June 1999 *Chem. Pharm. Bull.* **47**(6) 833—837 (1999) 833

The Diels–Alder Reaction Using a Vinyl Sulfoxide Activated by the Participation of a Neighboring Epoxide Group

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A vinyl sulfoxide, which is considered to be a moderately reactive dienophile, could be activated by neighboring participation of an epoxide group. The Diels–Alder reaction of *ortho*-epoxyphenyl vinyl sulfoxide with cyclopentadiene in the presence of Yb(OTf)$_3$ proceeded smoothly even at room temperature to afford the epoxy-opened cycloadducts with moderate stereoselectivity.

Key words Diels–Alder reaction; vinyl sulfoxide; epoxide; neighboring participation; sulfonium salt

α,β-Unsaturated sulfoxides bearing an electron-withdrawing group (EWG) on the olefinic carbon have been utilized as efficient dienophiles in Diels–Alder reactions.[1] Ester,[2] ketone,[3] sulfone,[4] sulfoxide,[5] phosphonate,[6] and nitro[7] groups have been incorporated into the α- and/or β-position of alkenyl sulfoxides to activate the dienophilicity. In contrast to such activated alkenyl sulfoxides bearing an EWG, simple vinyl sulfoxides show poor reactivity towards conjugated dienes.[8] For example, the [4+2] cycloaddition reaction between *p*-tolyl vinyl sulfoxide and cyclopentadiene could only reach completion when carried out at high temperature.[9] To activate simple vinyl sulfoxides, Kagan *et al.* employed Meerwein reagent or trimethylsilyl triflate (TMSOTf) as an additive to generate the corresponding sulfonium salts.[10] As a different activation method for simple vinyl sulfoxides, we report here that the reactivity of vinyl sulfoxides can be enhanced by the participation of an neighboring epoxide group with the aid of acid.[11] 2-Epoxyphenyl vinyl sulfoxides **1a** and **1b** were used as substrates, and their [4+2] cycloaddition with cyclopentadiene was investigated.

The diastereomeric vinyl sulfoxides **1a** and **1b** were prepared from chlorosulfide **2** (Chart 1). Oxidation of **2** with Oxone® followed by bromohydrination gave **4a** and **4b**, which were converted to epoxides **1a** and **1b**, respectively, by treatment with K_2CO_3. The stereostructure of **1a** was established by an X-ray analysis. The relative configuration at the sulfur atom and the C(2)-position of **1a** was (R^*_S, $R^*_{C(2)}$) as shown in Fig 1. Thus, the stereostructure of **1b** was deduced as (R^*_S, $S^*_{C(2)}$).

We examined the Diels–Alder reaction of **1a** with cyclopentadiene under various conditions (Table 1). When this reaction was carried out at room temperature without any additive, only starting sulfoxide **1a** was recovered in 98% yield (run 1). Both *p*-toluenesulfonic acid and $BF_3 \cdot Et_2O$ could activate **1a** as a dienophile to afford *endo*-adducts **5** and **6**, and *exo*-adducts **7** and **8** in moderate yields (runs 2 and 3). The optimum yield was obtained when Yb(OTf)$_3$ was employed in CH_3CN (run 4).[12] Lower yields were observed when CH_2Cl_2 or toluene was used as the solvent (runs 5 and 6). The use of 0.3 eq of Yb(OTf)$_3$ required a longer reaction time to give **5**—**8** in 55% yield with 10% recovery of **1a** (run 7). Sc(OTf)$_3$ also proved to be an excellent additive for this reaction (run 8). On the other hand, the activating ability of

