A New Synthetic Approach to the Bicyclo[3.2.1]octane Ring System, based on Intramolecular Photocycloaddition Involving Cyclopentane-1,3-dione Enol Esters

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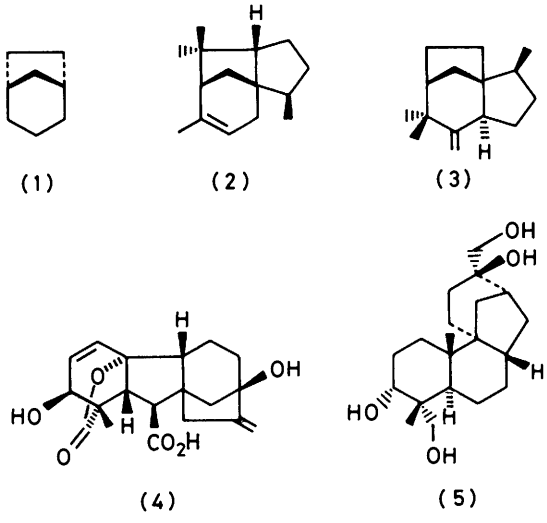
Irradiation of 1 : 1 mixtures of enol acetates derived from 4-prop-2-enylcyclopentane-1,3-diones [*i.e.* (9), (23), (27), (32a), (32b)], leads to 6-acetoxytricyclo[3.2.1.$0^{3,6}$]octan-2-ones [*i.e.* (12), (24), (28), (33a), (33b)] in high yield (>70%). The adducts result from regioselective intramolecular [2 + 2] cycloaddition in the 5-prop-2-enyl enol acetate isomers [*e.g.* (10)], suggesting that equilibration between the isomeric enol acetates [*e.g.* (10) and (11)] is rapid during the irradiations. Fragmentation of the 6-acetoxytricyclo[3.2.1.$0^{3,6}$]octan-2-ones, either directly [*e.g.* (12) ⟶ (16); KOH–EtOH] or *via* the corresponding acetoxy-mesylates [*e.g.* (24) ⟶ (25) ⟶ (26)] provides a facile route to a range of substituted bicyclo[3.2.1]octane ring systems.

Irradiation of the isomerically pure enol acetates (39), containing a methyl substituent at C-2, by contrast produce largely (ratio 3 : 2) 3-acetoxytricyclo[3.2.1.$0^{3,6}$]octan-7-one adducts (43) resulting from the alternative mode of intramolecular cycloaddition in the enol acetate (see Scheme 1); these adducts are also elaborated to bicyclo[3.2.1]octenones [*e.g.* (45)].

The bicyclo[3.2.1]octane carbon framework (1) is an important structural unit found in a wide range of terpenes of plant and fungal origin. Examples include the odoriferous sesquiterpenes α-cedrene (2) and zizaene (3), the plant growth regulator gibberellic acid (4) and the antiumoral diterpene aphidicolin (5). The interesting and diverse biological activities found amongst molecules (2)—(5) and related natural products, combined with their structural complexity, has made the design of routes to the bicyclo[3.2.1]octane ring system a particularly challenging problem in synthesis.[1,2] In this paper we describe a new approach to the bicyclo[3.2.1]octane ring system which is based on fragmentation of the tricyclo-[3.2.1.$0^{3,6}$]octane carbon framework (7)—(8) produced by intramolecular [2 + 2] photocycloaddition of enol acetates derived from 4-prop-2-enylcyclopentane-1,3-diones (6) (Scheme 1).[3]



(1) (2) (3) (4) (5)

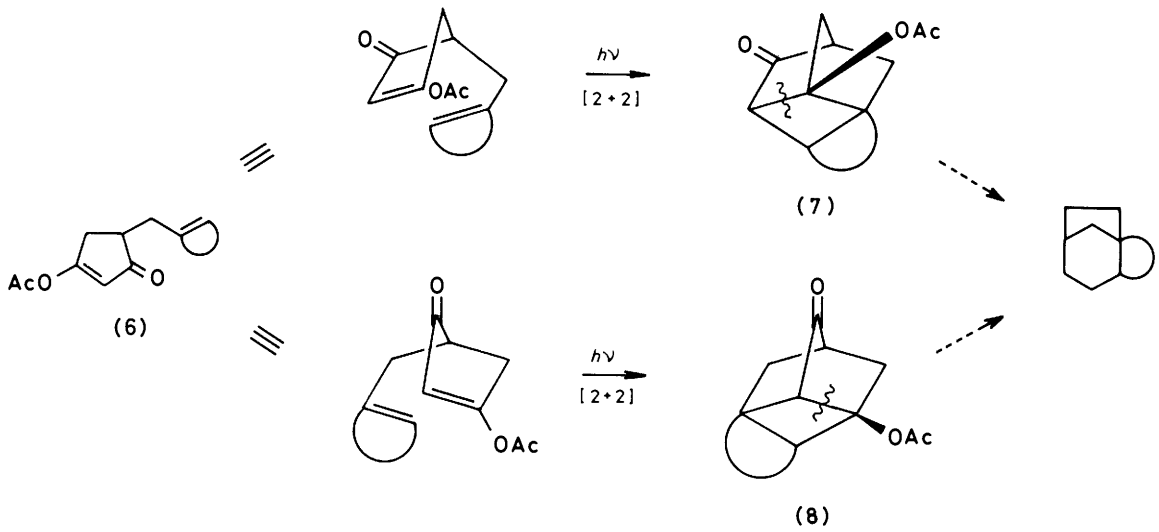
We began our studies of this design to bicyclo[3.2.1]octanes by first investigating the irradiation of the mixture of enol acetates (10) and (11) derived from the cyclopentane-1,3-dione (9).[4] *A priori* we might expect to observe the formation of all four cycloadducts (12)—(15) resulting from alternative modes of intramolecular [2 + 2] photocycloaddition in (10) and (11). Inspection of a simple electrostatic interaction mechanism for the various cycloadditions leading to (12)—(15), based on the establishment of an initial π-complex between the excited enone chromophores in (10) and (11), and the alkene,[5] suggests that the enol acetate (10) would lead preferentially to (12) and that (11) should produce the cycloadduct (15). Interestingly, the same products are also predicted by frontier orbital theory.[6]

In the event, irradiation of a 1 : 1 mixture of (10) and (11) in hexane, using Pyrex-filtered light from a medium-pressure lamp, resulted in the formation of a 4 : 1 mixture of two photoproducts in a combined yield of 82%. The major product separated as a colourless crystalline solid, m.p. 75—76 °C, in 62% yield, after chromatography. Although spectral data supported structure (12) (single epimer) for the cycloadduct, and eliminated the possibility of (13) [*i.e.* observed $\nu_{max.}$ 1 740 cm^{-1}, ring ketone; expected $\nu_{max.}$ 1 760 cm^{-1} for (13)[7]], the data did not entirely exclude the alternative possibilities of (14) and (15). Accordingly the structure was examined by *X*-ray measurements.

