

(11) (a) Braverman, S.; Mechoulam, H. *Isr. J. Chem.* **1967**, *5*, 71. (b) Stirling, C. J. M. *Chem. Commun.* **1967**, 131. (c) Smith, G.; Stirling, C. J. M. *J. Chem. Soc. C* **1971**, 1530. (d) Braverman, S.; Mechoulam, H. *Tetrahedron* **1974**, *30*, 3883.

(12) Attempts to promote the rearrangement with transition-metal catalysts[13a] or in DMF solvent[13b] were not successful.

(13) (a) Hiroi, K.; Kitayama, R.; Sato, S. *J. Chem. Soc., Chem. Commun.* **1984**, 303. (b) Hiroi, K.; Kityama, R.; Sato, S. *Ibid.* **1983**, 1470.

(14) Because of the large number of compounds resulting from permutations of **3** and **4** a simplified numbering system is employed. The structure of the allyl vinyl ether product is uniquely specified by Nxy, where N = 1 for β,γ isomers, N = 2 for α,β isomers, x = **a–i** for the substituents R^1, R^2, and R^3 as listed in Table I, and y = **a–n** for the substituents R^4, R^5, R^6, and R^7 as listed in Table II.

(15) (a) Denmark, S. E.; Jones, T. K. *J. Org. Chem.* **1982**, *47*, 4595. (b) Brown, C. D.; Ahuja, V. J. *J. Chem. Soc., Chem. Commun.* **1973**, *533*. (c) Brown, C. A.; Ahuja, V. J. *J. Org. Chem.* **1973**, *38*, 2226.

Table III. Preparation of Allyl Vinyl Ethers 1 and 2 Unsubstituted at C(1)

entry	educt	alcohol (equiv)	base (equiv)	solvent	conc, M	time[a]	product	yield,[b] %
1	**6**	**4a** (53)	NaH (0.07)	**4a**	0.28	10 min	**1aa**	84
2	**6**	**4a** (53)	NaH (0.88)	**4a**	0.28	30 min	**2aa**	52 (64)[c,d]
3	**3a**	**4b** (5)	Al_2O_3 (0.31)	THF	0.34	24 h	**1ab**	24 (30)[e]
4	**6**	**4b** (38)	NaH (0.7)	**4b**	0.31	12 h	**2ab**	31[d]
5	**3a**	**4d** (5)	Al_2O_3 (0.32)	THF	0.33	24 h	**1ad**	18 (44)[e]
6	**6**	**4e** (15)	NaH (0.13)	**4e**	0.78	30 min	**1ae**	77[d,f]
7	**6**	**4f** (10)	NaH (0.07)	THF	0.93	20 min	**2af**	75[d]
8	**3a**	**4g** (3)	NaH (0.20)	THF[g]	0.20	30 min[h]	**1ag**	26[i]
9	**6**	**4g** (3)	NaH (0.20)	THF[g]	0.30	15 min[j]	**2ag**	40
10	**6**	**4h** (2.9)	Al_2O_3 (0.13)	THF	0.67	24 h	**1ah**	4
11	**6**	**4i** (7.9)	NaH (0.04)	THF	0.79	10 min	**1ai**	55[d,f]

[a] All reactions were run at room temperature unless otherwise specified. [b] Yields refer to chromatographically homogeneous materials. [c] Yield corrected for isolated ketal product. [d] *E* configuration of the double bond was assigned. See text for explanation. [e] Yield corrected for recovered starting material. [f] Mixture of α,β- and β,γ-unsaturated isomers. [g] 3 equiv of *t*-BuOH was added. [h] Reaction run at −20 °C. [i] **1ag** rearranges at room temperature. [j] Reaction run at 0 °C.

Table IV. Preparation of Allyl Vinyl Ethers 1 and 2 Monosubstituted at C(1) or C(3)

entry	educt	alcohol (equiv)	base (equiv)	solvent	conc, M	time,[a] min	product	yield,[b] %
1	**3b**	**4a** (2)	NaH (0.05)	THF	0.48	4	**1ba**	90
2	**3b**	**4b** (2)	NaH (0.05)	THF	0.48	8	**1bb**	82
3	**3b**	**4c** (2)	NaH (0.05)	THF	0.48	2.5	**1bc**	67
4	**3b**	**4p** (2)	NaH (0.05)	THF	0.48	8	**1bp**	45
5	**3b**	**4r** (2)	NaH (0.05)	THF	0.48	15[c]	**1br**	62
6	**3h**	**4a** (54)	NaH (0.05)	**4a**	0.27	25	**1ha**	84
7	**7**	**4a** (57)	NaH (0.06)	**4a**	0.86	270	**1ia**	63
8	**7**	**4a** (54)	NaH (0.10)	THF	0.86	15	**1ie**	88[d]

[a] All reactions were run at room temperature unless otherwise specified. [b] Yields refer to chromatographically homogeneous materials. [c] Reaction run at 0 °C/5 min then 20 °C/15 min. [d] Mixture of α,β- and β,γ-unsaturated isomers.

to **2**, reactivity of **3a**, and its propensity toward polymerization. Two different methods were investigated and the results are collected in Table III. The first method involved the alumina-catalyzed[16] addition of the alcohol to the allenic sulfone (entries 3, 5, 10). Although this method was extensively examined with both basic and neutral activated alumina in many solvents,[17] the yields were generally low, and isolation of the product was always complicated by separation from starting material and hydrolysis products. Surprisingly, in these cases only the β,γ-isomers **1** were obtained. This method was abandoned when it was shown that secondary alcohols failed to add.

The second method, adapted from Stirling[7a] involved the addition of metal allyloxides to the allenes at ambient temperature in the alcohol or THF as solvent. Both isomers **1** and **2** are accessible by this method. With a higher concentration of base and longer reaction times the thermodynamically more stable α,β-isomer **2** can be obtained (compare entries 1 and 2, 8 and 9). Many bases (KH, NaH, *n*-BuLi, K_2CO_3, NaDMSO, NaOH, *n*-$Bu_4N^+OH^-$) and solvents (THF, HMPA, DMSO, DMF, *t*-BuOH, C_6H_6, H_2O) were examined as well as order of addition of reagents. By far the preferred procedure is to use ca. 7 mol% of NaH and the alcohol as solvent for **1** and ca. 1 equiv of NaH for the product **2**. For secondary alcohols, however, isomer **2** was the predominant product unless very low temperatures and added *t*-BuOH were used (entries 6–9). In some cases the yields are very good (entries 1, 6, 7), but the large excess of alcohol necessary to suppress polymerization of the resulting anion makes this approach very inefficient. In an effort to solve the problem of self-condensation and the use of excess alcohol, α,β-unsaturated β-halo sulfones were examined.[18] It was hoped that addition–elimination would proceed in good yield without the intermediacy of anions. Unfortunately, dehydrohalogenation proved to be a problem generating the allene and thus offering no advantage. Tertiary alcohols did not add to the sulfones under these conditions. At higher concentrations of alkoxide, only polymerization was observed.

2.2. C(3)-Monosubstituted Allyl Vinyl Ethers. This class of addition products could be prepared generally in good yields by using only 2.0 equiv of the allylic alcohol. The results for the C(3)-monosubstituted products are compiled in Table IV. The optimal protocol employs 5 mol% of NaH and 2.0 equiv of the alcohol in THF at ca. 0.5 M. The yields of the β,γ-isomers **1** range from 45% to 90%, the lowest being for secondary alcohols. The reaction proved to be quite general and also stereoselective. In entries 1–6 a single geometrical isomer was produced as judged by HPLC and ^1H or ^{13}C NMR analysis. Both primary and secondary alcohols could be used although *cis*-2-butenol (**4c**, entry 3) had a tendency to give the α,β-isomer **2bc** if the reaction was not quenched quickly.

C(1)-substituted allyl vinyl ethers could be prepared in good yields exclusively as β,γ-isomers **1** from both primary and secondary alcohols.

2.3. C(3)-Disubstituted Allyl Vinyl Ethers. Geminally substituted sulfonylallenes **3d–g** proved to be highly versatile substrates in this preparation. As in the previous cases only two equivalents of the allylic alcohol were necessary to obtain excellent yields of the allyl vinyl ethers (Table V). Not surprisingly, the additions of sodium allyl oxides to these substrates were considerably slower than to the less substituted allenes. However, upon switching to potassium salts, generated with KH, the additions were again complete within minutes. In all cases the β,γ-isomer **1** was formed exclusively. A wide variety of allenes and alcohols could be combined with few exceptions. On the allene, methyl, ethyl, and pentamethylene substituents do not interfere, but isopropyl groups (**3e**) proved too bulky

(16) Review: Posner, G. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 487.
(17) Cinnamyl alcohol was used as test substrate in THF, benzene, or CH_2Cl_2.
(18) (a) Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5875. (b) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73. (c) Sauvetre, R.; Normant, H. *Bull. Soc. Chim. Fr.* **1972**, 3202.

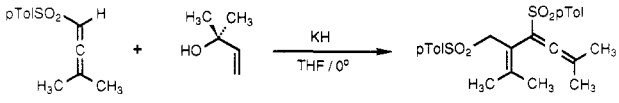
(19) Denmark, S. E.; Harmata, M. A., manuscript submitted.

Table V. Preparation of Allyl Vinyl Ethers 1 and 2 Disubstituted at C(1)

entry	educt	alcohol (equiv)	base (equiv)	solvent	conc, M	time,[a] min	product	yield,[b] %
1	**3c**	**4a** (65)	KH (0.74)	**4a**	0.23	285	**1ca**	59
2	**3c**	**4e** (2)	KH (0.28)	THF	0.45	11[d]	**8ce**[e]	87
3	**3c**	**4j** (2)	KH (0.21)	THF	0.46	17	**1cj**	88
4	**3c**	**4k** (2)	KH (0.25)	THF	0.10	10	**1ck**	86
5	**3c**	**4l** (2)	KH (0.25)	THF	0.10	10	**1cl**	88
6	**3c**	**4m** (2)	KH (0.15)	THF	0.45	12	**1cm**	79
7	**3c**	**4n** (2)	KH (0.25)	THF	0.45	10	**1cn**	82
8	**3c**	**4o** (2)	KH (0.24)	THF	0.45	10	**1co**	91
9	**3c**	**4p** (2)	KH (0.19)	THF	0.45	10	**1cp**	86
10	**3c**	**4e** (1.71)	KH (0.3)	THF	0.46	*c*	**1cq**	80
11	**3d**	**4a** (2)	KH (0.33)	THF	0.50	25	**1da**	89
12	**3d**	**4j** (2)	KH (0.25)	THF	0.1	10	**1dj**	80
13	**3d**	**4k** (2)	KH (0.25)	THF	0.1	10	**1dk**	86
14	**3e**	**4a** (2)	KH (1.0)	THF	0.2	*f*	**1ea**	0[g]
15	**3f**	**4a** (2)	KH (0.16)	THF	0.46	60	**1fa**	97
16	**3f**	**4j** (2)	KH (0.25)	THF	0.48	12	**1fj**	84
17	**3f**	**4m** (2)	KH (0.3)	THF	0.48	12	**1fm**	54
18	**3g**	**4a** (2)	KH (0.24)	THF	0.52	20	**1ga**	85

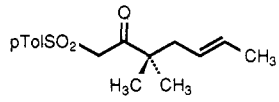
[a] All reactions were run at room temperature unless otherwise specified. [b] Yields refer to chromatographically homogeneous materials. [c] Reaction run at 0 °C/5 min, 20 °C/45 min, and then 50 °C/3 h. [d] Reaction run at 0 °C. [e] Rearrangement occurred upon workup. [f] Reaction run at 20 °C/30 min and then 50 °C/30 min. [g] >90% recovery of **3e**.

Scheme VI



9

to allow addition of even the least hindered allyloxide (entry 14). Primary alcohols with substituents on both olefinic carbons are all compatible—even two isopropyl groups do not suppress addition (entry 5). Secondary alcohols add (entries 2, 9), but tertiary alcohols failed to react. Under more forcing conditions an interesting dimer **9** was isolated in an attempted reaction of **3c** with 2-methyl-3-buten-2-ol (Scheme VI). The isolation of the rearranged product **8ce** (entry 2) has interesting implications for the carbanionic Claisen rearrangement as a "one-pot" process; however, we feel this occurred during workup and isolation.



8ce

Discussion

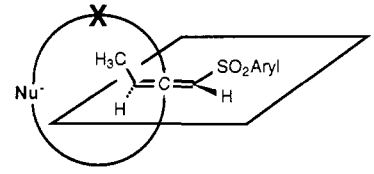
In 1969 Steele reported accurate heats of formation of a series of sulfones to investigate the existence of conjugative stabilization for the SO_2 group.[20] Those data are summarized in Table VI in the format of isomerization reactions in the exothermic direction with the appropriate $-\Delta H_f°$. These results confirmed the more qualitative observations of Stirling[7a] and others[21] that β,γ-unsaturated sulfones are more stable than their α,β-isomers by ca. 2.5 kcal/mol. In the allene series (entries 1–3), the stability of the propadienyl vis-a-vis the alkynyl isomers (**3a** > **6** > **6′**, Scheme III) is in accord with this class of compounds[22], but much greater in magnitude. The only α,β-unsaturated sulfone which is more stable than its β,γ-isomer is the 1-propenyl, 2-propenyl case (entry 4) presumably due to the hyperconjugative stabilization by the methyl group.

Table VI. Experimental Heats of Isomerization of Unsaturated Sulfones[a]

entry	reaction	$-\Delta H°_f$, kcal/mol
1	p-$TolSO_2C{\equiv}CCH_3 \rightarrow p$-$TolSO_2CH{=}C{=}CH_2$	10.2 ± 1.6
2	p-$TolSO_2CH_2C{\equiv}CCH_3 \rightarrow p$-$TolSO_2CH{=}C{=}CH_2CH_3$	7.9 ± 1.6
3	p-$TolSO_2C{\equiv}CCH_2CH_3 \rightarrow p$-$TolSO_2CH_2C{\equiv}CCH_3$	2.3 ± 1.5
4	p-$TolSO_2CH_2CH{=}CH_2 \rightarrow p$-$TolSO_2CH{=}CHCH_3$	1.4 ± 1.5
5	p-$TolSO_2CH{=}CHCH_2CH_3 \rightarrow p$-$TolSO_2CH_2CH{=}CHCH_3$	2.6 ± 1.5
6	p-$TolSO_2CH{=}C(CH_3)_2 \rightarrow p$-$TolSO_2CH_2C(CH_3){=}CH_2$	2.4 ± 1.4

[a] All data from ref 20.

