Reagent Design and Study of Allene as a Promising Class of Reagents (Synthons) for Cycloaddition. The Site Selective and Regioselective Diels-Alder Reactions of (Phenylsulfonyl)propadiene and Alkylation of the Adducts

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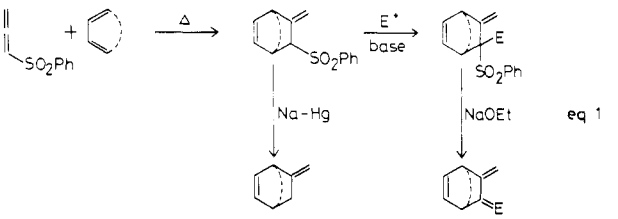
Received October 11, 1984

The cycloaddition reaction of title compound **1** with 1,3-dienes and troponoid compounds has been investigated. The reactions with dienes **2–8** proceeded in remarkable site selective and regioselective manners to give the Diels–Alder adducts **9–15** possessing an exocyclic allyl sulfone moiety. Allylation and desulfonylation of these adducts provide a convenient way of synthesis of exocyclic triene compounds **33–36**. In contrast, the reactions of **1** with tropone (**37**) and azaheptafulvenes (**40**) afforded only [8 + 2] adducts **38** and **41**, which underwent a series of hydrogen migrations to give finally the aromatized compounds **39** and **43**, respectively. The stereochemical assignments of these adducts were performed on the basis of the spectroscopic data.

The Diels–Alder reactions utilizing allene as a dienophile might provide a convenient way of synthesizing a variety of methylenecyclohexanes, a useful building block of terpenoid natural products.[1] However, the application of allene to the Diels–Alder reactions has been severely limited[2] because of its unreactive nature as a dienophile due to the lack of π-donor–acceptor complementarity between the diene and dienophile.[3] While the Diels–Alder reactions of some activated allenes have been reported,[4] cycloaddition reactions of these allenes have received less attention compared with the extensive studies on reactions of the corresponding vinylic dienophiles.

As a continuation of our systematic studies on the pericyclic reactions of organosulfur compounds,[5] we have investigated the cycloaddition reactions of (phenylsulfonyl)propadiene (**1**)[6] as a synthetic equivalent (synthon) of allene since the phenylsulfonyl group can be readily removed by various ways[7] after the cycloaddition reaction. Furthermore, the CNDO/2 calculations of (methylsulfonyl)propadiene indicate that the introduction of a sulfonyl group causes a remarkable lowering of the LUMO energy level compared with allene (ΔE = 3.07 eV) and that the largest LUMO coefficient locates on the central carbon (C-2) and the next on the C-1 position as shown in Figure 1. This suggests that **1** will be the more potent dienophile and undergo the Diels–Alder reaction with electron-rich dienes at the C-1,2 positions, due to the favorable LUMO(1)–HOMO(dienes) interactions, to produce the adducts possessing an allyl sulfone moiety, whose synthetic usefulness has been well documented.[7-9] This paper describes the highly site selective and regioselective cycloaddition reactions of **1** with various dienes as well as cyclic trienes. Moreover, the alkylation and desulfonylation of these adducts provides the highly functionalized methylenecyclohexanes (eq 1).



eq 1

Results and Discussion

Reactions of 1 with 1,3-Dienes. The previously reported Diels–Alder reactions of **1** have been restricted to those with symmetrical five-membered cyclic dienes such as cyclopentadiene[10] and furan.[11] In order to establish the utility of **1** as a dienophile, we have investigated the reactions of **1** with various 1,3-dienes. It was now found that **1** undergoes the Diels–Alder reaction with both cyclic and acyclic dienes (**2–8**) at 80–160 °C in a sealed tube (toluene) to give the adducts (**9–15**) in good to high yields (Table I). As Table I indicates, the cycloaddition takes place only at the C-1,2 double bond of **1**, affording the products containing the exocyclic allyl sulfone moiety. The reaction of **1** with cyclic dienes **3–5** gave adducts **10–12** as a mixture of endo and exo stereoisomers, each of which could be isolated in a pure form by a column chromatography except for **10**. The endo/exo ratio seemed to be influenced by the C-7 bridge substituents of these bicyclic adducts. Increasing steric bulk at this position caused a higher endo-selectivity, and thus the reaction of 6,6-diphenylfulvene (**2**) gave almost exclusively the endo adduct **9a** (entry 1). The generally available Lewis acid catalysts give no evidence of accelerating these reactions; some darkening and product destruction occur instead.

