tallization from acetone gave colorless crystals, mp 206-208 °C. Bicyclo[2.2.2]oct-1-yldiphenylphosphine oxide (8): MS, *m/e* (relative intensity) 311 (9), 310 (4), 297 (3), 282 (8), 201 (3), 109 (23), 77 (44), 67 (100), 55 (37), 47 (38), 41 (39), 27 (10), 18 (15); ^{1}H NMR ($CDCl_3$) δ 1.67 (13 H, m), 7.50 (6 H, m), 7.92 (4 H, m); ^{13}C NMR ($CDCl_3$, relative to TMS) δ 34.21 (J_{C-P} = 78.21 Hz, C_1), 24.89 (C_2), 25.15 (J_{C-P} = 11.59 Hz, C_3), 23.73 (C_4), 131.26 (J_{C-P} = 91.56 Hz, C_i), 132.29 (J_{C-P} = 7.93 Hz, C_o), 128.20 (J_{C-P} = 10.98 Hz, C_m), 131.32 (J_{C-P} = 2.44 Hz, C_p); ^{31}P NMR δ (ppm, relative to external 85% H_3PO_4) 35.30 (positive sign-downfield). Anal. Calcd for $C_{20}H_{33}PO$: C, 77.4; H, 7.5. Found: C, 77.3; H, 7.4.

Photostimulated Reaction of 1-Iodobicyclo[2.2.2]octane with Ph_2P^- Ions in the Presence of *p*-Dinitrobenzene. The procedure was similar to that for the previous reaction, except that 20 mol % of *p*-dinitrobenzene was added.

Photostimulated Reaction of 1-Iodobicyclo[2.2.2]octane with Ph_2P^- Ions in Liquid Ammonia-*tert*-Butylamine. To the 200 mL of freshly distilled liquid ammonia was added 80 mL of dry *tert*-butylamine, and the procedure was similar to that described above.

Photostimulated Reaction of 1-Bromo-4-iodobicyclo[2.2.2]octane and 1,4-Diiodobicyclo[2.2.2]octane with 6 in Liquid Ammonia. The procedure was similar to that described above except that the irradiation time was 60 min. The residue was chromatographed on a column of silica gel. Elution with diethyl ether and then ethanol afforded the monosubstitution and the disubstitution products, respectively. The 1,4-bis(diphenylphosphinyl)bicyclo[2.2.2]octane was recrystallized from benzene, mp 313 °C (hot plate mp apparatus). 1,4-Bis(diphenylphosphinyl)bicyclo[2.2.2]octane (14): MS, *m/e* (relative intensity) 509 (6), 508 (6), 386 (3), 325 (3), 309 (47), 281 (12), 201 (100), 183 (12), 108 (4), 107 (23), 91 (8), 77 (26), 47 (3); ^{1}H NMR ($CDCl_3$) δ 1.82 (12 H, t), 7.48 (12 H, m) 7.86 (8 H, m); ^{13}C NMR ($DCCl_3$, relative to Me_4Si)[20] δ 34.48 ($^1J_{C-P}$ = 79.35 Hz, $^4J_{C-P}$ = 1.52 Hz, C_1 + C_4), 24.51 (C_2 + C_3), 130.49 (J_{C-P} = 93.08 Hz, C_i), 132.14 (C_o), 128.37 (C_m), 131.64 (C_p); ^{31}P NMR δ (ppm, relative to external 85% H_3PO_4) 34.80 (positive sign—downfield shift). Anal. Calcd for $C_{32}H_{32}P_2O_2$; C, 75.3; H, 6.3. Found C, 75.6; H, 6.2.

Photostimulated Reaction of 1-Chloro-4-iodobicyclo[2.2.2]octane with 6 in Liquid Ammonia. The procedure was similar to that described above, except that the irradiation time was 240 min. The residue from the ether extract was chromatographed on a column of silica gel (elution with diethyl ether) afforded (4-chlorobicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide as a white solid, which was recrystallized from diethyl ether/benzene (1:1), mp 212 °C. (4-Chlorobicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide (12): MS, *m/e* (relative intensity) 344.6 (23), 309.4 (100), 281 (23), 237 (4), 201 (76), 183 (14), 107 (18), 91 (14), 77 (39), 67 (6), 51.1 (12), 47 (10); ^{1}H NMR ($CDCl_3$) δ 1.98 (12 H, br s), 7.51 (6 H, m), 7.89 (4 H, m); ^{13}C NMR ($DCCl_3$, relative to Me_4Si) δ 33.33 (J_{C-P} = 77.15 Hz, C_1), 27.48 (C_2), 35.29 (J_{C-P} = 11.23 Hz, C_3), 65.78 (J_{C-P} = 2.44 Hz, C_4), 130.41 (J_{C-P} = 92.77 Hz, C_i), 132.02 (J_{C-P} = 8.3 Hz, C_o), 128.4 (J_{C-P} = 11.23 Hz, C_m), 131.74 (J_{C-P} = 4.4 Hz, C_p); ^{31}P NMR δ (ppm, relative to external 85% H_3PO_4) 34.38 (positive sign—downfield shift). Anal. Calcd for $C_{20}H_{22}POCl$: C, 69.7; H, 6.4. Found: C, 70.0; H, 6.1.

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Registry No. 1, 89566-55-2; 5, 931-98-6; 8, 114378-27-7; 9, 2064-03-1; 10, 89566-54-1; 12, 114378-28-8; 14, 114378-29-9; 15, 10364-05-3; *p*-DNB, 100-25-4; $Ph_2P^-Na^+$, 15205-59-1; triphenylphosphine, 603-35-0.

(20) Resonances for C_2, C_3, C_o, and C_m of compound 14 exhibit second-order characteristics even at 100.4 MHz (X parts of ABX spin systems; see ref 21 and 22 for examples).

(21) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 2361.
(22) Olah, G. A.; Shih, J. G.; Krishnamurthy, V. V.; Singh, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4492.

Selective Cross Diels-Alder Reactions of 2-(Phenylsulfonyl) 1,3-Dienes

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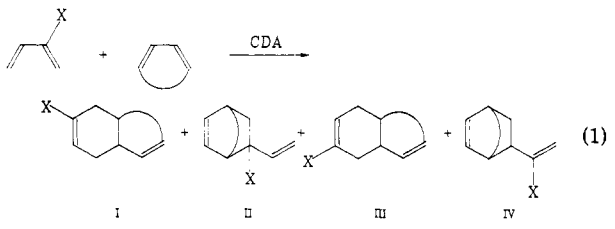
2-Sulfonylated 1,3-dienes have been prepared by way of their stable precursors, 3-sulfonylated 3-sulfolenes. These dienes underwent clean cross Diels-Alder reactions with Danishefsky diene, cyclopentadiene, cyclohexadiene, 6,6-dimethylfulvene, and norbornadiene at 130 °C. In the cross cycloaddition reactions, the sulfonylated 1,3-dienes may react as both the dienes and the dienophiles. When the sulfonylated 1,3-dienes were reacted with Danishefsky diene, they behaved as the dienophiles. When the sulfonylated 1,3-dienes were reacted with cyclopentadiene at room temperature, mixtures containing the cycloadducts from the reactions of sulfonylated dienes as the dienes with cyclopentadiene as the dienophile and those from the reactions of cyclopentadiene as the diene with the sulfonylated dienes as the dienophiles were obtained. The latter cycloadducts, being the major products of the reactions, could be converted completely to the former adducts by a sigmatropic rearrangement process at 130 °C. Thus, this paper illustrates successful examples of a cross Diels-Alder reaction between two different dienes where only one of the possible isomeric cycloadducts was obtained cleanly.

