Synthesis of Substituted Aromatic Compounds by Diels–Alder Reactions of Alkoxycyclobutenes Produced *via* Photocycloadditions between Vinyl Ethers and 1,3-Dione Enol Esters

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The adduct (5) obtained from [2 + 2] photocycloaddition of ethyl vinyl ether to the 1,3-dione enol acetate (4) rapidly loses acetic acid producing the ethoxycyclobutene (7). On being warmed in the presence of a dienophile, the ethoxycyclobutene (7) undergoes electrocyclic ring-opening to give the ethoxydienone (8) followed by [4 + 2] cycloaddition to produce Diels–Alder adducts [*e.g.* (10) with dimethyl acetylenedicarboxylate] ; elimination of ethanol from (10) gives the dimethyl phthalate (11). In a 'one-pot' reaction, heating a solution of (5) with 1,4-naphthaquinone in xylene containing alumina leads to the substituted anthraquinone (12) in 95% yield.

On storage at 0 °C for a few days the ethoxycyclobutene (7) is converted into the crystalline dimer (9) *via* the transient ethoxydienone (8) ; the structure of (9) followed from X-ray measurements. An analogous dimer (14) was produced during attempts to effect an intramolecular Diels–Alder reaction from the bicyclic ether (13).

The past few years have witnessed an explosion of interest in synthetic applications of light-induced reactions.[1] Without doubt, the formation of four-membered rings by [2 + 2] photocycloaddition involving unsaturated molecules (C–C double and triple bonds, carbonyl groups, and oxygen) is one of the most useful photochemical methods—made more so in those instances where the inherent strain in the four-ring adduct can be relieved in a subsequent chemical reaction. A striking illustration of this type of reaction is the intramolecular de Mayo reaction which we[2] and others[3] have used recently to elaborate a range of ring systems found in natural terpenoids. To explore further the scope of [2 + 2] photocycloaddition followed by cleavage of the four-ring adducts as a stratagem in ring synthesis, we have investigated the chemistry of the [2 + 2] adducts [*viz.* (1)] produced from photocycloaddition of 1,3-dione enol acetates to vinyl ethers. In this paper we show that the adducts rather than undergoing ring cleavage to give 1,5-diones, instead suffer elimination to produce alkoxycyclobutenes [*viz.* (2)] which are useful precursors of 1-alkoxy substituted butadienes [*viz.* (3)] ;[4] Diels–Alder reaction of the latter with appropriate dienophiles provides a facile synthesis of substituted aromatic compounds (Scheme 1).

We first examined the photocycloaddition of ethyl vinyl ether to the enol acetate(4) derived from dimedone. In agreement with an earlier observation made by Cantrell *et al.*[5] using 3-acetoxycyclohex-2-enone, the addition was regioselective producing a mixture of isomers of the cycloadduct (5) in a combined yield of 67%. Attempts to separate and purify the isomers of (5) by chromatography met with limited success. In only one instance did we succeed in separating a single isomer, believed to be the *trans* ring fused isomer (6) (*cf.* ref. 4). The major *cis* ring-fused adduct (5) produced from (4), was found to undergo rapid elimination of acetic acid on standing or in the presence of chromatography supports leading to the ethoxycyclobutene (7). Although the ethoxycyclobutene (7) could be stored at −78 °C for periods of months, at 0 °C during a few days it was found to undergo dimerisation to the crystalline adduct (9). The dimer, whose structure was confirmed by X-ray measurements (see Figure), arises from Diels–Alder reaction of the ethoxydienone (8) obtained by conrotatory opening of (7).

Reaction of the ethoxycyclobutene (7), in hot toluene, in the presence of dimethyl acetylenedicarboxylate afforded an

