[Chem. Pharm. Bull. 36(4)1371—1378(1988)]

7,7-Dimethyltricyclo[3.3.0.0^{2,8}]octan-3-ones as Synthetic Intermediates. II.[1] A Total Synthesis of (±)-Pentalenene, an Angular Triquinane Sesquiterpene[2]

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(Received October 7, 1987)

A total synthesis of (±)-pentalenene (**3**), one of the least-oxidized triquinane sesquiterpenes, is described. By a several-step sequence, 4,4-dimethyl-2-cyclopentenone (**5**) was derived to a tricyclooctanone (**4**), which was subjected to a reductive C_2–C_8 bond opening reaction to give **15**. The triquinane derivative (**20**), obtained from **15**, was transformed to (±)-pentalenene (**3**) and (±)-*epi*-pentalenene (**21**) in a 1.8 : 1 ratio.

On the other hand, hydroboration-oxidation of **4** followed by tosylation gave easily separable products, **23** and **24**, which were transformed to **20A** and **20B**, precursors for (±)-**3** and (±)-**21**, respectively.

Keywords——angular triquinane; sesquiterpene; pentalenene; *epi*-pentalenene; total synthesis; cyclopropane ring opening; Birch reduction; tricyclo[3.3.0.0^{2,8}]octane; bicyclo[3.3.0]octane; cyclopropanation

Recently, many kinds of angular triquinane sesquiterpenes have been isolated and have received much attention from the structural viewpoint.[3] In the previous paper we reported a preparation and cyclopropane ring cleavage of 7,7-dimethyl-5-(2-propenyl)tricyclo[3.3.0.0^{2,8}]octan-3-one (**1**).[1] Under the Birch reduction conditions, compound **1** was found to undergo the exclusive cleavage of the C_2–C_8 bond, yielding the bicyclo [3.3.0]octan-3-one (**2**), which seems to be a versatile intermediate for angular triquinanes. In this paper, we describe a total synthesis of an angular triquinane sesquiterpene, (±)-pentalenene (**3**).

Pentalenene was isolated from *Streptomyces griseochromogenes* in 1980 and its structure was determined as **3** on the basis of spectral considerations.[4] The least-oxidized triquinane is structurally related to other triquinane sesquiterpenes, *e.g.*, isocomene,[5] silphinene[6] and subergorgic acid,[7] and is biogenetically related to the pentalenolactone family.[8] Several synthetic routes to (±)-pentalenene (**3**) have been developed to date.[3,9] Our present strategy for construction of (±)-**3** is illustrated in Chart 1 and consists of utilizing the above C_2–C_8 bond cleavage reaction as a crucial step, starting from a tricyclo[3.3.0.0^{2,8}]octanone (**4**) which has a four-carbon alkyl unit at the 5-position.

Synthesis of the Starting Material, 7,7-Dimethyl-5-(1-methyl-2-propenyl)tricyclo[3.3.0.0^{2,8}]-octan-3-one (4)

Reaction of 4,4-dimethyl-2-cyclopentenone (**5**)[10] with crotylmagnesium chloride[11] in ether gave the 1,2-adduct (**6**) as a diastereomeric mixture. The constitutional isomer (**7**) could not be detected in this reaction. According to the known method,[12] the tertiary allylic alcohol (**6**) was transformed into the enone (**8**) in 84% yield from the starting material (**5**). Lithium aluminum hydride reduction of **8** in ether afforded almost quantitatively the alcohol (**9**).