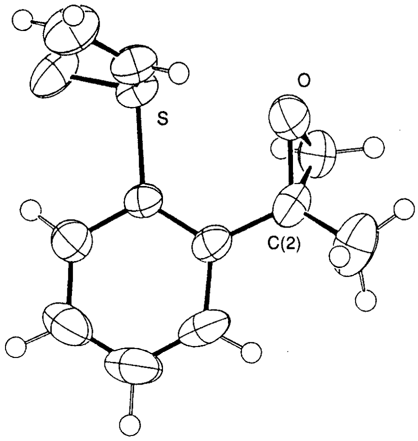

Fig. 1. ORTEP Drawing of **1a**

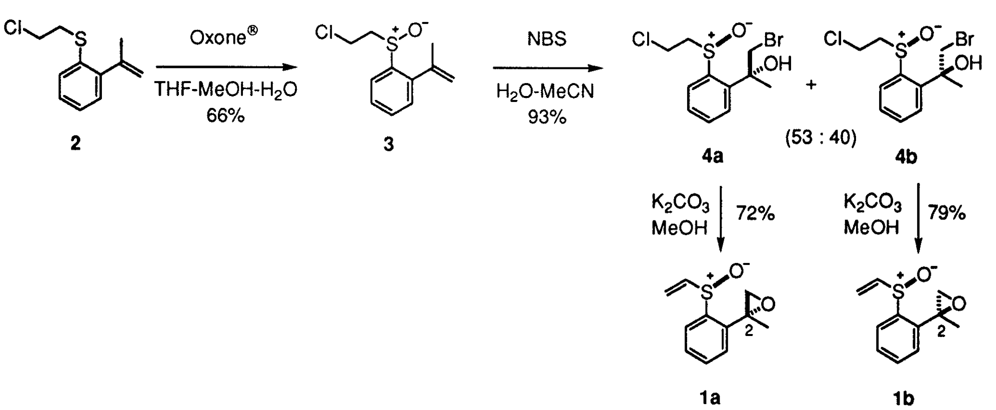

Chart 1

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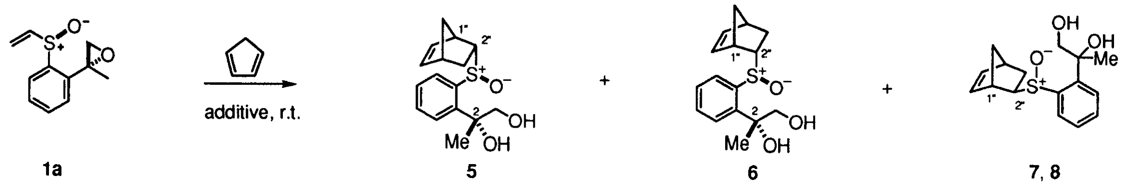
Table 1. The Diels–Alder Reaction of Vinyl Sulfoxide **1a** with Cyclopentadiene[a)]



Run	Acid (eq)		Solvent	Time	Yield (%)[b)] **5**:**6**:**7**:**8**	*endo*/*exo*	Total yield[c)] (%)	Recovered **1a** (%)
1	—	—	CH_2Cl_2	24 h	0: 0: 0:0	—	0	98
2	*p*-TSA	(1.1)	CH_2C_2	3 h	34:20:13:6	2.8	73	
3[d)]	$BF_3\cdot Et_2O$	(2.0)	$CHCl_3$	3 h	35:14:14:6	2.5	69	
4	$Yb(OTf)_3$	(1.0)	CH_3CN	5 h	60:17:11:8	4.1	96	
5	$Yb(OTf)_3$	(1.0)	CH_2Cl_2	5 h	35:15:13:5	2.8	68	
6	$Yb(OTf)_3$	(1.0)	Toluene	22 h	36:14: 8:5	3.8	63	
7	$Yb(OTf)_3$	(0.3)	CH_3CN	60 h	28:17: 7:3	4.5	55	10
8	$Sc(OTf)_3$	(1.0)	CH_3CN	10 min	59:12:10:7	4.2	88	
9	$Sc(OTf)_3$	(0.3)	CH_3CN	8 h	35:14: 9:6	3.3	64	5
10	$La(OTf)_3$	(1.0)	CH_3CN	32 h	33:16: 9:5	3.5	63	6
11	ZnI_2	(1.1)	CH_2Cl_2	1 h	~0:17:10:2	1.4	29	
12	$ZnBr_2$	(1.1)	CH_2Cl_2	3 h	~0:14:11:2	1.1	27	
13	$ZnCl_2$	(1.1)	CH_2Cl_2	22 h	0:11: 7:3	1.1	21	

a) 50 eq of cyclopentadiene was used. Each reaction was quenched by water. *b*) Product ratio was determined by ^{1}H-NMR integration. *c*) Isolated yield. *d*) 5 eq of cyclopentadiene was used.

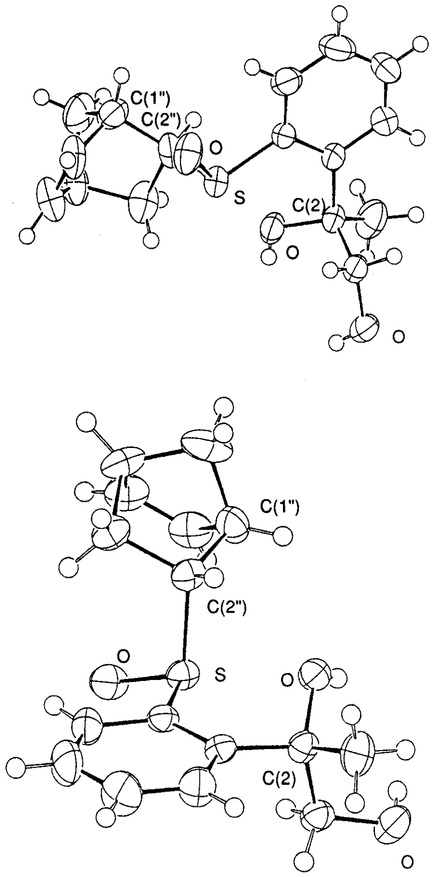


Fig. 2. ORTEP Drawings of *endo*-Major Adduct **5** (Top) and *endo*-Minor Adduct **6** (Bottom)

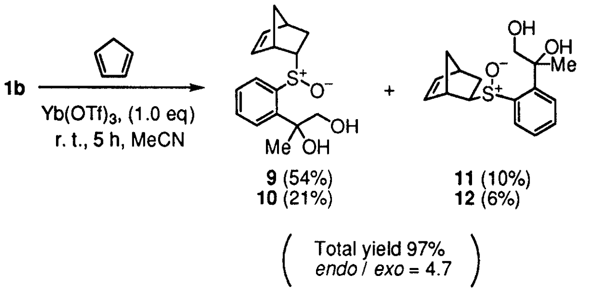


Chart 2

$La(OTf)_3$ was not notable (run 10). Interestingly, zinc halides gave no cycloadduct **5**, which was the major product under the reaction conditions shown in runs 2—10, in spite of the fact that the other cycloadducts **6**—**8** were produced in low yields (runs 11—13).

