New Synthetic Approaches to Fused-ring Carbocycles based on Intramolecular Photocycloadditions of 1,3-Dione Enol Esters

Michael J. Begley, Michael Mellor, and Gerald Pattenden *
Chemistry Department, The University, Nottingham NG7 2RD

Irradiation of 3-acetoxy-2-pent-4-enylcyclohex-2-enone (12) leads to the tricyclic adduct (18), in high yield (>95%), which on hydrolytic cleavage in ethanolic potassium hydroxide gives rise to bicyclo[6.3.0]-undecane-2,6-dione (20).

In contrast, irradiation of the isomeric enol acetate, 3-acetoxy-4-pent-4-enylcyclohex-2-enone (17) led to the two photoadducts (25) and (26) resulting from intramolecular photocycloaddition, and to the trione (24) produced *via* photo-Fries rearrangement of (17) ; the formation of (25) and (26) followed from the structures (29) and (27) produced after saponification-retroaldolisation of mixtures containing (25) and (26). Irradiation of the 6-pentenyl substituted enol ester (16) gave rise to only the photo-Fries rearrangement product (24).

Irradiation of 1-acetoxy-2-pent-4-enoylcyclopentene(39) led (93%) to a 2:3 mixture of the photo-adducts (41) and (42) whose structures followed from X-ray measurements. The corresponding cyclo-hexene (45), instead produced the product (46) of photo-Fries rearrangement on irradiation. Hydrolytic cleavage of (41) in KOH–EtOH leads to the bicyclo[5.3.0]decanone (47), whereas similar treatment of (42) instead gave directly the aldol (49) by way of the transient retro-aldol intermediate (48).

Photochemical [2 + 2] cycloaddition of an enolised 1,3-dione to an alkene, followed by retro-aldolisation of the 2-acylcyclo-butanol intermediate, *i.e.* de Mayo reaction (Scheme 1) [1] has been widely used in the construction of a range of ring systems found amongst natural products.[2] During 1978, Oppolzer *et al.*[3] and ourselves [4] demonstrated independently the synthetic utility of the intramolecular variant of the de Mayo reaction during synthetic investigations amongst the terpenes longi-folene (1) and zizaene (2). Since this time both our research groups have shown further scope for the intramolecular de Mayo reaction, culminating in the synthesis of a range of difficulty accessible fused ring systems.[5,6] In the preceding papers, we summarised our studies leading to a new synthesis of zizaene (2).[7] In this paper we describe some of our other investigations of the intramolecular de Mayo reaction, which have been directed largely towards the synthesis of the bicyclo[6.3.0]undecane, bicyclo[5.3.1]undecane, and bicyclo-[5.3.0]decane ring systems, (3) (4), and (5) respectively,[8] found in a range of interesting natural terpenes, *e.g.* ophiobolin F(6),[9] taxinine (7),[10] aromadendrene (8).[11]

We first investigated the photochemistry of the pent-4-enyl substituted cyclohexane-1,3-dione enol acetates (12) and (17), with a view to synthesis of the fused ring systems (3) and (4) respectively. The C-2 substituted enol acetate (12) was prepared from the corresponding cyclohexane-1,3-dione (11), which was easily produced by alkylation of the anion (9) obtained from 2,4-dimethoxycyclohexa-1,4-diene with 5-iodopent-1-ene [to (10)], followed by hydrolysis.[12] This method of synthesis of the dione (11) is far superior to that involving direct C-2 pent-4-enylation of cyclohexane-1,3-dione.[13]

The C-4 substituted enol acetate (17) was obtained by chromatographic separation from the 2:1 mixture of C-4 and C-6 (16) substituted compounds produced by acetylation of the cyclohexanedione (15). The dione (15) was easily prepared by hydrolysis of the substituted enol ether (14) produced from pentenylation of the kinetic enolate derived from 3-ethoxy-cyclohex-2-enone (13).[14]

Irradiation of the enol acetate (12) in hexane, using Pyrex-filtered light from a medium-pressure lamp, resulted in regiospecific intramolecular [2 + 2] photocycloaddition with the production of the isomerically pure crystalline tricyclic ketone (18) in almost quantitative yield. We were unable to
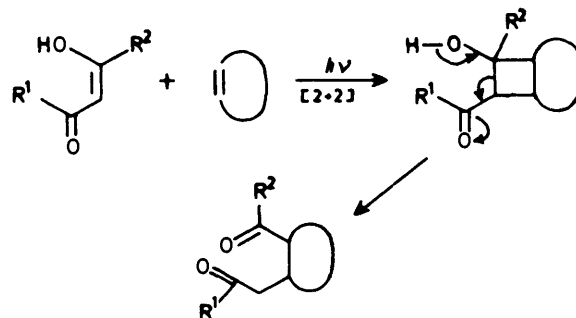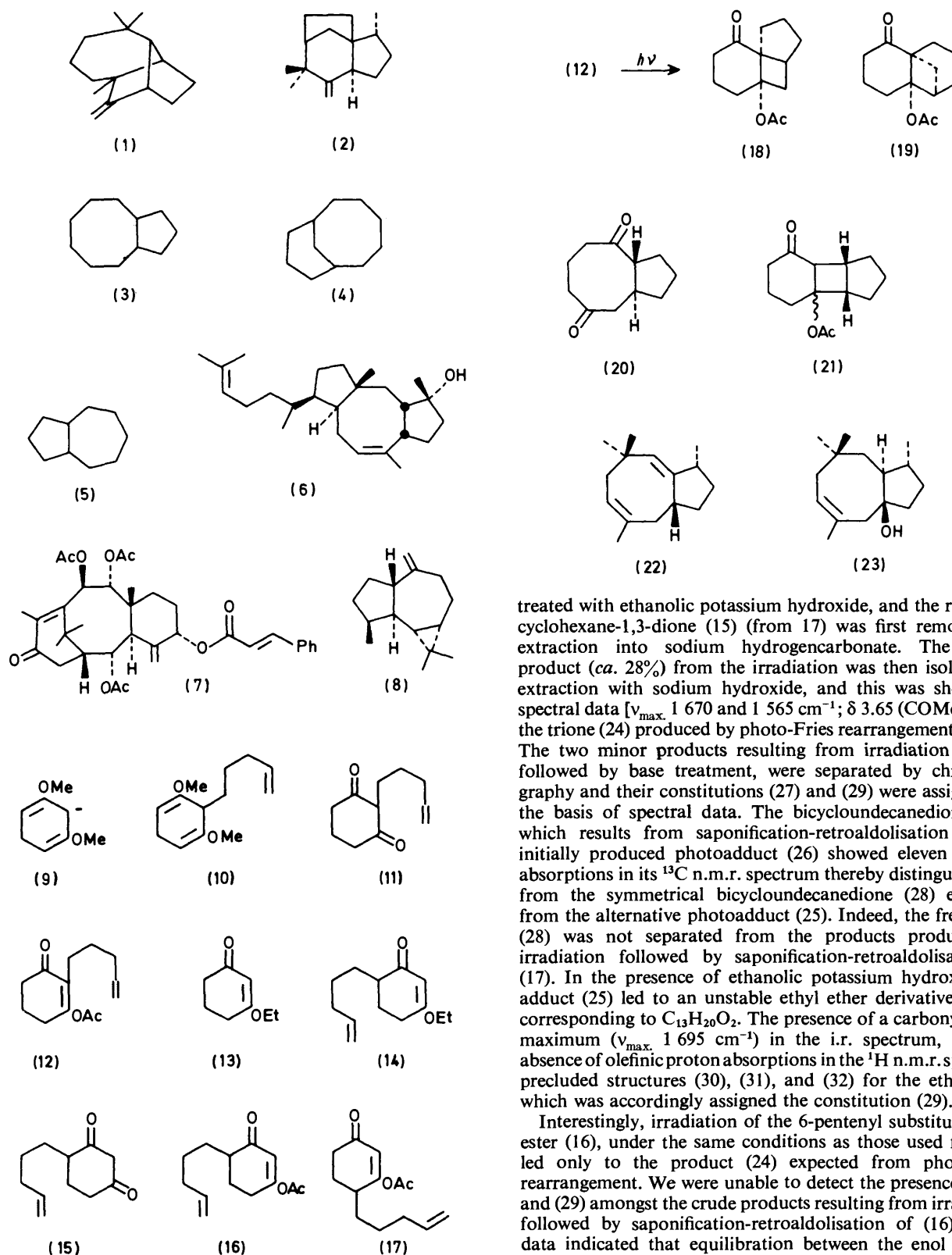

