Acid-catalysed Transformations of Substituted 4-Hydroxy-2-(prop-2-enyl)cyclopent-2-enones

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Treatment of the substituted 4-hydroxy- or 4-methoxy-3-methyl-2-(prop-2-enyl)cyclopent-2-enones (1a—c; R^2 = H or Me) with pyridine hydrochloride (PHC) or 6N-HCl gives the corresponding substituted 4-methyl-5-n-propylcyclopent-4-ene-1,3-diones (2a—c). Under the same conditions 4-methyl-5-(prop-2-enyl)cyclopent-4-ene-1,3-dione (3; R = H) produces only 4-methyl-5-(prop-1-enyl)cyclopent-4-ene-1,3-dione (4). Reduction of (3; R = H) with ZnHg–HCl or treatment of the hydroxycyclopentenone (1a; R^2 = H) with NaOMe–MeOH led to the crystalline enol 3-hydroxy-4-methyl-5-(prop-2-enyl)cyclopent-2-enone (6), which produced the cyclopentenedione (2a) with PHC or 6N-HCl. 4-Hydroxy-3-methyl-2-n-propylcyclopent-2-enone (7), showing no side-chain unsaturation, produced only 3-hydroxy-4-methyl-5-n-propylcyclopent-2-enone (8) with PHC. These data suggested that the isomerisations (1) ⟶ (2) probably proceed *via* intermediate enols [*viz.* (6)]. Conversion (1) ⟶ (6) is envisaged as an acid-catalysed enone–dienol type rearrangement and conversion (6) ⟶ (2) as a simple double bond migration proceeding by a series of prototropic shifts. An alternative scheme, involving initial side-chain double bond migration, followed by enol formation is also proposed under certain conditions.

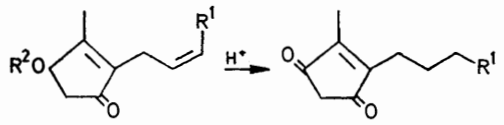
The analogue 4-hydroxy-3-methyl-2-[(*Z*)-penta-2,4-dienyl]cyclopent-2-enone (14) containing additional unsaturation in the prop-2-enyl side-chain produced largely 4-methyl-5-[(*E*)-pent-1-enyl]cyclopent-4-ene-1,3-dione (17) with PHC, accompanied by small amounts of positional isomers (16) and (18). In contrast to earlier reports, (14) produced only the enol 3-hydroxy-4-methyl-5-[(*Z*)-penta-2,4-dienyl]cyclopent-2-enone (19) in NaOMe–MeOH.

In the preceding paper [1] we reported that treatment of the methoxycyclopentenone (1a; R^2 = Me) with pyridine hydrochloride (PHC) resulted in exclusive formation of the cyclopentenedione (2a). As depicted, this novel transformation formally involves oxidation of the methoxycyclopentenone CH–O bond, and synchronous reduction of the side-chain C=C bond. The present paper describes our more detailed studies of this unusual transformation.[2]

[1] G. Pattenden and R. Storer, preceding paper.

[2] Preliminary account, G. Pattenden and R. Storer, *J.C.S. Chem. Comm.*, 1973, 875.

Treatment of methyl ether (1a; R^2 = Me) with PHC at 200° for 0·5 h produced a single, clean product which was homogenous in both t.l.c. and g.l.c. The product

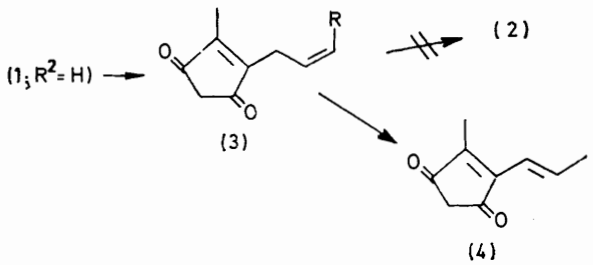


(1) (2)

a, R^1 = H; b, R^1 = Me; c, R^1 = Et.

had displayed i.r. data ($\nu_{max.}$ 1735 and 1700 cm^{-1}) characteristic of a cyclopentenedione,[3,4] and readily produced a bis-2,4-dinitrophenylhydrazone derivative. Its n.m.r. spectrum displayed triplet resonances associated with vinyl methylene [τ 7·56 (:C·CH_2CH$_2$)] and saturated methyl [τ 9·04 (·CH$_2$·CH_3)] protons which replaced resonances due to the pent-2-enyl side-chain protons in structure (1a), and a singlet at τ 7·19 (2H) replaced the ABX signals of the cyclopentenone protons in (1a). These data led to formulation (2a) for the product. An identical product was obtained when the free alcohol (1a; R^2 = H) was treated similarly with PHC, and when (1a; R^2 = H) was heated in 6N-hydrochloric acid (see below). Treatment of the corresponding but-2-enyl (1b) and pent-2-enyl (1c) derivatives (R^2 = H or Me) with PHC produced the homologous cyclopentenediones (2b) and (2c) respectively, which both exhibited closely similar spectral data to those of (2a).

