Intramolecular Diels–Alder Reactions via Sulfone-Substituted 3-Sulfolenes

Shang-Shing P. Chou,* Ching-Shien Lee, Meng-Chi Cheng, and Hai-Ping Tai

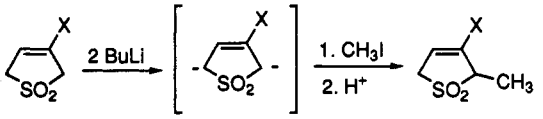
Department of Chemistry, Fu Jen Catholic University, Taipei, Taiwan 24205, Republic of China

Received November 15, 1993•

Regiospecific alkylation of the dianion of sulfone-substituted 3-sulfolenes **1–4** attached an unsaturated alkyl chain at the C2 position to form convenient precursors for IMDA reactions. The substituents on the diene moiety have a significant effect on the reactivity of the IMDA reactions (H > Me_3Si > PhS). The stereochemistry of the cyclization reaction depends on the chain length connecting the diene and dienophile. The hydronaphthalene products **12a** and **12b** are obtained only in the trans form, and the hydroindene products **10** and **11** have predominantly the trans ring structure. All the products have the useful vinylic sulfone structure.

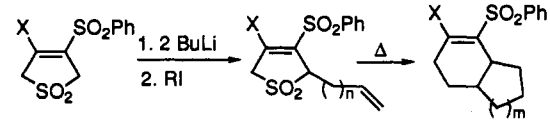
The Diels–Alder reaction is one of the most useful methods in organic synthesis.[1] The intramolecular version of this reaction (IMDA) has been widely used in the construction of polycyclic ring systems with different levels of stereocontrol.[2] The problem of using the IMDA reaction is often the efficient and selective synthesis of the required diene and dienophile within the same molecule. It is well established that 3-sulfolenes are useful precursors to 1,3-dienes[3] and have often been used in the IMDA reaction.[4] We have been interested in the synthesis and reactions of sulfur-substituted dienes via 3-sulfolenes.[5] Although there are many examples of sulfur-substituted dienes in the intermolecular Diels–Alder reaction,[6] they have not been used in the IMDA reaction[7] until recently when we reported that a sulfonyl group on the diene can facilitate its IMDA reaction with an unsaturated alkyl chain[8] and that a diene moiety bearing phenylthio and trimethylsilyl groups at the 2- and 3-positions can react efficiently in the IMDA reaction.[9]

It was reported that 3-sulfolenes substituted with a strongly electron-withdrawing group at C3 could be selectively methylated at C2 via the dianions (eq 1).[10] Using this strategy, we have now synthesized sulfone-substituted 3-sulfolenes bearing an unsaturated side chain for the IMDA reaction (eq 2).[11]



(eq 1)

X = CO_2Me, $PhSO_2$, CN



(eq 2)

X = H, Me_3Si, PhS n = 3, 4 m = 1, 2

Treatment of 3-(phenylsulfonyl)-3-sulfolene (**1**),[5j] 3-(phenylsulfonyl)-4-(trimethylsilyl)-3-sulfolene (**2**),[5o] or a 1:2 mixture[5b] of 3-sulfolene **3** and 2-sulfolene **4** with *n*-BuLi (2 equiv) in THF at −78 °C followed by the addition of 5-iodo-1-pentene or 6-iodo-1-hexene gave the alkylation products **5–9** (Table 1). The alkylation occurred regiospecifically at the C2 position of the sulfolenes as expected, but a mixture of double-bond isomers was obtained in most cases.

• Abstract published in *Advance ACS Abstracts,* March 15, 1994.

(1) Carruthers, W. *Some Modern Methods of Organic Synthesis*, 3rd ed.; Cambridge University Press: Cambridge, 1986; Chapter 3 and references therein.

(2) (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10. (b) Brieger, G.; Bennet, J. N. *Chem. Rev.* **1980**, *80*, 63. (c) Taber, D. F. *Intramolecular Diels-Alder Reactions and Alder Ene Reactions*; Springer Verlag: New York, 1984. (d) Ciganek, E. *Org. React.* **1984**, *32*, 1. (e) Craig, D. *Chem. Soc. Rev.* **1987**, *16*, 238.

(3) (a) Chou, T. S.; Tso, H. H. *Org. Prep. Proc. Int.* **1989**, *21*, 259. (b) Chou, T. S.; Chou, S. S. P. *J. Chin. Chem. Soc.* **1992**, *39*, 625.

(4) (a) Nicolaou, K. C.; Barnette, W. E.; Ma, P. *J. Org. Chem.* **1980**, *45*, 1463. (b) Schmitthenner, H. F.; Weinreb, S. M. *J. Org. Chem.* **1980**, *45*, 3372. (c) Martin, S. F., Tu, C.; Kimura, M.; Simonsen, S. H. *J. Org. Chem.* **1982**, *47*, 3634. (d) Nomoto, T.; Takayama, H. *Heterocycles* **1985**, *23*, 2913. (e) Chou, T. S.; Tso, H. H.; Chang, L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 236. (f) Tso, H. H.; Chang, L. J.; Lin, C. L.; Chou, T. S. *J. Chin. Chem. Soc.* **1985**, *32*, 333. (g) Lee, S. J.; Chou, T. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1188. (h) Cbou, T. S.; Lee, S. J.; Yao, N. K. *Tetrahedron* **1989**, *45*, 4113. (i) Leonard, J.; Fearnley, S. P.; Hickey, M. B. *Synlett* **1992**, 272.