Scheme 1.

obtain any evidence for the co-formation of the alternative photoadduct (19) from intramolecular [2 + 2] photocyclo-addition. Treatment of the tricyclic ketone (18) with ethanolic potassium hydroxide at 0 °C resulted in simultaneous saponification and retro-aldolisation leading to the bicyclo-[6.3.0]undecane-2,6-dione (20). The structure (20) was con-firmed by comparison with the same dione produced by retro-aldol cleavage of the tricyclic adduct (21) [15] resulting from intermolecular photocycloaddition of cyclopentene to cyclo-hexane-1,3-dione enol acetate.[16] The *trans*-fusion of the rings in the dione, which presumably results from epimerisation at the bridgehead centre during saponification retroaldolisation, was established by X-ray measurements.[17]

Natural products showing structures based on the linear fusion of 5- and 8-membered rings, although rare, are found amongst the fusicoccin [18] and ophiobolane groups of terpenes [*e.g.* ophiobolin F (6)], and also in a few sesquiterpenes, *e.g.* precapnelladiene (22),[19] dactylol (23) [20] of marine origin. In the following paper, we show how the intramolecular de Mayo reaction sequence shown above, was used in a total synthesis of the natural hydrocarbon (22).[21]

In contrast to the regiospecific behaviour observed with (12),† irradiation of the isomeric enol acetate (17) led to three photoproducts in a combined yield of *ca.* 47%. The photo-

---

† After publication of our preliminary results (ref. 6*b*), Oppolzer and Bird reported similar data from irradiation of (12) (ref. 5*a*).

(1)   (2)

(3)   (4)

(5)   (6)

(7)   (8)

(9)   (10)   (11)

(12)   (13)   (14)

(15)   (16)   (17)

(12) $\xrightarrow{h\nu}$

(18)   (19)

(20)   (21)

(22)   (23)

treated with ethanolic potassium hydroxide, and the resulting cyclohexane-1,3-dione (15) (from 17) was first removed by extraction into sodium hydrogencarbonate. The major product (ca. 28%) from the irradiation was then isolated by extraction with sodium hydroxide, and this was shown by spectral data [$\nu_{max.}$ 1 670 and 1 565 cm^{-1}; δ 3.65 (COMe)] to be the trione (24) produced by photo-Fries rearrangement in (17). The two minor products resulting from irradiation of (17) followed by base treatment, were separated by chromatography and their constitutions (27) and (29) were assigned on the basis of spectral data. The bicycloundecanedione (27), which results from saponification-retroaldolisation of the initially produced photoadduct (26) showed eleven distinct absorptions in its ^{13}C n.m.r. spectrum thereby distinguishing it from the symmetrical bicycloundecanedione (28) expected from the alternative photoadduct (25). Indeed, the free dione (28) was not separated from the products produced by irradiation followed by saponification-retroaldolisation of (17). In the presence of ethanolic potassium hydroxide the adduct (25) led to an unstable ethyl ether derivative of (28) corresponding to $C_{13}H_{20}O_2$. The presence of a carbonyl group maximum ($\nu_{max.}$ 1 695 cm^{-1}) in the i.r. spectrum, and the absence of olefinic proton absorptions in the ^{1}H n.m.r. spectrum precluded structures (30), (31), and (32) for the ethyl ether which was accordingly assigned the constitution (29).

Interestingly, irradiation of the 6-pentenyl substituted enol ester (16), under the same conditions as those used for (17), led only to the product (24) expected from photo-Fries rearrangement. We were unable to detect the presence of (27) and (29) amongst the crude products resulting from irradiation followed by saponification-retroaldolisation of (16). These data indicated that equilibration between the enol acetates (16) and (17) was not a major process on irradiation of (16).*

Exclusive formation of the photoadduct (18), at the expense of (19), from irradiation of the enol acetate (12) is entirely consistent with predictions based on the 'rule of five' for the

products were only poorly resolved from one another and from remaining starting material in chromatography, and attempted resolution of the mixture under a range of chromatographic conditions resulted in extensive losses due to concurrent hydrolysis and rearrangement. Accordingly, the crude mixture of photoproducts and residual starting material was

---

* This result is to be contrasted with data obtained for enol acetates derived from cyclopentane-1,3-diones: see ref. 7.

(24)　　　　(25)　　　　(26)

(27)　　　　(28)　　　　(29)

