Synthetic Photochemistry. XXXIV.[1] Synthetic Strategy of 5-8-5-Membered Tricyclic Higher Terpenoids Based on the Condensation of Two Optically-Active Iridoids, C_{10}-Synthons Obtained from Photo-Cycloadduct of Methyl 2,4-Dioxopentanoate-Isoprene, and Its Application to a Synthesis of the Basic Carbon Skeleton of Fusicoccane[2]

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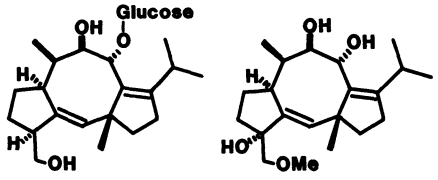
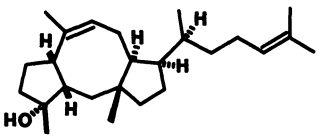
One of the photocycloadducts obtained during methyl 2,4-dioxopentanoate to isoprene was converted to optically active iridoids. Using a $CrCl_2$ reductive-coupling reaction, proper combinations of two kinds of enantiomeric iridoids, 1-iriden-7-al and 9-benzyloxy-7-chloro-1-iridene, produced versatile intermediates for various types of 5-8-5-membered tricyclic natural products. From one such product, fusicocca-2,8,10(14)-triene (**1**) was synthesized by sequential transformations.

There are several higher terpenoids that have 5-8-5-membered tricyclic frameworks e.g, fusicoccins (**A**) and cotylenins (**B**),[3] ophiobolins (**C**),[4] ceroplastols (**D**),[5] and several other recently found derivatives.[6,7] From their stereochemical characteristics, one can say that i) these tricyclic skeletons can be divided into two iridoid blocks, and ii) depending on their origins, these natural products possess different stereochemistries involving a basic carbon skeleton. Therefore, a synthetic strategy based on the dimerization of iridoid synthons to natural products, many of which possess heavy oxygenated functions, and are reported to be physiologically or biologically active, should be attractive. In addition, there are related tricyclic derivatives, e.g., marine metabolites, 6-7-5-membered tricyclo compounds, clavularenes (**E**) isolated from *Clavularia inflata*.[8] Their total synthesis might also be achieved by a slight modification of this method. Recently, we developed a facile preparation of iridoid synthons from the photoadduct of methyl 2,4-dioxopentanoate (**F**) to isoprene (**G**)[9] via titanium(II) chloride-mediated retro-ozonolysis.[10]

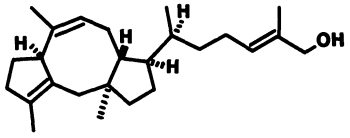
In this paper, the first synthesis of fusicocca-2,8,10(14)-triene (**1**) is described.[11] It is thought to be the missing link in the biogenesis of natural fusicoccins,[2] all of which possess the trans-8β,9α-diol function.[3]



fusicoccin H (A') cotylenol (B')



ophiobolin F (C')



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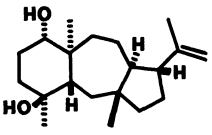
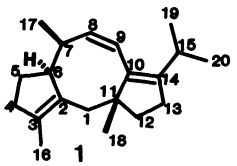


1α,4β-dihydroxyclavular-17-ene (E')



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Scheme 1.

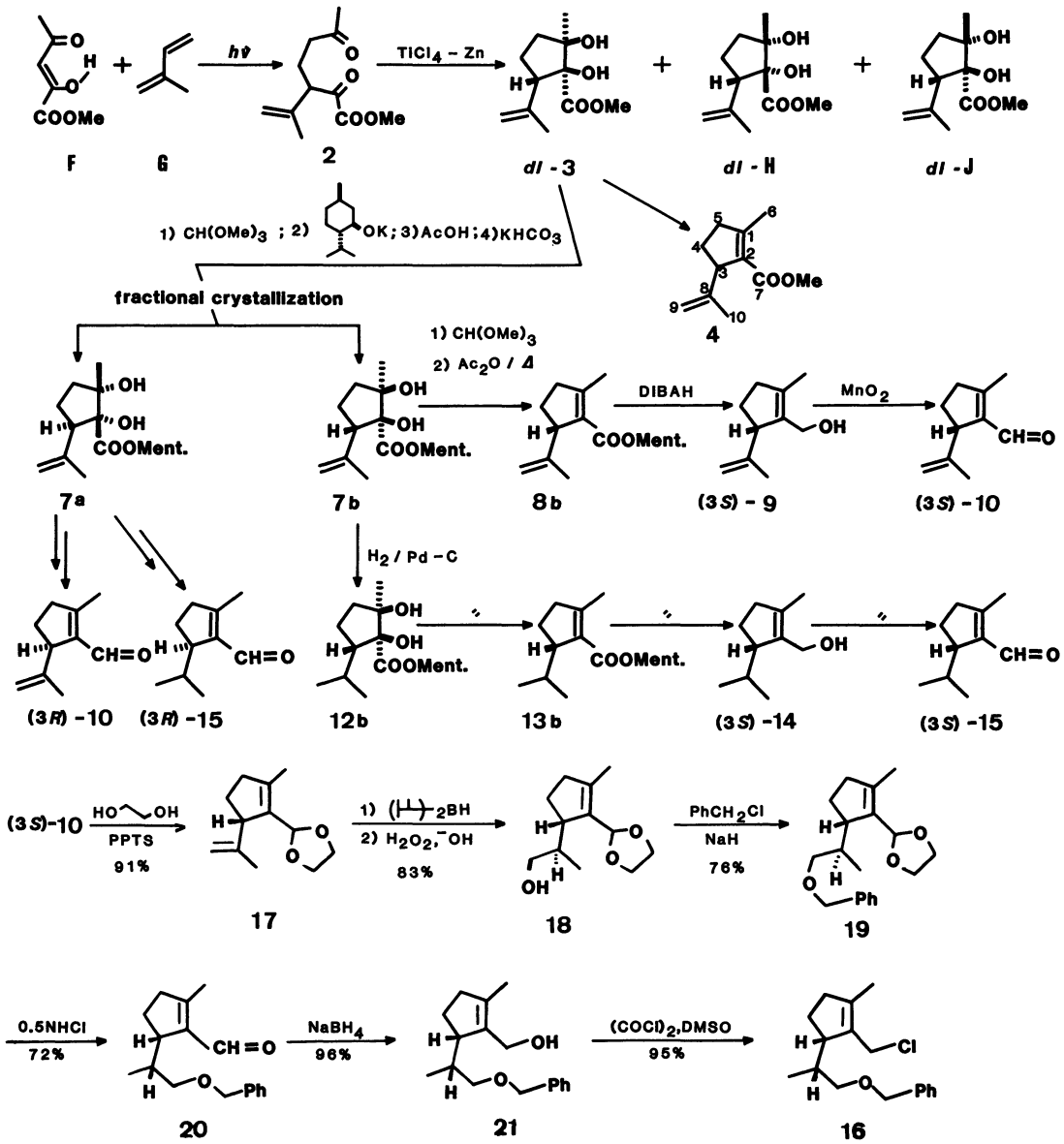
Results and Discussion

Optical Resolution. As previously described,[13] Mukaiyama's titanium(II) chloride-mediated reductive cyclization of photoadduct (**2**) from **F** to **G** gave three 1,2-diol derivatives (**3**, **H**, and **J**), among which the major product, **3**, was convertible to the olefin (**4**) in good yield. Since diols are appropriate for introducing an optically active segment for the resolution, we first investigated the optical resolution of these iridoids to minimize the number of isomers of the dimeric condensates in the subsequent steps. The **3** was treated with trimethoxymethane (**5**) and pyridinium *p*-toluenesulfonate (PPTS) in benzene and with potassium salt of *l*-menthol (**6**) followed by aqueous acetic acid-hydrolysis to form, via an orthoester, *l*-menthyl 1,2-dihydroxy-8-iriden-7-oates (**7a** and **7b**).[14]

Fractional recrystallization of **7a** and **7b** easily enabled the resolution; the isomer with a higher-melting point, mp 97—97.5 °C, showed $[\alpha]_D=-57.1°$, while the isomer with a lower-melting point, mp 81.5—82 °C, showed $[\alpha]_D=-40.8°$. The former was (3*S*)-**7b** and the latter was (3*R*)-**7a** based on the following transformations. The (3*S*)-**7b** was consecutively treated with **5** and PPTS and then with acetic anhydride under reflux[15] to give *l*-menthyl (3*S*)-1,8-iridadien-7-oate ((3*S*)-**8b**). This was, according to a known procedure, transformed to (3*S*)-1,8-iridadien-7-ol ((3*S*)-**9**) by diisobutylaluminum hydride (DIBAH)-reduction and (3*S*)-1,8-iridadien-7-al ((3*S*)-**10**) by manganese(IV) oxide-oxidation.[16] Previously, enantiomeric **10** was prepared and the absolute stereochemistry clarified.[16] For the preparation of **10** from **9**, a Collins oxidation produced a poor result due to the formation of a byproduct, (3*S*)-1,2-epoxy-8-iriden-7-ol (**11**). A catalytic reduction of (3*S*)-**7b** gave a dihydro derivative, *l*-menthyl (1*R*,2*S*,3*S*)-1,2-dihydroxyiridan-7-oate (**12b**), which, upon similar treatment with **5** and PPTS, followed by thermolytic deoxygenation, DIBAH-reduction and oxidation, formed *l*-menthyl (3*S*)-1-iriden-7-oate ((3*S*)-**13b**), (3*S*)-1-iriden-7-ol ((3*S*)-**14**), and (3*S*)-1-iriden-7-al ((3*S*)-**15**). The same transformations starting from (3*R*)-**7a** were carried out.

Chromium(II) Chloride-Mediated Coupling of Two Iridoids and the Stereochemistry. For the chromium(II) chloride-mediated coupling reaction, the required (3*S*)-9-benzyloxy-7-chloro-1-iridene ((3*S*)-**16**) was prepared by (3*S*)-**10** by treating 1,2-ethanediol to give an acetal (**17**), stereoselective hydroboration[9] to (3*S*,8*R*)-7,7-ethylenedioxy-1-iriden-9-ol (**18**), benzylation to 9-benzyloxy derivative (**19**), hydrolysis to 9-benzyloxy-1-iriden-7-al (**20**), reduction to 9-benzyloxy-1-iriden-7-ol (**21**), and treatment with oxalyl dichloride and dimethyl sulfoxide (DMSO)[17] to (3*S*)-**16**.

When (3*S*)-**15** and (3*S*)-**16** were treated with chromi-



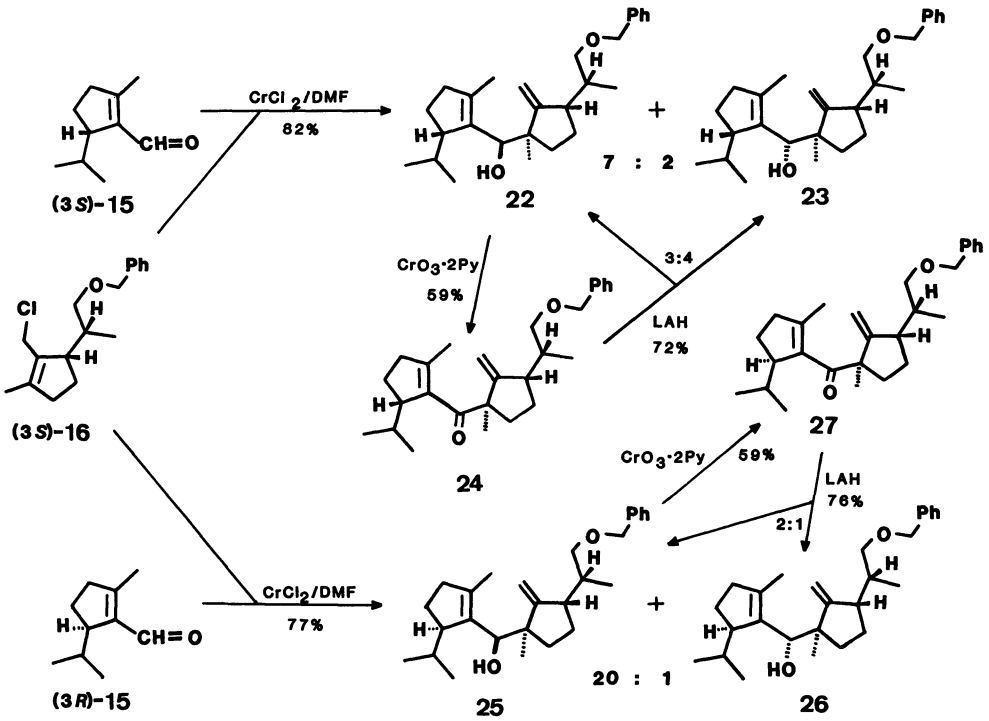
Scheme 2.

um(II) chloride in *N,N*-dimethylformamide (DMF), two condensates (**22** and **23**) were obtained in 82% yield with a ratio of 7:2. Collins oxidation of **22** gave a dehydro ketone (**24**), and its lithium aluminum hydride (LAH)-reduction in tetrahydrofuran (THF) reproduced **22** and **23** in a ratio of 3:4. Therefore, **22** and **23** are epimeric. In parallel, (3*R*)-**15** and (3*S*)-**16** also gave two condensates (**25** and **26**) in 20:1, and by Collins oxidation, the former, **25**, yielded another dehydro ketone (**27**) which was reduced to **25** and **26** by LAH.