Scheme VII



For C(3)-unsubstituted allyl vinyl ethers the α,β-isomer **2** appears to be more stable than the β,γ-isomer **1** contrary to the trend shown in Table VI, entry 6, but consistent with Stirling's observations with methoxide. This presumably derives from a synergistic interaction between the strong donor (RO) and acceptor (arylSO$_2$) groups. Consequently, the kinetic adduct **1** can only be obtained in good yield in protic media which suppress isomerization, namely, the alcohol. The α,β-isomers **2** are more readily obtained. Occasionally these isomers were contaminated with the β,γ-isomers particularly with secondary alcohols and were not chromatographically resolvable on silica gel. The relative proportion of the isomer **1** could be increased in these cases by operating at lower temperature and using t-BuOH as a substitute for the allylic alcohol. The acetal derived from a second addition of allyloxide was also occasionally observed. The E configuration of the double bond in **2** was assigned on the basis of the downfield shift of the allylic methyl group as described by Stirling.[7a] No other geometrical isomers were observed. Thus, for some of these substrates many of the criteria were not met, and

(20) (a) Mackle, H.; McNally, D. V.; Steele, W. V. *Trans. Faraday Soc.* **1969**, 2060. (b) Mackle, H.; Steele, W. V. *Ibid.* **1969**, 2069. (c) Mackle, H.; Steele, W. V. *Ibid.* **1969**, 2073.

(21) O'Connor, D. E.; Lyness, W. I. *J. Am. Chem. Soc.* **1964**, *86*, 3840.

(22) Deming, R. L.; Wulff, C. A. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: New York, 1980; Part 1, pp 155–164.

a general preparation remains to be developed.

The C(3)-monosubstituted cases could all be obtained as β,γ-isomers 1 by using only 2 equiv of allylic alcohol. The *E* configuration of the C(2)–C(3) double bond is assigned on the basis of the preferred approach of the nucleophilic allyl oxide from the less encumbered side of the allene (Scheme VII). This stereochemical outcome has precedent in the analogous addition of organocuprates to sulfonyl-, sulfinyl-, and phosphinylallenes[23] as well as the addition of alcohols to sulfinylallenes[24a] and ketene iminium ions.[24b] Interestingly, this stereocontrol element has also been documented in [4 + 2]-cycloadditions with sulfonylallenes.[25] The establishment of this double bond geometry with high selectivity is critical in the subsequent studies of internal asymmetric induction in the rearrangement.

The C(3)-disubstituted products were the most readily prepared. The added nucleophilicity of potassium allyl oxides nicely compensated for the diminished reactivity of the allenes. In these cases both sides of the allene are shielded to attack by the substituents. The preparation is general, proceeds in good yield, optimally with 2 equiv of alcohol, and gives exclusively the β,γ-unsaturated isomer.

In principle, it should be possible to formulate reaction conditions where the allyl oxide addition produces an anion that rearranges faster than polymerization processes, since (to a first approximation) it is the same ion that does the rearrangement. The isolation of **8ce** seemed to lend support to this notion. Although closer inspection revealed that the rearrangement occurred subsequent to addition. We believe this to be the case in another report involving phosphonylallenes as well.[5]

In conclusion, we have developed a workable method for the generation of a wide variety of substituted allyl vinyl ethers and have produced a multitude of substrates for the investigation of the scope of the carbanionic Claisen rearrangements. The results of these studies will be reported in the near future.[19]

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Varian EM 390 (90 MHz), HR 220 (220 MHz), XL 200 (MHz), or Nicolet NTC-360 (360 MHz) spectrometer with chloroform (7.26 ppm) or tetramethylsilane (0 ppm) as an internal standard in $CDCl_3$ solutions unless otherwise stated. Chemical shifts are given in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quadruplet, m (multiplet), or br (broadened). Coupling constants, *J*, are reported in Hz. Infrared spectra were obtained on a Perkin-Elmer 127, 1320, or Nicolet 7199c FT IR spectrometer as a neat liquid, chloroform solution or KBr pellet. Peaks are reported in cm^{-1} with the following relative intensities: s (strong, 67–100%), m (medium, 34–66%), w (weak, 0–33%). Mass spectra (EI) were obtained on a Finnigan MAT CH-5 spectrometer or a Finnigan MAT 311A with an ionization voltage of 10 or 70 eV. High-resolution (EI) mass spectra were obtained on a Finnigan MAT 731 spectrometer. High-resolution (FAB) mass spectra were obtained on a VG-ZAB-2F spectrometer.

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus in evacuated capillary tubes and are corrected. Bulb-to-bulb distillations were done on a Buchi GKR-50 Kugelrohr; boiling points (bp) refer to air bath temperatures and are uncorrected. Analytical TLC was performed on 0.25-mm silica gel plates (Merck) with QF-254 indicator. Visualization was accomplished with UV light, phosphomolybdic acid, iodine, sulfuric acid/methanol, vanillin, and/or 2,4-DNP solution. Flash chromatography[26] was performed on 32–63-μm silica gel (Woelm) with technical grade solvents distilled as follows: cyclohexane, pentane and hexane (from anhydrous $CaCl_2$), ethyl acetate (from anhydrous K_2CO_3), and ether (from $FeSO_4$ and anhydrous $CaSO_4$). Analytical gas chromatography was performed on a Varian 3700 chromatography with flame ionization detection. The carrier gas for packed columns was N_2 (30 mL/min) and H_2 (1 mL/min) for capillary columns. Columns used were a packed 5% Carbowax 20 M on non-acid washed Chromosorb W (12 ft × $^1/_8$ in.) and a capillary Carbowax 20 M (39 m). Retention times and integrals were obtained from a Hewlett-Packard 3390 recorder. High-pressure liquid chromatography (HPLC) was performed on a Perkin-Elmer Series 1 LC pump and LC-75 spectrophotometric detector (variable UV, 250 nm used for these studies). Columns used were Perkin-Elmer Silica B (5 m, 250 × 4.6 mm) and an Excalibur Spherisorb aminopropyl (5 μm, 250 × 4.6 mm). Solvents for HPLC were distilled in glass or UV grade and filtered and degassed immediately prior to use. Ozonolyses were performed on a Welsbach Ozonator. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

Alkyllithiums were titrated by the method of Gilman.[27] Dry solvents were distilled freshly prior to use: THF, Et_2O, DME (sodium/benzophenone), benzene, acetonitrile, TMEDA, and CH_2Cl_2 (CaH_2). DMSO, HMPA, and pyridine were distilled from CaH_2 and stored over activated 4-Å sieves. All other reagents were distilled or recrystallized as necessary. All air- and moisture-sensitive reactions were performed in oven (140 °C) or flame-dried glassware under an inert atmosphere of N_2 or Ar.

Starting Materials. The following compounds were prepared by the literature methods: *p*-toluenesulfinyl chloride,[28a] 1-phenyl-2-propyn-1-ol,[28b,c] 4-(1,1-dimethylethyl)-1-ethynylcyclohexanol,[28b,d] 3-ethyl-1-pentyn-3-ol,[28b,e] 3-(trimethylsilyl)-2-propen-1-ol,[28f] 2-butyn-1-ol,[28g] 2-cyclohexen-1-ol,[28h] 1-cyclohexenylmethanol,[28i] 3-methyl-2-buten-1-ol,[28j] cyclohexylidenemethanol,[28k,l] and 4-(1-dimethylethyl)cyclohexylidenemethanol.[28m]

General Procedure for the Synthesis of Sulfinate Esters 4–10. An oven-dried, three-necked, round-bottomed flask equipped with septa and a stirring bar was charged with 11.3 g (0.065 mol) of *p*-toluenesulfinyl chloride and 20 mL of dry pyridine and was cooled to 0 °C. A pear-shaped flask was charged with 0.062 mol of the acetylenic carbinol and 7 mL of dry pyridine and was also cooled to 0 °C. The alcohol solution was added to the sulfinyl chloride solution via cannula over 15 min. The thick mixture was allowed to stir at room temperature for 45 min. It was then diluted with 200 mL of Et_2O in a separatory funnel and washed with H_2O (1 × 75 mL), 2 N HCl (3 × 50), 10% $NaHCO_3$ (2 × 50 mL), H_2O (1 × 50 mL), and brine (1 × 50 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed. The crude product was then purified by distillation and/or recrystallization.

1-Methyl-2-propynyl 4-Methylbenzenesulfinate (5b). The crude product was distilled to give an 86% yield of **5b** as a faintly yellow liquid, bp 115–25 °C (0.05 Torr) [lit.[11c] bp 102 °C (0.05

(23) (a) Koosha, K.; Berlan, J.; Capmau, M.-L. *C. R. Seances Acad. Sci., Ser. C* **1973**, *276*, 1633. (b) Koosha, K.; Berlan, J.; Capmau, M.-L.; Chodkiewicz, W. *Bull. Soc. Chim. Fr.* **1975**, 1291. (c) Berlan, J.; Battioni, J.-P.; Koosha, K. *Tetrahedron Lett.* **1976**, 3351. (d) Ohmori, M.; Yamadu, S.; Takayama, H. *Ibid.* **1982**, *23*, 4709.

(24) Van Rheenan, V.; Shephard, K. P. *J. Org. Chem.* **1979**, *44*, 1582. (b) Bartlett, P. A.; Hahne, W. F. *Ibid.* **1979**, *44*, 882.

(25) (a) Barbarella, G.; Cinquini, M.; Colonna, S. *J. Chem. Soc., Perkin Trans. 1*, **1980**, 1646. (b) Hanack, M.; Massa, F. W. *Tetrahedron Lett.* **1981**, *22*, 557.

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

(27) Gilman, H.; Haubien, R. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515.

(28) (a) Kurzev, F. In *Organic Syntheses*; Rabjohn, N., Ed.; Wiley: New York, 1963; Collect. Vol. 4, p 937. (b) Skattebol, L.; Jones, E. R. H.; Whiting, M. C. In *Organic Syntheses*; Rabjohn, N., Ed.; Wiley: New York, 1963; Collect. Vol. 4, p 792. (c) Jones, E. R. H.; McCombie, J. J. *J. Chem. Soc.* **1942**, 773. (d) Garratt, D. B.; Beaulieu, P. L.; Morrisett, V. M. *Can. J. Chem.* **1981**, *59*, 927. (e) Papa, D.; Villani, F. J.; Ginsberg, H. F. *J. Am. Chem. Soc.* **1954**, *76*, 4446. (f) Denmark, S. E.; Jones, T. K. *Org. Synth.* **1985**, *64*, 182. (g) Brandsma, L.; Verkruisse, H. O. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981; p 58. (h) Mousseron, M.; Jacquier, R.; Mousseran-Canet, M.; Zagdoun, R. *Bull. Soc. Chim. Fr.* **1952**, 1042. (i) Dreiding, A. S.; Hartmann, J. A. *J. Am. Chem. Soc.* **1953**, *75*, 939. (j) Sargent, G. D.; Mason, J. J.; Harrison, M. J.; Hall, J. A. *Ibid.* **1973**, *95*, 1849. (k) Wadsworth, W. S.; Emmons, W. D. In *Organic Syntheses*; Baumgartner, H., Ed.; Wiley: New York, 1973; Collect. Vol. 5, p 547. (l) Viscontini, M.; Burgherr, H. D. *Helv. Chim. Acta* **1957**, *40*, 881. (m) House, H. O.; Lubikowski, J.; Good, J. J. *J. Org. Chem.* **1975**, *40*, 86.

Torr)]. It is extremely important that short-path distillation be used in this purification.

1,1-Dimethyl-2-propynyl 4-Methylbenzenesulfinate (5c). The crude product was recrystallized twice from pentane/CH_2Cl_2 to give a 65% yield of **5c** as colorless needles; mp 67–69 °C. IR ($CHCl_3$): 3303 m, 3020 s, 3017 s, 2035 w, 1596 w, 1520 w, 1494 w, 1463 w, 1450 w, 1437 w, 1425 w, 1383 w, 1367 w, 1221 s, 1211 s, 1142 m, 1120 m, 1112 m, 1082 m, 1045 w, 1017 w, 950 m, 927 w, 858 s, 810 m. ^1H NMR (220 MHz): 7.62 (d, 2 H, J = 8.1, Ar H ortho to SO_2), 7.33 (d, J = 8.1, 2 H, Ar H), 2.79 (s, 1 H, H-C(3)), 2.42 (s, 3 H, PhCH_3), 1.81 (s, 3 H, CH_3(1)), 1.68 (s, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 222 (M^+, 1.4), 165 (14), 140 (13), 139 (83), 124 (27), 123 (10), 92 (32), 91 (21), 83 (19), 67 (100), 41 (15). Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.86; H, 6.31; S, 14.41. Found: C, 64.81; H, 6.58; S, 14.52.

1,1-Diethyl-2-propynyl 4-Methylbenzenesulfinate (5d). The crude product was recrystallized twice from hexane to give an 84% yield of **5d** as colorless cubes, mp 54–56.5 °C. IR ($CHCl_3$): 3308 s, 3005 m, 2980 s, 2944 m, 2885 m, 2115 w, 1595 w, 1495 w, 1460 m, 1400 w, 1382 w, 1312 w, 1265 w, 1128 s, 1107 s, 1040 w, 1016 w, 949 m, 900 s. ^1H NMR (200 MHz): 7.62 (d, J = 8, 12 H, Ar H ortho to SO_2), 7.32 (d, J = 8.1, 2 H, Ar H), 2.86 (s, 1 H, C≡CH), 2.42 (s, 3 H, PhCH_3), 2.02 (q, J = 7.5, 2 H, CH_3CH_2), 1.86 (q, J = 7.25, 2 H, CH_3CH_2), 1.08 (t, J = 7.25, 3 H, CH_3), 1.03 (t, J = 7.5, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 250 (M^+, 0.56), 157 (43), 140 (14), 139 (57), 111 (22), 95 (71), 94 (28), 93 (21), 92 (13), 91 (11), 79 (24), 67 (100), 55 (48), 53 (14), 41 (13). Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.20; H, 7.20; S, 12.80. Found: C, 66.96; H, 7.11; S, 12.73.

1,1-Bis(1-methylethyl)-2-propynyl 4-Methylbenzenesulfinate (5e). The crude product was recrystallized from hexane to give a 73% yield of **5e** as white needles, mp 93–95 °C. IR ($CHCl_3$): 3300 s, 3060 w, 2980 s, 2940 s, 2880 m, 2300 w, 2110 w, 1700 w, 1600 w, 1500 w, 1470 m, 1420 w, 1390 m, 1370 m, 1320 m, 1305 m, 1260 s, 1220 m, 1140 s, 1125 s, 1114 m, 1090 m, 1080 m, 1020 m, 1000 m, 970 m, 910 s, 890 s. ^1H NMR (200 MHz): 7.66 (d, J = 8.3, 2 H, Ar H ortho to SO_2), 7.28 (d, J = 7.9, 2 H, Ar H), 2.95 (s, 1 H, C≡CH), 2.41 (s, 3 H, PhCH_3), 2.09 (septet, J = 6.7, 1 H, $(CH_3)_2CH$), 2.08 (septet, J = 6.7, 1 H, $(CH_3)_2CH$), 1.12 (d, J = 6.9, 3 H, CH_3), 1.06 (d, J = 7, 3 H, CH_3), 0.92 (d, J = 6.7, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 140 (M^+ 138, 16.8), 139 (46), 123 (23), 122 (34), 107 (16), 95 (12), 92 (28), 91 (34), 81 (100), 79 (20), 77 (14), 67 (21), 65 (25), 53 (14), 43 (61), 41 (40). Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.05; H, 7.97; S, 11.52. Found: C, 69.13; H, 8.09; S, 11.48.

