synthetic pathways are noted in Scheme II.

Experimental Section

Olefin/Maleic Anhydride Reactions. Reactants and solvent were used as received. A magnetic stirring bar and a heterogeneous mixture consisting of 750 mg of olefin (Wiley Organics), 500 mg of maleic anhydride (Aldrich), and 50 mg of phenothiazine (Aldrich) in 3 mL of Decalin (J. T. Baker) were sealed under nitrogen in a heavy-walled tube. The mixture was brought to 200 ± 5 °C in a thermostated oil bath and held at this temperature overnight (16 h). After cooling, the homogeneous mixture was transferred to a distillation flask for removal of solvent and unreacted starting materials under reduced pressure. The crude product was distilled (bulb-to-bulb) under vacuum and obtained as a colorless oil.

In a similar manner, *cis*-5-decene was reacted with maleic anhydride for 6-, 12-, 24-, 48-, and 120-h periods, and the products were isolated as above.

Instrumental Setup. The ^{13}C NMR spectra were recorded at 90.55 MHz at ambient temperature on a Nicolet NT 360 WB spectrometer equipped with Nicolet 1280 computer. Instrumental conditions used: pulse angle, 60°; pulse delay, 5 s; sweep width, 20 000 Hz. Under these conditions, the olefin region should be quantitative. The T_1's for most of these olefin carbons are in the range of 2 s. The only long T_1's are the terminal carbons of the vinyl groups ($RCH{=}CH_2$). These carbons have not been used in the calculations.

Acknowledgment. We are gratefully indebted to E. Laletas for excellent experimental work and Dr. R. W. Harrell and Elizabeth A. Demgar for the ^{13}C NMR spectra given in Figure 1. Thanks are also due to Professor Stephen R. Wilson for ^{13}C NMR spectra of resolved diastereoisomers related to **3**, **4**, and **5**.[39] We also thank Professor J. A. Berson for his helpful comments on the paper.

Registry No. 1, 81949-64-6; **2**, 81949-63-5; **3t**, 104947-44-6; **3e**, 104947-45-7; **4t**, 104947-46-8; **4e**, 104947-47-9; **5t**, 104947-48-0; **5e**, 104947-49-1; **6t**, 104947-50-4; **6e**, 104947-51-5; **7t**, 104947-52-6; **7e**, 104947-53-7; **8t**, 104947-54-8; **8e**, 104947-55-9; **9t**, 104947-56-0; **9e**, 104947-57-1; **10t**, 104947-58-2; **10e**, 104947-59-3; **11t**, 104947-62-8; **11e**, 104947-63-9; **12t**, 104947-60-6; **12e**, 104947-61-7; **13t**, 104975-79-3; **13e**, 104975-80-6; **14t**, 104947-64-0; **14e**, 104947-65-1; **15t**, 104947-66-2; **15e**, 104947-67-3; maleic anhydride, 108-31-6; 1-decene, 872-05-9; (*E*)-2-decene, 20063-97-2; (*Z*)-2-decene, 20348-51-0; (*E*)-3-decene, 19150-21-1; (*Z*)-3-decene, 19398-86-8; (*E*)-4-decene, 19398-89-1; (*Z*)-4-decene, 19398-88-0; (*E*)-5-decene, 7433-56-9; (*Z*)-5-decene, 7433-78-5.

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Addition Reactions of (Phenylsulfonyl)propadiene with 1-Pyrrolidinyl Enamines of Cyclic Ketones: Syntheses and Reactions of 1,3-Dienes Possessing an Allyl Sulfone Moiety

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Received May 30, 1986

Addition reactions of (phenylsulfonyl)propadiene (**1**) with various 1-pyrrolidinyl enamines have been investigated. Allene **1** and enamines of cyclic ketones (**2**, **7–14**) readily underwent the Michael-type addition reactions at −50 °C to give the adducts **3**, **15–20**, and/or their isomers **4** and **21–26**, which apparently arose by base-catalyzed isomerization of the former. These adducts were conveniently converted into the corresponding 1,3-dienes possessing allyl sulfone moiety (**28**, **38–45**) through allyl acetates (**27**, **30–37**) by base-promoted (*n*-BuLi, −50 °C) 1,4 elimination of acetic acid to vinyl sulfones followed by deconjugation to allyl sulfones. The synthetic versatility of these dienes was revealed by the Diels–Alder reactions with dimethyl acetylenedicarboxylate (DMAD) and alkylation reactions via α-sulfonyl carbanions.

Recently we reported[1] that (phenylsulfonyl)-1,2-propadiene (**1**), a readily preparable and stable crystalline compound,[2-4] proved to be the useful synthetic equivalent of allene[5] as a dienophile in the Diels–Alder reaction due to its enhanced reactivity as well as the easy removal of phenylsulfonyl group from the adducts. Compound **1** might be also activated toward nucleophilic addition because of its markedly lowered LUMO energy level compared with allene.[1] While the reactions with heteronucleophiles have been well investigated,[6-13] much less attention has been paid to the carbon–carbon bond-forming reactions of **1** with the C nucleophiles.[14] Therefore, we