(30)　　　　(31)　　　　(32)
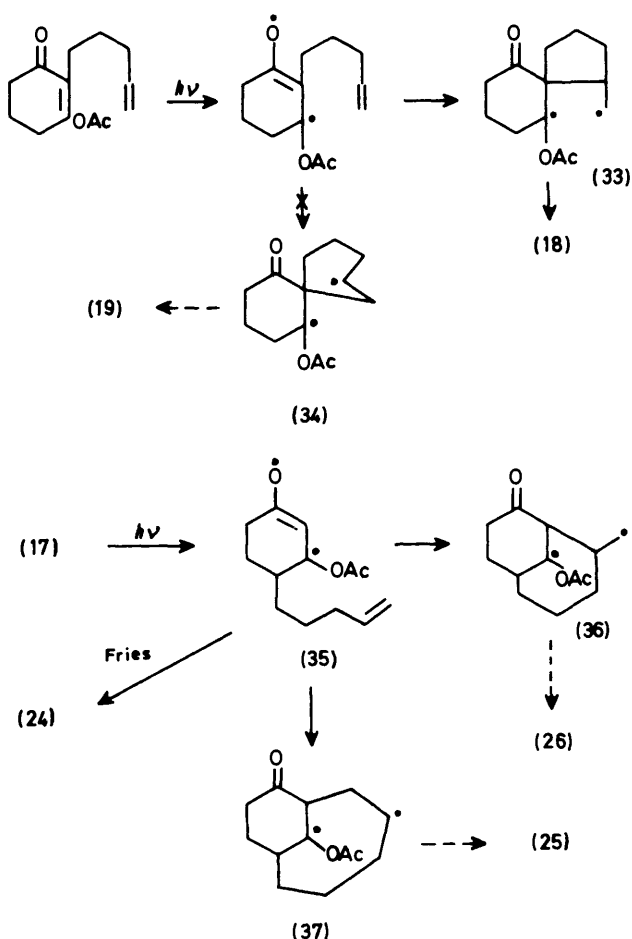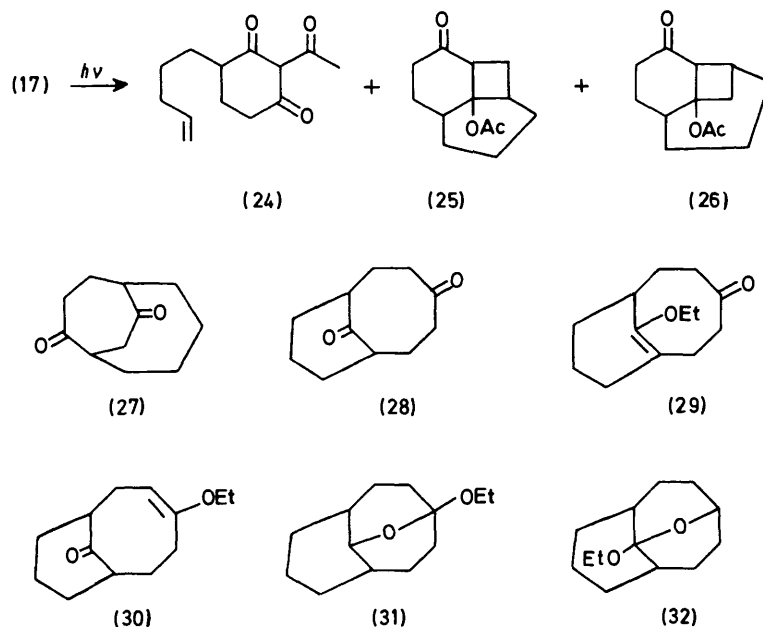
preferred mode of cyclisation of hex-1-enyl radicals,[22] *i.e.* closure to the five-ring biradical intermediate (33) favoured over closure to the corresponding six-ring intermediate (34). In addition, the lack of regioselectivity observed in the intramolecular photocycloaddition from (17) is not altogether

surprising, since there is little to choose on stability grounds between the anticipated seven-ring and eight-ring biradical intermediates, (36) and (37) respectively, produced in this reaction. Indeed, in the case of (17) [and of the isomeric enol acetate (16)] its photochemistry is dominated by facile acyl shift (*i.e.* Fries rearrangement) from the excited state (35) leading to the trione (24).

In a further examination of the scope of the intramolecular de Mayo reaction, we investigated irradiation of the enol acetate (39) with an eye to synthesis of the bicyclo[5.3.0]-undecanedione (47). The pentenoylcyclopentanone (38) was first prepared by treatment of 1-morpholinocyclopent-1-ene with pent-4-enoyl chloride. Acetylation of the dione (38) with acetic anhydride in the presence of toluene-*p*-sulphonic acid then led to the enol acetate (39) accompanied by the *exo*-isomer (40).

Irradiation of a 2 : 1 mixture of the enol acetates (39) and (40), led to the formation of two crystalline photoadducts (ratio 2 : 3) in a combined yield of 93%. Spectral data alone failed to distinguish between the four possible adducts resulting from intramolecular [2 + 2] cycloaddition in (39) and (40), and the structures were examined by *X*-ray measurements. The *X*-ray data (see Figures 1 and 2) showed that the photoadducts had the constitutions (41) (major product) and (42), both of which result from intramolecular cycloaddition in only the *endo*-enol acetate (39). Equilibration of the enol acetates (39) and (40) is therefore quite rapid under the irradiation conditions.

The lack of regioselectivity observed in the intramolecular photoaddition of (39) was disappointing, and is to be contrasted with the observation made by Oppolzer and Godel[3] that the corresponding irradiation of the analogue (43) affords the adduct (44), regioselectively and in high yield (78%). It is also interesting to compare the observation with the outcome of irradiation of the six-ring enol acetate analogue (45), where only the product (46) of Fries rearrangement was isolated. Not for the first time the dramatic effect of ring size in determining the course of a photochemical reaction is reflected in *these* studies.[23]

Treatment of the keto-acetate (41) with ethanolic *potassium* hydroxide at 0 °C led to the bicyclodecanone (47), whereas similar treatment of the adduct (42) instead gave the aldol (49),

(38)   (39)   (40)

(41)   (42)

Figure 2. Crystal structure of (42) with acetate group omitted for clarity
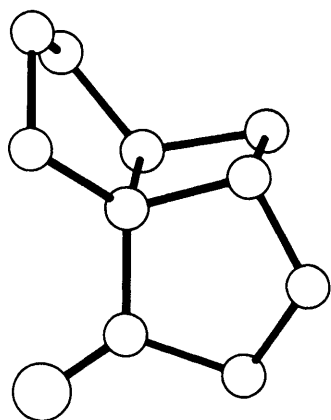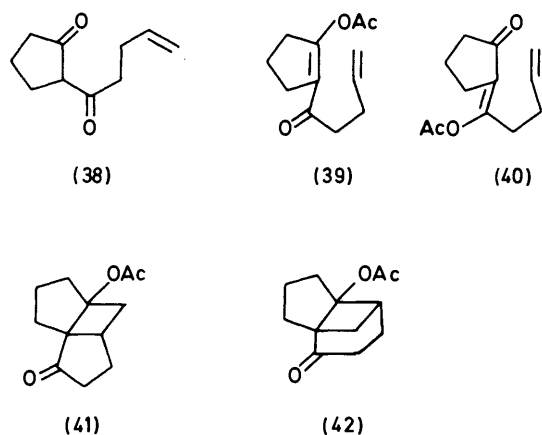

Figure 1. Crystal structure of (41) with acetate group omitted for clarity

a crystalline solid m.p. 104—108 °C, by way of the transient retro-aldol intermediate (48).

Experimental

For general experimental details see previous papers.[7]

2-Pent-4-enylcyclohexane-1,3-*dione* (11).—(*a*) Cyclohexane-1,3-dione (6.15 g) was added to a stirred solution of potassium methoxide (from 2.14 g potassium) in methanol (16.5 ml) at 0—5 °C. The mixture was stirred at 5 °C for 10 min and then treated with 5-iodopent-1-ene (11.2 g) and heated under reflux for 3.5 h. After cooling, the methanol was evaporated under reduced pressure and the residue extracted with dilute aqueous sodium carbonate. The aqueous solution was washed with ether, and then cooled to 0.5 °C and acidified to pH 4—5 with dilute hydrochloric acid. The precipitate was filtered off and dried *in vacuo* to give the dione (1.3 g, 13%) as a pale yellow powder, m.p. 103—108 °C, $v_{max.}$ (CHCl$_3$) 1 735, 1 705, and 1 620br cm^{-1}; δ 5.6—6.18 (m, C*H*:CH$_2$), 4.9—5.25 (m, :CH$_2$), 1.7—2.78 (m, 10 H), and 1.18—1.64 (m, 2 H) (Found: M^+, *m/z* 180.1156. C$_{11}$H$_{16}$O$_2$ requires *M*, 180.1150).

