Synthesis Based on Cyclohexadienes. Part 15.[1] Total Synthesis of (±)-Prezizaene, (±)-Prezizanol and (±)-Jinkohol II

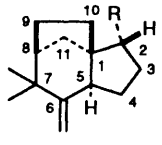
Natesan Selvakumar and G. S. R. Subba Rao*
Department of Organic Chemistry, Indian Institute of Science, Bangalore-560012, India

A new methodology for the synthesis of the complex ring system tricyclo[6.2.1.$0^{1,5}$]undecane, present in the zizaene group of sesquiterpenes, is described. Acid-catalysed rearrangement of the *endo* alcohol **20** afforded the enone **12**, which was transformed stereoselectively into the key intermediate, (±)-norprezizanone **10**. The features of the synthesis are the transformation of a bicyclo[2.2.2]octane framework into a bicyclo[3.2.1]octane system by an acid-catalysed rearrangement and a stereoselective conjugate addition of a methyl group on an α,β-unsaturated keto ester at −100 °C. Norprezizanone was converted into the sesquiterpenes (±)-prezizanol **5** and (±)-prezizaene **4**. The first total synthesis of (±)-jinkohol II **6** is also presented.

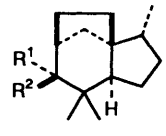
A large number of natural tricyclic sesquiterpenes possess the tricyclo[6.2.1.$0^{1,5}$]undecane skeleton. These include zizaene **1**,[2] khusimol **2**,[3] and zizanoic acid **3**,[4] which were isolated from vetiver oil of various regions, prezizaene **4**,[5] prezizanol **5** and jinkohol II **6**,[6] isolated from vetiver oil and japanese agarwood. It is interesting to note that these unusual tricyclic sesquiterpenes have been found only in vetiver oil and agarwood oil and possess a strong woody note. Two distinct biogenetic schemes have been postulated to rationalize the unusual ring system, substitution pattern and stereochemistry of zizaene and its congeners.[7,8]

Total synthesis of these sesquiterpenes is a challenge to synthetic chemists, since they possess (i) a novel tricyclo[6.2.1.$0^{1,5}$]undecane skeleton, (ii) four one-carbon substituents at C-7 (geminal dimethyl), C-6 and C-2, (iii) a spiro-fused ring system and (iv) a thermodynamically less stable *trans*-fused ethanohydrindane nucleus. Owing to their unique molecular structure, interesting biogenesis and their importance as perfumery products, several syntheses[9] of zizaene and its congeneric relatives have been reported.

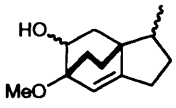
We have earlier reported[10] the preparation of the tricyclic compounds **8** and **9** required for the synthesis of cedrene and



1 R = Me zizaene
2 R = CH_2OH khusimol
3 R = CO_2H zizanoic acid



4 $R^1R^2 = CH_2$ prezizaene
5 R^1 = Me, R^2 = OH prezizanol
6 R^1 = H, $R^2 = CH_2OH$ jinkohol II



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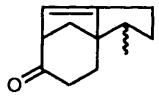

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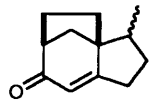

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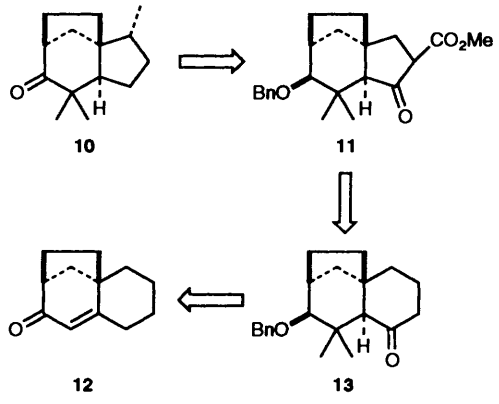
zizaene, by an acid-catalysed rearrangement of the alcohols **7**. Although the compound **9** could be converted[11] into zizaene by appropriate transformations, only an epimeric mixture (C-2) of zizaene was obtained. We now describe an efficient stereocontrolled total synthesis of (±)-prezizaene **4**, (±)-prezizanol **5** and (±)-jinkohol II **6**. A preliminary account of this work has been reported.[12]

Results and Discussion

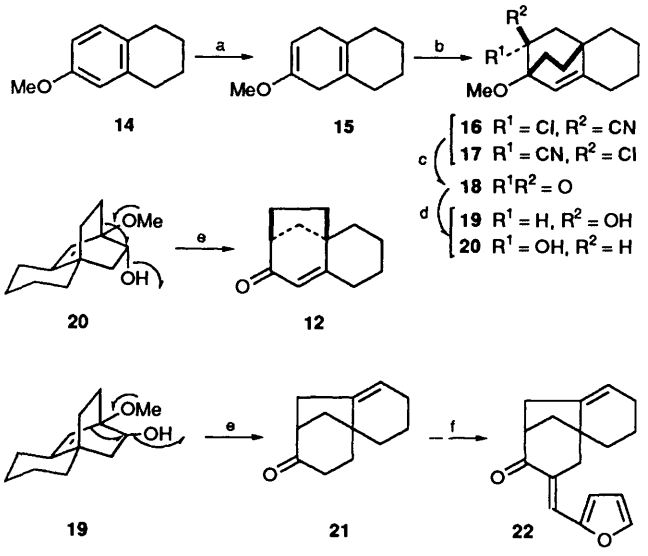
We have chosen norprezizanone **10** as the key intermediate of our synthesis and this can be made from the tricyclic enone **12** through the sequence of reactions outlined in Scheme 1.



10 **11** **12** **13**

Scheme 1

Preparation of the Intermediate **13**.—The starting material for the preparation of the tricyclic enone **12** is the readily available 6-methoxytetralin **14** which was converted into enone **12** as shown in Scheme 2. Birch reduction of compound **14** yielded the dihydro compound **15**, which was subjected to a (4 + 2) cycloaddition with α-chloroacrylonitrile in refluxing benzene for 48 h to afford a mixture of adducts **16** and **17** in 97% yield. Hydrolysis[13] of the mixture of adducts **16** and **17** with aq. KOH in dimethyl sulfoxide (DMSO) at 60 °C for 45 h gave the known tricyclic ketone **18**.[14] Compound **18** on reduction with $NaBH_4$ afforded a 2:1 mixture of the *endo* and the *exo* alcohols **20** and **19** respectively. However, reduction of the ketone **18** with diisobutylaluminium hydride (DIBALH) yielded a 19:1 mixture of *endo* and *exo* alcohols, which was separated by column chromatography. The alcohols were characterized on the basis of their ^1H NMR spectra, wherein the C-9 proton appeared as a doublet of a doublets due to a W-coupling in the spectrum of *exo*-compound **19**, while the *endo*-alcohol **20** displayed a broad doublet for the same proton. The *endo*-alcohol **20**, upon treatment with $BF_3{\cdot}Et_2O$ in refluxing benzene for 20 h, rearranged to the enone **12** in 94% yield. Under identical conditions the *exo*-alcohol **19** afforded the isomeric ketone **21**. The structures of the compounds **12** and **21** were deduced from their spectral data; in particular, the IR spectrum of compound **12** showed the presence of α,β-unsaturated



