Synthesis based on cyclohexadienes. Part 35:[1] Synthesis of some polyquinane derivatives

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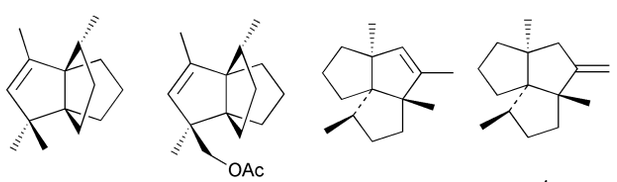
A new strategy for the synthesis of a [4.3.3]propellane derivative and an angular triquinane is described starting from the tetracyclic compounds **8** and **15**. The synthesis of the [4.3.3]propellane involved a radical cyclisation and a Beckmann fragmentation as the key steps. The angular triquinane was synthesised employing an oxidative cleavage of the tetracyclic system. A novel Wilkinson's catalyst-mediated carbon–carbon bond formation (**12** ⟶ **30**) is reported.

The polyquinane natural products have aroused a great deal of interest among synthetic chemists in recent years, primarily on account of the architecturally pleasing assembly of five-membered rings, embellished with a number of methyl groups and the wide range of biological activity exhibited by some members of this family. The literature on the subject has been periodically reviewed.[2–8]

As part of our ongoing interest to develop new strategies for the synthesis of complex sesquiterpenes,[9] we initiated a program for the synthesis of polyquinanes starting from readily available cyclohexadienes. The sesquiterpenes modhephene **1**



1 **2** **3** **4**

and 13-acetoxymodhephene **2** were isolated from the hexane extracts of the rayless golden rod plant *Isocoma wrightii*,[10] and have a diquinane moiety as part of their structure. The angular triquinanes constitute another class of polyquinane natural products and are abundantly present in Nature. The sesquiterpenes α- and β-isocomenes **3** and **4** belonging to the angular triquinane family were isolated by Zalkow *et al.*[11a] and Bohlmann *et al.*[11b] and are distinguished by an angular fusion of three cyclopentane rings; the tricyclo[6.3.0.0^{1,5}]undecane framework. The main challenge in the synthesis of angular triquinanes is the installation of a network of methyl groups and carbon centres in addition to the control of stereochemistry of the remote methyl group. Many syntheses of modhephene[12] and isocomenes[8] have appeared in the literature, employing a wide variety of strategies.

With this background, a new strategy for the synthesis of natural [3.3.3]propellanes **1** and **2** and isocomenes **3** and **4** from the tetracyclic ketone **8** was developed. Most of the strategies reported in the literature so far have employed cyclisation reactions to construct the third ring of the polyquinane natural products. However, our strategy involved the cleavage of an appropriate bond of a tetracyclic system, which has a hidden polyquinane framework, to give polyquinanes. Initially we contemplated the synthesis of the intermediates **10** and **12**, which could be elaborated to modhephene and isocomenes, respectively, by employing an appropriate sequence of reactions. The retro-synthesis of the intermediates **10** and **12** is depicted in Scheme 1. It was envisaged that the [4.3.3]propellane **10** could be obtained from the tetracyclic ketone **8** through the oxime **9** by the cleavage of the C8–C9 bond under Beckmann fragmentation conditions. The angular triquinane **12** can also be obtained from the same tetracyclic ketone **8**, through the intermediate **11**, by employing either an oxidative cleavage or a heteroatom-assisted Beckmann fragmentation strategy. The tetracyclic ketone **8** can be prepared by a 5-*exo-trig* allyl radical cyclisation of the bromide **7**, which in turn can be obtained from 5-methoxyindane **5** through the tricyclic ketone **6**. Thus, the synthesis of the [4.3.3]propellane derivative **10** and the triquinane derivative **12** was attempted[13] from a common intermediate and the results are discussed below.

Results and discussion

Synthesis of the tetracyclic ketone 8

The tricyclic ketone **6** was prepared according to the earlier procedure.[14] Thus, Birch reduction of 5-methoxyindane **5** with Li–NH_3 in the presence of ethanol as proton source furnished the corresponding diene, which on Diels–Alder reaction with α-chloroacrylonitrile followed by hydrolysis afforded the ketone **6** (Scheme 2). LDA alkylation of the ketone **6** with MeI at −78 °C furnished the *endo*-methylated product **13**. Initially we attempted to synthesise the tetracyclic ketone **15** by employing a 5-*exo-trig* allyl radical cyclisation[15] of the allyl bromide **7**. The allyl bromide **7** was obtained as a single regioisomeric product[16] by alkylation of the ketone **13** with LDA in the presence of the dibromide **16** and hexamethylphosphoric triamide (HMPA). Having obtained the bromide **7**, the crucial allyl radical cyclisation[15] was attempted on it. Thus, refluxing a benzene solution of the dibromide **7** in the presence of azoisobutyronitrile (AIBN) and tributyltin hydride (TBTH) (slow addition) furnished only the reduced product and not the cyclised product **15**. The failure of this cyclisation reflects the reactivity of the allyl radical (generated from **7**), which being less reactive undergoes reduction faster than cyclisation. Hence a more versatile vinyl radical cyclisation approach was employed for the synthesis of the ketone **8**. The precursor for the vinyl radical cyclisation, **14**, was obtained by the alkylation of the ketone **13** with LDA at −78 °C in the presence of propargyl (prop-2-ynyl) bromide and HMPA. The acetylenic ketone **14** underwent a smooth 5-*exo-dig* radical cyclisation when refluxed with TBTH and a catalytic amount of AIBN in benzene to furnish the tetracyclic ketone **8** after destannylation.

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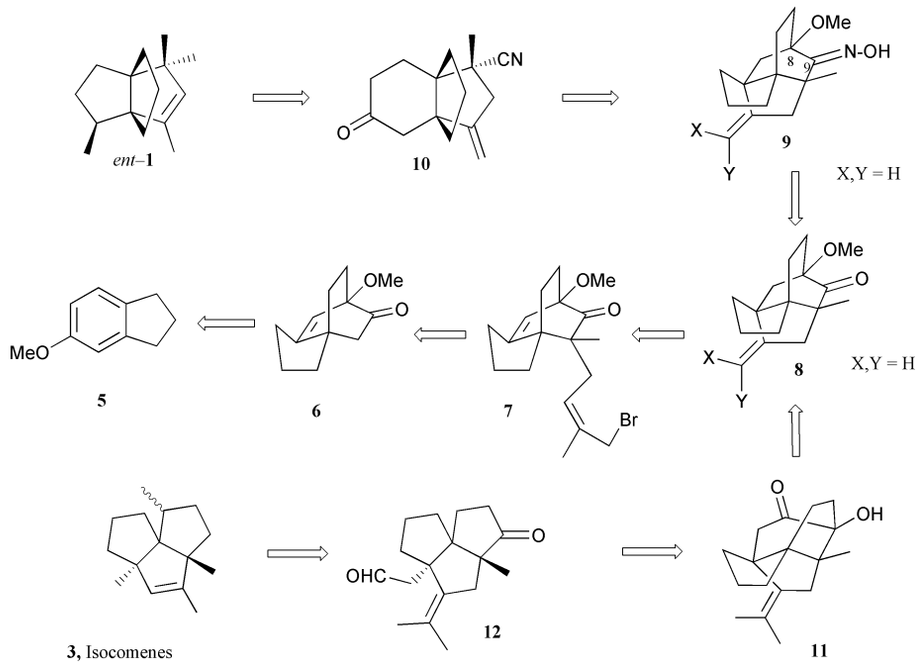
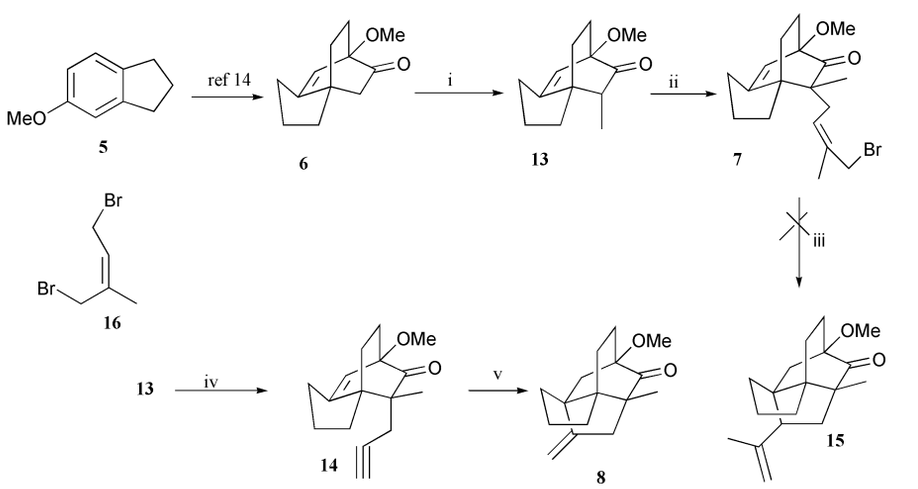


