

## Synthetic Photochemistry. A New Synthesis of ( $\pm$ )-Zizaene *via* an Intramolecular Variant of the de Mayo Reaction

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Irradiation of a 1 : 1 mixture of the enol acetates (10) and (31) derived from the cyclopentane-1,3-dione (30), is shown to produce a 7 : 3 mixture of the cycloadducts (32) and (33), resulting from intramolecular [2 + 2] photocycloaddition in the enol acetate (10).

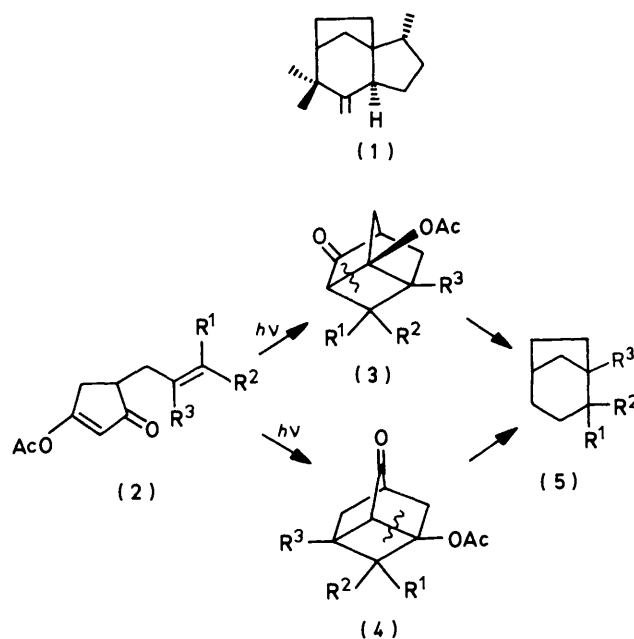
Fragmentation of the mesylate (34b) derived from the cycloadduct (32) then leads to the alkene (35), which on hydrogenation produces an unresolved mixture of  $\alpha$ -(minor) and  $\beta$ -(major) methyl epimers, (37) and (39) respectively, of the tricyclic ketone (36). The tricyclic ketone (37) has been converted previously into ( $\pm$ )-zizaene (1).

The new approach to (37) formally completes a new total synthesis of ( $\pm$ )-zizaene (1) and its methyl epimer.

Zizaene (1), which is also known as khusinene, khusene, or tricyclo-vetivene, is the parent hydrocarbon of the zizaene family of sesquiterpenes found in vetiver oil, *Vetiveria zizanioides* (L.) Nash.<sup>1</sup> The first syntheses of zizaene were published contemporaneously by Coates<sup>2</sup> and by Wiesner<sup>3</sup> and their respective collaborators. In the previous paper we described a novel approach to the bicyclo[3.2.1]octane ring system (5) present in zizaene and several other important natural terpenoids (*e.g.* gibberellins, cedranes, barbatanes, and aphidicolin). This approach was based on fragmentation of a tricyclo[3.2.1.0<sup>3,6</sup>]octane carbon framework, *i.e.* (3) or (4), produced by intramolecular [2 + 2] photocycloaddition of an enol acetate, *i.e.* (2), derived from a 4-prop-2-enylcyclopentane-1,3-dione (see Scheme 1).<sup>4</sup> In this paper we describe the application of this synthetic design to a new synthesis of the tricyclic ketone (37) which is a central intermediate in Coates' synthesis of zizaene.<sup>5</sup>

Our previous studies of intramolecular de Mayo reactions involving 4-prop-2-enyl substituted cyclopentane-1,3-dione enol acetates demonstrated that the cycloadditions showed considerable regioselectivity depending largely on the degree of alkyl substituents on the C-C double bonds taking part in the cycloadditions.<sup>4</sup> Thus, the enol acetates (6) having minimal substitutions on the C-C double bonds were found to produce the single cycloadducts (7) on irradiation. By contrast, irradiation of the more heavily substituted enol acetate (8) gave rise largely to the cycloadducts (9) resulting from the alternative mode of intramolecular [2 + 2] cycloaddition in (8) (*cf.* Scheme 1). We envisaged that introduction of additional alkyl substituents onto the C-C double bonds in (2) would further promote intramolecular cycloaddition in the direction of (4) rather than (3). Furthermore, in the special case of the 5-methylcyclopent-1-enylmethyl substituted derivative (10) we anticipated that irradiation would lead largely to the cycloadduct (11) suitably functionalised for elaboration to Coates' tricyclic ketone (37) *via* the intermediate mesylate (34b) and alkene (35). This was found to be the case.

