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High 1,2-Asymmetric Induction in Radical Reactions: Radical Addition to γ-Hydroxy α,β-Unsaturated Carboxylic Esters and Sulfones

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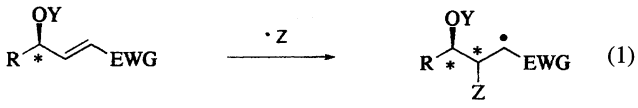
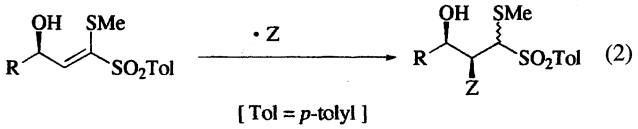
High 1,2-asymmetric induction was realized by the addition of a 1-hydroxy-1-methylethyl radical to conformationally flexible (*E*)-γ-hydroxy α,β-unsaturated carboxylic esters and sulfones (**1** and **2**, respectively). Upon the irradiation (> 290 nm) of (*E*)-**1** and benzophenone in 2-propanol, the 1-hydroxy-1-methylethyl radical was generated in situ and added to (*E*)-**1** with high *anti*-stereoselectivity. The bulkier is the γ-alkyl group of (*E*)-**1**, the higher does the selectivity become. Similarly, a radical addition to the acetates of (*E*)-**1** and (*E*)-**2** proceeded stereoselectively in an *anti* fashion, whereas (*Z*)-**2** exhibited *syn*-stereoselectivity. The mechanism for these stereoselective radical additions is discussed.

Over the past 10—15 years, much effort has been expanded in the development of free-radical reactions accompanied by asymmetric induction.[1—3] Although many methodologies have been reported for these reactions, the stereocontrol of the free-radical reaction in an acyclic system remains as one of the challenging problems. Although several types of reaction system have been exploited to solve this problem,[4,5] there are only a few reports on a 1,2-asymmetric induction in the intermolecular addition of an achiral radical to select a stereogenic π-face of acyclic chiral alkenes (Eq. 1).[4b,6]



(1)

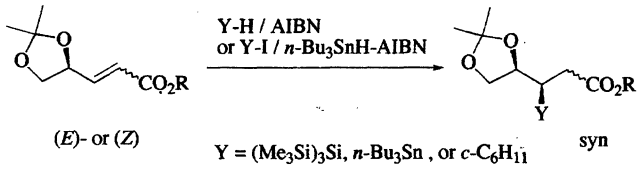
Since the radical addition to alkenes is generally exothermic, its transition state can be assumed to be reactant-like (the Hammond postulate).[7] Therefore, it seems to be important to the efficient 1,2-asymmetric induction of the above equation how the conformation of a chiral center is fixed so much as to direct an radical attack on the stereogenic π-face. Recently, we developed a new system for efficient 1, 2-asymmetric radical inductions: a 1-hydroxyalkyl radical adds to γ-hydroxy-α-methylthio α,β-unsaturated sulfones (Eq. 2) with a high degree of *syn*-selectivity.[8] The synergistic effect of an electron-donating methylthio group and an electron-withdrawing *p*-tolylsulfonyl group contributes toward the acceleration of the radical addition and fixation of the chiral center conformation.[8]



(2)

[Tol = *p*-tolyl]

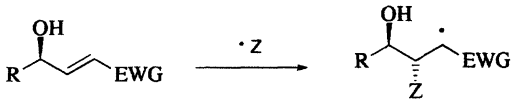
Smadja[4b,6c,6d] and Taguchi[6e] also reported on an intriguing stereoselective radical addition to a γ,δ-(isopropylidenedioxy) α,β-unsaturated carboxylic ester (Eq. 3). Bulky heteroatom-centered radicals (heteroatom=silicon or tin) add to the α,β-unsaturated carboxylic esters with high *syn*-selectivity, irrespective of the geometry of the double bond.



(*E*)- or (*Z*) Y = $(Me_3Si)_3Si$, *n*-Bu_3Sn , or *c*-C_6H_{11} syn

(3)

These facts prompted us to investigate the stereoselectivity in the radical addition of unadorned γ-hydroxy α,β-unsaturated esters and sulfones, as shown in Eq. 4.



(4)

(*E*)-**1** EWG=COOMe

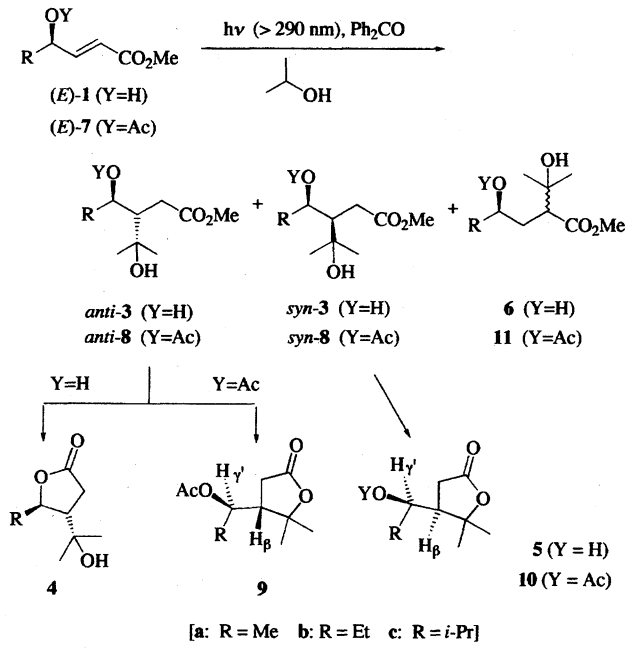
(*E*)-**2** EWG=SO_2Tol [Tol=*p*-tolyl]

Results and Discussion

For the radical species, we selected a 1-hydroxy-1-methylethyl radical that is sufficiently electron-rich to react favorably with an electron-poor alkene and, as a result, to attain a high regioselectivity.[1,2] The irradiation of methyl (*E*)-2-alkenoate[9] [(*E*)-**1**] and equimolar benzophenone in 2-propanol with a 100-W high-pressure Hg lamp (Pyrex fil-

ter)[10] gave two γ-lactones (**4** and **5**) (Scheme 1). Although an α-adduct (**6**) was also observed to form in low yield (less than 3%), it could not be isolated in a pure form. Photochemically excited benzophenone abstracted the α-hydrogen of 2-propanol to generate the 1-hydroxy-1-methylethyl radical. This radical added to (*E*)-**1** at the β-position to give intermediary adducts (*anti*-**3** and *syn*-**3**), which were transformed into the γ-lactone (**4** and **5**, respectively). Therefore, the ratio of **4** and **5** reflects the *anti* : *syn* selectivity of the radical addition. Table 1 (Entries 1—3) summarizes the yields and stereoselectivity of the products. The relatively low yields of **4** and **5** are attributable to the formation of a large amount of intractable oligomers, which were derived from **1** and the 1-hydroxy-1-methylethyl radical.

Similarly, the acetyl derivative [(*E*)-**7**][11] of (*E*)-**1** underwent the addition of 1-hydroxy-1-methylethyl radical



Scheme 1.

Table 1. Radical Addition to (*E*)-**1** and (*E*)-**7**[a]

Entry	Compound		Time	Radical adduct	
		R	h	Yield/%	Ratio[b]
1	(*E*)-**1a**	Me	4	38	**4** : **5**=68 : 32
2	(*E*)-**1b**	Et	5	42	**4** : **5**=77 : 23
3[c]	(*E*)-**1c**	*i*-Pr	6	28 (45)[d]	**4** : **5**=83 : 17
4	(*E*)-**7a**	Me	3	53	**9** : **10**=68 : 32
5	(*E*)-**7b**	Et	4	31	**9** : **10**=72 : 28
6	(*E*)-**7c**	*i*-Pr	4.5	43	**9** : **10**=91 : 9

a) Otherwise noted, a solution of (*E*)-**1** or **7** (2.00 mmol) and benzophenone (2.00 mmol) in 2-propanol (70 mL) was irradiated at room temperature. b) The product ratio that was determined by ^{1}H NMR (400 MHz, $CDCl_3$). c) (*E*)-**1c** (1.00 mmol) and benzophenone (2.00 mmol) were used because the reaction was slow (see Experimental Section). d) The yield based on the unrecovered (*E*)-**1c**.

(Entries 4—6 in Table 1), and high *anti*-selectivity was also observed. In this case, the corresponding α-adduct (**11**) was formed in 3—5% yield. It is noteworthy that the *anti*-selectivity in the present system contrasts with the results reported in the radical addition to γ,δ-(isopropylidenedioxy) α,β-unsaturated esters (Eq. 3). The *anti*-selectivity becomes higher as the alkyl group at the γ-position of **1** is bulkier.

