# Bicyclo[3.3.0]octenones in Synthesis. A New Synthesis of (±)-Cedrene using Sequential Inter- and Intra-molecular Michael Reactions

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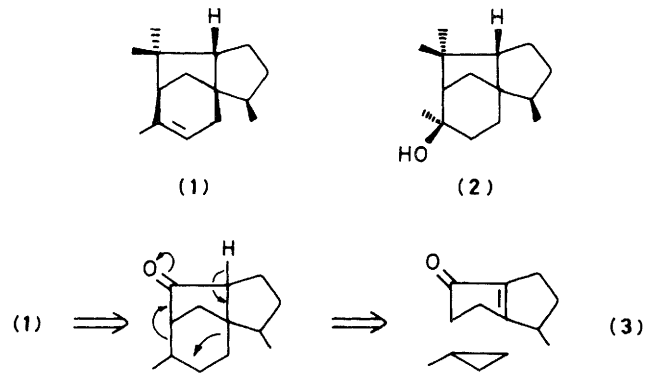
A new synthetic approach to cedrene (**1**) based on sequential inter- and intra-molecular Michael reactions using the bicyclo[3.3.0]octenone (**21**) as the key intermediate is described.

Michael addition of the enolate derived from (**21**) to 2-nitrobut-2-ene, led to a mixture of diastereoisomers of the nitro ketone (**22**), which was then converted into the 1,4-dione (**23**). Treatment of (**23**) with potassium t-butoxide in t-butyl alcohol resulted in smooth intramolecular Michael reaction leading to a mixture of α-(**24a**; major) and β-isomers of the tricyclo[5.3.1.$0^{1,5}$]undecanedione (**24**) in a combined yield of 73%. The undecanedione (**24**) was then converted into (±)-cedrene (**1**) and the corresponding methyl epimer (**31a**) *via* the intermediates (**25**), (**26**), (**27**), and (**28**).



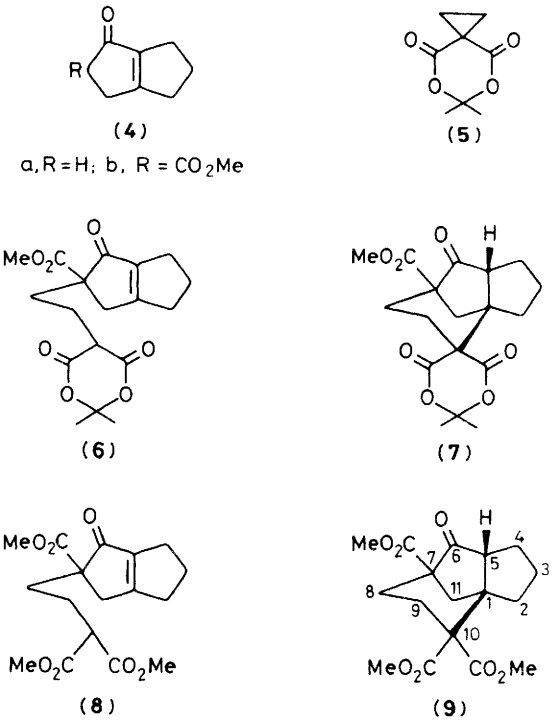
The tricyclic sesquiterpene cedrene (**1**) co-occurs with cedrol (**2**) in *Juniperus* oil; both molecules have useful odoriferous properties. Since the structures of cedrene and cedrol were firmly established in 1953,[1] they have been at the focus of many inspired syntheses of fused ring carbocycles.[2] In this paper we describe a conceptually new approach to (±)-cedrene which features the bicyclo[3.3.0]octenone (**21**) as the key intermediate.[3]

Our approach to the synthesis of cedrene was based on the retrosynthetic analysis summarised in the Scheme. In this approach we envisaged introducing the six-ring in the tricycle, using a single-step tandem Michael addition sequence involving the kinetic enolate derived from the bicyclo-octenone (**3**) and an activated cyclopropane.



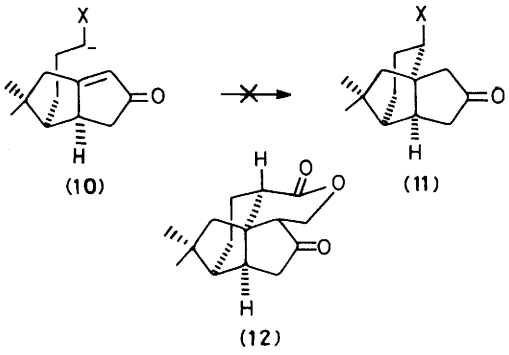

**Scheme.**

We began our investigation of this approach to cedrene by first examining some model reactions with the easily available bicyclo[3.3.0]octenone (**4a**)[4] and the cyclopropane (**5**).[5] The extensive studies by Danishefsky *et al.*[6] have firmly established that spiro-activated cyclopropanes like (**5**) are smoothly cleaved by a range of nucleophiles producing the corresponding Meldrum acid derivatives. In the event however, deprotonation of the bicyclo-octenone (**4a**) with lithium di-isopropylamide in tetrahydrofuran at −78 °C followed by treatment with the cyclopropane (**5**) and warming to 0 °C, led to the recovery of only starting material. Furthermore, although the enolate derived from the corresponding β-keto ester (**4b**) added smoothly to (**5**), producing the adduct (**6**), we were unable to induce this substrate, either *in situ* or in a separate operation, to undergo the second (intramolecular) Michael reaction leading to (**7**).

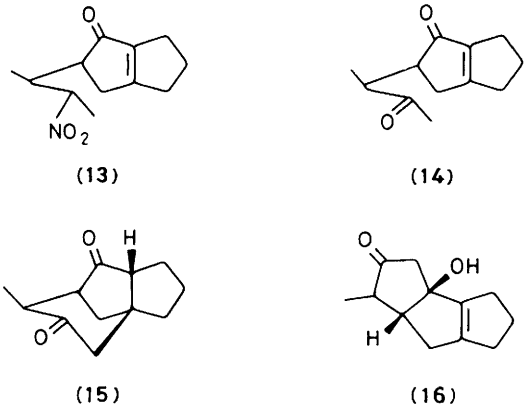



Reasoning that the failure to achieve this second Michael reaction *i.e.* (**6**) ⟶ (**7**) was probably associated with the low nucleophilicity of the carbanion derived from (**6**) in combination with its sterically encumbered nature,[7] we decided to convert (**6**) into the corresponding dimethyl ester (**8**) and examine its cyclisation. To our satisfaction, treatment of (**6**) with dry methanolic hydrogen chloride led to the trimethyl ester (**8**), which, in the presence of potassium t-butoxide in t-butyl alcohol underwent an intramolecular Michael reaction, producing the tricyclic ring system (**9**) found in cedrene, in 93% yield. The ease with which (**8**) undergoes intramolecular Michael reaction producing (**9**) is interesting and is to be contrasted with our earlier failure to induce a range of substrates of the type (**10**) to undergo a corresponding ring closure to the ring system found in quadrone (**12**); see discussion in preceding paper.[8]