1-Ethynylcyclohexyl 4-Methylbenzenesulfinate (5f). The crude product was recrystallized from hexane to give an 82% yield of **5f**, mp 73–74.5 °C. IR ($CHCl_3$): 3250 m, 2900 s, 2820 m, 2105 w, 1600 w, 1490 w, 1447 m, 1400 w, 1376 w, 1341 w, 1290 m, 1257 w, 1172 w, 1125 s, 1111 s, 1085 m, 1040 w, 920 s, 854 s, 833 m, 814 w. ^1H NMR (220 MHz): 7.63 (d, J = 7.9, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8, 2 H, Ar H), 2.83 (s, 1 H, C≡CH), 2.42 (s, 3 H, PhCH_3), 2.26–2.21 (m, 1 H), 2.07–1.92 (m, 2 H), 1.85–1.53 (m, 6 H), 1.34–1.26 (m, 1 H). MS (70 eV): m/e (relative intensity) 262 (M^+, 6.2), 123 (11), 107 (12), 106 (15), 91 (32), 79 (35), 67 (15), 65 (13), 58 (31), 44 (21), 43 (100), 41 (11). Anal. Calcd for $C_{15}H_{18}O_2$: C, 68.70; H, 6.87; S, 12.21. Found: C, 68.93; H, 6.83; S, 12.08.

4-(1,1-Dimethylethyl)-1-ethynylcyclohexan-1-yl 4-Methylbenzenesulfinate (5g). The crude product was recrystallized from petroleum ether to give a 68% yield of **5g**, mp 86–87 °C. IR ($CHCl_3$): 3309 s, 3006 m, 2962 s, 2910 m, 2875 m, 2119 w, 1598 w, 1495 w, 1475 m, 1455 m, 1397 w, 1368 m, 1347 w, 1320 w, 1305 w, 1285 w, 1265 w, 1134 s, 1123 s, 1113 s, 1083 m, 1042 m, 1021 s, 945 s, 929 s, 911 s. ^1H NMR (200 MHz): 7.62 (d, J = 8.3, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8.3, 2 H, Ar H), 2.85 (s, 1 H, C≡CH), 2.49–2.42 (m, 4 H, PhCH_3 at 2.42), 2.23-2.14 (m, 1 H), 1.89–1.35 (m, 6 H), 1.09–0.94 (m, 1 H), 0.88 (s, 9 H, $C(CH_3)_3$). MS (70 eV): m/e (relative intensity) 318 (M^+, 0.87), 157 (10), 139 (15), 121 (11), 107 (27), 106 (18), 105 (13), 93 (16), 91 (31), 79 (14), 77 (10), 69 (15), 65 (12), 57 (100), 55 (15), 43 (13), 41 (31). Anal. Calcd for $C_{19}H_{26}O_2S$: C, 71.66; H, 8.23; S, 10.07. Found: C, 71.53; H, 8.10; S, 10.11.

1-Phenyl-2-propynyl 4-Methylbenzenesulfinate (5h). The crude product was obtained as an oil in 93% yield, which decomposed on attempted distillation. An analytical sample could not be obtained. A small amount was purified by column chromatography (cyclohexane/EtOAc, 8/1) and identified by ^1H NMR (90 MHz): 7.66–7.18 (m, 9 H, Ar H), 5.92–5.87 (m, 1 H, HC(2)), 2.82 (d, J = 1.5, 1 H, HC(3), one diastereomer), 2.50 (d, J = 1.5, 1 H, HC(3), another diastereomer), 2.41 (s, 3 H, PhCH_3, one diastereomer), 2.38 (s, 3 H, PhCH_3, another diastereomer).

Sulfonylallenes and Acetylenes. [2-Propynylsulfonyl]benzene (6). Phenyl propargyl sulfide was oxidized with H_2O_2 according to the literature procedure[7a] in 83% yield to the title sulfone. Recrystallization from CCl_4 gave colorless needles, mp 90–93 °C (lit.[7a] mp 93 °C). The sulfide was prepared as follows:[29] A 250-mL, three-necked, round-bottomed flask fitted with a mechanical stirrer was charged with 3 g (0.75 mol) of NaOH, 40 mL of H_2O, and 5 g (45.4 mmol) of thiophenol. An 80% solution of propargyl bromide in toluene (6.82 g, 45.8 mmol) and 50 mL of benzene were added followed by 4 drops of Adogen 464. The reaction mixture, which became warm, was stirred vigorously for 20 min. The organic phase was separated and washed with H_2O (2 × 25 mL) and brine (1 × 25 mL). Drying ($MgSO_4$), filtering, and removing solvent gave an orange residue. Distillation through a Vigreux column afforded 6.09 g (90%) of phenylpropargyl sulfide as a clear colorless liquid, which yellowed quickly on exposure to the atmosphere [bp 74–75 °C (0.4 Torr); lit.[30] bp 104–110 °C (10 Torr)]. ^1H NMR (90 MHz): 7.5–7.1 (m, 5 H, Ar H), 3.59 (d, J = 2, 2 H, PhCH_2), 2.2 (t, J = 2, 1 H, C≡CH).

[1,2-Propadienylsulfonyl]benzene (3a). **6** (1 g, 5.6 mmol) was passed through a 20 × 2 cm column of basic alumina with 150 mL of CH_2Cl_2. Evaporation of solvent gave a quantitative yield of **3a** whose ^1H NMR spectrum was consistent with that reported in the literature.[7a]

[2-Butynylsulfonyl]benzene (7). 3-(Phenylsulfenyl)-1-butyne was oxidized with oxone according to the procedure of Trost[31] in 70% yield to the title sulfone. Recrystallization from hexane–isopropyl ether gave colorless needles, mp 65–67 °C (lit.[32] mp 68 °C). The sulfide was prepared as follows: A 250-mL, three-necked, round-bottomed flask fitted with a N_2 inlet, 25-mL dropping funnel, thermometer, and stirring bar was flame-dried and cooled under N_2. It was then charged with 5.0 g (71.3 mmol) of 3-butyn-2-ol, 7.58 g (1.05 equiv) of triethylamine and 70 mL of dry CH_2Cl_2. The flask was cooled in ice salt bath and methanesulfonyl chloride (8.58 g, 1.05 equiv) in 10 mL of CH_2Cl_2 was added over 45 min, keeping the temperature between +2 and −6 °C. The reaction mixture was stirred and monitored by GC (Carbowax column). After 30 min the reaction mixture was filtered through dry $MgSO_4$, and the solvent was removed. Dilution with dry Et_2O, filtration through $MgSO_4$, and removal of solvent afforded 11.3 g (>100%) of a yellow liquid, which was immediately treated with thiophenol and NaOH under phase-transfer conditions as in the preparation of **6** above. After 45 min workup and distillation gave 9.5 g (83%) of **7**, bp 80 °C (0.4 Torr) [lit.[32b] bp 73 °C (0.3 Torr)].

General Procedure for the Synthesis of Allenyl Sulfones. A 250-mL, round-bottomed flask equipped with a stirring bar and reflux condenser was charged with 11.3 mmol of the sulfinate ester and 80 mL of solvent (CCl_4 or C_6H_5Cl). The solution was refluxed and when the reaction was complete (TLC) the solvent was removed. The residue was purified by chromatography and/or recrystallization.

1-[1,2-Butadienylsulfonyl]-4-methylbenzene (3b). The crude product was purified by column chromatography (hexane/EtOAc, 3.5/1) followed by recrystallization from hexane/Et_2O. This gave a 59% yield of **3b** as colorless needles, mp 52–54 °C (lit.[11c] mp 47–48 °C).

1-[[3-Methyl-1,2-butadienyl]sulfonyl]-4-methylbenzene (3c). The crude product was recrystallized from benzene/hexane to give a 96% yield of **3c** as colorless needles, mp 77–78 °C. IR ($CHCl_3$): 3029 s, 3019 m, 2990 w, 2955 w, 2923 w, 1962 w, 1595 m, 1494 m, 1442 m, 1400 w, 1379 m, 1362 s, 1317 s, 1303 s, 1293 s, 1225 s, 1208 s, 1188 m, 1177 m, 1142 s, 1131 s, 1119 w, 1086 s, 1059 w, 1040 w, 928 w. ^1H NMR (220 MHz): 7.77 (d, J = 8.2,

(29) Herriott, H. A.; Picker, D. *Synthesis* **1975**, 447.
(30) Sato, K.; Mujamoto, O. *Bull. Chem. Soc. Jpn.* **1956**, *77*, 1409.
(31) Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, 1287.
(32) (a) Poucelot, G.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, *9*, 3024. (b) Poucelot, G.; Cadiot, P. *Ibid.* **1966**, *9*, 3016.

2 H, Ar H ortho to SO_2), 7.32 (d, J = 8.1, 2 H, Ar H), 6.03 (septet, J = 2.5, 1 H, =C*H*), 2.44 (s, 3 H, PhCH_3), 1.78 (d, 6 H, 2 × CH_3). MS (70 eV): m/e (relative intensity) 222 (M^+, 2.4), 139 (33), 124 (14), 92 (34), 91 (33), 83 (11), 67 (100), 65 (42), 51 (14), 41 (71). Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.86; H, 6.31; S, 14.41. Found: C, 64.58; H, 6.37; S, 14.68.

1-[[3-Ethyl-1,2-pentadienyl]sulfonyl]-4-methylbenzene (3d). The crude product was recrystallized from pentane/CH_2Cl_2 to give **3d** in 98% yield, mp 49–51 °C. IR ($CHCl_3$): 3022 m, 2978 s, 2940 m, 2915 m, 2880 m, 1958 m, 1918 w, 1599 m, 1495 w, 1459 m, 1370 m, 1315 s, 1303 s, 1295 s, 1174 m, 1139 s, 1082 s, 1040 w, 1019 w, 971 w, 940 w. ^1H NMR (200 MHz): 7.78 (d, J = 8.1, 2 H, Ar H ortho to SO_2), 7.33 (d, J = 8.1 , 2 H, Ar H), 6.24 (quintet, J = 3 Hz, 1 H =C*H*), 2.44 (s, 3 H, CH_3), 2.08 (dxq, J = 3, 7.25, 4 H, 2 × CH_2CH$_3$), 0.97 (t, J = 7.25, 6 H, 2 × CH$_2$CH_3). MS (70 eV): m/e (relative intensity) 250 (M^+, 2.2), 157 (27), 139 (14), 111 (23), 95 (47), 94 (20), 93 (22), 92 (12), 91 (33), 79 (22), 77 (14), 67 (100), 65 (34), 55 (73), 53 (36), 43 (10), 41 (40). Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.20; H, 7.20; S, 12.80. Found: C, 67.59; H, 7.27; S, 12.87.

1-[[4-Methyl-3-(1-methylethyl)-1,2-pentadienyl]sulfonyl]-4-methylbenzene (3e). The crude product was recrystallized from pentane to give **3e** in 89% yield, mp 52–55 °C. IR ($CHCl_3$): 3300 w, 2980 s, 2940 s, 2880 m, 2680 w, 2300 w, 1950 w, 1600 m, 1490 w, 1460 m, 1450 m, 1420 m, 1390 m, 1375 m, 1370 m, 1320 s, 1300 s, 1290 s, 1260 s, 1220 s, 1180 m, 1140 s, 1085 s, 1050 m, 1030 w, 1020 w, 1000 w, 915 m, 900 m. ^1H NMR: 7.79 (d, J = 8.3, 2 H, Ar H ortho to SO_2), 7.29 (d, J = 8.6, 2 H, Ar H), 6.27 (t, J = 2.0, 1 H, =C*H*), 2.43 (s, 3 H, PhCH_3), 2.28 (dx septet, J = 1.9, 6.7, 2 H, C*H*(CH$_3$)$_2$), 1.01 (d, J = 6.7, 6 H, 2 × CH_3), 0.99 (d, J = 7.0, 6 H, 2 × CH_3). MS (70 eV): m/e (relative intensity) 278 (M^+, 0.66), 123 (25), 122 (40), 107 (15), 92 (12), 91 (23), 81 (100), 79 (22), 67 (16), 65 (15), 53 (10), 43 (42), 41 (25). Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.05; H, 7.97; S, 11.52. Found: C, 69.31; H, 7.80; S, 11.43.

1-[[2-Cyclohexylideneethenyl]sulfonyl]-4-methylbenzene (3f). The crude product was recrystallized from hexane/diisopropyl ether to give a 67% yield of **3f**, mp 77–78 °C. IR ($CHCl_3$): 3030 m, 3020 m, 2940 m, 2899 w, 2860 m, 1958 w, 1598 w, 1494 w, 1449 m, 1441 w, 1392 w, 1342 m, 1320 s, 1304 s, 1293 m, 1230 m, 1219 m, 1211 m, 1185 w, 1163 m, 1143 s, 1130 s, 1087 s, 1019 w, 974 w. ^1H NMR (220 MHz): 7.78 (d, J = 8.1, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8.1, 2 H, Ar H), 6.05 (t, J = 1.6, 1 H, olefinic H), 2.44 (s, 3 H, PhCH_3), 2.16 (br s, 4 H), 1.54 (br s, 6 H). MS (70 eV): m/e (relative intensity) 262 (M^+, 5), 157 (20), 139 (12), 123 (36), 107 (32), 106 (38), 105 (10), 93 (17), 91 (91), 79 (100), 78 (14), 77 (26), 69 (41), 51 (11), 41 (22). Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.70; H, 6.87; S, 12.21. Found: C, 68.63; H, 6.94; S, 12.61.

1-[[2-(4-(1,1-Dimethylethyl)cyclohexylidene)ethenyl]sulfonyl]-4-methylbenzene (3g). The crude product was recrystallized from diisopropyl ether to give **3g** in 70% yield, mp 106–108 °C. IR ($CHCl_3$): 3040 w, 3029 m, 3019 m, 2955 s, 2927 m, 2909 m, 2868 m, 2845 w, 1957 w, 1606 w, 1502 w, 1486 w, 1476 w, 1449 m, 1439 w, 1400 m, 1373 m, 1365 w, 1331 s, 1321 s, 1311 s, 1299 m, 1247 m, 1230 m, 1217 m, 1191 m, 1154 s, 1094 s, 1042 w, 1026 w, 980 w, 931 w. ^1H NMR (200 MHz): 7.76 (d, J = 8.3, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8.3, 2 H, Ar H), 6.06 (t, J = 3.2, 1 H, =C*H*), 2.46–2.40 (m, 5 H, PhCH_3 at 2.46), 2.14–1.87 (m, 4 H), 1.16–1.04 (m, 3 H), 0.85 (s, 9 H, C(CH_3)$_3$). MS (70 eV): m/e (relative intensity) 318 (M^+, 3.1), 179 (12), 162 (12), 157 (11), 147 (10), 121 (13), 107 (34), 106 (20), 105 (16), 93 (18), 91 (41), 79 (16), 77 (12), 69 (12), 65 (15), 57 (100), 55 (14), 45 (37), 44 (17), 43 (27), 41 (39). Anal. Calcd for $C_{19}H_{26}O_2S$: C, 71.66; H, 8.23; S, 10.07. Found: C, 71.49; H, 8.23; S, 9.99.

1-[[3-Phenyl-1,2-propadienyl]sulfonyl]-4-methylbenzene (3h). The crude product was chromatographed (hexane/EtOAc, 3/1) and recrystallized twice from ethanol to give **3h** in 43% yield, mp 93–96 °C (lit.[8d] mp 89–90 °C).

