Synthesis and photoreaction of tricyclo[5.2.2.0^{2,6}]undecanes in the excited singlet (^1S) state: a novel and stereospecific route to protoilludanoids

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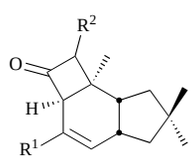
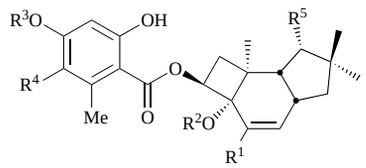
A novel and general approach to the synthesis of functionalised protoilludane skeletons having fused-four-, six- and five-membered rings is described. A photochemical sigmatropic 1,3-acyl shift in *endo*-tricyclo[5.2.2.0^{2,6}]undecanes having a β,γ-unsaturated carbonyl chromophore, and $\pi^{4s} + \pi^{2s}$ cycloaddition of spiro[cyclohexa-2,4-diene-oxiran]-6-one are the key features of this approach. An efficient one-step synthesis of the epoxy ketone 11 by $\pi^{4s} + \pi^{2s}$ cycloaddition of the *in situ* generated spiro[cyclohexa-2,4-diene-oxiran]one is reported. Further transformation of 11 to a variety of *endo*-tricyclo[5.2.2.0^{2,6}]-undecanes (20, 25, 28, 30 and 31) and their photochemical behaviour upon singlet (^1S) excitation is described. Direct excitation of all the tricyclic chromophoric systems in benzene neatly furnished the protoilludanoids 32–36.

A surge of interest in the sesquiterpenoids of protoilludane family,[1–2] is the result of the isolation of a large number of novel secondary metabolites of types **1**–**6** from various strains of



1 R^1 = CHO, R^2 = OH

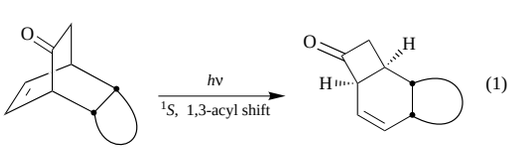


2 R^1 = CHO, R^2 = R^3 = R^4 = R^5 = H
3 R^1= CHO, R^2= R^3 = R^4 = H, R^5 = OH
4 R^1= CHO, R^2 = Me, R^3 = R^4 = H, R^5 = OH
5 R^1 = CHO, R^2 = R^4 = H, R^3 = Me, R^5 = OH
6 R^1 = CH_2OH, R^2 = R^4 = H, R^3 = Me, R^5 = OH

Basidiomycetes having a protoilludane skeleton, which exhibit antitumour, antibiotic and antibacterial activity.[1a,d] Moreover, some members of this family play an important role in the biosynthesis[3] of a host of biologically active sesquiterpenoids such as lactaranes, illudalanes and marasmanes *via* the protoilludyl cation. Further, the unique molecular architecture composed of four-, six- and five-membered rings fused in an angular *cis*:*anti*:*cis* fashion, together with the unusual functionalities, the promising biological activities and the biosynthetic connections of these compounds have kindled interest in their synthesis and chemistry.

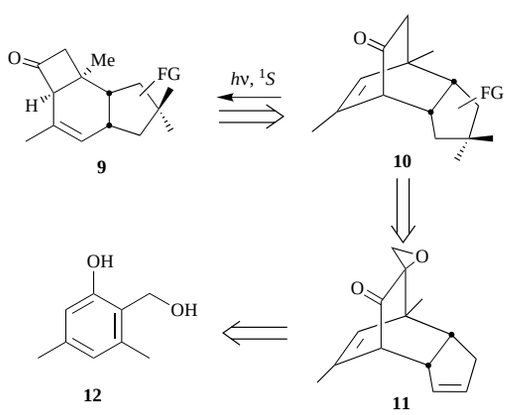
No attempts have been made to synthesize recently isolated protoilludanoids (*e.g.* **1**–**6** and related compounds) and, surprisingly, there are few routes [2a–e] to earlier discovered compounds.[1f]

In the context of our exploratory programme towards the development of novel methodologies employing photochemical reactions, we thought that a cyclobutane ring fused to a *cis* hydrindane skeleton could be efficiently formed stereoselectively *via* a symmetry-allowed[4] photochemical 1,3-sigmatropic acyl shift in an *endo* annulated tricyclic system such as **7**



7 **8** (1)

[Eqn. (1)].[5] Therefore, we designed a general strategy to synthesize tricyclic skeletons of type **9** disposed with all the essential features of protoilludanes such as angular and geminal methyl groups and functionalities in all the rings for further manipulation. We thought that the intermediate **9** and its congeners could be readily obtained from the *endo* annulated bicyclo[2.2.2]octenones having a β,γ-unsaturated carbonyl chromophore such as **10** (Scheme 1). This would, in turn, we



9 **10** **11** **12**

Scheme 1

thought be readily available from the epoxy ketone **11** which should itself be accessible from the appropriately substituted phenol **12** after its oxidation and subsequent interception of the resulting cyclohexa-2,4-dienone with cyclopentadiene.

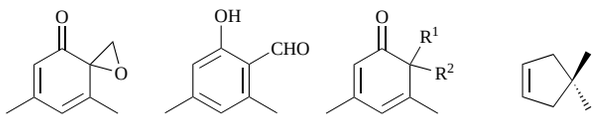
We report herein a novel, efficient and stereospecific route to functionalised protoilludanoids employing a photochemical 1,3-acyl shift upon singlet excitation of various tricyclo-[5.2.2.0^{2,6}]undecenones as a key step. A general synthesis of a variety of tricyclic chromophoric systems having β,γ-enone chromophore by oxidation of a simple aromatic precursor such as 4,6-dimethylsalicyl alcohol to a spiro[cyclohexa-2,4-diene-oxiran]one, subsequent interception with cyclopentadiene and manipulation of the resulting adduct is also reported.

Results and discussion

Synthesis of tricyclic chromophoric systems

Conceptually, the tricyclic systems of type **10** having a β,γ-

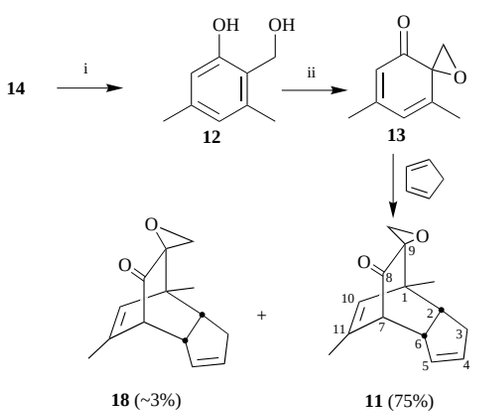
enone chromophore could be directly prepared by cycloaddition of 3,5-dimethylcyclohexa-2,4-dienone **16** and 4,4-dimethylcyclopentene **17**. However, while there are a few



13 **14** **15** R^1 = alkyl, R^2 = OAc; **16** $R^1 = R^2 = H$ **17**

methods[6,7] for the preparation of 6,6-disubstituted cyclohexa-2,4-dienones, there are no methods for the cyclohexadienones of type **16**. Moreover, the dienone **16** (actually a keto tautomer of the corresponding phenol) has been neither trapped, characterised nor prepared. Therefore, we considered an alternate indirect method for the synthesis of the desired chromophoric system of type **10** from the keto-epoxide **11**. The latter was available from 4,6-dimethylsalicyl alcohol **12** by its oxidation to the spiro[cyclohexa-2,4-diene-oxiran]one **13** and subsequent interception with cyclopentadiene. In this connection, we have recently developed a method for *in situ* generation of spiro-[cyclohexa-2,4-diene-oxiran]one by two-phase periodate oxidation of *o*-hydroxymethyl phenols.[8]

Towards the preparation of the phenol **12**, 4,6-dimethylsalicylaldehyde[9] **14** was reduced with sodium borohydride in methanol–water (80 : 20). Although we observed that the reduction proceeded smoothly (TLC), attempts to isolate the corresponding alcohol under a variety of conditions failed and led to polymerisation. Therefore, we thought to oxidize the reaction mixture containing 4,6-dimethylsalicyl alcohol **12** and intercept the resulting spiro[cyclohexa-2,4-diene-oxiran]one **13** with cyclopentadiene. Indeed, oxidation of the reaction mixture containing **12** with sodium metaperiodate in the presence of freshly cracked cyclopentadiene furnished the required adduct **11** in excellent yield (75%) along with its stereoisomer **18** as a minor product (~3%) in a single-pot reaction from the aldehyde **14** (Scheme 2). The adducts were obviously formed through gener-