Although the conversion of the bicyclo-octenone (**4b**) into (**9**), *via* (**6**), demonstrated the viability of our approach to cedrene (Scheme), the simultaneous incorporation of three methoxycarbonyl groups in strategically undesirable positions

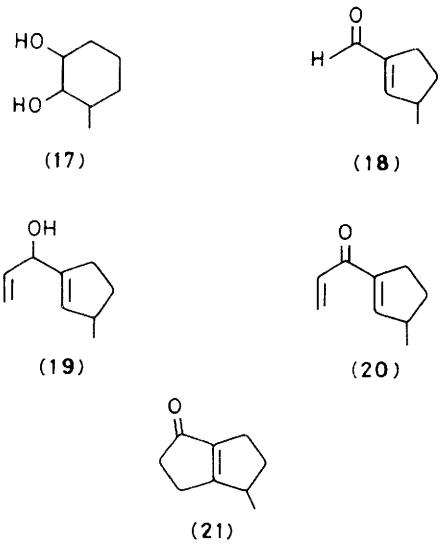



in the tricycle (**9**), did not augur well for an attractive conclusion to our proposed synthesis of cedrene. This problem was overcome when we decided to change to 2-nitrobut-2-ene instead of an activated cyclopropane as the three-carbon annelation reagent (*cf.* Scheme). Thus, Michael addition of the enolate derived from (**4a**) (LDA, HMPA, −78 °C) to 2-nitrobut-2-ene followed by quenching at −60 °C led to a mixture of diastereoisomers of the nitro enone (**13**) in a yield of 92%. Hydrolysis of (**13**), using sodium nitrite and n-propyl nitrite in dimethyl sulphoxide, then produced the 1,4-dione (**14**) which on treatment with potassium t-butoxide in t-butyl alcohol (25 °C, 15 min) underwent clean intramolecular Michael reaction leading to the tricyclo-[5.3.1.$0^{1,5}$]undecanedione (**15**).* We were not able to detect the co-formation or intermediacy of the product (**16**) expected from aldol condensation in the 1,4-dione (**14**), under these conditions.

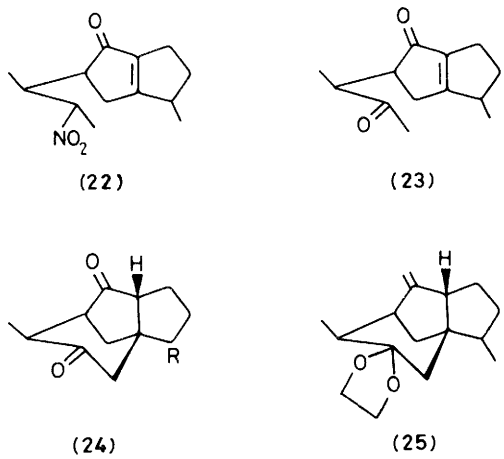



Having established an attractive new route to the tricyclic ring system present in cedrene, based on the approach summarised in the Scheme, we next turned to the synthesis of the substituted bicyclo-octenone (**21**) required for elaboration to the tricyclic precursor (**24**) to cedrene (**1**). The bicyclo-octenone (**21**) was obtained starting from 3-methylcyclohexane-1,2-diol (**17**). Thus, treatment of the diol with sodium periodate, followed by *in situ* aldolisation of the resulting 1,5-dialdehyde using potassium hydroxide, first produced the unsaturated aldehyde (**18**).[10] Reaction between the aldehyde (**18**) and vinylmagnesium bromide then led to the secondary alcohol (**19**), which after oxidation to the dione (**20**) using manganese dioxide, and Nazarov cyclisation in the presence of polyphosphoric acid produced the bicyclo-octenone (**21**).

* For other examples of the intramolecular Michael reaction in synthesis, see ref. 9.

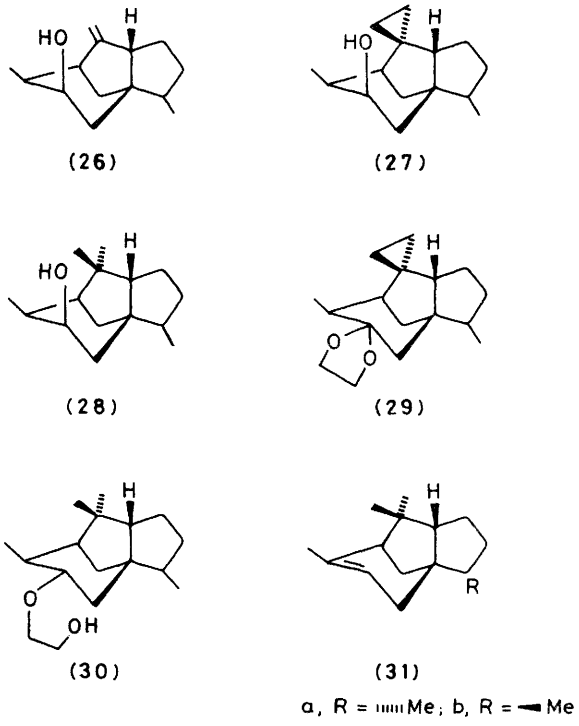



Deprotonation of (**21**), in a similar procedure to that described for (**4a**), followed by treatment with 2-nitrobut-2-ene [to (**22**)] and Nef reaction, led to the substituted 1,4-dione (**23**). When this 1,4-dione was treated with potassium t-butoxide in t-butyl alcohol it underwent smooth intramolecular Michael reaction leading to a 2:1 mixture of α- and β-methyl isomers of the corresponding tricyclic dione (**24**) in a combined yield of 73%; we have assigned the α-methyl isomer (**24a**) as the major product, on the basis of cyclisation on the least hindered β-face of (**23**) in its conversion into (**24**).




a, R = ⁞⁞⁞ Me, b, R = ◀ Me

After selective protection of the six-ring carbonyl group in (**24**) as the corresponding dioxolane, a Wittig reaction with methylenetriphenylphosphorane provided the alkene (**25**) as a colourless oil. In order to optimise yields in the Simmons-Smith reaction leading to (**27**), we next converted the dioxolane group in (**25**) into the axial carbinol (**26**) *via* reduction of the corresponding ketone using L-selectride. Cyclopropanation of the hydroxy-alkene (**26**) using diethylzinc–methylene di-iodide in the presence of catalytic oxygen, then led to (**27**) which on hydrogenation provided the carbinol (**28**). This route to the carbinol (**28**) from the dioxolane (**25**) was preparatively more convenient than an alternative procedure whereby (**25**) was first converted into the cyclopropane (**29**) which was then hydrogenated to (**30**). Comparison of $^1$H n.m.r. spectral data for our




synthetic carbinol (**28**) with those reported for authentic isomers of the carbinol produced from natural cedrene,[11] established the identity of our material and also confirmed the presence of α- (major) and β-methyl epimers. Dehydration of the carbinol (**28**), using phosphorus oxychloride in hot benzene containing pyridine, finally produced (±)-cedrene (**1**) and the corresponding methyl epimer (**31a**) as a colourless oil; the synthetic cedrene showed chromatographic and spectral data indistinguishable from naturally derived material.

