Photocycloaddition-cyclobutane rearrangement to spiro cyclopentanones: application in a formal synthesis of (±)-α-cedrene

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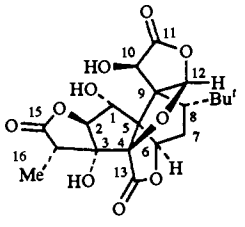
A novel four-step sequence has been developed for the construction of cyclopentanone at the carbonyl carbon of cyclic ketones **5** leading to the synthesis of functionalised spiro[4.*n*] systems **9**. The key steps involve a pinacol-type rearrangement of ethoxycyclobutane derivatives **8** obtained from copper(I)-catalysed photocycloaddition of the dienes **7** prepared from the cyclic ketones **5**. The methodology also works well on cyclic ketones with an additional functional group. For example, the ketones **13** and **20** produce the spiro ketone **19** ideally suited for synthesis of the acorane sesquiterpenes. The synthetic potential of this protocol has been demonstrated by a formal synthesis of α-cedrene **3**.

Spirocyclic systems are widely represented in natural products isolated from terrestrial as well as marine sources: ginkgolide B **1**,[1] α-acoradiene **2**,[2] α-cedrene **3**[3] and laurenene **4**[4] are examples. Since each of these structures contains a spiro[4.*n*]



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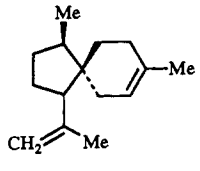

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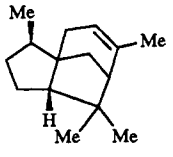

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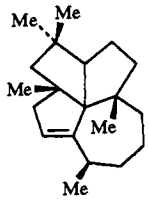

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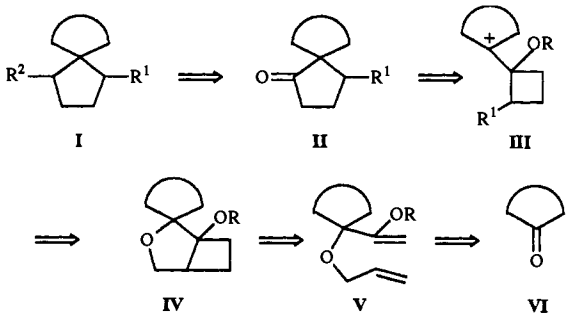
unit **I** with 1,4-bifunctionalisation on the cyclopentane ring, development[5] of a direct route to such a unit **I** is of considerable importance for the total synthesis of a wide variety[6] of natural products.

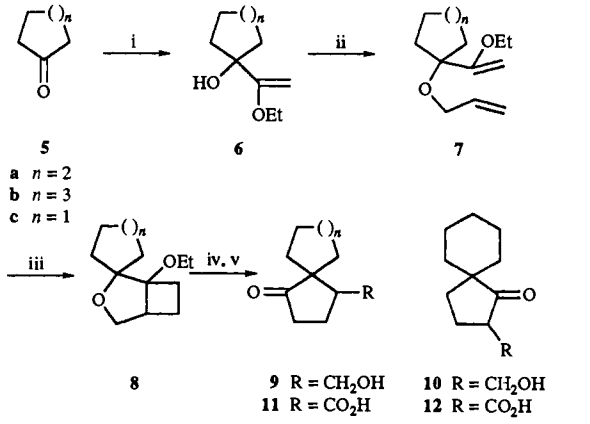
A retrosynthetic analysis (Scheme 1) suggests that the spiro cyclic unit **I** can be constructed from the spiro cyclopentanone **II** and, therefore, our primary concern was to develop a convenient route for the construction of the latter. This may be available by migration of the 1,5-bond in the cyclobutyl carbinyl cation **III**, itself generated from acid-induced opening of the tetrahydrofuran ring of the oxabicyclo[3.2.0]heptane **IV** available, in principle, from intramolecular [2 + 2] cycloaddition of the diene **V**. The diene **V** can be constructed easily from the ketone **VI**. Thus, appropriately chosen cyclic ketones will allow synthesis of the desired spiro cyclopentanones. Based on this retrosynthetic analysis,[7] we report a general convenient procedure for the construction of cyclopentanone at the carbonyl carbon of a cyclic ketone providing easy access to functionalised spiro[4.*n*] systems.[8]



Scheme 1

Results and discussion

The overall steps involved in the present protocol is illustrated by transformation of cyclohexanone **5a** to the spiro cyclopentanone **9a** (Scheme 2). Reaction of cyclohexanone **5a**



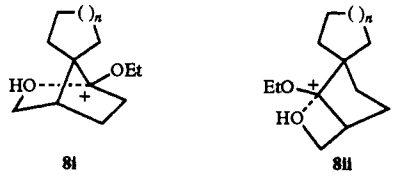
Scheme 2 *Reagents and conditions:* i, Bu^{t}Li, ethyl vinyl ether, THF −70 °C to room temp., 81–96%; ii, NaH–THF, allyl bromide, HMPA, reflux, 81–92%; iii, *hv*, Et_2O, CF_3SO_2Cu, 54–68%; iv, TfOH, CH_2Cl_2, −78 °C to room temp., 2 h, 50–82%; v, Jones oxidation, 0 °C to room temp., 1 h, 75%

with ethoxyvinyllithium,[9] generated *in situ* from reaction of ethyl vinyl ether with Bu^{t}Li afforded the vinyl carbinol **6a** (96%). The incorporation of ethyl vinyl moiety in **6a** was evident from the presence of two olefinic doublets at δ 3.94 and 4.23 (*J* 2.5 Hz), OCH_2 protons at δ 3.77 (q, *J* 7 Hz) and CH_3

protons at δ 1.31 (t, J 6 Hz) in ^{1}H NMR spectrum of **6a**. The carbinol **6a** was treated with NaH and then allyl bromide in THF–HMPA (4:1) under reflux to afford the diene **7a** (92%). The presence of three olefinic protons at δ 4.87–6.23 as a multiplet in addition to the olefinic protons present in the vinyl carbinol **6a** is in conformity with the diene structure **7a**. After successfully preparing the diene **7a**, recourse to the work of Mackor and Salomon was made for cycloaddition of the diene **7a**. Mackor[10] has shown for the first time that diallyl ether undergoes smooth photocycloaddition in the presence of cuprous triflate (CuOTf) as catalyst to form 3-oxabicyclo-[3.2.0]heptane. Subsequently, Salomon *et al.*[11] has demonstrated that CuOTf also catalyses intramolecular [2 + 2] photocycloaddition of homoallyl vinyl ethers to form 2-oxabicyclo[3.2.0]heptanes. Intrigued by these observations, the diene **7a** in diethyl ether was irradiated in presence of CuOTf to give the cyclobutane derivative **8a** (63%). The structure of the adduct was established by analysis of ^{1}H and ^{13}C NMR spectral data. While disappearance of the olefinic protons of the diene **7a** in the ^{1}H NMR spectrum of the photoadduct was an indication in favour of the structure **8a**, the most characteristic information was gained from the ^{13}C NMR spectrum. The presence of two downfield quaternary carbons at δ 89.6 and 82.7 attributable to the resonance of the carbons attached to oxygen, *i.e.* C-2 and C-1 and the two methylenes at δ 65.1 and 55.5 for the two OCH_2 units with a CH_3 at δ 15.7 indicates an ethoxy tetrahydrofuran structure as in **8a**. The deshielding of the only methine carbon at δ 42.7 over the reported chemical shift (26.5) for C-3 of tetrahydrofuran is quite expected as it is β to an ethoxy group. The presence of an additional seven CH_2 triplets coupled with the above structural information confirmed the structure of the photoadduct as **8a**