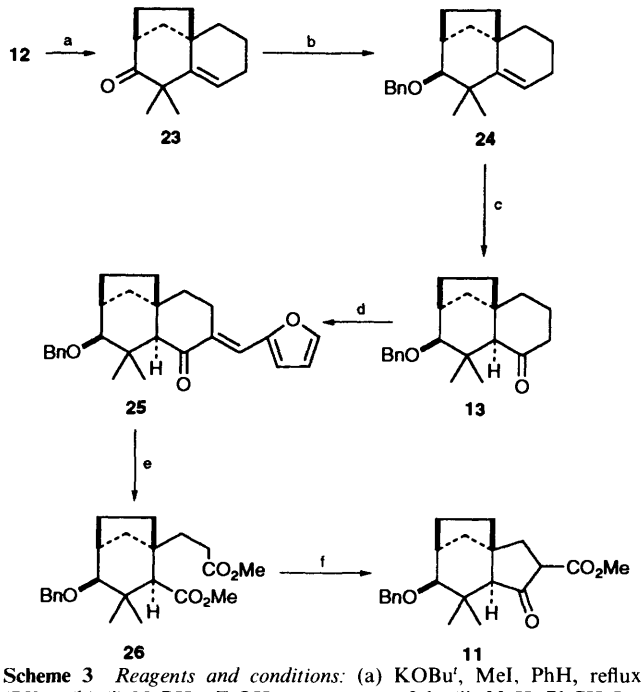
Scheme 2 *Reagents:* (a), Na, liq. NH_3; (b), CH_2=C(Cl)CN, PhH, reflux; (c) KOH, DMSO; (d) DIBALH; (e) BF_3·OEt_2; (f) NaOH, furfural (2-furaldehyde)

carbonyl absorptions at 1610 and 1680 cm^{-1} while that of compound **21** showed an absorption band at 1722 cm^{-1} due to the saturated ketone. In addition the ^1H and ^{13}C NMR spectra of the ketones **12** and **21** were consistent with the proposed structure. Furthermore, compound **21** gave a crystalline furfurylidene derivative, **22**, the structure of which was confirmed by X-ray crystallography. The mechanism of the formation of the ketones **12** and **21** from the *endo* and *exo* alcohols **20** and **19** can be visualized by the concerted migration of the antiperiplanar C–C bonds with respect to the OH group.

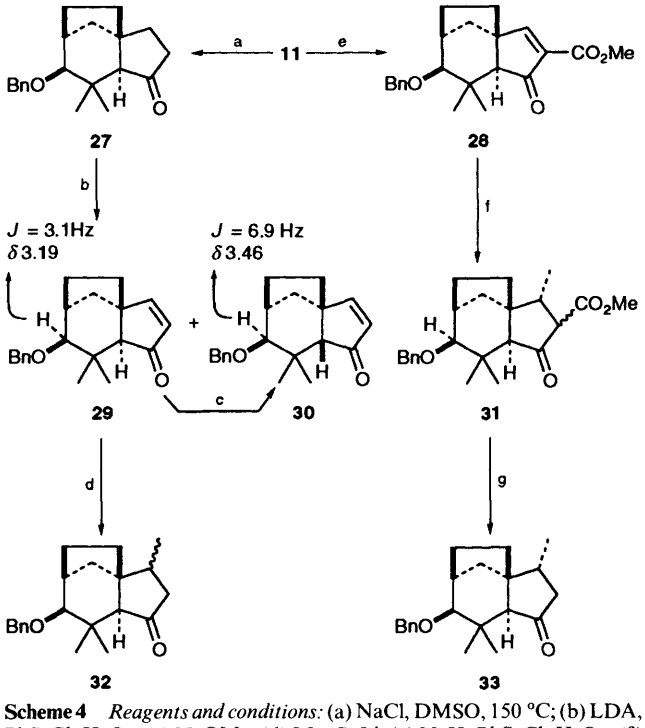
Synthesis of Tricyclic Ketone **33**.—Alkylation [15] of the enone **12** with KOBu^t and MeI in refluxing benzene furnished the ketone **23** in 75% yield (Scheme 3). Reduction of ketone **23** with $NaBH_4$ gave the alcohol, which was converted into its benzyl ether **24** on treatment with sodium hydride and benzyl bromide in excellent yield. Hydroboration of the cyclohexene **24** followed by oxidative work-up resulted in the expected secondary alcohol, which was oxidized with pyridinium chlorochromate (PCC) to the ketone **13** in high yield. The stereochemistry of the hydrogen at the ring junction was assumed to be α, since the addition of BH_3 is expected to take place from the less hindered α side of the molecule, as the β side is crowded by an axial ethano bridge and an axial methyl group. The tricyclic ketone **13** was converted [16] into the dicarboxylic ester **26** by ozonolysis of its furfurylidene derivative **25** followed by oxidative work-up and esterification of the resultant diacid. Dieckmann condensation of the diester **26** with KOBu^t in refluxing benzene afforded the β-keto ester **11**. The ^1H NMR spectrum of compound **11** showed distinct singlets for the two methyl groups and a doublet for the C-7 proton, indicating it to be a single diastereoisomer.

Having achieved the basic tricyclo[6.2.1.$0^{1,5}$]undecane framework, our next task was to introduce an α-methyl group at the C-2 position stereoselectively. This could in principle be achieved by a conjugate addition of Me_2CuLi on the unsaturated ketone **29**, since it was expected that the methyl group would approach from the less hindered α-face of the molecule.

Decarboxylation of the keto ester **11** with NaCl–DMSO [17] at 150 °C afforded the ketone **27** in 88% yield (Scheme 4). Treatment of **27** with lithium diisopropylamide (LDA) and PhSeCl [18] followed by oxidative elimination of the intermediate selenide with aq. H_2O_2 resulted in an inseparable mixture (4:1)



Scheme 3 *Reagents and conditions:* (a) KOBu^t, MeI, PhH, reflux (75%); (b) (i) $NaBH_4$, EtOH, room temp., 2 h; (ii) NaH, $PhCH_2Br$, Bu_4NI, THF, 0 °C to room temp., 24 h (98%); (c) (i) BH_3·THF, THF, 0 °C to room temp., 5 h, then aq. NaOH, 30% H_2O_2; (ii) PCC, CH_2Cl_2, 1 h (77%); (d) NaOH, furfural, EtOH, 0 °C to room temp., 7 h; (e) (i) O_3, EtOAc, −78 °C, then 30% H_2O_2, AcOH, 24 h; (ii) CH_2N_2, Et_2O, 0 °C (70%); (f) KOBu^t, PhH, reflux, 17 h (78%)



Scheme 4 *Reagents and conditions:* (a) NaCl, DMSO, 150 °C; (b) LDA, PhSeCl, H_2O_2; (c) NaOMe; (d) Me_2CuLi; (e) NaH, PhSeCl, H_2O_2; (f) Me_2CuLi, −100 °C; (g) DABCO, *o*-xylene