(*b*) By the general procedure described by Piers and Grierson [12] addition of 5-iodopent-1-ene to the anion derived from 2,4-dimethoxycyclohexa-1,4-diene (Bu^{t}Li in HMPA), followed by hydrolysis (HCl in acetone) of the intermediate 2,4-dimethoxy-3-pent-4-enylcyclohexa-1,4-diene, gave the dione (*ca.* 60% overall) showing identical spectral data to those described above.
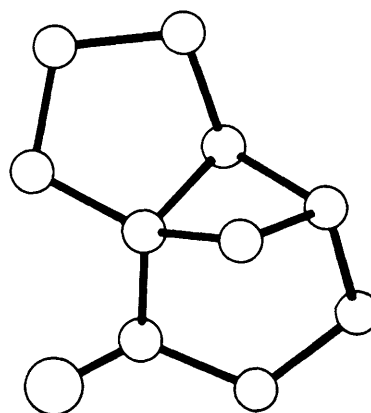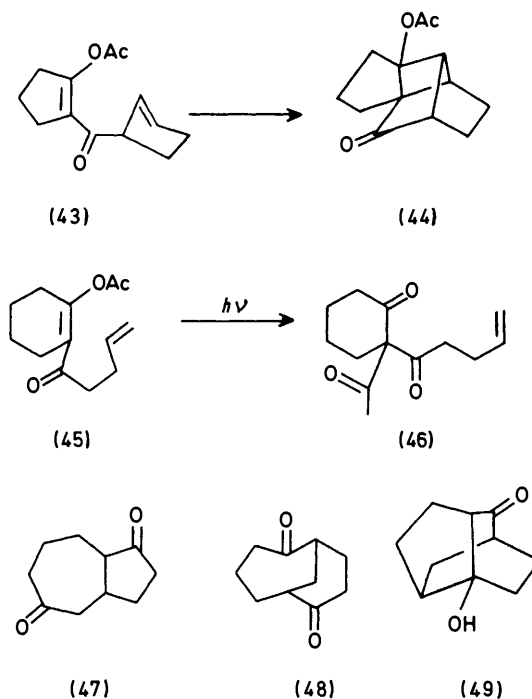

(43)   (44)

(45)   (46)

(47)   (48)   (49)

3-*Acetoxy*-2-*pent*-4-*enylcyclohex*-2-*enone* (12).—A mixture of 2-pent-4-enylcyclohexane-1,3-dione (1.95 g) and anhydrous sodium acetate (0.3 g) in acetic anhydride (45 ml) was stirred at 25 °C for 52 h, and then evaporated to dryness under reduced pressure. The residue was diluted with water, and then extracted with ether (4 × 30 ml). The combined ether extracts were washed with dilute aqueous sodium carbonate, and with water, and then dried and evaporated. The resulting brown oil was filtered through silica gel (50—100 mesh; 150 g) using ether–light petroleum (b.p. 40—60 °C) (1 : 1) as eluant, to give the enol acetate (2.2 g, 92%) as a pale yellow oil, $v_{max.}$ (CHCl$_3$) 1 755 and 1 640—1 680 cm^{-1}; δ 5.6—6.04 (m, C*H*:CH$_2$), 4.82—5.16 (m, :CH$_2$), 1.75—2.7 (m, 10 H), 2.24 (OAc), and 1.2—1.62 (m, 2 H) (Found: M^+, *m/z* 222.1243. C$_{13}$H$_{18}$O$_3$ requires *M*, 222.1256).

4-*Pent*-4-*enylcyclohexane*-1,3-*dione* (15).—Treatment of cyclohexane-1,3-dione with ethanol in the presence of toluene-*p*-sulphonic acid, by the general procedure, gave 3-

ethoxycyclohex-2-enone (80%), b.p. 89—92 °C at 0.9 mmHg, δ 5.38 (:CH), 3.96 (q, J 7, OCH$_2$CH$_3$), 2.2—2.55 (m, 4 H), 1.8—2.2 (m, 2 H), and 1.41 (t, J 7, OCH$_2$CH$_3$). Metallation of 3-ethoxycyclohex-2-enone at −78 °C, using lithium di-isopropylamide in the presence of hexamethylphosphoramide, by the procedure of Stork and Danheiser,[14] followed by alkylation with 5-iodopent-1-ene, led to 3-ethoxy-6-pent-4-enylcyclohex-2-ene (14) (ca. 68%) as a pale yellow liquid, b.p. 120—130 °C at 1 mmHg, $v_{max.}$ (CHCl$_3$) 1 595—1 660 cm^{-1}; δ 5.56—6.1 (m, ·CH:CH$_2$), 5.34 (CO·CH:CO), 4.82—5.16 (m, :CH$_2$), 3.92 (q, J 7, OCH$_2$CH$_3$), 1.16—2.54 (m, 11 H), 1.38 (t, J 7, OCH$_2$CH$_3$) (Found: M^+, m/z 208.1474. C$_{13}$H$_{20}$O$_2$ requires M, 208.1463).

A solution of 3-ethoxy-6-pent-4-enylcyclohex-2-ene (6.34 g) in tetrahydrofuran (45 ml) was treated with ice-cold 20% sulphuric acid (90 ml), and the mixture was stirred for 1 h; it was then poured into water and extracted with ether. The combined ether solutions were extracted with dilute aqueous sodium carbonate, and the aqueous solution then separated, acidified with dilute hydrochloric acid, and extracted with ether. Evaporation of the ether extracts left the dione (83%) as a viscous oil, which crystallised from ether–light petroleum at −20 °C to give white crystals, m.p. 42—43 °C, $v_{max.}$ (CHCl$_3$) 1 730 and 1 710 cm^{-1}; δ (oil) 8.24 (:COH), 5.55—6.04 (m, CH:CH$_2$), 5.52 (CH:COH), 4.82—5.16 (m, :CH$_2$), and 1.2—2.8 (m, 11 H) [δ (crystals) 3.48 (COCH$_2$CO) indicates 70% dione form] (Found: C, 73.4; H, 9.0%; M^+, m/z 180.1155. C$_{11}$H$_{16}$O$_2$ requires C, 73.3; H, 8.9%; M, 180.1150).