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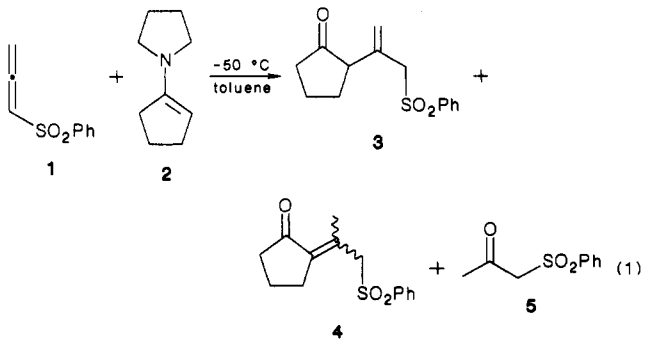
have explored the reactions of 1 and enamines of various cyclic ketones with the aim of raising its potential in organic synthesis. It was found that the reaction proceeded smoothly to give the Michael-type addition products, which were in turn conveniently converted into the corresponding 1,3-dienes consisting of a cycloalkene double bond and allyl sulfone moiety. The dual properties of these compounds as a 1,3-diene and allyl sulfone were revealed by the Diels–Alder reaction and the carbanion-mediated alkylation. Herein we describe the full details of our experimental results of these studies.

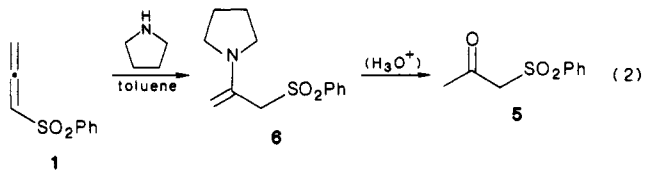
Results and Discussion

Reactions of Sulfonylallene 1 and Enamines of Cyclic Ketones. As compared with the extensively studied reactions of enamines with electron-deficient olefins and acetylenes,[15-17] reaction with allenic compounds has received less attention.[18,19] The [2+2] cycloaddition of 1 and aminoisobutenes was briefly reported, but no experimental details were described.[20] We have investigated the reaction of 1 with various 1-pyrrolidinyl enamines[21] under carefully controlled conditions. When 1 was treated with a slight excess of 1-(1-pyrrolidinyl)-cyclopentene (2) in dry toluene at −50 °C, it was consumed completely within 2 h. After removal of solvent, chromatography on silica gel gave the Michael-type adduct 3 (37%) and its isomer 4 (*E*:*Z* = 2:1) (46%) along with 1-(phenylsulfonyl)propan-2-one (5)[10] as a byproduct (7%) (eq 1). The reaction at ambient temperature (≃25 °C)



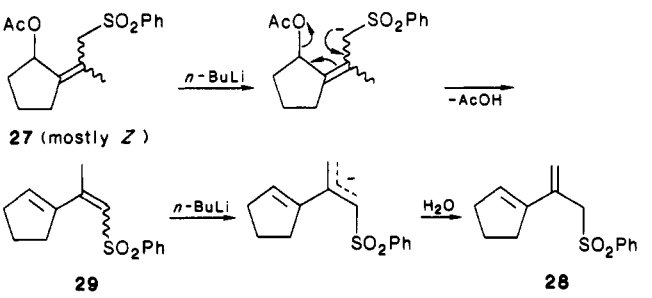
(1)

led to the formation of larger amount of 5 which was apparently formed by the nucleophilic addition to 1 of pyrrolidine contaminant in 2 via enamine 6. A control experiment showed that reaction of 1 and pyrrolidine under the similar reaction conditions resulted in a smooth formation of 5 in a quantitative yield (eq 2).



(2)

Scheme I

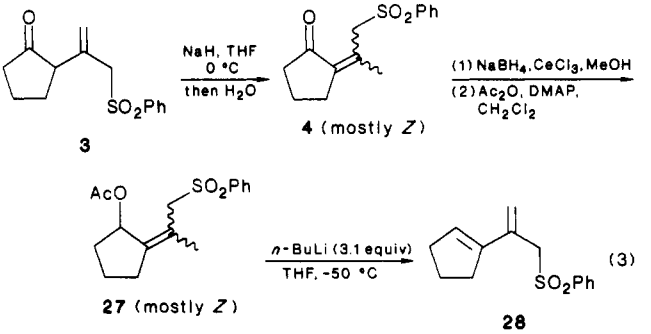


The addition reaction also proceeded in 73–86% yields in other solvents such as THF, CH_3CN, and CH_2Cl_2, but in these solvents, the product was the conjugated ketone 4 (~90% *Z*), arising from 3 by the base-catalyzed isomerization, probably facilitated in these polar solvents (vide infra).

The reactions of 1 with other pyrrolidinyl enamines derived from various cyclic ketones (7–14) were examined, and the results are summarized in Table I. While the primary addition products (3, 15–20) can be generally isolated under these reaction conditions (toluene, −50 °C), only α,β-unsaturated ketones (24, 26) were obtained in entries 7 and 9.

The structural assignment of these products was made on the basis of the spectroscopic data (Table III, supplementary material) as well as chemical transformations. In the ^1H NMR spectra, for example, adduct 3 displayed the characteristic signals due to two olefinic protons at δ 4.93 and 5.13 (each br s) and two allylic protons α to the phenylsulfonyl group at δ 3.79 and 4.44 (AB q, J_{AB} = 13.2 Hz), whereas 4 showed the methyl signal at δ 2.25 (s) for the *E* isomer and δ 2.03 (s) for the *Z* isomer, respectively.