The structural determination of these bicyclic adducts **9–12** was deduced from their ^{1}H NMR spectra (Table IV, see supplementary material). Especially, the following characteristic spectral features were instrumental in their stereochemical assignments:[12] (1) The methine proton (He) of the exo isomers **9b–12b** appears at higher field (δ 3.50–4.07) compared with that of the endo isomers **9a–12a**

(1) Heathcock, C. H.; Graham, S. L.; Pirrung, M. C.; Plavec, F.; White, C. T. "The Total Synthesis of Natural Products"; ApSimon, J., Ed.,; John Wiley: New York, 1983; Vol. 5.
(2) Taylor, D. R. *Chem. Rev.* **1967**, *67*, 317.
(3) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976.
(4) (a) Kurtz, P.; Gold, H.; Disselnkotter, H. *Liebigs Ann. Chem.* **1959**, *624*, 1. (b) Büchi, G.; Carlson, J. A. *J. Am. Chem. Soc.* **1968**, *90*, 5336. (c) Kozikowski, A. P.; Floyd, W. C.; Kuniak, M. P. *Chem. Commun.* **1977**, 582. (d) Gommper, R.; Wolf, U. *Liebigs Ann. Chem.* **1979**, 1388.
(5) (a) Hayakawa, K.; Mibu, N.; Osawa, E.; Kanematsu, K. *J. Am. Chem. Soc.* **1982** *104*, 7136. (b) Hayakawa, K.; Kamikawaji, Y.; Kanematsu, K. *Tetrahedron Lett.* **1982**, *23*, 2171.
(6) Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5856, 5863, 5875.
(7) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.
(8) (a) Julia, M.; Righini-Tapie, A.; Verpeaux, J.-N. *Tetrahedron* **1983**, *39*, 3283. (b) Julia, M.; Verpeaux, J.-N. *Ibid.* **1983**, *39*, 3289.
(9) Hirama, M. *Tetrahedron Lett.* **1981**, *22*, 1905.
(10) Veniard, L.; Benaim, J.; Pourcelot, G.; Normant, M.-H. *C. R. Acad. Sci. Ser. C* **1968**, 1092.
(11) Guildford, A. J.; Turner, R. W. *Chem. Commun.* **1983**, 466.
(12) Maccagnani, G.; Montanari, F.; Tadei, F. *J. Chem. Soc. B* **1968**, 453.

0022-3263/85/1950-0512$01.50/0

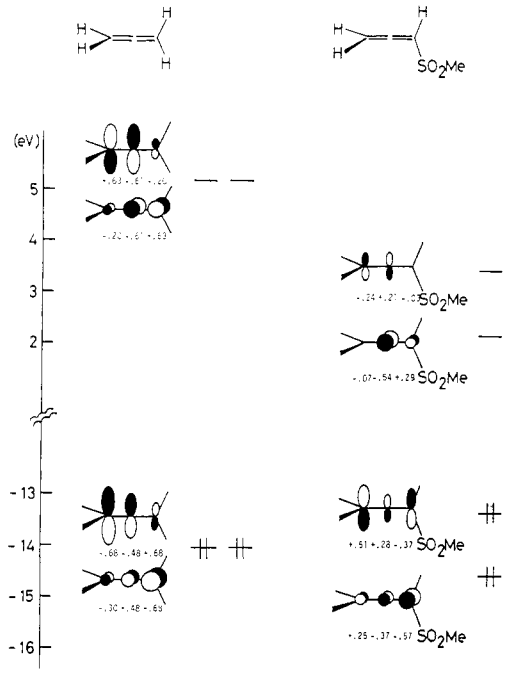
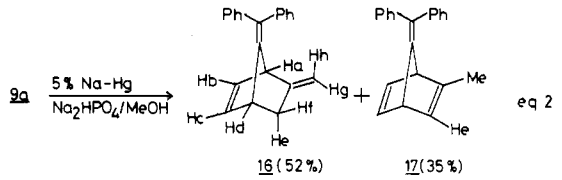


Figure 1. Frontier molecular orbitals of propadiene and (methylsulfonyl)propadiene calculated by the CNDO/2 method.

(δ 4.18–4.42) due to the shielding effect of the endocyclic double bond. (2) The coupling constant between two adjacent methine protons (*J*de) is generally larger in the endo isomers **9a–11a** (3.0–3.5 Hz) than that in the exo isomers **10a** and **11a** (2.0 Hz). (3) The *syn*-proton (Hh) at the C-7 bridge of *exo*-**11b** suffers a considerable downfield shift (δ 2.04) compared with that of *endo*-**11b** (δ 1.66) and the ethano bridge protons (Hh–j) of *exo*-**12b** appear as a much broader multiplet than those of *endo*-**12a** due to the anisotropic effect of the phenylsulfonyl group.

Reductive removal of the phenylsulfonyl group of these adducts can be readily achieved. For example, treatment of **9a** with 5% sodium amalgam in the presence of phosphate buffer[13] at the ambient temperature gave the desulfonylated products **16** and **17** in 52% and 35% yields, respectively (eq 2).



We also examined the Diels–Alder reactions of **1** with acyclic silyl enol ethers **6–8** (Table I). The reaction of **1** with 1-(trimethylsiloxy)buta-1,3-diene (**6**) at 160 °C (sealed tube, 8 h) followed by a rapid chromatography on a small amount of silica gel afforded the adduct **13a** in 72% yield. When the reaction mixture was treated with acetic acid prior to chromatography, the alcohol **13b** was obtained in 75% yield as a sole product. In the reaction of 2-(trimethylsiloxy)buta-1,3-diene (**7**), the acid-sensitive adduct **14** (79%) could be isolated as a primary product, whereas the similar reaction of 1-methoxy-3-(trimethylsiloxy)-buta-1,3-diene (**8**) gave only the phenolic product **15a** (82%) which might arise from the hydrolysis and subsequent aromatization of the initially formed adduct **15c**. The structure of **15a** was further confirmed by converting

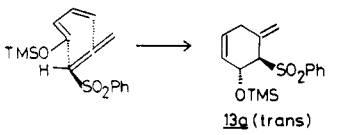


Figure 2.