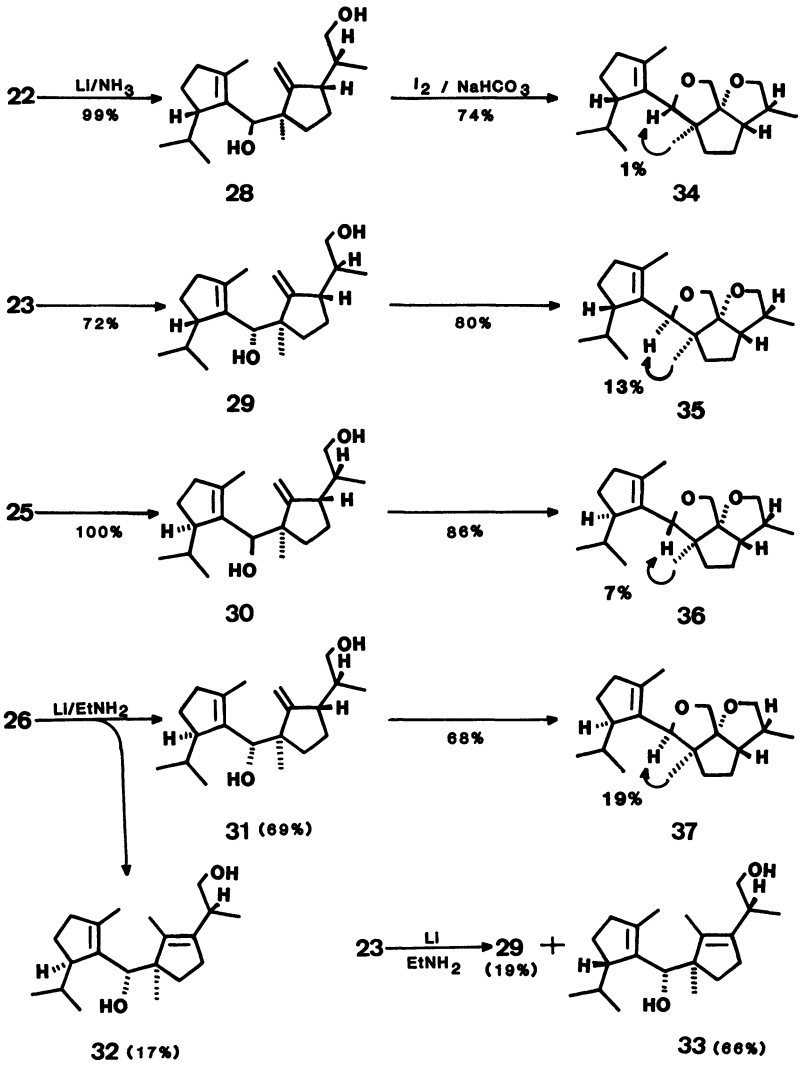
Nevertheless, in both cases the chromium(II) chloride condensation yielded only a pair of epimers. The observed product distributions might indicate the stereochemistry of the C–C bonding site as being an attack of carboanion from the less hindered side to produce a cis-relationship for the quaternary methyl and isopropyl groups.

This has been verified unambiguously as follows. The four condensates (**22**, **23**, **25**, and **26**) were easily debenzylated by a Birch reduction to give 1,2-diols (**28**, **29**, **30**, and **31**) in good yields. When the Birch reduction of **26** was carried out in ethylamine, the products were **31** and its bond-migrated isomer (**32**) with two tetrasubstituted double bonds. This was also the case when **23** was reduced in ethyl amine; the debenzylated products were **29** and the isomeric diene (**33**), the major product (66% yield). All of these (**28** to **31**) formed iodine-free bis-ether derivatives (**34**, **35**, **36**, and **37**). Since these are triply fused five-membered ring systems, their ring junctures should all be cis. From this requirement, quaternary methyl and isopropyl groups are cis, as depicted. The stereochemistry of the secondary hydroxyl groups were determined by the nuclear Overhauser effect between each singlet methyl signal and the proton signal from the carbinyl carbon. The observed enhancement of carbinyl proton signals upon irradiation with radio frequencies corresponding to the chemical shifts ascribable to the quaternary methyl singlets were shown to be 1% for **34**, 13% for **35**, 7% for **36**, and 19% for **37**, respectively. Thus, **35** and **37** possessed a cis-configuration, while their counterparts, **34** and **36**, showed a trans-relationship. The original stereochemistry of **22**, **23**, **25**, and **26** was established as shown.

Cope Rearrangement and the Singlet-Oxygen Oxidation. At first, the recently developed anionic *oxy*-Cope rearrangement[19] was attempted, but gave an inferior result. For instance, the thermolysis of the oxy anion species derived from a potassium hydride treatment of **25** in anhydrous THF caused the fragmentation to two iridoids ((3*R*)-**15** and **38**) and only a small amount of the products (**39a** and **39b**) were obtained as a mixture. The ^{1}H NMR spectra of **38** and **39** revealed that their structures are in agreement with those predicted from the reaction mechanism. On the other hand, the Cope rearrangement was dramatically improved when the secondary hydroxyl was protected by the trimethylsilyl (TMS) group. In this case, the TMS derivative (**40**, **42**, or **43**) prepared from **22**, **25**, or **26**, at 190°C in a sealed tube, a single thermolysate (**44**, **45**, or **46**) was produced each time. However, in the case of **41**, for the TMS derivative of **23**, it was necessary to heat above 200°C for 4 d to produce two products (**47** and **48**). This stereochemical behavior is attributable to the



Scheme 3.

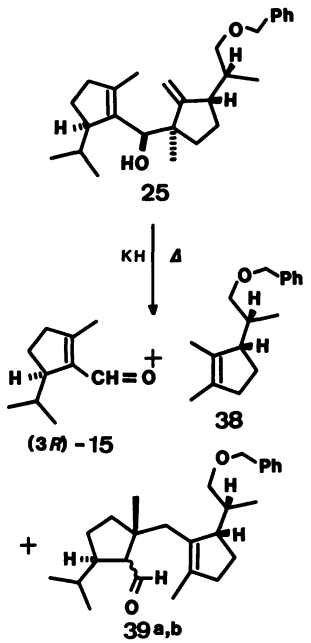


Scheme 4.

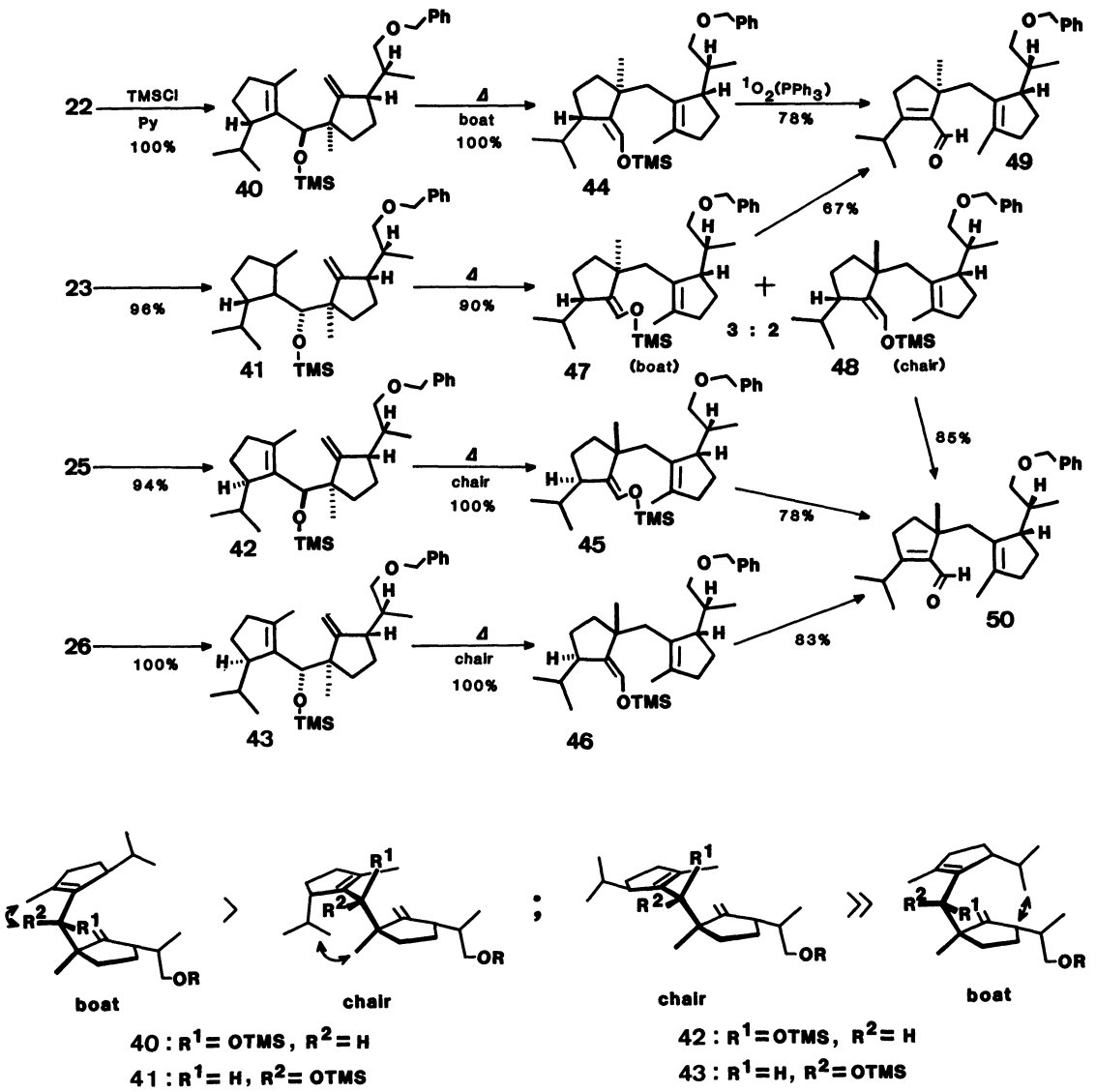
geometry of the transition state in the rearrangement, a concerted [3,3] sigmatropy.

According to a study using molecular models, it is certain that the predominant conformers in the transition state of the rearrangement should be chair-like for **42** and **43**, respectively (Scheme 6). Alternative boat-like conformers suffer heavy nonbonding interactions. On the other hand, the chair-like conformers for **40** and **41** suffer nonbonding interactions and, furthermore, in the boat-like conformer of **41** a considerable interaction also exists between the newly-formed quaternary methyl group and the trimethylsiloxy (TMSO) group due to a 1,3-diaxial mode. As a result, both conformations which are required for an electrocyclic reaction are more unstable than any other extended conformers. Indeed, the thermolysis of **41** required more severe conditions than others and gave two thermolysates, **47** and **48**, via the different transition states.

Although the reaction conditions were different and reflected the geometries of the transition states of



Scheme 5.



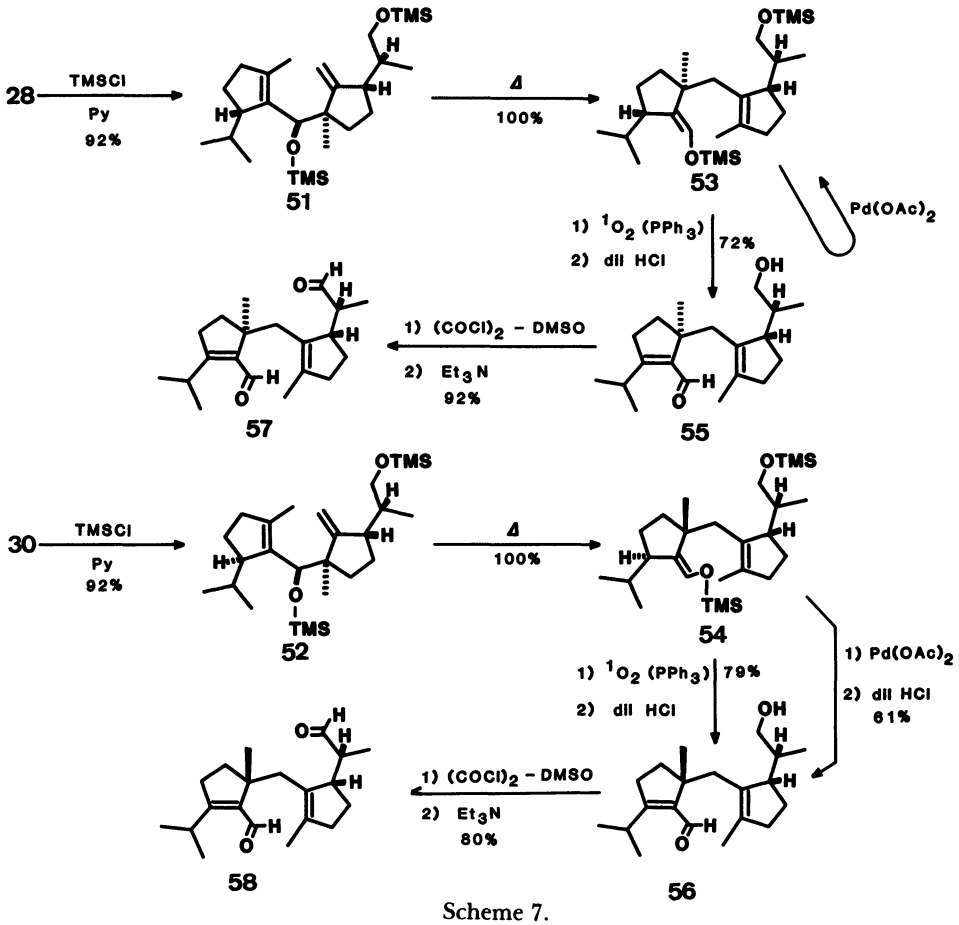
Scheme 6.

the compounds, the reaction mixture remained clean and neat, and the yields of the thermolysates were satisfactory.

Thus, Cope rearrangement worked to not only transfer an oxygen function to the required position for subsequent cyclization, but also worked to adjust the stereochemistry of fused tricyclic frameworks. This means one can synthesize various stereoisomers with or without a Cope rearrangement. In view of the oxidation state around the ring C of fusicoccane derivatives and for the sake of a convenient structural analysis, thermolysates were oxidized to α,β-unsaturated aldehydes (**49** and **50**). For this purpose either singlet oxygen ($^1O_2$)-oxidation[19] or palladium(II) acetate-oxidation[20] might be suitable. The former gave the better result. It is particularly advantageous that, at least for a preparative purpose, the separation of $CrCl_2$-induced condensation products was not necessary. The subsequent transformation of **25** and **26** resulted in the formation of the same compounds, while the thermolysis conditions of **22** and **23** were greatly different.

Dialdehyde Formation. Based on the establishment of a stereoelectronic course for the Cope rearrangement, we then investigated the thermolysis with more suitable reactants than the benzyloxy derivatives (**40**, **41**, **42**, and **43**): The bis-TMS derivatives (**51** and **52**) derived from **28** and **30**. Indeed, a clean stereospecific rearrangement occurred forming **53** and **54**. In parallel to **40**, and **42**, **53**, and **54** were each oxidized with $^1O_2$ to α,β-unsaturated aldehydes (**55** and **56**) which, by the advantage of TMS derivatives, generated the primary hydroxyl groups during the workup. An alternative palladium(II) acetate oxidation gave **56** from **54** in fair yield, but gave no **55** from **53**.