(5) (a) Chou, S. S. P.; Liou, S. Y.; Tsai, C. Y.; Wang, A. J. *J. Org. Chem.* **1987**, *52*, 4468. (b) Chou, T. S.; Lee, S. J.; Peng, M. L.; Sun, D. J.; Chou, S. S. P. *J. Org. Chem.* **1988**, *53*, 3027. (c) Chou, S. S. P.; Sun, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1176. (d) Chou, S. S. P.; Tsai, C. Y. *J. Org. Chem.* **1988**, *53*, 5305. (e) Chou, S. S. P.; Sun, D. J. *J. Chin. Chem. Soc.* **1988**, *35*, 437. (f) Chou, S. S. P.; Tsai, C. Y.; Sun, C. M. *J. Chin. Chem. Soc.* **1989**, *36*, 149. (e) Chou, S. S. P.; Sun, D. J. *J. Chin. Chem. Soc.* **1988**, *35*, 437. (f) Chou, S. S. P.; Tsai, C. Y.; Sun, C. M. *J. Chin. Chem. Soc.* **1989**, *36*, 149. (g) Chou, S. S. P.; Tsai, C. Y.; Sun, C. M. *J. Chin. Chem. Soc.* **1989**, *36*, 227. (h) Chou, S. S. P.; Sun, D. J.; Wey, S. J. *Synth. Commun.* **1989**, *19*, 1593. (i) Chou, S. S. P.; Sung, C. C. *J. Chin. Chem. Soc.* **1989**, *36*, 601. (j) Chou, S. S. P.; Sun, C. M. *Tetrahedron Lett.* **1990**, *31*, 1035. (k) Chou, S. S. P.; Lee, W. H. *Synthesis* **1990**, 219. (l) Chou, S. S. P.; Yuan, T. M. *Synthesis* **1991**, 171. (m) Chou, S. S. P.; Hsu, C. H.; Yeh, M. C. P. *Tetrahedron Lett.* **1992**, *33*, 643. (n) Chou, S. S. P.; Sung, C. C.; Sun, D. J. *J. Chin. Chem. Soc.* **1992**, *39*, 333. (o) Chou, S. S. P.; Cheng, M. C. *J. Org. Chem.* **1993**, *58*, 967. (p) Chou, S. S. P.; Tsao, H. J.; Lee, C. M.; Sun, C. M. *J. Chin. Chem. Soc.* **1993**, *40*, 53.

(6) Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753. (b) Cohen, C.; Kosarych, Z. *J. Org. Chem.* **1982**, *47*, 4005. (c) Kozikowski, A. P.; Huie, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 2923. (d) Overman, L. E.; Petty, C. B.; Ban, T.; Huang, G. T. *J. Am. Chem. Soc.* **1983**, *105*, 6335. (e) Bridges, A. J.; Fischer, J. W. *Tetrahedron Lett.* **1983**, *24*, 447. (f) Proteau, P. J.; Hopkins, P. B. *J. Org. Chem.* **1985**, *50*, 141. (g) Liotta, C. L.; Verbicky, J. W., Jr. *Tetrahedron Lett.* **1985**, *26*, 1395. (h) Bäckvall, J. E.; Juntunen, S. K. *J. Am. Chem. Soc.* **1987**, *109*, 6396. (i) Boucher, J. L.; Stella, L. *J. Chem. Soc., Chem. Commun.* **1989**, 187. (j) Kouklovsky, C.; Pouilhes, A.; Langlois, Y. *J. Am. Chem. Soc.* **1990**, *112*, 6672. (k) Posner, G. H.; Kinter, C. M. *J. Org. Chem.* **1990**, *55* 3967. (l) Padwa, A.; Gareau, Y.; Harrison, B.; Rodriguez, A. *J. Org. Chem.* **1992**, *57*, 3540.

(7) The closest system we could find was that reported by Craig et al. (Craig, D.; Fischer, S. A.; Kemal, O.; Plessner, T. *Tetrahedron Lett.* **1988**, *29*, 6369), where a sulfonyl-substituted dienophile was reacted with a diene intramolecularly.

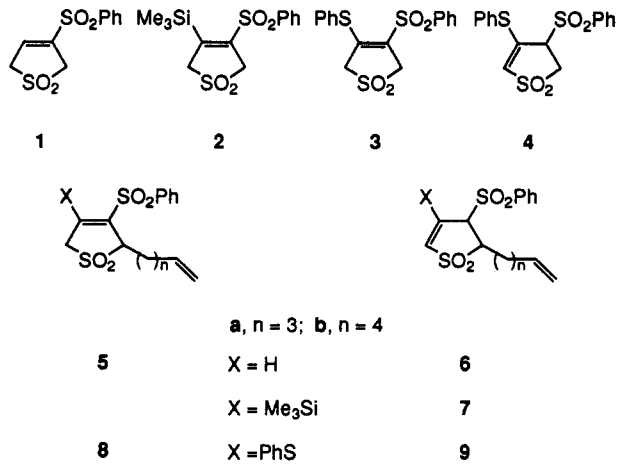
(8) Chou, S. S. P.; Wey, S. J. *J. Org. Chem.* **1990**, *55*, 1270.

(9) Chou, S. S. P.; Lee, C. M. *J. Chin. Chem. Soc.* **1991**, *38*, 491.

