Synthetic Photochemistry. Elaboration of the Tricyclo[6.3.0.0^{2,6}]-undecane ('Hirsutane') Carbon Skeleton by Intramolecular Photocyclisations of Dicyclopent-1-enylmethanes

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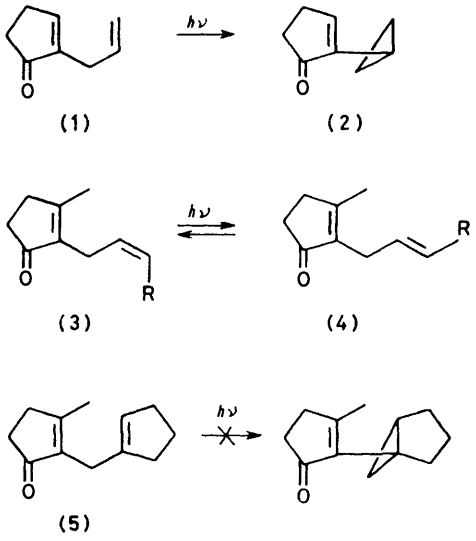
Irradiation of the dicylopent-1-enylmethane (5) in methanol is shown to lead to intramolecular [2 + 2] cycloaddition, followed by *in situ* addition of methanol to the presumed intermediate bicyclo[2.1.0]pentane (11), producing the *cis,syn,cis*-tricyclo[6.3.0.0^{2,6}]undecane (12) in >90% yield. The general method is applied in a synthesis of the hirsutane carbon skeleton [*viz.* (19)→(20)] found in hirsutic acid (7) and related natural sesquiterpenes.

Attempts to expand the scope of the photoprocess to other fused polycyclic systems met with mixed success. Thus, although irradiation of the cyclopentenone (24) in methanol led to the bicyclo[3.3.0]octenone (25), the cyclopentenone (29) instead produced the isomeric alkene (30) resulting from a 1,3-H shift, and irradiation of (31) led only to decomposition.

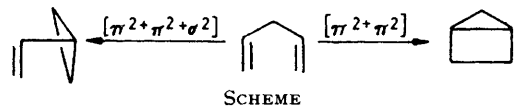
OUR investigations of the photochemistry of 2-prop-2-enyl-substituted cyclopentenones have demonstrated the potential for these substrates in the synthesis of 2-cyclopropylcyclopent-2-enones by way of photo-induced di-π-methane rearrangement [*i.e.* (1)→(2)].[1,2] In the preceding paper we illustrated the scope of the rearrangement in a synthesis of the vinylcyclopropane ring system present in the sesquiterpene taylorione from *Mylia taylorii*.[3]

A limitation to this photochemical method of vinylcyclopropane synthesis was found in those substrates containing prop-2-enyl side chains capable of exhibiting π-geometrical isomerism, where photo-stationary equilibrium mixtures of *E*- and *Z*-isomers were produced on irradiation, *e.g.* (3) and (4). In addition, in those



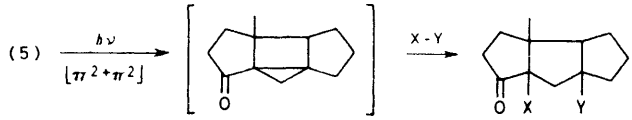
molecules where this alternative photoprocess was precluded, by incorporating the side-chain double bond in a small ring [*e.g.* (5)], only decomposition of the substrate was observed on irradiation (in hexane).

The di-π-methane rearrangement, which involves a [$_{\pi}2_{a} + {}_{\pi}2_{a} + {}_{\sigma}2_{a}$] process,[4] is known to compete with the alternative [$_{\pi}2 + {}_{\pi}2$] intramolecular cycloaddition reaction leading to bicyclo[2.1.0]pentanes (Scheme).[5] It occurred to us that this alternative pathway might be followed by substrates of type (5), which could not



SCHEME

dissipate energy by *E*—*Z* isomerisation, and furthermore did not undergo di-π-methane rearrangement. If this were the case, then it might prove possible to intercept the bicyclo[2.1.0]pentane intermediates, using Michael donors, providing an attractive synthesis of the tricyclo-[6.3.0.0^{2,6}]undecane ring system (6) found in several natural terpenes, *e.g.* hirsutic acid (7) from *Stereum*



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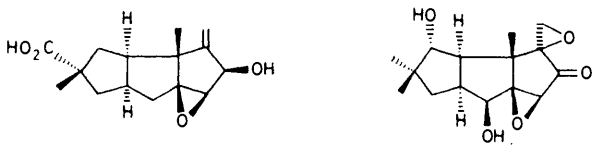


