5.7 Hz), 6.03 (dd, 1 H, J = 2.4, 5.7 Hz), 7.08 (dd, 1 H, J = 5.28, 5.28 Hz), 7.33–7.82 (m, 5 H); ^{13}C NMR (200 MHz) δ 20.42 (CH_3), 20.74 (CH_3), 26.71 (CH_2), 28.24 (CH_2), 39.59 (CH), 42.62 (CH), 122.17 (C), 127.81 (CH), 128.61 (CH), 131.63 (CH), 132.84 (CH), 136.31 (CH), 138.97 (C), 139.31 (CH), 141.18 (C), 141.98 (C); MS m/z 300 (M^+), 143, 142, 141, 129, 128, 115, 106 (100%), 91, 77. Calcd for $C_{18}H_{20}O_2S$: 300.1184. Found: m/z 300.1192. Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.97; H, 6.71. Found: C, 71.96; H, 6.96.

4,7-Dihydro-1-isopropyl-5-methyl-6-(phenylsulfonyl)-indene (23b): yellow oil; IR (neat) 3061, 2909, 2854, 1631, 1445, 1372, 1301, 1146, 1088, 804, 756, 723, 690 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.47 (s, 3 H), 1.49 (s, 3 H), 1.98–2.48 (m, 4 H), 2.23 (s, 3 H), 2.71–2.90 (m, 1 H), 3.07 (br s, 1 H), 5.45 (d, 1 H, J = 5.7 Hz), 6.05 (dd, 1 H, J = 2.2, 5.7 Hz), 7.32–7.93 (m, 5 H); ^{13}C NMR (200 MHz) δ 20.57 (CH_3), 20.95 (CH_3), 21.37 (CH_3), 29.42 (CH_2), 38.46 (CH_2), 40.01 (CH), 43.54 (CH), 122.59 (C), 127.17 (CH), 128.61 (CH), 129.00 (CH), 132.39 (CH), 132.61 (CH), 133.05 (C), 135.39 (CH), 141.58 (C), 142.16 (C), 151.27 (C); MS m/z 314 (M^+), 106 (100%), 91, 77. Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.58; H, 7.05. Found: C, 72.48; H, 6.99.

1,4,5,8,9,10-Hexahydro-1,4-methano-7-(phenylsulfonyl)-naphthalene (25a). The ^{13}C NMR spectrum, which contains more than one set of signals, indicates that **25a** is a mixture of the endo and exo isomers. However, separation and identification of each isomer were unsuccessful. Colorless liquid; IR (neat) 3060, 2961, 2845, 1632, 1559, 1445, 1306, 1151, 1095, 938, 760, 719, 690 cm^{-1}; ^{1}H NMR (80 MHz) δ 1.21–2.95 (m, 10 H), 6.05 (s, 2 H), 7.09–7.28 (m, 1 H), 7.41–8.00 (m, 5 H); MS m/z 221 (M^+ – 65, 100%), 143, 141, 125, 115, 91, 79, 78, 77, 66. Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 71.58; H, 6.55.

1,4,5,8,9,10-Hexahydro-1,4-methano-6-methyl-7-(phenylsulfonyl)naphthalene (25b). The ^{13}C NMR spectrum, which contains more than one set of signals, indicates that **25b** is a mixture of the endo and exo isomers. However, separation and identification of each isomer were unsuccessful. Colorless liquid; IR (neat), 3064, 2962, 1624, 1445, 1297, 1148, 1084, 1023, 758, 725, 690, 642 cm^{-1}; ^{1}H NMR (80 MHz) δ 1.22–2.96 (m, 10 H), 2.28 (s, 3 H), 6.04 (s, 2 H), 7.38–7.95 (m, 5 H); MS m/z 300 (M^+), 235 (100%), 234, 233, 159 ($M^+ - C_6H_5SO_2$), 143, 91, 77. Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.97; H, 6.71. Found: C, 72.05; H, 6.91.

Acid-Induced Elimination of Methanol from 12 To Give 13. A solution of **12a** or **12b** (1 mmol) in 1 N HCl (2 mL)/MeOH (2 mL) was stirred at room temperature for 24 h, after which time the excess methanol was evaporated under reduced pressure. The residual aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to give essentially pure **13a** and **13b**, respectively, in almost quantitative yields. Starting from a mixture of **12** and **13**, the same treatment gave **13** cleanly.

Cope Rearrangement of 15 to 14. A solution of **15a** or **15b** (1 mmol) in toluene (10 mL) was heated under reflux for 6 h. After removal of excess of toluene, **14a**, and **14b**, respectively, were produced in 85% yield.

Base-Induced Double-Bond Isomerization of 21b to 3-Isopropenyl-1,3-dimethyl-6-(phenylsulfonyl)cyclohexene (22). A solution of **21b** (0.2 mmol) and t-BuOK (0.19 mmol) in t-BuOH (2 mL) was stirred at room temperature for 64 h, after which time saturated brine (5 mL) was added. The aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude oil was purified by HPLC (LiChrosorb column, 8:1 hexane/EtOAc) to give the recovered **21b** in 43% yield and two diastereomeric products **22** in 31% and 27% yields, respectively. The faster moving minor diastereomer was unseparable from **21b** and their yields were calculated from the integrals of the methyl groups. ^{1}H NMR of the minor diastereomer: (200 MHz) δ 0.95 (s, 3 H), 1.31–2.00 (m, 4 H), 1.51 (s, 3 H), 1.96 (s, 3 H), 3.53–3.63 (m, 1 H), 4.38 (s, 1 H), 4.52 (s, 1 H), 5.52 (s, 1 H), 7.36–7.85 (m, 5 H). The slower moving diastereomer was the major component: white solid; mp 65–66 °C; IR (KBr) 3082, 2965, 2871, 1636, 1587, 1447, 1377, 1305, 1197, 1145, 1084, 1024, 1000, 898, 861, 809, 764, 720, 691 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.83 (s, 3 H), 1.57 (s, 3 H), 1.15–1.76 (m, 3 H), 1.98 (s, 3 H), 1.76–2.07 (m, 1 H), 3.53 (d, 1 H, J = 5.5 Hz), 4.46 (s, 1 H), 4.69 (s, 1 H), 5.57 (s, 1 H), 7.39–7.88 (m, 5 H); MS m/z 290 (M^+), 149, 133, 121 (100%), 119, 107, 105, 93, 91, 79, 77. Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.31; H, 7.64. Found: C, 70.33; H, 7.99.