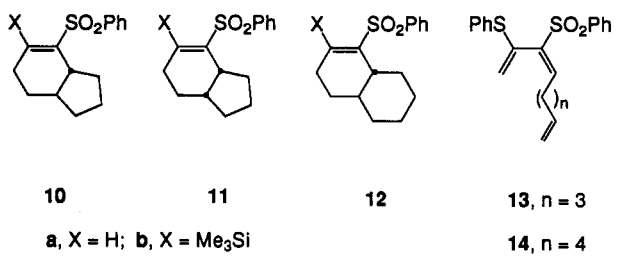
(10) Chou, T. S.; Tsai, C. Y.; Huang, L. J. *J. Org. Chem.* **1990**, *55*, 5410.

(11) Preliminary results were presented at the 9th International Conference on Organic Synthesis, Montreal, Canada, 1992 (Abstract p 143).

0022-3263/94/1959-2010$04.50/0



Although mixtures of double-bond isomers from the alkylation could be separated by HPLC in some cases (**5** and **6**), it was more convenient to use the mixture directly for the IMDA reactions (Table 2). Heating sulfolenes **5** and **6** in xylene at reflux (entries 1 and 2) gave the cyclization products in good yield. This indicates that the 2-sulfolenes **6** were first isomerized under the reaction conditions to the 3-sulfolenes **5**, which then underwent SO_2 extrusion[12] and IMDA reaction to give the products. The IMDA reactions of sulfolenes **7a** and **7b** (entries 3 and 4) also gave the cyclization products in excellent yields, but required higher temperatures. Dimethylaniline (DMA) was found to be a good solvent for these IMDA reactions.[13] Sulfolenes **8** and **9** did not give the expected cyclization products under conditions for entries 1–4, but trienes **13** and **14** could be obtained in good yields under mild heating (entries 5 and 6). These results show that the reactivity of the IMDA reaction varies significantly with the substituents on the diene moiety and follows the order H > Me_3Si > PhS, indicating that both steric and electronic effects of the substituents are important. Although the phenylthio group is smaller than the trimethylsilyl group, the stronger electron-donating ability of the former would cause a less favorable LUMO (diene)–HOMO (dienophile) interaction, which should be most important for determining the IMDA regioselectivity of these sulfone-substituted 1,3-butadienes.[14] This is also consistent with what we have observed for the higher IMDA reactivity of a sulfone-substituted diene than a thio-substituted diene.[8]



A single stereoisomer was obtained for hydronaphthalenes **12a** and **12b** (entries 2 and 4), but mixtures of trans and cis isomers were obtained for hydroindenes **10** and **11** (entries 1 and 3). The trans ring structure of **12a** was proven by X-ray crystallography (Figure 1). The stereochemistry of **12b** was established by comparing its spectral data with those of **12a**. The major isomers **10a** and **10b** were assigned to have trans ring structures on the basis of the ^{13}C NMR data, the trans isomers having more downfield chemical shifts for the aliphatic carbons at the ring junction than those of the cis isomers.[15]

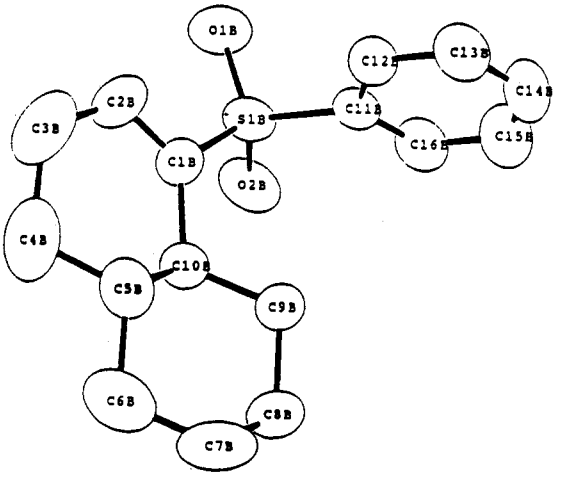


Figure 1. ORTEP representation of compound **12a**.

Table 1. Alkylation of Sulfolenes 1–4

entry	sulfolene	alkylating agent	products	yield, %
1	1	CH_2=$CH(CH_2)_3I$	**5a** + **6a** (3:1)	69
2	1	CH_2=$CH(CH_2)_4I$	**5b** + **6b** (3:1)	67
3	2	CH_2=$CH(CH_2)_3I$	**7a**	58
4	2	CH_2=$CH(CH_2)_4I$	**7b**	49
5	3 + 4	CH_2=$CH(CH_2)_3I$	**8a** + **9a** (1:2)	55
6	3 + 4	CH_2=$CH(CH_2)_4I$	**8b** + **9b** (1:2)	74