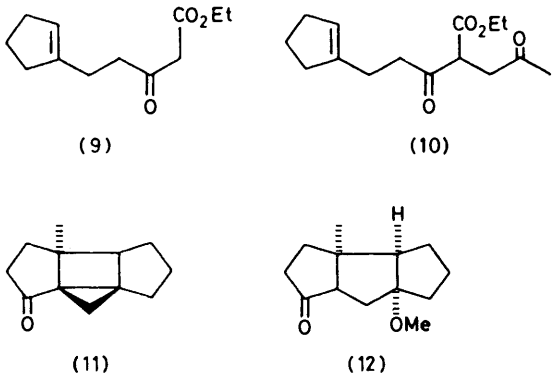
(7) (8)

hirsutum[6] and coriolin (8) from *Coriolus concors*.[7] In this paper we report a flexible synthesis of the ring system (6) based on the ideas presented above.[8]

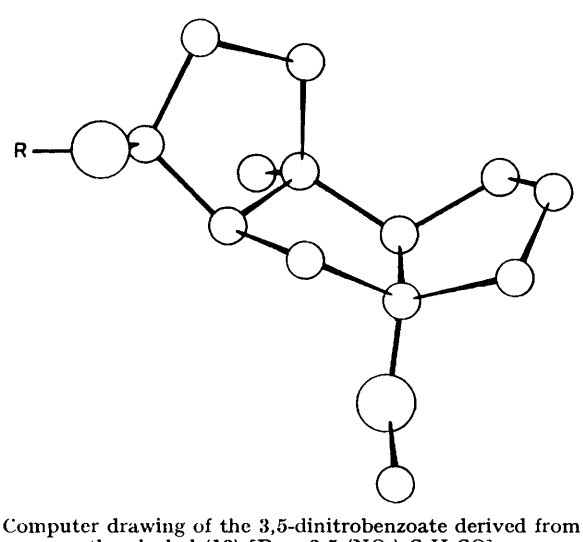
RESULTS AND DISCUSSION

We first examined the irradiation of the cyclopentenone (5), which is readily prepared by alkylation of the dianion derived from ethyl 3-oxobutanoate with cyclopent-1-enylmethyl bromide, followed by reaction of the resulting β-keto-ester (9) with bromoacetone [to give

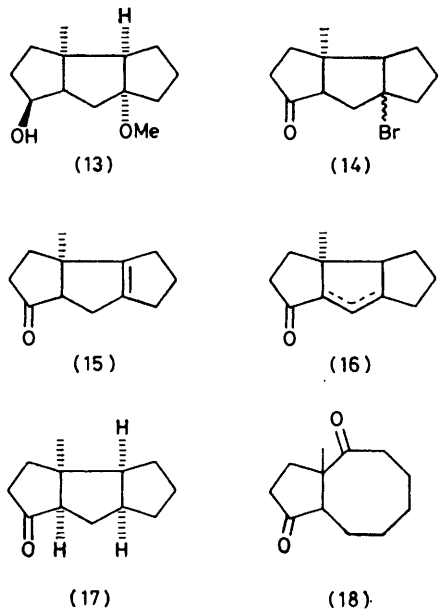
(10)] and aldol cyclisation. Irradiation of (5) in methanol through Pyrex led to the rapid production (<2 h) of a single volatile photoproduct (>90%) whose spectral data were consistent with the tricyclic structure (12) resulting from addition of methanol to the presumed intermediate (11) produced by intramolecular [$_{\pi}2 + _{\pi}2$] cycloaddition. Involvement of the ' hausane ' intermediate (11) implies that the conjugate addition of methanol will take place from the α-face leading to the *cis,syn,cis*-tricycle (12). Indeed the relatively small chemical shift of the methoxy-group protons in the [Eu(fod)$_3$]-shifted ^{1}H n.m.r. spectrum of (12) supported the *syn*-stereochemistry (see Experimental section), and unequivocal confirmation of this stereochemistry was provided by an *X*-ray crystallographic examination of the 3,5-dinitrobenzoate derivative of the corresponding *endo*-alcohol (13) prepared from (12) by reduction with lithium aluminium hydride. The structure thus revealed is shown in the Figure.[9]



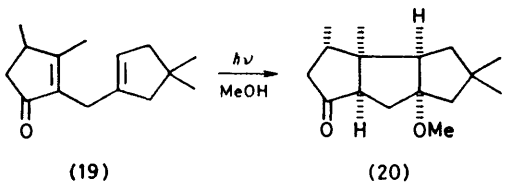
Treatment of the tricyclic ketone (12) with boron tribromide in methylene dichloride at −10 °C led to a mixture of the bromo-ketone (14) and the enone (15) resulting from sequential demethoxylation of the methyl ether, bromination [to give (14)], and dehydrobromination; further treatment of the mixture with ethanolic silver nitrate gave the pure enone (15) contaminated with small amounts of the positional isomers (16). Hydrogenation of (15) produced the parent tricyclic undecanone (17), whereas oxidation with osmium tetraoxide–sodium metaperiodate led to the bicyclo[6.3.0]-undecanetrione (18).



Computer drawing of the 3,5-dinitrobenzoate derived from the alcohol (13) [R = 3,5-(NO$_2$)$_2$C$_6$H$_3$CO]



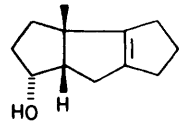
In a similar manner, irradiation of the dicyclopent-1-enylmethane (19) in methanol gave rise to the tricycle (20) containing the hirsutane carbon skeleton [*cf.* (7)].