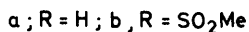
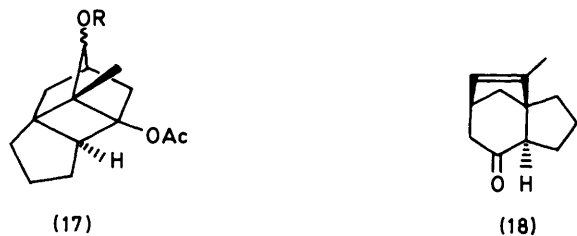
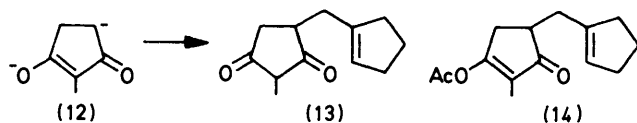
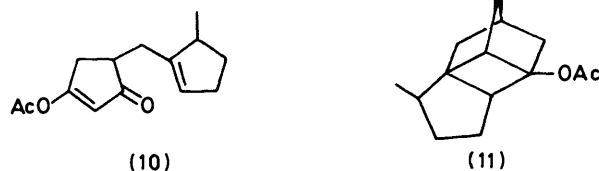
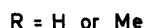
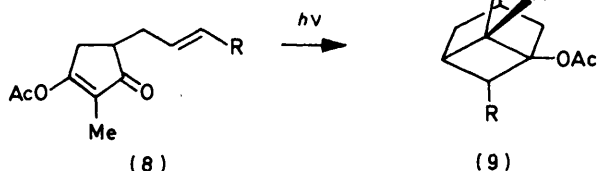
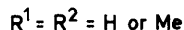
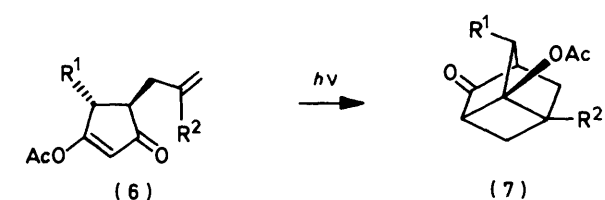
The feasibility of the above proposal was first examined using the enol acetate (14) derived from the cyclopentane-1,3-dione (13). This dione was easily prepared by alkylation of the bis-anion (12) derived from 2-methylcyclopentane-1,3-dione with cyclopent-1-enylmethyl bromide.<sup>6</sup> Irradiation of the enol acetate (14) in hexane, using Pyrex-filtered light from a medium-pressure mercury lamp resulted in the production of one major photoproduct (*ca.* 82%), which was isolated as a colourless oil by chromatography. The oil displayed *i.r.* ( $\nu_{\max}$ . 1760  $\text{cm}^{-1}$ ; ketone) and  $^1\text{H}$  n.m.r. ( $\delta$  2.04, OAc; 1.07, Me) spectral data consonant with the anticipated tetracyclic



Scheme 1.