Synthesis of 1,3-Dienes Possessing an Allyl Sulfone Moiety. Considering the great utility of 1,3-dienes[22] as well as allyl sulfones[23,24] in organic synthesis, conversion of the above adducts 3 and 15–20 and their isomers 4 and 21–26 (Table I) into the corresponding 1,3-dienes possessing an allyl sulfone moiety was investigated. Thus, the adduct of type 3 was first subjected to base-catalyzed isomerization to enone 4,[25] which was in turn transformed into the allyl acetate 27 by a sequence of $NaBH_4$ reduction and acetylation in almost quantitative yield (eq 3). The



(3)

attempted transformation of the allyl alcohol into another good leaving group such as mesylate or tosylate was un-

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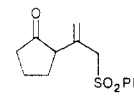
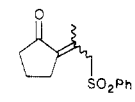
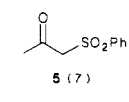
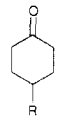
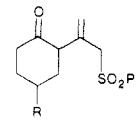
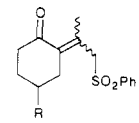
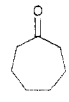
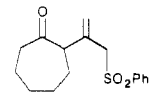
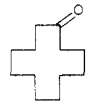
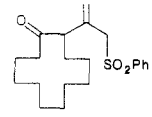
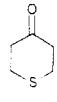
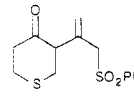
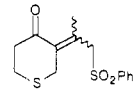
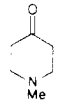
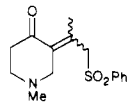
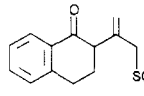
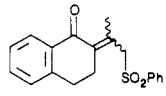
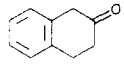
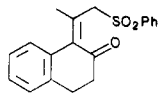
(24) Trost, B. M.; Schmuff, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 396 and references cited therein.
(25) For the synthesis of 1,3-dienes, prior isomerization of the Michael-type adducts (3) to the α,β-unsaturated carbonyl compounds (4) was necessary since the similar base treatment of the acetate derived from 3 resulted in no such elimination reaction.

Table I. Reactions of 1 with 1-Pyrrolidinyl Enamines of Cyclic Ketones[a]

entry	ketone[b]	product (% yield)[c]		
1	 2	 3 (37)	 4 (46) ($E:Z$ = 2:1)[d]	 5 (7)
2				5 (9)
3	 7, R = H; 8, R = Me	 15 (56); 16 (36)	 21 (29); 22 (33)	5 (4)
4	 9	 17 (57)		5 (17)
5	 10	 18 (17)		5 (73)
6	 11	 19 (6)	 23 (75)	5 (18)
7	 12		 24 (63)	5 (17)
8	 13	 20 (46)	 25 (11)	5 (29)
9	 14		 26 (71)	5 (12)

[a] The reactions were carried out in toluene at −50 °C, and the products were isolated by column chromatography on silica gel (*n*-hexane/EtOAc). [b] For the preparation of 1-pyrrolidinyl enamines, see the Experimental Section. [c] Isolated yields. [d] The *E*:*Z* ratio was determined by ^{1}H NMR.

successful. When the acetate **27** was treated with *n*-BuLi in THF (−50 °C), the 1,3-diene **28** was obtained in varying yields depending on the reaction conditions (eq 3). The conversion of **27** into **28** is considered to arise from the base-mediated 1,4 elimination of acetic acid (to vinyl sulfone **29**) followed by its deconjugation (to allyl sulfone **27**) via α-sulfonyl carbanion generated by action of the second mole of *n*-BuLi (Scheme I). In order to complete these reactions in one pot, however, it was required to use more than 3 equiv of *n*-BuLi, presumably due to the partial consumption of the base for formation of the dianion of the resulting acetic acid: thus, treatment of **27** with 2 equiv of *n*-BuLi at −50 °C (THF) resulted in a mixture of **28** and **29** (33:67), whereas the same treatment with 3.1 equiv of *n*-BuLi exclusively afforded **28**, mp 101.5–103 °C, in 92% yield.

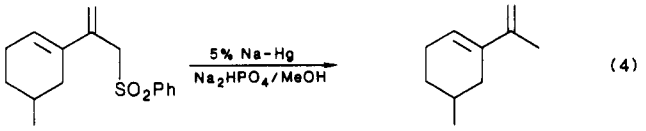
As shown in Table II, other adducts were similarly converted into the corresponding 1,3-dienes via the allyl acetates[25] with the exception of entry 8, where it was not necessary to pass through the acetate since the allyl alcohol **36** was directly dehydrated to diene **44** on treatment with acid (10% HCl).

The structures of these dienic compounds were confirmed by spectroscopic data (Table V, supplementary material) as well as their propensity for undergoing the Diels–Alder reactions with electron-deficient dienophiles (vide infra). In the ^{1}H NMR spectrum of **28**, for instance, most telling are three singlets at δ 5.04, 5.18 (each 1 H), and 4.05 (2 H) due to two exocyclic olefin protons and allylic methylene protons, respectively.

Since the phenylsulfonyl group may be reductively removed,[1] sulfonylallene **1** can be regarded as a synthetic equivalent of 2-propenyl cation in the above reactions. Thus, treatment of **39** (Table II, entry 3) with 5% sodium amalgam in the presence of phosphate buffer[26] at room temperature gave a terpenoid product, (±)-$\Delta^{3,8(9)}$-*m*-methadiene (**46**)[27] in 84% yield (eq 4).

