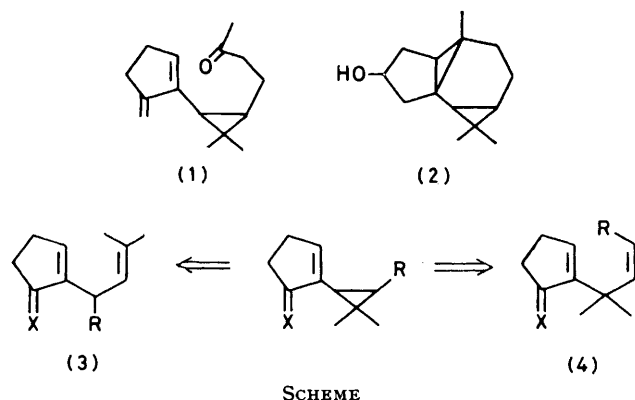


Synthetic Photochemistry. A Synthesis of the Carbon Skeleton found in Taylorione from *Mylia taylorii*, using the Di- π -methane Rearrangement

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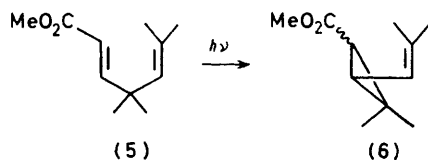
Synthetic routes to the *E*- and *Z*-cyclopentenones (20) and (25), which incorporate photosensitive 1,4-diene systems, are described. Irradiation of the *E*-cyclopentenone (20) is shown to result in efficient regiospecific di- π -methane rearrangement (>70%) to the vinylcyclopropane (26), which is then converted into *trans*-deoxytaylorione (28). Irradiation of the corresponding *Z*-cyclopentenone (25) also leads to (26), presumably by way of the *E*-cyclopentenone (20), produced by *Z*-*E* photoisomerisation.

TAYLORIONE (1) is a novel vinylcyclopropane sesquiterpenoid found in the liverwort *Mylia taylorii*¹ where it co-occurs with the bis-cyclopropane myliol (2).² The seco-aromadendrane structure followed for taylorione on the basis of chemical and spectroscopic evidence.¹ The presence of a conjugated vinylcyclopropane system in (1) suggested a design for the synthesis of the carbon skeleton in taylorione based on the photochemical 'di- π -methane' rearrangement of an appropriate 1,4-diene precursor (Scheme).³ Hitherto the only other demon-



SCHEME

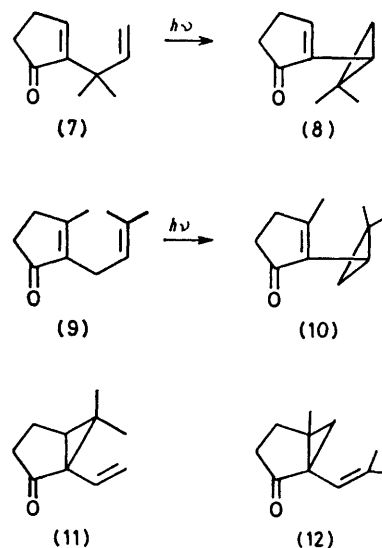
stration of the scope of this rearrangement in natural product synthesis has been in a synthesis of the chrysanthemyl carbon skeleton found in chrysanthemic acid [*viz.* (5)→(6)].⁴ In this paper, we describe a synthesis of the carbon skeleton found in taylorione (1) which uses the di- π -methane rearrangement as a key stage.⁵



RESULTS AND DISCUSSION

Model photochemical studies,⁶ using easily accessible 2-prop-2-enyl substituted cyclopent-2-enones, demonstrated the ease with which substrates of the type shown in the Scheme undergo regiospecific di- π -methane rearrangement to the corresponding vinylcyclopropanes (50–80%). Thus, irradiation of (7) in hexane led to the essentially quantitative conversion into (8) within 2 h, whereas irradiation of (9) produced (10) (66%) after

55 h. Significantly we were not able to detect the co-formation of photoproducts of the type (11) and (12) in these irradiations, resulting from the alternative mode

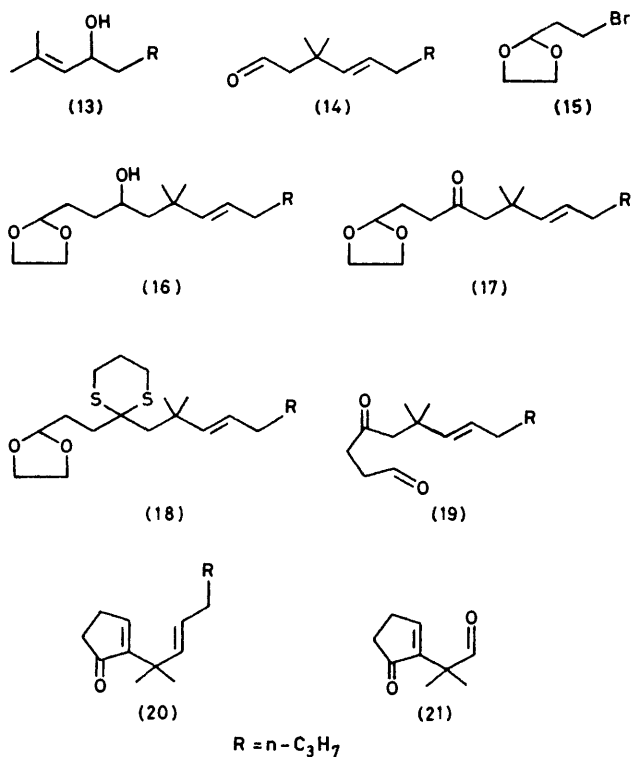


of di- π -methane rearrangement in the substrates (7) and (9). Either of the two 1,4-diene precursors (3) and (4) *a priori* could thus lead to the vinylcyclopropane system present in taylorione by photorearrangement; we have investigated the first approach using the *E*- and *Z*-cyclopentenones (20) and (25).