Several schemes can be advanced to rationalise the formation of (2) from (1) in the presence of acid. The possible involvement of the 5-(prop-2-enyl)cyclopentenedione (3) was quickly eliminated, by examining the reaction between authentic (3; R = H) and PHC. The dione (3; R = H) has been synthesised previously



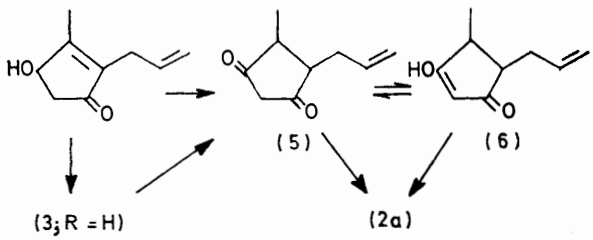
(1; R^2 = H) (3) (2) (4)

by the controlled oxidation of alcohol (1a; R^2 = H) with manganese dioxide.[4] When this dione was heated with either PHC or with 6N-hydrochloric acid, the only product isolated was the dione (4), resulting from straightforward acid-catalysed isomerisation of the side-chain double bond into conjugation. The isomeric dione displayed i.r. and n.m.r. spectral data expected on the basis of structure (4), and the olefinic proton coupling (J 16 Hz) observed for the side-chain C(1)-H established the E-geometry of the disubstituted double bond in (4).

[3] C. H. de Puy and P. R. Wells, *J. Amer. Chem. Soc.*, 1960, **82**, 2910.

[4] L. Crombie, J. A. Ellis, R. Gould, G. Pattenden, M. Elliott, N. F. Janes, and K. A. Jeffs, *J. Chem. Soc.* (*C*), 1971, 9.

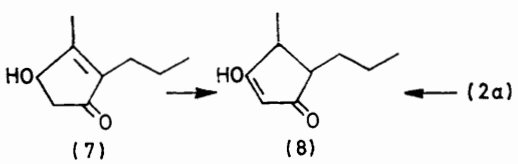
At this juncture, the supposition was made that the transformation of (1) into (2) proceeded by initial isomerisation to produce a cyclopentanedione [*viz.* (5)], and that this intermediate then reacted further in acid to produce (2). A mixture of enolic forms of the cyclopentanedione (5) has been prepared previously,[5] as a viscous oil, by treatment of alcohol (1a; R^2 = H) with sodium methoxide in methanol; both chemical and spectral data have suggested that formulation (6) best represents the structure of the enol. In the present study, we prepared (5) by using the procedure of Elliott,[5] and isolated the compound as a crystalline solid, m.p. 74—75°; the solid displayed spectral data closely identical with those described earlier, and interpreted in terms of the enol formulation (6). We also synthesised the



(5) (6) (3; R = H) (2a)

same enol by reduction of the cyclopentenedione (3; R = H) with zinc amalgam in hydrochloric acid, and during the attempted demethylation of (1a; R^2 = Me) with ethanethiolate anion.[6]

Treatment of the enol (6) with PHC under identical conditions to those used previously in reactions with (1a; R^2 = H or Me), produced a similar yield of the cyclopentenedione (2a), as did reaction of (6) with boiling 6N-hydrochloric acid. Although we were not able to detect the presence of (6) in the reactions between (1a; R^2 = H) and PHC, because its subsequent reaction to produce (2) was presumably too rapid, its intermediacy in the overall conversion (1a; R^2 = H or Me) ⟶ (2) was suggested strongly from the foregoing data. Further support came from separate studies of the reaction between PHC and the saturated-side-chain analogue (7). The hydroxycyclopentenone (7) was prepared by controlled hydrogenation of (1a; R^2 = H), and was treated with PHC to give a high yield of the saturated-side-chain analogue [*viz.* (8)] of (6). The compound was identical with that obtained by reduction of the cyclopentenedione (2a) with zinc amalgam in hydrochloric acid; an enol structure follows from spectral data, and formulation (8)



(7) (8) (2a)

is proposed by analogy with earlier work on hydroxycyclopentenone enols.[5]