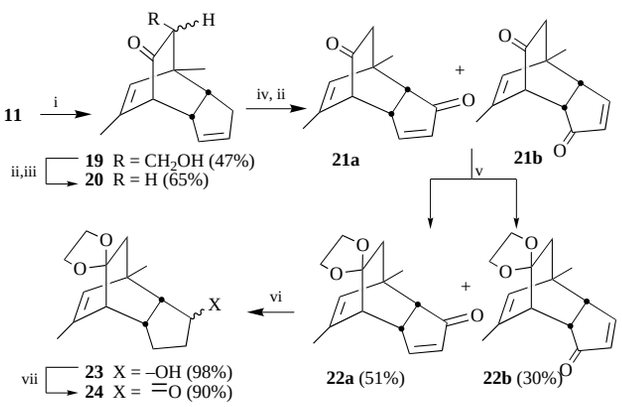
18 (~3%) **11** (75%)

Scheme 2 *Reagents and conditions*: i, $NaBH_4$, MeOH–H_2O; ii, $NaIO_4$, MeCN

ation of 3,5-dimethylspiro[cyclohexa-2,4-diene-6,2′-oxiran]one **13** and its cycloaddition with cyclopentadiene wherein the former species apparently behaved as a 4π and the latter as a 2π partner. It is interesting to note the selectivity in the above cycloaddition especially since there are various symmetry-allowed pericyclic modes of addition between spiro[cyclohexa-2,4-diene-oxiran]one **13** and cyclopentadiene.

The structures and stereochemistry of the adducts **11** and **18** were deduced from their highfield ^{1}H NMR spectra, ^{13}C NMR spectra, and comparison with other data.[10–12] The stereochemical orientation of the oxirane moiety was deduced on the basis of the general tendency of cyclohexa-2,4-dienones having 6-acetoxy functions during their cycloaddition, especially with themselves,[6] and comparison of the spectral features of **11** and **18** with similar adducts.

Towards the synthesis of the desired tricyclic chromophoric systems it was necessary to remove the oxirane moiety present at the bridge and introduce the geminal methyl groups in the five-membered ring of the adduct **11**; this was done as follows. The keto epoxide **11** was reduced[13] with zinc in MeOH–H_2O (7 : 1) to give the keto alcohol **19** as a major product (47%); this was oxidised with Jones' reagent and the resulting β-keto acid was subsequently decarboxylated[14] to give the tricyclic compound **20** (Scheme 3). Oxidation of compound **20** with



Scheme 3 *Reagents and conditions*: i, Zn, NH_4Cl, MeOH–H_2O, RT; ii, Jones'; iii, THF–H_2O, heat; iv, SeO_2, KH_2PO_4, dioxane–water, heat; v, $HOCH_2CH_2OH$, PTSA, PhH, heat; vi, $NaBH_4$, MeOH; vii, PCC, CH_2Cl_2

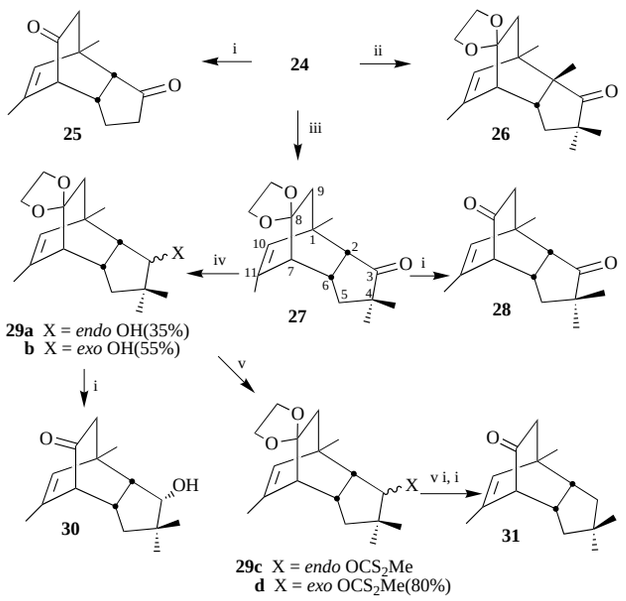
selenium dioxide gave a regioisomeric mixture of allylic alcohols which upon further oxidation with Jones' reagent[15] gave a mixture of the diene-diones **21a** and **21b**; these were separated after ketalization of the carbonyl group at the ethano bridge. Thus, the mixture of diene-diones **21a** and **21b** was treated with ethylene glycol and toluene-*p*-sulfonic acid to give the keto ketals **22a** and **22b** which were separated by a careful chromatography (Scheme 3).

In order to introduce geminal dimethyl groups in the five-membered ring, it was necessary to reduce the conjugated carbon–carbon π bond in the five-membered ring. Therefore, the ketal enone **22a** was treated with sodium borohydride which reduced both the double bond as well as carbonyl group (IR, ^{1}H NMR) and furnished the alcohol **23**; subsequent oxidation of this gave the keto ketal **24**. Hydrolysis of the ketal **24** gave the chromophoric system **25**. The structure of all the compounds are consistent with their spectral data.

Towards the introduction of the geminal methyl groups α to the carbonyl group of cyclopentane ring, the keto ketal **24** was first treated with methyl iodide in the presence of sodium hydride in THF. This, unfortunately, furnished the undesired trimethylated derivative **26**. Such exhaustive alkylation was avoided by selection of a bulky base. Thus, alkylation of the keto ketal **24** with methyl iodide in the presence of potassium *tert*-butoxide in dry *tert*-butyl alcohol smoothly furnished the desired dimethylated keto ketal **27** whose structure was clearly revealed from its spectral data.

The keto ketal **27** was reduced with sodium borohydride in THF–H_2O to give a stereoisomeric mixture of *endo* and *exo* alcohols **29a**,**b** which were separated by careful chromatography. The stereochemical orientation of the hydroxy groups was determined on the basis of the chemical shift and coupling constants of the *H*–C–OH proton. Thus, *H*–C–OH in the *endo* alcohol **29a** resonated at δ 3.52 (dd, *J* 12 and 8) in its ^{1}H NMR spectrum while *H*–C–OH in **29b** appeared at δ 3.17 (d, *J* 7), respectively. Hydrolysis of **29a** gave the hydroxy ketone **30**.

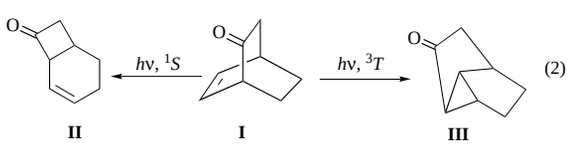
The alcohols **29a**,**b** were also converted into their thiocarbamates **29c**,**d** whose reduction with tributyltin hydride followed by hydrolysis furnished the chromophoric system **31** (Scheme 4).



Scheme 4 *Reagents and conditions*: i, HCl–H_2O; ii, NaH, THF, MeI, V; iii, KO′Bu, Bu′OH, MeI; iv, $NaBH_4$, THF–H_2O; v, NaH, THF, imidazole, CS_2, MeI; vi, TBTH, AIBN, Ph-Me, neat

Towards protoilludanes: photochemical reaction of the tricyclic systems 20, 25, 28, 30 and 31 upon singlet (^1S) excitation

There has been a great deal of research on the photochemistry of β,γ-enones,[17] stimulated initially by spectroscopic studies[17] and subsequently by observation of the then novel photochemical equilibration of bicyclo[3.2.0]heptenones through a process which was later termed a 1,3-sigmatropic acyl shift.[18] Ever since, many types of photoreactions have been discovered which are characteristic of alkenes and carbonyl chromophore. However, it has been observed that rigid β,γ-enones undergo two unusual molecular rearrangements upon electronic excitation involving a 1,3-sigmatropic acyl shift and a oxa-di-π-methane rearrangement.[19,20] The direct irradiation (^1S, π-π*) of β,γ-enones causes a 1,3-acyl shift leading to the formation of cyclobutanone derivatives while the triplet-sensitized irradiation (^3T, π-π*) leads to a 1,2-acyl shift or oxa-di-π-methane rearrangement [Eqn. (2)], though a mixture of products may

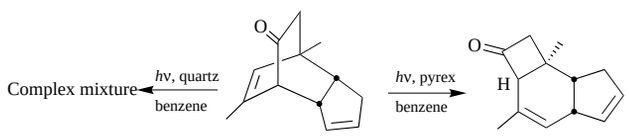


result because of indiscriminate population of the excited states. We realized that a 1,3-acyl shift in an appropriately designed tricyclic system having a β,γ-enone chromophore would provide a general, efficient and stereospecific route to protoilludanes, and hence this reaction was incorporated in the strategy.