Scheme 1



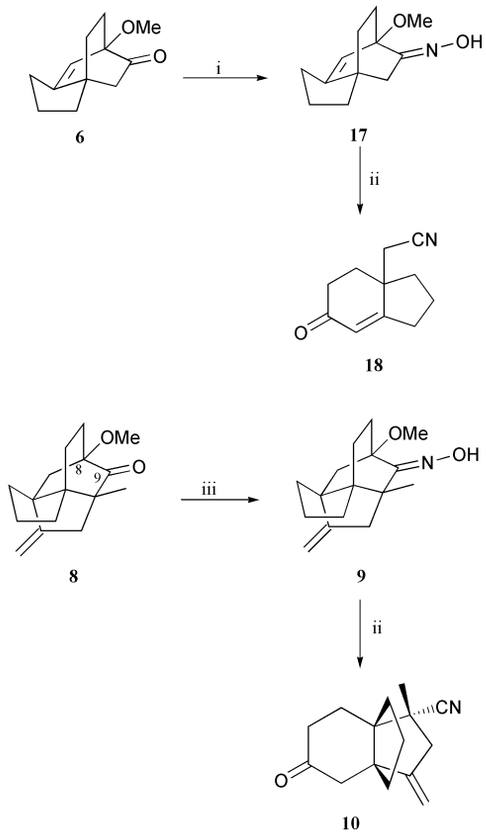
Scheme 2 *Reagents and conditions*: i) LDA, MeI, THF, −78 °C; ii) LDA, THF, HMPA, **16**, −78 °C; iii) TBTH (slow addition), AIBN, benzene, reflux; iv) LDA, propargyl bromide, THF, HMPA, −78 °C; v) TBTH, AIBN, benzene, reflux.

The structure of the tetracyclic ketone **8** was established from its spectral data. The IR spectrum of **8** showed the absence of acetylenic absorptions, and the ^{1}H NMR spectrum showed the presence of exocyclic olefinic protons at δ 4.7 and 5.01.

Synthesis of the [4.3.3]propellane 10

Having obtained the tetracyclic ketone **8** in good yield, we turned our attention towards the cleavage of the C8–C9 bond. The ketone **8** has a latent [4.3.3]propellane unit, and cleavage of the C8–C9 bond would furnish the propellane derivative **10**. The ketone **8** has a bridgehead methoxy group and a carbonyl group next to it; two requirements necessary for a heteroatom-assisted Beckmann fragmentation.[17] This fragmentation strategy was employed for the cleavage of the C8–C9 bond in the ketone **8**. As a model study, we decided to carry out the Beckmann fragmentation on the tricyclic ketone **6** before attempting it on the real system **8**. Thus, refluxing a solution of the ketone **6** with hydroxylamine hydrochloride and Na_2CO_3 in a mixture of EtOH and water furnished the oxime **17** (Scheme 3), which underwent a smooth Beckmann fragmentation[17] when treated with TsCl in pyridine to furnish the enone **18**. The fragmentation was more efficient in terms of reaction time and yield when Tf_2O was used[18] in place of TsCl. The structure of the enone **18** was delineated from its spectral data. The IR spectrum showed absorptions at ν_{max} 2225 and 1660 cm^{-1} due to the nitrile and enone functionalities, respectively, and the ^{1}H NMR spectrum showed the disappearance of signal at δ 3.53 due to the methoxy protons.

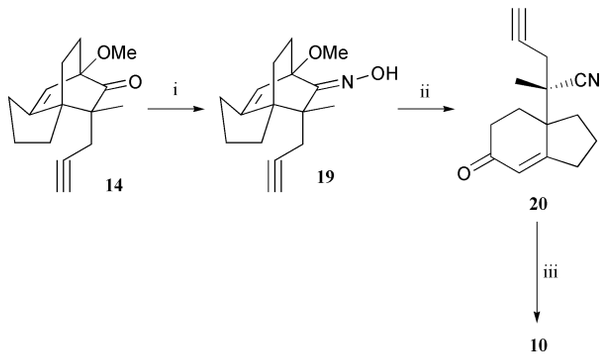
Having succeeded in the Beckmann fragmentation of the tricyclic oxime **17**, we attempted the same fragmentation on the tetracyclic oxime **9**. Preparation of the oxime **9** proved elusive in the beginning. Thus, reaction of the ketone **8** with hydroxylamine hydrochloride and Na_2CO_3 in a refluxing mixture of ethanol and water (2:1) furnished only the starting material. This was to be anticipated in view of the steric nature of the carbonyl group in **8**, which is flanked by two quaternary carbons. However, refluxing a mixture of the ketone **8** and hydroxylamine hydrochloride (8 equiv.) in pyridine[19] for 48 h neatly furnished the oxime **9** in good yield. The oxime **9** underwent the expected Beckmann fragmentation[17] on treatment with TsCl in pyridine for 24 h to furnish the propellane **10**. Again Tf_2O[18] was found to be superior to TsCl for this fragmentation, the reaction being over in just 3 h. The structure of the propellane **10** was established from its spectral characteristics. The IR spectrum showed absorptions at ν_{max} 2220 and



Scheme 3 *Reagents and conditions*: i) $NH_2OH{\cdot}HCl$, Na_2CO_3, EtOH–water (1 : 2), reflux; ii) TsCl, pyridine, or Tf_2O, CH_2Cl_2, pyridine, 0 °C; iii) $NH_2OH{\cdot}HCl$, pyridine, reflux.

1710 cm^{-1} due to the nitrile and carbonyl functionalities, respectively. The ^1H NMR spectrum showed the disappearance of methoxy protons, thus confirming that the fragmentation had occurred.

The propellane **10** can also be obtained by reversing the sequence of reactions. Thus, fragmentation of the oxime **19** was attempted first. Refluxing a pyridine solution of the ketone **14** with hydroxylamine hydrochloride (8 equiv.) for 48 h furnished the oxime **19**, which underwent a Beckmann fragmentation on treatment with either TsCl or Tf_2O to afford the enone **20** (Scheme 4). A 5-*exo-dig* radical cyclisation[20] of the ketone



Scheme 4 *Reagents and conditions*: i) $NH_2OH{\cdot}HCl$, pyridine, reflux; ii) TsCl, pyridine, or Tf_2O, CH_2Cl_2, pyridine, 0 °C; iii) (a) TBTH, AIBN, benzene, reflux, (b) 50% HCl, Et_2O.

20 with TBTH followed by destannylation furnished a compound which was identical with the propellane **10** (comparison of their spectral characteristics).