After firmly establishing the structure, the cyclobutane derivative **8a** was subjected to rearrangement, for which only trifluoromethanesulfonic acid (TfOH) was found to be effective. The single compound obtained in 78% yield after rearrangement of **8a** displayed IR absorptions at 1725s and 3240br cm^{-1} indicating it to be a hydroxy-cyclopentanone derivative. The ^{13}C NMR spectrum of the rearrangement product showed a carbonyl resonance at δ 223, deshielded from the usually observed cyclopentanone carbonyl signal (δ 213.8) indicating that the carbon α to the keto group is geminally substituted or, in other words, is the spiro centre. A triplet at δ 62.4 indicated the presence of a CH_2OH unit. Thus, the rearrangement product possesses either structure **9a** or **10** which may arise by migration of either the 1,5- or the 1,7-bond, respectively. If the rearrangement product has structure **10**, the methine carbon to which the CH_2OH unit is attached would display a signal at δ 56 in its ^{13}C NMR spectrum in contrast to a signal at δ 42 calculated for structure **9a**. The observed chemical shift (δ 44.0) for the only methine signal of the rearrangement product closely matches that calculated for structure **8a**. This clearly establishes that during rearrangement of the cyclobutane derivative **8a**, a 1,5-bond migrates exclusively to produce the spiro cyclopentanone **9a**. Further evidence in favour of structure **9a** was gained by oxidation of the compound to afford the keto acid **11** (86%). The failure of the keto acid thus obtained to undergo decarboxylation excluded the β-keto acid structure **12** which would arise if rearrangement of **8a** had involved migration of the 1,7-bond to produce **10**. The generality of this sequence was demonstrated by the transformation of cyclopentanone and cycloheptanone to the spiro[4.4] and [4.6] units **9c** and **9b**, the core structural units of ginkgolide B **1** and laurenene **4**. Thus, through a four-step sequence appropriately chosen cyclic ketones can be converted very efficiently into spiro[4.n] systems with the carbonyl and the hydroxymethylene groups on the 5-membered ring disposed in a manner so as to lead entry into a variety of natural products.

The specificity observed in migration of the 1,5-bond over the antiperiplanar 1,7-bond is interesting. Such specificity has also been observed[7] in the rearrangement of analogous cyclobutanes constructed from acyclic ketones to form vicinally substituted cyclopentanones. The observed specificity is possibly the result† of the stabilisation of the cation **8i** generated on 1,5-bond migration by the OH group that is formed during rearrangement. Stabilisation of the cation **8ii** generated after



8i **8ii**

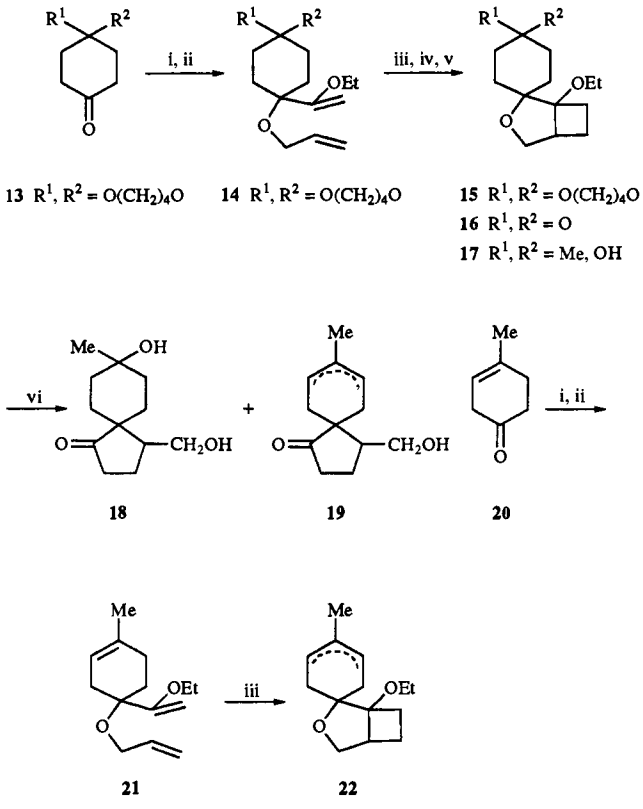
1,7-bond migration requires unfavourable formation of a strained oxetane and is thus inhibited.

The synthetic potential of this four-step sequence for spiro ring construction would be enhanced further if cyclic ketones with additional functional groups in it could be employed. This would then allow construction of spiro system with functional groups on both the rings. To illustrate, the mono ketal of cyclohexane-1,4-dione **13**[12] was chosen. The addition of ethoxyvinyllithium followed by reaction of its alkoxide with allyl bromide was uneventful and produced the diene **14** in overall excellent yield. The photoadduct **15** obtained from irradiation of the diene **14**, for convenience of operation, was deketalised with boiling aqueous acetic acid to give the ketone **16** in 59% overall yield. The structure of this adduct is in good agreement with its IR and ^{1}H NMR spectral data. The cyclobutane derivative **16** thus obtained is uniquely functionalised. It has a free carbonyl group on the six-membered ring ready for further functionalisation. On the other hand, the lower half, *i.e.* the 3-oxabicyclo[3.2.0]heptane unit is a ready source of cyclopentanone and can be generated on rearrangement‡ with only strong acid when required. Thus, without affecting the lower half, functional group manipulation is possible on the top half. To illustrate the chemoselectivity, the adduct **16** was allowed to react with an excess of MeLi to afford a diastereoisomeric mixture of the carbinols **17** in 1:2 ratio (GC and ^{1}H NMR) in 75% combined yield. The cyclopentanone unit was then generated as follows. Treatment of the carbinol mixture **17** with TfOH afforded, after chromatographic separation, the dihydroxycyclopentanone **18** (26%) and the hydroxycyclopentanone **19** (19%). The structural assignment to the hydroxycyclopentanone **19** is based on IR absorption at 1725 (CO) and 3440 (OH) cm^{-1} and the presence of two broad singlets at δ 1.64 and 5.4 for vinyl methyl and vinyl protons, respectively in the ^{1}H NMR spectrum. The structural identity of the dihydroxycyclopentanone **18** was obtained by its transformation to the spirocyclopentanone **19** through selective dehydration of the tertiary OH by heating of the compound in DMSO. The spiro ketone **19** is appropriately functionalised in both the rings for elaboration to the sesquiterpene acoradiene **2**.

A direct synthesis of the spiro ketone **19** is also possible starting from 4-methylcyclohex-3-enone **20**. The triene **21** was prepared in an analogous fashion in excellent yield.