Table 2. IMDA Reactions of Sulfolenes 5–9

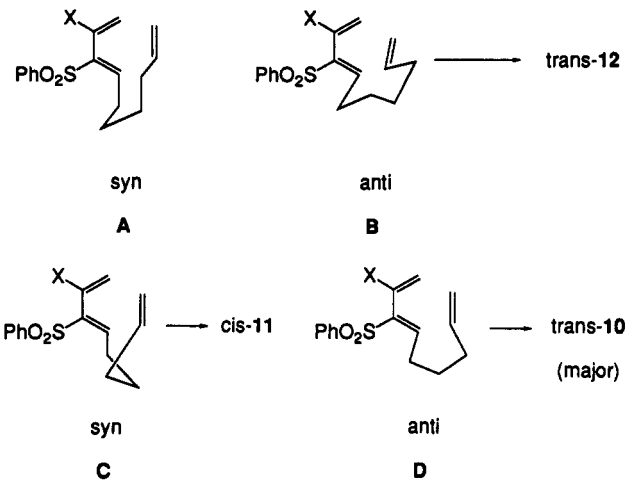
entry	sulfolene	IMDA condition	products	yield, %
1	**5a** + **6a**	xylene, reflux, 120 h	**10a** + **11a** (3:1)	75
2	**5b** + **6b**	xylene, reflux, 65 h	**12a**	98
3	**7a**	DMA, 310 °C, 12 h	**10b** + **11b** (2.3:1)	88
4	**7b**	DMA, 310 °C, 16 h	**12b**	83
5	**8a** + **9a**	toluene, 170 °C, 16 h	**13**	77
6	**8b** + **9b**	toluene, 180 °C, 19 h	**14**	75

The trienes **13** and **14** were found by NOE experiments to have unexpectedly the *E* configuration. Previously we observed that thermal desulfonylation of 2,3-disubstituted 3-sulfolenes gave solely or mainly the *Z* double bond.[5a,9] The trienes obtained from incomplete desulfonylation of sulfolenes **7a** and **7b** in refluxing xylene (compare with entries 3 and 4 in Table 2) also have the *Z* configuration. Thus, we propose that the trienes **13** and **14** initially generated (entries 5 and 6 in Table 2) also have the *Z* configuration, but the low IMDA reactivity caused by the phenylthio substituent then leads to the more stable *E* isomer.

The stereochemistry of the IMDA reaction can be explained by comparison of the various transition states involved in the cyclization. For the formation of hydronaphthalenes **12a** and **12b**, the syn transition state **A** is unfavorable because of the steric repulsion between the C3 phenylsulfonyl group and the C6 methylene group. Thus the anti transition state **B** is more favorable, leading to the formation of trans product **12**. Similar steric

(12) (a) Mock, W. L. *J. Am. Chem. Soc.* **1966**, *88*, 2857. (b) Kellog, S. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 2858. (c) Kellog, R. M.; Prins, W. L. *J. Org. Chem.* **1974**, *39*, 2366.
(13) Parker, K. A.; Iqbal, T. *Tetrahedron Lett.* **1986**, *27*, 6291.
(14) Alston, P. V.; Gordon, M. D.; Ottenbrite, R. M.; Cohen, T. *J. Org. Chem.* **1983**, *48*, 5051.
(15) Pretsch, E.; Seibl, J.; Simon, W.; Clerc, T. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, 1981; p C75.

interactions caused by other C3 substituents have been reported.[4f,9,16] On the other hand, for the formation of hydroindenes **10** and **11**, both the syn transition state **C** and the anti transition state **D** have unfavorable features. The former has steric interaction between the C3 phenylsulfonyl group and the C7 methylene group, and the latter has van der Waals repulsion between the C4 hydrogen and the connecting chain. In the unsubstituted parent system,[17] the syn transition state is slightly more favorable, leading to a cis/trans ratio of 70:30. In our system the large phenylsulfonyl group has a more significant effect so that the trans product predominated.



In summary, we have used regiospecific alkylation of the dianion of sulfone-substituted 3-sulfolenes to attach an unsaturated alkyl chain at the C2 position to form convenient precursors for IMDA reactions. The substituents on the diene moiety have a significant effect on the reactivity of the IMDA reactions (H > Me_3Si > PhS). The stereochemistry of the cyclization products varies with the chain length connecting the diene and the dienophile. The trans ring-fused hydronaphthalene products **12a** and **12b** containing the useful vinylic sulfone structure[18] have been synthesized in good yields and should be useful for further synthetic transformations.

Experimental Section

^1H and ^{13}C NMR spectra were measured in $CDCl_3$ at 300 and 75 MHz, respectively, with tetramethylsilane as the internal standard. HPLC was carried out with a LiChrosorb (Merck) column. The silica gel used for flash chromatography was made by Merck (60 H). The sealed tube used for thermolysis was made by Ace Glass (catalog no. 8648-23). All reagents were of reagent grade and were purified prior to use.[19]

General Procedure for Alkylation of Dianions of Sulfolenes 1-4. To a solution of sulfolene 1-4 (1.44 mmol) in THF (30 mL) at -78 °C was added *n*-BuLi/hexane (2.19 mL, 1.4 M, 2.96 mmol) dropwise. The mixture was stirred for 30 min, and 5-iodo-1-pentene or 6-iodo-1-hexene (3.00 mmol, see Table 1) was added in one portion. The solution was stirred at -78 °C for 1 h and then poured into a saturated NH_4Cl solution (20 mL). The solvent was removed under vacuum, and the residue was extracted with EtOAc (15 mL × 2). The organic solution was dried ($MgSO_4$) and evaporated. The crude product was purified by flash chromatography using hexane/ethyl acetate (2:1 for entries 1 and 2; 6:1 for entries 3 and 4; 3:1 for entries 5 and 6 of Table 1) to give alkylation products **5-9**. Separation of isomers **5a** and **6a**, **5b** and **6b**, was achieved by HPLC.