Analysis of the ^{1}H n.m.r. spectrum of (20) using the shift reagent [Eu(fod)$_3$] (see Experimental section) suggested that, like (12), the molecule had the *cis,syn,cis*-stereochemistry.

The foregoing experiments thus demonstrated the ease with which dicyclopent-1-enylmethanes undergo photocyclisation leading to *cis,syn,cis*-tricyclo[6.3.0.0^{2,6}]-undecanes. To our knowledge the only other reported synthesis of this ring system in the *cis,syn,cis*-series, is based on acid-catalysed cyclisation of dicyclopentyl ketone followed by hydrogenation.[10] Natural products like hirsutic acid (7) and coriolin (8) have the alternative *cis,anti,cis*-stereochemistry at the five-membered ring junctions, and our photochemical route is thus limited in scope for the synthesis of these molecules.[11] With a view to inverting the *syn*-stereochemistry of the tricycle (12) to the corresponding *anti*-geometry, using controlled intramolecular hydrogenation *via* an anion-co-ordinated Wilkinson catalyst [*cf.* complex (22)] [12] the enone (15) was first reduced stereoselectivity to the

endo-alcohol (21) with lithium tri-t-butoxyaluminium hydride. Treatment of the potassium salt of (21) with tris(triphenylphosphine)rhodium chloride led to a reduced product, however, whose spectral and chromatographic features were indistinct from those of the product (23) (presumed *cis,syn,cis*) obtained from straightforward hydrogenation of (21) over a heterogenous palladium catalyst.



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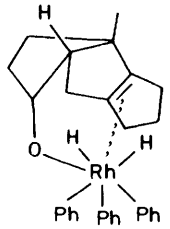

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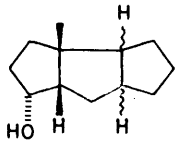

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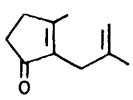
Efforts to expand the scope of intramolecular photocycloadditions amongst dicyclopent-1-enylmethanes to other fused polycyclic systems met with mixed success. Thus, although irradiation of the cyclopentenone (24) in methanol led to the bicyclo[3.3.0]octenone (25), accompanied by small amounts of the product (26) resulting from α-cleavage in (25), the cyclopentenone (27) instead led only to the corresponding geometrical isomer (28). In addition, it was found that neither of the cycloalkenones (29) and (31) gave rise to fused carbocycles on



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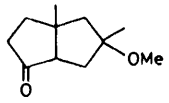

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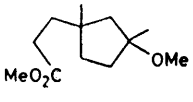

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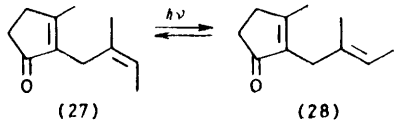

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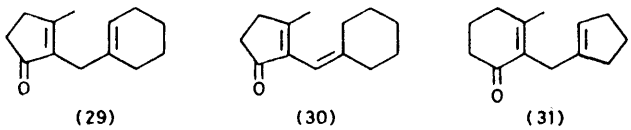


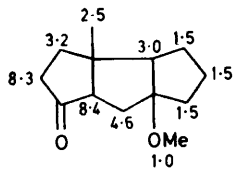
(29) (30) (31)

irradiation in methanol. Instead (29) produced the isomeric alkene (30) resulting from a 1,3-H shift, and irradiation of (31) led only to decomposition. Not for the first time, these latter observations demonstrate the remarkable effect of substitution on photo-reactivity amongst closely related molecules. Although a rational explanation as to the origin of the divergent photoreactivity in these chromophores is not immediately obvious, in the cases of *e.g.* (5) and (29), it is probable that the differing rigidity and flexibility of the cyclopentene and cyclohexene rings contribute significantly to their divergent photoreactivity.

EXPERIMENTAL

For general experimental details see ref. 1. ^{13}C N.m.r. spectra were recorded at 20 °C with a JEOL-PS-100 spectrometer operating at 25.15 MHz interfaced with a Nicolet 1085 20K computer.