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Preparation of 2,3-Dihetero-Substituted 1,3-Dienes from Brominated 2-Sulfolenes

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A general procedure for the preparation of 2,3-dihetero-substituted 1,3-butadienes is described. These dienes are obtained from the thermolysis of the corresponding 3,4-disubstituted 3-sulfolenes, which can be prepared by nucleophilic substitution reactions from 4-brominated 2-sulfolenes.

The use of hetero-substituted 1,3-dienes in Diels–Alder reactions has been an area of great synthetic activity.[1] The introduction of hetero substituents has a significant influence on the reactivity and regioselectivity of the diene, and these hetero substituents add versatility in further reactions of the cycloadducts.[1] The attachment of two hetero substituents at the 2- and 3-positions of a 1,3-diene further increases the potential utility, and several studies on the preparation and cycloaddition reactions of 2,3-dihetero-substituted 1,3-dienes have been reported.[2] In our recent studies of 3-sulfolenes as useful synthetic intermediates,[3] we have discovered that 4-bromo-2-sulfolene

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(2) For examples, see: (a) Bridges, A. J.; Fischer, J. W. *Tetrahedron Lett.* **1983**, *24*, 447. (b) Bridges, A. J.; Fischer, J. W. *J. Org. Chem.* **1984**, *49*, 2954. (c) Bridges, A. J.; Fischer, J. W. *J. Chem. Soc., Chem. Commun.* **1982**, 665. (d) Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3548. (e) McDonald, E.; Suksamrarn, A.; Wylie, R. D. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1893. (f) Clennan, E. L.; Nagraba, K. *J. Org. Chem.* **1987**, *52*, 294. (g) Jeganathan, S.; Okamura, W. H. *Tetrahedron Lett.* **1982**, *23*, 4763. (h) Garratt, P. J.; Tsotinis, A. *Tetrahedron Lett.* **1986**, *27*, 2761. (i) Pollok, T.; Schmidbaur, H. *Tetrahedron Lett.* **1987**, *28*, 1085.

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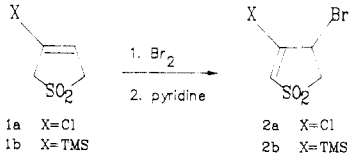
serves as a butadienyl cation equivalent when it is treated with certain nucleophiles.[4] We now report that this strategy can be extended to the preparation of 2,3-dihetero-substituted 1,3-dienes by way of their stable precursors, 3,4-disubstituted 3-sulfolenes.

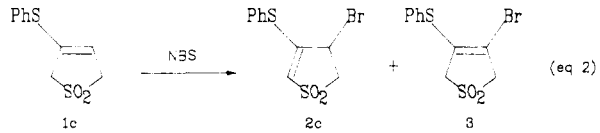
Results and Discussion

The preparation of 2,3-dihetero-substituted 3-sulfolenes commenced with the direct nucleophilic substitution reactions of 3-hetero-substituted 4-bromo-2-sulfolenes **2a–c**, which were prepared from the corresponding 3-sulfolenes **1a–c** via different routes. The known compounds **2a**[5] and **2b**[6] were prepared from **1a** and **1b**, respectively, by a known procedure[7] involving a bromination/partial dehydrobromination reaction sequence (eq 1). While the same



1a X=Cl
1b X=TMS
2a X=Cl
2b X=TMS
(eq 1)

reaction sequence could be used to prepare **2c**, this compound was more conveniently prepared by the NBS-induced allylic bromination of **1c**[8] in 76% yield (eq 2). In



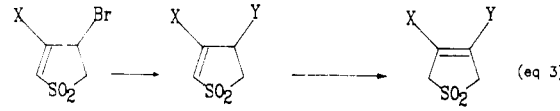
1c 2c 3 (eq 2)

this reaction, a dihetero-substituted 3-sulfolene **3** was formed as a minor product (19%). Preliminary attempts to increase the yield of **3** by varying the reaction conditions were not successful.

Attempted isomerization of **2a–c** to the corresponding 3-sulfolenes with bases resulted in dehydrobromination and some other side reactions.[4] On the other hand, substitution reactions of **2a–c** with the sodium salts of phenylthiolate, phenylsulfinate, and azide proceeded smoothly to give the disubstituted 2-sulfolenes **4**, which could be subsequently treated with bases to give the isomerized products, the 3,4-dihetero-substituted 3-sulfolenes **5** (Table I). Unfortunately, reactions of **2a–c** with other nucleophiles such as acetate, phenoxide, and diphenylphosphide did not give any substitution products.

Base-induced double-bond isomerization of **4** occurred very rapidly in some cases where 3-sulfolenes **5** were directly produced along with **4** before the base treatment (entries 1, 2, 6, and 7 of Table I). Compounds **4b** and **5b**, although they could be separated by careful HPLC technique, were found to exist in equilibrium under basic conditions. A similar phenomenon was also observed for compounds **4g** and **5g**. It is generally observed that when a sulfolene is substituted with an arylsulfonyl group at the 3-position, the double bond tends to equilibrate between C2–C3 and C3–C4.[9] Fortunately, separation of these pairs of positional isomers was unnecessary since each pair can be thermolyzed in the presence of pyridine to extrude SO_2 to give its corresponding diene. Presumably the isomerization of the double bond induced by pyridine is a rapid process during thermolysis.

