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Synthesis of 1,3-Dioxin-4-ones and Their Use in Synthesis. XX.1) (6*S*,7*S*,10*R*)- and (6*R*,7*S*,10*R*)-7-Isopropyl-10-methyl-4-oxo-1,5-dioxaspiro[5.5]undec-2-enes; Synthesis and Their Use in Enantiomerically Pure Corey Lactone Analogue Synthesis2)

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Two chiral spirocyclic dioxinones (*S*-5 and *R*-5) useful in the so-called de Mayo reaction as alternatives to β-diketones (enones) have been synthesized; they not only act as formylacetates (inactive by themselves as enones) but also display remarkable diastereofacial selectivities in photoaddition to alkenes. The synthesis of these dioxinones is described, together with a practical one-pot synthesis of enantiomerically pure (1*S*,4*R*)-(+)-6-formyl-2-oxabicyclo[3.3.0]oct-6-en-3-one, the key intermediate of prostaglandin synthesis, from the (6*S*)-spirocyclic dioxinone (*S*-5).

Keywords asymmetric synthesis; chiral enone component; Corey lactone analogue; de Mayo reaction; chiral spirocyclic 1,3-dioxin-4-one; prostaglandin synthesis; photo[2+2]cycloaddition; diastereofacial selectivity

We have already developed an efficient method for the introduction of carboxaldehyde and acetic acid appendages at the vicinal position of alkenes by an application of the de Mayo reaction3) using 5,6-unsubstituted 1,3-dioxin-4-ones as the photochemical equivalent of formylacetates, which are inactive as the enones in this reaction.4) Shortly thereafter, a practical one-pot synthesis of the Corey lactone analogue 6-formyl-*cis*-2-oxabicyclo[3.3.0]oct-6-en-3-one [(±)-4] from 2,2-dimethyl-1,3-dioxin-4-one5) (**1**) and *cis*-2-cyclopentene-1,4-diol6) by an application of the de Mayo reaction was accomplished in our laboratories.7)

Since the (+)-lactone [(+)-**4**] has considerable utility in the preparation of prostaglandin derivatives, namely, 11,12-difluoromethanoprostaglandin,8) prostaglandin C_2,9) and thromboxane B_2,10) it is desirable to synthesize the lactone as an enantiomerically pure compound (abbreviated hereafter as EPC), which would require a superior method to the previous ones.11-13)

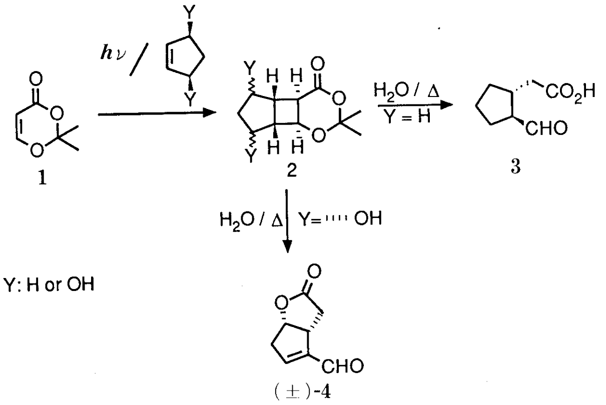
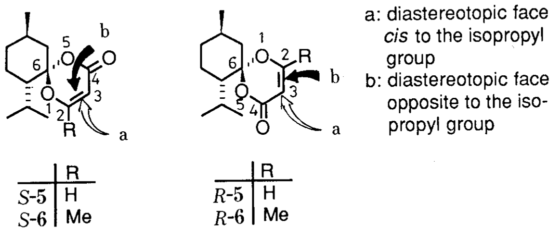


