Synthetic Photochemistry. LXXI. Photocycloaddition of Methyl 2,4-Dioxohexanoate to 3-Benzylozy-2-methylpropene

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Synthetic Photochemistry. LXXI. Photocycloaddition of Methyl 2,4-Dioxohexanoate to 3-Benzyloxy-2-methylpropene

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A useful C_{20} synthon for higher terpenoid syntheses was prepared by photocycloaddition of 3-benzyloxy-2-methylpropene to methyl 2,4-dioxohexanoate. In this combination of two sterically crowded components, a protic solvent, which normally reduces the enol content of β-diketones, unexpectedly made the reaction smooth. It plays probably a catalytic role on the re-enolization of the diketo-isomer which would be accumulated in the relatively slow photo-reaction. C_{20} synthons, prepared by low-valent chromium salt mediated coupling, were fully characterized by NMR spectral analysis as well as X-ray crystallographic analysis of the key isomer.

Introduction

The UV-light irradiated photochemical reaction of acetylacetone (**A**) with olefins, reported in 1962 by de Mayo and Takeshita,[1] is the first intermolecular photocycloaddition. Indeed, the de Mayo reaction has been regarded to be one of the most useful photocycloaddition reaction in organic syntheses, and there are many applications. In addition, the de Mayo reaction is different from the other enone photocycloadditions; its four-membered ring system in the *proto*-photoproducts, 2-acetylcyclobutanols, spontaneously dealdolizes into the 2,6-diketones, which are convertible to cyclohexenones. Thus, the formation of a six-membered ring system could be a photochemical substitute of the Diels-Alder reaction. Methyl 2,4-dioxopentanoate (**B**) is photochemically superior in many respects over acetylacetone; i) irrespective to the kind of medium, it shows a large enol content, ii) it is reactive towards a conjugated C=C system, iii) it smoothly cycloadds to olefins carrying various functional groups, and so on.[2] Taking these advantages, we have utilized **B** to synthesize various terpenoids.[3] In addition, from its homologue, methyl 2,4-dioxohexanoate (**1**), and 2-methylpropene (**C**) we have accomplished a total synthesis of deoxytrisporone, a trimethylcyclohexane sesquiterpenoid ketone.[4]

In this paper, we like to show the photochemical cycloaddition reaction of **1** with a heteroatom-substituted olefin, 3-benzyloxy-2-methylpropene (**2**). The products obtained should have a potential in syntheses of 6-7-5-membered tricyclic diterpenoids, such as dolastanes.[5]

Results and Discussion

Photoreaction of 3-Benzyloxy-2-methylpropene to Methyl 2,4-Dioxohexanoate. Solvent Effect and Polar Substituent Effect. When 3-benzyloxy-2-methylpropene (**2**) and methyl 2,4-dioxohexanoate (**1**)[6] were irradiated in a cyclohexane solution, two products (**3** and **4**) were formed in 60 and 19% yields, respectively. The reaction was slower than that of 2-methylpropene (**C**) and methyl 2,4-dioxopentanoate (**B**) suffering a considerable steric effect; when the reaction of **1** and **2** was carried out in ethyl acetate which has been the most prominent solvent in these photocycloadditions, no appreciable amount of product was isolated. Surprisingly,