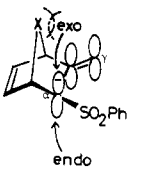
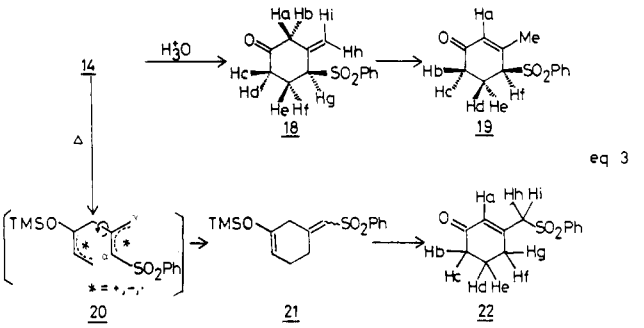


Figure 3.

to the acetate **15b**. When **14** was treated with acetic acid at room temperature, **18** was initially formed and then gradually isomerized to **19**. Interestingly, attempted distillation of **14** at 180 °C (Kugelrohr) led to the isolation of **22** in 71% yield (eq 3). The formation of **22** can be reasonably explained by assuming the thermal C-5,6 bond cleavage of **14** to give the diradical (or ionic) intermediate **20** and its recyclization at the γ-position to **21** as depicted in eq 3.



The spectroscopic data (Table IV) satisfied the assigned structures of all these products. Especially, the ^{1}H NMR spectra of **13** revealed a singlet of the Hf proton (**13a**, δ 3.78; **13b**, δ 3.93), i.e., neither vicinal coupling between Hf and He nor allylic coupling between Hf and Hg (or Hh) was appreciable, whereas the coupling between He and Hd (*J*ef) was shown to be 3.5 Hz. This is only compatible with trans stereochemistry at the C-5,6 positions as shown in **13**.

The above results reveal the remarkable site selectivity and regioselectivity in the Diels–Alder reactions of **1**. The reactions with **5** and **6** afforded only the ortho products (**12** and **13**), and those with **7** and **8** gave the para products (**14** and **15**). These regioselectivities can be reasonably understood by considering the preferential interaction between the LUMO of **1** and HOMO of dienes.[3] However, the stereoselectivities observed in these reactions were only moderate and strongly influenced by the steric factors. For example, the reaction of **1** with **6** proceeded favorably via an exo transition state to give only trans product **13a** (Figure 2). These results imply that the phenylsulfonyl group simply acts as an electron-withdrawing substituent[14] and displays no remarkable secondary orbital effects in controlling stereoselectivity of these reactions.[15]

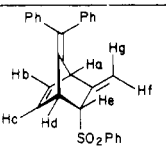
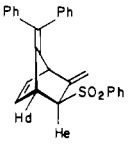
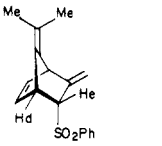
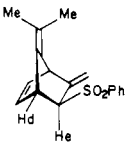
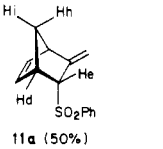
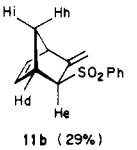
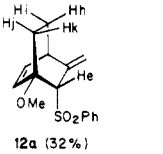
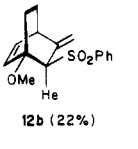
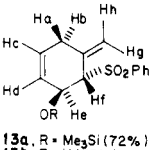
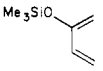
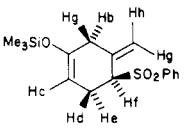
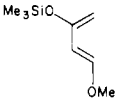
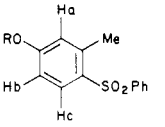
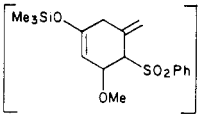
Alkylation of the Diels–Alder Adducts. In order to demonstrate the synthetic versatility of the Diels–Alder reaction of **1**, we have undertaken the alkylation of the adducts with allyl bromide as an electrophile. The α-

(13) Trost, B. M.; Arndt. H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

(14) Muller, C.; Schweig, A. *Tetrahedron* **1973**, *29*, 3973.

(15) Woodard, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.