The Swern oxidation[17] of **55** and **56** gave the desired dialdehydes (**57** and **58**) in good yields. From its stereostructure, **58** should be a precursor of diterpenoids such as cotylenins or fusicoccins while **57** should be a good precursor for sesterterpenoids such as ophio-

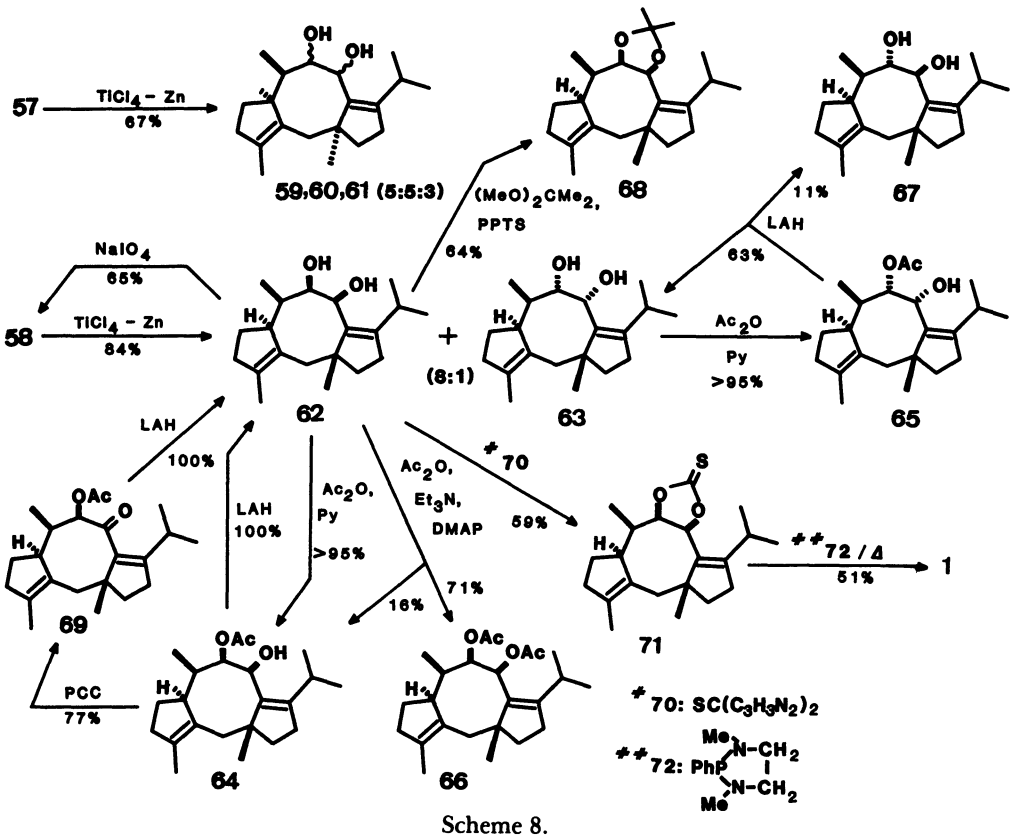


Scheme 7.

bolanes or ceroplastanes. This is true even though further transformations are required to furnish the correct stereochemistry on the side chains. Recently, several diterpenoids with a "sesterterpenoid-like" ring systems have been isolated.[7]

Titanium(II) Chloride-Mediated Reductive Cyclization. When **57** was reduced with titanium(II) chloride (generated in THF by Mukaiyama's method),[10] three cyclisates (**59**, **60**, and **61**) were formed (5:5:3) with a combined yield of 68%. However, it required high-dilution conditions to prevent an intermolecular condensation. Although the central eight-membered B-ring might be conformationally flexible, a careful inspection of the ^{1}H NMR spectra showed their stereostructures. Both **60** and **61** revealed large vicinal couplings (J=9 Hz) between the protons on the carbons of 1,2-diol functions, making them to be trans-diols. The **59** revealed a small coupling constant (J=4 Hz), indicating a cis-diol structure. Moreover, **59** and **61** exhibited relatively lower signals which were ascribable to the quaternary methyl singlets at δ=1.20, while the signal of the corresponding methyl of **60** was at 0.98. Accordingly, the quaternary methyl and C-9 hydroxyl of **59** and **61** are in cis-direction, and, thus, have a 1,3-diaxial relationship. From these facts, **59**, **60**, and **61** must be 8α,9α-diol, 8α,9β-diol, and 8β,9α-diol, respectively. The chemical shifts of their secondary methyl groups at C-7, were 0.93 for **59**, 0.96 for **60**, and 0.98 for **61**. These were also explainable in terms of an anisotropic effect due to adjacent C-8 hydroxyl groups.

On the other hand, the titanium(II) chloride-induced cyclization of **58** was much superior with respect to product distributions; it gave almost one product (**62**) in a yield greater than 80%. Although a byproduct (**63**) could not be isolated as diol, its formation was confirmed after silica-gel column chromatography of the monoacetates (**64** and **65**) prepared from a mixture of the cyclisates. Its yield was estimated to be ca. 11%. A diacetate (**66**) was obtained by the acetylation of **62** with acetic anhydride and 4-(dimethylamino)pyridine (DMAP) together with some amount of **64**. The removal of the acetyl group of **65** by LAH-reduction resulted in a solvolytic rearrangement; the major product was indeed **63** whose ^{1}H NMR spectrum had a close resemblance to that of **65**. The byproduct (**67**) showed the signal for the quaternary methyl group at relatively low-field to indicate an epimerization of C-9 hydroxyl to form 8α,9β-diol. It is certain that the original mixture did not contain **67**. A smooth sodium periodate-oxidation of **62** afforded **58**; therefore, the original configuration was retained during the cyclization. The structure of **62** resembles that of the natural fusicoccins; only the differences are orientation



Scheme 8.

of C-9 hydroxyl and the position of the double bond in the A/B rings. The stereochemistry of the 1,2-diol function of **62** was further confirmed by the formation of an acetonide (**68**) which could be prepared by a PPTS-treatment of **62** and 2,2-dimethoxypropane. The central eight-membered ring of **68** became rigid and showed sharp ^{1}H NMR signals which revealed the coupling patterns of the methine protons, i.e., the signals at δ=4.20 and 5.17 mutually coupled with 9 Hz to clarify the cis relationship. Also the former signal showed an additional coupling (1 Hz) to the vicinal methine proton at a carbon bearing the secondary methyl group. We tried hard to invert the hydroxyl group at C-9; for example, when the keto acetate (**69**), prepared from **64** by pyridinium chlorochromate (PCC)-oxidation, was reduced by LAH. The isolable product was only regenerated **62**. We are still studying this matter.[21]

Synthesis of Fusicoccatriene. According to the biogenetic concept, the C-8 and C-9 positions of these terpenoids correspond to one of the head-to-tail junctures of the isoprene units.[22] Therefore, in the original precursors (geranylgeraniol or geranylfarnesol) they were the sp^3-carbons. This means that the 1,2-diol function was derived via a dehydrogenation followed by epoxidation and hydrolysis. Consequently, the reductive elimination of the 1,2-diol to an olefin (**1**) should constitute a synthesis of a common intermediate during biogenesis. Following Corey's procedure,[23] **62** was converted by 1,1'-(thiocarbonyl)bis[diimidazole] (**70**) to a thiocarbonate (**71**). After several unsuccessful attempts, **71** was finally converted to **1**. Its heating in benzene to reflux with a thiophile, 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (**72**),[24] afforded a hydrocarbon whose NMR features and molecular weight (by mass spectrometry) were fully consistent with the structure of **1**.

Up to now, several synthetic studies regarding these tricyclic higher terpenoids have been reported, but most of the current effort seems to be concerned with the construction of model system.[25-27]

Experimental

All mps (measured by means of a Yanagimoto Micro-mp Apparatus) are uncorrected. Elemental analyses were performed by Miss S. Hirashima of Research Institute of Industrial Science, Kyushu University. The purity of the each analytical specimen was checked by high-pressure liquid chromatography (HPLC) on a Nippon Waters ALC 244 Model apparatus with a prepacked Micropolasil column (stainless steel, diameter; 7.8 mm, and length; 300 mm). Gas-liquid chromatography (GLC) was carried out by means of a Yanagimoto Model G 80 apparatus with a thermal-conductivity detector. Optical rotations were measured by means of a Union Model PM-101 apparatus. The NMR spectra were measured using a JEOL FX 100 Spectrometer with a $CDCl_3$ solutions. Chemical shifts measured were expressed in δ units from the internal Me_4Si. The mass spectra were measured by means of a JEOL 01SG-2 Spectrometer. The IR spectra were taken in either as KBr disks or as liquid film (NaCl plates) using a JASCO

IR-A 102 Spectrometer.

Optical Resolution of 3. A mixture of **3** (1.54g), **4** (15 cm³), and PPTS (100 mg) was kept room temperature for 16 h. Then, the mixture was partitioned between a 1:1-mixture of hexane and AcOEt and aqueous $NaHCO_3$. The organic layer was washed with brine, dried on $MgSO_4$ and chromatographed on a silica-gel column with AcOEt–hexane (1:8) to give a colorless oil (1.80 g; 98%). To a THF solution (25 cm³) containing potassium salt of **6** (prepared from **6** (7.5 g) and potassium (500 mg)), a THF solution (18 cm³) of the above oily product was added and refluxed under an N_2 atmosphere for 20 min with the gradual removal of THF (18 cm³). Subsequently, aqueous NH_4Cl was added to the cooled mixture and extracted with AcOEt and hexane (1:5). The organic extract was washed with aqueous $NaHCO_3$, water and brine and dried on $MgSO_4$. The evaporation of the solvent left a pale-yellow oil which was chromatographed on a silica-gel column to remove an excess of **6** from a diastereomeric mixture of *l*-menthyl ester (2.50 g; 94%).

This was dissolved in a mixture (40 cm³) of AcOH, THF, and water (2:2:1) and refluxed for 2 h. After dilution with water, K_2CO_3 was introduced to neutralize AcOH in the mixture. The mixture was then extracted with AcOEt and heated in vacuo to give a yellow-oily diastereomeric mixture of formates, which was further treated with saturated aqueous $KHCO_3$ (5 cm³) in MeOH (30 cm³) at room temperature for 45 min. After removal of MeOH in vacuo. The residue was diluted with water and extracted with AcOEt. A yellow oil from the extract was chromatographed on a silica-gel column to give a mixture of a *l*-menthyl ester of 1,2-dihydroxy-8-iriden-7-oate, **7a** and **7b** (2.125 g). Fractional recrystallizations from hexane by alternate seeding of **7a** and **7b** afforded, after repeating the operation several times, (3*S*)-**7b** [colorless prisms, mp 97—97.5°C, 1.007 g; 95%. Found: C, 71.21; H, 10.24%. Calcd for $C_{20}H_{34}O_4$: C, 70.97; H, 10.12%. $[\alpha]_D=-57.1°$ (*c* 2.10, $CHCl_3$). ^1H NMR δ=0.74 (3H, d, *J*=7 Hz), 0.91 (6H, d, *J*=7 Hz), 1.25 (3H, s), 1.73 (3H, br s), 3.02 (1H, br s, OH), 3.18 (1H, br m), 3.56 (1H, s, OH), 4.73 (1H, td, *J*=10, 4 Hz), 4.79 (1H, m), and 4.87 (1H, m). ^{13}C NMR δ=15.6, 20.8, 22.0, 22.5, 22.9, 24.7, 25.5, 25.8, 31.4, 34.2, 38.8, 40.6, 46.8, 51.4, 76.5, 81.2, 85.0, 112.8, 143.7, and 173.8. IR ν: 3425, 2970, 2940, 2880, 1720, 1638, 1448, 1377, 1290, 1254, 1128, 1023, and 884 cm⁻¹] and (3*R*)-**7a** [colorless plates, mp 81.5—82°C, 1.020 g; 96%. Found: C, 71.23; H, 10.18%. $[\alpha]_D=-40.8°$ (*c* 2.11, $CHCl_3$). ^1H NMR δ=0.74 (3H, d, *J*=7 Hz), 0.91 (6H, d, *J*=7 Hz), 1.25 (3H, s), 1.71 (3H, br s), 3.10 (1H, br m), 3.13 (1H, br s, OH), 3.71 (1H, s, OH), 4.77 (1H, td, *J*=10, 4 Hz), 4.78 (1H, m), and 4.85 (1H, m). ^{13}C NMR δ=15.5, 20.9, 22.0, 22.5, 22.8, 24.5, 25.7, 25.8, 31.4, 34.1, 38.8, 40.6, 47.0, 51.5, 76.7, 81.3, 84.6, 112.5, 143.7, and 174.3. IR ν: 3555, 3495, 2955, 2930, 2870, 1710, 1640, 1448, 1354, 1248, 1110, 970; and 898 cm⁻¹].

Reductive Elimination of (1*R*,2*S*,3*S*)-7b to *l*-Menthyl (3*S*)-1,8-Iridadien-7-oate ((3*S*)-8b). A mixture of (3*S*)-**7b** (249 mg), **5** (3 cm³) and PPTS (30 mg) was stirred at room temperature for 15 h. The resultant dioxolane derivative (after the usual workup) was heated in Ac_2O (3 cm³) for 3 h. The mixture was poured into aqueous $NaHCO_3$ and stirred an additional 1 h at room temperature and extracted with a mixture of hexane and ether. The organic extract was, after removing the solvent, chromatographed on a silica-gel column with hexane–ether (15:1) to give (3*S*)-**8b** [a colorless oil, 222 mg; 99%. Found: C, 79.12; H, 10.59%. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59%. $[\alpha]_D=-28.5°$ (*c* 1.86, $CHCl_3$). ^1H NMR δ=0.76 (3H, d, *J*=7 Hz), 0.88 (6H, d, *J*=7 Hz), 1.67 (3H, br s), 2.11 (3H, br s), 3.57 (1H, br m), 4.62 (2H, m), and 4.67 (1H, td, *J*=10, 4 Hz). ^{13}C NMR δ=16.2, 16.6, 20.4, 20.8, 22.1, 23.7, 26.5, 28.6, 31.4, 34.4, 39.3, 40.8, 47.2, 53.5, 73.3, 109.2, 130.1, 148.0, 155.2, and 165.6. IR ν: 2955, 1705, 1648, 1454, 1372, 1274, 1220, 1123, 1052, and 894 cm⁻¹].

Reductive Elimination of (1*S*,2*R*,3*R*)-7a to *l*-Menthyl (3*R*)-1,8-Iridadien-7-oate ((3*R*)-8a). Similarly, (3*R*)-**7a** (268 mg) was converted to (3*R*)-**8a** [a colorless oil, 239 mg; 99%. Found: C, 79.02; H, 10.65%. $[\alpha]_D=-112.9°$ (*c* 2.17, $CHCl_3$). ^1H NMR δ=0.69 (3H, d, *J*=7 Hz), 0.85 (3H, d, *J*=7 Hz), 0.89 (3H, d, *J*=7 Hz), 1.68 (3H, br s), 2.13 (3H, br s), 3.57 (1H, br m), 4.62 (2H, m), and 4.68 (1H, td, *J*=10, 4 Hz). ^{13}C NMR δ=15.7, 16.2, 20.8, 21.0, 22.1, 23.0, 25.4, 28.7, 31.5, 34.4, 39.2, 41.3, 47.3, 53.3, 73.2, 109.1, 130.1, 148.2, 155.8, and 165.6. IR ν: 2955, 1705, 1649, 1455, 1372, 1273, 1223, 1127, 1051, and 885 cm⁻¹].