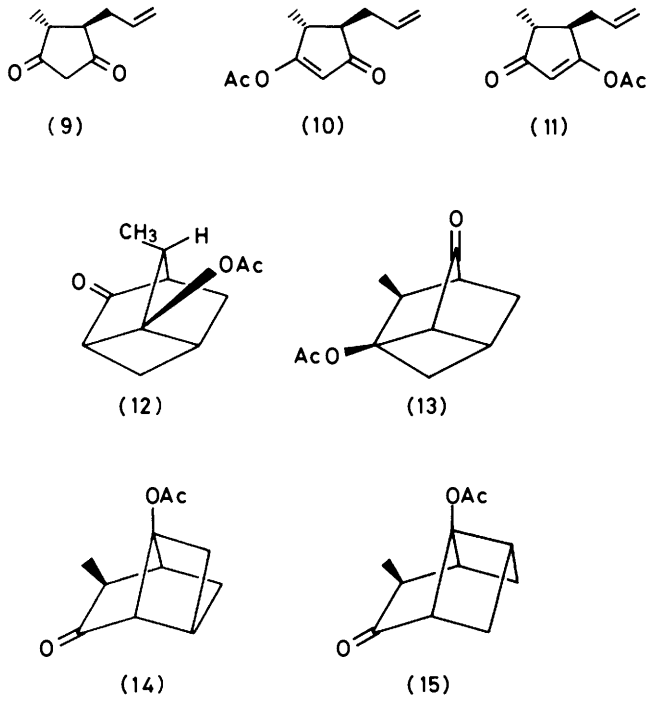
The *X*-ray structure, as revealed in the Figure, shows that the major product produced from irradiation of the mixture of (10) and (11) was indeed the cycloadduct (12) expected from (10) on the basis of the theoretical grounds mentioned earlier. Treatment of the cycloadduct with ethanolic potassium hydroxide resulted in concomitant saponification and retroaldolisation leading to a 2 : 1 mixture of *endo*- and *exo*-epimers of the bicyclo[3.2.1]octane-2,6-dione (16). In addition, reduction of (12) using aqueous methanolic sodium borohydride led to largely the β-carbinol (17a). Treatment of the mesylate (17b) derived from (17a) with hot aqueous sodium hydroxide in dioxane then resulted in simultaneous saponification and Grob fragmentation leading to the *endo*-bicyclo-[3.2.1]octenone (18).

The minor (*ca.* 16%) photoproduct obtained from irradiation of the mixture of enol acetates (10) and (11), an oil, showed closely similar spectral properties to those of (12), thereby supporting the *anti*-epimeric structure (19). This assignment was confirmed when the photoproduct was converted into the same mixture of epimers of the bicyclooctanedione (16) produced from (12) after saponification retroaldolisation.

The *syn*- and *anti*-tricyclic adducts (12) and (19) both result



Scheme 1.



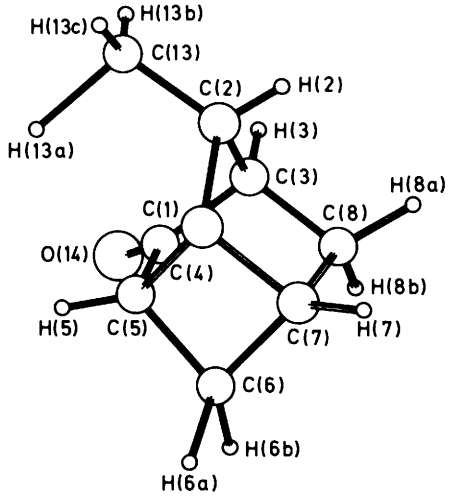
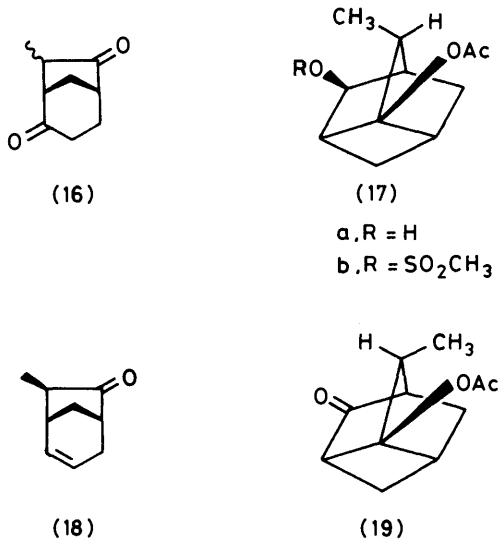


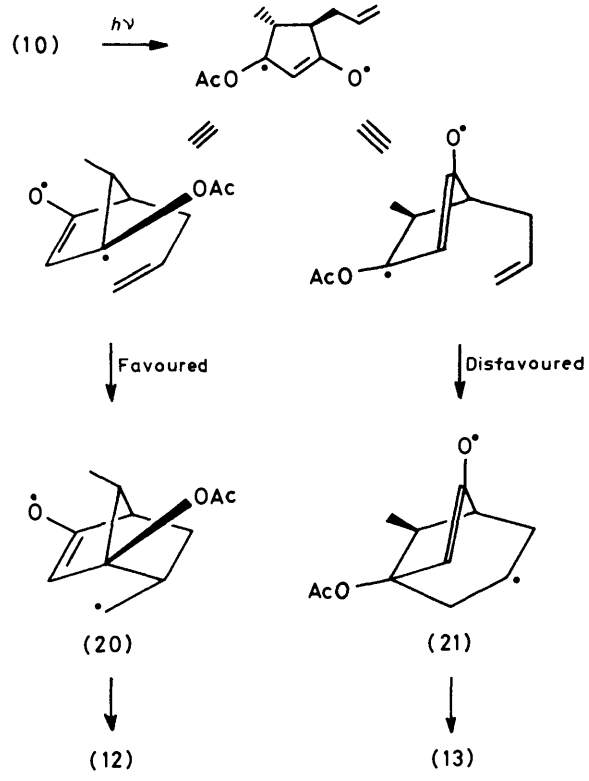
Figure. Crystal structure of (12) with acetate group omitted for clarity

from intramolecular [2 + 2] photocycloaddition in the enol acetate (10). It is significant that no cycloadducts [*i.e.* (14) and (15)] resulting from the isomeric enol acetate (11) (which constituted 50% of the original mixture) were detected in crude reaction mixtures. This feature suggests that equilibration between the enol acetates (10) and (11) must be quite rapid during the irradiation, the acyl transfer probably proceeding by a process not unrelated to the photo-Fries reaction.[8]

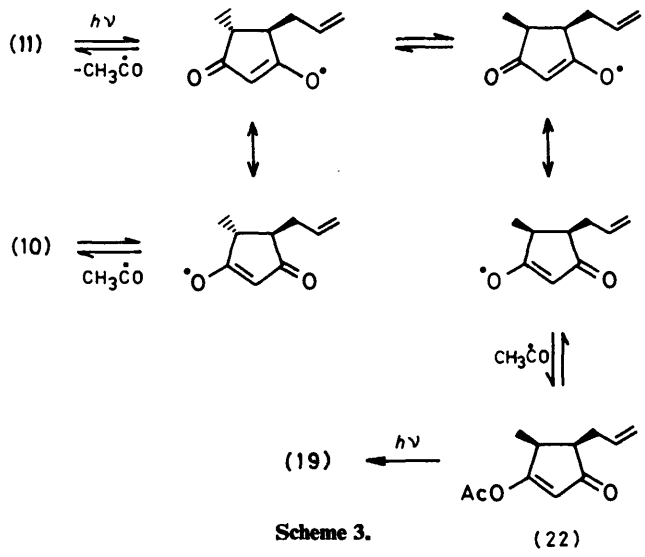
Sensitization and quenching experiments indicated that the intramolecular cycloaddition reaction leading to (12) and (19) from (10), proceeded *via* a triplet excited state, and most likely therefore through diradical intermediates. Thus, the cycloaddition was increased in rate by a factor of two in the presence of chlorobenzene as sensitizer, whereas in the presence of the radical scavenger 2,5-dimethylhexa-2,4-diene, the reaction was totally quenched. The formation of the cyclo-adduct (12) rather than (13) from irradiation of (10) is consistent with predictions based on the ' rule-of-five ' for the preferred mode of ring closure of hex-1-enyl radicals,[9] *i.e.* formation of five-ring enolate radical intermediate (20) favoured over the corresponding six-ring enolate radical intermediate (21) (Scheme 2). The isolation of the *anti*-(19) in addition to *syn*-epimer (12), from irradiation of the mixture of enol acetates (10) and (11), is most likely due to epimerisation at C-5 in the isomer (11) during photoequilibration with (10) (Scheme 3). Both ^{1}H n.m.r. and ^{13}C n.m.r. spectra failed to detect the presence of the *syn*-diastereoisomer (22) of (10) in the mixture of enol acetates derived from the cyclopentane-1,3-dione (9) (see discussion in previous paper).[4]