† Alternatively, as suggested by one referee, the selectivity in migration of the 1,5-bond over the 1,7-bond is the result of the greater electron donating power of the more substituted 1,5-bond.

‡ The cyclobutane ring in 3-oxabicyclo[3.2.0]heptane derivative **16** was totally resistant to TfOH. The δ (+) character of the carbonyl carbon probably inhibits the generation of the cyclobutyl carbinyl cation.

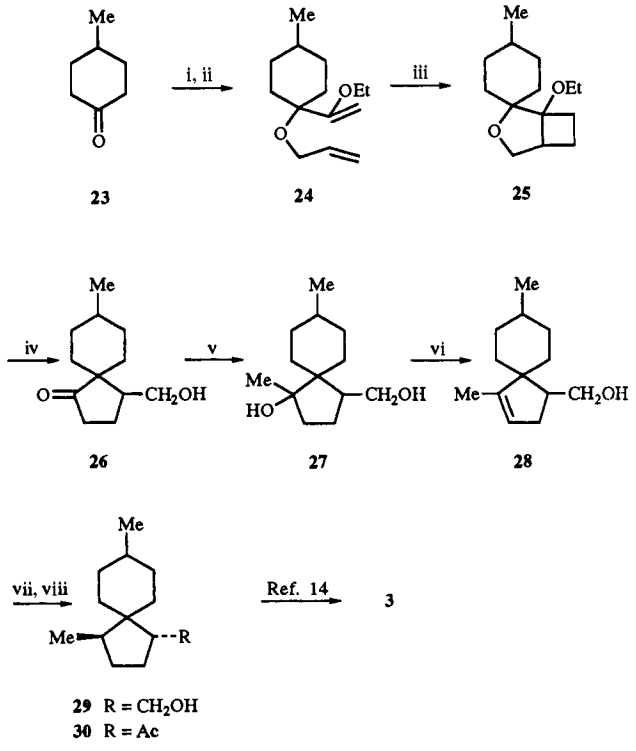


13 $R^1, R^2 = O(CH_2)_4O$ 14 $R^1, R^2 = O(CH_2)_4O$ 15 $R^1, R^2 = O(CH_2)_4O$
16 $R^1, R^2 = O$
17 R^1, R^2 = Me, OH

18 19 20

21 22

Scheme 3 *Reagents and conditions:* i, Bu^{t}Li, ethyl vinyl ether, THF, −70 °C to room temp.; ii, NaH, THF, allyl bromide, HMPA, reflux; iii, *hν*, Et_2O, CF_3SO_2Cu; iv, HOAc-H_2O, heat, 1 h; v, MeLi, Et_2O, room temp.; vi, TfOH, CH_2Cl_2, −78 °C to room temp.



23 24 25

26 27 28

3

29 R = CH_2OH
30 R = Ac

Scheme 4 *Reagents and conditions:* i, Bu^{t}Li, ethyl vinyl ether, THF, −70 °C, 81%; ii, NaH-THF, allyl bromide, HMPA, reflux, 89%; iii, *hν*, Et_2O, CF_3SO_2Cu, 58%; iv, TfOH, CH_2Cl_2, room temp., 76%; v, dihydropyran, PPTS, CH_2Cl_2; MeLi, THF, reflux; PPTS, MeOH, 67% overall; vi, Me_2SO, 165 °C, 73%; vii, H_2, PtO_2, EtOH, 99%; viii, Swern oxidation, −65 °C then MeLi, Et_2O then Jones oxidation, 55% overall

Photocycloaddition of the triene **21** in presence of CuOTf afforded the cyclobutane derivative **22** in 56% yield after chromatographic purification. The smooth cycloaddition of the triene **21** to afford the only isolable adduct **22** demonstrates that cycloaddition involved only those two alkene units which are properly orientated to form the required diene–copper(I) complex.[13] Rearrangement of the cyclobutane derivative **22** gave a mixture of the same spirocyclopentanones in comparable yields to those obtained from rearrangement of the cyclobutane derivatives **17**. The compatibility of the various functional groups present in the cyclic ketones **13** and **20** to the reaction conditions used in the spiro annulation strategy demonstrates its generality.

The four-step sequence developed, thus, has been employed to construct stereoselectively a spiro[4.5]decane with 1,4-disubstitution that had been used earlier as an advanced intermediate in a total synthesis of α-cedrene. The synthesis begins with transformation of 4-methylcyclohexanone **23** to the spirocyclopentanone **26**. The diene **24** prepared from the ketone **23**, on irradiation in the presence of CuOTf, afforded the cyclobutane derivative **25** (58%). Rearrangement of the cyclobutane derivative **25** was accomplished by treatment with TfOH to afford the spiro cyclopentanone **26** (76%). The carbonyl group in **26** has been elaborated to have a Me at this centre. The hydroxy group in **26** was first protected as a tetrahydropyranyl ether. Reaction of this hydroxy protected ketone with MeLi followed by removal of the protecting group afforded the diol **27** in 67% overall yield. Selective dehydration of the tertiary OH group was achieved by heating the diol **27** in DMSO to afford the cyclopentene derivative **28** (73%). Hydrogenation of the spiro cyclopentene **28** over Adam's catalyst afforded the spiro cyclopentane **29**. The stereochemical orientation of the Me and the CH_2OH groups on the cyclopentane ring could not be determined from ^1H NMR. The hydroxycyclopentane **29** was transformed to the ketone **30** through three consecutive steps involving Swern oxidation of the CH_2OH unit to CHO, MeLi addition to CHO and Jones oxidation of the resulting carbinol. The ^1H NMR spectrum of this product showed three COMe singlets at δ 2.14, 2.20 and 2.24 indicating the presence of three of the four possible diastereoisomers of the ketone **30**. The IR, ^1H NMR and mass spectra of this product were closely comparable to those reported by Lansburry.[14] When this mixture of the diastereoisomers was heated under reflux with NaOMe in MeOH, the components with COMe peak at δ 2.24 disappeared totally producing a mixture of two components (~3:1) with COMe peaks at δ 2.14 and 2.20. This indicated that in the components with COMe peaks at δ 2.24 and 2.20, comprising *ca.* 80–85% of the mixture, the Me and the COMe groups had the more stable *anti* orientation. The ketones **30** has already been transformed[14] to α-cedrene. Thus, with the synthesis of the ketones **30**, a formal synthesis of α-cedrene[15] is accomplished.

In conclusion, we have developed a general synthetic protocol for the construction of functionalised spiro[4.*n*] systems starting from a variety of cyclic ketones. The synthetic potential of this strategy has been demonstrated by a formal synthesis of α-cedrene.

Experimental

Bps of compounds reported here are uncorrected. Light petroleum refers to the fraction of bp 60–80 °C and ether refers to diethyl ether. Unless otherwise stated, organic extracts were dried with anhydrous sodium sulfate. ^1H NMR spectra were recorded at 60 MHz on a Varian EM-360L, at 100 MHz on a JEOL-JNM-FX 100, at 200 MHz on a Varian XL-200

spectrometer. ^{13}C NMR spectra were recorded at 25 MHz on JEOL-JNM-FX 100 spectrometer. Unless otherwise specified, ^1H NMR spectra were taken in CCl_4 solution at 60 MHz. *J* Values are given in Hz. IR spectra for solids (KBr) and liquids (neat) were recorded on Perkin-Elmer 298 IR spectrophotometer. Mass spectra were recorded at 70 eV on a JEOL-AX 500 mass spectrometer. Gas chromatographic analyses were done on a Shimadzu GC 9A instrument using column SE-30 (2 m × 3 mm) using nitrogen as carrier gas. Elemental analyses were performed by Mr S. Sarkar of this department. Owing to rapid decomposition, compounds having the vinyl ether moiety could not be analysed.