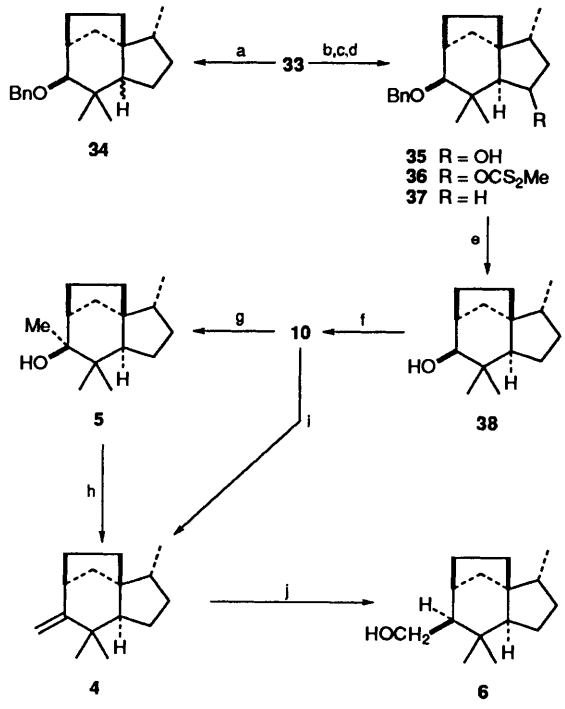
of enones **29** and **30**, as evidenced by the ^1H NMR spectrum, indicating that epimerization of the C-5 proton had taken place. When the spectrum of the above mixture was recorded after the sample had been kept in $CDCl_3$ for 24 h, we observed a rapid conversion of the *trans*-enone **29** into the *cis* compound **30** from an initial (4:1) ratio into a (1:1) mixture. The signal for the C-7 proton in the ^1H NMR spectrum was diagnostic for estimating the ratio of this mixture. In the *trans* compound the C-7 proton

appeared at δ 3.19 (J 3.1 Hz), while it appeared at δ 3.46 (J 6.9 Hz) for the *cis* compound. The peak positions were assigned for these epimers on the basis of the observed coupling constants. Examination of molecular models indicated that the 6-membered ring in the *trans* compound assumes a chair conformation, while in the *cis* compound it exists in a boat conformation. The dihedral angle of the proton on C-7 with C-8 changes from 60° for the *trans* compound to 40° for the *cis* compound and hence there is an increase in the coupling constant. This (1 : 1) mixture on being left in the NMR tube in $CDCl_3$ became a (1 : 4) mixture after 6 days. Furthermore, with a catalytic amount of NaOMe in refluxing methanol this mixture was completely converted into the *cis* compound **30**.

Owing to this unexpected isomerization at the ring junction, the enone **29** was subjected to a 1,4-addition reaction immediately after its preparation. Thus, reaction of compound **27** with LDA, PhSeCl and H_2O_2 resulted in an oil, which was allowed to react with Me_2CuLi[19] at 0 °C, to give the ketone **32**, whose ^1H NMR spectrum showed a pair of doublets for the C-2 methyl group, indicating the absence of selectivity during the 1,4-addition reaction. Owing to the poor selectivity during the addition of Me_2CuLi on the enone **29** at 0 °C, we anticipated that the addition might take place stereoselectively at low temperature on the enone ester **28**. Treatment of the keto ester **11** with NaH and PhSeCl gave the selenide, which was oxidized with H_2O_2 to yield the unstable enone ester **28**. Reaction of compound **28** with Me_2CuLi in dry diethyl ether at −100 °C, afforded the β-keto ester **31** in 88% yield as an unstable oil. The β-keto ester **31** was found to be a mixture of two diastereoisomers from its ^1H NMR spectrum, as it displayed two peaks for the methoxycarbonyl group, presumably due to epimers at the centre bearing the methoxycarbonyl group. This was confirmed by decarboxylation of the mixture of β-keto esters to give a single isomer of ketone **33**, whose ^1H NMR spectrum showed a lone doublet for the C-2 methyl group, indicating that a stereoselective conjugate addition of methyl group had taken place. It is of interest to note that the NaCl–DMSO decarboxylation procedure on the keto ester **31** failed to give good yields of the product **33**, although decarboxylation of the keto ester **11** afforded the ketone **27** in 88% yield. In search for a mild procedure for the decarboxylation of keto ester **31**, 1,4-diazabicyclo[2.2.2] octane (DABCO) in *o*-xylene[20] at 85 °C proved to be superior giving the ketone **33** in 84% yield.

Synthesis of (±)-*Norprezizanone* **10**.—Having achieved the stereoselective 1,4-addition, our next task was the reduction of compound **33** to ketone **10**. Attempted Wolff–Kishner reduction resulted in an epimeric mixture of the tricyclic compound **34**, wherein the C-5 proton isomerized under the reaction conditions (Scheme 5). Even the modified Wolff–Kishner reduction[21] with the mild base K_2CO_3 also led to isomerization. This problem could be circumvented by the use of Barton's deoxygenation protocol[22] on the alcohol **35**, obtained from the ketone **33**.

Reduction of the ketone **33** with $NaBH_4$, $LiAlH_4$ and BH_3 resulted in partial reduction to the alcohol **35**. However, with excess of DIBALH, the ketone **33** was reduced to the alcohol **35** in 93% yield. The xanthate **36** was obtained by treatment of the alcohol **35** with excess of NaH and successive quenches with CS_2 and MeI. Reduction of the xanthate **36** with tributyltin hydride (TBTH) in refluxing benzene resulted in only the recovery of the starting material. In refluxing toluene, a partial elimination of the xanthate was observed after 12 h. However, when the reduction was carried out by successive addition of TBTH twice with an interval of 3 h, the benzyl ether **37** was obtained in excellent yield. The ether **37**, thus obtained as a single isomer, was hydrogenolysed to the alcohol **38**, which was oxidized with pyridinium dichromate (PDC) to afford (±)-norprezizanone **10** in quantitative yield. The IR and ^1H NMR spectra of compound **10** were identical with those of an authentic sample provided by Professor Kenji Mori.



Scheme 5 *Reagents and conditions:* (a) Wolff–Kishner reaction; (b) DIBALH, THF, −78 °C to room temp. (93%); (c) NaH, CS_2, MeI, THF, reflux (98%); (d) TBTH, AIBN, PhMe, reflux (91%); (e) H_2, 10% Pd/C, EtOH, 2 h (100%); (f) PDC, CH_2Cl_2, 2 h (100%); (g) MeLi, Et_2O, −78 °C to room temp. (88%); (h) MsCl, Et_3N, CH_2Cl_2, 0 °C (76%); (i) Wittig reaction (78%); (j) BH_3-THF, THF, 0 °C then 30% H_2O_2 (72%)

The synthesis of prezizaene and prezizanol has been reported by three different groups[9d,e,h] and all of them involve norprezizanone **10** as the common intermediate. In all the syntheses either a mixture of products was formed which required HPLC separation or a large number of steps were involved to obtain norprezizanone. Our synthesis of norprezizanone was accomplished in 13 steps from 6-methoxytetralin **14**, with an overall yield of 10.6%.

Synthesis of Sesquiterpenes **4**, **5** *and* **6**.—Mori and coworkers[9h] have converted norprezizanone **10** into prezizanol and prezizaene. By application of the same sequence of reactions, compound **10** afforded (±)-prezizanol **5** with MeLi. Dehydration of alcohol **5** gave (±)-prezizaene **4**.