It is worth mentioning, however, that most of the investigations on the photoreactions of β,γ-enones were directed towards triplet-sensitized oxa-di-π-methane rearrangements;[19,20] further, that most of the studies on excited singlet (^1S) state photoreactions of β,γ-enones were carried out on simple bicyclic systems in conjunction with oxa-di-π-methane rearrangements in order to resolve the singlet–triplet dichotomy.[18] While the triplet excited state photochemistry of β,γ-enones has been exploited in organic synthesis, the synthetic potential of the photochemical 1,3-acyl shift in β,γ-enones has not been realized until recently.[5]

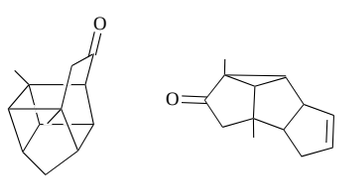
Although the photoreaction of β,γ-enones are characteristic of excited states, a mixture of products may be obtained due to unselective population of the excited states. Moreover, the photoreactions of β,γ-enones are quite sensitive to the nature of functional groups and substituent present on the chromophoric systems.[21] Considering the structural and functional complexity of the above chromophoric systems many photochemical reactions such as intramolecular cycloaddition,[22] epimerization,[23] photoreduction,[24] decarbonylation[25] and 1,3-acyl shift can be expected.

In view of the above, we first explored the photoreaction of compounds **20**. Thus, a solution of **20** in benzene was irradiated with a mercury vapour lamp (125 W, APP) in a quartz immersion well; it gave a complex mixture of products. Therefore, a benzene solution of **20** was irradiated in a Pyrex immersion well (>300 nm) for *ca.* 1 h; this gave the 1,3-acyl shift product **32** in reasonably good yield (31%) (Scheme 5) along with some



Scheme 5

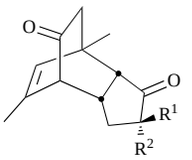
unchanged starting material. The structure of compound **32** was deduced from its spectral data. It is interesting to note the selectivity in the above photoreaction especially since products of type **37** and/or **38** were not formed because of



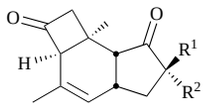
intramolecular $\pi^{2s} + \pi^{2s}$ cycloaddition or oxa-di-π-methane rearrangement.

Similar irradiation of compounds **30** and **31** under the aforementioned conditions also gave the protoilludanoids **35** and **36**, respectively. While the above photoreactions occurred smoothly we were a little concerned about the photoreaction of the diones **25** and **28** since these contain carbonyl groups in the five-membered ring which are also reactive chromophores and undergo α cleavage upon irradiation. It was a relief to find that the dione **25** underwent a clean photoreaction upon direct irradiation in benzene to furnish the desired 7-protoilludendione **33**. However, irradiation of the dione **28** gave a 1,3-acyl shift product **34** contaminated with a minor product, apparently formed due to α cleavage of the carbonyl group present in the five-membered ring as revealed through its high-field ^1H NMR spectrum; this showed a signal at δ 9.46 for an aldehydic proton. However, since the minor product could not be separated on column chromatography, the mixture of photoproducts was worked up with sodium bisulphite to remove the minor aldehydic product and give the desired compound **34** in pure form. The structure of the compound **34** is consistent with its spectral data.

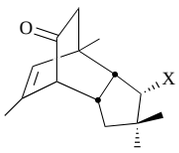
In summary we have described a novel and stereoselective route to protoilludanes employing a photochemical sigmatropic 1,3-acyl shift in appropriately constructed *endo*-tricyclo-[5.2.2.$0^{2,6}$]undecanes having a β,γ-unsaturated carbonyl chromophore. There are several noteworthy features of the present strategy. For example, it generates the angular *cis*:*anti*:



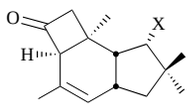
25 $R^1 = R^2 = H$
26 $R^1 = R^2 = Me$



33 $R^1 = R^2 = H$
34 $R^1 = R^2 = Me$



30 X = OH
31 X = H



35 X = OH
36 X = H

cis tricyclic protoilludane framework in a single stereoselective sequence from precursors in which most of the structural and stereochemical features of protoilludanes are present in latent form. Moreover, the penultimate precursors are easily derived from the keto epoxide **11** which is prepared from the aromatic compound **12** and cyclopentadiene in a single step. The present strategy also illustrates the principle of generation of maximum complexity[26] rapidly and efficiently at the very beginning of the synthetic route since 13 (out of 15) carbon atoms of protoilludanes are assembled with appropriate connectivity in just a single step. We have also presented a simple methodology for the synthesis of the desired tricyclic chromophoric systems from aromatic precursors by cycloaddition of an *in situ* generated spiro[cyclohexa-2,4-diene-oxiran]one and cyclopentadiene. The route described in the present paper provides opportunities for further investigation in the area of protoilludanes.

Experimental

Melting points were determined on a Veego apparatus of Buchi type and are uncorrected. TLC analyses were carried out on glass plates coated with TLC grade silica gel and spots were visualized with iodine vapour. Silica gel (100–200 mesh) was used for column chromatography. Laboratory solvents were purified and pre-dried before use according to standard procedures. Light petroleum (LP; bp 60–80 °C) was used for column chromatography. IR spectra were recorded on a Nicolet Impact 400 FT-IR instrument. UV spectra were recorded on a Shimadzu 260 instrument. NMR spectra were recorded on either Varian VXR 300, or Bruker AMX 500 instruments using $CDCl_3$ as the solvent containing $SiMe_4$ as an internal standard with chemical shifts (δ) expressed as ppm downfield with respect to $SiMe_4$; J values are given in Hz. Elemental analysis were performed on a CEST 1106 instrument. Mass spectra were recorded on a HP GCD 1800A mass spectrometer. All organic extracts were dried over anhydrous sodium sulfate.

1′,11″-Dimethylspiro[oxirane-2,9′-*endo*-tricyclo[5.2.2.0^{2,6}]-undeca-4′,10′-dien]-8′-one 11

Methanol–water (80:20; 60 cm^3) was added to the aldehyde **14** (2.5 g, 16.67 mmol) in a round bottom flask after which the mixture was stirred while sodium borohydride (0.63 g, 16.57 mmol) was added to it all at once. The mixture was then further stirred for 0.5 h at ambient temperature (~30 °C). After the reduction was over (~1 h, TLC), acetonitrile (25 cm^3), water (100 cm^3) and freshly cracked cyclopentadiene (10 cm^3) were added to the reaction mixture followed by finely powdered sodium metaperiodate (15 g, 70 mmol), added over a period of 0.5 h. After being stirred for 1 h the reaction mixture was treated with additional cyclopentadiene (5 cm^3) and then stirred for 8 h at ambient temperature (~30 °C); it was then poured into water (250 cm^3) and extracted with diethyl ether (3 × 75 cm^3). The combined extracts were washed with water (2 × 75 cm^3) and brine (1 × 75 cm^3), dried and evaporated under reduced pressure. The crude product was charged onto a column of silica gel and eluted with LP to remove unchanged dicyclopentadiene. Further elution with LP–ethyl acetate (98:2) gave the adduct **11** (2.7 g, 75%) as a colourless solid which was recrystallized from LP (bp 40–60 °C), mp 54–55 °C; ν_{max}(film)/cm^{-1} 1735; λ_{max}(MeOH)/nm 223.2 and 305.6; δ_H(300 MHz, $CDCl_3$) 5.72 (1H, m of d, J 6, olefinic H), 5.66 (1H, br m, γ-H of β,γ-enone moiety), 5.42 (1H, m of d, J 6, olefinic H), 3.34 (1H, complex m of d, J 9, methine H), 3.12 (1H, m, J 2, methine H), 3.04 (1H, part of an AB system, J_{AB} 6, OCH_2), 2.92 (1 H, part of an AB system, J_{AB} 6, OCH_2), 2.71 (1H, dd of d, J 9, 10 and 5, methine H), 2.47 (1H, m of dd, J 17 and 10, methylene H), 2.14 (1H, m of d, J 17, methylene H), 1.75 (3H, d, J 1.5, CH_3) and 1.04 (3H, s, CH_3); δ_C(25 MHz, $CDCl_3$) 205.6 (CO), 136.7, 133.1, 129.8, 128.9 (olefinic carbons), 59.9, 57.0, 50.8, 49.5, 41.9, 41.1, 36.5, 21.4, 14.9 (other methine, methylene methyl and quaternary carbons); *m/z* 216 (M$^+$, 4%), 151 (71, M$^+$ − C_5H_5), 123 (100, M$^+$ − C_5H_5 − CO), 91 (28) and 66 (41) (Found: C, 77.54; H, 7.50. $C_{14}H_{16}O_2$ requires C, 77.77; H, 7.40%).