Table I. Preparation of Dihetero-Substituted 2-Sulfolenes from Nucleophilic Substitution Reactions of 2 and 4 and Subsequent Base-Induced Isomerization to the Corresponding 3-Sulfolenes

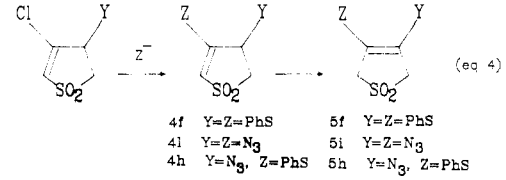


2 4 5 (eq 3)

entry	compd	Nu (equiv)	product and yield	base	product and yield
1	**2a**	PhS^- (0.95)	**4a** (68%) + **5a** (17%)	Et_3N	**5a** (quant)
2	**2a**	$PhSO_2^-$ (1.1)	**4b** (22%) + **5b** (45%)		
3	**2a**	N_3^- (1.1)	**4c** (61%)	DBN	**5c** (82%)
4	**2b**	PhS^- (0.9)	**4d** (87%)	DBN	**5d** (81%)
5	**2b**	N_3^- (1.9)	**4e** (86%)	DBN	**5e** (7%)[a]
6	**2c**	PhS^- (4)	**4f** (<1%) + **5f** (93%)		**5f** (quant)[b]
7	**2c**	$PhSO_2^-$ (5)	**4g** (66%) + **5g** (33%)		
8	**2c**	N_3^- (3)	**4h** (91%)	NaOH	**5h** (73%)
9	**2c**	MeO^- (2)	**4i** (98%)		
10	**2c**	C_4H_8NH (1.4)	**4j** (44%)		
11	**2c**	NO_2^- (2.2)	**4k** (40%)[c]		
12	**2a**	PhS^- (2.25)	**5a** (40%) + **5f** (40%)		
13	**2a**	N_3^- (1.95)	**4l** (30%) + **4c** (47%)	DBN	**5i** (75%)
14	**4c**	PhS^- (0.9)	**4h** (65%)		

[a] In addition to **5e** and recovered **4e** (9%), a significant amount (30%) of desilylated product, 3-azido-3-sulfolene, was obtained. [b] The **5f**/**4f** ratio was dependent upon the reaction time. If the reaction lasted longer than 5 h, compound **5f** was the only product. [c] The intermediate nitrite was not obtained. Presumably the nitrite underwent a rapid hydrolysis under the reaction conditions to give 4-hydroxy-3-(phenylthio)-2-sulfolene (**4k**).

Sulfolenes **2a** and **4a–c**, bearing a β-chloro-α,β-unsaturated sulfone functionality, could react with nucleophiles to undergo a Michael addition/dechlorination process so as to introduce some other hetero functionality in place of the chlorine (eq 4). A mixture of **5a** (40%) and **5f** (40%) was obtained directly from the reaction of **2a** with a large excess of phenylthiolate. The first equivalent of the phenylthiolate should have reacted with **2a** in a normal substitution mode to give the intermediate **4a**, whereas the excessive phenylthiolate then acted not only as a Michael donor to give **5f** but also as a base to induce the double-bond isomerization of intermediate **4a** to give **5a**. Such



(eq 4)

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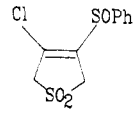
Table II. Thermal Extrusion of SO_2 from Dihetero-Substituted 3-Sulfolenes

entry	precursor	X	Y	product and yield
1	**5a**	Cl	PhS	**6a** (quant)
2	**4b + 5b**	Cl	$PhSO_2$	**6b** (87%)
3	**5d**	TMS	PhS	**6c** (81%)
4	**5f**	PhS	PhS	**6d** (quant)[a]
5	**4g + 5g**	PhS	$PhSO_2$	**6e** (75%)
6	**5j**	Cl	PhSO	**6f** (75%)

[a] A single product was obtained. However, this product **6d** was unstable and decomposed gradually upon standing.

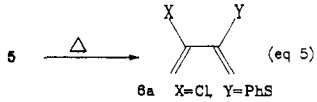
a dual behavior of thiolate was also observed in a separate experiment where **4a** was treated with 1 equiv of sodium phenylthiolate in methanol to give a mixture of **5a** and **5f** in about a 6:1 ratio. On the other hand, treatment of **2a** with 2 equiv of sodium azide gave a mixture of the direct substitution product **4c** (47%) and diazido-2-sulfolene (**4l**) (30%). Compound **4l** should be the product from the Michael addition/dechlorination reaction of intermediate **4c**. Similarly, treatment of **4c** with phenylthiolate gave **4h** in 65% yield. However, treatment of **4a** with acetate or pyrrolidine resulted only in the double-bond isomerization to give **5a** but did not produce any products resulting from a Michael addition/dechlorination reaction. Compound **4l** could readily be isomerized with DBN to diazido-3-sulfolene (**5i**) in 75% yield (Table I).

Phenylthio-containing dihetero-substituted 3-sulfolenes should be easily oxidized to the corresponding sulfoxides and sulfones. For example, a mixture of **4b** (22%) and **5b** (45%) could be obtained by treating **5a** with 2 equiv of *m*-CPBA, whereas 3-chloro-4-(phenylsulfinyl)-3-sulfolene (**5j**) (82%) was obtained when 1 equiv of *m*-CPBA was used.



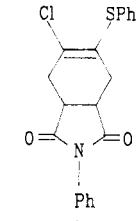
5j

The dihetero-substituted 3-sulfolenes **3** and **5a–j** should be good precursors for the corresponding dienes since it has been well established that the SO_2 extrusion from substituted 3-sulfolenes can be easily achieved by thermolysis[3,10] or by treatment with certain reducing agents.[11] Examples of thermolytic extrusion of SO_2 from **5** to give **6** (eq 5) are summarized in Table II. Compound **6a** was



6a X=Cl, Y=PhS
6b X=Cl, Y=$PhSO_2$
6c X=TMS, Y=PhS
6d X=Y=PhS
6e X=PhS, Y=$PhSO_2$
6f X=Cl, Y=PhSO

reported to be extremely unstable when prepared by a different route and had to be used immediately after its preparation.[2a] However, we have found that **6a**, if generated from the thermolysis of **5a**, could be stored as a dilute solution in benzene or other solvents for at least 2 weeks without appreciable decomposition. In addition, we have found that **5a** could be used directly in the Diels–Alder reaction with *N*-phenylmaleimide under thermal conditions to give the desired cycloadduct **7**. Therefore, isolation of the dihetero-substituted dienes could be avoided. This technique is especially useful when the dienes are unstable to handle.



