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Synthetic Photochemistry. XXVIII.[1] A Photochemical C_5-Homologation of 4-Isopropenyltoluene with Methyl 2,4-Dioxopentanoate to Isolaurene and a Formal Synthesis of Cuparene

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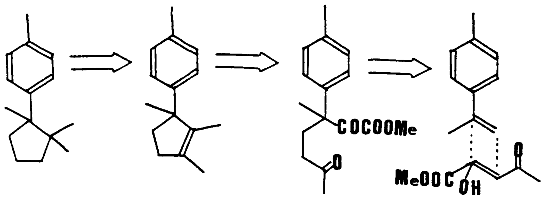
Starting from the photocycloaddition of methyl 2,4-dioxopentanoate with 4-isopropenyltoluene, isolaurene was synthesized, and its further conversion to 5-cuparenone constituted the formal synthesis of cuparene. For the first time, the *proto*-(2+2)π cycloadduct, a β-keto cyclobutanol derivative, has been isolated from the product mixture.

Recently, we have extended the use of the photocycloadducts of methyl 2,4-dioxopentanoate (**1**) with olefins to a facile cyclopentane ring construction.[2] The method must be applicable to a synthesis of laurenoids or cuparenoids.

An advantage of using **1** as a photocycloaddend is a capability of reaction with conjugated olefins; with cyclopentadiene[2] and with cycloheptatriene,[3] it gave the (2+2)π cycloadducts in addition to the (2+4)π and/or (2+6)π cycloadducts. Even with an acyclic diene, isoprene, **1** smoothly produced the (2+2)π cycloadducts, from which sesquiterpenoids, geijerone and an elemene derivative,[4] and monoterpenoids, dehydroiridodial, and chrysomelidial,[5] have been synthesized. This constitutes a proper head-to-tail homologation of terpenoids with the C_5-unit. Based on this method, cuparenoids and migrated cuparenoids, many of which are physiologically active, can be constructed as shown in the following *retro*-synthetic scheme (Scheme 1).



Scheme 1.

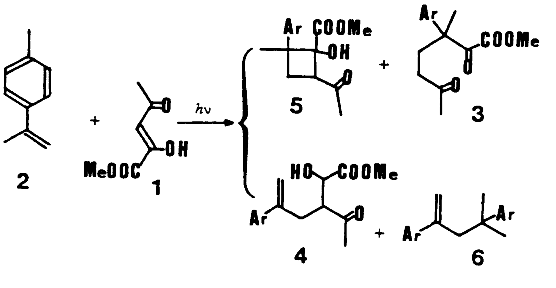
Since indene was photochemically reactive with **1**,[6] 4-isopropenyltoluene (**2**) should also be reactive enough to form the photoadduct (**3**) which could be just the proper starting material for the purpose.

When an ethyl acetate solution of **1** and **2** was internally irradiated by means of a high-pressure mercury lamp, formation of four photoproducts was recognized, as shown in Scheme 2. The major product (48% yield) was the desired (2+2)π cycloadduct (**3**). Its ^{1}H-NMR spectrum showed signals ascribable to the *p*-tolyl, acetyl, and methoxycarbonyl groups. Another compound (**4**, 10% yield) showed not only the NMR signals of acetyl and methoxycarbonyl groups, but those of a methine proton on the carbon bearing the methoxycarbonyl and hydroxyl groups and a terminal methylene group. Therefore, **4** must be an ene-reaction product.[7]

Another product (**5**), 0.2% yield, exhibited the $\nu_{C=O}$ band in the IR spectrum, and was converted into **3** under somewhat strong conditions. Therefore, **5** must be the *proto*-(2+2)π adduct. It is surprising that an intensive use of silica-gel column chromatography in the workup has not completed the *retro*-aldolization of such a strained aldol, **5**.