Although the Diels-Alder dimerization reactions of conjugated dienes are frequently observed, the cross Diels-Alder (CDA) reactions between two different conjugated dienes have not been systematically studied,[1] and their synthetic applications remain essentially unexplored so far. The major reason is that the CDA reactions usually nonselectively produce mixtures of all possible structural, stereoisomeric, and regioisomeric cycloadducts in addition to the dimers of each diene so they are synthetically useless. For example, there are four possible isomers in eq 1. Nevertheless, each of the four cycloadducts shown in eq 1 is suitably functionalized (if X is a heteroatom functionality), and they may be transformed into many mono- and multicyclic molecules that are not easily ac-

(1) For examples, see: (a) Johnstone, R. A. W.; Quan, P. M. *J. Chem. Soc.* **1963**, 935. (b) Stewart, C. A., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4815. (c) Houk, K. N.; Luckus, L. J. *J. Org. Chem.* **1973**, *38*, 3836. (d) Franck-Neumann, M.; Martina, D.; Brion, F. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 864. (e) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665.

0022-3263/88/1953-3020$01.50/0

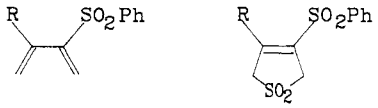


(1)

cessible by known procedures. Therefore, if the chemo-, stereo-, and regioselectivity of the CDA reactions can be controlled so that only one of the possible products is formed predominantly or exclusively, these reactions will become very useful. We describe herein our recent findings about the CDA reactions of 2-sulfonylated dienes with several typical dienes for the preparation of highly functionalized decalin and hydrindene systems.

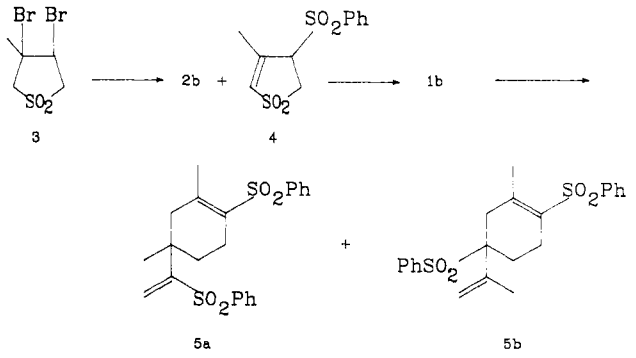
The study of the synthetic utility of 2-arylsulfonylated 1,3-dienes has recently drawn increasing attention.[2-4] These reagents may behave as Michael acceptors with nucleophiles to give β'-functionalized allylic sulfones.[2,3] They may be transformed into 1,4-difunctionalized olefins through a multistep reaction sequence.[2] They may also undertake [4 + 2] cycloaddition reactions regioselectively with both electron-rich and electron-deficient olefins to give functionalized cyclic systems.[2-4] Their Diels–Alder reactions are especially interesting because these sulfonylated dienes, although being electron deficient, display reasonably good reactivity as dienes.[5] Alternatively, these dienes could be viewed as potential dienophiles since they are olefins bearing electron-withdrawing sulfonyl and vinyl groups. For this reason, 2-sulfonylated dienes appeared to us to be ideal candidates for the study of CDA reactions.

Although some of the substituted 2-(phenylsulfonyl)-1,3-butadienes are stable for long-term storage, the parent compound **1a** itself is reportedly to undergo rapid Diels–



Alder dimerization at room temperature[2,3,6] so that its preparation in a pure state presents a synthetic challenge. As it is now well established that 3-sulfolenes are useful precursors for substituted 1,3-dienes,[7] we were able to apply this idea to partially circumvent this problem by developing a procedure for the preparation of **2a**, the stable precursor of **1a**.[6] As can be seen in the later discussion, for the cycloaddition reactions performed at 130 °C, compound **2a** was used directly since the extrusion of SO_2 proceeded rapidly at this temperature and diene **1a** was generated in the presence of other dienes. However, we had to be able to prepare **1a** in the unprotected form because sometimes it was desirable to perform CDA reactions at low temperature. To meet this purpose, compound **2a** was subjected to a brief thermolysis as a dilute solution in toluene under reflux for 7 h followed by flash column chromatographic separation to give a clean solution of **1a** free from dimers in about 35% yield. Compound **1a** dimerized completely in about 3 h after it was concentrated. Fortunately, a brief condensation of the dilute solution at room temperature could give an essentially pure sample for rapid spectral analysis. In fact, the percentage yield of **1a** was estimated by the amount of dimers collected after concentration. A dilute solution of **1a** in toluene (4 mg/mL) was found to be stable for at least 1 week at −10 °C with <5% of dimerization.

Scheme I

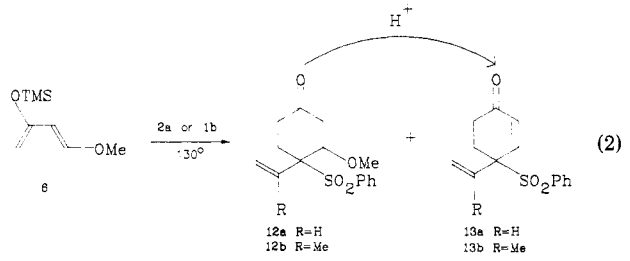


4-Methyl-3-(phenylsulfonyl)-3-sulfolene (**2b**), the stable precursor of **1b**, was prepared from the substitution reaction of the readily available compound **3**[6] (Scheme I). Treatment of **3** with sodium phenylsulfinate produced the desired product **2b**. The formation of **2b** was unavoidably accompanied by its double-bond isomer **4** in about a 1:2 ratio. These two isomers could be separated only with great difficulty and were found to exist in an about 1:1 equilibrium under basic conditions because all kinds of basic treatment of the mixture gave the mixture of the two components in approximately the same ratio.[6] Fortunately, the separation of **2a** from **4** was unnecessary because thermolysis of the mixture at 130 °C produced **1b** in good yield. Presumably, the conversion of **4** to **2b** through equilibration proceeded fast enough under thermal conditions. Diene **1b** is thermally much more stable than **1a**. A neat sample of **1b** remained essentially unchanged after standing at room temperature for a week and dimerizes <60% after being heated to 130 °C for 3 days. Unlike the situation for **1a**, we usually used the free diene **1b** in CDA reactions at various temperatures, although the mixture of **2b** and **4** could work as well.

With the requisite sulfonyl dienes at hand, the CDA reactions of several electron-rich dienes, including 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene (Danishefsky diene) (**6**), cyclopentadiene (**7**), 1,3-cyclohexadiene (**8**), 2,3-dimethyl-1,3-butadiene (**9**), 6,6-dimethylfulvene (**10**), and norbornadiene (**11**), were performed.

Treatment of Danishefsky diene (**6**) with **2a** or **1b** at 130 °C proceeded chemoselectively and regioselectively to give the cycloadducts **12a,b** and **13a,b**, respectively, in good yields (eq 2). No other isomers were detected. Isolation of products **12** and **13** was possible but unnecessary since treatment of the crude mixtures with dilute HCl induced the elimination of methanol from **12a,b** and resulted in the formation of essentially clean **13a,b**. The acid treatment