Synthesis of angular triquinane 12

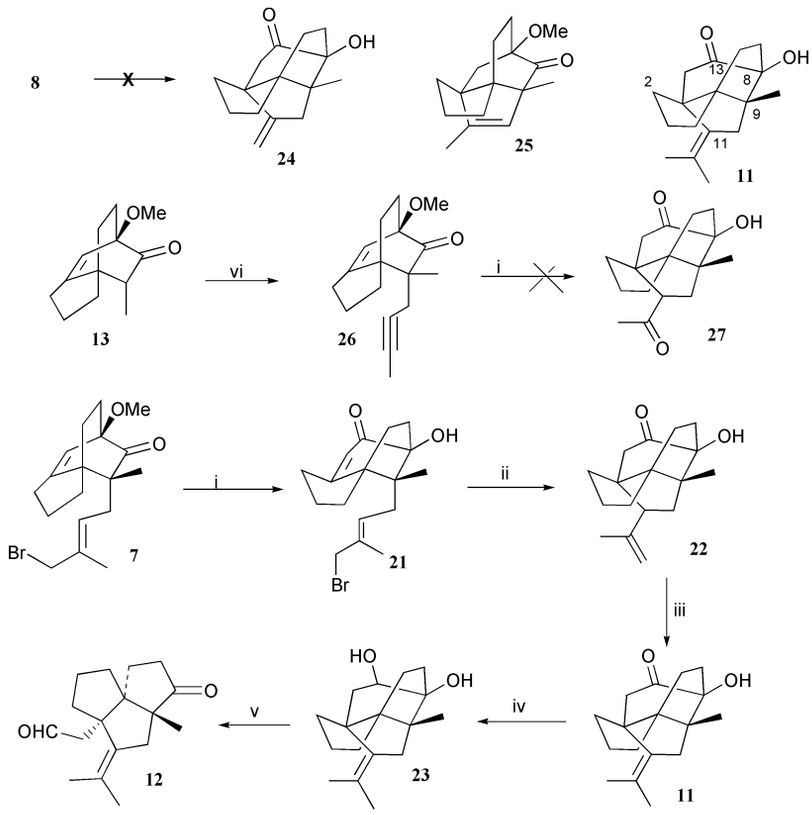
Having succeeded in the synthesis of the [4.3.3]propellane derivative **10** from the tetracyclic ketone **8**, we next focused on the synthesis of the angular triquinane **12**. It was anticipated that the triquinane **12** could be obtained by a heteroatom-assisted Beckmann fragmentation or an oxidative cleavage of the C8–C13 bond of the ketone **11**. There are enough reports in the literature, which employ a skeletal rearrangement[21] of a bicyclo[2.2.2]octane unit to a bicyclo[3.2.1]octane, for the synthesis of natural products. It was anticipated that a similar skeletal rearrangement of the tetracyclic ketone **8** would furnish the rearranged product **24**. However, all attempts[21] to rearrange the ketone **8** to the hydroxy ketone **24** resulted in only the isomerisation of the double bond to give **25** (Scheme 5). The failure of this rearrangement reaction may perhaps be attributed to the strain involved on going from **8** to **24**. We next investigated a one-pot cationic rearrangement–ene cyclisation[1] of the tricyclic ketone **26**. The ketone **26** was obtained by LDA alkylation of the ketone **13** with 1-brombut-2-yne in the presence of HMPA. The ketone **26** was expected to undergo a one-pot cationic rearrangement–ene cyclisation[1] to the dione **27**, on treatment with $HClO_4$. However, all attempts to convert the ketone **26** to the dione **27** were unsuccessful.

Since the rearrangement of the ketone **8** to **24** was unsuccessful, we attempted an acid-catalysed rearrangement of the ketone **7** before carrying out the radical cyclisation. Although attempted allyl radical cyclisation[15] of the bromide **7** was not successful, we anticipated that the same radical cyclisation on the enone **21** might be efficient since it has a better acceptor. Thus, the ketone **7** was rearranged to the hydroxy enone **21** by treatment with $HClO_4$ in CH_2Cl_2 (Scheme 5). Treatment of the hydroxy enone **21** with TBTH under standard conditions afforded the tetracyclic hydroxy ketone **22**, whose structure was established from its spectral characteristics. The IR spectrum showed absorptions at ν_{max} 3460 and 1700 cm^{-1} due to the hydroxy and carbonyl functionalities, respectively. The ^1H NMR spectrum showed the presence of exocyclic olefinic protons at δ 4.66 and 4.91. In addition, the mass spectrum showed the molecular-ion peak at *m*/*z* 260. Isomerisation of the double bond in **22** to the more substituted olefin **11** was carried out with a catalytic amount of toluene-*p*-sulfonic acid (PTSA) in refluxing toluene for 1 h.

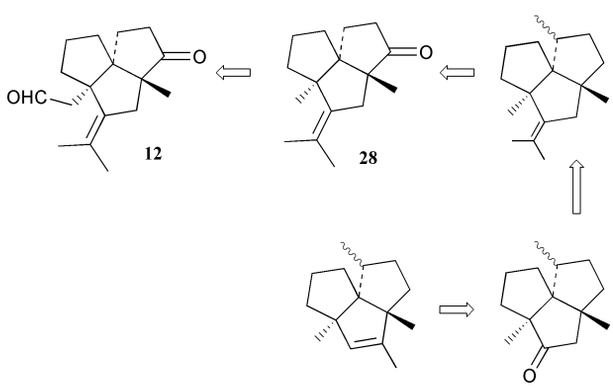
The next task in the synthetic sequence was to cleave the C8–C13 bond in the hydroxy ketone **11**. Although several methods are known in the literature for the direct cleavage of acyloins (α-hydroxy ketones) to keto carboxylic acids, reagents like HIO_4 and $Pb(OAc)_4$ were ineffective in bringing about this transformation. However, the diol **23**, obtained by $NaBH_4$ reduction of the ketone **11**, underwent smooth cleavage on treatment with HIO_4 in a mixture of ethanol and water to afford exclusively the angular triquinic aldehyde **12**. The structure of **12** was established from its spectral data. The IR spectrum showed absorptions at ν_{max} 2700, 1735 and 1710 cm^{-1} due to the aldehyde C–H, cyclopentanone and aldehyde carbonyls, respectively. The ^1H NMR spectrum showed three singlets at δ 1.18, 1.65, and 1.72 due to the three methyl-group protons. The aldehyde proton appeared at δ 9.78 as a singlet. The mass spectrum showed the molecular-ion peak at *m*/*z* 260 with a base peak at *m*/*z* 161.

After successfully completing the preparation of the triquinic aldehyde **12**, attention was next turned towards the synthesis of the angular triquinanes, isocomenes **3** and **4**. It was anticipated that decarbonylation of the angular triquinic aldehyde **12** would provide the ketone **28**, which can be transformed into isocomenes through the known sequence of reactions (Scheme 6).

Thus, decarbonylation of the triquinic aldehyde **12** was attempted with a stoicheiometric amount of Wilkinson's catalyst in benzonitrile at 160 °C. The reaction product upon purification afforded a compound whose spectral data were different from those of the expected product **28**. The IR spectrum of the product showed two carbonyl absorptions at 1740 and 1700 cm^{-1}. The ^1H NMR spectrum showed only three

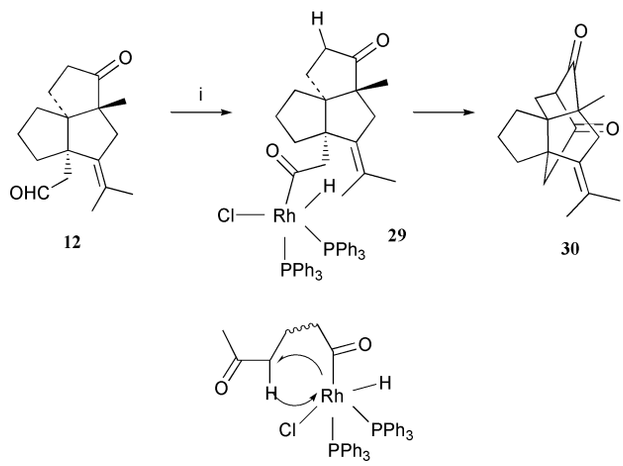


Scheme 5 *Reagents and conditions*: i) $HClO_4$ (catalytic), CH_2Cl_2; ii) TBTH, AIBN, benzene, reflux; iii) PTSA (catalytic), toluene, reflux; iv) $NaBH_4$, MeOH, 0 °C; v) HIO_4 (aq.), EtOH, 20 °C; vi) LDA, 1-bromobut-2-yne, THF, HMPA.