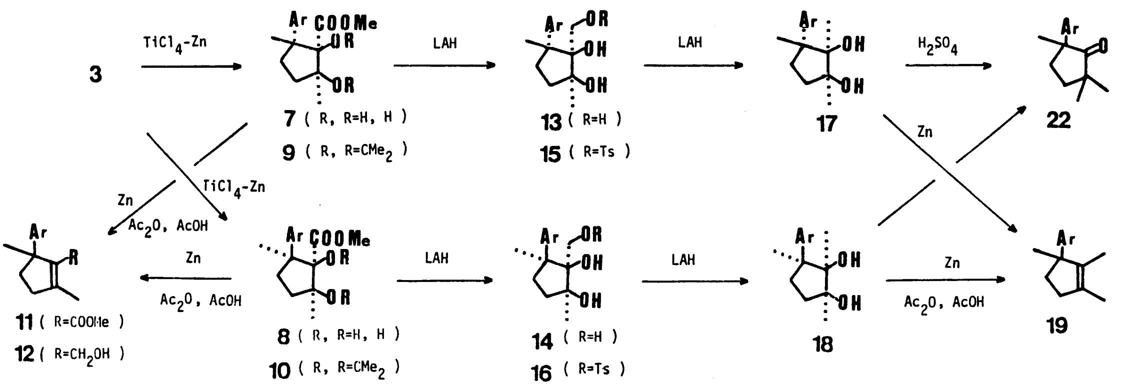
Although we have previously isolated the *proto*-(4+2)π[2] and (6+2)π[3] cycloadducts of **1** with conjugated olefins, this is the first example of an isolation of a *proto*-(2+2)π adduct.

From the less polar photoproduct mixture, 23% of a hydrocarbon (**6**) has been isolated; its NMR analysis determined the structure to be the ene-type dimer of **2**.



Scheme 2.

The formation of **3** from **2** can be regarded as a C_5 homologation of a monoterpene to sesquiterpenoid derivatives; subsequent transformations of **3**, in Scheme 3, may lead to a fundamental laurenoid skeleton. When **3** was treated with titanium(II) chloride,[5,8,9] generated *in situ* from titanium(IV) chloride and zinc dust, two *cis*-glycol derivatives (**7** and **8**) were formed in good yields. Both **7** and **8** formed the dioxolane derivatives (**9** and **10**) by treatment with 2,2-dimethoxypropane in the presence of pyridinium *p*-toluenesulfonate (PPTS) in benzene. Relative configurations of **7** and **9** *vs*. **8** and **10** were determined by the ^{1}H-NMR comparisons; the methoxyl signals of the ester groups of **7** and **9** appeared at $\delta=3.27$ and 3.21, while those of **8** and **10** at 3.80 and 3.76, and the difference can be explained in terms of the anisotropic high-field shift due to the proximate aromatic ring in the formers. Therefore, the *p*-tolyl and the methoxycarbonyl groups of **7** and **9** are in *cis*-rela-



Scheme 3.

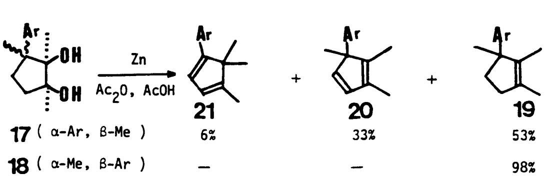
tionship.

The zinc-in-acetic acid reduction of both **7** and **8** afforded the same cyclopentene derivative (**11**), whose LAH (lithium aluminum hydride) reduction to an allyl alcohol (**12**) was unsatisfactory because of a low yield. Alternatively, **7** and **8** were at first reduced to the triols (**13** and **14**), and then their tosylates (**15** and **16**) were reduced again with LAH to the diols (**17** and **18**). The ^{1}H-NMR spectrum of **18** was identical with that of the osmium(VIII) oxide oxidation product of isolaurene, although the original workers[11] did not specify the stereochemistry.[11]

The reduction of **18** with zinc in acetic acid[12] gave a hydrocarbon (**19**) in 98% yield, whose reported NMR data in carbon tetrachloride was identical with isolaurene.[10] Consequently, an alternative synthesis of **19** has been completed.

