Photo-Induced Intermolecular Radical β-Addition to Chiral α-(Arylsulfinyl) Enones

Nobuyuki Mase, Yoshihiko Watanabe, and Takeshi Toru*

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555

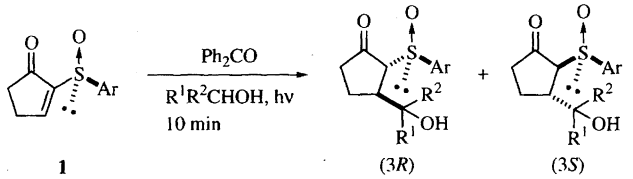
(Received July 17, 1998)

The reactions of α-(arylsulfinyl) enones with alkyl radicals having a hydroxy or acetal group were examined under photo-irradiation in the presence of benzophenone. High diastereoselectivity was observed in the photo-induced radical reaction of 2-(arylsulfinyl)-2-cyclopentenones having a bulky aryl group, such as the 2,4,6-triisopropylphenyl or 2,4,6-trimethylphenyl group. The photo-induced reaction of 3-[(2,4,6-triisopropylphenyl)sulfinyl]-3-pentene-2-one in 1,3-dioxolane also gave a single diastereomer of the 1,3-dioxolan-2-yl adduct.

A number of radical-mediated stereoselective reactions have provided synthetically useful methods.[1] In order to extend the synthetic utility of intermolecular radical reactions, it is important to develop new stereoselective reactions of radicals containing functional groups. From this point of view, the photo-induced radical reaction performed in alcohols[2] or in 1,3-dioxolane[3] is an attractive radical reaction. Indeed, several studies leading to high 1,2-asymmetric induction have been reported in the photo-induced radical reactions of α,β-unsaturated carbonyl compounds[4] and acyclic vinylsulfones.[5] Previously, we showed a highly efficient role of the bulky arylsulfinyl groups in the 1,3-asymmetric induction in the Et_3B-induced alkyl radical addition to 2-(arylsulfinyl)-2-cyclopentenones,[6] but, unfortunately, we failed to extend this reaction to acyclic α-(arylsulfinyl) enones, because a facile formation of the Pummerer-type rearranged products compensated the chiral center first formed via the radical addition.[7] We now report herein on a stereoselective reaction of chiral 2-(arylsulfinyl)-2-cyclopentenones **1** as well as 3-(arylsulfinyl)-3-penten-2-ones **26** with functionalized alkyl radicals generated by photo-irradiation in the presence of benzophenone.

Results and Discussion

First, we examined the reaction of 2-(arylsulfinyl)-2-cyclopentenones[6a] **1a—c** with 1-(hydroxyalkyl) radicals generated under photo-irradiation. A degassed solution (0.01 mol dm^{-3}) of **1** and benzophenone (1.0 equiv) as a sensitizer[8] in an alcohol was irradiated with a high-pressure mercury lamp (100 W) equipped with a water-cooled Pyrex jacket. The results are given in Table 1. All of the reactions completed within 10 min to give addition products **2—8** in high yields. Reactions of (*S*)-2-(*p*-tolylsulfinyl)-2-cyclopentenone (**1a**) gave an addition product with low diastereoselectivity in a ratio of 53 : 47 in methanol (Entry 1) and 70 : 30 in 2-propanol (Entry 2). The low stereochemical outcome is in accord with previous observations in the β-addition of alkyl radicals to **1a**.[6] On the other hand, both reactions of (*S*)-2-[(2,4,6-trimethylphenyl)sulfinyl]-2-cyclopentenone (**1b**) in methanol and in 2-propanol gave addition products comprising of a single diastereomer (Entries 5 and 6). The reaction in ethanol also showed a complete selection on the olefin face of the substrate, but gave a diastereomeric mixture resulting from the low face selection on the 1-hydroxyethyl radical (Entry 7).[9] As expected, the reactions of (*S*)-2-[(2,4,6-triisopropylphenyl)sulfinyl]-2-cyclopentenone (**1c**) also gave addition products with complete face selec-



a : Ar = *p*-tolyl
b : Ar = 2,4,6-trimethylphenyl
c : Ar = 2,4,6-triisopropylphenyl

2, 4, 7 : $R^1 = R^2 = H$
3, 5, 8 : $R^1 = R^2 = Me$
6 : $R^1 = H$, $R^2 = Me$

Table 1. Photo-Induced Radical β-Addition to 2-(Arylsulfinyl)-2-cyclopentenones **1** in Alcohols[a]

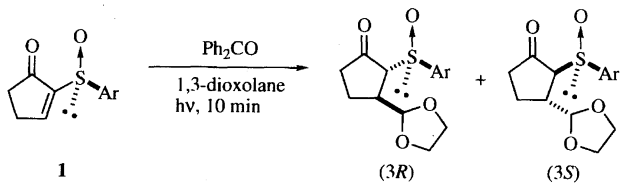
Entry	Enone	Alcohol	Product	Yield (%)[b]	(3*R*) : (3*S*)[c]
1	**1a**	MeOH	**2**	93	53 : 47
2	**1a**	*i*-PrOH	**3**	99	70 : 30
3[d]	**1a**	*i*-PrOH	**3**	98	68 : 32
4[e]	**1a**	*i*-PrOH	**3**	92	68 : 32
5	**1b**	MeOH	**4**	75	>98 : 2
6	**1b**	*i*-PrOH	**5**	99	>98 : 2
7	**1b**	EtOH	**6**	97	>98 : 2[f]
8	**1c**	MeOH	**7**	96	>98 : 2
9	**1c**	*i*-PrOH	**8**	99	>98 : 2

a) The reaction was carried out using 1.0 equiv of Ph_2CO unless otherwise noted. b) Isolated yield. c) The ratio was determined by the ^1H NMR spectrum. d) Ph_2CO (0.5 equiv) was used. e) Ph_2CO (0.1 equiv) was used. f) A mixture of two diastereomers was obtained in a ratio of 56 : 44.

tivity in methanol as well as in 2-propanol (Entries 8 and 9).

Complete diastereoselection was observed in the reactions of **1b** and **1c** with an 1,3-dioxolan-2-yl radical generated from 1,3-dioxolane upon benzophenone-sensitized photoirradiation. Thus, a solution of **1** in 1,3-dioxolane (0.01 mol dm^{-3}) was irradiated in the presence of benzophenone (1.0 equiv) to give 2-(arylsulfinyl)-3-(1,3-dioxolan-2-yl)-2-cyclopentanones **9**—**11**. The results are given in Table 2. All of the reactions completed within 10 min, and gave addition products **9**—**11** in high yields. The reaction of **1a** gave the addition product **9** in a ratio of 65 : 35, whereas reactions of **1b** and **1c** afforded the corresponding addition products **10** and **11** with complete diastereoselectivity.

As shown in Fig. 1, an X-ray crystallographic analysis[10] of 2-[(2,4,6-trimethylphenyl)sulfinyl]-2-cyclopentenone (**1b**) reveals that the olefin face is effectively shielded by a methyl group on the phenyl, where the carbonyl and sulfoxide oxygens are placed in an antiperiplanar orientation. The distance between the methyl proton and the β-proton on the cyclopentenone ring is 2.67 Å. A NMR study supported this structure in solution by a significant nuclear Overhauser effect (9%) between these protons. Since the transition state of the radical addition to a double bond is assumed to be reactant-like,[11] these data show that 1-(hydroxyalkyl) and 1,3-dioxolan-2-yl radicals approach preferentially from one of the olefin faces in the cyclopentenone ring opposite to the face shielded by the arylsulfinyl group.



a : Ar = *p*-tolyl
b : Ar = 2,4,6-trimethylphenyl
c : Ar = 2,4,6-triisopropylphenyl

Table 2. Photo-Induced Radical β-Addition to 2-(Arylsulfinyl)-2-cyclopentenones **1** in 1,3-Dioxolane

Entry	Enone	Product	Yield (%)[a]	(3*R*) : (3*S*)[b]
1	**1a**	**9**	96	65 : 35
2	**1b**	**10**	95	>98 : 2
3	**1c**	**11**	97	>98 : 2

a) Isolated yield. b) The ratio was determined by the ^{1}H NMR spectrum.