Table I. Cycloaddition Reactions of (Phenylsulfonyl)propadiene (1) with 1,3-Dienes (2-8)

diene	reactn conditn	product (yield, %)	
 2	100 °C, 8 h	 9a (80%)	 9b (<3%)
 3	100 °C, 15 h	 10a (50%)	 10b (37%)
 4	80 °C, 8 h	 11a (50%)	 11b (29%)
 5	130 °C, 8 h	 12a (32%)	 12b (22%)
 6	160 °C, 8 h	 13a, R = Me_3Si (72%) 13b, R = H (75%) 13c, R = Ac (82%)	
 7	160 °C, 3 h	 14 (79%)	
 8	130 °C, 4 h	 15a, R = H (82%) 15b, R = Ac (94%)	 15c

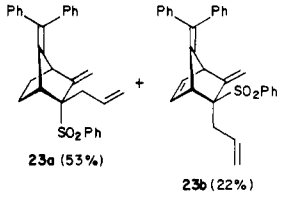
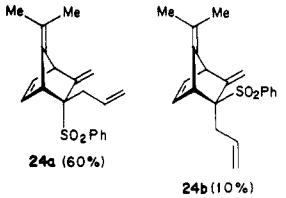
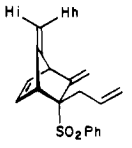
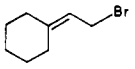
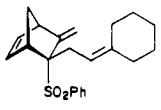
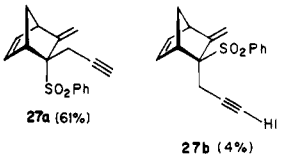
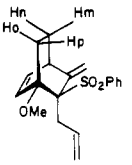
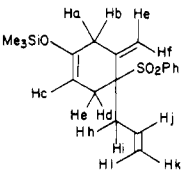
sulfonyl carbanion of the Diels–Alder adducts **9–14** generated by action of *n*-butyllithium (1.5 equiv) in tetrahydrofuran at −50 °C was treated with an excess of allyl bromide (5 equiv) to give the allylated products (**23–29** (Table II). As is generally known for allyl sulfones,[8,9] the alkylation of these adducts occurred exclusively at the α-carbon to the phenylsulfonyl group despite its sterically unfavorable position (Figure 3). However, the stereochemical outcome was remarkably affected by the structure of adducts and electrophiles employed. In the case of bicyclo[2.2.1]heptene systems, while exo alkylation is favored over endo alkylation, increasing steric bulk of the C-7 substituents causes an increased formation of endo alkylation products (e.g., **23b** and **24b**). Separate treatment of **11a** and **11b** (or a mixture of them) with *n*-BuLi followed by addition of allyl bromide afforded solely the same exo product **25a** in good yield regardless of stereochemical variation in the starting materials. In contrast, sterically less demanding propargylation of **11** gave a mixture of exo and endo products, **27a** and **27b**. These results indicate that the stereochemistry of alkylation is merely controlled by the steric factors, and this can be understood by assuming that the initially formed α-sulfonyl carbanions are almost planar by conjugation with the neighboring double bond (Figure 3). In the case of **12**, allylation of *endo*-**12b** gave a single product **28b** in 72% yield, while a similar treatment of *exo*-**12a** led to only the recovery of unchanged **12a**.[16]

The structural determination of these alkylation products was made on the basis of the ^1H NMR spectra (Table IV): the anisotropic effect of the phenylsulfonyl group was diagnostic for the sterochemical assignment as mentioned above. For instance, in the case of **27**, the Hg proton of exo product (*endo*-$PhSO_2$) **27a** appeared at δ 1.83 (bd, J = 7.5 Hz), while that of endo product (*exo*-$PhSO_2$) **27b** appeared at δ 2.60 (bd, J = 9.5 Hz). Furthermore, the olefinic protons of the endocyclic double bond (Hb and Hc) appear as two separate signals in the exo products **23a–27a** but as an inseparable 2H multiplet in the endo products **23b–27b**.

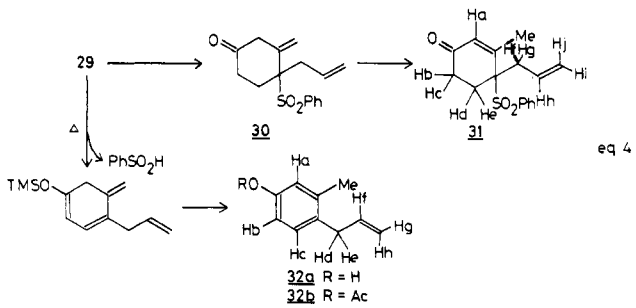
The structure of acid-labile **29** was supported by its conversion to the enone **31** via **30** on treating with acetic acid as seen in the case of **14**. In contrast to **14**, however,

(16) Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4976.