Continued elution with the same solvent gave the minor adduct **18** (0.1 g, ~3%) as a solid which was recrystallized from LP (bp 40–60 °C), mp 76–77 °C; ν_{max}(KBr)/cm^{-1} 1735; δ_H(300 MHz, $CDCl_3$) 5.72 (1H, m of d, J 6, olefinic H), 5.69 (1H, br m merged with the signal at 5.72, olefinic proton of bicyclo-[2.2.2]octene framework), 5.48 (1H, m of d, J 6, olefinic H), 3.30 (1H, complex m, methine H), 3.13 (1H, dd, J 3 and 2.5, methine proton at the bridgehead), 3.0 (1H, part of an AB system, J_{AB} 6, OCH_2), 2.89 (1 H, part of an AB system, J_{AB} 6, OCH_2), 2.56 (1H, dd of d, J 10 and 6, methine H), 2.46 (1H, m of dd, J 18 and 10, allylic methylene H), 2.20 (1H, m of d, J 18, methylene H), 1.77 (3H, d, J 1.5, CH_3) and 1.04 (3H, s, CH_3); *m/z* 216 (M$^+$, 10%), 151 (67), 123 (100), 91 (30) and 66 (38) (Found: C, 77.71; H, 7.45. $C_{14}H_{16}O_2$ requires C, 77.77; H, 7.40%).

1,11-Dimethyl-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-4,10-dien-8-one 20

To a suspension of activated zinc (7.15 g, excess) in MeOH–H_2O (7:1; 100 cm^3) was added a solution of compound **11** (4.7 g, 21.76 mmol) in methanol (25 cm^3), followed by ammonium chloride (2.7 g, excess). The reaction mixture was stirred at room temperature (~30 °C) for *ca.* 6 h after which it was filtered through a Celite pad and then concentrated *in vacuo*. After dilution of the residue with water (50 cm^3) it was extracted with ethyl acetate (3 × 75 cm^3). The combined extracts were washed with water (2 × 30 cm^3) and brine (1 × 30 cm^3), dried and evaporated under reduced pressure to give a crude product. Chromatography of this over silica gel with LP–ethyl acetate (90:10) as eluent furnished compound **19** (2.2 g, 47%) [ν_{max}(film)/cm^{-1} 3458 and 1711; *m/z* 218 (M$^+$, 8%), 153 (28), 131 (64) and 122 (100)]. This compound was oxidized as follows.

To a stirred solution of the keto alcohol **19** (3 g, 13.76 mmol) in acetone (80 cm^3) at ~10 °C was added dropwise freshly prepared Jones' reagent. After the reaction was complete (TLC, ~2 h) the mixture was evaporated under reduced pressure and the residue was diluted with water (100 cm^3) and extracted with ethyl acetate (3 × 50 cm^3). The combined extracts were washed with water (2 × 30 cm^3) and brine (1 × 25 cm^3), dried and evaporated to give the β-keto acid (3.1 g, 97%; ν_{max}/cm^{-1} 3500 and 1740) which was then directly subjected to decarboxylation as follows. A mixture of the β-keto acid (3.1 g, 13.36 mmol) in tetrahydrofuran–water (60:40; 50 cm^3) was refluxed for *ca.* 12 h after which the tetrahydrofuran was removed under reduced pressure and the residue was diluted with water (50 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined extracts were washed with saturated aqueous sodium hydrogen

carbonate (2 × 25 cm^3), water (1 × 25 cm^3) and brine (1 × 25 cm^3), dried and evaporated. Chromatography of the residue (LP–ethyl acetate, 95:5) gave the parent compound **20** which was recrystallized from LP (bp 40–60 °C); it was obtained as a low melting solid (1.62 g, 65%), mp 37–38 °C; ν_{max}(film)/cm^{-1} 1730; λ_{max}(MeOH)/nm 212 (s) and 294; δ_H(300 MHz, $CDCl_3$) 5.67–5.60 (2H, m merged with a br m, olefinic H), 5.42 (1H, m of d, *J* 6, olefinic H), 3.24 (1H, m of d, *J* 7, methine H), 2.92 (1H, dd, *J* 2.5 and 2.5, bridgehead H), 2.44–2.32 (2H, overlapped m, methine and allylic methylene H), 2.06 (1H, m of d, *J* 16, allylic methylene H), 1.94 (2H, AB system, J_{AB} 18, methylene protons α to ketone), 1.60 (3H, d, *J* 1.5, olefinic methyl) and 1.22 (3H, s, CH_3); δ_C(25 MHz, $CDCl_3$) 212.0 (CO), 136.1 (s), 132.3 (d), 130.9 (d) and 129.5 (d) (olefinic carbons), 58.1 (d), 50.5 (d), 47.4 (d), 45.8 (t), 39.9 (s), 36.4 (t), 22.0 (q) and 21.1 (q); *m*/*z* 188 (M^+, 10%) and 123 (100, $M^+ - C_5H_5$).

1,11-Dimethylspiro[1,3-dioxolane-2,8′-*endo*-tricyclo[5.2.2.0^{2,6}]-undeca-4′,10′-dien]-3′-one 22a and 1,11-dimethylspiro-[1,3-dioxolane-2,8′-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-3′,10′-dien]-5′-one 22b

To a stirred solution of selenium dioxide (10.32 g, 93 mmol) in dioxane–water (75:25; 80 cm^3) was added potassium dihydrogen orthophosphate (7.2 g, 53 mmol) followed by a solution of compound **20** (5.0 g, 26.6 mmol) in dioxane (10 cm^3), added dropwise. The reaction mixture was heated at 100 °C for 10 h after which it was filtered through a Celite pad; the pad was then washed with diethyl ether (2 × 20 cm^3). The combined filtrate and washings were concentrated under reduced pressure and then diluted with water (50 cm^3) and extracted with ethyl acetate (3 × 75 cm^3). The combined extracts were washed with water (2 × 50 cm^3) and brine (1 × 50 cm^3), dried and evaporated *in vacuo*. The residue was chromatographed over silica gel with LP–ethyl acetate (75:25) as eluent to yield a mixture of hydroxy ketones (3 g, 55%) (IR and ^{1}H NMR, 60 MHz) which was subjected to further oxidation with Jones' reagent as follows.

To a solution of the above mixture (3 g, 14.7 mmol) in acetone (100 cm^3), was added freshly prepared Jones' reagent dropwise at *ca.* 0–5 °C. After the reaction was over (TLC) the solvent was removed *in vacuo* and the residue was diluted with water and extracted with ethyl acetate (3 × 75 cm^3). The combined extracts were washed with water (2 × 75 cm^3), aqueous sodium hydrogen carbonate (1 × 75 cm^3) and brine (1 × 50 cm^3), dried and evaporated. Column chromatography (LP–ethyl acetate, 75:25) of the residue over silica gel furnished a mixture of the dienediones **21a** and **21b** (2.8 g, 94.26%) which was subjected to ketalization.