DIBAH-Reduction of (3*S*)-8b to (3*S*)-9. Following the method described by Paquette,[16] (3*S*)-**8b** (122 mg) was reduced with a toluene solution (1 cm³) of DIBAH (1.5 M) in anhydrous ether (8 cm³) at −78°C to (3*S*)-**9** [a colorless oil, 55 mg; 90%. $[\alpha]_D=+193.6°$ (*c* 1.40, $CHCl_3$ (lit,[16] +143.9°)). ^1H NMR δ=1.64 (3H, br s), 1.72 (3H, br s), 3.97 (1H, d, *J*=12 Hz), 4.20 (1H, d, *J*=12 Hz), and 4.75 (2H, m). IR ν: 3550, 2900, 1370, and 890 cm⁻¹].

MnO_2 Oxidation of (3*S*)-9 to (3*S*)-10. (3*S*)-**9** (1.00 g) was treated with MnO_2 (10 g) in CH_2Cl_2 (40 cm³) for 2 d to give, after chromatographic purification, (3*S*)-**10** [a colorless oil, 675 mg; 68%. $[\alpha]_D=+45.8°$ (*c* 1.40, $CHCl_3$ (lit,[16] +56.1°; lit,[28] +61.5°, EtOH)). ^1H NMR δ=1.68 (3H, br s), 2.18 (3H, br s), 3.60 (1H, br m), 4.64 (2H, m), and 9.91 (1H, s). ^{13}C NMR δ=14.5, 20.5, 28.6, 39.4, 50.8, 109.6, 139.1, 146.8, 163.4, and 187.8. IR ν: 3010, 2950, 2850, 2740, 1660, 1437, 1378, and 890 cm⁻¹].

Collins Oxidation of (3*S*)-9 to (3*S*)-10. To a CH_2Cl_2 solution (25 cm³) of (3*S*)-**9** (119 mg), Collins reagent (1.20 g) was added and stirred at room temperature for 45 h. The mixture was then diluted with hexane–AcOEt (1:1) and filtered on a short silica-gel column to remove the reagent. The organic filtrate was distilled in vacuo and further fractionated through a silica-gel column to give (3*S*)-**10** (62 mg; 53%) together with **11** [a colorless oil, 14.9 mg; 11%. Found: M.W., 168.1155. Calcd for $C_{10}H_{16}O_2$: 168.1150. ^1H NMR δ=1.44 (3H, s), 1.68 (3H, s), 2.97 (1H, br d, *J*=7 Hz), 3.58 (1H, d, *J*=12 Hz), 3.98 (1H, d, *J*=12 Hz), and 4.74 (2H, m). ^{13}C NMR δ=15.5, 20.9, 25.7, 32.7, 48.4, 60.1, 70.2, 72.4, 112.3, and 145.7. IR ν: 3450, 2950, 1450, 1380, 1030, 893, and 755 cm⁻¹].

Conversion of (3*R*)-8a to (3*R*)-10 via (3*R*)-9. Similarly, (3*R*)-**8a** was converted to (3*R*)-**9** [a colorless oil, 95%. $[\alpha]_D=-195.0°$ (*c* 0.80, $CHCl_3$)] which was then oxidized into (3*R*)-**10** [a colorless oil, 91%. $[\alpha]_D=-45.1°$ (*c* 3.66, $CHCl_3$)].

Catalytic Reduction of (3*S*)-7b to (3*S*)-12b. (3*S*)-**7b** (181 mg) was hydrogenated with Pd/carbon (5%, 15 mg) in MeOH (5 cm³) to give (3*S*)-**12b** [colorless prisms, mp 141—142°C, 182 mg; 100%. Found: C, 70.61; H, 10.76%. Calcd for $C_{20}H_{36}O_4$: C, 70.55; H, 10.66%. $[\alpha]_D=-40.0°$ (*c* 2.80, $CHCl_3$). ^1H NMR δ=0.72 (3H, d, *J*=7 Hz), 0.83 (3H, d, *J*=7 Hz), 0.88 (3H, d, *J*=7 Hz), 0.90 (6H, d, *J*=7 Hz), 1.20 (3H, s), 2.74 (1H, br s, OH), 3.62 (1H, br s, OH), and 4.73 (1H, td, *J*=10.5, 4 Hz). IR ν: 3420, 2955, 2870, 1725, 1378,

1250, 1117, and 1016 cm^{-1}].

Catalytic Reduction of (3*R*)-7a to (3*R*)-12a. Similarly, (3*R*)-**7a** (178 mg) was converted to (3*R*)-**12a** [colorless needles, mp 115—116°C, 179 mg; 100%. Found: C, 70.61; H, 10.76%. $[\alpha]_D=-65.4°$ (*c* 1.99, $CHCl_3$). ^1H NMR δ=0.74 (3H, d, *J*=7 Hz), 0.81 (6H, d, *J*=7 Hz), 0.91 (3H, d, *J*=7 Hz), 0.93 (3H, d, *J*=6 Hz), 1.22 (3H, s), 2.96 (1H, s, OH), 3.74 (1H, s, OH), and 4.74 (1H, td, *J*=10.5, 4 Hz). IR ν: 3565, 3510, 2960, 2870, 1717, 1353, 1250, 1138, and 1104 cm^{-1}].

Reductive Elimination of (3*S*)-12b to (3*S*)-13b. Similar to the case of **7** to **8**, (3*S*)-**12b** (173 mg) was treated with **5** (3 cm^3) and PPTS (30 mg) to yield a dioxolane derivative which was then heated in Ac_2O (3 cm^3) to give (3*S*)-**13b** [a colorless oil, 152 mg; 98%. Found: C, 78.43; H, 11.23%. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18%. $[\alpha]_D=-64.5°$ (*c* 2.20, $CHCl_3$). ^1H NMR δ=0.69 (3H, d, *J*=7 Hz), 0.77 (3H, d, *J*=7 Hz), 0.88 (6H, d, *J*=7 Hz), 0.91 (3H, d, *J*=6 Hz), 2.03 (3H, br s), 2.98 (1H, br m), and 4.74 (1H, td, *J*=10.5, 4 Hz). IR ν: 2955, 2930, 2870, 1706, 1646, 1468, 1369, 1240, 1220, 1108, and 1052 cm^{-1}].

Conversion of (3*R*)-12a to (3*R*)-13a. Similarly, (3*R*)-**12a** (170 mg) gave (3*R*)-**13a** [a colorless oil, 147 mg; 96%. Found: C, 78.36; H, 11.24%. $[\alpha]_D=-58.5°$ (*c* 1.95, $CHCl_3$). ^1H NMR δ=0.69 (3H, d, *J*=7 Hz), 0.76 (3H, d, *J*=7 Hz), 0.88 (9H, d, *J*=7 Hz), 2.03 (3H, br s), 2.98 (1H, br m), and 4.76 (1H, td, *J*=10.5, 4 Hz). IR ν: 2955, 2920, 2865, 1702, 1643, 1468, 1368, 1238, 1218, 1099, and 1050 cm^{-1}].

DIBAH-Reduction of (3*S*)-13b to (3*S*)-14. Similar to the case of **8** to **9**, (3*S*)-**13b** (132 mg) was treated with DIBAH to give (3*S*)-**14** [a colorless oil, 61 mg; 92%. Found: M. W., 154.1367. Calcd for $C_{10}H_{18}O$: 154.1357. $[\alpha]_D=+17.6°$ (*c* 3.76, $CHCl_3$). ^1H NMR δ=0.67 (3H, d, *J*=7 Hz), 0.92 (3H, d, *J*=7 Hz), 1.70 (3H, br s), 2.82 (1H, br m), 3.99 (1H, d, *J*=12 Hz), and 4.26 (1H, d, *J*=12 Hz). ^{13}C NMR δ=13.9, 15.9, 21.4, 21.8, 28.7, 38.0, 51.8, 57.3, 136.4, and 137.0. IR ν: 3350, 2900, 1470, 1380, 1360, and 1000 cm^{-1}].

MnO_2 Oxidation of (3*S*)-14 to (3*S*)-1-Iriden-7-al ((3*S*)-15). Similar to the case of **9** to **10**, (3*S*)-**14** (1.00 g) was oxidized with MnO_2 (10 g) in CH_2Cl_2 (40 cm^3) to (3*S*)-**15**[29] [a colorless oil, 893 mg; 90%. Found: M.W., 152.1199. Calcd for $C_{10}H_{16}O$: 152.1200. $[\alpha]_D=-5.5°$ (*c* 5.47, $CHCl_3$). ^1H NMR δ=0.65 (3H, d, *J*=7 Hz), 0.88 (3H, d, *J*=7 Hz), 2.14 (3H, s), 3.00 (1H, br m), and 9.97 (1H, s). ^{13}C NMR δ=14.3, 16.4, 21.3, 22.1, 28.9, 40.1, 50.0, 140.0, 163.1, and 188.2. IR ν: 2980, 1670, and 760 cm^{-1}].

Conversion of (3*R*)-13a to (3*R*)-15 via (3*R*)-14. Similarly, (3*R*)-**13a** was converted to (3*R*)-**14** [a colorless oil, 95%. $[\alpha]_D=-17.9°$ (*c* 2.79, $CHCl_3$)], which was then oxidized to (3*R*)-**15**[30] [a colorless oil, 70%. $[\alpha]_D=+6.9°$ (*c* 3.77, $CHCl_3$)].

Preparation of Ethylenedioxy Acetal of 1,8-Iridadien-7-al (17). An anhydrous benzene solution (330 cm^3) of (3*S*)-**10** (23.5 g) and 1,2-ethanediol (50 cm^3) was refluxed in the presence of PPTS (3.2 g) for 9 h along with the removal of liberated water by means of a Dean-Stark apparatus. To the mixture, aqueous $NaHCO_3$ was added and extracted with benzene. The organic extract was dried on K_2CO_3 and evaporated to leave a brown oil which was purified by distillation in vacuo (bp 60—70°C/2 mmHg) to give **17** [a colorless oil, 27.7 g; 91%. Found: M.W., 194.1315. Calcd for $C_{12}H_{18}O_2$: 194.1306. ^1H NMR δ=1.64 (3H, br s), 1.81 (3H, br s), 3.50 (1H, br m), 3.72—4.08 (4H, m), 4.58 (1H, br s), 4.67 (1H, br s), and 5.49 (1H, s). ^{13}C NMR δ=14.1, 18.7, 28.7, 38.6, 53.5, 64.8, 65.3, 100.3, 109.4, 132.9, 142.5, and 149.1. IR ν: 3070, 2945, 2890, 1677, 1642, 1437, 1390, 1185, 1100, 1055, 943, and 881 cm^{-1}].

Hydroboration of 17. To an anhydrous diethylene glycol dimethyl ether solution (40 cm^3) containing $NaBH_4$ (1.62 g), 2-methyl-2-butene (13.0 cm^3) was introduced at 0°C. Subsequently, BF_3–etherate (5.9 cm^3) was added dropwise and stirred at 0°C for 2 h. After this, an anhydrous diglyme solution (10 cm^3) of **17** (5.34 g) was added dropwise within a 20-min period. After keeping 0°C for another 30 min, the mixture was warmed to room temperature with stirring for 2 h. Then, the mixture was cooled again to below 0°C, aqueous 3M† NaOH (28 cm^3) was introduced, 30% H_2O_2 (25 cm^3) was also introduced within a 40-min period at 50°C, and further stirred for 1 h. The mixture was then extracted with ether, dried on K_2CO_3 and distilled by means of a Kugelrohr apparatus in vacuo to give **18** [a colorless oil, 4.86 g; 83%]. The sample obtained by this workup was suitable for subsequent reaction, but the analytical sample [Found: M.W., 212.1416. Calcd for $C_{12}H_{20}O_3$: 212.1411. ^1H NMR δ=0.88 (3H, d, *J*=7 Hz), 1.76 (3H, br s), 2.63 (1H, br, OH), 3.01 (1H, br m), 3.2—3.7 (2H, m) which changed to 3.31 (1H, dd, *J*=10.9, 7.8 Hz), and 3.54 (1H, dd, *J*=10.9, 5.9 Hz) by addition of D_2O, 3.8—4.2 (4H, m), and 5.51 (1H, s). ^{13}C NMR δ=13.8, 15.9, 23.2, 38.0, 38.2, 48.4, 63.9, 64.4, 64.6, 100.2, 131.1, and 143.3. IR ν: 3440, 2880, 1675, 1460, 1438, 1397, 1380, 1195, 1092, 1048, 980, and 943 cm^{-1}] was obtained by alumina column chromatography.

Preparation of 9-Benzyloxy-1-iriden-7-al (20) via Its Ethylenedioxy Acetal (19). To an anhydrous DMF solution (280 cm^3) of NaH (1.4 g), a DMF solution (20 cm^3) of **18** (4.45 g) was added and stirred for 1 h. Then, benzyl chloride (4.0 cm^3) was added and stirred at room temperature for 96 h. Ether extraction of the mixture yielded **19** [a colorless oil, 4.82 g; 76%. ^1H NMR δ=1.02 (3H, d, *J*=7 Hz), 1.75 (3H, br s), 3.00 (1H, br m), 3.19 (1H, t, *J*=9 Hz), 3.49 (1H, dd, *J*=9, 4 Hz), 3.7—4.0 (4H, m), 4.39 (1H, d, *J*=12 Hz), 4.47 (1H, d, *J*=12 Hz), 5.47 (1H, s), and 7.27 (5H, br s). ^{13}C NMR δ=14.2, 16.6, 23.9, 35.8, 38.3, 49.4, 64.4, 64.9, 72.7, 72.8, 100.6, 127.1, 127.3 (2C), 128.1 (2C), 131.6, 139.1, and 143.0. IR ν: 2955, 2880, 1677, 1498, 1455, 1095, 943, 735, and 696 cm^{-1}], which was without purification, treated with 0.5 M HCl (80 cm^3) in ether (150 cm^3) for 4 h. Subsequently, the mixture was treated with 10%-$NaHCO_3$, extracted with ether, chromatographed on a silica-gel column to give **20** [colorless needles, mp 53—53.5°C, 3.10 g; 72%. Found: C, 78.74; H, 8.76%. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58%. $[\alpha]_D=-12.2°$ (*c* 5.72, $CHCl_3$). ^1H NMR δ=0.95 (3H, d, *J*=7 Hz), 2.07 (3H, br s), 3.14 (1H, br m), 3.20 (1H, dd, *J*=9, 7 Hz), 3.34 (1H, dd, *J*=9, 5.5 Hz), 4.39 (2H, br s), 7.24 (5H, br s), and 9.92 (1H, s). ^{13}C NMR δ=14.3, 16.0, 24.2, 35.2, 39.6, 47.1, 72.7, 73.0, 127.2 (3C), 128.1 (2C), 138.7, 139.3, 163.4, and 188.1. IR ν: 2950, 2850, 2730, 1655, 1618, 1493, 1450, 1425, 1365, 1210, 1088, 990, 758, and 700 cm^{-1}].

