Total Synthesis of (±)-Pentalenene, (±)-Pentalenic Acid, and (±)-Deoxypentalenic Acid through an Intramolecular Double Michael Reaction

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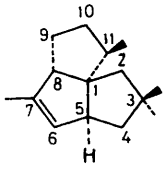
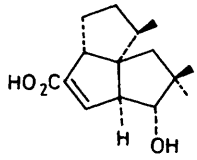
The angular triquinane sesquiterpenes, (±)-pentalenene (**1**), (±)-pentalenic acid (**2**), and (±)-deoxypentalenic acid (**4**), were synthesized *via* the intramolecular double Michael reaction as the key step. Heating the bis-enone (**10**), prepared from 4,4-dimethylcyclopent-2-enone (**11**) in six steps, with chlorotrimethylsilane, triethylamine, and zinc chloride gave the tricyclo[7.3.0.0^{1,5}]dodecanedione (**9**), which was converted into the above triquinanes after ring contraction.

Pentalenene (**1**),[1,2] pentalenic acid (**2**),[2e,3,4] and deoxypentalenylglucurone (**3**)[5] were isolated together with pentalenolactone (**5**)[6,7] from fermentation broths of several species of *Streptomyces*. The angular triquinanes (**1**), (**2**), and (**4**)[2e] are regarded as the biosynthetic precursors[8] of pentalenolactone, which has antibiotic activity against Gram-positive and -negative bacteria as well as fungi. These architecturally intriguing compounds have been attractive targets for synthetic



(**1**)



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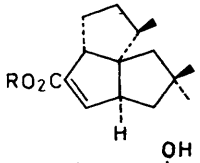
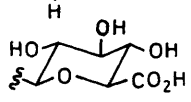
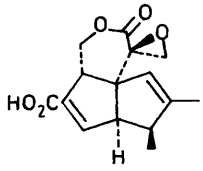
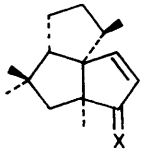


(**3**) R = 

(**4**) R = H



(**5**)

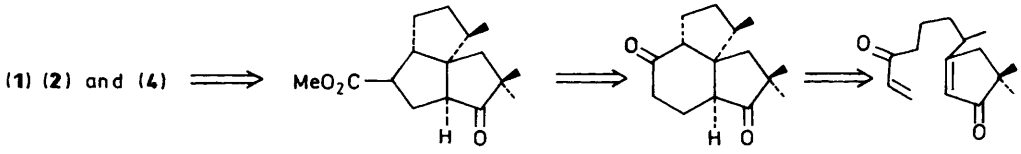


(**6**) X = O
(**7**) X = H_2

work. Recently we synthesized the racemate of 3-oxosilphinene (**6**),[9,10] the congener of silphinene (**7**),[11,12] *via* a tricyclo[7.3.0.0^{1,5}]dodecane derivative constructed by an intramolecular Diels–Alder reaction. As a further extension of this work, we deemed that the above three triquinanes (**1**), (**2**), and (**4**) could be synthesized from a common intermediate (**8**), which could be derived from a tricyclo[7.3.0.0^{1,5}]dodecanedione (**9**). Furthermore recent success in the assembly of polycyclic molecules by intramolecular double Michael reaction[13,14] inspired us to generate (**9**) from the bis-enone (**10**) (Scheme 1). We here report total syntheses of the triquinanes (**1**), (**2**), and (**4**) by an exploitation of this methodology.[15]

Results

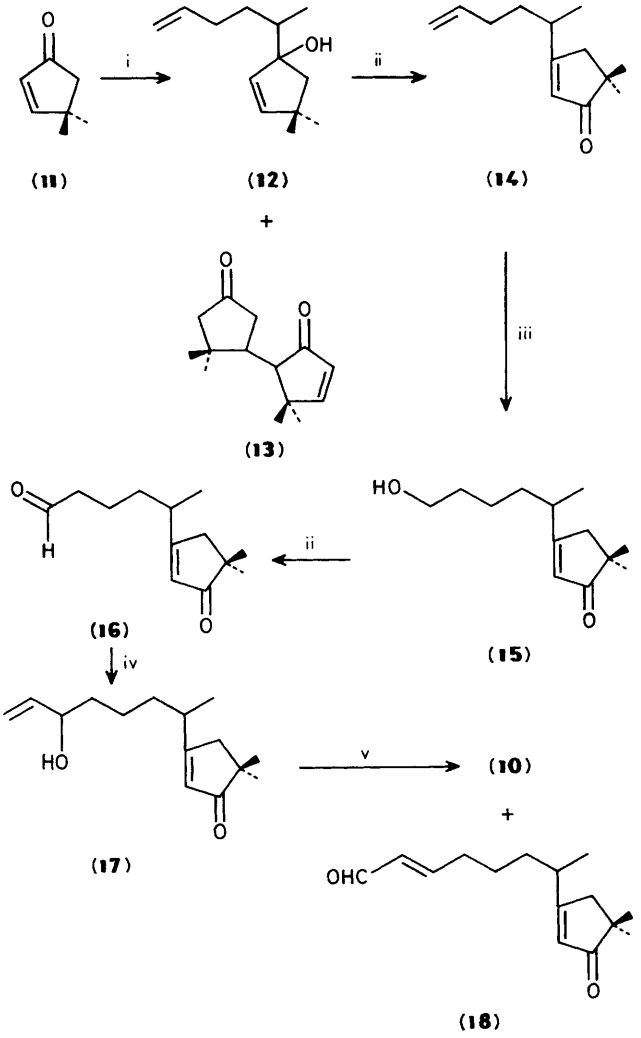
Synthesis of Bis-enone.—The cyclopent-2-enone (**11**), available in a large quantity by a known method,[16] was chosen as a starting material and its coupling reaction with 5-bromohex-1-ene[17] was studied first. Although the desired product (**12**) was not obtained by the reaction using the corresponding Grignard reagent, the 1,2-addition smoothly took place when the mixture of both compounds was treated with lithium in ether under ultrasonic irradiation.[18] Thus the tertiary alcohol (**12**) was obtained in 70% yield as a mixture of two diastereoisomers in the ratio ~1:1 along with the enone (**13**) in 5% yield. The allylic alcohol (**12**) was then oxidized by pyridinium chlorochromate (PCC)[19] in the presence of Florisil to the transposed α,β-unsaturated ketone (**14**) in 95% yield. Anti-Markovnikov hydration of the olefin (**14**) was first tested using borane–dimethyl sulphide complex but reaction at the α,β-unsaturated ketone function was also observed to some extent. Chemo- and regio-selective hydroboration–oxidation was achieved using dicyclohexylborane[20] to afford the primary alcohol (**15**) in 94% yield. Oxidation of compound (**15**) with PCC in the presence of Florisil gave in 91% yield the aldehyde (**16**), which was treated with vinylmagnesium bromide in a mixture of dichloromethane and tetrahydrofuran (THF) and then subjected to acidic treatment to provide the allylic alcohol (**17**) in 73% yield. The product (**17**) was obtained as a mixture of two diastereoisomers but the ratio of the two isomers was obscure. On oxidation of enol (**17**) with PCC the required bis-enone (**10**) was produced in 47% yield together with the rearranged product (**18**) in 9% yield (Scheme 2). On the other hand, oxidation of enol (**17**) utilizing pyridinium dichromate (PDC) in dichloromethane



(**8**) (**9**) (**10**)

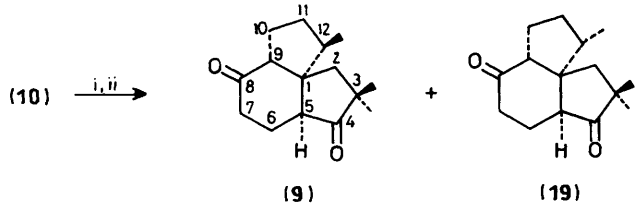
Scheme 1.

quantitatively formed the bis-enone (**10**). Thus the substrate of the key step, the intramolecular double Michael reaction, was synthesized in 41.5% overall yield from enone (**11**) in six steps.