Scheme 1.
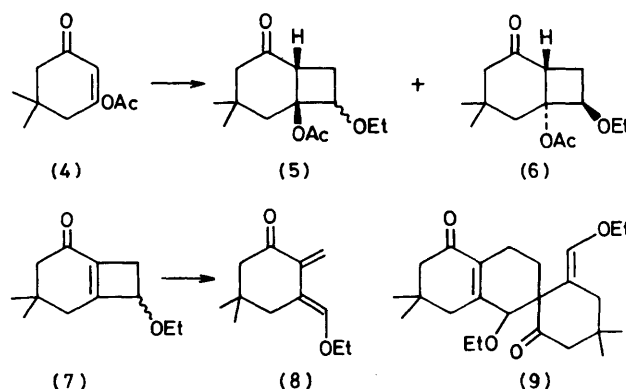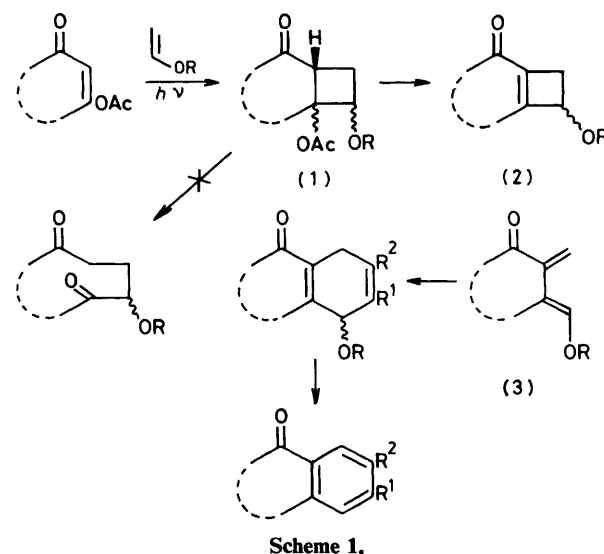
excellent yield (*ca.* 88%) of the oily cycloadduct (10), which eliminated ethanol in the presence of toluene-*p*-sulphonic acid to give the substituted dimethyl phthalate (11). In the case of a Diels–Alder reaction between the diene (8) and 1,4-naphthoquinone we found that it was necessary only to heat the
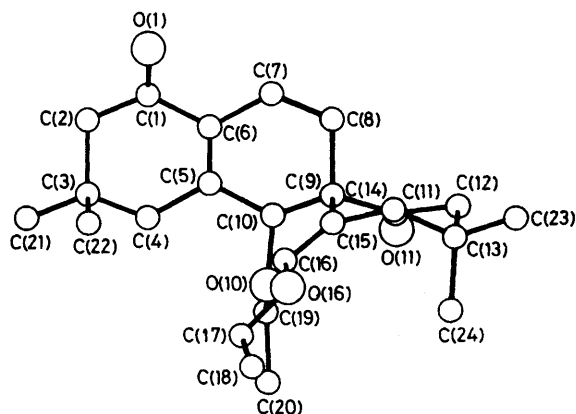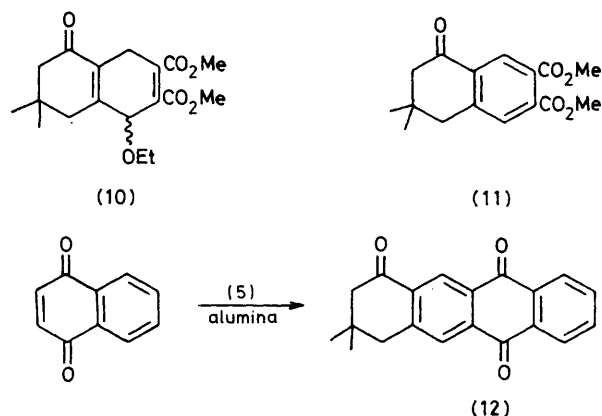
Figure. Crystal structure of the dimer (9)

(10)

(11)

(12)

(13)

(14)

(15)

(16)

(17)

(18)

(19)

photoadduct (5) and 1,4-naphthoquinone in xylene in the presence of basic alumina in order to obtain high yields of the yellow crystalline anthraquinone (12).

We next investigated the possibility of effecting the above Diels–Alder reaction in an intramolecular sense using the mixture of isomers of (13) obtained by photocycloaddition of (4) to the ethyl vinyl ether derived from pent-4-enol. Although a range of reaction conditions (*i.e.* different bases and reaction temperatures) were examined, the only product obtained from this study was the intermolecular dimer (14); we were unable to obtain any evidence for the co-formation of the product expected from intramolecular cycloaddition. Attempts to effect intramolecular [4 + 2] cycloaddition from the adduct (15) produced from the enol acetate (4) and citronellal ether were also unsuccessful.

In separate investigations, we synthesised the two tricyclic ethers (16) and (17) from 1-methoxycyclopent-1-ene and dihydropyran respectively, by photocycloaddition to the enol acetate (4). These photoadducts like (5) also resisted attempts to fragment them to cyclo-octane-1,5-diones, and under a range of conditions instead eliminated acetic acid to produce the corresponding alkoxycyclobutenes (18) and (19) respectively. Not surprisingly, the almost impossible steric demands imposed on the transition states leading to electrocyclic ring opening in (18) and (19) precluded the use of these molecules as precursors for 1,3-dienes in Diels–Alder reactions.