Preparation of 9-Benzyloxy-1-iriden-7-ol (21). An MeOH solution (130 cm^3) of **20** (5.07 g) was reduced with $NaBH_4$ (750 mg) to give **21** [colorless liquid, 4.947 g; 96.5%. Found: C, 78.45; H, 9.32%. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29%. ^1H NMR δ=0.91 (3H, d, *J*=7 Hz), 1.68 (3H, br s), 2.70 (1H, dd, *J*=7, 6 Hz, OH), 2.84 (1H, br m), 3.25 (1H, dd, *J*=9, 6 Hz), 3.36 (1H, dd, *J*=9, 7 Hz), 4.08 (2H, br m), 4.36 (1H, d, *J*=12 Hz), 4.45 (1H, d, *J*=12 Hz), and 7.25 (5H, br s). ^{13}C NMR δ=14.0, 16.6, 23.3, 35.5, 37.6, 50.6, 57.7, 72.9, 73.2, 127.5, 127.6 (2C),

† 1 M = 1 mol dm^{-3}.

128.7 (2C), 136.1, 137.1, and 138.1. IR ν: 3410, 2960, 1677, 1498, 1457, 1096, 1005, 736, and 698 cm^{-1}].

Preparation of 9-Benzyloxy-7-chloro-1-iridene (16). To an anhydrous CH_2Cl_2 solution (30 cm^3) of $(COCl)_2$ (0.8 cm^3), anhydrous DMSO (1.3 cm^3) was added at −60°C with stirring. After 5 min, an anhydrous CH_2Cl_2 solution (2 cm^3) of **21** (1.984 g) was added dropwise during a 15-min period. The mixture was then gradually warmed to 0°C within 1 h, extracted with ether, dried on $MgSO_4$, and distilled in vacuo to remove the solvent to leave **16** [pale yellow oil, 2.01 g; 95%. ^1H NMR δ=1.02 (3H, d, J=7 Hz), 1.71 (3H, br s), 2.93 (1H, br m), 3.20 (1H, dd, J=9, 7 Hz), 3.34 (1H, dd, J=9, 5 Hz), 4.05 (1H, br d, J=12 Hz), 4.20 (1H, d, J=12 Hz), 4.41 (2H, br s), and 7.25 (5H, br s)], which was very sensitive towards the acidic species that it prevented a further purification.

$CrCl_2$-Mediated Condensation of (3*S*)-16 and (3*S*)-15. To an anhydrous THF suspension (30 cm^3) of $CrCl_3$ (3.76 g) under an N_2 atmosphere at 0°C, LAH (440 mg) was added to form $CrCl_2$. After 30 min, the medium was changed, in vacuo, from THF to anhydrous DMF (40 cm^3) by transfer. Subsequently, a DMF solution (5 cm^3) of (3*S*)-**15** (1.80 g) and a DMF solution (5 cm^3) of (3*S*)-**16** (2.02 g) was added consecutively at 0°C. After 5 h under stirring, the mixture was treated with water, and extracted with ether. The organic extract was dried on K_2CO_3 and the solvent removed in vacuo, treated with $NaBH_4$ in MeOH to reduce any excess amount of (3*S*)-**15**, and chromatographed on a silica-gel column to give **22** [a colorless oil, 1.92 g; 64%. Found: C, 82.06; H, 10.36%. Calcd for $C_{27}H_{40}O_2$: C, 81.77; H, 10.17%. ^1H NMR δ=0.73 (3H, d, J=7 Hz), 0.90 (3H, d, J=7 Hz), 1.11 (3H, d, J=7 Hz), 1.15 (3H, s), 1.68 (3H, br s), 2.82 (1H, br m), 3.20 (1H, dd, J=9, 8 Hz), 3.45 (1H, dd, J=9, 4 Hz), 4.31 (1H, br s), 4.45 (2H, br s), 4.93 (1H, d, J=2.5 Hz), 5.03 (1H, d, J=3 Hz), and 7.28 (5H, br s). ^{13}C NMR δ=15.0, 15.7, 17.1, 21.5, 21.9, 22.1, 24.9, 30.4, 35.2, 35.7, 38.0, 47.6, 51.9, 53.4, 72.6, 73.0 (2C), 106.0, 127.3, 127.4 (2C), 128.2 (2C), 135.9, 138.7, 138.8, and 162.1. IR ν: 3545, 2955, 1642, 1498, 1467, 1456, 1367, 1099, 1012, 895, 733, and 697 cm^{-1}], and **23** [a colorless oil, 1.35 g; 18%. Found: C, 81.87; H, 10.32%. ^1H NMR δ= 0.75 (3H, d, J=7 Hz), 0.92 (3H, s), 0.93 (3H, d, J=7 Hz), 1.11 (3H, d, J=7 Hz), 1.88 (3H, br s), 2.48 (2H, br m), 3.21 (1H, dd, J=9, 8.5 Hz), 3.46 (1H, dd, J=9, 4 Hz), 4.26 (1H, br s), 4.41 (1H, d, J=12 Hz), 4.48 (1H, d, J=12 Hz), 4.93 (1H, d, J= 3 Hz), 4.96 (1H, d, J=2.5 Hz), and 7.28 (5H, br s). ^{13}C NMR δ=16.2, 16.8, 17.0, 21.7, 22.5, 24.9, 25.1, 29.4, 32.6, 34.6, 39.3, 49.6, 54.0, 56.5, 72.6, 72.9, 75.1, 104.4, 127.2, 127.3 (2C), 128.1 (2C), 136.3, 138.7, and 160.4. IR ν: 3570, 3500, 2955, 2875, 1642, 1498, 1465, 1457, 1368, 1100, 1029, 886, 735, and 698 cm^{-1}].

Collins Oxidation of 22 to 24. To an anhydrous CH_2Cl_2 solution (2 cm^3) containing CrO_3 (150 mg) and pyridine (245 mg), CH_2Cl_2 solution (2 cm^3) of **22** (95 mg) was added and stirred at room temperature for 1 h. The mixture was then diluted with ether, and passed through a Florisil column to remove inorganic material. The removal of the solvent in vacuo left a colorless oil, which was purified by a silica-gel column chromatography to yield **24** [a colorless oil, 56 mg; 59%. Found: C, 82.18; H, 9.80%. Calcd for $C_{27}H_{38}O_2$: C, 82.18; H, 9.71%. ^1H NMR δ=0.72 (3H, d, J=7 Hz), 0.84 (3H, d, J=7 Hz), 1.09 (3H, d, J=7 Hz), 1.21 (3H, s), 1.60 (3H, br s), 2.45 (1H, br m), 2.92 (1H, br m), 3.21 (1H, dd, J=9, 8 Hz), 3.45 (1H, dd, J=9, 4 Hz), 4.41 (1H, d, J=12 Hz), 4.46 (1H, d, J=12 Hz), 4.96 (1H, d, J=2.5 Hz), 4.99 (1H, d, J=3 Hz), and 7.26 (5H, br s). ^{13}C NMR δ=15.4, 16.5, 17.1, 21.3, 23.4, 25.3, 25.7, 30.8, 34.9, 35.7, 37.8, 48.4, 55.5, 59.5, 72.7, 73.0, 108.1, 127.4 (3C), 128.2 (2C), 138.7, 139.8, 141.4, 156.2, and 211.3. IR ν: 2960, 2875, 1677, 1455, 1368, 1098, 895, 735, and 696 cm^{-1}].

LAH-Reduction of 24. An anhydrous THF solution (2 cm^3) of **24** (50 mg) was reduced with LAH (10 mg) in THF (1 cm^3) at room temperature for 50 min. An ordinary work up of the mixture yielded **22** (15 mg; 30%) and **23** (21 mg; 42%), whose identity with the authentic samples were confirmed by direct comparisons.

$CrCl_2$-Mediated Condensation of (3*S*)-16 and (3*R*)-15. Similarly, (3*R*)-**15** (5.11 g) and (3*S*)-**16** (6.39 g) were condensed with $CrCl_2$, prepared from $CrCl_3$ (10.64 g), in DMF (80 cm^3) to form **25** [a colorless oil, 7.02 g; 73%. Found: C, 82.01; H, 10.25%. ^1H NMR δ=0.70 (3H, d, J=7 Hz), 0.85 (3H, d, J=7 Hz), 1.09 (3H, s), 1.10 (3H, d, J=7 Hz), 1.90 (3H, br s), 2.45 (2H, br s), 3.18 (1H, dd, J=9, 8 Hz), 3.45 (1H, dd, J=9, 4 Hz), 4.04 (1H, br s), 4.42 (1H, d, J=12 Hz), 4.47 (1H, d, J=12 Hz), 4.91 (1H, d, J=2.5 Hz), 4.99 (1H, d, J=3 Hz), and 7.27 (5H, br s). ^{13}C NMR δ=15.8, 16.9, 17.3, 21.7, 22.2, 23.5, 25.4, 28.9, 34.4, 35.2, 39.2, 48.4, 52.7, 55.8, 72.7, 72.9, 74.9, 105.9, 127.4 (3C), 128.2 (2C), 136.6, 137.4, 138.7, and 160.5. IR ν: 3510, 2955, 1643, 1599, 1455, 1367, 1098, 1028, 734, and 695 cm^{-1}], and **26** [a colorless oil, 0.37 g; 4%. Found: C, 81.98; H, 10.41%. ^1H NMR δ=0.71 (3H, d, J=7 Hz), 0.77 (3H, s), 0.87 (3H, d, J=7 Hz), 1.11 (3H, d, J=7 Hz), 1.73 (3H, br s), 2.72 (1H, br m), 3.21 (1H, t, J=9 Hz), 3.47 (1H, dd, J=9, 4 Hz), 4.42 (1H, d, J=12 Hz), 4.47 (1H, d, J=12 Hz), 4.65 (1H, br s), 4.96 (1H, d, J=2.5 Hz), 4.99 (1H, d, J=3 Hz), and 7.27 (5H, br s). ^{13}C NMR δ=15.0, 15.7, 17.2, 22.0, 22.1, 25.4 (2C), 30.4, 32.2, 38.0, 49.8, 52.5, 53.1, 72.7, 73.0, 75.2, 104.0, 127.4 (3C), 128.2 (2C), 135.4, 138.7, 139.1, and 161.4. IR ν: 3575, 3510, 2875, 1642, 1498, 1455, 1366, 1098, 1018, 882, 732, and 695 cm^{-1}].

Collins Oxidation of 25 to 27. Similarly, **25** (1.00 g) was oxidized with CrO_3 (1.5 g) and pyridine (245 mg) in CH_2Cl_2 (30 cm^3) to form **27** [a colorless oil, 585 mg; 59%. Found: C, 81.91; H, 9.68%. ^1H NMR δ=0.71 (3H, d, J=7 Hz), 0.80 (3H, d, J=7 Hz), 1.12 (3H, d, J=7 Hz), 1.17 (3H, s), 1.60 (3H, br s), 2.57 (1H, br m), 2.80 (1H, br m), 3.24 (1H, dd, J=9, 8 Hz), 3.46 (1H, dd, J=9, 4 Hz), 4.41 (1H, d, J=12 Hz), 4.46 (1H, d, J=12 Hz), 4.87 (1H, d, J=3 Hz), 4.92 (1H, d, J=2.5 Hz), and 7.27 (5H, br s). ^{13}C NMR δ=15.2, 15.9, 17.0, 21.5, 22.8, 24.7, 26.2, 30.1, 34.6, 35.9, 37.9, 48.8, 55.1, 59.5, 72.6, 72.9, 107.7, 127.3 (3C), 128.1 (2C), 138.6, 140.4, 141.0, 156.5, and 209.5. IR ν: 2960, 1677, 1455, 1368, 1098, 895, 735, and 696 cm^{-1}].

LAH-Reduction of 27 to 25 and 26. Similarly, **27** (315 mg) was treated in THF (5 cm^3) with LAH (100 mg) in THF (5 cm^3) to give **25** (167 mg; 53%) and **26** (72 mg; 23%). Their identities with the authentic samples were confirmed by direct comparisons.

Birch Reduction of 22 to 28. To liquid NH_3 (30 cm^3) containing lithium (50 mg), an anhydrous ether solution (2 cm^3) of **22** (780 mg) was added dropwise and refluxed for 2 h. The mixture was then treated with NH_4Cl and water, and almost all of NH_3 was allowed to evaporate. The residue was extracted with ether and dried on K_2CO_3. Silica-gel column chromatography of the mixture yielded, beside recovered **22** (30 mg; 3.8%), **28** [a colorless oil, 598 mg; 99.5%. Found: C, 78.48; H, 11.24%. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18%. ^1H NMR δ=0.71 (3H, d, J=7 Hz), 0.88 (3H, d, J=7 Hz), 1.05 (3H, d, J=7 Hz), 1.17 (3H, s), 1.67 (3H, br s), 2.82 (1H, br m),

3.36 (1H, dd, J=10, 8 Hz), 3.64 (1H, dd, J=10, 5 Hz), 4.31 (1H, br s), 4.97 (1H, d, J=2.5 Hz), and 5.07 (1H, d, J=3 HZ). ^{13}C NMR δ=14.9, 15.7, 16.6, 21.9 (2C), 22.1, 24.6, 30.4, 35.2, 37.9, 38.0, 47.6, 51.8, 53.3, 64.6, 73.2, 106.0, 136.1, 138.6, and 162.3. IR ν: 3410, 2960, 1645, 1470, 1385, 1370, 1020, and 900 cm^{-1}].

Birch Reduction of 23 to 29. Similarly, **23** (286 mg) was reduced to **29** [a colorless oil, 160 mg; 72%. Found: C, 78.21; H, 11.39%. ^{1}H NMR δ=0.76 (3H, d, J=7 Hz), 0.93 (3H, d, J=7 Hz), 0.96 (3H, s), 1.07 (3H, d, J=7 Hz), 1.90 (3H, br s), 2.51 (2H, br m), 3.40 (1H, dd, J=10, 8 Hz), 3.68 (1H, dd, J=10, 5 Hz), 4.28 (1H, br s), 4.98 (1H, d, J=3 Hz), and 5.03 (1H, d, J=2.5 Hz). ^{13}C NMR δ=16.2, 16.5, 16.8, 21.8, 22.6, 24.6, 25.2, 29.4, 32.6, 36.7, 39.4, 49.5, 54.0, 56.6, 64.9, 75.1, 104.5, 136.3, 136.9, and 160.8. IR ν: 3410, 2955, 1643, 1467, 1369, 1032, and 884 cm^{-1}].