2-(4-Pentenyl)-3-(phenylsulfonyl)-3-sulfolene (5a): yield 243 mg (52%); IR (neat) 3094, 2948, 1606, 1481, 1315, 1148, 762, 686 cm^{-1}; ^1H NMR δ 1.30-1.65 (2 H, m), 1.70-2.14 (4 H, m), 3.69 (1 H, dd, J = 7.5, 0.8 Hz), 3.67-4.02 (2 H, m), 4.82-5.06 (2 H, m), 5.58-5.78 (1 H, m), 7.08-7.12 (1 H, m), 7.49-7.80 (3 H, m), 7.85-7.98 (2 H, m); ^{13}C NMR δ 24.9, 28.0, 33.1, 56.0, 64.2, 115.5, 128.2, 129.8, 132.3, 134.6, 137.3, 137.9, 143.4; MS (rel intensity) m/z 326 (M^+, 1), 262 (12), 185 (25), 129 (38), 121 (90), 111 (60), 77 (55), 63 (100), 41 (30); exact mass calcd for $C_{15}H_{18}O_4S_2$ m/z 326.0647, found 326.0640.

2-(5-Hexenyl)-3-(phenylsulfonyl)-3-sulfolene (5b): yield 246 mg (50%); IR (neat) 3115, 2975, 1630, 1338, 1172, 755, 710 cm^{-1}; ^1H NMR δ 1.32-1.45 (4 H, m), 1.85-2.07 (4 H, m), 3.65 (1 H, br d, J = 8.5 Hz), 3.85-4.00 (2 H, m), 4.92-5.02 (2 H, m), 5.68-5.80 (1 H, m), 7.08-7.26 (1 H, m), 7.58-7.76 (3 H, m), 7.87-7.90 (2 H, m); ^{13}C NMR δ 25.2, 28.3 (×2), 33.1, 56.0, 64.1, 114.7, 128.2, 129.7, 132.2, 134.6, 137.8, 138.2, 143.4; MS (rel intensity) m/z 340 (M^+, 1), 276 (12), 199 (28), 143 (36), 135 (92), 125 (61), 91 (60), 77 (100), 55 (27); exact mass calcd for $C_{16}H_{20}O_4S_2$ m/z 340.0804, found 340.0801.

5-(4-Pentenyl)-4-(phenylsulfonyl)-2-sulfolene (6a): yield 81 mg (17%); IR (neat) 3094, 2948, 1631, 1481, 1315, 1138, 762, 686 cm^{-1}; ^1H NMR δ 1.30-1.65 (2 H, m), 1.73-2.11 (4 H, m), 3.28-3.39 (1 H, m), 4.11-4.20 (1 H, m), 4.88-5.02 (2 H, m), 5.65-5.82 (1 H, m), 6.70-6.73 (1 H, m), 6.82-6.85 (1 H, m), 7.49-7.98 (5 H, m); ^{13}C NMR δ 26.0, 28.2, 33.1, 58.5, 70.0, 115.6, 128.2, 129.2, 130.8, 135.2, 136.3, 137.2, 143.3; MS (rel intensity) m/z 326 (M^+, 1), 185 (30), 129 (35), 121 (90), 111 (58), 77 (60), 63 (100), 41 (25); exact mass calcd for $C_{16}H_{20}O_4S_2$ m/z 326.0647, found 326.0645.

5-(5-Hexenyl)-4-(phenylsulfonyl)-2-sulfolene (6b): yield 82 mg (17%); IR (neat) 3110, 2965, 1643, 1340, 1185, 760, 706 cm^{-1}; ^1H NMR δ 1.36-1.49 (4 H, m), 1.95-2.07 (4 H, m), 3.31-3.38 (1 H, m), 4.12-4.15 (1 H, m), 4.95-5.04 (2 H, m), 5.72-5.82 (1 H, m), 6.71 (1 H, dd, J = 7.0, 2.4 Hz), 6.82 (1 H, dd, J = 7.0, 2.3 Hz), 7.61-7.91 (5 H, m); ^{13}C NMR δ 26.3, 28.3, 28.7, 33.1, 58.5, 70.1, 114.9, 128.2, 129.3, 129.8, 130.8, 135.3, 136.4, 138.1; MS (rel intensity) m/z 340 (M^+, 1), 276 (12), 199 (28), 143 (36), 135 (92), 125 (61), 91 (60), 77 (100), 55 (27); exact mass calcd for $C_{16}H_{20}O_4S_2$ m/z 340.0800, found 340.0801.

5-(4-Pentenyl)-4-(phenylsulfonyl)-3-(trimethylsilyl)-2-sulfolene (7a): yield 139 mg (58%); mp 153-154 °C; IR (neat) 3040, 2930, 1605, 1540, 1505, 1470, 1300, 1210, 1150, 880, 790 cm^{-1}; ^1H NMR δ 0.38 (9 H, s), 0.88-1.45 (3 H, m), 1.62-1.88 (3 H, m), 3.09-3.16 (1 H, m), 4.17-4.19 (1 H, m), 4.81-4.90 (2 H, m), 5.45-5.65 (1 H, m), 6.87 (1 H, d, J = 1.3 Hz), 7.58-7.80 (3 H, m), 7.85-7.93 (2 H, m); ^{13}C NMR δ 0.0, 26.5, 30.1, 33.6, 59.5, 74.6, 116.0, 130.0, 130.5, 135.7, 137.0, 137.9, 144.1, 147.7; MS (rel intensity) m/z 398 (M^+, 1), 383 (23), 257 (21), 135 (35), 73 (100); exact mass calcd for $C_{18}H_{26}O_4S_2Si$ m/z 398.1046, found 398.1042.