Experimental

For general experimental details see previous papers.[2,6]

6-Acetoxy-7-ethoxy-4,4-dimethylbicyclo[4.2.0]*octan-2-one* (5).—A solution of 3-acetoxy-5,5-dimethylcyclohex-2-enone
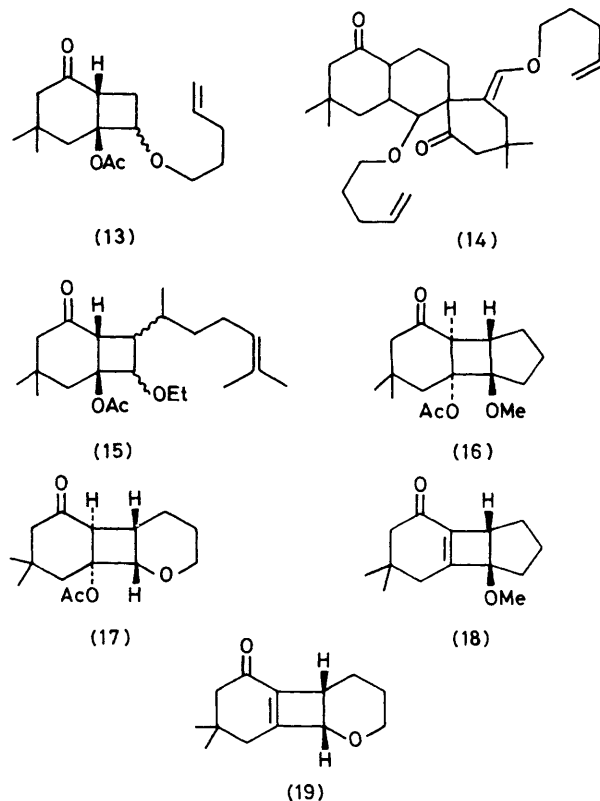
(2 g)[6] and ethyl vinyl ether (30 ml) in n-hexane (100 ml) was purged with nitrogen, and then irradiated at 0 °C (ice bath) through Pyrex with a 100-W medium-pressure mercury lamp for 7 h (g.l.c. monitoring on 10% SE-30 at 180 °C). The solution was evaporated at 25 °C under reduced pressure and the residue was immediately chromatographed on alumina using chloroform as eluant to give the bicyclo-octanone (1.87 g, 67%) as a mixture of isomers which showed $\nu_{max.}$ (film) 1 735 and 1 700 cm^{-1}; δ 4.09 (apparent t, *J ca.* 7, C*H*OEt), 3.6 and 3.54 (q, *J* 8, OC*H*$_2$CH$_3$ isomers), 3.14—1.85 (m, 3 H), 1.99 (OAc), 1.75—1.37 (m, 2 H), 1.23 and 1.18 (t, *J* 8, OCH$_2$C*H*$_3$ isomers), 1.12, 1.08, 1.05, 0.93 (CMe, isomers); *m/z* 254, (C$_{14}$H$_{22}$O$_4$). Distillation of a portion of the bicyclo-octanone gave the *trans*-isomer (6) b.p. 100—110 °C at 0.6 mmHg, δ 4.1 (apparent t, *J* 8, C*H*OEt), 3.96—3.3 (m, 2 H), 3.57 (q, *J* 8, OC*H*$_2$CH$_3$), 2.95—2.0 (m, 3 H), 2.01 (OAc), 1.81—1.46 (m, 2 H), 1.2 (t, *J* 8, OCH$_2$C*H*$_3$), 1.09 (CMe), and 0.95 (CMe); *m/z* 254.

7-Ethoxy-4,4-dimethylbicyclo[4.2.0]*oct-*1(6)*-en-2-one* (7).— A solution of 6-acetoxy-7-ethoxy-4,4-dimethylbicyclo[4.2.0]-octan-2-one (1 g) in chloroform (100 ml) was shaken at 25 °C for 3 h in the presence of basic alumina. The mixture was filtered and the filtrate was then evaporated under reduced pressure to leave a pale yellow oil. Chromatography on alumina using chloroform as eluant then gave the bicyclo-octenone (0.55 g, 71%) as an unstable oil showing, $\lambda_{max.}$ (EtOH) 242 nm; $\nu_{max.}$ (film) 1 680 and 1 650 cm^{-1}; δ 3.62 (t, *J* 6, C*H*OEt), 3.53 (q, *J* 8, OC*H*$_2$CH$_3$), 2.59—1.9 (m, 6 H), 1.2 (t, *J* 8, OCH$_2$C*H*$_3$), 1.04 (CMe), and 1.01 (CMe). The same bicyclo-octenone, in varying forms of purity, was also obtained during lengthy chromatographic purification of the bicyclo-octan-2-one (5), and after warming solutions of (5) in benzene at 80 °C for a few minutes.