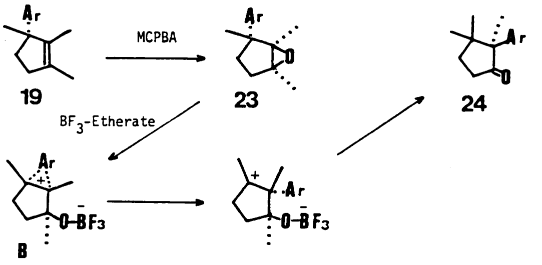
On the other hand, the same treatment of **17** yielded **19** in a lower yield, 53%, together with the formation of two cyclopentadiene derivatives (**20** and **21**) in 33 and 6% yields. The structures of **20** and **21** were clarified by the NMR analysis; the formation of **20** from **17** in a substantial amount confirmed the assignment for the stereochemistry of the glycols, **7** and **8** (Scheme 4).

Following the conversion of **18** to 2,5,5-trimethyl-2-(*p*-tolyl)cyclopentanone (**22**),[10] **17** was also treated with methanolic sulfuric acid briefly; an exclusive product was the cyclopentanone (**22**) whose structure was firmly established by the NMR comparisons. In any case, the protic acid-induced rearrangement of **17** and **18** never furnished the cuparene skeleton. Probably, this comes from a preferential protonation to the C-3 hydroxyl groups over the C-2 hydroxyl group on steric grounds.



Scheme 4.

These results of the protic acid-catalyzed dehydration of **17** and **18** made us examine the Lewis acid-promoted reaction of an oxygenated isolaurene derivative. Indeed, when an epoxide (**23**) prepared from **19** and *m*-chloroperbenzoic acid (MCPBA) was treated with boron trifluoride etherate in benzene, a facile rearrangement occurred. The sole product formed was a cyclopentanone derivative (**24**) whose NMR data measured in carbon tetrachloride were identical with those of 2,3,3-trimethyl-2-(*p*-tolyl)cyclopentanone (5-cuparenone) already prepared by de Mayo and Suau.[13] As proposed in Scheme 5, the rearrangement of **23** to **24** involved migrations of the *p*-tolyl and the methyl groups *via* formation of the spirocyclic phenonium ion (**B**). Since cuparene[14] has been synthesized from **24**,[13] the present study constitutes another total synthesis of it.



Scheme 5.

Experimental

The elemental analyses were performed by Miss M. Yamaguchi of This Institute. The NMR spectra were measured by an FX 100 Model spectrometer, JEOL, in $CDCl_3$ solutions unless otherwise specified, and the chemical shifts were expressed in δ units from the internal Me_4Si. The mass spectra were measured by an O1SG Model spectrometer, JEOL, and the IR spectra were taken either in solution (CCl_4 or $CHCl_3$) or as KBr disks, by an A 102 Model spectrometer, JASCO.

Photocycloaddition Reaction of 4-Isopropenyltoluene (2) with 1. An EtOAc solution (50 cm^3) of **2** (27.6 g) and **1** (9.2 g) was placed in an immersion well cooled with running water, and was internally irradiated with a 400-W high-pressure mercury lamp with an occasional check of the reaction with $FeCl_3$ coloration. After 25 h, the mixture was evaporated *in vacuo* at room temperature to remove the volatile material, and fractionated with benzene and aqueous Na_2CO_3. The organic layer containing the photoadducts was then dried on $MgSO_4$, and chromatographed on a silica-gel column; from the least polar fractions eluted with hexane was the hydrocarbon, **6**, 10.2 g (23%) [Found: M$^+$, 264.1857. Calcd for $C_{20}H_{24}$: M$^+$, 264.1875. δ=1.16 (6H, s), 2.24 (3H, s), 2.75 (2H, s), 4.70 (1H, dm, J=2 Hz), 5.09 (1H, d, J=2 Hz), and 6.8—7.2 (8H, m). δ(C)=20.8, 21.0, 28.8 (2C), 38.3, 49.6, 116.2, 125.9 (2C), 126.5 (2C), 128.7 (2C), 128.9 (2C), 134.8, 136.5, 140.8, 146.7, and 146.8. ν: 3200—2800, 1625, 1520, 900, 830, 817 cm^{-1}].