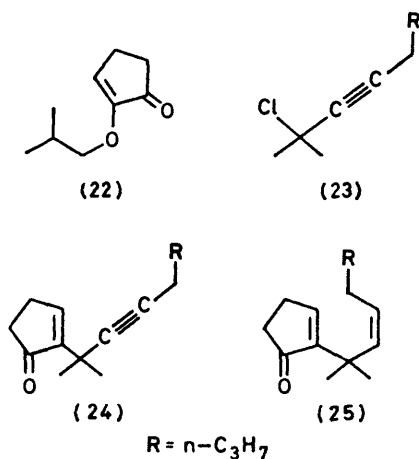
The *E*-cyclopentenone (20) was synthesised starting from the alcohol (13),⁷ obtained by a Grignard reaction between 2-methylprop-1-enylmagnesium bromide and pentan-1-al. Conversion of the alcohol into the corresponding vinyl ether and Claisen rearrangement first gave the *E*-unsaturated aldehyde (14), which by reaction with the Grignard reagent derived from the bromide (15), followed by oxidation of the resulting secondary alcohol (16) with pyridine chlorochromate, afforded the dioxolan ketone (17). In an alternative, but less practical approach to (17), the aldehyde (14) was first converted into the corresponding dithian, which was then metallated and reacted with (15) giving the substituted dithian (18) (*ca.* 16%), accompanied by considerable amounts of starting dithian. Selective unmasking of the ketone group, using *N*-chlorosuccinimide-silver nitrate in aqueous acetonitrile, then led to (17). The *E*-stereochemistry of the disubstituted double

bond in (17) followed from i.r. (ν_{\max} 975 cm^{-1}) and ^1H n.m.r. (J_{vic} 15 Hz) data.

Hydrolysis of the dioxolan (17) then produced the γ -keto-aldehyde (19) which was cyclised in ethanolic



sodium hydroxide, under high dilution, to the *E*-cyclopentenone (20). In another approach to (20), the allyl-substituted molecule (7) was first converted into the corresponding aldehyde (21) using osmium tetroxide-sodium periodate. Surprisingly, and in spite of several attempts under a variety of reaction conditions, we were unable, however, to effect olefination of the aldehyde

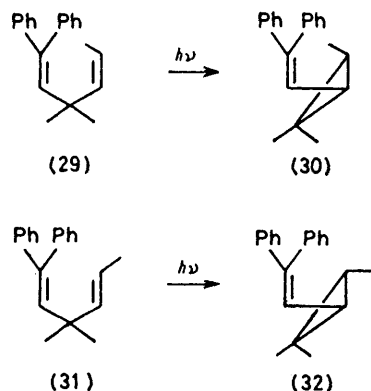
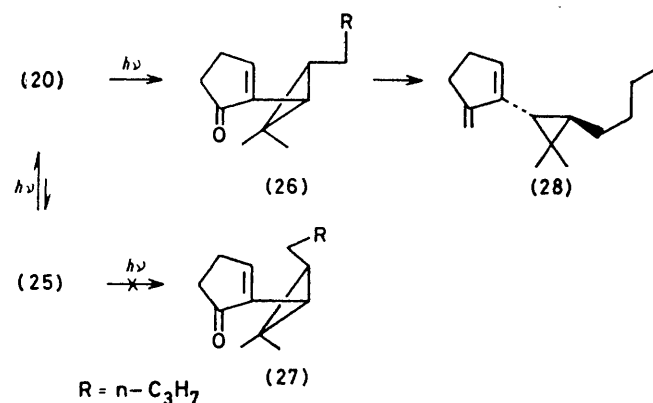


with a range of alkylphosphoranylides. This feature is presumably associated with steric crowding of the formyl group in (21) by the adjacent *gem*-methyl groups.

The *Z*-cyclopentenone (25) was prepared from the

vinyl ether (22),⁸ following reaction with the Grignard reagent from the chloro-octyne (23), hydrolysis-dehydration, and hydrogenation of the resulting dehydroderivative (24) over the Lindlar catalyst. The configuration about the double bond in (25) followed from the magnitude of the vicinal olefinic coupling (J_{vic} 12 Hz) in the ^1H n.m.r. spectrum. Although the *Z*- and *E*-cyclopentenones (20) and (25) were each isomerically homogenous in g.l.c. analysis on SCOT capillary columns, complete resolution between the isomers could not be accompanied.