Dimer (9) *of 3-Ethoxymethylene-5,5-dimethyl-2-methylene-cyclohexanone* (8).—The dimer was obtained by the following methods: (*a*) prolonged storage (*ca.* 1 week) of the bicyclo-octan-2-one (5) at 0 °C; (*b*) warming solutions of either the bicyclo-octan-2-one (5) or the bicyclo-octenone (7) in light petroleum (b.p. 60—80 °C) for 3 h. The dimer recrystallised from n-hexane–toluene (30 : 1) [60% overall yield from (5)] as colourless crystals, m.p. 148—149 °C, $\lambda_{max.}$ (EtOH) 249 nm (5 100); $\nu_{max.}$ (KBr) 1 760, 1 665, and 1 635 cm⁻¹; δ 5.85 (C*H*OEt), 4.41 (C*H*OEt), 3.58 (q, *J* 7.5, OC*H₂*CH₃), 2.63—1.85 (m, 12 H), 1.14 (t, *J* 7.5, OCH₂C*H₃*), 1.1 (t, *J* 7.5, OCH₂C*H₃*), 1.04 (CMe), 1.02 (2 × CMe), and 0.9 (CMe); δ_C 212.5, 199.0, 154.4, 144.4(d), 129.8, 110.5, 78.4(t), 69.1(t), 67.0(t), 57.3, 52.0(t), 51.1(t), 40.8(t), 34.6(t), 33.0, 30.1, 28.9, 28.7, 27.9, 26.5, 19.7(q), 15.8(q), 15.8(q), and 15.4(q) p.p.m. (Found: C, 74.2; H, 9.6. $C_{24}H_{36}O_4$ requires C, 74.2; H, 9.3%).

Crystal Structure Determination of the Dimer (9).—*Crystal data.* $C_{24}H_{36}O_4$, *M* = 388.6. Monoclinic *a* = 16.232(3), *b* = 13.588(3), *c* = 21.055(4) Å, β = 94.22(2)°, *U* = 4 631.3 Å³, *Z* = 8, D_c = 1.11 g cm⁻³, *F*(000) = 1 696. Space group *C2/c* from systematic absences and subsequent refinement. Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 0.80 cm⁻¹.

A crystal of approximate dimensions 0.5 × 0.35 × 0.2 mm³ was mounted on a Hilger Y290 four-circle 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°. A total of 4 095 independent reflections was measured of which 2 202 had *I* ≥ 3σ(*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. 280 Reflections with *E* > 1.76 were used and the *E* map from the best set of phases revealed the positions of all non-hydrogen atoms as 28 of the 30 highest peaks in the map. These positions were refined initially isotropically and subsequently anisotropically. A difference map revealed the approximate positions of all hydrogen atoms. Accurate positions of hydrogen atoms were then calculated from bond length and angle considerations. They were then included in structure factor calculations with isotropic temperature factors but without refinement. Refinement terminated at *R* 0.060 with maximum δ/σ 0.05. A final difference map showed no features in excess of 0.2 e Å⁻³. Final atomic co-ordinates are listed in Table 1 with bond lengths and angles in Tables 2 and 3. These values are unexceptional with the possible exception of the carbon–carbon bond lengths of the terminal ethyl groups which have been foreshortened by large thermal vibrations. The cyclohexenone ring has the double bonds twisted 10° out of conjugation about the C(1)⁻C(6) bond. Temperature factors and observed and calculated structure factors are listed in supplementary publication No. 23627 (25 pp.).

2,3-Bis(methoxycarbonyl)-7,7-dimethyl-5,6,7,8-tetrahydro-naphthalen-5-one (11).—A solution of 7-ethoxy-4,4-dimethyl-bicyclo[4.2.0]oct-1(6)-en-2-one (0.39 g) and dimethyl acetylenedicarboxylate (0.29 g) in dry toluene (12 ml) was heated under reflux for 3 h, and then evaporated to dryness under reduced pressure. Distillation of the residue then gave the cycloadduct (10) (0.59 g, 88%) as a pale yellow liquid, b.p. 85—90 °C at 0.04 mmHg, $\lambda_{max.}$ (EtOH) 210(5 900), 215(6 300), and 224 nm (5 300); $\nu_{max.}$ (film) 1 725, 1 700, and 1 630 cm⁻¹; δ 4.05 (q, *J* 7, OC*H₂*CH₃), 3.82 (2 × OMe), 3.91—3.27 (m, 3 H), 2.9—1.49 (m, 2 H), 1.99 (CH₂CO), 1.19 (t, *J* 7, OCH₂-C*H₃*), 1.1(CMe), and 0.94(CMe); δ_C 209.5, 197.4, 194.9,