Isocomenes **3**

Scheme 6

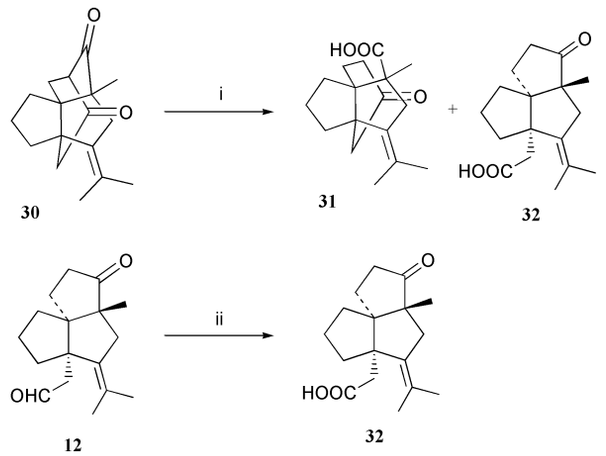


Scheme 7 *Reagents and conditions*: i) $ClRh(PPh_3)_3$, PhCN, reflux.

singlets, at δ 1.11, 1.52 and 1.66, for the tertiary methyl and two vinylic methyl groups, respectively, which confirmed that decarbonylation had not taken place. An interesting observation in the ^{1}H NMR spectrum was the presence of a doublet at δ 3.30 (J 4.2 Hz), which cannot be explained with the structure **28**. The ^{13}C NMR spectrum showed the presence of 17 carbons, of which the resonance at δ_C 65.7 was attributed to the presence of a methine carbon. The resonances at δ_C 214.5 and 202.6 were attributed to the presence of cyclopentane and cyclohexane carbonyls, respectively. The mass spectrum showed the molecular-ion peak at m/z 258, two units less than the starting material, and the base peak appeared at m/z 160. Based on the above spectral data, the compound was assigned the structure **30**.

The formation of the tetracyclic 1,3-dione **30** presumably involves the acylrhodium complex **29** of the triquinic aldehyde **12**, which undergoes an intramolecular C–H insertion[22] reaction to the weakly acidic CO–C–H bond by the CO–Rh bond as shown in Scheme 7.

The structure of the dione **30** was further confirmed by subsequent chemical transformations. Treatment of **30** in methanol with 10% KOH (1 equiv.) in a sealed tube at 100 °C for 4 h furnished a 1:4 mixture of the [4.3.3]propellane **31** and the triquinic acid **32**, in nearly quantitative yield, which can be separated by chromatography (Scheme 8). The structures of these two acids were deduced from their spectral data. The IR spectrum of the mixture of acids **31** and **32** showed absorptions at 1731 and 1713 cm^{-1} due to the cyclopentanone and the acid carbonyl group, respectively. The ^{1}H NMR spectrum showed three singlets at δ 0.98, 1.51 and 1.64 due to the three methyls besides the methylene protons. The ^{13}C NMR spectrum of **32** showed seventeen resonances with the cyclopentanone carbonyl resonance appearing at δ_C 222.6. To confirm the structure of the triquinic acid **32**, the triquinic keto aldehyde **12** was oxidised to the corresponding acid using Jones' reagent. The spectral data of this acid were found to be identical with those of the major compound **32** in all respects. Conversion of the triquinanes **22** and **32** into the natural isocomenes is under progress.



Scheme 8 *Reagents and conditions*: i) 10% KOH, MeOH; ii) Jones' reagent.

In conclusion, a general methodology was developed for the synthesis of [4.3.3]propellanes and angular triquinanes starting from readily available cyclohexadienes. The synthesis of [4.3.3]-propellane involved a combination of 5-*exo* radical cyclisation and Beckmann fragmentation, while the angular triquinane was synthesised employing an oxidative cleavage of a substituted tetracyclo[6.3.2.0^{1,5}.0^{5,9}]tridecane as the key step. During the course of the synthesis, a novel Wilkinson's catalyst-mediated carbon–carbon bond formation was observed, which strongly supports the acylrhodium complex intermediate in the decarbonylation reactions.

Experimental

General

All mps and bps are uncorrected. Mps were recorded on a Mettler FP1 instrument. IR spectra were recorded as neat liquids or in Nujol mull for solids on Perkin-Elmer 780 and JASCO FT/IR-410 spectrophotometers. NMR spectra were recorded on JEOL FX-90Q, Bruker ACF-200 and JEOL JNM LA-300 and spectrometers. The chemical shifts (δ/ppm) and coupling constants (J/Hz) are reported with reference to standard tetramethylsilane (for ^{1}H) or the central line of $CDCl_3$ (for ^{13}C). Mass spectra were recorded on a JEOL MS-DX 303 with inbuilt direct-inlet system, and relative intensities of the ions are given in parentheses. Microanalysis was carried out using a Carlo Erba 1106 instrument. Analytical and preparative TLC were performed on glass plates coated with Acme's Silica gel G containing 13% calcium sulfate as the binder. Visualisation of the spot was accomplished by exposure to iodine vapour. Acme's silica gel (60–120 mesh) was used for column chromatography. 'Hexane' refers to petroleum spirit fraction boiling at 60–80 °C, and ether refers to diethyl ether. All dry solvents were prepared by standard procedures. Liquid ammonia was distilled over sodamide before use. All reactions involving air- and moisture-sensitive reagents were performed under either a blanket of nitrogen or argon-filled balloons. Wherever it is mentioned, 'the usual work-up' means the reaction mixture was washed successively with water and brine, dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator at aspirator pressure for the isolation of the product mixture. Unless otherwise stated, all the materials were obtained from commercial suppliers and were used without further purification.

7-Methoxy-9-*endo*-methyltricyclo[5.2.2.0^{1,5}]undec-5-en-8-one 13

To a freshly prepared LDA solution [prepared from 14 ml of 1.7 M BuLi (24 mmol) and diisopropylamine (3.5 ml, 24.5 mmol)] in 140 ml of THF at −78 °C under argon was added a solution of the ketone[14] **6** (4.2 g, 20.4 mmol) in THF (30 ml) dropwise. The resultant solution was stirred for 1 h at the same temperature and quenched with methyl iodide (2.5 ml, 40.78 mmol). The reaction mixture was stirred overnight, poured into water and extracted with ether. The extract was washed successively with dil. HCl, water, and brine and dried over Na_2SO_4. Evaporation of the solvent gave a product, which was purified by chromatography on a silica gel column and eluted with ethyl acetate–hexane (1 : 10) to furnish the *ketone* **13** (4 g, 89%); ν_{max}/cm^{-1} 1720, 1650 and 925; δ_H (300 MHz) 1.0 (3H, d, J 7.5, CHCH_3), 1.29–1.96 (8H, m), 2.02–2.09 (1H, q, J 7.2, 9-H), 2.19–2.57 (2H, m, allylic CH_2), 3.51 (3H, s, OMe) and 5.84 (1H, br s, olefinic); m/z 207 (M$^+$), 150, 121 and 91 (Found: M$^+$, 206.1313. $C_{13}H_{18}O_2$ requires M, 206.1310).