The structures and stereochemistry of the products obtained herein were deduced based on their satisfactory spectral data. Furthermore, the benzophenone-sensitized irradiation of 4-methyl-2-penten-4-olide[12] in 2-propanol afforded **4a** in 83% yield as a single isomer (see Experimental Section), and the spectral data of **4a** agreed with those reported in the literature.[13] The stereochemistry of **4b** was assigned by a differential NOE experiment (Fig. 1). A single-crystal X-ray crystallographic analysis elucidated the structures of **5b** and **5c** [Fig. 2: (a) and (b)]. The structure of **10a**, which was also derived by the acetylation of **5a**,[11] was also confirmed by X-ray crystallography [Fig. 2: (c)]. In addition, the configurations of **9a—c** and **10a—c** were confirmed to be the same by a comparison of the coupling constants between their C_β–*H* and C'_γ–*H* in ^{1}H NMR (Table 2).

The conformational preference of allylic alcohols was reported to be quite sensitive to substitution on the C=C double bond and, in particular, electron-withdrawing groups (EWG) favor a conformation in which the C–O linkage eclipses the double bond.[14] Hence, our attention was paid to radical addition to 3-hydroxy-1-(*p*-tolylsulfonyl)-1-alkenes (**2**) because a sulfonyl group is well-known to be stable and remarkably electron-withdrawing. When a 2-propanol solution of (*E*)-**2** or its acetate [(*E*)-**13**][15] in the presence of benzophenone was irradiated, an adduct (**12** or **14**, respectively)[16] was formed as a mixture of two diastereomers (Scheme 2). The results are summarized in Table 3, showing the following distinct features: (1) high *anti*-selectivity was also observed; (2) the *anti* : *syn* ratio of the adduct (**12** or **14**) was enhanced

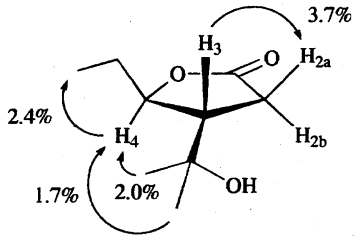


Fig. 1. The observed differential NOE of **4b**.

Table 2. Comparison of the Coupling Constants and Chemical Shifts of **9** and **10**[a,b]

Compound	R	$J_{H_\beta,H_{\gamma'}}$/Hz		δ_{H_β}/ppm		$\delta_{H_{\gamma'}}$/ppm	
		9	**10**	**9**	**10**	**9**	**10**
a	Me	4.70	11.0	2.33	2.53	5.09	4.92
b	Et	4.03	9.90	2.40	2.59	5.03	4.98
c	*i*-Pr	3.66	10.6	2.50	2.64	4.94	5.04

a) The measurement was performed by ^{1}H NMR (400 MHz, $CDCl_3$). b) For the positions (β, γ'), see Scheme 1.

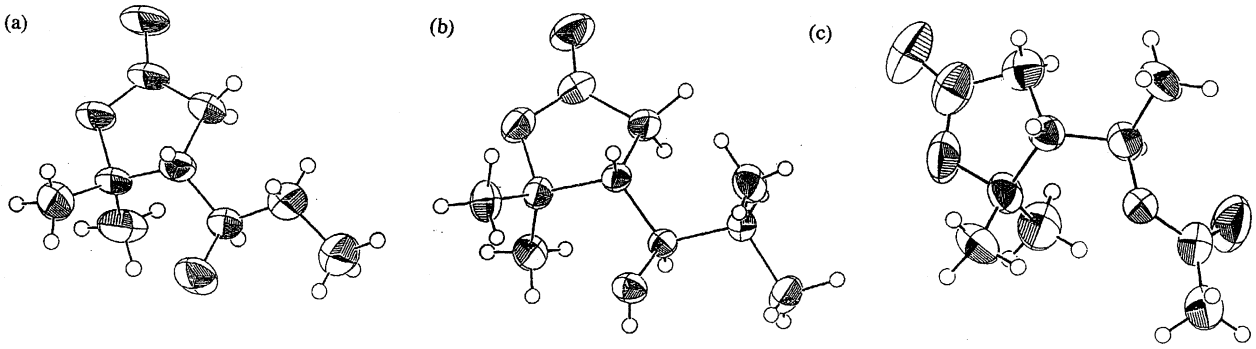
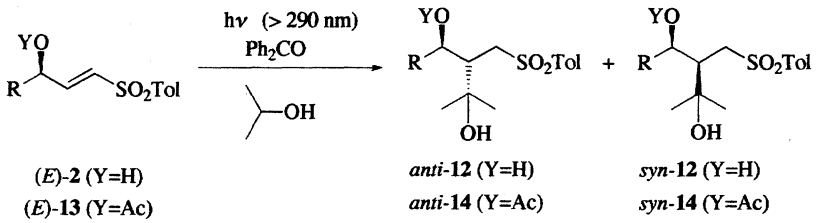


Fig. 2. ORTEP drawing. (a) **5b**. (b) **5c**. (c) **10a**.



[a: R=Me **b**: R=Et **c**; R=*i*-Pr]

Scheme 2.

Table 3. Radical Addition to a Molar Amount of (*E*)-**2** and (*E*)-**13**[a)]

Entry	Compound			Time	Molar amounts of	Addition product		
		Y	R	h	benzophenone	Yield/%[b)]		*anti* : *syn*[c)]
1	(*E*)-**2a**	H	Me	6.0	2.0	**12a**	43 (52)	80 : 20
2	(*E*)-**2b**	H	Et	9.0	3.0	**12b**	74 (80)	84 : 16
3	(*E*)-**2c**	H	*i*-Pr	10.0	3.0	**12c**	36 (57)	95 : 5
4	(*E*)-**13a**	Ac	Me	3.5	1.0	**14a**	90 (93)	71 : 29
5	(*E*)-**13b**	Ac	Et	4.5	2.0	**14b**	77 (89)	79 : 21
6	(*E*)-**13c**	Ac	*i*-Pr	5.5	2.0	**14c**	61 (64)	95 : 5

a) A solution of (*E*)-**2** or (*E*)-**13** (1.00 mmol) and benzophenone in 2-propanol (70 mL) was irradiated with a 100-W high-pressure Hg lamp at room temperature. b) The value in parenthesis means the yield based on the unrecovered starting material. c) The ratio was determined by ^{1}H NMR (270 MHz, $CDCl_3$).

with the increasing bulkiness of the alkyl group (R). In the case of R=isopropyl, the *anti* : *syn* ratio was extremely high (95 : 5) compared to the radical 1,2-asymmetric induction of a simple and flexible acyclic system; (3) the addition was so regiospecific that no γ-adduct was detected in the reaction mixture; and (4) the *anti*-selectivity of the present reaction is in a sharp contrast with the *syn*-selective addition observed in the radical additions of Eqs. 2 and 3.

Furthermore, we investigated the radical addition to (*Z*)-**2** and (*Z*)-**13**,[17] which, as summarized in Table 4, preferably gave *syn*-**12** and *syn*-**14**, respectively (Scheme 3). The *syn* selectivity increased as the substituent (R) became smaller. Since the photochemical isomerization of (*Z*)-**2** did not occur under the present conditions,[18] the reverse of the selectivity was considered to come from the geometry of (*Z*)-**2**.

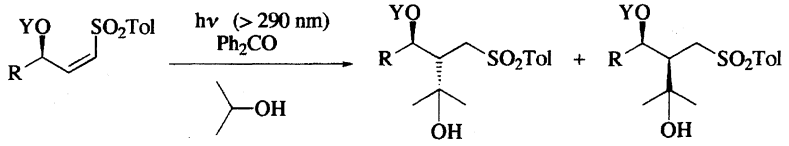
As mentioned above, the addition of the 1-hydroxyalkyl radical to the alkenes is so exothermic in that its transition state must be reactant-like.[7] Indeed, the addition of the methyl radical to (*E*)-**2** is calculated by the MNDO/PM3 method[19] to be exothermic by 27 kcal mol^{-1}. This supports the idea that the favorable transition state of the present radical addition can be estimated by considering a radical approach from a less hindered site of the starting α,β-unsaturated sulfones. Hence, we attempted to analyze the conformations of (*E*)-**2** and (*Z*)-**2** by ^{1}H NMR and X-ray crystallography. The X-ray crystallographic analysis of (*E*)-**13b** [Fig. 3(a)][20] showed that the preferred conformation of (*E*)-**13b** in a crystalline state possesses an acetoxyl group inside of the double bond and the methine proton (H_γ) outside.

In the ^{1}H NMR spectra of (*E*)-**2a**—**c** and (*E*)-**13a**—**c** in $CDCl_3$ or CD_3OD the coupling constants between H_β and H_γ[21] are relatively small (3.60—4.95 Hz), and differential NOE was observed between these protons, indicating that the predominant conformation of (*E*)-**2** and (*E*)-**13** around the C_β–C_γ bond is almost similar to that of crystalline (*E*)-**13b**. These facts are in good accordance with a confor-

Table 4. Radical Addition to a Molar Amount of (*Z*)-**2** and (*Z*)-**13**[a)]

Entry	Compound			Time	Molar amounts of	Addition product		
		Y	R	h	benzophenone	Yield/%[b)]		*anti* : *syn*[c)]
1	(*Z*)-**2a**	H	Me	4.0	2.0	**12a**	63 (76)	9 : 91
2	(*Z*)-**2b**	H	Et	4.3	2.0	**12b**	77 (80)	21 : 79
3	(*Z*)-**2c**	H	*i*-Pr	4.5	2.0	**12c**	59 (67)	31 : 69
4	(*Z*)-**13a**	Ac	Me	4.5	2.0	**14a**	76 (89)	28 : 72
5	(*Z*)-**13b**	Ac	Et	7.0	3.0	**14b**	70 (78)	31 : 69
6	(*Z*)-**13c**	Ac	*i*-Pr	7.0	3.0	**14c**	43 (77)	43 : 57

a) A solution of (*Z*)-**2** or (*Z*)-**13** (0.50 mmol) and benzophenone in 2-propanol (25 mL) was irradiated a 100-W high-pressure Hg lamp at room temperature. b) The value in parenthesis means the yield based on the unrecovered starting material. c) The ratio was determined by ^{1}H NMR (270 MHz, $CDCl_3$).