5-(5-Hexenyl)-4-(phenylsulfonyl)-3-(trimethylsilyl)-2-sulfolene (7b); yield 121 mg (49%); mp 148-149 °C; IR (neat) 3040, 2945, 1615, 1540, 1505, 1470, 1300, 1210, 1150, 880, 780 cm^{-1}; ^1H NMR δ 0.41 (9 H, s), 0.95-1.35 (5 H, m), 1.72-1.97 (3 H, m), 3.10-3.20 (1 H, m), 4.15-4.25 (1 H, m), 4.90-5.02 (2 H, m), 5.63-5.80 (1 H, m), 6.87 (1 H, d, J = 1.3 Hz), 7.61-7.82 (3 H, m), 7.87-7.97 (2 H, m); ^{13}C NMR δ -0.1, 26.0, 28.3, 30.0, 33.7, 58.8, 74.3, 115.1, 129.7, 129.9, 135.3, 136.4, 138.3, 143.5, 147.2; MS (rel intensity) m/z 412 (M^+, 1), 397 (32), 199 (21), 135 (35), 73 (100); exact mass calcd for $C_{19}H_{28}O_4S_2Si$ m/z 412.1209, found 412.1200.

2-(4-Pentenyl)-3-(phenylsulfonyl)-4-(phenylthio)-3-sulfolene (8a) and 5-(4-pentenyl)-4-(phenylsulfonyl)-3-(phenylthio)-2-sulfolene (9a): yield 267 mg (55%, 1:2). These two isomers could not be separated by HPLC, and the following data were measured for the mixture; IR (film) 3055, 2987, 2360, 1444, 1408, 1265, 1153, 1128, 896, 828, 753, 706 cm^{-1}; ^1H NMR δ 1.49-1.64 (m), 1.98-2.10 (m), 3.42 (d), 3.63 (d), 3.60-3.66 (m), 4.01-4.08 (m), 4.22 (dd), 4.94-5.03 (m), 5.59 (d), 5.65-5.76 (m), 7.30-7.52 (m), 7.55-7.80 (m), 8.04-8.08 (m); ^{13}C NMR δ 24.9, 25.9, 29.9, 30.0, 32.9, 33.1, 59.2, 62.1, 68.4, 72.7, 115.5, 124.9, 127.6, 128.3, 129.3, 130.0, 130.4, 130.7, 131.3, 134.3, 134.8, 135.1, 135.2, 137.2, 137.4, 139.7, 146.0, 148.6; MS (rel intensity) m/z 434 (M^+, 11),

(16) Tao, Y. T.; Chen, M. L. *J. Org. Chem.* **1988**, *53*, 69.
(17) Lin, Y. T.; Houk, K. N. *Tetrahedron Lett.* **1985**, *26*, 2269.
(18) (a) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. (b) Fuchs, P. L.; Braish, T. F. *Chem. Rev.* **1986**, *86*, 903.
(19) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

293 (100), 229 (83), 147 (34), 119 (82), 91 (64), 77 (50), 65 (27); exact mass calcd for $C_{21}H_{22}O_4S_3$ m/z 434.0683, found 434.0682. These two isomers have some distinct ^1H and ^{13}C NMR absorptions. **8a**: ^1H NMR δ 3.42 (1 H, d, J = 17.1 Hz), 3.63 (1 H, d, J = 17.1 Hz), 4.01–4.08 (1 H, m); ^{13}C NMR δ 24.9, 30.0, 33.1, 59.2, 68.4. **9a**: ^1H NMR δ 4.22 (1 H, dd, J = 3.8, 1.1 Hz), 5.59 (1 H, d, J = 1.1 Hz); ^{13}C NMR δ 25.9, 29.9, 32.9, 62.1, 72.7.

2-(5-Hexenyl)-3-(phenylsulfonyl)-4-(phenylthio)-3-sulfolene (8b) and 5-(5-hexenyl)-4-(phenylsulfonyl)-3-(phenylthio)-2-sulfolene (9b): yield 480 mg (74%, 1:2). These two isomers could not be separated by HPLC, and the following data were measured for the mixture: IR (film) 3055, 2985, 2928, 2856, 1445, 1264, 1126, 895, 828, 762, 748 cm^{-1}; ^1H NMR δ 1.37–1.61 (m), 1.99–2.07 (m), 3.42 (d), 3.58–3.66 (m), 3.64 (d), 4.00–4.05 (m), 4.22 (dd), 4.94–5.03 (m), 5.59 (d), 5.72–5.81 (m), 7.35–7.37 (m), 7.60–7.64 (m), 8.05–8.90 (m); ^{13}C NMR δ 25.0, 26.4, 28.1, 28.3, 30.7, 30.9, 33.1, 33.4, 59.0, 62.9, 68.3, 72.5, 114.9, 115.1, 124.1, 125.1, 128.0, 128.2, 128.9, 129.0, 129.1, 129.8, 129.9, 130.8, 131.1, 131.2, 132.3, 134.0, 135.0, 135.1, 135.6, 135.7, 138.7, 138.8, 140.0, 146.3; MS (rel intensity) m/z 448 (M$^+$, 32), 307 (53), 243 (100), 133 (86), 91 (88), 65 (40); exact mass calcd for $C_{22}H_{24}O_4S_3$ m/z 448.0842, found 448.0838. These two isomers have some distinct ^1H and ^{13}C NMR absorptions. **8b**: ^1H NMR δ 3.42 (1 H, d, J = 17.1 Hz), 3.64 (1 H, d, J = 17.1 Hz), 4.00–4.05 (1 H, m); ^{13}C NMR δ 25.0, 28.3, 30.7, 33.1, 59.0, 68.3. **9b**: ^1H NMR δ 4.22 (1 H, dd, J = 3.9, 1.1 Hz), 5.59 (1 H, d, J = 1.1 Hz); ^{13}C NMR δ 26.4, 28.1, 30.9, 33.4, 62.9, 72.5.