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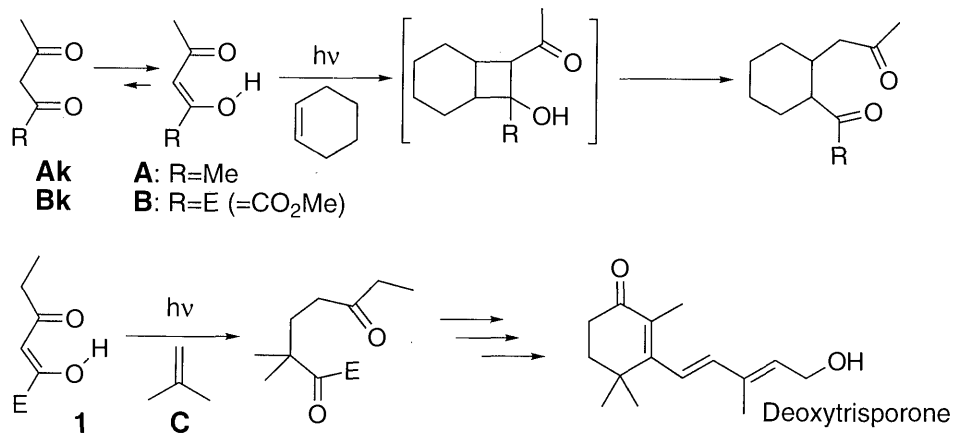
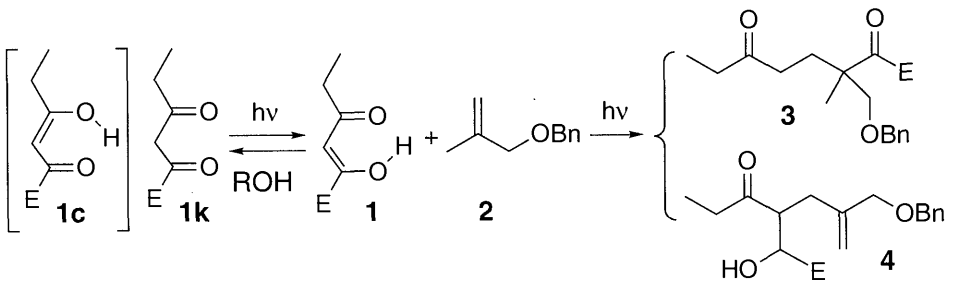


Scheme 1

Table 1. Photochemical reaction of **1** and **2** under various conditions.

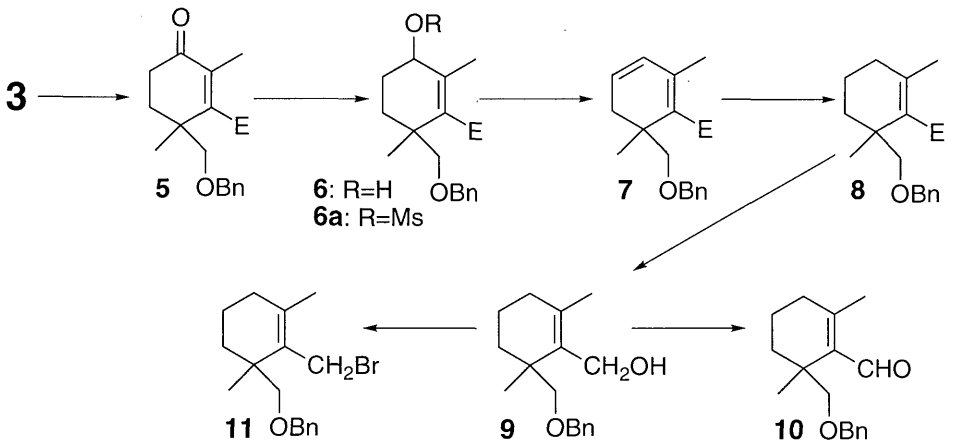
Temp./Solvent	Mol ratio of **1** : **2**	irradiation time/h	Yield/% of **3**	Yield/% of **4**
r.t./AcOEt	1 : 10	48	0	0
r.t./MeOH	1 : 5	48	28	0
r.t./MeOH	1 : 8	48	46	0
−30℃/MeOH	1 : 5	48	24	0
r.t./cyclohexane	1 : 8	10	60	19



Scheme 2

the reaction was better in methanol to form **3** in 28 to 46% yields. The improvement of the yields in protic solvent is rather unpredicted, since the enol contents of the β-diketones are smaller in protic solvents.