## Experimental

For general experimental details see preceding paper.[8]

3-*Methoxycarbonylbicyclo*[3.3.0]*oct*-1(5)-*en*-2-*one* (**4b**).—A solution of bicyclo[3.3.0]oct-1(5)-en-2-one[4] (2.0 g) in dimethylformamide (5 $cm^3$) was added to a solution of methylmagnesium carbonate (16.9 g)[12] in dimethylformamide (65 $cm^3$), and the resulting mixture was then heated at 100 °C, under nitrogen, for 2 h. The cooled solution was added to methanol (160 $cm^3$) at −60 °C, that had been previously saturated with dry hydrogen chloride. The solution was allowed to warm to room temperature with continuous stirring (care, $CO_2$ evolution), where it was kept for a further 24 h. The methanol was removed under reduced pressure and the residue then extracted with ether (3 × 100 $cm^3$). The dimethylformamide layer was diluted with an equal volume of water, and the mixture then extracted with ether (3 × 100 $cm^3$). The combined ether extracts were washed with saturated aqueous sodium chloride (100 $cm^3$), and then dried. Evaporation of the ether extracts left the crude β-keto ester (3.34 g) as a dark red oil. Chromatography on Kieselgel G using light petroleum (b.p. 40—60 °C)–ether (1:1) as eluant gave the pure β-keto ester (1.992 g, 68%) as a pale yellow oil, $\nu_{max.}$(film) 1 740, 1 700, and 1 640 $cm^{-1}$; δ 2.25—2.95 (m, 8 H) and 3.77 (m, $CH_3$, $MeO_2CCHCO$); $\delta_C$ 195.8, 187.4, 169.8, 147.2, 57.8 (d), 52.5 (q), 31.9 (t), 30.0 (t), 27.8 (t), and 24.6 (t); *m/z* 180.0769 ($C_{10}H_{12}O_3$ requires *M*, 180.0785).

3-*Methoxycarbonyl*-3-[2-(2,2-*dimethyl*-4,6-*dioxo*-1,3-*dioxacyclohexyl*)*ethyl*]*bicyclo*[3.3.0]*oct*-1(5)-*en*-2-*one* (**6**).—A solution of 3-methoxycarbonylbicyclo[3.3.0]oct-1(5)-en-2-one (600 mg) in dry t-butyl alcohol (12 $cm^3$) was added to a stirred solution of potassium t-butoxide (from 195 mg potassium) in dry t-butyl alcohol (36 $cm^3$) at 20 °C under nitrogen. A solution of 6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione[5] (612 mg) in dry t-butyl alcohol (12 $cm^3$) was then added, and the resulting dark red solution was stirred at 25 °C for 18 h and then at 75 °C for a further 5 h. The mixture was cooled, and then quenched with 2% aqueous citric acid (30 $cm^3$), and extracted with chloroform (4 × 50 $cm^3$). Evaporation of the dried organic extracts left an orange oil which was purified by chromatography on Kieselgel G using light petroleum (b.p. 40—60 °C)–acetone (3:1) as eluant to give the triester (750 mg, 65%) as colourless crystals, m.p. 97—99 °C (hexane), $\nu_{max.}$(film) 1 800, 1 750, 1 700, and 1 640 $cm^{-1}$; δ 1.75 ($CH_3$), 1.84 ($CH_3$), 1.95—3.10 (m, 13 H), and 3.74 ($CO_2Me$); $\delta_C$ 198.1, 186.8, 171.2, 165.3, 146.5, 105.1, 65.3, 52.4 (q), 46.2 (d), 35.8 (t), 31.9 (t), 31.3 (t), 28.4 (q), 27.6 (t), 26.2 (q), 24.6 (t), and 21.3 (t) (Found: C, 61.2; H, 6.3. $C_{18}H_{22}O_7$ requires C, 61.7; H, 6.45%); *m/z* 266.1154 ($M - C_4H_4O_2$ requires 266.1154).

3-*Methoxycarbonyl*-3-(3,3-*dimethoxycarbonylpropyl*)-bicyclo[3.3.0]*oct*-1(5)-*en*-2-*one* (**8**).—Dry methanol (14 $cm^3$) that had been saturated with dry hydrogen chloride was added to a solution of 3-methoxycarbonyl-3-[2-(2,2-dimethyl-4,6-dioxo-1,3-dioxacyclohexyl)ethyl]bicyclo[3.3.0]oct-1(5)-en-2-one (200 mg) in dry methanol (14 $cm^3$), and the resulting solution was heated under reflux for 45 min. The cooled mixture was set aside for 18 h at 25 °C, and then evaporated to leave the crude triester (193 mg). Chromatography on Kieselgel G using hexane–acetone (4:1) as eluant, gave the pure trimethyl ester (127 mg, 66%) as a colourless oil, $\nu_{max.}$(film) 1 740, 1 700, and 1 640 $cm^{-1}$; δ 1.7—2.1 (m, 4 H), 2.2—3.5 (m, 9 H), 3.72 (OMe), 3.74 (OMe), and 3.76 (OMe); $\delta_C$ 198.1, 186.8, 171.2, 169.4, 146.8, 65.3, 52.5 (q), 51.6 (d), 35.8 (t), 32.0 (t), 27.6 (t), 24.6 (t), and 24.2 (t); *m/z* 338.1365 ($C_{17}H_{22}O_7$ requires *M*, 338.1365).

7,10,10-*Trimethoxycarbonyltricyclo*[5.3.1.$0^{1,5}$]*undecan*-6-*one* (**9**).—A solution of 3-methoxycarbonyl-3-(3,3-dimethoxycarbonylpropyl)bicyclo[3.3.0]oct-1(5)-en-2-one (100 mg) in dry t-butyl alcohol (2 $cm^3$) was added to a stirred solution of potassium t-butoxide (from 6 mg potassium) in dry t-butyl alcohol (2 $cm^3$) at room temperature under nitrogen. The mixture was stirred at room temperature for 18 h, and then at 90 °C for a further 2 h; it was then allowed to cool to room temperature. Citric acid (300 mg) was added, followed by saturated aqueous ammonium chloride (10 $cm^3$), and the mixture was then extracted with chloroform (4 × 10 $cm^3$). The combined chloroform extracts were washed with saturated aqueous sodium chloride (15 $cm^3$), and then dried and evaporated to leave a viscous yellow oil (109 mg), $\nu_{max.}$(film) 3 600—2 500 $cm^{-1}$. The crude product was dissolved in dry methanol (10 $cm^3$) and then treated with dry methanol (5 $cm^3$) that had been saturated with dry hydrogen chloride. The solution was heated under reflux for 2 h, and then cooled and allowed to stand at room temperature for a further 18 h. The methanol was removed under reduced pressure, and the residue, an orange oil (115 mg), was then chromatographed on Kieselgel G using hexane–acetone (3:1) as eluant to give the pure tricyclic ketone (95 mg, 95%) as a pale yellow oil; $\nu_{max.}$(film) 1 750 and 1 730 $cm^{-1}$; δ 1.6—2.7 (m, 12 H), 3.1—3.45 (m, OCC*H*), 3.76 (2 × $CO_2CH_3$), 3.83 ($CO_2CH_3$); $\delta_C$ 214.2, 171.1, 170.9, 170.8, 61.1, 59.9, 56.4 (d), 54.0, 52.4 (q), 52.3 (q), 40.6 (t), 34.7 (t), 28.8 (t), 28.0 (t), 27.8 (t), and 25.6 (t); *m/z* 338.1359 ($C_{17}H_{22}O_7$ requires *M*, 338.1365).

