

Photochemical Transformations. Part 10.¹ Photocycloaddition Reactions of 4-Hydroxycoumarin with Cycloalkenes

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Irradiation of 4-hydroxycoumarin in the presence of an excess of cyclohexene leads to the cyclobutane adduct, 6a,6b,7,8,9,10,10a,10b-octahydro-10b-hydroxybenzo[3,4]cyclobuta[1,2-c]chromen-6-one, in high yield. Analogous additions occur with cyclopentene, cycloheptene, cyclo-octene, norbornene, and 2,3-dimethylbut-2-ene. On treatment with triethylamine in methanol, the cyclohexene adduct is converted into methyl 2-*o*-hydroxybenzoyl-cyclohexylacetate and not the desired oxocin.

THE [$\pi 2 + \pi 2$] photocycloaddition of enolised β -dicarbonyl compounds to alkenes has been widely used in organic synthesis;² the cyclobutanol derivatives thus formed readily undergo retro-aldol cleavage, a reaction sequence which in the case of cyclic β -diketones leads to ring expansion.³ Earlier studies have been principally concerned with aliphatic and alicyclic β -dicarbonyl compounds and their derived enol ethers and esters. For some time now, we have been concerned with the extension of this reaction to heterocyclic systems with a view to developing a novel synthesis of medium-sized ring heterocycles.

4-Hydroxycoumarin exists in solution as the enol tautomer (1) and thus provides a readily available model

¹ For Part 9, see J. S. Cridland, P. J. Moles, S. T. Reid, and K. T. Taylor, *Tetrahedron Letters*, 1976, 4497.

² P. de Mayo, *Accounts Chem. Research*, 1971, 4, 41.

³ B. D. Challand, H. Hikino, G. Kornis, G. Lange, and P. de Mayo, *J. Org. Chem.*, 1969, 34, 794.

⁴ R. Anet, *Canad. J. Chem.*, 1962, 40, 1249; G. O. Schenck, I. von Wiluchi, and C. H. Krauch, *Chem. Ber.*, 1962, 95, 1409; G. S. Hammond, C. A. Stout, and A. A. Lamola, *J. Amer. Chem. Soc.*, 1964, 86, 3103; H. Morrison, H. Curtis, and T. McDonnell, *J. Amer. Chem. Soc.*, 1966, 88, 5415; C. H. Krauch, S. Farid, and G. O. Schenck, *Chem. Ber.*, 1966, 99, 625.

for this investigation. Coumarin itself has been reported to form photodimers⁴ and alkene cycloaddition products⁵ on both direct and sensitised irradiation. The sensitised photodimerisation of 3-chlorocoumarin has also been described,⁶ as have the photodimerisation and alkene photoaddition reactions of 3-acetylcoumarin.⁷

4-Hydroxycoumarin is not readily soluble in alkenes and the cycloadditions were therefore carried out in *t*-butyl alcohol-alkene mixtures using a *ca.* 40-fold molar excess of alkene. Methanol-alkene mixtures were used in our preliminary investigation,⁸ but the use of *t*-butyl alcohol is now preferred to minimise competing reactions arising by hydrogen abstraction from the solvent. Pyrex-filtered irradiation of a 0.25M-solution of 4-hydroxycoumarin in *t*-butyl alcohol-cyclohexene gave, on removal of the solvent, a crystalline product in 67%

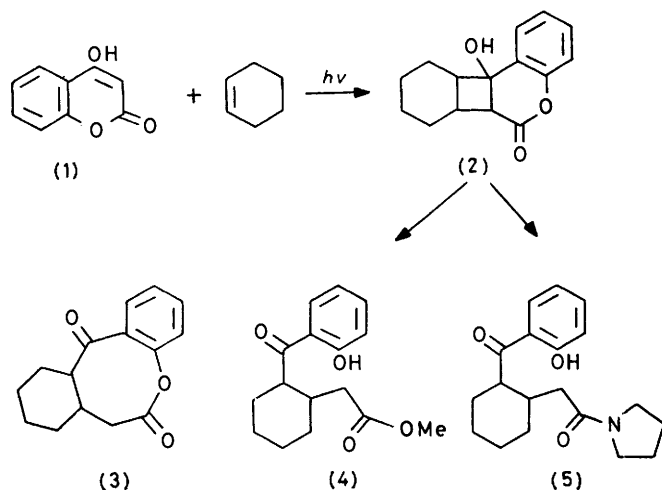
⁵ J. W. Hanifin and E. Cohen, *Tetrahedron Letters*, 1966, 1419; G. O. Schenck, W. Hartmann, S.-P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, 1962, 95, 1642.