Irradiation of the *E*-cyclopentenone (20) in hexane through Pyrex using a 100-W mercury lamp resulted in the rapid (<2 h) establishment of a photostationary equilibrium mixture of (20) and a single photoproduct corresponding to 70% conversion (g.l.c. monitoring). The irradiation was interrupted at this point, and separation by chromatography gave the photoproduct as an oil, whose spectroscopic data (Experimental) were consistent with the *trans*-cyclopropane (26) resulting



from regiospecific di- π -methane rearrangement of (20). The *trans*-configuration (26) followed from inspection of the magnitude of the vicinal coupling constant (J 6 Hz) across the cyclopropane ring in the $[\text{Eu}(\text{fod})_3]$ -shifted ^1H n.m.r. spectra of (26). Isomeric 1,2-disubstituted cyclopropanes of the type shown in (26) typically show vicinal H-H couplings of 8.2 Hz (*cis*), e.g. *cis*-chrysanthemic acid and bicyclogermacrene, and 6.4 Hz (*trans*), e.g. *trans*-chrysanthemic acid.⁹ At the outset of our investigations, the geometry of natural taylorione was

not known with certainty; recent studies have now confirmed however, that as expected the molecule has the *cis*-configuration (J_{vic} 8 Hz).¹⁰

Preservation of the stereochemical integrity of the migrating (*E*)-double bond in the rearrangement of (20) to the *trans*-cyclopropane (26) is consistent with studies carried out some time ago by Zimmerman and his co-workers.¹¹ These workers showed *e.g.* that the photochemical di- π -methane rearrangements of *Z*- and *E*-1,1-diphenyl-3,3-dimethylhexa-1,4-dienes (29) and (30) were completely stereospecific, leading to the corresponding *cis*- and *trans*-cyclopropanes (31) and (32), respectively. It was surprising to find then, that irradiation of the *Z*-cyclopentenone (25), under identical conditions to those used for (20), led to the same *trans*-cyclopropane (26) as that obtained from (20). We were unable to obtain any evidence for the co-formation of the anticipated *cis*-cyclopropane (27) from the irradiation. This was also the case when the irradiation of (25) was interrupted after short periods of conversion (<10%). Under these circumstances the only photoproduct in addition to (26) that could be detected was the corresponding *E*-cyclopentenone (20), resulting from *Z*—*E* isomerisation in (25). It seems probable, therefore, that the di- π -methane rearrangement of (25) to the *cis*-cyclopropane (27) is precluded as a result of efficient competitive *Z*—*E* photoisomerisation of (25) to the *E*-cyclopentenone (20), which then undergoes rapid rearrangement to (26).

Wittig reaction between (26) and methylenetriphenylphosphoranylide then led to the diene (28), completing a synthesis of *trans*-deoxytaylorione. After completion of our studies Nakayama *et al.*¹⁰ published a multi-stage synthesis of (–)-taylorione using a strategy whereby the carbon skeleton was elaborated from optically pure chrysanthemyl precursors.

EXPERIMENTAL

For general experimental details see ref. 6.

3-Methyl-2-(3-methylbut-2-enyl)cyclopent-2-enone (9) (with *J. S. H. Kueh*).—A solution of ethyl 7-methyl-3-oxo-oct-6-enoate (9 g)⁶ in dry dioxan (20 ml) was added to a suspension of sodium hydride (1.5 g) in dry dioxan (20 ml). The mixture was cooled to –15 °C, and then a solution of bromopropanone (10 g) in dry dioxan (10 ml) was added all at once. The mixture was heated under reflux for 1 h, and then evaporated to dryness. The residue was warmed to 70 °C for 1.75 h with aqueous sodium hydroxide solution (200 ml, 3%), then treated with 20% sulphuric acid (50 ml) and heated at 100 °C for 1 h. The solution was extracted with light petroleum (b.p. 40–60 °C) and the extracts were dried. Evaporation of the light petroleum, and distillation of the residue, gave the enone (3.5 g, 45%) as a colourless oil, b.p. 72–74 °C/0.1 mmHg; ν_{max} 1 690, 1 640, and 850 cm^{-1} ; τ 4.92 (br t, J ca. 7 Hz, =CH), 7.1 (d, J 7 Hz, CH₂), 7.29–8.0 (m, 4 H), 7.92 (MeC=), and 8.3 (=CMe) (M^+ , 164. C₁₁H₁₆O requires M , 164), homogenous by g.l.c. (10% Apiezon L; 140 °C).

3-Methyl-2-(2,2-dimethylcyclopropyl)cyclopent-2-enone (10).—By the general procedure, irradiation of 3-methyl-2-(3-methylbut-2-enyl)cyclopent-2-enone (0.9 g) in hexane (800 ml) for 55 h led to a 2 : 1 mixture of product and start-

ing material. Chromatography (g.l.c. OV-17; 190 °C) gave the *cyclopropylcyclopentenone* (eluted first) as an oil; ν_{max} (film) 1 690, 1 640, and 915 cm^{-1} ; τ 7.4–7.8 m (4 H), 7.96 (MeC=), 8.25–9.4 m (3 H), 8.82 (Me), and 9.16 (Me) (M^+ , 164.118; C₁₁H₁₆O requires M , 164.120 1).