Diels–Alder Reactions. Diene **28** was found to undergo the Diels–Alder reaction with dimethyl acetylenedicarboxylate (DMAD) at 110 °C (toluene) to give adduct

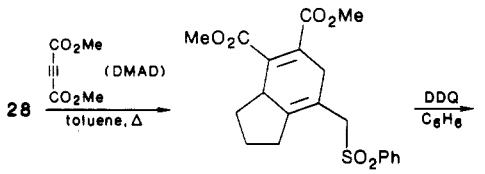
(26) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.
(27) Luff, B. D. W.; Perkin, W. H., Jr. *J. Chem. Soc.* **1911**, *99*, 518.



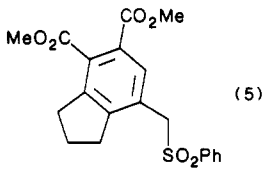
(4)

39 (±)-$\Delta^{3,8(9)}$-*m*-menthadiene (46)

47, which was, however, inseparably contaminated with a substantial amount of aromatized compound. Hence, the crude product was treated with DDQ in refluxing benzene, leading to isolation of a pure aromatic product **48** in 59% overall yield (eq 5): IR 1725 cm^{-1}; ^1H NMR δ 1.80–2.20 (m, 2 H), 2.51–3.08 (m, 4 H), 3.83 (s, 3 H), 3.90 (s, 3 H), 4.33 (s, 2 H), 7.44 (s, 1 H), 7.38–7.90 (m, 5 H).



47



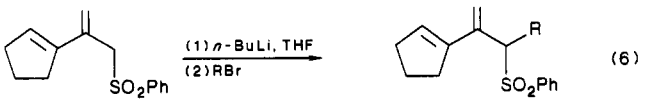
(5)

48

Table II summarizes the results obtained in similar cycloaddition reactions of dienes **38–45**[28] with DMAD followed by a DDQ treatment. In entries 8 and 9, compounds **53** and **54** were obtained as the stable products and no further dehydrogenation to phenanthrene derivatives occurred even after a prolonged treatment with excess of DDQ. In contrast, the reactions of heterocyclic compounds such as **42** and **43** resulted in a complex mixture, and no stable adducts could be obtained (entries 6 and 7).

The spectroscopic data of all these products were compatible with the assigned structures and summarized in Table V (supplementary material).

Alkylation Reactions of Diene 28. In order to demonstrate the synthetic versatility of the above dienes, alkylation reactions of diene **28** were studied. The α-sulfonyl carbanion of **28** generated by the action of *n*-BuLi (THF, −50 °C) was treated with an excess of allylic bromides to give selectively the α-allylated products[29] (**55a–c**) in good yields (eq 6). The same products could be also obtained directly from the acetate **27** by the similar treatment using excess of *n*-BuLi (>3 equiv), albeit in the less satisfactory yields.



(6)

28

55a, R = $CH_2CH{=}CH_2$ (100%)
b, R = CH_2Ph (85%)
c, R = $CH_2C{\equiv}CH$ (98%)

In summary, the present work has demonstrated that sulfonylallene **1** smoothly undergoes the Michael-type addition reactions with various enamines of cyclic ketones in good yields. The adducts can be conveniently converted into the synthetically more useful 1,3-dienes possessing the allyl sulfone moiety. The synthetic versatility of these dienes is revealed by their facile Diels–Alder reactions and alkylation reactions. Further development of the synthetic utility of these dienes is now in progress.

(28) These dienic compounds similarly underwent the Diels–Alder reactions with *N*-phenylmaleimide to give the corresponding adducts in moderate yields.

(29) (a) Julia, M.; Righini-Tapie, A.; Vereax, J.-N. *Tetrahedron* **1983**, *39*, 3283. (b) Julia, M.; Vereaux, J.-N. *Tetrahedron* **1983**, *39*, 3289.

Experimental Section

The melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. The ^1H NMR spectra were taken with a JEOL PS-100 and Hitachi R-600 spectrometer with tetramethylsilane as an internal standard, and the chemical shifts are expressed in δ values. The IR spectra were taken with a Jasco IR A-100 infrared spectrophotometer. Mass spectra were determined with a JEOL 01SG double-focusing spectrometer operated at an ionization potential of 75 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 150–200 °C. Column chromatography was performed by using E. M. Merck Kieselgel 60 (70–200 mesh) as stationary phase.

1-Pyrrolidino-1-cyclopentene (2). General Procedure for Preparation of 1-Pyrrolidinyl Enamines. A mixture of cyclopentanone (5.7 g, 68 mmol), pyrrolidine (5.7 g, 80 mmol), and *p*-toluenesulfonic acid monohydrate (650 mg, 3.4 mmol) in toluene (50 mL) was heated to reflux with azeotropic separation of water using a Dean–Stark apparatus. After separation of the stoichiometric amount of water (about 2 h), the solution was evaporated under reduced pressure to give a brown residual liquid, which upon Kugelrohr distillation afforded pure **2**: 6.5 g (95%); pale yellow liquid; bp 120 °C (10 mmHg).