9-*endo*-(4-Bromo-3-methylbut-2-enyl)-7-methoxy-9-methyltricyclo[5.2.2.0^{1,5}]undec-5-en-8-one 7

To a freshly prepared LDA solution [prepared from 1.0 M solution of *n*-BuLi (14.4 ml, 14.4 mmol) and diisopropylamine (2 ml, 14.4 mmol) in 20 ml of THF] at −78 °C under argon was added a solution of the ketone **13** (1.5 g, 7.3 mmol) in THF (15 ml) dropwise. The resultant solution was stirred for 1 h at −78 °C and quenched with 1,4-dibromo-2-methylbut-2-ene **16** (4.1 g, 18.02 mmol) followed by the addition of HMPA (1.25 ml, 7.2 mmol). The reaction mixture was stirred for 12 h, poured into ice-cold water and extracted with ether (4 × 50 ml). The combined organic layer was washed successively with 2 M HCl, water and brine and dried over anhydrous Na_2SO_4. Removal of the solvent afforded the crude bromo ketone **7** (2.1 g, 82%); ν_{max}/cm^{-1} 2950, 1720 and 1640; δ_H (90 MHz) 1.02 (3H, s, Me), 1.12–2.46 (12H, m), 1.67 (3H, br s, allylic Me), 3.48 (3H, s, OMe), 3.99 (3H, s, CH_2Br), 5.68 (1H, t, J 6.8, olefinic) and 5.87 (1H, br s, olefinic).

7-Methoxy-9-*exo*-methyl-9-(prop-2-ynyl)tricyclo[5.2.2.0^{1,5}]-undec-5-en-8-one 14

To a freshly prepared solution of LDA [prepared from 15 ml of 1.475 M BuLi (22.12 mmol) and diisopropylamine (4 ml, 28 mmol)] at −78 °C was added dropwise a solution of the ketone **13** (3.14 g, 15.2 mmol) in THF (20 ml). The resultant solution was stirred for 1 h at the same temperature and quenched with a solution of propargyl bromide (2.7 ml, 30 mmol) in THF followed by the addition of HMPA (5.45 ml, 30 mmol). The reaction mixture was stirred overnight, and poured into 2 M HCl. Usual work-up with column chromatography on silica gel [ethyl acetate–'hexane' (1 : 9)] afforded the *ketone* **14** as a colourless oil (3 g, 81%), ν_{max}/cm^{-1} 3290, 2220, 1725 and 900; δ_H (300 MHz) 1.191 (3H, s, Me), 1.223–2.03 (10H, m), 2.04 (1H, d, J 2.4), 2.16 (1H, dd, J 17.4 and 2.4), 2.45 (1H, dd, J 17.4 and 2.4), 3.51 (3H, s, OMe) and 5.82 (1H, br s, olefinic); δ_C (75 MHz) 19.64, 25.52, 26.575, 27.093, 28.00, 30.794, 31.378, 47.08, 52.935, 53.00, 70.9, 80.9, 84.6, 115.2, 155.7 and 213.04; m/z 244 (M$^+$), 177, 149, 122, 106, 90 and 66 (Found: M$^+$, 244.331. $C_{16}H_{20}O_2$ requires M, 244.332).

8-Methoxy-10-methyl-12-methylenetetracyclo[6.4.1.0^{1,5}.0^{5,10}]-tridecan-9-one 8

To a solution of compound **14** (1.8 g, 7.3 mmol) in degassed benzene (350 ml) were added TBTH (2.8 ml, 9.5 mmol) and AIBN (catalytic) under nitrogen atmosphere and the mixture was refluxed overnight. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in ether, and the solution was washed successively with 50% aq. HCl, water, 1% NH_4OH, water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent followed by column chromatography (1 : 19 ethyl acetate–'hexane') afforded the *tetracyclic ketone* **8** as a colourless oil (1.4 g, 78%); ν_{max}/cm^{-1} 1720, 1650 and 900; δ_H (300 MHz) 1.14 (3H, s, Me), 1.16–2.23 (12H, m),

2.39 (2H, t, *J* 2.1), 3.31 (3H, s, OMe), 4.7 (1H, t, *J* 2.1) and 5.01 (1H, t, *J* 2.1); δ_C (75 MHz) 15.239 (q), 22.95 (t), 24.18 (t), 29.79 (t), 29.94 (t), 36.23 (t), 41.34 (t), 41.4 (t), 51.82 (q), 55.19 (s), 56.42 (s), 57.18 (s), 80.03 (s), 107.3 (t), 156.58 (s) and 218.8 (s); *m*/*z* 246 (M^+, 6%), 218 (27), 134 (100) and 83 (72) (Found: M^+, 246.3468. $C_{16}H_{22}O_2$ requires *M*, 246.3478).

7-Methoxytricyclo[5.2.2.0^{1,5}]undec-5-en-8-one oxime 17

A magnetically stirred solution of the ketone **6** (0.5 g, 2.6 mmol), hydroxylamine hydrochloride (0.36 g, 5.2 mmol) and sodium carbonate (0.83 g, 7.8 mmol) in a mixture of ethanol (6 ml) and water (12 ml) was refluxed for 4 h. The reaction mixture was cooled and the product was extracted with ether. The organic layer was subjected to the usual work-up followed by chromatography on silica gel [ethyl acetate–'hexane' (1 : 10)] which furnished the *oxime* **17** (0.49 g, 90%), which was crystallised from ethyl acetate–'hexane', mp 108–109 °C; ν_{max}/cm^{-1} 3300, 1650 and 930; δ_H (90 MHz) 1.21–1.86 (8H, m), 2.12 (1H, dd, J_1 17.4, J_w 3.3, H-9 *endo*), 2.18–2.39 (2H, m, allylic CH_2), 2.46 (1H, d, *J* 17.4, H-9 *endo*), 3.53 (3H, s, OMe) and 5.98 (1H, br s, olefinic) (Found: C, 69.8; H, 8.3; N, 6.5. $C_{12}H_{17}NO_2$ requires C, 69.5; H, 8.3; N, 6.8%).

6-(Cyanomethyl)bicyclo[4.3.0]non-1-en-3-one 18

Method A. Beckmann fragmentation with *p*-TsCl. To a solution of the oxime **17** (0.4 g, 1.9 mmol) in dry pyridine (5 ml) was added a solution of *p*-TsCl (0.44 g, 2.3 mmol) in dry pyridine (3 ml) at 0 °C over a period of 10 min. The reaction mixture was stirred at room temperature for 36 h and poured into dil. HCl. Usual work-up followed by chromatography on silica gel [ethyl acetate–'hexane' (1 : 10)] afforded the *keto nitrile* **18** (0.3 g, 88%), which was recrystallised from 'hexane', mp 68 °C; ν_{max}/cm^{-1} 2225 and 1660; δ_H (300 MHz) 1.55–1.66 (2H, m), 1.84–2.04 (4H, m), 2.19–2.26 (1H, m), 2.39–2.78 (5H, m) and 5.9 (1H, t, *J* 2.4); δ_C (22.5 MHz) 20.3 (t), 22.4 (t), 29.9 (t), 32.1 (t), 32.3 (t), 37.4 (t), 43.8 (s), 116.9 (s), 122.7 (d), 172.2 (s) and 197.2 (s) (Found: C, 75.4; H, 7.5; N, 8.0. $C_{11}H_{13}NO$ requires C, 75.4; H, 7.6; N, 8.0%).

Method B. Beckmann fragmentation with trifluoromethanesulfonic anhydride. To a magnetically stirred solution of the oxime **17** (0.12 g, 0.58 mmol) and dry pyridine (0.005 ml, 0.7 mmol) in dry methylene dichloride (1 ml) at 0 °C was added trifluoromethanesulfonic anhydride (0.1 ml, 0.64 mmol) slowly dropwise. After being stirred at the same temperature for 3 h the mixture was treated with aq. $NaHCO_3$ and the product was extracted with ether. The extract was submitted to the usual work-up, followed by chromatography to furnish the keto nitrile **18** (83 mg, 81%), which was recrystallised from 'hexane', mp 68–69 °C, identical with the sample obtained in the above experiment.

