# A formal total synthesis of (±)-homogynolide-B

**Adusumilli Srikrishna,*[a] Sankuratri Nagaraju,[a] Somepalli Venkateswarlu,[a] Uma S. Hiremath,[a] T. Jagadeeswar Reddy[a] and Paloth Venugopalan[b]**

[a] *Department of Organic Chemistry, Indian Institute of Science, Bangalore 56012, India*
[b] *Department of Chemistry, Panjab University, Chandigarh 160014, India*

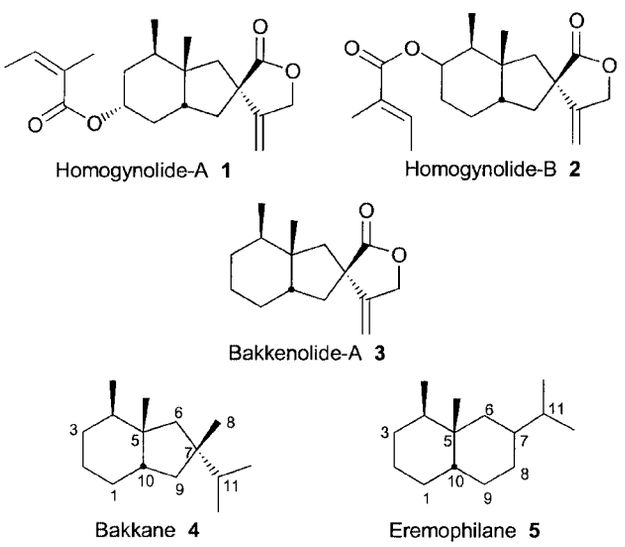
***Received (in Cambridge) 14th May 1999, Accepted 15th June 1999***

A formal total synthesis of (±)-homogynolide-B, a sesquiterpene containing an α-spiro-β-methylene-γ-butyrolactone moiety spirofused to a bicyclo[4.3.0]nonane framework, is described. Thus, Hagemann's ester **11** was converted into the allyl alcohol **16** in three steps. One-pot Claisen rearrangement of the allyl alcohol **16** and 2-methoxypropene in the presence of a catalytic amount of propionic acid afforded a 3:2 epimeric mixture of the ketone **15** and further rearranged product **19**. Ozonolysis followed by intramolecular aldol condensation and hydrogenation transformed the enones **15a**,**b** into the key intermediate keto ketals **13a** and **13b**. Methoxymethylene Wittig reaction followed by bromoacetalisation converted the keto ketal **13a** into the radical precursor bromo acetal **22a**. The 5-*exo-dig* radical cyclisation of the bromo acetal **22a**, followed by acid catalysed hydrolysis and oxidation, led to the keto spirolactone **12**, Greene's precursor of homogynolide-B. The same sequence transformed the keto ketal **13b** into a 3:2 mixture of the spirolactones **12** and **25**, which on equilibration furnished the spirolactone **12**. The stereostructure of the keto spirolactone **12** was unambiguously established by single-crystal X-ray diffraction analysis.

## Introduction

The creativity of nature in devising varied molecular architecture is revealed through the isolation of a wide range of natural products with remarkable skeletal make-up and multifarious functionalities. Among the natural products, terpenoids (isoprenoids) occupy a special position on account of their widespread occurrence and the bewildering array of carbocyclic skeleta that they embody. Sesquiterpenes, biogenetically derived from farnesyl pyrophosphate, are assembled in acyclic, monocyclic, bicyclic, tricyclic and even tetracyclic structures containing small, medium and large rings with a wide range of functionalities.[1] The great diversity in their molecular architecture has made terpene synthesis a challenging and exciting area of research.[2] In 1976, Sorm and co-workers[3] reported, for the first time, the isolation of homogynolides A **1** and B **2** along with bakkenolide A **3** from *Homogyne alpina*. (L.) Cass. Homogynolides A and B belong to a small group of sesquiterpenes, the bakkanes **4**,[4] which are biogenetically derived from eremophilanes **5**, containing a novel α-spiro-β-methylene-γ-butyrolactone moiety spirofused to a hydrindane framework. The homogynolides A **1** and B **2** were found to possess antifeedant activity against certain types of beetle adults (*Sitophilus granarius*, *Tribolium confusum*) and larvae (*Trogoderma granarium*, *Tribolium confusum*).[5] The structures of homogynolides A **1** and B **2** were established as the (*Z*)-2-methylbut-2-enoyl ester of 2-hydroxybakkenolide-A and the (*E*)-2-methylbut-2-enoyl ester of 3-hydroxybakkenolide-A, respectively, *via* chemical degradation and spectral comparison with other bakkenolides. The unusual structural features of homogynolides coupled with their biological activities made them attractive and challenging synthetic targets. Despite their biological properties, homogynolides and bakkenolides have received only limited attention from synthetic chemists.[6–9] For example, only one approach, by Greene and co-workers,[6,7] was reported in the literature for the total synthesis of homogynolides A and B prior to the completion of work in our laboratory.[9]

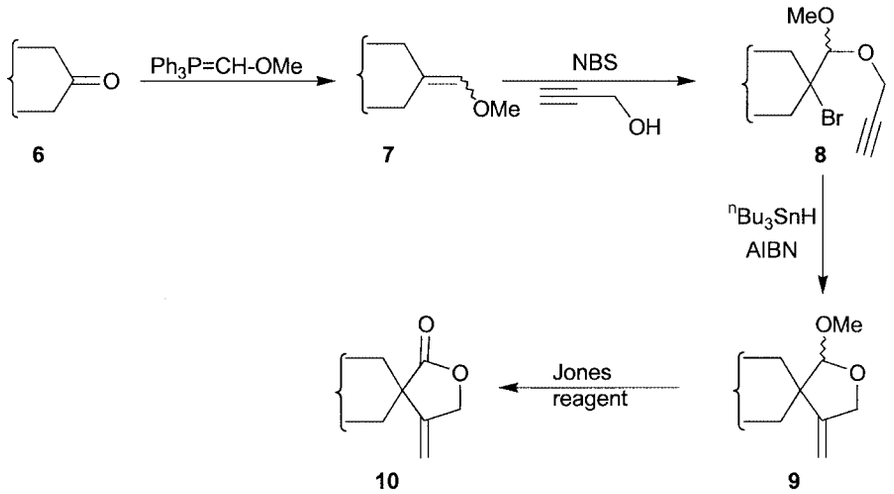
Recently, we have developed a general, radical cyclisation-based methodology[10] for the construction of α-spiro-β-methylene-γ-butyrolactones starting from cyclic ketones, Scheme 1.



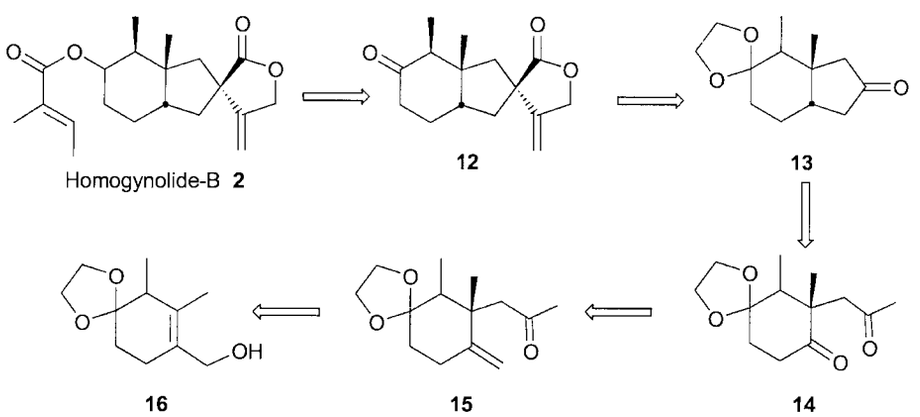

Methoxymethylene Wittig reaction of a cyclic ketone **6** followed by bromoacetalisation of the resultant enol ether **7** with *N*-bromosuccinimide (NBS) and propargyl alcohol (prop-2-yn-1-ol) generates the bromo acetal **8**. The 5-*exo-dig*-radical cyclisation of the bromo acetal **8** followed by one-step hydrolysis and oxidation of the resultant spiroacetal **9** furnishes the spirolactone **10**. Based on this methodology we have achieved a formal total synthesis of (±)-homogynolide-B starting from Hagemann's ester **11**, and herein we describe the details of these investigations.[9]