From the subsequent fractions eluted by hexane–EtOAc (9:1) gave a colorless oil, **3**, 8.0 g (48%). Cold finger distillation of a part of this sample yielded the analytical specimen, a colorless liquid [Found: C, 69.58; H, 7.36%. M$^+$, 276.1361. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30%; M$^+$, 276.1361. δ=1.57 (3H, s), 1.99 (3H, s), 2.0—2.3 (4H, m), 2.26 (3H, s), 3.50 (3H, s), and 7.07 (4H, s). δ(C)=20.8, 21.0, 29.6, 31.4, 38.3, 52.0, 52.8, 126.5 (2C), 129.5 (2C), 136.9, 137.0, 162.7, 197.3, and 207.1. ν: 1743, 1722 cm^{-1}].

Subsequently, the fractions from hexane-EtOAc (8:2) yielded a pale yellow oil, **4**, 1.7 g (10%) [Found: C, 69.47; H, 7.39%. M$^+$, 276.1358. δ=2.10 (3H, s), 2.34 (3H, s), 2.8—3.2 (4H, m, diminished to 3H by adding D_2O), 3.69 (3H, s), 4.21 (1H, d, J=3.2 Hz), 5.13 (1H, d, J=1.3 Hz), 5.53 (1H, d, J=1.3 Hz), and 6.8—7.3 (4H, m). δ(C)=21.1, 30.4, 33.8, 52.5, 53.0, 70.9, 115.0, 126.0 (2C), 129.3 (2C), 136.7, 137.7, 144.5, 173.8, and 210.9. ν: 3500, 1740, 1715 cm^{-1}]. An oily material obtained from more polar fractions was further purified by means of preparative thin-layer chromatography (PTLC) to yield a colorless oil, **5**, 29 mg (0.2%) [Found: M$^+$, 276.1367. Calcd for $C_{16}H_{20}O_4$: 276.1362. δ=1.44 (3H, s), 2.10 (3H, s), 2.0—2.4 (4H, m, diminished to 3H by adding D_2O), 2.31 (3H, s), 3.83 (3H, s), and 6.8—7.2 (4H, m). δ(C)=21.2, 24.8, 30.2, 31.5, 37.7, 39.7, 52.6, 62.3, 129.5 (2C), 129.8 (2C), 136.4, 173.3, and 208.7. ν: 3460, 1725, 1710 cm^{-1}].

Conversion of 5 to 3. A benzene solution (2 cm^3) of **5** (5 mg) and TsOH (1 mg) was refluxed for 1 h. PTLC of the reaction mixture afforded **3**, 3.5 mg (70%), whose identity with the authentic sample was confirmed by direct comparisons.

Reductive Cyclization of 3. Formation of 7 and 8. To an anhydrous tetrahydrofuran (THF, 60 cm^3) of $TiCl_4$ (650 mg), Zn (450 mg) and pyridine (240 mg) were added at 0 °C. The mixture, containing Ti(II) salt, was then cooled by ice-water, and a THF solution (20 cm^3) of **3** (631 mg) was added for 0.5 h at 0 °C with vigorous stirring. After 3 h, the mixture was poured into ice-water, and extracted with ether, and the ether extract was chromatographed on a silica-gel column with hexane-EtOAc (3:1) to give colorless crystals, mp 126—126.5 °C, **7**, 213 mg (34%) [Found: C, 69.29; H, 8.01%; M$^+$, 278.1509. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97%; M$^+$, 278.1520. δ=1.12 (3H, s), 1.50 (3H, s), 2.26 (3H, s), 2.4—2.8 (4H, m), 3.27 (3H, s), 3.4 (1H, br. s, disappeared by adding D_2O), 4.24 (1H, br. s, disappeared by adding D_2O), and 6.8—7.2 (4H, m). δ(C)=20.8, 25.5, 28.0, 32.9, 35.8, 51.8, 52.1, 80.3, 89.4, 124.9 (2C), 128.5 (2C), 135.0, 144.8, and 175.4. ν=3460, 1720, 1515, 1260 cm^{-1}], and a colorless oil, **8**, 219 mg (35%) [Found: M$^+$, 278.1520. δ=1.23 (3H, s), 1.37 (3H, s), 1.8—2.2 (3H, m), 2.28 (3H, s), 2.4—2.8 (2H, m), 3.48 (1H, br. s), 3.80 (3H, s), and 7.04 (4H, m). δ(C)=20.8, 25.4, 26.8, 34.6, 37.7, 52.3 (2C), 81.4, 88.6, 127.6 (2C), 128.4 (2C), 135.7, 141.7, and 174.1. ν: 3470, 1515, 1250 cm^{-1}].