Reaction of cyclic ketones with ethoxyvinyllithium

Reaction of cyclohexanone **5a** with ethoxyvinyllithium is an illustrative procedure.

1-(1-Ethoxyvinyl)cyclohexanol 6a. To a solution of ethyl vinyl ether (5.3 g, 74 mmol) in anhydrous THF (20 cm^3) cooled to −70 °C, was added Bu^{t}Li (12% in pentane; 12 cm^3, 22 mmol) dropwise with constant stirring under an argon atmosphere. After addition the reaction mixture was allowed to warm to −10 °C and stirred for 15 min at that temperature. It was cooled again to −70 °C and to it a solution of cyclohexanone **5a** (1.47 g, 15 mmol) in THF (15 cm^3) was added slowly over a period of 15 min. The reaction mixture was stirred at −70 °C for 30 min and then allowed to attain room temperature slowly. The reaction mixture was quenched by slow addition of 15% aqueous NH_4Cl at 0 °C and then extracted with ether (2 × 50 cm^3). The combined ether extracts were dried and concentrated and the residue mixed with 1–2% of NEt_3 and distilled under reduced pressure to afford a clear liquid **6a** (2.46 g, 96%), bp 135–137 °C (10 mmHg); δ_H(200 MHz) 1.31 (3 H, t, *J* 7), 1.48–1.82 (11 H, m), 3.77 (2 H, q, *J* 7), 3.94 (1 H, d, *J* 2.5) and 4.23 (1 H, d, *J* 2.5).

1-(1-Ethoxyvinyl)cycloheptanol 6b. Reaction of cycloheptanone **5b** (1.14 g, 10 mmol) with ethoxyvinyllithium prepared from ethyl vinyl ether (3.8 g, 52 mmol) and Bu^{t}Li (12% in pentane; 8 cm^3, 15 mmol) afforded the carbinol **6b** (1.52 g, 81%); bp 130–132 °C (0.5 mmHg); δ_H(200 MHz) 1.29 (3 H, t, *J* 7), 1.43–2.06 (13 H, m), 3.72 (2 H, q, *J* 6.9), 3.87 (1 H, d, *J* 2.4) and 4.18 (1 H, d, *J* 2.6).

1-(1-Ethoxyvinyl)cyclopentanol 6c. Reaction of the cyclopentanone **5c** (1.26 g, 15 mmol) with ethoxyvinyllithium [prepared from ethyl vinyl ether (5.3 g, 74 mmol) and Bu^{t}Li (12% solution in pentane; 12 cm^3, 22 mmol)] afforded the carbinol **6c** (2.15 g, 92%); bp 100–102 °C (10 mmHg); δ_H 1.33 (3 H, t, *J* 7), 1.57–2.20 (9 H, m), 3.77 (2 H, q, *J* 7) merged with d at 3.83 (1 H, *J* 2) and 4.20 (1 H, d, *J* 2).

Transformation of the vinyl carbinols to the diallyl ether derivatives

The following preparation is an illustrative procedure.

1-Allyloxy-1-(1-ethoxyvinyl)cyclohexane 7a. NaH (40% in oil; 1.74 g, 29 mmol) was placed in a three-necked flask under nitrogen atmosphere and washed repeatedly with light petroleum to free it from adhering oil. To it was added sequentially THF (35 cm^3) and a solution of the carbinol **6a** (2.43 g, 14.3 mmol) in THF (15 cm^3). The mixture was gently refluxed for 2 h with constant stirring and then cooled to room temperature and treated with HMPA (10 cm^3) followed by allyl bromide (3.51 g, 29 mmol). After this mixture had been refluxed for 2 h, it was cooled in ice, slowly diluted with cold water (20 cm^3) and then extracted with ether (3 × 40 cm^3). The combined extracts were washed with aqueous $NaHCO_3$ and water, dried (K_2CO_3) and concentrated. The residue was mixed with 1–2% of NEt_3 and distilled under reduced pressure to afford **7a** (2.77 g, 92%) as a colourless liquid; bp 105–107 °C (0.5 mmHg); δ_H 1.30 (3 H, t, *J* 7) partly merged within m centred at 1.50 (10 H), 3.67–3.87 (4 H, m), 3.90 (1 H, d, *J* 2), 4.10 (1 H, d, *J* 2) and 4.87–6.23 (3 H, m).

1-Allyloxy-1-(1-ethoxyvinyl)cycloheptane 7b. Alkylation of the carbinol **7b** (1.44 g, 8.3 mmol) with NaH (40% in oil; 1.02 g, 17 mmol) and allyl bromide (2.06 g, 17 mmol) in the presence of HMPA (8 cm^3) afforded the diallyl ether derivative **7b** (1.46 g, 87%); bp 150–152 °C (0.5 mmHg); δ_H(200 MHz) 1.28 (3 H, t, *J* 7), 1.40–1.80 (8 H, m), 1.88 (4 H, m), 3.74 (2 H, q, *J* 7), 3.82 (2 H, m), 4.03 (1 H, d, *J* 2.4), 4.19 (1 H, d, *J* 2.4), 5.06–5.38 (2 H, m) and 5.84–6.10 (1 H, m).

1-Allyloxy-1-(1-ethoxyvinyl)cyclopentane 7c. Alkylation of the carbinol **6c** (2.11 g, 13.5 mmol) with NaH (1.7 g, 27 mmol, 40% in oil) and allyl bromide (3.23 g, 27 mmol) in the presence of HMPA (10 cm^3) afforded the diallyl ether derivative **7c** (2.3 g, 87%); bp 125–127 °C (10 mmHg); δ_H 1.30 (3 H, t, *J* 7), 1.75 (8 H, br s), 3.47–3.97 (m) merged with d at 3.87 (*J* 2) (total 5 H), 4.10 (1 H, d, *J* 2) and 4.80–6.13 (3 H, m).

Irradiation of diallyl ether derivatives

The following preparation is an illustrative procedure.

1-Ethoxyspiro[3-oxabicyclo[3.2.0]heptane-2,1′-cyclohexane] 8a. A solution of the diallyl ether derivative **7a** (1.2 g, 5.7 mmol) and cuprous triflate (200 mg) in anhydrous ether (250 cm^3) was irradiated with a Hanovia medium-pressure mercury-vapour lamp (450 W) through a water-cooled (10–12 °C) quartz immersion well for 7 h. The ether solution was washed with aqueous NH_4OH and water, and evaporated. Column chromatography of the residue with light petroleum–ethyl acetate (19:1) as eluent afforded the pure product **8a** (750 mg, 63%) as a clear liquid (Found: C, 74.1; H, 10.4. $C_{13}H_{22}O_2$ requires C, 74.24; H, 10.54%); δ_H(200 MHz) 1.16 (3 H, t, *J* 7), 1.40–2.34 (14 H, m), 2.66–2.82 (1 H, m), 3.40–3.64 (3 H, m) and 3.86 (1 H, AB_q, *J* 10); δ_C {^1H} 15.7 (q), 19.3 (t), 21.1 (t), 22.4 (t), 22.9 (t), 25.7 (t), 26.9 (t), 31.7 (t), 42.7 (d), 59.5 (t), 69.1 (t), 82.6 (s) and 89.6 (s).