The stereostructures of the *endo*-adducts **5** and **6** were unambiguously determined based on X-ray analyses (Fig. 2). It was found that the relative configurations regarding the sulfur atom, the C(2), and the C(2″) positions were (R^*_S, $R^*_{C(2)}$, $R^*_{C(2'')}$) for **5** and (R^*_S, $R^*_{C(2)}$, $S^*_{C(2'')}$) for **6**, respectively. Based on the ^{1}H-NMR analysis, the coupling constants between H(1″) and H(2″) in both *endo*-cycloadducts **5** and **6** was 3.5—4.0 Hz. On the other hand, each coupling constant ($J_{H(1'')-H(2'')}$) for the adducts **7** and **8** was *ca.* 1.5 Hz. These results were indicative of the *exo*-stereochemistry for the products **7** and **8**.[9)]

The epoxy sulfoxide **1b** was also activated by $Yb(OTf)_3$. The reaction of **1b** with cyclopentadiene using $Yb(OTf)_3$ (1.0 eq) afforded the *endo*-adducts **9** and **10**, and the *exo*-adducts **11** and **12**,[13)] which were not identical with **5**—**8** (Chart 2). The yields of **9**, **10**, **11**, and **12** were 54%, 21%, 10%, and 6%, respectively.

In order to check the effect of the neighboring epoxide function on the activation of the vinyl sulfoxide, we examined the reaction of isopropenylphenyl vinyl sulfoxide (**13**). $Yb(OTf)_3$ (1.0 eq) did not enhance the dienophilicity of **13** in the Diels–Alder reaction with cyclopentadiene, and resulted

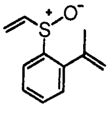


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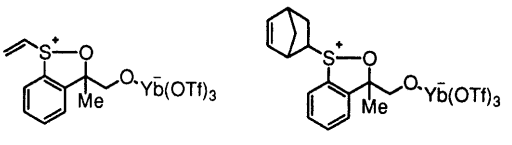
Chart 3



14 **15**

Chart 4

in only a quantitative recovery of the starting sulfoxide **13** (Chart 3).

We propose that a five-membered ring sulfonium intermediate **14**, which may be caused by the interaction between Yb(OTf)$_3$ and the epoxide oxygen, is the reactive species in this reaction. The cycloaddition of **14** with cyclopentadiene and successive hydrolysis of the resulting sulfonium ion **15** during the work-up stage would produce the epoxy-opened cycloadducts (Chart 4).

In conclusion, we demonstrated that an epoxide group located at a neighboring position could activate simple vinyl sulfoxides as dienophiles in the presence of a protonic or Lewis acid. This method is expected to be applicable to asymmetric reactions of chiral sulfinyl compounds.

Experimental

Melting points were measured with a Yanagimoto micro melting point hot-plate apparatus and are uncorrected. IR spectra were recorded on a JASCO A-102 or FTIR-350 spectrometer. NMR spectra were taken with a Varian VXR-500 or VXR-200 instrument with chemical shifts reported as δ ppm and couplings expressed in Hertz. Fast atom bombardment-mass spectra (FAB-MS) were obtained with VG-70SE mass spectrometer. Elemental analyses were carried out on a Yanaco MT-5 CHN analyzer. Column chromatography was performed using silica gel (Wako-gel C-200 or Merck No. 9385). Yb(OTf)$_3$ and Sc(OTf)$_3$ were dried for 2 d at 200 °C under vacuum pressure before use.

1-(2-Chloroethylthio)-2-isopropenylbenzene (2) A solution of 2-(2-mercaptophenyl)-2-propanol (1.00 g, 5.94 mmol) in MeOH (2.7 ml) was treated with an aqueous NaOH (0.245 g, 6.11 mmol) solution (2.7 ml) at room temperature. After 5 min, ethylene chlorohydrin (13.8 ml, 205 mmol) was added to the mixture. After stirring for 80 min at room temperature, the reaction mixture was poured into saturated NaHCO$_3$ aqueous solution and extracted with AcOEt. The organic layer was washed with brine, dried over MgSO$_4$, and evaporated to leave a white solid. Recrystallization from ether gave pure 2-[2-(2-hydroxyethylthio)]phenyl-2-propanol (1.10 g, 87.6%) as colorless prisms, mp 109—110.5 °C. IR (KBr) cm^{-1}: 3310. ^{1}H-NMR (200 MHz, DMSO-d_6) δ: 1.59 (6H, s), 3.02 (2H, t, J=7.0 Hz), 3.71 (2H, t, J=7.0 Hz), 7.12 (1H, td, J=7.0, 1.8 Hz), 7.19 (1H, td, J=7.0, 1.8 Hz), 7.40 (1H, dd, J=7.0, 1.8 Hz), 7.58 (1H, dd, J=7.0, 1.8 Hz). *Anal.* Calcd for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60. Found: C, 62.27; H, 7.45.