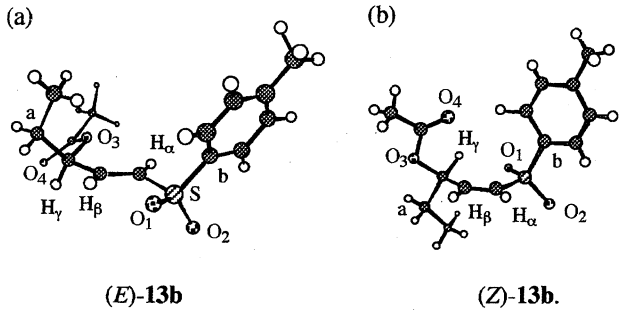
(*Z*)-**2** (Y=H)
(*Z*)-**13** (Y=Ac)

anti-**12** (Y=H)
anti-**14** (Y=Ac)

syn-**12** (Y=H)
syn-**14** (Y=Ac)

[**a**: R=Me **b**: R=Et **c**: R=*i*-Pr]

Scheme 3.



(*E*)-**13b** (*Z*)-**13b**.

Fig. 3. Chem 3D representation of the X-ray structures. (a) (*E*)-**13b** (R=Et). (b) (*Z*)-**13b** (R=Et).

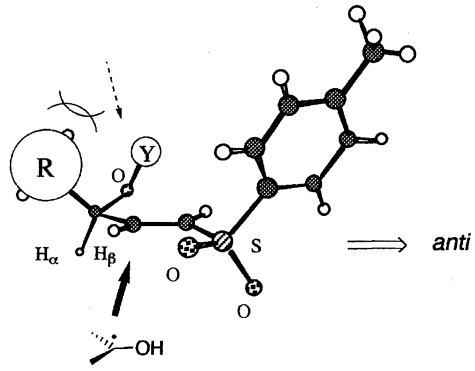


Fig. 4. A proposed mechanism for 1,2-asymmetric induction in radical addition to (*E*)-**2**.

mational analysis of the γ-hydroxy α,β-unsaturated esters reported by Gung et al.[14] Thus, the observed *anti*-selectivity is rationalized in terms of a radical attack from the less crowded side, which is opposite to the alkyl (R) group. The steric effect of the *p*-tolyl group of (*E*)-**2** was thought to be not so large because almost the same degree of diastereoselectivity (*anti* : *syn*=79 : 21) was observed in a reaction of (*E*)-**3**-hydroxy-1-butenyl methyl sulfone (**15**) (see Experimental Section) (Fig. 4).

On the other hand, it is speculated from its crystal structure [Fig. 3(b)] that (*Z*)-**13** favors a conformation around the C_β–C_γ bond, which has the acetoxy group outside of the double bond and the methine proton (H_γ) inside.[22] The preference of this conformation in a solution was supported by the ^{1}H NMR spectra: Large coupling constants ($^3J_{H_\beta,H_\gamma}$=7.58—8.90 Hz) and no NOE between H_β and H_γ were observed. In this conformation, a radical approaches from the side opposite to the alkyl (R) to lead to the *syn*-adduct. A MNDO/PM3 calculation[19] of (*Z*)-**13a** showed that two conformations, **I** and **II**, in Fig. 5 are very close in energy. Since the radical approaches to the β-carbon while avoiding the OH (or OAc) group and inclining toward a relatively smaller H_β, a *syn* attack of a radical in the conformation (**II**) is likely to suffer from a steric repulsion of the *p*-tolysulfonyl group. With the increasing bulkiness of the alkyl (R) group, the conformation (**I**) is reasonably assumed to become less favorable and, consequently, make the *syn*-selectivity in (*Z*)-**12** and (*Z*)-**14** lower.

In conclusion, we found an efficient 1,2-asymmetric induction in an intermolecular radical addition to simple and conformationally flexible γ-hydroxy α,β-unsaturated carboxylic esters and sulfones, in which the electron-withdrawing methoxycarbonyl or sulfonyl group contributes to the fixation of the chiral center adjacent to the C=C double bond. The high asymmetric induction is reasonably explained by the radical approching from a less-hindered site to the most

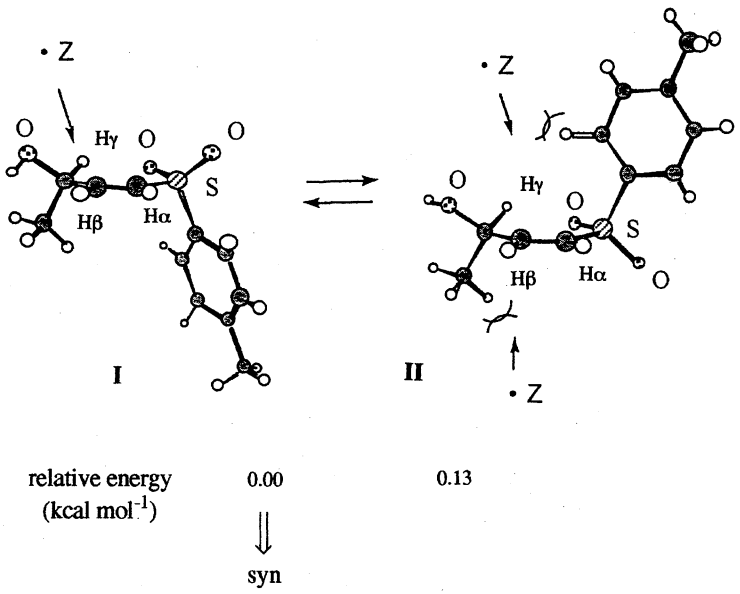


Fig. 5. A proposed mechanism for radical addition to (*Z*)-**2**.

stable conformer of the α,β-unsaturated esters and sulfones. This is in contrast with the explanation that was given by Smadja[4b] for the radical addition to a γ,δ-(isopropylidenedioxy) α,β-unsaturated carboxylic ester (Eq. 3): the radical addition will occur by the selection of the diastereotopic face of the double bond of a less stable (high energy) conformer and their transition state resembles the Cieplak model[23] or the Felkin–Anh model.[24] In consequence, the present radical addition to simple γ-hydroxy α,β-unsaturated carboxylic esters and sulfones was shown to make a new entry in acyclic radical 1,2-asymmetric induction.

Experimental

General Procedure. The melting points were determined on a hot-stage microscope apparatus (Yanagimoto) and are uncorrected. ^{1}H NMR spectra were obtained on a JOEL FX 270 (270 MHz) and a JOEL JNM-GSX 400 (400 MHz). Infrared spectra were measured with a JASCO A-200 and the data are present for important and diagnostic absorptions. The high-resolution mass spectra were recorded on a JEOL JMS-HX 110 instrument. Microanalytical data were provided by the Chemical Analysis Center of Chiba University. Chromatography was conducted on Merck silica gel 60 (70—230 mesh).

X-Ray Crystallography. Data collection was performed on a Mac Science MXC18 four-circle diffractometer with monochromated Cu $K\alpha$ (λ=1.54178 Å) or Mo $K\alpha$ (λ=0.7103 Å) radiation using the 2θ–ω scan technique, and the X-ray intensities were measured up to 2θ=140° or 55° at 298 K, respectively. Three standard reflections were monitored every 100 reflections; there were no significant variations in the intensities. The structure was solved by a direct method with Sir 92,[25] and refined by full-matrix least-squares method using the Crystan GM package.[26] All of the non-hydrogen atoms were refined anisotropically. Hydrogens were localized from a difference Fourier synthesis and refined isotropically. Tables of the coordinates, thermal parameters, bond lengths, and angles for all compounds have been deposited as Document No. 70043 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Photochemical Addition to (*E*)-1a in 2-Propanol. A Typical Procedure. A solution of (*E*)-**1a** (260 mg, 2.00 mmol) and benzophenone (364 mg, 2.00 mmol) in 2-propanol (70 mL) was irradiated with a 100-W high-pressure Hg arc lamp (Shigemi Standard) with a water-cooled Pyrex jacket under bubbling N_2 at room temperature for 4 h. After evaporation of the solvent in vacuo, the residue was purified by column chromatography on silica gal (hexane/ethyl acetate, 10 : 1 to 2 : 1) and preparative HPLC (GPC, $CHCl_3$ as an eluent) to afford a 68 : 32 mixture of **4a** and **5a** (119 mg, 38% yield). Separation of **4a** and **5a** was achieved by preparative HPLC (column: D-SIL-5-06-B YMC-Pack, eluent: hexane/ethyl acetate, 1 : 2.5).