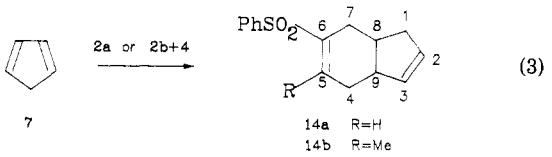
(2) Bäckvall, J.-E.; Juntunen, S. K. *J. Am. Chem. Soc.* **1987**, *109*, 6396 and references cited therein.
(3) Cuvigny, T.; Herve du Penhoat, C.; Julia, M. *Tetrahedron* **1986**, *42*, 5329.
(4) Inomata, K.; Kinoshita, H.; Takemoto, H.; Murata, Y.; Kotake, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3341.
(5) Carruthers, W. *Some Modern Methods of Organic Synthesis*; Cambridge University Press: Cambridge, 1978; pp 161–230.
(6) Chou, T. S.; Hung, S. C.; Tso, H. H. *J. Org. Chem.* **1987**, *52*, 3394.
(7) (a) Chou, T. S.; Tso, H. H.; Chang, L. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1323. (b) Chou, T. S.; Tso, H. H.; Chang, L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 236. (c) Chou, T. S.; Tso, H. H.; Chang, L. J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 515. (d) Chou, T. S.; Chang, L. J.; Tso, H. H. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1039. (e) Chou, T. S.; Tso, H. H.; Lin, L. C. *J. Org. Chem.* **1986**, *51*, 1000. (f) Chou, T. S.; You, M. L. *Bull. Inst. Chem., Acad. Sin.* **1986**, *33*, 13. (g) Yamada, S.; Ohsawa, H.; Suzuki, T.; Takayama, H. *J. Org. Chem.* **1986**, *51*, 4934. (h) Tao, Y. T.; Liu, C. L.; Lee, S. J.; Chou, S. S. P. *J. Org. Chem.* **1986**, *51*, 4718. (i) Chou, T. S.; Tso, H. H.; Tao, Y. T.; Lin, L. C. *J. Org. Chem.* **1987**, *52*, 244. (j) Tso, H. H.; Chou, T. S.; Lee, W. C. *J. Chem. Soc., Chem. Commun.* **1987**, 934. (k) Chou, S. S. P.; Liou, S. Y.; Tsai, C. Y.; Wang, A. J. *J. Org. Chem.* **1987**, *52*, 4468.



(2)

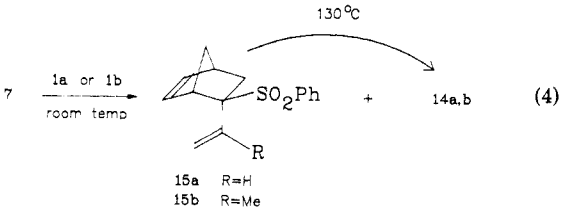
of an isolated, pure sample of **12a** or **12b** gave **13a** and **13b**, respectively, in almost quantitative yields. The CDA reactions in eq 2 exemplify that sulfonylated dienes **1a,b** indeed may react as dienophiles specifically at only one of the double bonds as we originally anticipated. Products **13a,b** are expected to be useful intermediates for synthesis since they are functionalized with an α,β-unsaturated ketone as well as a doubly allylic sulfone group.[8]

The CDA reactions of cyclopentadiene (**7**) with **2a** or **1b** at 130 °C resulted in the formation of only one type of product, **14a** and **14b**, respectively, in good yields (eq 3). These are the cycloadducts of the apparent cycloaddition reaction of **1a,b** as the dienes with **7** as the dienophile.



(3)

Since **7** is electron rich and the sulfonylated dienes are electron poor, one would have expected the CDA reactions to proceed contrariwise, favoring the electron-rich diene to react as the diene and **1** to react as the dienophile.[5] In order to examine this problem in more detail, we performed the room temperature CDA reactions between **7** and the free dienes **1a** and **1b** (eq 4). Under these reaction

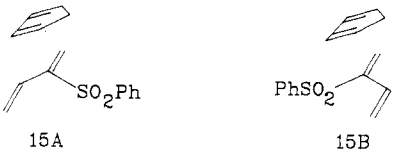


(4)

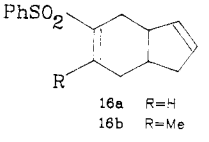
conditions, **14a** (16%) and **14b** (29%) were still obtainable, however, as minor components. The major products of these CDA reactions are the bicyclic compounds **15a** (55%) and **15b** (58%), the expected cycloadducts from the consideration of the electronic nature of the reactants. Heating **15a** or **15b** at 130 °C for 5 h completely gave **14a** and **14b**, respectively, whereas stirring **15a,b** at room temperature for 2–3 days did not cause any conversion.

This observation indicates that two different modes of cross cycloaddition reactions took place at room temperature. The first route involves the cross cycloaddition of **7** as the diene with **1a,b** as the dienophiles, giving **15a,b**, while the second route involves the cross cycloaddition of **1a,b** as the dienes with **7** as the dienophile, giving **14a,b**. The conversion of **15a,b** to **14a,b** at 130 °C presumably involves the sigmatropic Cope rearrangement, which is well-known to take place readily in similar systems.[9] It also seemed reasonable to assume that, at 130 °C, **15a,b** were formed from **14a,b** by way of reversible Diels–Alder reactions since the process would ultimately produce the more stable Diels–Alder adducts. However, such a possibility was ruled out because no trace of **14b** could be detected when **15a** was heated at 130 °C in the presence of 2 mol equiv of **1b**, nor was any trace of **14a** detected when **15b** was heated in the presence of 2 mol equiv of **2a** under similar conditions. These observations evidenced the intramolecular nature of the conversion from **15** to **14**. The structure of **14a** was so assigned on the basis of its ^{1}H NMR data and the result of a 2D-COSY experiment, while the structural assignment of **14b** could not be achieved simply by similar spectral analyses. However, since **14b** could be obtained from **15b** by Cope rearrangment, the only possible structure is the one shown in eq 3.

Several points about these reactions merit mentioning. First, in the room temperature CDA reactions, the reaction route involving **7** as the diene appears to be the major but not the sole route. This is somewhat different from the results of the CDA reactions of Danishefsky diene where only one mode of cycloaddition was observed (eq 2). The divergence in product formation of the two reactions indicates that, although **1a** and **1b** are electron deficient, they still have the ability to react as dienes with electron-rich dienes. Second, the reaction route leading to products **15a,b** is very regioselective; i.e., only the double bond directly attached to the sulfonyl group of **1** is reacting as the dienophilic part. This is conceivable since there is a significant difference in electron deficiency between the two double bonds in **1**. Third, this reaction route is highly stereoselective because the other possible stereoisomers of **15a,b** with the vinyl group on the exo face and the sulfonyl group on the endo face were not present in the product mixtures. The transition state leading to the formation of **15a** can be shown as in **15A**, which is more favored than **15B** probably for both steric and secondary



orbital overlapping reasons. Fourth, since compounds **14** and **15** are not interconvertible at room temperature, compounds **14a,b** formed under room temperature conditions must be the primary products of a regioselective cycloaddition reaction. It is known that in the Diels–Alder reactions of 2-arylsulfonyl 1,3-dienes with unsymmetrical dienophiles,[2,4] the sulfonyl group is an effective directing element favoring the formation of "para" adducts. Therefore, it is not surprising to observe that **14a** was formed in the absence of its regioisomer **16a**. The situ-



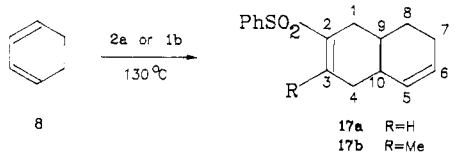
ation should be more complex for **1b** to react as the diene since both methyl and sulfonyl groups may effect the regioselectivity. The result that the isomer **16b** was not detected indicates that the phenylsulfonyl group is a much more powerful "para"-directing element than the methyl group for the control of regioselectivity of Diels–Alder reactions. The regioselectivity is comparable to that of the Diels–Alder reactions of 2-methyl-3-(phenylsulfenyl)-1,3-butadiene, where the sulfenyl group is the more powerful

(8) (a) Trost, B. M.; Schmuff, N. R.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5981. (b) Cuvigny, T.; Julia, M.; Rolando, C. *J. Organomet. Chem.* **1985**, *285*, 395. (c) Masaki, Y.; Sakuma, K.; Kaji, K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1171. (d) Julia, M.; Righini-Tapie, A.; Verpeaux, J. N. *Tetrahedron* **1985**, *39*, 3283.