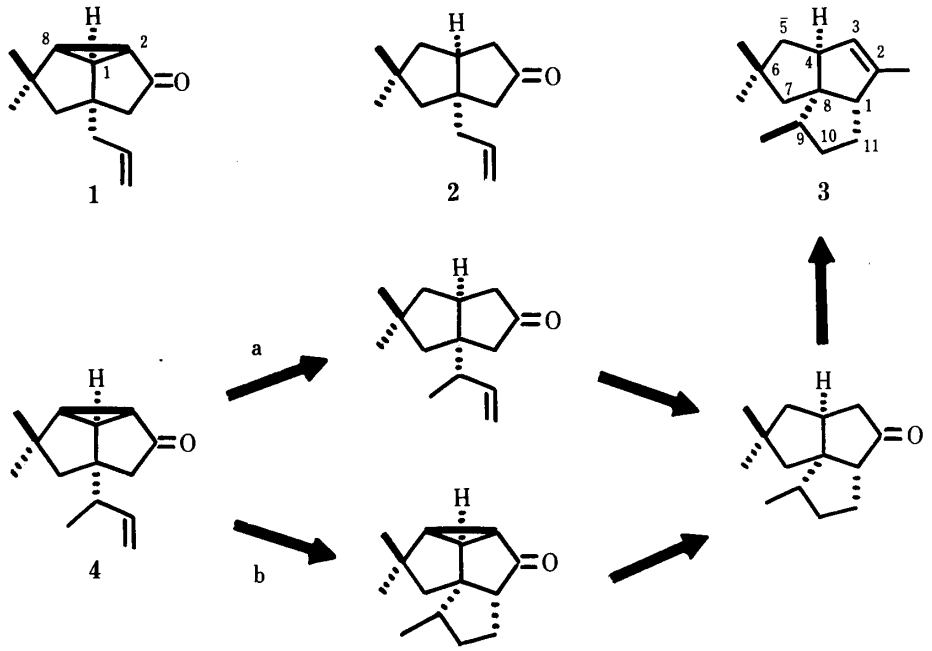

Chart 1

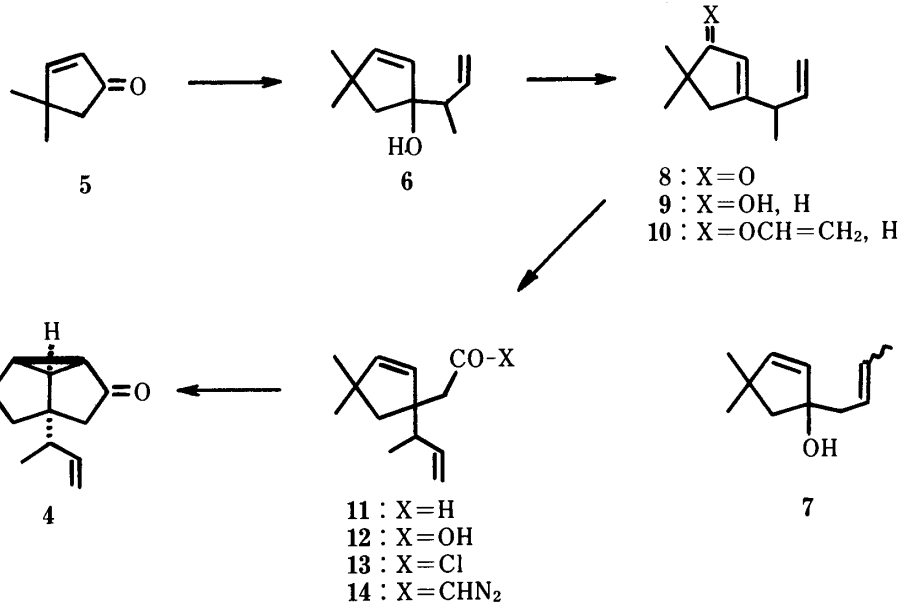

Chart 2

Although the product showed one spot on thin layer chromatography (TLC) and its proton magnetic resonance (^{1}H-NMR) spectrum gave no information about the stereochemistry at the C-1 position, it is likely that the product is a C-1 epimeric mixture.[13] Several attempts were made to separate the isomers, but all were unsuccessful. Therefore, a diastereomeric mixture of **9** was used without separation in the next steps. Heating of **9** in ethyl vinyl ether containing mercuric acetate at 200 °C afforded the aldehyde (**11**) *via* the Claisen rearrangement of the intermediate (**10**). Oxidation of **11** gave the carboxylic acid (**12**). The same compound (**12**) was also obtainable by means of an orthoester Claisen rearrangement. Namely, the reaction of **9** with a large excess of triethyl orthoacetate in the presence of hydroquinone at 180 °C, followed by alkaline hydrolysis, afforded **12** in 57% yield.

The intramolecular cyclopropanation was accomplished as follows. The acid chloride

(**13**), prepared from **12** by the reaction with oxalyl chloride, was treated with diazomethane in ether to afford the diazoketone (**14**), which was heated with anhydrous copper bronze in cyclohexane solution to give the tricyclooctanone (**4**) in 82% yield from **12**. Its structural assignment was confirmed by spectral considerations (see Experimental).

Total Synthesis of (±)-Pentalenene (3) and (±)-*epi*-Pentalenene (21)

According to our previous report,[1] compound **4** was converted to the bicyclo[3.3.0]-