cis,syn,cis-6-*Methoxy*-1-*methyltricyclo*[6.3.0.$0^{2,6}$]*undecan*-9-*one* (12).—A solution of 2-(cyclopent-1-enyl)methyl-3-methylcyclopent-2-enone (1 g) [1] in methanol (1 000 ml) was irradiated for 2 h (monitoring by g.l.c.) under nitrogen through Pyrex with a 100-W medium-pressure lamp. After this period of time g.l.c. analysis (10% Apiezon L; 180 °C) showed the presence of one volatile photoproduct (>93%). The methanol was evaporated at room temperature *in vacuo*, and the residue was chromatographed on silica using ether–light petroleum (b.p. 40—60 °C) (1 : 1) as eluant to give the *tricyclic ketone* as an oil; $\nu_{max.}$ (film) 1 720 cm^{-1}; τ 6.77 (OMe), 7.34—7.92 (m, 5 H, CH_2COCH-CH_2), 7.92—8.76 (m, 9 H), and 8.77 (Me); δ_C 220.5 (C-9), 98.8 (C-6), 61.4 (d, C-8), 61.2 (C-2), 51.1 (q, O*Me*), 50.1 (C-1), 37.5 (t, C-10), 36.0 (t, C-7), 35.0 (t, C-11), 29.4 (t, C-5), 28.0 (q, C-1-*Me*), 27.1 (t, C-3), and 26.2 (t, C-4) (M^+, 208.147 9; $C_{13}H_{20}O_2$ requires *M*, 208.146 3). The semicarbazone was obtained as an amorphous white solid, m.p. 189—191 °C. The tricyclic ketone was treated with an equimolar amount of the shift reagent [Eu(fod)$_3$] and the chemical shifts for protons in the ^1H n.m.r. spectrum are summarised below.



endo-cis,syn,cis-6-*Methoxy*-1-*methyltricyclo*[6.3.0.$0^{2,6}$]-*undecan*-9-*ol* (13).—A solution of 6-methoxy-1-methyltricyclo[6.3.0.$0^{2,6}$]undecan-9-one (0.26 g) in dry ether (5 ml) was added to a suspension of lithium aluminium hydride (0.055 g) in dry ether (100 ml), and the mixture was refluxed for 0.5 h. The mixture was cooled to 5 °C and then treated with dilute sulphuric acid. The ether layer was separated and the aqueous layer was extracted with ether (2 × 50 ml). Evaporation of the dried ether extracts left the alcohol (0.24 g, 91%), homogeneous on t.l.c. [silica; ether–light petroleum (b.p. 40—60 °C) (1 : 1)] as a 3 : 1 mixture of *endo*- and *exo*-isomers; $\nu_{max.}$ ($CHCl_3$) 3 450 cm^{-1}; τ 5.66 (m, C*H*OH, *endo*-epimer), 5.95 (m, C*H*OH, *exo*-epimer), 6.77 (OMe), 7.4—9.2 m (15 H), 8.72 (Me, *exo*-epimer), 8.90 (Me, *endo*-epimer). The 3,5-dinitrobenzoate was prepared, and the *endo*-isomer crystallised from ether–light petroleum (b.p. 40—60 °C) as long pale yellow needles, m.p. 112—115 °C.

cis-1-*Methyltricyclo*[6.3.0.$0^{2,6}$]*undec*-2(6)-*en*-9-*one* (15).—Boron tribromide (0.1 g) was added to a stirred solution of

1-methyl-6-methoxytricyclo[6.3.0.0^{2,6}]undecan-9-one (0.19 g) in dry methylene chloride (25 ml) at −10 °C. The mixture was stirred for 5 min and then water (5 ml) was added. The mixture was extracted with ether, and the ether extracts were then dried and evaporated to leave a mixture of the unsaturated ketone and 6-bromo-1-methyltricyclo[6.3.0.0^{2,6}]undecan-9-one (14). The mixture was treated with an ethanolic solution of silver nitrate for 0.5 h, and then worked-up as before to give the *undecenone* (0.15 g, 92%) as an oil; $\nu_{max.}$ ($CHCl_3$) 1 720 cm^{-1}; τ 7.3—8.7 (m, 13 H), and 8.76 (Me) (M^+ 176.119 3. $C_{12}H_{16}O$ requires *M*, 176.120 1).

cis,syn,cis-1-*Methyltricyclo*[6.3.0.0^{2,6}]*undecan*-9-*one* (17).—(*a*) A solution of 1-methyltricyclo[6.3.0.0^{2,6}]undec-2(6)-en-9-one (65 mg) in methanol (5 ml) was shaken in the presence of hydrogen and Adams catalyst for 3.5 h. The mixture was filtered and then evaporated to dryness. The residue was dissolved in ether, and the ether solution was then dried and evaporated to leave the *undecan*-9-*one* (45 mg) as an oil; $\nu_{max.}$ ($CHCl_3$) 1 725 cm^{-1}; τ 7.1—9.3 (m, 15 H), 8.8 (Me) (M^+, 178.134 2. $C_{12}H_{18}O$ requires *M*, 178.135 8).

(*b*) A solution of 1-methyltricyclo[6.3.0.0^{2,6}]undecan-9-ol (23) (40 mg) in methylene chloride (0.5 ml) was added to pyridinium chlorochromate (74 mg) in methylene chloride (1 ml), and the mixture was then stirred at 25 °C for 2 h. The mixture was diluted with ether and after decanting the ether, the residue was washed twice with more ether. Evaporation of the combined ether extracts left the undecan-9-one (35 mg), identical with that obtained above.