Birch Reduction of 25 to 30. Similarly, **25** (7.39 g) was reduced with lithium (390 mg) in liquid NH_3 (250 cm^3) to give **30** [a colorless oil, 5.12 g; 100%. Found: C, 78.24; H, 11.24%. ^{1}H NMR δ=0.71 (3H, d, J=7 Hz), 0.87 (3H, d, J=7 Hz), 1.06 (3H, d, J=7 Hz), 1.12 (3H, s), 1.91 (3H, br s), 3.33 (1H, dd, J=10, 8 Hz), 3.64 (1H, dd, J=10, 5 Hz), 4.07 (1H, br s), 4.97 (1H, d, J=2.5 Hz), and 5.04 (1H, d, J=3 Hz). ^{13}C NMR δ=15.9, 16.8, 16.9, 21.7, 22.3, 23.5, 25.0, 29.0, 34.5, 37.4, 39.2, 48.4, 52.8, 55.9, 65.1, 74.9, 106.0, 136.6, 137.5, and 161.1. IR ν: 3410, 2960, 2880, 1644, 1465, 1368, 1024, and 893 cm^{-1}] together with the recovered **25** (866 mg; 12%).

Birch Reduction of 26 to 31 and 32. To an anhydrous $EtNH_2$ solution (8 cm^3) of lithium (100 mg), an anhydrous ether solution (2 cm^3) of **26** (85 mg) was added and stirred at 0 °C for 2 h. The usual work up yielded a C=C bond-migrated diol (**32**) [a colorless oil, 11 mg; 17%. ^{1}H NMR δ=0.72 (3H, d, J=7 Hz), 0.84 (3H, d, J=7 Hz), 0.89 (3H, d, J=7 Hz), 0.99 (3H, s) 1.64 (3H, t, J=1 Hz), 1.70 (3H, br s), 2.78 (1H, br m), 2.81 (1H, sext, J=7 Hz), 3.45 (2H, br s), and 4.61 (1H, br s)], and **31** [a colorless oil, 45 mg; 69%. Found: C, 78.25; H, 11.32%. ^{1}H NMR δ=0.70 (3H, d, J=7 Hz), 0.81 (3H, s), 0.87 (3H, d, J=7 Hz), 1.06 (3H, d, J=7 Hz), 1.73 (3H, br s), 3.36 (1H, dd, J=10, 8 Hz), 3.68 (1H, dd, J=10, 5 Hz), 4.68 (1H, br s), and 5.03 (2H, br d, J=2.5 Hz). ^{13}C NMR δ=15.0, 15.7, 16.7, 22.0, 22.2, 25.0, 25.6, 30.5, 32.1, 36.3, 38.1, 49.8, 52.5, 53.1, 65.2, 75.3, 104.1, 135.3, 139.4, and 162.2. IR ν: 3400, 2950, 1645, 1470, 1025, and 885 cm^{-1}] was obtained.

The Birch Reduction of 23 in Ethylamine. Formation of 29 and Its Isomer, 33. Similar to this, the reduction of **23** (67 mg) in $EtNH_2$ (10 cm^3) with lithium (25 mg) afforded **29** (a colorless oil, 10 mg; 19%) and **33** [colorless prisms, mp 119.5—120 °C, 34 mg; 66%. Found: C, 78.52; H, 11.29%. ^{1}H NMR δ=0.74 (3H, d, J=7 Hz), 0.91 (3H, d, J=7 Hz), 0.98 (3H, d, J=7 Hz), 1.03 (3H, s), 1.63 (3H, t, J=1 Hz), 1.92 (3H, br s), 2.45 (1H, br m), 2.71 (1H, sext, J=7 Hz), 3.45 (2H, br m), and 4.16 (1H, br s). ^{13}C NMR δ=10.3, 15.2, 16.1, 16.5, 21.7, 22.5, 22.9, 29.0, 29.5, 32.3, 35.7, 39.4, 56.0, 57.9, 66.0, 73.2, 136.5, 137.2, 138.7, and 138.9. IR ν: 3300, 2950, 1667, 1465, 1452, 1366, 1020, 1000, and 765 cm^{-1}].

Bis-Etherification of 28 to 34 with I_2 and a Base. To an ether solution (10 cm^3) of **28** (240 mg), saturated $NaHCO_3$ (20 cm^3) and an excess of I_2 were added and kept room temperature for 3 h. The mixture was then treated with $NaHSO_3$ and saturated K_2CO_3 and extracted with ether. Silica-gel column chromatography of the extract afforded **34** [a colorless oil, 192 mg; 74%. Found: C, 78.98; H, 10.71%. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59%. ^{1}H NMR δ=0.69 (3H, d, J=7 Hz), 0.83 (3H, s), 0.88 (3H, d, J=7 Hz), 0.95 (3H, d, J=7 Hz), 1.65 (3H, br s), 2.68 (1H, br m), 3.23 (1H, dd, J=10, 8 Hz), 3.71 (1H, d, J=9 Hz), 3.80 (1H, d, J=9 Hz), 3.88 (1H, dd, J=8, 7 Hz), and 4.64 (1H, br s). ^{13}C NMR δ=11.2, 14.9, 15.8, 16.4, 22.3, 22.7, 24.9, 30.5, 36.2, 38.1, 40.3, 53.4, 53.8, 57.7, 74.1, 76.8, 86.4, 102.2, 135.8, and 136.3. IR ν: 2960, 2880, 1470, 1455, 1380, and 1053 cm^{-1}].

Bis-Etherification of 29 to 35 with I_2 and a Base. A similar treatment of **29** (40 mg) with I_2 (55 mg) and saturated $NaHCO_3$ solution (4 cm^3) yielded **35** [a colorless oil, 35 mg; 80%. Found: C, 79.04; H, 10.70%. ^{1}H NMR δ=0.71 (3H, d, J=7 Hz), 0.87 (3H, d, J=7 Hz), 0.94 (3H, d, J=7 Hz), 1.01 (3H, s), 1.89 (3H, br s), 2.60 (1H, br m), 3.28 (1H, dd, J=10, 8 Hz), 3.31 (1H, d, J=9 Hz), 3.81 (1H, d, J=9 Hz), 3.86 (1H, dd, J=8, 7 Hz), and 4.00 (1H, br s). ^{13}C NMR δ=10.8, 15.3, 15.7, 18.8, 21.6, 21.9, 24.6, 28.6, 35.3, 35.5, 39.4, 53.6, 55.6, 55.8, 73.2, 76.1, 87.7, 101.1, 132.0, and 136.0. IR ν: 2960, 2845, 1465, 1379, 1063, and 995 cm^{-1}].

Bis-Etherification of 30 to 36 with I_2 and a Base. Similarly, **30** (60 mg) was converted to **36** [a colorless oil, 51 mg; 86%. Found: C, 78.98; H, 10.82%. ^{1}H NMR δ=0.73 (3H, d, J=7 Hz), 0.87 (3H, s), 0.89 (3H, d, J=7 Hz), 0.96 (3H, d, J=7 Hz), 1.85 (3H, br s), 3.25 (1H, dd, J=10, 8 Hz), 3.67 (1H, d, J=9 Hz), 3.90 (1H, dd, J=8, 7 Hz), 3.93 (1H, d, J=9 Hz), and 4.21 (1H, br s). IR ν: 2955, 2875, 1466, 1455, 1378, and 1050 cm^{-1}].

Bis-Etherification of 31 to 37 with I_2 and a Base. Similarly, **31** (22 mg) was converted to **37** [colorless needles, mp 69.5—70 °C, 15 mg, 68%. Found: C, 79.02; H, 10.81%. ^{1}H NMR δ=0.67 (3H, d, J=7 Hz), 0.85 (3H, d, J=7 Hz), 0.88 (3H, s), 0.94 (3H, d, J=7 Hz), 1.68 (3H, br s), 2.70 (1H, br m), 3.23 (1H, dd, J=10.5, 8 Hz), 3.37 (1H, d, J=9 Hz), 3.83 (1H, d, J=9 Hz), 3.85 (1H, dd, J=8, 7 Hz), and 4.23 (1H, br s). IR ν: 2960, 2840, 1460, 1373, and 1051 cm^{-1}].

Attempted Anionic Oxy-Cope Rearrangement with 25. To an anhydrous THF suspension (3 cm^3) of KH (35% in a mineral oil, 100 mg), **25** (55 mg) was added under ice-cooling. After standing at room temperature for 20 h, the mixture was treated with aqueous ether and extracted. HPLC with AcOEt–hexane eluted **38** [a colorless oil, 3 mg; 11%. ^{1}H NMR δ=1.01 (3H, d, J=7 Hz), 1.56 (6H, br s), 2.56 (1H, br m), 3.16 (1H, t, J=10 Hz), 3.30 (1H, dd, J=10, 4 Hz), 4.42 (2H, br s), and 7.30 (5H, br s)], a colorless-oily mixture of **39a** and **39b** (1:1) [10 mg; 23%. ^{1}H NMR δ=0.82 (1.5H, d, J=7 Hz), 0.83 (1.5H, d, J=7 Hz), 0.87 (1.5H, d, J=7 Hz), 0.92 (1.5H, d, J=7 Hz), 0.97 (1.5H, s), 1.01 (1.5H, s), 1.02 (3H, d, J=7 Hz), 1.58 (3H, br s), 3.07 (0.5H, t, J=9.5 Hz), 3.09 (0.5H, t, J=9.5 Hz), 3.22 (0.5H, dd, J=9.5, 4.5 Hz), 3.24 (0.5H, dd, J=9.5, 4.5 Hz), 4.40 (2H, br s), 7.27 (5H, br s), 9.65 (0.5H, d, J=7 Hz), and 9.66 (0.5H, d, J=4 Hz)], (3*R*)-**15** (1 mg; 6%), and the recovered **25** (11 mg; 20%), which were identified by direct comparisons.

Preparation of the TMS Derivative (40) from 22. To a pyridine solution (1 cm^3) of **22** (15 mg), trimethylsilyl chloride (TMSCl, 200 mg) was added and stirred at 15—25 °C for 24 h. The mixture was then treated with aqueous $NaHCO_3$, extracted with hexane–ether, dried on K_2CO_3, and chromatographed on a silica-gel column to give colorless oily **40** [18 mg; 100%. Found: C, 76.83; H, 10.44%. Calcd for $C_{30}H_{48}O_2Si$: C, 76.86; H, 10.32%. ^{1}H NMR δ=0.04 (9H, s), 0.67 (3H, d, J=7 Hz), 0.86 (3H, d, J=7 Hz), 1.09 (3H, d, J=7 Hz), 1.11 (3H, s), 1.64 (3H, br s), 2.77 (1H, br m), 3.17 (1H, t, J=9 Hz), 3.46 (1H, dd, J=9, 4 Hz), 4.30 (1H, s), 4.40 (1H, d, J=12 Hz), 4.48 (1H, d, J=12 Hz), 4.80 (2H, br d, J=2.5 Hz), and 7.28 (5H, br s). ^{13}C NMR δ=0.7 (3C), 15.1, 16.1, 17.3, 21.9,

22.4, 23.9, 25.0, 29.5, 34.9, 35.3, 37.8, 47.9, 51.2, 53.1, 72.9 (2C), 74.5, 106.0, 127.2, 127.4 (2C), 128.2 (2C), 136.8, 136.9, 138.8, and 160.2. IR ν: 2960, 2875, 1645, 1455, 1250, 1062, 880, 837, and 695 cm^{-1}].

Preparation of the TMS Derivative (41) from 23. Similarly, **23** (29 mg) was converted to **41** [a colorless oil, 33 mg; 96%. Found: C, 77.08; H, 10.34%. ^1H NMR δ=0.03 (9H, s), 0.75 (3H, d, J=7 Hz), 0.92 (3H, d, J=7 Hz), 0.92 (3H, s), 1.11 (3H, d, J=7 Hz), 1.84 (3H, br s), 3.21 (1H, dd, J=9, 8 Hz), 3.48 (1H, dd, J=9, 4 Hz), 4.24 (1H, br s), 4.43 (1H, d, J=12 Hz), 4.45 (1H, d, J=12 Hz), 4.82 (2H, br d, J=2.5 Hz), and 7.28 (5H, br s). ^{13}C NMR δ=0.4 (3C), 16.3, 16.5, 17.3, 22.4 (2C), 25.0, 25.5, 29.5, 33.4, 34.8, 39.6, 49.8, 54.0, 56.2, 73.0, 73.2, 77.1, 103.8, 127.3, 127.4 (2C), 128.2 (2C), 136.5, 137.7, 139.1, and 161.5. IR ν: 2955, 2865, 1645, 1366, 1246, 1077, 876, 835, 745, 730, and 694 cm^{-1}].

Preparation of the TMS Derivative (42) from 25. Similarly, **25** (77 mg) was treated with TMSCl (200 mg) to give **42** [a colorless oil, 85 mg; 94%. Found: C, 76.89; H, 10.36%. ^1H NMR δ=0.08 (9H, s), 0.71 (3H, d, J=7 Hz), 0.82 (3H, d, J=7 Hz), 1.01 (3H, s), 1.08 (3H, d, J=7 Hz), 1.84 (3H, br s), 3.18 (1H, dd, J=9, 8 Hz), 3.47 (1H, dd, J=9, 4 Hz), 4.12 (1H, br s), 4.40 (1H, d, J=12 Hz), 4.48 (1H, d, J=12 Hz), 4.81 (1H, d, J=2 Hz), 4.87 (1H, d, J=3 Hz), and 7.28 (5H, br s). ^{13}C NMR δ=0.3 (3C), 15.9, 16.8, 17.3, 22.1, 22.3, 25.7, 26.7, 28.8, 33.1, 34.7, 39.3, 49.5, 52.6, 55.4, 72.9, 73.1, 77.8, 105.4, 127.3, 127.4 (2C), 128.2 (2C), 136.9, 137.0, 138.8, and 160.2. IR ν: 2960, 2880, 1645, 1456, 1250, 1066, 880, 835, and 695 cm^{-1}].

Preparation of the TMS Derivative (43) from 26. Similarly, **26** (24 mg) was converted to **43** [colorless prisms, mp 67—67.5 °C, 29 mg; 100%. Found: C, 76.71; H, 10.26%. ^1H NMR δ=0.01 (9H, s), 0.66 (3H, d, J=7 Hz), 0.72 (3H, s), 0.84 (1H, d, J=7 Hz), 1.11 (3H, d, J=7 Hz), 1.60 (3H, br s), 2.64 (1H, br s), 3.19 (1H, dd, J=8.8, 8.5 Hz), 3.49 (dd, J=8.8, 3.5 Hz), 4.42 (1H, d, J=12 Hz), 4.49 (1H, d, J=12 Hz), 4.54 (1H, s), 4.83 (1H, d, J=2.5 Hz), 4.89 (1H, d, J=3 Hz), and 7.27 (5H, br s). ^{13}C NMR δ=0.5 (3C), 14.7, 16.1, 17.6, 22.1, 26.1 (2C), 29.7, 32.3, 33.7, 37.9, 50.3, 51.2, 52.7, 72.9 (2C), 136.7, 136.9, 138.8, and 162.7. IR ν: 2955, 2865, 1644, 1453, 1368, 1246, 1101, 1064, 878, 833, 745, and 696 cm^{-1}].