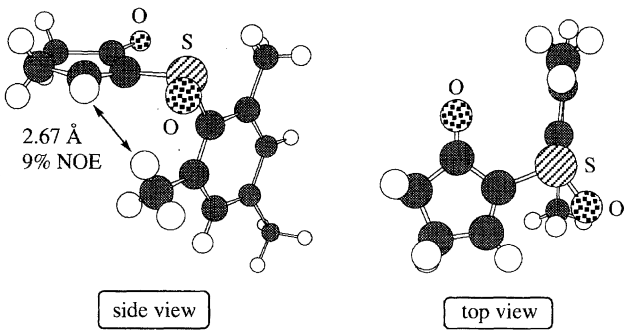
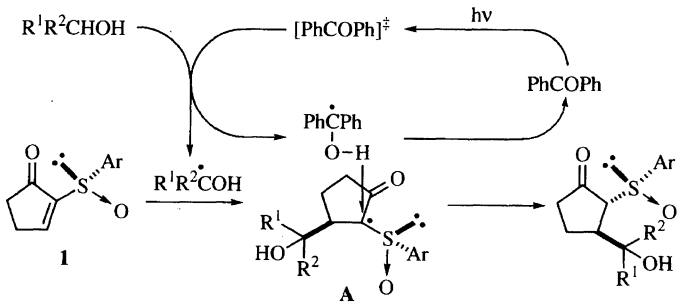


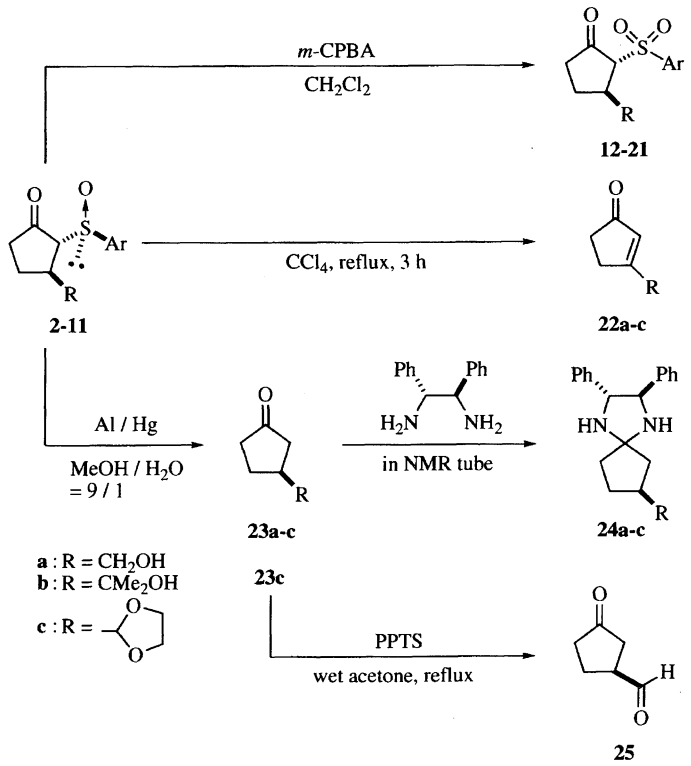
Fig. 1. Chem 3D representation of X-ray structure of **1b**.

Scheme 1 shows an assumed reaction mechanism[12] in the presence reaction. A 1-(hydroxyalkyl) radical generated from an alcohol by abstraction of a hydrogen with the ^{3}(n, π*) state of benzophenone attacks the olefinic carbon β to the carbonyl to form the intermediate radical **A**. The bulky aryl substituent on the sulfinyl group in radical **A** would be arranged at a position opposite to the added alkyl group by avoiding a steric interaction, and the transfer of a hydrogen from the hydroxydiphenylmethyl radical occurs from the side opposite to the aryl group to give trans compounds. It is known that benzophenone is regenerated via dehydrogenation from the hydroxydiphenylmethyl radical.[12] We also observed that a high yield of the addition product was obtained in the presence of 0.5 or 0.1 equiv of benzophenone (Table 1, Entries 3 and 4). It should be noted that the present reaction of 2-(arylsulfinyl)-2-cyclopentenones **1** proceeded quite smoothly and completed within 10 min, even in the presence of a catalytic amount of benzophenone, as compared with the results of the reaction of 2-cyclopentenone (2-propanol, 1 h, 57%; methanol, 2 h, 87%; 1,3-dioxolane, 2 h, 88%); furthermore, the reaction of 2-cyclohexenone has been reported to give addition products in low yield in methanol or ethanol after 24 h of photo-irradiation.[4e,4f]

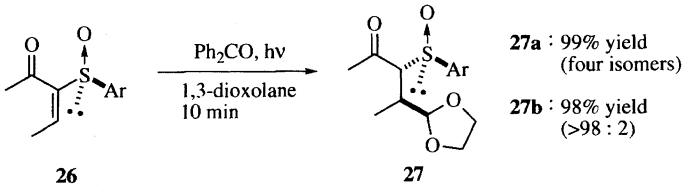
The stereochemistry of addition products **2**—**11** was determined as follows (Scheme 2). In addition to the fact that the oxidation of a mixture of diastereomers **2**—**11** with *m*-chloroperbenzoic acid (*m*-CPBA) gave a single diastereomer of sulfones **12**—**21**, the *trans* configuration of the addition products **2**—**11** was chemically confirmed by a facile *syn*-elimination[13] of the sulfenic acid to 3-alkyl-2-cyclopentenones **22** by heating at reflux in CCl_4. The addition products **2**—**11** were subjected to desulfurization[14] with



Scheme 1.



Scheme 2.



Scheme 3.

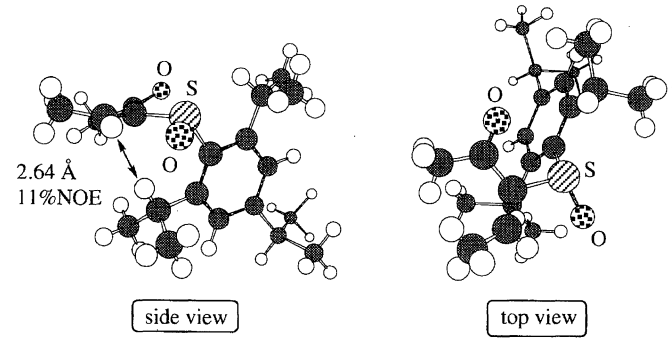
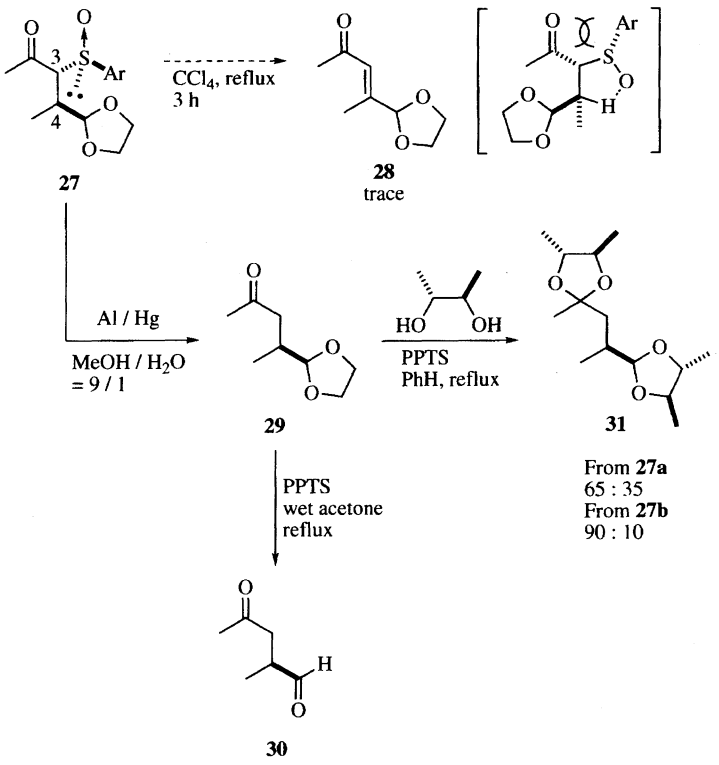