Table 1. Fractional atomic co-ordinates for dimer (9)

Atom	*x/a*	*y/b*	*z/c*
C(1)	0.009 4(2)	0.229 3(3)	0.040 1(2)
C(2)	0.026 6(2)	0.124 6(3)	0.056 5(2)
C(3)	0.086 5(2)	0.115 3(3)	0.115 4(2)
C(4)	0.166 0(2)	0.172 0(3)	0.103 6(2)
C(5)	0.151 6(2)	0.272 5(3)	0.075 3(2)
C(6)	0.079 0(2)	0.299 5(3)	0.045 7(2)
C(7)	0.061 9(2)	0.399 9(3)	0.019 1(2)
C(8)	0.139 8(2)	0.458 6(3)	0.012 6(2)
C(9)	0.199 6(2)	0.451 1(3)	0.073 4(2)
C(10)	0.225 2(2)	0.342 7(3)	0.078 8(2)
C(11)	0.273 5(2)	0.515 2(3)	0.059 7(2)
C(12)	0.262 8(2)	0.624 7(3)	0.062 3(2)
C(13)	0.224 4(2)	0.660 8(3)	0.122 6(2)
C(14)	0.144 2(2)	0.602 0(3)	0.128 8(2)
C(15)	0.159 9(2)	0.493 3(3)	0.130 8(2)
C(16)	0.146 9(2)	0.437 9(3)	0.181 8(2)
C(17)	0.118 3(4)	0.417 8(4)	0.288 1(2)
C(18)	0.094 4(4)	0.467 0(5)	0.342 5(2)
C(19)	0.355 6(3)	0.280 0(4)	0.123 8(2)
C(20)	0.407 8(3)	0.279 2(6)	0.183 2(3)
C(21)	0.108 4(3)	0.007 2(3)	0.127 1(3)
C(22)	0.047 7(3)	0.157 6(4)	0.173 3(2)
C(23)	0.204 1(3)	0.769 5(3)	0.115 7(2)
C(24)	0.284 1(3)	0.644 4(3)	0.180 8(2)
O(1)	−0.059 4(2)	0.258 7(2)	0.021 3(2)
O(10)	0.278 7(1)	0.326 8(2)	0.134 6(1)
O(11)	0.336 7(2)	0.479 0(2)	0.043 4(2)
O(16)	0.115 1(2)	0.477 8(2)	0.233 6(1)
H(2a)	−0.0270	0.0894	0.0646
H(2b)	0.0506	0.0899	0.0195
H(4a)	0.2009	0.1771	0.1452
H(4b)	0.1988	0.1312	0.0734
H(7a)	0.0258	0.4372	0.0490
H(7b)	0.0289	0.3944	−0.0232
H(8a)	0.1265	0.5294	0.0032
H(8b)	0.1688	0.4311	−0.0249
H(10)	0.2607	0.3245	0.0428
H(12a)	0.3180	0.6580	0.0596
H(12b)	0.2257	0.6468	0.0239
H(14a)	0.1179	0.6236	0.1688
H(14b)	0.1032	0.6187	0.0913
H(16)	0.1609	0.3638	0.1815
H(17a)	0.1761	0.3881	0.2953
H(17b)	0.0796	0.3578	0.2785
H(18a)	0.0975	0.4231	0.3818
H(18b)	0.1338	0.5246	0.3531
H(18c)	0.0373	0.4942	0.3363
H(19a)	0.3858	0.3158	0.0890
H(19b)	0.3472	0.2095	0.1074
H(20a)	0.4623	0.2496	0.1819
H(20b)	0.4158	0.3512	0.2001
H(20c)	0.3772	0.2448	0.2185
H(21a)	0.0582	−0.0330	0.1340
H(21b)	0.1496	−0.0007	0.1643
H(21c)	0.1343	−0.0214	0.0880
H(22a)	−0.0055	0.1222	0.1809
H(22b)	0.0862	0.1508	0.2127
H(22c)	0.0343	0.2298	0.1670
H(23a)	0.2554	0.8103	0.1111
H(23b)	0.1759	0.7953	0.1533
H(23c)	0.1653	0.7821	0.0761
H(24a)	0.3375	0.6816	0.1772
H(24b)	0.2595	0.6675	0.2211
H(24c)	0.2984	0.5723	0.1867

169.4, 86.9; 77.1(q), 65.7, 53.4, 51.2(t), 42.3(d), 36.5(t), 34.0, 31.5(q), 28.5(t), 26.5(q), 21.9(q), and 15.4(q) p.p.m.; *m/z* 290 (*M⁺* − EtOH).