To a solution of 2-[2-(2-hydroxyethylthio)]phenyl-2-propanol (201 mg, 0.946 mmol) in dry pyridine (184 μl) was added dropwise SOCl$_2$ (145 μl, 1.99 mmol) at room temperature. The reaction mixture was stirred for 10 min, poured into water, and extracted with ether. The organic layer was washed with brine, dried over MgSO$_4$, and evaporated to give a crude oil which was purified by silica gel column chromatography. Elution with hexane afforded pure **2** (139 mg, 68.9%) as a pale yellow oil. IR (CHCl$_3$) cm^{-1}: 900. ^{1}H-NMR (200 MHz, CDCl$_3$) δ: 2.11 (3H, t, J=1.2 Hz), 3.16—3.24 (2H, m), 3.55—3.63 (2H, m), 4.91 (1H, sextet, J=0.9 Hz), 5.23 (1H, quintet, J=1.6 Hz), 7.11—7.41 (4H, m). *Anal.* Calcd for $C_{11}H_{13}ClS$: C, 62.10; H, 6.16. Found: C, 61.78; H, 6.15.

1-(2-Chloroethylsulfinyl)-2-isopropenylbenzene (3) To a solution of **2** (139 mg, 0.652 mmol) in tetrahydrofuran (THF) (1 ml), MeOH (0.5 ml), and H$_2$O (1 ml) was added Oxone® (265 mg, 0.430 mmol) at 0 °C. The mixture was stirred for 10 min at 0 °C, and then filtered. The filtrate was poured into water and extracted with ether. The ether layer was washed with brine, dried over MgSO$_4$, and evaporated. The resulting crude oil was purified by silica gel chromatography with AcOEt–hexane (1 : 2) to give **3** (97.8 mg, 65.6%). An analytical sample was obtained by recrystallization from hexane to leave pale yellow prisms, mp 44—45 °C. IR (CHCl$_3$) cm^{-1}: 1020—1080. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 2.13 (3H, dd, J=0.8, 1.8 Hz), 3.02 (1H, ddd, J=13.5, 7.5, 4.5 Hz), 3.26 (1H, ddd, J=13.5, 8.5, 8.0 Hz), 3.68 (1H, ddd, J=11.5, 8.5, 4.5 Hz), 3.97 (1H, ddd, J=11.5, 8.0, 7.5 Hz), 5.02 (1H, br s), 5.33 (1H, quintet, J=1.5 Hz), 7.25 (1H, dd, J=8.0, 1.5 Hz), 7.47 (1H, td, J=7.5, 1.5 Hz), 7.52 (1H, td, J=7.5, 1.5 Hz), 7.98 (1H, dd, J=8.0, 1.5 Hz). *Anal.* Calcd for $C_{11}H_{13}ClOS$: C, 57.76; H, 5.73. Found: C, 57.52; H, 5.71.

1-Bromo-2-[2-(2-chroloethylsulfinyl)]phenyl-2-propanol (4a and 4b) To a mixture of **3** (15.01 g, 65.6 mmol), H$_2$O (59 ml), and CH$_3$CN (280 ml) was added portionwise *N*-bromosuccinimide (NBS) (12.85 g, 72.2 mmol) at room temperature. After stirring for 10 min, the mixture was poured into 10% Na$_2$S$_2$O$_3$ aqueous solution and extracted with CH$_2$Cl$_2$. The combined organic layer was washed with saturated NaHCO$_3$ aqueous solution and brine, and dried over MgSO$_4$. Evaporation of the solvent gave a crude oil which was purified by silica gel chromatography with AcOEt–hexane (1 : 2). **4a** (11.42 g, 53%) was obtained as a colorless oil from the less polar fraction, and **4b** (9.12 g) as a white solid from the polar fraction. **4b** was recrystallized from ether to leave colorless prisms (8.50 g, 40%). **4a**: IR (CHCl$_3$) cm^{-1}: 1010, 3200—3300. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 1.78 (3H, s), 3.04 (1H, ddd, J=12.5, 7.0, 4.0 Hz), 3.56 (1H, br s, exchangeable with D$_2$O), 3.61 (1H, d, J=11.0 Hz), 3.68 (1H, dt, J=12.5, 8.5 Hz), 3.79 (1H, ddd, J=12.5, 8.5, 4.0 Hz), 3.89 (1H, d, J=11.0 Hz), 4.01 (1H, ddd, J=12.5, 8.5, 7.0 Hz), 7.30 (1H, dd, J=8.0, 1.5 Hz), 7.49 (1H, td, J=8.0, 1.5 Hz), 7.56 (1H, td, J=8.0, 1.5 Hz), 8.22 (1H, dd, J=8.0, 1.5 Hz). FAB-MS (positive ion mode) *m/z*: 325 (^{35}Cl, ^{79}Br), 327 (^{35}Cl, ^{81}Br and ^{37}Cl, ^{79}Br), 329 (^{37}Cl, ^{81}Br) [(M+1)$^+$]. **4b**: mp 124—125 °C. IR (KBr) cm^{-1}: 1000, 3160. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 1.76 (3H, s), 3.11 (1H, ddd, J=12.0, 7.0, 4.5 Hz), 3.58 (1H, s, exchangeable with D$_2$O), 3.65 (1H, dt, J=12.0, 10.5 Hz), 3.78 (1H, ddd, J=11.5, 10.5, 4.5 Hz), 3.86 (2H, s), 4.02 (1H, ddd, J=11.5, 10.5, 7.0 Hz), 7.20 (1H, dd, J=8.0, 1.5 Hz), 7.48 (1H, td, J=8.0, 1.5 Hz), 7.53 (1H, td, J=8.0, 1.5 Hz), 8.20 (1H, dd, J=8.0, 1.5 Hz). FAB-MS (positive ion mode) *m/z*: 325 (^{35}Cl, ^{79}Br), 327 (^{35}Cl, ^{81}Br and ^{37}Cl, ^{79}Br), 329 (^{37}Cl, ^{81}Br) [(M+1)$^+$]. *Anal.* Calcd for $C_{11}H_{14}BrClO_2S$: C, 40.57; H, 4.33. Found: C, 40.66; H, 4.26.