***trans*-7-(Phenylsulfonyl)-2,3,3a,4,5,7a-hexahydroindene (10a) and *cis*-7-(Phenylsulfonyl)-2,3,3a,4,5,7a-hexahydroindene (11a).** A 3:1 mixture of sulfolenes **5a** and **6a** (35 mg, 0.11 mmol) and hydroquinone (3 mg) in xylene (5 mL) was heated at reflux under nitrogen for 120 h. The solvent was removed by rotary evaporation, and the crude product was purified by flash chromatography using hexane/ethyl acetate (6:1) as eluent to give a 3:1 mixture of **10a** and **11a** (21.2 mg, 75% yield). These two isomers could not be separated by HPLC. The following spectral data were measured for the mixture: IR (neat) 3131, 3066, 1640, 1460, 1328, 1156, 778, 726; ^1H NMR δ 1.08–2.04 (m), 2.26–2.56 (m), 6.99–7.02 (m), 7.15–7.21 (m), 7.48–7.61 (m), 7.84–7.88 (m); MS (rel intensity) m/z 262 (M$^+$, 4), 121 (100), 93 (20), 79 (38), 67 (22), 41 (20); exact mass calcd for $C_{15}H_{18}O_2S$ m/z 262.1068, found 262.1031. The two isomers have different ^1H NMR absorptions for the vinylic proton: **10a**, δ 6.99–7.02; **11a**, δ 7.15–7.21. The ratio of these two isomers was determined by integration of the vinylic proton. The ^{13}C NMR absorptions of these two isomers could be assigned due to the difference in peak intensities between these two isomers. **10a**: δ 21.9, 26.3, 27.9, 28.1, 28.8, 43.0, 45.1, 127.7, 129.0, 132.8, 139.9, 141.0, 142.5. **11a**: δ 23.3, 24.6, 25.8, 30.9, 31.3, 37.9, 38.0, 127.9, 128.9, 132.9, 138.7, 140.5, 143.8.

***trans*-7-(Phenylsulfonyl)-6-(trimethylsilyl)-2,3,3a,4,5,7a-hexahydroindene (10b) and *cis*-7-(Phenylsulfonyl)-6-(trimethylsilyl)-2,3,3a,4,5,7a-hexahydroindene (11b).** A mixture of **7a** (100 mg, 0.25 mmol) and hydroquinone (5 mg) in dimethylaniline (7 mL) was heated in a sealed tube at 310 °C for 12 h. After the solution was cooled to rt, ether (30 mL) was added to the solution. The mixture was then washed with aqueous HCl (2 M, 10 mL × 2), dried ($MgSO_4$), and evaporated under vacuum. The crude product was purified by flash chromatography using hexane/ethyl acetate (10:1) as eluent to give a 2.3:1 mixture of **10b** and **11b** (74 mg, 88% yield). These two isomers could not be separated by HPLC, and the following spectral data were measured for the mixture: IR (neat) 3010, 2950, 1580, 1550, 1475, 1350, 1245 cm^{-1}; ^1H NMR δ 0.33 (s), 0.34 (s), 1.00–1.80 (m), 1.87–2.00 (m), 2.27–2.78 (m), 7.45–7.62 (m), 7.78–7.90 (m); MS (rel intensity) m/z 334 (M$^+$, 5), 320 (10), 319 (100), 135 (30), 91 (11), 73 (30); exact mass calcd for $C_{18}H_{26}O_2SSi$ m/z 334.1420, found 334.1424. The ^{13}C NMR absorptions of these two isomers could be assigned due to the difference in peak intensities between these two isomers. **10b**: δ 1.7, 22.0, 27.9, 28.8, 29.0, 35.9, 44.2, 45.7, 126.9, 128.8, 132.6, 142.0, 146.5, 156.0. **11b**: δ 1.9, 23.1, 25.8, 31.1, 32.2, 32.7, 37.1, 40.4, 116.1, 127.6, 132.8, 141.2, 149.2, 154.1.

***trans*-1-(Phenylsulfonyl)-3,4,4a,5,6,7,8,8a-octahydronaphthalene (12a).** A 3:1 mixture of **5b** and **6b** (25 mg, 0.074 mmol) and hydroquinone (3 mg) in xylene (5 mL) was heated at reflux under nitrogen for 65 h. The solvent was removed by rotary evaporation, and the crude product was purified by flash chromatography using hexane/ethyl acetate (6:1) as eluent to give **12a** (20 mg, 98% yield): mp 69–72 °C; IR (neat) 3090, 2940, 1636, 1310, 1162, 740, 708 cm^{-1}; ^1H NMR δ 0.69–0.78 (1 H, m), 1.14–1.35 (6 H, m), 1.61–1.68 (3 H, m), 2.06–2.09 (1 H, m), 2.22 (1 H, br d, J = 14.0 Hz), 2.33–2.38 (2 H, m), 7.08–7.10 (1 H, m), 7.48–7.60 (3 H, m), 7.82–7.85 (2 H, m); ^{13}C NMR δ 26.1, 26.3, 26.6, 28.8, 30.0, 33.6, 41.1, 42.1, 127.3, 129.0, 132.7, 141.1, 141.8, 142.9; MS (rel intensity) m/z 276 (M$^+$, 43), 211 (13), 135 (100), 93 (34), 91 (42), 77 (29), 67 (62), 55 (19), 41 (29), 28 (51); exact mass calcd for $C_{16}H_{20}O_2S$ m/z 276.1185, found 276.1170.