Table II. Alkylation Reactions of Adducts

adduct	electrophile	product (yield, %)
9a		 23a (53%) 23b (22%)
10a/10b		 24a (60%) 24b (10%)
11a/11b		 25a (97%)
11a/11b		 26a (74%)
11a/11b		 27a (61%) 27b (4%)
12b		 28b (72%)
14		 29 (65%)

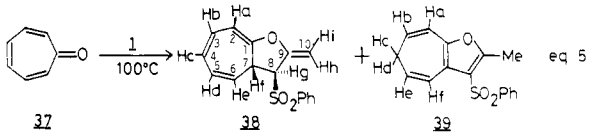
heating of **29** at 180 °C resulted in desulfonylation to give **32a** which was further converted to the acetate **32b** by the usual method (eq 4).



eq 4

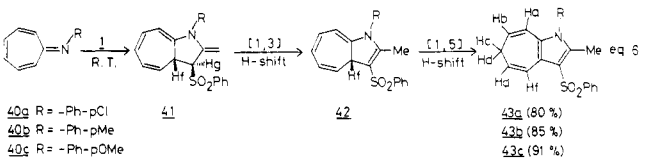
The above obtained alkylation products **23a–26a** underwent the elimination of sulfinic acid on treating with sodium ethoxide in ethanol to yield the exocyclic triene compounds **33–36** as an *E*/*Z* mixture (Table III). This indicates that the Diels–Alder reaction of **1** combined with the subsequent alkylation and $PhSO_2H$ elimination offers a convenient way of synthesis of the 5,6-dimethylenebicyclo[2.2.1]hept-2-ene derivatives which are of both theoretical and synthetical interest.[17,18]

Reaction of 1 with Tropone and Azaheptafulvenes. We next investigated the reaction of **1** with cyclic trienes such as tropone (**37**)[19–21] and azaheptafulvenes (**40**),[22] whose reactions with heterocumulenes were well studied. When a mixture of **1** and tropone (**37**) (1.5 equiv) was heated at 100 °C without solvent or in benzene (sealed tube), a sole [8 + 2] adduct (**38**) was obtained in 41% or 31% yield (eq 5). A similar reaction in acetonitrile afforded **38** (21%) as well as an aromatized product **39** (10%): ^{1}H NMR δ 2.69 (s, 3 H). A control experiment confirmed that the latter was formed from **38** under the reaction conditions presumably by the successive [1,3]- and [1,5]-sigmatropic hydrogen shifts.[23] A trace of acid present in acetonitrile seemed to facilitate these hydrogen shifts since much higher temperatures were needed for these isomerizations in acid-free solvents. The trans stereochemistry of Hf and Hg in **38** was assigned by the small coupling (Jfg = 3.0 Hz)[24] in the ^{1}H NMR spectra (Table IV).



eq 5

In contrast, the reaction of **1** and azaheptafulvenes (**40**) in acetonitrile took place much more readily at room temperature to produce the relatively unstable [8 + 2] adducts **41** which isomerized gradually at room temperature or more rapidly at the elevated temperatures via **42** to the stable crystalline products **43** in 80–90% yields (eq 6). The ^{1}H NMR spectra of **43** were similar to that of **39** except for the additional signals of the N-substituents. The intermediary formation of **41** and **42** was confirmed by monitoring the reaction with ^{1}H NMR spectroscopy, for example, **41a**, δ 3.31 (m, Hf) and 4.38 (ddd, Hg); **42a**, δ 2.36 (s, CH) and 3.30 (d, Hf).

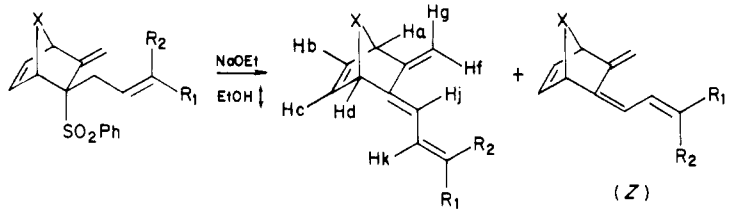


eq 6

The above results can be reasonably understood in terms of the concerted mechanism based on the FMO interaction. Since the HOMO of both tropone (**37**)[25] and azaheptafulvenes (**40**)[26] are known to possess the largest coefficient on the heteroatom and the next on the C-2 position, the exclusive formation of [8 + 2] adducts (**38** and **41**) in these reactions might be a result of the HOMO(triene)–LUMO(1) interaction. Moreover, this agrees with the

(17) Pinkerton, A. A.; Schwaezenbach, D. *J. Am. Chem. Soc.* **1981**, *103*, 2095.
(18) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328.
(19) Ciabattoni, L.; Anderson, H. W. *Tetrahedron Lett.* **1967**, 3377.
(20) Gommper, R.; Studeneer, A.; Elser, W. *Tetrahedron Lett.* **1968**, 1019.
(21) Truce, W. E.; Lin, C. I. M. *J. Am. Chem. Soc.* **1973**, *95*, 4426.
(22) (a) Iwasaki, T.; Kajigaeshi, S.; Kanemasa, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 229. (b) Sanechika, K.; Kajigaeshi, S.; Kanemasa, S. *Chem. Lett.* **1977**, 861. (c) Yamamoto, K.; Kajigaeshi, S.; Kanemasa, S. *Chem. Lett.* **1977**, 85, 91.
(23) Liu, C.-Y.; Mareda, J.; Houk, K. N. *J. Am. Chem. Soc.* **1983**, *105*, 6714.
(24) Ciabattoni, J.; Cabell, M. *Tetrahedron Lett.* **1968**, 2693.
(25) Mukherjee, D.; Watts, C. R.; Houk, K. N. *J. Org. Chem.* **1978**, *43*, 817.
(26) Kuroda, H.; Kumii, T. *Theor. Chim. Acta* **1967**, *7*, 220.