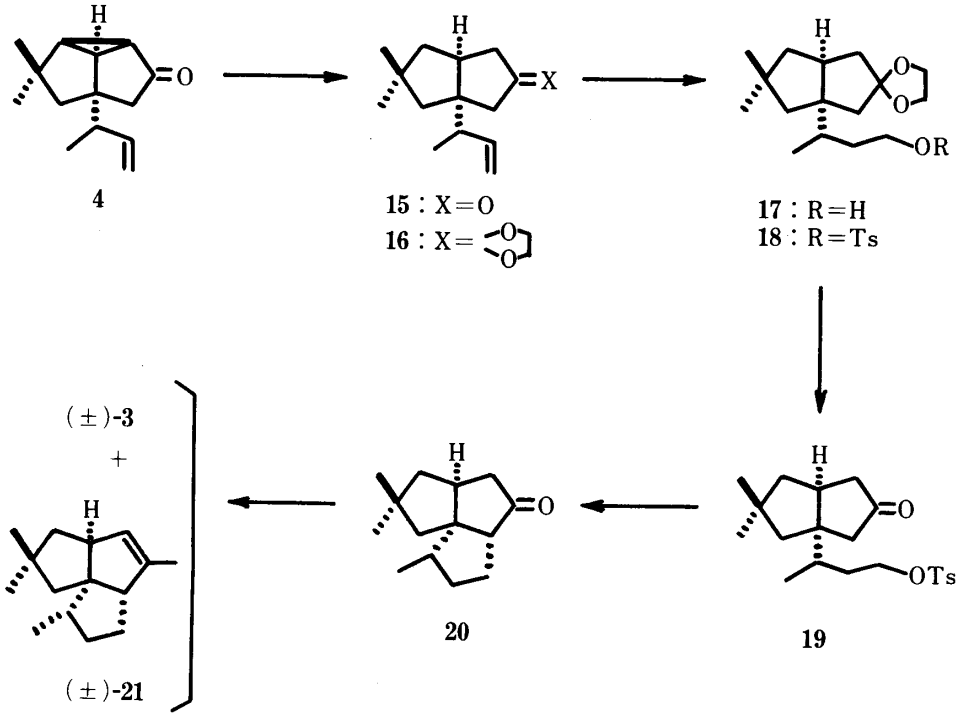

Chart 3

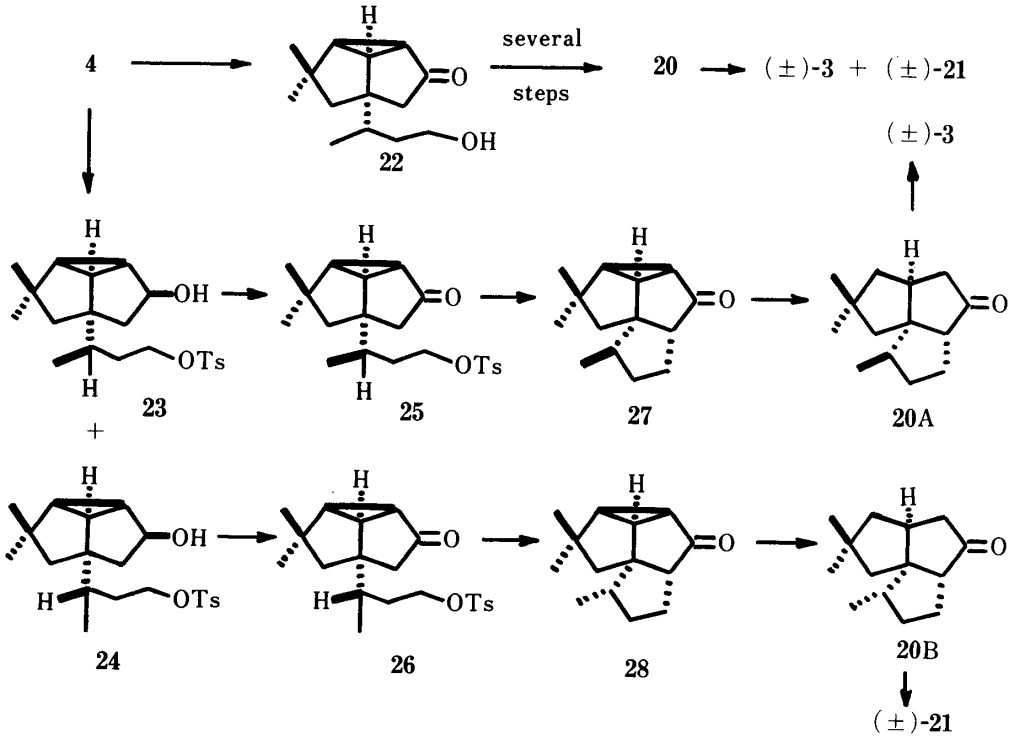

Chart 4

octanone (**15**) in 80% yield by an exclusive C_2–C_8 bond cleavage with lithium in ammonia. Acetalization of **15** to give **16**, followed by hydroboration-oxidation, provided the primary alcohol (**17**), which was converted into the tosylate (**18**). After hydrolysis of the acetal moiety, the formed keto-tosylate (**19**) was subjected to intramolecular alkylation to give the triquinane (**20**). Finally, the treatment of **20** with methyllithium in ether followed by *p*-toluenesulfonic acid furnished (±)-pentalenene (**3**) and (±)-*epi*-pentalenene (**21**) in a 1.8 : 1 ratio.

In all steps of the above route, the epimeric mixtures at the center bearing the methyl group were used because of their inseparability. Although a chemoselective hydroboration of **4** followed by oxidation gave the ketol (**22**) in 45% yield as an inseparable diastereoisomeric mixture, the same reaction using a large excess of diborane and subsequent tosylation resulted in the formation of two separable isomers (**23** and **24**) in 24 and 23% yields, respectively. The base-catalyzed cyclization of the ketones (**25** and **26**), which were obtained from **23** and **24** quantitatively by pyridinium chlorochromate (PCC) oxidation, gave the corresponding tetracyclic compounds (**27** and **28**). The external bond of the cyclopropane ring in each of **27** and **28** was also easily cleaved under the Birch reduction conditions to result in the exclusive formation of **20A** and **20B**, respectively. In the same manner as mentioned above, the former (**20A**) was transformed into (±)-pentalenene (**3**), while the latter (**20B**) was converted into (±)-*epi*-pentalenene (**21**). The ketol (**22**) was also convertible to a mixture of (±)-**3** and (±)-**21**. The synthetic (±)-pentalenene was identical with an authentic sample on the basis of spectral comparison.[14]

Experimental

The instruments used to obtain physical data, and the notations, were the same as described in the previous paper.[1]

5,5-Dimethyl-3-(1-methyl-2-propenyl)-2-cyclopentenone (8)——A solution of **5** (5.0 g, 0.045 mol) in dry ether (30 ml) was added dropwise to a stirred solution of crotylmagnesium chloride [prepared from Mg (3.0 g) and crotyl chloride (9.0 g)] in dry ether (10 ml) over a period of 30 min under ice cooling. Stirring was further continued at room temperature for 3 h and then the reaction mixture was poured into ice water. After acidification with 2 N HCl, the ethereal layer was separated and the aqueous layer was extracted with ether. The combined ethereal extract was washed with saturated $NaHCO_3$ and brine. This ethereal solution containing the alcohol (**6**) was used for the next step without purification. A solution of CrO_3 (6.4 g, 64 mmol) in 5% H_2SO_4 (65 ml) was added dropwise to the above stirred solution under ice cooling over a period of 1 h. Stirring without cooling was continued for another 1 h and the organic layer was separated. The aqueous layer was extracted with ether. The combined extract was washed with saturated $NaHCO_3$ and brine, dried, and concentrated to leave an oil, which was distilled under reduced pressure to give **8** (6.3 g, 84%) as a colorless oil, bp 90—100 °C (7 mmHg). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 1710, 1610, 990, 920. ^{1}H-NMR (CCl_4) δ: 1.02 (6H, s, 5-CH_3), 1.30 (3H, d, J=7 Hz, 3-CHC$\underline{H}_3$), 2.40 (2H, m, 4-H), 3.14 (1H, m, 3-CH), 4.8—5.3 (2H, m, CH=C$\underline{H}_2$), 5.4—6.2 (2H, m, 2-H and C$\underline{H}$=CH_2). MS m/z (%): 164 (M^+, 28), 149 (100). UV λ_{max}^{EtOH} nm (log ε): 229 (4.16).

2,4-Dinitrophenylhydrazone: Red needles, mp 175—178 °C (from EtOH–AcOEt). *Anal.* Calcd for $C_{17}H_{20}O_4N_2$: C, 59.29; H, 5.85; N, 16.27. Found: C, 58.99; H, 5.87; N, 16.21.