## Results and discussion

The retrosynthetic analysis of homogynolide-B **2** is depicted in Scheme 2. The keto spirolactone **12**, the penultimate precursor in Greene's[6] synthesis of (−)-homogynolide-B, was identified as the target molecule. Based on the radical-cyclisation-mediated general methodology,[10] *cf.* Scheme 1, the monoprotected bicyclic dione **13** was readily recognised as the key



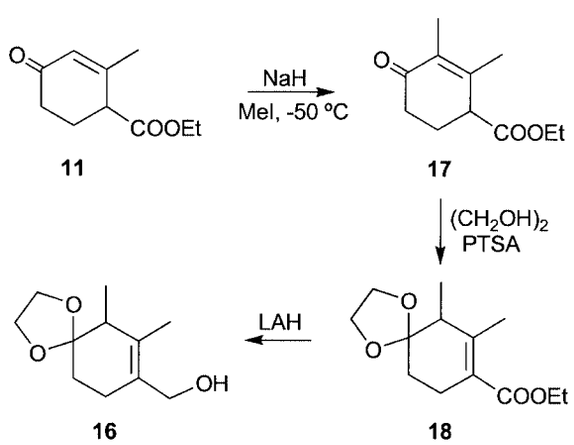

**Scheme 1**




**Scheme 2**

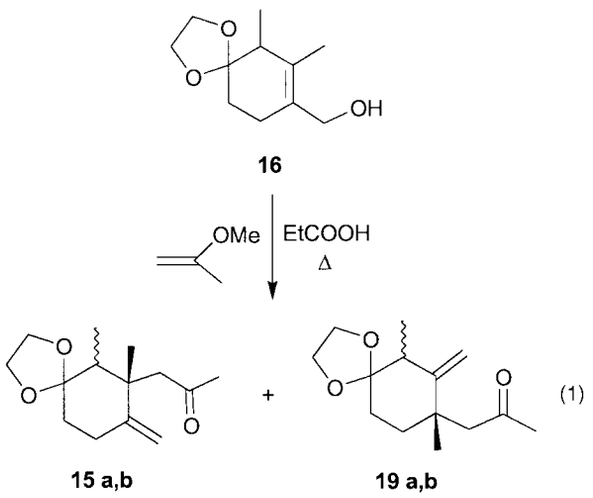
intermediate. It was envisaged that intramolecular aldol condensation followed by hydrogenation could convert the dione **14** into the keto ketal **13**. The dione **14** could itself be obtained by oxidative cleavage of the enone **15**. The enone **15**, a γ,δ-unsaturated ketone, could in turn be obtained from the allyl alcohol **16** *via* a Claisen rearrangement.

To begin with, the allyl alcohol **16** was synthesised starting from Hagemann's ester **11**.[11] Thus, low-temperature (−50 °C) alkylation of the sodium dienolate of Hagemann's ester **11**, generated at 0 °C using sodium hydride in dry THF, with methyl iodide furnished the γ-methylated ester **17** in almost quantitative yield with a high degree of regioselectivity (>20:1). For the conversion of the ester **17** into the allyl alcohol **16**, in addition to protection of the ketone as its ketal, the isomerisation of the olefin was also required, and this was achieved by exploiting the well established fact that the double bond isomerises to the β,γ-position from the α,β-position during the ketalisation of a cyclohexenone.[12] Thus, refluxing a benzene solution of the ester **17**, ethylene glycol and a catalytic amount of toluene-*p*-sulfonic acid (PTSA) using a Dean–Stark water trap furnished the ketal **18**. Regioselective reduction of the ketal ester **18** with lithium aluminium hydride (LAH) in diethyl ether at −70 °C furnished the requisite allyl alcohol **16** in 97% yield (Scheme 3).



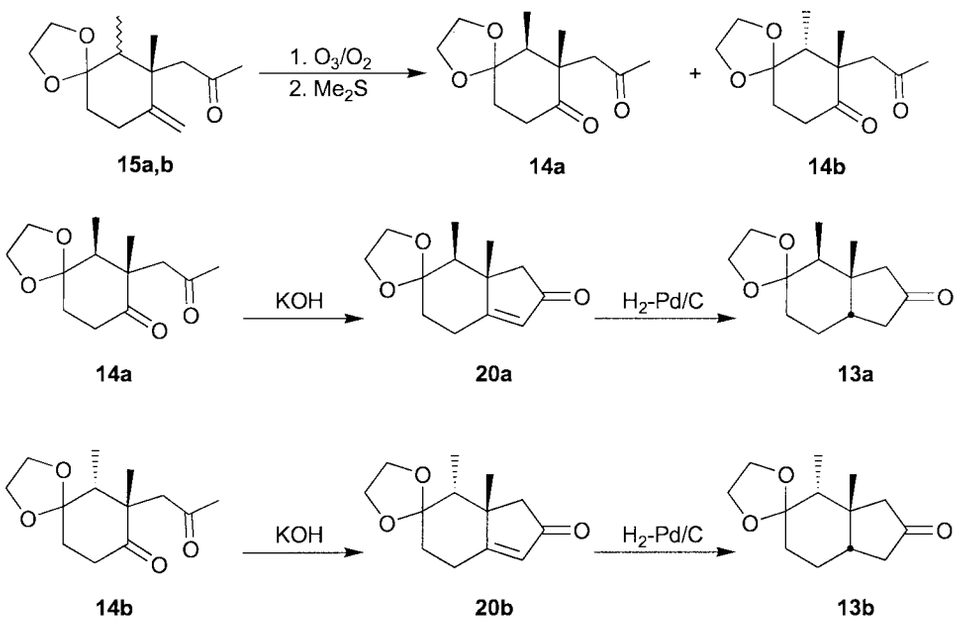

**Scheme 3**

The regio- and stereospecific formation of γ,δ-unsaturated carbonyl systems coupled with the ease of creation of a quaternary centre from a γ,γ-disubstituted allyl alcohol prompted us to choose the Claisen rearrangement[13] for the generation of the quaternary carbon atom. Thermal activation of a mixture of the allyl alcohol **16**, 2-methoxypropene and a catalytic amount of propionic acid in a sealed tube first at 100 °C for 12 h and later at 190 °C for 48 h furnished a 3:2 epimeric mixture of the enones **15a**,**b** in 75% yield and an epimeric mixture of the rearranged product **19** in 11% yield [reaction (1)], whose structure was established from its spectral data. The rearranged product **19** was obtained by an intramolecular enol-ene reaction followed by a retro-ene reaction.[14] The stereochemistry of the two methyl groups was assigned as *cis* for the major isomer **15a** of the enones on the basis of the assumption that during the Claisen rearrangement the enol ether moiety approaches the olefin from the *anti* side of the secondary methyl group. This was confirmed by the conversion of the major isomer **15a** into the target molecule, the keto spirolactone **12**. The enones **14a**,**b** were converted into the keto ketals **13a**,**b** *via* ozonolysis, intramolecular aldol condensation and catalytic hydrogenation. Thus, ozonation of the epimeric mixture of the enone **15a**,**b** in methanol–methylene dichloride (1:5) at −70 °C followed by