Fig. 2. Chem 3D representation of the X-ray structure of **26b**.

aluminum amalgam to give 3-alkyl-1-cyclopentanones[15] **23a—c**. The absolute configuration of 3-(1,3-dioxolan-2-yl)-1-cyclopentanone (**23c**) was determined by comparing of the value of the optical rotation of 3-oxocyclopentanecarboxaldehyde (**25**), obtained by deacetalization[16] with pyridinium *p*-toluenesulfonate (PPTS) at reflux in wet acetone, with the known value[17] for the (*R*)-isomer. Other 3-(hydroxyalkyl)-1-cyclopentanones **23a—b** were deduced to have the same stereochemistry at the 3-position as **23c**. The absolute configuration of **23a—c** was further confirmed by ^{13}C NMR analyses of the aminals **24a—c**, produced upon the treatment of **23a—c** with (1*R*,2*R*)-1,2-diphenylethylenediamine in a NMR tube.[18] The ^{13}C NMR spectra of aminals **24a—c** showed chemical shifts having consistency with the general tendency in the change of the chemical shifts differentiating (*R*)-3-alkyl-1-cyclopentanones from the (*S*)-



Scheme 4.

Table 3. Crystallographic Data of **1b** and **26b**

	1b	**26b**
Chemical formula	$C_{14}H_{16}O_2S$	$C_{20}H_{30}O_2S$
Formula weight	248.34	334.52
Crystal dimensions/mm	$0.20 \times 0.20 \times 0.30$	$0.20 \times 0.10 \times 0.30$
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$ (#19)	$P2_1$ (#4)
a/Å	14.474(1)	9.458(4)
b/Å	16.280(1)	11.333(5)
c/Å	5.491(1)	9.754(3)
α/°	90.000(0)	90.000(0)
β/°	90.000(0)	108.59(3)
γ/°	90.000(0)	90.000(0)
V/Å^3	1293.8(2)	991.10(7)
Z	4	2
D_{calcd}/g cm^{-3}	1.275	1.121
μ(Cu $K\alpha$)/cm^{-1}	21.170	14.930
Radiation	Cu $K\alpha$ (λ = 1.5418 Å)	Cu $K\alpha$ (λ = 1.5418 Å)
T/K	296	296
Computer program	teXsan	teXsan
Structure solution	Direct method	Direct method
No. of measured reflections	1109	1713
No. of unique reflections	1079	1570
No. of observations ($I > 3\sigma(I)$)	1026	1514
No. of variables	218	327
Refinement	Full matrix	Full matrix
R; R_w	0.048; 0.068	0.051; 0.035

isomers.[18] The chemical shifts of the C7 carbons appeared at δ = 38.15, 46.76, and 40.61 for (7*S*)-**24a**, (7*S*)-**24b**, and (7*S*)-**24c**, whereas the corresponding carbons appeared at lower fields, such as at δ = 39.78, 48.30, and 41.05 for (7*R*)-**24a**, (7*R*)-**24b**, and (7*R*)-**24c**, respectively. From these results, the addition products **2**—**11** were determined to have the (2*R*, 3*R*, S_S)-configuration.

The high stereoselection observed in the reaction of 2-(arylsulfinyl)-2-cyclopentenones **1** with 1-(hydroxyalkyl) and 1,3-dioxolan-2-yl radicals prompted us to study the

photo-induced radical reaction of acyclic α-(arylsulfinyl) enones **26**. Previously, we had shown that the addition of alkyl radicals, generated from alkyl iodide and triethylborane, to **26** did not afford the desired addition products in high yield, but mainly gave unexpected Pummerer-type rearrangement products, which were formed via alkyl radical addition followed by the formation of the cyclic boronenolate.[7] We attempted reactions of **26** under various radical reaction conditions; e.g., Bu_3SnH/*t*-BuI/$(Bu_3Sn)_2$/$h\nu$; Bu_3SnH/*t*-BuI/AIBN/heat; the thiohydroxamate method; *t*-BuHgCl/$NaBH_4$, etc. We, however, failed to produce any radical addition products by all these methods. We were pleased to find that the photo-induced radical reaction of (*S*,*E*)-3-(*p*-tolylsulfinyl)-3-pentene-2-one (**26a**) in 1,3-dioxolane afforded addition product **27a** in 99% yield.[19] The product was comprised of a mixture of four diastereomers, as in the reaction of **26a**. Surprisingly, the reaction of (*S*,*E*)-3-[(2,4,6-triisopropylphenyl)sulfinyl]-3-penten-2-one (**26b**) gave the addition product **27b** in 98% yield as a single diastereomer (> 98 : 2), which was confirmed by the ^{1}H and ^{13}C NMR spectra (Scheme 3).

The stereochemistry of **27b** was in accord with that expected from a mechanistic consideration on the basis of a X-ray analysis and a ^{1}H NMR study of **26b**. As shown in the X-ray diagram of **26b** (Fig. 2), it is amazing that even in the acyclic α-(arylsulfinyl) enone **26b** the carbonyl and sulfinyl groups are arranged in an antiperiplanar orientation, and the carbonyl and the double bond have a *s-trans* configuration, where the olefin face is effectively shielded by one of the *o*-isopropyl groups on the phenyl. The distance between the isopropyl methine proton and the β-proton was 2.64 Å, and a significant nuclear Overhauser effect (11%) was observed between these protons in the ^{1}H NMR spectrum. The structure informed by these analyses was substantially similar to that of 2-(arylsulfinyl)-2-cyclopentenones **1**, showing the critical role of the dipole–dipole interaction between the carbonyl and sulfinyl groups in fixing the conformation. From the above observations, it is likely that the 1,3-dioxolan-2-yl radical attacks the olefinic carbon from the *Si* face.

The stereochemistry was determined in a similar way to the cyclic system mentioned before (Scheme 4). The *anti* configuration between the acetyl group and the sulfinyl oxygen of **27b** was deduced from the chemical reactivity for the *syn*-elimination of sulfenic acid,[20] where only a trace amount of the 4-alkyl-3-penten-2-one **28** was formed at reflux in CCl_4, a large amount of **27b** being recovered (93% yield). A model study showed a strained transition-state structure for *syn* elimination from *anti*-**27b**. The addition products **27** were subjected to desulfurization[14] with aluminum amalgam to give 4-(1,3-dioxolan-2-yl)-2-pentanone **29**. The absolute configuration of **29** was determined by a comparison of the optical rotation of the corresponding aldehyde **30** with the known value[21] for (*S*)-2-methyl-4-oxopentanal. Thus, the stereochemistry of addition product **27b** was assigned to be (3*R*, 4*R*, S_S). The acetal **29** could not be transformed to the chiral aminal upon a treatment with (1*R*,2*R*)-1,2-diphenylethylenediamine.[18] A transformation of the acetal **29** derived from the diastereomerically pure **27b** into the chiral acetal **31** was attempted.[22] The acetal **29** was treated with 1 equiv of (1*R*,2*R*)-2,3-butanediol in the presence of PPTS[16] in the refluxing benzene to give a mixture of the acetals. The acetal **29** was treated with more than 2 equiv of the butanediol to afford the bisacetal **31**. The ^{13}C NMR spectrum, however, showed that **31** comprised a diastereomeric mixture in a ratio of 90 : 10, possibly due to partial racemization of **29** occurring during the acetalization under weakly acidic conditions.