5,5-Dimethyl-3-(1-methyl-2-propenyl)-2-cyclopentenol (9)——$LiAlH_4$ (1.56 g, 41 mmol) was added portionwise to a stirred solution of **8** (13.5 g, 82 mmol) in dry ether (150 ml) under ice cooling over a period of 30 min. Stirring under cooling was continued for 3 h and then saturated potassium sodium tartrate aqueous solution was added to decompose the excess reagent and the complex salt. The mixture was filtered and the mass was washed with ether. The filtrate was dried and evaporated to give **9** (13.5 g, 99%) as a colorless oil, which showed one spot on TLC. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600, 3350, 3080, 1630. ^{1}H-NMR (CCl_4) δ: 1.00 (3H, s, 5-CH_3), 1.04 (3H, s, 5-CH_3), 1.15 (3H, d, J=7 Hz, 3-CHC$\underline{H}_3$), 1.9—2.2 (2H, m, 4-H), 2.85 (1H, m, 3-CH), 4.08 (1H, br, 1-H), 4.8—5.1 (2H, m, CH=C$\underline{H}_2$), 5.25—5.4 (1H, m, 2-H), 5.5—6.0 (1H, m, C$\underline{H}$=CH_2). MS m/z (%): 166 (M^+, 1.9), 111 (100). High MS Calcd for $C_{11}H_{18}O$: 166.1355. Found: 166.1349.

4,4-Dimethyl-1-(1-methyl-2-propenyl)-2-cyclopentene-1-acetic Acid (12)——a) *via* the Claisen Rearrangement: A mixture of **9** (0.50 g, 3.0 mmol), Hg $(OAc)_2$ (0.40 g, 1.26 mmol), and ethyl vinyl ether (5 ml) was heated in a sealed tube at 200 °C for 36 h. The reaction mixture was diluted with ether and the resulting solution was washed with brine. The dried organic layer was concentrated to give the crude aldehyde (**11**), which was used in the next step without further

purification. A standard Jones reagent (8 N) was added dropwise under ice cooling to a solution of the crude **11** in purified acetone (5 ml) until the color of the reagent no longer disappeared within a few minutes. After decomposition of the excess reagent with methanol, acetone was evaporated off under reduced pressure. Water was added to the residue and the resulting mixture was extracted with ether. The extract was washed with brine, dried, and concentrated. The oily residue was chromatographed on silica gel with $CHCl_3$ to give **12** (385 mg, 61%) as a colorless oil. *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.58; H, 9.85. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500—2400, 1710, 1640, 990, 920. ^{1}H-NMR ($CDCl_3$) δ: 0.93 and 0.97 (total 3H, each d, $J \simeq 7$ Hz, 1-CHC$\underline{H}_3$), 1.08 (6H, s, 4-CH_3), 1.71 (2H, s, 5-H), 2.42 (2H, s, 1-CH_2), 5.42 (2H, s, 2- and 3-H), 4.7—5.2 (2H, m, CH=C$\underline{H}_2$), 5.2—6.0 (1H, m, C$\underline{H}$=CH_2), 10.20 (1H, br s, COOH). CI-MS *m/z* (%): 209 ($M^+ + 1$, 15), 58 (100).

b) *via* the Orthoester Claisen Rearrangement: A mixture of **8** (13.5 g, 81 mmol), hydroquinone (a catalytic amount), and triethyl orthoacetate (40 ml) was heated at 180 °C for 3 d. During this time, the ethanol formed was removed by distillation. After evaporation of the excess orthoester, methanol (190 ml) and 10% NaOH aqueous solution (190 ml) were added to the residue and the resulting mixture was stirred at 60 °C for 8 h. Almost of the solvent was evaporated off and the aqueous residue was washed with $CHCl_3$ to remove neutral substances. The aqueous layer was acidified with concentrated HCl and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with brine, dried, and concentrated to leave an oil, which was purified by column chromatography on silica gel to give **12** (9.6 g 57%).

***rel*-(1*R*,2*S*,5*S*,8*S*)-7,7-Dimethyl-5-(1-methyl-2-propenyl)tricyclo[3.3.0.0^{2,8}]octan-3-one (4)**——Oxalyl chloride (1.46 g, 11.5 mmol) was added dropwise to a stirred solution of **12** (450 mg, 2.2 mmol) in dry benzene (5 ml) under ice cooling. After the addition, stirring was continued under cooling for 1 h. Evaporation of the solvent and reagent gave the crude acyl chloride (**13**), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1810, which was immediately used in the next step. A solution of the acyl chloride in dry benzene (5 ml) was added to a stirred solution of a large excess of diazomethane in ether and the resulting mixture was stirred under ice cooling for 30 min. Evaporation of the solvent gave the crude diazoketone (**14**). ^{1}H-NMR ($CDCl_3$) δ: 0.92 and 0.98 (total 3 H, each d, J=7 Hz, 1-CHC$\underline{H}_3$), 1.07 (6H, s, 4-CH_3), 1.69 (2H, s, 5-H), 2.0—2.4 (1H, m, 1-C$\underline{H}$$CH_3$), 2.40 (2H, s, 1-$CH_2$), 4.7—5.25 (3H, m, CH=C$\underline{H}_2$ and COC$\underline{H}$$N_2$), 5.40 (2H, s, 2- and 3-H), 5.3—6.0 (1H, m, C$\underline{H}$=CH_2). A mixture of the diazoketone, Cu bronze (2.5 g, 39.4 mmol), and cyclohexane (30 ml) was heated at 80 °C with vigorous stirring for 3 h. The inorganic substances were removed by filtration and the filtrate was concentrated to leave an oil, which was chromatographed on silica gel with $CHCl_3$ to give **4** (345 mg, 82%) as a colorless oil. *Anal.* Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.96, H, 10.09. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1640, 995, 920. ^{1}H-NMR (CCl_4) δ: 1.00 and 1.03 (total 3H, each d, J= 7 Hz, 5-CHC$\underline{H}_3$), 1.10, 1.20, and 1.21 (total 6H, each s, 7-CH_3), 4.8—5.2 (2H, m, CH=C$\underline{H}_2$), 5.2—6.0 (1H, m, C$\underline{H}$=CH_2). MS *m/z* (%): 204 (M^+, 3.7), 93 (100).