Chart 1



a: diastereotopic face *cis* to the isopropyl group

b: diastereotopic face opposite to the isopropyl group

Fig. 1. Diastereotopic Faces of the Chiral Dioxinones

In our recent communication, we have reported that when the title dioxinones (*S*- and *R*-**5**) are photoadded to cyclopentene, the addition occurs predominantly at a-side with complete formation of *cis–anti–cis* adducts.14) The same a-side preference (with almost stereoselective formation of the *cis–anti–cis* adduct) was also observed by Demuth and his collaborators in the photoaddition of the corresponding 2-methyl derivatives (*S*- and *R*-**6**).15)

Considering these facts, it seemed desirable to examine the photoaddition of 6*S*-spirocyclic dioxinone (*S*-**5**) with *cis*-2-cyclopentene-1,4-diol in order to synthesize the desired lactone as an EPC. This paper presents the details of 1) the synthesis of chiral spirocyclic dioxinones and 2) their photoaddition to cyclopentene, both of which have already been reported in a communication,14) as well as 3) the novel asymmetric de Mayo reaction utilizing the dioxinone (*S*-**5**) as the chiral enone by which the EPC synthesis of the lactone [(+)-**4**] has been successfully accomplished.

Synthesis of Chiral Spirocyclic Dioxinones (*S*-5 and *R*-5) According to the general synthetic method of 5,6-unsubstituted dioxinones developed in our laboratories,5) formyl Meldrum's acid and *l*-menthone were heated in toluene under reflux. As a result, a mixture of diastereomers (*ca.* 1 : 1 ratio) was obtained in 27% yield. When 2,2-dimethyl-1,3-dioxin-4-one (**1**) was used instead of the Meldrum's acid in the above reaction, the same adducts (again in *ca.* 1 : 1 ratio) were obtained in 59% yield. The diastereoisomers