1-Ethoxyspiro[3-oxabicyclo[3.2.0]heptane-2,1′-cycloheptane] 8b. Irradiation of the diallyl ether derivative **7b** (0.5 g, 2.2 mmol) for 7 h in the presence of CuOTf (200 mg) afforded, after column chromatography [light petroleum–ethyl acetate (19:1)], the cycloadduct **8b** (270 mg, 54%) (Found: C, 74.6; H, 10.6. $C_{14}H_{24}O_2$ requires C, 74.95; H, 10.78%); δ_H(200 MHz) 1.18 (3 H, t, *J* 7), 1.36–1.90 (12 H, m), 2.02–2.38 (4 H, m), 2.70–2.98 (1 H, m), 3.46–3.64 (3 H, m) and 3.84 (1 H, AB_q, *J* 10).

1-Ethoxyspiro[3-oxabicyclo[3.2.0]heptane-2,1′-cyclopentane] 8c. Irradiation of the diallyl ether derivative **7c** (1.25 g, 7.3 mmol) for 7 h in the presence of CuOTf (200 mg) afforded, after column chromatography [light petroleum–ethyl acetate (19:1)], the cycloadduct **8c** (850 mg, 68%) (Found: C, 73.0; H, 10.1. $C_{12}H_{20}O_2$ requires C, 73.43; H, 10.27%); δ_H(200 MHz) 1.18 (3 H, t, *J* 7), 1.34–1.88 (8 H, m), 2.04–2.26 (4 H, m), 2.68–2.88 (1 H, m), 3.40–3.62 (3 H, m), 3.78 (1 H, AB_q, *J* 10); δ_C {^1H} 15.7 (q), 18.6 (t), 23.8 (t), 24.9 (t), 25.0 (t), 30.7 (t), 34.2 (t), 42.2 (d), 59.4 (t), 69.7 (t), 87.6 (s) and 94.1 (s).

Rearrangement of cyclobutane derivatives

The following preparation is a representative procedure.

4-Hydroxymethylspiro[4.5]decan-1-one 9a. Trifluoromethanesulfonic acid (0.13 cm^3, 1.4 mmol) was added to a solution of the photoadduct **8a** (300 mg, 1.4 mmol) in CH_2Cl_2 (5 cm^3) at −78 °C. After the reaction mixture had been allowed to attain room temperature it was stirred for additional 2 h at that temperature and then diluted with ether, washed with 10% aqueous NaOH and brine and dried and evaporated under reduced pressure. Column chromatography of the residual mass with light petroleum–ether (3:2) as eluent afforded the spiro derivative **9a** as a clear liquid (210 mg, 78%) (Found: C, 72.5; H, 9.9. $C_{11}H_{18}O_2$ requires C, 72.49; H, 9.96); ν_{max}/cm^{-1}

3440, 2940, 2860, 1725, 1505, 1410, 1220, 1160, 1080 and 1020; δ_H 1.47 (13 H, br s), 1.97–2.37 (3 H, m) and 3.27–3.90 (2 H, m); δ_C {^{1}H} 21.4 (t), 21.9 (t), 25.5 (t), 26.7 (t), 32.6 (t), 35.1 (t), 44.9 (d), 50.8 (s), 62.4 (t) and 223.1 (s).

4-Hydroxymethylspiro[4.6]undecan-1-one 9b. Treatment of a solution of the photoadduct **8b** (300 mg, 1.3 mmol) in CH_2Cl_2 (4 cm^3) with trifluoromethanesulfonic acid (0.12 cm^3, 1.3 mmol) furnished after column chromatography [light petroleum–ether (3:2)] the spiro derivative **9b** (200 mg, 76%) (Found: C, 73.3; H, 10.2. $C_{12}H_{20}O_2$ requires C, 73.43; H, 10.27); ν_{max}/cm^{-1} 3449, 2930, 1730, 1460, 1150. 1115, 1035, 1020 and 960; δ_H(100 MHz) 1.32–2.44 (18 H, m), 3.56 (1 H, q, A of ABX, J_{AB} 10, J_{AX} 3), 3.89 (1 H, q, B of ABX, J_{AB} 10, J_{BX} 3).

4-Hydroxymethylspiro[4.4]nonan-1-one 9c. Treatment of a solution of the photoadduct **8c** (300 mg, 1.5 mmol) in CH_2Cl_2 (4 cm^3) with trifluoromethanesulfonic acid (0.14 cm^3, 1.5 mmol) furnished after column chromatography [light petroleum–ether (3:2)] the spiro derivative **9c** (210 mg, 82%) as clear liquid (Found: C, 71.2; H, 9.4. $C_{10}H_{16}O_2$ requires C, 71.39; H, 9.59); ν_{max}(neat)/cm^{-1} 3430, 2960, 2870, 1725, 1450, 1405, 1045 and 1025; δ_H(100 MHz) 1.08–1.96 (11 H, m), 1.98–2.52 (3 H, m), 3.64 (1 H, q, A of ABX, J_{AB} 10, J_{AX} 6), 3.89 (1 H, q, B of ABX, J_{AB} 10, J_{BX} 6); δ_C {^{1}H} 22.9 (t), 25.3 (t), 25.9 (t), 29.1 (t), 34.9 (t), 35.9 (t), 47.9 (d), 58.3 (s), 63.0 (t) and 223.1 (s).

4-Oxospiro[4.5]decane-1-carboxylic acid 11. Jones reagent (0.7 mol dm^{-3}; 3 cm^3) was added with magnetic stirring to an ice-cooled solution of the keto alcohol **9a** (300 mg, 1.6 mmol) in acetone (5 cm^3). After 15 min the cooling bath was removed and stirring was continued for 1 h. The reaction mixture was diluted with water (15 cm^3) and extracted with ethyl acetate (4 × 10 cm^3) and the extracts were washed with water (10 cm^3) and aqueous saturated $NaHCO_3$ (3 × 5 cm^3). The combined basic aqueous washings were cooled, acidified with 6 mol dm^{-3} HCl and extracted with ethyl acetate (3 × 5 cm^3). The combined extracts were washed with brine (2 × 10 cm^3), dried and evaporated to afford the acid **11** (250 mg, 75%), mp 103 °C (Found: C, 67.2; H, 8.2. $C_{11}H_{16}O_3$ requires C, 67.32; H, 8.22); ν_{max}/cm^{-1} 2945, 1740, 1690, 1445, 1340, 1240, 1190, 1160, 1130, 1015, 950, 765 and 680; ^{1}H NMR (as Me ester) δ 1.50 (10 H, br s), 1.90–2.67 (4 H, m), 2.93 (1 H, t, J 5) and 3.67 (3 H, s).