1-*Methylbicyclo*[6.3.0]*undecane*-2,6,9-*trione* (18).—A solution of 1-methyltricyclo[6.3.0.0^{2,6}]undec-2(6)-en-9-one (0.15 g) in ether (3 ml) and water (3 ml) containing osmium tetraoxide (1 mg) was treated portionwise during 0.5 h with sodium metaperiodate (0.4 g). The mixture was stirred at 25 °C for 17 h, then poured into water and extracted with ether (3 × 30 ml). The washed (aqueous $NaHCO_3$) and dried ether extracts were evaporated to leave a residue which was chromatographed on silica using ether as eluant to give the *trione* as a glass; $\nu_{max.}$ ($CHCl_3$) 1 725 cm^{-1}; τ 7.3—8.8 (m, 13 H) and 8.76 (Me) (M^+, 208.112 6. $C_{12}H_{16}O_3$ requires *M*, 208.109 9).

endo-cis-1-*Methyltricyclo*[6.3.0.0^{2,6}]*undec*-2(6)-*en*-9-*ol* (21).—Lithium tri-t-butoxyaluminium hydride (0.15 g) was added to a solution of 1-methyltricyclo[6.3.0.0^{2,6}]undec-2(6)-en-9-one (47 mg) in dry ether (20 ml) and the mixture was stirred at 25 °C for 20 h, and then diluted with water. The mixture was extracted with ether (3 × 40 ml), and the ether extracts were then dried and evaporated. The residue was chromatographed on silica using ether–light petroleum (1 : 1) as eluant to give the endo-*alcohol* (41 mg, 85%), as an oil; $\nu_{max.}$ ($CHCl_3$) 3 610 and 3 500 cm^{-1}; τ 5.88 (m, C*H*OH), 7.1—9.2 (m, 14 H), and 8.87 (Me) (M^+, 178.135 6. $C_{12}H_{18}O$ requires *M*, 178.135 8).

1-*Methyltricyclo*[6.3.0.0^{2,6}]*undecan*-9-*ol* (23).—A solution of 1-methyltricyclo[6.3.0.0^{2,6}]undec-2(6)-en-9-ol (43 mg) in methanol (5 ml) was shaken in the presence of hydrogen and Adams catalyst (*ca.* 3 mg) for 19 h. The mixture was filtered and the filtrate evaporated to dryness to leave the alcohol as a colourless gum (39 mg); τ 5.85 m (C*H*OH), 7.25—9.25 m (15 H + OH), and 8.92 (Me), homogenous in g.l.c. (10% SE-30, 147 °C).

2-(4,4-*Dimethylcyclopent*-1-*enylmethyl*)-3,4-*dimethylcyclopent*-2-*enone* (19).—Reduction of 4,4-dimethylcyclopent-1-enecarbaldehyde [13] in ether, using lithium aluminium hydride in the usual way, gave 4,4-dimethylcyclopent-1-enylmethyl alcohol as a liquid (75%), b.p. 46—52 °C/0.7 mmHg; τ 4.55 (br, =C*H*), 5.9 (br, CH_2OH), 7.65 (br, OH), 7.85 (br, 4 H), and 8.9 (CMe_2); δ_C 142.8 (C-1), 123.7, (d, C-2), 61.9 (t, C-6), 47.7 (t, C-5), 47.6 (t, C-3), 38.6 (C-4), and 29.9 (C-4-Me_2).

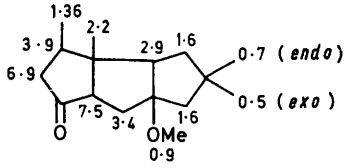
Phosphorus tribromide (28 g) in dry ether (60 ml) was added dropwise over 0.5 h to a stirred solution of the alcohol (13 g) in dry ether at −22 °C. The mixture was allowed to warm to 0 °C, and then stirred at this temperature for 4 h. The mixture was added cautiously to saturated sodium hydrogencarbonate solution and then extracted with ether (3 × 100 ml). Evaporation of the dried ether extracts, and chromatography of the residue on silica using 1 : 1 ether–light petroleum as eluant, gave 4,4-dimethylcyclopent-1-enylmethyl bromide (11.5 g, 56%) as an oil; τ 4.3 (br, =C*H*), 5.95 (br, CH_2Br), 7.8 (br, 4 H), and 8.9 (=CMe_2) homogeneous in t.l.c.

A solution of ethyl 3-oxobutanoate (11.4 g) in dry tetrahydrofuran (10 ml) was added dropwise over 10 min to a stirred suspension of sodium hydride (2.4 g) in dry tetrahydrofuran (175 ml) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 20 min and then treated with a solution of n-butyl-lithium (1 mol equiv.) in hexane during 0.5 h. The mixture was stirred for a further 0.5 h and then treated with a solution of 4,4-dimethylcyclopent-1-enylmethyl bromide (14.4 g) in dry tetrahydrofuran (20 ml) during 0.25 h. The mixture was stirred at 5—15 °C for 0.5 h and then diluted with 4N-hydrochloric acid (70 ml) followed by ether (150 ml). The mixture was extracted with ether and the ether extracts were combined, dried, and evaporated to leave *ethyl* 5-(4,4-*dimethylcyclopent*-1-*enyl*)-3-*oxopentanoate* (19.1 g, 85%) as an oil; τ 4.75 (br, =C*H*), 5.77 (q, OCH_2), 6.53 ($COCH_2CO$), 7.29 (t, C$H_2$$COCH_2$), 7.68 (t, CH_2CH_2CO), 7.92 (m, 4 H), 8.72 (t, OCH_2*Me*), and 8.92 (CMe_2) (M^+, 238.158 4. $C_{14}H_{22}O_3$ requires *M*, 238.156 9).