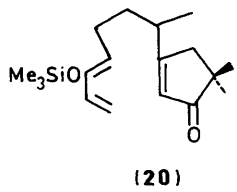
Scheme 2. *Reagents and conditions:* i, CH_2=CH[CH_2]$_2$CHBrMe, Li, ultrasound; ii, PCC, Florisil; iii, $(C_6H_{11})_2BH$; H_2O_2, NaOH; iv, CH_2=CHMgBr; aq. NH_4Cl; v, PDC

Intramolecular Double Michael Reaction.—Previously we were able to control the stereoselection in the construction of spiro-fused bicyclo[2.2.2]octanes by an intramolecular double Michael reaction employing lithium amides.[13] Therefore the bis-enone (**10**) was first treated with several lithium amides, such as lithium di-isopropylamide (LDA). However, the vinyl ketone function was too reactive and intractable polar products incorporating the amine moiety were formed, even though bulky bases such as lithium 2,2,6,6-tetramethylpiperidide were used. Reaction of compound (**10**) with dimethyl-t-butylsilyl trifluoromethanesulphonate in the presence of triethylamine [13d] also yielded no objective product. The annulation was eventually achieved by heating the bis-enone (**10**) together with chlorotrimethylsilane, triethylamine, and zinc chloride.[21,22] On this reaction two separable diastereoisomers, tricyclic compounds (**9**) and (**19**), were obtained (Scheme 3) but both yield and ratio of those depended on the reaction temperature and the solvent. For example, heating the mixture of compound (**10**)



Scheme 3. *Reagents and conditions:* i, Me_3SiCl, Et_3N, $ZnCl_2$, heat; ii, H_3O^+

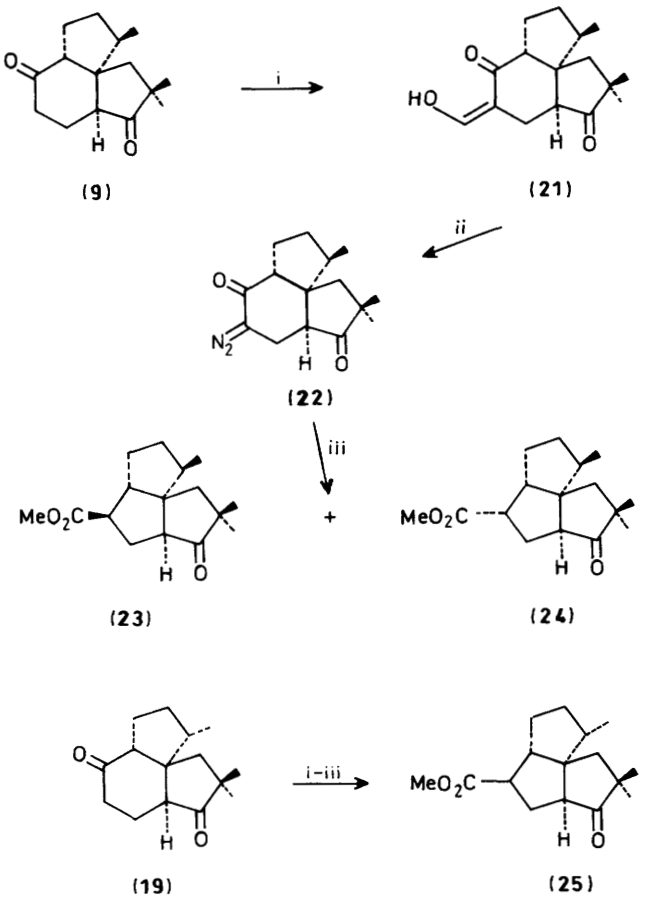
and the above three reagents in toluene in a sealed tube for 24 h at 160 °C, followed by treatment with 10% perchloric acid in THF, afforded the diketones (**9**) and (**19**) in 65 and 35% yield, respectively, after chromatographic separation. On the other hand, the annulation, carried out in dichloromethane in a sealed tube at 160 °C for 24 h, produced the diketones (**9**) and (**19**) in 52 and 10% yield, respectively. The course of the above reactions was carefully examined using t.l.c. and it was observed that the bis-enone (**10**) was directly converted into the tricyclic compounds, which were then gradually transformed into a mixture of silyl enol ethers. Therefore we consider that the cyclization occurs not through the intramolecular Diels–Alder reaction of the siloxydiene (**20**), but through the tandem conjugate addition, the intramolecular double Michael reaction.



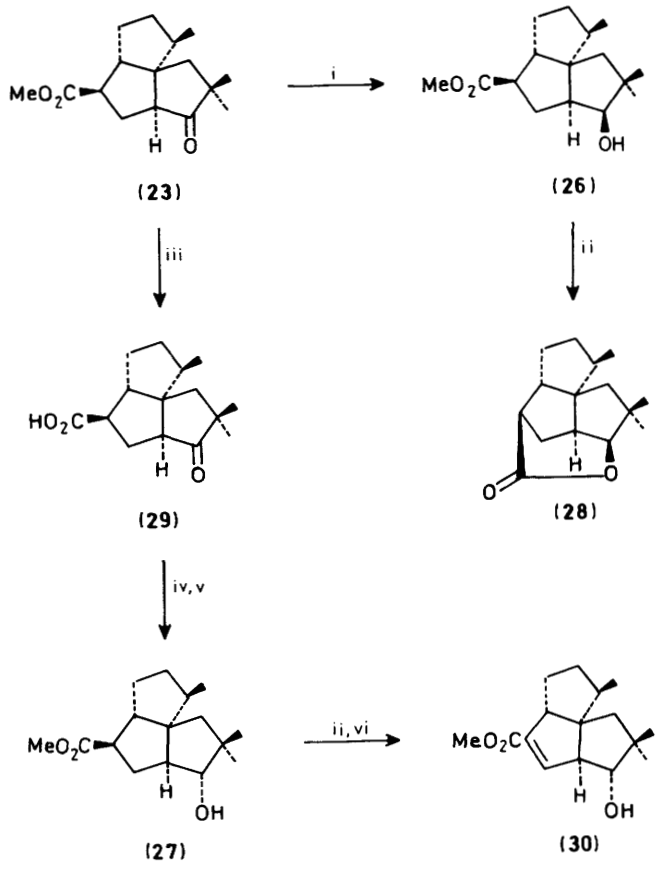
I.r. and ^{1}H n.m.r. (500 MHz) spectra of the above two products (**9**) and (**19**) firmly indicated their planar structures as 3,3,12-trimethyltricyclo[7.3.0.0^{1,5}]dodecane-4,8-dione. Their relative configurations were deduced by ^{1}H n.m.r. spectroscopy after ring contraction. The ring transformations of the diketones (**9**) and (**19**) were effectively carried out by Wolff rearrangement [23] without protection of the carbonyl group at C-4. For example reaction of compound (**9**) with ethyl formate in the presence of sodium methoxide gave in 90% yield the hydroxymethylene compound (**21**), which was subjected to diazo-exchange using toluene-*p*-sulphonyl azide and triethylamine. Irradiation of the resulting diazo ketone (**22**) in methanol with a 400-W high-pressure lamp through a Pyrex filter formed a mixture of the two keto esters (**23**) and (**24**) in 83% overall yield in the ratio of 3.6:1. Separation of the two diastereoisomers was performed by h.p.l.c. Similarly the other diketone (**19**) was converted in 70% overall yield into the keto ester (**25**), which was obtained as a single stereoisomer (Scheme 4). In the 500 MHz ^{1}H n.m.r. spectra, compound (**23**) showed no nuclear Overhauser effect (n.O.e.) between the hydrogen at C-5 (C-8)* and the methyl group at C-11 (C-2),* while about 10% n.O.e. between those was observed for the keto ester (**25**). This fact suggested that the four contiguous asymmetric centres around the spiro atom of the major product (**9**) of the key step were correctly arranged and this was confirmed by its conversion into the natural products.