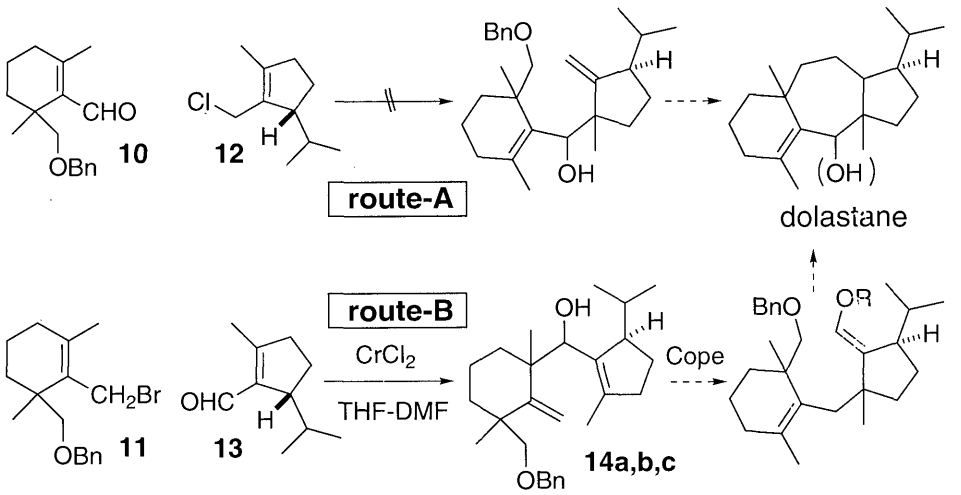
The present results should be explained in terms of enhanced rate for the re-enolization of the photogenerated keto-isomer **1k** of **1**. Namely, the triplet carbonyl of photo-excited **1** abstracts enolic hydrogen to give a cross-conjugated oxo ester, methyl 4-hydroxy-2-oxo-4-hexenoate (**1c**) whose photochemically-allowed 1,3-hydrogen shift furnishes **1k**. Accordingly, irradiation of **2** with less reactive ethenes should accumulate **1k**. In a protic solvent, such a diketo-isomer can be enolized by catalytic action of protons. In other words, assistance of protons for re-enolization overtakes the disfavored ability of diminishment in enol content of β-diketones in original ground state. The present substrate **2** has a bulky benzyloxy substituent in the vicinity of ethene moiety, and since the photochemical reactivity of **1** towards **C** is smooth, it should be concluded that the steric hindrance of **2** is large enough to retard the addition reaction. Conversely, **B** reacts smoothly to many bulky ethenes, such as adamantylidenethene and terpinolene, an introduction of one methyl group in **1** also retarded the reaction in a great deal. Table 1 summarizes the solvent effect of the photocycloaddition.



Scheme 3

Nevertheless, **3** possessed an appropriate arrangement of substituents for construction of trimethylcyclohexenyl moiety found in many natural products including carotenoids. Thus, acid catalyzed cyclization of **3** in benzene with azeotropic removal of water quantitatively gave methyl 6-(benzyloxymethyl)-3-oxo-2,6-dimethyl-1-cyclohexenecarboxylate (**5**). Structure of **5** was deduced straightforward from the observation of ^{1}H and ^{13}C NMR spectroscopy. Removal of the keto function in **5** was achieved by sodium borohydride reduction and subsequent elimination of the mesyloxy derivative derived therefrom and reduction with rhodium catalyst to give (*via* **6** and **7**) methyl 6-(benzyloxymethyl)-2,6-dimethyl-1-cyclohexenecarboxylate (**8**). The oxidation of **9** with pyridinium dichromate (PDC) gave a corresponding aldehyde **10** and the phosphorus tribromide-treatment of **9** afforded an allyl bromide **11**.