7,7-Dimethyl-1-(1-methyl-2-propenyl)bicyclo[3.3.0]octan-3-one (15)——A solution of **4** (520 mg, 2.6 mmol) in dry ether (10 ml) was added to a stirred mixture of Li (137 mg, 19.6 mg-atom) and liquid ammonia (50 ml) at −78 °C. After the addition, the reaction mixture was further stirred at −78 °C for 30 min and at −33 °C for 30 min. Solid NH_4Cl was added to the mixture and ammonia was evaporated off. The residue was diluted with water and extracted with ether. The extract was washed with dilute HCl and brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with $CHCl_3$ to give the starting material (49 mg, 9%) and **15** [388 mg, 74% (80% based on the consumed starting material)], both as colorless oils. *Anal.* Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found : C, 81.47; H, 10.71. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 1740, 1640, 1000, 920. ^{1}H-NMR (CCl_4) δ: 0.95 and 1.00 (total 3H, each d, J=7 Hz, 1-CHC$\underline{H}_3$), 1.02 (3H, s, 7-CH_3), 1.07 (3H, s, 7-CH_3), 4.8—5.2 (2H, m, CH=C$\underline{H}_2$), 5.2—5.9 (1H, m, C$\underline{H}$=CH_2). MS *m/z* (%): 206 (M^+, 10), 109 (100).

7,7-Dimethyl-1-(1-methyl-2-propenyl)bicyclo[3.3.0]octan-3-one Ethylene Acetal (16)——A mixture of **15** (130 mg, 0.63 mmol), *p*-TsOH (trace), ethylene glycol (156 mg, 2.52 mmol), and benzene (15 ml) was heated under reflux for 1.5 h with removal of the formed water by using a Dean-Stark apparatus. The reaction mixture was washed with saturated $NaHCO_3$ and brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with benzene to give **16** (145 mg, 92%) as a colorless oil. *Anal.* Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.93; H, 10.54. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 3040, 1640, 990, 920. ^{1}H-NMR (CCl_4) δ: 0.91 and 0.98 (total 3H, each d, J=7 Hz, 1-CHC$\underline{H}_3$), 0.96 (3H, s, 7-CH_3), 1.03 (3H, s, 7-CH_3), 3.6—3.9 (4H, m, OCH_2CH_2O), 4.7—5.1 (2H, m, CH=C$\underline{H}_2$), 5.1—5.9 (1H, m, C$\underline{H}$=CH_2). MS *m/z* (%): 250 (M^+, 7.1), 195 (100).

1-(3-Hydroxy-1-methylpropyl)-7,7-dimethylbicyclo[3.3.0]octan-3-one Ethylene Acetal (17)——A solution of BH_3 in dry tetrahydrofuran (THF) (1 M, 2.5 ml) was added dropwise to a stirred solution of **16** (205 mg, 0.82 mmol) in dry THF (10 ml) under ice cooling. After the addition, the mixture was stirred under cooling for 3h. Water was added in order to decompose excess BH_3 and then a mixture of 6 N NaOH (6 ml) and 30% H_2O_2 (4 ml) was added. The whole mixture was stirred at room temperature for 12 h and extracted with $CHCl_3$. The extract was washed with brine, dried, and concentrated to leave an oil, which was chromatographed on alumina with benzene and then with $CHCl_3$ to give **17** (188 mg, 86%) as a colorless oil. *Anal.* Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.52. Found: C, 71.77; H, 10.50. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630, 3450. ^{1}H-NMR (CCl_4) δ: 0.85 (3H, d, J=7 Hz, 1-CHC$\underline{H}_3$), 0.95 (3H, s, 7-CH_3), 1.04 (3H, s, 7-CH_3), 3.3—3.7 (2H, m, C$\underline{H}_2$OH), 3.7—4.0 (4H, m, OCH_2CH_2O). MS *m/z* (%): 268 (M^+, 7.2), 153 (100).

7,7-Dimethyl-1-(1-methyl-3-tosyloxypropyl)bicyclo[3.3.0]octan-3-one Ethylene Acetal (18)——A mixture of **17** (34 mg, 0.13 mmol), *N*,*N*-dimethylaminopyridine (DMAP) (2 mg), triethylamine (0.04 ml), *p*-TsCl (31 mg,

0.16 mmol), and CH_2Cl_2 (2 ml) was stirred at room temperature for 16 h. After dilution with CH_2Cl_2, the reaction mixture was successively washed with water, saturated $NaHCO_3$, and brine. The organic layer was dried and concentrated to leave an oil, which was chromatographed on silica gel with $CHCl_3$ to give **18** (45 mg, 84%) as a colorless oil. *Anal.* Calcd for $C_{23}H_{34}O_5S$: C, 65.37; H, 8.11; S, 7.59. Found: C, 65.27; H, 8.16; S, 7.60. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1600, 1500, 1360, 1180. ^{1}H-NMR (CCl_4) δ: 0.74 and 0.81 (total 3H, each d, J=7 Hz, 1-CHC$\underline{H}_3$), 0.90 (3H, s, 7-CH_3), 1.01 (3H, s, 7-CH_3), 2.42 (3H, s, Ar-CH_3), 3.6—3.8 (4H, m, OCH_2CH_2O), 3.8—4.1 (2H, m, CH_2OTs), 7.20 (2H, d, J=9 Hz, aromatic H), 7.63 (2H, d, J=9 Hz, aromatic H). MS *m/z* (%): 422 (M^+, 2.6), 153 (100).