1-[2-(1,2-Epoxypropyl)]-2-(vinylsulfinyl)benzene (1a and 1b) To a solution of **4a** (475 mg, 1.46 mmol) in MeOH (15 ml) was added portionwise K$_2$CO$_3$ (806 mg, 5.83 mmol) at room temperature. The mixture was stirred for 1 h at room temperature, and then the undisolved solid was filtered off. Approximately 10 ml of MeOH was evaporated off under reduced pressure. The concentrated mixture was poured into water (10 ml), and extracted with ether four times. The organic layers were combined, washed with brine, dried over MgSO$_4$. After the solvent was evaporated off, the resulting crude mixture was purified by silica gel chromatography with ether–hexane (2 : 1). Recrystallization from hexane afforded **1a** (219 mg, 72%) as colorless prisms, mp 63 °C. IR (CHCl$_3$) cm^{-1}: 950, 1000—1080, 2980. ^{1}H-NMR (500 MHz, CD$_3$CN) δ: 1.73 (3H, s), 2.89, 3.03 (each 1H, ABq, J=5.0 Hz), 5.84 (1H, d, J=9.5 Hz), 6.06 (1H, d, J=16.0 Hz), 6.94 (1H, dd, J=16.0, 9.5 Hz), 7.48—7.56 (3H, m), 7.82—7.85 (1H, m). ^{13}C-NMR (125 MHz, CD$_3$CN) δ: 23.9, 56.7, 59.1, 119.7, 124.4, 128.8, 129.9, 131.7, 139.9, 142.9, 145.1. *Anal.* Calcd for $C_{11}H_{12}O_2S$: C, 63.44; H, 5.81. Found: C, 63.33; H, 5.73.

In a way similar to the above procedure, **1b** (4.29 g, 79%) was obtained as a pale yellow oil from **4b** (8.50 g, 26.1 mmol). IR (CHCl$_3$) cm^{-1}: 950, 1000—1080, 2980. ^{1}H-NMR (200 MHz, CDCl$_3$) δ: 1.73 (3H, s), 2.88, 2.98 (each 1H, ABq, J=5.1 Hz), 5.82 (1H, d, J=9.7 Hz), 6.21 (1H, d, J=16.5 Hz), 6.85 (1H, dd, J=16.5, 9.7 Hz), 7.36—7.52 (3H, m), 7.84—7.89 (1H, m). ^{13}C-NMR (50 MHz, CDCl$_3$) δ: 24.1, 52.9, 58.3, 118.1, 123.8, 127.1, 129.1, 130.6, 138.4, 142.4, 142.7. HRMS (FAB) Calcd for $C_{11}H_{13}O_2S$ (M+H)$^+$: 209.0636. Found: 209.0624.