Wittig olefination of compound **10** also directly yielded (±)-prezizaene **4**, which upon hydroboration followed by oxidation gave (±)-jinkohol II **6** in good yield. The spectral data of compound **6** were identical[6] with those reported, thus completing the first total synthesis of this compound. Since prezizaene **4** has been converted[5] into zizaene **1**, a formal total synthesis of zizaene has also been achieved.

In conclusion, we describe a novel and efficient method of total synthesis of the sesquiterpenes prezizaene **4**, prezizanol **5** and jinkohol II **6**, which contain the complex tricyclo-[6.2.1.$0^{1,5}$]undecane ring system, from readily available dihydroanisole derivatives.

Experimental[23]

M.p.s (measured on Mettler FP1) and b.p.s are uncorrected. IR spectra were recorded on either neat samples or solutions in $CHCl_3$. ^1H NMR and ^{13}C NMR spectra were recorded on

solutions in $CDCl_3$ with $SiMe_4$ as internal standard. Chemical shifts are reported in δ-units, and J-values are in Hz. The usual work-up involved dilution of the reaction mixture with water, extraction with diethyl ether, washing of the organic extract with water and brine, followed by drying over Na_2SO_4, and evaporation at aspirator pressure. Column chromatography was performed on silica gel (60–120 mesh) by elution with a light petroleum (boiling range 60–80 °C)–ethyl acetate mixture (9:1). Liquid ammonia was distilled over sodium amide. Sodium hydride was 60% in oil, and was used after washing with light petroleum.

9-Chloro-8-methoxytricyclo[6.2.2.0^{1,6}]*dodec-6-ene-9-carbonitrile* **16** *and* **17**.—A solution of 6-methoxytetralin **14** (24.3 g, 0.15 mol) in dry tetrahydrofuran (THF) (15 cm^3)–*tert*-butyl alcohol (30 cm^3) was added to stirred, distilled ammonia (500 cm^3). Sodium (6.9 g, 0.3 mol) was added and the resulting blue solution was stirred for 2.5 h. Solid NH_4Cl was added until the blue colour was discharged. NH_3 was allowed to evaporate, and the residue was worked up with light petroleum to give the diene **15** as a liquid, ν_{max}/cm^{-1} 1670, 1450 and 1220.

The diene **15**, 2-chloroacrylonitrile (35.5 cm^3, 0.45 mol) and hydroquinone (10 mg) were refluxed in dry, stirred benzene (120 cm^3) for 48 h. The reaction mixture was concentrated under reduced pressure and distilled at reduced pressure (b.p. 132–135 °C at 0.1 mmHg) to give the adducts **16** and **17** as a viscous oil (36.6 g, 97%); ν_{max}/cm^{-1} 2225; δ_H(60 MHz) 1.30–2.40 (14 H, m), 3.52 (3 H, s, OMe) and 5.83 and 6.00 (1 H, two br s, olefinic) (Found: C, 66.7; H, 7.2. $C_{14}H_{18}ClNO$ requires C, 66.8; H, 7.2%).

8-Methoxytricyclo[6.2.2.0^{1,6}]*dodec-6-en-9-one* **18**.—The adducts **16** and **17** (25.1 g, 0.10 mol) and 20% aq. KOH (56 cm^3, 0.20 mol) were stirred in DMSO (110 cm^3) at 60 °C for 40 h. The reaction mixture obtained after the usual work-up furnished by chromatography a yellow oil, which was distilled under reduced pressure to provide the tricyclic ketone **18** as an oil, b.p. 105 °C (0.1 mmHg); ν_{max}/cm^{-1} 1733; δ_H(90 MHz) 1.50–2.40 (14 H, m), 3.52 (3 H, s, OMe) and 5.82 (1 H, br s, olefinic); δ_C(50 MHz) 18.30, 20.44, 25.98, 27.03, 30.49, 31.24, 38.48, 45.16, 52.44, 84.20, 119.39, 148.57 and 209.17 (Found: C, 75.3; H, 9.2%; M$^+$, 206.1315. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.8%; M, 206.1307).

endo-*8-Methoxytricyclo*[6.2.2.0^{1,6}]*dodec-6-en-9-ol* **20**.—A 1.2 mol dm^{-3} solution of DIBALH (45.8 cm^3, 55 mmol) in toluene was added to a solution of ketone **18** (10.30 g, 50 mmol) in dry THF (160 cm^3) dropwise at −78 °C under argon. The mixture was stirred at −78 °C for 30 min, warmed to room temp. over a period of 15 min, and quenched with methanol (20 cm^3). The resulting solution was treated with saturated aq. sodium potassium tartrate (500 cm^3) to get a clear solution, which after the usual work-up showed two closely moving spots on TLC (R_f-values 0.35 and 0.30; 20% EtOAc in light petroleum). The mixture was chromatographed; the less polar component was the *exo*-alcohol **19** (469 mg), ν_{max}/cm^{-1} 3440; δ_H(90 MHz) 1.30–2.60 (15 H, m), 3.22 (3 H, s, OMe), 3.86 (1 H, dd, J 2.5 and 10.8, C*H*OH) and 5.40 (1 H, br s, olefinic). The more polar component was the *endo*-alcohol **20** (8.91 g, 90% overall yield, *exo*:*endo* ratio 5:95); ν_{max}/cm^{-1} 3440; δ_H(90 MHz) 1.20–2.40 (15 H, m), 3.40 (3 H, s, OMe), 3.92 (1 H, d, J 9, C*H*OH) and 5.72 (1 H, br s, olefinic) (Found: C, 74.85; H, 9.6. $C_{13}H_{20}O_2$ requires C, 75.0; H, 9.6%).

Tricyclo[7.2.1.0^{1,6}]*dodec-6-en-8-one* **12**.—A solution of *endo*-alcohol **20** (6.24 g, 30 mmol) in dry benzene (150 cm^3) was heated under reflux with BF_3·Et_2O (1 cm^3) for 20 h. The reaction mixture was diluted with benzene (300 cm^3), washed successively with aq. $NaHCO_3$, water, and brine, and was dried. Evaporation of the solvent followed by purification by chromatography afforded the enone **12** as an oil (4.96 g, 94%), ν_{max}/cm^{-1} 1680 and 1610; δ_H(90 MHz) 1.40–2.50 (14 H, m), 2.78–2.9 (1 H, m, 9-H) and 5.66 (1 H, br s, olefinic); δ_C(22.5 MHz) 22.58 (t), 24.27 (t), 26.74 (t), 30.64 (t), 34.54 (t), 35.19 (t), 45.34 (t), 46.25 (s), 48.98 (d), 122.07 (d), 170.32 (s) and 202.71 (s) (Found: C, 81.7; H, 9.2%; M$^+$, 176.1210. $C_{12}H_{16}O$ requires C, 81.8; H, 9.15%; M, 176.1201).