Synthesis of (±)-*Pentalenic Acid.*—Reduction of the above keto ester (**23**) with sodium borohydride at 0 °C gave a

* Systematic name locants given in parentheses—see Experimental section.



Scheme 4. *Reagents and conditions:* i, HCO_2Et, NaOMe; ii, TsN_3, Et_3N; iii, *hν*



Scheme 5. *Reagents:* i, $NaBH_4$; ii, LDA; iii, KOH; iv, Li, NH_3, MeOH; v, CH_2N_2; vi, PhSeCl; then H_2O_2, AcOH

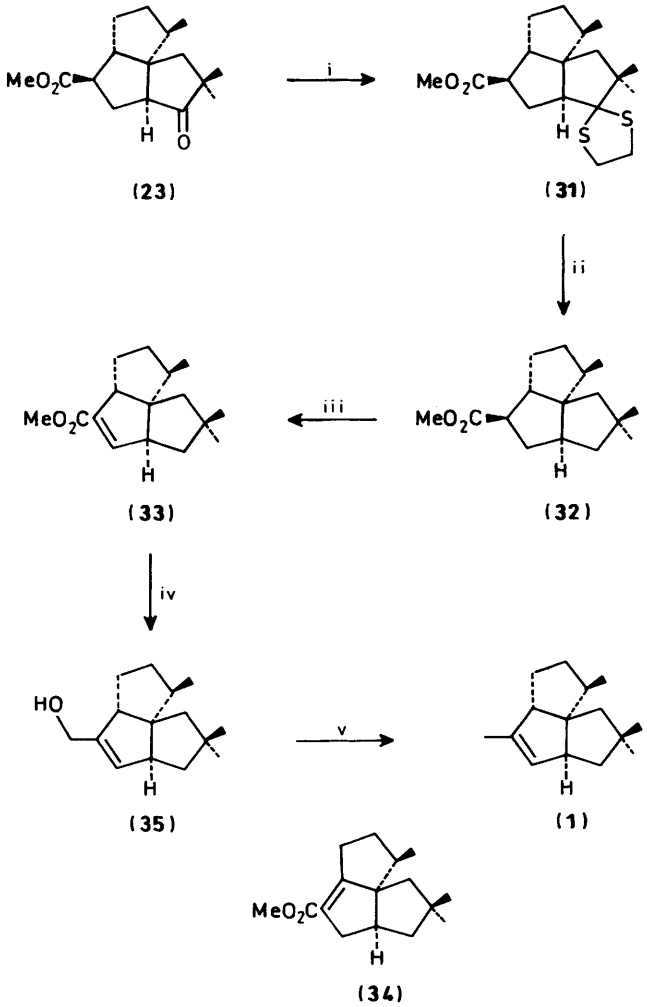
separable mixture of two alcohols (**26**) and (**27**) in 94% yield and in the ratio ~6:1. The preferred formation of epimer (**26**) possessing the β-oriented hydroxy group is presumably due to the less hindered α-side attack of the hydride. This was confirmed by the formation of the lactone (**28**) in 90% yield on treatment of compound (**26**) with LDA. It is expected from considerations of Dreiding models that lactone formation is possible only when both the ester group and the hydroxy group are orientated to the β-side. Selective construction of the desired alcohol (**27**) was accomplished by reduction using a dissolving metal. Thus the keto ester (**23**) was initially hydrolysed to the corresponding acid (**29**), which, after treatment with sodium hydride, was reduced with lithium in liquid ammonia in the presence of methanol.[2e] Esterification of the resulting crude product with excess of diazomethane afforded the α-oriented alcohol (**27**) in 85% overall yield. The double bond between C-6 and C-7 was introduced by benzeneselenenylation followed by oxidative elimination.[24] The spectra data of the α,β-unsaturated ester (**30**), obtained in 75% overall yield (Scheme 5), were identical with those of authentic methyl pentalenate.[3] Since the ester (**30**) has previously been hydrolysed to (±)-pentalenic acid (**2**),[4a] the total synthesis of the triquinane is achieved.

Synthesis of (±)-*Deoxypentalenic Acid and* (±)-*Pentalenene.* Lastly synthesis of (±)-pentalenene (**1**) was investigated from the keto ester (**23**), by means of the ester of deoxypentalenic acid (**4**). Reduction of the carbonyl group of compound (**23**) to methylene was performed by the standard method. Thus, treatment of ketone (**23**) with ethanedithiol in the presence of boron trifluoride–diethyl ether in dichloromethane followed by desulphurization of the dithioacetal (**31**) with Raney nickel in a mixture of methanol and dioxane at 80 °C furnished the ester (**32**) in 90% overall yield. Oxidation of (**32**) to the olefin (**33**) was conducted under the same conditions as the conversion of (**27**) into (**30**). However, the target olefin (**33**) was obtained in 46% yield along with the isomer (**34**) in 37% yield. ^1H N.m.r. ($CDCl_3$; 500 MHz) and i.r. ($CHCl_3$) spectral data of compound (**33**) were consistent with those reported[2e] for (±)-methyl deoxypentalenate, which has already been hydrolysed to (±)-deoxypentalenic acid (**4**).[2e] Reduction of ester (**33**) with diisobutylaluminium hydride (DIBAL) at 0 °C gave in 91% yield the allylic alcohol (**35**), which was treated with pyridine–sulphur trioxide complex and the product then reduced with lithium aluminium hydride[25] to provide (±)-pentalenene (**1**) in 47% overall yield without allylic rearrangement (Scheme 6). The spectral data of the product (**1**) were consistent with those of natural pentalenene.

In conclusion, the total syntheses of (±)-pentalenic acid, (±)-pentalenene, and (±)-deoxypentalenic acid have been accomplished through a common intermediate. The crucial role of the intramolecular double Michael reaction is certainly noteworthy.

Experimental

M.p.s were determined on a Yanako micromelting-point apparatus and are uncorrected. ^1H N.m.r. spectra were recorded on JEOL FX-90 (90 MHz) and JEOL GX-500 (500 MHz) spectrometers with tetramethylsilane as the internal standard. I.r. spectra were obtained on a Hitachi 260-10 spectrophotometer. Ordinary mass spectra were measured with a Hitachi M-



Scheme 6. *Reagents:* i, $HSCH_2CH_2SH$, BF_3·Et_2O; ii, Raney Ni; iii, LDA; then PhSeCl; then H_2O_2, AcOH; iv, DIBAL; v, SO_3–pyridine; then $LiAlH_4$

52G instrument while high-resolution mass spectroscopy was performed on a JEOL DX-300 spectrometer. All reactions were run under an atmosphere of dry nitrogen or argon. Solvents were freshly distilled prior to use: THF and ether were distilled from sodium–benzophenone; dichloromethane was distilled from phosphorus pentaoxide and kept over 4 Å molecular sieves. Unless otherwise noted, all reaction mixtures were dried, after work-up, over anhydrous Na_2SO_4. Silica gel column chromatography was carried out with Wako gel C-200. High-performance liquid chromatography (h.p.l.c.) was carried out with Gilson h.p.l.c. system Model 302/303 equipped with 4.6 × 250 mm column of Dynamax microsorb silica 5 μm and monitored using u.v. and refractive index detectors.