A solution of the cycloadduct (0.2 g) (from above) in

Table 2. Bond lengths in Å for dimer (9)

C(1)–C(2)	1.487(5)	C(9)–C(15)	1.523(5)
C(1)–C(6)	1.477(5)	C(10)–O(10)	1.425(4)
C(1)–O(1)	1.223(4)	C(11)–C(12)	1.500(6)
C(2)–C(3)	1.524(6)	C(11)–O(11)	1.210(4)
C(3)–C(4)	1.538(5)	C(12)–C(13)	1.534(5)
C(3)–C(21)	1.528(6)	C(13)–C(14)	1.541(5)
C(3)–C(22)	1.526(6)	C(13)–C(23)	1.519(6)
C(4)–C(5)	1.501(5)	C(13)–C(24)	1.521(6)
C(5)–C(6)	1.342(5)	C(14)–C(15)	1.499(5)
C(5)–C(10)	1.526(5)	C(15)–C(16)	1.341(5)
C(6)–C(7)	1.493(5)	C(16)–O(16)	1.354(4)
C(7)–C(8)	1.510(5)	C(17)–C(18)	1.405(7)
C(8)–C(9)	1.553(5)	C(17)–O(16)	1.407(5)
C(9)–C(10)	1.533(5)	C(19)–C(20)	1.458(7)
C(9)–C(11)	1.528(5)	C(19)–O(10)	1.434(5)

Table 3. Bond angles in degrees for dimer (9)

C(2)–C(1)–C(6)	118.0(3)	C(11)–C(9)–C(15)	108.7(3)
C(2)–C(1)–O(1)	122.6(3)	C(5)–C(10)–C(9)	113.0(3)
C(6)–C(1)–O(1)	119.4(4)	C(5)–C(10)–O(10)	111.9(3)
C(1)–C(2)–C(3)	111.5(3)	C(9)–C(10)–O(10)	110.6(3)
C(2)–C(3)–C(4)	108.7(3)	C(9)–C(11)–C(12)	117.6(3)
C(2)–C(3)–C(21)	109.7(4)	C(9)–C(11)–O(11)	121.0(4)
C(2)–C(3)–C(22)	110.0(3)	C(12)–C(11)–O(11)	121.2(4)
C(4)–C(3)–C(21)	108.7(3)	C(11)–C(12)–C(13)	113.8(3)
C(4)–C(3)–C(22)	110.0(3)	C(12)–C(13)–C(14)	107.6(3)
C(21)–C(3)–C(22)	109.8(4)	C(12)–C(13)–C(23)	100.3(4)
C(3)–C(4)–C(5)	114.3(3)	C(12)–C(13)–C(24)	100.3(4)
C(4)–C(5)–C(6)	122.6(3)	C(14)–C(13)–C(23)	109.5(3)
C(4)–C(5)–C(10)	116.8(3)	C(14)–C(13)–C(24)	110.3(3)
C(6)–C(5)–C(10)	120.6(3)	C(23)–C(13)–C(24)	109.9(3)
C(1)–C(6)–C(5)	120.1(3)	C(13)–C(14)–C(15)	111.7(3)
C(1)–C(6)–C(7)	116.1(3)	C(9)–C(15)–C(14)	115.4(3)
C(5)–C(6)–C(7)	123.8(3)	C(9)–C(15)–C(16)	121.7(3)
C(6)–C(7)–C(8)	112.5(3)	C(14)–C(15)–C(16)	122.7(3)
C(7)–C(8)–C(9)	111.5(3)	C(15)–C(16)–O(16)	120.8(4)
C(8)–C(9)–C(10)	105.9(3)	C(18)–C(17)–O(16)	113.1(5)
C(8)–C(9)–C(11)	104.9(3)	C(20)–C(19)–O(10)	108.9(4)
C(8)–C(9)–C(15)	110.8(3)	C(10)–O(10)–C(19)	114.9(3)
C(10)–C(9)–C(11)	110.5(3)	C(16)–O(16)–C(17)	115.6(3)
C(10)–C(9)–C(15)	115.5(3)		