Tricyclo[6.3.1.0^{1,6}]*dodec-5-en-9-one* **21**.—When the *exo*-alcohol **19** (312 mg, 1.5 mmol) in dry benzene was refluxed with BF_3·Et_2O (cat.) as described above, the ketone **21** (227 mg, 86%) was obtained as an oil, ν_{max}/cm^{-1} 1722; δ_H(90 MHz) 1.20–2.80 (15 H, m) and 5.60 (1 H, br s, olefinic); δ_C(22.5 MHz) 18.28 (t), 24.79 (t), 32.59 (t), 34.15 (t), 34.41 (t), 35.71 (t), 41.18 (s), 44.56 (t), 48.20 (d), 120.12 (d), 141.32 (s) and 212.72 (s) (Found: M$^+$, 176.1215).

7,7-Dimethyltricyclo[7.2.1.0^{1,6}]*dodec-5-en-8-one* **23**.—To a slurry of KOBu^t in *tert*-butyl alcohol, prepared from potassium (2.93 g, 75 mmol) and dry *tert*-butyl alcohol (40 cm^3), was added a solution of the enone **12** (4.40 g, 25 mmol) in dry benzene (100 cm^3). After stirring of the mixture for 30 min, MeI (15.6 cm^3, 0.25 mol) was added rapidly and the mixture was refluxed for 2 h before being brought to room temp. and a further quantity of MeI (4 cm^3) was added. The resulting solution was stirred for 6 h and the usual work-up followed by chromatographic purification afforded the ketone **23** (3.83 g, 75%), which crystallized upon refrigeration. An analytical sample was obtained by bulb-to-bulb distillation (125 °C, bath temperature; 0.1 mmHg), m.p. 47 °C; ν_{max}/cm^{-1} 1712 and 1672; δ_H(90 MHz) 1.28 (6 H, s, Me), 1.40–2.20 (12 H, m), 2.86 (1 H, m, 9-H) and 5.52 (1 H, t, J 4, olefinic); δ_C(22.5 MHz) 20.23 (q), 25.57 (t), 27.91 (t), 30.25 (t), 31.81 (q), 36.23 (t), 37.27 (t), 39.74 (t), 44.17 (s), 46.51 (s), 50.54 (d), 119.21 (d), 148.99 (s) and 217.80 (s) (Found: C, 82.4; H, 10.0%; M$^+$, 204.1529. $C_{14}H_{20}O$ requires C, 82.3; H, 9.9%; M, 204.1514).

8-Benzyloxy-7,7-dimethyltricyclo[7.2.1.0^{1,6}]*dodec-5-ene* **24**.—To a solution of ketone **23** (3.06 g, 15 mmol) in ethanol (100 cm^3) was added $NaBH_4$ (284 mg, 7.5 mmol) at room temp. After being stirred for 2 h, the reaction mixture was concentrated under reduced pressure and was poured into aq. NH_4Cl (500 cm^3). The usual work-up followed by chromatography afforded the corresponding alcohol, ν_{max}/cm^{-1} 3355.

A mixture of this alcohol and benzyl bromide (1.87 cm^3, 15.7 mmol) in dry THF (30 cm^3) was added to a suspension of NaH (660 mg, 16.5 mmol) and tetrabutylammonium iodide (cat.) in dry THF (90 cm^3) at 0 °C dropwise under argon. The reaction mixture was brought to room temp. during 1 h and was stirred for 24 h at ambient temperature. The usual work-up, followed by filtration through a column of silica gel, yielded the ether **24** as an oil (4.35 g, 98%). An analytical sample was obtained by bulb-to-bulb distillation (180 °C, bath temperature; 0.1 mmHg), ν_{max}/cm^{-1} 1452, 732 and 696; δ_H(90 MHz) 1.14 (3 H, s, Me), 1.18 (3 H, s, Me), 1.26–2.10 (12 H, m), 2.44–2.64 (1 H, m, 9-H), 3.18 (1 H, d, J 3, 8-H), 4.38 and 4.72 (2 H, AB_q, J 12, OCH_2Ph), 5.44 (1 H, t, J 4, olefinic) and 7.28–7.44 (5 H, m, Ph); δ_C(22.5 MHz) 21.23 (t), 23.47 (q), 26.69 (t), 27.96 (q), 31.17 (d), 37.90 (t), 40.63 (s), 43.56 (t), 44.73 (s), 71.15 (t), 88.02 (d), 117.77 (d), 127.22 and 128.30 (2 d, 5 aromatic carbons), 139.80 (s) and 151.70 (s) (Found: C, 84.6; H, 9.4%; M$^+$, 296.2130. $C_{21}H_{28}O$ requires C, 85.1; H, 9.5%; M, 296.2140).

8-Benzyloxy-7,7-dimethyltricyclo[7.2.1.0^{1,6}]*dodecan-5-one* **13**.—To a solution of compound **24** (3.55 g, 12 mmol) in dry THF (100 cm^3) was added 1.2 mol dm^{-3} BH_3·THF (30 cm^3, 36 mmol) dropwise at 0 °C under argon. The resultant mixture was

brought to room temp. during 1 h and was stirred for a further 5 h at ambient temperature before being carefully quenched with drops of water, and 20% aq. NaOH (3.6 cm^3, 18 mmol) and 30% aq. H_2O_2 (4.1 cm^3, 36 mmol) were added with occasional cooling. After stirring of the mixture for 3 h, the usual work-up and chromatography afforded the C-5 alcohol (2.90 g, 77%), ν_{max}/cm^{-1} 3418.

The alcohol (2.83 g, 9 mmol), PCC (2.44 g, 11.3 mmol) and silica gel (3 g) were stirred in dry CH_2Cl_2 (60 cm^3) at room temp. for 1 h. The solvent was removed, and the resultant powder was dissolved in diethyl ether and filtered through a pad of Celite. The filtrate was evaporated, and the residue was passed through a column of silica gel to give the ketone **13** as a viscous oil (2.81 g, 100%), which crystallized upon storage. An analytical sample was obtained by recrystallization in light petroleum, m.p. 72 °C; ν_{max}/cm^{-1} 1704; δ_H(90 MHz) 1.18 (3 H, s, Me), 1.34 (3 H, s, Me), 1.52–2.56 (14 H, m), 3.04 (1 H, d, *J* 3, 8-H), 4.42 and 4.70 (2 H, AB_q, *J* 12, OCH_2Ph) and 7.28–7.44 (5 H, m, Ph); δ_C(22.5 MHz) 16.08 (q), 22.84 (t), 24.79 (t), 31.68 (q), 32.59 (d), 37.53 (s), 38.57 (t), 43.00 (t), 46.51 (t), 48.46 (s), 64.71 (d), 71.22 (t), 88.25 (d), 127.01 and 128.18 (2 d, 5 aromatic carbons), 139.37 (s) and 209.21 (s) (Found: C, 80.5; H, 9.1%; M^+, 312.2087. $C_{21}H_{28}O_2$ requires C, 80.7; H, 9.0%; M, 312.2090).

Methyl 4-Benzyloxy-1-[2-(methoxycarbonyl)ethyl]-3,3-dimethylbicyclo[3.2.1]octane-2-carboxylate **26**.—To a solution of the ketone **13** (2.25 g, 7.2 mmol) in ethanol (60 cm^3) at 0 °C under argon was added 20% aq. NaOH (1.44 cm^3, 7.2 mmol) dropwise, and the resultant solution was stirred for 30 min. A solution of freshly distilled furfuraldehyde (0.6 cm^3, 7.2 mmol) in ethanol (1 cm^3) was added, and the reaction mixture was warmed to room temp. and stirred for 7 h. Usual work-up gave the condensation product **25** as a yellow solid which was used directly in the next step without purification.