1-(*Hex-5-en-2-yl*)-4,4-*dimethylcyclopent-2-enol* (**12**).—To a mixture of lithium (500 mg, 72.3 mmol) in dry ether (30 ml) was added a mixture of the enone (**11**) (2.25 g, 20.4 mmol) and 5-bromohex-1-ene (3.60 g, 22.1 mmol) in dry ether (30 ml) under ultrasonic irradiation (30-W) during 30 min. After the addition was over, the irradiation was continued for 50 min. Then the mixture was quenched with saturated aqueous ammonium chloride in a cooling bath and diluted with ether. The organic layer was washed successively with 10% hydrochloric acid and saturated aqueous sodium chloride, dried, and concentrated. The residue was chromatographed on silica gel with hexane–ethyl acetate (95:5 v/v) as eluant to afford the *alcohol* (**12**) (2.76 g, 70%) as a pale yellow oil. Further elution with hexane–ethyl acetate (85:15 v/v) gave the *ketone* (**13**) (112 mg, 5%) as needles, m.p. 114—115 °C.

For the alcohol (**12**) (Found: C, 79.95; H, 11.9. $C_{13}H_{22}O$ requires C, 80.35; H, 11.4%); $\nu_{max.}(CHCl_3)$ 3 600 and 3 400 (OH) and 1 640 cm^{-1} (C=C); δ_H(90 MHz; $CDCl_3$) 6.00—5.74 (1 H, m, C*H*=CH_2), 5.65 and 5.45 (each 1 H, each d, each *J* 5.7 Hz, 2- and 3-H), 5.20—4.90 (2 H, m, CH=CH_2), 2.30—0.80 (6 H, m), 1.85 and 1.30 (each 1 H, each d, each *J* 14.2 Hz, 5-H_2), 1.17 and 1.07 (each 3 H, each s, 4-Me_2), and 0.97 and 0.86 (each 1.5 H, each d, each *J* 7.1 Hz, *Me*CH<); *m/z* 176 ($M^+ - H_2O$).

For the ketone (**13**); $\nu_{max.}(CHCl_3)$ 1 735 (C=O) and 1 705 cm^{-1} (C=O); δ_H(90 MHz; $CDCl_3$) 7.45 (1 H, d, *J* 6.3 Hz, C=CH), 6.00 (1 H, d, *J* 6.3 Hz, C=CH), 3.10—1.40 (6 H, m), and 1.05, 1.10, 1.16, and 1.26 (each 3 H, each s, 4 × Me); *m/z* 220 (M^+) (Found: M^+, 220.1455. $C_{14}H_{20}O_2$ requires *M*, 220.1464).

3-(*Hex-5-en-2-yl*)-5,5-*dimethylcyclopent-2-enone* (**14**).—A mixture of the alcohol (**12**) (1.90 g, 9.78 mmol), PCC (4.21 g, 19.60 mmol), and Florisil (4.21 g) in dry CH_2Cl_2 (35 ml) was stirred at room temperature for 1 h. The reaction mixture was then treated with ether and filtered through Celite. The filtrate was washed successively with 10% aqueous potassium hydroxide and saturated aqueous sodium chloride, and dried. Evaporation of the solvent gave a residue, which was chromatographed on silica gel with hexane–ethyl acetate (95:5 v/v) as eluant to yield the *enone* (**14**) (1.78 g, 95%) as an oil (Found: C, 81.35; H, 10.7. $C_{13}H_{20}O$ requires C, 81.2; H, 10.9%); $\nu_{max.}(CHCl_3)$ 1 695 (C=O) and 1 610 cm^{-1} (C=C); δ_H(90 MHz; $CDCl_3$) 5.90—5.50 (1 H, m, C*H*=CH_2), 5.85 (1 H, br s, 2-H), 5.10—4.90 (2 H, m, CH=CH_2), 2.60 (1 H, m, MeC*H*<), 2.45 (2 H, br s, 4-H_2), 2.05 (2 H, br q, *J* 7.0 Hz, CH_2CH=CH_2), 1.70—1.40 (2 H, m, CH_2), 1.15 (3 H, d, *J* 7.0 Hz, *Me*CH<), and 1.10 (6 H, s, 5-Me_2); *m/z* 192 (M^+).

3-(6-*Hydroxyhexan-2-yl*)-5,5-*dimethylcyclopent-2-enone* (**15**).—To a solution of the enone (**14**) (1.5 g, 7.80 mmol) in dry THF (70 ml) at 0 °C was added a suspension of dicyclohexylborane in THF [23.4 ml; prepared from cyclohexene (4.61 g, 56.2 mmol) and borane–dimethyl sulphide complex (10M solution; 2.81 ml) in dry THF (28.1 ml)]. The reaction mixture was stirred for 1 h at the same temperature, and then carefully treated in turn with methanol (40 ml), 3M aqueous sodium hydroxide (2.6 ml), and 30% aqueous hydrogen peroxide (3.98 ml). After the resulting mixture had been heated at 50 °C for 1 h, 10% aqueous hydrochloric acid was added to the cooled mixture. The mixture was evaporated to give a residue, which was taken up into ether. The solution was washed with saturated aqueous sodium chloride, dried, and evaporated to give a residue, which was chromatographed on silica gel with hexane–ethyl acetate (2:1 v/v) as eluant to afford the *alcohol* (**15**) (1.54 g, 94%) as an oil (Found: C, 73.85; H, 11.0. $C_{13}H_{22}O_2$ requires C, 74.25; H, 10.55%); $\nu_{max.}(CHCl_3)$ 3 650 and 3 450 (OH) and 1 680 cm^{-1} (C=O); δ_H(90 MHz; $CDCl_3$) 5.85 (1 H, br s, 2-H), 3.90—3.55 (2 H, m, CH_2OH), 2.55 (1 H, m, MeC*H*<), 2.40 (2 H, br s, 4-H_2), 1.85—1.20 (7 H, m, 3 × CH_2 and OH), 1.15 (3 H, d, *J* 7.1 Hz, *Me*CH<), and 1.10 (6 H, s, 5-Me_2); *m/z* 210 (M^+).

5-(4′,4′-*Dimethyl-3′-oxocyclopent-1′-enyl*)*hexanal* (**16**).—A mixture of PCC (1.02 g, 4.75 mmol), Florisil (1.02 g), and the alcohol (**15**) (500 mg, 2.38 mmol) in dry CH_2Cl_2 (8.5 ml) was stirred at room temperature for 1.5 h. The reaction mixture was diluted with ether and filtered through Celite. The filtrate was washed successively with 10% aqueous potassium hydroxide and saturated aqueous sodium chloride, dried, and evaporated.