7

In summary, the reaction sequence described herein presents a convenient and general method for the preparation of 2,3-dihetero-substituted 1,3-dienes from the corresponding 3-sulfolenes where the hetero substituents may be chloro, bromo, azido, trimethylsilyl, phenylthio, phenylsulfinyl, and phenylsulfonyl. This strategy should be applicable to the preparation of other dihetero-substituted 1,3-dienes.

Experimental Section

General Method. NMR spectra were determined on a Bruker AW-80, a Bruker MSL-200, or a Varian 360L spectrometer as solutions in $CDCl_3$. IR spectra were determined on a Beckman Acculab TM1 or a Perkin-Elmer 882 IR spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 5995B or a Jeol JMS-D-100 mass spectrometer. Elemental analyses were performed at the microanalysis laboratory of National Taiwan University using a Perkin-Elmer 240C analyzer. All reactions were performed under an atmosphere of dry nitrogen. All anhydrous solvents were freshly distilled before use.

4-Bromo-3-(phenylthio)-2-sulfolene (2c) and 4-Bromo-3-(phenylthio)-3-sulfolene (3). A solution of 3-(phenylthio)-3-sulfolene (**1c**) (2 g, 8.9 mmol) and *N*-bromosuccinimide (NBS, 1.8 g, 10.2 mmol) in CH_3CN (50 mL) was heated under reflux for 2 h. After removal of the excess solvent under reduced pressure, CCl_4 was added to cause precipitation. The precipitate was removed by filtration, and the filtrate was concentrated under reduced pressure. The crude oil was purified by column chromatography (Lobar column, 4:1 hexane/EtOAc) to give **2c** in 76% yield and **3** in 19% yield. Compound **2c**: white solid; mp 96–97 °C; IR (KBr) 1560, 1300, 1240, 1140, 1120, 910, 750 cm^{-1}; ^1H NMR (60 MHz) δ 3.80–3.97 (m, 2 H), 5.17 (dd, 1 H, J = 4, 7 Hz), 5.93 (s, 1 H), 7.63 (s, 5 H); MS m/z 306 (M^+ + 2), 304 (M^+), 160 (100%), 128, 109, 65, 51. Anal. Calcd for $C_{10}H_9BrO_2S_2$: C, 39.35; H, 2.97. Found: C, 39.31; H, 2.96. Compound **3**: white solid; mp 110–111 °C; IR (KBr) 1583, 1430, 1310, 1230, 1130, 1035, 915, 745 cm^{-1}; ^1H NMR (60 MHz) δ 3.57 (t, 2 H, J = 1 Hz), 4.15 (t, 2 H, J = 1 Hz), 7.50 (s, 5 H); MS m/z 306 (M^+ + 2), 304 (M^+), 242, 240, 161 (100%), 128, 65, 51. Anal. Calcd for $C_{10}H_9BrO_2S_2$: C, 39.35; H, 2.97. Found: C, 39.38; H, 2.95.

General Procedure for the Nucleophilic Substitution Reaction of 4-Brominated 2-Sulfolenes. The solution of a 2-sulfolene **2a–c** and a nucleophile, whose molar equivalents used are as indicated below, in a proper solvent was stirred for a period of time. The solvent was then removed under reduced pressure and the crude mixture was purified by HPLC (LiChrosorb column, hexane/EtOAc) to give the pure product(s). The yields of the products are summarized in Table I.

3-Chloro-4-(phenylthio)-2-sulfolene (4a) and 3-Chloro-4-(phenylthio)-3-sulfolene (5a). These compounds were obtained from the substitution reaction of **2a** with sodium phenylthiolate [0.95 equiv (generated from 1.1 equiv of thiophenol and 0.95 equiv of NaOMe)] in 1:1 MeOH/EtOH under reflux for 48 h. In the product mixture were also found recovered starting material **2a** (9%) and 3-chloro-3-sulfolene (7%). Compound **4a**: white solid; mp 83.5–85 °C; IR (neat) 1600, 1478, 1440, 1400, 1300, 1280, 1230, 1200, 1130, 1040, 979, 918, 800, 750 cm^{-1}; ^1H NMR (80 MHz) δ 3.40 (dd, 1 H, J = 4, 14 Hz), 3.8 (dd, 1 H, J = 8, 14 Hz), 4.34 (dd, 1 H, J = 4, 8 Hz), 6.66 (s, 1 H), 7.36 (s, 5 H); MS

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m/z 262 ($M^+ + 2$), 260 (M^+), 198, 196, 161, 128, 110, 109 (100%), 65, 51. Anal. Calcd for $C_{10}H_9ClO_2S_2$: C, 46.06; H, 3.48. Found: C, 45.98; H, 3.42. Compound **5a**: yellow solid; mp 48–49 °C; IR (KBr) 1605, 1584, 1480, 1441, 1401, 1330, 1243, 1142, 1051, 941, 750 cm^{-1}; ^1H NMR (200 MHz) δ 3.66 (s, 2 H), 4.08 (s, 2 H), 7.39 (s, 5 H); MS m/z 262 ($M^+ + 2$), 260 (M^+), 198, 196, 161 (100%), 135, 128, 91, 87, 65, 51. Anal. Calcd for $C_{10}H_9ClO_2S_2$: C, 46.06; H, 3.48. Found: C, 46.05; H, 3.48.

3-Chloro-4-(phenylsulfonyl)-2-sulfolene (4b) and 3-Chloro-4-(phenylsulfonyl)-3-sulfolene (5b). These compounds were obtained from the substitution reaction of **2a** with sodium phenylsulfinate (1.1 equiv) in DMF at 60 °C for 18 h. The mixture is a white solid, and separation of the two components was unsuccessful. However, the peaks of the ^1H NMR spectrum of the mixture are well resolved so they can be assigned easily. The IR, MS, and elemental analysis data were taken on the mixture. IR (KBr) 1597, 1450, 1318, 1288, 1134, 1084, 951, 780, 758 cm^{-1}; ^1H NMR (200 MHz) of **4b**: δ 3.71 (dd, 1 H, J = 9.5, 15 Hz), 3.88 (dd, 1 H, J = 3.2, 15 Hz), 4.63 (dd, 1 H, J = 3.2, 9.5 Hz), 6.79 (s, 1 H), 7.58–7.99 (m, 5 H); ^1H NMR (200 MHz) of **5b**: δ 4.15 (s, 2 H), 4.23 (s, 2 H), 7.58–7.99 (m, 5 H); MS m/z 294 ($M^+ + 2$), 292 (M^+), 228, 129, 87, 77 (100%). Anal. Calcd for $C_{10}H_9ClO_4S_2$: C, 41.02; H, 3.10. Found: C, 40.80; H, 2.86.