In a similar study, irradiation of a 1 : 1 mixture of enol acetates derived from the dione (23) [4] led to a 3 : 2 mixture of *syn*- and *anti*-epimers of the tricyclic adduct (24) (72%). After conversion into the acetate-mesylate (25), fragmentation then gave the angular methyl substituted bicyclo-octenone (26). Likewise the mixture of enol acetates derived from (27) led to the adduct (28), which underwent fragmentation in base to a mixture of epimers of the dione (29). A second product (<5%)

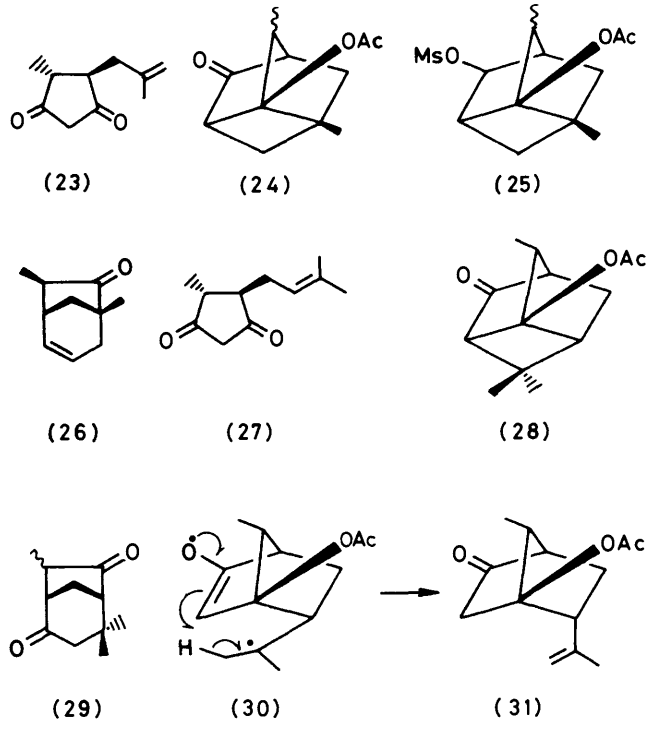




Scheme 2.



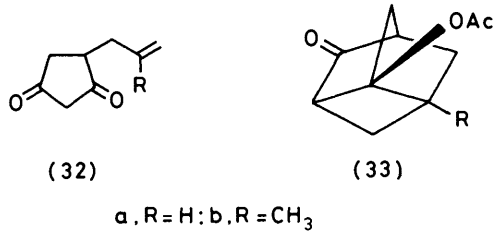
Scheme 3.



was separated by chromatography from the irradiation of the enol acetate derived from (27). Spectral data showed that this was the propenyl substituted bicyclo[2.2.1]heptanone (31) which is most likely derived by H-abstraction from the presumed di-radical intermediate (30) [*cf.* intermediate (20), Scheme 2].

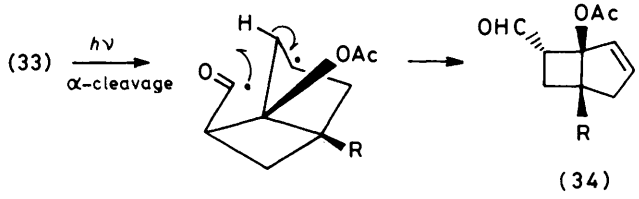
Irradiations of the mixtures of enol acetates derived from the 4-prop-2-enyl substituted cyclopentane-1,3-diones (32a) and (32b), lacking methyl groups at C-5, gave rise to single cycloadducts corresponding to structures (33a) and (33b) respectively. Interestingly, these adducts were found to be more photolabile than the analogues (12), (24), and (28), and underwent smooth Norrish type cleavage to bicyclo[3.2.0]-heptene (34).[5]

Irrespective of the compositions of the enol acetate starting materials, all the intramolecular photocycloadditions cited above showed high regioselectivity, and led to the 6-acetoxy-tricyclo[3.2.1.$0^{3,6}$]octan-2-one adducts [*i.e.* (7), Scheme 1] in high yield. This same regioselectivity, but with an important difference, was also observed during studies of the irradiation of enol *ethers* derived from 4-prop-2-enyl substituted cyclopentane-1,3-diones. Thus, irradiation of the 1 : 1 mixture of isobutyl ethers (35a) and (36a), produced from (9), resulted in slow conversion into a poor yield (>40%) of the *syn*-epimer (37) of 6-isobutoxy-7-methyltricyclo[3.2.1.$0^{3,6}$]octan-2-one; the structure followed from comparison of spectral data with those of the corresponding 6-acetoxy adducts [*e.g.* (12)]. Large amounts (>40%) of enol ether starting material were

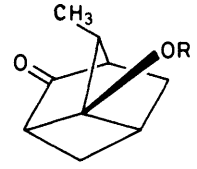


(32) (33)

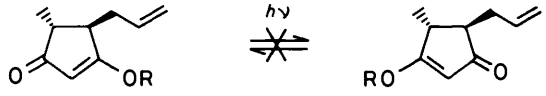
a, R = H; b, R = CH_3



(34)

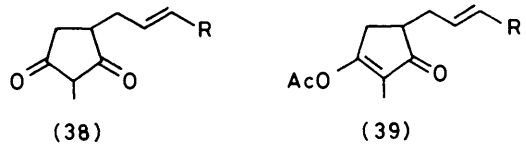


(37)



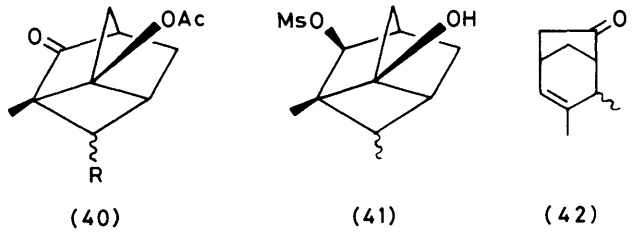
(35) (36)

a, R = CH_2CHMe_2;
b, R = Me



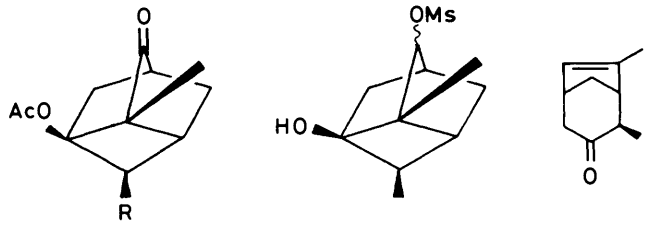
(38) (39)

a, R = Me; b, R = H



(40) (41) (42)

a, R = Me; b, R = H



(43) (44) (45)

a, R = Me; b, R = H

recovered in this experiment, and spectral data showed this to consist principally of the enol ether isomer (35a). A similar result was obtained on irradiation of the mixture of enol methyl ethers (35b) and (36b). In contrast with the corresponding enol acetates (10) and (11), these data show that a photochemical process for the interconversion of the isomeric enol ethers (35) and (36) is not available, and that the isomer (35) is unreactive towards intramolecular [2 + 2] photocycloaddition.