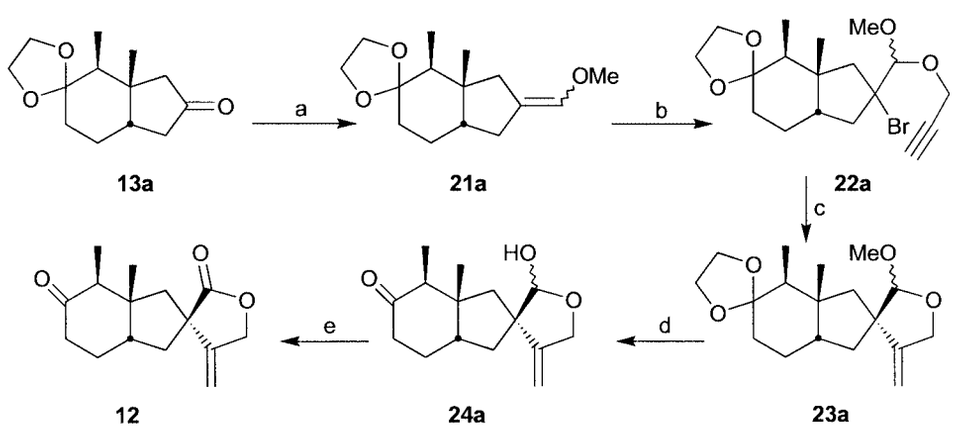



reductive work-up with dimethyl sulfide furnished a 3:2 mixture of the diones **14a** and **14b**, which was separated by column chromatography on alumina. The intramolecular aldol condensation of the dione **14a** with 10% aq. KOH in refluxing methanol furnished the enone **20a** in quantitative yield. Catalytic hydrogenation using 10% Pd on carbon in ethyl acetate at 40 psi for 3 h transformed the enone **20a** into the keto ketal **13a**. In a similar manner, intramolecular aldol condensation of the minor dione **14b** followed by catalytic hydrogenation of the resulting enone **20b** furnished the epimeric keto ketal **13b** (Scheme 4).

For the completion of the formal total synthesis of homogynolide-B **2**, the keto ketal **13a** was transformed into the keto spirolactone **12**, Greene's precursor of homogynolide-B, by employing the radical-cyclisation-mediated spiroannulation[10] of the butyrolactone moiety, Scheme 5. Thus, Wittig reaction of the keto ketal **13a** with methoxymethylenetriphenylphosphorane in THF furnished a 1:1 *E*,*Z* mixture of the enol ether **21a** in 75% yield. Treatment of the enol ether **21a** with NBS and propargyl alcohol in methylene dichloride[15] at −50 °C furnished the radical precursor, the bromo acetal **22a**. The 5-*exo*-dig radical cyclisation of the bromo acetal **22a** using an *in situ*-generated catalytic tributyltin hydride ($^nBu_3SnCl$ and $NaCNBH_3$)[16] in the presence of a catalytic amount of azoisobutyronitrile (AIBN) in refluxing tertiary butyl alcohol furnished a 1:1 mixture of methoxy epimers of the spiroacetal **23a**. As the direct oxidation of the spiroacetal **23a** using Jones' reagent[17] led to an epimeric mixture of spirolactones **12** and **25**, a two-step process, *i.e.* hydrolysis of acetal and ketal moieties followed by oxidation of the resultant keto lactol, was resorted to. Hydrolysis of the spiroacetal **23a** with 2 M aq. HCl in THF at room temperature for 3 h furnished the keto lactol **24a**. Finally, oxidation of the keto lactol **24a** with a 1:1 mixture of silica gel and pyridinium chlorochromate (PCC)[18] in methylene dichloride at room temperature furnished the keto spirolactone **12**, mp 110–112 °C, which exhibited IR and $^1H$ NMR spectra



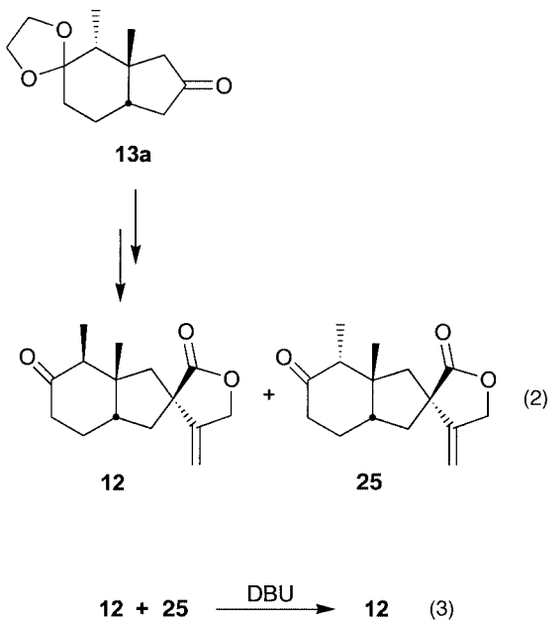

**Scheme 4**




**Scheme 5** *Reagents*: (a) $Ph_3P{=}CHOMe$; (b) NBS, $HC{\equiv}CCH_2OH$; (c) $^nBu_3SnCl$, $NaCNBH_3$, AIBN; (d) 2 M HCl; (e) PCC–silica gel.

identical with those of the sample obtained by Greene and co-workers.

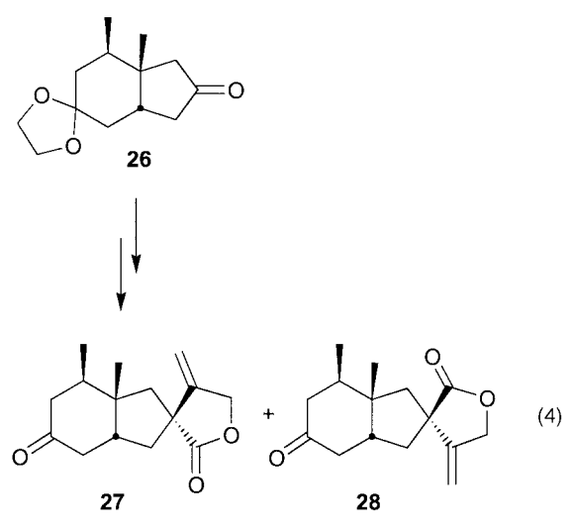
In a similar manner, methoxymethylene Wittig reaction of the keto ketal **13b**, followed by bromoacetalisation of the resulting enol ether **21b** with NBS and propargyl alcohol furnished the bromo acetal **22b**, which on radical cyclisation generated the spiroacetal **23b**. Hydrolysis of the spiroacetal using 2 M aq. HCl followed by oxidation of the resulting keto-lactol with PCC and silica gel furnished a 3:2 epimeric mixture of the spriolactones **12** and **25** due to the partial epimerisation of the secondary methyl group during the hydrolysis of the ketal moiety [reaction (2)]. Finally, complete epimerisation of




the mixture of keto spirolactones **12** and **25** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in methylene dichloride generated the keto spirolactone **12** [reaction (3)]. Since Greene and co-workers have already converted[8] the keto spirolactone **12** into (±)-**2** by regioselective reduction of the ketone followed by esterification, the present synthesis of keto spirolactone **12** constitutes a formal total synthesis of (±)-homogynolide-B **2**.