In summary, highly efficient 1,3-asymmetric induction by chiral arylsulfinyl groups, such as (2,4,6-triisopropylphenyl)- and (2,4,6-trimethylphenyl)sulfinyl groups, was achieved in benzophenone-sensitized photo-induced radical reactions in alcohols and in 1,3-dioxolane. The bulkyl arylsulfinyl groups having ortho substituents effectively shield the olefin face, not only in the 2-(arylsulfinyl)-2-cyclopentenones, but also in the 3-(arylsulfinyl)-3-pentene-2- one. Since the sulfinyl groups can be removed, these reactions provide a method for preparing chiral 3-alkyl-1-cyclopentanones and 4-alkyl-2-pentanones containing a functinalized alkyl group.

Experimental

General. CH_2Cl_2 was distilled from calcium hydride. All of the reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm Merck silica gel (60F-254) precoated glass plates. TLC plates were visualized with UV light and 7% phosphomolybdic acid or *p*-anisaldehyde in ethanol. Column chromatography was carried out on a column packed with Fuji Silysia silica-gel BW-200. ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra for solutions in $CDCl_3$ were recorded on a Varian Gemini-200 instrument; the chemical shifts (δ) are expressed in ppm downfield from internal tetramethylsilane, and the *J* values are given in Hz. Infrared spectra were recorded on a JASCO FT/IR-200 spectrometer. Mass spectra (eV) were recorded on a Hitachi M-2000 spectrometer. Microanalyses were performed with a Perkin–Elmer-240. Optical rotations were measured on a JASCO DIP-4 polarimeter operating at λ = 589 nm corresponding to the sodium D line. HPLC analyses were performed on a JASCO TRI ROTOR IV using a 4.6×150 mm COSMOSIL packed column (500 μl min^{-1}).

X-Ray Crystallographic Determination of 1b and 26b. General Procedures. Diffraction data for two compounds were collected with graphite-monochromated Cu $K\alpha$ radiation on a Rigaku AFC-5R automatic four-cycle diffractometer and 2θ–ω scan mode up to 126° in 2θ at room temperature (Table 3). A structure analysis software package, called teXan,[23] with INDIGO2, was used for all computations. The structure was solved by direct methods using MITHRIL[24] in combination with difference Fourier recycling. A full-matrix least-squares refinement was carried out using ORFLS[25] with non-H atoms treated anisotropically. The ideal positions for hydrogen atoms were calculated and verified on a difference Fourier map. Then they underwent further refinement. [$R_w = \Sigma s^2(|F_o| - |F_c|)^2 / \Sigma s^2 |F_o|^2)^{1/2}$].

General Procedure for the Photo-Induced Radical β-Addition to 2-(Arylsulfinyl)-2-cyclopentenones 1. A solution of the 2-(arylsulfinyl)-2-cyclopentenone **1**[6] and benzophenone (1.0 equiv) in alcohol or in 1,3-dioxolane (0.01 mol dm^{-3}) was degassed under reduced pressure using a sonicator. The solution was irradiated for 10 min with a high-pressure mercury lamp (100 W) equipped with a Pyrex water jacket. The reaction mixture was concentrated under

vacuum to give the crude product, which was purified by column chromatography to give the addition product **2**—**11**. Diastereomeric ratios were determined by integration of the methine proton α to the sulfoxide in the ^{1}H NMR spectra. These addition products could not be stored in a freezer for a long time without decomposition, because of a facile *syn*-elimination of sulfenic acid. The spectral data concerning the addition products are listed below.

(2*R*,3*R*,*S*$_S$)- and (2*S*,3*S*,*S*$_S$)-3-(Hydroxymethyl)-2-(*p*-tolylsulfinyl)-1-cyclopentanone (2): R_f = 0.35 (hexane/ethyl acetate = 30/70); HPLC t_R = 24.84 min for (3*S*)-isomer, 28.18 min for (3*R*)-isomer (hexane/ethyl acetate = 20/80); ^{1}H NMR δ = 1.38—2.00 (m, 2H), 2.01—3.05 (m, 3H), 2.42 (s, 3H), 3.20—3.54 (m, 2H), 3.60—3.79 (m, 1H), 3.48 (d, J = 8.0 Hz, 1H for (3*S*)-isomer) and 3.94 (d, J = 9.1 Hz, 1H for (3*R*)-isomer), 7.26—7.65 (m, 4H); IR (neat) 3600—3100, 2920, 1730, 1140, 1040, 795 cm^{-1}.

(2*R*,3*R*,*S*$_S$)- and (2*S*,3*S*,*S*$_S$)-3-(1-Hydroxy-1-methylethyl)-2-(*p*-tolylsulfinyl)-1-cyclopentanone (3): R_f = 0.42 (hexane/ethyl acetate = 30/70); ^{1}H NMR δ = 1.07, 1.10 (2s, 6H for (3*S*)-isomer) and 1.19, 1.28 (2s, 6H for (3*R*)-isomer), 1.40—2.00 (m, 3H), 2.05—2.90 (m, 3H), 2.42 (s, 3H), 3.59 (d, J = 6.0 Hz, 1H for (3*S*)-isomer) and 4.09 (d, J = 8.0 Hz, 1H for (3*R*)-isomer), 7.25—7.68 (m, 4H); IR (neat) 3650—3150, 2980, 1740, 1380, 1170, 1045, 810 cm^{-1}.

(2*R*,3*R*,*S*$_S$)-3-(Hydroxymethyl)-2-[(2,4,6-trimethylphenyl)sulfinyl]-1-cyclopentanone (4): R_f = 0.10 (hexane/ethyl acetate = 50/50); ^{1}H NMR δ = 1.55—1.95 (m, 2H), 2.10—3.19 (m, 3H), 2.30 (s, 3H), 2.51 (s, 6H), 3.50—3.70 (m, 1H), 3.52 (dd, J = 6.3, 10.7 Hz, 1H), 3.63 (dd, J = 5.3, 10.7 Hz, 1H), 3.66 (d, J = 5.7 Hz, 1H), 6.86 (s, 2H); IR (neat) 3650—3150, 2930, 1740, 1450, 1130, 740 cm^{-1}.

(2*R*,3*R*,*S*$_S$)-3-(1-Hydroxy-1-methylethyl)-2-[(2,4,6-trimethylphenyl)sulfinyl]-1-cyclopentanone (5): R_f = 0.33 (hexane/ethyl acetate = 50/50); ^{1}H NMR δ = 1.19 and 1.28 (2s, 6H), 1.50—2.01 (m, 2H), 2.11—2.89 (m, 4H), 2.30 (s, 3H), 2.46 (s, 6H), 3.54 (d, J = 5.2 Hz, 1H), 6.86 (s, 2H); IR (neat) 3600—3100, 2980, 1740, 1470, 1155, 1060, 1005, 730 cm^{-1}.

(2*R*,3*R*,*S*$_S$)-3-(1-Hydroxyethyl)-2-[(2,4,6-trimethylphenyl)sulfinyl]-1-cyclopentanone (6): R_f = 0.19 (hexane/ethyl acetate = 50/50); HPLC t_R = 15.96 min for major, 16.97 min for minor (hexane/ethyl acetate = 30/70); ^{1}H NMR δ = 1.19 (d, J = 7.4 Hz, 3H-minor) and 1.23 (d, J = 7.2 Hz, 3H-major), 1.58—2.00 (m, 2H), 2.01—2.88 (m, 3H), 2.29 (s, 3H), 2.48 (s, 6H), 3.52—3.92 (m, 3H), 6.87 (s, 2H); IR (neat) 3650—3150, 2980, 1740, 1470, 1155, 1030, 790 cm^{-1}.