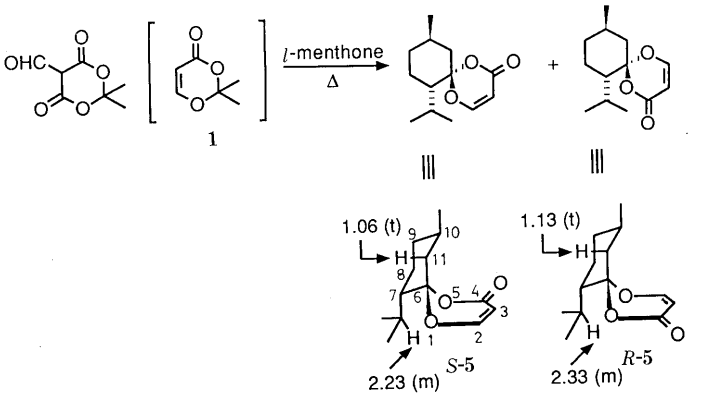


Chart 2

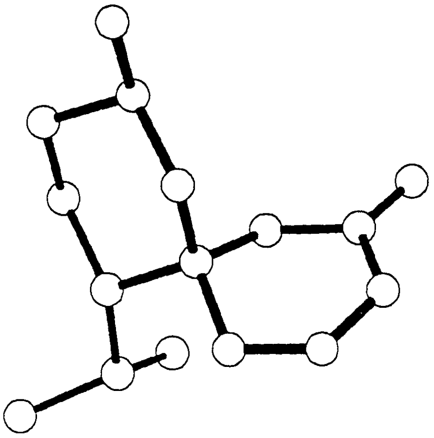


Fig. 2. Molecular Structure of S-5

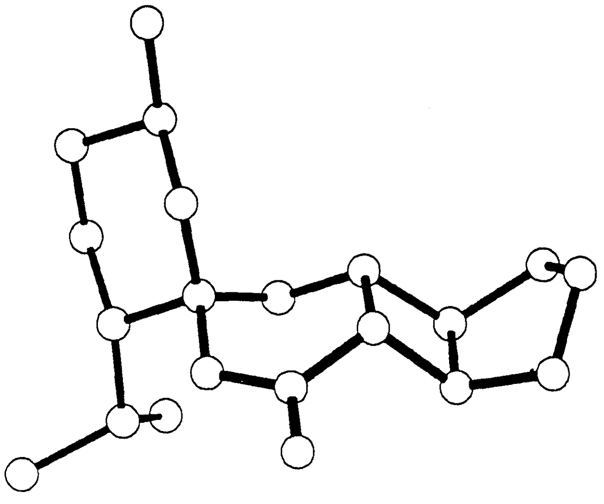


Fig. 3. Molecular Structure of **7a**

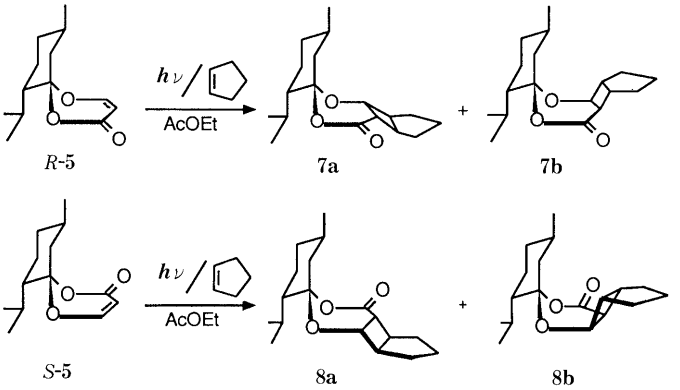


Chart 3

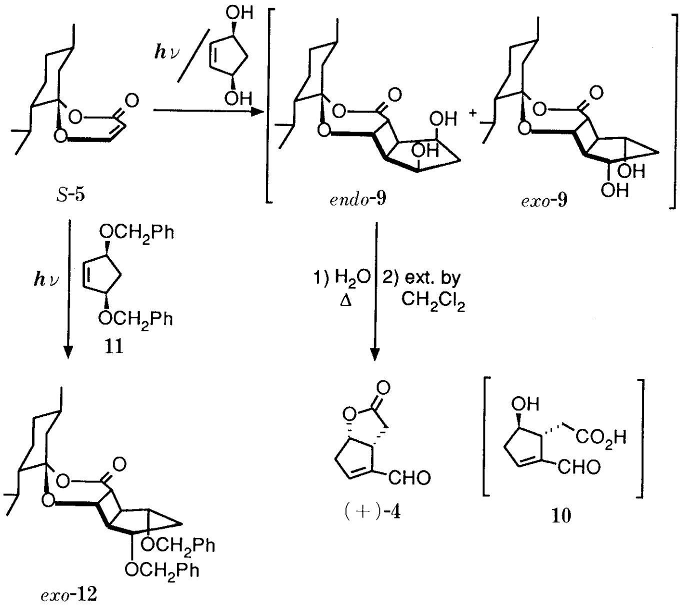


Chart 4

were separated by column chromatography to give the less (S-**5**) and more polar adducts (R-**5**). The structure of the former (the less polar) adduct was determined as the 6S-isomer (S-**5**) unequivocally by X-ray crystallographic analysis (Fig. 2).

The two diastereoisomers can also be distinguished by their nuclear magnetic resonance (NMR) spectra. Thus, the signals of C_{11}-H_{axial} and the methine proton in the isopropyl group of the 6S-isomer (S-**5**) appear at higher fields than those of the corresponding 6R-isomer (R-**5**).[16)]

Photoaddition of S-5 and R-5 to Cyclopentene: Preliminary Studies on the Use of Chiral Dioxinones in the Asymmetric de Mayo Reaction As a preliminary study, we have examined the photoaddition of these dioxinones to cyclopentene. When R-**5** was photoadded to cyclopentene in ethyl acetate (room temperature), two adducts (**7a** and **7b**) were obtained in *ca.* 6 : 1 ratio.

From the NMR spectra, both adducts were determined as having *cis–anti–cis* structure. The structure of the major adduct was determined to have arisen from a-side attack of the alkene by X-ray crystallographic analysis (Fig. 3).