### X-Ray crystal structure of the keto spirolactone 12

Subsequent to the completion of formal total synthesis[9] of homogynolide-B, application of the spiroannulation methodology for the formal total synthesis of homogynolide-A,[7c] starting from the keto ketal **26**, generated a mixture of one major and one minor keto spirolactone **27** and **28**, which are epimeric at the spiro-centre, contrary to the formation of a single isomer



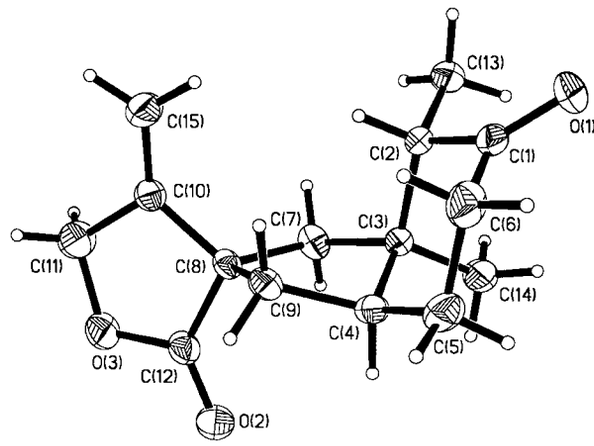




**Fig. 1** ORTEP plot of the keto spirolactone **12**, with crystallographic numbering scheme.

**12** from the keto ketal **13** [reaction (4)]. Formation of the epimeric spirolactone **27** as the major product in this reaction, coupled with the fact that there exists only marginal differences in the NMR spectra of the two lactones **27** and **28**, prompted us to resort to single-crystal X-ray diffraction analysis of the keto spirolactone **12** for unambiguously establishing its stereostructure. Good single crystals of the spirolactone **12** were grown from 1:6 methylene dichloride–hexane mixture and a single crystal with dimensions 0.24 × 0.21 × 0.17 mm was mounted along the largest dimension and used for data collection. The intensity data were collected on a Siemens P4 single-crystal diffractometer equipped with molybdenum sealed tube ($\lambda$ = 0.710 73 Å) and highly oriented graphite monochromator. The lattice parameters and standard deviations were obtained by least-squares fit to 50 reflections (9.81° < 2$\theta$ < 29.50°). The data were collected by 2$\theta$–$\theta$ scan mode with a variable scan speed ranging from 2.0 to a maximum of 25.0° min$^{-1}$. The data were corrected for Lorentz and polarisation factors, but no absorption correction was applied. All other relevant information about data collection is given in the Experimental section. The structure was solved by direct methods using the SHELX-97[19] package and was also refined using this. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the ideal positions with fixed isotropic $U$-values and were riding. A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $a = 0.0654$ and $b = 0.4275$ Å was used. The refinement converged to a final $R$-value of 0.0511 ($wR2$ 0.1279 for 1540 reflections [$I > 2\sigma(I)$]). The final difference map was featureless. Final atomic coordinates, bond lengths and bond angles, anisotropic thermal parameters, hydrogen-atom positions and observed and calculated structure factors are deposited at the Cambridge Crystallographic Data Centre. A perspective view of the molecule with atom-numbering scheme is given in Fig. 1. The X-ray molecular structure unambiguously established the stereostructure of the keto spirolactone **12**. The origin of the difference in stereoselectivity during the spiroannulation of the keto ketals **13** and **26** is not clear; perhaps the conformational preference of the intermediate radicals may be responsible.

## Experimental

Mps were recorded in capillaries and are not corrected. IR spectra were recorded on Perkin-Elmer 781 and Hitachi 270-50 spectrophotometers. $^1$H (60, 90, 200, 270 and 300 MHz) and $^{13}$C NMR (22.5, 50 and 75 MHz) spectra were recorded on Varian T-60, JEOL FX-90Q and JNM $\lambda$-300, Bruker ACF-200 and WH-270 spectrometers. The chemical shifts ($\delta$/ppm) and the coupling constants ($J$/Hz) are reported in the standard fashion with reference to either internal tetramethylsilane (for $^1$H) or the central line ($\delta_C$ 77.1) of $CDCl_3$ (for $^{13}$C). In the $^{13}$C NMR

spectra off-resonance multiplicities, when recorded, are given in parentheses. Low- and high-resolution mass measurements were carried out with a JEOL JMS DX 303 GC MS instrument using a direct inlet mode. Relative intensities of the ions are given in parentheses. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with Acme's silica gel G containing 13% calcium sulfate as binder. Acme's silica gel (100–200 mesh) and Qualigens neutral alumina were used for column chromatography. All small-scale dry reactions were carried out using standard syringe-septum techniques. Low-temperature reactions were conducted in a bath made of alcohol and liquid nitrogen. Potassium was obtained from Riedel. PCC was prepared according to the literature procedure. AIBN was recrystallised from methanol and stored in the dark. All the other commercial reagents were used without further purification. Ether refers to diethyl ether.

### Ethyl 2,3-dimethyl-4-oxocyclohex-2-enecarboxylate 17

To a magnetically stirred, ice-cold suspension of sodium hydride (60% dispersion in oil; 1.1 g, 27.5 mmol, washed with dry hexane) in dry THF (125 ml) was added Hagemann's ester **11** (5 g, 27.5 mmol) and the mixture was stirred for 30 min, cooled to −50 °C, methyl iodide (3 ml, 48 mmol) was added, and the mixture was stirred for 2 h at the same temperature before being allowed to attain room temperature over a period of 30 min, and the solvent was removed under reduced pressure. The residue was taken in water (30 ml) and extracted with ether (3 × 30 ml). The extract was washed with brine and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1 : 20) as eluent furnished the γ-methylated ester **17** (5.2 g, 97%) as an oil,[12] $\nu_{max}$(neat) 1720, 1670, 1630, 1250, 1170, 1030 $cm^{-1}$; $\delta_H$(300 MHz; $CDCl_3$) 4.21 (2 H, q, *J* 6.9, $OCH_2CH_3$), 3.30 (1 H, br s, H-1), 2.10–2.60 (4 H, m, $H_2$-5 and -6), 1.97 (3 H, s, $C^2$-$CH_3$), 1.81 (3 H, s, $C^3$-$CH_3$), 1.29 (3 H, t, *J* 6.9, $OCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 197.7 (s, C=O), 172.3 (s, O–C=O), 149.7 (s, C-2), 133.1 (s, C-3), 61.1 (t, $OCH_2$), 47.6 (d, C-1), 34.5 (t, C-5), 25.5 (t, C-6), 20.6 (q), 14.1 (q), 11.1 (q).

### Ethyl 4,4-(ethylenedioxy)-2,3-dimethylcyclohex-1-enecarboxylate 18

To a magnetically stirred, refluxing solution of the keto ester **17** (5 g, 25.5 mmol) and ethylene glycol (5 ml, 89 mmol) in benzene (80 ml) was added a catalytic amount of PTSA and the reaction mixture was refluxed for 40 h with a Dean–Stark water trap. Excess of benzene was distilled off and the residue was treated with saturated aq. $NaHCO_3$ (20 ml) and extracted with ether (2 × 25 ml). The ether layer was washed successively with water and brine and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1 : 20) as eluent furnished the ketal ester **18** (3.2 g, 52%) as an oil,[12] $\nu_{max}$(neat) 1700, 1630 $cm^{-1}$; $\delta_H$(90 MHz; $CDCl_3$) 4.18 (2 H, q, *J* 7.2, $OCH_2CH_3$), 4.00 (4 H, s, $OCH_2$-$CH_2O$), 2.50 (1 H, m, H-3), 2.04 (3 H, t, *J* 2.0, olefinic $CH_3$), 1.50–2.40 (4 H, m), 1.30 (3 H, t, *J* 7.2, $OCH_2CH_3$), 1.18 (3 H, d, *J* 7.2, *sec*-$CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 168.6 (O–C=O), 147.5 (C-1), 123.1 (C-2), 109.5 (O–C–O), 64.6 and 64.3 ($OCH_2$-$CH_2O$), 60.0 ($OCH_2CH_3$), 45.5 (C-3), 26.5, 25.6, 20.8, 15.6 and 14.3.

Further elution of the column with the same solvent furnished unchanged starting material **17** (1.5 g, 30%).