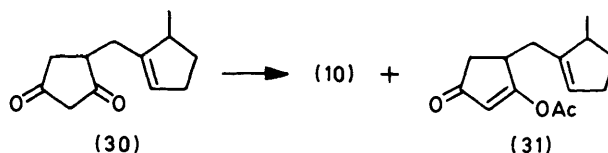
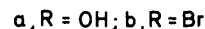
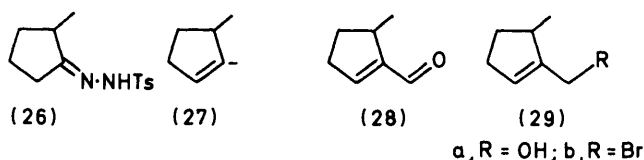
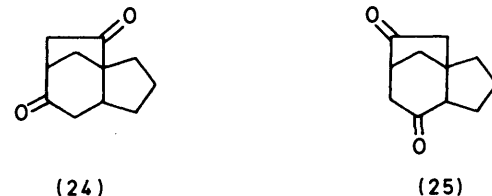
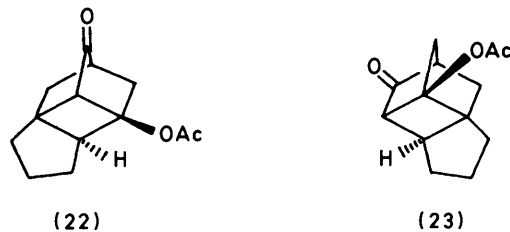
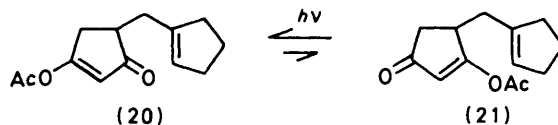
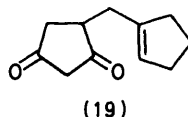
ketone (15) (see Discussion in preceding paper<sup>4</sup>); we were unable to detect any of the cycloadduct (16) resulting from the alternative mode of intramolecular cycloaddition in (14). Treatment of the adduct (15) with sodium borohydride gave rise to a mixture of  $\alpha$ - and  $\beta$ -carbinols (17a) which was converted into the corresponding mesylate (17b). Fragmentation of the mesylate mixture, in the presence of aqueous sodium hydroxide in dioxane at 60 °C then produced the unsaturated ketone (18) containing the zizaene carbon framework.

In another model study of the regioselectivity of intramolecular de Mayo reactions amongst 4-cyclopent-1-enylmethyl substituted cyclopentane-1,3-dione enol esters, we examined the irradiation of a 1 : 1 mixture of enol acetates (20) and (21) derived from the dione (19). This led to a mixture (*ca.* 6 : 4) of cycloadducts, which by comparison of their spectral data with those of the adducts derived from (6) and (8) were assigned constitutions (22) and (23). Our previous investigations have shown that equilibration between the enol acetates (20) and (21) is quite rapid under irradiation, and



that the enol acetate (21) is relatively 'unreactive' towards intramolecular [2 + 2] cycloaddition (see Discussion in preceding paper).<sup>4</sup> Treatment of the crude mixture of aldol esters (22) and (23) with ethanolic potassium hydroxide at 0 °C resulted in saponification and retro-aldolisation leading to the two diones (24) (major) and (25) (minor) which were separated by chromatography. Although a clear distinction between the diones proved difficult by inspection of their lowfield <sup>1</sup>H n.m.r. data, since our own investigations, Oppolzer and Burford<sup>7</sup> have inspected the 360 MHz <sup>1</sup>H n.m.r. data of the same diones obtained by a similar pathway, which have clearly established their constitutions.

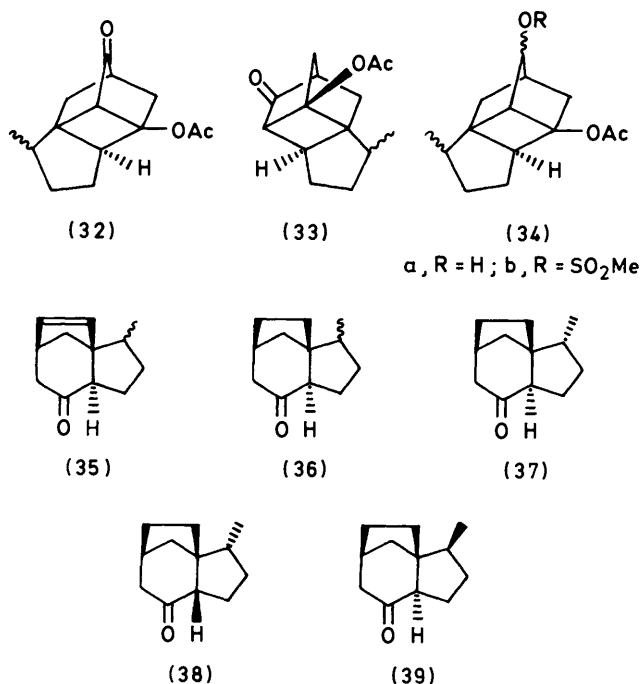
We next turned to the synthesis of the tricyclic unsaturated