Addition Reaction of 2 with (Phenylsulfonyl)propadiene (1). General Procedure for Addition Reactions. To a stirred solution of **1** (6.3 g, 35 mmol) in toluene (30 mL) was added **2** (5.8 g, 42 mmol) at −50 °C in one portion. The reaction mixture was stirred for 2 h at −50 °C and then warmed to room temperature. After removal of the solvent, the residual oil was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (7:3) as an eluant to give, in the order of elusion, the adducts **3** [3.42 g (37%)], **4** [4.26 g (46%); *E*:*Z* = 2:1), and (phenylsulfonyl)acetone [**5**; 486 mg (7%)] as colorless plates: mp 40–43 °C; ^1H NMR ($CDCl_3$) δ 8.04–7.30 (m, 5 H), 4.11 (s, 2 H), 2.35 (s, 3 H); IR ($CHCl_3$) 1730, 1345, 1175 cm^{-1}; MS, *m*/*e* 198 (M^+), 77.

Compound 3: ^1H NMR ($CDCl_3$) δ 8.01–7.44 (m, 5 H), 5.13 (s, 1 H), 4.93 (d, 1 H, J = 1.2 Hz), 4.44 and 3.79 (AB q, 2 H, J_{AB} = 13.2 Hz), 3.39–2.99 (m, 1 H), 2.63–1.70 (m, 6 H); IR ($CHCl_3$) 1735, 1310, 1150 cm^{-1}; MS, *m*/*e* 264 (M^+).

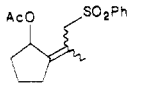
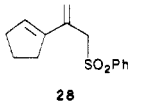
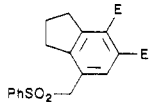
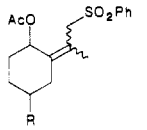
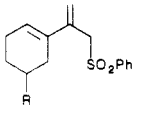
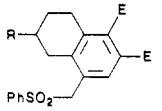
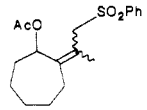
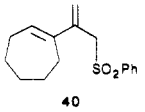
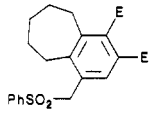
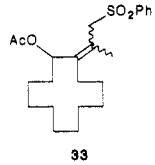
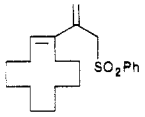
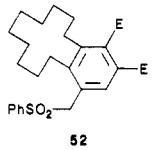
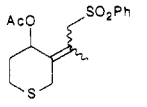
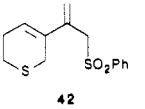
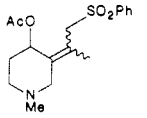
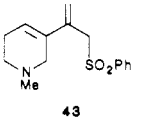
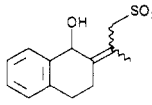
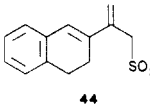
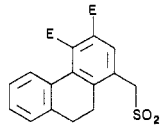
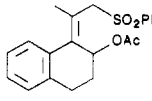
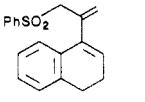
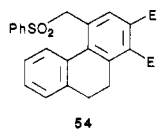
Compound 4 (*E*:*Z* = 2:1): ^1H NMR ($CDCl_3$) δ 8.14–7.38 (m, 5 H), 4.75 [s, 1.75 H, CH_2SO_2 (*Z*)], 3.93 [s, 0.25 H, CH_2SO_2 (*E*)], 2.25 [s, 0.4 H, Me (*E*)], 2.03 [s, 2.6 H, Me (*Z*)], 2.80–1.23 (m, 6 H); IR ($CHCl_3$) 1725, 1335, 1170 cm^{-1}; MS, *m*/*e* 264 (M^+), 123.

The results for the reactions of **1** and the enamines of ketones **7–14** are summarized in Table I, and the spectroscopic data of adducts are given in Table III (supplementary material).

Allyl Acetate 27 (General Procedure). To a suspension of sodium hydride (50% NaH in mineral oil, 240 mg, 5 mmol), washed several times with *n*-hexane prior to use, in THF (20 mL) was added a solution of **3** (1.10 g, 4.16 mmol) in THF (10 mL) at 0 °C. After it was stirred for 30 min at this temperature, the reaction mixture was diluted with a cold 10% aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layers were washed with brine (2 × 50 mL) and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave crude enone **4**: 1.09 g (100%); *E*:*Z* = 1:7; colorless solid; mp 60–63 °C.

To a solution of crude **4** (1.05 g, 3.97 mmol) and cerium(III) chloride heptahydrate (1.49 g, 4.0 mmol) in methanol (50 mL) was added sodium borohydride (150 mg, 3.96 mmol) in portions with stirring at room temperature. The mixture was allowed to react for 5 min, then concentrated to about one-fourth under the reduced pressure, and diluted with a cold 10% aqueous hydrochloric acid (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were washed with brine (3 × 75 mL) and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave crude alcohol: 1.22 g (100%); *E*:*Z* = 1:7; yellow oil; ^1H NMR ($CDCl_3$) δ 8.04–7.44 (m, 5 H), 4.60 [br s, 0.12 H (*E*)], 4.42 [br s, 0.88 H (*Z*)], 4.19 [d, 0.88 H, J = 13.0 Hz, CH_2SO_2 (*Z*)],

Table II. Synthesis of 1,3-Dienes from the Allyl Acetates and the Diels–Alder Reactions with DMAD followed by Aromatization[a]

entry	starting acetate[b]	diene	% yield[c]	aromatized adduct[f]	% yield[c]
1	 **27**	 **28**	92	 **48**	59
2	 **30**, R = H **31**, R = Me	 **38**, R = H **39**, R = Me	100	 **49**, R = H **50**, R = Me	46
3			98		47
4	 **32**	 **40**	75	 **51**	87
5	 **33**	 **41**	44	 **52**	19
6	 **34**	 **42**	44	*e*	
7	 **35**	 **43**	11	*e*	
8	 **36**	 **44**	(62)[d]	 **53**	75
9	 **37**	 **45**	65	 **54**	63

[a] For the reaction conditions, see eq 3 and 5. [b] Prepared in 46–95% overall yields from the corresponding adducts according to the method described in Scheme I. [c] Isolated yields. [d] Yield from enone **25**; see the text. [e] A complex mixture is formed. [f] E = CO_2Me.