Isopropylidenedioxy Derivative (9) from 7. To an anhydrous benzene solution (2 cm^3) of **7** (27.6 mg), 2,2-dimethoxypropane (2 cm^3) and PPTS (10 mg) were added at once, this mixture was kept at 15—25 °C for 8 h. It was then diluted with ether and washed with aqueous K_2CO_3 solution. PTLC of the organic extracts with hexane-EtOAc (4:1) yielded a colorless oil, 15 mg (55%), **9** [Found: M$^+$, 318.1839. Calcd for $C_{19}H_{26}O_4$: M$^+$ 318.1831. δ=1.38 (3H, s), δ=1.45 (3H, s), 1.50 (3H, s), 1.63 (3H, s), 1.8—2.9 (4H, m), 2.27 (3H, s), 3.21 (3H, s), and 7.03 (4H, s). δ(C)=21.0, 27.4, 27.6, 28.1, 28.4, 37.1, 39.6, 51.2, 54.5, 93.7, 100.0, 115.4, 125.3 (2C), 128.6 (2C), 135.2, 144.7, and 172.7. ν: 1750 cm^{-1}].

Isopropylidenedioxy Derivative (10) from 8. Similarly, **8** (52 mg) was converted to **10**, a colorless oil, 67.5 mg (74%) [Found: M$^+$, 318.1839. δ=1.28 (3H, s), 1.35 (6H, s), 1.58 (3H, s), 1.6—2.0 (4H, m), 2.29 (3H, s), 3.76 (3H, s), and 7.08 (4H, s). δ(C)=20.9, 24.9, 26.9, 27.2, 27.4, 34.7, 38.8, 51.6, 54.6, 93.4, 95.7, 109.8, 126.5 (2C), 128.6 (2C), 135.5, 141.5, and 171.8. ν: 1720 cm^{-1}].

Reduction of 7 with Zinc in Acetic Acid. To a mixed solution of Ac_2O (18 cm^3) and AcOH (9 cm^3) of **7** (142.5 mg), powdered Zn (3 g) was added in portions while refluxing for 6 h. The mixture was then evaporated *in vacuo* to remove the solvent, and the residue was poured into ice-water, and extracted with benzene. The extracts were purified by PTLC to give a colorless oil, 80 mg (64%), **11** [Found: M$^+$, 244.1463. Calcd for $C_{16}H_{20}O_2$: M$^+$, 244.1463. δ=1.61 (3H, s), 1.8—2.3 (4H, m), 2.14 (3H, s), 2.27 (3H, s), 3.50 (3H, s), and 7.0—7.1 (4H, m). δ(C)=16.9, 20.9, 25.0, 37.8, 42.5, 50.5, 53.8, 125.4 (2C), 128.7 (2C), 134.7, 135.1, 146.1, 155.1, and 166.3. ν: 1715, 1520, 1268 cm^{-1}].

Reduction of 8 with Zinc in Acetic Acid. Similarly, **8** (41 mg) was reduced with powdered Zn (670 mg) in Ac_2O (4 cm^3) and AcOH (2 cm^3) for 9.5 h to give a colorless oil, 35 mg (85%), which was identical with the sample of **12** obtained from the reduction of **7**.

LAH-Reduction of 11 to Give 12 An anhydrous ether solution (25 cm^3) of **11** (46.5 mg) was treated with LAH (22 mg) at 15—25 °C for 1.5 h. The mixture was then treated with EtOAc, and poured into ice-water, and extracted with ether. The PTLC of the extracts with hexane-EtOAc (3:1) gave a colorless oil, 2.4 mg (6%), **12** [Found: M$^+$, 216.1514. Calcd for $C_{15}H_{20}O$: M$^+$, 216.1514. δ=1.51 (3H, s), 1.83 (3H, s), 2.30 (3H, s), 3.83 (1H, d, J=12.5 Hz), 4.05 (1H, d, J=12.5 Hz), and 7.0—7.2 (4H, m). δ(C)=14.4, 20.9, 25.1, 36.1, 41.7, 53.9, 57.2, 125.9 (2C), 128.9 (2C), 135.2, 138.4, 141.1, and 146.1. ν: 3420, 1520 cm^{-1}].