(2*R*,3*R*,*S*$_S$)-3-(Hydroxymethyl)-2-[(2,4,6-triisopropylphenyl)-sulfinyl]-1-cyclopentanone (7): R_f = 0.05 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ = 1.13—1.42 (m, 18H), 1.80—2.50 (m, 4H), 2.52—2.70 (m, 1H), 2.80—3.00 (m, 1H), 3.45—4.15 (m, 5H), 3.74 (d, J = 4.9 Hz, 1H), 7.09 (s, 2H); IR (neat) 3600—3100, 2965, 1740, 1470, 1045, 730 cm^{-1}.

(2*R*,3*R*,*S*$_S$)-3-(1-Hydroxy-1-methylethyl)-2-[(2,4,6-triisopropylphenyl)sulfinyl]-1-cyclopentanone (8): R_f = 0.18 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ = 1.10—1.40 (m, 24H), 1.85—2.50 (m, 5H), 2.62—2.75 (m, 1H), 2.80—3.00 (m, 1H), 3.45—4.15 (m, 2H), 3.65 (d, J = 4.6 Hz, 1H), 7.08 (s, 2H); IR (neat) 3600—3200, 2970, 1740, 1470, 1140, 1055, 790 cm^{-1}.

(2*R*,3*R*,*S*$_S$)- and (2*S*,3*S*,*S*$_S$)-3-(1,3-Dioxolan-2-yl)-2-(*p*-tolylsulfinyl)-1-cyclopentanone (9): R_f = 0.37 (hexane/ethyl acetate = 30/70); ^{1}H NMR δ = 1.45—2.60 (m, 4H), 2.42 (s, 3H), 2.95—3.20 (m, 1H), 3.33 (d, J = 5.0 Hz, 1H for (3*S*)-isomer), 3.65—4.10 (m, 5H including 1H for (3*R*)-isomer), 4.42 (d, J = 2.8 Hz, 1H for (3*S*)-isomer) and 4.98 (d, J = 2.9 Hz, 1H for (3*R*)-isomer), 7.23—7.56 (m, 4H); IR (neat) 2950, 2890, 1720, 1400, 1180, 1030 cm^{-1}.

(2*R*,3*R*,*S*$_S$)-3-(1,3-Dioxolan-2-yl)-2-[(2,4,6-trimethylphenyl)sulfinyl]-1-cyclopentanone (10): R_f = 0.27 (hexane/ethyl acetate = 50/50); ^{1}H NMR δ = 1.95—2.65 (m, 4H), 2.30 (s, 3H), 2.48 (s, 6H), 2.82—2.98 (m, 1H), 3.57 (d, J = 3.0 Hz, 1H), 3.75—4.08 (m, 4H), 4.87 (d, J = 3.0 Hz, 1H), 6.87 (s, 2H); IR (neat) 2960, 2890, 1730, 1450, 1135, 1045, 910, 730 cm^{-1}.

(2*R*,3*R*,*S*$_S$)-3-(1,3-Dioxolan-2-yl)-2-[(2,4,6-triisopropylphenyl)sulfinyl]-1-cyclopentanone (11): R_f = 0.22 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ = 1.09—1.40 (m, 18H), 1.93—2.60 (m, 4H), 2.63—2.79 (m, 1H), 2.80—3.00 (m, 1H), 3.45—4.15 (m, 6H), 3.73 (d, J = 2.5 Hz, 1H), 4.78 (d, J = 2.9 Hz, 1H), 7.08 (s, 2H); IR (neat) 2965, 1735, 1460, 1180, 1045, 790 cm^{-1}.

General Procedure for Oxidation of the Addition Products 2—11 to the Sulfones 12—21. To a solution of addition products **2**—**11** in CH_2Cl_2 (0.1 mol dm^{-3}) was added portionwise *m*-chloroperbenzoic acid (2 equiv) at 0 °C; the mixture was stirred for 3—5 h. The reaction mixture was then poured into a mixture of saturated $NaHSO_3$ and Et_2O. The aqueous layer was extracted with Et_2O (3 times), and the combined organic extracts were washed successively with saturated $NaHCO_3$, water, and brine. The solution was dried over $MgSO_4$ and concentrated to give the crude product, which was purified by column chromatography to give the corresponding sulfones **12**—**21**.

3-(Hydroxymethyl)-2-(*p*-tolylsulfonyl)-1-cyclopentanone (12): Yield 99%; R_f = 0.55 (hexane/ethyl acetate = 20/80); ^{1}H NMR δ = 1.58—1.89 (m, 1H), 2.09—2.60 (m, 3H), 2.47 (s, 3H), 2.98—3.26 (m, 1H), 3.70—3.80 (m, 1H), 3.73 (dd, J = 5.5, 10.9 Hz, 1H), 3.76 (d, J = 7.7 Hz, 1H), 3.91 (dd, J = 4.7 Hz, 10.9 Hz, 1H), 7.37 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H); ^{13}C NMR δ = 21.7, 23.1, 38.6, 40.2, 64.4, 71.8, 129.2, 129.8, 134.6, 145.4, 206.5; IR (neat) 3650—3200, 2955, 1750, 1600, 1405, 1305, 1150, 1090, 795 cm^{-1}; MS (EI) *m*/*z* 268 (M$^+$; 43), 237 (21), 195 (100). Found: C, 57.95; H, 5.79%. Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01%.

3-(1-Hydroxy-1-methylethyl)-2-(*p*-tolylsulfonyl)-1-cyclopentanone (13): Yield 85%; R_f = 0.58 (hexane/ethyl acetate = 60/40); ^{1}H NMR δ = 1.19, 1.34 (2s, 6H), 1.60—2.00 (m, 1H), 2.05—2.70 (m, 4H), 2.47 (s, 3H), 2.99—3.16 (m, 1H), 3.81 (d, J = 4.7, 1H), 7.38 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H); ^{13}C NMR δ = 21.7, 22.2, 25.6, 29.4, 38.4, 47.3, 71.8, 129.1, 129.8, 134.5, 145.4, 207.2; IR (neat) 3650—3200, 2980, 1750, 1600, 1305, 1150, 1090 cm^{-1}; MS (EI) *m*/*z* 296 (M$^+$; 0.6), 281 (6), 238 (57), 141 (86), 83 (100). Found: C, 60.82; H, 6.97%. Calcd for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80%.

(2*R*,3*R*)-3-(Hydroxymethyl)-2-[(2,4,6-trimethylphenyl)sulfonyl]-1-cyclopentanone (14): Yield 83%; R_f = 0.73 (hexane/ethyl acetate = 50/50); ^{1}H NMR δ = 1.58—1.89 (m, 1H), 2.09—2.70 (m, 3H), 2.32 (s, 3H), 2.59 (s, 6H), 3.10—3.38 (m, 1H), 3.70—3.80 (m, 1H), 3.73 (dd, J = 5.6, 10.6 Hz, 1H), 3.86 (d, J = 7.4 Hz, 1H), 3.79 (dd, J = 4.4, 10.6 Hz, 1H), 6.99 (s, 2H); ^{13}C NMR δ = 21.1, 22.9, 23.3, 38.9, 39.5, 64.4, 71.2, 132.4, 140.6, 143.9, 207.0; IR (neat) 3600—3200, 2930, 1750, 1605, 1310, 1145 cm^{-1}; MS (EI) *m*/*z* 296 (M$^+$; 14), 265 (90), 119 (100). Found: C, 60.58; H, 6.71%. Calcd for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80%.