ketone (35) based on the strategy outlined above, and using the enol acetate (10).

The cyclopentene-1-carbaldehyde (28) was first prepared starting from 2-methylcyclopentanone. Thus, treatment of the tosylhydrazone (26) derived from 2-methylcyclopentanone with four equivalents of *n*-butyl-lithium led to the vinyl anion (27) which on treatment with dimethylformamide gave the aldehyde (28).<sup>8</sup> Reduction of (28) with lithium aluminium hydride then produced the carbinol (29a), which was converted into the corresponding bromide (29b) using phosphorus tribromide. Alkylation of the bis-anion derived from cyclopentane-1,3-dione with the bromide (29b) then led to the substituted dione (30) which was converted into a 6 : 4 mixture of (10) and the isomeric enol acetate (31).

Irradiation of the mixture of enol acetates (10) and (31) gave rise to a 7 : 3 mixture of the two photoadducts (32) and (33), in a combined yield of 69%, which was separated by chromatography. The major photoadduct showed spectral data [ $\nu_{\text{max}}$ , 1765  $\text{cm}^{-1}$ ;  $\delta$  2.04, 2.02 (OAc) and 0.77, 0.75 (CHMe)] consistent with a 1 : 3 mixture of methyl epimers of the tetracycloundecan-9-one adduct (32); the minor product was separated as a mixture of methyl epimers of the alternative



cycloadduct (33). Reduction of the tetracyclic undecan-9-one (32), using sodium borohydride in methanol at 0 °C, followed by mesylation of the resulting mixture of isomeric carbinols (34a) led to a mixture of isomers of the mesylate (34b). Treatment of the mesylate (34b) with sodium hydroxide in aqueous dioxane at 60 °C for 1 h then resulted in fragmentation leading to a 1 : 2 mixture of  $\alpha$ - and  $\beta$ -methyl epimers of the fragrant smelling alkenone (35). Hydrogenation of the alkenone (35) over 10% palladium on charcoal, finally produced an epimeric mixture of Coates' tricyclic ketone (36).

Comparison of the  $^1H$  n.m.r. spectrum of our synthetic tricyclic ketone (36) with those obtained by Coates for the isomer (37)<sup>2</sup> and by Piers<sup>9</sup> for the bridgehead epimer (38), and correlation of shift data for the secondary methyl group resonances in the various isomers, [*i.e.* (37) ( $\delta$  0.97), (38) ( $\delta$  0.94), our synthetic ketone (36)  $\delta$  0.97, 0.92] established that our tricyclic ketone was composed of a mixture of the  $\alpha$ - and  $\beta$ -methyl epimers (37) (minor) and (39) (major). Significantly, the data established that little or no epimerisation at the ring fused position occurred during the fragmentation reaction leading to (35) from (34b).\*

Since Coates and Sowerby<sup>2</sup> have converted the tricyclic ketone (37) into ( $\pm$ )-zizaene (1) our new approach to (37) constitutes a new total synthesis of racemic zizaene and its methyl epimer.