In the previous paper,[4] we showed that acetylation of the cyclopentane-1,3-diones (38a) and (38b), containing a methyl substituent at C-2, led to the single enol acetates (39a) and (39b) respectively. Irradiation of the enol acetate (39a) resulted in the formation of two cycloadducts, in the ratio of 3 : 2, which were separated by chromatography. The minor photoproduct exhibited spectral data closely similar to those recorded for the photoadducts (12), (24), and (28), and accordingly was assigned constitution (40a). Significantly, the 6-acetoxytricyclo[3.2.1.$0^{3,6}$]octan-2-one adducts (12), (24), (28), and (40a) show a maximum at 1 715 cm^{-1} ($\nu_{max.}$ ketone) in their i.r. spectra, and the acetate methyl group hydrogen atoms absorb at δ 2.15 in their ^{1}N n.m.r. spectra. Confirmation of structure (40a) was obtained when the adduct was converted into the bicyclo[3.2.1]octenone (42) ($\nu_{max.}$ 1 735 cm^{-1}, 5-ring ketone) following fragmentation *via* the corresponding mesylate (41).

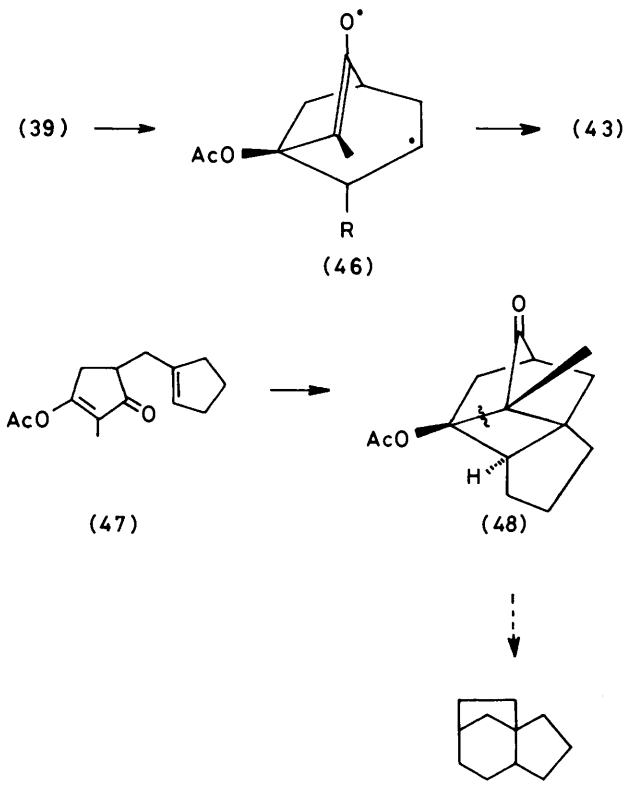
The major cycloadduct derived from irradiation of (39a), exhibited a high frequency maximum at 1 765 cm^{-1} in its i.r. spectrum,[7] suggestive of the tricyclo[3.2.1.$0^{3,6}$]octan-7-one structure (43a). This assignment was supported by inspection and comparison of other spectral data with those of the isomeric adduct (40a), and also by the fact that fragmentation of the mesylate (44) derived from the adduct led to the isomeric bicyclo[3.2.1]oct-6-en-3-one (45) ($\nu_{max.}$ 1 705 cm^{-1}, 6-ring ketone). In a similar manner, the enol acetate (39b) produced a 7 : 3 mixture of the two photoproducts (40b) and (43b).

The 3-acetoxytricyclo[3.2.1.$0^{3,6}$]octan-7-one adducts (43) result from the alternative mode of intramolecular [2 + 2] photocycloaddition in (39), to that encountered previously in the case of enol acetates derived from (9), (23), (27), and (32) [*cf.* (7) and (8) in Scheme 1]. Since steric crowding close to the radical centres undergoing cyclisation of hex-1-enyl radicals is known to result in significant amounts of 6-ring over 5-ring radical formation,[9] it seems likely that the 6-ring diradical intermediate (46) [*cf.* (21), Scheme 2], is implicated in the pathway leading to (43) from (39).

It is significant that when the prop-2-enyl side chain in (39) is replaced with the more bulky cyclopent-1-enylmethyl group, irradiation of this ester [*viz.* (47)] leads almost entirely to the 3-acetoxytricyclo[3.2.1.$0^{3,6}$]octan-7-one adduct (48). This observation has been exploited in a synthesis of the tricyclo-[6.2.1.$0^{1,5}$]undecane carbon framework found in zizaene (3), which is described in the accompanying paper.[10]

Experimental

For general experimental details, and for the preparation of the enol acetates used in this work, see previous paper.[4]



Irradiation of Prop-2-enyl Substituted Cyclopentane-1,3-dione Enol Acetates: General Procedure.—A solution of the enol acetate (5 g, mixture of positional isomers) in dry aromatic-free n-hexane (500 ml) was purged with dry nitrogen for 0.5 h, and then irradiated for *ca.* 5 h (monitoring by g.l.c.) under nitrogen through Pyrex with a 100-W medium-pressure lamp. The irradiation was stopped when either all the starting material was consumed or when a photostationary state had been established. The hexane was evaporated at room temperature under reduced pressure, and the residue was then chromatographed, on Woelm alumina using chloroform as eluant, to give the tricyclo-octanones.

syn- *and* anti-*Isomers of* 6-*Acetoxy*-7-*methyltricyclo*-[3.2.1.0^{3,6}]*octan*-2-*one* (12) *and* (19).—By the general procedure, irradiation of a 1 : 1 mixture of the enol acetates (10) and (11) (5 g),[4] led in 6 h, to a 4 : 1 mixture of the cycloadducts (12) and (19), in a combined yield of 82%. Chromatography, gave the following. (i) *syn*-6-Acetoxy-7-methyltricyclo-[3.2.1.0^{3,6}]octan-2-one (12) (62%, eluted second) as a colourless crystalline solid, which recrystallised from light petroleum (b.p. 40—60 °C), and had m.p. 75.5—76 °C, $\lambda_{max.}$ (EtOH) 222 (ε 1 600) and 293 nm (85); $\nu_{max.}$ (KBr) 1 735, 1 720, and 1 245 cm^{-1}; δ_H 2.71—3.06 (m, 3 H), 2.47—2.69 (m, 2 H), 2.15—2.47 (m, 1 H), 2.13 ($OCOCH_3$), 1.54—1.91 (m, 2 H), and 0.8 (d, *J* 7, CH*Me*); δ_C 212.6 (C-2), 170 ($OCOCH_3$), 91.5 (C-6), 56.1 (d, C-3), 46.3 (d, C-1), 44.9 (d, C-7), 36.9 (d, C-5), 35.7 (t, C-8), 34.6 (t, C-4), 21.2 (q, CO*Me*), and 8.8 p.p.m. (q, C-9) (Found: C, 68.2; H, 7.40; *M*, *m/z* 194.0962. $C_{11}H_{14}O_3$ requires: C, 68.0, H, 7.3%; *M* 194.0963). (ii) *anti*-6-Acetoxy-7-methyltricyclo[3.2.1.0^{3,6}]octan-2-one (19) (16%, eluted first) as a colourless oil, $\lambda_{max.}$ (EtOH) 222 (ε 1 500), 294 nm (ε 90); $\nu_{max.}$ (film) 1 745, 1 730, and 1 230 cm^{-1}; δ_H 2.7—3.0 (m, 3 H), 2.2—2.52 (m, 1 H), 2.15 (OCO*Me*), 1.4—1.79 (m, 2 H), and 0.91 (d, *J* 7, CH*Me*); δ_C 211.5 (C-2), 169.9 ($OCOCH_3$), 91.3 (C-6), 55.4 (d, C-3), 48.9 (d, C-1), 43.7 (d, C-7), 37.0 (d, C-5), 34.0 (t, C-4), 31.3 (t, C-8), 21.1 (q, CO*Me*), and 8.3 p.p.m. (q, C-9) (Found: *M*, *m/z* 194.0946).