The residue was chromatographed on silica gel with hexane–ethyl acetate (7:3 v/v) as eluant to yield the *aldehyde* (**16**) (452 mg, 91%) as a pale yellow oil; $\nu_{max.}$($CHCl_3$) 1 730 and 1 690 cm^{-1} (C=O); δ_H(90 MHz; $CDCl_3$) 9.75 (1 H, br s, CHO), 5.85 (1 H br s, 2′-H), 2.70—2.35 (5 H, m, 5′-H_2, CH_2, and CH), 1.80—1.40 (4 H, m, 2 × CH_2), 1.15 (3 H, d, *J* 7.1 Hz, *Me*CH<), and 1.10 (6 H, s, 4′-Me_2) (Found: M^+, 208.1487. $C_{13}H_{20}O_2$ requires *M*, 208.1464).

3-(6-*Hydroxyoct*-7-*en*-2-*yl*)-5,5-*dimethylcyclopent*-2-*enone* (**17**).—To a stirred solution of the aldehyde (**16**) (240 mg, 1.15 mmol) in dry CH_2Cl_2 (9 ml) at −78 °C was added vinylmagnesium bromide in dry THF (2.3 ml, 2.3 mmol) [*ca.* 1M solution, prepared from vinyl bromide (40.0 g, 0.374 mol) and magnesium (10.0 g, 0.411 mol) in dry THF (374 ml)]. After having been stirred for 15 min at the same temperature, the mixture was quenched with saturated aqueous ammonium chloride, and extracted with ether. The extracts were washed with saturated aqueous sodium chloride, dried, and evaporated to give a residue, which was chromatographed on silica gel. Elution with hexane–ethyl acetate (7:3 v/v) yielded the *alcohol* (**17**) (200 mg, 73%) as a mixture of diastereoisomers of a pale yellow oil; $\nu_{max.}$($CHCl_3$) 3 600 and 3 450 (OH) and 1 690 cm^{-1} (C=O); δ_H(90 MHz; $CDCl_3$) 6.05—5.65 (1 H, m, C*H*=CH_2), 5.85 (1 H, br s, 2-H), 5.30—5.00 (2 H, m, C=CH_2), 4.20—3.95 (1 H, m, >C*H*OH), 2.55 (1 H, m, MeC*H*), 2.45 (2 H, br s, 4-H_2), 2.70—2.30 (7 H, m, 3 × CH_2 and OH), 1.15 (3 H, d, *J* 7.1 Hz, *Me*CH<), and 1.10 (6 H, s, 5-Me_2) (Found: M^+, 236.1789. $C_{15}H_{24}O_3$ requires *M*, 236.1776).

7-(4′,4′-*Dimethyl*-3′-*oxocyclopent*-1′-*enyl*)*oct*-1-*en*-3-*one* (**10**).—*Method* (*A*). A mixture of PDC (923 mg, 2.45 mmol) and the alcohol (**17**) (276 mg, 1.17 mmol) in dry CH_2Cl_2 (4.0 ml) was stirred at room temperature for 7 h and the reaction mixture was diluted with ether and filtered through Celite. The filtrate was washed successively with 10% aqueous potassium hydroxide and saturated aqueous sodium chloride, dried, and evaporated. The residue was chromatographed on silica gel with hexane–ethyl acetate (7:3 v/v) as eluant to afford *bis-enone* (**10**) (273 mg, 100%) as a slightly yellow oil.

Method (*B*). A mixture of PCC (364 mg, 1.69 mmol), Florisil (364 mg), and the alcohol (**17**) (197 mg, 0.83 mmol) in dry CH_2Cl_2 (5.0 ml) was stirred at room temperature for 6 h, and the reaction mixture was diluted with ether and filtered through Celite. The filtrate was washed successively with 10% aqueous potassium hydroxide and saturated aqueous sodium chloride, dried, and evaporated. The residue was chromatographed on silica gel with hexane–ethyl acetate (8:2 v/v) as eluant to yield bis-enone (**10**) (92 mg, 47%) as an oil, which was identical with the above compound prepared by the Method (A). Further elution gave the *aldehyde* (**18**) (17 mg, 9%) as an oil.

For the bis-enone (**10**) (Found: C, 76.45; H, 9.75. $C_{15}H_{22}O_2 \cdot 0.1H_2O$ requires C, 76.3; H, 9.5%); $\nu_{max.}$($CHCl_3$) 1 700 (C=O), 1 615 (C=C), and 1 140 cm^{-1}; δ_H(500 MHz; $CDCl_3$) 6.35 (1 H, dd, *J* 17.2 and 10.3 Hz, C*H*=CH_2), 6.22 (1 H, dd, *J* 17.3 and 1.5 Hz, H\C=C<H/H), 5.83 (1 H, dd, *J* 10.3 and 1.5 Hz, H\C=C<H/H), 5.86 (1 H, br s, 2′-H), 2.60 (2 H, t, *J* 7.1 Hz, CH_2), 2.57 (1 H, m, MeC*H*<), 2.45 (2 H, s, 5′-H_2), 1.65—1.40 (4 H, m, 2 × CH_2), 1.15 (3 H, d, *J* 7.1 Hz, *Me*CH<), and 1.10 (6 H, s, 4-Me_2); *m/z* 234 (M^+) (Found: M^+, 234.1627. $C_{15}H_{22}O_2$ requires *M*, 234.1618).

For the aldehyde (**18**); $\nu_{max.}$($CHCl_3$) 1 690 cm^{-1} (C=O); δ_H(90 MHz; $CDCl_3$) 9.36 (1 H, br s, CHO), 6.40—6.10 (1 H, m, 3-H), 6.00—5.75 (2 H, m, 2 × olefinic H), 2.90—2.00 (5 H, m), 1.70—1.30 (4 H, m), 1.15 (3 H, d, *J* 5.8 Hz, >CH*Me*), and 1.13 and 1.11 (each 3 H, each s, 5-Me_2); *m/z* 234 (M^+) (Found: M^+, 234.1595. $C_{15}H_{22}O_2$ requires *M*, 234.1618).

(±)-(1RS,5RS,9SR,12SR)-(**9**) *and* (±)-(1RS,5RS,9SR,12RS)-3,3,12-*Trimethyltricyclo*[7.3.0.$0^{1,5}$]*dodecane*-4,8-*dione* (**19**).—*Method* (*A*). A mixture of the bis-enone (**10**) (20.0 mg, 0.094 mmol), zinc chloride (100 mg), triethylamine (0.1 ml), and chlorotrimethylsilane (0.1 ml) in dry toluene (3.0 ml) was heated in a sealed tube at 160 °C for 24 h. The reaction mixture was then diluted with benzene, washed successively with 10% hydrochloric acid and saturated aqueous sodium chloride, and dried. After evaporation, the residue was dissolved in THF–10% perchloric acid (1:1 v/v; 3.0 ml) and the mixture was stirred at room temperature for 30 min. The mixture was extracted with ether, and the extract was washed successively with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried, and evaporated. The residue was chromatographed on silica gel with hexane–ethyl acetate (95:5 v/v) as eluant to afford the *ketone* (**9**) (13.0 mg, 65%) as plates, m.p. 62—63 °C; and the *ketone* (**19**) (7.0 mg, 35%) as plates, m.p. 73—74 °C.

Method (*B*). A mixture of the enone (**10**) (29.0 mg, 0.124 mmol), zinc chloride (150 mg), triethylamine (0.15 ml), and chlorotrimethylsilane (0.15 ml) in dry CH_2Cl_2 (3.0 ml) was heated in a sealed tube at 160 °C for 24 h. The reaction mixture was diluted with ether, washed successively with 10% hydrochloric acid and saturated aqueous sodium chloride, and dried. After evaporation, the resulting mixture was dissolved in THF–10% perchloric acid (1:1 v/v; 3.0 ml) and the mixture was stirred at room temperature for 30 min. After having been worked up as described in Method (A), the crude product was chromatographed on silica gel with hexane–ethyl acetate (95:5 v/v) as eluant to afford the ketone (**9**) (15.3 mg, 52%) and the ketone (**19**) (2.7 mg, 10%).