⁶ J. W. Hanifin and E. Cohen, *J. Org. Chem.*, 1968, 33, 2811.

⁷ K.-H. Pfoertner, *Helv. Chim. Acta*, 1976, 59, 834.

⁸ R. G. Hunt, C. J. Potter, S. T. Reid, and M. L. Roantree, *Tetrahedron Letters*, 1975, 2327.

yield. The molecular formula was established as $C_{15}H_{16}O_3$ by analysis and mass spectra, and the adduct was assigned the benzo[3,4]cyclobuta[1,2-*c*]chromen-6-one structure (2) on the basis of the following spectral evidence; ν_{\max} (CCl_4) 3 590, 1 755, and 1 613 cm^{-1} ; δ_H ($CDCl_3$) 1.20 (8 H, m), 2.84 (2 H, m), 3.37 (1 H, s), 3.50 (1 H, d, J 8Hz), and 7.30 (4 H, m). The ^{13}C n.m.r. spectrum confirmed this structure (Table 4). The stereochemistry of the adduct remains uncertain but must presumably be *cis*, *cisoid*, *cis* or *cis*, *transoid*, *cis*. The alternative isomer may be present in low yield.



Analogous crystalline adducts were obtained with cyclopentene (51%), cycloheptene (55%), cyclo-octene (58%), and norbornene (30%). Addition to the acyclic alkene 2,3-dimethylbut-2-ene also took place in high yield (75%); ^{13}C n.m.r. assignments for the corresponding carbon atoms of this adduct are also shown in the Table for comparison. Addition was induced more rapidly by silica-filtered irradiation, but the yields of adducts isolated from these photoreactions were considerably lower. This is presumably due to competing shorter-wavelength photoreactions or, more likely, to photodecomposition of the adducts.

With the successful formation of the desired cycloadducts accomplished, attention was directed to the study of ring cleavage reactions of the cyclohexene adduct. Attempts to effect a base-catalysed retro-aldol cleavage of the adduct (2) with *n*-butyl-lithium, sodium carbonate in acetone, triethylamine, or 1,8-bis(dimethylamino)naphthalene to give the oxocin (3) were unsuccessful, starting material being recovered in all cases. In the analogous retro-aldol cleavage observed in the dimedone-cyclohexene adduct,³ cyclobutanol ring opening occurs either spontaneously or as the result of treatment with aqueous sodium hydroxide during the isolation procedure.

Treatment of the adduct (2) with triethylamine in dry methanol gave not the desired oxocin but methyl 2-*o*-hydroxybenzoylcyclohexylacetate (4) in high yield. In a similar fashion, treatment of the adduct (2) with pyrrolidine in benzene gave the corresponding amide (5). Both structures were unambiguously established

by spectral evidence and are formally the result of ring opening of the cyclobutanol and the lactone. It is not clear from these results whether nucleophilic attack on the lactone precedes or follows cyclobutane ring opening. The possibility that cyclobutane ring cleavage is reversible in the absence of strong nucleophiles, and that this is responsible for the failure to obtain the oxocin (3), cannot be ignored.

In an effort to clarify the behaviour of this system and to facilitate ring opening of the cyclobutane in an alternative sense, the acetate (6) was prepared and studied. The acetate itself was obtained in 68% yield by treatment of the cyclohexene adduct (2) with boron trifluoride-ether in acetic acid; other standard methods