7,7-Dimethyl-1-(1-methyl-3-tosyloxypropyl)bicyclo[3.3.0]octan-3-one (19)——A mixture of **18** (113 mg, 0.27 mmol), 1 N HCl (5 ml), and acetone (5 ml) was stirred at room temperature for 1.5 h. Acetone was evaporated off and the residue was extracted with ether. The ethereal extract was washed with saturated $NaHCO_3$ and brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with $CHCl_3$ to give **19** (97 mg, 96%) as a colorless oil. *Anal.* Calcd for $C_{21}H_{30}O_4S$: C, 66.63; H, 7.99; S, 8.47. Found: C, 66.43; H, 8.06; S, 8.86. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1600, 1500, 1370, 1180. ^{1}H-NMR (CCl_4) δ: 0.77 and 0.85 (total 3H, each d, J=7 Hz, 1-CHC$\underline{H}_3$), 1.00 (3H, s, 7-CH_3), 1.04 (3H, s, 7-CH_3), 2.38 (3H, s, Ar-CH_3), 3.8—4.1 (2H, m, CH_2OTs), 7.15 (2H, d, J=9 Hz, aromatic H), 7.60 (2H, d, J=9 Hz, aromatic H). MS *m/z* (%): 378 (M^+, 5.2), 151 (100).

5-(3-Hydroxy-1-methylpropyl)-7,7-dimethyltricyclo[3.3.0.0^{2,8}]octan-3-one (22)——A solution of BH_3 in dry THF (1 M, 1 ml) was added to a stirred solution of **4** (195 mg, 0.98 mmol) in dry THF (10 ml) under ice cooling, and the stirring was continued for 3 h. Water was added in order to decompose excess BH_3 and then a mixture of 6 N NaOH (0.3 ml) and 30% H_2O_2 (0.3 ml) was added to the reaction mixture. The whole mixture was stirred at room temperature for 12 h and work-up as described for **17** gave an oily crude product, which was chromatographed on silica gel with $CHCl_3$ to give **22** (95 mg, 45%) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3420, 1710. ^{1}H-NMR ($CDCl_3$) δ: 0.95 (3H, d, J=7 Hz, 5-CHC$\underline{H}_3$), 1.09 (3H, s, 7-CH_3), 1.20 (3H, s, 7-CH_3), 3.3—4.0 (2H, m, C$\underline{H}_2$OH). MS *m/z* (%): 222 (M^+, 1.3), 107 (100). High MS Calcd for $C_{14}H_{22}O_2$: 222.1617. Found: 222.1594.

***rel*-(1*R*,1′*S*)- and *rel*-(1*R*,1′*R*)-7,7-Dimethyl-5-(1-methyl-3-tosyloxypropyl)tricyclo[3.3.0.0^{2,8}]octan-3-ol (23 and 24)**——A solution of BH_3 in dry THF (1 M, 15 ml) was added to a stirred solution of **4** (0.30 g, 1.5 mmol) in dry THF (5 ml) and the stirring was continued for 3 h. After addition of water to the mixture, a mixture of 6 N NaOH (2 ml) and 30% H_2O_2 (2 ml) was added, and the whole was stirred at room temperature for 12 h. Work-up as usual afforded an oily residue, which was chromatographed on silica gel with $CHCl_3$–methanol (100 : 1) to give a diol-A (111 mg) and a diol-B (123 mg).

A mixture of the diol-A (111 mg), triethylamine (0.2 ml), *p*-TsCl (104 mg, 0.55 mmol), and dry CH_2Cl_2 (6 ml) was stirred at room temperature for 12 h and then diluted with CH_2Cl_2 (20 ml). The resulting solution was washed with brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with $CHCl_3$ to give **24** (125 mg, 23%) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 1600, 1370, 1180. ^{1}H-NMR ($CDCl_3$) δ: 0.80 (3H, d, J=7 Hz, 5-CHC$\underline{H}_3$), 1.13 (3H, s, 7-CH_3), 1.35 (3H, s, 7-CH_3), 2.42 (3H, s, Ar-CH_3), 4.0—4.3 (2H, m, CH_2OTs), 4.7—5.0 (1H, m, 3-H), 7.30 (2H, d, J=8 Hz, aromatic H), 7.74 (2H, d, J=8 Hz, aromatic H). MS *m/z* (%): 378 (M^+, 0.2), 133 (100). High MS Calcd for $C_{21}H_{30}O_4S$: 378.1862. Found: 378.1839.

A mixture of the diol-B (123 mg), triethylamine (0.2 ml), *p*-TsCl (104 mg, 0.55 mmol), and dry CH_2Cl_2 (6 ml) was stirred at room temperature, and work-up as above gave **23** (131 mg, 24%) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 1600, 1370, 1180. ^{1}H-NMR ($CDCl_3$) δ: 0.74 (3H, d, J=7 Hz, 5-CHC$\underline{H}_3$), 1.11 (3H, s, 7-CH_3), 1.34 (3H, s, 7-CH_3), 2.44 (3H, s, Ar-CH_3), 3.9—4.3 (2H, m, CH_2OTs), 4.7—5.0 (1H, m, 3-H), 7.33 (2H, d, J=8 Hz, aromatic H), 7.78 (2H, d, J=8 Hz, aromatic H). MS *m/z* (%): 378 (M^+, 0.2), 133 (100). High MS Calcd for $C_{21}H_{30}O_4S-H_2O$: 360.1759. Found: 360.1785.

***rel*-(1*R*,1′*S*)-7,7-Dimethyl-5-(1-methyl-3-tosyloxypropyl)tricyclo[3.3.0.0^{2,8}]octan-3-one (25)**——A mixture of **23** (151 mg, 0.40 mmol), pyridinium chlorochromate (PCC) (259 mg, 1.20 mmol), NaOAc (33 mg, 0.40 mmol), and dry CH_2Cl_2 (15 ml) was stirred at room temperature for 1 h. The reaction mixture was diluted with ether and passed through a pad of Florisil. The filtrate was concentrated to leave an oily residue, which was chromatographed on silica gel with $CHCl_3$ to give **25** (151 mg, 100%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1600, 1370, 1180. ^{1}H-NMR ($CDCl_3$) δ: 0.86 (3H, d, J=7 Hz, 5-CHC$\underline{H}_3$), 1.08 (3H, s, 7-CH_3), 1.20 (3H, s, 7-CH_3), 2.45 (3H, s, Ar-CH_3), 4.0—4.3 (2H, m, CH_2OTs), 7.33 (2H, d, J=8 Hz, aromatic H), 7.78 (2H, d, J=8 Hz, aromatic H). MS *m/z* (%): 376 (M^+, 15), 149 (100). High MS Calcd for $C_{21}H_{28}O_4S$: 376.1709. Found: 376.1730.