For the ketone (**9**) (Found: C, 76.65; H, 9.75. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.45%); $\nu_{max.}$($CHCl_3$) 1 735 and 1 710 cm^{-1} (C=O); δ_H(500 MHz; $CDCl_3$) 2.51 (1 H, dd, *J* 5.0 and 2.5 Hz), 2.47 (3 H, m), 2.26—2.16 (2 H, m), 1.91—1.84 (1 H, m), 1.86 and 1.57 (each 1 H, each d, *J* 14.0 Hz, 2-H_2), 1.78—1.70 (2 H, m), 1.30—1.15 (1 H, m), 1.24 and 1.17 (each 3 H, each s, 3-Me_2), and 0.92 (3 H, d, *J* 6.3 Hz, 12-Me); *m/z* 234 (M^+).

For the ketone (**19**) (Found: C, 76.9; H, 9.65%); $\nu_{max.}$($CHCl_3$) 1 730 and 1 710 cm^{-1} (C=O); δ_H(500 MHz; $CDCl_3$) 2.58 (1 H, t, *J* 4.7 Hz), 2.48—2.41 (2 H, m), 2.38—2.28 (2 H, m), 2.16—2.07 (1 H, m), 1.97 and 1.84 (each 1 H, each d, *J* 14.0 Hz, 2-H_2), 2.00—1.40 (2 H, m), 1.15 and 1.13 (each 3 H, each s, 3-Me_2), and 0.87 (3 H, d, *J* 7.0 Hz, 12-Me); *m/z* 234 (M^+).

(±)-(1RS,5RS,9SR,12SR)-7-*Hydroxymethylene*-3,3,12-*trimethyltricyclo*[7.3.0.$0^{1,5}$]*dodecane*-4,8-*dione* (**21**).—A suspension of 60% sodium hydride (53.0 mg, 1.33 mmol) in dry ether (4.20 ml) at 0 °C was treated with methanol (0.06 ml), and a solution of the ketone (**9**) (52.0 mg, 0.22 mmol) in dry ether (1.00 ml) was then added dropwise. To the mixture, still at 0 °C, was added ethyl formate (0.35 ml). After having been stirred for 40 min, the reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with ether. The extract was washed successively with water and saturated aqueous sodium chloride, dried, and evaporated. The residue was chromatographed on silica gel with hexane–ethyl acetate (4:1 v/v) as eluant to give the *hydroxymethylene compound* (**21**) (52.4 mg, 90%) as an oil; $\nu_{max.}$($CHCl_3$) 3 300 (OH), 1 740, 1 670 (C=O), and 1 600 cm^{-1} (C=C); δ_H(90 MHz; $CDCl_3$) 14.20 (1 H, br s, OH), 8.66 (1 H, br s, C=CH), 3.00—1.20 (10 H, m), 1.86 and 1.55 (each 1 H, each d, *J* 13.2 Hz, 2-H_2), 1.10 and 0.98 (each 3 H, each s, 3-Me_2), and 1.00 (3 H, d, *J* 5.3 Hz, 12-Me) (Found: M^+, 262.1530. $C_{16}H_{22}O_3$ requires *M*, 262.1568).

Methyl (±)-(1RS,2SR,5RS,6SR,8RS)-(**23**) *and* (±)-(1RS,2SR,5RS,6RS,8RS)-2,10,10-*Trimethyl*-9-*oxotricyclo*-[6.3.0.0^{1,5}]*undecane*-6-*carboxylate* (**24**).—A solution of the mixture of the hydroxymethylene (**21**) (43 mg, 0.16 mmol) in dry CH_2Cl_2 (4.00 ml) was treated with triethylamine (0.07 ml, 0.50 mmol) and toluene-*p*-sulphonyl azide (48 mg, 0.25 mmol) at room temperature. The resulting mixture was stirred for 2 h at the same temperature. After evaporation of the solvent, the residue was subjected to chromatography on silica gel with hexane–ethyl acetate (4:1 v/v) as eluant to give the diazo ketone (**22**) as a yellowish oil; $\nu_{max.}$($CHCl_3$) 2 100 (N_2), 1 740 (C=O), 1 600, and 1 350 cm^{-1}.

The diazo ketone (**22**) was dissolved in dry methanol (6 ml) and the solution was irradiated for 30 min at 0 °C with a 400-W high-pressure mercury lamp with a Pyrex filter. Evaporation of the solvent gave a residue, which was chromatographed on silica gel and eluted with hexane–ethyl acetate (4:1 v/v) to afford the esters [32.2 mg, 83% from (**21**)] as a mixture of two epimers (**23**) and (**24**). The mixture was further purified by h.p.l.c. with hexane–ethyl acetate (95:5 v/v; 1.5 ml min^{-1}) as eluant to give the *keto ester* (**23**) (27.6 mg, 65%) as an oil and the *keto ester* (**24**) (4.6 mg, 18%) as an oil.

For the keto ester (**23**); $\nu_{max.}$($CHCl_3$) 1 730 cm^{-1} (C=O); δ_H(500 MHz; $CDCl_3$) 3.65 (3 H, s, OMe), 2.63 (1 H, q, *J* 7.3 Hz, 6-H), 2.51 (1 H, t, *J* 7.9 Hz, 8-H), 2.11 and 1.75 (each 1 H, each d, *J* 12.8 Hz, 11-H_2), 2.15—1.20 (8 H, m), 1.14 and 1.06 (each 3 H, each s, 10-Me_2), and 0.97 (3 H, d, *J* 6.7 Hz, 2-Me) (Found: M^+, 264.1725. $C_{16}H_{24}O_3$ requires *M*, 264.1726).

For the keto ester (**24**); $\nu_{max.}$($CHCl_3$) 1 735 cm^{-1} (C=O); δ_H(90 MHz; $CDCl_3$) 3.66 (3 H, s, OMe), 2.20 and 1.45 (each 1 H, each d, *J* 15.7 Hz, 11-H_2), 2.60—1.10 (8 H, m), 1.10 and 1.06 (each 3 H, each s, 10-Me_2), and 1.00 (3 H, d, *J* 7.1 Hz, 2-Me) (Found: M^+, 264.1706).

Methyl (±)-(1RS,2RS,5RS,8RS)-2,10,10-*Trimethyl*-9-*oxotricyclo*[6.3.0.0^{1,5}]*undecane*-6-*carboxylate* (**25**).—The ester (**25**) (15.8 mg, 70%) was prepared from the dione (**19**) (20.2 mg, 0.085 mmol) by the same procedure as the case of the *isomer* (**23**); $\nu_{max.}$($CHCl_3$) 1 730 cm^{-1} (C=O); δ_H(500 MHz; $CDCl_3$) 3.64 (3 H, s, OMe), 2.66 (1 H, m, 6-H), 2.50 (1 H, m, 8-H), 2.29 and 2.14 (each 1 H, each m, 11-H_2), 1.90—1.10 (6 H, m), 1.15 and 1.08 (each 3 H, each s, 10-Me_2), and 0.97 (3 H, d, *J* 7.2 Hz, 2-Me) (Found: M^+, 264.1727).