## Experimental

For general experimental details see previous papers.<sup>4,6</sup>

**6-Acetoxy-10-methyltetracyclo[6.2.1.0<sup>1,5</sup>.0<sup>6,10</sup>]undecan-9-one (15).**—By the general procedure,<sup>4</sup> irradiation of 3-acetoxy-5-cyclopent-1-enylmethyl-2-methylcyclopent-2-enone (0.4 g),<sup>6</sup> led in 8.5 h, to one major photoproduct (*ca.* 82%) accompanied by a minor product and starting material (*ca.* 9% each). Chromatography gave the undecanone (0.31 g, 76%) as a colourless oil,  $\nu_{max}$  (film) 1 760, 1 730, 1 235, and 1 170  $cm^{-1}$ ;

$\delta$  1.3–2.9 (m, 12 H), 2.04 (OAc), 1.07 (Me);  $m/z$  234. ( $C_{14}H_{18}O_3$ ).

**10-Methyltricyclo[6.2.1.0<sup>1,5</sup>]undec-9-en-6-one (18).**—By the general procedures described previously,<sup>4</sup> reduction of the undecanone (15), led (72%) to an epimeric mixture of isomers of 6-acetoxy-10-methyltetracyclo[6.2.1.0<sup>1,5</sup>.0<sup>6,10</sup>]undecan-9-ol,  $\nu_{max}$  (film) 3 430, 1 735, 1 240, 1 175, 1 060, and 1 035  $cm^{-1}$ ;  $\delta$  3.42, 3.84 (CHOH, epimers), 1.27–2.89 (m, 13 H), 2.0, 2.07 (OAc, epimers), and 1.1, 1.14 (Me, epimers);  $m/z$  236. This was converted into the corresponding mixture of mesylates, a pale yellow semicrystalline gum (52%),  $\nu_{max}$  (film) 1 735 and 1 175  $cm^{-1}$ ;  $\delta$  4.46, 4.61br CHO, epimers) 2.94, 2.98 ( $SO_2Me$ , epimers), 1.28–2.87 (m, 12 H), 1.98, 2.05 (OAc, epimers), and 1.11, 1.15 (Me, epimers). Fragmentation of the mesylate in the presence of sodium hydroxide then gave the tricyclic undecanone (33%) as a colourless viscous oil,  $\nu_{max}$  ( $CHCl_3$ ) 1 730 and 1 660  $cm^{-1}$ ;  $\delta$  5.4–5.55 (m, :CH), 2.6–2.84 (m, 2 H), 1.26–2.58 (m, 10 H), and 1.66 (:CMe) (Found:  $M^+$ ,  $m/z$  176.1212.  $C_{12}H_{16}O$  requires  $M$ , 176.1201); unchanged mesylate (*ca.* 19%) was also recovered.

**Tricyclo[6.2.1.0<sup>1,5</sup>]undecane-6,9-dione (24) and Tricyclo[6.2.1.0<sup>1,5</sup>]undecane-7,10-dione (25) (with M. Mellor).**—By the general procedure<sup>4</sup> irradiation of a 1 : 1 mixture of the enol acetates (20) and (21) derived from 4-cyclopent-1-enylmethylcyclopentane-1,3-dione (19),<sup>6</sup> led in 2.5 h, to a 6 : 4 mixture of the photoproducts (22) ( $\delta$  2.01, OAc) and (23) ( $\delta$  2.12, OAc) (85%). The mixture was treated with ethanolic potassium hydroxide, according to the general procedure, which led to a 7 : 3 mixture of the diones (24) and (25). Repeated chromatography on silica using 1 : 1 ether–light petroleum (b.p. 40–60 °C) as eluant gave the following. (i) The undecane-6,9-dione (eluted first), as a semi-crystalline oil,  $\nu_{max}$  ( $CHCl_3$ ) 1 730 and 1 715  $cm^{-1}$ ;  $\delta$  3.03 (dd,  $J$  3, 6, 1 H), 2.59 (m, 1 H), and 1.25–2.50 (m, *ca.* 12 H). (ii) The undecane-7, 10-dione (eluted second), an oil  $\nu_{max}$  ( $CHCl_3$ ) 1 735 and 1 706  $cm^{-1}$ ;  $\delta$  2.81 (m, 1 H), 2.63 (t,  $J$  8, 1 H), 2.43 (d, dd,  $J$  1, 5 and 12, 1 H), and 1.32–3.0 (m, *ca.* 11 H).<sup>7</sup>