Cope Rearrangement of 40 to 44. An anhydrous oxygen-free toluene solution (5 cm^3) of **40** (18 mg) was sealed and heated in an autoclave at 190 °C for 12 h. The mixture was then distilled in vacuo to remove the solvent. The residue was practically pure thermolysate, **44** [a colorless oil, 18 mg; 100%. ^1H NMR δ=0.16 (9H, s), 0.74 (3H, d, J=7 Hz), 0.89 (3H, d, J=7 Hz), 1.03 (3H, d, J=7 Hz), 1.04 (3H, s), 1.58 (3H, br s), 2.75 (2H, br m), 3.08 (1H, dd, J=9, 8 Hz), 3.27 (1H, dd, J=9, 4 Hz), 4.39 (1H, d, J=12 Hz), 4.44 (1H, d, J=12 Hz), 6.03 (1H, d, J=2 Hz), and 7.25 (5H, br s)].

Cope Rearrangmement of 42. Formation of 45. Similarly, a toluene solution (5 cm^3) of **42** (82 mg) was heated in an autoclave at 190 °C for 8 h to give **45** [a colorless oil, 82 mg; 100%. ^1H NMR δ=0.19 (9H, s), 0.81 (3H, d, J=7 Hz), 1.02 (3H, d, J=7 Hz), 1.05 (3H, s), 1.62 (3H, br s), 2.68 (1H, d, J=14 Hz), 2.74 (1H, br m), 3.10 (1H, t, J=9 Hz), 3.27 (1H, dd, J=9, 4 Hz), 4.36 (1H, d, J=12 Hz), 4.46 (1H, d, J=12 Hz), 5.93 (1H, d, J=2 Hz), and 7.26 (5H, br s)].

Cope Rearrangement of 43. Formation 46. Similarly, a toluene solution of **43** (29 mg) was heated at 190 °C for 8 h in an autoclave to give **46** [a colorless oil, 29 mg; 100%. ^1H NMR δ=0.16 (9H, s), 0.75 (3H, d, J=7 Hz), 0.88 (3H, d, J=7 Hz), 0.94 (3H, s), 1.00 (3H, d, J=7 Hz), 1.58 (3H, br s), 3.08 (1H, t, J=9 Hz), 3.26 (1H, dd, J=9, 4 Hz), 4.36 (1H, d, J=12 Hz), 4.45 (1H, d, J=12 Hz), 6.08 (1H, d, J=2 Hz), and 7.24 (5H, br s)].

Cope Rearrangement of 41. Formation of 47 and 48. A toluene solution of **41** (74 mg) was heated at 200 °C for 4 d in an autoclave to give a mixture of **47** and **48** (3:2, 67 mg; 90%), which was separated by GLC (SE 30 column, 300 cm in length; column temperature, 285 °C; and He-flow, 25 $cm^3 min^{-1}$) to obtain **47** [a colorless oil. ^1H NMR δ= 0.16 (9H, s), 0.80 (3H, d, J=7 Hz), 0.90 (3H, d, J=7 Hz), 1.03 (3H, d, J=7 Hz), 1.17 (3H, s), 1.56 (3H, br s), 2.78 (1H, br m), 3.10 (1H, t, J=9 Hz), 3.28 (1H, dd, J=9, 4 Hz), 4.33 (1H, d, J= 12 Hz), 4.46 (1H, d, J=12 Hz), 5.97 (1H, d, J=2 Hz), and 7.24 (5H, br s)] and **48** [a colorless oil. ^1H NMR δ=0.16 (9H, s), 0.81 (3H, d, J=7 Hz), 0.89 (3H, d, J=7 Hz), 0.93 (3H, s), 1.02 (3H, d, J=7 Hz), 1.60 (3H, br s), 3.08 (1H, t, J=9 Hz), 3.25 (1H, dd, J=9, 4 Hz), 4.36 (1H, d, J=12 Hz), 4.43 (1H, d, J= 12 Hz), 6.10 (1H, d, J=2 Hz), 7.25 (5H, br s)].

The $^1O_2$-Oxidation of 44. Formation of 49. An anhydrous toluene solution (5 cm^3) of **44** (82 mg), pyridine (0.03 cm^3), *meso*-5,10,15,20-tetraphenylporphine (TPP, 2 mg) was externally irradiated by means of a 500-W tungsten lamp with an O_2-stream under ice-cooling for 50 min. The mixture was then treated with PPh_3 to neutralize peroxy derivatives, solvent removed in vacuo, and chromatographed on a silica-gel column to give **49** [a colorless oil, 54 mg; 78%. Found: C, 82.38; H, 9.96%. Calcd for $C_{27}H_{38}O_2$: C, 82.18; H, 9.71%. ^1H NMR δ=1.01 (3H, d, J=7 Hz), 1.03 (3H, d, J= 7 Hz), 1.10 (3H, d, J=7 Hz), 1.29 (3H, s), 1.47 (3H, br s), 2.68 (1H, br m), 3.09 (1H, t, J=9 Hz), 3.24 (1H, dd, J=9, 4.5 Hz), 3.38 (1H, sept, J=7 Hz), 4.37 (1H, d, J=12 Hz), 4.44 (1H, d, J=12 Hz), 7.25 (5H, br s), and 9.95 (1H, s). ^{13}C NMR δ=15.2, 16.9, 21.2, 21.5, 23.8, 26.7, 27.3, 30.0, 35.0 (2C), 36.3, 37.2, 51.1, 52.8, 72.2, 127.2, 127.4 (2C), 128.2 (2C), 134.6, 135.8, 138.8, 141.4, 171.8, and 188.2. IR ν: 2970, 2940, 2875, 2745, 1670, 1615, 1456, 1373, 1100, 732, and 695 cm^{-1}].

The $^1O_2$-Oxidation of 45. Formation of 50. Similarly, an anhydrous benzene solution (5 cm^3) of **45** (82 mg) and pyridine (0.03 cm^3) was irradiated 50 min under an O_2 atmosphere; after PPh_3-treatment, the mixture was chromatographed on a silica-gel column to give **50** [a colorless oil, 54 mg; 78%. Found: C, 82.42; H, 9.94%. ^1H NMR δ=0.87 (3H, d, J=7 Hz), 1.08 (6H, d, J=7 Hz), 1.18 (3H, s), 1.62 (3H, br s), 3.07 (1H, dd, J=9, 8 Hz), 3.21 (1H, dd, J=9, 4 Hz), 3.40 (1H, sept, J=7 Hz), 4.34 (1H, d, J=12 Hz), 4.42 (1H, d, J=12 Hz), 7.25 (5H, br s), 9.96 (1H, s). ^{13}C NMR δ=14.8, 17.0, 21.1, 21.5, 23.2, 26.2, 26.7, 30.1, 34.3 (2C), 36.2, 37.0, 50.7, 52.0, 72.1, 72.9, 127.1, 127.3 (2C), 128.1 (2C), 134.8, 135.4, 138.9, 141.7, 171.4, 188.1. IR ν: 2960, 2740, 1670, 1455, 1100, 735, 696 cm^{-1}].

The $^1O_2$-Oxidation of 46. Formation of 50. Similarly, **46** (29 mg) was converted to **50** (20 mg; 83%).

The $^1O_2$-Oxidation of 47. Formation of 49. Similarly, **47** (7.0 mg) was oxidized with $^1O_2$ by irradiation for 5 min to give **49** (a colorless oil, 4.0 mg; 67%).

The $^1O_2$-Oxidation of 48. Formation of 50. Similarly, **48** (7.0 mg) was converted to **50** (5.0 mg; 85%).

Preparation of the TMS Derivative (51) from 28. To an anhydrous pyridine solution (5 cm^3) of **28** (298 mg), TMSCl (0.7 cm^3) was added dropwise at room temperature. After being stirred for 12 h, the mixture was then diluted with water, extracted with hexane–ether (1:1), dried on K_2CO_3, and distilled in vacuo to remove the solvent. The residue was chromatographed quickly on a silica-gel column to give

51 [a colorless oil, 405 mg; 92%. Found: C, 69.38; H, 11.27%. Calcd for $C_{26}H_{50}O_2Si_2$: C, 69.27; H, 11.18%. ^{1}H NMR δ= 0.04 (9H, s), 0.09 (9H, s), 0.86 (3H, d, J=7 Hz), 1.03 (3H, d, J=7 Hz), 1.13 (3H, s), 1.65 (3H, br s), 2.80 (2H, br m), 3.21 (1H, t, J=9.5 Hz), 3.59 (1H, dd, J=9.5, 4 Hz), 4.31 (1H, s), and 4.82 (2H, br d, J=2.5 Hz). ^{13}C NMR δ=−0.4 (3C), 0.7 (3C), 15.1, 16.1, 16.8, 21.9, 22.4, 23.9, 24.8, 29.5, 35.0, 37.6, 37.8, 47.7, 51.3, 53.1, 64.6, 74.4, 106.0, 136.8, 137.0, and 160.3. IR ν: 2955, 1647, 1468, 1250, 1087, 1066, 879, and 746 cm^{-1}].

Preparation of the TMS Derivative (52) from 30. Similarly, **30** (5.123 g) in pyridine (35 cm^3) was treated with TMSCl (7.5 cm^3) to give **52** [a colorless oil, 6.913 g; 92%. Found: C, 69.56; H, 11.23%. ^{1}H NMR δ=0.09 (18H, s), 0.71 (3H, d, J=7 Hz), 0.82 (3H, d, J=7 Hz), 1.02 (3H, d, J=7 Hz), 1.04 (3H, s), 1.84 (3H, br s), 3.22 (1H, t, J=9.5 Hz), 3.60 (1H, dd, J=9.5, 4 Hz), 4.12 (1H, br s), 4.82 (1H, d, J=2 Hz), and 4.88 (1H, d, J=2.5 Hz). ^{13}C NMR δ=−0.4 (3C), 0.3 (3C), 15.9, 16.8 (2C), 22.1, 22.3, 25.6, 26.8, 28.9, 33.3, 37.1, 39.4, 49.4, 52.7, 55.5, 64.9, 77.9, 105.5, 137.2, 137.3, and 160.6. IR ν: 2955, 2875, 1643, 1250, 1068, 878, and 836 cm^{-1}].

Cope Rearrangement of 51 to 53. An anhydrous toluene solution (5 cm^3) of **51** (857 mg) was placed in a sealed tube and heated in an autoclave at 190 °C for 12 h. The mixture was then heated in vacuo to remove the solvent to give **53** [a colorless oil, 857 mg; 100%. Found: C, 69.33; H, 11.19%. ^{1}H NMR δ=0.08 (9H, s), 0.16 (9H, s), 0.75 (3H, d, J=7 Hz), 0.88 (3H, d, J=7 Hz), 0.95 (3H, d, J=7 Hz), 1.04 (3H, s), 1.60 (3H, br s), 2.74 (2H, br m), 3.15 (1H, t, J=10 Hz), 3.38 (1H, dd, J=10, 4 Hz), and 6.05 (1H, d, J=2.5 Hz). ^{13}C NMR δ=−0.4(6C), 15.1, 16.6, 18.0, 21.8, 23.4, 23.9, 27.9, 28.4, 37.0, 37.4, 38.4, 38.6, 46.2, 47.9, 52.7, 64.1, 132.7, 134.9, and 135.5 (2C). IR ν: 2955, 2875, 1667, 1252, 1154, 1081, 873, 838, and 748 cm^{-1}].

Cope Rearrangement of 52 to 54. Similarly, a toluene solution of **52** (238 mg) was heated in an autoclave to give **54** [a colorless oil, 238 mg; 100%. Found: C, 69.02; H, 11.09%. ^{1}H NMR δ=0.06 (9H, s), 0.18 (9H, s), 0.79 (3H, d, J=7 Hz), 0.92 (6H, d, J=7 Hz), 1.04 (3H, s), 1.63 (3H, br s), 2.70 (1H, br m), 2.66 (1H, d, J=14 Hz), 3.12 (1H, t, J=10 Hz), 3.37 (1H, dd, J=10, 4 Hz), and 5.91 (1H, d, J=2 Hz). ^{13}C NMR δ=−0.5 (3C), −0.4 (3C), 14.8, 16.8 (2C), 22.0, 23.2, 24.8, 24.9, 28.7, 34.5, 36.6, 37.2, 38.5, 46.4, 49.4, 51.9, 63.9, 132.2, 132.5, 134.3, and 136.1. IR ν: 2960, 2875, 1668, 1252, 1160, 1082, 872, 840, and 748 cm^{-1}].

Conversion of 53 to Unsaturated Aldehyde (55). An anhydrous toluene solution (25 cm^3) of **53** (857 mg), TPP (9 mg), and pyridine (0.05 cm^3) was irradiated with a 500-W tungsten lamp under an O_2 atmosphere at −70 °C for 30 min. The mixture was then treated with PPh_3 and extracted with ether. The ether extract was hydrolyzed with dil HCl and chromatographed on a silica-gel column, from benzene–hexane (2:1) to hexane–AcOEt (5:1), to give **55** [a colorless oil, 417 mg; 72%. Found: C, 78.95; H, 10.68%. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.60%. ^{1}H NMR δ=0.97 (3H, d, J=7 Hz), 1.08 (3H, d, J=7 Hz), 1.13 (3H, d, J=7 Hz), 1.32 (3H, s), 1.53 (3H, br s), 2.73 (1H, br m), 3.26 (1H, dd, J=11, 7.5 Hz), 3.41 (1H, sept, J=7 Hz), 3.50 (1H, dd, J=11, 6 Hz), and 9.97 (1H, s). ^{13}C NMR δ=14.9, 16.2, 21.0, 21.2, 23.2, 26.4, 26.9, 29.8, 34.7, 36.0, 37.0 (2C), 50.8, 52.5, 64.0, 134.7, 135.6, 141.1, 172.0, and 188.0. IR ν: 3430, 2950, 1670, 1613, 1460, and 1025 cm^{-1}].