Methyl (±)-(1RS,2SR,5RS,6SR,8RS,9RS)-9-*Hydroxy*-2,10,10-*trimethyltricyclo*[6.3.0.0^{1,5}]*undecane*-6-*carboxylate* (**26**).—The ester (**23**) (17.8 mg, 0.067 mmol) was dissolved in dry methanol (3.0 ml) and the solution was cooled to 0 °C. Solid sodium borohydride (25 mg, 0.66 mmol) was added in portions and the mixture was stirred at 0 °C for 30 min. After concentration, the resulting mixture was partitioned between ether and saturated aqueous sodium chloride. The organic layer was dried and evaporated to give a residue which was chromatographed on silica gel with hexane–ethyl acetate (4:1 v/v) as eluant to afford a mixture of the alcohols (**26**) and (**27**) (16.8 mg, 94%). Purification by h.p.l.c. with hexane–ether (9:1 v/v; 1.0 ml min^{-1}) as eluant gave the *alcohols* (**26**) (13.9 mg) and (**27**) (2.3 mg).

For the alcohol (**26**); $\nu_{max.}$($CHCl_3$) 3 350 (OH) and 1 730 cm^{-1} (C=O); δ_H(90 MHz; $CDCl_3$) 3.68 (3 H, s, OMe), 2.60 (1 H, br d, *J* 6.9 Hz, 9-H), 2.70—1.20 (13 H, m), 1.10 and 0.96 (each 3 H, each s, 10-Me_2), and 0.90 (3 H, d, *J* 7.1 Hz, 2-Me) (Found: M^+, 266.1875. $C_{16}H_{26}O_3$ requires *M*, 266.1882).

(±)-(1RS,2SR,5RS,6SR,8RS,9RS)-2,10,10-*Trimethyltricyclo*-[6.3.0.0^{1,5}]*undecane*-6,9-*carbolactone* (**28**).—To a solution of LDA [prepared from di-isopropylamine (0.04 ml, 0.28 mmol) and butyl-lithium (1.25M solution; 0.2 ml, 0.25 mmol)] in dry THF (1.0 ml) at −78 °C was added a solution of the ester (**26**) (6.7 mg, 0.025 mmol) in dry THF (1.0 ml). The resulting mixture was stirred for 1 h at the same temperature. After addition of saturated aqueous ammonium chloride, the mixture was extracted with ethyl acetate. The extract was washed successively with water and saturated aqueous sodium chloride, dried, and evaporated. The residue was chromatographed on silica gel with hexane–ethyl acetate (4:1 v/v) as eluant to afford the *lactone* (**28**) (5.3 mg, 90%) as needles, m.p. 84—86 °C; $\nu_{max.}$($CHCl_3$) 1 730 cm^{-1} (C=O); δ_H(90 MHz; $CDCl_3$) 4.10 (1 H, d, *J* 4.6 Hz, 9-H), 2.63 (1 H, br s, 6-H), 2.55—1.20 (11 H, m), 1.10 and 0.96 (each 3 H, each s, 10-Me_2), and 1.03 (3 H, d, *J* 7.0 Hz, 2-Me) (Found: M^+, 234.1623. $C_{15}H_{22}O_2$ requires *M*, 234.1620).

(±)-(1RS,2SR,5RS,6SR,8RS)-2,10,10-*Trimethyl*-9-*oxo-tricyclo*[6.3.0.0^{1,5}]*undecane*-6-*carboxylic Acid* (**29**).—A solution of the keto ester (**23**) (25.3 mg, 0.096 mmol) in 10% (w/v) potassium hydroxide–methanol (8.0 ml) was stirred at room temperature for 20 h. After the reaction mixture had been concentrated under reduced pressure the residue was acidified at 0 °C with 10% hydrochloric acid and extracted with ethyl acetate. The extract was washed with saturated aqueous sodium chloride, dried, and evaporated to give a residue, which was chromatographed on silica gel. Elution with hexane–ethyl acetate (7:3 v/v) gave the *carboxylic acid* (**29**) (24.0 mg, 100%) as an oil; $\nu_{max.}$($CHCl_3$) 1 735 and 1 710 cm^{-1} (C=O); δ_H(500 MHz; $CDCl_3$) 2.66 (1 H, q, *J* 6.7 Hz, 6-H), 2.55—2.48 (2 H, m, 8- and 7-H), 2.55—2.48 (2 H, m), 2.30—1.80 (5 H, m), 2.12 and 1.75 (each 1 H, each d, *J* 13.4 Hz, 11-H_2), 1.50—1.40 (2 H, m), 1.15 and 1.07 (each 3 H, each s, 10-Me_2), and 0.96 (3 H, d, *J* 6.7 Hz, 2-Me) (Found: M^+, 250.1561. $C_{15}H_{22}O_3$ requires *M*, 250.1568).

Methyl (±)-(1RS,2SR,5RS,6SR,8RS,9SR)-9-*Hydroxy*-2,10,10-*trimethyltricyclo*[6.3.0.0^{1,5}]*undecane*-6-*carboxylate* (**27**).—A solution of the carboxylic acid (**29**) (11.0 mg, 0.044 mmol) in dry THF (1.2 ml) was treated at 0 °C with 60% sodium hydride (5.0 mg, 0.13 mmol) for 30 min. To the mixture were added anhydrous liquid NH_3 (4 ml), anhydrous methanol (1.2 ml), and freshly scraped Li wire (9.0 mg, 1.3 mmol). The resulting mixture was stirred for 30 min at −33 °C, after which saturated aqueous ammonium chloride was added and the NH_3 was allowed to evaporate. The residue was carefully acidified with 10% hydrochloric acid and extracted with ethyl acetate. The extract was washed with saturated aqueous sodium chloride, dried, and evaporated. The resulting crude oil was dissolved in methanol (2.0 ml) and treated with an excess of diazomethane in ether. The crude ester was purified by chromatography on silica gel with hexane–ethyl acetate (9:1 v/v) as eluant to afford the *ester* (**27**) (10.0 mg, 85%) as a yellowish oil; $\nu_{max.}$($CHCl_3$) 3 350 (OH) and 1 730 cm^{-1} (C=O); δ_H(90 MHz; $CDCl_3$) 3.68 (3 H, s, OMe), 3.45 (1 H, br d, *J* 7.5 Hz, 9-H), 2.75—2.40 (2 H, m), 2.30—1.20 (11 H, m), 1.05 and 0.90 (each 3 H, each s, 10-Me_2), and 0.95 (3 H, d, *J* 5.8 Hz, 2-Me) (Found: M^+, 266.1895. $C_{16}H_{26}O_3$ requires *M*, 266.1882).

(±)*Methyl Pentalenate* (**30**).—To a solution of LDA [prepared from di-isopropylamine (0.06 ml, 0.43 mmol) and butyl-lithium (1.25M solution; 0.30 ml, 0.38 mmol] in dry THF (1.0 ml) at −78 °C was added a solution of the ester (**27**) (5.0 mg, 0.019 mmol) in dry THF (0.5 ml). The resulting mixture was stirred at between −78 and −15 °C for 1.5 h. To the above solution cooled at −78 °C was added a solution of benzeneselenenyl chloride (108 mg, 0.56 mmol) in dry THF (0.5 ml) in one portion. The mixture was allowed to warm to 0 °C during 1 h. After addition of 1M hydrochloric acid at 0 °C, the mixture was extracted with ethyl acetate. The extract was washed successively with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried, and

evaporated. The residue was chromatographed on silica gel with hexane–ethyl acetate (6:4 v/v) as eluant to give a mixture of the epimeric selenenyl compounds, which was oxidized without further purification.