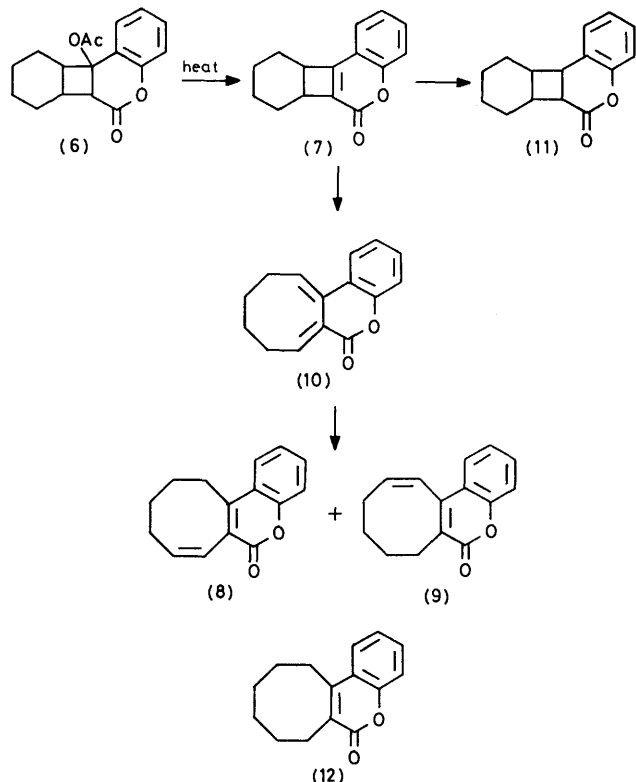
Provisional ^{13}C n.m.r. assignments

	δ (p.p.m. from $SiMe_4$)	Corresponding δ value for 2,3-dimethylbut-2-ene adduct †
C-1	130.3	129.8
C-2	125.0	124.4
C-3	128.6	129.0
C-4	117.6	117.3
C-4a	150.3	150.7
C-6	166.9	166.1
C-6a	48.5	54.2
C-6b	29.5	39.7
C-7		
C-8	23.5, 22.6,	
C-9	21.0, and 20.9	
C-10		
C-10a	44.2	48.3
C-10b	72.1	71.6
C-10c	123.9	124.0

† Methyl signals at 25.1, 21.6, 21.1, and 20.9.

failed to give the acetate of this tertiary alcohol. Reaction of the acetate (6) with triethylamine in methanol and with pyrrolidine again gave the ester (4) and the amide (5), respectively. Pyrolysis of the acetate (6) was accompanied by elimination of acetic acid and gave three isomeric products, the amount of each being dependent upon the reaction conditions. The major product of pyrolysis at 190 °C *in vacuo* for 1.5 h was the benzocyclobutachromenone (7). I.r. absorptions at 1 738 and 1 640 cm^{-1} were in agreement with the presence of an $\alpha\beta$ -unsaturated lactone, and 1H n.m.r. absorptions at δ 3.5–3.8 (2 H, m) were assigned to the cyclobutyl methine protons. The two vinyl cyclobutene carbon signals occurred at δ 41.4 in the ^{13}C n.m.r. spectrum. Pyrolysis under identical conditions but continued for 16 h led to the cyclo-octachromenones (8) and (9), arising presumably by a thermal electrocyclic pathway from the cyclobutene (7) to the cyclo-octadiene (10)

followed by two competing 1,5-hydrogen migrations to give the more stable chromenones. The cyclo-octadienes (8) and (9) are more readily obtained by pyrolysis of the acetate (6) in refluxing quinoline.



Evidence in favour of structures (8) and (9) comes from ^1H n.m.r. spin decoupling studies; on irradiation at methylene resonance frequencies, the signals for the two vinyl protons collapse to doublets with $J_{1,2}$ 11 Hz, indicating that both protons are on the same double bond and have *cis*-stereochemistry. The cyclo-octadienes with the lower and higher R_F values are tentatively assigned structures (8) and (9), respectively, on the basis of ^1H and ^{13}C n.m.r. spectra.

Hydrogenation of the cyclobutene (7) over 5% palladium-charcoal gave the octahydrobenzocyclobuta-chromenone (11), whereas hydrogenation of a mixture of the cyclo-octadienes (8) and (9) gave the hexahydrocyclo-octachromenone (12). Analytical and spectral data agreed with these assignments.

EXPERIMENTAL

Photoreactions were carried out using a 450 W Hanovia medium-pressure mercury arc surrounded by a water-cooled silica or Pyrex jacket and fitted with a reactor. Dry oxygen-free nitrogen was bubbled through the reaction solution for 1 h prior to irradiation and bubbling was continued throughout the irradiation. The progress of the reaction was followed either by the reduction in intensity of the i.r. band at 1720 cm^{-1} or by the disappearance of 4-hydroxycoumarin (t.l.c. on silica gel; CH_2Cl_2).