Selected Allylic Alcohols. Preparation of *trans*-2-Butenol (4b). A flame-dried, 250-mL, three-necked, round-bottomed flask equipped with an N_2 inlet, 50-mL addition funnel, septum, and stirring bar was charged with 6.5 g (0.17 mol, 1.2 equiv) of $LiAlH_4$. Dry DME (120 mL) was added, and the mixture was cooled in an ice bath. The addition funnel was charged with 10 g (0.14 mol) of 2-butyn-1-ol and 30 mL of DME. This was added to the $LiAlH_4$ dropwise over 35 min. The ice bath was then removed, and the reaction was stirred for 24 h at room temperature. The reaction was quenched by the sequential addition of H_2O (6.5 mL), 15% NaOH (6.5 mL), and H_2O (19.5 mL). The resulting precipitate was filtered off with Et_2O. Removal of solvent by distillation followed by distillation of product through a column packed with glass helices gave 7.87 g (78%) of *trans*-2-butenol, bp 71–72 °C (89–94 Torr) [lit.[33] bp 121.6 °C]. GC analysis (12 ft, packed Carbowax, t_R 5.94 min) showed the presence of *only* trans alcohol. GC conditions below.

Preparation of *cis*-2-Butenol (4c). A 250-mL, three-necked, round-bottomed flask equipped with septa and a stirring bar was charged with 7 g (0.1 mol) of 2-butyn-1-ol, 5 mL of collidine, 500 mg of 5% Pd of $BaSO_4$, and 70 mL of MeOH. After 1 h on a hydrogenator at atmospheric pressure, no reaction had taken place so the reaction mixture was filtered. It was then added to 500 mg of preactivated catalyst via syringe. The reaction was monitored by GC (12 ft, packed Carbowax; temperature program, 50 °C for 2 min to 150 °C at 15 deg/min). After 10.25 h, the incomplete reaction was stopped to avoid isomerization or saturation. Filtration followed by distillation gave 3.3 g (47%) of *cis*-2-butenol, bp 74–77 °C (% Torr) [lit.[33] bp 123.6 °C]. The material was 99% cis by GC (t_R 6.43 min).

Preparation of 1-Penten-3-ol (4f). A flame-dried, 1-L, round-bottomed flask equipped with an N_2 inlet, thermometer, addition funnel, and stirring bar was charged with 18 g (0.75 mol, 1.1 equiv) of Mg and 150 mL of dry Et_2O. Ethyl bromide (73 g, 0.66 mol) in 150 mL of Et_2O was added over 2.5 h, and the mixture was refluxed for 1.25 h. This mixture was cooled to −25 °C. Acrolein (25 g, 0.44 mol) in 150 mL of Et_2O was added over 1 h, keeping the temperature below −10 °C. After the addition was complete, 50 g of ice was added followed by slow addition of 200 mL of 15% aqueous H_2SO_4. The layers were separated, and the aqueous phase was saturated with NaCl and extracted with Et_2O (2 × 200 mL). The combined Et_2O layers were dried ($MgSO_4$) and filtered, and the solvent was removed by distillation. Continued distillation afforded 17.2 g (45%) of product as a colorless liquid, bp 111–115 °C [lit.[34] bp 114–116 °C].

Preparation of 4-Methyl-1-penten-3-ol (4g). A flame-dried, 500-mL, three-necked, round-bottomed flask equipped with a thermometer, stirring bar, septum, condenser, and N_2 inlet was charged with 12.3 g (0.51 mol) of Mg, 100 mL of dry THF, and a crystal of iodine. Vinyl bromide (51.5 g, 0.48 mol) in 20 mL of THF was added dropwise via cannula over 1 h. The brown heterogeneous mixture was cooled in an ice bath, and 23.8 g (0.33 mol) of isobutyraldehyde was added over 30 min. The cold bath was removed and the reaction was allowed to stir for 30 min. Workup proceeded as in the previous experiment except that here the combined Et_2O layers were washed with $NaHCO_3$ saturated aqueous solution before distillation. A 67% yield (22.1 g) of product was obtained, bp 122–127 °C [lit.[35] bp 125 °C].

Preparation of 4-Methyl-3-(1-methylethyl)-2-penten-1-ol (4l). A 100-mL, three-necked, round-bottomed flask equipped with a stirring bar, nitrogen inlet, dropping funnel, and reflux condenser was charged with resublimed magnesium turnings (1.92 g, 0.08 mol) and 6 mL of THF. Vinyl bromide (5.64 mL, 0.08 mol) in 4 mL of THF was added dropwise over 20 min. The mixture was stirred for 45 min. Diisoproyl ketone **11** (4.57 g, 0.04 mol) was dissolved in 40 mL of THF and added dropwise over 20 min to the reaction flask. The mixture was stirred 1 h and poured carefully onto 200 mL of crushed ice and 200 mL of 2 N HCl and 200 mL of Et_2O were added. The organic layer was washed with 100 mL of saturated $NaHCO_3$ and 100 mL of brine. The organic layer was dried over $MgSO_4$, and the solvent was removed. Distillation of the crude product afforded 5.3 g (71%) of 4-methyl-3-(1-methylethyl)-1-penten-3-ol, bp 72–73 °C (30 Torr). ^1H NMR (90 MHz): 5.5–5.0 (m, 1 H, C*H*=CH$_2$), 5.0–5.3 (m, 2 H, CH=CH_2), 1.7–2.1 (m, 2 H, C*H*(CH$_3$)$_2$), 1.2 (s, 1 H, OH), 0.8–1.0 (m, 12 H, CH(CH_3)$_2$).

(33) Hiskey, C. F.; Slates, H. C.; Wendler, N. L. *J. Org. Chem.* **1956**, *21*, 429.
(34) *Dictionary of Organic Compounds*; Buckingham, J., Ed.; Chapman and Hall: New York, 1982; Vol. 4, p 4542.
(35) *Beilsteins Handbuch der Organische Chemie*; Springer-Verlag: Berlin, 1941; Band I, E II, p 487.

A 250-mL, three-necked, round-bottomed flask equipped with a stirring bar, reflux condenser, and nitrogen inlet was charged with pyridinium chlorochromate (20.5 g, 95 mmol) and 100 mL of CH_2Cl_2. A solution of 4-methyl-3-(1-methylethyl)-1-penten-3-ol (6.8 g, 47.5 mmol) in 50 mL of CH_2Cl_2 was added in one portion to the slurry. The mixture was stirred at room temperature for 24 h, and an additional 6.8 g of PCC was added to the reaction mixture. After being stirred another 48 h, the reaction mixture was diluted with an equal volume of Et_2O and decanted. The black precipitate was washed with three 20-mL portions of Et_2O, and the Et_2O layers were combined. The organic layers were washed with 5% aqueous NaOH (2 × 200 mL), 5% HCl (200 mL), and saturated $NaHCO_3$ (2 × 75 mL). The organic layers were dried over $MgSO_4$, and the solvent was removed. The crude aldehyde was used directly in the reduction step to the alcohol.

A flame-dried, 50-mL, three-necked, round-bottomed flask equipped with a stirring bar, nitrogen inlet, and septum was charged with $NaBH_4$ (0.51 g, 13.5 mmol) and 6.8 mL of ethanol. The mixture was cooled in an ice bath, and the crude aldehyde (3.77 g, 27 mmol) was added dropwise via syringe. The mixture was stirred at room temperature and monitored by TLC. Upon completion, the reaction was quenched with 1 N HCl, extracted into Et_2O, and washed with water and brine. The organic layer was dried ($MgSO_4$), and the solvent was removed. The product was chromatographed (hexane/EtOAc, 4/1) and then bulb-to-bulb distilled to afford **4l** in 40% yield for the two steps, bp 85 °C (29 Torr). IR ($CHCl_3$): 3160 s, 3450 w, 2960 s, 2930 s, 2870 s, 1650 w, 1460 s, 1380 m, 1360 m, 1155 w, 1000 s, 975 m, 950 m. ^1H NMR (200 MHz): 5.36 (t, J = 7, 1 H, C=CH), 4.21 (t, J = 6, 2 H, CH_2OH), 2.78 (m, 1 H, $CH(CH_3)_2$), 2.32 (m, 1 H, $CH(CH_3)_2$), 1.17 (m, 1 H, $CH(CH_3)_2$, 1.02 (d, J = 7, 12 H, $CH(CH_3)_2$). MS (70 eV): m/e (relative intensity) 124 (36), 111 (21), 109 (40), 99 (51), 98 (11), 83 (70), 82 (12), 81 (90), 79 (17), 71 (24), 69 (56), 67 (36), 57 (22), 56 (10), 55 (86), 43 (19), 43 (100), 41 (86). Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 75.93; H, 13.00.

Preparation of Allyl Vinyl Ethers. General Procedure for the Alumina-Catalyzed Addition of Allylic Alcohols to (1,2-Propadienylsulfonyl)benzene. A flame-dried, 250-mL, round-bottomed flask equipped with a mechanical stirrer, septum, and N_2 inlet was charged with 54 g (0.53 mol) of activated basic alumina. Dry THF (50 mL), **3a** (3 g, 17 mmol), and 5 equiv of allyl alcohol were added. After 24 h, the reaction mixture was filtered, and the alumina was rinsed thoroughly with Et_2O and CH_2Cl_2. Removal of solvent gave a crude product, which was purified by column chromatography and recrystallization. Column chromatography and recrystallization solvents will be specified for each compound. Consult Table II for more information. This method will be denoted method A.

General Procedure for the Allyl Oxide Initiated Additions of Allylic Alcohols to Sulfones. An oven-dried, three-necked, round-bottomed flask equipped with an N_2 inlet, two septa, and a stirring bar was charged with KH or NaH dispersion. This was rinsed with hexane (3x), and solvent was added. If the solvent was THF the appropriate amount of allylic alcohol was then added. The reaction mixture was cooled as specified, and sulfone was added in one portion. The reaction mixture was monitored by TLC or just worked up after a short time. The reaction was quenched by addition to water. Ether extraction followed by water and brine washes, drying ($MgSO_4$), and solvent removal gave the crude product. This was purified by flash chromatography and/or recrystallization. Column chromatography and recrystallization solvents will be specified for each compound. Consult Tables III–V for more information. This method will be denoted method B.

[[2-(2-Propenyloxy)-2-propenyl]sulfonyl]benzene (1aa). Method B. In one run the crude product was purified by two recrystallizations from diisopropyl ether. This gave a 65% yield of **1aa** as colorless cubes, mp 43–53 °C. IR ($CHCl_3$): 2900 w, 1665 w, 1630 s, 1440 m, 1390 m, 1318 s, 1290 s, 1210 m, 1155 s, 1130 m, 1085 s, 1047 m, 1005 m, 935 m, 914 m, 872 w, 830 m. ^1H NMR (90 MHz): 7.94–7.78 (m, 2 H, Ar H ortho to SO_2), 7.78–7.34 (m, 3 H, Ar H), 5.87–5.37 (m, 1 H, CH=CH_2), 5.21–4.80 (m, 2 H, CH=CH_2), 4.23–4.10 (dxd, J = 3, 2 H, C=CH_2), 4.01 (br d, J = 5, 2 H, OCH_2), 3.83 (s, 2 H, SO_2CH_2). MS (10 eV): m/e (relative intensity) 238 (M^+, 0.45), 141 (19), 97 (54), 96 (100), 83 (21), 79 (11), 77 (10), 67 (12), 55 (27), 43 (23), 41 (39). Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.50; H, 5.88; S, 13.45. Found: C, 60.50; H, 5.80; S, 13.56. The wide melting range was due to the presence of ca. 4% of the (*Z*)-**2aa** isomer which was isolated by MPLC (aminopropyl column; hexane/isopropyl alcohol, 4/1) and identified by NMR (90 MHz): 8.03–7.86 (m, 2 H, Ar H ortho to SO_2), 7.57–7.34 (m, 3 H, Ar H), 5.90–5.48 (m, 1 H, at 5.77, CH=CH_2), 5.77 (s, 1 H, $PhSO_2CH$=), 5.27–4.97 (m, 2 H, CH=CH_2), 4.39 (br d, J = 5, 2 H, OCH_2), 1.97 (s, 3 H, CH_3). In another run of this reaction, the crude product was first purified by column chromatography to give an 84% yield of product. Severl recrystallizations from diisopropyl ether gave a 55% yield of **1aa**, mp 52–55 °C.

(*E*)-[[2-(2-Propenyloxy)-1-propenyl]sulfonyl]benzene (2aa). Method B. Chromatographic purification of the crude product (hexane/EtOAc, 2.5/1) gave 52% yield of **2aa** and an 18% yield of the corresponding diallyl acetal. The corrected yield for **2aa** is 64%. IR ($CHCl_3$): 3189 w, 3070 w, 3024 m, 2931 w, 1611 s, 1479 w, 1462 w, 1448 m, 1426 w, 1414 w, 1388 m, 1362 w, 1321 s, 1311 s, 1305 s, 1228 m, 1209 m, 1180 w, 1144 s, 1087 s, 1070 m, 1054 m, 1026 w, 1000 w, 985 w, 930 m. ^1H NMR (220 MHz): 7.90 (dxd, J = 1.2, 7.6, 2 H, Ar H ortho to SO_2), 7.62–7.47 (m, 3 H, Ar H), 5.99–5.82 (m, 1 H, CH=CH_2), 5.55 (s, 1 H, $PhSO_2CH$=), 5.37–5.26 (m, 2 H, CH=CH_2), 4.27 (d, J = 5.3, 2 H, OCH_2), 2.25 (s, 3 H, CH_3). MS (10 eV): m/e (relative intensity) 238 (M^+, 1.1), 97 (100), 96 (29), 83 (40), 77 (10), 55 (14), 43 (82), 41 (44). Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.50; H, 5.88; S, 13.45. Found: C, 60.59; H, 6.01; S, 13.43. The following data obtains for the acetal. ^1H NMR (90 MHz): 7.97–7.80 (m, 2 H, Ar H ortho to SO_2), 7.60–7.42 (m, 3 H, Ar H), 5.90–5.48 (m, 2 H, 2 × CH=CH_2), 5.20–4.91 (m, 4 H, 2 × CH=CH_2), 3.81 (d, J = 5, finely split, 4 H, 2 × OCH_2), 3.44 (s, 2 H, SO_2CH_2), 1.73 (s, 3 H, CH_3).