2-Methyloct-2-en-4-ol (13).—A solution of pentan-1-ol (25.8 g) in dry tetrahydrofuran (100 ml) was added dropwise over 1 h at room temperature to a solution of the Grignard reagent formed by addition of 1-bromo-2-methylprop-1-ene to activated magnesium [prepared from potassium (30 g), anhydrous magnesium chloride (42 g), and dry potassium iodide (50 g)]¹² in dry tetrahydrofuran (800 ml) under nitrogen. The mixture was stirred for 0.5 h, and then treated with a 20% aqueous solution of ammonium chloride until two clear layers were produced. The organic layer was separated and then washed with 10% aqueous sodium hydrogencarbonate (5 × 100 ml). The tetrahydrofuran layer was evaporated *in vacuo*, and the residue was then taken up in ether (150 ml), washed with water (25 ml), and dried (MgSO₄). Evaporation of the ether, and distillation of the residue gave the alcohol (36 g, 64%) as a colourless oil, b.p. 45–49 °C/0.2 mmHg, n_D^{20} 1.445 2 (lit.,⁷ b.p. 85–87 °C/13 mmHg, n_D^{20} 1.443 8); ν_{max} (film) 3 350 and 1 670 cm^{-1} , τ 4.77 (d, br J ca. 8 Hz, =CH), 5.36–5.90 (m, CHOH), 8.25 (Me₂C=C), and 8.35–9.2 (m, 9 H).

Vinyl Ether of 2-Methyloct-2-en-4-ol (13).—A mixture of 2-methyloct-2-en-4-ol (107 g), ethyl vinyl ether (380 g), and mercury(II) acetate (5.35 g) was refluxed for 6 h in a nitrogen atmosphere; the reflux temperature of the solution rose from 39.5 to 41 °C during this period. Potassium carbonate (12.0 g) was then added, and the excess of ethyl vinyl ether was removed under reduced pressure. Distillation of the residue gave the *vinyl ether*, b.p. 40–41 °C/0.15 mmHg, contaminated (ca. 20%) with 2-methyloct-2-en-4-ol, which was purified (31.2 g, 25%; 70% based on recovered alcohol) by chromatography on silica gel using benzene-ether (9 : 1) as eluant. A sample had b.p. 60–62 °C/1.5 mmHg, n_D^{25} 1.438 1; ν_{max} (film) 1 631 and 1 608 cm^{-1} ; τ 3.66 (dd, J 6, 14 Hz, CH=CH₂), 4.86 (br d, J ca. 9 Hz, C=CH-CH), 5.38–5.73 m (CHO), 5.80–6.18 (m, CH₂=C), 8.25 (MeC=C), 8.31 (MeC=C), and 8.35–9.25 (m, 9 H); (M^+ , 168.150 8; C₁₁H₂₀O requires M , 168.151 4).

(E)-3,3-Dimethylnon-4-enal (14).—A solution of the vinyl ether of 2-methyloct-2-en-4-ol (31.2 g) was refluxed in xylene (500 ml) for 4 h. Removal of the xylene *in vacuo* left a yellow oil which on distillation gave the *aldehyde* (22.7 g, 73%), as a colourless liquid, b.p. 82.5–84.5 °C/11 mmHg, n_D^{21} 1.445 0; ν_{max} (film) 2 700, 1 710, and 980 cm^{-1} ; τ 0.24 (t, J 3 Hz, CHO), 4.5 m (CH=CH), 7.70 (d, J 3 Hz, CH₂CHO), 7.8–8.2 (m, 2 H), 8.85 (Me₂C=C), and 8.6–9.2 (7 H) (M^+ , 168.153. C₁₁H₂₀O requires M , 168.151). The 2,4-dinitrophenylhydrazone was recrystallised from ethanol and had m.p. 79.5–80 °C (Found: C, 58.3; H, 7.15; N, 16.0. C₁₇H₂₄N₄O₄ requires C, 58.6; H, 6.9; N, 16.1%).

2-[(E)-2,2-Dimethyloct-3-enyl]-1,3-dithian.—A solution of 3,3-dimethylnon-4-enal (14) (11.3 g) and propane-1,3-dithiol (7.3 g) in chloroform (500 ml) was stirred at room temperature for 1 h. The solution was cooled to –20 °C and boron trifluoride-ether (9.45 ml, 48% by weight of boron trifluoride) was then added *via* a syringe. The solution was allowed to reach room temperature overnight with continued stirring. The organic solution was washed successively with water (2 × 200 ml), 20% aqueous potassium hydroxide (2 × 200 ml), and water (2 × 200 ml), and then dried (MgSO₄). Removal of the solvent and distil-

lation of the residue gave the *dithian* (17.0 g, 95%), b.p. 94—96 °C/0.01 mmHg, n_D^{20} 1.525 2; ν_{\max} (film) 1 618 and 970 cm^{-1} ; τ 4.6 (m, $\text{CH}=\text{CH}$), 6.07 (t, J 5.5 Hz, $\text{S}-\text{CH}-\text{S}$), 6.92—7.32 (m, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$), 7.7—8.2 (m, 2 H), 8.33 (d, J 5.5 Hz, CHCH_2), 8.5—9.3 (m, 7 H), and 9.84 (Me_2C) (M^+ , 258.147. $\text{C}_{14}\text{H}_{28}\text{S}_2$ requires M , 258.148).