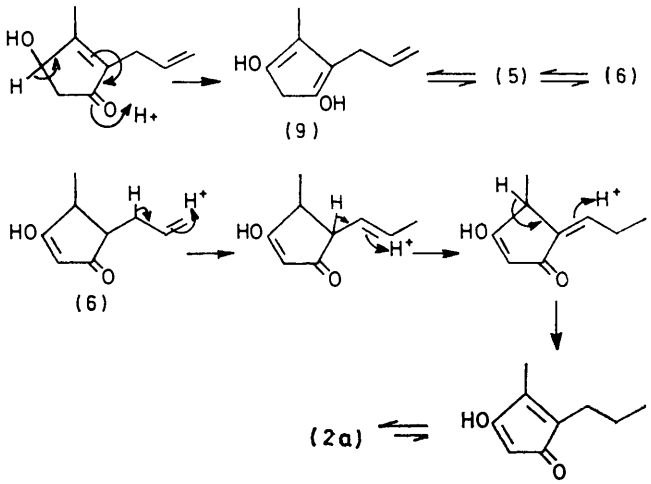
[5] M. Elliott, *J. Chem. Soc.*, 1965, 3097, and references cited therein.

[6] G. I. Feutrill and R. N. Millington, *Austral. J. Chem.*, 1972, **25**, 1719.

The data above therefore suggested a scheme from (1a; R^2 = Me) to (2a) involving (1a; R^2 = H) and (6) as probable intermediates. The transformation (1a; R^2 = H) ⟶ (6) can be depicted as involving a familiar enone–dienol rearrangement (Scheme 1).[7] The usual

SCHEME 1

enone–dienol rearrangement, however, follows a concerted [1,5] sigmatropic pathway, and the groups must necessarily adopt a *cisoid* conformation (see Scheme 1). The transformation of (1a; R^2 = H) to (6) is either acid or base promoted, and under no circumstances could the appropriate groups in (1a; R^2 = H) assume a *cisoid* conformation. We therefore envisage the isomerisation (1a; R^2 = H) ⟶ (6) in PHC proceeding *via* the bis-enol (9) formed from an acid-promoted enone–dienol rearrangement, followed by ketonisation [to (5)] and re-enolisation (Scheme 2). Transformation of (6) to (2a)



SCHEME 2

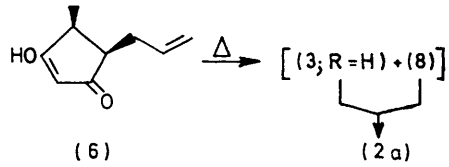
then proceeds simply by initial protonation of the side-chain double bond followed by stepwise migration of the double bond along the side-chain to the ring position *via* a series of prototropic shifts.

The possibility that (2a) might be formed from (6) by a thermal process, involving concerted intermolecular transfer of two hydrogen atoms from C-2 and C-3 to the side-chain double bond,[8] was briefly examined (Scheme 3), but by using enol (6) as model compound, we were not able to detect the presence of (2a) during attempted thermal transformations of (6). The enol (6) was thermally stable at several elevated temperatures and was recovered largely unchanged; under more extreme thermal conditions complex mixtures of products were produced.

* The configurations of the side chain double bonds in (16) and (18) are not known with certainty.

[7] See E. N. Marvell and M. Whalley, ' Uncatalysed Rearrangements Involving the Hydroxyl Group ' in ' The Chemistry of the Hydroxy Group, Part 2, ed. S. Patai, Interscience, New York, 1971, p. 719.

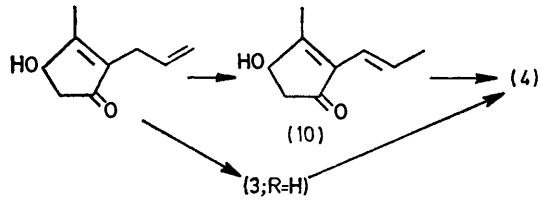
Earlier we pointed out that transformation (1) ⟶ (2) was brought about by 6N-HCl as well as by PHC. Studies with the alcohol (1a; R^2 = H) showed that in 6N-HCl, the dione (4) was concurrently produced (*ca.* 20% total product); the identity of (4) followed from spectral data, and from g.l.c. comparison with authentic material. The formation of (4) under these conditions is difficult to explain, but can be rationalised in terms of either (i) ' initial ' prototropic migration of the side-chain



SCHEME 3

double bond, to produce (10), followed by oxidation of the CH–OH bond in (10), or (ii) initial oxidation to (3; R = H), followed by double bond migration (see Scheme 4). The concurrent formation of (2a) and (4) from (1a; R^2 = H) in 6N-HCl naturally raises the possibility that (2) could be formed from (1) *via* an intermediate [*viz.* (11)] resulting from ' initial ' migration of the side-chain double bond (see Scheme 5). Subsequent transformation of (1) to (2) could then proceed by way of either of the two enols (12) and (13)[9] followed by normal prototropic isomerisation. The paucity of suitable model compounds prevented us from examining this alternative scheme in any detail.