A solution of enone **25** in ethyl acetate (80 cm^3) was ozonized at −78 °C until TLC indicated the disappearance of starting material. The solvent was removed at 10 °C under reduced pressure, and the resultant gum was treated with acetic acid (40 cm^3), 30% aq. H_2O_2 (10 cm^3) and dil. H_2SO_4 (1 cm^3). The mixture was stirred overnight and concentrated at 40 °C under reduced pressure. The residue was dissolved in diethyl ether (400 cm^3), and washed with brine, and the solvent was evaporated to give a solid.

A solution of the above dicarboxylic acid in dry diethyl ether (200 cm^3) was esterified with ethereal diazomethane. The solvent was evaporated off and the residue was purified on a column to obtain the diester **26** as a solid (1.96 g, 70%), which was recrystallized from ethyl acetate, m.p. 67 °C; ν_{max}/cm^{-1} 1737; δ_H(90 MHz) 1.08 (3 H, s, Me), 1.10 (3 H, s, Me), 1.20–2.60 (12 H, m), 3.14 (1 H, d, *J* 3, 4-H), 3.68 (6 H, s, CO_2Me), 4.36 and 4.68 (2 H, AB_q, *J* 12, OCH_2Ph) and 7.32 (5 H, br s, Ph); δ_C(22.5 MHz) 19.06 (q), 24.01 (q), 29.86 (t), 30.51 (t), 33.11 (t), 33.37 (t), 37.79 (t), 41.57 (t), 45.73 (s), 50.54 (q), 51.19 (q), 58.99 (d), 71.22 (t), 86.82 (d), 127.01 and 127.92 (2 d, 5 aromatic carbons), 138.98 (s), 172.53 (s) and 173.70 (s) (Found: C, 71.1; H, 8.4. $C_{23}H_{32}O_5$ requires C, 71.1; H, 8.3%).

Methyl 7-Benzyloxy-6,6-dimethyl-4-oxotricyclo[6.2.1.0^{1,5}]undecane-3-carboxylate **11**.—To a freshly prepared solution of KOBu^t in *tert*-butyl alcohol prepared from potassium (211 mg, 5.4 mmol) and dry *tert*-butyl alcohol (7 cm^3), was added a solution of the diester **26** (1.75 g, 4.5 mmol) in dry benzene (80 cm^3) at room temp. under argon. The solution was refluxed for 6 h and then was allowed to cool to room temp. The reaction mixture was added to aq. NH_4Cl and extracted with ethyl acetate (4 × 200 cm^3). The usual work-up followed by chromatography afforded the β-keto ester **11** as an unstable oil (1.25 g, 78%), ν_{max}/cm^{-1} 1755 and 1731; δ_H(200 MHz) 1.13 (3 H, s, Me), 1.19 (3 H, s, Me), 1.25–2.55 (10 H, m), 3.17 (1 H, d, *J* 3, 7-H), 3.26 (1 H, dd, *J* 8.3 and 11.7, 3-H), 3.74 (3 H, s, CO_2Me), 4.42 and 4.69 (2 H, AB_q, *J* 12, OCH_2Ph) and 7.28–7.35 (5 H, m, Ph); δ_C(67.89 MHz) 16.53 (q), 24.66 (t), 32.48 (q), 33.04 (t), 36.14 (t), 38.60 (s), 39.92 (d), 43.36 (t), 47.87 (s), 53.00 (q), 55.99 (d), 67.36 (d), 72.71 (t), 89.05 (d), 128.02 and 128.94 (2 d, 5 aromatic carbons), 139.97 (s), 170.85 (s) and 208.73 (s) (Found: M^+, 356.1981. $C_{22}H_{28}O_4$ requires M, 356.1988).

7-Benzyloxy-6,6-dimethyltricyclo[6.2.1.0^{1,5}]undecan-4-one **27**.—A mixture of the β-keto ester **11** (356 mg, 1 mmol), NaCl (64 mg, 1.1 mmol), water (0.04 cm^3) and DMSO (5 cm^3) was heated to 150 °C for 8 h. The reaction mixture was cooled, and the usual work-up followed by chromatography yielded the ketone **27** (262 mg, 88%), ν_{max}/cm^{-1} 1734; δ_H(90 MHz) 1.18 (3 H, s, Me), 1.24 (3 H, s, Me), 1.36–2.64 (12 H, m), 3.18 (1 H, d, *J* 3, 7-H), 4.44 and 4.72 (2 H, AB_q, *J* 12, OCH_2Ph) and 7.36 (5 H, br s, Ph); δ_C(100 MHz) 15.90, 23.91, 31.20, 31.26, 32.50, 37.69, 38.52, 39.13, 42.95, 49.53, 66.68, 71.80, 88.51, 127.25 and 128.20 (5 aromatic carbons), 139.31 and 216.38 (Found: M^+, 298.1958. $C_{20}H_{26}O_2$ requires M, 298.1933).

7-Benzyloxy-6,6-dimethyltricyclo[6.2.1.0^{1,5}]undec-2-en-4-one **29** *and* **30**.—A 1.6 mol dm^{-3} solution of BuLi in hexane (0.63 cm^3, 1 mmol) was added to a solution of diisopropylamine (0.14 cm^3, 1 mmol) in THF (1 cm^3) at −78 °C under argon. After this mixture had been stirred for 30 min, a solution of the ketone **27** (268 mg, 0.9 mmol) in THF (2 cm^3) was added dropwise. The resultant mixture was stirred for 1 h, and a solution of PhSeCl (192 mg, 1 mmol) in THF (1 cm^3) was added at once. After being stirred for 15 min, the cold reaction mixture was poured into aq. NH_4Cl and worked up to afford the corresponding seleno compound.

To a mixture of the above crude seleno compound in CH_2Cl_2 (4 cm^3) was added 30% aq. H_2O_2 (0.26 cm^3, 2.25 mmol) at 5 °C. After being stirred for 30 min, the reaction mixture was diluted with CH_2Cl_2, washed with water, and dried. The residue obtained after chromatography afforded the enones **29** and **30** (165 mg, 62%), ν_{max}/cm^{-1} 1713.

Enone **29**: δ_H(200 MHz) 1.19 (3 H, s, Me), 1.26 (3 H, s, Me), 1.34–2.52 (8 H, m), 3.19 (1 H, d, *J* 3.1, 7-H), 4.44 and 4.70 (2 H, AB_q, *J* 12, OCH_2Ph), 5.94 (1 H, d, *J* 5.7, 3-H), 7.28–7.36 (5 H, m, Ph) and 7.42 (1 H, d, *J* 5.7, 2-H).

Enone **30**: δ_H(200 MHz) 1.01 (3 H, s, Me), 1.32–2.60 (8 H, m), 1.39 (3 H, s, Me), 3.46 (1 H, d, *J* 6.9, 7-H), 4.37 and 4.55 (2 H, AB_q, *J* 12, OCH_2Ph), 6.09 (1 H, d, *J* 5.7, 3-H), 7.26–7.34 (5 H, m, Ph) and 7.51 (1 H, d, *J* 5.7, 2-H) (Found: M^+, 296.1790. $C_{20}H_{24}O_2$ requires M, 296.1776).