***rel*-(1*R*,1′*R*)-7,7-Dimethyl-5-(1-methyl-3-tosyloxypropyl)tricyclo[3.3.0.0^{2,8}]octan-3-one (26)**——A mixture of **24** (131 mg, 0.35 mmol), PCC (226 mg, 1.05 mmol), NaOAc (29 mg, 0.35 mmol), and dry CH_2Cl_2 (10 ml) was stirred at room temperature for 1 h, and work-up as described for **25** gave **26** (131 mg, 100%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1600, 1370, 1180. ^{1}H-NMR ($CDCl_3$) δ: 0.86 (3H, d, J=7 Hz, 5-CHC$\underline{H}_3$), 1.07 (3H, s, 7-CH_3), 1.18 (3H, s, 7-CH_3), 2.42 (3H, s, Ar-CH_3), 4.0—4.3 (2H, m, CH_2OTs), 7.33 (2H, d, J=8 Hz, aromatic H), 7.78 (2H, d, J=8 Hz, aromatic H). MS *m/z* (%): 376 (M^+, 9.1), 149 (100). High MS Calcd for $C_{21}H_{28}O_4S$: 376.1706. Found: 376.1706.

***rel*-(7*R*,8*R*)-7,10,10-Trimethyltetracyclo[6.3.0.0^{2,11}.0^{4,8}]undecan-3-one (27)**——Freshly sublimed potassium *tert*-butoxide (44 mg, 0.39 mmol) was added all at once to a stirred solution of **25** (99 mg, 0.26 mmol) in dry THF (10 ml) under ice cooling. The stirring was continued for 2 h and the reaction mixture was neutralized with AcOH. The solvent was evaporated off and the residue was taken up in $CHCl_3$. The $CHCl_3$ solution was washed with

saturated $NaHCO_3$ and brine, dried, and concentrated. The crude product was chromatographed on alumina with benzene to give **27** (51 mg, 95%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720. ^{1}H-NMR (CCl_4) δ: 0.82 (3H, d, J=7 Hz, 7-CH_3), 1.05 (3H, s, 10-CH_3), 1.22 (3H, s, 10-CH_3). MS m/z (%): 204 (M^+, 28), 133 (100). High MS Calcd for $C_{14}H_{20}O$: 204.1515. Found: 204.1528.

***rel*-(7*R*,8*S*)-7,10,10-Trimethyltetracyclo[6.3.0.0^{2,11}.0^{4,8}]undecan-3-one (28)**——Freshly sublimed potassium *tert*-butoxide (134 mg, 1.20 mmol) was added all at once to a stirred solution of **26** (0.30 g, 0.80 mmol) in dry THF (20 ml) under ice cooling. The stirring was continued for 2 h, and work-up as described for **27** gave **28** (153 mg, 94%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1715. ^{1}H-NMR (CCl_4) δ: 1.08 (3H, s, 10-CH_3), 1.11 (3H, d, J=7 Hz, 7-CH_3), 1.21 (3H, s, 10-CH_3). MS m/z (%): 204 (M^+, 38), 133 (100). High MS Calcd for $C_{14}H_{20}O$: 204.1515. Found: 204.1514.

***rel*-(7*R*,8*R*)-and *rel*-(7*R*,8*S*)-7,10,10-Trimethyltricyclo[6.3.0.0^{4,8}]undecan-3-one (20A and 20B)**——a) From **27**: A solution of **27** (23 mg, 0.11 mmol) in dry ether (2 ml) was added to a stirred mixture of Li (7 mg, 1 mg-atom) in liquid NH_3 (10 ml) at −78 °C. After addition, the reaction mixture was further stirred at −78 °C for 30 min and then at −33 °C for 30 min. Work-up as described for **15** afforded an oily crude product, which was chromatographed on silica gel with benzene to give **20A** (18 mg, 78%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740. ^{1}H-NMR (CCl_4) δ: 0.95 (3H, d, J=7 Hz, 7-CH_3), 1.00 (3H, s, 10-CH_3), 1.09 (3H, s, 10-CH_3). MS m/z (%): 206 (M^+, 59), 164 (100). High MS Calcd for $C_{14}H_{22}O$: 206.1670. Found: 206.1670.

b) From **28**: A solution of **28** (23 mg, 0.11 mmol) in dry ether (2 ml) was added to a stirred mixture of Li (5.4 mg, 0.77 mg-atom) in liquid NH_3 (10 ml) at −78 °C, and treatment as described for **20A** gave **20B** (0.010 g, 43%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740. ^{1}H-NMR (CCl_4) δ: 0.95 (3H, d, J=7 Hz, 7-CH_3), 1.02 (6H, s, 10-CH_3). MS m/z (%): 206 (M^+, 33), 149 (100). High MS Calcd for $C_{14}H_{22}O$: 206.1675. Found: 206.1676.

c) From **19**: Freshly sublimed potassium *tert*-butoxide (35 mg; 0.31 mmol) was added all at once to a stirred solution of **19** (0.10 g, 0.26 mmol) in dry THF (12 ml) under ice cooling. The stirring was continued for 2 h and the reaction mixture was neutralized with AcOH. The solvent was evaporated off and the residue was taken up in $CHCl_3$. The $CHCl_3$ solution was washed with saturated $NaHCO_3$ and brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with benzene to give an inseparable mixture of **20A** and **20B** (55 mg, 100%) as a colorless oil, which was characterized by comparison of its IR and ^{1}H-NMR spectra with those of **20A** and **20B**.