4a: A colorless oil; IR (neat) 3450, 2975, 1750, 1380, 1290, 1183, 946 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.68 (dq, 1H, J=5.50 and 6.23 Hz), 2.65 (dd, 1H, J=9.53 and 18.3 Hz), 2.58 (dd, 1H, J=7.32 and 18.3 Hz), 2.16 (ddd, 1H, J=5.50, 7.32, and 9.53 Hz), 1.71 (br, 1H, OH), 1.44 (d, 3H, J=6.23 Hz), 1.25 (s, 3H), 1.23 (s, 3H). These spectral data agreed with those of the literature.[13]

5a: Colorless crystals; mp 105.5—107 °C (hexane–ether); IR (KBr) 3445, 1759(shoulder), 1718, 1292, 1138, 950 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.82 (dq, 1H, J=3.67 and 5.86 Hz), 2.39 (dd, 1H, J=8.43 and 13.6 Hz), 2.26—2.15 (m, 2H), 1.90 (br, 1H, OH), 1.57 (s, 3H), 1.40 (s, 3H), 1.24 (d, 3H, J=5.86 Hz). Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92%. Found: C, 60.52; H, 9.06%.

Similarly, one molar amount of **1a**, **7a**, **7b**, and **7c** were irradiated in 2-propanol containing 2.0 molar amounts of benzophenone to give the corresponding γ-lactones.

4b: A colorless oil; IR (neat) 3465, 2980, 1759, 1187, 1140, 974 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.49 (dt-like, 1H, J=7.58 and 4.62 Hz), 2.64 (dd, 1H, J=9.89 and 18.5 Hz), 2.53 (dd, 1H, J=5.60 and 18.5 Hz), 2.19 (ddd, 1H, J=4.29, 5.60, and 9.89 Hz), 2.07 (br, 1H, OH), 1.77—1.60 (m, 2H), 1.23 (s, 3H), 1.22 (s, 3H), 1.02 (t, 3H, J=7.58 Hz). HRMS (FAB) Calcd for $C_9H_{17}O_3$: (M+H$^+$), 173.1178. Found: m/z 173.1187.

5b: Colorless crystals; mp 90.5 °C (decomp, hexane–CH_2Cl_2); IR (KBr) 3490, 1730, 1282, 1238, 1132, 1082 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.58 (dt-like, 1H, J=2.64 and 8.57 Hz), 2.49—2.23 (m, 3H), 1.60—1.24 (m, 3H, CH_3CH_2 and O*H*), 1.58 (s, 3H), 1.40 (s, 3H), 1.00 (s, 3H). HRMS (FAB) Calcd for $C_9H_{17}O_3$:

(M+H$^+$), 173.1178. Found: *m/z* 173.1175. A single crystal for X-ray crystallography was obtained by recrystallization from a mixture of hexane and CH_2Cl_2 (Table 5).

9a (a more polar isomer): A colorless oil; IR (neat) 1770, 1730, 1373, 1240, 1122, 962 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=5.09 (dq, 1H, J=4.76 and 6.23 Hz), 2.68 (d, 2H, J=8.79 Hz), 2.33 (dt, 1H, J=4.76 and 8.79 Hz), 2.04 (s, 3H), 1.47 (s, 3H), 1.32 (s, 3H), 1.27 (d, 3H, J=6.59 Hz). Anal. Calcd for $C_{10}H_{16}O_4 \cdot 0.2H_2O$: C, 58.92; H, 8.10%. Found: C, 58.93; H, 8.08%.

10a (a less polar isomer): Colorless crystals; mp 79.0—80.5 °C (hexane–CH_2Cl_2); IR (KBr) 1769, 1723, 1374, 1270, 1236, 1079 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.92 (dq, 1H, J=11.0 and 6.33 Hz), 2.55 (dd, 1H, J=8.06 and 15.8 Hz), 2.56—2.49 (m, 1H), 2.37 (dd, 1H, J=4.40 and 15.8 Hz), 2.07 (s, 3H), 1.26 (s, 6H), 1.27 (d, 3H, J=6.33 Hz). Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05%. Found: C, 59.92; H, 7.99%. A single crystal for X-ray crystallography was obtained by recrystallization from a mixture of hexane and CH_2Cl_2.

11a: A colorless oil; a mixture (diastereomeric ratio of isomer A and B=49 : 51); ^{1}H NMR (400 MHz, $CDCl_3$) of the isomer A: δ=4.88 (ddq, 1H, J=2.17, 5.13, and 5.13 Hz), 3.73 (s, 3H), 2.49 (br, 1H, OH), 2.38 (dd, 1H, J=2.57 and 10.6 Hz), 2.09 (ddd, 1H, J=8.06, 10.6, and 14.3 Hz), 1.99 (s, 3H), 1.86 (ddd, 1H, J=2.57, 5.13 and 14.3 Hz), 1.239 (d, 3H, J=6.33 Hz), 1.236 (s, 3H), 1.231 (s, 3H); ^{1}H NMR of the isomer B: δ=4.80 (ddq, 1H, J=3.29, 9.89, and 6.23 Hz), 3.71 (s, 3H), 2.74 (br, 1H, OH), 2.55 (dd, 1H, J=3.29 and 11.7 Hz), 2.04 (s, 3H), 2.01 (ddd, 1H, J=3.30, 9.89, and 13.9 Hz), 1.86 (ddd, 1H, J=3.30, 11.3, and 14.5 Hz), 1.243 (d, 3H, J=6.33 Hz), 1.236 (s, 3H), 1.232 (s, 3H). HRMS (FAB) Calcd for $C_{11}H_{21}O_5$: (M+H$^+$), 233.1389. Found: *m/z* 233.1371.

9b (a more polar isomer): A colorless oil; IR (neat) 1773, 1733, 1369, 1234, 1115, 960 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=5.03 (ddd, 1H, J=4.03, 5.86, and 7.06 Hz), 2.71 (dd, 1H, J=9.52 and 17.6 Hz), 2.62 (dd, 1H, J=8.43 and 17.6 Hz), 2.40 (ddd, 1H, J=4.03, 8.43, and 9.52 Hz), 2.06 (s, 3H), 1.47 (s, 3H), 1.31 (s, 3H), 0.91 (d, 3H, J=7.33 Hz). HRMS (FAB) Calcd for $C_{11}H_{19}O_4$: (M+H$^+$), 215.1283. Found: *m/z* 215.1298.

10b (a less polar isomer): A colorless oil; IR (neat) 2986, 1769, 1730, 1369, 1235, 958 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.98 (ddd, 1H, J=3.66, 6.96, and 9.90 Hz), 2.59 (dd, 1H, J=8.43, 9.89, and 12.5 Hz), 2.54 (dd, 1H, J=9.63 and 16.4 Hz), 2.37 (dd, 1H, J=12.5 and 16.9 Hz), 2.09 (s, 3H), 1.76—1.68 (m, 1H), 1.51—1.43 (m, 1H), 1.49 (s, 3H), 1.27 (s, 3H), 0.90 (t, 3H, J=7.33 Hz). HRMS (FAB) Calcd for $C_{11}H_{19}O_4$: (M+H$^+$), 215.1283. Found: *m/z* 215.1289.

11b: A colorless oil; a mixture (diastereomeric ratio of isomer A and B=42 : 58); IR (neat) 3450, 2960, 1750, 1720, 1365, 1232 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) of the isomer **A**: δ=4.90—4.88 (m, 1H), 3.63 (s, 3H), 2.64 (br, 1H, OH), 2.31 (dd, 1H, J=2.56 and 10.3 Hz), 2.01—2.00 (m, 2H), 1.94 (s, 3H), 1.57—1.47 (m, 2H), 1.18 (s, 3H), 1.16 (s, 3H), 0.81 (t, 3H, J=7.32 Hz); ^{1}H NMR of the isomer **B**: δ=4.80—4.70 (m, 1H), 3.65 (s, 3H), 2.64 (br, 1H, OH), 2.44 (dd, 1H, J=3.30 and 11.7 Hz), 1.98 (s, 3H), 1.90—1.72 (m, 2H), 1.57—1.47 (m, 2H), 1.17 (s, 3H), 1.16 (s, 3H), 0.81 (t, 3H, J=7.32 Hz). HRMS (FAB) Calcd for $C_{12}H_{23}O_5$: (M+H$^+$), 247.1545. Found: *m/z* 247.1531.

9c (a more polar product): A colorless oil; IR (neat) 2985, 1767, 1733, 1371, 1230, 960 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.94 (dd, 1H, J=3.36 and 5.49 Hz), 2.75 (dd, 1H, J=9.53 and 16.9 Hz), 2.57 (dd, 1H, J=8.43 and 16.9 Hz), 2.50 (ddd, 1H, J=3.66, 8.43, and 9.89 Hz), 2.08 (s, 3H), 1.82 (d and septet, 1H, J=5.49 and 6.96 Hz), 1.47 (s, 3H), 1.28 (s, 3H), 0.92 (d, 6H, J=6.96 Hz).