(9) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1974**, *22*, 1.

directing element.[10] Fifth, compound **1b**, with an extra methyl group, is more electron rich than **1a** and accordingly should have a higher tendency to react as a diene. This tendency is clearly reflected in the higher ratio of **14b**/**15b** than **14a**/**15a** under room temperature reaction conditions. Sixth, although the exclusive formation of **14a,b** at 130 °C might have been entirely produced from the primary cross cycloaddition reaction of **1a,b** as the dienes with **7** as the dienophile, it is most likely that only part of **14a** or **14b** was produced by this manner while another good part was produced by a tandem Diels–Alder reaction–Cope rearrangement sequence, that is, the cross cycloaddition reaction of **7** as the diene with **1a,b** as the dienophiles followed by Cope rearrangement of the intermediates **1a,b**. The regioselectivity and stereoselectivity of the two modes of cross cycloaddition reactions are the key to the result that the two sequences bring about identical final products, **14a** and **14b**. Finally, the reactions in eq 3 and 4 demonstrate a very good example of controlling the results of CDA reactions by temperature. At room temperature, we could obtain mainly one type of cycloadducts while at 130 °C we could obtain completely the other type of cycloadducts. Both types of cycloadducts are useful intermediates since they are functionalized with either an allylic[8] or a vinylic sulfonyl group.[11]

The CDA reactions of 1,3-cyclohexadiene **8** with **2a** and **1b** at 130 °C proceeded with similarly high regioselectivity to give the cycloadducts **17a** and **17b**, respectively (eq 5). Again, these are the products from the apparent cross cycloaddition of **1a,b** as the dienes with **8** as the dienophile.



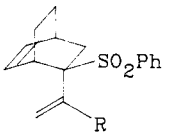
8

17a R=H
17b R=Me

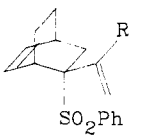
(5)

The structure of **17a** was unambiguously determined by ^{1}H NMR spectral data and a 2D-COSY experiment. Structural assignment of **17b** was determined by several comparison studies. The ^{1}H NMR spectra of **17a** and **17b** are almost identical except for the proton (**17a**) and the methyl group (**17b**) on the vinyl carbon β to the phenylsulfonyl group and thus suggest the two compounds have analogous skeletons. Besides, the ^{13}C NMR spectra revealed that the lines corresponding to the chemical shifts of C5 through C8 are almost superimposable (with a difference of no more than 0.2 ppm each pair) for these two compounds, and the chemical shift of C10 of **17a** (δ 30.82) is only slightly different from that of **17b** (δ 31.72). These small differences again suggest the structural similarity. Furthermore, we examined the ^{13}C NMR spectra of **14a** and **14b** and found that the chemical shift differences of the two ring-junction carbons are in good agreement with those for **17a** and **17b**, i.e., small differences for the ring-junction carbons farther from the sulfonyl group (δ 41.68 for C9 of **14a** and δ 44.17 for C9 of **14b** with a difference of 2.49 ppm; δ 30.82 for C10 of **17a** and δ 31.72 for C10 of **17b** with a difference of 0.90 ppm) and even smaller differences for the ones closer to the sulfonyl group (δ 34.97 for C8 of **14a** and δ 35.05 for C8 of **14b** with a difference of 0.09 ppm; δ 30.23 for C9 of **17a** and δ 30.60 for C9 of **17b** with a difference of 0.37 ppm). Finally, since **17b** was the only cycloadduct obtained in the CDA reaction and we do not expect an entirely different regioselectivity from that of the CDA reaction of **1b** with cyclopentadiene, it was therefore assigned to be the structure as shown in eq 5.

To examine if the Cope rearrangement reactions of the intermediates **18a** and **18b** were involved as intermediates



18a R=H
18b R=Me

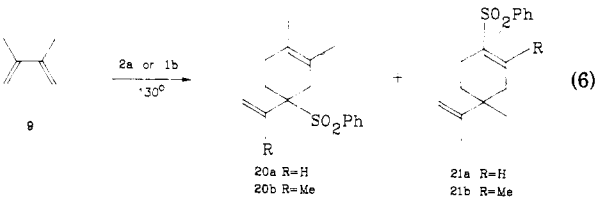


19a R=H
19b R=Me

in the CDA reactions producing **17a,b**, we studied the room temperature CDA reactions of **8** with the free dienes **1a** and **1b**. However, we were disappointed to see that all efforts toward the identification of the formation of **18** were in vain. For example, stirring **1a** with **8** at room temperature for 9 days gave results similar to those in eq 5 in lower yields. Stirring of **8** and **1b** at room temperature for 4 days gave **17b** in barely detectable amount and almost complete recovery of starting materials. On the other hand, as we carefully analyzed the minor products from the CDA reactions, we could observe some components (<1%) whose ^{1}H NMR spectral and mass spectral data fit well to the structures **18a,b**. But treatment of them at 130 °C did not bring about any rearrangement giving **17a** or **17b**. These minor products were thus tentatively assigned to be **19a** and **19b**.

The relatively low reactivity of **8** toward the dienes **1a,b** at low temperature as compared with cyclopentadiene suggests that cyclohexadiene is less reactive than cyclopentadiene both as a diene and as a dienophile. Since a Cope rearrangement of **18** would give the corresponding **17**, there is still a possibility that some **18a,b** did form during the reaction processes and rearranged to **17a,b** so rapidly that we were unable to detect the existence of these intermediates.

Treatment of 2,3-dimethyl-1,3-butadiene (**9**) with **2a** or **1b** at 130 °C led to the formation of two types of cycloadducts **20a,b** and **21a,b** in addition to the dimers of the starting materials (eq 6).



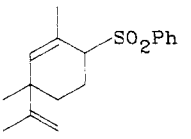
9

20a R=H
20b R=Me

21a R=H
21b R=Me

(6)

The structures of **20a,b** were easily assigned since there are no other possible regioisomers. The structure of **21a** was determined by its ^{1}H NMR spectrum and a 2D-COSY experiment while that of **21b** was unambiguously determined by a base-induced deconjugation process of the vinylic sulfone to the allylic sulfone **22**.[12] Thus, treatment



22

of **21b** with *t*-BuOK/*t*-BuOH at room temperature resulted in the formation of, in addition to the recovered

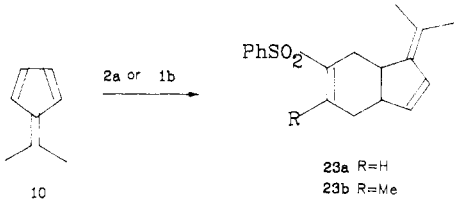
(10) Proteau, P. J.; Hopkins, P. B. *J. Org. Chem.* **1985**, *50*, 141.
(11) (a) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. (b) Posner, G. H.; Brunell, D. J. *J. Org. Chem.* **1973**, *38*, 2747. (c) Kinney, W. A.; Crouse, G. D.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4986. (d) Fuchs, P. L.; Braish, T. F. *Acc. Chem. Res.* **1986**, *86*, 903.

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

starting material, **22** as a mixture of diastereomers. The sharp singlet signals in the ^1H NMR spectra (δ 5.57 and 5.52) of the two diastereomers revealed that the vinyl protons do not couple with any methylene protons, confirming that they are the double-bond isomers of **21b**. Had **21b** been the other regioisomer, its deconjugated product would have shown a vinyl proton signal as a triplet or at least a broad singlet in ^1H NMR spectrum.