[[2-(2-Butenyloxy)-2-propenyl]sulfonyl]benzene (1ab). Method A. Commecial *trans*-crotyl alcohol was used in this preparation. Chromatographic purification of the crude product (hexane/EtOAc, 2/1) gave a 24% yield of **1ab** (30% corrected for recovered starting material). Two recrystallizations from hexane/diisopropyl ether produced **1ab** in 17% yield as colorless needles, mp 59–60 °C. IR ($CHCl_3$): 3025 m, 2972 w, 2940 w, 2919 w, 1715 w, 1670 w, 1629 m, 1587 w, 1521 w, 1480 w, 1463 w, 1449 m, 1398 w, 1322 s, 1310 s, 1300 s, 1228 m, 1210 m, 1180 w, 1155 s, 1141 m, 1085 m, 1028 m, 999 w, 968 m, 922 w, 896 w, 860 w, 827 m. ^1H NMR (220 MHz): 7.90 (d, J = 7.6, 2 H, Ar H ortho to SO_2), 7.67–7.49 (m, 3 H, Ar H), 5.64–5.48 (m, 1 H, CH=$CHCH_3$) 5.34–5.21 (m, 1 H CH=$CHCH_3$), 4.19 (d, J = 2.8, 1 H, C=CHH), 4.17 (d, J = 2.7, 1 H, C=CHH), 3.93 (d, J = 5.9, 2 H, OCH_2), 3.86 (s, 2 H, SO_2CH_2), 1.66 (d, J = 6.5, 3 H, CH_3). MS (10 eV): m/e (relative intensity) 252 (M^+, 0.64), 198 (18), 141 (14), 134 (20), 126 (28), 125 (100), 111 (39), 110 (92), 95 (10), 93 (16), 77 (12), 55 (75), 43 (12). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.90; H, 6.35; S, 12.70. Found: C, 61.91; H, 6.34; S, 12.74.

(*E*)-[[2-[(*E*)-(2-Butenyloxy)]-1-propenyl]sulfonyl]benzene (2ab). Method B. Column chromatographic purification of the crude product gave a 75% yield of a mixture of **1ab** and **2ab**. This was isomerized to **2ab** by treatment with a catalytic amount of KO-*t*-Bu in THF at room temperature for 5 h. Column chromatographic purification (hexane/EtOAc, 2/1) of this product gave a 31% yield of **2ab**. IR ($CHCl_3$): 3063 w, 3019 s, 2971 w, 2942 w, 2919 w, 1719 w, 1675 w, 1609 s, 1587 m, 1522 w, 1480 w, 1462 w, 1448 m, 1440 w, 1424 w, 1322 s, 1311 s, 1305 s, 1227 s, 1208 s, 1145 s, 1085 s, 1070 w, 1044 m, 1024 w, 999 w, 967 m, 927 w, 898 w. ^1H NMR (220 MHz): 7.90 (br d, J = 7.2, 2 H, Ar H ortho to SO_2), 7.68–7.49 (m, 3 H, Ar H), 5.78–5.54 (m, s at 5.54, 3 H, olefinic H), 4.18 (d, J = 6.9, 2 H, OCH_2), 2.23 (s, 3 H, CH_3), 1.73 (d, J = 6.1, 3 H, CH_3). MS (10 eV): m/e (relative intensity) 199 (17), 198 (23), 134 (10), 111 (100), 110 (16), 94 (21), 83 (27), 55 (24), 43 (29). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.90; H, 6.35; S, 12.70. Found: C, 61.79; H, 6.48; S, 12.82.

[[2-[(2-Methyl-2-propenyl)oxy]-2-propenyl]sulfonyl]-benzene (1ad). Method A. Chromatography solvent, hexane-/EtOAc, 2/1. Yield, 18% (44% corrected for recovered starting material). Two recrystallizations from hexane/diisopropyl ether gave a 12% (30% corrected) yield of **1ad**, mp 57.5–60 °C. IR ($CHCl_3$): 3071 w, 3030 m, 3020 m, 2981 w, 2940 w, 2921 w, 2865 w, 1985 w, 1965 w, 1920 w, 1900 w, 1812 w, 1720 w, 1660 w, 1632 s, 1588 w, 1520 w, 1478 w, 1449 s, 1435 w, 1400 w, 1390 w, 1378 w, 1321 s, 1309 s, 1301 s, 1231 m, 1211 m, 1155 s, 1132 m, 1092 m, 1076 w, 1000 w, 985 w, 960 w, 912 m, 871 w, 828 m. ^1H NMR

(220 MHz): 7.90 (d, J =7, 2 H, Ar H ortho to SO_2), 7.63–7.49 (m, 3 H, Ar H), 4.81 (br s, 1 H, CH=C*H*), 4.76 (br s, 1 H, CH=CH*H*), 4.19 (s, 2 H, C=CH_2), 3.93 (s, 2 H, OCH_2), 1.56 (s, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 253 (M^+ + 1, 0.78), 141 (18), 111 (80), 110 (23), 95 (17), 93 (23), 77 (46), 69 (27), 55 (100), 51 (16), 43 (20), 41 (15). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.90; H, 6.35; S, 12.70. Found: C, 61.84; H, 6.33; S, 12.89.

(*E*)-[[2-[(1-Methyl-2-propenyl)oxy]-1-propenyl]sulfonyl]benzene (2ae). Method B. Chromatography solvent, hexane/EtOAc, 3/1. Yield, 77%. IR ($CHCl_3$): 3084 w, 3065 w, 3019 w, 2985 w, 2932 w, 1740 w, 1604 s, 1585 m, 1542 w, 1479 w, 1448 w, 1422 w, 1411 w, 1385 w, 1366 w, 1302 s, 1225 s, 1218 s, 1209 s, 1178 w, 1142 s, 1084 s, 1058 m, 1038 w, 1024 w, 999 w, 988 w, 969 w, 930 w, 890w, 840w. ^1H NMR (220 MHz): 7.88 (d, J = 7, 2 H, Ar H ortho to SO_2), 7.65–7.43 (m, 3 H, Ar H), 5.81–5.65 (m, 1 H, C*H*=CH_2), 5.56 (s, 1 H, $PhSO_2CH$=), 5.19 (d, J = 11.4, 1 H, CH=C*H*$_c$H$_t$), 5.17 (d, J = 16.3, 1 H, CH=CH$_c$*H*$_t$), 4.57 (br quintet, J = 6.1, 1 H, OC*H*(CH_3)), 2.19 (s, 3 H, CH_3), 1.34 (d, J = 6.2, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 253 (M^+ + 1, 0.32), 198 (15), 141 (14), 125 (11), 111 (57), 95 (13), 94 (33), 78 (12), 77 (48), 55 (100), 43 (55). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.90; H, 6.35;, S, 12.70. Found: C, 61.86; H, 6.32; S, 12.94.

(*E*)-[[2-[(1-Ethyl-2-propenyl)oxy]-1-propenyl]sulfonyl]benzene (2af). Method B. Chromatography solvent, hexane/EtOAc, 4/1. Yield, 75%. IR ($CHCl_3$): 3088 w, 3071 w, 3030 m, 3020 m, 2973 m, 2940 m, 2881 w, 1722 w, 1600 s, 1481 w, 1466 w, 1458 w, 1449 s, 1424 m, 1414 w, 1388 m, 1305 s, 1230 m, 1218 m, 1209 m, 1179 w, 1144s, 1087 s, 1070 m, 1066 m, 1044 m, 991 m, 978 w, 929 m, 918 m, 875 w, 860 w. ^1H NMR (220 MHz): 7.87 (dxd, J = 7.7, 1.3, 2 H, Ar H ortho to SO_2), 7.61–7.50 (m, 3 H, Ar H), 5.67–5.56 (m, 1 H, C*H*=CH_2), 5.56 (s, 1 H, $PhSO_2CH$=), 5.22 (d, J = 10.6, 1 H, CH=C*H*$_c$H$_t$), 5.15 (d, J = 18.3, 1 H, CH=CH$_c$*H*$_t$), 4.33 (br q, J = 6.3, 1 H, OC*H*Et), 2.20 (s, 3 H, CH_3), 1.68 (quintet, J = 6.3, 2 H, CH_2), 0.91 (t, J = 6.3, 3 H, CH_2CH_3). MS (70 eV): m/e (relative intensity) 266 (M^+, 0.9), 199 (28), 141 (14), 125 (41), 96 (26), 94 (14), 81 (14), 78 (12), 77 (72), 69 (55), 68 (49), 67 (18), 53 (13), 51 (27), 43 (100), 41 (99). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.16; H, 6.77; S, 12.03. Found: C, 63.25; H, 6.96; S. 12.07.

(*E*)-[[2-[[1-(1-Methylethyl)-2-propenyl]oxy]-1-propenyl]sulfonyl]benzene (2ag). Chromatography solvent, hexane/EtOAc, 2/1. Yield, 41%. Though chromatographically homogeneous, it appeared that the product contained a considerable amount of the β,γ-unsaturated isomer. NMR assignments for this compound are included below when possible. IR ($CHCl_3$): 3089 w, 3071 m, 3025 s, 3019 s, 2966 s, 2934 m, 2915 m, 2900 m, 2878 m, 1722 m, 1610 s, 1598 s, 1480 w, 1471 m, 1465 m, 1449 s, 1425 m, 1412 m, 1387 s, 1369 m, 1320 s, 1310 s, 1305 s, 1230 s, 1221 s, 1214 s, 1210 s, 1179 m, 1143 s, 1086 s, 1071 m, 1060 m, 1042 m, 1038 m, 993 m, 978 m, 960 w, 892 w, 857 w. ^1H NMR (220 MHz): 7.92–7.84 (m, 2 H, Ar H ortho to SO_2), 7.63–7.43 (m, 3 H, Ar H), 5.69–5.03 (m, s at 5.55, 4 H, olefinic H), 4.16 (t, J = 5.9, 1 H, OC*H*-*i*-Pr α,β isomer), 4.11 (s, 2 H, methylidene H, β,γ isomer), 3.93 (br t, J =5, OC*H*-*i*-Pr β,γ isomer), 3.87 (s, 2 H, SO_2CH_2, β,γ isomer), 2.20 (s, 3 H, CH_3, α,β isomer), 1.87 (septet, J = 6.7, 1 H, C*H*(CH_3)$_2$), 0.92 (d, J = 6.8, CH_3, α,β isomer), 0.90 (d, J = 6.7, 3 H, CH_3, α,β isomer), 0.75 (apparent t, J = 7, 6 H, 2 × CH_3, β,γ isomer). MS (10 eV): m/e (relative intensity) 280 (M^+, 4.7), 199 (17), 141 (12), 139 (31), 138 (15), 125 (17), 95 (32), 82 (100), 81 (20), 67 (18), 55 (72), 43 (47), 41 (12). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.29; H, 7.14; S, 11.43. Found: C, 64.44; H, 7.31; S. 11.38.

[[2-[(*E*)-(3-Phenyl-2-propenyl)oxy]-2-propenyl]sulfonyl]benzene (1ah). Method A. Chromatography solvent, hexane/EtOAc, 2/1. Yield, 9.5%. Two recrystallizations from diisopropyl ether/ethyl acetate gave **1ah** (4%) as colorless flakes, mp 91–92.5 °C. IR (KBr): 3081 m, 3065 m, 3058 m, 3029 m, 2979 m, 2929 m, 1718 m, 1639 m, 1598 w, 1586 w, 1575 w, 1496 w, 1479 w, 1447 w, 1425 w, 1400 w, 1385 w, 1373 w, 1319 s, 1310 s, 1301 s, 1292 s, 1246 w, 1169 s, 1139 m, 1096 m, 1085 m, 1071 w, 1055 w, 1032 w, 1024 w, 1016 w, 1000 w, 990 w, 985 w, 975 w, 970 w, 921 w, 912 w, 897 m. ^1H NMR (220 MHz): 7.92 (br d, J = 7.6, 2 H, Ar H ortho to SO_2), 7.59–7.47 (m, 3 H, Ar H), 7.37–7.27 (m, 5 H, Ph H), 6.39 (d, J = 15, 1 H, CH=C*H*Ph), 5.96 (dxt, J = 15.9, 1 H, C*H*=CHPh), 4.26 (d, J = 3, 1 H, C=C*H*H), 4.24 (d, J = 3, 1 H, C=CH*H*), 4.19 (br d, J = 5.6, 2 H, OCH_2), 3.91 (s, 2 H, SO_2CH_2). MS (70 eV): m/e (relative intensity) 172 (M^+ – 152, 18), 118 (11), 117 (100), 115 (25), 92 (14), 77 (10). Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.79; H, 5.73; S, 10.19. Found: C, 68.76; H, 5.82; S, 10.36.

[[2-[(3-(Trimethylsilyl)-2-propenyl)oxy]-2-propenyl]sulfonyl]benzene (1ai). Method B. Chromatography solvent, hexane/EtOAc, 7/1. Yield, 55%. Though chromatographically homogeneous, the product appeared to be a 1:1 mixture of α,β- and β,γ-unsaturated isomers. IR (neat): 3071 m, 3005 w, 2980 s, 2901 m, 2870 w, 1613 s, 1479 m, 1448 s, 1390 m, 1370 m, 1152 s, 1249 s, 1217 s, 1145 s, 1085 s, 1046 s, 1023 m, 999 m, 985 s, 938 m, 862 s, 840 s, 810 s. ^1H NMR (200 MHz): 7.92–7.87 (m, 2 H, Ar H ortho to SO_2, both isomers), 7.62–7.47 (m, 3 H, Ar H, both isomers), 6.00–5.97 (m, 2 H, olefinic H, one isomer), 5.74–5.71 (m, 2 H, olefinic H, one isomer), 5.52 (s, 1 H, $PhSO_2HC$=C, α,β isomer), 4.30 (d, J = 3.3, 2 H, OCH_2, α,β isomer), 4.21 (d, J =2.9, 1 H, C=C*H*H, β,γ isomer), 4.16 (d, J = 2.9, 1 H, C=CH*H*, β,γ isomer), 4.02 (d, J = 3.2, 2 H, OCH_2, β,γ isomer), 3.89 (s, 2 H, $PhSO_2CH_2$), 2.26 (s, 3 H, CH_3), 0.06 (s, 9 H, Si(CH_3)$_3$), 0.05 (s, 9 H, Si(CH_3)$_3$). MS (10 eV): m/e (relative intensity) 310 (M^+, 0.33), 295 (18), 255 (19), 199 (15), 169 (34), 168 (44), 166 (13), 153 (26), 137 (13), 136 (14), 135 (100), 129 (10), 125 (23), 115 (40), 113 (17), 112 (20), 97 (23), 85 (40), 83 (14), 77 (16), 75 (64), 73 (98), 61 (12), 59 (56), 58 (12), 43 (35). Anal. Calcd for $C_{15}H_{22}O_3SiS$: C, 58.06; H, 7.10; S, 10.32. Found: C, 57.95; H, 6.98; S, 10.11.

(*E*)-1-[[2-(2-Propenyloxy)-2-butenyl]sulfonyl]-4-methylbenzene (1ba). Method B. Chromatography solvent, cyclohexane/EtOAc, 4/1. Yield, 90%. Recrystallization from hexane/diisopropyl ether gave **1ba** (78%) as colorless cubes, mp 44.5–46.5 °C. IR ($CHCl_3$): 3070 w, 2950 m, 1945 w, 1685 m, 1610 m, 1500 w, 1460 m, 1410 m, 1355 m, 1322 s, 1310 s, 1305 s, 1255 m, 1155 s, 1142 s, 1110 s, 1095 s, 1029 m, 1005 s, 935 m, 880 m, 819 w. ^1H NMR (220 MHz): 7.76 (d, J = 8.3, 2 H Ar H ortho to SO_2), 7.30 (d, J = 8.2, 2 H, Ar H), 5.70–5.53 (m, 1 H, C*H*=CH_2), 5.09–5.01 (m, 2 H, CH=CH_2), 4.73 (q, J = 7.1, 1 H, C=C*H*CH_3), 3.97 (s, 2 H, $PhSO_2CH_2$), 3.94 (d, J = 5.4, 2 H, OCH_2), 2.43 (s, 3 H, $C_6H_4CH_3$), 1.57 (d, J = 7, 3 H, C=CHCH_3). MS (70 eV): m/e (relative intensity) 266 (M^+, 1.1), 155 (19), 139 (11), 110 (66), 95 (11), 93 (14), 92 (14), 91 (78), 81 (12), 69 (23), 67 (16), 65 (28), 57 (12), 55 (47), 53 (15), 43 (37), 41 (100). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.16; H, 6.77; S, 12.03. Found: C, 63.17; H, 6.70; S, 12.01.