4-Azido-3-chloro-2-sulfolene (4c). This compound was obtained from the substitution reaction of **2a** with sodium azide (1.1 equiv) in 1:1 CH_2Cl_2/H_2O under reflux for 24 h. White solid; mp 92.5–93.5 °C; IR (KBr) 2476, 2205, 2115, 2066, 1612, 1560, 1508, 1407, 1324, 1289, 1247, 1223, 1209, 1132, 1049, 997, 958, 913, 819, 802 cm^{-1}; ^1H NMR (200 MHz) δ 3.40 (dd, 1 H, J = 4, 14 Hz), 3.81 (dd, 1 H, J = 8, 14 Hz), 4.77 (dd, 1 H, J = 4, 8 Hz), 6.85 (s, 1 H); MS m/z 195 ($M^+ + 2$), 193 (M^+), 115, 66, 51, 41 (100%). Anal. Calcd for $C_4H_4ClN_3O_2S$: C, 24.82; H, 2.08; N, 21.70. Found: C, 24.81; H, 1.95; N, 21.58.

4-(Phenylthio)-3-(trimethylsilyl)-2-sulfolene (4d). This compound was obtained from the substitution reaction of **2b** with sodium phenylthiolate (0.9 equiv) in 1:1 MeOH/EtOH under reflux for 48 h. Colorless oil; IR (neat) 1580, 1473, 1442, 1404, 1292, 1247, 1219, 1181, 1125, 1111, 1049, 1024, 965, 927, 844, 753 cm^{-1}; ^1H NMR (200 MHz) δ 0.31 (s, 9 H), 3.31 (dd, 1 H, J = 3.5, 14 Hz), 3.46 (dd, 1 H, J = 7.2, 14 Hz), 4.54 (dd, 1 H, J = 3.5, 7.2 Hz), 6.69 (s, 1 H), 7.35 (s, 5 H); MS m/z 298 (M^+), 167, 160, 110, 109, 73 (100%). Anal. Calcd for $C_{13}H_{18}O_2S_2Si$: C, 52.31; H, 6.08. Found: C, 52.32; H, 6.22.

4-Azido-3-(trimethylsilyl)-2-sulfolene (4e). This compound was obtained from the substitution reaction of **2b** with sodium azide (1.9 equiv) in 1:1 CH_2Cl_2/H_2O under reflux for 48 h. Light yellow solid; mp 81–82 °C; IR (KBr) 2164, 2101, 2024, 1657, 1407, 1337, 1299, 1129, 1049, 920, 844, 760 cm^{-1}; ^1H NMR (200 MHz) δ 0.26 (s, 9 H), 3.25 (dd, 1 H, J = 4.4, 13.8 Hz), 3.60 (dd, 1 H, J = 7.8, 13.8 Hz), 4.68 (dd, 1 H, J = 4.4, 7.8 Hz), 6.73 (s, 1 H); MS m/z 216 ($M^+ - 15$), 124, 100, 97, 83, 73 (100%). Anal. Calcd for $C_7H_{13}N_3O_2SSi$: C, 36.34; H, 5.66. Found: C, 36.22; H, 5.61.

3,4-Bis(phenylthio)-2-sulfolene (4f) and 3,4-Bis(phenylthio)-3-sulfolene (5f). These compounds were obtained from the substitution reaction of **2c** with sodium phenylthiolate (4 equiv) in MeOH under reflux for 5 h. Compound **4f** existed only in trace amount: colorless oil; IR (neat) 3073, 1567, 1475, 1303, 1129, 749, 690 cm^{-1}; ^1H NMR (80 MHz) δ 3.36 (dd, 1 H, J = 7, 14 Hz), 3.69 (dd, 1 H, J = 8, 14 Hz), 4.47 (dd, 1 H, J = 7, 8 Hz), 5.65 (s, 1 H), 7.45 (s, 10 H); MS m/z 334 (M^+), 270, 161, 160, 159, 135, 128 (100%), 115, 109, 91, 65. Compound **5f**: white solid; mp 72–74 °C; IR (KBr) 1575, 1470, 1310, 1228, 1130, 940, 750, 690 cm^{-1}; ^1H NMR (60 MHz) δ 3.72 (s, 4 H), 7.5 (s, 10 H); MS m/z 334 (M^+, 100%), 270, 161. Anal. Calcd for $C_{16}H_{14}O_2S_3$: C, 57.46; H, 4.22. Found: C, 57.47; H, 4.09.

4-(Phenylsulfonyl)-3-(phenylthio)-2-sulfolene (4g) and 4-(Phenylsulfonyl)-3-(phenylthio)-3-sulfolene (5g). These compounds were obtained from the substitution reaction of **2c** with sodium phenylsulfinate (5 equiv) in DMF at room temperature for 1 h. These two compounds were unseparable by chromatography. However, a very small quantity of **5g** could be obtained by recrystallization of the mixture from CH_2Cl_2/Et_2O. **5g**: white solid; mp 178–179 °C; IR (KBr) 1575, 1325, 1270, 1150, 1100, 780, 740, 670 cm^{-1}; ^1H NMR (60 MHz) δ 3.55 (t, 2 H, J = 1 Hz), 4.03 (t, 2 H, J = 1 Hz), 7.33 (s, 5 H), 7.5–8.10 (m, 5 H); MS m/z 366 (M^+), 302, 177, 160 (100%), 147, 128. The peaks of the ^1H NMR spectrum of the mixture of **4g** and **5g** are resolved so that those of **4g** can be assigned: δ 3.63 (d, 2 H, J = 7 Hz), 4.70 (m, 1 H), 5.55 (d, 1 H, J = 1 Hz), 7.3–8.1 (m, 10 H). The elemental analysis was performed on the mixture. Anal. Calcd for $C_{16}H_{14}O_4S_3$: C, 52.44; H, 3.85. Found: C, 52.24; H, 3.87.