The same a-side preference was also observed when S-**5** was photoadded to cyclopentene. Again, two *cis–anti–cis* adducts were obtained in *ca.* 6 : 1 ratio in 70% yield. The major adduct (**8a**) is obviously the one as formed by a-side attack of the alkene (this assumption was verified, for example, in the synthesis of the Corey lactone analogue using S-**5** as the enone, *vide infra*).

Synthesis of the Corey Lactone Analogue by Novel Asymmetric de Mayo Reaction Using S-5 as the Enone Component According to our previous practical one-pot synthesis of the Corey lactone (racemic) from 2,2-dimethyl-1,3-dioxin-4-one (**1**) and *cis*-2-cyclopentene-1,4-diol by an application of the de Mayo reaction (*cf.* Chart 1),[7)] the chiral dioxinone (S-**5**) was irradiated at 300 nm in ethyl acetate containing an excess of the diol. After S-**5** was consumed (the reaction was monitored by thin layer chromatography (TLC)), the whole was washed with water to remove the unused diol from the organic layer, which was then evaporated *in vacuo*. The residue thus obtained was refluxed in water until all of the adducts were consumed and, after cooling, extracted with dichloromethane. Separation of the products soluble in dichloromethane by silica gel column chromatography afforded, in addition to *l*-menthone (the molar amount of which was nearly equal to the total molar amount of the dioxinone (S-**5**) used in the reaction), the desired lactone [(+)-**4**] in *ca.* 25% yield as a semi-crystalline solid which showed a single spot on TLC. The sign (+) of the specific rotation of this sample confirmed that the major diastereomers in the product have the absolute structure corresponding to *cis–anti–cis* adducts (*endo*-**9** and *exo*-**9**) formed by a-side attack of the alkene, as shown in the model experiment using cyclopentene. Consequently, compound **10** derived from *exo*-**9** should also be formed by the hydrolysis and remain in the aqueous layer. The isolation of **10** was not attempted, since in the previous study using **1** only a small amount of racemic **10** was isolated as its benzyl ester.[7] The enantiomeric excess (ee) of the lactone is 82% based on a comparison of its specific rotation value (+170°) with that (+200°) of the authentic (+)-lactone.[17]

Thus, we have now established the synthesis of the lactone in a satisfactory ee by a practical one-pot reaction. Furthermore, recrystallization of the crude lactone from ether afforded an enantiomerically pure lactone as crystals; this product was identical with authentic sample (see Experimental).

It should be noted that the photoaddition of *S*-**5** to *cis*-1,4-dibenzyloxycyclopent-2-ene (**11**) afforded *exo*-**12** as the sole adduct. The high *exo*-selectivity as well as complete a-side attack in the above reaction are probably due to steric effects. This result suggests that a-side preference in these dioxinones does hold generally, irrespective of the kind of olefins used.

Conclusion

In addition to the afore-mentioned synthesis of the Corey lactone analogue, the studies presented in this paper are important in the following respects. 1) The chiral spirocyclic dioxinones could serve as an excellent alternative to formyl acetates, which are by themselves neither photoactive nor capable of inducing asymmetric induction in the photo[2+2]addition. 2) The a-side preference in these dioxinones in the intermolecular photoaddition to cyclopentenes is a general phenomenon and hence it should be possible to choose any dioxinone as a suitable synthon in planning the synthetic route to the desired chiral target molecules.

We assume that the a-side preference is due to the sofa-conformation (verified by X-ray analysis) whose a-side is more exposed than the other side (b-side), as proposed in our previous communication.[14] This explanation is the same as that proposed by Demuth *et al.*[15] who for the first time found preferential a-side photoaddition of *R*-**6** (or *S*-**6**) to alkenes, but differs from that of Seebach *et al.*[18] who proposed that the selectivity is based on a pyramidalization in the triplet excited state of these dioxinones.

Efforts are now being made to clarify further this remarkable diastereofacial selectivity by examining the intramolecular photoaddition reaction of chiral dioxinones having an ω-alkenyl chain at the 2- or 3-position. The results will be reported in due course.