(*E*)-1-[[2-[(*E*)-(2-Butenyloxy)]-2-butenyl]sulfonyl]-4-methylbenzene (1bb). Chromatography solvent, hexane/EtOAc, 4/1. Yield, 82%. Two recrystallizations from hexane/EtOAc gave **1bb** (62%) as colorless needles, mp 86.7–88 °C. IR ($CHCl_3$): 2910 m, 2860 m, 1670 m, 1600 m, 1495 w, 1470 m, 1405 m, 1380 m, 1349 m, 1318 s, 1300 s, 1292 s, 1245 s, 1152 s, 1135 s, 1105 s, 1090 s, 1020 m, 971 m, 918 w, 880 m, 815 m. ^1H NMR (220 MHz): 7.76 (d, J = 8.3, 2 H, Ar H ortho to SO_2), 7.31 (d, J = 8.1, 2 H, Ar H), 5.59–5.43 (m, 1 H, CH=C*H*CH_3), 5.28–5.15 (m, 1 H, C*H*=$CHCH_3$), 4.72 (q, J = 7.1, 1 H, enol ether H), 3.96 (s, 2 H, *p*-TolSO_2CH_2), 3.85 (d, J = 5.9, 2 H, OCH_2), 2.44 (s, 3 H, $C_6H_4CH_3$), 1.64 (d, J = 6.1, 3 H, CH=CHCH_3), 1.57 (d, J = 6.9, 3 H, C=CHCH_3). ^{13}C NMR (90.7 MHz) 145.27 (s), 144.31 (s), 136.70 (s), 129.41 (d), 129.16 (d), 128.66 (d), 125.84 (d), 100.04 (d), 67.83 (t), 58.49 (t), 21.55 (q), 17.68 (q), 12.03 (q). MS (10 eV): m/e (relative intensity) 280 (M^+, 1.67), 226 (79), 208 (55), 157 (48), 140 (20), 139 (100), 125 (16), 124 (46), 107 (20), 83 (17), 71 (70), 55 (23), 43 (11). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.29; H, 7.14; S, 11.43. Found: C, 64.48; H, 7.36; S, 11.76.

(*E*)-1-[[2-[(*Z*)-(2-Butenyloxy)]-2-butenyl]sulfonyl]-4-methylbenzene (1bc). Chromatography solvent, hexane/EtOAc, 4/1. Yield, 67%. Recrystallization from pentane/ether (2×) gave **1bd** (36%) as colorless needles, mp 62–62.7 °C. IR ($CHCl_3$): 2900 m, 2850 w, 1672 m, 1600 m, 1495 w, 1450 m, 1401 m, 1380 w, 1347 w, 1320 s, 1292 s, 1250 s, 1153 s, 1138 s, 1105 s, 1090 s, 1023 m, 977 w, 880 m, 815 m. ^1H NMR (220 MHz): 7.76 (d, J = 8.2, 2 H, Ar H ortho to SO_2), 7.30 (d, J = 8.2, 2 H, Ar H), 5.58–5.50 (m, 1 H, C*H*=CH), 5.19–5.13 (m, 1 H, CH=C*H*), 4.74 (q, J = 7, 1 H, C=C*H*CH_3), 4.01 (d, J = 6.3, 2 H, OCH_2), 3.96 (s, 2 H, *p*-TolSO_2CH_2), 2.43 (s, 3 H, $C_6H_4CH_3$), 1.56–1.10 (overlapping a's, 6 H, 2 × CH_3). ^{13}C NMR (90.7 MHz): 145.22, 144.33, 136.22, 129.34, 128.54, 127.22, 125.54, 100.05, 63.10, 58.45, 21.52, 13.07, 11.99. MS (10 eV): m/e (relative intensity) 280 (M^+, 1.53), 226 (27), 208 (22), 157 (35), 155 (11), 140 (16), 139 (88), 124 (12), 92

(16), 91 (68), 71 (86), 65 (26), 55 (100), 53 (35), 43 (21), 41 (30). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.29; H, 7.14; S, 11.43. Found: C, 64.27; H, 7.28; S, 11.57.

(*E*)-1-[[2-(2-Cyclohexenyloxy)-2-butenyl]sulfonyl]-4-methylbenzene (1bp). Method B. Chromatography solvent, hexane/EtOAc, 4/1. Yield, 45%. IR ($CHCl_3$): 3017 m, 2945 m, 2895 w, 2875 w, 2840 w, 1721 w, 1668 m, 1601 m, 1497 w, 1455 m, 1440 m, 1404 m, 1345 m, 1320 s, 1307 s, 1295 s, 1151 s, 1135 s, 1095 s, 1061 m, 1038 s, 1031 m, 1020 m, 1008 m, 968 m, 886 m, 868 m. ^1H NMR (220 MHz): 7.77 (d, J = 8.1, 2 H, Ar H ortho to SO_2), 7.30 (d, J = 8.1, 2 H, Ar H), 5.85–5.75 (m, 1 H, CH=C*H*), 5.54–5.46 (m, 1 H, C*H*=CH), 4.77 (q, J = 7, 1 H, CH_3CH=), 4.29–4.21 (m, 1 H, OC*H*), 3.96 (d, J = 16, 1 H, $SO_2CH_aCH_b$), 3.94 (d, J = 16, 1 H, $SO_2CH_aCH_b$), 2.44 (s, 3 H, $C_6H_4CH_3$), 1.97–1.89 (m, 2 H, CH_2CH=), 1.68–1.39 (m, 4 H, $(CH_2)_2$), 1.55 (d, J = 7, 3 H, CH_3CH=). MS (10 eV): m/e (relative intensity) 306 (M^+, 0.61), 227 (49), 226 (11), 208 (17), 157 (42), 140 (12), 139 (66), 99 (21), 81 (100), 80 (38), 79 (12), 71 (39), 57 (11), 53 (15). Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.67; H, 7.19; S, 10.46. Found: C, 66.36; H, 7.24; S, 10.46.

(*E*)-1-[[2-(2-Butynyloxy)-2-butenyl]sulfonyl]-4-methylbenzene (1br). Method B. Two recrystallizations from diisopropyl ether gave **1br** (62%) as colorless needles, mp 65–66.5 °C. IR ($CHCl_3$): 3050 w, 2910 w, 2230 w, 1675 m, 1605 w, 1495 w, 1450 w, 1401 m, 1370 w, 1352 m, 1319 s, 1295 s, 1250 m, 1150 s, 1138 s, 1097 s, 1090 s, 1015 m, 995 w, 875 m, 817 w. ^1H NMR (220 MHz): 7.78 (d, J = 8.2, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8, 2 H, Ar H), 4.86 (q, J = 6.9, 1 H, C=C*H*CH_3), 4.11 (br d, J = 2, 2 H, OCH_2), 3.95 (s, 2 H, p-TolSO_2CH_2), 2.45 (s, 3 H, $C_6H_4CH_3$), 1.83 (t, J = 2, 3 H, C≡CCH_3), 1.52 (d, J = 6.9, 3 H, C=CHCH_3). MS (70 eV) m/e (relative intensity) 139 (M^+ – 139, 13), 122 (21), 91 (22), 58 (24), 53 (19), 44 (12), 43 (100). Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.75; H, 6.47; S, 11.51. Found: C, 64.54; H, 6.65; S, 11.58.

1-[[3-Methyl-2-(2-propenyloxy)-2-butenyl]sulfonyl]-4-methylbenzene (1ca). Method B. The crude product was recrystallized from pentane/diisopropyl ether to give a 59% yield of **1ca** as fluffy needles, mp 47–51 °C. IR ($CHCl_3$): 3080 w, 3065 w, 3025 m, 3019 m, 2923 w, 2880 w, 1716 w, 1672 w, 1647 w, 1598 m, 1520 w, 1496 w, 1452 w, 1424 w, 1404 w, 1382 w, 1375 w, 1358 w, 1319 s, 1305 s, 1290 s, 1273 m, 1226 s, 1209 s, 1183 m, 1150 s, 1119 w, 1087 s, 1040 w, 1020 m, 995 m, 932 m, 873 w, 851 w, 818 w. ^1H NMR (220 MHz): 7.78 (d, J = 8.3, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8.3, 2 H, Ar H), 5.91–5.74 (m, 1 H, C*H*=CH_2), 5.22–5.09 (m, 2 H, CH=CH_2), 4.11 (d, J = 5.6, 2 H, OCH_2), 3.98 (s, 2 H, p-TolSO_2CH_2), 2.44 (s, 3 H, $C_6H_4CH_3$), 1.66 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 280 (M^+, 4.8), 155 (35), 139 (14), 125 (23), 124 (30), 107 (24), 105 (12), 97 (11), 92 (21), 91 (99), 83 (48), 82 (15), 81 (14), 79 (18), 71 (13), 69 (32), 67 (36), 65 (35), 55 (97), 53 (10), 43 (49), 42 (12), 41 (100). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.29; H, 7.19; S, 11.43. Found: C, 64.31; H, 7.31; S, 11.70.

1-[[3-Methyl-2-[(3-methyl-2-butenyl)oxy]-2-butenyl]sulfonyl]-4-methylbenzene (1cj). Method B. Chromatography solvent, cyclohexane/EtOAc, 4/1. Yield, 88%. An analytical sample was prepared by recrystallization from diisopropyl ether and hexane to give **1cj** as colorless needles, mp 49.5–51.5 °C. IR ($CHCl_3$): 3030 w, 3001 m, 2985 m, 2865 m, 1670 w, 1599 m, 1497 w, 1451 m, 1387 m, 1325 s, 1310 s, 1296 m, 1279 m, 1160 s, 1099 s, 1052 w, 1031 w, 990 m, 939 w, 890 w. ^1H NMR (200 MHz): 7.78 (d, J = 8.2, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 7.9, 2 H, Ar H), 5.21 (t, J = 7.4, finely split, =C*H*), 4.09 (d, J = 7.0, 2 H, CH_2O), 3.99 (s, 2 H, CH_2SO_2), 2.44 (s, 3 H, $C_6H_4CH_3$), 1.71 (s, 3 H), 1.66 (s, 3 H), 1.62 (s, 3 H), 1.36 (s, 3 H). MS (70 eV): m/e (relative intensity) 240 (M^+ –68, 15.5), 222 (19), 157 (12), 140 (13), 139 (13), 91 (29), 85 (100), 69 (67), 67 (45), 65 (12), 41 (70). Anal. Calcd for $C_{17}H_{24}O_3S$: C, 66.23; H, 7.79; S, 10.40. Found: C, 65.93; H, 7.57; S, 10.31.

1-[[2-[(3-Ethyl-2-pentyl)oxy]-3-methyl-2-butenyl]sulfonyl]-4-methylbenzene (1ck). Method B. Chromatography solvent, hexane/EtOAc, 4/1. Yield, 86%. Oil. IR ($CHCl_3$): 3000 s, 1700 w, 1640 m, 1480 w, 1400 w, 1340 s, 1230 s, 1160 s, 1100 s, 1000 m. ^1H NMR (200 MHz): 7.80 (d, J = 7.0, 2 H, Ar H ortho to SO_2), 7.34 (d, J = 7.9, 2 H, Ar H), 5.15 (t, J = 6.4, 1 H, C=CH), 4.14 (d, J = 6.1, 2 H, OCH_2), 4.01 (s, 2 H, p-TolSO_2CH_2), 2.46 (s, 3 H, $C_6H_4CH_3$), 2.04 (q, J = 7.3, 4 H, CH_2CH_3), 1.68 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 1.01 (t, J = 7.3, 3 H, CH_2CH_3), 0.95 (t, J = 7.6, 3 H, CH_2CH_3). MS (70 eV): m/e (relative intensity) 111 (20), 105 (14), 97 (23), 96 (17), 91 (18), 85 (41), 81 (13), 77 (13), 71 (11), 69 (20), 67 (32), 65 (10), 57 (22), 56 (10), 55 (100), 53 (10), 43 (32), 41 (53). Anal. Calcd for $C_{19}H_{28}O_3S$: C, 67.86; H, 8.39; S, 9.52. Found: C, 67.51; H, 8.54; S, 9.35.

1-[[3-Methyl-2-[[4-methyl-3-(1-methylethyl)-2-pentenyl]oxy]-2-butenyl]sulfonyl]-4-methylbenzene (1cl). Method B. Chromatography solvent, benzene/acetone, 200/1. Yield, 88%. Oil. IR ($CHCl_3$): 3290 s, 2930 s, 2870 m, 1920 w, 1820 w, 1710 w, 1600 m, 1460 m, 1400 w, 1380 w, 1360 w, 1320 s, 1300 s, 1290 m, 1270 m, 1140 s, 1080 s, 980 m. ^1H NMR (200 MHz): 7.77 (d, J = 8.2, 2 H, Ar H ortho to SO_2), 7.31 (d, J = 7.9, 2 H, Ar H), 5.13 (t, J = 6.7, 1 H, C=C*H*), 4.15 (d, J = 7.0, 2 H, OCH_2), 3.97 (s, 2 H, p-TolSO_2CH_2), 2.67 (m, 1 H, $CH(CH_3)_2$), 2.43 (s, 3 H, $C_6H_4CH_3$), 2.27 (m, 1 H, $CH(CH_3)_2$), 1.65 (s, 3 H, C=C(CH_3)), 1.38 (s, 3 H, C=C(CH_3)), 0.97 (d, J = 6.7, 6 H, $CH(CH_3)_2$), 0.94 (d, J = 6.9, 6 H, $CH(CH_3)_2$). MS (70 eV): m/e (relative intensity) 58 (35), 57 (17), 55 (30), 44 (13), 43 (100), 41 (34). Anal. Calcd for $C_{21}H_{32}O_3S$: C, 69.19; H, 8.85; S, 8.80. Found: C, 69.03; H, 8.71; S, 8.62.