d) From **22**: A mixture of **22** (145 mg, 0.65 mmol), DMAP (10 mg), triethylamine (0.2 ml), *p*-TsCl (160 mg, 0.84 mmol), and dry CH_2Cl_2 (10 ml) was stirred at room temperature for 12 h. Work-up as described for **18** gave the corresponding *O*-tosyl derivative (a mixture of **25** and **26**) (185 mg, 75%) as a colorless oil. Treatment of the product (170 mg, 0.45 mmol) with potassium *tert*-butoxide (0.060 g, 0.54 mmol) as described for **27** afforded a mixture of **27** and **28** (77 mg, 83%) as a colorless oil. The tetracyclic product (0.040 g, 0.19 mmol) was reacted with Li (0.010 g, 1.43 mg-atom) in liquid NH_3 (20 ml) as described for **20A** to afford a mixture of **20A** and **20B** (0.030 g, 75%), which was found to be identical with the product obtained in c) by means of IR and ^{1}H-NMR comparisons.

(±)-Pentalenene (3) and (±)-*epi*-Pentalenene (21)——a) From the mixture of **20A** and **20B**: A solution of MeLi in dry ether (1 M, 3.8 ml) was added to a stirred solution of the mixture of **20A** and **20B** (64 mg, 0.31 mmol) in dry ether (6 ml) under ice cooling over a period of 10 min. Stirring under cooling was continued for 30 min. The reaction mixture was successively washed with brine, 5% HCl, brine, saturated $NaHCO_3$, and brine. The dried organic layer was concentrated to give an oily residue. A mixture of the residue, *p*-TsOH (trace), and dry benzene (20 ml) was heated under reflux using a Dean–Stark apparatus for 1 h. The reaction mixture was washed with saturated $NaHCO_3$ and brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with hexane to give a mixture of (±)-**3** and (±)-**21** (49 mg, 77%). The ratio of (±)-**3** and (±)-**21** was found to be *ca.* 1.8 : 1 by means of GLC analysis. [Column: OV-17 (3 mm × 1 m). Flow rate: 40 ml/min. Temp: 100 °C. Retention time: 14.1 min for (±)-**3** and 11.3 min for (±)-**21**.] The isomers were partially separable from each other by column chromatography on 10% $AgNO_3$–silica gel eluted with hexane.

(±)-Pentalenene (**3**). A colorless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3030, 2955, 2935, 2870, 1650, 1465, 1380, 1370, 1220, 1120. ^{1}H-NMR (CCl_4) δ: 0.89 (3H, d, J=7 Hz, 9-CH_3), 0.98 (6H, s, 6-CH_3), 1.60 (3H, br s, 2-CH_3), 2.3—2.8 (2H, m, 1-H and 4-H), 5.14 (1H, m, 3-H). ^{13}C-NMR ($CDCl_3$) δ: 15.52 (2-$\underline{C}H_3$), 17.03 (9-$\underline{C}H_3$), 27.71 (C-11), 29.22 (6-$\underline{C}H_3$), 30.05 (6-$\underline{C}H_3$), 33.66 (C-7), 40.63 (C-6), 44.73 (C-9), 46.97 (C-10), 49.07 (C-5), 59.50 (C-1), 62.23 (C-4), 64.91 (C-8), 129.61 (3-C), 140.68 (2-C). MS m/z (%): 204 (M^+, 37), 69 (100). High MS Calcd for $C_{15}H_{24}$: 204.1877. Found: 204.1898.

(±)-*epi*-Pentalenene (**21**). A colorless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3030, 2955, 2935, 2870, 1650, 1465, 1380, 1370, 1220, 1120. ^{1}H-NMR (CCl_4) δ: 0.93 (3H, d, J=7 Hz, 9-CH_3), 0.97 (6H, s, 6-CH_3), 1.61 (3H, br s, 2-CH_3), 2.5—2.7 (1H, m, 1-H), 2.7—3.0 (1H, m, 4-H), 5.16 (1H, m, 3-H). ^{13}C-NMR ($CDCl_3$) δ: 13.41 (9-$\underline{C}H_3$), 15.26 (2-$\underline{C}H_3$), 28.52 (C-11), 29.16 (6-$\underline{C}H_3$), 31.50 (6-$\underline{C}H_3$), 32.96 (C-7), 39.69 (C-6), 45.00 (C-9), 46.17 (C-10), 50.51 (C-5), 54.75 (C-1), 63.38 (C-4), 63.92 (C-8), 131.30 (C-3), 140.58 (C-2). MS m/z (%): 204 (M^+, 71), 147 (100). High MS Calcd for $C_{15}H_{24}$: 204.1877. Found: 204.1871.

b) From **20A**: On treatment according to the procedure described in a), **20A** (18 mg, 0.09 mmol) afforded (±)-pentalenene (**3**) (11 mg, 78%), which was found to be identical with the sample obtained in a) by means of TLC, GLC, IR, ^{1}H-NMR, and MS comparisons.

c) From **20B**: On treatment according to the procedure described in a), **20B** (0.010 g, 0.05 mmol) afforded (±)-*epi*-pentalenene (**21**) (4.8 mg, 48%), which was found to be identical with the sample obtained in a) by means of TLC,

GLC, IR, ^{1}H-NMR, and MS comparisons.

Acknowledgement We are grateful to Prof. H. Seto, The University of Tokyo, for providing spectral copies of natural pentalenene.

References and Notes

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13) The ^{1}H-NMR spectrum of **12**, obtained from **9**, indicates that **12** (or **9**) is a diastereomeric mixture (see Experimental).
14) The ^{1}H- and ^{13}C-NMR spectra of the synthetic (±)-**21** were in good accord with those of authentic (±)-*epi*-pentalenene reported in reference 9*b*.