Preparation of a C_{20} Synthon *via* Low-Valent Chromium Salt-Mediated Coupling Reaction. Next step to the C_{20} synthons leading to the dolastane skeleton is the low-valent chromium(Ⅱ) salt-mediated condensations of **10** or **11** to an iridenyl derivative as an another C_{10} unit. There are two routes in this type of strategy as has been employed in the synthetic studies of our 5-8-5-membered tricyclic higher terpenoids and sesterterpenoids.[2),3)] The route A should start with a condensation of **10** and (3*R*)-7-chloro-1-iridene (**12**), but in the present case, since the reaction site of the cyclohexenyl component **10** is sterically hindered, the reaction could not give any desired products. We could, however, overcome the problem by using the combination of (3*R*)-1-iriden-7-al (**13**) and the bromide **11**, the combination for the route B, to give three



Scheme 4

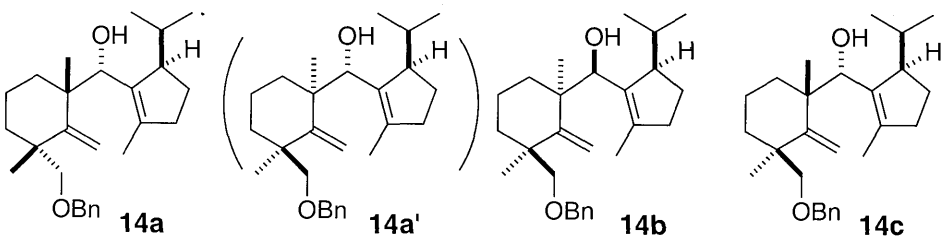


Fig. 1

products (**14a**, **b**, and **c**) in 29, 6, and 11% yields, respectively.

Stereochemistries of these isomers were deduced by NOE experiments on the ^{1}H NMR spectroscopy. Thus, the major product, **14a**, showed the NOE effect between the both singlet methyl signals on the sp^3-carbons and the proton signals of methylene group, indicating these methyl groups are in *syn*-orientation. This was also the case for the isomer, **14c**, but not in **14b**. At the same time, the vinyl methyl signal, at $\delta=1.60$, showed the NOE effect with the methine proton of hydroxyl-bearing carbon, which further showed the NOE effect with one of the methylene protons on the benzyloxy group. Due to the facile rotation around the connecting carbon (hydroxylated carbon), these observations allow to formulate the major product as **14a** or an alternative, **14a'**, but elimination of one from the other was not conclusive.

The X-ray crystallographic analysis of its single crystal, obtained by recrystallization from hexane provided a solution.[7] The ORTEP drawing, illustrated in Fig. 3 , clearly showed that **14a** is the structure. Taking this into account, the structures of other isomers, **14b** and **14c**, are deduced to be as depicted, respectively.

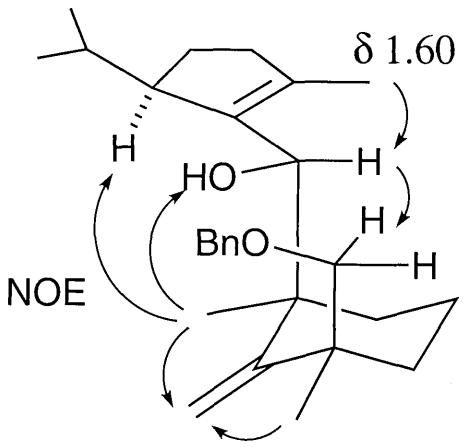


Fig. 2 The NOE illustration of **14a**.

At the present stage, the Cope rearrangement of the trimethysilyl ether of **14** to the B-*seco*-dolastanes has been unsuccessful, probably, due to the severe steric hindrance of the quaternary carbon in the vicinity of the reaction site. The local-minimum conformation, obtained by the Chem3D Pro calculation,[8] of the trimethylsilyl ether of **14a** leading to a chair Cope-transition state is shown in Fig. 4, from which it was easily expected that a bond rotation to shorten the distance of terminals of 1,5-diene system (C-1 and C-6 in Fig. 4) would cause a severe steric repulsion between the allylic methyl on C-1 and the axial-

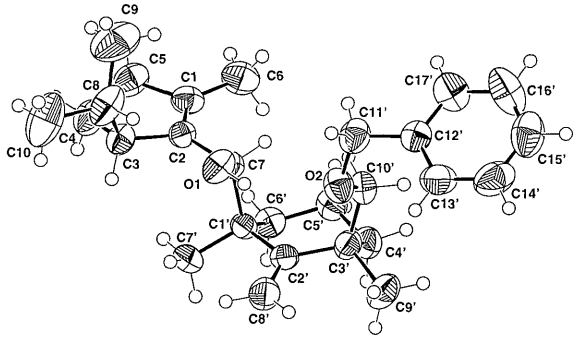


Fig. 3 The ORTEP drawing of **14a** showing 50% probability displacement ellipsoids.