4-Azido-3-(phenylthio)-2-sulfolene (4h). This compound was obtained from the substitution reaction of **2c** with sodium azide (3 equiv) in DMF at room temperature for 2 h. White solid; mp 102–103 °C; IR (KBr) 2110, 1575, 1300, 1230, 1130, 920, 760 cm^{-1}; ^1H NMR (60 MHz) δ 3.37 (dd, 1 H, J = 4, 14 Hz), 3.80 (dd, 1 H, J = 8, 14 Hz), 4.80 (dd, 1 H, J = 4, 8 Hz), 5.92 (s, 1 H), 7.63 (s, 5 H); MS m/z 267 (M^+, 100%), 174, 160, 147, 134, 104. Anal. Calcd for $C_{10}H_9N_3O_2S_2$: C, 44.93; H, 3.39; N, 15.73. Found: C, 44.96; H, 3.49; N, 15.79.

4-Methoxy-3-(phenylthio)-2-sulfolene (4i). This compound was obtained from the substitution reaction of **2c** with sodium hydroxide (2 equiv) in dry MeOH at room temperature for 2 h followed by aqueous treatment. White solid; mp 81–82 °C; IR (KBr) 1577, 1300, 1140, 1085, 765 cm^{-1}; ^1H NMR (60 MHz) δ 3.17–3.87 (m, 2 H), 3.47 (s, 3 H), 4.67–4.90 (m, 1 H), 5.73 (d, 1 H, J = 1 Hz), 7.43 (s, 5 H); MS m/z 256 (M^+, 100%), 160, 134. Anal. Calcd for $C_{11}H_{12}O_3S_2$: C, 51.54; H, 4.72. Found: C, 51.54; H, 4.67.

3-(Phenylthio)-4-pyrrolidino-2-sulfolene (4j). This compound was obtained from the substitution reaction of **2c** with pyrrolidine (1.4 equiv) in dry MeOH at room temperature for 1 h. White solid; mp 110–111 °C; IR (KBr) 1570, 1292, 1215, 1119, 935, 754 cm^{-1}; ^1H NMR (60 MHz) δ 1.63–2.0 (m, 4 H), 2.43–2.83 (m, 4 H), 3.31 (d, 2 H, J = 6 Hz) 3.56 (d, 1 H, J = 2 Hz), 4.63 (dt, 1 H, J = 2, 6 Hz), 7.43 (s, 5 H); MS m/z 295 (M^+), 97 (100%). Anal. Calcd for $C_{14}H_{17}NO_2S_2$: C, 56.73; H, 6.10; N, 4.73. Found: C, 56.94; H, 5.88; N, 4.75.

4-Hydroxy-3-(phenylthio)-2-sulfolene (4k). This compound was obtained from the substitution reaction of **2c** with sodium nitrite (2.2 equiv) in DMF at 0 °C for 2 h. White solid; mp 140–141 °C; IR (neat) 3452, 1571, 1289, 1229, 1124, 957, 753 cm^{-1}; ^1H NMR (60 MHz) δ 3.30 (dd, 1 H, J = 4, 14 Hz), 3.70 (dd, 1 H, J = 7, 14 Hz), 3.63 (br s, 1 H), 5.07 (dd, 1 H, J = 4, 7 Hz), 5.67 (s, 1 H), 7.45 (s, 5 H); MS m/z 242 (M^+, 100%), 176. Anal. Calcd for $C_{10}H_{10}O_3S_2$: C, 49.57; H, 4.16. Found: C, 49.45; H, 4.18.

General Procedure for the Michael Addition/Dechlorination Reaction of 4-Substituted 3-Chloro-2-sulfolenes. The solution of **2a** or **4c** and a nucleophile, whose molar equivalents used are as indicated below, in a proper solvent was stirred for a certain period of time. The solvent was then removed under reduced pressure and the crude mixture was purified by HPLC (LiChrosorb column, hexane/EtOAc) to give the pure product(s).

3,4-Bis(phenylthio)-3-sulfolene (5f). This compound was obtained in 40% yield from the reaction of **2a** with sodium phenylthiolate (2.25 equiv) in 1:1 MeOH/EtOH under reflux for 18 h. Compound **5a**, presumably formed by the thiolate-induced double-bond isomerization of the intermediate **4a**, was also obtained in 40% yield. These two components were readily separated by HPLC. A trace amount of **2c** (<2%) was also detected in the product mixture. This minor component is presumably formed from the direct Michael addition/dechlorination reaction of **2a** without touching the bromide.

3,4-Diazido-2-sulfolene (4l). This compound was obtained in 30% yield from the reaction of **2a** with sodium azide (1.95 equiv) in 1:1 CH_2Cl_2/H_2O under reflux for 24 h. Compound **4c** was also obtained in 47% yield from this reaction. The two products were readily separated by HPLC. Compound **4l**: yellow solid; mp 82–83.5 °C; IR (neat) 2177, 2143, 2101, 1605, 1410, 1320, 1285, 1268, 1233, 1216, 1132, 1097, 892, 743 cm^{-1}; ^1H NMR (200 MHz) δ 3.32 (dd, 1 H, J = 4.8, 15.2 Hz), 3.75 (dd, 1 H, J = 6.4, 15.2 Hz), 4.61 (dd, J = 4.8, 6.4 Hz), 6.37 (s, 1 H); MS m/z 200 (M^+), 66, 52, 48, 41 (100%). This compound decomposed gradually upon standing so that a satisfactory microanalysis was not obtainable.

4-Azido-3-(phenylthio)-2-sulfolene (4h). This compound was obtained in 65% yield from the reaction of **4c** with sodium phenylthiolate (0.9 equiv) in 1:1 MeOH/EtOH under reflux for 48 h.

General Procedure for the Base-Induced Double-Bond Isomerization Reaction from 2-Sulfolenes 4 to the Corresponding 3-Sulfolenes 5. The solution of **4** and a base in a proper solvent was stirred for a certain period of time. The base

was then removed by passing the reaction mixture through a silica gel column. The resulting solution was concentrated under reduced pressure and purified by HPLC (LiChrosorb column, hexane/EtOAc) to give the pure product **5**. The yields of isomerization reactions are summarized in Table I.