A solution of the keto-ester (13.9 g) in dioxan (25 ml) was added over 0.5 h to a stirred suspension of sodium hydride (1.5 g) in dioxan (25 ml) at 25 °C under nitrogen. The mixture was stirred at 25 °C for 0.5 h and then cooled to −20 °C and treated with 1-bromoethyl methyl ketone (12.1 g) in dioxan (10 ml) during 2 min. After warming to room temperature, the mixture was refluxed for 10 min, and then cooled. The mixture was treated with sodium hydroxide (7.4 g) in water (230 ml), and then slowly warmed to 70 °C over 2 h. After cooling, the mixture was treated with dilute sulphuric acid, and extracted with ether. Evaporation of the dried ether extracts left a residue which was distilled to give the *cyclopentenone* (7.1 g, 56%) as an oil, b.p. 105—125 °C/0.7 mm, which was purified by chromatography [silica gel; 1 : 1 ether–light petroleum (b.p. 40—60 °C)]; $\nu_{max.}$ 1 695 and 1 645 cm^{-1}, 4.87 (br, =C*H*), 7.08 (=C−CH_2C=), 7.1—7.5 (m, $COCH_2$–C*H*–), 7.7—8.2 (m, CH_2C=CH−CH_2), 7.98 (=CMe), 8.8 (d, *J* 7 Hz, *Me*CH), and 8.95 (CMe_2) (M^+, 218.166 1. $C_{15}H_{22}O$ requires *M*, 218.167 1).

exo-cis,syn,cis-6-*Methoxy*-1,4,4,11-*tetramethyltricyclo*-[6.3.0.0^{2,6}]*undecan*-9-*one* (20).—Irradiation of a solution of 2-(4,4-dimethylcyclopent-1-enyl)methyl-3,4-dimethylcyclopent-2-enone in hexane under identical conditions to those used for the analogue (5), and purification by chromatography in chloroform, gave the *tricyclic ketone* (*ca* 60%) as an oil; $\nu_{max.}$ (film) 1 720 cm^{-1}; τ 6.82 (OMe), 7.16—9.1 (m, 11 H), 8.88 (CMe), 8.9 (CMe), 8.94 (CMe), and 9.02 (d, *J* 7 Hz, CH*Me*); δ_C 219.3 (C-9), 99.5 (C-6), 64.7

(d, C-8), 62.9 (d, C-2), 51.0 (q, OMe), 50.1 (C-1), 47.1 (t, C-10), 46.7 (t, C-7), 42.9 (C-4), 41.5 (t, C-5), 36.8 (t, C-3), 33.5 (d, C-11), 30.5 (q, C-1-*Me*), 27.8 (q, C-11-*Me*), 22.5 (q, C-4-*Me*), and 15.3 (q, C-4-*Me*) (M^+, 250.197 4. $C_{16}H_{26}O_2$ requires M, 250.193 3). The tricyclic ketone was treated with an equimolar amount of the shift reagent [Eu(fod)$_3$], and the chemical shifts for protons in the ^{1}H n.m.r. spectrum are summarised below.



1,4,4,11-*Tetramethyltricyclo*[6.3.0.0^{2,6}]*undec*-2(6)-*en*-9-*one*.—Demethoxylation of 6-methoxy-1,4,4,11-tetramethyltricyclo[6.3.0.0^{2,6}]undecan-9-one (20) under identical conditions to those described for the analogue (12) gave the *enone* (90%) as an oil; $\nu_{max.}$ ($CHCl_3$) 1 725 and 1 615 cm^{-1}; τ 7.3—8.20 (10 H), 8.82 (C*Me*), 8.85 (C*Me*), 8.88 (C*Me*), 8.95 (d, J 7 Hz, CH*Me*), 8.88 (C*Me*), and 8.95 (d, J 7 Hz, CH*Me*) (M^+, 218.165 1. $C_{15}H_{22}O$ requires M, 218.167 1).