Experimental

All melting points were determined on a micro-hot stage (Yanagimoto) and are uncorrected. Optical rotations were measured with a JASCO DIP-340 digital polarimeter. Infrared (IR) spectra were recorded on a JASCO A-102 spectrometer and proton nuclear magnetic resonance (^{1}H-NMR) spectra on a JNM-PMX60SI or JEOL JNM-FX500 spectrometer (with tetramethylsilane as an internal standard). Mass spectra (MS) were taken either with a Hitachi M-52 spectrometer or with a JEOL JMS-01SG-2 spectrometer. Silica gel used for column chromatography was Wakogel C-200. TLC was performed on Merck Kieselgel 60 F254. High-pressure liquid chromatography (HPLC) was performed with a Waters μ-PORASIL column (30 cm). Medium-pressure liquid chromatography was performed with a Merck Lobar column (LiChroprep Si 60). The ratio of solvent mixtures for chromatography is shown as volume/volume.

Irradiation Conditions A: The photoreaction was carried out at room temperature in a quartz vessel with Rayonet RPR 3000 Å lamps.

B: The photoreaction was carried out using an Ushio 400 W high-pressure mercury lamp with a Vycor filter (immersion type) under ice-cooling.

(6*S*,7*S*,10*R*)- and (6*R*,7*S*,10*R*)-7-Isopropyl-10-methyl-4-oxo-1,5-dioxaspiro[5.5]undec-2-enes (*S*-5 and *R*-5) a: A solution of *l*-menthone (7.71 g, 50 mmol) in dry toluene (20 ml) was refluxed. Formylated Meldrum's acid[19] (1.72 g, 10 mmol) was added to the solution portionwise over 15 min. The solution was refluxed for an additional 30 min and then evaporated *in vacuo*. The residue was chromatographed on a silica gel (150 g) column. Elution with hexane–ethyl acetate (50 : 1) gave unreacted *l*-menthone (6 g). Further elution with hexane–ethyl acetate (30 : 1) gave a crystalline mixture of *S*-**5** and *R*-**5** (1 : 1). Yield, 605 mg (27%).

Purification of this mixture by medium-pressure column chromatography (hexane–ether, 30 : 1) gave *S*-**5** (less polar) and *R*-**5** (more polar). *S*-**5**. Prisms of mp 115—116 °C (from pentane). $[\alpha]_D^{24}$ −51.6° (c=1.1, CHCl$_3$). *Anal.* Calcd for C$_{13}$H$_{20}$O$_3$: C, 69.61; H, 8.99. Found: C, 69.41; H, 9.12. IR (CHCl$_3$): 1730, 1620 cm^{-1}. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 0.90 (3H, d, J=6.5 Hz, C$_{10}$-Me), 0.92 and 0.96 (each 3H, d, J=6.5 Hz, –CHMe$_2$), 1.06 (1H, t, J=12.5 Hz, C$_{11}$-H$_{\text{axial}}$), 2.23 (1H, m, –C$\underline{\text{H}}$Me$_2$), 2.69 (1H, ddd, J=12.5, 3.5, 2.5 Hz, C$_{11}$-H$_{\text{equatorial}}$), 5.33 (1H, d, J=5.6 Hz, C$_2$-H), 7.13 (1H, d, J=5.6 Hz, C$_3$-H). MS m/z: 224 (M$^+$). *R*-**5**. Prisms of mp 102—103 °C (from pentane). $[\alpha]_D^{26}$ −17.7° (c=1.3, CHCl$_3$). *Anal.* Calcd for C$_{13}$H$_{20}$O$_3$: C, 69.61; H, 8.99. Found: C, 69.51; H, 9.24. IR (CHCl$_3$): 1730, 1620 cm^{-1}. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 0.88 and 0.95 (each, 3H, d, J=6.5 Hz, –CHMe$_2$), 0.90 (3H, d, J=6.5 Hz, C$_{10}$-Me), 1.13 (1H, t, J=12.5 Hz, C$_{11}$-H$_{\text{axial}}$), 2.33 (1H, m, –C$\underline{\text{H}}$Me$_2$), 2.69 (1H, ddd, J=12.5, 3.5, 2.5 Hz, C$_{11}$-H$_{\text{equatorial}}$), 5.37 (1H, d, J=6.2 Hz, C$_2$-H), 7.13 (1H, d, J=6.2 Hz, C$_3$-H).