(2*R*,3*R*)-3-(1-Hydroxy-1-methylethyl)-2-[(2,4,6-trimethylphenyl)sulfonyl]-1-cyclopentanone (15): Yield 92%; R_f = 0.68 (hexane/ethyl acetate = 50/50); ^{1}H NMR δ = 1.17, 1.36 (2s, 6H), 1.75—2.15 (m, 1H), 2.20—2.79 (m, 3H), 2.32 (s, 3H), 2.57 (s, 6H), 2.85—3.16 (m, 2H), 3.90 (d, J = 4.4 Hz, 1H), 6.99 (s, 2H); ^{13}C NMR δ = 21.1, 22.7, 23.0, 25.3, 29.5, 38.4, 46.9, 71.3, 72.0, 132.3, 140.7, 143.9, 207.9; IR (neat) 3600—3200, 2980, 1750, 1600, 1460, 1300, 1150, 930, 845 cm^{-1}; MS (EI) *m*/*z* 324 (M$^+$; 9),

306 (7), 248 (34), 201 (63), 166 (80), 119 (87), 83 (100). Found: C, 63.22; H, 7.71%. Calcd for $C_{17}H_{24}O_4S$: C, 62.94; H, 7.46%.

(2*R*,3*R*)-3-(1-Hydroxyethyl)-2-[(2,4,6-trimethylphenyl)sulfonyl]-1-cyclopentanone (16): Yield 86%; R_f = 0.75 (hexane/ethyl acetate = 50/50); ^{1}H NMR δ = 1.28 (t, J = 5.7 Hz, 3H-minor) and 1.29 (t, J = 6.1 Hz, 3H-major), 1.45—2.00 (m, 2H), 2.01—2.75 (m, 3H), 2.32 (s, 3H), 2.57 (s, 6H), 2.85—3.18 (m, 1H), 3.61—3.83 and 4.14—4.36 (2m, 1H), 3.87 (d, J = 5.5 Hz, 1H-major) and 3.96 (d, J = 7.7 Hz, 1H-minor), 6.98 (s, 2H); IR (neat) 3600—3200, 2970, 1745, 1605, 1460, 1385, 1300, 1130, 870 cm^{-1}; MS (EI) m/z 310 (M$^+$; 2), 266 (24), 201 (27), 119 (100). Found: C, 62.14; H, 7.35%. Calcd for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.14%.

(2*R*,3*R*)-3-(Hydroxymethyl)-2-[(2,4,6-triisopropylphenyl)sulfonyl]-1-cyclopentanone (17): Yield 79%; R_f = 0.16 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ = 1.18—1.40 (m, 18H), 1.70—2.00 (m, 1H), 2.20—2.70 (m, 3H), 2.82—3.03 (m, 1H), 3.12—3.30 (m, 1H), 3.65—4.03 (m, 4H), 7.20 (s, 2H); ^{13}C NMR δ = 23.2, 23.5, 24.5, 25.3, 29.8, 34.2, 38.8, 39.7, 64.4, 72.8, 124.2, 127.8, 151.6, 154.0, 206.9; IR (neat) 3600—3200, 2970, 1750, 1600, 1465, 1300, 1135 cm^{-1}; MS (EI) m/z 380 (M$^+$; 2), 362 (3), 307 (7), 267 (100). Found: C, 66.28; H, 8.48%. Calcd for $C_{21}H_{32}O_4S$: C, 66.28; H, 8.48%.

(2*R*,3*R*)-3-(1-Hydroxy-1-methylethyl)-2-[(2,4,6-triisopropylphenyl)sulfonyl]-1-cyclopentanone (18): Yield 82%; R_f = 0.47 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ = 1.18, 1.37 (2s, 6H), 1.27 (d, J = 6.9 Hz, 18H), 1.75—2.00 (m, 1H), 2.28—2.79 (m, 4H), 2.82—3.05 (m, 1H), 3.07—3.25 (m, 1H), 3.77—4.03 (m, 3H), 7.20 (s, 2H); ^{13}C NMR δ = 22.9, 23.5, 24.4, 25.1, 25.3, 29.5, 29.7, 34.2, 38.5, 47.2, 71.8, 72.9, 124.2, 130.8, 151.8, 154.0, 207.6; IR (neat) 3600—3200, 2970, 1750, 1600, 1465, 1300, 1135 cm^{-1}; MS (EI) m/z 408 (M$^+$; 1), 350 (36), 307 (24), 267 (100). Found: C, 67.56; H, 8.81%. Calcd for $C_{23}H_{36}O_4S$: C, 67.61; H, 8.88%.

(2*R*,3*R*)- and (2*S*,3*S*)-3-(1,3-Dioxolan-2-yl)-2-(*p*-tolylsulfonyl)-1-cyclopentanone (19): Yield 84%; R_f = 0.60 (hexane/ethyl acetate = 30/70); ^{1}H NMR δ = 1.85—2.08 (m, 1H), 2.09—2.60 (m, 3H), 2.47 (s, 3H), 3.27—3.42 (m, 1H), 3.73 (d, J = 3.4 Hz, 1H), 3.75—4.05 (m, 4H), 5.02 (d, J = 2.6 Hz, 1H), 7.37 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H); ^{13}C NMR δ = 21.2, 21.7, 36.9, 40.2, 65.2, 65.4, 70.5, 104.6, 129.1, 129.8, 134.9, 145.3, 207.3; IR (neat) 2960, 2890, 1750, 1600, 1405, 1315, 1150, 1090, 950, 915, 810, 730 cm^{-1}; MS (EI) m/z 310 (M$^+$; 0.5), 252 (6), 228 (5), 155 (51), 91 (50), 73 (100). Found: C, 57.88; H, 5.74%. Calcd for $C_{15}H_{18}O_5S$: C, 58.05; H, 5.85%.

(2*R*,3*R*)-3-(1,3-Dioxolan-2-yl)-2-[(2,4,6-trimethylphenyl)sulfonyl]-1-cyclopentanone (20): Yield 89%; R_f = 0.72 (hexane/ethyl acetate = 50/50); ^{1}H NMR δ = 1.92—2.13 (m, 1H), 2.22—2.70 (m, 3H), 2.32 (s, 3H), 2.58 (s, 6H), 3.30—3.45 (m, 1H), 3.82 (d, J = 3.1 Hz, 1H), 3.84—3.98 (m, 4H), 5.03 (d, J = 2.7 Hz, 1H), 6.98 (s, 2H); ^{13}C NMR δ = 21.1, 21.7, 22.7, 37.1, 39.7, 65.2, 65.4, 69.9, 104.8, 132.3, 140.4, 143.7, 207.9; IR (neat) 2945, 2890, 1750, 1600, 1460, 1405, 1310, 1150, 950, 850, 820, 730 cm^{-1}; MS (EI) m/z 338 (M$^+$; 13), 248 (81), 201 (46), 119 (100). Found: C, 60.41; H, 6.82%. Calcd for $C_{17}H_{22}O_5S$: C, 60.34; H, 6.55%.

(2*R*,3*R*)-3-(1,3-Dioxolan-2-yl)-2-[(2,4,6-triisopropylphenyl)sulfonyl]-1-cyclopentanone (21): Yield 86%; R_f = 0.49 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ = 1.81—1.40 (m, 18H), 1.95—2.18 (m, 1H), 2.32—2.65 (m, 3H), 2.80—3.03 (m, 1H), 3.38—3.50 (m, 1H), 3.78—4.05 (m, 7H), 5.03 (d, J = 2.6 Hz, 1H), 7.19 (s, 2H); ^{13}C NMR δ = 21.9, 23.5, 24.5, 25.2, 29.7, 34.2, 37.0, 39.8, 65.3, 71.3, 104.9, 124.1, 130.2, 151.5, 153.9, 207.8; IR (neat) 2970, 2890, 1750, 1600, 1470, 1390, 1305, 1145, 950 cm^{-1}; MS (EI) m/z 422 (M$^+$; 2), 404 (5), 307 (10), 267 (100). Found: C, 65.18; H, 8.03%. Calcd for $C_{23}H_{34}O_5S$: C, 65.37; H, 8.11%.

General Procedure for *syn*-Elimination of the Addition Products 2-11 to the 2-Cyclopentenones 22a—c. A solution of addition products **2—11** in CCl_4 (0.1 mol dm^{-3}) was refluxed for 3 h. The reaction mixture was concentrated and purified by column chromatography to give the enones **22a—c** in almost quantitative yields.