Isomerization of trans-*Enone* **29** *to* cis-*Enone* **30**.—To a mixture of enones **29** and **30** (27 mg, 0.1 mmol) in dry benzene (3 cm^3) was added NaOMe (cat.) and the solution was refluxed for 4 h. The resultant mixture was cooled, poured into ice-cold 1 mol dm^{-3} HCl, and worked up as usual. The enone **30** was obtained after filtration through a short column of silica gel (23 mg, 86%).

7-Benzyloxy-2,6,6-trimethyltricyclo[6.2.1.0^{1,5}]undecan-4-one **33**.—A solution of β-keto ester **11** (445 mg, 1.25 mmol) in dry THF (5 cm^3) was added to a suspension of NaH (75 mg, 1.88 mmol) in dry THF (10 cm^3) over a period of 10 min at 0 °C under argon. After the mixture had been stirred for 15 min, a solution of PhSeCl (264 mg, 1.38 mmol) in THF (5 cm^3) was added rapidly, and the mixture was stirred for an additional 15 min. The cold reaction mixture was poured into an ice-cold mixture of diethyl ether (50 cm^3) and saturated aq. $NaHCO_3$ (50 cm^3), and was worked up as usual to obtain the selenide as a pale orange solid.

To a mixture of this crude selenide in CH_2Cl_2 (10 cm^3) was added 30% aq. H_2O_2 (0.27 cm^3, 2.4 mmol) dropwise at 5 °C. After being stirred at 5 °C for 10 min, the reaction mixture was warmed to room temp. over a period of 15 min. The resultant product mixture was diluted with CH_2Cl_2, washed with water, and dried. The residue was chromatographed to afford the unsaturated keto ester **28**, which was immediately used in the next step (412 mg, 93%), ν_{max}/cm^{-1} 1752 and 1725.

To a suspension of CuI (221 mg, 1.16 mmol) in dry diethyl ether (10 cm^3) at 0 °C under argon was added 0.87 mol dm^{-3} MeLi (2.65 cm^3, 2.32 mmol) in diethyl ether. The resultant solution of Me_2CuLi was stirred for 5 min and cooled to −100 °C. A solution of the unsaturated keto ester **28** (411 mg, 1.16 mmol) in dry diethyl ether (10 cm^3) was added slowly, and the reaction mixture, after being stirred for 30 min, was quenched with aq. NH_4Cl. The usual work-up followed by chromatography furnished the β-keto ester **31** as an oil. (378 mg, 88%), ν_{max}/cm^{-1} 1755 and 1731; δ_H(200 MHz) 1.02 (3 H, d, *J* 7.3, 2-Me), 1.13, 1.17, 1.18 and 1.23 (6 H, 4 s, Me), 1.35–2.56 (9 H, m), 2.96 (dd, *J* 2.1 and 1.4) and 3.42 (d, *J* 8.6) (together 1 H, 3-H), 3.10 (1 H, 2 dd, 2-H), 3.71 and 3.73 (3 H, 2 s, CO_2Me), 4.55 (2 H, AB_q, *J* 12, OCH_2Ph) and 7.36 (5 H, m, Ph).

A mixture of the β-keto ester **31** (370 mg, 1 mmol), DABCO (1.12 g, 10 mmol) and *o*-xylene (5 cm^3) was heated to 85 °C under argon for 7 h. The reaction mixture was cooled, acidified with 0.5 mol dm^{-3} HCl and worked up as usual. The ketone **33** was obtained as a crystalline solid after purification by chromatography (262 mg, 84%), and was recrystallized from light petroleum, m.p. 126 °C; ν_{max}/cm^{-1} 1740; δ_H(200 MHz) 1.04 (3 H, d, *J* 7.2, 2-Me), 1.14 (3 H, s, Me), 1.21 (3 H, s, Me), 1.26–2.55 (11 H, m), 3.11 (1 H, dd, *J* 3.0 and 1.1, 7-H), 4.42 and 4.70 (2 H, AB_q, *J* 12, OCH_2Ph) and 7.29–7.37 (5 H, m, Ph); δ_C(100 MHz) 16.09, 17.66, 23.68, 32.58, 34.03, 35.66, 37.41, 38.89, 39.14, 46.57, 52.11, 60.95, 71.60, 88.19, 127.10 and 128.03 (5 aromatic carbons), 139.13 and 216.30 (Found: C, 80.7; H, 9.4%; M^+, 312.2090. $C_{21}H_{28}O_2$ requires C, 80.7; H, 9.0%, M, 312.2090).

7-Benzyloxy-2,6,6-trimethyltricyclo[6.2.1.$0^{1,5}$]*undecane* **37**.—A 1 mol dm^{-3} solution of DIBALH in hexane (0.90 cm^3, 0.90 mmol) was added to a mixture of ketone **33** (140 mg, 0.45 mmol) in dry THF (5 cm^3) under argon at −78 °C. The mixture was stirred for 1 h and a further quantity of DIBALH (0.90 cm^3, 0.90 mmol) was added. After being stirred for 1 h at −78 °C, the reaction mixture was left at room temp. for another 1 h before being quenched with MeOH (1 cm^3) and poured into saturated aq. sodium potassium tartrate. The usual work-up and chromatography afforded the alcohol **35** (131 mg, 93% yield), ν_{max}/cm^{-1} 3360; δ_H(90 MHz) 0.92 (3 H, d, *J* 7.2, 2-Me), 1.10 (3 H, s, Me), 1.32 (3 H, s, Me), 1.36–2.60 (12 H, m), 3.10 (1 H, d, *J* 3, 7-H), 4.32–4.78 (3 H, m, OCH_2Ph and 4-H) and 7.22–7.44 (5 H, m, Ph); δ_C(22.5 MHz) 18.10 (q), 18.69 (q), 23.18 (t), 33.32 (q), 36.73 (t), 39.01 (d), 39.36 (d), 40.73 (s), 45.70 (t), 51.55 (s), 60.04 (d), 71.54 (t), 73.10 (d), 88.22 (d), 127.22 and 128.10 (2 d, 5 aromatic carbons) and 139.51 (s).

To a suspension of NaH (64 mg, 1.6 mmol) and imidazole (cat.) in dry THF (2 cm^3) was added a solution of the alcohol **35** (126 mg, 0.4 mmol) in dry THF (2 cm^3) under argon, and the mixture was refluxed for 2 h before being cooled, a solution of freshly distilled CS_2 (0.24 cm^3, 4 mmol) in THF (1 cm^3) was added, and this mixture was heated at reflux. After 45 min, the reaction mixture was cooled, a solution of MeI (0.25 cm^3, 4 mmol) in THF (1 cm^3) was added, and the mixture was refluxed for 30 min. After the usual work-up, the residue was filtered through a column of silica gel with light petroleum as eluent to yield the xanthate **36** as a yellow oil (159 mg, 98%), ν_{max}/cm^{-1} 1450 and 1050.