2-[(E)-2,2-Dimethyloct-3-enyl]-2-[2-(1,3-dioxolan-2-yl)-ethyl]-1,3-dithian (18).—A solution of *n*-butyl-lithium in hexane (36.3 ml, 87 mmol) was added by syringe to a stirred solution of 2-(2,2-dimethyloct-3-enyl)-1,3-dithian (22.45 g) in dry tetrahydrofuran (600 ml) at -40 °C. The solution was stirred for a further 2 h between -30 and -15 °C, then cooled to -70 °C and treated with 2-(2-bromoethyl)-1,3-dioxolan¹³ (14.3 g) by syringe during 10 min. The solution was allowed to reach 0 °C over a period of 1 h, and then stirred at 0 °C. A sample (2 ml) was removed every hour for analysis by ^1H n.m.r. until no further bromide remained. The mixture was added to water, and the organic layer was then separated, washed with water, and dried (K_2CO_3). Evaporation of the solvent followed by distillation to remove unreacted dithian left a residue which was chromatographed on alumina using benzene–light petroleum (b.p. 40–60 °C) (97 : 3) as eluant to give the *dioxolan-dithian* (4.7 g, 16%; 78% based on recovered starting dithian) as a colourless liquid; ν_{\max} (film) 980 cm^{-1} ; τ 4.33 (d, J 15 Hz, $\text{CH}=\text{CH}-\text{CH}_2$), 4.58—5.87 (m, $\text{CH}=\text{CH}-\text{CH}_2$), 5.00—5.27 (m, OCHO), 5.95—6.36 (m, $\text{OCH}_2\text{CH}_2\text{O}$), 7.07—7.56 (m, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$), 8.84 (Me_2C), and 7.8—9.2 (m, 17 H), (M^+ , 358.197. $\text{C}_{19}\text{H}_{34}\text{O}_2\text{S}_2$ requires M , 358.200).

2-[(6E)-3-Hydroxy-5-dimethylundec-6-enyl]-1,3-dioxolan (16).—A solution of (E)-3,3-dimethylnon-4-enal (7.34 g) in dry tetrahydrofuran (100 ml) was added to a solution of the Grignard reagent [prepared from 2-(2-bromoethyl)-1,3-dioxolan (8.6 g) and magnesium (1.14 g)] in dry tetrahydrofuran (70 ml) at such a rate that the temperature of the solution did not rise above 35 °C. After stirring at room temperature for 1 h, excess of aqueous ammonium chloride was added, followed by ether (30 ml). The organic layer was separated and the aqueous layer was then extracted with ether (20 ml). The combined organic extracts were washed with water (10 ml) and then dried. Evaporation of the ether, followed by chromatography of the residue on alumina, using benzene–ether (9 : 1) as eluant, gave the alcohol (6.7 g, 58%; 85% based on recovered starting aldehyde). A sample had b.p. 109—110 °C/0.01 mmHg, n_D^{22} 1.465 8; ν_{\max} (film) 3 475 and 975 cm^{-1} ; τ 4.42 d (J 15 Hz, $\text{CH}=\text{CH}$), 4.42—4.63 (m, $\text{CH}=\text{CH}-\text{CH}_2$), 5.10 (t, J 5 Hz, OCHO), 5.88—6.39 (m, 5 H, $\text{OCH}_2-\text{CH}_2\text{O}$ and CHOH), 7.88 (OH), 7.33—8.82 (m, 12 H), 8.93 (Me_2C), and 9.12 (t, J 7 Hz, CH_2Me).

2-[(6E)-5,5-Dimethyl-3-oxoundec-6-enyl]-1,3-dioxolan (17).—(a) A solution of the dithian (18) (3 g) in acetonitrile (8 ml) was added to a stirred solution of *N*-chlorosuccinimide (4.4 g) and silver nitrate (6.45 g) in acetonitrile (120 ml) and water (30 ml) with the exclusion of light. The solution was stirred for 10 min at room temperature, and then saturated solutions of sodium sulphate (8 ml), sodium carbonate (8 ml), and brine (8 ml) were added successively at 1-min intervals, followed by addition of hexane–dichloromethane (160 ml, 1 : 1 v/v). The mixture was filtered, and the filtrate was then dried (MgSO_4) and evaporated. Distillation of the residue gave the *ketone* (1.95 g, 97%) as an oil, b.p. 109—110 °C/0.025 mmHg, n_D^{19} 1.462 0; ν_{\max} (film) 1 705 and 974 cm^{-1} ; τ 4.54 (d, J 15 Hz, $\text{CH}=\text{CH}-\text{CH}_2$), 5.62—4.92 (m, $\text{CH}=\text{CH}-\text{CH}_2$), 5.17 (t, J 5 Hz, OCHO),

5.99—5.35 (m, $\text{OCH}_2\text{CH}_2\text{O}$), 7.55 (t, J 7.5 Hz, $\text{OC}-\text{CH}_2-\text{CH}_2$), 7.63 ($\text{OC}-\text{CH}_2-\text{CMe}_2$), 7.90—8.24 (m, $\text{OC}-\text{CH}_2-\text{CH}_2-\text{CH}$), 8.90 (Me_2C), and 8.6—9.7 (m, 9 H) (m/e 143.070 7. $\text{C}_7\text{H}_{11}\text{O}_3$ requires 143.070 8, M^+ not observed).