cis-7-*Methoxy*-5,7-*dimethylbicyclo*[3.3.0]*octan*-2-*one* (25) (*with M. J. Bullivant*).—A solution of 3-methyl-2-(2-methylprop-2-enyl)cyclopent-2-enone (1.3 g) [1] in methanol (1 000 ml) was irradiated for 52 h (monitoring by g.l.c.; 10% Apiezon L; 140 °C) under nitrogen through Pyrex with a 100-W medium-pressure lamp. After this period of time g.l.c. analysis showed the presence of one major volatile photoproduct (*ca.* 90%). The methanol was evaporated at room temperature *in vacuo* and the residue chromatographed on silica using chloroform as eluant to give the *bicyclic ketone* as an oil; $\nu_{max.}$ (film) 1 734 and 1 074 cm^{-1}; τ 6.9 (OMe), 7.45—8.45 (m, 9 H), 8.72 (Me), and 8.8 (Me); δ_C 239.5 (C-1), 99.8 (C-6), 72.9 d (C-8), 64.9 (t, C-7), 63.4 (q, OMe), 61.5 (C-4), 54.6 (t, C-2), 51.5 (t, C-3), 49.1 (t, C-5), 41.6 (q, C-4-Me), and 36.8 (q, C-6-Me) (M^+, 182.131 1. $C_{11}H_{18}O_2$ requires M, 182.130 7).

In some experiments, using longer periods of irradiation, a second photoproduct accumulated (<20%). Separation and purification by chromatography (silica; chloroform) gave methyl 3-(3-methoxy-1,3-dimethylcyclopentyl)propanoate (26); $\nu_{max.}$ (film) 1 740 cm^{-1}; τ 6.46 (CO_2Me), 6.8 (OMe), 7.5—8.6 m (10 H), 8.75 (Me), and 8.94 (Me) (M^+, 214. $C_{12}H_{22}O_3$ requires M, 214).

3-*Methyl*-2-[(E)-2-*methylbut*-2-*enyl*]*cyclopent*-2-*enone* (27).—Reaction between (*E*)-2-methylbut-2-enyl bromide (12 g) and ethyl 3-oxobutanoate (40 g) in the presence of sodium methoxide, in the usual way [1] gave 5-methylhept-5-en-2-one (7.3 g) as an oil; τ 4.31—4.62 (m, =C*H*), 6.0 (CH_2CO), 7.04 (CO*Me*), and 8.32 (2× =C*Me*). Treatment with diethyl carbonate in the presence of sodium hydride then led to ethyl 6-methyl-3-oxo-oct-6-enoate; τ 4.6—4.9 (m, =C*H*), 5.72 (q, J 7 Hz, MeCH_2), 6.51 (COCH_2CO), 7.2—7.8 (m, 4 H), 8.38 (2 × C*Me*), 8.71 (t, J 7 Hz, CH_2Me), which was converted to the cyclopentenone in an identical manner to that described for the analogue (19). Purification by chromatography on silica using chloroform as eluant gave the *cyclopentenone* as a colourless liquid; $\nu_{max.}$ (film) 1 695 and 1 645 cm^{-1}, τ 4.62—4.96 (m, =C*H*), 7.12 (=C–CH_2C=), 7.35—7.75 (m, 4 H), 7.94 (=CMe), and 8.42 (2 × =CMe) (M^+, 164.116 5. $C_{11}H_{16}O$ requires M, 164.120 1).

3-*Methyl*-2-[(Z)-2-*methylbut*-2-*enyl*]*cyclopent*-2-*enone* (28).—A solution of 3-methyl-2-[(E)-2-methylbut-2-enyl]-cyclopent-2-enone (0.2 g) in hexane (200 ml) was irradiated for 8 h under nitrogen through Pyrex with a 100-W medium-pressure lamp. After this period of time g.l.c. analysis (10% Apiezon L; 150 °C) showed the presence of one photoproduct (60%). The hexane was evaporated *in vacuo*, and the residue was purified by chromatography on silica using chloroform as eluant to give the *Z-alkene*; τ 4.65—4.95 m (=CH), 7.04 (=C–CH_2C=), 7.3—7.8 (m, 4 H), 7.94 (=CMe), and 8.41 (2 × CMe) (M^+, 164.115 1. $C_{11}H_{16}O$ requires M, 164.120 1).

2-(*Cyclohex*-1-*enylmethyl*)-3-*methylcyclopent*-2-*enone* (29).—Ethyl 5-cyclohexyl-3-oxopentanoate was first prepared (66%) from ethyl 3-oxobutanoate and 1-cyclohexenylmethyl bromide, in an identical manner to that described for the keto-ester (9). Chromatography on silica gel using 1 : 1 ether–light petroleum (b.p. 40—60 °C) as eluant gave the *keto-ester* as an oil; τ 4.6 (br, =CH), 5.8 (q, J 7 Hz, OCH_2Me), 6.56 (=C–CH_2C=), 7.36 (t, J 6 Hz, CH_2-$COCH_2$), 7.79 (t, J 6 Hz, CH_2CH_2CO), 7.85—8.3 (m, 4 H), 8.2—8.7 (m, 4 H), and 8.72 (t, J 7 Hz, OCH_2Me) (152.119 2, base peak. $C_{10}H_{16}O$ requires *m/e*, 152.120 1).