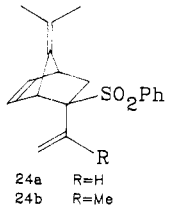
Compounds **20** and **21** were found not to be interconvertible when heated at 130 °C for a few days. This result is consistent with reports that the Cope rearrangement of 4-vinylcycloalkenes could be achieved only under extreme conditions.[13] The formation of **21a** and **21b** revealed again that the phenylsulfonyl group is the controlling element for regioselectivity in Diels–Alder reactions. Comparison of the ratios of **21a/20a** (ca. 1:3) and **21b/20b** (ca 1:4.5) shows that the competition between **9** and **1a,b** in the two modes of CDA reactions favors the more electron rich diene **9** to react as the diene moiety. The higher ratio of **21a/20a** than that of **21b/20b** indicates that the dienic character of **1a** is higher than that of **1b** in these reactions. This relative dienic character is different from that observed in the reactions of **1a,b** with cyclopentadiene where the more electron rich **1b** appears to be a better diene than **1a**. These results suggest that the pathway leading to the formation of **21a** and **21b** might possibly involve an inverse electron demand Diels–Alder reaction, while that leading to the formation of **14a,b** at room temperature involves a normal Diels–Alder reaction. It is known that **1a** reacts with both electron-rich and electron-deficient dienophiles.[2] The formation of mixtures of cycloadducts in eq 6 supports our early speculation that two modes of cross cycloaddition reactions might have both occurred in the CDA reactions of 1,3-cyclohexadiene.

The reactions of 6,6-dimethylfulvene (**10**) with **2a** and **1b** at 130 °C cleanly produced only one type of cycloadduct, **23a** and **23b**, respectively (eq 7). These are the cycloadducts from the apparent cross cycloaddition reactions of **1a,b** as the dienes with **10** as the dienophile.



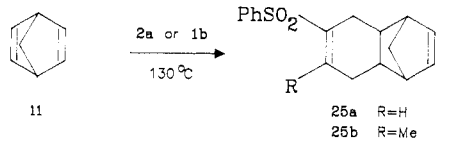
(7)

The structure of **23a** was easily determined by its ^1H NMR spectrum and a 2D-COSY experiment, whereas the structure of **23b** was determined indirectly by an approach similar to that used for the determination of structure **17b**, i.e., by comparison of its ^1H NMR and ^{13}C NMR spectra with those of **22a**. In an attempt to find out whether **23a** and **23b** were formed entirely from the primary CDA reaction of **1a,b** as the dienes and **10** as the dienophile or if the tandem Diels–Alder reaction–Cope rearrangments sequence by way of the intermediate bridged-bicyclic systems **24a,b** was involved, we performed the room temperature CDA reactions of **10** with **1a** and **1b**. It was found that, after a few days of reaction, the main products were still **23a** and **23b**. Our results are comparable with those of a report on the chemoselective CDA reactions of substituted fulvenes with cyclopentadiene where the C2–C3 double bond of the fulvenes reacted as the dienophile.[1c] As also was discussed by Houk,[1c] the inability to detect



the formation of the intermediates is insufficient to exclude the possibility that the final products were partially formed from a tandem Diels–Alder reaction–Cope rearrangement sequence.

The CDA reactions of norbornadiene (**11**) and **2a** or **1b** proceeded smoothly and chemoselectively to give only one type of products **25a,b** in good yields (eq 8). Efforts to



(8)

find products from the other mode of cycloaddition by lowering reaction temperature proved futile because under all conditions only the products **25a,b** and/or the recovered starting materials along with the dimers were obtainable.

Conclusion

2-Sulfonylated 1,3-dienes, either in the free dienic form as **1a,b** or in the sulfolene-protected form as **2a,b**, undergo cross Diels–Alder reactions with a variety of electron-rich dienes successfully to give one major product in each reaction except for the reactions of 2,3-dimethyl-1,3-butadiene. Some clues of the reaction mechanism could be drawn by examining the CDA reactions of **1a,b** with cyclopentadiene. The cycloadducts **14a,b** formed exclusively in the high-temperature CDA reactions are believed to be produced partially from one mode of cycloaddition directly giving **14a,b** and partially from the tandem Diels–Alder reaction–Cope rearrangement sequence of the other mode of cycloaddition involving **15a,b** as intermediates. The sulfonyl group is essential to the success of these CDA reaction. On the one hand, the electron-withdrawing nature of the sulfonyl group significantly differentiates the dienophilicity of the two double bonds of compounds **1a,b** so that only the double bond directly attached to the sulfonyl group is reactive as a dienophile. On the other hand, the sulfonyl group exhibits a powerful directing effect on the regioselectivity when **1a** and **1b** react as the dienes. Putting the two factors together excludes the possibility of the formation of the cycloadducts of type III and IV as described in eq 1 (X = phenylsulfonyl). The high "exo" stereoselectivity displayed by the phenylsulfonyl group of **1a,b** when reacting as dienophiles further permits the proper turn-out of the geometry of the intermediate (type II) for subsequent Cope rearrangement leading to the identical cycloadducts as produced from the CDA reactions of **1a,b** reacting as the dienes (type I). While mechanistic details are uncertain in several other cases owing to the lack of evidence for the existence of the intermediates, the facile Cope rearrangement from type II products to type I products is still possible so that only type I products were obtained at moderately elevated temperature. The nature of the counterpart dienes in the CDA reactons is also very important so that the very electron-rich dienes obviously react with 1 chemoselectivity to give the type II products as shown in eq 1. It is noticeable that, as compared with **1a**, the extra methyl group on **1b** had no effect on the regioselectivity. The CDA

(13) (a) Doering, W. von E.; Brenner, D. M. *Tetrahedron Lett.* **1976**, 899. (b) Baldwin, J. E.; Andrews, G. D.; Parker, D. W. *J. Org. Chem.* **1987**, *52*, 676.

Table I. Cross Diels–Alder Reactions of Sulfonylated 1,3-Dienes

reactants (molar ratio)	solvent	temp, °C	time	products and yields, %
2a + **6** (1:4)	toluene	130	16 h	**12a** (13%) + **13a** (82%)
1b + **6** (1:4)	toluene	130	24 h	**12b** (9%) + **13b** (76%)
2a + **7** (1:6)	toluene	130	29 h	**14a** (90%)
1b + **7** (1:20)	toluene	130	24 h	**14b** (89%)
1a + **7** (1:100)	toluene	25	24 h	**14a** (16%) + **15a** (55%) + dimers of **1a** (24%)
1b + **7** (1:100)	toluene	25	42 h	**14b** (29%) + **15b** (58%)
2a + **8** (1:55)	8	130	24 h	**17a** (75%) + **19a** (<1%)
1b + **8** (1:30)	toluene	130	4 days	**17b** (44%) + **19b** (<1%)
1a + **8** (1:70)	8	25	9 days	**17a** (28%) + **19a** (<1%) + dimers of **1a** (67%)
1b + **8** (1:20)	toluene	25	4 days	**1b** (85%) + **17b** (3%)
2a + **9** (1:6)	toluene	130	18 h	**20a** (40%) + **21a** (13%) + dimers of **1a** (47%)
1b + **9** (1:50)	toluene	130	6 days	**20b** (68%) + **21b** (15%)
2a + **10** (1:10)	toluene	130	48 h	**23a** (88%)
1b + **10** (1:10)	toluene	130	18 h	**23b** (90%)
1a + **10** (1:20)	toluene	25	48 h	**23a** (63%) + **24a** (<3%)
1b + **10** (1:10)	toluene	25	24 h	**1b** (53%) + **23b** (36%) + **24b** (<1%)
2a + **11** (1:50)	toluene	130	3 days	**25a** (82%)
1b + **11** (1:40)	**11**	130	24 h	**25b** (84%)
1a + **11** (1:100)	**11**	25	6 days	**25a** (57%) + dimers of **1a** (12%)
1b + **11** (1:80)	**11**	25	3 days	**1b** (75%) + **25b** (5%)

reaction products are usually obtained in high yields and easily separable from the much more polar dimers of **1** and much less polar dimers of the counterpart dienes by column chromatography. Since these cycloadducts, containing either an allylic or vinylic sulfone functionality, are versatile intermediates, the CDA reactions of **1** should find useful applications in organic synthesis.