LAH-Reduction of 7. Formation of 13. An anhydrous ether solution (30 cm^3) of **7** (188 mg) was treated with LAH (102 mg) at 15—25 °C for 0.5 h, and subsequently refluxed for 5 h. The mixture was then poured into ice-water and extracted with ether. Silica-gel column chromatography of the extracts yielded colorless needles, mp 126—127 °C, 168 mg (99%), **13** [Found: C, 72.09; H, 8.90; M$^+$, 250.1569. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86%; M$^+$, 250.1569. δ=1.12 (3H, s), 1.43 (3H, s), 1.8—2.4 (5H, m, diminished to 4H by adding D_2O), 2.29 (3H, s), 2.74 (1H, br. s, disappeared by adding D_2O), 3.33 (1H, d, J=12 Hz), 3.53 (1H, d, J=12 Hz), 3.84 (1H, br. s, disappeared by adding D_2O), and 7.0—7.2 (4H, m). δ(C)=20.8, 26.2, 26.7, 33.6, 38.0, 51.3, 64.7, 81.4, 83.3, 127.2 (2C), 129.0 (2C), 136.0, and 143.6. ν: 3500, 1360 cm^{-1}].

LAH-Reduction of 8. Formation of 14. Similarly, **8** (679 mg) was converted by the LAH reduction to colorless needles, mp 107—108 °C, 605 mg (99%), **14** [Found: C, 71.99; H, 8.98%; M$^+$, 250.1563. δ=1.35 (3H, s), 1.41 (3H, s), 2.0—2.3 (4H, m), 2.29 (3H, s), 3.00 (3H, br. s, disappeared by adding D_2O), 3.55 (1H, d, J=12 Hz), 3.70 (1H, d, J=12 Hz), and 6.8—7.2 (4H, m). δ(C)=20.7, 24.7, 25.4, 35.9, 38.7, 50.7, 63.1, 81.1, 81.2, 127.8 (2C), 128.5 (2C), 135.8, and 142.1. ν: 3450, 3300, 1510 cm^{-1}].

LAH-Reduction of a Monotosylate (15) Derived from 13. Preparation of 17. To a cold pyridine solution (5 cm^3) containing TsCl (380 mg), **13** (331 mg) was added and kept at 10—15 °C for 24 h. The mixture was then heated *in vacuo* to remove the volatile material, and the residue was washed with water, and extracted with $CHCl_3$. The extracts yielded colorless oily monotosylate, **15**, 528 mg (99%) [δ=1.18 (3H, s), 1.36 (3H, s), 1.6—2.3 (4H, m), 2.28 (3H, s), 2.41 (3H, s), 2.68 (1H, d, J=10 Hz), 2.83 (2H, br. s), 3.91 (1H, d, J=10 Hz), and 6.9—7.5 (8H, m). δ(C)=20.8, 21.6, 26.1, 26.5, 32.8, 38.1, 51.6, 72.0, 80.8, 81.8, 126.6 (2C), 127.8 (2C), 128.7 (2C), 129.6 (2C), 131.9, 135.6, 142.3, and 144.6. ν: 3500, 1360 cm^{-1}], on silica-gel column chromatography. Subsequently, **15** (145 mg) was dissolved in an anhydrous ether (10 cm^3), and was reduced with LAH (30 mg) in ether (25 cm^3) at 15—25 °C for 3 h. Then, the mixture was treated with EtOAc, poured into ice-water, and extracted with ether. The extracts were chromatographed on a silica-gel column to give colorless needles, mp 91—92 °C, 81 mg (96%), **17** [Found: M^+, 234.1621. Calcd for $C_{15}H_{22}O_2$: M^+, 234.1620. δ=0.78 (3H, s), 1.21 (3H, s), 1.42 (3H, s), 1.8—2.1 (4H, m), 2.30 (3H, s), 2.6 (2H, br. s, disappeared by adding D_2O), and 7.0—7.2 (4H, m). δ(C)=21.0, 22.4, 25.5, 26.5, 31.9, 37.1, 51.7, 80.4, 82.5, 126.3 (2C), 128.6 (2C), 135.1, and 145.4. ν: 3600—3300, 1510 cm^{-1}].