3-*Acetoxy*-4-*pent*-4-*enylcyclohex*-2-*enone*　(17)　*and*　3-*Acetoxy*-6-*pent*-4-*enylcyclohex*-2-*enone* (16).—A 2 : 1 mixture of the enol acetates, b.p. 122—124 °C at 0.01 mmHg was prepared from 4-pent-4-enylcyclohexane-1,3-dione according to the general procedure described for the positional isomer (12). Chromatography on silica gel using 1 : 2 ether–light petroleum (b.p. 40—60 °C) as eluant gave the following. (i) The 4-pentenyl isomer (17) (eluted first) $v_{max.}$ (CHCl$_3$) 1 765, 1 675, and 1 660 cm^{-1}; δ 5.5—6.02 (m, CH:CH$_2$), 5.89 (:CHCO), 4.8—5.16 (m, :CH$_2$), 1.1—2.8 (m, 11 H), and 2.22 (OAc) (Found: M^+, m/z 222.1241. C$_{13}$H$_{18}$O$_3$ requires M, 222.1256). (ii) The 6-pentenyl isomer (16) (eluted second) $v_{max.}$ (CHCl$_3$) 1 760 and 1 660 cm^{-1}; δ 5.55—6.0 (m, CH:CH$_2$), 5.85 (:CHCO), 4.8—5.1 (m, :CH$_2$), 2.57 [t, J 5, CH$_2$C(OAc)], 1.2—2.4 (m, 9 H), and 2.22 (OAc) (Found: M^+, m/z 180.1173. M − C$_2$H$_2$O requires 180.1150).

7-*Acetoxytricyclo*[5.4.0.^{1,5}]*undecan*-11-*one* (18).—A solution of 3-acetoxy-2-pent-4-enylcyclohex-2-enone (2.2 g) in hexane (500 ml) was irradiated through Pyrex using a 450-W medium-pressure lamp for 1.75 h (g.l.c. monitoring). The solution was evaporated to dryness to leave the adduct (2.1 g) as a viscous oil which crystallised from light petroleum (b.p. 40—60 °C) as colourless crystals, m.p. 71—72 °C, $v_{max.}$ (CHCl$_3$) 1 720 and 1 690 cm^{-1}; δ 1.4—2.8 (m, 15 H) and 2.06 (OAc) (Found: C, 70.3; H, 8.3%; M^+, m/z 222.1236. C$_{13}$H$_{18}$O$_3$ requires C, 70.2; H, 8.2%, M, 222.1256).

Bicyclo[6.3.0]*undecane*-2,6-*dione* (20).—A solution of the photoadduct (18) (1.1 g) in 5% ethanolic potassium hydroxide solution (30 ml) was stirred at 0 °C for 2 h, and then poured into water (40 ml). The solution was acidified with dilute hydrochloric acid and then extracted with ether. Evaporation of the dried ether extracts left the crude dione (0.7 g, 78%) (>90% pure by g.l.c.) which was purified by chromatography on silica using ether as eluant (ca. 40% recovery). Crystallisation from ether–n-hexane gave the *trans*-dione as hexagonal plates, m.p. 64.5 °C, $v_{max.}$ (KBr) 1 695 cm^{-1}; δ 1.2—3.0 (m); δ$_C$ 214.4, 211.8, 56.2(d) 46.5(t), 44.5(d), 43.2(t), 43.0(t), 34.1(t),

29.4(t), 22.6(t), and 21.4(t) p.p.m. (Found: C, 73.0; H, 9.3%; M^+, m/z 222.1245. C$_{11}$H$_{16}$O$_2$ requires C, 73.3; H, 9.0%; M, 222.1256).

The same dione (mixed m.p. 63—65 °C, identical spectral data) was also obtained (ca. 65%) by cleavage of the photo-adduct (21), in the presence of methanol–sulphuric acid.

Irradiation of 3-*Acetoxy*-4-*pent*-4-*enylcyclohex*-2-*enone* (17). —The enol ester (1 g) was irradiated in a similar manner to that described for the isomer (16) (see below), and the crude mixture of photoproducts was worked up by the same procedure. 4-Pent-4-enylcyclohexane-1,3-dione (15) (0.4 g) was recovered from the sodium hydrogencarbonate washings, and 2-acetyl-4-pent-4-enylcyclohexane-1,4-dione (24) (0.33 g) was recovered from the sodium hydroxide washings.

Evaporation of the final, combined ether extracts left a residue (0.13 g) which showed two peaks (ratio 2 : 1) in g.l.c. analysis. The residue was chromatographed on silica using ether–light petroleum (b.p. 40—60 °C) (4 : 1) as eluant to give the following. (i) Mixed fractions (40 mg). (ii) Major product (44 mg) homogeneous in g.l.c. showing the following spectral data: $v_{max.}$ (CHCl$_3$) 1 695 cm^{-1}; δ 3.16—3.56 (m, OCH$_2$), 1.1—2.96 (m, 15 H), 1.16 (t, J 7, CH$_2$CH$_3$); m/z 208 (C$_{12}$H$_{20}$O$_2$), 179 (M^+ − Et), 153, and 148. These support the enol ether structure (29). (iii) Mixed fractions (6 mg). (iv) Minor product (25 mg), homogeneous in g.l.c. and showing the following spectral data: $v_{max.}$ (CHCl$_3$) 1 720 and 1 690 cm^{-1}; δ 1.2—3.3 (m); δ$_C$ 219.6, 2 184, 50.2(d), 47.4(d), 42.7(t), 42.4(t), 33.3(t), 32.1(t), 25.1(t), and 22.3(t) p.p.m.; m/z 180 (C$_{11}$H$_{16}$O$_2$) and 152 (M^+ − CO). These were consistent with the dione structure (27).
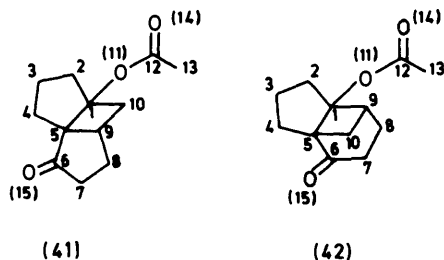
Irradiation of 3-*Acetoxy*-6-*pent*-4-*enylcyclohex*-2-*enone* (16). —A solution of the enol acetate (0.4 g) in n-hexane (350 ml) was irradiated through Pyrex using a 450-W medium-pressure lamp for 10 h; prolonged irradiation resulted in extensive decomposition (g.l.c. monitoring). The solution was evaporated to dryness, and the residue was then dissolved in 5% ethanolic potassium hydroxide (10 ml) at 0 °C. The solution was stirred at 0 °C for 2 h, and then diluted with water (20 ml), acidified with dilute hydrochloric acid, and thoroughly extracted with ether. The combined ether extracts were washed successively with saturated aqueous sodium hydrogencarbonate, 5% aqueous sodium hydroxide, and water, and then dried and evaporated. The residue (53 mg) exhibited a number of components in g.l.c. analysis, and was not further investigated.

The sodium hydrogencarbonate extracts were acidified with dilute hydrochloric acid, and the solution was extracted with ether. Evaporation of the dried ether extracts left 4-pent-4-enylcyclohexane-1,3-dione (15) (0.18 g), which was homogeneous in g.l.c. analysis, and showed spectral data identical with an authentic sample.