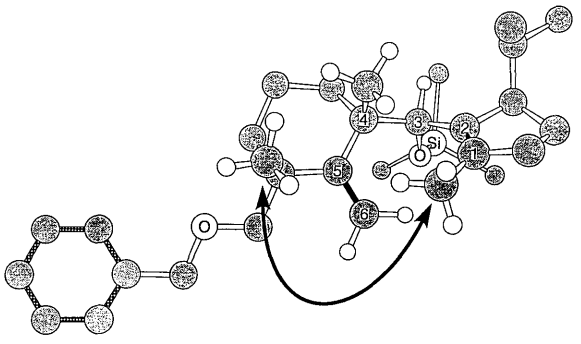


Fig. 4 The Chem3D Pro-calculated conformer for TMS-ether of **14a**. Non-hydrogen atoms and selected hydrogens are shown for clarity.

oriented methyl on the cyclohexane ring (shown as an arrow). The benzyloxymethyl group would take a similar role in an alternative boat-transition state, in which the opposite face of the exo-methylene would be involved in the rearrangement.

Although this could be overcome if other isomers would be selected, we had to terminate the study of this line. We are currently undertaking an improved synthesis of more appropriate C_{20} synthons. And, since trimethylcyclohexene derivatives obtained in this study are appropriately functionalized for the synthesis of highly oxygenated terpenoids, such as abscisic acid-related natural products, synthetic studies utilizing these photochemically-derived synthons are also in due course.

Experimental

Melting points were measured with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. Elemental analyses were performed at the Institute of Advanced Material Study, Kyushu University. The NMR spectra were measured on a GSX 270H Model spectrometer in $CDCl_3$; the chemical shifts are expressed in δ unit. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The stationary phase for the column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate, chloroform, and hexane.

Photochemical Reaction of 1 and 2. Formation of 3 and 4. An cyclohexane solution (7.5 cm^3) of **1** (200 mg, 1.26 mmol) and **2** (1.63 g, 10.08 mmol) was irradiated under N_2 atmosphere by means of 400-W high-pressure Hg lamp for 10 h. The mixture was then heated in vacuo to remove the volatile material, and the residue was chromatographed on a silica-gel column to give **3** [a colorless oil, 241 mg, 60%. ^{1}H NMR δ=1.01 (3H, t, J=7.3 Hz), 1.24 (3H, s), 1.90 (1H, m), 2.10 (1H, m), 2.38 (2H, q, J=7.3 Hz), 2.39 (2H, m), 3.58 (1H, d, J=9.2 Hz), 3.70 (1H, d, J=9.2 Hz), 3.73 (3H, s), 4.43 (2H, s), and 7.23 (5H, m); ^{13}C NMR δ=7.8, 19.6, 28.9, 35.9, 37.0, 50.5, 52.3, 73.3, 74.7, 127.5 (2C), 127.7, 128.3 (2C), 137.6, 162.9, 198.9, and 210.4] and **4** [a colorless oil, 76 mg, 19%. ^{1}H NMR δ=0.99 (3H, t, J=7.3 Hz), 2.39-2.55 (3H, m), 3.23 (1H, m), 3.45 (1H, d, J=8.8 Hz), 3.74 (3H, s), 4.01 (2H, d, J=2.6 Hz), 4.22 (1H, dd, J=8.8, 3.3 Hz), 4.50 (1H, d, J=11.9 Hz), 4.52 (1H, d, J=11.9 Hz), 5.07 (1H, s), 5.19 (1H, d, J=1.1 Hz), and 7.28-7.37 (5H, m)].