When a mixture (0.5 g) of the enol acetates (10) and (11) in hexane (500 ml) was irradiated in the presence of chlorobenzene (5.65 g) as sensitizer, a photostationary 4 : 1 mixture of (12) and (19) was achieved after 3.5 h (control, 5 h). The same irradiation in the presence of 2,5-dimethylhexa-2,4-diene (11.5 g) as triplet quencher, led to no appreciable conversion into (12) and (19) after 12 h.

Crystal Structure Determination of the Cycloadduct (12).—*Crystal data:* $C_{11}H_{14}O_3$, M = 194.2. Monoclinic a = 8.993(2), b = 8.646(2), c = 12.760(3) Å, β = 96.16(3)°, U = 986.4 Å^3, Z = 4, D_c = 1.31 g cm^{-3}, $F(000)$ = 416. Space group $P2_1/c$ uniquely from systematic absences. Mo-K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 1.02 cm^{-1}.

A crystal of approximate dimensions 0.6 × 0.5 × 0.3 mm was mounted on a Hilger Y290 diffractometer. 23 Reflections were used to determine accurate lattice parameters by least-squares. Intensity data were collected with Mo-K_α radiation using an ω—2θ scan for 1° ≤ θ ≤ 27.5°. A total of 2 276 independent reflections was measured of which 1 475 had $I \geq 3\sigma(I)$ and were considered observed and used in the subsequent refinement. The data were corrected for Lorentz and polarisation factors, but no absorption corrections were made. Crystallographic calculations were performed using the CRYSTALS system of programs. The structure was solved by direct methods using the MULTAN program. 100 Reflections with $E > 2.0$ were used and the E map from the best set of phases revealed the positions of all non-hydrogen atoms as 14 of the 15 highest peaks in the map. These positions were refined initially isotropically and subsequently anisotropically. A difference map revealed the positions of all hydrogen atoms as the 14 highest peaks. These were included in the refinement with isotropic vibrations. Refinement terminated at R 0.069 with maximum δ/σ 0.2. A final difference map showed no features in excess of 0.24e Å^{-3}. Final atomic co-ordinates are listed in Table 1 with bond lengths and angles in Tables 2 and 3. Temperature factors and observed and calculated structure factors are listed in Supplementary publication No. 23625 (16 pp.).*

7-*Methylbicyclo*[3.2.1]*octane*-2,6-*dione* (16).—A solution of the *syn*-epimer (12) (2 g) in ethanol (40 ml) was stirred at 0 °C in the presence of potassium hydroxide (5.5 g) in ethanol (80 ml) for 2 h, then poured into water (250 ml) and extracted with ether (6 × 50 ml). Evaporation of the dried ether extracts and chromatography of the residue on silica using chloroform–methanol (99 : 1) as eluant gave the *dione* (1.21 g, 77%) as a 2 : 1 mixture of *endo*- and *exo*-epimers, $\lambda_{max.}$ (EtOH) 213 (ε 1 400) nm; $\nu_{max.}$ (film) 1 735 and 1 705 cm^{-1}; δ_H 1.84—2.8 (m, 9 H), 1.25 (d, *J* 7, *exo*-CH*Me*), 1.07 (d, *J* 7.5, *endo*-CH*Me*) (Found: M^+, *m/z* 152.0833. $C_9H_{12}O_2$ requires *M* 152.0837). The dione formed a *bis*-(2,4-*dinitrophenylhydrazone*) which crystallised from aqueous ethanol and had m.p. 227—228 °C (Found: C, 49.1; H, 4.1; N, 21.6. $C_{21}H_{20}N_8O_8$ requires C, 49.2; H, 3.9; N, 21.9%).

Saponification and retro-aldolisation of the *anti*-epimer (19), under the same conditions, led to the same proportion of *syn* and *anti*-diones (16) in 72% combined yield.

6-*Acetoxy*-7-*methyltricyclo*[3.2.1.0^{3,6}]*octan*-2-*yl Mesylate* (17b).—A solution of *syn*-6-acetoxy-7-methyltricyclo-[3.2.1.0^{3,6}]octan-2-one (2 g) in methanol (80 ml) was added dropwise over 0.25 h to a stirred solution of sodium boro-

* For details of the Supplementary publications scheme, see Instructions for Authors (1983), *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

Table 1. Fractional co-ordinates with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
C(1)	0.148 1(3)	0.287 4(3)	0.149 9(2)
C(2)	0.253 2(3)	0.149 8(4)	0.149 3(2)
C(3)	0.394 0(3)	0.250 2(4)	0.175 3(3)
C(4)	0.357 0(3)	0.331 6(4)	0.274 1(2)
C(5)	0.195 1(3)	0.381 3(4)	0.250 5(2)
C(6)	0.192 4(4)	0.529 7(4)	0.181 7(3)
C(7)	0.210 7(4)	0.423 2(4)	0.087 8(2)
C(8)	0.374 5(4)	0.371 6(5)	0.086 8(3)
O(9)	−0.009 0(2)	0.260 3(2)	0.136 5(1)
C(10)	−0.071 4(3)	0.214 7(3)	0.040 8(2)
O(11)	−0.001 0(5)	0.191 0(3)	−0.031 9(2)
C(12)	−0.236 0(4)	0.197 8(5)	0.038 8(3)
C(13)	0.228 3(4)	0.025 3(4)	0.229 6(3)
O(14)	0.436 8(3)	0.353 6(4)	0.354 7(2)
H(2)	0.250(4)	0.105(4)	0.083(3)
H(3)	0.490(5)	0.198(5)	0.183(3)
H(5)	0.137(4)	0.384(4)	0.310(2)
H(6a)	0.099(4)	0.578(4)	0.177(3)
H(6b)	0.269(4)	0.610(5)	0.203(3)
H(7)	0.163(4)	0.457(4)	0.016(3)
H(8a)	0.383(4)	0.329(5)	0.021(3)
H(8b)	0.446(4)	0.471(5)	0.102(3)
H(12a)	−0.270(4)	0.274(5)	0.074(3)
H(12b)	−0.285(5)	0.212(5)	−0.033(4)
H(12c)	−0.261(5)	0.106(6)	0.071(3)
H(13a)	0.220(4)	0.073(5)	0.308(3)
H(13b)	0.310(5)	−0.048(5)	0.234(3)
H(13c)	0.139(5)	−0.032(5)	0.210(3)

Table 2. Bond lengths in Å with standard deviations in parentheses

C(1)–C(2)	1.520(4)	C(4)–C(5)	1.517(4)
C(1)–C(5)	1.540(4)	C(4)–O(14)	1.204(4)
C(1)–C(7)	1.555(4)	C(5)–C(6)	1.554(5)
C(1)–O(9)	1.424(3)	C(6)–C(7)	1.534(5)
C(2)–C(3)	1.542(4)	C(7)–C(8)	1.540(5)
C(2)–C(13)	1.520(5)	O(9)–C(10)	1.347(3)
C(3)–C(4)	1.512(5)	C(10)–O(11)	1.195(4)
C(3)–C(8)	1.538(5)	C(10)–C(12)	1.485(4)