Conversion of 54 to Unsaturated Aldehyde (56). a) Similarly, **54** (223 mg) was oxidized with $^1O_2$ and hydrolyzed with dil HCl to give **56** [a colorless oil, 119 mg; 79%. Found: C, 78.77; H, 10.77%. ^{1}H NMR δ=0.84 (3H, d, J=7 Hz), 1.09 (6H, d, J=7 Hz), 1.20 (3H, s), 1.62 (3H, br s), 3.21 (1H, dd, J=10.5, 7 Hz), 3.40 (1H, sept, J=7 Hz), 3.46 (1H, dd, J=10.5, 6 Hz), and 9.97 (1H, s). ^{13}C NMR δ=14.8, 16.5, 21.1, 21.5, 22.9, 26.6, 26.7, 30.2, 34.3, 35.9, 36.7, 37.1, 50.7, 51.9, 64.7, 135.6, 135.7, 141.6, 171.9, and 188.3. IR ν: 3440, 2960, 2870, 1670, 1610, 1465, 1455, and 1025 cm^{-1}].

b) An acetonitrile solution (10 cm^3) of **54** (778 mg) was mixed with $Pd(OAc)_2$ (420 mg) and maintained at room temperature for 72 h. The mixture was then extracted with ether, hydrolyzed with dil HCl in aqueous ether, washed with water and dried on K_2CO_3. Silica-gel column chromatography of the organic extract gave **56** (322 mg; 61%).

The Oxidation of 55 to a Dialdehyde (57). To an anhydrous CH_2Cl_2 solution (10 cm^3) of $(COCl)_2$ (72 mg), DMSO (122 mg) was added at −70 °C, and stirred for 5 min. Then CH_2Cl_2 solution (2 cm^3) of **55** (202 mg) was introduced to the mixture. After stirring for another 20 min at this temperature it was further stirred with NEt_3 (650 mg) added. The reaction mixture was warmed to room temperature, extracted with ether, and chromatographed on a silica-gel column to give **57** [a colorless oil, 186 mg; 92%. Found: M.W., 302.2247. Calcd for $C_{20}H_{30}O_2$: 302.2244. ^{1}H NMR δ=1.03 (3H, d, J= 7 Hz), 1.08 (3H, d, J=7 Hz), 1.13 (3H, d, J=7 Hz), 1.31 (3H, s), 1.55 (3H, br s), 2.98 (1H, br m), 3.41 (1H, sept, J=7 Hz), 9.53 (1H, d, J=1 Hz), and 9.96 (1H, s). ^{13}C NMR δ=12.0, 15.1, 21.3, 21.5, 25.0, 26.7, 26.8, 29.9, 34.9, 36.3, 37.0, 47.8, 51.3, 52.1, 133.5, 137.5, 141.7, 172.0, 188.2, and 206.0. IR ν: 2970, 2940, 2875, 2840, 2740, 1722, 1668, 1612, and 1460 cm^{-1}].

The Oxidation of 56 to a Dialdehyde (58). Similarly, **56** (119 mg) was oxidized with $(COCl)_2$ (40 mg) and DMSO (70 mg) to give **58** [a colorless oil, 80 mg; 80%. Found: M.W., 302.2245. ^{1}H NMR δ=0.93 (3H, d, J=7 Hz), 1.05 (6H, d, J=7 Hz), 1.22 (3H, s), 1.62 (3H, br s), 3.41 (1H, sept, J= 7 Hz), 9.48 (1H, br s), and 10.00 (1H, s). ^{13}C NMR δ=12.3, 14.8, 21.3, 21.5, 24.3, 26.8 (2C), 30.2, 34.5, 35.7, 38.8, 47.1, 50.8, 51.3, 133.9, 137.0, 141.4, 172.3, 188.2, and 206.4. IR ν: 2970, 2750, 1725, 1668, 1613, and 1460 cm^{-1}].

$TiCl_2$-Mediated Cyclization of 57. To an anhydrous THF solution (60 cm^3) of $TiCl_4$ (1 cm^3) prepared at 0 °C, pyridine (0.5 cm^3) and powdered Zn (1.3 g) were added in portions, and stirred for 30 min. Then, a THF solution (15 cm^3) of **57** (184 mg) was slowly introduced over a 2-h period to maintain high-dilution conditions, and stirred for another 40 min. The mixture was then treated with aqueous K_2CO_3, extracted with ether and dried on K_2CO_3. Silica-gel column chromatography and further HPLC of the extract afforded **59** [a colorless oil, 47 mg; 25%. Found: C, 78.76; H, 10.73%. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.60%. ^{1}H NMR δ=0.92 (3H, d, J=7 Hz), 0.93 (6H, d, J=7 Hz), 1.20 (3H, s), 1.64 (3H, br s), 2.61 (1H, sept, J=7 Hz), 2.98 (1H, br), 3.53 (1H, dd, J=6, 4 Hz), and 4.97 (1H, d, J=4 Hz). IR ν: 3450, 2950, 1470, 1382, and 1105 cm^{-1}], **60** [colorless prisms, mp 146.5—148 °C, 53 mg; 28%. Found: C, 78.93; H, 10.67%. ^{1}H NMR δ=0.86 (3H, d, J=7 Hz), 0.96 (6H, d, J=7 Hz), 0.98 (3H, s), 1.64 (3H, br s), 2.85 (2H, br), 3.04 (1H, sept, J=7 Hz), 3.76 (1H, dd, J=9, 2 Hz), and 4.10 (1H, d, J=9 Hz). IR ν: 3420, 2950, 1465, 1450, 1375, 1200, 1013, and 983 cm^{-1}], and **61** [a colorless oil, 27 mg; 14%. Found: M.W., 304.2388. Calcd for $C_{20}H_{32}O_2$: 304.2401. ^{1}H NMR δ=0.76 (3H, d, J=7 Hz), 0.95 (3H, d, J=7 Hz), 0.98 (3H, d, J=7 Hz), 1.20 (3H, s), 1.64 (3H, br s), 2.80 (1H, br), 2.82 (1H, sept, J=7 Hz), 4.18 (1H, d, J=9 Hz), and 4.49 (1H, d, J=9 Hz). IR ν: 3610, 3570, 2960, 2930, 1463, 1370, and 996 cm^{-1}].

$TiCl_2$-Mediated Cyclization of 58. To an anhydrous THF

solution (5 cm³) of $TiCl_4$ (106 mg) prepared carefully at 0 °C, pyridine (51 mg) and powdered Zn (126 mg) were added, and stirred for 30 min. Then, the THF solution (2 cm³) of **58** (97 mg) was introduced dropwise under stirring for 1 h. After being diluted with aqueous K_2CO_3, the mixture was extracted with ether and chromatographed on a silica-gel column to give **62** [a colorless oil, 82 mg; 84%. Found: M.W., 304.2404. ^1H NMR δ=0.94 (3H, d, J=7 Hz), 0.97 (3H, d, J=7 Hz), 1.14 (3H, d, J=7 Hz), 1.24 (3H, s), 1.67 (3H, br s), 3.54 (1H, br t, J=5 Hz), and 4.87 (1H, br). IR ν: 3350, 2950, 2880, 1460, 1385, 1370, and 1030 cm^{-1}].

Acetylation of a Mixture of 62 and 63. A pyridine solution (4 cm³) of the whole product (485 mg) was mixed with Ac_2O (0.5 cm³) and kept at room temperature for 16 h. The mixture was then diluted with water, extracted with hexane–ether (9:1) and chromatographed on a silica-gel column to give **64** [a colorless oil, 461 mg; 84%. Found: M.W., 346.2515. Calcd for $C_{22}H_{34}O_3$: 346.2506. ^1H NMR δ=0.92 (3H, d, J=7 Hz), 1.02 (6H, d, J=7 Hz), 1.21 (3H, s), 1.62 (3H, br s), 2.11 (3H, s), 2.64 (1H, sept, J=7 Hz), 4.76 (1H, br t, J=5 Hz), and 5.04 (1H, br). IR ν: 3550, 2950, 2870, 1745, 1720, 1465, 1384, 1370, 1242, 1028, and 964 cm^{-1}], and **65** [colorless needles, mp 117—120 °C, 72 mg; 13%. Found: M.W., 346.2510. ^1H NMR δ=0.93 (3H, d, J=7 Hz), 0.98 (3H, d, J=7 Hz), 1.01 (3H, d, J=7 Hz), 1.07 (3H, s), 1.60 (3H, br s), 2.10 (3H, s), 3.18 (1H, sept, J=7 Hz), 4.29 (1H, d, J=11 Hz), and 5.28 (1H, br). IR ν: 3490, 2950, 1725, 1452, 1377, 1260, and 1030 cm^{-1}].

Hydrolysis of 65. An anhydrous ether solution (3 cm³) of **65** (20 mg) was treated with LAH (10 mg) at room temperature for 1 h, after which the mixture was extracted with ether. Silica-gel column chromatography of the extract gave **63** [a colorless oil, 11 mg; 63%. Found: M.W., 304.2388. ^1H NMR δ=0.97 (9H, br d, J=7 Hz), 1.06 (3H, br s), 1.62 (3H, br s), 3.18 (1H, br), 3.90 (1H, br), and 4.23 (1H, br)] and an isomer, **67** [a colorless oil, 2 mg; 11%. Found: M.W., 304.2404. ^1H NMR δ=0.96 (6H, d, J=7 Hz), 1.02 (3H, d, J=7 Hz), 1.16 (3H, s), 1.61 (3H, br s), 2.59 (1H, br), 2.88 (1H, sept, J=7 Hz), 2.97 (1H, br), 3.97 (1H, dd, J=10, 8 Hz), and 4.38 (1H, d, J=10 Hz). IR ν: 3630, 3600, 2960, 2880, 1460, 1380, 1240, 1015 cm^{-1}].

Acetylation of 62 to a Diacetate (66). An anhydrous CH_2Cl_2 solution (3 cm³) of **62** (246 mg), DMAP (20 mg), AC_2O (300 mg) and Et_3N (100 mg) was kept at room temperature for 16 h. The mixture was then diluted with water, extracted with ether, and chromatographed on a silica-gel column to give **64** (46 mg; 16%) and **66** [a colorless oil, 223 mg; 71%. Found: C, 74.14; H, 9.36%. Calcd for $C_{24}H_{36}O_4$: C, 74.19; H, 9.34%. ^1H NMR δ=0.92 (3H, d, J=7 Hz), 1.00 (3H, s), 1.04 (3H, d, J=7 Hz), 1.07 (3H, d, J=7 Hz), 1.60 (3H, br s), 2.01 (3H, s), 2.08 (3H, s), 2.78 (1H, br), 2.84 (1H, sept, J=7 Hz), 4.80 (1H, dd, J=5.5, 3 Hz), and 6.30 (1H, br). IR ν: 2950, 2870, 1750, 1460, 1370, 1245, 1230, and 1030 cm^{-1}].

Hydrolysis of 64. Similarly, **64** (20 mg) was reduced with LAH in ether to give **62** (19 mg; 100%).

Formation of Dimethyl Acetal, 68, from 62. To an anhydrous benzene solution (4 cm³) of **62** (46 mg), $Me_2C(OMe)_2$ (1 cm³) was added and stirred with PPTS (3 mg) at room temperature for 72 h. The mixture was then treated with aqueous K_2CO_3 and extracted with ether. Silica-gel column chromatography of the extract yielded **68** [a colorless oil, 33 mg; 64%. Found: M.W., 344.2716. Calcd for $C_{23}H_{36}O_2$: 344.2713. ^1H NMR δ=0.94 (3H, d, J=7 Hz), 1.00 (3H, d, J=7 Hz), 1.11 (3H, d, J=7 Hz), 1.24 (3H, s), 1.28 (3H, s), 1.37 (3H, s), 1.60 (3H, br s), 2.52 (1H, sept, J=7 Hz), 2.59 (1H, br), 4.20 (1H, dd, J=9, 1 Hz), and 5.17 (1H, br d, J=9 Hz). IR ν: 2950, 1460, 1380, 1205, 1042, and 886 cm^{-1}].

$NaIO_4$-Cleavage of 62. Formation of 58. A THF solution (2 cm³) of **62** (29 mg) was treated with $NaIO_4$ (40 mg) dissolved in water (2 cm³) at room temperature for 12 h. The mixture was then, diluted with water and extracted with ether. Silica-gel column chromatography of the extract afforded **58** (19 mg; 65%), which was identical with the authentic sample in every respect.

PCC-Oxidation of 64 to 69. To an anhydrous CH_2Cl_2 suspension (2 cm³) of PCC (64 mg), NaOAc (9 mg), and Celite (40 mg), a CH_2Cl_2 solution of **64** (5 mg) was added dropwise. After 3 h, the mixture was diluted with ether and filtered on a short Florisil column to give **69** [a colorless oil, 33 mg; 77%. Found: M.W., 344.2353. Calcd for $C_{22}H_{32}O_3$: 344.2350. ^1H NMR δ=0.96 (6H, d, J=7 Hz), 1.06 (3H, d, J=7 Hz), 1.16 (3H, s), 1.60 (3H, br s), 2.15 (3H, s), 2.80 (1H, br), 3.10 (1H, br), and 5.25 (1H, d, J=5 Hz). IR ν: 2950, 1753, 1705, 1460, 1372, 1240, 1045, and 808 cm^{-1}].

LAH-Reduction of 69 to 62. An anhydrous ether solution of **69** (5.0 mg) was treated with LAH (5 mg) to give **62** (4.5 mg; 100%), whose identity as the authentic sample was confirmed by direct comparisons.

Conversion of 62 to Fusicoccatriene (1) via Elimination of Cyclic Thiocarbonate (71). To an anhydrous toluene solution (4 cm³) of **62** (277 mg), 1,1′-(thiocarbonyl)bis[imidazole] (**70**, 540 mg; 90%) was added and refluxed for 5 h. The mixture was then diluted with ether, passed through a short silica-gel filter, heated in vacuo to remove the solvent, and chromatographed to obtain **71** [a colorless oil, 185 mg; 59%. Found: M.W., 346.1963. Calcd for $C_{21}H_{30}O_2S$: 346.1965. ^1H NMR δ=0.95 (3H, d, J=7 Hz), 1.01 (3H, d, J=7 Hz), 1.16 (3H, d, J=7 Hz), 1.27 (3H, s), 1.66 (3H, br s), 4.91 (1H, dd, J=10, 1 Hz), and 5.82 (1H, d, J=10 Hz)]. Without further purification, **71** (174 mg) was dissolved together with 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (**72**, 1 cm³) in benzene (1.5 cm³), and refluxed for 9 h. After dilution with ether, the extract was passed through a short silica-gel column to obtain **1** [a colorless oil, 65 mg; 51%. Found: M.W., 270.2347. Calcd for $C_{20}H_{30}$: 270.2346. ^1H NMR δ=0.92 (6H, d, J=7 Hz), 0.95 (3H, s), 0.96 (3H, d, J=7 Hz), 1.58 (3H, br s), 2.51 (1H, sept, J=7 Hz), 2.60 (1H, br), 5.40 (1H, br dd, J=11, 7 Hz), and 5.79 (1H, br d, J=11 Hz). IR ν: 2960, 2880, 1460, 1370, 1110, and 1025 cm^{-1}], together with the recovered **71** (46 mg; 26%).

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