1-[[2-(2-Cyclohexylideneethoxy)-3-methyl-2-butenyl]sulfonyl]-4-methylbenzene (1cm). Method B. Chromatography solvent, cyclohexane/EtOAc, 7/1. Yield, 76%. Oil. IR (neat): 3029 w, 2929 s, 2854 s, 1737 m, 1668 m, 1598 m, 1494 w, 1448 s, 1402 m, 1379 m, 1370 m, 1319 s, 1302 s, 1289 s, 1270 s, 1247 m, 1200 s, 1181 m, 1150 s, 1087 s, 1044 w, 1019 m, 989 m, 934 w, 892 w, 879 w, 852 w, 817 m. ^1H NMR (220 MHz): 7.78 (d, J = 8.3, 2 H, Ar H ortho to SO_2), 7.23 (d, J = 8.3, 2 H, Ar H), 5.15 (br t, J = 7.2, 1 H, C=C*H*), 4.10 (d, J = 7.2, 2 H, CH_2O), 3.99 (s, 2 H, p-TolSO_2CH_2), 2.44 (s, 3 H, $C_6H_4CH_3$), 2.13–2.05 (m, 4 H, =CCH_2CH_2), 1.66 (s, 3 H, CH_3), 1.56–1.43 (m, 6 H, 3 × CH_2), 1.36 (s, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 240 (M^+ – 108, 18.3), 222 (21), 157 (11), 140 (11), 139 (11), 109 (28), 91 (19), 85 (70), 69 (13), 67 (65), 57 (13), 55 (22), 43 (100), 41 (30). Anal. Calcd for $C_{20}H_{28}O_3S$: C, 68.97; H, 8.05; S, 9.20. Found: C, 68.69; H, 8.18; S, 9.10.

1-[[2-(1-Cyclohexenylmethoxy)-3-methyl-2-butenyl]sulfonyl]-4-methylbenzene (1cn). Method B. Chromatography solvent, hexane/EtOAc, 6/1. Yield, 82%. Oil. IR (neat): 3035 w, 3000 m, 2931 s, 2861 s, 2840 m, 1714 w, 1671 w, 1598 m, 1495 w, 1449 m, 1438 m, 1402 m, 1379 m, 1318 s, 1304 s, 1288 s, 1261 s, 1234 m, 1197 s, 1180 m, 1148 s, 1085 s, 1017 m, 991 m, 922 w, 906 w, 873 w, 860 w, 818 m, 801 m. ^1H NMR (200 MHz): 7.76 (d, J = 8.2, 2 H, Ar H ortho to SO_2), 7.30 (d, J = 8.0, 2 H, Ar H), 5.58–5.51 (m, 1 H, C=C*H*), 3.97 (s, 2 H), 3.87 (s, 2 H), 2.43 (s, 3 H, $C_6H_4CH_3$), 2.09–1.79 (m, 4 H, allylic CH_2), 1.66 (s, 3 H, CH_3), 1.66–1.47 (m, 4 H, CH_2CH_2), 1.40 (s, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 240 (M^+ – 94, 20.9), 222 (18), 198 (14), 157 (13), 140 (15), 139 (17), 95 (54), 94 (12), 92 (14), 91 (36), 85 (100), 81 (14), 79 (21), 67 (60), 65 (18), 57 (22), 55 (18), 53 (11), 43 (36), 41 (45). Anal. Calcd for $C_{19}H_{26}O_3S$: C, 68.26; H, 7.78; S, 9.58. Found: C, 68.57; H, 7.75; S, 9.42.

1-[[2-[2-(4-(2,2-Dimethylethyl)cyclohexylidene)ethoxy]-3-methyl-2-butenyl]sulfonyl]-4-methylbenzene (1co). Method B. Chromatography solvent, hexane/EtOAc, 8/1. Yield, 91%. Oil. IR ($CHCl_3$): 3002 w, 2947 s, 2870 m, 1714 w, 1670 w, 1599 m, 1465 m, 1448 m, 1395 m, 1368 m, 1319 s, 1305 s, 1291 m, 1272 m, 1152 s, 1084 s, 1032 w, 1017 m, 982 m. ^1H NMR (200 MHz): 7.79 (d, J = 8, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8, 2 H, Ar H), 5.14 (br t, J = 7.2, 1 H, C*H*=), 4.11 (d, J = 7.2, 2 H, OCH_2), 3.99 (s, 2 H, p-TolSO_2CH_2), 2.64–2.52 (m, 1 H), 2.44 (s, 3 H, $C_6H_4CH_3$), 2.28–2.16 (m, 1 H), 2.09–1.61 (m, 7 H, s at 1.66, CH_3), 1.37 (s, 3 H, CH_3), 1.19–0.84 (m, 12 H), 0.84 (s, 9 H, $(CH_3)_3C$). MS (70 eV): m/e (relative intensity) 240 (M^+ – 164, 5.3), 222 (14), 155 (64), 105 (11), 93 (14), 92 (19), 91 (100), 85 (25), 79 (24), 71 (42), 67 (15), 65 (26), 57 (45), 43 (43), 41 (32). Satisfactory analytical data on this compound could not be obtained.

1-[[2-(2-Cyclohexenyloxy)-3-methyl-2-butenyl]sulfonyl]-4-methylbenzene (1cp). Method B. Chromatography solvent, hexane/EtOAc, 4/1. Yield, 86%. Oil. IR (neat): 3062 w, 3032 m, 2990 m, 2935 s, 2870 m, 2842 m, 1739 w, 1669 w, 1652 w, 1600 m, 1493 w, 1450 m, 1439 m, 1404 m, 1380 m, 1372 w, 1319 s, 1303 s, 1290 s, 1271 s, 1238 m, 1200 s, 1184 m, 1145 s, 1087 s, 1059 m, 1048 m, 1020 m, 964 m, 923 m, 905 w, 891 w, 887 w, 857 w, 838 w, 818 m. ^1H NMR (200 MHz): 7.77 (d, J = 8.2, 2 H, Ar

H ortho to SO_2), 7.30 (d, J = 8.2, 2 H, Ar H), 5.86–5.77 (m, 1 H, C*H*=CH), 5.54–5.45 (m, 1 H, CH=C*H*), 4.16–4.06 (m, 1 H, C*H*O), 4.01 (s, 2 H, p-TolSO_2CH_2), 2.44 (s, 3 H, $C_6H_4CH_3$), 2.03–1.91 (m, 2 H, =CHCH_2), 1.73–1.40 (m, 4 H, CH_2CH_2), 1.64 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 240 (M^+ – 80, 3.5), 85 (17), 81 (15), 43 (100), 41 (14). Anal. Calcd for $C_{18}H_{24}O_3S$: C, 67.50; H, 7.50; S, 10.00. Found: C, 67.12; H, 7.34; S, 9.64.

1-[(3-Methyl-2-(phenylmethoxy)-2-butenyl)sulfonyl]-4-methylbenzene (1cq). Method B. Chromatography solvent, hexane/EtOAc, 2/1. Yield, 80%. One recrystallization from hexane and one from diisopropyl ether gave **1cq** (51%) as colorless needles, mp 73.5–75 °C. IR ($CHCl_3$): 3025 w, 2890 m, 1720 w, 1670 w, 1600 m, 1445 m, 1400 w, 1373 w, 1312 s, 1300 s, 1270 m, 1140 s, 1085 s, 1020 m, 879 w, 817 w. ^{1}H NMR (200 MHz): 7.78 (d, J = 8, 2 H, Ar H ortho to SO_2), 7.36–7.17 (m, 7 H, Ar H), 4.60 (s, 2 H, p-TolSO_2CH_2), 4.60 (s, 2 H, p-TolSO_2CH_2), 4.00 (s, 2 H, $C_6H_5CH_2$), 2.43 (s, 3 H, $C_6H_4CH_3$), 1.67 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 155 (M^+ – 175, 25.8), 92 (20), 91 (100), 85 (13), 71 (17), 65 (25), 58 (11), 43 (45), 41 (15). HRMS calcd for $C_{19}H_{22}O_3S$: 330.1290. Found: 330.1283.

1-[[3-Ethyl-2-(2-propenyloxy)-2-pentenyl]sulfonyl]-4-methylbenzene (1da). Method B. Chromatography solvent, hexane/EtOAc, 4/1. Yield, 80%; mp 31–32 °C. IR ($CHCl_3$): 3015 m, 2975 s, 2940 m, 2880 m, 1658 w, 1600 m, 1495 w, 1463 m, 1425 w, 1402 m, 1379 w, 1360 w, 1320 s, 1305 s, 1290 m, 1145 s, 1101 m, 1085 s, 1020 m, 990 m, 935 m. ^{1}H NMR (200 MHz): 7.79 (d, J = 8.3, 2 H, Ar H ortho to SO_2), 7.31 (d, J = 8.1, 2 H, Ar H), 5.90–5.74 (m, 1 H, C*H*-CH_2), 5.22–5.07 (m, 2 H, CH=CH_2), 4.08 (dxt, J = 5.4, 1.3, 2 H, CH_2O), 3.98 (s, 2 H, p-TolSO_2CH_2), 2.43 (s, 3 H, $C_6H_4CH_3$), 2.08 (q, J = 7.5, 2 H, CH_2CH_3), 1.75 (q, J = 7.5, 2 H, CH_2CH_3), 0.88 (t, J = 7.5, 3 H, CH_2CH_3), 0.82 (t, J = 7.5, 3 H, CH_2CH_3). MS (70 eV): m/e (relative intensity) 308 (M^+, 0.6), 152 (13), 97 (21), 91 (34), 83 (25), 69 (37), 67 (14), 65 (13), 57 (14), 55 (79), 43 (27), 41 (100). Anal. Calcd for $C_{17}H_{24}O_3S$: C, 66.23; H, 7.79; S, 10.39. Found: C, 66.26; H, 7.96; S, 10.20.

1-[[3-Ethyl-2-[(3-methyl-2-butenyl)oxy]-2-pentenyl]sulfonyl]-4-methylbenzene (1dj). Method B. Chromatography solvent, hexane/EtOAc, 3/1. Yield, 80%. Oil. IR ($CHCl_3$): 3010 s, 1780 w, 1720 w, 1700 m, 1500 m, 1440 w, 1420 w, 1350 s, 1240 s, 1180 s, 1110 s, 1040 m, 1000 m. ^{1}H NMR (200 MHz): 7.79 (s, J = 8.3, 2 H, Ar H ortho to SO_2), 7.31 (d, J = 8.3, 2 H, Ar H), 5.21–5.16 (m, 1 H, C*H*=C$(CH_3)_2$), 4.07 (d, J = 7.0, 2 H, OCH_2), 3.99 (s, 2 H, p-TolSO_2CH_2), 2.43 (s, 3 H, $C_6H_4CH_3$), 2.10 (q, J = 7.3, 2 H, CH_2CH_3), 1.74 (q, J = 7.3, 2 H, CH_2CH_3) 1.71 (s, 3 H, C=C(CH_3)), 1.62 (s, 3 H, C=C(CH_3)), 0.87 (t, J = 7.6, 3 H, CH_2CH_3), 0.81 (t, J = 7.6, 3 H, CH_2CH_3). MS (70 eV): m/e (relative intensity) 113 (34), 112 (96), 111 (22), 97 (31), 95 (74), 91 (41), 83 (10), 71 (26), 69 (100), 67 (26), 65 (14), 57 (36), 53 (14), 43 (88), 41 (95). Anal. Calcd for $C_{19}H_{28}O_3S$: C, 67.82; H, 8.39; S, 9.53. Found: C, 67.53; H, 8.46; S, 9.33.

1-[[3-Ethyl-2-[(3-ethyl-2-pentenyl)oxy]-2-pentenyl]sulfonyl]-4-methylbenzene (1dk). Method B. Chromatography solvent, benzene/acetone, 100/1. Yield, 86%. Oil. IR ($CHCl_3$): 2970 s, 2940 s, 2880 s, 1730 w, 1660 w, 1600 m, 1460 s, 1320 s, 1140 s, 1080 s, 1020 m, 980 m. ^{1}H NMR (200 MHz): 7.79 (d, J = 8.0, 2 H, Ar H ortho to SO_2), 7.31 (d, J = 8.6, 2 H, Ar H), 5.10 (t, J = 6.4, 1 H, C*H*=C$(CH_2CH_3)_2$), 4.10 (d, J = 6.7, 2 H, OCH_2), 3.99 (s, 2 H, p-TolSO_2CH_2), 2.43 (s, 3 H, $C_6H_4CH_3$), 2.10 (q, J = 7.6, 2 H, OC=C(CH_2CH_3), 2.01 (q, J = 7.5, 4 H, C=C(CH_2CH_3)$_2$), 1.75 (q, J = 7.5, 2 H, OC=C(CH_2CH_3)), 0.98 (t, J = 7.5, 3 H, OC=C(CH_2CH_3)), 0.88 (t, J = 7.5, 6 H, C=C(CH_2CH_3)$_2$), 0.82 (t, J = 7.5, 3 H, OC=C(CH_2CH_3). MS (70 eV): m/e (relative intensity) 113 (23), 112 (62), 111 (12), 97 (28), 95 (39), 91 (22), 71 (11), 69 (17), 67 (15), 57 (22), 55 (100), 43 (48), 41 (29). Anal. Calcd for $C_{21}H_{32}O_3S$: C, 69.19; H, 8.85; S, 8.80. Found: C, 69.06; H, 9.06; S, 8.38.

1-[[2-Cyclohexylidene-2-(2-propenyloxy)ethyl]sulfonyl]-4-methylbenzene (1fa). Method B. Chromatography solvent, cyclohexane/EtOAc, 4/1. Yield, 97%. Recrystallization from hexane gave **1fa** (79%) as a colorless solid, mp 36.5–42 °C. IR ($CHCl_3$): 2900 s, 2820 m, 1670 w, 1605 w, 1498 w, 1445 m, 1400 m, 1315 s, 1302 s, 1262 m, 1140 s, 1090 s, 1033 m, 1020 m, 997 m, 935 m, 873 m, 854 w, 822 w. ^{1}H NMR (220 MHz): 7.79 (d, J = 8.3, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8.3, 2 H, Ar H), 5.91–5.73 (m, 1 H, C*H*=CH_2), 5.21–5.09 (m, 2 H, CH=CH_2), 4.13 (d, J = 5.4, 2 H, OCH_2), 3.99 (s, 2 H, p-TolSO_2CH_2), 2.44 (s, 3 H, $C_6H_4CH_3$), 2.22–2.17 (m, 2 H), 1.85 (br t, J = 5.8, 2 H), 1.46–1.30 (m, 6 H). MS (70 eV): m/e (relative intensity) 320 (M^+, 3), 165 (12), 164 (32), 139 (11), 136 (18), 126 (25), 123 (26), 109 (28), 107 (12), 105 (11), 95 (13), 91 (56), 83 (42), 81 (72), 79 (31), 77 (14), 69 (16), 67 (47), 65 (17), 57 (68), 55 (58), 53 (14), 43 (23), 41 (100). Anal. Calcd for $C_{18}H_{24}O_3S$: C, 67.50; H, 7.50; S, 10.00. Found: C, 67.28; H, 7.47; S, 10.06.