Cyclization of 3 to 5. An anhydrous benzene solution (50 cm^3) of **3** (3.0 g) and TsOH (catalytic amount) was refluxed with attached a Dean-Stark equipment for 5 h. Then, the reaction mixture was heated in vacuo, and chromatographed on a silica-gel column to give **5** [a yellow oil, 2.80 g, 100%. ^{1}H NMR δ = 1.25 (3H, s), 1.74 (3H, s), 1.77 (1H, m), 2.22 (1H, m), 2.48-2.58 (2H, m), 3.41 (1H, d, J=9.2 Hz), 3.47 (1H, d, J=9.2 Hz), 3.73 (3H, s), 4.47 (1H, d, J=12.1 Hz), 4.51 (1H, d, J=12.1 Hz), and 7.32 (5H, m); ^{13}C NMR δ=11.3, 22.0, 32.4, 33.6, 38.8, 51.6, 73.3, 75.4, 127.4 (2C), 127.5, 128.3 (2C), 133.1, 137.9, 151.4, 168.4, and 198.6].

Removal of the Oxo Function of 5 via 6. Formation of a Diene 7. To an MeOH solution of **5** (100 mg) was treated with $NaBH_4$ (25 mg) for 1 h at 0 ℃. The mixture was then diluted with water and extracted with CH_2Cl_2. Silica-gel column chromatography of the organic extract afforded **6** [a colorless oil, 89 mg, 88%. ^{1}H NMR (a 1 : 1 mixture of diastereomers) δ= 1.10 (1.5H, s), 1.15 (1.5H, s), 1.31-1.54 (2H, m), 1.77 (1.5H, s), 1.78 (1.5H, s), 1.82-1.99 (2H, m), 3.28 (0.5H, d, J=8.8 Hz), 3.31 (1H, s), 3.39 (0.5H, d, J=8.8 Hz), 3.66 (3H, s), 3.94 (1H, m), 4.45 (0.5H, d, J=12.2 Hz), 4.48 (1H, s), 4.50 (0.5H, d, J=12.2 Hz), and 7.25-7.35 (5H, m)].

Then, a part of the resultant **6** (130 mg) was treated with MsCl (1.55 cm^3) in CH_2Cl_2 (80 cm^3) containing Et_3N (10 cm^3) at 0℃, and allowed stand for 17 h to form a mesylate, which was without purification, dissolved in DMF (10 cm^3) containing Li_2CO_3 (156 mg) and LiBr (130 mg) and heated at 120 ℃ for 10 h. The mixture was then treated with aq. AcOH and extracted with

CH_2Cl_2. Silica-gel column chromatography of the organic extract afforded a diene **7** [a colorless oil, 135 mg, 94%. ^1H NMR $\delta=1.10$ (3H, s), 1.84 (3H, s), 1.89 (1H, dm, $J=17.2$ Hz), 2.67 (1H, dm, $J=17.2$ Hz), 3.23 (1H, d, $J=8.8$ Hz), 3.54 (1H, d, $J=8.8$ Hz), 3.69 (3H, s), 4.47 (2H, s), 5.77-5.90 (2H, m), and 7.24-7.32 (5H, m); ^{13}C NMR $\delta=20.0$, 21.1, 34.1, 36.2, 50.9, 73.2, 74.1, 127.4 (2C), 127.5, 128.1, 128.2 (2C), 128.7, 129.0, 135.1, 138.6, and 169.7].