M.p.s were determined with a Kofler hot-stage apparatus. I.r. and u.v. spectra were recorded on a Perkin-Elmer 257 and a Unicam SP 800 spectrophotometer, respectively, and n.m.r. spectra were obtained using a JEOL PS-100 spectrometer with SiMe_4 as reference. Mass spectra were determined using an A.E.I. MS 902 instrument.

Solvents were purified prior to use for all irradiations. Cyclohexene was purified by washing with an aqueous iron(II) sulphate solution prior to distillation; immediately before use, cyclohexene was passed through a column of 'Camag' neutral alumina.

6a, 6b, 7, 8, 9, 10, 10a, 10b-Octahydro-10b-hydrobenzo[3,4]-cyclobuta[1,2-c]chromen-6-one (2).—A solution of 4-hydroxycoumarin (10.0 g) in cyclohexene (410 ml) and *t*-butyl alcohol (100 ml) was irradiated through Pyrex until reaction was complete (80 h). Distillation left an oil which crystallised from petroleum-benzene to give the adduct (10.0 g, 67%), m.p. $116\text{--}117^\circ$; ν_{max} (CH_2Cl_2) $2910, 1755$, and 1190 cm^{-1} ; δ_{H} (CDCl_3) $0.6\text{--}2.0\text{br}$ (8 H), $2.3\text{--}3.0$ (2 H, m), 3.42 (1 H, d), 3.82 (1 H, s), and $6.8\text{--}7.6\text{br}$ (4 H); δ_{C} (CDCl_3) $166.8, 150.3, 130.3, 128.6, 124.9, 123.9, 117.6, 72.2, 48.5, 44.2, 29.5, 23.5, 22.6, 21.9$, and 20.9 ; m/e 244 (M^+ , 1%), 163 (100), 162 (34), and 120 (56); (Found: C, 73.7; H, 6.5. $\text{C}_{15}\text{H}_{16}\text{O}_3$ requires C, 73.7; H, 6.55%).

An analogous reaction using a silica filter gave the adduct (50%) after 20 h irradiation.