**5-Methylcyclopentene-1-carbaldehyde (28).**—A solution of 2-methylcyclopentanone (11.6 g)<sup>11</sup> and *p*-tolylsulphonylhydrazine (25.3 g) in ethanol (175 ml) and concentrated hydrochloric acid (0.1 ml) was heated under reflux for 2.5 h, cooled, and then evaporated almost to dryness. The residue was filtered to leave 2-methylcyclopentanone *p*-tolylsulphonylhydrazone (26) as a white solid. Crystallisation from aqueous ethanol gave white crystals (24.3 g, 77%), m.p. 133.5–135.0 °C,  $\lambda_{max}$  (EtOH) 206 ( $\epsilon$  11 200), 229 ( $\epsilon$  11 900), and 275 nm ( $\epsilon$  830);  $\nu_{max}$  (KBr) 1 650 and 1 590  $cm^{-1}$ ;  $\delta$  7.76 (d,  $J$  8, 2 H), 7.2 (d,  $J$  8, 2 H), 7.2–7.7br (NH), 2.4 (Me), 1.1–2.3 (m, 7 H), and 1.01 (d,  $J$  7, CHMe).

A solution of *n*-butyl-lithium (4 equiv.; 1.43M) in hexane (162 ml) was added over 0.5 h to a stirred solution of the tosylhydrazone (15.4 g) in tetramethylethylenediamine (85 ml) maintained at –78 °C under nitrogen. The deep red solution was allowed to warm to 25 °C over 1 h, and then kept at 25 °C for a further 1 h. The solution was cooled to 0 °C, and then treated with dry *N,N*-dimethylformamide (10 g) and stirred at 0 °C for 1 h. The mixture was diluted with water (125 ml) and then extracted with ether (4  $\times$  50 ml). The ether extracts were combined, then washed with dilute hydrochloric acid (3  $\times$  100 ml) and water (3  $\times$  100 ml), and dried. Evaporation of the ether and distillation of the residue gave the aldehyde (5.4 g, 84%)<sup>12</sup> as a pale yellow oil, b.p. 80–85 °C at 14 mmHg,  $\lambda_{max}$  (EtOH) 237.5 nm ( $\epsilon$  10 300);  $\nu_{max}$  (film) 1 685 and 1 615  $cm^{-1}$ ;  $\delta$  9.72 (CHO), 6.77 (m, :CH), 3.0 (m, CHMe), 1.8–2.8 (m, 4 H), and 1.13 (d,  $J$  7, CHMe);  $m/z$  110. ( $C_7H_{10}O$ ).

\* Since publication of our work<sup>5</sup> another synthesis of this ketone has been announced.<sup>10</sup>

**1-Bromomethyl-5-methylcyclopentene (29b).**—Reduction of 5-methylcyclopentene-1-carbaldehyde, using lithium aluminium hydride, in the usual manner gave 5-methylcyclopent-1-enylmethanol (89%) as an oil,  $\nu_{\max}$  (film) 3 335 and 1 615  $\text{cm}^{-1}$ ;  $\delta$  5.65 (m, :CH), 4.16 ( $\text{CH}_2\text{OH}$ ), 3.4—4.2 (OH), 2.73 (m, 1 H, *CHMe*), 1.23—2.56 (m, 4 H), and 1.05 (d, *J* 7, *CHMe*) (Found:  $M^+$ ,  $m/z$  112.  $\text{C}_7\text{H}_{12}\text{O}$  requires  $M$ , 112). Bromination of the carbinol, using phosphorus tribromide, in the usual manner, then led to the bromide (38%), an unstable oil, b.p. 65—68 °C at 16 mmHg,  $\nu_{\max}$  (film) 1 660  $\text{cm}^{-1}$ ;  $\delta$  5.75 (m, :CH), 4.02 ( $\text{CH}_2\text{Br}$ ), 1.28—3.03 (m, 5 H), and 1.09 (d, *J* 7 *CHMe*).