8-Methoxy-10-methyl-12-methylenetetracyclo[6.4.1.0^{1,5}.0^{5,10}]-tridecan-9-one oxime 9

A solution of the ketone **8** (0.5 g, 2 mmol) and hydroxylamine hydrochloride (1.13 g, 16 mmol) in pyridine (7 ml) was refluxed for 48 h. The solution was poured in to dil. HCl and the product was extracted with ether. The organic layer was subjected to the usual work-up, followed by chromatography [ethyl acetate–'hexane' (1 : 10)] to afford the *tetracyclic oxime* **9** (0.4 g, 75%), which was recrystallised from 'hexane'–ethyl acetate, mp 176–177 °C; ν_{max}/cm^{-1} 3250, 1650 and 890; δ_H (300 MHz) 1.42 (3H, s, Me), 1.44–2.17 (10H, m), 1.89 (2H, d, *J* 1.5, CH_2), 2.33 (2H, td, *J* 16.5 and 2.1), 3.0 (1H, t, *J* 16.5, allylic CH), 3.3 (3H, s, OMe), 4.7 (1H, t, *J* 2.1) and 4.96 (1H, t, *J* 2); δ_C (75 MHz) 15.6 (q), 22.9 (t), 24.8 (t), 29.4 (t), 29.6 (t), 36.8 (t), 39.0 (t), 45.6 (t), 49.2 (s), 51.1 (q), 54.7 (s), 56.8 (s), 75.6 (s), 106.8 (t), 158.9 (s) and 164.4 (s) (Found: C, 73.3; H, 8.9; N, 5.3. $C_{16}H_{23}NO_2$ requires C, 73.5, H, 8.9; N, 5.4%).

7-Methyl-9-methylene-3-oxotricyclo[4.3.3.0^{1,6}]dodecane-7-carbonitrile 10

Method A. Beckmann fragmentation with *p*-TsCl. To a stirred solution of the oxime **9** (0.4 g, 1.5 mmol) in dry pyridine (7 ml) was added a solution of *p*-TsCl (0.35 g, 1.8 mmol) in dry pyridine (2 ml) at 0 °C over a period of 10 min. The reaction mixture was stirred at room temperature for 24 h and poured into dil. HCl. Usual work-up followed by chromatography on silica gel [ethyl acetate–'hexane' (1 : 10)] furnished the *nitrile* **10** (0.29 g, 83%) as a colourless oil, ν_{max}/cm^{-1} 2220, 1710, 1650 and 900; δ_H (300 MHz) 1.50 (3H, s, Me), 1.54–2.55 (10H, m), 2.52 (1H, d, *J* 15.3, H^a-8), 2.6 and 2.68 (2H, ABq, *J* 16.2), 2.89 (1H, d, *J* 15.3, H^b-8) and 4.95 and 5.07 (2H, br s, olefinic); δ_C (75 MHz) 20.6 (q), 24.6 (t), 30.4 (t), 34.5 (t), 34.7 (t), 43.0 (t), 46.3 (s), 46.8 (t), 49.0 (t), 55.2 (s), 56.4 (s), 108.2 (t), 124.7 (s), 155.0 (s) and 211.6 (s); *m*/*z* 229 (M^+, 52%), 213 (21), 202 (88), 162 (68), 91 (100), 55 (72) (Found: M^+, 229.3217. $C_{15}H_{19}NO$ requires *M*, 229.3211).

Method B. Beckmann fragmentation with trifluoromethanesulfonic anhydride. To a magnetically stirred solution of the oxime **9** (0.13 g, 0.5 mmol) and dry pyridine (0.047 ml, 0.6 mmol) in dry dichloromethane (2 ml) at 0 °C was added trifluoromethanesulfonic anhydride (0.09 ml, 0.55 mmol) slowly dropwise. After being stirred for 3 h at the same temperature, aqueous $NaHCO_3$ solution was added and the product was extracted with ether. The organic layer was washed with water, brine and dried over anhydrous Na_2SO_4. Removal of the solvent followed by chromatography on silica gel furnished the keto nitrile **10** (91 mg, 83%), identical with the sample obtained as above.

7-Methoxy-9-*exo*-methyl-9-(prop-2-ynyl)tricyclo[5.2.2.0^{1,5}]-undec-5-en-8-one oxime 19

A stirred solution of the ketone **14** (0.5 g, 2 mmol) and hydroxylamine hydrochloride (1.13 g, 16 mmol) in pyridine (10 ml) was refluxed for 48 h. After cooling to room temperature, the reaction mixture was poured into dil. HCl and extracted with ether. The extract was subjected to the usual work-up, followed by chromatography on silica gel and elution with ethyl acetate–'hexane' (1 : 10) to afford the *oxime* **19** as a white solid, which was crystallised from ethyl acetate–'hexane' (0.4 g, 75%), mp 132–133 °C; ν_{max}/cm^{-1} 3300, 1650 and 900; δ_H (300 MHz) 1.5 (3H, s, Me), 1.2–1.77 (8H, m), 1.95 (1H, t, *J* 2.7), 2.28 (1H, dd, *J* 17.7 and 2.7), 2.35–2.52 (2H, m, allylic CH_2), 2.99 (1H, dd, *J* 17.7 and 2.7), 3.51 (3H, s, OMe) and 5.90 (1H, br s, olefinic) (Found: C, 74.2; H, 8.1; N, 5.3. $C_{16}H_{21}NO_2$ requires C, 74.1; H, 8.2; N, 5.4%).

2-Methyl-2-(4-oxobicyclo[4.3.0]non-5-en-1-yl)pent-4-ynonitrile 20

Method A. Beckmann fragmentation with *p*-TsCl. To a stirred solution of the oxime **19** (0.4 g, 1.5 mmol) in dry pyridine (5 ml) was added a solution of *p*-TsCl (0.36 g, 1.8 mmol) in dry pyridine (3 ml) dropwise over a period of 10 min at 0 °C. After the addition was over the reaction mixture was stirred at room temperature for 24 h and poured into dil. HCl. Usual work-up followed by chromatography on silica gel and elution with ethyl acetate–'hexane' (1 : 10) afforded the *keto nitrile* **20** (0.29 g, 82%) as a white solid, mp 128–129 °C; ν_{max}/cm^{-1} 3250, 2220 and 1660; δ_H (300 MHz) 1.56 (3H, s, Me), 1.59–1.93 (4H, m), 2.25 (1H, t, *J* 3, acetylenic CH), 2.32–2.97 (8H, m), 6.13 (1H, d, *J* 2.4, olefinic); *m*/*z* M^+ (227, 16%), 212 (6), 199 (27), 184 (25), 160 (41), 135 (89), 107 (100), 93 (48) (Found: M^+, 227.3043. $C_{15}H_{17}NO$ requires *M*, 227.3052).

Method B. Beckmann fragmentation with trifluoromethanesulfonic anhydride. To a magnetically stirred solution of the

oxime **19** (0.18 g, 0.69 mmol) and dry pyridine (0.066 ml, 0.83 mmol) in dry methylene dichloride (5 ml) was added trifluoromethanesulfonic anhydride (0.13 ml, 0.76 mmol) slowly dropwise. After the mixture had been stirred at the same temperature for 3 h, aq. $NaHCO_3$ was added and the product was extracted with ether. The extract was subjected to the usual work-up, followed by chromatography to furnish the keto nitrile **20** (0.14 g, 89%), mp 128–129 °C, identical with the sample obtained in the earlier experiment.