Reduction of 14 to 18 via *Monotosylate (16).* Similarly, **14** (558 mg) was converted to a monotosylate (**16**), a colorless oil, 887 mg (99%) [δ=1.32 (3H, s), 1.41 (3H, s), 1.8—2.3 (4H, m), 2.27 (3H, s), 2.37 (3H, s), 2.62 (2H, br. s), 4.09 (1H, d, J=10 Hz), 4.23 (1H, d, J=10 Hz), and 7.0—7.5 (8H, m). δ(C)=20.8, 21.6, 24.2, 25.7, 36.7, 39.1, 50.8, 71.4, 80.6, 80.7, 126.6 (2C), 127.8 (2C), 128.6 (2C), 129.8 (2C), 132.4, 136.1, 140.8, and 144.9. ν: 3500, 1360 cm^{-1}]. Then, an anhydrous ether solution (30 cm^3) of **16** (465 mg) was reduced by LAH (95 mg) to a colorless oil, 268 mg (99%), **18** [Found: M^+, 234.1622. δ=1.12 (3H, s), 1.28 (3H, s), 1.34 (3H, s), 2.0—2.3 (4H, m), 2.30 (3H, s), 2.6 (2H, br. s, disappeared by adding D_2O), and 7.1—7.3 (4H, m). δ^{CCl_4}=1.08 (3H, s), 1.20 (3H, s), 1.29 (3H, s), 1.8—2.3 (4H, m), 2.30 (3H, s), and 7.0—7.1 (4H, m). δ(C)=19.4, 20.8, 25.6, 26.1, 33.9, 38.3, 51.4, 80.9, 82.4, 127.3 (2C), 128.9 (2C), 136.0, and 141.9. ν: 3450, 1515 cm^{-1}], of which the NMR taken in CCl_4 was in accord with that (lit, mp 114—116 °C) prepared by Irie *et al.*[10]

Reduction of 17 with Zinc in Acetic Acid. Formation of 19, 20, and 21. To a mixed solution of Ac_2O (12 cm^3) and AcOH (6 cm^3) of **17** (145 mg), powdered Zn (617 mg) was added in portions, and the mixture was refluxed for 3 h. It was then filtered, and the residue was washed with water, dil HCl, and ether. The filtrate was extracted with ether, and the combined organic layer was evaporated *in vacuo* to remove the volatile material. Then the residue was chromatographed on a silica-gel column. From the less polar fractions, a hydrocarbon, **19**, a colorless oil, 65 mg (53%) [Found: M^+, 200.1575. Calcd for $C_{15}H_{20}$: 200.1563. δ=1.37 (3H, s), 1.39 (3H, s), 1.71 (3H, s), 2.0—2.3 (4H, m), 2.30 (3H, s), and 7.07 (4H, s). δ^{CCl_4}=1.32 (3H, s), 1.35 (3H, s), 1.69 (3H, s), 1.8—2.3 (4H, m), 2.26 (3H, s), and 6.92 (4H, s). δ(C)=10.3, 14.3, 20.9, 34.3, 35.9, 41.6, 54.6, 126.1 (2C), 128.7 (2C), 131.8, 134.6, 137.5, and 146.2], was isolated, and was in accord with isolaurene in respects of the reported NMR.[10] From the more polar fractions, other hydrocarbons, **20**, 42 mg (33%) [Found: M^+, 198.1406. Calcd for $C_{15}H_{18}$: 198.1406. δ=1.44 (3H, s), 1.55 (3H, s), 1.85 (3H, s), 2.28 (3H, s), 6.10 (H, d, J=6.5 Hz), 6.28 (1H, d, J=6.5 Hz), and 6.9—7.05 (4H, m). ν: 2960, 2930, 1510, 815 cm^{-1}], and **21**, 7 mg (6%) [Found: M^+, 198.1392. δ=1.19 (6H, s), 1.87 (3H, d, J=2 Hz), 2.30 (3H, s), 5.94 (1H, quint, J=2 Hz), 6.53 (1H, d, J=2 Hz), and 7.05—7.35 (4H, m). δ(C)=12.4, 21.0, 22.5 (2C), 53.0, 123.3, 125.2, 125.8 (2C), 128.9 (2C), 133.6, 135.6, 145.1 and 155.5], were isolated.