Addition of 4-Hydroxycoumarin to Other Alkenes.—The photoaddition of 4-hydroxycoumarin to other alkenes was carried out in essentially the same fashion to give (i) the cyclopentane adduct (51%), m.p. $161\text{--}162^\circ$ (from petroleum-benzene); ν_{max} (CH_2Cl_2) $2910, 1755$, and 1190 cm^{-1} ; δ_{H} (CDCl_3) $0.4\text{--}2.0\text{br}$ (6 H), $2.6\text{--}3.2$ (2 H, m), 3.5 (1 H, d), 3.86 (1 H, s), and $6.9\text{--}7.5\text{br}$ (4 H); δ_{C} (CDCl_3) $167.1, 150.6, 130.3, 127.9, 124.9, 121.1, 117.2, 72.3, 52.3, 46.8, 37.7, 28.9, 28.0$, and 25.4 ; m/e 230 (M^+ , 0.3%), 163 (100), 162 (48), and 120 (67) (Found: C, 73.2; H, 6.0. $\text{C}_{14}\text{H}_{14}\text{O}_3$ requires C, 73.0; H, 6.13%); (ii) the cycloheptene adduct (43%), m.p. $165\text{--}166^\circ$ (from petroleum-benzene); ν_{max} (CH_2Cl_2) $2910, 1755$, and 1200 cm^{-1} ; δ_{H} (CDCl_3) $0.6\text{--}2.0\text{br}$ (10 H), $2.4\text{--}3.0$ (2 H, m), 3.65 (1 H, d), 3.86 (1 H, s), and $6.8\text{--}7.5\text{br}$ (4 H); δ_{C} (CDCl_3) $166.0, 150.8, 130.3, 129.2, 124.5, 122.3, 117.5, 72.1, 50.4, 49.4, 36.8, 30.7, 27.9, 25.2$, and 23.4 ; m/e 258 (M^+ , 0.03%), 163 (100), 162 (15), and 120 (25) (Found: C, 74.7; H, 6.9. $\text{C}_{16}\text{H}_{18}\text{O}_3$ requires C, 74.4; H, 7.0%); (iii) the cyclo-octene adduct (50%), m.p. $178\text{--}180^\circ$ (from methanol); ν_{max} $2910, 1755, 1205$, and 1185 cm^{-1} ; δ_{H} (CDCl_3) $0.6\text{--}2.0\text{br}$ (12 H), $2.6\text{--}3.0$ (2 H, m), 3.63 (1 H, d), 3.90 (1 H, s), and $6.8\text{--}7.5\text{br}$ (4 H); δ_{C} (CDCl_3) $166.0, 150.8, 130.3, 129.2, 124.5, 122.4, 117.5, 72.1, 50.4, 49.4, 36.8$ (2 C), $30.7, 27.9, 25.4$ (2 C), and 23.4 ; m/e 272 (M^+ , 0.1%), 163 (100), 162 (18), and 120 (26) (Found: C, 75.1; H, 7.5. $\text{C}_{17}\text{H}_{20}\text{O}_3$ requires C, 74.8; H, 7.4%); (iv) the norbornene adduct (30%), m.p. $177\text{--}178^\circ$ (from benzene); ν_{max} $2940, 1755$, and 1180 cm^{-1} ; δ_{H} (CDCl_3) $0.8\text{--}3.0\text{br}$ (10 H), 3.42 (1 H, dd), 3.8 (1 H, s), and $6.9\text{--}7.4$ (4 H, m); δ_{C} (CDCl_3) $168.1, 150.8, 130.2, 127.5, 125.1, 122.8, 117.1, 72.4, 55.3, 46.8, 41.9, 36.6, 35.3, 33.1, 28.0$, and 27.5 ; m/e 256 (M^+ , 0.06%), 163 (100), 162 (35), and 120 (41) (Found: C, 74.8; H, 6.1. $\text{C}_{16}\text{H}_{16}\text{O}_3$ requires C, 75.0; H, 6.3%); and (v) the 2,3-dimethylbut-2-ene adduct (75%), m.p. $132\text{--}133^\circ$ (from petroleum-benzene); ν_{max} 1745 and 1195 cm^{-1} ; δ_{H} (CDCl_3) 0.70 (3 H, s), 0.73 (3 H, s), 1.10 (3 H, s), 1.20 (3 H, s), 3.10 (1 H, s), 3.50 (1 H, s), $6.8\text{--}7.4\text{br}$ (4 H); δ_{C} (CDCl_3) $166.1, 150.7, 129.8, 128.9, 124.4, 124.0, 117.3, 71.6, 54.2, 48.3, 39.7, 25.1, 21.6, 21.1$, and 20.9 ; m/e 163 (100%)

(Found: C, 73.3; H, 7.0. $C_{15}H_{18}O_3$ requires C, 73.2; H, 7.4%).

10b-Acetoxy-6a,6b,7,8,9,10,10a,10b-octahydrobenzo[3,4]-cyclobuta[1,2-c]chromen-6-one (6).—Boron trifluoride-diethyl ether (5.0 ml) was added gradually to the cyclohexene adduct (2) (5.0 g) in glacial acetic acid (5.0 ml) and the resulting solution was kept at room temperature for 48 h. The product obtained on cooling was recrystallised from chloroform to give the acetate (4.0 g, 68%), m.p. 189–193° (decomp.); $\nu_{\max.}$ (CH_2Cl_2) 2 940, 1 764, 1 740, and 1 215 cm^{-1} ; δ_H ($CDCl_3$) 0.8–2.0br (8 H), 1.96 (3 H, s), 2.6–3.2 (2 H, m), 3.63 (1 H, d), and 7.0–7.5 (4 H, m); δ_C ($CDCl_3$) 169.9, 165.0, 151.7, 130.4, 127.7, 124.3, 120.6, 117.3, 76.6, 46.9, 41.2, 31.4, 23.8, 22.6, 21.8, 21.1, and 20.9; m/e 205 (32%) and 163 (100) (Found: C, 71.1; H, 6.2. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.3%).