Experimental Section

General Methods. NMR spectra were determined on a Bruker AW-80 or a Bruker MSL-200 spectrometer as solutions in $CDCl_3$. IR spectra were determined on a Perkin-Elmer 290 IR or a Perkin-Elmer 882 spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 5995B mass spectrometer. High-resolution mass spectra were recorded on a Jeol JMS-D-10 mass spectrometer. Elemental analyses were performed at the microanalysis laboratory of the National Taiwan University using a Perkin-Elmer 240C analyzer. All reactions were carried out under an atmosphere of dry nitrogen. All anhydrous solvents were freshly distilled before use.

2-(Phenylsulfonyl)-1,3-butadiene (1a). A very dilute solution of 3-(phenylsulfonyl)-3-sulfolene (**2a**) or a mixture of **1a** and 4-(phenylsulfonyl)-2-sulfolene (4:1) in toluene (5 mg/mL) containing pyridine (2 equiv) and hydroquinone (catalytic amount) was heated under reflux for 7 h. The cooled reaction solution was eluted through a column of neutral aluminum oxide with toluene to yield a dilute solution of diene **1a** in toluene free from its dimers. The yield of the diene **1a** was estimated to be 35% by weighing the dimers after concentrating an exactly measured amount of the dilute solution to dryness. The dilute solution of **1a** in toluene (4 mg/mL) remained almost unchanged after standing at −10 °C for 1 week. Compound **1a**: ^{1}H NMR (80 MHz) δ 5.30 (d, 1 H, J = 11 Hz), 5.63 (d, 1 H, J = 17 Hz), 5.99 (s, 1 H), 6.34 (dd, 1 H, J = 11, 17 Hz), 6.34 (s, 1 H), 7.30–8.00 (m, 5 H).

3-Methyl-4-(phenylsulfonyl)-3-sulfolene (2b) and 3-Methyl-4-(phenylsulfonyl)-2-sulfolene (4). To a mixture of 3,4-dibromo-3-methylsulfolene (**3**) (15 g, 51.4 mmol) and sodium phenylsulfinate (25.3 g, 154.1 mmol) in dry methanol (100 mL) was added a solution of sodium hydroxide (2.26 g, 56.5 mmol) in methanol (100 mL). The resulting mixture was stirred under reflux for 7 h, after which time methanol was evaporated under reduced pressure to give a white solid. The white solid was dissolved in water (80 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting white solid was purified with a silica gel column (1:1 hexane/EtOAc) to give a 2:1 mixture of **2b** and **4**, which could be used without further purification. Treatment of this mixture with triethylamine or DBN at room temperature or elevated temperatures all gave a ca. 1:1 mixture of **2b** and **4**. These two compounds could be separated by careful HPLC (LiChrosorb column, 1:1 hexane/EtOAc). Compound **2b**: white solid; mp 113–114 °C; IR (KBr) 3066, 2986, 2967, 2933, 1633, 1583, 1446, 1387, 1308, 1257, 1150, 1137, 1084, 1019, 808, 756, 727, 686 cm^{-1}; ^{1}H NMR (80 MHz) δ 2.31 (s, 3 H), 3.94 (s, 4 H), 7.38–7.98 (m, 5 H); MS m/z 272 (M^+), 208, 141 ($C_6H_5SO_2^+$), 131 ($M^+ - C_6H_5SO_2$), 129, 125, 86, 84, 77, 67 (100%). Anal. Calcd for $C_{11}H_{12}O_4S_2$: C, 48.51; H, 4.44. Found: C, 48.67; H, 4.22. Compound **4**: white solid; mp 126–127 °C; IR (KBr) 3058, 3021, 2972, 2950, 1631, 1583, 1449, 1409, 1317, 1307, 1293, 1238, 1157, 1147, 1102, 1084, 998, 928, 850, 804, 756, 729, 696, 629 cm^{-1}; ^{1}H NMR (200 MHz) δ 2.28 (s, 3 H), 3.41 (dd, 1 H, J = 8.4, 14.8 Hz), 3.51 (dd, 1 H, J = 4.3, 14.8 Hz), 4.49 (dd, 1 H, J = 4.3, 8.4 Hz), 6.48 (s, 1 H), 7.51–7.88 (m, 5 H); MS m/z 272 (M^+), 208, 141, 129, 125 (100%), 86, 84, 83, 78, 77. Anal. Calcd for $C_{11}H_{12}O_4S_2$: C, 48.51; H, 4.44. Found: C, 48.38; H, 4.40.

2-Methyl-3-(phenylsulfonyl)-1,3-butadiene (1b). A solution of the mixture of **2b** and **4** (10.68 g, 39.3 mmol) and pyridine (5 mL) in toluene (250 mL) was heated under reflux for 51 h. After removal of toluene under reduced pressure, the black oily residue was eluted through a silica gel column (5:1 hexane/EtOAc) to give the pure diene **1b** in 86% yield: colorless oil; IR (neat) 3066, 2979, 2954, 2924, 1617, 1585, 1447, 1385, 1305, 1160, 1125, 1080, 1024, 999, 952, 917, 833, 741, 688 cm^{-1}; ^{1}H NMR (80 MHz) δ 1.85 (s, 3 H), 5.11 (s, 1 H), 5.30 (s, 1 H), 5.89 (s, 1 H), 6.42 (s, 1 H), 7.34–7.95 (m, 5 H); MS m/z 208 (M^+), 144, 143, 129, 125, 86, 84, 78, 77, 67, 65, 51, 49 (100%).

Dimerization of 2-Methyl-3-(phenylsulfonyl)-1,3-butadiene (1b). A solution of **1b** in toluene (50 mg/mL) was heated under reflux for 3 days. After removal of the excess solvent under reduced pressure, the crude product mixture was purified by HPLC (LiChrosorb column, 1:1 hexane/EtOAc) to give **1b** in 33% yield, along with dimers **5a** and **5b** in 4% and 53%, respectively. Compound **5a**: colorless liquid; IR (neat) 3063, 2930, 1641, 1585, 1446, 1381, 1302, 1147, 1087, 1023, 999, 963, 850, 755, 723, 689 cm^{-1}; ^{1}H NMR (80 MHz) δ 1.14 (s, 3 H), 1.47–2.95 (m, 6 H), 2.01 (s, 3 H), 5.70 (s, 1 H), 6.15 (s, 1 H), 7.24–7.95 (m, 10 H); MS m/z 416 (M^+), 275, 274, 149, 143, 141, 133 (100%), 125, 117, 115, 105, 91, 77. Calcd for $C_{22}H_{24}O_4S_2$: 416.1116. Found: m/z 416.1143. Compound **5b**: white solid; mp 163–164 °C; IR (KBr) 3096, 3068, 2954, 2919, 1640, 1584, 1445, 1302, 1148, 1086, 1072, 1024, 997, 909, 865, 765, 721, 694 cm^{-1}; ^{1}H NMR (80 MHz) δ 1.67 (s, 3 H), 1.86–3.15 (m, 6 H), 2.11 (s, 3 H), 4.56 (s, 1 H), 5.11 (s, 1 H), 7.30–7.91 (m, 10 H); MS m/z 416 (M^+), 275 ($M^+ - C_6H_5SO_2$), 274, 273, 149, 143, 141, 134, 133 (100%), 132, 125, 119, 117, 105, 93, 91, 77. Anal. Calcd for $C_{22}H_{24}O_4S_2$: C, 63.43; H, 5.81. Found: C, 63.50; H, 5.83.

General Procedure of Cross Diels–Alder Reactions. A sealed tube containing suitable amounts of dienes and solvent as shown in Table I along with a catalytic amount of hydroquinone under nitrogen was heated at 130 °C for a certain length of time. After the removal of the excess of solvent, saturated brine was added and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layers were dried ($MgSO_4$) and eluted through a silica gel column (5:1 hexane/EtOAc) to give the products. Analytical samples were obtained by HPLC pu-

rification (LiChrosorb column, 5:1 hexane/EtOAc). The room temperature cross Diels–Alder reactions were carried out similarly by stirring the reaction mixtures in round-bottomed flasks under nitrogen and were worked up as described above.