3-(1-*Methyl*-2-*oxopropyl*)*bicyclo*[3.3.0]*oct*-1(5)-*en*-2-*one* (**14**).—A solution of n-butyl-lithium (28.2 $cm^3$; 1.42M) in hexane was added to a stirred solution of di-isopropylamine (4.16 g) in dry tetrahydrofuran (100 $cm^3$) at −20 °C under nitrogen. The solution was stirred at −20 °C for 15 min and then cooled to −78 °C. Hexamethylphosphoramide (7.16 g) was introduced, and after a further 30 min a solution of bicyclo[3.3.0]oct-1(5)-en-2-one[4] (4.88 g) in dry tetrahydrofuran (50 $cm^3$) was added during 30 min. The resulting yellow solution was stirred at −78 °C for 2.5 h, and then 2-nitrobut-2-ene (6.06 g, 0.06 mol) was added in one portion. The orange solution was stirred at −60 °C for 3 h, and then quenched by the addition of 3M-acetic acid (20 $cm^3$). The mixture was allowed to warm to 25 °C and the organic phase was then separated. The aqueous phase was extracted with ether (3 × 50 $cm^3$), and the combined organic extracts were then washed successively with dilute hydrochloric acid (2M; 2 × 50 $cm^3$), saturated aqueous sodium hydrogen carbonate (50 $cm^3$), and saturated sodium chloride solution (50 $cm^3$). Evaporation of the dried organic extracts left the crude nitro enone (**13**) (8.2 g, 92%) as an orange oil, $\nu_{max.}$(film) 1 685, 1 640, and 1 550 $cm^{-1}$; δ 0.90 (d, *J* 6, $CH_3$), 1.5—1.7 [m, $CH(NO_2)CH_3$], 2.0—3.1 (m, 10 H), and 4.50—5.30 (m, $CHNO_2$).

Dry sodium nitrite (10.3 g) was added to dry freshly distilled dimethyl sulphoxide (60 $cm^3$) followed by the nitro enone (**12**) (7 g) and n-propyl nitrite (5.34 g).[13] The resulting mixture was stirred under nitrogen in subdued light at room temperature for 6 days. The mixture was poured into a mixture of dichloromethane (250 $cm^3$) and water (250 $cm^3$), and the organic phase then separated. The aqueous phase was extracted with dichloromethane (2 × 100 $cm^3$), and the combined organic extracts were then washed with water (100 $cm^3$) followed by saturated aqueous sodium chloride (100 $cm^3$). Evaporation of the dried organic extracts left a dark red oil which was chromatographed on Kieselgel G using chloroform–ether (4 : 1) as eluant to give the ene dione (2.84 g, 49%; 65% based on recovered starting material) as a pale yellow oil, $\nu_{max.}$(KBr) 1 710, 1 695, and 1 640 $cm^{-1}$; δ 0.95, 1.15 (d, *J* 7, $CH_3$, diastereoisomers), 2.14, 2.22 ($COCH_3$, diastereoisomers), and 2.05—3.4 (m, 10 H); *m*/*z* 192.1143 ($C_{12}H_{16}O_2$ requires *M*, 192.1150).

8-*Methyltricyclo*[5.3.1.$0^{1,5}$]*undecane*-6,9-*dione* (**15**).—A solution of 3-(1-methyl-2-oxopropyl)bicyclo[3.3.0]oct-1(5)-en-2-one (1.0 g) in dry t-butyl alcohol (40 $cm^3$) was added in one portion to a stirred solution of potassium t-butoxide [from potassium (2.0 g, 52.1 mg-atom)] in dry t-butyl alcohol (200 $cm^3$). The solution was stirred at room temperature under nitrogen for 10 min and then water (400 $cm^3$) was added. The solution was extracted with ether (3 × 100 $cm^3$), and the combined ether extracts were then washed with saturated aqueous sodium chloride (3 × 100 $cm^3$). Evaporation of the dried ether layer left a yellow glassy solid which was purified by chromatography on Kieselgel G using chloroform–ether (50:1) as eluant to give the tricyclic dione (710 mg, 71%) as a white crystalline solid, m.p. 60—61 °C (hexane), $\nu_{max.}$(film) 1 740 and 1 715 $cm^{-1}$; δ 1.04, 1.22 (d, *J* 7, $CH_3$, diastereoisomers), and 1.4—3.0 (m, 13 H); major diastereoisomer: 217.0, 209.1, 56.4 (d), 55.5 (d), 53.6 (t), 51.1, 49.2 (d), 38.9 (t), 36.8 (t), 27.8 (t), 25.0 (t), and 12.5 (q) (Found: C, 75.1; H, 8.6. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.4%); *m*/*z* 192.1152 ($C_{12}H_{16}O_2$ requires *M*, 192.1150).

3-*Methylcyclohexane*-1,2-*diol* (**17**).—A solution of 3-methylpyrocatechol (55 g) in ethanol (40 $cm^3$) was heated at 150 °C in the presence of Raney nickel (9 g) and hydrogen at 100 atm pressure in a rocking autoclave, until hydrogen uptake ceased (*ca.* 12 h). The mixture was allowed to cool to 25 °C, and the hydrogen pressure was then released. The catalyst was filtered off, and the filtrate was then evaporated under reduced pressure. Distillation of the residue gave the diol (45.22 g, 77%) as a colourless viscous oil, b.p. 95—100 °C at 2 mmHg (lit.,[10] b.p. 78—80 °C at 0.8 mmHg); $\nu_{max.}$(film) 3 350 $cm^{-1}$; δ 0.9—1.05 (m, $CH_3$), 1.1—2.3 (m, 7 H), 2.7—4.4 (m, 2 × C*H*·OH); *m*/*z* 130.0987 ($C_7H_{14}O_2$ requires *M*, 130.0994).