To a solution of the above mixture in THF (1.0 ml) at 0 °C were added acetic acid (0.01 ml) and 30% aqueous hydrogen peroxide (0.02 ml), and the resulting mixture was stirred for 30 min at 0 °C. Then the reaction mixture was poured into ice-cold saturated aqueous sodium hydrogen carbonate (1.0 ml), which was then extracted with ethyl acetate. The extract was washed with saturated aqueous sodium chloride, dried, and evaporated to give a residue, which was chromatographed on silica gel. Elution with hexane–ethyl acetate (9:1 v/v) yielded (±)-methyl pentalenate (**30**) (3.7 mg, 75%) as an oil whose spectral data were identical with those of the authentic compound.[3]

Methyl (±)-(1RS,2RS,5SR,6RS,8RS)-2,10,10-*Trimethyltricyclo*[6.3.0.$0^{1,5}$]*undecane-6-carboxylate* (**32**).—To a stirred solution of the keto ester (**23**) (39.9 mg, 0.15 mmol) and ethanedithiol (0.4 ml) in dry CH_2Cl_2 (4.0 ml) was added BF_3·Et_2O (0.2 ml) at room temperature and the mixture was stirred for 1 h. After addition of water, the mixture was extracted with ether. The extract was washed successively with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried, and evaporated to afford the *dithioacetal* (**31**) (64.1 mg) as an oil, which was used in the next step without further purification; $\nu_{max.}$($CHCl_3$) 1 730 cm^{-1} (C=O) (Found: M^+, 240.1531. $C_{18}H_{28}O_2S_2$ requires M, 340.1531).

To a stirred solution of the dithioacetal (**31**) (64.1 mg) in a mixture of dry dioxane (6.0 ml) and dry methanol (0.8 ml) was added Raney-Ni W_2 (2.0 g). The mixture was heated at 80 °C for 4.5 h. The reaction mixture was treated with ethyl acetate and filtered through Celite. After evaporation of the solvents, the residue was chromatographed on silica gel with hexane–ethyl acetate (95:5 v/v) as eluant to give the *ester* (**32**) as an oil (33.1 mg, 90%); $\nu_{max.}$($CHCl_3$) 1 730 cm^{-1} (C=O); δ_H(90 MHz; $CDCl_3$) 3.65 (3 H, s, OMe), 2.70—2.40 (1 H, m, 6-H), 2.30—1.20 (11 H, m), 1.65 and 1.35 (each 1 H, each d, J 14.1 Hz, 11-H_2), 1.08 and 0.95 (each 3 H, each s, 10-Me_2), and 0.89 (3 H, d, J 7.0 Hz, 2-Me) (Found: M^+, 250.1927. $C_{18}H_{26}O_2$ requires M, 250.1933).

Methyl (±)-*Deoxypentalenate* (**33**) *and its Isomer* (**34**).—To a stirred solution of LDA [prepared from di-isopropylamine (0.04 ml, 0.29 mmol) and butyl-lithium (1.54M solution; 0.14 ml, 0.22 mmol)] in dry THF (1.0 ml) at −78 °C was added dropwise a solution of the ester (**32**) (5.5 mg, 0.022 mmol) in dry THF (0.9 ml). The resulting mixture was stirred at between −78 and +10 °C for 1.5 h. To the above solution cooled at −78 °C was added a solution of benzeneselenenyl chloride (63.2 mg, 0.33 mmol) in dry THF (0.5 ml) in one portion. The mixture was allowed to warm to 0 °C during 1.5 h. After addition of 10% hydrochloric acid at 0 °C, the mixture was extracted with ether. The extract was washed successively with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried, and evaporated to give a residue, which was dissolved in THF (2.5 ml). To the solution at 0 °C were added acetic acid (0.1 ml) and 30% aqueous hydrogen peroxide (0.2 ml), and the mixture was stirred for 30 min at the same temperature. Then dimethyl sulphide (0.4 ml) was added to the resulting mixture at room temperature and the mixture was stirred for 8 h. After extraction with ether, the extract was washed successively with water and saturated aqueous sodium chloride, dried, and evaporated. The residue was purified by h.p.l.c. with hexane–ether (97:3 v/v; 1 ml min^{-1}) as eluant to give the *esters* (**33**) (2.5 mg, 46%) and (**34**) (2.0 mg, 37%) as oils.

For the ester (**33**); $\nu_{max.}$($CHCl_3$) 1 710 (C=O) and 1 630 cm^{-1} (C=C); δ_H(500 MHz; $CDCl_3$) 6.63 (1 H, br s, 7-H), 3.73 (3 H, s, OMe), 3.04 (1 H, br d, J 9.3 Hz), 2.87 (1 H, m), 2.00—1.10 (9 H, m), 1.10 and 1.00 (each 3 H, each s, 10-Me_2) and 0.93 (3 H, d, J 7.0 Hz, 2-Me) (Found: M^+, 248.1785. $C_{16}H_{24}O_2$ requires M, 248.1776).

For the ester (**34**); $\nu_{max.}$($CHCl_3$) 1 700 (C=O) and 1 650 cm^{-1} (C=C); δ_H($CDCl_3$) 3.70 (3 H, s, OMe), 3.10—1.10 (12 H, m), 1.07 and 1.00 (each 3 H, each s, 10-Me_2), and 0.93 (3 H, d, J 5.7 Hz, 2-Me) (Found: M^+, 248.1776).

(±)-(1RS,2RS,5RS,8SR)-(2,10,10-*Trimethyltricyclo*-[6.3.0.$0^{1,5}$]*undec-6-en-6-yl*)*methanol* (**35**).—To a stirred solution of the ester (**33**) (15.0 mg, 0.06 mmol) in dry THF (6.0 ml) at 0 °C was added dropwise a solution of DIBAL in hexane (1M solution; 0.4 ml, 0.4 mmol). The reaction mixture was stirred at the same temperature for 30 min. After addition of water (0.4 ml), the mixture was stirred for 1 h, and then filtered through Celite. The filtrate was dried and evaporated to give a residue, which was chromatographed on silica gel. Elution with hexane–ethyl acetate (4:1 v/v) afforded the *alcohol* (**35**) (12.1 mg, 91%) as an oil; $\nu_{max.}$($CHCl_3$) 3 300 cm^{-1} (OH); δ_H(90 MHz; $CDCl_3$) 5.50 (1 H, br s, 7-H), 4.10 (2 H, br s, CH_2OH), 2.60—2.10 (2 H, m, 5- and 8-H), 2.20—1.10 (10 H, m), 1.00 (6 H, s, 10-Me_2), and 0.94 (3 H, d, J 7.1 Hz, 2-Me) (Found: M^+, 220.1826. $C_{15}H_{24}O$ requires M, 220.1827).

(±)-*Pentalenene* (**1**).—To a solution of the alcohol (**35**) (13.7 mg, 0.06 mmol) in dry THF (5.00 ml) at 0 °C was added pyridine–sulphur trioxide complex (51.7 mg, 0.32 mmol), and the mixture was stirred at 0 °C for 12 h. A solution of lithium aluminium hydride (41.8 mg, 1.10 mmol) in dry THF (1.10 ml) was added to this solution at 0 °C and then the mixture was stirred at 0 °C for 30 min and at room temperature for 8.5 h. After successive addition of water (0.02 ml), 15% aqueous sodium hydroxide (0.02 ml), and water (0.06 ml) to the mixture at 0 °C, ether was added and the precipitate was filtered off through Celite. The filtrate was dried over anhydrous $MgSO_4$ and concentrated to give a residue, which was chromatographed on silica gel. Elution with pentane yielded (±)-pentalenene (**1**) (6.0 mg, 47%) as an oil, whose n.m.r. spectrum was identical with that of natural pentalenene.

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