Dihydro Derivative of 7 Formation of 8. An anhydrous EtOH solution of **7** (80 mg) and Rh/Al_2O_3 catalyst (5 mg) was stirred under H_2 atmosphere to give a dihydro derivative **8** [a colorless oil, 80 mg, 100%. ^1H NMR $\delta=1.14$ (3H, s), 1.27 (1H, td, $J=6.2$, 4.8 Hz), 1.59-1.66 (2H, m), 1.67 (3H, s), 1.81 (1H, m), 2.00 (2H, t, $J=6.2$ Hz), 3.33 (1H, d, $J=9.0$ Hz), 3.38 (1H, d, $J=9.0$ Hz), 3.65 (3H, s), 4.46 (1H, d, $J=12.2$ Hz), 4.49 (1H, d, $J=12.2$ Hz), and 7.24-7.32 (5H, m); ^{13}C NMR $\delta=18.2$, 21.5, 23.7, 31.3, 32.7, 37.9, 51.1, 73.2, 76.6, 127.3, 127.4 (2C), 128.2 (2C), 132.2, 137.0, 138.8, and 170.9].

DIBALH-Reduction of 8 Formation of 9. A toluene solution (2 cm^3) of **8** (18 mg) was treated with DIBALH (0.093mmol) at 0 ℃ for 30 min. The mixture was then treated with aq. Na_2SO_4 and extracted with EtOAc. Silica-gel column chromatography of the organic fractions afforded a primary alcohol **9** [a colorless oil, 11 mg, 65%. ^1H NMR $\delta=0.95$ (3H, s), 1.29 (1H, td, $J=8.4$, 3.7 Hz), 1.46-1.66 (2H, m), 1.77 (3H, s), 1.83 (1H, m), 1.95-2.07 (2H, m), 2.73 (1H, br d, $J=6.6$ Hz), 3.20 (1H, d, $J=9.2$ Hz), 3.54 (1H, d, $J=9.2$ Hz), 3.99 (1H, d, $J=11.7$ Hz), 4.13 (1H, dm, $J=11.7$ Hz), 4.49 (1H, d, $J=11.9$ Hz), 4.55 (1H, d, $J=11.9$ Hz), and 7.28-7.35 (5H, m)].

PDC-Oxidation of 9 to an Aldehyde 10. An CH_2Cl_2 solution (20 cm^3) of **9** (261 mg) was oxidized with PDC (460 mg) in a presence of Molecular Sieve (MS 4A, 500 mg) for 12 h at room temperature. The mixture was then diluted with ether and filtered on Florisil column. Silica-gel column chromatography of the residue obtained by evaporation of the solvent afforded **10** [a colorless oil, 121 mg, 47%. 1H NMR $\delta=1.07$ (3H, s), 1.18-1.29 (2H, m), 1.51-1.68 (2H, m), 1.86 (1H, td, $J=9.5$, 4.0 Hz), 2.02 (3H, s), 2.14 (1H, m), 3.27 (1H, d, $J=8.8$ Hz), 3.72 (1H, d, $J=8.8$ Hz), 4.37 (2H, s), 7.15-7.25 (5H, m), and 10.04 (1H, s)].

Conversion of the Primary Alcohol 9 to the Bromomethyl Derivative 11. An anhydrous ether solution (5 cm^3) of **9** (62 mg) was treated with PBr_3 (0.02 cm^3) at 0 ℃ for 20 h. The mixture was then treated with ice-water, and extracted with ether. The crude product **11** was employed for the reaction without purification.