3-*Methylcyclopent*-1-*ene*-1-*carbaldehyde* (**18**).—Concentrated nitric acid (4.6 $cm^3$) was added to a stirred suspension of sodium periodate (20.02 g) in water (240 $cm^3$) at 25 °C, and after the solid had dissolved, the solution was adjusted to pH 4 with dilute sodium hydroxide (2M). A solution of 3-methylcyclohexane-1,2-diol (10 g) in water (25 $cm^3$) was added, whereupon the temperature of the mixture rose to 35 °C. After 30 min, the mixture was cooled to 25 °C and then ether (32 $cm^3$) followed by aqueous potassium hydroxide (28 $cm^3$; 20%) were added; the mixture was then stirred vigorously for 30 min. The organic layer was separated, and the aqueous layer was then extracted with ether (2 × 50 $cm^3$). The combined ether extracts were dried and then evaporated to leave the crude aldehyde (8.02 g, 95%). A small portion of the aldehyde was distilled to give a pure sample as a colourless oil, b.p. 48—52 °C at 10 mmHg (extensive decomp.) (lit.,[10] b.p. 56—57 °C at 20 mmHg), $\nu_{max.}$(film) 2 710, 1 680, and 1 620 $cm^{-1}$; δ 1.15 (d, *J* 7, $CHCH_3$), 1.3—1.72 (m, 1 H), 2.12—2.35 (m, 1 H), 2.39—2.69 (m, 2 H), 2.75—3.2 (m, 1 H), 6.78 (m, :CH), and 9.83 (CHO).

1-(1-*Hydroxyprop*-2-*enyl*)-3-*methylcyclopent*-1-*ene* (**19**).—A solution of vinyl bromide (64 g) in dry tetrahydrofuran (80 $cm^3$) was added to a stirred suspension of magnesium turnings (13.2 g) in dry tetrahydrofuran (260 $cm^3$) under nitrogen, at such a rate so as to maintain gentle reflux. The mixture was heated under reflux for a further 30 min and then allowed to cool to 25 °C. The Grignard solution was added dropwise over 30 min to a stirred solution of 3-methylcyclopentene-1-carbaldehyde (54.2 g) in dry tetrahydrofuran (200 $cm^3$) at −10 °C under nitrogen. The mixture was allowed to warm to 0 °C where it was stirred for a further 2 h. Saturated ammonium chloride solution (250 $cm^3$) was added, and the tetrahydrofuran was then removed under reduced pressure. The residue was extracted with ether (4 × 200 $cm^3$), and the combined ether extracts were dried and evaporated. Distillation of the residue gave the dienol (24.62 g, 33% from diol) as a colourless oil, b.p. 38—40 °C at 0.1 mmHg, $\nu_{max.}$(film) 3 350 and 1 640 $cm^{-1}$; δ 1.03 (d, *J* 7, $CHCH_3$), 1.25—1.55 (m, 1 H), 1.85 (br, O*H*), 1.95—2.5 (m, 3 H), 2.6—3.0 (m, 1 H), 4.7 (br, C*H*OH), 5.1—5.4 (m, :$CH_2$), 5.58 (m, :CH), 5.78—6.15 (m, C*H*:$CH_2$); $\delta_c$ 147.8, 139.4 (d), 131.6 (d), 114.65 (t), 72.2 (d), 39.85 (d), 32.5 (dd), 31.3 (t), and 21.0 (q); *m*/*z* 138.1050 ($C_9H_{14}O$ requires *M*, 138.1045).

3-*Methyl*-1-(1-*oxoprop*-2-*enyl*)*cyclopent*-1-*ene* (**20**).—A solution of 3-methyl-1-(1-hydroxyprop-2-enyl)cyclopent-1-ene (5 g) in chloroform (20 $cm^3$) was added to a stirred suspension of manganese dioxide (50 g) in chloroform (500 $cm^3$). After being stirred in subdued light for 18 h the mixture was filtered through silica, and the filtrate was evaporated to leave the crude dienone (4.95 g, 100%). A small portion of the dienone was distilled to give a pure sample as a pale yellow oil, b.p. 84—86 °C at 12 mmHg, $\nu_{max.}$(film) 1 660 and 1 610 $cm^{-1}$; δ 1.13 (d, *J* 7, $CH_3$), 1.30—1.70 (m, 1 H), 1.95—2.50 (m, 1 H) 2.5—2.80 (m, 2 H), 2.80—3.25 (m, 1 H), 5.60 (dd, *J* 11 and 2, CH:CH*H*), 6.30 (dd, *J* 17 and 2, CH:CH*H*), 6.70 (m, 1 H), 6.94 (dd, *J* 17 and 11, C*H*:$CH_2$); $\delta_C$ 188.3, 149.8 (d), 144.8, 132.6 (d), 127.2 (t), 41.6 (d), 31.6 (t), 30.5 (t), and 19.8 (q).

6-*Methylbicyclo*[3.3.0]*oct*-1(5)-*en*-2-*one* (**21**).—3-Methyl-1-(1-oxopropyl-2-enyl)cyclopent-1-ene (10 g) was added in one portion to stirred polyphosphoric acid (150 g) at 55—60 °C

under $N_2$. After the mixture had been stirred for 10 min, iced water (500 $cm^3$) was added rapidly, while the reaction flask was cooled in ice. The resulting solution was extracted with ether (4 × 200 $cm^3$) and the combined ether extracts were then washed successively with water (200 $cm^3$), saturated aqueous sodium hydrogen carbonate (200 $cm^3$), and saturated saline (200 $cm^3$). The extracts were then dried and evaporated to leave the crude enone, which was purified by column chromatography on Kieselgel G using ether–n-hexane (5 : 4) to give the bicyclo-[3.3.0]octenone (3.2 g, 32%) as a red oil. A small portion of the enone was distilled to give a pure sample as a colourless oil, b.p. 50—51 °C at 0.1 mmHg, $\nu_{max.}$(film) 1 700 and 1 640 $cm^{-1}$; δ 1.16 (d, *J* 7, $CH_3$), 1.75—2.05 (m, 1 H), and 2.20—3.15 (m, 8 H); $\delta_c$ 204.2, 190.5, 147.6, 40.9 (t), 38.9 (d), 37.0 (dd), 23.9 (t), 23.8 (t), and 18.3 (q); *m/z* 136.0899 ($C_9H_{12}O$ requires *M*, 136.0888). The 2,4-dinitrophenylhydrazone derivative crystallised from ethanol and had m.p. 166—168 °C (Found: C, 57.2; H, 5.1; N, 17.9. $C_{15}H_{16}N_4O_4$ requires C, 57.0; H, 5.1; N, 17.7%).