Table 3. Bond angles with standard deviations in parentheses

C(2)–C(1)–C(5)	107.5(2)	C(5)–C(4)–O(14)	126.6(3)
C(2)–C(1)–C(7)	109.2(2)	C(1)–C(5)–C(4)	100.8(2)
C(2)–C(1)–O(9)	118.7(2)	C(1)–C(5)–C(6)	88.7(2)
C(5)–C(1)–C(7)	86.8(2)	C(4)–C(5)–C(6)	107.6(3)
C(5)–C(1)–O(9)	111.5(2)	C(5)–C(6)–C(7)	87.1(2)
C(7)–C(1)–O(9)	118.2(2)	C(1)–C(7)–C(6)	88.9(2)
C(1)–C(2)–C(3)	93.2(2)	C(1)–C(7)–C(8)	100.6(2)
C(1)–C(2)–C(13)	114.5(3)	C(6)–C(7)–C(8)	111.3(3)
C(3)–C(2)–C(13)	115.5(3)	C(3)–C(8)–C(7)	103.0(2)
C(2)–C(3)–C(4)	101.1(2)	C(1)–O(9)–C(10)	118.0(2)
C(2)–C(3)–C(8)	101.5(3)	O(9)–C(10)–O(11)	123.3(3)
C(4)–C(3)–C(8)	106.1(3)	O(9)–C(10)–C(12)	111.2(3)
C(3)–C(4)–C(5)	105.0(2)	O(11)–C(10)–C(12)	125.5(3)
C(3)–C(4)–O(14)	128.4(3)		

hydride (0.75 g) in methanol (30 ml) and water (5 ml) maintained at 0—5 °C. The mixture was stirred at 0—5 °C for 0.5 h and then diluted with water (200 ml) and extracted with ether (5 × 50 ml). The aqueous layer was saturated with sodium chloride, and again extracted with ether. Evaporation of the dried ether extracts left 6-acetoxy-7-methyltricyclo-[3.2.1.$0^{3,6}$]octan-2-ol (17a) (1.9 g, 94%) as a clear gum, $\nu_{max.}$ (film) 3 450 and 1 715 cm^{-1}; δ_H 3.95br (C*H*OH), 3.12br (OH), 2.32—2.8 (m, 6 H), 2.12 (OAc), 1.2—1.52 (m, 2 H), and 1.03 (d, *J* 7, CH*Me*) (Found: *M*, *m/z* 196.109856. $C_{11}H_{16}O_3$ requires *M*, 196.109937).

A solution of the carbinol (1.9 g) in dichloromethane (65 ml) was cooled to 0 °C and treated with a solution of triethylamine (35 ml) in dichloromethane (65 ml). The mixture was stirred at 0 °C for 0.25 h, and then treated with a solution of methanesulphonyl chloride (9 ml) in dichloromethane (40 ml), dropwise over 0.25 h. The mixture was allowed to reach room temperature over 1 h when it was washed with water (4 × 100 ml). Evaporation of the dried dichloromethane extracts left the mesylate (2.4 g, 92%) as a red oil, $\nu_{max.}$ (film) 1 735 cm^{-1}; δ_H 4.75 (m, CH-O), 3.01 (SO_2Me), 2.52—2.88 (m, 6 H), 2.1 (OAc), 1.2—1.4 (m, 2 H), and 0.96 (d, *J* 7, CH*Me*) (*m/z* 274) which was used without further purification.

endo-7-*Methylbicyclo*[3.2.1]*oct*-2-*en*-6-*one* (18).—A solution of 6-acetoxy-7-methyltricyclo[3.2.1.$0^{3,6}$]octan-2-yl mesylate (2.7 g) in 1,4-dioxane (85 ml) was heated at 65 °C for 1 h in the presence of 0.5M-aqueous sodium hydroxide (85 ml). The mixture was cooled to room temperature, and then extracted with ether (5 × 30 ml). Evaporation of the washed (water) and dried ether extracts, followed by chromatography of the residue on silica using chloroform as eluant gave the *enone* (54%) as a colourless liquid, b.p. 70—75 °C at 14 mmHg, $\lambda_{max.}$ (EtOH) 204 nm (ε 950); $\nu_{max.}$ (film) 1 730 and 1 635 cm^{-1}; δ_H 5.96 (m, :CH), 5.58 (dt, *J* 10 and 6, CH_2CH:), 2.03—2.8 (m, 7 H), and 1.09 (d, *J* 7, CH*Me*) (Found: M^+, *m/z* 136.0889. $C_9H_{12}O$ requires *M*, 136.0888). The enone formed a 2,4-*dinitrophenylhydrazone* which recrystallised from ethanol and had m.p. 207.5—208 °C (Found: C, 56.9; H, 4.9; N, 17.8. $C_{15}H_{16}N_4O_4$ requires C, 57.0; H, 5.1; N, 17.7%).

syn- *and* anti-*Isomers of* 6-*Acetoxy*-5,7-*dimethyltricyclo*-[3.2.1.$0^{3,6}$]*octan*-2-*one* (24).—By the general procedure, irradiation of a 1 : 1 mixture of enol acetates (0.95 g) derived from the dione (23) [4] led in 6 h, to a 3 : 2 mixture of *syn*- and *anti*-isomers of the adduct (24) (0.64 g, 67%), $\nu_{max.}$ (film) 1 755sh, 1 735, and 1 235 cm^{-1}; δ_H 2.59—3.04 (m, 3 H), 2.21 (m, 1 H), 2.1, 2.14 (OCO*Me*, epimers), 1.7—1.97 (m, 3 H), 1.16, 1.20 (C*Me*, epimers), 0.87 (d, *J* 7.5, *anti*-CH*Me*), and 0.85 (d, *J* 7.5, *syn*-CH*Me*) (Found: M^+, *m/z* 208.1128. $C_{12}H_{16}O_3$ requires *M*, 208.1100).

Saponification and retro-aldolisation of the epimeric mixture, in an identical manner to that described for the analogue (12), led (60%) to a mixture of *exo*- and *endo*-epimers of 5,7-dimethylbicyclo[3.2.1]octane-2,6-dione, $\nu_{max.}$ (film) 1 740 and 1 710 cm^{-1}; δ_H 2.9—3.17 (m, 1 H), 1.62—2.88 (m, 7 H), 1.32 (*endo*-CMe), 1.21 (*exo*-CMe), 1.20 (d, *J* 7, *exo*-CH*Me*), and 1.08 (d, *J* 7, *endo*-CH*Me*) (Found: M^+, *m/z* 166.0987. $C_{10}H_{14}O_2$ requires *M*, 166.0993).

endo-5,7-*Dimethylbicyclo*[3.2.1]*oct*-2-*en*-6-*one* (26).—By the general procedure described for the preparation of the analogue (18), reduction of the mixture of *syn*- and *anti*-isomers of the tricyclo-octanone (24) led to the corresponding carbinol (95%), a crystalline solid, m.p. 71—73 °C (diethyl ether), $\nu_{max.}$ (KBr) 3 490 and 1 730 cm^{-1}; δ_H 3.98, 4.03 (C*H*OH, epimers), 2.87br, (OH), 2.0—2.83 (m, 4 H), 2.10, 2.17 (OAc, epimers), 1.3—1.6 (m, 3 H), 1.12, 1.15 (CMe, epimers), and 0.97, 1.07 (d, *J* 7.5, CH*Me* epimers) (Found: M^+, *m/z* 210.1277. $C_{12}H_{18}O_3$ requires *M*, 210.1256). The carbinol was then converted into the corresponding mesylate, a pale yellow gum, $\nu_{max.}$ 1 730 cm^{-1}; δ_H 4.54—4.6 (m, CHO), 2.9,

2.94 (SO_2Me, epimers), 1.92—3.05 (m, 4 H), 1.93, 2.02 (OAc, epimers), 1.18—1.59 (m, 3 H), 0.99, 1.03 (CMe, epimers), and 0.90, 0.98 (d, *J* 7.5, CH*Me*, epimers) (Found: M^+, *m/z* 288.1045. $C_{13}H_{20}O_5$ requires *M* 288.1025) which on fragmentation in the presence of sodium hydroxide gave the *endo*-bicyclo-octenone (38%) as a colourless oil, $\nu_{max.}$ (film) 1 735 and 1 640 cm^{-1}; δ_H 5.92 (dd, *J* 10 and 8, CH·C*H*:CH), 5.57 (dt, *J* 10 and 3, CH_2C*H*:CH), 2.59—2.82 (m, 1 H), 2.42 (q, *J* 7, C*H*Me), 2.05 (m, 2 H), 1.71—1.98 (m, 2 H), 1.15 (CMe), 1.08) d, *J* 7, CH*Me*) (Found: M^+, *m/z* 150.1047. $C_{10}H_{14}O$ requires *M*, 150.1045). Substantial amounts of the starting mesylate and hydroxy-mesylate, corresponding to saponified starting mesylate, were recovered.