1-Ethoxyspiro[3-oxabicyclo[3.2.0]heptane-2,1′-cyclohexan]-3-one 16. Reaction of 7,12-dioxaspiro[5.6]dodecan-3-one **13** (1.84 g, 9.6 mmol) with ethoxyvinyllithium [prepared from ethyl vinyl ether (4.0 g, 56 mmol) and Bu^{t}Li (12% solution in pentane; 8 cm^3, 15 mmol)] afforded the corresponding vinyl carbinol (1.90 g, 75%); bp 135–137 °C (0.5 mm); δ_H 1.33 (3 H, t, J 7) partly merged with m centred at 1.67 (13 H), 3.47–3.93 (m) merged with d at 3.80 (J 2) (total 7 H), 4.13 (1 H, d, J 2). This carbinol (1.85 g, 7 mmol) was alkylated, using NaH (40% in oil; 0.84 g, 14 mmol), with allyl bromide (1.69 g, 14 mmol) in presence of HMPA (7 cm^3) to afford the diene **14** (1.96 g, 92%); bp 160–163 °C (0.5 mmHg); δ_H 1.30 (3 H, t, J 7), 1.47–2.00 (12 H, m), 3.47–3.87 (8 H, m), 3.92 (1 H, d, J 2), 4.10 (1 H, d, J 2) and 4.87–6.20 (3 H, m).

Irradiation of the diene **14** (0.90 g, 2.9 mmol) for 7 h in the presence of CuOTf (200 mg) afforded the adduct **15** (0.9 g). This was heated on a steam-bath with 80% aqueous acetic acid (9 cm^3) for 1 h after which it was cooled to room temperature and extracted with ether. The ether extract was washed with water and aqueous $NaHCO_3$, dried and concentrated and the residue subjected to column chromatography with light petroleum–ether (4:1) as eluent to afford the pure ketone **16** (0.45 g, 59%) overall (Found: C, 69.3; H, 9.1. $C_{13}H_{20}O_3$ requires C, 69.61; H, 8.99%); ν_{max}/cm^{-1} 2960, 2870, 1715, 1440, 1280, 1250, 1230, 1220, 1110, 1065, 995, 980 and 900; δ_H(100 MHz) 1.18 (3 H, t, J 7), 1.36–3.12 (13 H, m), 3.52 (2 H, q, J 7), 3.67 (1 H, d, J 10) and 3.92 (1 H, ABq, 10).

1-Ethoxy-4′-methylspiro[3-oxabicyclo[3.2.0]heptane-2,1′-cyclohexan]-4′-ol 17

To a solution of the ketone **16** (250 mg, 1 mmol) in dry ether (10 cm^3) cooled in ice, was added MeLi (1.5 mol dm^{-3} solution in ether; 2 cm^3, 3.0 mmol) dropwise under N_2 atmosphere. The reaction mixture was stirred overnight at room temperature and then quenched with saturated aqueous NH_4Cl (2 cm^3) and extracted with ether (3 × 10 cm^3). The combined extracts were washed with brine, dried and evaporated and the residue was column chromatographed with light petroleum–ether (4:1) as eluent to give the unchanged ketone **16** (50 mg) and the desired alcohol **17** (160 mg, 75% based on recovered ketone) [eluent light petroleum–ether (3:2)] as a clear liquid; t_R 1.55 min (34%) and 1.72 min (65%) at 200 °C (Found: C, 69.6; H, 10.3. $C_{14}H_{24}O_3$ requires C, 69.96; H, 10.07%); ν_{max}/cm^{-1} 3420, 2960, 2870, 1440, 1370, 1270, 1230, 1110, 1070, 1000, 920 and 880; δ_H(100 MHz) 1.20 (3 H, t, J 7), 1.24 (3 H, s), 1.36–2.48 (13 H, m), 2.60–2.92 (1 H, m), 3.50 (2 H, q, J 7), 3.56 (1 H, d, merged under q of OCH_2CH_3, J 10) and 3.84 (1 H, ABq, J 10).

Rearrangement of the cyclobutane derivative 17: synthesis of 4-hydroxymethyl-8-methylspiro[4.5]dec-7-en-1-one 19

Treatment of a solution of the photoadduct **17** (130 mg, 0.54 mmol) in CH_2Cl_2 (3 cm^3) with TfOH (0.04 cm^3) furnished, after column chromatography (1:1 ether–light petroleum), first the olefin **19** (20 mg, 19%) (Found: C, 74.3; H, 9.6. $C_{12}H_{18}O_2$ requires C, 74.19; H, 9.34%); ν_{max}/cm^{-1} 3440, 2930, 1725, 1400, 1150, 1080 and 1030; δ_H(100 MHz) 1.32–2.60 (15 H, m, with a br s at 1.64), 3.40–4.02 (2 H, m), 5.40 (1 H, br s) and then the dihydroxy compound **18** (30 mg, 26%); δ_H 0.70–2.40 (22 H, m, with a s at 1.13), 3.30–4.00 (2 H, m). The diol was characterised by its transformation to the olefin **19** by heating in DMSO in an NMR tube at 165 °C (oil bath) for 2 h.

1-Ethoxy-4′-methylspiro[3-oxabicyclo[3.2.0]heptane-2,1′-cyclohex-3′-ene] 22

Reaction of 4-methylcyclohex-3-enone **20** (1.65 g, 15 mmol) with ethoxyvinyllithium [prepared from ethyl vinyl ether (5.5 g, 78 mmol) and Bu^{t}Li (12% solution in pentane; 12.5 cm^3, 23 mmol)] afforded the corresponding vinyl carbinol (2.10 g, 77%); bp 125–127 °C (0.2 mmHg); δ_H 1.30 (3 H, t, J 7), 1.53–2.47 (10 H, m), 3.73 (q, J 7) merged with d at 3.83 (J 2) (total 3 H), 4.20 (1 H, d, J 2) and 5.10–5.37 (1 H, m). This carbinol (1.84 g, 10.1 mmol) was alkylated, using NaH (40% in oil; 1.2 g, 20 mmol), with allyl bromide (2.42 g, 20 mmol) in the presence of HMPA (10 cm^3) to afford the diallyl ether derivative **21** (2.04 g, 91%), bp 143–145 °C (0.2 mmHg); δ_H 1.30 (3 H, t, J 7), 1.53–2.57 (9 H, m), 3.43–3.90 (4 H, m), 3.93 (1 H, d, J 2), 4.10 (1 H, d, J 2) and 4.70–6.17 (4 H, m).

Irradiation of the diallyl ether derivative **21** (1.2 g, 5.4 mmol) in the presence of CuOTf (350 mg) afforded after column chromatography [light petroleum–ethyl acetate (19:1)] the adduct **22** (0.67 g, 56%) (Found: C, 74.9; H, 9.85. $C_{14}H_{22}O_2$ requires C, 75.63; H, 9.97%); δ_H 1.13 (3 H, t, J 7), 1.33–2.43 (13 H, m), 2.50–2.93 (1 H, m), 3.23–3.97 (4 H, m) and 4.97–5.43 (1 H, m).