Table 5. Crystallographic Data of **5b**, **5c**, and **10a**

	5b	**5c**	**10a**
Chemical formula	$C_9H_{16}O_3$	$C_{10}H_{18}O_3 \cdot H_2O$	$C_{10}H_{16}O_4$
Formula weight	172.20	204.27	200.23
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	$P2_12_12_1$ (#19)	$P2_12_12_1$ (#19)	P-1 (#2)
a/Å	8.877(3)	9.680(2)	8.125(8)
b/Å	14.896(5)	14.965(4)	11.858(7)
c/Å	7.380(3)	8.074(3)	12.898(5)
α/°	90.000(0)	90.000(0)	87.70(4)
β/°	90.000(0)	90.000(0)	74.84(5)
γ/°	90.000(0)	90.000(0)	72.74(6)
V/Å^3	975.9(5)	1169.6(6)	1145(1)
Z	4	4	4
D_{calcd}/g cm^{-3}	1.17	1.16	1.16
Radiation	Cu $K\alpha$ (λ=1.54178 Å)	Cu $K\alpha$ (λ=1.54178 Å)	Mo $K\alpha$ (λ=0.71073 Å)
Monochrometer	Graphite	Graphite	Graphite
T/K	298	298	298
Computer program	Crystan GM[a)]	Crystan GM[a)]	Crystan GM[a)]
Structure solution	Sir92[b)]	Sir92[b)]	Sir92[b)]
No. of measured reflections	1143	1361	5813
No. of unique reflections	1089	1299	5269
No. of observetions[c)]	910	1200	1647
No. of variables	145	207	300
Refinement	Full matrix	Full matrix	Full matrix
R; R_W	0.0813; 0.0708	0.0429; 0.0387	0.0649; 0.0668

a) See Ref. 23. b) Direct method, see Ref. 24. c) $I>3.00\sigma(I)$.

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83%. Found: C, 62.90; H, 9.12%.

10c (a less polar product): Colorless crystals; mp 74.5—76.0 °C (hexane–CH_2Cl_2); IR (KBr) 2970, 1762, 1721, 1270, 1233, 958 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=5.04 (dd, 1H, J=2.57 and 11.6 Hz), 2.64 (ddd, 1H, J=8.06, 10.4, and 13.2 Hz), 2.50 (dd, 1H, J=8.06 and 16.9 Hz), 2.39 (dd, 1H, J=13.2 and 16.9 Hz), 2.10 (s, 3H), 1.78—1.71 (m, 1H), 1.46 (s, 3H), 1.29 (s, 3H), 0.92 (d, 3H, J=6.96 Hz), 0.91 (d, 3H, J=6.96 Hz). Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83%. Found: C, 63.12; H, 8.79%.

11c: A colorless oil; a mixture (diastereomeric ratio of isomer **A** and isomer **B**=41 : 59); IR (neat) 3420, 2960, 1720, 1362, 1236, 1020 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) of isomer **A**: δ=4.80 (quintet-like, 1H, J=4.40 Hz), 3.712 (s, 3H), 2.69 (br, 1H, OH), 2.35 (dd, 1H, J=3.29 and 9.52 Hz), 2.01 (s, 3H), 2.00—1.79 (m, 3H), 1.54 (s, 3H), 1.39 (s, 3H), 0.90 (d, 3H, J=6.96 Hz), 0.88 (d, 3H, J=6.59 Hz); ^1H NMR of isomer **B**: δ=4.62 (ddd, 1H, J=2.57, 5.86, and 8.43 Hz), 3.713 (s, 3H), 2.69 (br, 1H, OH), 2.46 (dd, 1H, J=3.30 and 12.1 Hz), 2.06 (s, 3H), 2.00—1.79 (m, 3H), 1.23 (s, 3H), 1.22 (s, 3H), 0.90 (d, 6H, J=6.96 Hz). HRMS (FAB) Calcd for $C_{13}H_{25}O_5$: M, 261.1702. Found: m/z 261.1693.

Photochemical Addition to (*E*)-1c in 2-Propanol. A solution of (*E*)-**1c** (158 mg, 1.00 mmol) and benzophenone (182 mg, 1.00 mmol) in 2-propanol (70 mL) was irradiated with a 100-W high-pressure Hg arc lamp (Shigemi Standard) with a water-cooled Pyrex jacket under bubbling N_2 at room temperature for 3 h. After a further addition of benzophenone (182 mg, 1.00 mmol), the irradiation was continued for 3 h. Evaporation and chromatographic separation of the residue afforded a 83 : 17 mixture of **4c** and **5c** (55 mg, 28% yield). The starting (*E*)-**1c** (60 mg, 38%) was recovered.

4c: A colorless oil; IR (neat) 3460, 2980, 1763, 1369, 1188, 993 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=4.34 (dd, 1H, J=2.93 and 5.13 Hz), 2.62 (dd, 1H, J=10.3 and 18.7 Hz), 2.49 (dd, 1H, J=4.66 and 18.7 Hz), 2.25 (ddd, 1H, J=4.66, 5.13, and 10.3 Hz), 1.90—1.82 (m, 1H), 1.72 (br, 1H, OH), 1.23 (s, 3H), 1.22 (s, 3H), 1.00 (d, 3H, J=6.96 Hz), 0.97 (d, 3H, J=6.60 Hz). HRMS (FAB) Calcd for $C_{10}H_{19}O_3$: ($M+H^+$), 187.1334. Found: m/z 187.1325.

5c: Colorless crystals; mp 65.0—66.8 °C (hexane–ether); IR (KBr) 3600, 3260, 1750, 1723, 1379, 1276, 1137, 950 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=3.55 (dd, 1H, J=2.20 and 7.33 Hz), 2.42—2.27 (m, 3H), 1.62 (d and septet, 1H, J=2.20 and 6.96 Hz), 1.58 (s, 3H), 1.41 (d, 1H, J=5.13 Hz, OH), 1.39 (s, 3H), 1.01 (d, 3H, J=6.96 Hz), 0.87 (d, 3H, J=6.59 Hz). HRMS (FAB) Calcd for $C_{10}H_{19}O_3$: ($M+H^+$), 187.1332. Found: m/z 187.1318. A single crystal for X-ray crystallography was obtained by recrystallization from a mixture of hexane and ether.

Photochemical Addition of 2-Propanol to 4-Methyl-2-pentenolide. Irradiation of a solution of 4-methyl-2-penten-4-olide (196 mg, 2.00 mmol) in 2-propanol (70 mL) containing benzophenone (36.4 mg, 0.20 mmol) for 1.5 h afforded **4a** (262 mg, 83% yield) as a single diastereomer. Its spectral data agreed with those of the adduct (**4a**) obtained in the reaction of (*E*)-**1a**.

Preparation of (*E*)-2a. Typical Procedure. This compound [(*E*)-**2a**] was prepared according to the method described in the literature, except for the use of (methylsulfinyl)methyl *p*-tolyl sulfone instead of (*p*-chlorophenylsulfinyl)methyl phenyl sulfone[27] or (*p*-tolylsulfinyl)methyl phenyl sulfone.[27]

(Methylsulfinyl)methyl *p*-tolyl sulfone was obtained by oxidation of (methylthio)methyl *p*-tolyl sulfone with either hydrogen peroxide in acetic acid–CH_2Cl_2 or *m*-chloroperbenzoic acid in CH_2Cl_2 as colorless crystals: Mp 118.0—119.9 °C (ethyl acetate); IR (KBr) 1598, 1313, 1148, 1122, 1082, 1048 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.85 (d, 2H, J=8.24 Hz), 7.41 (d, 2H, J=7.91 Hz), 4.37 (ABq, 2H, J=2.31 Hz), 2.94 (s, 3H), 2.48 (s, 3H). Anal. Calcd for $C_9H_{12}O_3S_2$: C, 46.53; H, 5.21%. Found: C, 46.66; H, 5.16%.

To a stirring solution of (methylsulfinyl)methyl *p*-tolyl sulfone (1.48 g, 6.37 mmol) in acetonitrile (20 mL) were added piperidine (1.35 mL, 12.7 mmol) and propionaldehyde (0.93 mL, 12.7 mmol) at 0 °C. After the mixture was stirred at room temperature for 4 h, the reaction mixture was neutralized by 2.4 M HCl, (1 M=1 mol dm^{-3}), and the aqueous layer was then extracted with CH_2Cl_2 (20 mL×3). The extracts were dried over $MgSO_4$ and concentrated in vacuo to give a crude product. Purification by flash column chromatography on silica gel (hexane/ethyl acetate, 1.45 : 1) afforded (*E*)-**2a** (1.44 g) as a colorless oil: IR (neat) 3450, 2990, 1585, 1140, 1085, 960 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.76 (d, 2H, J=8.24 Hz), 7.33 (d, 2H, J=7.91 Hz), 6.94 (dd, 1H, J=3.63 and 15.0 Hz), 6.57 (dd, 1H, J=1.70 and 15.0 Hz), 4.54 (ddq, 1H, J=1.65, 3.63, and 6.60 Hz), 2.44 (s, 3H), 1.90—1.60 (br, 1H, OH), 1.35 (d, 3H, J=6.60 Hz). The ^1H NMR data agreed with those of the literature.[28]

To a solution of (*E*)-**2a** (315 mg, 1.39 mmol) in pyridine (2 mL) was added acetic anhydride (2 mL) at 0 °C. The mixture was stirred at room temperature for 19 h. The usual workup and column chromatography on silica gel (hexane/ethyl acetate, 3 : 1) gave (*E*)-**13a**[28,29] (368 mg, 99% yield) as a colorless oil; IR (neat) 1730, 1590, 1310, 1230, 1140, 1080 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.76 (d, 2H, J=8.24 Hz), 7.35 (d, 2H, J=7.91 Hz), 6.88 (dd, 1H, J=4.26 and 15.0 Hz), 6.46 (dd, 1H, J=1.65 and 15.0 Hz), 5.51 (ddq, 1H, J=1.65, 4.62, and 6.52 Hz), 2.45 (s, 3H), 2.06 (s, 3H), 1.37 (d, 3H, J=6.59 Hz). Anal. Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01%. Found: C, 58.25; H, 6.27%.