Typical Procedure for Diels–Alder Reaction of 1a (Table 1, Run 4) Yb(OTf)$_3$ (299.0 mg, 0.482 mmol) was added to a mixture of **1a** (100.3 mg, 0.482 mmol), freshly distilated cyclopentadiene (2.0 ml), and CH$_3$CN (4 ml). The reaction mixture was stirred for 5 h at room temperature, and then filtered to remove undissolved Yb(OTf)$_3$. The filtrate was poured into water, extracted with CH$_2$Cl$_2$, washed with brine, and dried over MgSO$_4$. The solvent was removed under reduced pressure to give an oil. The crude oil was subjected to silica gel chromatography with AcOEt–hexane (2 : 1) to remove cyclopentadiene dimer, and with AcOEt to give a mixture of four diastereomers **5**—**8** (135.0 mg, 96%) as a colorless oil. The diastereomer ratio was determined by ^{1}H-NMR integration of their olefinic and 2′-protons. Analytical samples were obtained by further purification with silica gel chromatography and recrystallization. *endo*-Adducts **5** and **6**, and *exo*-major-adduct **7** could be isolated in pure form. However, all attempts to isolate the *exo*-minor-adduct **8** were unsuccessful. **5** (*endo*-Major): colorless prisms, mp 117—118 °C (AcOEt–hexane). IR (KBr) cm^{-1}: 980—1000, 3200—3500. ^{1}H-NMR (500 MHz, CD$_3$OD) δ: 1.34 (1H, d, J=8.5 Hz), 1.47 (1H, ddd, J=12.5, 4.5, 3.0 Hz), 1.52 (1H, d, J=8.5 Hz), 1.59 (3H, s), 1.72 (1H, ddd, J=12.5, 9.5, 3.5 Hz), 2.88 (1H, br s), 3.25 (1H, br s), 3.60, 3.66 (each 1H, ABq, J=11.0 Hz), 3.69 (1H, ddd, J=9.0, 4.5, 3.5 Hz), 6.26 (2H, m), 7.45 (1H, td, J=7.5, 1.5 Hz), 7.48 (1H, dd, J=7.5, 1.5 Hz), 7.52 (1H, td, J=7.5, 1.5 Hz), 8.12 (1H, dd, J=7.5, 1.5 Hz). ^{13}C-NMR (125 MHz, CD$_3$OD) δ: 26.8, 29.8, 43.8, 45.8, 50.1, 69.6, 72.0, 77.4, 127.2, 128.3, 129.2, 131.8, 133.6, 139.0, 143.7, 146.1. FAB-MS (positive ion mode) *m/z*: 293 (M+1)$^+$. *Anal.* Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89. Found: C, 65.45; H, 6.84. **6** (*endo*-Minor): colorless needles, mp 158—160 °C (MeOH–ether). IR (KBr) cm^{-1}: 1010, 3300—3500. ^{1}H-NMR (500 MHz, CD$_3$OD) δ: 1.30 (1H, d, J=8.5 Hz), 1.42 (1H, d, J=8.5 Hz), 1.53 (1H, ddd, J=12.5, 9.0, 4.0 Hz), 1.65 (3H, s), 1.76 (1H, ddd, J=12.5, 4.5, 3.0), 2.92 (1H, br s), 3.61, 3.70 (each 1H, ABq, J=11.0 Hz), 3.80 (1H, ddd, J=9.0, 4.5, 4.0 Hz), 6.10 (1H, dd, J=5.5, 3.0 Hz), 6.23 (1H, dd, J=5.5, 3.0 Hz), 7.36 (1H, dd, J=7.0, 2.5 Hz), 7.40—7.42 (2H, m), 7.86 (1H, dd, J=6.5, 2.5 Hz). ^{13}C-NMR (125 MHz, CD$_3$OD) δ: 23.0, 26.3, 43.6, 47.4, 50.9, 66.3, 71.4, 77.9, 125.3, 128.4, 128.6, 131.1, 131.6, 139.4, 144.2, 145.8. FAB-MS (positive ion mode) *m/z*: 293 (M+1)$^+$. *Anal.* Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89. Found: C, 65.60; H, 6.61. **7** (*exo*-Major): colorless prisms, mp 197—197.5 °C (ether). IR (KBr) cm^{-1}: 990, 3100—3500. ^{1}H-NMR (500 MHz, CD$_3$OD) δ: 0.90 (1H, ddd, J=12.5, 8.5, 2.0 Hz), 1.34 (1H, d, J=8.0 Hz), 1.59 (3H, s), 1.80 (1H, d, J=8.0 Hz), 2.14 (1H, dt, J=12.5, 4.0 Hz), 2.89 (1H, br s), 3.14 (1H, ddd, J=8.5, 4.0, 1.5 Hz), 3.17 (1H, br s), 3.61, 3.69 (each 1H, ABq, J=11.0 Hz), 6.13 (1H, dd, J=5.5, 3.0 Hz), 6.20 (1H, dd, J=5.5, 3.0 Hz), 7.34—7.37 (1H, m), 7.42—7.46 (2H, m), 7.97—7.99 (1H, m). ^{13}C-NMR (125 MHz, CD$_3$OD) δ: 23.8, 26.5, 42.4, 46.2, 65.3, 71.7, 78.0, 125.5, 128.4, 128.6, 131.2, 137.1, 140.8, 144.6, 144.8. FAB-MS (positive ion mode) *m/z*: 293 (M+1)$^+$. *Anal.* Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89. Found: C, 65.61; H, 6.89.

Selected signals of **8** (*exo*-minor) in ^{1}H-NMR spectrum (500 MHz, CD$_3$OD) δ: 2.97 (1H, ddd, J=8.5, 5.0, 1.5 Hz), 5.98 (1H, dd, J=5.5, 3.5 Hz), 8.12 (1H, d, J=7.5 Hz). *Anal.* for the mixture of **6** and **8** (*ca.* 2 : 1). Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89. Found: C, 65.76; H, 6.81.

Diels–Alder Reaction of 1b In a way similar to the above procedure, a mixture of four diastereomers **9**—**12** (127.7 mg, 91%) was obtained from **1b** (99.5 mg, 0.478 mmol), cyclopentadiene (2.0 ml), Yb(OTf)$_3$ (296.5 mg, 0.478 mmol), and CH$_3$CN (4 ml). The ratio of the four diastereomers was determined by ^{1}H-NMR integration of their olefinic and 2′-protons. Analytical samples of **9** and **11** were obtained by purification with silica gel chromatography (AcOEt) and recrystallization. However, all attempts to isolate **10** and **12** were unsuccessful. **9** (*endo*-Major): colorless prisms, mp 136.5—137 °C (AcOEt–hexane). IR (KBr) cm^{-1}: 990, 3300—3500. ^{1}H-NMR (500 MHz, CD$_3$OD) δ: 1.34 (1H, d, J=8.5 Hz), 1.38 (1H, ddd, J=13.0, 4.5, 2.5 Hz), 1.50 (1H, d, J=8.5 Hz), 1.53 (3H, s), 1.79 (1H, ddd, J=13.0, 9.0, 4.5 Hz), 2.87 (1H, br s), 3.18 (1H, br s), 3.71, 3.79 (each 1H, ABq, J=11.5 Hz), 3.83 (1H, ddd, J=9.0, 4.5, 3.5 Hz), 6.25 (2H, m), 7.46—7.51 (3H, m), 8.10 (1H, dd, J=6.0, 2.0 Hz). FAB-MS (positive ion mode) m/z: 293 (M+1)$^+$. *Anal.* Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89. Found: C, 65.72; H, 6.79. **11** (*exo*-Major): colorless plates, mp 183—185.5 °C (ether). IR (KBr) cm^{-1}: 1000, 3200—3500. ^{1}H-NMR (500 MHz, CD$_3$OD) δ: 0.86 (1H, dd, J=12.0, 9.5 Hz), 1.33 (1H, d, J=8.5 Hz), 1.54 (3H, s), 1.83 (1H, d, J=8.5 Hz), 2.07 (1H, dt, J=12.0, 4.0 Hz), 2.86 (1H, br s), 3.17 (1H, br s), 3.68, 3.78 (each 1H, ABq, J=11.5 Hz), 6.15 (1H, dd, J=5.5, 3.0 Hz), 6.18 (1H, dd, J=5.5, 3.0 Hz), 7.30—7.36 (1H, m), 7.41—7.45 (2H, m), 7.96—8.00 (1H, m). The solvent signals (3.30 ppm) overlapped with the one of proton α to the sulfinyl group. When measured in dimethyl sulfoxide-d_6 (DMSO-d_6), its signals appeared at 3.21 ppm with a coupling patern of dd (J=8.0, 4.5 Hz). FAB-MS (positive ion mode) *m/z*: 293 (M+1)$^+$. *Anal.* Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89. Found: C, 65.70; H, 6.93.