7-Methyl-9-methylene-3-oxotricyclo[4.3.3.0^{1,6}]dodecane-7-carbonitrile 10 (alternative preparation)

A 0.02 M degassed benzene solution of the enone **20** (40 mg, 0.19 mmol), TBTH (0.07 ml, 0.24 mmol) and a catalytic amount of AIBN was refluxed for 12 h under nitrogen atmosphere. Benzene was removed by distillation, the residue was taken up in ether, and the extract was washed successively with 50% aq. HCl, dil. NH_4OH water, and brine and dried over anhydrous Na_2SO_4. Removal of the solvent followed by chromatography on silica gel [ethyl acetate–hexane (1 : 10)] furnished the tricyclic ketone **10** (25 mg, 63%), identical with the sample obtained earlier.

8-Methoxy-10,12-dimethyltetracyclo[6.4.1.0^{1,5}.0^{5,10}]tridec-11-en-9-one 25

The ketone **8** (0.12 g, 0.49 mmol) was stirred with $HClO_4$ (2 drops) in methylene dichloride (3 ml). After being stirred for 2 h the solution was treated with aq. $NaHCO_3$ and the product was extracted with ether. The extract was subjected to the usual work-up, followed by chromatography on silica gel [ethyl acetate–'hexane' (1 : 9)] to furnish the ketone **25** as a colourless oil (0.11 g, 92%); ν_{max}/cm^{-1} 2920, 1720 and 1630; δ_H (300 MHz) 1.18 (3H, s, Me), 1.65 (3H, s, allylic Me), 1.35–2.17 (12H, m), 3.33 (3H, s, OMe) and 4.98 (1H, br s, olefinic).

9-*endo*-(But-2-ynyl)-7-methoxy-9-methyltricyclo[5.2.2.0^{1,5}]-undec-5-en-8-one 26

To a freshly prepared solution of LDA [prepared from 2.4 ml of 1.47 M BuLi (3.5 mmol) and diisopropylamine (0.64 ml, 4.5 mmol) in 10 ml of dry THF] at −78 °C was added dropwise a solution of the ketone **13** (0.5 g, 2.4 mmol) in THF (10 ml). The resultant solution was stirred for 1 h at the same temperature and quenched with a solution of 1-bromobut-2-yne (0.64 ml, 4.85 mmol) in 2 ml of THF followed by the addition of HMPA (0.5 ml, 2.8 mmol). The reaction mixture was stirred overnight and poured into 2 M HCl. Usual work-up followed by column chromatography [ethyl acetate–'hexane' (1 : 9)] afforded the ketone **26** as an oil (0.48 g, 76%); ν_{max}/cm^{-1} 2240, 1720 and 1630; δ_H (300 MHz) 1.14 (3H, s, Me), 1.2–2.03 (8H, m), 1.78 (3H, t, *J* 2.4, acetylenic Me), 2.16 and 2.37 (2H, q of d, *J* 13.8 and 2.6, $CCCH_2$), 2.31–2.58 (2H, m, allylic CH_2), 3.5 (3H, s, OMe) and 5.79 (1H, br s, olefinic); δ_C (75 MHz) 3.6, 20.2, 25.7, 27.1, 27.3, 28.3, 30.9, 31.6, 47.7, 52.8, 53.2, 75.9, 78.6, 84.8, 114.8, 156.1 and 213.5.

11-*endo*-(4-Bromo-3-methylbut-2-enyl)-8-hydroxy-11-methyltricyclo[6.2.1.0^{1,5}]undec-5-en-7-one 21

A solution of the ketone **7** (2.1 g, 5.95 mmol) in CH_2Cl_2 (50 ml) was stirred with $HClO_4$ (70%; 0.3 ml) at room temperature. After 30 min, the reaction mixture was diluted with CH_2Cl_2, washed successively with water, saturated aq. $NaHCO_3$, and brine, and dried over Na_2SO_4. Evaporation of the solvent followed by chromatography of the crude product over silica gel [ethyl acetate–'hexane' (1 : 30)] as eluent gave the *ketone* **21** (1.86 g, 91%) as a viscous liquid; ν_{max}/cm^{-1} 3450, 2960 and 1660; δ_H (300 MHz) 1.13 (3H, s, Me), 1.50–2.10 (10H, m), 1.65 (3H, s, Me), 2.46–2.79 (2H, m, allylic CH_2), 3.95 (2H, s, CH_2Br), 5.75 (1H, t, *J* 7.2, olefinic) and 6.04 (1H, s, olefinic); δ_C (75 MHz) 14.4 (q), 16.2 (q), 23.4 (t), 29.7 (t), 30.2 (t), 31.5 (t), 31.9 (t), 33.0 (t), 41.8 (t), 54.5 (s), 60.5 (s), 87.5 (s), 116.9 (d), 127.7 (d), 132.3 (s), 180.6 (s) and 202.0 (s); *m*/*z* 339 (M^+, 38%), 259 (34), 241 (19), 231 (88), 191 (40) and 121 (100) (Found: M^+ 339.0938. $C_{17}H_{23}O_2Br$ requires *M*, 339.0944).

8-Hydroxy-11-isopropenyl-9-methyltetracyclo[6.3.2.0^{1,5}.0^{5,9}]-tridecan-13-one 22

To a solution of the allylic bromide **21** (1.02 g, 3 mmol) in degassed benzene (600 ml) was added dropwise a solution of TBTH (0.8 ml, 3 mmol) and AIBN (30 mg) in dry benzene (10 ml) using a syringe pump for 2 h under nitrogen atmosphere. After refluxing for 6 h, the reaction mixture was concentrated *in vacuo* and the residue was taken up in ether; the extract was submitted to the usual work-up, followed by column chromatography [ethyl acetate–'hexane' (1 : 30)] which afforded the *hydroxy ketone* **22** (0.62 g, 79%) as a colourless oil; ν_{max}/cm^{-1} 3460, 2950, 1700 and 1630; δ_H (300 MHz) 1.09 (3H, s, Me), 1.73 (3H, s, Me), 1.50–2.06 (12H, m), 2.25 (1H, dd, *J* 1.5 and 16.2, COCH), 2.50 (1H, d, *J* 16.2, COCH), 2.64 (1H, t, *J* 9.9, allylic H), 3.78 (1H, s, OH), 4.66 (1H, s, olefinic) and 4.91 (1H, s, olefinic); *m*/*z* 260 (M^+, 10%), 243 (6), 232 (9), 164 (17), 150 (100) and 136 (41) (Found: C, 78.6; H, 9.1. $C_{17}H_{24}O_2$ requires C, 78.4; H, 9.3%).

8-Hydroxy-11-isopropylidene-9-methyltetracyclo[6.3.2.0^{1,5}.0^{5,9}]-tridecan-13-one 11

A solution of the hydroxy olefin **22** (0.6 g, 2.28 mmol) and PTSA (catalytic) in dry toluene (90 ml) was refluxed for 1 h. The reaction mixture was cooled, washed successively with saturated aq. $NaHCO_3$ (10 ml) and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified over a silica gel column [ethyl acetate–'hexane' (1 : 30)] to afford the *isomeric hydroxy ketone* **11** (0.55 g, 91%) as an oil; ν_{max}/cm^{-1} 3460, 2940 and 1710; δ_H (300 MHz) 1.12 (3H, s, Me), 1.54 (3H, s, Me), 1.66 (3H, s, Me), 1.50–2.00 (10H, m), 2.05 (1H, d, *J* 12.6, CHCO), 2.19 (2H, s, allylic CH_2) and 2.35 (1H, dd, *J* 6.9 and 10.2, CHCO); δ_C (75 MHz) 15.2 (q), 20.8 (q), 22.5 (q), 24.2 (t), 24.6 (t), 30.1 (t), 32.8 (t), 36.1 (t), 40.7 (t), 44.9 (t), 54.9 (s), 56.1 (s), 56.3 (s), 75.4 (s), 126.0 (s), 137.6 (s) and 221.9 (s); *m*/*z* 260 (M^+, 55%), 242 (34), 232 (62), 217 (40), 189 (41), 161 (100) and 147 (54) (Found: C, 78.3; H, 9.5. $C_{17}H_{24}O_2$ requires C, 78.4; H, 9.3%).