6-*Methyl*-3-(1-*methyl*-2-*oxopropyl*)*bicyclo*[3.3.0]*oct*-1(5)-*en*-2-*one* (**23**).—A solution of n-butyl-lithium (4.2 mmol; 1.46M) in hexane (3 $cm^3$) was added to a stirred solution of di-isopropylamine (444 mg) in dry tetrahydrofuran (10 $cm^3$) at −20 °C under nitrogen. The solution was stirred at −20 °C for 15 min and then cooled to −78 °C. Hexamethylphosphoramide (733 mg) was introduced, and after a further 40 min a solution of 6-methylbicyclo[3.3.0]oct-1(5)-en-2-one (544 mg) in tetrahydrofuran (5 $cm^3$) was added during 30 min. The resulting yellow solution was stirred at −78 °C for 2.5 h, and then 2-nitrobut-2-ene (606 mg, 6.0 mmol) was added in one portion. The resulting orange solution was stirred at −60 °C for 3 h, and then quenched by the addition of 3M-acetic acid (3 $cm^3$). The mixture was allowed to warm to 25 °C when the organic phase was then separated. The aqueous phase was extracted with ether (3 × 40 $cm^3$) and the combined organic layers were then washed successively with dilute hydrochloric acid (1M; 2 × 20 $cm^3$), saturated aqueous sodium hydrogen carbonate (25 $cm^3$), and saturated saline (25 $cm^3$). Evaporation of the dried organic layers left a mixture of isomers of the nitroenone (22) (0.85 g, 95%) as an oil, $\nu_{max.}$(film) 1 685, 1 640, and 1 550 $cm^{-1}$; δ 0.90 (d, *J* 6, $CH_3$), 1.2 (d, *J* 7, $CH_3$), 1.50—1.70 [m, $CH(NO_2)CH_3$], 1.70—3.10 (m, 9 H), and 4.60—5.30 (m, $CHNO_2$).

Dry sodium nitrite (18.0 g) was added to dry freshly distilled dimethyl sulphoxide (150 $cm^3$), followed by the nitroenone (**22**) (8.4 g) and n-propyl nitrite (9.35 g).[13] The resulting mixture was stirred under nitrogen in subdued light at room temperature for 6 days. The mixture was poured into a mixture of dichloromethane (250 $cm^3$) and water (250 $cm^3$) and the organic phase was then separated. The aqueous phase was extracted with dichloromethane (3 × 100 $cm^3$), and the combined organic extracts were then washed with water (100 $cm^3$) followed by saturated saline (100 $cm^3$). Evaporation of the dried organic extracts left a dark red oil which was chromatographed on Kieselgel G using chloroform–ether (4:1) as eluant to give the ene dione (3.2 g, 44%) as a pale yellow oil, $\nu_{max.}$(film) 1 710, 1 695, and 1 640 $cm^{-1}$; δ 0.96, 1.16 (d, *J* 7, $CH_3$ diastereoisomers), 1.26 (d, *J* 7, $CHMe$, diastereoisomers), and 1.7—3.3 (m, 9 H); $\delta_c$ (major diastereoisomer) 210.6, 210.3, 188.6, 147.0, 54.7 (d), 46.9 (d), 38.9 (d), 36.7 (dd), 29.2 (q), 27.9 (t), 24.0 (t), 18.2 (q), and 14.5 (q); *m/z* 206.1318 ($C_{13}H_{18}O_2$ requires *M*, 206.1307).

2,8-*Dimethyltricyclo*[5.3.1.0$^{1,5}$]*undecane*-6,9-*dione* (**24**).—A solution of 6-methyl-3-(1-methyl-2-oxopropyl)bicyclo[3.3.0]-oct-1(5)-en-2-one (1.1 g) in dry t-butyl alcohol (50 $cm^3$) was added in one portion to a stirred solution of potassium t-butoxide (from 2.23 g potassium) in dry t-butyl alcohol (160 $cm^3$). The solution was stirred at room temperature under nitrogen for 30 min and then water (300 $cm^3$) was added. This solution was extracted with ether (5 × 100 $cm^3$), and the combined ether extracts were then washed with saturated saline (300 $cm^3$). Evaporation of the dried ether layer left a viscous red oil which was purified by chromatography on silica using chloroform–ether (4:1) as eluant to give the tricyclic dione (0.869 g, 79%) as a yellow oil, $\nu_{max.}$(film) 1 740 and 1 715 $cm^{-1}$; δ 0.86, 1.0 (d, *J* 7, $CH_3$ diastereoisomers), 1.10, 2.3 (d, *J* 7, $CH_3$ diastereoisomers), 1.35—2.90 (m, 12 H); $\delta_c$ (major diastereoisomer) 217.9, 209.8, 56.4 (d), 54.8 (d), 52.3 (t), 49.9, 49.4 (d), 41.3 (d), 33.8 (t), 32.5 (t), 25.7 (t), 16.5 (q), and 12.6 (q); *m/z* 206.1307 ($C_{13}H_{18}O_2$ requires *M*, 206.1307).

The bis-2,4-dinitrophenylhydrazone derivative crystallised from ethanol and had m.p. 140—142 °C (decomp.) (Found: C, 52.9; H, 4.8; N, 19.3. $C_{25}H_{26}N_8O_8$ requires C, 53.0; H, 4.6; N, 19.8%).

2,8-*Dimethyl*-6-*methylenetricyclo*[5.3.1.0$^{1,5}$]*undecan*-9-*one Ethylene Acetal* (**25**).—A mixture of 2,8-dimethyltricyclo-[5.3.1.0$^{1,5}$]undecane-6,9-dione (613 mg), ethylene glycol (1.48 g), triethyl orthoformate (1.48 g), and toluene-*p*-sulphonic acid (5 mg) was stirred at room temperature for 2 h. The mixture was cooled to 25 °C and then diluted with benzene (40 $cm^3$) and washed with water (10 $cm^3$) followed by saturated aqueous sodium hydrogen carbonate (5 $cm^3$). Evaporation of the dried organic extracts left an oil which was chromatographed on Kieselgel G using light petroleum (b.p. 40—60 °C)–ether (4:1) as eluant to give the corresponding six-ring dioxolane (472 mg, 64%) as a pale yellow oil, $\nu_{max.}$(film) 1 740 $cm^{-1}$; δ 0.76—1.05 (m, 2 × $CH_3$), 1.10—3.05 (m, 12 H), 3.80—3.98 (m, $OCH_2CH_2O$).