Selected signal of **10** (*endo*-minor) in ^{1}H-NMR spectrum (200 MHz, CD$_3$OD) δ: 3.99 (1H, ddd, J=8.6, 4.4, 3.6 Hz), 6.10 (1H, dd, J=5.6, 2.8 Hz), 7.86 (1H, m). Selected signals of **12** (*exo*-minor) in ^{1}H-NMR spectrum (200 MHz, CD$_3$OD) δ: 3.18 (1H, ddd, J=8.6, 5.0, 1.6 Hz), 5.96 (1H, dd, J=5.6, 3.2 Hz), 8.13 (1H, m). *Anal.* for the mixture of **10** and **12** (*ca.* 3 : 1). Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89. Found: C, 65.85; H, 6.83.

1-Isopropenyl-2-(vinylsulfinyl)benzene (13) To a solution of **3** (9.52 g, 41.7 mmol) in THF (260 ml) was added a solution of *tert*-BuOK (10.00 g, 87.5 mmol) in THF (400 ml) at −78 °C. After stirring for 10 min at −78 °C, the mixture was poured into saturated NH$_4$Cl aqueous solution and extracted with Et$_2$O. The organic layer was washed with brine, dried over MgSO$_4$, and evaporated to give a brown oil. Purification by silica gel chromatography with ether–hexane (1 : 2) afforded pure **13** (6.27 g, 78.3%) as a yellow oil. IR (CHCl$_3$) cm^{-1}: 910, 1020—1080. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 2.13 (3H, dd, J=1.5, 1.0 Hz), 5.00 (1H, dd, J=2.0, 1.0 Hz), 5.33 (1H, m), 5.83 (1H, d, J=9.5 Hz), 6.13 (1H, d, J=16.5 Hz), 6.65 (1H, dd, J=16.5, 9.5 Hz), 7.23 (1H, dd, J=7.5, 1.5 Hz), 7.42 (1H, td, J=7.5, 1.5 Hz), 7.47 (1H, td, J=7.5, 1.5 Hz), 7.86 (1H, dd, J=7.5, 1.5 Hz). HRMS (FAB) Calcd for $C_{11}H_{13}OS$ (M+H)$^+$: 193.0687. Found: 193.0692.

X-Ray Analysis for 1a, 5, and 6 Diffraction data for **1a**, **5**, and **6** were measured on a Rigaku AFC 5R diffractometer with Mo*Kα* radiation using ω–2θ scans. The structures were solved by direct methods and anisotropically refined for non-hydrogen atoms and isotropically for hydrogen atoms by a full-matrix least-squares technique. **1a**: $C_{11}H_{12}O_2S$, M_r=208.27, monoclinic, space group *C*2/*c*, Z=8, a=20.775 (12), b=7.970 (2), c=14.254 (9) Å, β=115.83 (4)°, V=2125 (4) Å^3, D_x=1.302 g cm^{-3}, μ (Mo$K\alpha$)=0.263 mm^{-1}. The final R=0.053, R_w=0.054 for 1684 reflections [$I_0>2\sigma(I_0)$, $2\theta\leq60.0°$] and 176 parameters. **5**: $C_{16}H_{20}O_3S$, M_r=292.39, monoclinic, space group $P2_1/n$, Z=4, a=9.393 (3), b=9.731 (3), c=16.310 (5) Å, β=95.25 (2)°, V=1485 (1) Å^3, D_x=1.308 g cm^{-3}, μ (Mo$K\alpha$)=0.212 mm^{-1}. The final R=0.069, R_w=0.056 for 2113 reflections [$I_0>1\sigma(I_0)$, $2\theta\leq52.0°$] and 262 parameters. **6**: $C_{16}H_{20}O_3S$, M_r=292.39, monoclinic, space group *C*2/*c*, Z=8, a=18.206 (17), b=8.276 (5), c=20.168 (7) Å, β=96.92 (3)°, V=3017 (4) Å^3, D_x=1.288 g cm^{-3}, μ (Mo$K\alpha$)=0.209 mm^{-1}. The final R=0.065, R_w=0.060 for 2507 reflections [$I_0>1.5\sigma(I_0)$, $2\theta\leq58.0°$] and 261 parameters.