(*E*)-2b:[28] Colorless crystals; mp 85.0—85.3 °C (hexane–CH_2Cl_2); IR (KBr) 3500, 2960, 1595, 1290, 1135, 1080 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.76 (d, 2H, J=8.24 Hz), 7.33 (d, 2H, J=7.91 Hz), 6.94 (dd, 1H, J=3.93, and 15.0 Hz), 6.58 (dd, 1H, J=1.65 and 15.0 Hz), 4.31 (dddd, 1H, J=1.65, 3.93, 5.40, and 7.25 Hz), 2.44 (s, 3H), 1.90—1.80 (br, 1H, OH), 1.76—1.50 (m, 2H), 0.96 (t, 3H, J=7.40 Hz). Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71%. Found: C, 60.00; H, 6.68%.

(*E*)-13b:[28] Colorless crystals; mp 68.5—69.0 °C (hexane–CH_2Cl_2); IR (KBr) 1740, 1590, 1370, 1290, 1140, 1080 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.75 (d, 2H, J=8.52 Hz), 7.34 (d, 2H, J=7.91 Hz), 6.86 (dd, 1H, J=4.62, and 15.0 Hz), 6.44 (dd, 1H, J=1.65 and 15.0 Hz), 5.40 (ddt, 1H, J=1.65, 4.62, and 6.28 Hz), 2.44 (s, 3H), 2.07 (s, 3H), 1.78—1.66 (m, 2H), 0.91 (t, 3H, J=7.36 Hz). Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43%. Found: C, 59.46; H, 6.29%. A single crystal for X-ray crystallographic analysis was obtained by recrystallization from hexane–CH_2Cl_2 (Table 6).

(*E*)-2c: Colorless crystals; mp 116.5—117.5 °C (hexane–CH_2Cl_2); IR (KBr) 3500, 2960, 1620, 1275, 1135, 1078 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.76 (d, 2H, J=8.24 Hz), 6.96 (dd, 1H, J=3.93 and 15.0 Hz), 7.33 (d, 2H, J=8.24 Hz), 6.59 (dd, 1H, J=1.85 and 15.0 Hz), 4.18 (ddd, 1H, J=1.85, 3.69, and 5.24 Hz), 2.44 (s, 3H), 1.86 (d and septet., 1H, J=5.24 and 6.92 Hz), 1.50—1.92 (br, 1H, OH), 0.94 (d, 3H, J=6.92 Hz), 0.92 (d, 3H, J=6.92 Hz). Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13%. Found: C, 61.32; H, 7.00%.

(*E*)-13c: A colorless oil; IR (neat) 1740, 1595, 1370, 1313, 1140, 1083 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.75 (d, 2H, J=8.24 Hz); 7.34 (d, 2H, J=7.91 Hz), 6.88 (dd, 1H, J=4.92 and 15.0 Hz), 6.42 (dd, 1H, J=1.65 and 15.0 Hz), 5.30 (dt, 1H, J=1.65 and 5.26 Hz), 2.44 (s, 3H), 2.07 (s, 3H), 2.06—1.92 (m, 1H), 0.93 (d, 3H, J=6.58 Hz), 0.91 (d, 3H, J=6.58 Hz). Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80%. Found: C, 60.47; H, 6.63%.

Table 6. Crystallographic Data of (*E*)-**13b** and (*Z*)-**13b**

	(*E*)-**13b**	(*Z*)-**13b**
Chemical formula	$C_{14}H_{18}O_4S$	$C_{14}H_{18}O_4S$
Formula weight	282.40	282.40
Crystal system	Triclinic	Monoclinic
Space group	*P*-1 (#2)	$P2_1/n$ (#14)
a/Å	7.458 (4)	17.193 (7)
b/Å	9.430 (2)	8.994 (3)
c/Å	11.331 (8)	10.092 (4)
α/°	76.54 (3)	90.000 (0)
β/°	84.09 (6)	106.03 (3)
γ/°	74.67 (3)	90.000 (0)
V/Å^3	746.7 (8)	1500 (1)
Z	2	4
D_{calcd}/g cm^{-3}	1.26	1.25
Radiation	Mo $K\alpha$ (λ=0.71073 Å)	Mo $K\alpha$ (λ=0.71073 Å)
Monochrometer	Graphite	Graphite
T/K	298	298
Computer program	Crystan GM[a)]	Crystan GM[a)]
Structure solution	Sir92[b)]	Sir92[b)]
No. of measured reflections	3720	4003
No. of unique reflections	3436	3458
No. of observetions[c)]	3006	2029
No. of variables	244	217
Refinement	Full matrix	Full matrix
R; R_W	0.0552; 0.0545	0.0676; 0.0692

a) See Ref. 23. b) Direct method, see Ref. 24. c) $I>3.00\sigma(I)$.

Photochemical Addition of 2-Propanol to (*E*)-2a. Typical Procedure. A solution of (*E*)-**2a** (229 mg, 1.01 mmol) and benzophenone (184 mg, 1.01 mmol) in 2-propanol (70 mL) was irradiated with a 100-W high-pressure Hg arc lamp equipped with a water-cooled Pyrex jacket under bubbling N_2 at room temperature for 6 h. After the addition of benzophenone (184 mg, 1.01 mmol), irradiation was continued for an additional 2 h. Evaporation of the solvent in vacuo and purification of the residue (657 mg) by column chromatography on silica gel (hexane/ethyl acetate, 3 : 1 to 1.5 : 1) and preparative HPLC (GPC columns, $CHCl_3$ as an eluent) afforded a diastereomeric mixture (*anti* : *syn*=80 : 20) of **12a** (123 mg, 43% yield) and the recovered (*E*)-**2a** (43.3 mg, 19% yield). The spectral data of **12a** agreed with those of our previous report.[8)]

In a similar manner, **2b** and **2c** were irradiated in 2-propanol containing benzophenone to give the corresponding adducts (**12**).

Photochemical Addition of 2-Propanol to (*E*)-13a. A Typical Procedure. A solution of (*E*)-**13a** (287 mg, 1.00 mmol) and benzophenone (182 mg, 1.00 mmol) in 2-propanol (70 mL) was irradiated with a 100-W high-pressure Hg arc lamp (Sigemi Standard) equipped with a water-cooled Pyrex jacket under bubbling N_2 at room temperature for 3 h. After the solvent was evaporated in vacuo, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 4 : 1 to 1 : 1) and preparative HPLC (GPC, $CHCl_3$ as an eluent) to afford a diastereomeric mixture of **14a** (310 mg, 90% yield) along with (*E*)-**13a** (16 mg, 6% yield).

(*E*)-14a: A colorless viscous oil; a mixture of two diastereomers (*anti* : *syn*=71 : 29); IR (neat) 3500, 2980, 1725, 1370, 1140, 1085 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) of *anti*-**14a**: δ=7.85 (d, 2H, *J*=8.24 Hz), 7.38 (d, 2H, *J*=7.91 Hz), 5.22 (dq, 1H, *J*=1.26 and 6.59 Hz), 3.47 (dd, 1H, *J*=4.62 and 14.8 Hz), 3.33 (dd, 1H, *J*=3.63 and 14.8 Hz), 2.62 (ddd, 1H, *J*=0.99, 3.63, and 4.62 Hz), 2.47 (s, 3H), 1.99 (s, 3H), 1.33 (s, 3H), 1.24 (d, 3H, *J*=6.59 Hz), 1.04 (s, 3H); ^{1}H NMR of *syn*-**14a**: δ=7.81 (d, 2H, *J*=8.58 Hz), 7.36 (d, 2H, *J*=7.91 Hz), 5.16 (dq, 1H, *J*=4.26 and 6.60 Hz), 3.45 (dd, 1H, *J*=4.92 and 14.8 Hz), 3.17 (dd, 1H, *J*=4.26 and 15.0 Hz), 2.54 (q-like, 1H, *J*=4.26 Hz), 2.45 (s, 3H), 1.96 (s, 3H), 1.32 (s, 3H), 1.23 (d, 3H, *J*=6.60 Hz), 1.22 (s, 3H). Anal. Calcd for $C_{16}H_{24}O_5S\cdot0.06CH_2Cl_2$: C, 57.84; H, 7.29%. Found: C, 57.82; H, 7.29%.