3-(Hydroxymethyl)-2-cyclopentenone (22a): R_f = 0.12 (hexane/ethyl acetate = 40/60); ^{1}H NMR δ = 1.91—3.00 (m, 5H), 4.50 (s, 2H), 6.20 (t, J = 1.6 Hz, 1H); IR (neat) 3600—3100, 2920, 1705, 1615, 1435, 1125, 910, 730 cm^{-1}; MS (EI) m/z 112 (M$^+$; 63), 70 (100). HRMS (EI) Calcd for $C_6H_8O_2$: M, 112.0524. Found: m/z 112.0547.

3-(1-Hydroxy-1-methylethyl)-2-cyclopentenone (22b): R_f = 0.19 (hexane/ethyl acetate = 40/60); ^{1}H NMR δ = 1.45—1.95 (m, 1H), 1.48 (s, 6H), 2.43—2.54 (m, 2H), 2.65—2.78 (m, 2H), 6.12 (t, J = 1.4 Hz, 1H); ^{13}C NMR δ = 27.6, 29.0, 35.6, 71.8, 127.5, 187.2, 209.7; IR (neat) 3650—3100, 2980, 1710, 1605, 1385, 1190 cm^{-1}; MS (EI) m/z 140 (M$^+$; 39), 125 (96), 97 (92), 43 (100). HRMS (EI) Calcd for $C_8H_{12}O_2$: M, 140.0837. Found: m/z 140.0939.

3-(1,3-Dioxolan-2-yl)-2-cyclopentenone (22c): R_f = 0.14 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ = 2.39—2.52 (m, 2H), 2.60—2.75 (m, 2H), 3.90—4.10 (m, 4H), 5.64 (s, 1H), 6.24 (s, 1H); ^{13}C NMR δ = 26.6, 35.1, 65.5, 100.6, 131.2, 175.0, 209.4; IR (neat) 2965, 2890, 1715, 1155, 1090 cm^{-1}; MS (EI) m/z 154 (M$^+$; 6), 126 (98), 73 (100). HRMS (EI) Calcd for $C_8H_{10}O_3$: M, 154.0630. Found: m/z 154.0648.

Determination of Enantiomeric Purity of 3-Alkyl-1-cyclopentanones 23a—c. To a solution of addition products **2—11** and a small amount of NaH_2PO_4 in a mixed solvent of MeOH and H_2O (MeOH/H_2O = 90/10) was added an excess amount of freshly prepared aluminum amalgam at room temperature to give the 3-alkyl-1-cyclopentanones **23a—c**, which were then converted to the cyclic aminals **24a—c** by mixing with (1*R*,2*R*)-1,2-diphenylethylenediamine in the NMR tubes in the presence of 4 Å molecular sieves.[18] The ^{13}C NMR spectra showed clearly separated signals of (7*R*)- and (7*S*)-isomers. Spectral data of 3-alkyl-1-cyclopentanones **23a—c** and their aminals **24a—c** are indicated below. It was difficult to completely remove the solvent from **23a—c** due to their volatility.

(*S*)-3-(Hydroxymethyl)-1-cyclopentanone (23a):[15a] R_f = 0.14 (hexane/ethyl acetate = 30/70); $[\alpha]_D^{28}$ = −44.4 (*c* 0.216, acetone); ^{1}H NMR δ = 1.52—2.63 (m, 7H), 1.73 (s, 1H), 3.69 (d, J = 5.9 Hz, 2H); IR (neat) 3700—3100, 2970, 1725, 1400, 1150, 1090, 1015 cm^{-1}.

(*S*)-3-(1-Hydroxy-1-methylethyl)-1-cyclopentanone (23b):[15b] R_f = 0.17 (hexane/ethyl acetate = 60/40); $[\alpha]_D^{27}$ = −56.9 (*c* 0.538, acetone); ^{1}H NMR δ = 1.22, 1.25 (2s, 6H), 1.46—1.93 (m, 2H), 1.95—2.48 (m, 5H), 2.22 (s, 1H); ^{13}C NMR δ = 23.8, 27.7, 28.5, 39.0, 40.0, 47.7, 70.8, 219.5; IR (neat) 3630—3200, 2980, 1725, 1380, 1170 cm^{-1}.

(*S*)-3-(1,3-Dioxolan-2-yl)-1-cyclopentanone (23c): R_f = 0.31 (hexane/ethyl acetate = 60/40); $[\alpha]_D^{27}$ = −28.6 (*c* 0.710, acetone); ^{1}H NMR δ = 1.72—2.69 (m, 7H), 3.75—4.10 (m, 4H), 4.88 (d, J = 3.9 Hz, 1H); ^{13}C NMR δ = 23.8, 37.4, 39.1, 39.6, 42.2, 65.1, 65.3, 98.3, 105.9, 218.8; IR (neat) 2960, 2890, 1730, 1415, 1130 cm^{-1}; MS (EI) m/z 156 (M$^+$; 2), 28 (100); HRMS (EI) Calcd for $C_8H_{12}O_3$: M, 156.0786. Found: m/z 156.0785.

(2*R*,3*R*,7*S*)-1,4-Diaza-7-(hydroxymethyl)-2,3-diphenylspiro[4.4]nonane ((7*S*)-24a): ^{13}C NMR δ = 25.67, 38.15, 40.67, 44.30, 66.12, 69.16, 69.68, 86.36, 106.97, 128.85, 126.98, 127.79, 128.18, 128.44, 128.58, 140.71, 141.13.

(2*R*,3*R*,7*R*)-1,4-Diaza-7-(hydroxymethyl)-2,3-diphenylspiro-[4.4]nonane ((7*R*)-24a): ^{13}C NMR δ = 26.57, 39.78, 40.78, 44.43, 66.66, 70.28, 86.61, 106.97, 126.85, 126.98, 127.79, 128.18, 128.44, 128.58, 140.44, 140.71.

(2*R*,3*R*,7*S*)-1,4-Diaza-7-(1-hydroxy-1-methylethyl)-2,3-diphenylspiro[4.4]nonane ((7*S*)-24b): ^{13}C NMR δ = 24.90, 27.78, 30.13, 40.46, 41.28, 46.76, 68.71, 70.19, 70.68, 85.91, 126.80, 127.01, 127.37, 128.11, 128.35, 128.44, 140.53, 140.95.

(2*R*,3*R*,7*R*)-1,4-Diaza-7-(1-hydroxy-1-methylethyl)-2,3-diphenylspiro[4.4]nonane ((7*R*)-24b): ^{13}C NMR δ = 25.17, 27.78, 28.76, 40.79, 42.01, 48.30, 69.38, 71.32, 86.28, 126.80, 127.01, 127.37, 128.11, 128.35, 128.44, 140.23, 140.53.

(2*R*,3*R*,7*S*)-1,4-Diaza-2,3-diphenyl-7-(1,3-dioxolan-2-yl)spiro[4.4]nonane ((7*S*)-24c): ^{13}C NMR δ = 25.17, 40.18, 40.61, 41.57, 65.01, 69.97, 70.24, 86.40, 106.97, 126.86, 126.97, 127.31, 128.16, 128.39, 128.60, 140.80, 141.25.

(2*R*,3*R*,7*R*)-1,4-Diaza-2,3-diphenyl-7-(1,3-dioxolan-2-yl)spiro[4.4]nonane ((7*R*)-24c): ^{13}C NMR δ = 25.43, 40.37, 41.05, 42.06, 65.01, 70.40, 86.65, 106.97, 126.86, 126.97, 127.31, 128.16, 128.39, 128.60, 140.38, 140.99.