11-Isopropylidene-9-methyltetracyclo[6.3.2.0^{1,5}.0^{5,9}]tridecane-8,13-diol 23

To a solution of the ketone **11** (0.5 g, 1.9 mmol) in methanol (75 ml) at 0 °C was added $NaBH_4$ (0.15 g, 3.84 mmol) and the reaction mixture was stirred at room temperature for 2 h. Saturated aq. NH_4Cl was added to the reaction mixture and methanol was removed at reduced pressure. The residue was treated with water and extracted with ether (4 × 25 ml). The combined organic layer was subjected to the usual work-up to give a crude alcohol, which was purified by column chromatography over silica gel. Elution with 'hexane'–ethyl acetate (10 : 1) gave the *pure alcohol* **23** (0.47 g, 93%) as a colourless liquid; ν_{max}/cm^{-1} 3450 and 2910; δ_H (300 MHz) 1.02 (3H, s, Me), 1.61 (3H, s, Me), 1.73 (3H, s, Me), 1.15–2.20 (13H, m), 2.60 (1H, d, *J* 15.3, allylic) and 3.49 (1H, d, *J* 3, CHOH); δ_C (75 MHz) 16.7 (q), 20.1 (q), 22.5 (q), 23.4 (t), 27.6 (t), 31.6 (t), 32.8 (t), 33.3 (t), 37.6 (t), 37.8 (t), 51.1 (s), 57.1 (s), 64.3 (s), 77.4 (d), 83.0 (s), 124.9 (s) and 140.9 (s); *m*/*z* 262 (M^+, 6%), 244 (19), 194 (32), 150 (96) and 136 (100) (Found: C, 77.6; H, 9.7. $C_{17}H_{26}O_2$ requires C, 77.8; H, 9.9%).

(6-Isopropylidene-8-methyl-9-oxotricyclo[6.3.0.0^{1,5}]undecan-5-yl)acetaldehyde 12

The diol **23** (0.3 g, 1.14 mmol) was dissolved in ethanol (12 ml)

and aq. periodic acid (0.29 g, 1.26 mmol in 3 ml) was added. The reaction mixture was stirred for 30 min at 20 °C, the solution was poured into water, and the product was extracted with ether. Removal of the solvent gave the *triquinic aldehyde* **12** (0.294 g, 100%) as an oil; ν_{max}/cm^{-1} 2910, 2700, 1735 and 1710; δ_H (300 MHz) 1.18 (3H, s, Me), 1.65 (3H, s, Me), 1.72 (3H, s, Me), 1.50–2.30 (11H, m), 2.40 (1H, d, *J* 15.3, allylic), 2.80 (1H, d, *J* 15.3, allylic), 2.83 (1H, m, CHCO) and 9.78 (1H, t, *J* 3, CHO); *m*/*z* 260 (M^+, 22%), 244 (54), 232 (55), 217 (29), 189 (60), 173 (62), 161 (100), 147 (66) and 105 (43) (Found: C, 78.2; H, 9.1. $C_{17}H_{24}O_2$ requires C, 78.4; H, 9.3%).

11-Isopropylidene-9-methyltetracyclo[5.4.2.0^{1,5}.0^{5,9}]tridecane-8,13-dione 30

To a degassed solution of the aldehyde **12** (260 mg, 1 mmol) in benzonitrile (10 ml) was added Wilkinson's catalyst (925 mg, 1 mmol) under argon atmosphere and the resulting solution was heated at 160 °C for 1.5 h. The reaction mixture was allowed to cool, solvent was evaporated *in vacuo* and the residue obtained was purified by column chromatography [ethyl acetate–'hexane' (3:7)] to afford the *tetracyclic 1,3-dione* **30** (180 mg, 69%) as an oil; ν_{max}/cm^{-1} 2960, 1740, 1700; δ_H (300 MHz) 1.11 (3H, s, Me), 1.52 (3H, s, Me), 1.66 (3H, s, Me), 1.70–1.85 (3H, m), 1.90–2.26 (5H, m), 2.26 (1H, d, *J* 12.9), 2.60 (1H, d, *J* 16.8, allylic), 2.63 (1H, d, *J* 16.8, CHCO), 2.93 (1H, d, *J* 16.8, allylic), 3.3 (1H, d, *J* 4.2, bridgehead H); δ_C (75 MHz) 17.4 (q), 20.7 (q), 22.6 (q), 26.2 (t), 31.6 (t), 32.7 (t), 41.2 (t), 44.4 (t), 49.4 (t), 54.2 (s), 55.6 (s), 62.6 (s), 65.7 (d), 125.8 (s), 139.3 (s), 202.6 (s) and 214.5 (s); *m*/*z* 258 (M^+, 14%), 230 (16), 215 (5), 160 (100), 145 (23), 131 (8) and 105 (8) (Found: C, 79.3; H, 8.7. $C_{17}H_{22}O_2$ requires C, 79.1; H, 8.5%).

9-Isopropylidene-7-methyl-3-oxotricyclo[4.3.3.0^{1,6}]dodecane-7-carboxylic acid 31 and (6-isopropylidene-8-methyl-9-oxotricyclo[6.3.0.0^{1,5}]undecan-5-yl)acetic acid 32

A solution of the 1,3-dione **30** (25 mg, 0.096 mmol) and 10% aq. KOH (0.05 ml) in methanol was heated to 100 °C in a sealed tube for 4 h. The reaction mixture was allowed to cool, then was diluted with water and extracted with ether (2 × 10 ml). Removal of the solvent gave the product as a mixture (**31** and **32**) (25 mg, 93%) in the ratio 1:4. The major compound **32** was separated by chromatography and crystallised from methanol, mp 140–142 °C; ν_{max}/cm^{-1} 2962, 1731, 1713 and 1642; δ_H (300 MHz) 0.98 (3H, s, Me), 1.51 (3H, s, Me), 1.64 (3H, s, Me), 1.50–2.60 (13H, m), 2.41 (1H, d, *J* 15.3, allylic) and 2.68 (1H, d, *J* 15.3, allylic); δ_C (75 MHz) 18.4 (q), 21.2 (q), 22.7 (q), 25.1 (t), 29.3 (t), 35.0 (t), 37.0 (t), 39.2 (t), 40.8 (t), 41.6 (t), 57.2 (s), 58.1 (s), 66.9 (s), 125.0 (s), 141.4 (s), 178.4 (s) and 222.6 (s) (Found: C, 74.1; H, 8.6. $C_{17}H_{24}O_3$ requires C, 73.9; H, 8.8%).

The minor compound **31** had δ_C 20.8 (q), 22.5 (q), 23.1 (q), 26.8 (t), 29.6 (t), 32.8 (t), 35.6 (t), 41.4 (t), 41.9 (t), 50.6 (t), 53.1 (s), 57.9 (s), 58.7 (s), 123.5 (s), 139.9 (s), 182.6 (s) and 213.9 (s); *m*/*z* 276 (M^+, 13%), 258 (14), 248 (30), 230 (24), 220 (56), 189 (22), 160 (95), 145 (43), 123 (29), 83 (100) and 69 (37).

(6-Isopropylidene-8-methyl-9-oxotricyclo[6.3.0.0^{1,5}]undecan-5-yl)acetic acid 32 (alternative preparation)

To a solution of the aldehyde **12** (230 mg, 1 mmol) in acetone (20 ml) was added Jones' reagent (1 ml, 1 M soln.) and the reaction mixture was stirred at 0 °C for 2 h. The reaction mixture was poured into water and extracted with ethyl acetate, and the extract was submitted to the usual work-up to give the crude acid, which was purified by chromatography on silica gel. Elution with ethyl acetate–'hexane' (2:5) afforded the title product which crystallised from methanol, mp 140–142 °C, identical with the sample obtained as above.

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