3-Chloro-4-(phenylthio)-3-sulfolene (5a). This compound was obtained from the isomerization reaction of **4a** with Et_3N (3 equiv) in $CHCl_3$ at room temperature for 12 h.

3-Azido-4-chloro-3-sulfolene (5c). This compound was obtained from the isomerization reaction of **4c** with Et_3N (3 equiv) in $CHCl_3$ at room temperature for 24 h. Yellow solid; mp 104–105 °C; IR (KBr) 2158, 2129, 1651, 1402, 1315, 1254, 1141, 1130, 1109, 1077, 973 cm^{-1}; ^1H NMR (80 MHz) δ 3.98 (s, 2 H), 4.05 (s, 2 H); MS m/z 193 (M^+), 66 (100%), 61, 41.

3-(Phenylthio)-4-(trimethylsilyl)-3-sulfolene (5d). This compound was obtained from the isomerization reaction of **4d** with DBN (1 equiv) in CH_2Cl_2 at room temperature for 1 h. White solid; mp 94–95 °C; IR (KBr) 1562, 1309, 1246, 1230, 1132, 839, 750 cm^{-1}; ^1H NMR (200 MHz) 0.30 (s, 9 H), 3.66 (s, 2 H), 3.94 (s, 2 H), 7.31 (s, 5 H); MS m/z 298 (M^+), 234, 167, 157, 129, 109, 73 (100%).

3-Azido-4-(trimethylsilyl)-3-sulfolene (5e). This compound was obtained from the isomerization reaction of **4e** with DBN (1 equiv) in CH_2Cl_2 at room temperature for 8 h. Colorless oil; IR (neat) 2105, 1705, 1597, 1315, 1251, 1127, 969, 842, 758 cm^{-1}; ^1H NMR (200 MHz) δ 0.17 (s, 9 H), 3.88 (s, 2 H), 3.96 (s, 2 H); MS m/z 231 (M^+), 189, 138, 125, 99, 84, 73 (100%). In addition to **5e** and recovered **4e**, 3-azido-3-sulfolene was also obtained in 30% yield as a yellow solid: mp 99–100.5 °C; IR (neat) 2411, 2366, 2208, 2170, 2120, 1423, 1401, 1326, 1288, 1123, 1089, 1007, 903, 801 cm^{-1}; ^1H NMR (200 MHz) δ 3.76–3.78 (m, 2 H), 3.95–3.98 (m, 2 H), 5.52–5.56 (m, 1 H); MS m/z 159 (M^+), 95, 67, 66, 53, 41 (100%).

3-Azido-4-(phenylthio)-3-sulfolene (5h). This compound was obtained from the isomerization reaction of **4h** with methanolic NaOH (0.8 equiv) at room temperature for 1 h. White solid; mp 80–88 °C (dec); IR (KBr) 2120, 1610, 1315, 1245, 1145, 1130, 970, 746 cm^{-1}; ^1H NMR (60 MHz) δ 3.68 (t, 2 H, J = 1 Hz), 3.97 t, 2 H, J = 1 Hz), 7.28 (s, 5 H); MS m/z 267 (M^+), 239, 175, 135 (100%), 117, 110. Anal. Calcd for $C_{10}H_9N_3O_2S_2$: C, 44.93; H, 3.39; N, 15.72. Found: C, 44.91; H, 3.40; N, 15.73.

3,4-Diazido-3-sulfolene (5i). This compound was obtained from the isomerization reaction of **4l** with DBN (1 equiv) in CH_2Cl_2 at room temperature for 45 min. Yellow solid; mp 82–83.5 °C; IR (KBr) 2151, 2090, 1355, 1317, 1144, 1129, 1088, 874, 700 cm^{-1}; ^1H NMR (200 MHz) δ 3.96 (s); MS m/z 200 (M^+), 104, 64, 53 (100%). This compound decomposed gradually upon standing so that satisfactory microanalysis was not obtainable.

Oxidation of 3-Chloro-4-(phenylthio)-3-sulfolene (5a) with *m*-Chloroperbenzoic Acid (*m*-CPBA). A solution of **5a** and *m*-CPBA (1 or 2 equiv) in CH_2Cl_2 was stirred at room temperature for 24 h. The solution was then washed with aqueous $Na_2S_2O_3$. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give essentially pure product. The reaction using 2 equiv of *m*-CPBA gave a mixture of **4b** (22%) and **5b** (45%) while the reaction using 1 equiv of *m*-CPBA gave **5j** in 82% yield. Compound **5j**: white solid; mp 110.5–111.5 °C; IR (neat) 1609, 1475, 1445, 1403, 1328, 1246, 1136, 1077, 1035, 937, 752 cm^{-1}; ^1H NMR (80 MHz) δ 3.53 (d, 1 H, J = 16.8 Hz), 4.14 (s, 2 H), 4.25 (d, 1 H, J = 16.8 Hz), 7.60 (s, 5 H); MS m/z 278 (M^+ + 2), 276 (M^+), 214, 212, 164, 129, 109, 78, 77, 51 (100%). Anal. Calcd for $C_{10}H_9ClO_3S_2$: C, 43.40; H, 3.28. Found: C, 43.46; H, 3.05.

General Procedure for the Thermolysis of 3-Sulfolenes 5 to the Corresponding 1,3-Dienes 6. A suspension of **5** and a trace amount of hydroquinone (<5%) in completely degassed toluene (100 mg/20 mL) was either heated to 130 °C in a sealed tube or refluxed under nitrogen for 2 h. The solvent was removed under reduced pressure, and the crude product was eluted through silica gel (hexane) to remove hydroquinone to give essentially pure product. Analytical samples were obtained by purification with HPLC (LiChrosorb column). The yields of the dienes are summarized in Table II. We were unable to obtain satisfactory elemental analyses of most of these dienes owing to their instability.