A mixture of methyltriphenylphosphonium iodide (5.97 g) and potassium t-butoxide (1.51 g) was stirred at 0 °C in dry di-isopropyl ether (25 cm) under nitrogen for 45 min. A solution of the six-ring dioxolane {2,8-dimethyltricyclo[5.3.1.0$^{1,5}$]unde-cane-6,9-dione 9-ethylene acetal} (672 mg) in dry di-isopropyl ether (10 $cm^3$) was then added, and the resulting solution heated under reflux for 22 h. The solution was cooled, then diluted with water (20 $cm^3$), and the organic layer separated. The aqueous layer was extracted with light petroleum (b.p. 40—60 °C) (4 × 25 $cm^3$), and the combined organic extracts were then evaporated to leave an oily solid. The oily solid was triturated with light petroleum (b.p. 40—60 °C) (15 $cm^3$) and the light petroleum was evaporated to leave the crude olefin as a viscous oil. Chromatography on Kieselgel G using light petroleum (b.p. 40—60 °C)–ether (10:1) as eluant gave the pure olefin (566 mg, 85%) as a colourless oil, $\nu_{max.}$(film) 1 660 $cm^{-1}$; δ 0.80—1.00 (m, 2 × $CH_3$), 1.08—2.30 (m, 10 H), 2.34—2.53 (m, 1 H), 2.84—3.11 (m, 1 H), 3.72—4.12 (m, $OCH_2CH_2O$), 4.88 (m, $=CH_2$); $\delta_c$ (major diastereoisomer) 160.2, 111.0, 106.2 (t), 65.4 (t), 63.9 (t), 55.2, 50.9 (d), 49.9 (d), 46.0 (t), 45.35 (d), 42.55 (d), 37.6 (t), 32.6 (t), 31.4 (t), 14.2 (q), and 12.2 (q) (Found: C, 77.65; H, 9.95%; *m/z* 248.1789. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%; *M*, 248.1776).

2,8-*Dimethyl*-6-*methylenetricyclo*[5.3.1.0$^{1,5}$]*undecan*-9-*one*.—A solution of the 9-ethylene acetal (**25**) (10 $cm^3$) and water (0.1 $cm^3$) containing pyridinium toluene-*p*-sulphonate (80 mg, 0.32 mmol) was heated under reflux for 12 h. The mixture was allowed to cool, and the acetone was then removed under reduced pressure. The residue was diluted with ether (25 $cm^3$), and the solution was then washed with saturated sodium hydrogen carbonate (3 $cm^3$) followed by 5% aqueous copper sulphate (5 $cm^3$). Evaporation of the dried ether extracts left the ketone (160 mg, 94%) as a yellow oil, $\nu_{max.}$(film) 1 765 and 1 655 $cm^{-1}$; δ 0.80—1.10 (m, 2 × $CH_3$), 1.22—2.80 (m, 12 H), and 4.88 (m, $=CH_2$); *m/z* 204.1442 ($C_{14}H_{20}O$ requires *M*, 204.1476).

9-*Hydroxy*-2,8-*dimethyl*-6-*methylenetricyclo*[5.3.1.0$^{1,5}$]*un-decane* (**26**).—A solution of 2,8-dimethyl-6-methylenetricyclo-

[5.3.1.0$^{1,5}$]undecan-9-one (160 mg) in dry tetrahydrofuran (0.5 cm$^3$) was added to a solution of L-selectride (2.5 cm$^3$; 1.0 mol) in tetrahydrofuran under nitrogen at −78 °C. The solution was stirred at −70 °C for 2 h, then allowed to warm to room temperature when it was stirred for a further 4 h. The excess of hydride was destroyed by careful addition of wet tetrahydrofuran (0.5 cm$^3$). Aqueous 2M-sodium hydroxide (2 cm$^3$) was added followed by hydrogen peroxide (30%; 4 cm$^3$); the mixture was then stirred for 12 h. The organic phase was separated, and the aqueous layer was then extracted with ether (3 × 5 ml). The combined organic extracts were washed with aqueous sodium metabisulphite (5%; 10 cm$^3$) followed by saturated saline (5 cm$^3$), and then dried and evaporated to leave the alcohol (162 mg, 99%) as a colourless oil, $\nu_{max.}$(film) 3 425 and 1 650 cm$^{-1}$; δ 0.92 (d, *J* 7, $CH_3$), 1.08 (d, *J* 7, $CH_3$), 1.25—2.20 (m, 10 H), 2.36 (m, 1 H), 3.00 (m, 1 H), 3.90 (m, C*H*OH), and 4.92 (m, :$CH_2$); *m/z* 206.1542 ($C_{14}H_{22}O$ requires *M*, 206.1504).

9-*Hydroxy*-2,8-*dimethyltricyclo*[5.3.1.0$^{1,5}$]*undecane*-6-*spiro*-1′-*cyclopropane* (**27**).—A solution of diethylzinc (148 mg, 1.0 cm$^3$; 15% by wt., 1.2 mmol) in toluene (1 cm$^3$) was added to a stirred solution of 9-hydroxy-2,8-dimethyl-6-methylenetricyclo[5.3.1.0$^{1,5}$]undecane (50 mg) in dry toluene (0.5 cm$^3$) at room temperature under nitrogen. The solution was warmed to 50 °C, and a solution of methylene di-iodide (337 mg) in dry toluene (1 cm$^3$) was then slowly added during 90 min. Dry oxygen was passed over the mixture for 30 min, and the mixture was then allowed to cool to room temperature in an atmosphere of nitrogen.[14] A second portion of diethylzinc (74 mg) in toluene (0.5 cm$^3$) was added, and the mixture was again warmed to 50 °C when a further portion of methylene di-iodide (168 mg) in dry toluene (0.5 cm$^3$) was added over 1 h. Oxygen was again passed over the mixture for 30 min, after which the mixture was allowed to cool to room temperature; it was then quenched by addition of dilute hydrochloric acid (5 cm$^3$). The organic phase was separated, and the aqueous layer was then extracted with light petroleum (b.p 40—60 °C) (3 × 5 cm$^3$). The combined organic extracts were dried and evaporated to leave a red oil, which was chromatographed on Kieselgel G using light petroleum (b.p. 40—60 °C)–ether (20:1) as eluant to give the cyclopropyl alcohol (40 mg, 75%) (89% pure by g.l.c.), as a colourless oil, δ 0.87 (d, *J* 7, $CH_3$), 1.08 (d, *J* 7, $CH_3$), 0.7—2.60 (m, 12 H), 3.95 (m, C*H*OH), *m/z* 220.1833 ($C_{15}H_{24}O$ requires *M*, 220.1827).

9-*Hydroxy*-2,6,6,8-*tetramethyltricyclo*[5.3.1.0$^{1,5}$]*undecane* (**28**).—A solution of 9-hydroxy-2,8-dimethyl-6,6-spirocyclopropyltricyclo[5.3.1.0$^{1,5}$]undecane (109 mg) in ethyl acetate (1 cm$^3$) was added in one portion to a mixture of rhodium–platinum oxide catalyst[15] (125 mg) in glacial acetic acid (10 cm$^3$) containing sodium acetate (300 mg) that had been treated with hydrogen for 12 h. The mixture was stirred at room temperature under hydrogen at 1 atm for 6 h during which time 11.6 cm$^3$ of hydrogen was absorbed. The catalyst was filtered off and the filtrate was then evaporated under reduced pressure. The residue was treated with water (8 cm$^3$), and then extracted with hexane (4 × 10 cm$^3$). Evaporation of the dried hexane extracts left a residue which was chromatographed on Kieselgel G using hexane–ether (10:1) as eluant to give the tetramethyl alcohol (52 mg, 47%) (93% pure by g.l.c.), as a colourless viscous oil, $\nu_{max.}$(film) 3 350 cm$^{-1}$; δ 0.84 (d, *J* 6, $CH_3$), 0.91 ($CH_3$), 1.18 (d, *J* 7, $CH_3$), 1.29 ($CH_3$), 1.10—2.60 (m, 13 H), and 4.03 (m, C*H*OH); $\delta_c$ (major diastereoisomer) 70.5 (d), 54.8, 53.3 (d), 52.9 (d), 45.9 (t), 45.0, 43.6 (d), 42.6 (t), 40.2 (d), 33.85 (t), 28.5 (q), 27.55 (q), 24.6 (t), 17.3 (q), and 13.9 (q); *m/z* 222.1985 ($C_{15}H_{26}O$ requires *M*, 222.1984).