1-Ethoxy-4′-methylspiro[3-oxabicyclo[3.2.0]heptane-2,1′-cyclohexane] 25

Reaction of 4-methylcyclohexanone **23** (1.14 g, 10 mmol) with ethoxyvinyllithium [prepared from ethyl vinyl ether (6 g, 84 mmol) and Bu^{t}Li (12% solution in pentane; 13 cm^3, 25 mmol) afforded the corresponding carbinol (2.4 g, 81%); bp 128–130 °C (0.5 mmHg); δ_H 0.83–1.07 (3 H, m), 1.33 (t, J 7) merged under m at 1.27–2.40 (total 13 H), 3.70 (2 H, q, J 7), 3.90 (1 H, d, J 2) and 4.10–4.20 (1 H, m).

This carbinol (2.4 g, 13 mmol) was alkylated using NaH (40% in oil; 1.56 g, 26 mmol) with allyl bromide (3.14 g, 26 mmol) in

the presence of HMPA (10 cm^3) to afford the diene **24** (2.6 g, 89%); bp 145–147 °C (0.5 mmHg): δ_H 0.63–1.07 (3 H, m), 1.27–2.37 (12 H, m), 3.43–3.83 (5 H, m), 3.90 (1 H, d, *J* 2) and 4.80–6.23 (3 H, m).

Irradiation of the diene **24** (1.25 g, 5.6 mmol) in the presence of CuOTf (350 mg) afforded after column chromatography [light petroleum–ethyl acetate (19:1)] the adduct **25** (0.72 g, 58%) (Found: C, 75.25; H, 10.28. $C_{14}H_{24}O_2$ requires C, 74.95; H, 10.78%); δ_H(100 MHz) 0.90, 0.96 (3 H, two s), 1.08–2.44 (16 H, m with two t at 1.18 and 1.20), 2.64–2.94 (1 H, m), 3.36–3.72 (3 H, m) and 3.87 (1 H, m).

4-Hydroxymethyl-8-methylspiro[4.5]decan-1-one 26

TfOH (0.25 cm^3, 2.8 mmol) was added to a solution of the photoadduct **25** (0.63 g, 2.8 mmol) in CH_2Cl_2 (6 cm^3) at −78 °C. The reaction mixture was allowed slowly to attain room temperature after which it was stirred for an additional 2 h at that temperature. It was then diluted with ether, washed with 10% aqueous NaOH and brine, dried and evaporated. Column chromatography of the residue with light petroleum–ether (3:2) as eluent afforded **26** (420 mg, 76%) (Found: C, 73.3; H, 10.5. $C_{12}H_{20}O_2$ requires C, 73.43; H, 10.27%); ν_{max}/cm^{-1} 3430, 2920, 2860, 1730, 1450, 1410, 1080, 1030, 1015 and 970; δ_H(100) 0.76–1.00 (3 H, m), 1.04–2.52 (15 H, m) and 3.44–3.92 (2 H, m).

4-Hydroxymethyl-1,8-dimethylspiro[4.5]dec-1-ene 28

A solution of the hydroxy compound **26** (0.28 g, 1.43 mmol) and dihydropyran (0.18 g, 2.1 mmol) in dry CH_2Cl_2 (6 cm^3) containing pyridinium toluene-*p*-sulfonate (PPTS) (40 mg, 0.15 mmol) was stirred for 4 h at room temperature after which it was evaporated. Rapid column chromatography of the residue with light petroleum–ether (4:1) as eluent, afforded the THP ether (0.38 g, 95%); δ_H 0.70–1.07 (3 H, m), 1.13–2.50 (H, m) 3.07–3.97 (6 H, m) and 4.47 (1 H, br s).

To a solution of the THP ether (0.38 g, 1.36 mmol) in THF (10 cm^3), cooled in ice, was added dropwise MeLi (1.5 mol dm^{-3} solution in ether, 4.5 cm^3, 6.8 mmol). The mixture was stirred at room temperature for 12 h after which it was gently refluxed for 4 h and then quenched with saturated aqueous NH_4Cl at 0 °C and extracted with ether (2 × 25 cm^3). The combined extracts were dried and evaporated to afford the crude product in quantitative yield. The crude material was used in the next step without further purification.

A solution of the THP ether, thus obtained (400 mg, 1.36 mmol) and PPTS (35 mg, 0.14 mmol) in ethanol (8 cm^3) was stirred at 55 °C for 3 h after which it was evaporated under reduced pressure. The residue was chromatographed to afford the unchanged ketone **26** (30 mg) [light petroleum–ethyl acetate (4:1)] and the desired diol **27** (0.180 g, 67% overall yield) [light petroleum–ethyl acetate (7:3)]; ν_{max}/cm^{-1} 3360, 2920, 2870, 1735 (week), 1460, 1380, 1150, 1120, 1020 and 930; δ_H 1.00 (3 H, d, *J* 6), 1.20 (3 H, s), 1.53–2.20 (14 H, m), 3.36 (1 H, q, A of ABX, J_{AB} 10, J_{AX} 2.5), 3.73 (1 H, q, B of ABX, J_{AB} 10, J_{BX} 2.5) and 5.10–5.90 (2 H, br s). The diol **27** was directly dehydrated as follows:

A solution of the diol **27** (60 mg, 0.28 mmol) and DMSO (0.5 cm^3) in a sealed tube was heated at 165–170 °C (bath temperature) for 2.5 h after which it was cooled to room temperature, poured into water (2 cm^3) and extracted with ether (3 × 5 cm^3). The combined extracts were washed with water, dried and evaporated and the residue was column chromatographed with light petroleum–ethyl acetate (9:1) as eluent to afford the unsaturated alcohol **28** (40 mg, 73%) (Found: C, 80.2; H, 11.25. $C_{13}H_{22}O$ requires C, 80.35; H, 11.41); δ_H(100 MHz) 0.90 (3 H, d, *J* 6), 1.16–2.60 (16 H, m), 3.37 (1 H, q, A of ABX, J_{AB} 10, J_{AX} 6), 3.89 (1 H, q, B of ABX, J_{AB} 10, J_{BX} 6) and 5.28 (1 H, br s).

1-Hydroxymethyl-4,8-dimethylspiro[4.5]decane 29

Hydrogenation of a solution of the unsaturated alcohol **28** (40 mg, 0.21 mmol) in ethyl acetate (5 cm^3) was achieved by stirring it over Adam's catalyst (10 mg) under an H_2 atmosphere for 4 h. The catalyst was filtered off and the filtrate evaporated to afford the saturated alcohol **29** (40 mg, 99%) (Found: C, 79.4; H, 12.2. $C_{13}H_{24}O$ requires C, 79.53; H, 12.32); δ_H(100 MHz) 0.76–1.02 (6 H, m), 1.08–2.26 (16 H, m) and 3.18–3.94 (2 H, m).