b: A solution of 2,2-dimethyl-1,3-dioxin-4-one (**1**,[5] 1.28 g, 10 mmol) and *l*-menthone (7.71 g, 50 mmol) in dry benzene (20 ml) was refluxed for 2.5 h. The reaction mixture was worked up according to method a to give a mixture of *S*-**5** and *R*-**5** (1 : 1). Yield, 1.32 g (59%).

Crystallographic Measurements of *S*-5 Colorless prismatic crystals were grown in pentane solution. A crystal of approximate dimensions of 0.5 × 0.2 × 0.2 mm^3 was used for data collection on a Rigaku AFC-5R diffractometer with graphite-monochromated CuK_α radiation (λ=1.54184 Å). The crystal data are as follows: C$_{13}$H$_{20}$O$_3$. M_r=224.30, orthorhombic, space group $P2_12_12_1$, a=10.490(3), b=13.52(3), c=9.121(2) Å; Z=4, $D_{\text{calc.}}$=1.152 g/cm^3. Intensities were measured in the $\theta-2\theta$ scan mode with a scanning speed of 8° (2θ)/min. Of 1145 independent reflections with $2\theta<120°$, 51 weak reflections below the background were considered to be zero reflections; the observational threshold value, F_{lim}, was 0.061. Corrections were made for Lorentz and polarization factors but not for absorption.

The structure was solved by the direct method using the program MULTAN84[20] and the atomic parameters were refined by the block-diagonal least-squares method. The refinements were performed first isotropically and then anisotropically for non-hydrogen atoms. Hydrogen atoms were all located from difference Fourier maps. The final R value was 0.056 (R_w=0.061) for reflections with $|F_O|>3\sigma|F_O|$.

(1*R*,2*S*,4*S*,7*R*,8*R*,2′*S*,5′*R*)- and (1*S*,2*R*,4*S*,7*S*,8*R*,2′*S*,5′*R*)-6-Oxo-3,5-dioxatricyclo[6.3.0.0^{2,7}]undecane-4-spiro-(2′-isopropyl-5′-methyl)cyclohexane (7a and 7b) A solution of *S*-**5** (112 mg, 0.5 mmol) and cyclopentene (340 mg, 5 mmol) in dry hexane (25 ml) was irradiated under condition A for 3.5 h. The solvent was evaporated off *in vacuo* and the residue was purified by medium-pressure column chromatography (hexane–ether, 20 : 1) to give **7b** (less polar) and **7a** (more polar).

7a: Prisms of mp 66—68 °C (from pentane). Yield, 74 mg (51%). $[\alpha]_D^{24}$ −6.6° (c=1, CHCl$_3$). High-resolution (HR) MS m/z: 292.2013. M$^+$ Calcd for C$_{18}$H$_{28}$O$_3$: 292.2037. ^{1}H-NMR (CDCl$_3$) δ: 4.21 (1H, dd, J=6, 2 Hz, C$_2$-H). IR (CHCl$_3$): 1722 cm^{-1}.

7b: Prisms of mp 84—86 °C (from pentane). Yield, 10 mg (7%). $[\alpha]_D^{22}$ −22.6° (c=0.8, CHCl$_3$). HRMS m/z: 292.2031. M$^+$ Calcd for C$_{18}$H$_{28}$O$_3$: 292.2037. ^{1}H-NMR (CDCl$_3$) δ: 4.22 (1H, dd, J=8, 2 Hz, C$_2$-H). IR (CHCl$_3$): 1722 cm^{-1}.