A mixture of ethylene glycol (2 cm^3, excess) and toluene-*p*-sulfonic acid (10 mg) in dry benzene (50 cm^3) was refluxed in a Dean-Stark apparatus, in order to remove traces of water after which the mixture of dienediones **21a** and **21b** (2.8 g, 13.9 mmol) was added to it; the reaction mixture was then refluxed until completion of the reaction (TLC, ~4 h). The reaction mixture was then cooled and washed with saturated aqueous sodium hydrogen carbonate (2 × 25 cm^3) and brine (1 × 25 cm^3), dried and evaporated under reduced pressure to furnish a mixture of compounds **22a** and **22b** (3.17 g). The crude product was charged onto a column of silica gel and eluted with LP–ethyl acetate (80:20) to give the ketal **22a** (1.75 g, 51%), mp 92 °C; ν_{max}(KBr)/cm^{-1} 1699.9; λ_{max}(MeOH)/nm 223.8; δ_H(300 MHz, $CDCl_3$) 7.38 (1H, dd, *J* 5.8 and 3, β-H of the α,β-enone moiety), 6.1 (1H, dd, *J* 5.8 and 1.8, α-H of α,β-enone moiety), 5.44 (1H, br s, olefinic H), 3.93 [4H, br s, $(CH_2O)_2$], 3.47 (1H, m, methine H), 2.52 (1H, m, methine H), 2.1 (1H, d, *J* 5.7, methine H, α to carbonyl), 1.67 (3H, s, CH_3), 1.65 (1H, part of an AB system, J_{AB} 15, methylene H), 1.53 (1H, part of an AB system, J_{AB} 15, methylene H) and 1.4 (3H, s, CH_3); δ_C(75 MHz, $CDCl_3$) 210.3, 163.7, 136.8, 128.1, 113.2, 64.4, 64.3, 52.5, 48.4, 48.1, 43.3, 39.1, 29.7, 21.8 and 21.5; *m*/*z* 246 (M^+, 3%), 160 [33, $M^+ - (CH_2O)_2{=}CH_2$], 145 [100, $M^+ - \{(CH_2O)_2{=}CH_2\} - CH_3$], 118 (26) and 87 (64) (Found: C, 73.57; H, 7.66. $C_{15}H_{18}O_3$ requires C, 73.17; H, 7.32%).

Continued elution with the same solvent furnished the minor isomeric ketal **22b** as a viscous liquid (1.02 g, 30%); ν_{max}(film)/cm^{-1} 1703; λ_{max}(MeOH)/nm 224.4; δ_H(300 MHz, $CDCl_3$) 7.54 (1H, dd, *J* 6 and 1, β-H of the enone moiety), 6.20 (1H, d, *J* 6, α-H of the enone group), 5.26 (1H, br m, olefinic proton), 3.96 [4H, m, $(CH_2O)_2$], 2.8 (3H, m, methine H), 1.76 (1H, part of an AB system, J_{AB} 15, methylene H), 1.7 (3H, d, *J* 1.5, olefinic CH_3), 1.65 (1H, part of an AB system, J_{AB} 15, methylene H) and 1.24 (3H, s, CH_3); *m*/*z* 246 (M^+, 8%), 160 [25, $M^+ - (CH_2O)_2{=}CH_2$], 145 [100, $M^+ - \{(CH_2O)_2{=}CH_2\} - CH_3$], 118 (27) and 87 (67).

1′,11″-Dimethyl-3′-hydroxyspiro[1,3-dioxolane-2,8′-*endo*-tricyclo[5.2.2.0^{2,6}]undec-10′-en]-3′-one 24

Sodium borohydride (0.843 g, 22.18 mmol) was added as a single portion to a solution of the ketal enone **22a** (2.5 g, 10.16 mmol) in methanol (100 cm^3) at room temperature (~30 °C). After being stirred for 1 h the reaction mixture was concentrated *in vacuo* to ~20 cm^3, diluted with water (100 cm^3) and extracted with dichloromethane (3 × 100 cm^3). The combined extracts were washed with water (2 × 75 cm^3), dried and concentrated by removal of solvent. Column chromatography of the residue (LP–ethyl acetate, 90:10) furnished the alcohol **23** (2.5 g, 98%); ν_{max}(film)/cm^{-1} 3535; δ_H(300 MHz, $CDCl_3$) 5.83 (1H, br m, olefinic H), 4.20 (1H, complex m, *HC*OH), 3.91 [4H, $(CH_2O)_2$], 2.62 (1H, complex m, methine H), 2.43 (1H, superimposed dd, *J* 2.5 and 2.5, methine H at the bridgehead), 1.99 (1H, dd, *J* 12 and 7, methine H), 1.88 (3H, d, *J* 1.5, CH_3), 1.80–1.60 (2H, merged multiplets, methylene H), 1.53 (2H, AB system, J_{AB} 15, methylene H), 1.44–1.38 (3H, complex m, methylene H + OH), 1.26 (3H, s, CH_3) and 1.06–0.92 (1H, complex m, methylene H); *m*/*z* 250 (M^+, 2%), 164 (48, $M^+ - (CH_2O)_2{=}CH_2$), 120 (100), 107 (31) and 87 (17). The alcohol **23** was then oxidized as described below.

A suspension of PCC (3.54 g, 16.44 mmol) in dichloromethane (50 cm^3) in a 250-cm^3 flask equipped with addition funnel was treated with a solution of the alcohol **23** in dichloromethane (25 cm^3), added dropwise with stirring over a period of 30 min. After being stirred for 1 h (TLC) the reaction mixture was diluted with ether (75 cm^3), stirred for additional 30 min and then filtered through a short column of silica gel. After removal of solvent, the brown residue was dissolved in ether (150 cm^3) and washed with 5% aqueous sodium hydroxide (2 × 25 cm^3), cold 5% aqueous hydrochloric acid (25 cm^3), saturated aqueous sodium hydrogen carbonate (1 × 25 cm^3) and brine (1 × 25 cm^3) and then dried and evaporated *in vacuo* to yield a yellow oil. This was chromatographed on silica gel to furnish the ketone **24** as a colourless oil (2.23 g, 90%); ν_{max}(film)/cm^{-1} 1730; λ_{max}(MeOH)/nm 211s and 300w; δ_H(500 MHz, $CDCl_3$) 5.52 (1H, br m, olefinic H), 3.9 [4H, m, $(CH_2O)_2$], 3.0 (1H, complex m, methine H), 2.4 (1H, br m, methine H), 2.08 (1H, d with str., *J* 8, methine H), 2.05–1.90 (3H, overlapped m), 1.85 (3H, d, *J* 1.5, CH_3), 1.55 (1H, part of an AB system, J_{AB} 14, methylene H), 1.50 (1H, m), 1.42 (1H, part of an AB system, J_{AB} 14, methylene H) and 1.30 (3H, s, CH_3); δ_C(125 MHz, $CDCl_3$) 220.9 (CO), 139.9, 129.9, 113.4, 64.3, 64.2, 55.5, 50.5, 48.6, 39.4, 39.2, 35.6, 24.9, 23.2 and 21.9; *m*/*z* 248 (M^+, 4%), 162 [100, $M^+ - (CH_2O)_2{=}CH_2$], 134 (43), 106 (48), 91 (23), 87 (59) and 56 (22).

1,11-Dimethyl-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-10-ene-3,8-dione 25

A solution of compound **24** (0.12 g, 0.48 mmol) in acetone–water (90:10) (20 cm^3) was treated with a few drops of concentrated hydrochloric acid and then stirred for 4 h at room temperature (~30 °C) after which it was evaporated *in vacuo*. The residue was diluted with ethyl acetate (1 × 50 cm^3). The organic layer was separated and washed with saturated aqueous

sodium hydrogen carbonate (1 × 20 cm^3), water (1 × 20 cm^3) and brine (1 × 25 cm^3) and then dried and evaporated *in vacuo*. Column chromatography (LP–ethyl acetate, 95:5) of the residue furnished compound **25** (0.095 g, 96%); ν_{max}(film)/cm^{-1} 1730; λ_{max}(MeOH)/nm 293.4 and 208.6; δ_H(300 MHz, $CDCl_3$) 5.74 (1H, m, olefinic H), 3.08 (1H, dd, *J* 1.5 and 2.6), 2.95 (1H, m), 2.31 (1H, d, *J* 9.3), 2.22–2.02 (3H, complex m), 1.96 (1H, part of AB system, J_{AB} 18.3, methylene H), 1.89 (3H, d, *J* 1.65, CH_3), 1.82 (1H, part of AB system, J_{AB} 18.3, methylene H), 1.72–1.64 (1H, m) and 1.46 (3H, s, CH_3); *m/z* 204 (M^+, 6%), 162 (100, $M^+ - COCH_2$), 134 [34, $M^+ - \{(COCH_2) + CO\}$], 119 [37, $M^+ - \{(COCH_2) + CO + CH_3\}$], 106 [65, $M^+ - \{(COCH_2) + CO + C_2H_6\}$], 91 (35) and 77 (14).