Treatment of the keto-ester with bromopropanone, in an identical manner to that described for the preparation of the analogue (5), gave the cyclopentenone, which was purified by chromatography on silica gel using 1 : 1 ether–light petroleum (b.p. 40—60 °C) as eluant. The pure *cyclopentenone* was obtained as a colourless oil; $\nu_{max.}$ 1 690 and 1 640 cm^{-1}; τ 4.7 (br, =C*H*), 7.18 (br, =C–CH_2C=), 7.38—7.74 (m, 4 H), 7.95 (=CMe), 7.9—8.3 (m, 4 H), and 8.25—8.7 (m, 4 H); δ_C 209.1, 170.9, 138.5, 134.8, 121.6 (d), 34.3 (t), 31.6 (t), 31.0 (t), 28.7 (t), 25.3 (t), 23.0 (t), 22.5 (t), and 17.3 (q) (M^+, 190.133 5. $C_{13}H_{18}O$ requires M, 190.135 8), homogeneous by g.l.c. (10% Apiezon L, 184 °C).

2-(*Cyclohexylidenemethyl*)-3-*methylcyclopent*-2-*enone* (30).—A solution of 2-(cyclohex-1-enylmethyl)-3-methyl-2-cyclopentenone (0.5 g) in n-hexane (500 ml) was irradiated for 30 h (monitoring by g.l.c.) under nitrogen through Pyrex with a 100-W medium-pressure lamp. After this period of time g.l.c. analysis (10% Apiezon L, 194 °C) showed the presence of one major volatile photoproduct (73%). The solution was evaporated to dryness and the residue was chromatographed on silica gel using ether–light petroleum (b.p. 40—60 °C) as eluant to give the *conjugated diene*; $\nu_{max.}$ ($CHCl_3$) 1 690 cm^{-1}; τ 4.48 (br, =C*H*), 7.2—7.9 (m, 8 H), 8.0 (=CMe), and 8.2—8.7 (m, 6 H); δ 209.0, 171.0, 146.9, 138.4, 111.2 (d), 36.9 (t), 34.7 (t), 31.7 (t), 31.0 (t), 28.4 (t), 27.6 (t), 26.5 (t), 18.5 (q) (M^+, 190.135 0. $C_{13}H_{18}O$ requires M, 190.135 8).

2-(*Cyclopent*-1-*enylmethyl*)-3-*methylcyclohex*-2-*enone* (31).—A solution of Hagemann's ester [14] (4.6 g) in dry ethanol (5 ml) was added dropwise over 10 min to a stirred solution of sodium ethoxide (from 0.6 g sodium) in dry ethanol (15 ml) at 25 °C under argon. The orange mixture was stirred for 0.5 h and then treated with a solution of cyclopent-1-enylmethyl bromide (4.1 g) in ethanol (5 ml). The mixture was refluxed for 3 h, then cooled, filtered, and evaporated to dryness. The residue was dissolved in water (150 ml) and then extracted with ether (3 × 50 ml). Evaporation of the dried ether extracts left *ethyl* 2-(*cyclopent*-1-*enylmethyl*)-3-*methyl*-4-*oxocyclohex*-2-*enecarboxylate* (6.4 g, 95%) as an oil; τ 4.76 (br, =C*H*), 5.76 (q, J 7 Hz, OCH_2Me), 6.66 (t, J *ca.* 6 Hz, C*H*CO_2Et), 6.9 (br, =C–CH_2C=), 7.0—8.5 (m, 10 H), 8.01 (=CMe), and 8.71 (t, J 7 Hz, OCH_2Me) (M^+, 262.156 5. $C_{16}H_{22}O_3$ requires M, 262.156 9).

The crude keto-ester (6.4 g) was dissolved in ethanolic potassium hydroxide solution (1.5 g KOH in 15 ml C_2H_5OH) and the mixture was stirred at 25 °C for 20 h and then poured into water (150 ml) and extracted with ether (3 × 50 ml). The ether extracts were extracted with sodium hydrogencarbonate solution (2 × 50 ml), and the aqueous extracts were then acidified (10% HCl) and extracted with ether. Evaporation of the dried ether extracts gave 2-(cyclopent-1-enylmethyl)-3-methyl-4-oxocyclohex-2-enecarboxylic acid (4.4 g, 74%) as a yellow oil; τ 4.2 (br, CO_2H), 4.8 (br, =C*H*), 6.65 (t, *J ca.* 6 Hz, $CHCO_2H$), 6.9 (br, =C–CH_2–C=), 7.1—8.4 (m, 10 H), and 8.0 (=CMe).

The keto-acid (4.4 g) was heated at 90—100 °C for 1 h, then cooled to 25 °C and extracted with ether. The ether extracts were washed with sodium hydrogencarbonate solution, then dried and evaporated to leave the cyclohexenone (2.8 g, 78% and 58% overall from Hagemann's ester) as a pale yellow oil; $\nu_{max.}$ 1 660 and 1 630 cm^{-1}; τ 4.8 (br, =CH), 6.9 (br, =C–CH_2C=), 7.5—8.4 (m, 12 H), and 8.07 (=CMe), homogenous in g.l.c. (10% Apiezon L; 160 °C).

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