Condensation Reaction of 11 with (3*R*)-1-Iriden-7-al (13). Formation of 14a, 14b and 14c. To an anhydrous THF solution (3 cm^3) of $CrCl_3$ (91 mg) was reduced with LAH (12 mg) at 0 ℃ for 30 min to generate $CrCl_2$. The mixture was once raised to room temperature, and cooled down to 0 ℃ again and the iridenal (**13**) (73 mg) in DMF (1 cm^3) and DMF solution (3 cm^3) of **11** (ca. 70 mg) was added and stirred for 44 h. The mixture was treated with water to terminate the reaction, and extracted with ether. Silica-gel column chromatography afforded three products; **14a** [a colorless crystals, mp 79 ℃, 80 mg, 29%. Found: C, 81.48; H, 10.09%. Calcd for $C_{27}H_{40}O_2$: C, 81.77; H, 10.17%. ^1H NMR $\delta=0.72$ (3H, d, $J=7.0$ Hz), 0.88 (3H, d, $J=7.0$ Hz), 1.09 (3H, s), 1.19 (3H, s), 1.29-1.41 (2H, m), 1.60 (3H, d, $J=1.1$ Hz), 1.61-1.70 (4H, m), 2.17 (1H, m), 2.41 (1H, d, $J=2.2$ Hz), 2.45 (1H, m), 2.81 (1H, br d, $J=8.1$ Hz), 3.20 (1H, d, $J=9.2$ Hz), 3.61(1H, d, $J=9.2$ Hz), 4.51 (2H, s), 4.57 (1H, s), 5.25 (1H, s), 5.30 (1H, s), and 7.23-7.32 (5H, m); ^{13}C NMR $\delta=15.7$, 15.9, 18.7, 22.3, 25.3, 29.1 (2C), 30.8, 35.7, 36.5, 38.6, 40.7, 47.4, 54.2, 69.8, 73.2, 73.5, 116.8, 127.4 (2C), 127.6, 128.2 (2C), 136.4, 137.8, 138.1, and 159.5], **14b** [a colorless oil, 16 mg, 6%. ^1H NMR $\delta=0.81$ (3H, d, $J=7.0$ Hz), 0.96 (3H, d, $J=7.0$ Hz), 1.09 (3H, s), 1.18 (3H, s), 1.22-1.48 (4H, m), 1.53-1.80 (4H, m), 1.90 (3H, s), 2.09-2.27 (2H, m), 2.43 (1H, d, $J=2.2$ Hz), 2.50 (1H, m), 3.15 (1H, d, $J=9.2$ Hz), 3.61 (1H, d, $J=9.2$ Hz), 4.40 (1H, d, $J=12.5$ Hz), 4.43 (1H, d, $J=2.2$ Hz), 4.57 (1H, d, $J=12.5$ Hz), 5.25

(1H, s), 5.31 (1H, s), and 7.22-7.34 (5H, m); ^{13}C NMR δ=16.5, 17.0, 18.2, 22.0, 24.2, 29.5, 29.7, 30.3, 36.8, 36.9, 39.3, 40.6, 48.0, 56.5, 68.2, 69.9, 73.4, 116.0, 127.5, 127.6 (2C), 128.3 (2C), 130.9, 134.9, 138.1, and 154.1], and **14c** [a colorless oil, 30 mg, 11%. ^{1}H NMR δ=0.71 (3H, d, J=7.0 Hz), 0.88 (3H, d, J=7.0 Hz), 1.11 (3H, s), 1.23 (3H, s), 1.24-1.80 (8H, m), 1.75 (3H, s), 1.87 (1H, s), 2.10-2.29 (2H, m), 2.43 (1H, m), 2.83 (1H, br s), 3.32 (1H, d, J=8.8 Hz), 3.40 (1H, d, J=8.8 Hz), 4.52 (1H, d, J=12.5 Hz), 4.54 (1H, d, J=12.5 Hz), 4.73 (1H, s), 5.15 (1H, s), 5.29 (1H, s), and 7.24-7.33 (5H, m); ^{13}C NMR δ=15.6, 15.8, 18.1, 22.2, 24.9, 25.9, 30.8 (2C), 34.8, 35.2, 38.5, 40.6, 46.8, 54.1, 70.5, 73.3, 79.7, 113.3, 127.5 (3C), 128.3 (2C), 135.7, 138.8, 139.4, and 158.0].

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6) The compound **6** was prepared according to our previous method (ref. 4) with slightly modified procedure.
7) The crystallographic data for **14a** are as follows: Crystal system, Orthorhombic; Space group, $P2_12_12_1$; a=10.228 (1) Å, b=31.827 (4) Å, c=7.462 (4) Å; V=2429 (1) Å^3; Z=4; D_{calc}=1.084g cm; 1638 reflections; 1511 obsd. reflections [$I > 2\sigma(I)$]; 264 parameters; Refined on F^2; $wR(F^2)$=0.1003; $R[F^2 > 2\sigma(F^2)]$=0.0361.
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