(*S*)-3-Oxocyclopentanecarboxaldehyde (25).[17] To a solution of the cyclopentenone **23c** (39.9 mg, 0.256 mmol) in wet acetone (acetone 5 ml/H_2O 0.5 ml) was added pyridinium *p*-toluenesulfonate (19.3 mg, 76.8 μmol). After the reaction mixture was stirred for 5 d at reflux, it was cooled to room temperature and concentrated under reduced pressure to give the crude product, which was purified by column chromatography (silica gel, hexane/Et_2O = 90/10) to give the aldehyde **25** (11.7 mg) and the starting cyclopentenone **23c** (19.1 mg, 48%). The absolute $[\alpha]_D$ value of **25** was smaller than the one estimated as 100% ee from the reported value, probably because of its high volatility to strip off the solvent and possible partial epimerization occurring during deacetalization: R_f = 0.19 (hexane/ethyl acetate = 60/40); $[\alpha]_D^{26}$ = −35.0 (*c* 0.234, acetone) (lit,[17] $[\alpha]_D^{26}$ = +19.1 (*c* 1.00, acetone, 39% ee) for (*R*)-3-oxocyclopentanecarboxaldehyde); ^{1}H NMR δ = 1.60—2.65 (m, 6H), 3.03—3.32 (m, 1H), 9.78 (d, *J* = 1.4 Hz, 1H); IR (neat) 2975, 1730, 1405, 1165 cm^{-1}.

Radical β-Addition to the 3-(Arylsulfinyl)-3-pentene-2-ones 26. The reaction was carried out as described in the general procedure for the photo-induced radical β-addition to 2-(arylsulfinyl)-cyclopentenones **1**, using the 3-(arylsulfinyl)-3-pentene-2-ones **26**[7] to give the sulfoxides **27**.

5,5-Ethylenedioxy-4-methyl-3-(*p*-tolylsulfinyl)-2-pentanone (27a): R_f = 0.34 (hexane/ethyl acetate = 50/50); ^{1}H NMR δ = 1.05—1.53 (m, 3H), 1.65—2.68 (m, 4H), 2.41 (s, 3H), 3.60—4.10 (m, 5H), 4.75—5.13 (m, 1H), 7.20—7.60 (m, 4H); IR (neat) 2980, 2890, 1710, 1500, 1470, 1410, 1360, 1175, 1100, 1070 cm^{-1}; MS (EI) *m/z* 296 (M$^+$; 7), 279 (27), 139 (78), 91 (48), 73 (100). Found: C, 60.91; H, 6.98%. Calcd for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80%.

(3*R*,4*R*,S$_S$)-5,5-Ethylenedioxy-4-methyl-3-[(2,4,6-triisopropylphenyl)sulfinyl]-2-pentanone (27b): R_f = 0.32 (hexane/ethyl acetate = 70/30); $[\alpha]_D^{21}$ = +172 (*c* 0.306, $CHCl_3$); ^{1}H NMR δ = 1.10—1.45 (m, 21H), 1.65—1.88 (m, 1H), 2.34 (s, 3H), 2.75—2.98 (m, 1H), 3.35—3.63 (m, 1H), 3.70—3.98 (m, 4H), 4.21—4.52 (m, 1H), 4.67 (d, *J* = 3.5 Hz, 1H), 4.81 (d, *J* = 3.3 Hz, 1H), 7.01, 7.16 (2s, 2H); ^{13}C NMR δ = 11.5, 22.6, 23.2, 23.6, 25.5, 25.7, 27.3, 28.9, 34.2, 36.7, 64.8, 64.9, 71.5, 105.1, 121.6, 125.1, 131.7, 150.0, 152.1, 153.0, 203.7; IR (neat) 2960, 1720, 1600, 1470, 1360, 1270, 1120, 1050 cm^{-1}; MS (EI) *m/z* 408 (M$^+$; 6), 233 (100). Found: C, 67.69; H, 8.71%. Calcd for $C_{23}H_{36}O_4S$: C, 67.61; H, 8.88%.

Thermal Treatment of 27b to 5,5-Ethylenedioxy-4-methyl-3-penten-2-one (28). Although the addition product **27b** (4.5 mg, 11.0 μmol) was treated as in the preparation of **22a—c**, only a trace amount of the enone **28** was formed along with the recovery of the starting sulfoxide (4.2 mg, 93%). **28**: R_f = 0.36 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ = 2.09 (s, 3H), 2.24 (s, 3H), 3.90—4.10 (m, 4H), 5.18 (s, 1H), 6.38 (s, 1H); MS (EI) *m/z* 156 (M$^+$; 5), 73 (100).

Desulfurization of 27b to 5,5-Ethylenedioxy-4-methyl-2-pentanone (29). The addition product **27b** (114.8 mg, 0.281 mmol) was treated with aluminum amalgam as in the preparation of **23a—c** to give the pentanone **29** (45.9 mg). The pentanone **29** was too volatile to completely remove the solvent: R_f = 0.41 (hexane/ethyl acetate = 70/30); $[\alpha]_D^{26}$ = −6.9 (*c* 0.654, $CHCl_3$); ^{1}H NMR δ = 0.98 (d, *J* = 6.7 Hz, 3H), 2.15 (s, 3H), 2.12—2.73 (m, 3H), 3.78—4.02 (m, 4H), 4.73 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR δ = 14.7, 30.2, 32.9, 45.0, 65.0, 106.6, 207.8; IR (neat) 2970, 2890, 1710, 1370, 1165, 1105 cm^{-1}; MS (EI) *m/z* 158 (M$^+$; 4), 73 (100).

Deacetalization of 29 to (*S*)-2-Methyl-4-oxopentanal (30).[21] The pentanone **29** (26.5 mg, 168 μmol), derived from the addition product **27b**, was treated as in the preparation of **25** to give the aldehyde **30** (10.8 mg containing a small amount of the solvents). The solvents could not be removed due to the volatility: R_f = 0.26 (hexane/ethyl acetate = 70/30); $[\alpha]_D^{26}$ = −18.6 (*c* 0.156, $CHCl_3$) (lit,[21] (*S*)-isomer $[\alpha]_D^{25}$ = −40.8 (*c* 1.00, $CHCl_3$)); ^{1}H NMR δ = 1.17 (d, *J* = 7.2 Hz, 3H), 2.20 (s, 3H), 2.30—3.01 (m, 3H), 9.69 (s, 1H); IR (neat) 2925, 1715, 1370, 1090 cm^{-1}.

Preparation of 1,4-Bis[(2*R*,3*R*)-2,3-dimethylethylenedioxy]-2-methylpentane (31). A mixture of the ketone **29** (11.3 mg, 71.4 μmol) derived from **27b**, (2*R*,3*R*)-2,3-butanediol (16.3 μl, 179 μmol), and PPTS (1.8 mg, 7.16 μmol) in benzene (5 ml) was heated at reflux for 15 h. The solvent was removed under vacuum to give a crude product, which was purified by column chromatography (silica gel, hexane/Et_2O = 98/2), affording the acetal **31** (17.2 mg, 93%): R_f = 0.67 (hexane/ethyl acetate = 70/30); ^{1}H NMR (3*S*)-isomer δ = 1.04 (d, *J* = 6.9 Hz, 3H), 1.15—1.35 (m, 12H), 1.36 (s, 3H), 1.42—1.68 (m, 1H), 1.83—2.05 (m, 2H), 3.48—3.76 (m, 4H), 4.97 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR (3*S*)-isomer δ = 14.9, 16.6, 16.7, 17.2, 17.3, 26.1, 33.2, 40.8, 77.9, 78.6, 78.8, 79.6, 106.4, 109.4. (3*R*)-isomer δ = 14.8, 16.6, 16.7, 17.2, 17.3, 26.2, 33.0, 41.2, 78.1, 78.4, 78.6, 79.7, 106.3, 109.4; IR (neat) 2975, 2880, 1465, 1385, 1245, 1100 cm^{-1}.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 06805079 from the Ministry of Education, Science and Culture. We thank Dr. Shinya Kusuda, Mr. Takeo Inohara, and Ono Pharmaceutical Co., Ltd., for X-ray crystallographic analysis.

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