### 4,4-(Ethylenedioxy)-2,3-dimethylcyclohex-1-enemethanol 16

To a magnetically stirred, cold (−70 °C) suspension of LAH (500 mg, 13 mmol) in dry ether (75 ml) was added dropwise a solution of the ketal ester **18** (5 g, 20.8 mmol) in dry ether (15 ml) over a period of 10 min. The reaction mixture was stirred at −70 °C for 2 h and allowed to attain room temperature over a period of 30 min. Ethyl acetate (2 ml) was added to the reaction mixture to consume the excess of reagent and the reaction was quenched by careful addition of water (0.5 ml). The solids were filtered off and the residue was washed with ether (25 ml). The combined organic phase was dried ($Na_2SO_4$), and solvent was evaporated. Purification of the residue over a silica gel column using ethyl acetate–hexane (1 : 20) as eluent furnished the allyl alcohol **16** (4 g, 97%) as an oil, $\nu_{max}$(neat) 3330 $cm^{-1}$; $\delta_H$(90 MHz; $CDCl_3$) 4.12 (2 H, m, $CH_2OH$), 4.00 (4 H, s, $OCH_2$-$CH_2O$), 2.34 (1 H, m), 1.20–2.20 (4 H, m), 1.76 (3 H, s, olefinic $CH_3$), 1.10 (3 H, d, *J* 7.2, *sec*-$CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 133.4 (C-4), 128.6 (C-3), 110.3 (O–C–O), 64.5 ($OCH_2$), 64.3 and 62.7 ($OCH_2CH_2O$), 43.9, 27.2, 26.7, 17.4 and 15.5; HRMS: *m*/*z* (Calc. for $C_{11}H_{18}O_3$: *M*, 198.1256. Found: $M^+$, 198.1269).

### *cis*- and *trans*-1,1-(Ethylenedioxy)-2,3-dimethyl-4-methylene-3-(2-oxopropyl)cyclohexane 15 and *cis*- and *trans*-1,1-(ethylenedioxy)-2,4-dimethyl-3-methylene-4-(2-oxopropyl)cyclohexane 19

A solution of the allyl alcohol **16** (3.5 g, 17.6 mmol), 2-methoxypropene (15 ml, 156 mmol) and propionic acid (catalytic) in toluene (15 ml) was taken up in four Carius tubes under nitrogen atmosphere and heated first at 100 °C for 12 h, and later at 190 °C for 48 h. The Carius tubes were cooled, and the contents were pooled, then diluted with ether (20 ml) and washed successively with saturated aq. $NaHCO_3$ and brine, and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the residue on a neutral alumina column using ethyl acetate–hexane (1 : 40) as eluent furnished a 3 : 2 diastereomeric mixture of the enone **15** (3.16 g, 75%), $\nu_{max}$(neat) 1700, 1635, 910 $cm^{-1}$; $\delta_H$(90 MHz; $CDCl_3$; 3 : 2 mixture of epimers) 4.88 (s) and 4.78 (s), and 4.88 (s) and 4.72 (s) (2 H, C=$CH_2$), 3.80–4.20 (4 H, m, $OCH_2CH_2O$), 1.40–3.30 (7 H, m), 2.10 and 2.12 (3 H, 2 s, $CH_3C$=O), 1.26 and 1.20 (3 H, 2 s, *tert*-$CH_3$), 0.94 and 0.88 (3 H, 2 d, *J* 7.2, *sec*-$CH_3$); $\delta_C$(22.5 MHz; $CDCl_3$; 3 : 2 mixture of epimers) 208.5 and 207.7 (s, C=O), 151.9 and 150.1 (s, *C*=$CH_2$), 111.0 and 109.7 (s, OCO), 109.5 and 108.9 (t, C=*C*$H_2$), 65.0 (t) and 63.7 (t), and 64.1 (t) and 63.3 (t) ($OCH_2CH_2O$), 51.7 (t), 49.4 (d), 46.4 (t), 42.4 (s), 41.9 (d), 36.0 (t), 32.0 (t), 31.5 (t), 30.4 (q), 29.8 (t), 23.3 (q) and 23.0 (q, *tert*-$CH_3$), 11.4 (q) and 7.7 (q) (*sec*-$CH_3$); *m*/*z* 238 (30%, $M^+$), 209 (35), 195 (10), 181 (100), 153 (47), 137 (15), 125 (12), 109 (13), 100 (25), 99 (53); HRMS: *m*/*z* (Calc. for $C_{14}H_{22}O_3$: *M*, 238.1569. Found: $M^+$, 238.1569).

Further elution of the column furnished an epimeric mixture of the rearranged enone **19** (500 mg, 11%) as an oil,[14] $\nu_{max}$(neat) 1700, 1630, 910 $cm^{-1}$; $\delta_H$(90 MHz; $CDCl_3$; for the major epimer) 4.83 (1 H, d, *J* 2) and 4.79 (1 H, d, *J* 2) (olefinic), 3.98 (4 H, m, $OCH_2CH_2O$), 1.85–2.90 (3 H, m), 2.19 (3 H, s, $CH_3C$=O), 1.50–1.85 (4 H, m), 1.28 (3 H, s, *tert*-$CH_3$), 1.06 (3 H, d, *J* 7.2, *sec*-$CH_3$); *m*/*z* 238 (25%, $M^+$), 223 (15), 205 (18), 181 (95), 180 (40), 165 (15), 136 (60), 129 (20), 121 (65), 101 (75), 100 (100), 99 (100).

### *cis*- and *trans*-4,4-(Ethylenedioxy)-2,3-dimethyl-2-(2-oxopropyl)-cyclohexanone 14

An epimeric mixture of the enone **15** (2 g, 8.4 mmol) and solid $NaHCO_3$ (100 mg) were taken up in 1 : 5 methanol–$CH_2Cl_2$ (30 ml) and cooled to −78 °C. Precooled ozone in oxygen was passed through the solution till the reaction mixture turned blue (≈30 min). Excess of ozone was flushed off with oxygen, dimethyl sulfide (10 ml) was added to the reaction mixture and the mixture was allowed to warm up to room temperature over a period of 30 min. After stirring for a further 2 h period, excess of dimethyl sulfide and solvent were evaporated under reduced pressure and the residue was purified on a neutral alumina column using ethyl acetate–hexane (1 : 9) as eluent to furnish, first, the minor dione **14b** (608 mg, 30%) as an oil, $\nu_{max}$(neat) 1700 $cm^{-1}$; $\delta_H$(90 MHz; $CDCl_3$) 3.80–4.10 (4 H, m, $OCH_2CH_2O$), 3.00 and 2.50 (2 H, AB q, *J* 18, $CH_2C$=O), 1.60–2.70 (5 H, m),

2.06 (3 H, s, $CH_3C$=O), 1.06 (3 H, s, *tert*-$CH_3$), 0.85 (3 H, d, *J* 7.5, *sec*-$CH_3$); $\delta_C$(22.5 MHz; $CDCl_3$) 213.0 (s, ring C=O), 206.2 (s, $CH_3C$=O), 108.8 (s, OCO), 65.1 (t) and 63.6 (t) ($OCH_2CH_2O$), 49.5 (t, $CH_2C$=O), 49.1 (s, C-2), 41.5 (d, C-3), 35.2 (t, C-5), 31.7 (t, C-6), 29.8 (q, $CH_3C$=O), 20.5 (q, *tert*-$CH_3$), 7.5 (q, *sec*-$CH_3$); *m*/*z* 240 (18%, $M^+$), 197 (12), 183 (20), 100 (42), 99 (100); HRMS: *m*/*z* (Calc. for $C_{13}H_{20}O_4$: *M*, 240.1362. Found: $M^+$, 240.1365).