(b) A solution of the alcohol (16) (6.7 g) in dichloromethane (25 ml) was added to a stirred suspension of pyridinium chlorochromate (10 g) in dichloromethane (150 ml), and the resulting mixture was stirred at 25 °C for 2.5 h. The mixture was washed with ether (3×100 ml) and the combined ether extracts were dried and evaporated. Distillation of the residue gave the *ketone* (6.6 g, 95%), identical to that obtained by method (a).

(7E)-6,6-Dimethyl-4-oxododec-7-enal (19).—A solution of 2-[(6E)-5,5-dimethyl-3-oxoundec-6-enyl]-1,3-dioxolan (1.3 g) in tetrahydrofuran (90 ml) was shaken with 10% dilute hydrochloric acid (30 ml) for 27 h. The solution was extracted with ether and the combined extracts were washed with water (2×50 ml), and then dried (MgSO_4) and evaporated. Chromatography of the residue on alumina using benzene–light petroleum (b.p. 40–60 °C) (95 : 5) as eluant gave the *keto-aldehyde* (741 mg, 64%) as an oil, n_D^{22} 1.463 0; ν_{\max} (film), 2 700, 1 707, 1 705, and 980 cm^{-1} ; τ 0.16 (CHO), 4.45 (d, J 16 Hz, $\text{CH}=\text{CH}-\text{CH}_2$), 4.45—4.68 (m, $\text{CH}=\text{CH}-\text{CH}_2$), 7.32 ($\text{CHO}-\text{CH}_2-\text{CH}_2\text{CO}$), 7.58 ($\text{Me}_2\text{C}-\text{CH}_2\text{CO}$), 7.79—8.28 (m, 2 H), 8.50—8.83 (m, 4 H), 8.88 (Me_2C), and 9.11 (t, J 7 Hz, CH_2Me) (M^+ , 167.141 6. $\text{C}_{11}\text{H}_{19}\text{O}$ requires M , 167.143 6). The *bis-2,4-dinitrophenylhydrazone* recrystallised from ethanol, and had m.p. 198—199 °C (Found: C, 52.9; H, 5.8; N, 19.10. $\text{C}_{26}\text{H}_{32}\text{N}_8\text{O}_8$ requires C, 53.40; H, 5.5; N, 19.20%).

2-[(2E)-1,1-Dimethylhept-2-enyl]cyclopent-2-enone (20).—A solution of (E)-6,6-dimethyl-4-oxododec-7-enal (1.0 g) in ethanol (1 080 ml), water (176 ml), and 0.5M sodium hydroxide (108 ml) was refluxed for 1.5 h. The solution was cooled and then dilute hydrochloric acid was added until a clear aqueous layer was obtained. The organic layer was separated, and the aqueous layer was then washed with ether. The combined organic extracts were washed with water (2×100 ml) and then dried (MgSO_4). Evaporation of the ether, and chromatography of the residue on alumina using benzene–light petroleum (b.p. 40–60 °C) as eluant gave the *cyclopentenone* (440 mg, 48%), n_D^{20} 1.484 0; λ_{\max} (EtOH) 225 nm (ϵ 6 305); ν_{\max} (film) 1 700, 1 608, and 980 cm^{-1} ; τ 2.75 (t, J 3 Hz, $\text{CH}_2\text{CH}=\text{C}$), 4.35 (d, J 16 Hz, $\text{CH}_2-\text{CH}=\text{CH}$), 4.50—4.36 (m, $\text{CH}_2-\text{CH}=\text{CH}$), 7.42—7.83 (m, 4 H of ring), 7.9—8.2 m (2 H), 8.6—9.0 (m, 4 H), 8.81 (Me_2C), 9.2 (t, J 7 Hz, Me) (M^+ , 206.167 07. $\text{C}_{14}\text{H}_{22}\text{O}$ requires M , 206.167 06), which was homogeneous on g.l.c. analysis (50-ft SCOT capillary column, OV-17; 160 °C).

2-(1,1-Dimethyl-2-oxoethyl)cyclopent-2-enone (21).—Osmium tetroxide (0.1 g) was added to a stirred solution of 2-(1,1-dimethylprop-2-enyl)cyclopent-2-enone (7.7 g) in dioxan (80 ml) and water (24 ml) under nitrogen. The mixture was stirred at 25 °C for 2 h, and then sodium periodate (60 g) was added portionwise over 2 h. The mixture was stirred at 25 °C for a further 15 h and then extracted with ether (3×100 ml). Evaporation of the washed (5% aqueous Na_2CO_3) and dried ether extracts left the *aldehyde* (4.6 g, 58%) as a liquid; ν_{\max} (film) 2 690, 1 713, and 1 693 cm^{-1} ; τ 0.4 (CHO), 2.5 (t, J 3 Hz, $=\text{CH}$), 7.2—7.7 (m, 4 H), and 8.66 (CMe_2), which was used without further purification. The *bis-2,4-dinitrophenylhydrazone* of (21) was recrystallised from ethanol, and had m.p. 137.5—138 °C (Found: C, 53.9; H, 4.7; N, 16.9. $\text{C}_{21}\text{H}_{20}\text{N}_8\text{O}_8$ requires C, 54.2; H, 4.9; N, 16.9%).