The sodium hydroxide extracts from above, were acidified with dilute hydrochloric acid, and the solution was extracted with ether. Evaporation of the dried ether extracts left 2-acetyl-4-pent-4-enylcyclohexane-1,3-dione (24) (80 mg) as an oil, $v_{max.}$ (film) 1 670 and 1 565 cm^{-1}; δ 5.68—6.14 (m, CH:CH$_2$), 4.96—5.25 (m, :CH$_2$), 3.65 (COCH$_3$), and 1.2—2.9 (m, 11 H) (Found: M^+, m/z 222.1249. C$_{13}$H$_{18}$O$_3$ requires M, 222.1255). The trione formed a blue amorphous copper complex, m.p. 98—100.5 °C on treatment with aqueous copper acetate.

1-*Acetoxy*-2-*pent*-4-*enoylcyclopentene* (39).—Addition of pent-4-enoyl chloride to the morpholine enamine derived from cyclopentanone, by the usual procedure, gave 2-pent-4-enoyl-cyclopentanone (25%), $v_{max.}$ (film) 1 740, 1 710, 1 650, and

Table 1. Fractional atomic co-ordinates for cycloadduct (41)

(41)　　　　　　　　(42)

Atom	x/a	y/b	z/c
C(1)	0.294 9(2)	0.392 8(3)	0.499 9(2)
C(2)	0.366 8(3)	0.273 6(5)	0.464 8(4)
C(3)	0.333 9(5)	0.100 5(5)	0.489 9(5)
C(4)	0.293 0(3)	0.115 4(4)	0.584 3(3)
C(5)	0.284 5(2)	0.300 6(3)	0.601 1(2)
C(6)	0.178 8(2)	0.367 0(3)	0.612 6(2)
C(7)	0.176 5(3)	0.552 8(4)	0.623 4(3)
C(8)	0.266 8(4)	0.647 6(4)	0.597 9(4)
C(9)	0.361 8(3)	0.533 3(4)	0.591 3(3)
C(10)	0.402 1(3)	0.400 5(5)	0.690 6(3)
O(11)	0.175 2(2)	0.429 5(2)	0.396 2(1)
C(12)	0.173 6(3)	0.538 4(4)	0.314 6(2)
C(13)	0.045 1(4)	0.566 8(6)	0.214 7(4)
O(14)	0.265 0(2)	0.603 0(3)	0.325 2(2)
O(15)	0.100 0(2)	0.280 0(3)	0.613 5(2)
H(2a)	0.448(4)	0.286(5)	0.512(3)
H(2b)	0.357(3)	0.282(4)	0.384(3)
H(3a)	0.406(4)	0.031(6)	0.514(4)
H(3b)	0.267(5)	0.073(6)	0.408(5)
H(4a)	0.355(3)	0.063(4)	0.664(3)
H(4b)	0.208(3)	0.069(4)	0.549(3)
H(7a)	0.194(3)	0.571(4)	0.709(3)
H(7b)	0.091(4)	0.584(5)	0.568(4)
H(8a)	0.313(3)	0.718(5)	0.666(3)
H(8b)	0.214(3)	0.712(4)	0.514(3)
H(9)	0.421(3)	0.589(4)	0.580(3)
H(10a)	0.409(3)	0.428(4)	0.768(3)
H(10b)	0.477(3)	0.342(4)	0.707(3)
H(13a)	0.043(4)	0.612(5)	0.152(4)
H(13b)	−0.008(4)	0.469(6)	0.193(4)
H(13c)	0.006(4)	0.625(6)	0.245(4)

Table 2. Fractional atomic co-ordinates for cycloadduct (42)

Atom	x/a	y/b	z/c
C(1)	0.294 9(2)	0.392 8(3)	0.499 9(2)
C(2)	0.366 8(3)	0.273 6(5)	0.464 8(4)
C(3)	0.333 9(5)	0.100 5(5)	0.489 9(5)
C(4)	0.293 0(3)	0.115 4(4)	0.584 3(3)
C(5)	0.284 5(2)	0.300 6(3)	0.601 1(2)
C(6)	0.178 8(2)	0.367 0(3)	0.612 6(2)
C(7)	0.176 5(3)	0.552 8(4)	0.623 4(3)
C(8)	0.266 8(4)	0.647 6(4)	0.597 9(4)
C(9)	0.361 8(3)	0.533 3(4)	0.591 3(3)
C(10)	0.402 1(3)	0.400 5(5)	0.690 6(3)
O(11)	0.175 2(2)	0.429 5(2)	0.396 2(1)
C(12)	0.173 6(3)	0.538 4(4)	0.314 6(2)
C(13)	0.045 1(4)	0.566 8(6)	0.214 7(4)
O(14)	0.265 0(2)	0.603 0(3)	0.325 2(2)
O(15)	0.100 0(2)	0.280 0(3)	0.613 5(2)
H(2a)	0.448(4)	0.286(5)	0.512(3)
H(2b)	0.357(3)	0.282(4)	0.384(3)
H(3a)	0.406(4)	0.031(6)	0.514(4)
H(3b)	0.267(5)	0.073(6)	0.408(5)
H(4a)	0.355(3)	0.063(4)	0.664(3)
H(4b)	0.208(3)	0.069(4)	0.549(3)
H(7a)	0.194(3)	0.571(4)	0.709(3)
H(7b)	0.091(4)	0.584(5)	0.568(4)
H(8a)	0.313(3)	0.718(5)	0.666(3)
H(8b)	0.214(3)	0.712(4)	0.514(3)
H(9)	0.421(3)	0.589(4)	0.580(3)
H(10a)	0.409(3)	0.428(4)	0.768(3)
H(10b)	0.477(3)	0.342(4)	0.707(3)
H(13a)	0.043(4)	0.612(5)	0.152(4)
H(13b)	−0.008(4)	0.469(6)	0.193(4)
H(13c)	0.006(4)	0.625(6)	0.245(4)

Table 3. Bond lengths in Å

Bond lengths	(41)	(42)
C(1)–C(2)	1.518(3)	1.514(4)
C(1)–C(5)	1.562(2)	1.534(3)
C(1)–C(9)		1.535(4)
C(1)–C(10)	1.530(3)	
C(1)–O(11)	1.446(2)	1.444(3)
C(2)–C(3)	1.524(3)	1.528(5)
C(3)–C(4)	1.521(3)	1.508(5)
C(4)–C(5)	1.512(2)	1.518(4)
C(5)–C(6)	1.505(3)	1.483(3)
C(5)–C(9)	1.547(2)	
C(5)–C(10)		1.557(4)
C(6)–C(7)	1.492(3)	1.504(5)
C(6)–O(15)	1.204(2)	1.204(3)
C(7)–C(8)	1.514(4)	1.510(5)
C(8)–C(9)	1.532(3)	1.526(5)
C(9)–C(10)	1.541(3)	1.531(5)
O(11)–C(12)	1.343(2)	1.344(3)
C(12)–C(13)	1.486(4)	1.483(5)
C(12)–O(14)	1.193(3)	1.190(3)

1 620 cm⁻¹; δ 5.59—6.04 (m, CH:CH₂), 4.86—5.18 (m, :CH₂), 3.4 (t, J ca. 6, COCHCO), and 1.7—3.14 (m, 10 H) after purification by chromatography on silica using ether–light petroleum (b.p. 40—60 °C) (2 : 3) as eluant. Acetylation of the dione, using acetic anhydride in the presence of toluene-*p*-sulphonic acid, gave the crude enol acetate, which was purified by chromatography on silica using ether–light petroleum (b.p. 60—80 °C) (1 : 1) as eluant. G.l.c. analysis (SE-30, 165 °C) of the acetate, $v_{max.}$ (film) 1 755, 1 715, and 1 640 cm⁻¹; δ 5.6— 6.08 (m, CH:CH₂), 4.88—5.2 (m, :CH₂), 1.7—3.06 (m, 10 H), and 2.26, 2.22 (OAc, two isomers) showed the presence of the two isomers (39) and (40) (R_F 12.6 and 13.9 min; 40 ml/min) in the ratio 2 : 1.