Methyl 2-o-Hydroxybenzoylcyclohexylacetate (4).—The cyclohexene adduct (1.0 g) was dissolved in reagent grade methanol (20 ml) containing triethylamine (1 ml) and the solution was stirred at room temperature for 24 h. The solvent was removed by distillation and the product purified by t.l.c. (silica gel; 25 : 75 ethyl acetate–benzene). The ester (0.91 g, 80%) was extracted from the plates with 50 : 50 acetone–dichloromethane; $\nu_{\max.}$ (CH_2Cl_2) 2 870, 1 740, 1 640, 1 160, and 1 040 cm^{-1} ; δ_H ($CDCl_3$) 1.0–2.6br (11 H), 3.25 (1 H, m), 3.55 (3 H, s), 6.6–7.9 (4 H, m), and 12.62 (1 H, s); δ_C 209.7, 172.5, 163.3, 136.5, 130.0, 118.9 (3 C), 51.3, 49.0, 39.2, 35.4, 34.8, 31.8, 31.4, and 25.8; m/e 276 (M^+ , 7%), 245 (5), 203 (7), and 121 (100%) (Found: C, 69.3; H, 7.5. $C_{16}H_{20}O_4$ requires C, 69.6; H, 7.3%).

2-o-Hydroxybenzoylcyclohexylacetopiperidine (5).—A solution of the cyclohexene adduct (1.0 g) in benzene (20 ml) containing pyrrolidine (1.0 ml) was stirred at room temperature for 24 h. The solvent was removed by distillation and the product purified by t.l.c. (silica gel; 25 : 75 ethyl acetate–benzene). The amide (0.88 g, 68%) was obtained as a light yellow oil by extraction from the plates with dichloromethane; $\nu_{\max.}$ (CH_2Cl_2) 2 940, 1 640, 1 345, and 1 160 cm^{-1} ; δ_H ($CDCl_3$) 1.0–2.6br (15 H), 3.1–3.7 (5 H, m), 6.6–8.1br (4 H), and 12.5 (1 H, s); δ_C ($CDCl_3$) 210.0, 170.0, 163.1, 136.4, 130.1, 118.9 (2 C), 118.6, 49.3, 46.7, 45.5, 39.7, 35.6, 31.7 (2 C), 26.1, 25.8 (2 C), and 24.3; m/e 315 (M^+ , 6%), 121 (20), and 113 (100) (Found: C, 72.3; H, 8.0; N, 4.3. $C_{18}H_{25}NO_3$ requires C, 72.4; H, 8.0; N, 4.4%).

6b,7,8,9,10,10a-Hexahydrobenzo[3,4]cyclobuta[1,2-c]-chromen-6-one (7).—The acetate (6) (1.0 g) was placed in a break-seal pyrolysis tube, and the tube evacuated, sealed, and placed in an oven at 190 °C for 1.5 h. The product mixture was separated by repeated t.l.c. (silica gel; 50 : 50 petroleum–benzene), and the cyclobutene extracted from the plates with ethyl acetate. After recrystallisation from petroleum, it had m.p. 70–71° (0.52 g, 63%); $\nu_{\max.}$ (CH_2Cl_2) 2 940, 1 738, and 1 640 cm^{-1} ; $\lambda_{\max.}$ (EtOH) 275 (ϵ 4 520), 285 (ϵ 4 500), and 311 nm (ϵ 3 700); δ_H ($CDCl_3$) 1.1–2.4br (8 H), 3.5–3.8 (2 H, m), and 7.1–7.6 (4 H, m); δ_C ($CDCl_3$) 165.0, 157.0, 156.3, 131.8, 130.9, 124.0, 123.2, 122.7, 117.8, 41.4 (2 C), 23.4, 23.1, 18.6, and 18.2; m/e 226 (M^+ , 96%) and 197 (100) (Found: C, 79.7; H, 6.1. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%).

9,10,11,12-(8) and 7,8,9,10-Tetrahydrocyclo-octa[c]chromen-6-one (9).—A solution of the acetate (6) (2.0 g) in redistilled quinoline (20 ml) was heated under reflux for 1.5 h. The solution was allowed to cool, diluted with chloroform (200 ml), and extracted with dilute hydrochloric acid (6 × 200 ml) to remove the quinoline. The cyclo-octadienes were separated by repeated t.l.c. (silica gel; 50 : 50 petroleum–benzene) and extracted from the plates with ethyl acetate.