Table III. Desulfonylation Reactions of Alkylated Adducts



alkylated adduct	X	R_1		R_2	reactn time, h	product (yield, %)	E/Z ratio[a]
23a	C=C(Ph)$_2$	Hl		Hm	12	**33** (57%)	1.8:1
24a	C=C(Me)$_2$	Hl		Hm	5	**34** (68%)	1.8:1
25a	Hh-C-Hi	Hl		Hm	3	**35** (78%)	4.5:1
26a	Hh-C-Hi		-(CH$_2$)$_5$-		10	**36** (88%)	5.0:1

[a] The E/Z ratio was determined by ^{1}H NMR.

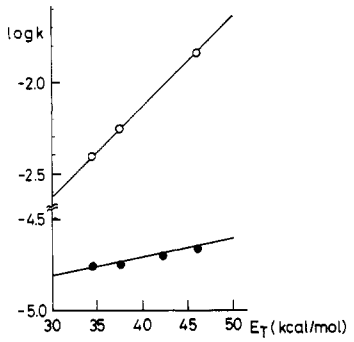
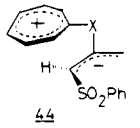


Figure 4. Plots of log k vs. E_T value for the reactions of 1 with tropone (**37**) (●) and 8-azaheptafulvene (**40b**) (○).

observed higher reactivity of **40** compared with **37** (see Figure 4) because the HOMO energy level of **40** is higher than that of **37**.[26]

On the other hand, considering the highly electrophilic nature of 1,[6,27] the stepwise formation of these [8 + 2] adducts via an ionic intermediate **44** is also conceivable.



44

Therefore, in order to investigate the solvent effects on these reactions, the reaction rates were measured in various solvents of different polarity and the results are summarized in Figure 4. While the reactions of tropone (**37**) show almost no solvent dependency, those of azaheptafluvene (**40b**) reveal the noticeable rate enhancement with increase of the solvent polarity. This indicates that the latter reaction proceeds via the more polar transition states rather than the former, or some involvement of zwitterionic intermediates may be also plausible.

Conclusion

The present results have demonstrated an interesting periselectivity in cycloaddition reactions of (phenylsulfonyl)propadiene (1), which is reasonably expected by the FMO considerations. While 1 undergoes the Diels–Alder ([4 + 2]) reactions with the electron-rich 1,3-dienes, the reaction with troponoid compounds (cyclic trienes) such as **37** and **40** affords exclusively [8 + 2] adducts. The reactions proceed in highly site selective and regioselective manners but the stereoselectivity seems to be governed mainly by the steric factors. These results are noteworthy since the corresponding cumulenes and heterocumulenes undergo preferentially [2 + 2] cycloadditions in rather nonselective manners.[28] Furthermore, facile alkylation and desulfonylation of these adducts indicates the versatility of 1 as an allene equivalent. Further development of the synthetic utility of these reactions is now in progress in our laboratory.

Experimental Section

The melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. The ^{1}H NMR spectra were taken with a JEOL PS-100 and Hitachi R-600 spectrometer with tetramethylsilane as an internal standard; chemical shifts are expressed in δ values. The ^{13}C NMR spectra were determined with a JEOL PS-100 and refer to solutions in deuteriochloroform concomitant standard, downfield chemical shifts being computed relative to tetramethylsilane. The IR spectra were taken with a JASCO IRA-1 infrared spectrometer. Mass spectra were determined with a JEOL-01SG double-focusing spectrometer operated at an ionization potential of 75 eV. The solid samples were ionizing by electron bombardment after sublimation directly into the electron beam at 150–200 °C. All crystalline products gave correct elemental analyses. The reaction rates were measured with a Iatroscan TH-10 TLC analyzer. Preparative thin-layer chromatography was performed by using E. M. Merck silica gel 60 PF-254, and column chromatography was done by using E. M. Merck Kieselgel 60 (70–200 mesh) as the stationary phase. Calculations were performed on the FACOM M-200 in the computer center of Kyushu University.

Materials. (Phenylsulfonyl)propadiene (1),[6] dimethylfulvene (3)[29] 1-(trimethylsiloxy)-1,3-butadiene (6),[30] 2-(trimethylsiloxy)-1,3-butadiene (7),[31] 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene (8)[32] and azaheptafulvenes (**40**)[33] were prepared according to the reported methods.

CNDO/2 Calculations of Propadiene and (Methylsulfonyl)propadiene. CNDO/2 calculations were carried out by using the following geometrical parameters: S—O, 1.434 Å; =C—S, 1.732 Å; C=C, 1.288 Å; =C—H, 1.023 Å; OSO, 109°; =C—H, 121.95°.[28,34] Torsion angle (C=CS—C) was treated at 90° and 108°, and the calculations indicated that the case of 90° had the lower total energy (90°, −2184.16 eV; 180°, −2183.65 eV). Therefore, FMO energies and coefficients of π(C) orbitals in the

(27) (a) Denmark, S. E.; Harmata, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 4974. (b) Denmark, S. E.; Harmata, M. A. *J. Org. Chem.* **1983**, *48*, 3369.