Irradiation of the Mixture of Enol Acetates (39) *and* (40) *derived from 2-Pent-4-enoylcyclopentanone* (38).—A solution of the 2 : 1 mixture of enol acetates (1 g) in n-hexane (500 ml) was irradiated through Pyrex using a 450-W medium-pressure lamp for 2.5 h. G.l.c. analysis (SE-30, 165 °C) after this time showed the formation of the photoproducts present in the ratio 2 : 3. The solution was evaporated to dryness to leave a residue (0.94 g) which was chromatographed on silica using ether–light petroleum (b.p. 40—60 °C) (1 : 2) as eluant to give

the following. (i) Mixed fractions (0.26 g). (ii) The cyclo-adduct (41) (0.14 g, 22%) (eluted second) which crystallised from light petroleum (b.p. 40—60 °C) as large colourless plates, m.p. 78—79 °C, $v_{max.}$ (KBr) 1 720 cm⁻¹; δ 2.03 (OAc), 1.15—2.98 (m, 13 H) (Found: M⁺, m/z 208.1115. C₁₂H₁₆O₃ requires M, 208.1099). (iii) A mixture of the two photoadducts (41) and (42) (0.23 g). (iv) The cycloadduct (42) (0.27 g, 45%) (eluted last), which crystallised from light petroleum (b.p. 40—60 °C) as small colourless crystals, m.p. 74—75 °C $v_{max.}$ (KBr) 1 725 and 1 705 cm⁻¹; δ 3.0—3.17 (m, 1 H), 2.04 (OAc), and 1.4—2.8 (m, 12 H) (Found: C, 69.5; H, 7.9%; M⁺, m/z 208.1119. C₁₂H₁₆O₃ requires C, 69.2; H, 7.7%).

Table 4. Bond angles in degrees

Bond angles	(41)	(42)
C(2)–C(1)–C(5)	105.4(1)	103.6(2)
C(2)–C(1)–C(9)		120.6(3)
C(2)–C(1)–C(10)	118.9(2)	
C(2)–C(1)–O(11)	112.2(2)	110.7(2)
C(5)–C(1)–C(9)		88.2(2)
C(5)–C(1)–C(10)	90.2(1)	
C(5)–C(1)–O(11)	111.8(1)	112.5(2)
C(9)–C(1)–O(11)		117.6(2)
C(10)–C(1)–O(11)	115.5(1)	
C(1)–C(2)–C(3)	105.5(2)	105.4(2)
C(2)–C(3)–C(4)	104.1(2)	108.4(3)
C(3)–C(4)–C(5)	103.8(2)	105.1(3)
C(1)–C(5)–C(4)	106.6(1)	108.7(2)
C(1)–C(5)–C(6)	114.9(1)	110.1(2)
C(1)–C(5)–C(9)	88.8(1)	
C(1)–C(5)–C(10)		85.5(2)
C(4)–C(5)–C(6)	118.4(1)	119.5(2)
C(4)–C(5)–C(9)	119.4(2)	
C(4)–C(5)–C(10)		120.3(3)
C(6)–C(5)–C(9)	105.2(1)	
C(6)–C(5)–C(10)		107.4(2)
C(5)–C(6)–C(7)	108.8(2)	115.1(2)
C(5)–C(6)–O(15)	125.1(2)	123.1(2)
C(7)–C(6)–O(15)	126.1(2)	121.8(3)
C(6)–C(7)–C(8)	104.2(2)	115.9(3)
C(7)–C(8)–C(9)	104.9(2)	112.0(3)
C(1)–C(9)–C(8)		109.8(2)
C(5)–C(9)–C(8)	105.9(2)	
C(1)–C(9)–C(10)		86.4(2)
C(6)–C(9)–C(10)	90.3(1)	
C(8)–C(9)–C(10)	117.4(2)	109.2(3)
C(1)–C(10)–C(9)	90.2(1)	
C(5)–C(10)–C(9)		87.5(2)
C(1)–O(11)–C(12)	116.8(1)	116.6(2)
O(11)–C(12)–C(13)	110.8(2)	110.9(3)
O(11)–C(12)–O(14)	123.5(2)	122.9(3)
C(13)–C(12)–O(14)	125.7(2)	126.2(3)

Treatment of the photoadducts (41) and (42) separately with 5% ethanolic potassium hydroxide, in the usual manner, led to bicyclo[6.3.0]undecane-1,6-dione (47) [$\nu_{max.}$ 1 725 and 1 705 cm^{-1}; m/z 166 $C_{10}H_{14}O_2$] and to the aldol (49) [m.p. 104—108 °C, $\nu_{max.}$ (CHCl$_3$) 3 450 and 1 720 cm^{-1}; δ 1—2.5 (m) (Found: C, 72.3; H, 9.0. $C_{10}H_{14}O_2$ requires C, 72.3; H, 8.4%); m/z 166.094] respectively.

Crystal Structure Determination of the Cycloadducts (41) *and* (42).—*Crystal data* (*a*) Cycloadduct (41). $C_{12}H_{16}O_3$, $M = 208.26$. Monoclinic $a = 12.002(3)$, $b = 8.338(2)$, $c = 11.253(3)$ Å, $\beta = 98.92(3)$ °, $U = 1112.5$ Å^3, $Z = 4$, $D_c = 1.24$ g cm^{-3}, $F(000) = 544$. Space group $P2_1/c$ uniquely from systematic absences. Mo-K_α radiation, $\lambda = 0.71069$ Å, μ (Mo-K_α) = 0.95 cm^{-1}. (*b*) Cycloadduct (42). $C_{12}H_{16}O_3$, $M = 208.26$. Monoclinic $a = 12.361(3)$, $b = 8.057(2)$, $c = 12.585(3)$ Å, $\beta = 119.34(3)°$, $U = 1092.6$ Å^3, $Z = 4$, $D_c = 1.27$ g cm^{-3}, $F(000) = 544$. Space group $P2_1/c$, μ (Mo-K_α) = 0.97 cm^{-1}.