syn-6-*Acetoxy*-4,4,7-*trimethyltricyclo*[3.2.1.$0^{3,6}$]*octan*-2-*one* (28).—By the general procedure, irradiation of a 1 : 1 mixture of enol acetates derived from the dione (27),[4] led in 5 h, to the tricyclo-octenone (70%) as a semi-crystalline oil, $\nu_{max.}$ 1 735 and 1 235 cm^{-1}; δ_H 2.2—3.14 (m, 5 H), 2.14 (OAc), 1.44—1.78 (m, 1 H), 1.37 (Me), 0.84 (Me), and 0.8 (d, *J* 7, CH*Me*), (Found: M^+, *m/z* 222.1238. $C_{13}H_{18}O_3$ requires *M*, 222.1256). A small amount of the bicyclo[2.2.1]heptane (31) (<5%), $\nu_{max.}$ (film) 1 735 cm^{-1}; δ_H 4.84—5.04 (m, :C*H*), 4.34 (d, *J* 6, :C*H*H), 1.92—3.04 (m, 7 H), 2.03 (OAc), 1.76 (:CMe), and 1.12 (d, *J* 7, CH*Me*) was also separated from some preparations, by chromatography.

4,4,7-*Trimethylbicyclo*[3.2.1]*octane*-2,6-*dione* (29).—The dione was prepared in a similar manner to that described for the analogue (16). Chromatography led to a mixture of *endo*- and *exo*-isomers (62%) as an oil, $\nu_{max.}$ 1 735 and 1 710 cm^{-1}; δ_H 1.48—3.12 (m, 7 H), 1.27 (Me), 1.1 (Me), 1.09 (d, *J* 7, *exo*-CH*Me*), 0.95 (d, *J* 7, *endo*-CH*Me*); (*m/z* 180); this formed a *bis*-(2,4-*dinitrophenylhydrazone*), m.p. 103—105 °C (EtOH) (Found: C, 50.6, H, 4.7; $C_{23}H_{24}N_8O_8$ requires C, 51.1, H, 4.5%).

6-*Acetoxytricyclo*[3.2.1.$0^{3,6}$]*octan*-2-*one* (33a).—By the general procedure, irradiation of a 1 : 1 mixture of enol acetates derived from the cyclopentane-1,3-dione (32a),[4] led in 4 h, to a mixture of two photoproducts. Chromatography gave the following. (i) The tricyclo-octanone (33a) (eluted first), as a crystalline solid, m.p. 50—52 °C [light petroleum (b.p. 40—60 °C)], $\nu_{max.}$ (KBr) 1 740 and 1 245 cm^{-1}; δ 2.56—3.0 (m, 3 H), 1.98—2.44 (m, 4 H), 2.15 (OAc), and 1.58—1.98 (m, 2 H); δ_C 211.8 (C-2), 170.1 (*C*OCH$_3$), 88.9 (C-6), 50.6 (d, C-3), 47.8 (C-1) 40.1, 36.9, 36.4, 34.9, and 21.3 (q, *C*H$_3$) (Found: M^+, *m/z* 180.0791. $C_{10}H_{12}O_3$ requires *M*, 180.0786). (ii) 1-*Acetoxybicyclo*[3.2.0]*hex*-2-*ene*-7-*carbaldehyde* (34a) (eluted second), as a colourless oil, $\nu_{max.}$ (film) 1 730 and 1 705 cm^{-1}; δ_H 9.91 (d, *J* 2, CHO), 6.18 (d, *J* 7, CH:CH), 5.94 (dt, *J* 7 and 2, CH_2C*H*:CH), 3.52 (td, *J* 9 and 2, C*H*·CHO), 1.89—2.15 (m, 3 H), 2.07 (OAc), and 1.17—1.83 (m, 2 H) (*m/z* 180).

6-*Acetoxy*-5-*methyltricyclo*[3.2.1.$0^{3,6}$]*octan*-2-*one* (33b).—By the general procedure, irradiation of a mixture of enol acetates derived from the cyclopentane-1,3-dione (32b),[4] led in 3 h, to a 2 : 1 mixture of two photoproducts. Chromatography gave an incomplete separation of a mixture of the tricyclo-octanone (33b) (major product) and 1-acetoxy-5-methylbicyclo[3.2.0]hept-2-ene-7-carbaldehyde (34b) (minor product), $\nu_{max.}$ (film) 1 735 and 1 235 cm^{-1}; δ_H 10.01 (d, *J* 2.5, CHO), 6.19 (dd, *J* 2 and 6, C*H*:CH), 6.01 (dt, *J* 6 and 3, C:C*H*·CH_2), 3.47 (dt, *J* 2 and 9, C*H*·CHO), 1.9—2.8 (m), 2.1 [OAc, (31b)], 2.02 [OAc, (32b)], 1.66—1.88 (m), 1.31 [Me, (32b)], and 1.23 [Me, (31b)].

4-*Methyl*-5-*prop*-2-*enylcyclopentane*-1,3-*dione Isobutyl Enol Ethers* (35a) and (36a).—A solution of 4-methyl-5-prop-2-enylcyclopentane-1,3-dione (10 g) and isobutyl alcohol (15 ml) in dry benzene (60 ml) containing toluene-*p*-sulphonic acid (0.25 g) was heated under reflux for 20 h using a Dean and Stark trap. The cooled solution was washed with aqueous sodium hydrogen carbonate (5 × 30 ml) and water (2 × 30 ml), and then dried and evaporated to dryness under reduced pressure. Distillation gave a 1 : 1 mixture of the isobutyl ethers as a pale yellow oil (7.9 g, 58%), b.p. 87—89 °C at 0.03 mmHg, $\nu_{max.}$ (film) 1 695, 1 645, and 1 595 cm^{-1}; δ 5.36—5.96 (m, C*H*:CH_2), 5.16 (COC*H*:C), 4.87—5.22 (m, :CH_2), 3.7—3.8 (m, OCH_2), 1.89—2.82 (m, 5 H), 1.27 and 1.24, (d, *J* 7, CH*Me* isomers), and 1.14 (d, *J* 7, CHMe_2); δ_C 207.4, 189.7, 135.6(d), 116.8(t), 102.6(d), 77.9(t), 53.4(d), 40.9(d), 35.7(t), 27.9(d), 18.9(q), 17.5(q) [isomer (35a)], 206.0, 191.9, 134.6d, 117.5(t), 103.1(d), 77.9(t), 48.7(d), 45.6(d), 35.2(t), 27.9(d), 18.9(q), and 16.5(q) p.p.m. [isomer (36a)].

syn-6-*Isobutoxy*-7-*methyltricyclo*[3.2.1.$0^{3,6}$]*octan*-2-*one* (37a).—By the general procedure, irradiation of a 1 : 1 mixture of the isobutyl ethers (35a) and (36a) (1.04 g), led in 37 h, to a photostationary equilibrium mixture of one photoproduct, accompanied by 40% remaining starting material. Chromatography on silica, using ether as eluant gave the following. (i) The tricyclo-octanone, an oil, $\nu_{max.}$ (film) 1 740 cm^{-1}; δ_H 3.1—3.3 (m, CH_2O), 1.91—2.93 (m, 7 H), 1.43—1.9 (m, 2 H), 0.97 (d, *J* 7, CHMe_2), and 0.8 (d, *J* 7, CH*Me*) (Found: M^+, *m/z* 208.1477. $C_{13}H_{20}O_2$ requires *M*, 208.1463). (ii) 3-Isobutoxy-5-methyl-4-prop-2-enylcyclopent-2-enone (36a), δ 5.3—5.95 (m, C*H*:CH_2), 5.14 (m, COC*H*:C), 4.83—5.2 (m, :CH_2), 3.7—3.8 (m, OCH_2), 2.0—2.8 (m, 4 H), 1.23 (d, *J* 7, CH*Me*), and 1.13 (d, *J* 7, CHMe_2).