3.84 [d, 0.88 H, J = 13.0 Hz, CH_2SO_2 (Z)], 3.81 [s, 0.24 H, CH_2SO_2 (E)], 1.98 [s, 0.37 H, Me (E)], 1.73 [s, 2.63 H, Me (Z)], 2.55–1.39 (m, 6 H); IR (neat) 3500, 1310, 1150 cm^{-1}.

To a solution of the above alcohol (1.22 g, 4.58 mmol) and 4-(dimethylamino)pyridine (DMAP; 560 mg, 4.58 mmol) in CH_2Cl_2 (50 mL) was added dropwise acetic anhydride (2 mL) at room temperature. After stirring for additional 30 min at this temperature, the resulting mixture was poured into a cold 10% aqueous hydrochloric acid (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were washed with brine (2 × 50 mL) and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave crude **27**: 1.40 g (99%); E:Z = 1:7; solid recrystallized from ether to give a pure sample of the Z isomer of **27** as colorless needles: mp 99–101 °C; ^1H NMR ($CDCl_3$) δ 8.04–7.42 (m, 5 H), 5.27 (br s, 1 H), 4.30 and 3.69 (AB q, 2 H, J_{AB} = 14.0 Hz), 1.99 (s, 3 H), 2.30–1.40 (m, 6 H); IR ($CHCl_3$) 1720, 1350, 1150 cm^{-1}; MS, m/e 308 (M^+), 249.

The acetates **30–35** and **37** (Table II) were similarly prepared from the corresponding adducts, and the spectroscopic data as well as physical properties of their major Z isomers are given in Table IV (supplementary material).

Reduction of **24** was carried out as follows: To a stirred solution of lithium aluminum hydride (15.2 mg, 0.4 mmol) in THF (10 mL) was added dropwise **24** (117 mg, 0.4 mmol) in THF (10 mL) at 0 °C under Ar. After stirring for 1 h at this temperature, the reaction was quenched with ethyl acetate (1 mL) and added the wet Celite (100 mg). The mixture was stirred for additional 5 min, and then the precipitate was filtered off, washed with ether (3 × 5 mL), and dried over Na_2SO_4. Evaporation of the solvent gave the allylic alcohol: 64.5 mg (55%); yellow oil; ^1H NMR ($CDCl_3$) δ 8.00–7.44 (m, 5 H), 4.57 (t, 1 H, J = 3.0 Hz), 4.29 and 3.70 (AB q, 2 H, J_{AB} = 14.0 Hz), 3.39 and 2.91 (AB q, 2 H, J_{AB} = 13.0 Hz), 2.33 (s, 3 H), 2.70–2.15 (m, 4 H), 1.74 (s, 3 H); IR (neat) 3525, 1305, 1140 cm^{-1}. This alcohol was similarly acetylated as above to give **35**.

2-[3-(Phenylsulfonyl)propen-2-yl]-3,4-dihydronaphthalene (44) (Table II, Entry 8). To a stirred solution of **25** (Table I, entry 8; 450 mg, 1.38 mmol; *E*:*Z* = 1:2) and cerium(III) chloride heptahydrate (521 mg, 1.4 mmol) in methanol (20 mL) was slowly added sodium borohydride (60 mg, 1.59 mmol) at room temperature. After stirring for 3 h at this temperature, the mixture was concentrated under the reduced pressure to one-fourth and then poured into 10% aqueous hydrochloric acid (30 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 40 mL). The combined organic layers were washed with brine (2 × 50 mL), dried over Na_2SO_4, and evaporated under the reduced pressure. The residual oil was chromatographed on silica gel with *n*-hexane/ethyl acetate (7:3) to give **44**: 264 mg (62%); yellow oil; IR (neat) 1300, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.11–6.75 (m, 9 H), 6.38 (s, 1 H), 5.48 (s, 1 H), 5.16 (s, 1 H), 4.18 (s, 2 H), 2.74–2.36 (m, 4 H); high-resolution mass spectrum (*m*/*e*) for $C_{19}H_{18}O_2S$, calcd 310.4107, obsd 310.4099.

2-[3-(Phenylsulfonyl)propen-2-yl]cyclopentene (28) (Table II, Entry 1). General Procedure for the Preparation of Dienes. To a stirred solution of **27** (528 mg, 1.71 mmol) in THF (20 mL) was added a hexane solution of *n*-butyllithium (5.30 mmol, 3.1 equiv) at −50 °C under Ar. After stirring was continued for 1 h at this temperature, the reaction was quenched with AcOH/THF (1:1; 2 mL). The resulting mixture was warmed to room temperature and further diluted with ether (50 mL) and brine (30 mL). The organic layer was separated, and the aqueous layer was extracted with ether (2 × 30 mL). The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate (30 mL) and brine (2 × 30 mL) and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the residual solid was chromatographed on silica gel with *n*-hexane/ethyl acetate (7:3) to give pure **28**: 391 mg (92%); colorless needles; mp 101.5–103 °C; ^1H NMR ($CDCl_3$) δ 8.00–7.42 (m, 5 H), 5.61 (small m, 1 H), 5.18 (s, 1 H), 5.04 (s, 1 H), 4.05 (s, 2 H), 2.60–1.55 (m, 6 H); IR ($CHCl_3$) 1310, 1150 cm^{-1}; MS, *m*/*e* 248 (M^+). Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. Found: C, 67.75; H, 6.52.