(1*S*,2*R*,4*R*,7*S*,8*R*,2′*S*,5′*R*)- and (1*R*,2*S*,4*R*,7*R*,8*S*,2′*S*,5′*R*)-6-Oxo-3,5-dioxatricyclo[6.3.0.0^{2,7}]undecane-4-spiro-(2′-isopropyl-5′-methyl)cyclohex-

ane (8a and 8b) Following the procedure given for preparation of **7a** and **7b**, compound *R*-**5** (224 mg, 1 mmol) was reacted with cyclopentene to give **8b** (less polar) and **8a** (more polar).

8a: Prisms of mp 109—110 °C (from pentane). Yield, 142 mg (48%). $[\alpha]_D^{23}$ $-33.2°$ ($c=2$, $CHCl_3$). *Anal.* Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 74.07; H, 9.69. ^1H-NMR (500 MHz, $CDCl_3$) δ: 0.91 (3H, d, $J=6.7$ Hz, $C_{5'}$-Me), 0.95 (6H, d, $J=7.2$ Hz, $-CH\underline{Me_2}$), 1.24 (1H, t, $J=13.5$ Hz, $C_{6'}$-H_{axial}), 2.33 (1H, m, $-C\underline{H}Me_2$), 2.54 (1H, dt, $J=5.4$, 1.5 Hz, C_1-H), 2.68 (1H, br t, $J=6.5$ Hz, C_7-H), 3.09 (1H, dt, $J=6.5$, 5.4 Hz, C_8-H), 4.01 (1H, dd, $J=6.5$, 1.5 Hz, C_2-H). IR ($CHCl_3$): 1720 cm^{-1}. MS *m/z*: 292 (M^+).

8b: Prisms of mp 146.5—148 °C (from pentane). Yield, 23.8 mg (8%). $[\alpha]_D^{24}$ $-13.3°$ ($c=0.9$, $CHCl_3$). *Anal.* Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.72; H, 9.92. IR ($CHCl_3$): 1720 cm^{-1}. ^1H-NMR (500 MHz, $CDCl_3$) δ: 0.84 and 0.90 (each 3H, d, $J=6.9$ Hz, $-CH\underline{Me_2}$), 0.94 (3H, d, $J=6.4$ Hz, $C_{5'}$-Me), 2.04 (1H, m, $-C\underline{H}Me_2$), 2.34 (1H, dt, $J=13.2$, 2.3 Hz, $C_{6'}$-$H_{equatorial}$), 2.74 (1H, ddd, $J=8.0$, 5.1, 1.7 Hz, C_1-H), 2.82 (1H, br t, $J=6.3$ Hz, C_7-H), 3.03 (1H, q, $J=6.3$ Hz, C_8-H), 4.14 (1H, dd, $J=8.0$, 3.2 Hz, C_2-H). MS *m/z*: 292 (M^+).

Crystallographic Measurements of 7a Colorless prismatic crystals were grown in pentane solution. A crystal of approximate dimensions of $0.2 \times 0.2 \times 0.1$ mm^3 was used for data collection on a Rigaku AFC-5R diffractometer with graphite-monochromated CuK_α radiation ($\lambda=1.54184$ Å). The crystal data are as follows: $C_{18}H_{28}O_3$, $M_r=292.42$, orthorhombic, space group $P2_12_12_1$, $a=8.439(5)$, $b=28.86(3)$, $c=6.893(4)$ Å, $Z=4$, $D_{calc.}=1.157$ g/cm^3. Intensities were measured in the $\theta-2\theta$ scan mode with a scanning speed of $4°(2\theta)$/min. Of 1489 independent reflections with $2\theta<120$, 180 weak reflections below the background were considered to be zero reflections; the observational threshold value, F_{lim}, was 0.536. Corrections were made for Lorentz and polarization factors but not for absorption.

The structure was solved by the direct method using the program MULTAN84[20] and the atomic parameters were refined by the block-diagonal least-squares method. The refinements were performed first isotropically and then anisotropically for non-hydrogen atoms. Hydrogen atoms were all located from difference Fourier maps. The final R value was 0.070 ($R_w=0.0869$) for reflections with $|F_O|>3\sigma|F_O|$.