toluene (5 ml) was heated under reflux for 2 h in the presence of toluene-*p*-sulphonic acid (1 mg). The solution was cooled to 25 °C washed with aqueous sodium carbonate (2 × 2 ml) and then dried and evaporated. Distillation of the residue gave the naphthalenone (0.13 g, 76%) as a pale yellow viscous oil, b.p. 145—148 °C at 0.45 mmHg; $\lambda_{max.}$ (EtOH) 249 and 297 nm; $\nu_{max.}$ (film) 1 730, 1 690, and 1 605 cm^{-1}; δ 8.26 (:CH). 7.41 (:CH), 3.87 (2 × O*Me*), 2.9 (CH$_2$CO), 2.5 (ArCH$_2$), and 1.1 (CMe$_2$); *m/z* 290, C$_{16}$H$_{18}$O$_5$.

8,8-*Dimethyl*-7,8,9,12-*tetrahydronaphthacene*-5,10,12-*trione* (12).—A solution of 6-acetoxy-4,4-dimethyl-7-ethoxybicyclo-[4.2.0]octan-2-one (0.5 g) and 1,4-naphthoquinone (0.8 g) in xylene (20 ml) was heated under reflux for 3.5 h in the presence of suspended basic alumina (0.1 g; Brockmann Grade I). The cooled mixture was filtered, and the filtrate was then evaporated to dryness under reduced pressure. Chromatography of the residue on silica using chloroform as eluant then gave the quinone (0.59 g, 95%) as an amorphous solid which crystallised from toluene–ethyl acetate (4 : 1) as pale yellow needles, m.p. 217—218 °C, $\lambda_{max.}$ (EtOH) 221, 265, and 328 nm; $\nu_{max.}$ (KBr) 1 690, 1 675, and 1 585 cm^{-1}; δ 8.76 (:CH), 8.27—8.09 (m, 2 × :CH), 7.81—7.55 (m, 2 × :CH), 8.05 (:CH), 2.98 (CH$_2$), 2.56 (CH$_2$), and 1.12 (CMe$_2$); δ$_C$ 196.7, 182.5, 181.8, 148.2, 135.9(d), 135.6(d), 134.4(d), 134.1(d), 133.5, 133.3, 131.9(d), 128.5, 127.3, 127.2, 126.4, 52.3(t), 43.8(t), 33.5, and 28.2(q) p.p.m. (Found: C, 78.7; H, 5.4%; *M*$^+$, *m/z* 304.1082. C$_{20}$H$_{16}$O$_3$ requires C, 78.9; H, 5.3%; *M*, 304.1099).

Dimer (14).—The dimer was prepared from 3-acetoxy-5,5-dimethylcyclohex-2-enone and pent-4-enyl ether[7] in a manner identical to that described for the analogue (9). Irradiation of the cyclohexanone (4) in the presence of pent-4-enyl ether gave (*ca.* 58%) a mixture of isomers of the photoadduct (13) [$\nu_{max.}$ 1 730, 1 700, and 1 630 cm^{-1}; δ 6.0—5.5 (m, C*H*:CH$_2$), 5.12— 4.83 (m, CH$_2$), 4.3—3.85 (CH–O), 3.7—3.1 (m, 3 H), 2.75— 1.82 (m, *ca.* 5 H) 2.03 (OAc), 1.66—1.41 (m, *ca.* 9 H), 1.07 (CMe), *ca.* 0.95 (CMe)] which on warming in light petroleum (b.p. 40—60 °C) preferably in the presence of KOBu^t or DBN) produced the dimer [*ca.* 70% overall from (13)] as a colourless oil, $\lambda_{max.}$ (EtOH) 239 nm; $\nu_{max.}$ (film) 1 705 and 1 665 cm^{-1}; δ 6.04 (:CHO), 6.0—5.5 (m, 2 × C*H*:CH$_2$), 5.1—4.85 (m, 2 × CH$_2$), 4.6 (CHO), 3.77—3.53 (m, 2 × OC*H*$_2$), 2.73—1.89 (m, *ca.* 6 H), 1.09 (CMe), 1.07 (2 × CMe), and 0.93 (CMe); *M*$^+$ not observed.