(28) Ghosez, L.; O'Donnell, M. J. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II.

(29) Hein, R. W.; Astle, M. J.; Schelton, J. R. *J. Org. Chem.* **1961**, *26*, 4874.

(30) Ishida, A.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1161.

(31) Jung, M. E.; McCombs, C. A. *Org. Synth.* **1977**, *58*, 163.

(32) Danishefsky, S.; Kitahara, T.; Schuda, P. *Org. Synth.* **1980**, *61*, 147.

(33) Sanetica, K.; Kajigawase, S.; Kanemasa, S. *Synthesis* **1977**, 202.

(34) Bullough, R. K.; Wheatley, P. J. *Acta Crystallogr.* **1957**, *10*, 233.

former case were depicted in Figure 1 and listed in Table VII (Supplementary Material).

General Procedure for Cycloaddition Reactions of 1 with Dienes. A solution of **1** and an appropriate diene (ca. 1.5 equiv) in toluene was heated in a sealed tube at given temperatures as listed in Table I. The reaction was monitored by TLC. When **1** completely disappeared, heating was stopped and the reaction mixture was evaporated in vacuo. The oily residue was chromatographed on a silica gel column with *n*-hexane–ethyl acetate as an eluant to give the adduct. ^{1}H NMR and IR data are listed in Table IV.

Cycloaddition Reaction of 1 with 1-(Trimethylsiloxy)-1,3-butadiene (6). A solution of **1** (91.5 mg, 0.508 mmol) and **6** (108.5 mg, 0.763 mmol) in toluene (0.5 mL) was heated in a sealed tube at 160 °C for 8 h. After cooling, the reaction mixture was evaporated in vacuo, dissolved in 2 mL of a AcOH–THF–H_2O (8:8:1) mixture, and stirred at room temperature for 30 min. After 20 mL of water was added, the product was extracted with ether (3 × 10 mL), washed with aqueous Na_2CO_3 solution and brine, dried over Na_2SO_4, and subjected to chromatography on silica gel with *n*-hexane–ethyl acetate (1:1) to give 95 mg (75%) of **13**.

Acetylation of 13b. A mixture of **13b** (100.5 mg, 0.401 mmol), 4-(dimethylamino)pyridine (59.3 mg, 0.485 mmol), and acetic anhydride (0.5 mL) in dichloromethane was stirred at room temperature for 1 h. The mixture was diluted by water (20 mL), extracted by ether (3 × 10 mL), washed with water (2 × 10 mL) and brine, dried over Na_2SO_4, and chromatographed on silica gel to give 96.2 mg (82%) of pure **13c**. Spectral data are summarized in Table IV.

Cycloaddition of 1 with 2-(Trimethylsiloxy)-1,3-butadiene (7). A solution of **1** (90.2 mg, 0.500 mmol) and **7** (110.2 mg, 0.775 mmol) in toluene (0.5 mL) was heated in a sealed tube at 160 °C for 8 h. After cooling, the reaction mixture was evaporated in vacuo and treated with AcOH–THF–H_2O (8:8:1) at room temperature for 30 min. The usual workup and chromatography on silica gel with *n*-hexane–ethyl acetate (3:2) gave 74.8 mg (60%) of **18** and 8.4 mg (6.7%) of **22** in the order of elution. ^{1}H NMR and IR spectral data are summarized in Table IV.

Thermal Rearrangement of 14. In Kugelrohr, **14** (106.3 mg, 0.330 mmol) was placed and heated at 180 °C (1 mmHg) for 2 h. The resulting mixture was chromatographed on silica gel with *n*-hexane–ethyl acetate (3:2) to give 58.9 mg (71%) of **22**. ^{1}H NMR and IR spectral data are summarized in Table IV.

Acetylation of 15a. A mixture of **15a** (146.9 mg, 0.632 mmol), (dimethylamino)pyridine (94.0 mg, 0.769 mmol), and acetic anhydride (1 mL) in dichloromethane (2 mL) was stirred at room temperature for 3 h. The usual workup and chromatography on silica gel using *n*-hexane–ethyl acetate (4:1) gave 152.7 mg (94%) of pure **15b**. ^{1}H NMR and IR spectral data are summarized in Table IV.

Reductive Desulfonylation of Adduct 9a. To a solution of **9a** (76.5 mg, 0.186 mmol) and anhydrous disodium hydrogen phosphate (120.8 mg, 0.85 mmol) in methanol (2 mL) was added pulverized 5% sodium amalgam (0.6 g). The reaction mixture was stirred for 4 h at room temperature and then poured on to water (10 mL). The product was extracted with ether (2 × 10 mL), washed with brine and water, dried over Na_2SO_4, and chromatographed on a silica gel column with *n*-hexane–ethyl acetate (5:1) to give a mixture of **16** and **17**. The mixture was further subjected to a preparative TLC (*n*-hexane, developed five times) to give 17.5 mg (35%) of **17** and 26.3 mg (52%) of **16** in the order of elution. ^{1}H NMR and IR data are summarized in Table IV.