Further elution of the column with the same solvent furnished the major dione **14a** (1.012 g, 50%) as a solid, which was recrystallised from hexane–$CH_2Cl_2$, mp 90–92 °C; $\nu_{max}$(neat) 1705 $cm^{-1}$; $\delta_H$(270 MHz; $CDCl_3$) 3.90–4.11 (4 H, m, $OCH_2CH_2O$), 3.43 and 2.70 (2 H, AB q, *J* 17.4, $CH_2COCH_3$), 2.74 (1 H, d of t, *J* 13.1 and 5.5, H-$6_{ax}$), 2.40 (1 H, t of d, *J* 13.1 and 4.8, H-$6_{eq}$), 2.12 (1 H, t of d, *J* 13.3 and 5.2, H-$5_{eq}$), 2.12 (3 H, s, $COCH_3$), 2.02 (1 H, q, *J* 7, H-3), 1.79 (1 H, d of t, *J* 13.3 and 4.8, H-$5_{ax}$), 1.17 (3 H, s, *tert*-$CH_3$), 0.95 (3 H, d, *J* 6.9, *sec*-$CH_3$); $\delta_C$(22.5 MHz; $CDCl_3$) 213.0 (s, C=O), 207.3 (s, $CH_3C$=O), 108.9 (s, OCO), 64.4 (t) and 65.5 (t) ($OCH_2CH_2O$), 49.7 (2 C, s and d, C-2 and -3), 47.6 (t, $CH_2COCH_3$), 35.6 (t, C-6), 35.4 (t, C-5), 31.3 (q, $COCH_3$), 21.2 (q, *tert*-$CH_3$), 9.0 (q, *sec*-$CH_3$); *m*/*z* 240 (62%, $M^+$), 197 (55), 183 (100), 155 (12), 141 (27), 127 (30), 111 (20), 100 (100), 99 (100); HRMS: *m*/*z* (Calc. for $C_{13}H_{20}O_4$: *M*, 240.1362. Found: $M^+$, 240.1296).

### (1β,2β)-3,3-(Ethylenedioxy)-1,2-dimethylbicyclo[4.3.0]non-6-en-8-one 20a

To solution of the dione **14a** (600 mg, 2.5 mmol) in methanol (3 ml) was added 10% aq. KOH (0.14 ml, 2.5 mmol) and the reaction mixture was refluxed for 4 h. The solvent was evaporated under reduced pressure. The residue was taken up in water (5 ml) and extracted with ether (3 × 10 ml). The combined extract was washed with brine and dried ($Na_2SO_4$). Evaporation of the solvent followed by purification of the product on a neutral alumina column using ethyl acetate–hexane (1:9) as eluent furnished the enone **20a** (549 mg, 99%) as an oil, $\nu_{max}$(neat) 1700 $cm^{-1}$; $\delta_H$(60 MHz, $CCl_4$) 5.80 (1 H, br s, olefinic H), 3.70–4.20 (4 H, m, $OCH_2CH_2O$), 2.73 (1 H, m), 2.13 and 1.86 (2 H, AB q, *J* 8, $CH_2CO$), 1.60–2.00 (4 H, m), 1.55 (3 H, s, *tert*-$CH_3$), 0.92 (3 H, d, *J* 7, *sec*-$CH_3$); $\delta_C$(22.5 MHz; $CDCl_3$) 208.2 (s, C=O), 184.0 (s, C=CHC=O), 127.9 (d, C=CHC=O), 110.4 (s, OCO), 63.5 (t) and 64.6 (t) ($OCH_2CH_2O$), 49.0 (t, $CH_2C$=O), 47.3 (s, C-1), 45.3 (d, C-2), 30.7 (t, C-4), 28.2 (q, *tert*-$CH_3$), 24.9 (t, C-5), 12.7 (q, *sec*-$CH_3$); *m*/*z* 222 (50%, $M^+$), 207 (50), 193 (25), 179 (10), 121 (27), 107 (18), 99 (30), 93 (38), 87 (45), 86 (100); HRMS: *m*/*z* (Calc. for $C_{13}H_{18}O_3$: *M*, 222.1256. Found: $M^+$, 222.1254).

### (1β,2β,6β)-3,3-(Ethylenedioxy)-1,2-dimethylbicyclo[4.3.0]-nonan-8-one 13a

To a solution of the enone **20a** (500 mg, 2.25 mmol) in ethyl acetate (25 ml) in a 250 ml pressure bottle was added 10% Pd/C (25 mg) and the system was hydrogenated at 40 psi at room temperature for 3 h in a Parr-type hydrogenation apparatus. The reaction mixture was filtered through a short neutral alumina column using $CH_2Cl_2$ as eluent. Evaporation of the solvent furnished the saturated ketone **13a** (500 mg, 99%) as an oil, $\nu_{max}$(neat) 1730 $cm^{-1}$; $\delta_H$(270 MHz; $CDCl_3$) 3.80–4.05 (4 H, m, $OCH_2CH_2O$), 2.83 and 1.79 (2 H, AB q, *J* 18.6, $H_2$-9), 2.61 (1 H, dd, *J* 18.7 and 7.5, H-$7_A$), 1.90 (1 H, d, *J* 18.7, H-$7_B$), 1.30–2.00 (6 H, m), 1.10 (3 H, s, *tert*-$CH_3$), 0.91 (3 H, d, *J* 6.7, *sec*-$CH_3$); $\delta_C$(22.5 MHz; $CDCl_3$) 219.5 (s, C=O), 109.9 (s, OCO), 64.0 (t) and 65.6 (t) ($OCH_2CH_2O$), 45.4 (d, C-2), 44.2 (2 C, t, C-7 and -9), 43.6 (s, C-1), 42.0 (d, C-6), 33.8 (t, C-4), 28.0 (2 C, q and t, *tert*-$CH_3$ and C-5), 8.6 (q, *sec*-$CH_3$); *m*/*z* 224 (22%, $M^+$), 209 (5), 152 (5), 140 (20), 127 (15), 109 (10), 99 (100), 87 (25), 86 (100); HRMS: *m*/*z* (Calc. for $C_{13}H_{20}O_3$: *M*, 224.1412. Found: $M^+$, 224.1408).

### (1β,2α)-3,3-(Ethylenedioxy)-1,2-dimethylbicyclo[4.3.0]non-6-en-8-one 20b

Intramolecular aldol condensation of the dione **14b** (250 mg, 1.04 mmol) with 10% aq. KOH (0.6 ml, 1.07 mmol) in methanol (2 ml) for 4 h, followed by purification of the product as described for the enone **20a**, furnished the enone **20b** (224 mg, 97%), which was recrystallised from $CH_2Cl_2$–hexane, mp 98–100 °C; $\nu_{max}$($CCl_4$) 1700, 1620 $cm^{-1}$; $\delta_H$(90 MHz; $CDCl_3$) 5.80 (1 H, br s, olefinic H), 3.80–4.20 (4 H, m, $OCH_2CH_2O$), 2.68 (2 H, m, $CH_2C$=O), 1.40–2.40 (5 H, m), 1.24 (3 H, s, *tert*-$CH_3$), 0.89 (3 H, d, *J* 7.2, *sec*-$CH_3$); *m*/*z* 222 (50%, $M^+$), 207 (45), 193 (25), 121 (25), 113 (8), 107 (18), 100 (28), 99 (72), 93 (38), 86 (100); HRMS: *m*/*z* (Calc. for $C_{13}H_{28}O_3$: *M*, 222.1256. Found: $M^+$, 222.1269).

### (1β,2α,6β)-3,3-(Ethylenedioxy)-1,2-dimethylbicyclo[4.3.0]-nonan-8-one 13b

Hydrogenation of the enone **20b** (250 mg, 1.1 mmol) in ethyl acetate (25 ml) using 10% Pd/C (25 mg) as catalyst at 40 psi for 3 h, followed by purification of the product over a neutral alumina column using ethyl acetate–hexane (1:20) as eluent, furnished the ketone **13b** (252 mg, 100%), which was recrystallised from $CH_2Cl_2$–hexane, mp 78–81 °C; $\nu_{max}$(neat) 1737 $cm^{-1}$; $\delta_H$(60 MHz, $CCl_4$) 3.70–4.10 (4 H, m $OCH_2CH_2O$), 2.42 and 1.83 (2 H, AB q, *J* 18, $H_2$-9), 1.90–2.50 (3 H, m), 1.30–2.35 (3 H, m), 1.16 (3 H, s, *tert*-$CH_3$), 0.83 (3 H, d, *J* 8, *sec*-$CH_3$); $\delta_C$(22.5 MHz; $CDCl_3$) 218.3 (s, C=O), 110.0 (s, OCO), 63.9 (t) and 65.2 (t) ($OCH_2CH_2O$), 53.9 (t, C-9), 43.1 (s, C-1), 41.7 (d, C-2), 40.6 (d, C-6), 39.9 (t, C-7), 28.7 (t, C-4), 21.4 (q, *tert*-$CH_3$), 21.1 (t, C-5), 7.8 (q, *sec*-$CH_3$); *m*/*z* 224 (27%, $M^+$), 209 (5), 100 (30), 99 (100), 86 (100); HRMS: *m*/*z* (Calc. for $C_{13}H_{20}O_3$: *M*, 224.1412. Found: $M^+$, 224.1408).