1-Acetyl-4,8-dimethylspiro[4.5]decane 30

To a solution of oxalyl chloride (0.40 cm^3, 0.40 mmol) in CH_2Cl_2 (1 cm^3) at −60 °C, was added DMSO (0.5 cm^3, 0.63 mmol) dissolved in CH_2Cl_2 (0.25 cm^3) with stirring under a N_2 atmosphere. After 5 min at this temperature the mixture was treated with a solution of the alcohol **29** (50 mg, 0.25 mmol) in CH_2Cl_2 (0.5 cm^3). Stirring was continued for additional 15 min at −60 °C after which Et_3N (0.9 cm^3, 1.7 mmol) was added to the mixture and stirring continued for 5 min. After the mixture had been allowed to attain room temperature it was treated with water (2 cm^3) and the aqueous layer separated and extracted with CH_2Cl_2 (3 × 5 cm^3). The combined extracts were washed successively with aqueous HCl (1%), water, aqueous $NaHCO_3$ (5%) and brine and then dried and evaporated. Filtration of the residue through short column of neutral Al_2O_3 [light petroleum–ether (1:1)] afforded the corresponding aldehyde (40 mg, 81%) as a clear liquid; δ_H 0.70–1.07 (6 H, m), 1.10–2.53 (15 H, m) and 9.70–9.83 (1 H, m). Without further purification this aldehyde was directly treated with MeLi according to the following procedure.

To a solution of the aldehyde (40 mg, 0.21 mmol) in ether (2 cm^3) was added MeLi (1.2 mol dm^{-3} in ether; 1 cm^3, 1.2 mmol) at 0 °C under a N_2 atmosphere. The reaction mixture was stirred at room temperature for 12 h and then quenched with saturated aqueous NH_4Cl at 0 °C and extracted with ether (2 × 10 cm^3). The combined extracts were washed with brine, dried and evaporated and the residue chromatographed to afford a liquid (30 mg, 70%); δ_H 0.70–2.33 (24 H, m) and 3.23–4.17 (2 H, m). Without further purification this alcohol (30 mg, 0.14 mmol) in acetone (2 cm^3) was oxidised with Jones reagent (0.7 mol dm^{-3}; 0.3 cm^3) to afford a mixture of the diastereoisomeric ketones **30** (20 mg, 67%); ν_{max}/cm^{-1} 2960, 2930, 2880, 1710, 1455, 1380, 1355 and 1170; δ_H(100 MHz) 0.68–2.48 (20 H, m), 2.14, 2.20, 2.24 (3 H, all s, COMe) and 2.52–3.16 (1 H, m), *m/z* 208 (M^+), 190, 150, 138, 123, 109, 95, 84 and 81. Spectral data were closely comparable to those reported.

The ketone thus obtained (20 mg, 0.1 mmol) was refluxed with a solution of sodium methoxide in methanol (0.8 mol dm^{-3}; 2.5 cm^3) for 4 h. Standard ether work-up gave a liquid (15 mg); δ_H 0.68–2.48 (20 H, m), 2.14, 2.20 (3 H, two s) and 2.52–3.16 (1 H, m).

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References

1 N. Sakabe, S. Takada and K. Okabe, *J. Chem. Soc., Chem. Commun.*, 1967, 259.
2 (*a*) B. Tomita and Y. Hirose, *Tetrahedron Lett.*, 1970, 143; (*b*) B. Tomita, T. Isono and Y. Hirose, *Tetrahedron Lett.*, 1970, 1371.
3 G. Stork and R. Breslow, *J. Am. Chem. Soc.*, 1953, **75**, 3291.
4 (*a*) R. E. Corbett, D. R. Lauren and R. T. Weavers, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1774; (*b*) R. E. Corbett, C. M. Couldwell, D. R. Lauren and R. T. Weavers, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1791.
5 (*a*) For a comprehensive account of synthetic approaches to spiro cyclopentanes see: (i) C. H. Heathcock, S. L. Graham, M. C.

Pirrung, F. Plavac and C. T. White, *The Total Synthesis of Sesquiterpenes*, ed. J. ApSimon, Wiley, New York, 1983, vol. 5, pp. 264–313; (ii) M. Vandewalle and P. De Clercq, *Tetrahedron*, 1985, **41**, 1767; (*b*) For some selected recent work see: (i) P. A. Wender and A. W. White, *J. Am. Chem. Soc.*, 1988, **110**, 2218; (ii) D. L. J. Clive and R. J. Bengstra, *J. Org. Chem.*, 1990, **55**, 1786; (iii) P. Canonne, R. Boulanger and P. Angers, *Tetrahedron Lett.*, 1991, **32**, 5861; (iv) T. Imanishi, T. Ohra, K. Sugiyama, Y. Ueda, T. Takemoto and C. Iwata, *J. Chem. Soc., Chem. Commun.*, 1992, 269; (v) J. R. Hwu and J. M. Wetzel, *J. Org. Chem.*, 1992, **57**, 922; (vi) F. Camps, A. Llebaria, J. M. Moreto and L. Pages, *Tetrahedron Lett.*, 1992, **33**, 113; (vii) F. Kido, T. Abiko and M. Kato, *J. Chem. Soc., Perkin Trans. 1*, 1992, 229; (viii) H. Huang and C. J. Forsyth, *Tetrahedron Lett.*, 1993, **34**, 7889; (iv) M. Mori, M. Ishono, N. Kaneta and M. Shibasaki, *J. Org. Chem.*, 1993, **58**, 2972.

6 For the synthesis of bridged and condensed ring natural products through spirocyclic intermediates see: (*a*) A. J. Robichaud and A. I. Meyers, *J. Org. Chem.*, 1991, **56**, 2607; (*b*) Y.-J. Wu and D. J. Burnell, *J. Chem. Soc., Chem. Commun.*, 1991, 764.

7 Using this sequence the synthesis of vicinally substituted cyclopentanones from acyclic ketones has been reported by us: (*a*) S. Ghosh and D. Patra, *Tetrahedron Lett.*, 1993, **34**, 4565; (*b*) D. Patra and S. Ghosh, *J. Org. Chem.*, 1995, **60**, 2526.

8 A portion of this work appeared as a preliminary communication: S. Ghosh, D. Patra and G. Saha, *J. Chem Soc., Chem. Commun.*, 1993, 783.

9 J. E. Baldwin, G. A. Hofle and O. W. Lever, Jr., *J. Am. Chem. Soc.*, 1974, **96**, 7125.

10 J. T. M. Evers and A. Mackor, *Tetrahedron Lett.*, 1978, 821.

11 S. R. Raychaudhuri, S. Ghosh and R. G. Salomon, *J. Am. Chem. Soc.*, 1982, **104**, 6841.

12 J. Hyatt, *J. Org. Chem.*, 1983, **48**, 129.

13 R. G. Salomon, *Tetrahedron*, 1983, **39**, 485.

14 P. T. Lansburry, V. R. Haddon and R. C. Stewert, *J. Am. Chem. Soc.*, 1974, **96**, 896.

15 For other approaches to cedranes see: (*a*) Ref. 5*a* (i), pp. 484–488; (*b*) K. Pramod and G. S. R. Subba Rao, *J. Chem. Soc., Chem. Commun.*, 1982, 761; (*c*) N. Selvakumar and G. S. R. Subba Rao, *Tetrahedron Lett.*, 1993, **34**, 7789; (*d*) Y. J. Chen and W. Y. Lin, *Tetrahedron Lett.*, 1992, **33**, 1749 and references cited therein.

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