The cyclo-octadiene with the higher R_F value (0.62 g, 39%) was assigned structure (9) and had m.p. 101.5–102.5° (from petroleum); $\nu_{\max.}$ (CH_2Cl_2) 2 940, 1 720, 1 615, and 1 060 cm^{-1} ; $\lambda_{\max.}$ (MeOH) 280 (ϵ 5 650) and 310 nm (ϵ 4 180); δ_H ($CDCl_3$) 1.0–4.0br (8 H), 6.0–6.8 (2 H, m), and 6.9–8.2br (4 H); δ_C ($CDCl_3$) 161.6, 152.0, 145.4, 138.8, 130.3, 125.3, 124.5, 124.0, 121.9, 119.5, 116.5, 29.2, 26.7, 24.3, and 21.7; m/e 226 (M^+ , 95%), 198 (33), and 197 (100) (Found: C, 79.4; H, 6.0. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%).

The cyclo-octadiene with the lower R_F value (0.65 g, 41%) was assigned structure (8) and had m.p. 142–144° (from methanol); $\nu_{\max.}$ (CH_2Cl_2) 2 940, 1 720, 1 610, and 1 055 cm^{-1} ; $\lambda_{\max.}$ (MeOH) 257 (ϵ 4 080), 301 (ϵ 4 760), and 317 nm (ϵ 5 390); δ_H ($CDCl_3$) 1.0–2.1br (4 H), 2.1–2.5 (2 H, m), 2.7–3.2 (2 H, m), 5.9–6.5 (2 H, m), and 7.0–7.8br (4 H); δ_C ($CDCl_3$) 160.8, 152.8, 149.1, 136.3, 130.8, 124.7, 124.4, 123.3, 122.2, 119.5, 117.0, 30.1, 27.5, 24.6, and 21.8; m/e 226 (M^+ , 96%), 198 (32), and 197 (100) (Found: C, 79.8; H, 6.0. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%).

6a,6b,7,8,9,10,10a,10b-Octahydrobenzo[3,4]cyclobuta[1,2-c]-chromen-6-one (11).—The cyclobutene (7) (0.5 g) was hydrogenated in ethanol (50 ml) at room temperature and atmospheric pressure over 5% palladium–charcoal (0.1 g). After uptake of 1 mol. equiv., the solution was filtered and the solvent removed by distillation. The product was purified by t.l.c. (silica gel; benzene) to give the octahydro-derivative, m.p. 87–88° (0.47 g, 93%); $\nu_{\max.}$ (CH_2Cl_2) 2 950, 1 760, 1 165, and 1 130 cm^{-1} ; δ_H ($CDCl_3$) 0.6–1.9br (8 H), 2.5–4.1 (4 H), and 6.8–7.5 (4 H, m); δ_C ($CDCl_3$) 167.8, 150.0, 128.5, 128.3, 124.3, 121.0, 117.1, 37.7 (2 C), 36.3, (2 C), 23.7 (2 C), 21.8, and 21.6; m/e 228 (M^+ , 1%) and 147 (100) (Found: C, 79.1; H, 6.9. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.1%).

7,8,9,10,11,12-Hexahydrocyclo-octa[c]chromen-6-one (12).—A mixture (0.5 g) of the cyclo-octadienes (8) and (9), obtained by pyrolysis of the acetate (6) in quinoline, was hydrogenated as above to give the hexahydrocyclo-octa[c]-chromen-6-one (0.45 g, 89%), m.p. 99.5–101.5°; $\nu_{\max.}$ (CH_2Cl_2) 2 940, 2 870, 1 715, 1 612, and 1 385 cm^{-1} ; δ_H ($CDCl_3$) 0.9–2.1br (8 H), 2.65–3.15 (4 H, m), and 7.1–7.8 (4 H, m); δ_C ($CDCl_3$) 161.4, 152.6, 150.2, 130.3, 126.8, 124.0 (2 C), 119.3, 117.0, 29.7, 29.2, 26.9, 26.3 (2 C), and 25.8; $\lambda_{\max.}$ (MeOH) 275 (ϵ 10 100), 285 (9 850), 307 (7 750), and 313 nm (7 750); m/e 228 (M^+ , 100%) (Found: C, 79.0; H, 7.2. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.1%).

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