2-Chloro-3-(phenylthio)-1,3-butadiene (6a). This compound was obtained from the sealed-tube thermolysis of **5a**. Colorless oil; IR (neat) 1608, 1583, 1568, 1479, 1440, 891, 740 cm^{-1}; ^1H NMR (80 MHz) δ 5.51 (s, 1 H), 5.66 (s, 1 H), 5.99 (s, 1 H), 6.19 (s, 1 H), 7.30 (s, 5 H); MS m/z 198 (M^+ + 2), 196 (M^+), 161, 128, 109, 86, 84 (100%), 51.

2-Chloro-3-(phenylsulfonyl)-1,3-butadiene (6b). This compound was obtained from the sealed-tube thermolysis of a mixture of **4b** and **5b** in the presence of pyridine (1 equiv). Colorless oil; IR (neat) 3064, 1584, 1368, 1308, 1148, 1069, 961 cm^{-1}; ^1H NMR (80 MHz) δ 5.66 (s, 1 H), 6.11 (s, 1 H), 6.46 (s, 1 H), 6.74 (s, 1 H), 7.53–7.94 (m, 5 H); MS m/z 230 (M^+ + 2), 228 (M^+), 129, 125, 77, 68, 51 (100%). Anal. Calcd for $C_{10}H_9ClO_2S$: C, 52.52; H, 3.97. Found: C, 52.52; H, 4.08.

2-(Phenylthio)-3-(trimethylsilyl)-1,3-butadiene (6c). This compound was obtained from the thermolysis of **5d**. Colorless oil; IR (neat) 1583, 1403, 1319, 936, 904, 885, 843, 757 cm^{-1}; ^1H NMR (200 MHz) δ 4.96 (s, 1 H), 5.20 (s, 1 H), 5.48 (s, 1 H), 6.02 (s, 1 H), 7.25–7.35 (m, 5 H); MS m/z 234 (M^+), 219, 167, 151, 129, 125, 109, 73 (100%).

2,3-Bis(phenylthio)-1,3-butadiene (6d). This compound was obtained from the thermolysis of **5f**. Colorless oil; IR (neat) 3071, 1556, 1477, 1115, 1024, 939, 739, 688 cm^{-1}; ^1H NMR (60 MHz) δ 5.4 (s, 2 H), 6.06 (s, 2 H), 7.43 (s, 10 H).

2-(Phenylsulfonyl)-3-(phenylthio)-1,3-butadiene (6e). This compound was obtained from the sealed-tube thermolysis of a mixture of **4g** and **5g** in the presence of pyridine (1 equiv). Colorless oil; IR (neat) 3065, 1584, 1308, 1148, 1077, 747, 695 cm^{-1}; ^1H NMR (60 MHz) δ 5.48 (s, 1 H), 6.07 (s, 1 H), 6.3 (s, 1 H), 6.63 (s, 1 H), 6.90–8.00 (m, 10 H); MS m/z 302 (M^+), 177, 160 (100%), 147. Anal. Calcd for $C_{16}H_{14}O_2S_2$: C, 63.55; H, 4.67. Found: C, 63.48; H, 4.65.

2-Chloro-3-(phenylsulfinyl)-1,3-butadiene (6f). This compound was obtained from the thermolysis of **5j**. Light yellow oil; IR (neat) 3059, 1618, 1584, 1476, 1022, 998, 934, 891, 750, 687 cm^{-1}; ^1H NMR (200 MHz) δ 5.46 (s, 1 H), 5.61 (s, 1 H), 6.27 (s, 1 H), 6.36 (s, 1 H), 7.45–7.66 (m, 5 H); MS m/z 214 (M^+ + 2), 212 (M^+), 125, 123, 109, 97, 77, 51 (100%).

Diels–Alder Reaction of 5a with *N*-Phenylmaleimide Giving 4-Chloro-1-phenyl-5-(phenylthio)-2a,3,6,6a-tetrahydrophthalimide (7). A suspension of **5a**, *N*-phenylmaleimide (5 equiv), and a trace of hydroquinone (<5%) in completely degassed benzene (100 mg/5 mL) was heated to 150 °C in a sealed tube for 24 h. The solvent was removed under reduced pressure, and the crude oil was purified by HPLC (LiChrosorb column, 3:2 hexane/EtOAc) to give the pure product **7** in 87% yield. White solid; mp 134–135 °C; IR (KBr) 3068, 1713, 1598, 1379, 1174, 889, 774, 697 cm^{-1}; ^1H NMR (80 MHz) δ 2.45–2.66 (m, 2 H), 2.74–3.05 (m, 2 H), 3.14–3.37 (m, 2 H), 7.11–7.56 (m, 10 H); MS m/z 371 (M^+ + 2), 369 (M^+), 262, 260, 188, 186, 109 (100%), 77. Anal. Calcd for $C_{20}H_{16}ClNO_2S$: C, 64.95; H, 4.36; N, 3.79. Found: C, 64.86; H, 4.21; N, 3.43.

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Registry No. **1a**, 7311-87-7; **1b**, 104692-94-6; **1c**, 64741-13-5; **2a**, 114079-02-6; **2b**, 111379-47-6; **2c**, 114397-08-9; **3**, 114397-09-0; **4a**, 114397-10-3; **4b**, 114397-11-4; **4c**, 114397-12-5; **4d**, 114397-13-6; **4e**, 114397-14-7; **4f**, 114397-15-8; **4g**, 114422-69-4; **4h**, 114397-16-9; **4i**, 114397-17-0; **4j**, 114397-18-1; **4k**, 114397-19-2; **4l**, 114397-20-5; **5a**, 114397-22-7; **5b**, 114397-23-8; **5c**, 114397-24-9; **5d**, 114397-25-0; **5e**, 114397-26-1; **5f**, 102058-95-7; **5g**, 114397-27-2; **5h**, 114397-28-3; **5i**, 114397-29-4; **5j**, 114397-21-6; **6a**, 85972-11-8; **6b**, 114397-31-8; **6c**, 91312-41-3; **6d**, 102058-98-0; **6e**, 114397-32-9; **6f**, 114397-33-0; **7**, 114397-34-1; 3-azido-3-sulfolene, 114397-30-7; sodium phenylthiolate, 930-69-8; sodium phenylsulfinate, 873-55-2; pyrrolidine, 123-75-1; *N*-phenylmaleimide, 941-69-5.