Crystals of approximate dimensions 0.6 × 0.4 × 0.3 mm^3 (41) and 0.6 × 0.5 × 0.2 mm^3 (42) were 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 < 25°. Totals of 1 958 (41) and 1 927 (42) independent reflections were measured of which 1 533 (41) and 1 290 (42) had $I > 3\sigma(I)$ 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. Both structures were solved by direct methods using the MULTAN program. In each case 140 reflections with $E > 1.7$ were used and the E maps from the best sets of phases revealed the positions of all non-hydrogen atoms among the highest peaks in the map. These positions were refined initially isotropically and subsequently anisotropically. Difference maps revealed the positions of the hydrogen atoms. These were included in the refinements with isotropic vibrations. Refinement terminated at convergence with final R values of 0.045 (41) and 0.048 (42). Final atomic co-ordinates are listed in Tables 1 and 2 with bond lengths and angles in Tables 3 and 4. Temperature factors and observed and calculated structure factors are listed in supplementary publication No. 23626 (31 pp.).*

1-*Acetoxy-2-pent-4-enoylcyclohexene* (45).—Addition of pent-4-enoyl chloride (13.2 g) to the morpholine enamine derived from cyclohexanone, by the usual procedure, gave 2-pent-4-enoylcyclohexanone (45%), b.p. 80—90 °C at 0.05 mmHg, $\nu_{max.}$ (film) 1 595—1 620 cm^{-1}; δ 15.24 (OH), 5.5—6.06 (m, CH:CH$_2$), 4.8—5.2 (m, :CH$_2$), 2.1—2.84 (m, 8 H), and 1.45—1.9 (m, 4 H). Acetylation of the dione, using acetic anhydride in the presence of toluene-*p*-sulphonic acid, gave the crude acetate, which was purified by chromatography on silica using chloroform–methanol (97 : 3) as eluant. The acetate (59%) showed b.p. 96—106 °C at 0.3 mmHg, $\nu_{max.}$ (film) 1 750, 1 690, 1 660, and 1 645 cm^{-1}; δ 5.48—5.96 (m, CH:CH$_2$), 4.8—5.12 (m, :CH$_2$), 2.62 (t, J, CH_2COAc), 2.1—2.5 (m, 6 H), 2.18 (OAc), and 1.44—1.86 (m, 4 H); m/z 222 ($C_{13}H_{18}O_3$).

2-*Acetyl-2-pent-4-enoylcyclohexanone* (46).—A solution of 1-acetoxy-2-pent-4-enoylcyclohexene (0.6 g) in hexane (500 ml) was irradiated through Pyrex, using a 450-W medium-pressure lamp for 10 h (g.l.c. monitoring). The solution was evaporated to dryness, and the residue was chromatographed on silica using ether–light petroleum (b.p. 40—60 °C) (2 : 3) as eluant to give the following. (i) Unchanged starting material (0.25 g) (eluted first). (ii) The cyclohexanone (46) (0.15 g) (eluted second), $\nu_{max.}$ (CHCl$_3$) 1 720 and 1 700 cm^{-1}; δ 5.58—6.08 (m, CH:CH$_2$), 4.88—5.2 (m, :CH$_2$), 2—2.8 (m, 8 H), 2.19 (COCH_3), and 1.5—2.0 (m, 4 H); m/z 222. ($C_{13}H_{18}O_3$).

References

1 P. de Mayo, *Pure and Appl. Chem.*, 1964, **9**, 597; *Acc. Chem. Res.*, 1971, **4**, 41.
2 See ref. 1 and also: (*a*) S. W. Baldwin, R. E. Gawley, R. J. Doll, and K. H. Leung, *J. Org. Chem.*, 1975, **40**, 1865; (*b*) S. W. Baldwin and R. E. Gawley, *Tetrahedron Lett.*, 1975, 3969.
3 W. Oppolzer and T. Godel, *J. Am. Chem. Soc.*, 1978, **100**, 2583.
4 M. Mellor, D. A. Otieno, and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1978, 138.
5 (*a*) W. Oppolzer and T. G. C. Bird, *Helv. Chim. Acta*, 1979, **62**, 1199; (*b*) W. Oppolzer and S. C. Burford, *ibid.*, 1980, **63**, 788; (*c*) W. Oppolzer and R. D. Wylie, *ibid.*, 1980, **63**, 1198.
6 (*a*) M. Mellor and G. Pattenden, *Synthetic Commun.*, 1979, 1; (*b*) M. J. Begley, M. Mellor, and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1979, 235; (*c*) A. J. Barker and G. Pattenden,

Tetrahedron Lett., 1980, **21**, 3513; (*d*) A. M. Birch and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1980, 1195; (*e*) A. J. Barker and G. Pattenden, *Tetrahedron Lett.*, 1981, **22**, 2599.

7 A. J. Barker and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1885; A. J. Barker, M. J. Begley, M. Mellor, D. A. Otieno, and G. Pattenden, *ibid.*, 1983, 1893; A. J. Barker and G. Pattenden, *ibid.*, 1983, preceding paper.

8 Preliminary communication: see ref. 6*b*.

9 G. A. Cordell, *Phytochemistry*, 1974, **13**, 2343; J. S. Calderon, L. Quijano and T. Rios, *Chem. Ind. (London)*, 1978, 584.

10 See: ' Natural Products Chemistry,' ed. K. Nakanishi, T. Goto, S. Itô, S. Natori, and S. Nozoe, Academic Press, London and New York, 1975, vol. 1, p. 281.

11 See ref. 10, p. 115—127.

12 A. J. Birch, *J. Chem. Soc.*, 1947, 102; A. J. Birch and H. Smith, *ibid.*, 1951, 1882; E. Piers and J. R. Grierson, *J. Org. Chem.*, 1977, **42**, 3755.

13 *cf.* G. Mandville, F. Leyendecker, and J. M. Conia, *Bull. Soc. Chim. Fr.*, 1973, 963.

14 G. Stork and R. L. Danheiser, *J. Org. Chem.*, 1973, **38**, 1775.

15 T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, 1969, **34**, 509.

16 *Cf.* M. Umehara, T. Oda, Y. Ikebe, and S. Hishida, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1075.

17 Unpublished work. The *X*-ray data will be published separately at a later date.

18 K. D. Barrow, D. H. R. Barton, E. B. Chain, U. F. W. Ohnsorge, and R. P. Sharma, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1590.

19 E. Ayanoglu, T. Gebreyesus, C. M. Beechan, and C. Djerassi, *Tetrahedron*, 1979, **35**, 1035.

20 F. J. Schmitz, K. H. Hollenbeak, and D. J. Vanderah, *Tetrahedron*, 1978, **34**, 2719.

21 A. M. Birch and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1913.

22 C. Walling and A. Cioffari, *J. Am. Chem. Soc.*, 1972, **94**, 6059; R. Srinivasan and K. H. Carlough, *ibid.*, 1967, **89**, 4932; M. Julia, *Accounts Chem. Res.*, 1971, **4**, 386; A. L. J. Beckwith, *Tetrahedron*, 1981, **37**, 3073, and refs. cited therein.

23 For other examples see: A. J. Barker, J. S. H. Kueh, M. Mellor, D. A. Otieno, and G. Pattenden, *Tetrahedron Lett.*, 1979, 1881.