1′,2′,4′,4′,11′-Pentamethylspiro[1,3-dioxolane-2,8′-*endo*-tricyclo[5.2.2.0^{2,6}]undec-10′-en]-3′-one 26

Sodium hydride (60% w/w suspension, 0.155 g; 3.2 mmol) in a dry two-necked flask was washed with dry hexane after which tetrahydrofuran (15 cm^3) was added to it. A solution of the ketone **24** (0.2 g, 0.8 mmol) in tetrahydrofuran (5 cm^3) was added to the reaction mixture followed by methyl iodide (2 cm^3, excess). The mixture was refluxed for *ca.* 0.5 h after which it was quenched with cold water and the tetrahydrofuran then removed *in vacuo*. The residue was extracted with ethyl acetate (3 × 15 cm^3), and the combined extracts were washed with water (2 × 10 cm^3) and brine (15 cm^3), dried and evaporated. Chromatography of the residue over silica gel (LP–ethyl acetate, 95:5) furnished the alkylated product **26** as a colourless liquid (0.14 g, 60%); ν_{max}(film)/cm^{-1} 1735; δ_H(500 MHz, $CDCl_3$) 5.61 (1H, s, olefinic H), 3.92 [4H, m, $(CH_2O)_2$], 2.47 (1H, d of dd, *J* 10.5, 5 and 2.5, ring junction H), 2.29 (1H, br s), 2.05 (1H, dd, *J* 14 and 10, methylene H), 1.9 (1H, d, *J* 14, methylene H), 1.82 (3H, d, *J* 1.25, CH_3), 1.31 (1H, d, *J* 14, methylene H), 1.25 (1H, d, *J* 14, methylene H), 1.28 (3H, s, CH_3), 1.16 (3H, s, CH_3), 1.04 (3H, s, CH_3) and 0.89 (3H, s, CH_3); *m/z* 290 (M^+, 3%), 204 (47), 178 (22) and 120 (100).

1′,4′,4′,11′-Tetramethylspiro[1,3-dioxolane-2,8′-*endo*-tricyclo-[5.2.2.0^{2,6}]undec-10′-en]-3′-one 27

tert-Butyl alcohol was added to potassium *tert*-butoxide (3.6 g, 32.2 mmol) in a flask (100 cm^3) equipped with a reflux condenser, nitrogen inlet and addition funnel and after which the flask was cooled to 10 °C. A solution of the ketone **24** (2.66 g, 10.72 mmol) in *tert*-butyl alcohol (20 cm^3) was then added rapidly with stirring to the flask followed by the immediate addition of methyl iodide (5 cm^3, 80.3 mmol). Once the initial exothermic reaction had subsided, the reaction mixture was refluxed for 5 h and then cooled and poured into cold water (50 cm^3). After removal of the *tert*-butyl alcohol under reduced pressure, the residue was extracted with ether (3 × 50 cm^3). The combined extracts were washed with water (2 × 30 cm^3) and brine (1 × 25 cm^3), dried and evaporated *in vacuo*. Column chromatography (LP–ethyl acetate, 90:10) of the crude product furnished the alkylated compound **27** (1.33 g, 45%); ν_{max}(film)/cm^{-1} 1734; λ_{max}(MeOH)/nm 208.6 and 293.4; δ_H(300 MHz, $CDCl_3$) 5.62 (1H, br m, olefinic H), 3.93 [4H, m, $(CH_2O)_2$], 3.05 (1H, d of dd, *J* 10.4, 9 and 2.7, methine proton at C-2′), 2.40 (1H, br m, methine proton at C-1′), 2.36 (1H, d, *J* 10.4, methine proton at C-6′), 1.86 (1H, dd, *J* 13 and 9, *exo* methylene proton at C-3′), 1.80 (3H, d, *J* 1.5, CH_3), 1.58 (1H, part of an AB system, J_{AB} 13.5, methylene proton at C-8′), 1.44 (1H, part of an AB system, J_{AB} 13.5, methylene proton at C-8′), 1.43 (3H, s, CH_3), 1.10 (1H, m of d, *J* 13, *endo* methylene proton at C-3′), 0.98 (3H, s, CH_3) and 0.90 (3H, s, CH_3); δ_C(125 MHz, $CDCl_3$) 222.3 (CO), 139.7, 130.4 (olefinic carbons), 113.5 [=*C*$(OCH_2)_2$], 64.3, 64.2, 53.1, 49.9, 49.2, 46.7, 39.9, 38.7, 32.6, 26.3, 23.5, 22.4 and 22.0 (all the carbons); *m/z* 276 (M^+, 2%), 190 [54, $M^+ - (CH_2O)_2{=}CH_2$], 162 [24, $M^+ - (CH_2O)_2{=}CH_2 + CO$], 106 [100, $M^+ - \{(CH_2O)_2{=}CH_2 + CO + (Me)_2C{=}CH_2\}$], 119 (49) and 87 (55).

1,4,4,11-Tetramethyl-*endo*-tricyclo[5.2.2.0^{2,6}]undec-10-ene-3,8-dione 28

Hydrolysis of compound **27** (0.1 g, 0.36 mmol) as described above and chromatography of the crude product furnished compound **28** (0.08 g, 95%); ν_{max}(film)/cm^{-1} 1730; λ_{max}(MeOH)/nm 207.8; δ_H(300 MHz, $CDCl_3$) 5.81 (1H, m, olefinic H), 3.0–2.9 (2H, m), (1H, d, *J* 10.4), 1.96 (1H, d, *J* 13.2), 1.93 (1H, part of AB system, J_{AB} 18.5, methylene H), 1.82 (1H, part of AB system, J_{AB} 18.5, methylene H), 1.79 (3H, d, *J* 1.65, CH_3), 1.55 (3H, s, CH_3), 1.21 (1H, m), 1.02 (3H, s, CH_3) and 0.95 (3H, s, CH_3); *m/z* 232 (M^+, 4%), 190 [66, $M^+ - (COCH_2)$], 162 [20, $M^+ - \{(COCH_2) + CO\}$], 106 [100, $M^+ - \{(COCH_2) + CO + C_4H_8\}$], 119 (45) and 91 (28).

1′,4′,4′,11′-Tetramethyl-3′-*endo*-hydroxy-spiro[1,3-dioxolane-2,8′-*endo*-tricyclo-[5.2.2.0^{2,6}]undec-10-ene] 29a and 1′,4′,4′,11′-tetramethyl-3′-*exo*-hydroxy-spiro[1,3-dioxolane-2,8′-*endo*-tricyclo[5.2.2.0^{2,6}]undec-10′-ene] 29b

Sodium borohydride (0.5 g, 13.16 mmol) was added to a solution of the ketone **27** (1.2 g, 4.35 mmol) in tetrahydrofuran (50 cm^3) and water (1 cm^3) and the reaction mixture was stirred for 12 h at room temperature (~30 °C, TLC). After the mixture had been concentrated by removal of the solvent under reduced pressure, it was diluted with water (30 cm^3) and extracted with dichloromethane (3 × 50 cm^3). The combined extracts were washed with water (2 × 30 cm^3) and brine (1 × 25 cm^3) dried and evaporated *in vacuo*. Column chromatography (LP–ethyl acetate, 90:10) of the crude product gave the alcohol **29a** (0.43 g, 35%); ν_{max}(film)/cm^{-1} 3543; δ_H(300 MHz, $CDCl_3$) 5.82 (1H, br m, olefinic H), 3.93 [4H, m, $(CH_2O)_2$], 3.52 (1H, dd, *J* 12 and 8, *H*COH), 2.78 (1H, complex m, methine H), 2.35 (1H, br m, methine H), 2.28 (1H, dd, *J* 12 and 7, methine H), 1.87 (3H, d, *J* 1.5, CH_3), 1.7 (1H, br s, OH), 1.59 (1H, part of an AB system, J_{AB} 14, methylene H), 1.49 (1H, part of an AB system, J_{AB} 14, methylene H), 1.40 (1H, m, methylene H), 1.26 (3H, s, CH_3), 0.98 (3H, s, CH_3) and 0.90 (4H, s merged with m, CH_3 + 1H); *m/z* 278 (M^+, 1%), 192 [90, $M^+ - (CH_2O)_2{=}CH_2$], 177 (21), 120 (100), 105 (22) and 87 (26).