1-[[2-Cyclohexylidene-2-[(3-methyl-2-butenyl)oxy]ethyl]sulfonyl]-4-methylbenzene (1fj). Method B. Chromatography solvent, cyclohexane/EtOAc; 8/1. IR (neat): 3063 w, 3025 w, 2970 m, 2930 s, 2857 s, 1739 m, 1653 w, 1598 m, 1495 w, 1449 m, 1401 m, 1378 m, 1319 s, 1303 s, 1289 m, 1274 m, 1259 m, 1239 m, 1189 m, 1152 s, 1139 s, 1103 m, 1086 s, 1078 w, 1041 m, 1029 m, 1018 m, 978 m, 926 w, 898 w, 874 w, 851 w, 817 w. ^{1}H NMR (220 MHz): 7.79 (d, J = 8.2, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8.2, 2 H, Ar H), 5.22 (br t, J = 7, 1 H, C=C*H*), 4.08 (d, J = 7, 2 H, CH_2O), 4.00 (s, 2 H, p-TolSO_2CH_2), 2.44 (s, 3 H, $C_6H_4CH_3$), 2.20 (br s, 2 H), 1.84–1.23 (m, 8 H), 1.71 (s, 3 H, CH_3), 1.62 (s, 3 H, (CH_3). MS (70 eV): m/e (relative intensity) 280 (M^+ – 68, 8.3), 125 (36), 124 (100), 123 (12), 109 (11), 107 (19), 91 (39), 83 (14), 81 (31), 79 (30), 69 (60), 67 (50), 65 (13), 55 (17), 43 (46), 41 (70). Anal. Calcd for $C_{20}H_{28}O_3S$: C, 68.51; H, 8.05; S, 9.20. Found: C, 68.76; H, 8.01; S, 9.51.

1-[[2-Cyclohexylidene-2-(2-cyclohexylideneethoxy)ethyl]sulfonyl]-4-methylbenzene (1fm). Method B. Chromatography solvent, cyclohexane/EtOAc, 8/1. Yield, 54%. An analytical sample was prepared by recrystallization from diisopropyl ether, mp 60–62 °C. IR ($CHCl_3$): 3030 w, 3005 w, 2935 s, 2859 s, 1659 w, 1599 w, 1495 w, 1450 m, 1401 w, 1320 s, 1310 s, 1294 m, 1277 m, 1263 m, 1195 m, 1157 s, 1141 s, 1110 m, 1091 s, 1067 w, 1075 m, 979 m. ^{1}H NMR (200 MHz): 7.79 (d, J = 8.2, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 7.9, 2 H, Ar H), 5.16 (br t, J = 7.3, 1 H, C*H*=), 4.10 (d, J = 7.0, 2 H, CH_2O), 4.00 (s, 2 H, p-TolSO_2CH_2), 2.44 (s, 3 H, $C_6H_4CH_3$), 2.26–2.06 (m, 6 H, allylic H), 1.86–1.75 (m, 2 H, allylic H), 1.49–1.12 (m, 12 H). MS (70 eV): m/e (relative intensity) 280 (M^+ – 118, 6.8), 125 (32), 124 (100), 109 (28), 107 (14), 91 (22), 81 (24), 79 (22), 67 (73), 55 (22), 43 (27), 41 (27). Anal. Calcd for $C_{23}H_{32}O_3S$: C, 71.13; H, 8.25; S, 8.25. Found: C, 71.10; H, 8.28; S, 8.25.

1-[[2-[4-(2,2-Dimethylethyl)cyclohexylidene]-2-(2-propenyloxy)ethyl]sulfonyl]-4-methylbenzene (1ga). Method B. Chromatography solvent, hexane/EtOAc, 5/1. Yield, 85%. An analytical sample was prepared by recrystallization from hexane, mp 59.5–69 °C. IR ($CHCl_3$): 3011 w, 2960 s, 2870 m, 1708 w, 1599 m, 1495 w, 1479 w, 1470 m, 1448 m, 1425 w, 1397 m, 1319 s, 1305 s, 1290 m, 1271 m, 1159 s, 1085 s, 1030 m, 1019 m, 989 m, 933 m, 873 w, 850 w. ^{1}H NMR (200 MHz): 7.79 (d, J = 8.3, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8.3, 2 H, Ar H), 5.93–5.76 (m, 1 H, C*H*=CH_2), 5.26–5.11 (m, 2 H, CH=CH_2), 4.14 (d, J = 5.6, 2 H, OCH_2), 4.03 (d, J = 15, 1 H, p-Tol$SO_2CH_aH_b$), 3.98 (d, J = 15, 1 H, p-Tol$SO_2CH_aH_b$), 2.98–2.88 (m, 1 H), 2.43 (s, 3 H, $C_6H_4CH_3$), 2.16–2.08 (m, 1 H), 1.80–1.44 (m, 5 H), 1.10–0.50 (m, 2 H), 0.78 (s, 9 H, C(CH_3)$_3$). MS (70 eV): m/e (relative intensity) 376 (M^+, 0.34), 220 (11), 179 (13), 165 (10), 137 (11), 123 (31), 109 (21), 95 (18), 91 (34), 83 (17), 81 (29), 79 (15), 67 (23), 57 (100), 55 (24), 43 (19), 41 (51). Anal. Calcd for $C_{22}H_{32}O_3S$: C, 70.21; H, 8.51; S, 8.51. Found: C, 70.25; H, 8.66; S, 8.46.

1-[[3-Phenyl-2-(2-propenyloxy)-2-propenyl]sulfonyl]-4-methylbenzene (1ha). Method B. Two recrystallizations from hexane/EtOAc gave **1ha** as white needles, mp 104.5–106 °C. IR ($CHCl_3$): 3085 w, 3060 w, 3015 w, 2935 w, 2870 w, 1646 s, 1600 m, 1577 w, 1496 w, 1458 w, 1448 w, 1451 m, 1322 s, 1309 m, 1298 m, 1158 s, 1090 s, 1025 m, 1002 w, 926 m, 881 w. ^{1}H NMR (200 MHz): 7.73 (d, J = 8.1, 2 H, Ar H ortho to SO_2), 7.34–7.16 (m, 7 H, Ar H), 5.90 (s, 1 H, C=C*H*Ph), 5.81–5.64 (m, 1 H, C*H*=CH_2), 5.23–5.12 (m, 2 H, CH=CH_2), 4.24 (br d, J = 5.2, 2 H, OCH_2), 4.13 (s, 2 H, p-TolSO_2CH_2), 2.44 (s, 3 H, $C_6H_4CH_3$). MS (70 eV): m/e (relative intensity) 328 (M^+, 11.4), 181 (12), 174 (12), 173 (91), 172 (20), 145 (29), 132 (15), 131 (100), 117 (14), 115 (16), 105 (12), 104 (15), 103 (41), 91 (65), 77 (12), 65 (15), 41 (78). Anal. Calcd for $C_{19}H_{20}O_3S$: C, 69.51; H, 6.10; S, 9.76. Found: C, 69.33; H, 6.29; S, 9.78.

1-[[1-Methyl-2-(2-propenyloxy)-2-propenyl]sulfonyl]benzene (1ia). Method B. Chromatography solvent hexane/EtOAc, 4/1. Yield, 63%. Oil. IR (neat): 3127 w, 3075 m, 3021

w, 2995 m, 2948 m, 2880 m, 1722 w, 1629 s, 1589 m, 1480 m, 1449 s, 1429 m, 1415 m, 1387 m, 1306 s, 1240 s, 1209 s, 1148 s, 1073 s, 1027 s, 1000 s, 937 s, 828 s. ^{1}H NMR (200 MHz): 7.88–7.83 (m, 2 H, Ar H ortho to SO_2), 7.66–7.46 (m, 3 H, Ar H), 5.71–5.52 (m, 1 H, C*H*=CH_2), 5.14–5.04 (m, 2 H, CH=CH_2), 4.24 (d, J = 3.0, 1 H, C=C*H*H), 4.13 (d, J = 3.0, 1 H, C=CH*H*), 4.02 (dxd, J = 12.6, 5.4, 1 H, OCH_aH_b), 3.91 (dxd, J = 12.6, 5.4, 1 H, OCH_aH_b), 3.79 (q, J = 7.2, 1 H, SO_2CHCH_3), 1.57 (d, J = 7.2, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 252 (M^+, 0.49), 111 (12), 110 (33), 91 (11), 83 (12), 81 (10), 78 (11), 77 (54), 69 (12), 55 (56), 53 (18), 51 (32), 43 (52), 41 (100). Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.90; H, 6.35; S, 12.70. Found: C, 61.79; H, 6.60, S, 12.76.

1-[[1-Methyl-2-[(1-methyl-2-propenyl)oxy]-2-propenyl]-sulfonyl]benzene (1ie). Method B. Chromatography solvent, hexane/EtOAc, 4/1. Yield, 88%. Though chromatographically homogeneous, the compound consisted of a mixture of two β,γ-unsaturated isomers and one α,β-unsaturated isomer in a ratio of 40:40:20. IR (neat): 3071 w, 2990 w, 2940 w, 1712 w, 1622 w, 1588 w, 1479 w, 1448 m, 1420 w, 1372 w, 1305 s, 1290 s, 1248 m, 1207 w, 1148 s, 1072 m, 1071 w, 998 m, 989 m, 930 w, 895 w, 817 m. ^{1}H NMR (200 MHz): 7.89–7.46 (m, 5 H, Ar H, all isomers), 5.89–5.39 (m, 1 H, C*H*=CH_2, all isomers), 5.20–4.97 (m, 2 H, CH=CH_2, all isomers), 4.75 (quintet, J = 6.7, 1 H, $OCHCH_3$, α,β isomer), 4.34–4.17 (m, 1 H, $OCHCH_3$, 1st β,γ isomer), 4.20 (d, J = 3.0, 1 H, C=C*H*H, β,γ isomers), 4.18 (d, J = 3.0, 1 H, C=CH*H*, 1st β,γ isomer), 4.12 (d, J = 3.0, 1 H, C=C*H*H, 2nd β,γ isomer), 4.09 (d, J = 3.0, 1 H, C=CH*H*, 2nd β,γ isomer), 3.82–3.67 (m, 1 H, $PhSO_2CHCH_3$, β,γ isomers), 2.42 (q, J = 1.4, 3 H, =C(CH_3), α,β isomer), 1.92 (q, J = 1.4, 3 H, $O(CH_3)C$=C, α,β isomer), 1.56 (d, J = 7.2, 3 H, SO_2CHCH_3, β,γ isomer), 1.54 (d, J = 7.1, 2 H, $PhSO_2CHCH_3$, β,γ isomer), 1.33 (d, J = 6.3, 3 H, $OCHCH_3$, α,β isomer), 1.13 (d, J = 6.4, 3 H, $OCHCH_3$, β,γ isomer), 0.97 (d, J = 6.4, 3 H, $OCHCH_3$, β,γ isomer). MS (10 eV): m/e (relative intensity) 266 (M^+, 1.3), 212 (21), 145 (14), 143 (22), 126 (27), 125 (51), 124 (57), 109 (20), 105 (12), 81 (12), 78 (16), 77 (10), 71 (88), 69 (13), 57 (18), 55 (97), 53 (21), 43 (100). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.16; H, 6.77; S, 12.03. Found: C, 63.13; H, 6.83; S, 11.93.

(*E*)-3,3-Dimethyl-1-[(4-methylphenyl)sulfonyl]-5-hepten-2-one (8ce). Method B. This compound was formed during workup. Chromatography solvent, hexane/EtOAc, 4/1. Yield, 87%. IR ($CHCl_3$): 3029 s, 3019 m, 2971 m, 2938 w, 2920 w, 2880 w, 1717 s, 1648 w, 1492 w, 1468 m, 1450 w, 1439 w, 1401 w, 1389 w, 1380 w, 1368 w, 1326 s, 1306 m, 1292 m, 1230 m, 1226 m, 1211 s, 1208 m, 1187 w, 1152 s, 1119 w, 1087 m, 1070 w, 1037 m, 1018 m, 1004 m, 970 m, 955 w, 927 w, 875 w, 812 m. ^{1}H NMR (200 MHz): 7.83 (d, J = 8, 2 H, Ar H ortho to SO_2), 7.36 (d, J = 8, 2 H, Ar H), 5.46–5.36 (m, 1 H, C*H*=CH), 5.22–5.12 (m, 1 H, CH=C*H*), 4.27 (s, 2 H, p-$TolSO_2CH_2$), 2.45 (s, 3 H, $C_6H_4CH_3$), 2.12 (d, J = 7, 2 H, CH_2), 1.60 (d, J = 7, 3 H, =$CHCH_3$), 1.11 (s, 6 H, 2 × CH_3). MS (70 eV): m/e (relative intensity) 294 (M^+, 3), 240 (50), 222 (20), 155 (13), 139 (20), 138 (16), 121 (27), 97 (41), 95 (19), 92 (13), 91 (51), 85 (26), 81 (15), 69 (51), 67 (22), 65 (24), 57 (11), 55 (100), 53 (10), 44 (41), 43 (47), 39 (22). Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.31; H, 7.48; S, 10.80. Found: C, 65.40; H, 7.91; S, 11.02.

1-[[3-Methyl-1-[2-methyl-1-[[(4-methylphenyl)sulfonyl]-methyl]-1-propenyl]-1,2-propadienyl]sulfonyl]-4-methyl-benzene (9). Method B. Chromatography solvent, hexane/EtOAc, 3/1. Yield, 76%; mp 142–144 °C. IR ($CHCl_3$): 2995 w, 2970 w, 2900 w, 2840 w, 1950 w, 1905 w, 1648 w, 1599 m, 1490 w, 1385 w, 1357 m, 1310 s, 1298 s, 1282 s, 1260 w, 1235 w, 1180 w, 1145 s, 1119 w, 1085 s, 1070 w, 1040 w, 1020 w, 950 w, 899 w, 815 w. ^{1}H NMR (220 MHz): 7.72 (d, J = 8.4, 2 H, Ar H ortho to SO_2), 7.71 (d, J = 8, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8, 2 H, Ar H), 7.30 (d, J = 8.2, 2 H, Ar H), 4.23 (s, 2 H, p-$TolSO_2CH_2$), 2.44 (s, 6 H, 2 × $C_6H_4CH_3$), 1.75 (s, 6 H, =CCH_3), 1.54 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 289 (M^+ – 189, 25), 225 (11), 157 (21), 149 (13), 139 (28), 133 (100), 132 (42), 117 (31), 115 (16), 105 (49), 93 (14), 92 (20), 91 (81), 79 (21), 77 (34), 65 (31), 55 (12), 51 (12), 44 (44), 43 (13). Anal. Calcd for $C_{24}H_{28}O_4S_2$: C, 64.86; H, 6.31; S, 14.41. Found: C, 64.54; H, 6.41; S, 14.43.

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A Combined Microbial/Chemical Synthesis of (+)-(*R*)-Methyloxirane Having High Enantiomeric Excess[1]

Ethan S. Simon[†] and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Douglas C. Cameron, David J. Weitz, and Charles L. Cooney*

Department of Applied Biological Sciences and Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Clostridium thermosaccharolyticum (ATCC 31960) converts glucose to (–)-(*R*)-propylene glycol; standard procedures transform this substance to (+)-(*R*)-methyloxirane ((+)-(*R*)-propylene oxide) with enantiomeric excess >99%. This procedure is capable of generating this useful chiral synthon on a large scale.

Enantiomerically pure (+)-(*R*)-methyloxirane (**4**) is a valuable chiral synthon.[2-4] This paper details a new method for the production of multigram quantities of optically pure (>99% ee) **4** from glucose (**1**) (Scheme I). Previous syntheses of this substance have started with ethyl (+)-(*S*)-lactate,[5,6] alanine,[7,8] propene,[9] and acetol.[10] Methods developed for butene oxide could also be applied to **4**.[11]

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