### (1β,2β,6β,8β)-1,2-Dimethyl-4′-methylenespiro(bicyclo[4.3.0]-nonane-8,3′-tetrahydrofuran)-2′,3-dione 12

To a magnetically stirred solution of potassium *tert*-amylate (310 mg, 2.46 mmol) in dry THF (15 ml) at room temperature was added (methoxymethyl)triphenylphosphonium chloride (1 g, 2.9 mmol), and the resulting red coloured solution was stirred at room temperature for 15 min. To the ylide thus formed was added the keto ketal **13a** (180 mg, 0.8 mmol) and the mixture was stirred for 2 h at room temperature. It was then diluted with ether (15 ml), washed with brine and dried ($Na_2SO_4$). Evaporation of the solvent followed by purification of the residue on a neutral alumina column using ethyl acetate–hexane (1:40) as eluent furnished an *E*,*Z* mixture of the enol ether **21a** (152 mg, 75%) as an oil, $\nu_{max}$(neat) 1680, 890 $cm^{-1}$; $\delta_H$(60 MHz, $CCl_4$; 1:1 mixture of the *E*,*Z* isomers) 5.87 (1 H, br s), 3.70–4.05 (4 H, m), 3.55 and 3.53 (3 H, s), 2.30–2.90 (2 H, m), 1.00–2.20 (8 H, m), 0.95 (3 H, s), 0.91 and 0.90 (3 H, d, *J* 7).

To a cold (−40 °C), magnetically stirred solution of NBS (105 mg, 0.52 mmol) and propargyl alcohol (0.5 ml, 8.5 mmol) in $CH_2Cl_2$ (10 ml) was added a solution of the enol ether **21a** (130 mg, 0.5 mmol) in 2 ml of $CH_2Cl_2$ over a period of 15 min. The reaction mixture was stirred for 45 min at the same temperature, diluted with $CH_2Cl_2$ (10 ml), washed successively with 1% aq. NaOH and brine and dried ($Na_2SO_4$). Evaporation of the solvent followed by purification of the product on a neutral alumina column using ethyl acetate–hexane (1:20) as eluent furnished a diastereomeric mixture of the bromo acetal **22a** (178 mg, 89%) as an oil, $\nu_{max}$ 3280, 2120 $cm^{-1}$; $\delta_H$(90 MHz; $CDCl_3$; mixture of two isomers) 4.30–4.50 (3 H, m), 3.80–4.05 (4 H, m), 3.72 (3 H, s), 1.20–3.20 (11 H, m), 1.40 and 1.06 (3 H, s), 0.96 (3 H, d, *J* 7.2).

A solution of the bromo acetal **22a** (165 mg, 0.42 mmol), $^nBu_3SnCl$ (0.02 ml, 0.075 mmol), $NaBH_3CN$ (75 mg, 1.2 mmol) and AIBN (catalytic) in *tert*-butyl alcohol (4 ml) was refluxed for 1.5 h. The solvent was evaporated under reduced pressure,

the residue was taken up in ether, washed successively with 1% aq. ammonia and brine, and dried ($Na_2SO_4$). Evaporation of the solvent followed by purification of the product over a silica gel column using ethyl acetate–hexane (1:40) as eluent furnished an epimeric mixture of the spiroacetal **23a** (100 mg, 76%) as an oil, $\nu_{max}$(neat) 3060, 1660, 880 $cm^{-1}$; $\delta_H$(270 MHz; $CDCl_3$; mixture of methoxy epimers) 5.18, 5.05, 5.02 and 4.90 (2 H, 4 t, *J* 2.3, C=$CH_2$), 4.93 and 4.61 (1 H, 2 s, OC*H*$OCH_3$), 4.20–4.50 (2 H, m, $OCH_2C$=), 3.80–4.05 (4 H, m, $OCH_2CH_2O$), 3.36 and 3.34 (3 H, 2 s, $OCH_3$), 1.20–2.50 (10 H, m), 1.05 and 1.03 (3 H, 2 s, *tert*-$CH_3$), 0.95 and 0.85 (3 H, 2 d, *J* 6.8, *sec*-$CH_3$)].

A solution of the spiroacetal **23a** (150 mg, 0.48 mmol) in THF (2 ml) and 2 M aq. HCl (2.5 ml) was stirred for 3 h at room temperature. The reaction mixture was diluted with ether (15 ml), washed successively with saturated aq. $NaHCO_3$ and brine, and dried ($Na_2SO_4$). The solvent was evaporated and the residue was filtered through a neutral alumina column using $CH_2Cl_2$ as eluent to furnish the keto spirolactol **24a** (97 mg, 80%) as an oil, $\nu_{max}$(neat) 3380, 1700, 1660, 880 $cm^{-1}$; $\delta_H$(90 MHz; $CDCl_3$; mixture of hydroxy epimers) 4.90–5.30 (3 H, m, C=$CH_2$ and OCHOH), 4.54 (2 H, m, $OCH_2C$=), 1.20–2.80 (10 H, m), 1.10 (3 H, d, *J* 7.2, *sec*-$CH_3$), 0.98 (3 H, s, *tert*-$CH_3$).

To a magnetically stirred suspension of PCC (65 mg, 0.3 mmol) and silica gel (65 mg) in dry $CH_2Cl_2$ (3 ml) was added a solution of the keto spirolactol **24a** (65 mg, 0.26 mmol) in $CH_2Cl_2$ (1 ml). The reaction mixture was stirred for 3 h at room temperature and then filtered through a silica gel column using $CH_2Cl_2$ as eluent. Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:9) as eluent furnished the keto lactone **12** (60 mg, 93%), which was recrystallised twice from $CH_2Cl_2$–hexane, mp 110–112 °C (lit.,[6] 99–102 °C); $\nu_{max}$(neat) 1760, 1700, 1670, 900 $cm^{-1}$; $\delta_H$(270 MHz; $CDCl_3$) 5.10 (2 H, t, *J* 2.0, C=$CH_2$), 4.90 and 4.82 (2 H, t of AB q, *J* 11, 2.1, $OCH_2C$=), 2.58 (1 H, q, *J* 7, *H*$CCH_3$), 2.13 and 2.09 (2 H, AB q, *J* 14, $H_2$-9), 1.95–2.55 (7 H, m), 1.02 (3 H, d, *J* 6.6, *sec*-$CH_3$), 0.98 (3 H, s, *tert*-$CH_3$); $\delta_C$(50 MHz; $CDCl_3$) 212.4 (ring C=O), 181.6 (OC=O), 149.5 (C=$CH_2$), 106.3 (C=$CH_2$), 70.5 ($OCH_2$), 50.3 (C-2), 49.4 (2 C, C-4 and spiro C), 48.4 (C-1), 45.5 (C-6), 42.8 (C-9), 36.7 (C-7), 24.6 (*tert*-$CH_3$), 21.6 (C-5), 8.14 (*sec*-$CH_3$); *m*/*z* 248 (18%, $M^+$), 177 (20), 138 (100), 137 (65), 132 (30), 123 (35), 112 (40), 111 (30), 105 (20); HRMS: *m*/*z* (Calc. for $C_{15}H_{20}O_3$: *M*, 248.1412. Found: $M^+$, 248.1427).