***trans*-8-(Phenylsulfonyl)-7-(trimethylsilyl)-1,2,3,4,4a,5,6,8a-octahydronaphthalene (12b).** A mixture of **7b** (100 mg, 0.24 mmol) and hydroquinone (5 mg) in dimethylaniline (7 mL) was heated in a sealed tube at 310 °C for 16 h. After the same workup as for **10b** and **11b**, the purified product **12b** (70 mg, 83% yield) was obtained: IR (neat) 3010, 2950, 2850, 1585, 1560, 1475, 1440, 1435, 1245 cm^{-1}; ^1H NMR δ 0.33 (9 H, s), 0.80–2.72 (14 H, m), 7.47–7.63 (3 H, m), 7.78–7.82 (2 H, m); ^{13}C NMR δ 1.1, 25.8, 26.2, 30.0, 31.2, 33.5, 33.7, 41.8, 44.5, 126.2, 128.2, 132.0, 142.8, 147.1, 158.5; MS (rel intensity) m/z 348 (M$^+$, 15), 333 (100), 305 (3), 135 (30), 91 (11), 73 (35); exact mass calcd for $C_{12}H_{21}O_2SSi$ m/z 348.1580, found 348.1581.

(*E*)-3-(Phenylsulfonyl)-2-(phenylthio)-1,3,8-nonatriene (13). A 1:2 mixture of **8a** and **9a** (70 mg, 0.16 mmol) and hydroquinone (3 mg) in toluene (2 mL) was heated in a sealed tube at 170 °C for 16 h. The solvent was removed under vacuum, and the crude product was purified by flash chromatography using hexane/ethyl acetate (6:1) as eluent to give **13** (46 mg, 77% yield): IR (film) 3050, 2990, 1440, 1410, 1265, 1145, 1128, 897, 825, 736, 705 cm^{-1}; ^1H NMR δ 1.53 (2 H, quintet, J = 7.5 Hz), 2.09 (2 H, q, J = 7.2 Hz), 2.27–2.37 (2 H, m), 4.85 (1 H, s), 4.98–5.07 (3 H, m), 5.72–5.85 (1 H, m), 7.09 (1 H, t, J = 7.6 Hz), 7.26–7.36 (5 H, m), 7.51–7.63 (3 H, m), 7.89–7.92 (2 H, m); ^{13}C NMR δ 27.7, 29.1, 33.3, 115.3, 117.6, 127.5, 128.7, 129.0, 129.3, 129.4, 130.8, 133.3, 135.3, 136.5, 137.8, 140.9, 145.0; MS (rel intensity) m/z 370 (M$^+$, 9), 305 (22), 229 (100), 187 (36), 119 (39), 91 (42), 77 (38); exact mass calcd for $C_{11}H_{22}O_2S_2$ m/z 370.1066, found 370.1063.

(*E*)-3-(Phenylsulfonyl)-2-(phenylthio)-1,3,8-decatriene (14). A 1:2 mixture of **8b** and **9b** (140 mg, 0.25 mmol) and hydroquinone (5 mg) in toluene (2 mL) was heated in a sealed tube at 180 °C for 19 h. The solvent was then removed by rotary evaporation, and the crude product was purified by flash chromatography using hexane/ethyl acetate (5:1) as eluent to give **14** (90 mg, 75% yield): IR (film) 3055, 2987, 1442, 1408, 1265, 1147, 1128, 896, 826, 738, 705 cm^{-1}; ^1H NMR δ 1.32–1.42 (4 H, m), 1.95–1.99 (2 H, m), 2.18–2.25 (2 H, m), 4.77 (1 H, s), 4.85–4.95 (3 H, m), 5.62–5.80 (1 H, m), 7.01 (1 H, t, J = 7.6 Hz), 7.12–7.38 (5 H, m), 7.40–7.60 (3 H, m), 7.81–7.94 (2 H, m); ^{13}C NMR δ 27.8, 28.4, 29.4, 33.3, 114.7, 117.5, 127.9, 129.1, 129.2, 129.4, 130.8, 132.8, 133.2, 135.2, 136.4, 138.3, 140.7, 145.2; MS (rel intensity) m/z 384 (M$^+$, 22), 319 (68), 275 (56), 243 (70), 161 (33), 147 (29), 133 (77), 91 (100), 77 (93), 65 (32), 55 (31); exact mass calcd for $C_{22}H_{24}O_2S_2$ m/z 384.1226, found 384.1219.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support (NSC 81-0208-M-030-03).

Supplementary Material Available: ^1H and ^{13}C NMR spectra of **5a**, **5b**, **5a + 6a**, **6b**, **7a**, **7b**, **8a + 9a**, **8b + 9b**, **10a + 11a**, **10b + 11b**, **12a**, **12b**, **13**, and **14** and table of bond distances and bond angles of IC 2152 (29 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.