2-Methyloct-3-yn-2-ol.—A solution of hex-1-yne (4.9 g) in dry ether (70 ml) was added dropwise to a solution of ethyl magnesium bromide [formed from magnesium (1.5 g) and ethyl bromide in dry ether (20 ml)] under nitrogen. A solution of dry acetone (5 g) in dry ether (70 ml) was added dropwise over 10 min, and the mixture was stirred at 25 °C for 0.5 h and then treated with aqueous ammonium chloride solution. The organic layer was separated, and the aqueous layer was then extracted with ether (2 × 20 ml). Evaporation of the dried ether extracts left the *alcohol* (7 g, 84%), as a colourless oil, $n_D^{20.5}$ 1.430 0; ν_{\max} (film) 3 414 and 2 285 cm^{-1} ; τ 7.70—7.91 (m, $\text{C}\equiv\text{C}-\text{CH}_2$), 7.94 (OH), 8.53 (Me_2C), 8.82 ($\text{CH}_2-\text{CH}_2\text{Me}$), and 9.08 (t, J 7 Hz, CH_2Me) (M^+ 140.122; $\text{C}_9\text{H}_{16}\text{O}$ requires M , 140.120).

2-Chloro-2-methyloct-3-yne (23).—2-Methyloct-3-yn-2-ol (3.5 g) was added to a mixture of calcium chloride (1.58 g), copper(i) chloride (1.13 g), copper-bronze powder (ca. 25 mg),¹⁴ and concentrated hydrochloric acid (12.5 ml) at 0 °C. The mixture was stirred at 0 °C for 1 h and then carefully poured into an excess of aqueous sodium hydrogen-carbonate and filtered. The filtrate was extracted with ether, and the ether extracts were then dried. Evaporation of the ether and distillation of the residue gave the *chloride* (3 g, 76%) as an oil, b.p. 75—78 °C/10 mmHg, n_D^{24} 1.448 5; ν_{\max} (film) 2 290 cm^{-1} ; τ 7.64—7.85 (m, $\text{C}\equiv\text{C}-\text{CH}_2$), 8.15 (Me_2C), 8.33—8.80 (m, $\text{CH}_2\text{CH}_2\text{Me}$), and 9.09 (t, J 7 Hz, CH_2Me) (M^+ , 158.085. $\text{C}_9\text{H}_{15}\text{Cl}$ requires M , 158.086).

2-Isobutoxy-1-(1,1-dimethylhept-2-ynyl)cyclopent-2-enol.—A solution of 2-isobutoxycyclopent-2-enone (0.97 g) in dry tetrahydrofuran (10 ml) was added dropwise at room temperature during 0.5 h to a stirred solution of the Grignard reagent formed from 2-chloro-2-methyloct-3-yne (1.0 g) and activated magnesium¹² [prepared from anhydrous magnesium chloride (1.05 g), potassium iodide (1.25 g), and potassium metal (0.76 g)]. The mixture was stirred at 25 °C for 0.5 h, and then excess of aqueous ammonium chloride was added. The organic layer was separated, and the aqueous layer was extracted with ether (2 × 20 ml). Evaporation of the dried ether organic extracts and chromatography of the residue on silica gel using benzene-ether (85 : 15) as eluant gave the *alcohol* (0.8 g, 46%) as a colourless liquid, n_D^{22} 1.473 7; ν_{\max} (film) 3 463 and 1 645 cm^{-1} ; τ 5.40 (m, $\text{CH}_2\text{CH}=\text{C}$), 6.42—6.60 (m, OCH_2CH), 7.43 (br, OH), 7.61—8.24 (6 H), 8.45—8.68 (m, $\text{CH}_2\text{CH}_2\text{Me}$), 8.77 (Me_2C), 9.04 (d, J 7 Hz, Me_2CH), and 9.96—9.21 (CH_2Me), [M^+ , 260.210. $\text{C}_{18}\text{H}_{28}\text{O}$ requires ($M - 18$), 260.214].

2-(1,1-Dimethylhept-2-ynyl)cyclopent-2-enone (24).—A solution of 2-isobutoxy-1-(1,1-dimethylhept-2-ynyl)cyclopent-2-enol (1.6 g) in ether (15 ml) and dilute hydrochloric acid (15 ml) was stirred for 4 days. The organic layer was separated and then washed with 5% aqueous sodium hydroxide (2 × 10 ml), water (2 × 10 ml), and then dried (MgSO_4). Evaporation of the solvent gave *2-hydroxy-2-(1,1-dimethylhept-2-ynyl)cyclopentanone* (1.3 g, >95%) as a colourless oil, n_D^{21} 1.474 0; ν_{\max} (film) 3 515 and 1 733 cm^{-1} ; τ 7.43 (br, OH), 7.53—8.24 (8 H), 8.50—8.77 (m, $\text{CH}_2\text{CH}_2\text{Me}$), 8.80 (MeC), 8.86 (MeC), and 9.18 (t, J 7 Hz, CH_2Me) (M^+ , 222.160; $\text{C}_{14}\text{H}_{22}\text{O}_2$ requires M , 222.162).