In a similar manner, irradiation of a 4 : 6 mixture of the corresponding methyl ethers (35b) and (36b), led in 30 h, largely to the *syn*-tricyclo-octanone (37b) (35%), $\nu_{max.}$ 1 740 cm^{-1}; δ_H 3.38 (OMe), 2.28—2.68 (m, 6 H), 172 (m, 2 H), and 0.82 (d, *J* 7, CH*Me*) (Found: M^+, *m/z* 166.0993. $C_{10}H_{14}O_2$ requires *M*, 166.0994).

6-*Acetoxy*-3,4-*dimethyltricyclo*[3.2.1.$0^{3,6}$]*octan*-2-*one* (40a) *and* 3-*Acetoxy*-4,6-*dimethyltricyclo*[3.2.1.$0^{3,6}$]*octan*-7-*one* (43a).—By the general procedure, irradiation of 3-acetoxy-5-but-2-enyl-2-methylcyclopent-2-enone (39a)[4] (1.5 g) in hexane (250 ml), led in 4.5 h, to a 2 : 3 mixture of the cyclo-adducts (40a) and (43a). Chromatography gave the following. (i) The tricyclo-octan-2-one (40a) (0.3 g, eluted first) (mixture of epimers) an oil, $\nu_{max.}$ (film) 1 740, 1 370, 1 245, 1 225, and 1 210 cm^{-1}; δ_H 2.26—2.9 (m, 4 H), 2.14, 2.12 (OAc, epimers), 1.93—2.04 (m, 1 H), 1.69—1.92 (m, 2 H), 1.22, 0.76 (d, *J* 7, CH*Me* epimers), and 1.04, 1.02 (Me, epimers) (Found: M^+, *m/z* 208. $C_{12}H_{16}O_3$ requires *M*, 208). (ii) The tricyclo-octan-7-one (43a) (0.4 g, eluted second) (single epimer), an oil, $\nu_{max.}$ (film) 1 765, 1 738, 1 375, 1 255, 1 235, 1 225, 1 190, 1 075, and 1 065 cm^{-1}; δ_H 2.08—2.7 (m, 5 H), 2.03 (OAc), 1.64—1.91 (m, 2 H), 1.31 (d, *J* 7, CH*Me*), and 1.28 (Me) (Found: *M*, *m/z* 208.1123; $C_{12}H_{16}O_3$ requires *M*, 208.1100).

3,4-*Dimethylbicyclo*[3.2.1]*oct*-2-*en*-6-*one* (42).—By the general procedure described for the preparation of the analogue (18), reduction of the photoadduct (40a) (mixture of epimers) led to the corresponding carbinol (82%), a viscous oil, $\nu_{max.}$ (film) 3 475, 1 735sh, and 1 720 cm^{-1}; δ 3.86 (m, C*H*OH), 2.61 (OH), 1.87—2.54 (m, 5 H), 2.1 (OAc), 1.47—1.84 (m, 2 H), 1.04, 1.1 (d, *J* 7.5, CH*Me* epimers), and 0.97, 1.02 (Me epimers), which was converted into 6-acetoxy-3,4-dimethyltricyclo[3.2.1.$0^{3,6}$]octan-2-yl mesylate (95%) (mixture

of epimers), $\nu_{max.}$ (film) 1 735 and 1 725sh cm^{-1}; δ 4.16, 4.22 (CHO, epimers), 3.23 (SO_2Me), 1.55—1.92 (m, 7 H), 2.07 (OAc), and 0.92—1.22 (m, 2 × Me, epimers). Fragmentation of the mesylate then led to the *octenone* (22%) (mixture of epimers) as a colourless volatile oil, $\nu_{max.}$ (film) 1 735 and 1 650 cm^{-1}; δ_H 5.44—5.67 (m, :CH), 1.65—2.77 (m, 7 H), 1.53 (:CMe), and 1.02, 1.11 (d, *J* 7, CHMe epimers) (Found: *M*, *m/z* 150. $C_{10}H_{14}O$ requires *M*, 150.1045). The 2,4-dinitrophenylhydrazone derivative recrystallised from aqueous ethanol and had m.p. 213.5—214.5 °C.

2,7-*Dimethylbicyclo*[3.2.1]*oct*-6-*en*-3-*one* (45).—By the general procedure described for the preparation of the analogue (18), reduction of the photoadduct (40a) led to the corresponding carbinol (98%) a viscous oil, $\nu_{max.}$ (film) 3 480, 1 730, and 1 710 cm^{-1}; δ_H 3.53, 3.83 (epimeric, C*H*OH), 2.58—2.72 (OH), 1.62—2.34 (m, 6 H), 2.03, 2.07 (OAc, epimers), 1.39—1.68 (m, 1 H), 1.34, 1.37 (Me, epimers), and 1.14, 1.21 (d, *J* 7, CH*Me*, epimers), which was converted into 3-acetoxy-4,6-dimethyltricyclo[3.2.1.$0^{3,6}$]octan-7-yl mesylate (83%) (1 : 1 mixture of C-7 epimers), an oil, $\nu_{max.}$ 1 730 cm^{-1}; δ_H 4.01—4.69 (m, CHO), 3.0, 3.17 (SO_2Me epimers), 1.26—2.77 (m, 7 H), 2.03 (OAc), 1.39 (Me), and 1.14, 1.16 (d, *J* 7, CH*Me*, epimers). Fragmentation of the mesylate then led to the *octenone* (30%) (single epimer) as a colourless volatile liquid, $\nu_{max.}$ 1 705 and 1 635 cm^{-1}; δ_H 5.38—5.52 (m, C:C*H*·CH), 2.63—2.83 (m, 1 H), 1.93—2.62 (m, 6 H), 1.76 (:CMe), and 1.07 (d, *J* 7, CH*Me*) (Found: *M*, *m/z* 150.1062; $C_{10}H_{14}O$ requires *M*, 150.1045). The 2,4-dinitrophenylhydrazone derivative recrystallised from ethanol and had m.p. 121.5—123 °C.

6-*Acetoxy*-3-*methyltricyclo*[3.2.1.$0^{3,6}$]*octan*-2-*one* (40b) and 3-*Acetoxy*-6-*methyltricyclo*[3.2.1.$0^{3,6}$]*octan*-7-*one* (43b).—By the general procedure, irradiation of 3-acetoxy-2-methyl-5-prop-2-enylcyclopent-2-enone (39b),[4] led to a 3 : 7 mixture (93%) of the cycloadducts (40b) and (43b). Chromatography gave the following. (i) The tricyclo-octan-2-one (43b), a colourless gum, $\nu_{max.}$ 1 760 and 1 725 cm^{-1}; δ 2.71—2.98 (m, 1 H), 2.1—2.7 (m, 6 H), 2.17 (OAc), 1.6—2.2 (m, 1 H), and 1.06 (Me) (Found: *M*, *m/z* 194.0921. $C_{11}H_{14}O_3$ requires *M*, 194.0943). (ii) The tricyclo-octan-7-one (40b), $\nu_{max.}$ 1 735 cm^{-1}; δ_H 2.68—3.04 (m, 1 H), 2.11—2.5 (m, 6 H), 2.06 (OAc), 1.5—1.75 (m, 1 H), and 1.18 (Me) (Found: *M*, *m/z* 194.0926).

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