**3-Acetoxy-5-(5-methylcyclopent-1-enylmethyl)cyclopent-2-en-1-one (10) and 3-Acetoxy-4-(5-methylcyclopent-1-enylmethyl)cyclopent-2-en-1-one (31).**—By the general procedure,<sup>6</sup> alkylation of cyclopentane-1,3-dione with 1-bromomethyl-5-methylcyclopentene gave 4-(5-methylcyclopent-1-enylmethyl)cyclopentane-1,3-dione (55%) as a yellow oil,  $\nu_{\max}$  (film) 2 770—2 150, 1 640, and 1 625—1 355  $\text{cm}^{-1}$ ;  $\delta$  12.64 (OH), 5.41 br (:CH, enol), 1.2—3.2 (m, 10 H), and 1.05 (d, *J* 7, *CHMe*) (Found:  $M^+$ ,  $m/z$  192.1141.  $\text{C}_{12}\text{H}_{16}\text{O}_2$  requires  $M$ , 192.1150).

Treatment of the dione, with acetic anhydride-sodium acetate, in the usual manner,<sup>6</sup> led to a 1 : 1 mixture of the enol acetates (10) and (31) (90%),  $\lambda_{\max}$  (EtOH) 236 nm (11 000);  $\nu_{\max}$  (film) 1 785, 1 705, 1 600, and 1 150  $\text{cm}^{-1}$ ;  $\delta$  6.19 [d, *J* 1, :*CHCO*, isomer (31)], 6.14 [t, *J* 1, :*CHCO*, isomer (10)], 5.34 (m, :*CHCH}\_2*), 1.71—3.3 (m, 10 H), 2.26, 2.31 (OAc, two isomers), and 1.02 (d, *J* 7, *CHMe*) (Found:  $M^+$ ,  $m/z$  234.1269.  $\text{C}_{14}\text{H}_{18}\text{O}_3$  requires  $M$ , 234.1256).

**6-Acetoxy-2-methyltetracyclo[6.2.1.0<sup>1,5</sup>.0<sup>6,10</sup>]undecan-9-one (32) and 10-Acetoxy-2-methyltetracyclo[6.2.1.0<sup>1,5</sup>.0<sup>6,10</sup>]undecan-7-one (33).**—By the general procedure,<sup>4</sup> irradiation of the 1 : 1 mixture of enol acetates (0.71 g) derived from 4-(5-methylcyclopent-1-enylmethyl)cyclopentane-1,3-dione, led in 7 h, to a 7 : 3 mixture of the photoproducts (32) and (33) (69%) (g.l.c. retention times 11.5 and 12.5 min respectively, 10% SE-30 at 190 °C). Chromatography gave the following. (i) The tetracycloundecan-7-one (56 mg) (eluted first) as an oily 1 : 1 mixture of C-2-methyl epimers,  $\nu_{\max}$  1 745  $\text{cm}^{-1}$ ;  $\delta$  1.5—3.13 (m, 10 H), 2.13, 2.14 (OAc, epimers), 1.08—1.5 (m, 2 H), and 0.9, 0.88 (d, *J* 7, *CHMe* epimers) (Found:  $M^+$ ,  $m/z$  234.1267.  $\text{C}_{14}\text{H}_{18}\text{O}_3$  requires  $M$ , 234.1256). (ii) The tetracycloundecan-9-one (65 mg) (eluted second) as an oily 3 : 1 mixture of 2-methyl epimers,  $\nu_{\max}$  1 765 and 1 735  $\text{cm}^{-1}$ ;  $\delta$  2.69—3.07 (m, 2 H), 1.41—2.69 (m, 9 H), 2.01, 2.04 (OAc, epimers), 1.09—1.39 (m, 1 H), and 0.78, 0.80 (d, *J* 7, *CHMe*, epimers) (Found:  $M^+$ ,  $m/z$  234.1242); (iii) An unresolved mixture of the undecanones (0.45 g).