Atomic coordinates, bond lengths and angles of these compounds have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements We are grateful to the X-ray Laboratory and the SC-NMR Laboratory of Okayama University for the use of their facilities.

References and Notes

1) Drabowicz J., Kielbasinski P., Lyzwa P., *Sulfur Reports*, **12**, 213—296 (1992); Carreno M. C., *Chem. Rev.*, **95**, 1717—1760 (1995).

2) Hogeveen H., Maccagnani G., Montanari F., *J. Chem. Soc.*, (*C*), **1966**, 1585—1591; Danishefsky S., Harayama T., Singh R. K., *J. Am. Chem. Soc.*, **101**, 7008—7012 (1979); Danishefsky S., Hirama M., Fritsch N., Clardy J., *ibid.*, **101**, 7013—7018 (1979); Koizumi T., Hakamada I., Yoshii E., *Tetrahedron Lett.*, **25**, 87—90 (1984); Maignan C., Guessous A., Rouessac F., *ibid.*, **25**, 1727—1728 (1984); Brimble M. A., Davis B. R., *Tetrahedron*, **41**, 4965—4972 (1985); Arai Y., Kuwayama S., Takeuchi Y., Koizumi T., *Tetrahedron Lett.*, **26**, 6205—6208 (1985); Takayama H., Hayashi K., Takeuchi Y., Koizumi T., *Heterocycles*, **24**, 2137—2140 (1986); Takayama H., Iyobe A., Koizumi T., *J. Chem. Soc., Chem. Commun.*, **1986**, 771—772; Alonso I., Carretero J. C., Garcia Ruano J. L., *J. Org. Chem.*, **59**, 1499—1508 (1994).

3) Danishefsky S., Walker F. J., *J. Am. Chem. Soc.*, **101**, 7018—7020 (1979); Carreno M. C., Garcia Ruano J. L., Urbano A., *J. Org. Chem.*, **57**, 6870—6876 (1992); Alonso I., Carretero J. C., Garcia Ruano J. L., Martin Cabrejas L. M., Lopez-Solera I., Raithby P. R., *Tetrahedron Lett.*, **35**, 9461—9464 (1994); Carreno M. C., Garcia Ruano J. L., Toledo M. A., Urbano A., *ibid.*, **35**, 9759—9762 (1994).

4) De Lucchi O., Lucchini V., Marchioro C., Valle G., Modena G., *J. Org. Chem.*, **51**, 1457—1466 (1986); Lopez R., Carretero J. C., *Tetrahedron:Asymmetry*, **2**, 93—96 (1991).

5) Arai Y., Kuwayama S., Takeuchi Y., Koizumi T., *Synth. Commun.*, **16**, 233—244 (1986).

6) Mikolajczyk M., Midura W. H., *Tetrahedron*: *Asymmetry*, **3**, 1515—1518 (1992).

7) Ono N., Kamimura A., Kaji A., *J. Org. Chem.*, **51**, 2139—2142 (1986); Jung M. E., Grove D. D., *J. Chem. Soc., Chem. Commun.*, **1987**, 753—755; Ono N., Kamimura A., Kaji A., *J. Org. Chem.*, **53**, 251—258 (1988); Fuji K., Tanaka K., Abe H., Itoh A., Node M., Taga T., Miwa Y., Shiro M., *Tetrahedron: Asymmetry*, **2**, 1319—1327 (1991); Fuji K., Tanaka K., Abe H., Matsumoto K., Harayama T., Ikeda A., Taga T., Miwa Y., Node M., *J. Org. Chem.*, **59**, 2211—2218 (1994); Abe H., Fujii H., Masunari C., Itani J., Kashino S., Shibaike K., Harayama T., *Chem. Pharm. Bull.*, **45**, 778—785 (1997).

8) Prilezhaeva E. N., Tsymbal L. V., Shostakovskii M. F., *Dokl. Akad. Nauk SSSR*, **138**, 1122—1125 (1961); Paquette L. A., Moerck R. E., Harirchian B., Magnus P. D., *J. Am. Chem. Soc.*, **100**, 1597—1599 (1978); Little R. D., Brown L., *Tetrahedron Lett.*, **21**, 2203—2204 (1980).
9) Maignan C., Raphael R., *Tetrahedron*, **39**, 3245—3249 (1983).
10) Ronan B., Kagan H. B., *Tetrahedron*: *Asymmetry*, **2**, 75—90 (1991).
11) Recently, the activation of a vinyl sulfone by neighboring participation of an intramolecular epoxide was reported: Zanon J., Lucchini V., Pasquato L., De Lucchi O., *Chem. Commun.*, **1996**, 709—710.
12) An example of $Yb(OTf)_3$ promoted Diels–Alder reaction using sulfinyl compounds: Arai Y., Masuda T., Masaki Y., *Chem. Pharm. Bull.*, **46**, 1078—1083 (1998).
13) The stereostructures were assigned based on their $J_{H(1'')-H(2'')}$ values[9]: 3.5 Hz for **9**, 3.6 Hz for **10**, ~0 Hz for **11**, and 1.6 Hz for **12**.