14b: A colorless viscous oil; a diastereomeric mixture (*anti* : *syn*, 79 : 21); a colorless oil; IR (neat) 3500, 1720, 1280, 1140, 1080, 1015 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) of *anti*-**14b**: δ=7.84 (d, 2H, *J*=8.24 Hz), 7.39 (d, 2H, *J*=7.91 Hz), 5.02 (t-like, 1H, *J*=7.10 Hz), 3.43 (dd, 1H, *J*=4.95 and 14.8 Hz), 3.32 (dd, 1H, *J*=3.63 and 14.8 Hz), 2.47 (s, 3H), 2.38 (t-like, 1H, *J*=3.80 Hz), 1.72—1.60 (broad, 1H, OH), 1.60—1.48 (m, 2H), 1.97 (s, 3H), 1.35 (s, 3H), 1.03 (s, 3H), 0.90 (t, 3H, *J*=7.33 Hz); ^{1}H NMR of *syn*-**14b**: δ=7.84 (d, 2H, *J*=8.58 Hz), 7.36 (d, 2H, *J*=7.91 Hz), 3.42 (dd, 1H, *J*=3.92 and 14.8 Hz), 3.20 (dd, 1H, *J*=4.62 and 14.8 Hz), 2.56—2.53 (m, 1H), 2.45 (s, 3H), 2.03 (s, 3H), 1.31 (s, 3H), 1.24 (s, 3H), 0.89 (t, 3H, *J*=7.33 Hz). The diastereomeric mixture was converted to **12b** by deacetylation (K_2CO_3, MeOH, 0 °C, 1.5 h; 98% yield), and its spectral data agreed completely with those of the above **12b**.

14c: A colorless oil; a diastereomeric mixture (*anti* : *syn*= 95 : 5); IR (neat) 3500, 1723, 1595, 1280, 1140, 1080 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) of *anti*-**14c**: δ=7.84 (d, 2H, *J*=8.24 Hz), 7.38 (d, 2H, *J*=7.91 Hz), 4.83 (d-like, 1H, *J*=9.90 Hz), 3.40 (dd, 1H, *J*=4.61 and 14.8 Hz), 3.33 (dd, 1H, *J*=3.62 and 14.8 Hz), 2.56 (t-like, 1H, *J*=3.96 Hz), 2.47 (s, 3H), 1.99 (s, 3H), 1.97—1.83 (m, 1H), 1.60—1.50 (broad, 1H, OH), 1.36 (s, 3H), 1.02 (s, 3H), 1.01 (d, 3H, *J*=6.59 Hz), 0.85 (d, 3H, *J*=6.60 Hz); the signal of ^{1}H NMR of *syn*-**14c**: δ=2.08 (s, 3H), 1.31 (s, 3H), 1.22 (s, 3H),

0.98 (d, 3H, J=6.59 Hz), 0.88 (d, 3H, J=6.59 Hz). Anal. Calcd for $C_{18}H_{28}O_5S$: C, 60.65; H, 7.92%. Found: C, 60.82; H, 7.97%.

Preparation of (*Z*)-2a. Typical Procedure.[17] Pyridinium chlorochromate (1.86 g, 8.61 mmol) was ground with silica gel (1.86 g) in a mortar. The resulting light-orange solid was suspended in CH_2Cl_2 (30 mL). (*E*)-**2a** (1.30 g, 5.74 mmol) was added in one portion to the suspension. The mixture was sonicated at room temperature for 2 h. After ether (30 mL) was added, a brown suspension was filtered off through celite and washed with ether. The filtrate was concentrated in vacuo, purified by column chromatography on silica gel (hexane/ethyl acetate, 6 : 1 to 3 : 1) and recrystallization from hexane–CH_2Cl_2 to afford (*E*)-4-(*p*-tolylsulfonyl)-3-beten-2-one (914 mg, 71% yield) as colorless crystals: Mp 46.5—51.0 °C (hexane–CH_2Cl_2); IR (KBr) 3050, 1690, 1590, 1280, 1140, 1080 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.80 (d, 2H, J=8.24 Hz), 7.38 (d, 2H, J=7.91 Hz), 7.13 (d, 1H, J=15.5 Hz), 7.13 (d, 1H, J=15.5 Hz), 2.47 (s, 3H), 2.35 (s, 3H). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39%. Found: C, 59.06; H, 5.36%.

A solution of (*E*)-4-(*p*-tolysulfonyl)-3-buten-2-one (100 mg, 0.46 mmol) in $CHCl_3$ (25 mL) was irradiated with a 100-W high-pressure Hg arc lamp (Pyrex filter) under bubbling a N_2 for 4 h. Evaporation gave a mixture of (*E*)- and (*Z*)-isomers (9 : 91) of 4-(*p*-tolysulfonyl)-3-buten-2-one, which was separated by preparative HPLC (YMC-Pack column; hexane/ethyl acetate, 1.5 : 1) to give (*Z*)-4-(*p*-tolylsulfonyl)-3-buten-2-one (80 mg, 80% yield) as a colorless oil: IR (neat) 1710, 1350, 1300, 1160, 1135, 1080 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.81 (d, 2H, J=8.57 Hz), 7.36 (d, 2H, J=8.24 Hz), 6.56 (d, 1H, J=12.9 Hz), 6.36 (d, 1H, J=12.9 Hz), 2.51 (s, 3H), 2.45 (s, 3H). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39%. Found: C, 59.20; H, 5.30%.

To a solution of (*Z*)-4-(*p*-tolylsulfonyl)-3-buten-2-one (185.5 mg, 0.83 mmol) in methanol (8.0 mL) were added $CeCl_3 \cdot 7H_2O$ (369 mg, 0.99 mmol) and $NaBH_4$ (33.0 mg, 0.87 mmol), and the resulting mixture was then stirred at the same temperature for 10 min. After the addition of water (5 mL), the aqueous layer was extracted with ether (10 mL×3). The combined organic layers were dried over $MgSO_4$, evaporated, and purified by column chromatography on silica gel (hexane/ethyl acetate, 3 : 1 to 2 : 1) to afford (*Z*)-**2a** (171 mg, 91% yield) as a colorless oil: IR (neat) 3450, 1440, 1360, 1290, 1140, 1080 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.80 (d, 2H, J=8.57 Hz), 7.36 (d, 2H, J=7.91 Hz), 6.24 and 6.20 (AB system, 2H, J=11.6 Hz), 5.39 (ddq, 1H, J=1.65, 3.96, and 6.23 Hz), 2.75 (d, 1H, J=1.65 Hz, OH), 2.45 (s, 3H), 1.35 (d, 3H, J=6.26 Hz). Anal. Calcd for $C_{11}H_{14}O_3S \cdot 0.10H_2O$: C, 57.92; H, 6.27%. Found: C, 57.99; H, 6.35%.

(*Z*)-13a: Colorless crystals; mp 50.5—52.0 °C (hexane–CH_2Cl_2); IR (KBr) 1718, 1629, 1302, 1240, 1142, 1039 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.90 (d, 2H, J=8.24 Hz), 7.36 (d, 2H, J=8.24 Hz), 6.42 (quintet, 1H, J=6.59 Hz), 6.18 (dd, 1H, J=0.66 and 11.5 Hz), 6.10 (dd, 1H, J=7.59 and 11.2 Hz), 2.44 (s, 3H), 2.04 (s, 3H), 1.48 (d, 3H, J=6.59 Hz). Anal. Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01%. Found: C, 58.18; H, 5.88%.

(*Z*)-2b: A colorless oil; IR (neat) 3450, 1622, 1595, 1298, 1141, 1082 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.80 (d, 2H, J=8.43 Hz), 7.36 (d, 2H, J=8.06 Hz), 6.31 (dd, 1H, J=1.10 and 11.4 Hz), 6.31 (dd, 1H, J=8.06 and 11.4 Hz), 5.12 (q-like, 1H, J=7.01 Hz), 2.67 (br, 1H, OH), 2.45 (s, 3H), 1.71—1.54 (m, 2H), 0.97 (t, 3H, J=7.33 Hz). Anal. Calcd for $C_{12}H_{16}O_3S \cdot 0.09H_2O$: C, 59.59, H, 6.74%. Found: C, 59.59; H, 6.71%.

(*Z*)-13b: Colorless crystals; mp 81.5—82.5 °C (hexane–CH_2Cl_2); IR (KBr) 2980, 1720, 1290, 1230, 1140, 1080 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.91 (d, 2H, J=8.24 Hz), 7.36 (d, 2H, J=7.91 Hz), 6.30 (ddt, 1H, J=0.99, 7.91, and 8.24 Hz), 6.21 (dd, 1H, J=0.99 and 8.24 Hz), 6.05 (dd, 1H, J=0.99 and 11.2 Hz), 2.44 (s, 3H), 2.06 (s, 3H), 1.83 (dq, 2H, J=6.92 and 7.58 Hz), 1.03 (t, 3H, J=7.58 Hz). Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43%. Found: C, 59.44; H, 6.34%. A single crystal for X-ray crystallographic analysis was obtained by recrystallization from a mixture of hexane and CH_2Cl_2.