2,8-*Dimethyltricyclo*[5.3.1.0$^{1,5}$]*undecane*-6-*spiro*-1′-*cyclopropan*-9-*one Ethylene Acetal* (**29**).—A solution of diethylzinc (124 mg) in toluene (1 cm$^3$) was added to a stirred solution of 2,8-dimethyl-6-methylenetricyclo[5.3.1.0$^{1,5}$]undecan-9-one ethylene acetal (100 mg) in dry toluene (0.5 ml) at room temperature under nitrogen. The solution was warmed to 50 °C, and a solution of methylene di-iodide (308 mg) in dry freshly distilled toluene (1 cm$^3$) was then added slowly over 30 min. Dry oxygen was slowly passed over the reaction mixture for 30 min, after which the oxygen was replaced by nitrogen and the mixture allowed to cool to room temperature. A second portion of diethylzinc (124 mg) in toluene (0.5 cm$^3$) was added, and the mixture was then warmed to 50 °C when a further portion of methylene di-iodide (308 mg) in dry toluene (1 cm$^3$) was slowly added over 30 min. Oxygen was again passed over the mixture for 30 min, after which the mixture was allowed to cool to room temperature where it was quenched by addition of dilute hydrochloric acid (3 ml; 1M). The organic phase was separated, and the aqueous layer was extracted with light petroleum (b.p. 40—60 °C) (2 × 10 cm$^3$). The combined organic solutions were washed with saturated aqueous sodium hydrogen carbonate (5 cm$^3$) and saturated saline (5 cm$^3$), dried, and evaporated to leave the crude dioxolanespirocyclopropane as a pale yellow oil. Chromatography on Kieselgel G using light petroleum (b.p. 40—60 °C)–ether (10:1) as eluant gave the pure dioxolanespirocyclopropane (78 mg, 74%) as a colourless oil, $\nu_{max.}$(film) 3 070 cm$^{-1}$; δ 0.0—0.8 (m, 4 H), 0.95 (d, *J* 7, 2 × $CH_3$), 1.1—2.5 (m, 12 H), 3.7—4.1 (m, $OCH_2CH_2O$); *m/z* 262.1924 ($C_{17}H_{26}O_2$ requires *M*, 262.1933).

2-(2,6,6,8-*Tetramethyltricyclo*[5.3.1.0$^{1,5}$]*undecan*-9-*yloxy*)-*ethanol* (**30**).—A solution of 2,8-dimethyltricyclo-[5.3.1.0$^{1,5}$]undecane-6-spiro-1′-cyclopropan-9-one 9-ethylene acetal (78 mg) in glacial acetic acid (1 cm$^3$) containing sodium acetate (20 mg) was added in one portion to a mixture of platinum oxide (100 mg), sodium acetate (60 mg), and glacial acetic acid (2 cm$^3$) that had been treated with hydrogen until it was saturated (*ca.* 2 h). The mixture was stirred at room temperature under hydrogen at 1 atm for 3 h during which time 11 cm$^3$ of hydrogen was absorbed. The catalyst was removed by filtration, and washed with methanol (3 cm$^3$) and hexane (3 cm$^3$). The filtrate was evaporated, and the residue was then extracted with hexane (3 × 10 cm$^3$). The combined organic solutions were washed with saturated sodium hydrogen carbonate (5 cm$^3$), and then dried and evaporated to leave the tetramethyltricyclo-oxyethanol (67 mg, 85%) as a colourless oil, $\nu_{max.}$(film) 3 375 cm$^{-1}$; δ 0.8—0.94 (m, 2 × $CH_3$), 1.05—1.27 (m, 2 × $CH_3$), 0.9—2.5 (m, 1 H), 3.2—3.9 (m, C*H*O$CH_2$-$CH_2$OH); *m/z* 266.2246 ($C_{17}H_{30}O_2$ requires *M*, 226.2246).

(±)-α-*Cedrene and* (±)-2-epi-*Methyl*-α-*cedrene* (1) *and* (**31a**).—A solution of 9-hydroxy-2,6,6,8-tetramethyltricyclo-[5.3.1.0$^{1,5}$]undecane (48 mg) in dry benzene (0.5 cm$^3$) was added to a stirred solution of phosphorus oxychloride (50 mg, 0.327 mmol) and pyridine (256 mg, 0.324 mmol) in dry benzene (3.5 cm$^3$) under nitrogen at room temperature. The mixture was stirred at 50 °C for 12 h, and then cooled to room temperature and treated with water (5 cm$^3$). The mixture was extracted with hexane (3 × 10 cm$^3$), and the combined hexane extracts were then washed with dilute hydrochloric acid (10 cm$^3$). Evaporation of the dried hexane extracts left an oil which was chromatographed on Kieselgel G impregnated with 17% silver nitrate, using hexane as eluant, to give a mixture of (±)-α-cedrene and (±)-2-*epi*-methyl-α-cedrene (23 mg, 52) (99% pure by g.l.c.) as a colourless oil, $\nu_{max.}$(film) 3 025, 2 960, 2 830, 1 460, 1 380, 1 360, and 800 cm$^{-1}$; δ 0.8—0.90 (m, C$H_3$), 0.92 (C$H_3$), 1.02 (C$H_3$), 1.07—2.55 (m, 14 H), 5.27 (m, :CH); $\delta_c$ (2-*epi*-methylcedrene) 140.8, 119.9 (d), 58.5 (d), 55.0, 53.55 (d), 49.05,

41.8 (d), 41.4 (t), 34.6 (t), 34.3 (t), 27.8 (q), 24.9 (q), 24.8 (q), 24.14 (t), and 13.67 (q); (cedrene) 140.57, 119.24 (d), 59.09 (d), 55.01, 53.9 (d), 48.1, 41.6 (t), 40.70 (d), 38.85 (t), 36.1 (t), 27.6 (q), 25.6 (q), 24.9 (t), 24.8 (q), and 15.4 (q) p.p.m.; *m/z* 204.1840 ($C_{15}H_{24}$ requires *M*, 204.1878).

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