Reduction of 18 with Zinc in Acetic Acid to 19. Similarly, **18** (231.5 mg) was refluxed with powdered Zn (980 mg) in Ac_2O (20 cm^3) and AcOH (10 cm^3) for 3 h. The mixture was then washed with water and with dil HCl, and extracted with ether. The ether extracts were heated *in vacuo* to remove the solvent, and the residue was chromatographed on a silica-gel column to give a colorless oil, **19**, 194 mg (98%) which was identical with the sample obtained from **17**.

Sulfuric Acid Treatment of 17. A methanolic H_2SO_4 solution (10%, 2 cm^3) of **17** (26.5 mg) was treated at 20—25 °C for 5 min. The mixture was then poured into water and extracted with benzene. The extracts were purified by PTLC to give **22**, 23.2 mg (95%) [Found: M^+, 216.1508. Calcd for $C_{15}H_{20}O$: M^+, 216.1514. δ=1.00 (3H, s), 1.14 (3H, s), 1.37 (3H, s), 1.6—2.3 (4H, m), 2.30 (3H, s), and 7.05—7.2 (4H, m). δ^{CCl_4}=0.94 (3H, s), 1.08 (3H, s), 1.29 (3H, s), 1.6—2.3 (4H, m), 2.28 (3H, s), and 6.95—7.1 (4H, m). δ(C)=20.9, 25.1, 25.5, 26.5, 34.7, 34.9, 45.5, 53.4, 126.3 (2C), 129.4 (2C), 136.2, 140.6, and 224.7. ν: 1735 cm^{-1}], which was identical with the product prepared by Irie *et al.* from **18**.[10]

Epoxidation of 19 to 23. A CH_2Cl_2 solution (25 cm^3) of **19** (200 mg) was mixed with MCPBA (90%, 345 mg), and kept at 15—25 °C for 24 h. After filtration of the resultant *m*-chlorobenzoic acid, the filtrate was washed with aqueous $NaHCO_3$, and chromatographed on a silica-gel column to give a colorless oil, 147 mg (68%), **23** [Found: M^+, 216.1512. Calcd for $C_{15}H_{20}O$: M^+, 216.1512. δ=1.12 (3H, s), 1.47 (3H, s), 1.49 (3H, s), 1.8—2.8 (4H, m), 2.32 (3H, s), and 7.0—7.1 (4H, m). δ(C)=11.7, 15.9, 20.2, 20.9, 31.8, 37.3, 48.5, 70.4, 72.7, 125.8 (2C), 129.0 (2C), 135.4, and 143.8. ν: 3150—2800, 1520, 1243, 815 cm^{-1}].

BF_3-Catalyzed Rearrangement of 23. Formation of 24. An anhydrous benzene solution (1 cm^3) of **23** (11.9 mg) was mixed with BF_3 etherate (0.05 cm^3), and kept at 20—25 °C for 5 min. The mixture was then poured into ice-water and extracted with $CHCl_3$. The extracts were chromatographed on a silica-gel column to give a colorless oil, 10.9 mg (92%), **24** [Found: M^+, 216.1512. Calcd for $C_{15}H_{20}O$: M^+, 216.1512. δ=0.67 (3H, s), 1.06 (3H, s), 1.32 (3H, s), 1.8—2.8 (4H, m), 2.30 (3H, s), and 6.95—7.1 (4H, m). δ^{CCl_4}=0.65 (3H, s), 1.04 (3H, s), 1.24 (3H, s), 1.8—2.8 (4H, m), 2.28 (3H, s), and 6.92 (4H, s). δ(C)=19.3, 20.9, 23.9, 26.5, 33.5, 36.0, 42.7, 59.9, 127.7 (2C), 128.4 (2C), 135.9, 137.9, and 222.1. ν: 3200—2800, 1742, 1510 cm^{-1}], which was in good agreement with the reported NMR data (in CCl_4) of de Mayo and Suau.[13]

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