(*Z*)-2c: A colorless oil; IR (neat) 3500, 1625, 1460, 1300, 1143, 1083 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.81 (d, 2H, J=8.57 Hz), 7.36 (d, 2H, J=7.91 Hz), 6.33 (dd, 1H, J=0.66 and 11.5 Hz), 6.22 (dd, 1H, J=8.57 and 11.5 Hz), 4.94 (dd-like, 1H, J=7.25 and 8.57 Hz), 2.80—2.50 (br, 1H, OH), 2.45 (s, 3H), 1.90—1.72 (m, 1H), 0.99 (s, 3H), 0.90 (s, 3H). Anal. Calcd for $C_{13}H_{18}O_3S \cdot 0.12H_2O$: C, 60.87; H, 7.17%. Found: C, 60.90; H, 7.20%.

(*Z*)-13c: Colorless crystals; mp 62.0—62.6 °C (hexane–ether–CH_2Cl_2); IR (KBr) 1721, 1629, 1364, 1312, 1238, 1142 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=7.93 (d, 2H, J=8.57 Hz), 7.36 (d, 2H, J=7.91 Hz), 6.25 (ddd, 1H, J=0.99, 5.28, and 8.90 Hz), 6.24 (dd, 1H, J=0.99 and 11.5 Hz), 6.02 (dd, 1H, J=8.90 and 11.5 Hz), 2.43 (s, 3H), 2.16—2.09 (m, 1H), 2.06 (s, 3H), 1.04 (s, 3H), 1.02 (s, 3H). Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.78; H, 6.80%. Found: C, 61.15; H, 6.97%.

Photochemical Addition of 2-Propanol to (*Z*)-2a. A distereomeric mixture (*syn* : *anti*=91 : 9) of **12a** (91 mg, 63% yield) was obtained by the irradiation of (*Z*)-**2a** (115 mg, 0.51 mmol) and benzophenone (185.6 mg, 1.02 mmol) in 2-propanol (25 mL) for 4 h. (*Z*)-**2a** (20 mg, 17%) was also recovered.

Photochemical Addition of 2-Propanol to (*Z*)-2b. A diastereomeric mixture (*syn* : *anti*=79 : 21) of **12b** (117.4 mg, 77% yield) was obtained by the irradiation of (*Z*)-**2b** (122 mg, 0.51 mmol) and benzophenone (185.2 mg, 1.02 mmol) in 2-propanol (25 mL) for 4.3 h. (*Z*)-**2b** (17.4 mg, 14%) was also recovered.

Photochemical Addition of 2-Propanol to (*Z*)-2c. A diastereomeric mixture (*syn* : *anti*=69 : 31) of **12c** (93.3 mg, 59% yield) was obtained by the irradiation of (*Z*)-**2c** (127 mg, 0.50 mmol) and benzophenone (182.2 mg, 1.00 mmol) for 4.5 h. (*Z*)-**2c** (14.1 mg, 11%) was also recovered.

Photochemical Addition of 2-Propanol to (*Z*)-13a. In a similar manner to the described above experiments, a solution of (*Z*)-**13a** (138 mg, 0.51 mmol) and benzophenone (186.7 mg, 1.02 mmol) in 2-propanol (25 mL) was irradiated at room temperature for 4.5 h. The usual workup gave a diastereomeric mixture (*syn* : *anti*= 72 : 28) of **14a** (128 mg, 76% yield). (*Z*)-**13a** (20 mg, 14%) was recovered.

Photochemical Addition of 2-Propanol to (*Z*)-13b. Similarly, a diastereomeric mixture (*syn* : *anti*=69 : 31) of 4-acetoxy-2-methyl-[(*p*-tolylsulfonyl)methyl]-2-hexanol (**14b**) (120 mg, 70% yield) was obtained by the irradiation of a solution of (*Z*)-**13b** (141 mg, 0.50 mmol) and benzophenone (91 mg) in 2-propanol (25 mL) for 7 h. Two 91 mg-portions of benzophenone were added after irradiation for 2 h and 4 h. (*Z*)-**13b** (14.4 mg, 10%) was also recovered.

Photochemical Addition of 2-Propanol to (*Z*)-13c. Similarly, a diastereomeric mixture (*syn* : *anti*=43 : 57) of 4-acetoxy-2,5-dimethyl-3-[(*p*-tolylsulfonyl)methyl]-2-hexanol (**14c**) (74.7 mg, 43% yield) was obtained after the irradiation of a solution of (*Z*)-**13c** (155 mg, 0.52 mmol) and benzophenone (94.7 mg×3) in 2-propanol (25 mL) for 7 h. (*Z*)-**13c** (68 mg, 52%) was also recovered.

Preparation of (*E*)-4-(Methylsulfonyl)-3-buten-2-ol [(*E*)-15]. To a solution of (methylsulfinyl)methyl methyl sulfone (1.07 g, 6.84 mmol) and piperidine (1.45 mL, 13.7 mmol) in a mixture of methanol (7 mL) and acetonitrile (33 mL), was dropwise added propion-

aldehyde (0.99 mL, 13.7 mmol) at room temperature. The mixture was stirred at room temperature for 20 h. After evaporation of the solvent in vacuo, the resulting mixture was diluted with ether (30 mL) and then washed with a 4 M HCl solution. The aqueous layer was extracted with successively ether (30 mL×2), ethyl acetate (30 mL×2), and CH_2Cl_2 (30 mL×2). The combined extracts were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 2 : 1 to 1 : 2) to afford **15** (324 mg, 31% yield) as colorless crystals: Mp 67.0—68.0 °C (hexane–ethyl acetate); IR (KBr) 3445, 1630, 1297, 1129, 976, 836 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=6.96 (dd, 1H, J=3.63 and 15.2 Hz), 6.66 (dd, 1H, J=1.98 and 15.2 Hz), 4.58 (ddq, 1H, J=1.98, 3.63, and 6.59 Hz), 2.96 (s, 3H), 2.40—1.84 (br, 1H, OH), 1.38 (d, 3H, J=6.59 Hz). Anal. Calcd for $C_5H_{10}O_3S$: C, 39.98; H, 6.71%. Found: C, 39.76; H, 6.71%.

Photochemical Addition of 2-Propanol to (*E*)-4-(Methylsulfonyl)-3-buten-2-ol [(*E*)-15]. In a similar manner to photoreaction of (*E*)-**2a**, a solution of (**15**) (150 mg, 1.00 mmol) and benzophenone (182 mg, 1.00 mmol) in 2-propanol (70 mL) was irradiated at room temperature for 2.5 h. After an additional one molar amount of benzophenone was added, irradiation was then continued for 3 h. After evaporation in vacuo, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 1 : 3) and preparative HPLC (GPC, $CHCl_3$ as an eluent) to afford a diastereomeric mixture (*anti* : *syn*=77 : 23) of 3-hydroxy-2-(1-hydroxyethyl)-3-methylbutyl methyl sulfone (**16**) (71.8 mg, 34% yield) as a colorless viscous oil and the starting (*E*)-**15** was also recovered (63.8 mg, 42% recovered yield). **16**: A colorless viscous oil; IR (neat) 3430, 2990, 1382, 1296, 1133, 1052 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) of *anti*-**16**: δ=4.41 (dq, 1H, J=1.98 and 6.59 Hz), 3.38 (d, 2H, J=3.96 Hz), 3.09 (s, 3H), 2.50—2.00 (br, 2H, OH), 2.01 (dt, 1H, J=1.98 and 4.29 Hz), 1.39 (s, 3H), 1.33 (s, 3H), 1.28 (d, 3H, J=6.26 Hz); ^1H NMR of *syn*-**16**: δ=4.17 (dq, 1H, J=4.29 and 6.27 Hz), 3.35 (dd, 1H, J=3.63 and 14.5 Hz), 3.18 (dd, 1H, J=6.26 and 14.5 Hz), 3.09 (s, 3H), 2.50—2.00 (br, 2H, OH), 2.01 (ddd, 1H, J=3.63, 6.26, and 7.91 Hz), 1.35 (s, 3H), 1.28 (s, 3H), 1.29 (d, 3H, J=6.26 Hz). The diastereomeric mixture were subjected to elemental analysis. Anal. Calcd for $C_8H_{18}O_4S$: C, 45.69; H, 8.63%. Found: C, 45.89; H, 8.62%.

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15) (*E*)-**2** was easily synthesized by Knoevenagel condensations of (methylsulfinyl)methyl *p*-tolyl sulfone with an appropriate aldehyde using piperidine. (*E*)-**13** was prepared by an acetylation of (*E*)-**11** with Ac_2O and pyridine. See Experimental Section.

16) The data for determining the structures of **12** and **14** were given in our previous reports.[8)]

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20) Important torsion angles (degree): H_β–C_β–C_γ–H_γ=−77.8, H_β–C_β–C_γ–C_a = 45.1, H_β–C_β–C_γ–O_3 = 165.7, O_1–S–C_α–C_β = −11.4, C_b–S–C_α–C_β = −127.7, H_α–C_α–C_β–H_β=−177.6.

21) (*E*)-**2** and (*E*)-**13** also exhibited small coupling constants (4.60—5.60 Hz) between H_β and H_γ, indicating that their conformations around C_β–C_γ bond are almost similar. a) M. Karplus, *J.*

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