3-Methoxy-4-(phenylsulfonyl)-4-vinylcyclohexanone (12a): white solid; ^{1}H NMR (80 MHz) δ 2.18–2.90 (m, 6 H), 3.26 (s, 3 H), 4.29 (br s, 1 H), 5.35–6.10 (m, 3 H), 7.30–7.92 (m, 5 H).

4-Isopropenyl-3-methoxy-4-(phenylsulfonyl)cyclohexanone (12b). Two diastereomeric components were obtained. Each was isolated as a colorless liquid. ^{1}H NMR (80 MHz) of the major component: δ 2.04 (s, 3 H), 2.16–2.90 (m, 6 H), 3.33 (s, 3 H), 4.54 (br s, 1 H), 5.26 (s, 1 H), 5.49 (s, 1 H), 7.40–7.92 (m, 5 H). ^{1}H NMR (200 MHz) of the minor component: δ 1.85 (s, 3 H), 2.13–2.50 (m, 3 H), 2.68 (dd, 1 H, J = 7.6, 15 Hz), 2.77–2.93 (m, 1 H), 3.12 (dd, 1 H, J = 3.5, 15 Hz), 3.27 (s, 3 H), 4.32 (dd, 1 H, J = 3.5, 7.6 Hz), 4.90 (s, 1 H), 5.08 (s, 1 H), 7.38–7.88 (m, 5 H).

4-(Phenylsulfonyl)-4-vinyl-2-cyclohexenone (13a): white solid; mp 96–97 °C; IR (KBr) 3062, 2963, 1689, 1681, 1585, 1447, 1379, 1299, 1149, 1085, 984, 975, 941, 874, 794, 765, 726, 692 cm^{-1}; ^{1}H NMR (80 MHz) δ 2.00–2.86 (m, 4 H), 5.18 (d, 1 H, J = 16.8 Hz), 5.50 (d, 1 H, J = 11 Hz), 6.06 (dd, 1 H, J = 11, 16.8 Hz), 6.21 (d, 1 H, J = 10.4 Hz), 6.86 (d, 1 H, J = 10.4 Hz), 7.40–7.98 (m, 5 H); MS m/z 262 (M$^+$), 141 ($C_6H_5SO_2^+$), 121 (M$^+$ – $C_6H_5SO_2$, 100%), 120, 119, 103, 93, 91, 79, 77. Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38. Found: C, 64.20; H, 5.39.

4-Isopropenyl-4-(phenylsulfonyl)-2-cyclohexenone (13b): white solid; mp 111–112 °C; IR (KBr) 3068, 2968, 2932, 1689, 1674, 1636, 1620, 1586, 1446, 1381, 1306, 1217, 1145, 1084, 999, 916, 867, 825, 722, 690 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.94 (s, 3 H), 2.18–2.57 (m, 4 H), 4.89 (s, 1 H), 5.28 (s, 1 H), 6.06 (d, 1 H, J = 10.4 Hz), 7.11 (d, 1 H, J = 10.4 Hz), 7.41–7.87 (m, 5 H); MS m/z 276 (M$^+$), 135 (M$^+$ – $C_6H_5SO_2$, 100%), 134, 117, 107, 105, 93, 91, 79, 77. Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84. Found: C, 65.14; H, 5.94.

4,7-Dihydro-6-(phenylsulfonyl)indene (14a): colorless liquid; IR (neat) 3055, 2928, 2845, 1634, 1586, 1445, 1304, 1151, 1092, 998, 857, 754, 721, 689 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.58–2.52 (m, 7 H), 2.84 (br s, 1 H), 5.38–5.56 (m, 2 H), 7.04–7.16 (m, 1 H), 7.38–7.87 (m, 5 H); ^{13}C NMR (200 MHz) δ 26.63 (CH_2), 28.29 (CH_2), 34.97 (CH), 39.13 (CH_2), 41.68 (CH), 127.69 (CH), 128.79 (CH), 129.89 (CH), 132.89 (CH), 134.36 (CH), 139.03 (C), 139.34 (CH), 140.14 (C); MS m/z 260 (M$^+$), 195, 143, 125, 119 (M$^+$ – $C_6H_5SO_2$), 118, 117, 77, 66 (100%). Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19. Found: C, 69.26; H, 6.32.

4,7-Dihydro-5-methyl-6-(phenylsulfonyl)indene (14b): colorless liquid; IR (neat) 3051, 2921, 2848, 1625, 1586, 1445, 1299, 1147, 1090, 1023, 999, 884, 788, 756, 724 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.51–2.59 (m, 7 H), 2.21 (s, 3 H), 2.89 (br s, 1 H), 5.25–5.38 (m, 1 H), 5.38–5.56 (m, 1 H), 7.30–7.86 (m, 5 H); ^{13}C NMR (200 MHz) δ 21.32 (CH_3), 30.90 (CH_2), 35.06 (CH), 38.77 (CH_2), 39.42 (CH_2), 44.17 (CH), 126.92 (CH), 128.78 (CH), 130.79 (CH), 132.53 (CH), 132.62 (CH), 132.80 (C), 141.66 (C), 151.91 (C); MS m/z 274 (M$^+$), 209, 143, 133 (M$^+$ – $C_6H_5SO_2$, 100%), 132, 125, 117, 91, 77. Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61. Found: C, 70.07; H, 6.62.

5-*exo*-(Phenylsulfonyl)-5-*endo*-vinylbicyclo[2.2.1]-2-heptene (15a): colorless liquid; IR (neat) 3064, 2985, 2952, 2900, 1636, 1586, 1445, 1299, 1143, 1083, 998, 921, 757, 716, 690 cm^{-1}; ^{1}H NMR (80 MHz) δ 1.35–1.68 (m, 2 H), 2.43–2.72 (m, 2 H), 3.01 (br s, 1 H), 3.43 (br s, 1 H), 4.72 (d, 1 H, J = 17.6 Hz), 5.11 (d, 1 H, J = 11 Hz), 5.74 (dd, 1 H, J = 17.6, 9.6 Hz), 5.86–6.02 (m, 1 H), 6.12–6.28 (m, 1 H), 7.30–7.95 (m, 5 H); MS m/z 260 (M$^+$), 196 (M$^+$ – SO_2), 195, 143, 120, 119 (M$^+$ – $C_6H_5SO_2$, 100%), 91, 77. Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19. Found: C, 69.14; H, 6.16.

5-*endo*-Isopropenyl-5-*exo*-(phenylsulfonyl)bicyclo[2.2.1]-2-heptene (15b): white solid; mp 129.5–130.5 °C, IR (KBr) 3081, 3003, 2978, 2961, 1631, 1580, 1445, 1376, 1335, 1286, 1136, 1125, 1083, 1041, 986, 909, 760, 717, 687 cm^{-1}; ^{1}H NMR (80 MHz) δ 1.58 (s, 3 H), 1.17–1.96 (m, 2 H), 2.49–2.83 (m, 2 H), 3.00 (br s, 1 H), 3.64 (br s, 1 H), 4.49 (br s, 1 H), 4.90 (br s, 1 H), 6.01 (br s, 1 H), 6.15–6.37 (m, 1 H), 7.24–7.95 (m, 5 H); MS m/z 274 (M$^+$), 209, 143, 133 (M$^+$ – $C_6H_5SO_2$, 100%), 105, 91, 77. Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61. Found: C, 70.06; H, 6.67.