General Procedure for Alkylation of Diels–Alder Adducts 9–14 with Allyl Bromide. To a stirred solution of adducts (1 equiv) in THF was added a hexane solution of *n*-butyllithium (1.5 equiv) at −50 °C. After stirring for 1 h, allyl bromide (5 equiv) was added at −50 °C and the reaction mixture was stirred at this temperature for an additional 1 h. After a mixture of AcOH–THF (1:1) was added, the reaction mixture was allowed to warm to room temperature. The product was extracted with ether, washed with aqueous Na_2CO_3 solution and brine, dried over Na_2SO_4, and chromatographed on silica gel with *n*-hexane–ethyl acetate to give alkylated products. The results are summarized in Table II and the spectral data of the product are listed in Table IV.

Thermolysis of 29. Into Kugelrohr was placed freshly prepared **29** (100.5 mg, 0.291 mmol) and the reaction was heated at 180 °C (1 mmHg) for 2 h. The resulting mixture was chromatographed on silica gel with *n*-hexane–ethyl acetate (4:1) to give 5.6 mg (13%) of **32a**. A solution of thus obtained **32a**, (dimethylamino)pyridine (7 mg, 0.0573 mol), and acetic anhydride (0.2 mL) in dichloromethane (0.5 mL) was stirred at room temperature for 5 h. The usual workup and chromatography on silica gel with *n*-hexane–ethyl acetate (5:1) gave 7.1 mg (79%) of **32b**. ^{1}H NMR and IR spectral data of **32a** and **32b** were summarized in Table IV.

Elimination Reaction of Alkylated Adducts 23a–26a. General Procedure. A solution of sodium ethoxide (10 equiv) and an appropriate adduct (1 equiv) in ethanol was heated under reflux for 3–10 h. After water was added, the products were extracted with pentane and washed with water. Careful evaporation of pentane and chromatography of the residue on silica gel gave product as a *E*/*Z* mixture. The results are summarized in Table III and ^{1}H NMR and IR spectral data are summarized in Table IV.

Cycloaddition Reactions of 1 with Tropone (37). A solution of **1** (95.2 mg, 0.528 mmol) and tropone (84.6 mg, 84.6 mmol) in acetonitrile was heated in a sealed tube at 100 °C for 16 h. After cooling, the reaction mixture was evaporated in vacuo. The residual oil was chromatographed on silica gel with *n*-hexane–ethyl acetate (7:3) to give **39** (15.1 mg, 10.0%), **38** (32.4 mg, 21.4%), and unreacted **1** (46.5 mg, 48.8%) in the order of elution.

The similar reaction (16 h) with benzene as a solvent gave **38** (30.8%) and **1** (63.1%). The reaction without solvent (8 h) gave **38** (41.1%) and **1** (36.8%). ^{1}H NMR and IR spectral data are summarized in Table IV.

Cycloaddition Reactions of 1 with 8-Aryl-8-azaheptafulvene (40). A solution of **1** (90.2 mg, 0.50 mmol) and **40a** (1.5 equiv) in acetonitrile was stirred at room temperature for 3.5 h. After evaporation of the solvent, chromatography on silica gel with *n*-hexane–ethyl acetate (7:3) and recrystallization from dichloromethane–ether gave pure **43a** (158 mg, 79.8%), mp 181–183 °C.

The similar reaction (5 h) of **1** with **40b** gave **43b** (84.6%), mp 193–194.5 °C, and the reaction (10 h) of **1** with **40c** gave **43c** (90.7%), mp 149–152 °C. The ^{1}H NMR and IR spectral data are summarized in Table IV.

Kinetics. Measurements of Rates of Reactions of (Phenylsulfonyl)propadiene (1) with Tropone (37) and 8-(*p*-Methylphenyl)-8-azaheptafulvene (40b). The kinetic run was carried out with a solution of **1** (0.2894 M) and **37** (0.8085 M) at 101 ± 1 °C or a solution of **1** (0.01287 M) and **40b** (0.01096 M) at 34 ± 0.1 °C in an appropriate solvent. The reaction rates were measured by following the disappearance of **1** with thin-layer chromatograph analyzer (Iatroscan TH-10 TLC Analyzer Iatron Laboratories Inc, Tokyo). The rate constants were calculated from the plots of log $[(a - x)/(b - x)]$ vs. time by the least-squares method, where a and b are the initial concentrations of **1** and **37** (or **40b**), and x is the consumed amount of **1** at time t. The kinetic data are listed in Table V and VI (supplementary materials) and depicted in Figure 4.

Acknowledgment. We thank Yasushi Okamoto for the helpful discussions in the MO calculations and Makoto Takewaki for the experimental assistance.

Supplementary Material Available: The spectral data of products (Table IV), the second-order rate constants for cycloaddition of **1** with **37** (Table V) and with **40b** (Table VI) in various solvents, and FMO coefficients of allene and (methylsulfonyl)propadiene calculated by CNDO/2 (Table VII) (12 pages). Ordering information is given on any current masthead.