Further elution with LP–ethyl acetate (80:20) gave the alcohol **29b** (0.67 g, 55%); ν_{max}(film)/cm^{-1} 3482; δ_H(300 MHz, $CDCl_3$) 5.60 (1H, br m, olefinic H), 3.91 [4H, m, $(CH_2O)_2$], 3.17 (1H, d, *J* 7, *H*COH), 2.68 (1H, complex m, methine H), 2.20 (1H, br m, bridgehead H), 1.82 (3H, d, *J* 1.5, CH_3), 1.72 (1H, dd, *J* 12 and 9, methine H), 1.55–1.44 (3H, m), 1.24 (1H, br s), 1.18 (3H, s, CH_3), 0.92 (3H, s, CH_3), 0.88 (3H, s, CH_3) and 0.80 (1H, superimposed dd, *J* 12 and 12, methylene H); *m/z* 278 (M^+, 1%), 192 [43, $M^+ - (CH_2O)_2{=}CH_2$], 177 (8), 120 (100), 105 (16) and 87 (12).

1,4,4,11-Tetramethyl-3-*endo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]-undec-10-en-8-one 30

Hydrolysis of compound **29a** (0.1 g, 0.36 mmol) as described above furnished the title compound **30** (0.080 g, 95%), mp 119 °C; ν_{max}(KBr)/cm^{-1} 3500 and 1722; λ_{max}(MeOH)/nm 206, 296; δ_H(500 MHz, $CDCl_3$) 5.99 (1H, br m, olefinic H), 3.60 (1H, dd, *J* 10 and 6, *H*COH), 2.91 (1H, superimposed dd, *J* 2.5 and 2.5, bridgehead H), 2.70 (1H, dd of dd, *J* 10.5, 6 and 3, ring junction H), 2.44 (1H, dd, *J* 10 and 6, ring junction H), 1.88 (2H, AB system, J_{AB} 18, methylene H), 1.84 (3H, d, *J* 2, CH_3), 1.50 (1H, dd with str., *J* 13 and 8, methylene H), 1.36 (4H, s overlapped with a signal, CH_3 + 1H), 1.60 (1H, d, *J* 3, methylene H), 1.0 (3 H, br s, CH_3) and 0.92 (3H, s, CH_3); δ_C(125 MHz, $CDCl_3$) 212.6 (CO), 136.2, 134.8, 81.3, 58.1, 54.8, 48.0, 45.7, 42.6, 40.1, 39.3, 25.6, 22.6, 22.3 and 22.2 (all the 15 carbons); *m/z* 234 (M^+, 5%), 192 [26, $M^+ - (CH_2{=}C{=}O)$], 120 [100, $M^+ - (CH_2{=}C{=}O) - (C_5H_{12})$], 107 (25) and 91 (15) (Found: C, 76.64; H, 9.35. $C_{15}H_{22}O_2$ requires C, 76.92; H, 9.40%).

1,4,4,11-Tetramethyl-*endo*-tricyclo-[5.2.2.0^{2,6}]undec-10-en-8-one 31

A mixture of the alcohol **29b** (1.1 g, 3.96 mmol), sodium hydride (50% suspension in oil; 0.57 g, 12 mmol) and imidazole (0.005 g) in dry tetrahydrofuran (20 cm^3) under nitrogen in a three-necked flask (50 cm^3) was refluxed and stirred for 3 h. After this, carbon disulfide (2 cm^3) in tetrahydrofuran (5 cm^3) was added to the reaction mixture and refluxing continued for a further 45 min; methyl iodide (2 cm^3, excess) was then added to the mixture and refluxing continued for a further 0.5 h. After the reaction mixture had been brought to room temperature (~30 °C) it was treated with acetic acid (0.5 cm^3) to quench the reaction and then diluted with water (30 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined extracts were washed with aqueous sodium hydrogen carbonate (2 × 10 cm^3), water (2 × 15 cm^3) and brine (1 × 20 cm^3), dried and evaporated *in vacuo*. The crude product was charged onto a silica gel column and eluted with LP to remove non-polar impurities; further elution with LP–ethyl acetate (98:2) furnished the *S*-methyl dithiocarbamate derivative **29c** (1.16 g, 80%); ν_{max}(film)/cm^{-1} 1461, 1220 and 1179; δ_H(500 MHz, $CDCl_3$) 5.66 (1H, s, olefinic H), 5.55 (1H, d, *J* 8, *H*CCS$_2$Me), 3.9 [4H, m, (CH$_2$O)$_2$], 2.82 (1H, dd, *J* 10 and 8), 2.55 (3H, s, CS$_2$CH$_3$), 2.22 (2H, m), 1.86 (3H, s, CH$_3$), 1.57–1.49 (4H, m), 1.03 (3H, s, CH$_3$), 0.97 (3H, s, CH$_3$) and 0.95 (3H, s, CH$_3$). The above thiocarbamate was reduced with tributyltin hydride as described below.

A three-necked round-bottom flask (50 cm^3) fitted with an argon inlet, reflux condenser and septum was charged with tributyltin hydride (1.8 g, 6.2 mmol) in dry toluene (25 cm^3). The reaction mixture was refluxed whilst a solution of the *S*-methyl dithiocarbamate **29c** (0.9 g, 2.45 mmol) in dry toluene (10 cm^3) was slowly injected into it. After the reaction mixture had been refluxed for 12 h, toluene was removed under reduced pressure and the residue was charged onto a silica gel column. Elution with LP removed the organotin impurities whilst further elution with LP–ethyl acetate (98:2) furnished the ketal (0.66 g). This was taken up in acetone–water (90:10, 40 cm^3) and treated with a drop of concentrated hydrochloric acid. The reaction mixture was stirred at ambient temperature (~30 °C) for 3 h after which the acetone was removed under reduced pressure and the residue dissolved in ethyl acetate (50 cm^3). The solution was then washed with saturated aqueous sodium hydrogen carbonate (1 × 20 cm^3), water (1 × 20 cm^3) and brine (1 × 20 cm^3) and then dried and evaporated *in vacuo*. Column chromatography of the crude material on silica gel and elution with LP–ethyl acetate (95:5) furnished the desired compound **31** (0.28 g, 52%); ν_{max}(film)/cm^{-1} 1726; λ_{max}(MeOH)/nm 208s and 296w; δ_H(300 MHz, $CDCl_3$) 5.71 (1H, br m, olefinic H), 2.82 (1H, superimposed dd, *J* 3 and 3, methine H at C-1), 2.62 (1H, m of dd, *J* 18 and 9, methylene H), 2.20 (1H, dd with str., *J* 18 and 9, methylene H), 1.86 (2H, AB system, J_{AB} 16, methylene protons α to CO), 1.80 (3H, d, *J* 1.5, CH$_3$), 1.50 (2H, dd with str., *J* 20 and 9, methylene H), 1.12 (3H, s, CH$_3$), 0.98 (3H, s, CH$_3$), 0.94 (2H, m merged between the methyl signals, methylene H) and 0.92 (3H, s, CH$_3$); δ_C(75 MHz, $CDCl_3$) 213.6 (CO), 136.3 (s), 133.0 (d), 58.6 (d), 49.4 (d), 47.5 (q), 44.3, 44.1, 41.8, 39.6, 39.5, 39.0, 28.5 (q), 27.4 (q) and 22.2; *m*/*z* 218 (M$^+$, 9%), 176 [100, M$^+$ − (CH$_2$=C=O)], 161 [69, M$^+$ − (CH$_2$=C=O + CH$_3$)], 120 (31), 105 (36) and 91 (14).