The cyclopentanone and toluene-*p*-sulphonic acid (200 mg) in dry benzene (250 ml) were refluxed for 2 h with continuous removal of water (Dean and Stark). After cooling, the solution was washed with 5% aqueous sodium hydroxide (2 × 25 ml), water (2 × 25 ml), and then dried (MgSO_4). Evaporation of the benzene gave the *cyclopentenone* (1.1 g,

92%) as a colourless liquid, $n_D^{24.5}$ 1.483 2; λ_{\max} (EtOH) 225 nm (ϵ 8 041); ν_{\max} (film) 1 696 cm^{-1} ; τ 2.41 (m, $\text{C}=\text{CH}$), 7.37—7.68 (m, 4 H, ring- CH_2), 7.68—7.94 (m, $\text{C}=\text{C}-\text{CH}_2$), 8.55 (Me_2C), 8.42—9.83 m ($\text{CH}_2\text{CH}_2\text{CH}$), and 9.07 (t, J 7 Hz, CH_2Me) (M^+ , 204.152. $\text{C}_{14}\text{H}_{20}\text{O}$ requires M , 204.151).

2-[(2Z)-1,1-Dimethylhept-2-enyl]cyclopent-2-enone (25).—Hydrogenation of 2-(1,1-dimethylhept-2-ynyl)cyclopent-2-enone (203 mg) in ethyl acetate (8 ml) using the Lindlar catalyst (70 mg), followed by filtration of the solution through a short alumina column and evaporation of the solvent, afforded the *cyclopentenone* (195 mg, 95%) as a colourless liquid, n_D^{20} 1.483 0; λ_{\max} (EtOH) 227 nm (ϵ 7 175); ν_{\max} (film) 1 698 cm^{-1} ; τ 2.70 (m, $\text{C}=\text{CH}$, of ring), 4.58 (d, J 12 Hz, $\text{CH}=\text{CH}-\text{CH}_2$), 4.66—4.98 (m, $\text{CH}=\text{C}-\text{CH}_2$), 7.42—7.74 (m, 4 H, ring- CH_2), 7.98—8.26 (m, $\text{CH}=\text{CH}-\text{CH}_2$), 8.6—9.3 (m, 7 H), and 8.71 (Me_2C) (M^+ , 206.168 7; $\text{C}_{14}\text{H}_{22}\text{O}$ requires M , 206.167 1), which was homogeneous on g.l.c. analysis (50-ft SCOT capillary column, OV-17; 160 °C).

trans-2-(2,2-Dimethyl-3-butylcyclopropyl)cyclopent-2-enone (26).—By the general procedure,⁶ irradiation of 2-[(2E)-1,1-dimethylhept-2-enyl]cyclopent-2-enone (0.73 g) in hexane (1 200 ml) for 1.25 h led to a 7 : 3 mixture (by g.l.c., 50-ft SCOT capillary column, OV-17, 160 °C) of product and starting material. Chromatography on alumina, using benzene-light petroleum (b.p. 40—60 °C) (95 : 5) as eluant gave the *cyclopropane* (eluted second) as an oil, n_D^{24} 1.479 9; λ_{\max} (EtOH) 219 (ϵ 4 300) and 242 (4 100) nm; ν_{\max} (film) 1 697 and 1 624 cm^{-1} ; τ 2.93 (t, J 3 Hz, $=\text{CH}$), 7.34—7.69 (m, 4 H), 8.4—9.4 (m, 11 H), 8.87 (CMe), 9.14 (CMe); ¹³C n.m.r., δ 209.8 (CO), 154.4 ($=\text{CH}$), 145.8 ($=\text{C}$), 34.9 (CH_2CO), 32.2 (CH_2CH), 31.1 ($\text{CH}_2\text{C}=\text{C}$), 28.9 (CH_2), 26.3 (CMe), 26.1 (CMe), 23.7 (CMe₂), 22.5 (CH_2), 21.6 (CH), 21.2 (CH), and 14.2 p.p.m. (CH_2Me) (M^+ , 206.169 9. $\text{C}_{14}\text{H}_{22}\text{O}$ requires M , 206.167 1).

An irradiation of 2-[(2Z)-1,1-dimethylhept-2-enyl]cyclopent-2-enone (0.1 g) in hexane (150 ml) was interrupted after 10% conversion. Chromatography separated the *trans-cyclopropane* identical with that obtained above.

1-Methylene-2-(trans-2,2-dimethyl-3-butylcyclopropyl)-cyclopent-2-ene (28).—A solution of 2-(2,2-dimethyl-3-butylcyclopropyl)cyclopent-2-enone (150 mg) in dry tetrahydrofuran (1 ml) was added at room temperature to methylenetriphenylphosphorylide [prepared from methyl-triphenylphosphonium iodide (1.75 g) and *n*-butyl-lithium (4 mmol)] in dry tetrahydrofuran (30 ml) under nitrogen, and the mixture was then refluxed for 20 h. The mixture was added to water and extracted with ether. Removal of the ether gave a residue which was extracted with hexane. Evaporation of the hexane, followed by chromatography of the residue on silica using hexane as eluant, gave the *diene* (75 mg, 51%) as a volatile liquid, $n_D^{24.5}$ 1.474 8; λ_{\max} (EtOH) 244 nm (ϵ 8 450); ν_{\max} (film) 1 633, 873, and 860 cm^{-1} ; τ 4.14 (br, $=\text{CH}$), 5.0—5.19 ($=\text{CH}_2$), 7.2—7.7 (4 H), 4.7 (CMe), 8.8 (CMe), 8.6—9.2 (m, 11 H) (M^+ , 204.188 2; $\text{C}_{15}\text{H}_{24}$ requires M , 204.187 8).

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