(1*S*,4*S*)-3-Oxo-2-oxabicyclo[3.3.0]oct-6-en-6-carbaldehyde [(+)-4] A solution of *S*-**5** (448 mg, 2 mmol) and *cis*-2-cyclopentene-1,4-diol (2.0 g, 20 mmol)[6] in ethyl acetate (170 ml) was irradiated under condition B until *S*-**5** was consumed. The reaction was followed by TLC. The reaction mixture was washed with water. Evaporation of the water layer gave the unreacted diol (1.6 g). The organic layer was evaporated *in vacuo*. The residue was heated with water (30 ml) under reflux for 2 h. The reaction mixture was extracted with dichloromethane. The aqueous layer was again refluxed for 2 h and then extracted with dichloromethane. The combined extract was subjected to silica gel (10 g) column chromatography. Elution with hexane–ether (20 : 1) gave *l*-menthone as an oil (250 mg). Further elution with hexane–ether (10 : 1) gave (+)-**4** as a solid. Yield, 76 mg (25%). The IR and ^1H-NMR spectral data were identical with reported values. $[\alpha]_D^{22}$ $+164°$ ($c=1.0$, EtOH). Recrystallization of this sample from ether gave enantiomerically pure (+)-**4** as prisms of mp 79—80 °C. $[\alpha]_D^{23}$ $+200°$ ($c=1.0$, EtOH). An authentic sample of (+)-**4** was prepared from commercial Corey's lactone (benzoxy derivative) according to the reported procedure.[17] $[\alpha]_D^{26}$ $+200°$ ($c=1.0$, EtOH), mp 79—80 °C.

(1*S*,2*S*,4*S*,7*R*,8*S*,9*S*,11*R*,2′*S*,5′*R*)-9,11-Dibenzyloxy-6-oxo-3,5-dioxatricyclo[6.3.0.0^{2,7}]undecane-4-spiro-(2′-isopropyl-5′-methyl)cyclohexane (*exo*-12) A solution of *S*-**5** (112 mg, 0.5 mmol) and *cis*-1,4-dibenzyloxycyclopent-2-ene (**11**,[21] 1.40 g, 5 mmol) in hexane (25 ml) was irradiated under condition A for 6 h. The reaction mixture was evaporated *in vacuo* and the residue was subjected to silica gel column chromatography. Elution with hexane–ether (30 : 1) gave the cyclopentene (1.2 g). Further elution with hexane–ether (10 : 1) gave the [2+2]adduct (*exo*-**12**) as crystals. Yield, 151 mg (60%). Needles of mp 136—138 °C. HRMS *m/z*: 504.2866. Calcd for $C_{32}H_{40}O_5$: 504.2874. IR ($CHCl_3$): 1730 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 3.6—4.3 (2H, m, C_9-H, C_{11}-H), 4.34, 4.77 (each 1H, d, $J=11$ Hz, $C\underline{H}_2C_6H_5$), 4.46 (2H, s, $C\underline{H}_2C_6H_5$), 4.78 (1H, m, C_2-H), 7.34 (10H, br s, $2 \times C_6H_5$), $[\alpha]_D^{25}$ $-21.4°$ ($c=2.0$, $CHCl_3$).

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16) So far, we have prepared many chiral derivatives of *S*- and *R*-**5**, such as the 2-methyl, 3-methyl, and 2,3-dimethyl derivatives, and measured their NMR spectra. It is obivous that the less polar dioxinones show these signals at higher field than the more polar ones as in the case of the unsubstituted dioxinones (*S*- and *R*-**5**). Since some of them had already been determined as having the assigned absolute configurations by X-ray analysis by us[14] and Demuth *et al.*,[15] the above-mentioned typical characteristics in the NMR spectra should hold for all of these dioxinones, irrespective of the pattern of the substituents. Details of these studies will be reported separately in due course.
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