### (1β,2α,6β,8β)- and (1β,2β,6β,8β)-1,2-Dimethyl-4′-methylenespiro(bicyclo[4.3.0]nonane-8,3′-tetrahydrofuran)-2′,3-dione 25 and 12

Wittig reaction of the ketone **13b** (200 mg, 0.89 mmol) with the ylide prepared from (methoxymethyl)triphenylphosphonium chloride (1.5 g, 4.4 mmol) and potassium *tert*-amylate (441 mg, 3.5 mmol) in dry THF (25 ml) for 5 h at room temperature, followed by purification of the product on a neutral alumina column using ethyl acetate–hexane (1:40) as eluent, furnished an *E*,*Z* mixture of the enol ether **21b** (190 mg, 84%) as an oil, $\nu_{max}$(neat) 1680, 1270, 1220, 1180, 1120 $cm^{-1}$; $\delta_H$(90 MHz; $CDCl_3$; mixture of *E*,*Z* isomers) 5.88 (1 H, br s), 3.80–4.10 (4 H, m), 3.58 (3 H, s), 1.40–2.60 (10 H, m), 1.05 (3 H, s), 0.88 and 0.84 (3 H, d, *J* 7.2).

Bromoalkoxylation of the enol ether **21b** (180 mg, 0.714 mmol) with NBS (143 mg, 0.8 mmol) and propargyl alcohol (0.5 ml, 8.5 mmol) in dry $CH_2Cl_2$ (20 ml) at −40 °C for 45 min as described for the bromo acetal **22a**, followed by purification of the product on a neutral alumina column using ethyl acetate–hexane (1:20) as eluent, furnished a diastereomeric mixture of the bromo acetal **22b** (256 mg, 92%) as an oil, $\nu_{max}$(neat) 3280, 2100, 1350, 1280, 1120 $cm^{-1}$; $\delta_H$(90 MHz; $CDCl_3$) 4.60 (1 H, s), 4.46 (2 H, d, *J* 2.5), 3.75–4.10 (4 H, m), 3.64 (3 H, s), 1.30–2.70 (11 H, m), 1.18 (3 H, s), 0.84 (3 H, d, *J* 7.2).

Radical cyclisation of the bromo acetal **22b** (256 mg, 0.66 mmol) with $^nBu_3SnCl$ (0.03 ml, 0.11 mmol), $NaBH_3CN$ (75 mg, 0.12 mmol) and AIBN (catalytic) in *tert*-butyl alcohol (5 ml) as described for the acetal **23a**, followed by purification of the product on a neutral alumina column using ethyl acetate–hexane (1:40) as eluent, furnished an epimeric mixture of the spiroacetal **23b** (159 mg, 78%) as an oil, $\nu_{max}$(neat) 3060, 1660, 880 $cm^{-1}$; $\delta_H$(90 MHz; $CDCl_3$; mixture of isomers) 4.50–5.10 (3 H, br m), 4.20 (2 H, m), 3.80–4.10 (4 H, m), 3.38 and 3.40 (3 H, s), 1.20–2.50 (10 H, m), 1.14 and 1.06 (3 H, s), 0.92 and 0.88 (3 H, d, *J* 7.2).

Hydrolysis of the spiroacetal **23b** (115 mg, 0.5 mmol) in THF (2 ml) and 2 M HCl (2 ml) for 3 h at room temperature as described for the keto lactol **24a**, followed by quick filtration of the crude lactol through a silica gel column using $CH_2Cl_2$ as eluent, furnished a mixture of the keto lactols **24a**,**b** (95 mg, 76%) as an unstable oil. Oxidation of the lactol mixture **24a**,**b** (50 mg, 0.2 mmol) with PCC (100 mg, 0.46 mmol) and silica gel (100 mg) in dry $CH_2Cl_2$ (3 ml) for 3 h, followed by purification as described for spirolactone **12**, furnished a 3:2 mixture (by $^1H$ NMR) of the keto spirolactones **12** and **25** (48 mg, 96%), $\nu_{max}$(neat) 1770, 1705, 1660, 895 $cm^{-1}$; $\delta_H$(270 MHz; $CDCl_3$) for the spirolactone **25**: 5.16 (1 H, t, *J* 2), 5.09 (1 H, t, *J* 2) (olefinic H), 4.85 (2 H, t, *J* 2, $OCH_2C$=), 3.08 (1 H, q, *J* 6.4, *H*$CCH_3$), 2.72 (1 H, t, *J* 12.7, H-$9_A$), 2.48 and 1.69 (2 H, AB q, *J* 14.2, H-7), 2.50 (1 H, m), 1.90–2.30 (5 H, m), 0.98 (3 H, d, *J* 6.5, *sec*-$CH_3$), 0.95 (3 H, s, *tert*-$CH_3$).

### Equilibration of the keto spirolactones 12 and 25

A solution of the 3:2 mixture of the keto spirolactones **12** and **25** (45 mg, 0.18 mmol) and DBU (0.1 ml) in $CH_2Cl_2$ (2 ml) was magnetically stirred at room temperature for 4 h. The reaction mixture was then diluted with $CH_2Cl_2$ (10 ml), washed successively with 1 M aq. HCl, saturated aq. $NaHCO_3$ and brine, and dried ($Na_2SO_4$). Evaporation of the solvent, followed by purification of the product on a silica gel column using ethyl acetate–hexane (1:9) as eluent, furnished the keto spirolactone **12** (45 mg, 100%) which was identified by comparison (mp, IR, $^1H$ NMR) with the sample obtained earlier.

### X-Ray data for the keto spirolactone 12

Molecular formula $C_{15}H_{20}O_3$, $M = 248.31$, colourless crystals from 1:6 methylene dichloride–hexanes, monoclinic, space group $P2_1/c$, $a = 6.998(1)$ Å, $b = 18.070(2)$ Å and $c = 14.825(2)$ Å, $\alpha = 90°$, $\beta = 104.53(1)°$, $\gamma = 90°$, $V = 1350.3(3)$ Å$^3$, $Z = 4$, $D_c = 1.221$ Mg $m^{-3}$, $T = 293(2)$ K, Absorption coefficient 0.084 $mm^{-1}$, $F(000) = 536$, crystal dimensions 0.24 × 0.21 × 0.17 mm. Data were collected on a Siemens P4 diffractometer, graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda = 0.710\,73$ Å) by $2\theta$–$\theta$ scan method, in the range 2.22° to 24.01°, with variable scan speed 2.0 to 45.0° $min^{-1}$ in $\omega$, scan range ($\omega$) 1.30° plus $K_\alpha$-separation. Background measurement: stationary crystal and stationary counter at the beginning and end of scan each for 25.0% of total scan time; index ranges: $0 \leqslant h \leqslant 8$, $0 \leqslant k \leqslant 20$, $-12 \leqslant l \leqslant 12$; 2282 reflections were collected, of which 2099 were unique with $R_{int} = 0.021$. 95.8% completeness to $2\theta = 24.01$. Refinement method: Full-matrix least-squares on $F^2$. Goodness-of-fit on $F^2$: 1.020. Final *R* indices [$I > 2\sigma(I)$] $R1 = 0.0511$, $wR2 = 0.1279$; *R* indices (all data) $R1 = 0.0742$, $wR2 = 0.1425$. Largest difference peak and hole: 0.185 and −0.177 e Å$^{-3}$. CCDC reference number 207/339. See http://www.rsc.org/suppdata/p1/1999/2069 for crystallographic files in .cif format.

## Acknowledgements

We thank Professor A. E. Greene for providing the copies of

the IR and $^1$H NMR spectra of the keto spirolactone **12**, and Professor K. Venkatesan for helpful discussions. We are grateful to the Department of Science and Technology, Council of Scientific and Industrial Research and the University Grants Commission for financial support.

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*Paper 9/03866C*