The dienes **38–45** were similarly prepared from the acetates **30–37**, respectively (Table II), and their spectroscopic data are given in Table V (supplementary material).

2-[3-(Phenylsulfonyl)propen-2-yl]cyclopentene (29). A mixture of **27** (524 mg, 1.7 mmol) and *n*-BuLi (1.7 mmol) in THF (30 mL) was stirred at −50 °C for 1 h. The same workup as above gave **29**: 347 mg (82%); yellow oil; ^1H NMR ($CDCl_3$) δ 8.05–7.35 (m, 5 H), 6.30 (s, 1 H), 6.22 (br s, 1 H), 2.28 (s, 3 H), 2.60–1.40 (m, 6 H). Similar treatment of **29** with *n*-BuLi (1 equiv) at −50 °C afforded **28**.

(±)-$\Delta^{3,8(9)}$-*m*-Menthadiene (46). To a solution of **39** (386 mg, 1.41 mmol) and anhydrous disodium hydrogen phosphate (801 mg, 5.64 mmol) in methanol (10 mL) was added pulverized 5% sodium amalgam (4.2 g). The reaction mixture was stirred for 3 h and then poured into water (140 mL). The product was extracted with ether (2 × 70 mL), washed with brine (2 × 100 mL), and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the residual oil was chromatographed on silica gel with *n*-hexane/ethyl acetate (5:1) to give **46**:[27] 160 mg (83.5%); colorless oil; ^1H NMR ($CDCl_3$) δ 5.87 (t, 1 H, *J* = 4.2 Hz), 4.95 (s, 1 H), 4.82 (s, 1 H), 2.44–1.25 (m, 7 H), 1.89 (s, 3 H), 1.00 (d, 3 H, *J* = 5.4 Hz); MS, *m*/*e* 136 (M^+).

Diels–Alder Reaction of 28 with Dimethyl Acetylenedicarboxylate (DMAD) and Aromatization of the Adduct. General Procedure. A solution of **28** (53.6 mg, 0.236 mmol) and DMAD (0.04 mL, 0.30 mmol) in toluene (10 mL) was heated under reflux (110 °C). The reaction was monitored by TLC. When **28** completely disappeared (3 h), heating was stopped and the reaction mixture concentrated under the reduced pressure. The residue was chromatographed on silica gel with *n*-hexane/ethyl acetate (4:1 to 1:1) to give a mixture of **47** and **48**: 54.2 mg (59%); IR ($CHCl_3$) 1725, 1305, 1160 cm^{-1}.

The above inseparable mixture of **47**/**48** (46.0 mg, 0.118 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ; 27.3 mg, 0.12 mmol) was dissolved in benzene (5 mL), and the solution was heated under reflux (80 °C) for 2 h. The resulting precipitate was filtered off and washed with ether (2 × 5 mL). The filtrate was concentrated under reduced pressure, and chromatography of the residual mixture on alumina with CH_2Cl_2 gave **48**: 45.8 mg (100%); ^1H NMR ($CDCl_3$) δ 7.90–7.38 (m, 5 H), 7.44 (s, 1 H), 4.33 (s, 2 H), 3.90 (s, 3 H), 3.83 (s, 3 H), 3.08–2.51 (m, 4 H), 2.20–1.80 (m, 2 H); IR (neat) 1725, 1305, 1155 cm^{-1}; high-resolution mass spectrum (*m*/*e*) for $C_{20}H_{20}O_6S$, calcd 388.4352, obsd 388.4348. The results in similar Diels–Alder reactions of dienes **38–45** are summarized in Table II, and the spectroscopic data and physical roperties of aromatized products **48–54** are given in Table V (supplementary material).

Alkylation Reaction of 28. To a stirred solution of **28** (166.7 mg, 0.670 mmol) in THF (15 mL) was added a hexane solution of *n*-butyllithium (1.5 equiv) at −50 °C under Ar. After the mixture stirred for 1 h, allyl bromide (0.08 mL, 0.924 mmol) was added at −50 °C and the reaction mixture was stirred at this temperature for additional 1 h. After a mixture of AcOH/THF (1:1; 1 mL) was added, the reaction mixture was allowed to warm to room temperature and then diluted with ether (50 mL). The reaction mixture was washed with 5% aqueous sodium hydroxide (30 mL) and brine (30 mL) and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was chromatographed on a short silica gel column with ethyl acetate to give **55a**: 193.2 mg (100%); yellow oil; ^1H NMR ($CDCl_3$) δ 7.96–7.36 (m, 5 H), 5.48 (br s, 1 H), 5.39 (s, 1 H), 5.31 (s, 1 H), 5.19 (br s, 1 H), 5.09 (d, 1 H, *J* = 1.2 Hz), 4.99–4.85 (m, 1 H), 4.10 (dd, 1 H, *J* = 11.4, 7.2 Hz), 3.10–1.10 (m, 8 H); IR (neat) 1305, 1145 cm^{-1}; MS, *m*/*e* 288 (M^+).