**2-Methyltricyclo[6.2.1.0<sup>1,5</sup>]undec-9-en-6-one (35).**—By the general procedures described previously,<sup>4</sup> reduction of the tetracycloundecan-9-one (32) (56 mg) led to 6-acetoxy-2-methyltetracyclo[6.2.1.0<sup>1,5</sup>.0<sup>6,10</sup>]undecan-9-ol (34a) (79%), a colourless gum, homogeneous in chromatography (silica, 25 : 1  $\text{CHCl}_3$ -MeOH) but consisting of a mixture of diastereoisomers,  $\nu_{\max}$  ( $\text{CHCl}_3$ ) 3 580, 3 400, and 1 720  $\text{cm}^{-1}$ ;  $\delta$  4.35—5.05 (m, *CHOH*), 3.63—3.93 br (OH), 1.15—2.85

(m, 12 H), 1.99, 2.0 (OAc, isomers), and 0.82 and 0.72 (d, *J* 7, *CHMe*, isomers). Reaction of the carbinol with methanesulphonyl chloride led to the corresponding mixture of isomeric mesylates (34b) (57 mg, 96%), a colourless semisolid,  $\nu_{\max}$  1 730 and 1 170  $\text{cm}^{-1}$ ;  $\delta$  4.59—5.17 (m,  $\text{CH-OSO}_2$ ), 3.01, 3.03 ( $\text{SO}_2\text{Me}$  isomers), 1.09—2.91 (m, 12 H), 1.98, 2.01 (OAc, isomers), 0.79, 0.81 (d, *J* 7, *CHMe*, isomers), which was then converted into a 2 : 1 mixture of 2-Me epimers of the *undec-9-en-6-one* (29 mg, 71%), a fragrant volatile oil, homogeneous in g.l.c. (SE-30, 90 °C), showing  $\nu_{\max}$  ( $\text{CHCl}_3$ ) 1 695 and 1 650  $\text{cm}^{-1}$ ;  $\delta$  5.99, 6.04 (dd, *J* 6 and 3,  $\text{HC}\cdot\text{CH}\cdot\text{CH}$ , isomers), 5.68, 5.83 (d, *J* 6,  $\text{CH}\cdot\text{CH}\cdot\text{C}$ , isomers), 1.15—2.50 (m, 11 H), and 0.94, 0.96 (d, *J* 7, *CHMe* isomers) (Found:  $M^+$ ,  $m/z$  176.1211.  $\text{C}_{12}\text{H}_{16}\text{O}$  requires  $M$ , 176.1201).

**2-Methyltricyclo[6.2.1.0<sup>1,5</sup>]undecan-6-one (36).**—A solution of 2-methyltricyclo[6.2.1.0<sup>1,5</sup>]undec-9-en-6-one (20 mg) in ether (1 ml) and hexane (4 ml) was shaken under hydrogen in the presence of 10% palladium on carbon (4 mg) for 4 h, and then filtered and evaporated. Chromatography of the residue on silica using 49 : 1 chloroform-methanol as eluant gave the *undecan-6-one* (18 mg), homogeneous in g.l.c. (SE-30, 190 °C), as a 3 : 1 mixture of methyl epimers (39) and (37),  $\nu_{\max}$  1 695  $\text{cm}^{-1}$ ,  $\delta$  1.2—2.7 (m, 15 H), 0.92, 0.97 (d, *J* 7, *CHMe* epimers) (Found:  $M^+$ ,  $m/z$  178.1366.  $\text{C}_{12}\text{H}_{18}\text{O}$  requires  $M$ , 178.1358).

#### Acknowledgements

We thank Professors Coates and Piers for providing <sup>1</sup>H n.m.r. spectral data on their synthetic tricyclic ketones (37) and (38) respectively. We also thank the S.E.R.C. for a studentship (to A. J. B.) and the Royal Society for an equipment grant.

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Received 10th November 1982; Paper 2/1902