2-*Methoxy*-10,10-*dimethyltricyclo*[5.4.0.0$^{2.6}$]*undec*-1-*en*-8-*one* (18).—A solution of 3-acetoxy-5,5-dimethylcyclohex-2-

enone (2.5 g) and 1-methoxycyclopent-1-ene (23 g)[8] in n-hexane (100 ml) was irradiated through Pyrex with a 100-W medium-pressure mercury lamp for 5 h (g.l.c. monitoring on 10% SE-30 at 190 °C). After this period of time g.l.c. analysis indicated the formation of two photoproducts in the ratio 1 : 1.3. The solution was evaporated to dryness under reduced pressure to leave a yellow semisolid. Crystallisation from light petroleum (b.p. 40—60 °C) at −40 °C gave 1-acetoxy-2-methoxy-10,10-dimethyltricyclo[5.4.0.0$^{2.6}$]undecan-8-one (0.94 g, 26%) (minor photoproduct of unknown stereochemistry, but presumed *cis, anti, cis*), as colourless crystals, m.p. 95—96 °C, $\lambda_{max.}$ (EtOH) 280 nm; $\nu_{max.}$ (KBr) 1 730 and 1 700 cm^{-1}; δ 3.34 (OMe), 2.42—2.15 (m, 6 H), 2.04 (OAc), 1.96—1.66 (m, 6 H), 1.09 (CMe), and 0.95 (CMe); δ$_C$ 210.2, 169.2, 91.3, 85.1, 52.3(t), 51.9(t), 48.1(d), 45.0(d), 36.9(t), 33.5, 31.4, 31.1, 29.4, 26.8(q), 25.5(q), and 21.7(q) p.p.m. (Found: C, 68.5; H, 8.7. C$_{16}$H$_{24}$O$_4$ requires C, 68.5; H, 8.6%).

Evaporation of the light petroleum solution remaining after the crystallisation left the undec-1-en-8-one as a pale yellow liquid (1.07 g, 34%) (major photoproduct) (95% pure) showing $\lambda_{max.}$ (EtOH) 240 nm; $\nu_{max.}$ (film) 1 680 and 1 640 cm^{-1}; δ 3.4 (OMe), 2.4—1.36 (m, 11 H) 1.15 (CMe), and 1.08 (CMe); δ$_C$ 195.3, 168.4, 138.5, 94.1, 54.0, 52.8, 48.4, 37.3, 36.8, 30.4, 29.1, 28.8, 24.7, 23.7 p.p.m.; *m/z* 220, C$_{14}$H$_{20}$O$_2$.

11,11-*Dimethyl*-6-*oxatricyclo*[6.4.0.0$^{2.7}$]*dodec*-1-*en*-9-*one* (19).—A solution of 3-acetoxy-5,5-dimethylcyclohex-2-enone (1 g) and dihydropyran (25 ml) in n-hexane (100 ml) was irradiated through Pyrex with a 100-W medium-pressure mercury lamp for 7 h (g.l.c. monitoring, 10% SE-30, 170 °C). The solution was evaporated under reduced pressure to leave a residue which was chromatographed on silica using chloroform as eluant to give 1-acetoxy-11,11-dimethyl-6-oxatricyclo-[6.4.0.0$^{2.7}$]dodecan-9-one (1.2 g, 96%) as a colourless oil of unknown stereochemistry (but presumed *cis, anti, cis*), $\nu_{max.}$ (film) 1 735 and 1 700 cm^{-1}; δ 4.03 (d, *J* 6, CHO), 3.81 (m, 2 H), 3.0—3.2 (m, 2 H), 2.53—1.15 (m, 8 H), 1.93 (OAc), 1.04 (CMe), and 0.94 (CMe) (Found: *M*$^+$, *m/z* 266.1527; C$_{15}$H$_{22}$O$_4$ requires *M*, 266.1518).

A solution of the photoadduct (0.1 g) (from above) in

benzene (10 ml) was stirred at 25 °C for 12 h in the presence of potassium t-butoxide (0.1 g). The mixture was diluted with water (5 ml) and then extracted with ether. Evaporation of the combined organic extracts left a yellow gum which was chromatographed on silica using 2 : 1 ether–light petroleum (b.p. 30—40 °C) as eluant to give the tricyclic ether (0.4 g, 55%) as a pale yellow liquid, $\lambda_{max.}$ (EtOH) 238 nm; $\nu_{max.}$ (film) 1 685 cm^{-1}; δ 4.48 (d, J 10, CHO), 3.67 (dt, J 3 and 15, CH$_2$O), 3.26—3.04 (m, 1 H), 2.16 (4 H), 2.13—1.33 (m, 2 H), 1.11 (CMe), and 1.08 (CMe) (Found: M^+, m/z 206.1317. C$_{13}$H$_{18}$O$_2$ requires M, 206.1307).

Acknowledgements

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