A solution of TBTH (0.21 cm^3, 0.78 mmol) in dry toluene (5 cm^3) was refluxed for 5 min under argon. To this refluxing solution was added dropwise a mixture of the xanthate **36** (158 mg, 0.39 mmol) and azoisobutyronitrile (AIBN) (cat.) in toluene (2 cm^3). Refluxing was continued for 6 h, and a further quantity of TBTH (0.21 cm^3, 0.78 mmol) with AIBN (cat.) in toluene (1 cm^3) was added. The resultant mixture was refluxed for an additional 5 h and all volatiles were then removed under reduced pressure. The residue obtained upon chromatography on neutral alumina and elution with light petroleum yielded the benzyl ether **37** (106 mg, 91%) as an oil, ν_{max}/cm^{-1} 1455, 732 and 696; δ_H(200 MHz) 0.87 (3 H, d, *J* 7.2, 2-Me), 0.97 (3 H, s, Me), 0.98 (3 H, s, Me), 1.06–1.98 (12 H, m), 2.02–2.49 (1 H, m, 8-H), 3.15 (1 H, dd, *J* 3.0 and 1.1, 7-H), 4.41 and 4.70 (2 H, AB_q, *J* 12, OCH_2Ph) and 7.25–7.40 (5 H, m, Ph); δ_C(22.5 MHz) 16.21 (q), 18.81 (q), 21.67 (t), 22.19 (t), 31.20 (q), 32.42 (t), 36.75 (s), 37.79 (t), 38.05 (d), 38.83 (d), 51.98 (s), 52.70 (d), 70.47 (t), 87.63 (d), 126.12 and 126.99 (2 d, 5 aromatic carbons) and 138.69 (s) (Found: M^+, 298.2300. $C_{21}H_{30}O$ requires M, 298.2296).

2,6,6-*Trimethyltricyclo*[6.2.1.$0^{1,5}$]*undecan-7-ol* **38**.—A solution of the benzyl ether **37** (89 mg, 0.3 mmol) in absolute ethanol (6 cm^3) was stirred with 10% Pd/C (10 mg) under H_2. After 2 h the catalyst was filtered off on Celite and the filtrate was chromatographed to give the alcohol **38** (62 mg) in quantitative yield, ν_{max}/cm^{-1} 3345; δ_H(200 MHz) 0.81 (3 H, d, *J* 7.2, 2-Me), 0.85 (3 H, s, Me), 0.94 (3 H, s, Me), 1.01–1.96 (13 H, m), 2.14 (1 H, m, 8-H) and 3.41 (1 H, dd, *J* 3.0 and 0.7, 7-H); δ_C(100 MHz) 16.51, 19.83, 22.90, 22.91, 32.54, 33.22, 33.35, 37.80, 39.52, 39.99, 44.69, 53.72, 53.80 and 81.20 (Found: M^+, 208.1852. Calc. for $C_{16}H_{24}O$: M, 208.1827).

2,6,6-*Trimethyltricyclo*[6.2.1.$0^{1,5}$]*undecan-7-one* **10**.—A mixture of alcohol **38** (52 mg, 0.25 mmol), PDC (188 mg, 0.5 mmol) and silica gel (200 mg) in dry CH_2Cl_2 (5 cm^3) was stirred for 2 h. The solvent was completely removed to give a dark powder, which was taken in diethyl ether and filtered through a pad of Celite and silica gel. The filtrate was concentrated and the residue was chromatographed to obtain the ketone **10** (51 mg) in quantitative yield, ν_{max}/cm^{-1} 1700; δ_H(400 MHz) 0.91 (3 H, d, *J* 7.2, 2-Me), 1.068 (3 H, s, Me), 1.072 (3 H, s, Me), 1.13–2.14 (12 H, m) and 2.76 (1 H, m, 8-H); δ_C(100 MHz) 19.93, 22.54, 24.37, 27.59, 28.81, 31.98, 32.09, 37.94, 39.86, 45.70, 52.22, 53.72, 54.09 and 219.62 (Found: M^+, 206.1697. Calc. for $C_{14}H_{22}O$: M, 206.1671).

(±)-*Prezizanol* **5**.—When the ketone **10** (33 mg, 0.16 mmol) was treated with 0.85 mol dm^{-3} MeLi (0.56 cm^3, 0.48 mmol) as per the procedure of Mori,[9h] prezizanol **5** (31 mg, 88%) was obtained, ν_{max}/cm^{-1} 3420; δ_H(90 MHz) 0.87 (3 H, s, Me), 0.88 (3 H, d, *J* 7, 2-Me), 1.01 (3 H, s, Me), 1.23 (3 H, s, Me) and 1.40–2.10 (13 H, m) (Found: M^+, 222.1983. Calc. for $C_{15}H_{26}O$: M, 222.1984).

(±)-*Prezizaene* **4**.—According to Mori,[9h] when prezizanol **5** (22 mg, 0.1 mmol) in dry CH_2Cl_2 (3 cm^3) was treated with Et_3N (0.5 cm^3) and $MeSO_2Cl$ (0.3 cm^3), prezizaene **4** was obtained as an oily liquid (15 mg, 76%), ν_{max}/cm^{-1} 3070, 1625 and 890; δ_H(90 MHz) 0.87 (3 H, d, *J* 7, 2-Me), 1.07 (3 H, s, Me), 1.10 (3 H, s, Me), 1.15–2.08 (12 H, m), 2.81 (1 H, t, 8-H) and 4.65 and 4.71 (2 H, AB_q, *J* 1.8, olefinic) (Found: M^+, 204.1855. Calc. for $C_{15}H_{24}O$: M, 204.1878).

(±)-*Jinkohol II* **6**.—To a solution of K^{t}OAm [prepared from potassium (12 mg, 0.3 mmol) and dry *tert*-amyl alcohol (1 cm^3)] in dry benzene (3 cm^3) was added solid PPh_3MeI (121 mg, 0.3 mmol) under argon. A solution of norprezizanone **10** (15 mg, 0.075 mmol) in benzene (2 cm^3) was added to the above yellow solution, and the resultant mixture was refluxed for 4 h,

then was cooled, and the usual work-up followed by chromatography afforded prezizaene **4** (12 mg, 78%).

A solution of prezizaene **4** (10 mg, 0.05 mmol) in dry THF (1 cm^3) at 0 °C under argon was treated with 0.6 mol dm^{-3} BH_3·THF (0.17 cm^3, 0.1 mmol). After being stirred for 30 min at 0 °C, the reaction mixture was allowed to warm to room temp. After stirring of the mixture for 2 h, water was added carefully, followed by aq. NaOH (4 mg, 0.1 mmol) and 30% aq. H_2O_2 (0.023 cm^3, 0.2 mmol). After being stirred for a further 30 min, the reaction mixture was worked up as usual. Jinkohol II **6** was obtained after short column chromatography (8 mg, 72%), ν_{max}/cm^{-1} 3320; δ_H(200 MHz) 0.75 (3 H, s, Me), 0.89 (3 H, d, *J* 7, 2-Me), 1.00 (3 H, s, Me), 1.02–1.97 (13 H, m), 2.39 (1 H, br s, 8-H), 3.52 (1 H, t, *J* 10.2, CH_2OH) and 3.77 (1 H, dd, *J* 10.5 and 3.5, CH_2OH).

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