The similar alkylation of **28** (125.0 mg, 0.503 mmol) with benzyl bromide (0.06 mL, 0.503 mmol) gave **55b**: 144.1 mg (85%); colorless plates; mp 83–84 °C; ^1H NMR ($CDCl_3$) δ 8.00–6.96 (m, 10 H), 5.54 (s, 1 H), 5.3 (br s, 1 H), 5.30 (s, 1 H), 4.33 (dd, 1 H, *J* = 12.0, 4.0 Hz), 3.66 (dd, 1 H, *J* = 14.0, 4.0 Hz), 3.18 (dd, 1 H, *J* = 14.0, 12.0 Hz), 2.50–0.75 (m, 6 H); IR (KBr) 1300, 1140 cm^{-1}; MS, *m*/*e* 338 (M^+). Anal. Calcd for $C_{21}H_{22}O_2S$: C, 74.52; H, 6.55. Found: C, 74.49; H, 6.55.

The similar alkylation of **28** (102.0 mg, 0.411 mmol) with propargyl bromide (0.05 mL, 0.561 mmol) afforded **55c**: 115.3 mg (98%); colorless plates; mp 74–76 °C; ^1H NMR ($CDCl_3$) δ 8.00–7.31 (m, 5 H), 5.55 (br s, 1 H), 5.41 (s, 1 H), 5.35 (s, 1 H), 4.29 (dd, 1 H, *J* = 10.0, 5.0 Hz), 3.16 (ddd, 1 H, *J* = 17.0, 5.0, 2.4 Hz), 2.85 (ddd, 1 H, *J* = 17.0, 10.0, 2.4 Hz), 1.91 (t, 1 H, *J* = 2.4 Hz), 2.64–1.48 (m, 6 H); IR ($CHCl_3$) 3315, 2120, 1310, 1150 cm^{-1}; MS, *m*/*e* 286 (M^+), 144.

Registry No. **1**, 2525-42-0; **2**, 7148-07-4; **3**, 105064-92-4; (*E*)-**4**, 105064-93-5; (*Z*)-**4**, 105065-33-6; **5**, 5000-44-2; **7**, 108-94-1; **8**, 589-92-4; **9**, 502-42-1; **10**, 830-13-7; **11**, 1072-72-6; **12**, 1445-73-4; **13**, 529-34-0; **14**, 530-93-8; **15**, 105064-94-6; **16**, 105064-95-7; **17**, 105064-96-8; **18**, 105064-97-9; **19**, 105064-98-0; **20**, 105089-46-1; (*E*)-**21**, 105064-99-1; (*Z*)-**21**, 105065-34-7; (*E*)-**22**, 105065-00-7; (*Z*)-**22**, 105065-35-8; (*E*)-**23**, 105065-01-8; (*Z*)-**23**, 105065-36-9; (*E*)-**24**, 105065-02-9; (*Z*)-**24**, 105065-37-0; (*E*)-**25**, 105065-03-0; (*Z*)-**25**, 105065-38-1; (*Z*)-**26**, 105065-04-1; (*E*)-**27**, 105065-05-2; (*E*)-**27**(alcohol), 105065-39-2; (*Z*)-**27**, 105065-41-6; (*Z*)-**27**(alcohol), 105065-40-5; **28**, 105065-06-3; **29**, 105065-07-4; (*E*)-**30**, 105065-08-5; (*Z*)-**30**, 105065-44-9; (*E*)-**31**, 105065-09-6; (*Z*)-**31**, 105065-45-0; (*E*)-**32**, 105065-10-9; (*Z*)-**32**, 105065-46-1; (*E*)-**33**, 105065-11-0; (*Z*)-**33**, 105065-47-2; (*E*)-**34**, 105065-12-1; (*Z*)-**34**, 105065-48-3; (*E*)-**35**, 105065-13-2; (*E*)-**35**(alcohol), 105065-42-7; (*Z*)-**35**, 105065-49-4; (*Z*)-**35**(alcohol), 105065-43-8; (*E*)-**36**, 105065-14-3; (*Z*)-**36**, 105065-50-7; **37**, 105065-15-4; **38**, 105065-16-5; (±)-**39**, 105065-17-6; **40**, 105065-18-7; **41**, 105065-19-8; **42**, 105065-20-1; **43**, 105065-21-2; **44**, 105065-22-3; **45**, 105065-23-4; (±)-**46**, 105065-24-5; **47**, 105065-25-6; **48**, 105065-26-7; **49**, 105065-27-8; **50**, 105065-28-9; **51**, 105065-29-0; **52**, 105065-30-3; **53**, 105065-31-4; **54**, 105065-32-5; **55a**, 105065-51-8; **55b**, 105065-52-9; **55c**, 105065-53-0; DMAD, 762-42-5; $H_2C{=}CHCH_2Br$, 106-95-6; $PhCH_2Br$, 100-39-0; $HC{\equiv}CCH_2Br$, 106-96-7; cyclopentanone, 120-92-3; pyrrolidine, 123-75-1.

Supplementary Material Available: The spectral (^1H NMR, IR, MS) data of adducts **3**, **4**, and **15–26** (Table III), of acetates **27** and **30–35** (Table IV), and of dienes **28** and **38–45** as well as Diels–Alder adducts **48–54** (Table V) (5 pages). Ordering information is given on any current masthead.