1,4,7,8,9,10-Hexahydro-2-(phenylsulfonyl)naphthalene (17a): white solid; mp 54–55 °C; IR (KBr) 3064, 3018, 2925, 2842, 1657, 1647, 1586, 1445, 1304, 1147, 1092, 1021, 999, 962, 759, 722, 690 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.27–1.56 (m, 2 H), 1.82–2.59 (m, 8 H), 5.54 (s, 2 H), 6.90–7.05 (m, 1 H), 7.40–7.89 (m, 5 H); ^{13}C NMR (200 MHz) δ 23.90 (CH_2), 24.43 (CH_2), 26.36 (CH_2), 30.23 (CH), 30.33 (CH_2), 30.82 (CH), 126.81 (CH), 127.72 (CH), 128.82 (CH), 130.44 (CH), 132.87 (CH), 135.95 (CH), 138.37 (C), 139.25 (C); MS m/z 274 (M$^+$), 232, 195, 143, 133 (M$^+$ – $C_6H_5SO_2$), 125, 117, 91, 80 (100%), 79, 77. Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61. Found: C, 70.05; H, 6.55.

1,4,7,8,9,10-Hexahydro-3-methyl-2-(phenylsulfonyl)naphthalene (17b): white solid; mp 96–97 °C; IR (KBr) 3032, 2919, 2902, 1640, 1442, 1284, 1203, 1139, 1090, 1000, 758, 740, 725, 711, 690 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.30–1.50 (m, 2 H), 2.04 (s, 3 H), 1.77–2.54 (m, 8 H), 5.51 (s, 2 H), 7.30–7.88 (m, 5 H); ^{13}C NMR (200 MHz) δ 20.62 (CH_3), 23.86 (CH_2), 24.41 (CH_2), 29.87 (CH_2), 30.60 (CH), 31.72 (CH), 39.51 (CH_2), 126.80 (CH), 126.90 (CH), 128.80 (CH), 130.40 (CH), 131.75 (C), 132.62 (CH), 141.91 (C), 145.85 (C); MS m/z 288 (M$^+$), 210, 209, 147 (100%), 146, 145, 143, 131, 125, 105, 91, 80, 79, 77. Anal. Calcd for $C_{17}H_{20}O_2S$: C, 70.80; H, 7.00. Found: C, 70.80; H, 7.32.

5-*endo*-(Phenylsulfonyl)-5-*exo*-vinylbicyclo[2.2.2]-2-octene (19a): colorless liquid; IR (neat) 3050, 2941, 2876, 1636, 1446, 1370, 1301, 1140, 1081, 1025, 1000, 924, 750, 714, 690 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.13–1.40 (m, 2 H), 1.70–1.73 (m, 2 H), 2.46–2.77 (m, 3 H), 3.03 (br s, 1 H), 4.79 (d, 1 H, J = 17.4 Hz), 5.08 (d, 1 H, J = 10.7 Hz), 5.54 (dd, 1 H, J = 10.7, 17.4 Hz), 6.03–6.22 (m, 2 H), 7.37–7.88 (m, 5 H); MS m/z 274 (M$^+$), 245, 232, 195, 143, 133, 125, 105 (100%), 104, 91, 80, 79, 77.

5-*exo*-Isopropenyl-5-*endo*-(phenylsulfonyl)bicyclo[2.2.2]-2-octene (19b): colorless liquid; ^{1}H NMR (200 MHz) δ 1.13–1.31 (m, 2 H), 1.5 (s, 3 H), 1.73–1.79 (m, 2 H), 2.41–2.68 (m, 3 H), 3.39 (br s, 1 H), 4.58 (br s, 1 H), 4.85 (s, 1 H), 6.09–6.19 (m, 2 H), 7.32–7.74 (m, 5 H).

1,2-Dimethyl-4-(phenylsulfonyl)-4-vinylcyclohexene (20a): colorless liquid; IR (neat) 3064, 2915, 1636, 1586, 1445, 1300, 1234, 1150, 1082, 999, 926, 835, 759, 718, 691 cm^{-1}; ^{1}H NMR (80 MHz) δ 1.74–2.46 (m, 5 H), 1.54 (s, 3 H), 1.60 (s, 3 H), 2.70 (d, 1 H, J = 18 Hz), 4.97 (d, 1 H, J = 17 Hz), 5.31 (d, 1 H, J = 10 Hz), 5.75 (dd, 1 H, J = 10, 17 Hz), 7.33–7.98 (m, 5 H); MS m/z 276 (M$^+$), 165, 143, 141, 135 (M$^+$ – $C_6H_5SO_2$), 134 (100%), 119, 107, 106, 105, 93, 91, 79, 77. Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29. Found: C, 69.22; H, 7.52.

4-Isopropenyl-1,2-dimethyl-4-(phenylsulfonyl)cyclohexene (20b): white solid; mp 114–115 °C; IR (KBr) 3096, 3070, 2958, 2896, 1634, 1586, 1447, 1375, 1287, 1138, 1076, 1025, 999, 929, 916, 818, 766, 726, 693 cm^{-1}; ^{1}H NMR (80 MHz) δ 1.48 (s, 3 H), 1.55 (s, 3 H), 1.75 (s, 3 H), 1.46–2.50 (m, 5 H), 2.71 (d, 1 H, J = 17 Hz), 4.67 (s, 1 H), 5.14 (s, 1 H), 7.34–7.88 (m, 5 H); MS m/z 290 (M$^+$), 149, 148, 134, 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, 70.54; H, 7.83.

4-Isopropenyl-4-methyl-1-(phenylsulfonyl)cyclohexene (21a): colorless liquid; IR (neat) 3088, 3066, 2950, 1647, 1637, 1587, 1446, 1374, 1306, 1154, 1088, 894, 755, 726, 690 cm^{-1}; ^{1}H NMR (80 MHz) δ 0.95 (s, 3 H), 1.67 (s, 3 H), 1.20–2.68 (m, 6 H), 4.58 (s, 1 H), 4.71 (s, 1 H), 7.02 (br s, 1 H), 7.3–8.0 (m, 5 H); MS m/z 276 (M$^+$), 233, 220, 219, 195, 151, 143, 141, 135, 134 (100%), 125, 119, 107, 106, 105, 93, 91, 82, 77. Calcd for $C_{16}H_{20}O_2S$: 276.1184. Found: m/z 276.1185. Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29. Found: C, 69.33; H, 7.13.

4-Isopropenyl-2,4-dimethyl-1-(phenylsulfonyl)cyclohexene (21b): colorless liquid; IR (neat) 3086, 2929, 2874, 1640, 1587, 1447, 1379, 1304, 1203, 1149, 1088, 892, 757, 723, 690, 648 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.87 (s, 3 H), 1.57 (s, 3 H), 1.24–1.76 (m, 2 H), 2.02 (s, 3 H), 1.85–2.45 (m, 4 H), 4.35 (s, 1 H), 4.60 (s, 1 H), 7.31–7.82 (m, 5 H); ^{13}C NMR (200 MHz) δ 18.35 (CH_3), 20.38 (CH_3), 24.09 (CH_2), 25.14 (CH_3), 31.58 (CH_2), 37.00 (C), 45.35 (CH_2), 109.50 (CH_2), 126.30 (CH), 128.49 (CH), 131.79 (C), 132.39 (CH), 141.51 (C), 146.56 (C), 148.82 (C); MS m/z 290 (M$^+$), 234, 233, 149, 148 (100%), 143, 141, 133, 125, 121, 120, 119, 107, 105, 93, 91, 82, 79, 77. Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.32; H, 7.64. Found: C, 70.27; H, 7.91.

4,7-Dihydro-1-isopropylidene-6-(phenylsulfonyl)indene (23a): yellow oil; IR (neat) 3065, 2976, 2912, 2855, 1636, 1586, 1445, 1372, 1304, 1145, 1092, 1070, 999, 916, 749, 722, 689, 639 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.38 (s, 3 H), 1.41 (s, 3 H), 1.85–2.53 (m, 4 H), 2.73–2.90 (m, 1 H), 3.08 (br s, 1 H), 5.48 (d, 1 H, J =

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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