2,6-Dimethyltricyclo[6.3.0.0^{2,5}]undeca-6,9-dien-4-one 32

A solution of compound **20** (0.086 g, 0.46 mmol) in benzene (100 cm^3) was irradiated under nitrogen with a mercury vapour lamp (125 W; Applied Photophysics) in a Pyrex immersion well for *ca.* 1.5 h after which the solvent was removed *in vacuo*. The photolysate was then chromatographed over silica gel with LP–ethyl acetate (98:2) as eluent to furnish compound **32** (0.027 g, 31%). Continued elution with the same solvent gave unchanged starting material (0.018 g); ν_{max}(film)/cm^{-1} 1777; λ_{max}(MeOH)/nm 207.2; δ_H(500 MHz, $CDCl_3$) 5.85 (1H, m), 5.66 (1H, m), 5.25 (1H, br m), 3.16 (1H, br m, methine H), 3.10 (1H, dd, *J* 16 and 2, COCH$_2$), 3.0 (1H, br m, methine H at the cyclobutanone ring junction), 2.55 (1H, dd, *J* 16 and 4,5, COCH$_2$), 2.45 (1H, overlapped dd of d, *J* 9 and 10, methine H adjacent to the allylic methylene), 2.28 (1H, m of dd, *J* 16 and 9, allylic methylene), 1.95 (1H, m of d, *J* 16, allylic methylene), 1.68 (3H, d, *J* 1.5, CH$_3$) and 1.26 (3H, s, CH$_3$); δ_C(125 MHz, $CDCl_3$) 205.8, 133.4, 130.3, 125.4, 122.2, 66.7, 43.4, 42.7, 34.1, 30.4, 26.4, 22.2 and 21.3 (all the carbons); *m*/*z* 188 (M$^+$, 6%), 142 [10, M$^+$ − (CH$_2$=C=O)], 131 (61), 123 (100), 94 (24) and 79 (19).

2,6-Dimethyltricyclo[6.3.0.0^{2,5}]undeca-6-ene-4,11-dione 33

Irradiation of compound **25** (0.056 g, 0.27 mmol) in dry benzene (100 cm^3) under nitrogen in a Pyrex immersion well as described above for 1.5 h followed by chromatography (LP–ethyl acetate, 95:5) of the photolysate gave compound **33** (0.017 g, 30%) followed by unchanged starting material (0.012 g); ν_{max}(film)/cm^{-1} 1777 and 1737; λ_{max}(MeOH)/nm 260.0, 207.6; δ_H(500 MHz, $CDCl_3$) 5.41 (1H, br m, olefinic H), 3.10–2.90 (3H, overlapped m), 2.56 (1H, dd, *J* 16 and 5.5, methylene H), 2.40 (1H, d, *J* 7, methine H), 2.20 (2H, m), 2.10 (1H, complex m), 1.96 (1H, m), 1.71 (3H, d, *J* 1, CH$_3$) and 1.63 (3H, s, CH$_3$); *m*/*z* 204 (M$^+$, 13), 162 [100, M$^+$ − (CH$_2$=C=O)], 91 (28) and 79 (15).

2,6,10,10-Tetramethyltricyclo[6.3.0.0^{2,5}]undeca-6-ene-4,11-dione 34

Irradiation of compound **28** (0.060 g, 0.26 mmol) in dry benzene (100 cm^3) under nitrogen in a Pyrex immersion well as described above for 1 h followed by chromatography (LP–ethyl acetate, 95:5) of the photolysate gave compound **34** (0.017 g, 28%) followed by unchanged starting compound (0.008 g); ν_{max}(film)/cm^{-1} 1779 and 1735; λ_{max}(MeOH)/nm 302.2w and 213.2s; δ_H(300 MHz, $CDCl_3$) 5.43 (1H, m, olefinic H), 3.15 (1H, m), 3.04–2.88 (2H, m), 2.64 (1H, d, *J* 7.3), 2.56 (1H, dd, *J* 16.5 and 5.8), 2.09 (1H, dd, *J* 13.2 and 1.1), 1.9 (1H, d with fine str., *J* 13.2), 1.7 (3H, m, CH$_3$), 1.64 (3H, d, *J* 0.6, CH$_3$), 1.07 (3H, s, CH$_3$) and 1.02 (3H, s, CH$_3$); *m*/*z* 190 [60%, M$^+$ − O=C=CH$_2$)], 162 [17, M$^+$ − {(COCH$_2$) + CO}], 119 [46, M$^+$ − {(COCH$_2$) + CO + C$_3$H$_7$}], 106 [100, M$^+$ − {(COCH$_2$) + CO + C$_4$H$_8$}] and 91 [31, 106 − CH$_3$].

2,6,10,10-Tetramethyl-11-*endo*-hydroxytricyclo[6.3.0.0^{2,5}]-undeca-6-en-4-one 35

Irradiation of compound **30** (0.070 g, 0.3 mmol) in dry benzene (100 cm^3) under nitrogen in a Pyrex immersion well as described above for 1.5 h followed by chromatography (LP–ethyl acetate, 95:5) of the photolysate gave compound **35** (0.031 g, 44%) followed by unchanged starting compound (0.022 g); ν_{max}(film)/cm^{-1} 3427 and 1774; λ_{max}(MeOH)/nm 207s, 305w; δ_H(500 MHz, $CDCl_3$) 5.53 (1H, s, olefinic H), 3.52 (1H, dd, *J* 10 and 4, *H*COH), 3.10 (1H, m, methine H), 3.02 (1H, dd, *J* 16.5 and 2.5, methylene H), 2.78 (1H, m, methine H), 2.61 (1H, dd, *J* 16.5 and 6, methylene H), 2.41 (1H, dd, *J* 10 and 5, methine H), 2.02 (1H, dd, *J* 12.5 and 10, methylene H), 1.71 (3H, br s, CH$_3$), 1.46 (1H, dd, *J* 12.5 and 4, methylene H), 1.44 (3H, s, CH$_3$), 1.18 (1H, d, *J* 10.2), 1.06 (3H, s, CH$_3$) and 1.01 (3H, s, CH$_3$); δ_C(125 MHz, $CDCl_3$) 206.3, 130.1, 127.3, 83.4, 68.1, 57.2, 45.6, 45.0, 43.2, 35.4, 29.9, 29.2, 25.4, 24.6 and 22.2; *m*/*z* 234 (M$^+$, 1%), 192 [22, M$^+$ − O=C=CH$_2$], 120 [100, M$^+$ − (CH$_2$=C=O + C$_5$H$_{12}$)], 105 (29) and 91 (15).

2,6,10,10-Tetramethyltricyclo[6.3.0.0^{2,5}]undeca-6-en-4-one 36

Irradiation of compound **31** (0.120 g, 0.55 mmol) in dry benzene (100 cm^3) under nitrogen in a Pyrex immersion well as described above for 1 h followed by chromatography (LP–ethyl acetate, 95:5) of the photolysate gave compound **36** (0.041 g, 34%) followed by unchanged starting compound (0.027 g); ν_{max}(film)/cm^{-1} 1778; δ_H(300 MHz, $CDCl_3$) 5.30 (1H, br m), 3.0

(1H, d with str. overlapped onto another m, J 18, $COCH_2$), 2.99 (1H, m, methine H at cyclobutanone ring junction), 2.63 (1H, br m, methine H at the allylic ring junction), 2.50 (1H, dd, J 18 and 5, $COCH_2$), 2.26 (1H, d of dd, J 12 and 9, methine H at the ring junction), 1.86 (1H, dd, J 12 and 7.5, methylene H), 1.69 (3H, br m, CH_3), 1.52–1.42 (2H, complex m, methylene H), 1.23 (3H, s, CH_3), 1.1 (1H, superimposed dd, J 12 and 12, methylene H), 1.02 (3H, s, CH_3) and 1.00 (3H, s, CH_3); δ_C(75 MHz, $CDCl_3$) 206.0 (s), 127.8 (d), 125.4 (s), 66.5 (d), 55.5 (t), 47.9 (t), 43.3 (t), 42.9 (d), 39.2 (d), 37.9 (s), 32.2 (q), 32.1 (q), 30.8 (s), 26.4 (q) and 22.1 (q); *m/z* 218 (M^+, 2%), 176 [94, $M^+ - O{=}C{=}CH_2$], 161 [100, $M^+ - (CH_2{=}C{=}O + CH_3)$], 120 (44), 105 (68), 91 (21) and 77 (11).

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