It has been reported[5] that reaction between the 2-(penta-2,4-dienyl)cyclopentenone (14) and sodium methoxide largely results in the formation of a mixture of cyclopentenediones (15) and (16). In view of the close similarity between this transformation and those described earlier in this paper, we examined the reaction between (14) and PHC. This reaction produced a mixture of three 5-pentenylcyclopentenediones in the approximate proportion 1 : 3 : 6. Inspection of the n.m.r. spectrum of the mixture, and comparison with n.m.r.[10] and other data for diones (3; R = Me and Et),



SCHEME 4

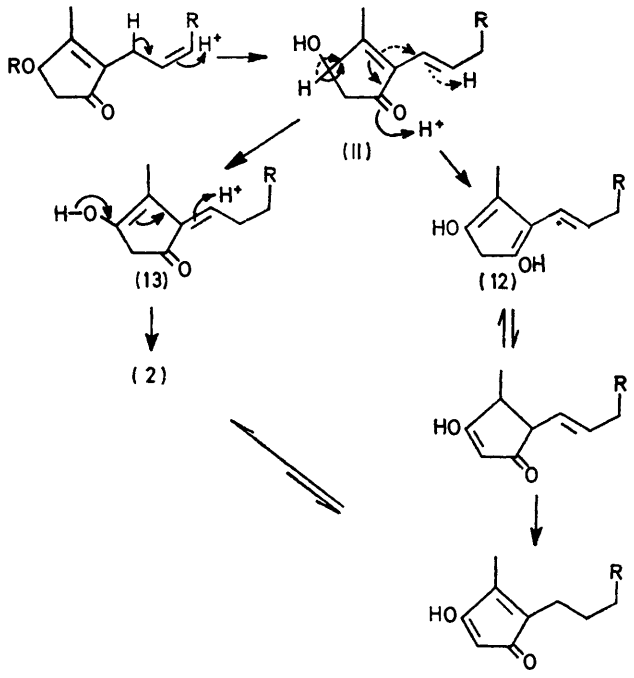
(4), and (2) showed that they had structures corresponding to (16)—(18).* The presence of two types of 5-substituted cyclopentene-1,3-dione followed from the presence of two singlet resonances, due to $-COCH_2CO-$, at

[8] R. B. Woodward and R. Hoffmann, ' Group Transfers and Eliminations ' in ' The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

[9] *Cf.* C. Maignan and F. Rouessae, *Bull. Soc. chim. France*, 1973, 1454.

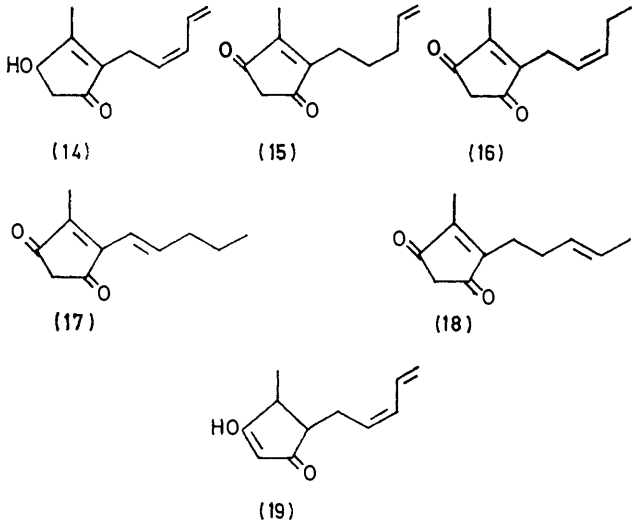
[10] A. F. Bramwell, L. Crombie, P. Hemesley, G. Pattenden, M. Elliott, and N. F. Janes, *Tetrahedron*, 1969, **25**, 1727.

τ 7·24 and 7·19. The 5-(pent-1-enyl)cyclopentenedione isomer (17), which was also the major product, showed



SCHEME 5

one olefinic resonance (d, J 16 Hz) at τ 3·7, and another at *ca.* 2·85 (dt), the observed vicinal olefinic coupling establishing the *E*-geometry of side-chain double bond.



The cyclopentenedione (16) was eluted second in g.l.c. (*ca.* 30% total) and co-chromatographed with an authentic sample of (16) obtained earlier.[4] The presence of (18) as a minor 5-pentenylcyclopentenedione product was suggested by the presence of a doublet at τ 8·25 (J *ca.* 6 Hz) due to the side-chain vinyl methyl group.[10] Separate analysis and comparison of mass spectral data[11] obtained from g.l.c.–m.s. studies confirmed the structural assignments given to these products; we were not able to obtain evidence to support the presence of isomer (15) amongst the products of reaction between (14) and PHC. In view of the above findings, we repeated the earlier work on the reaction between (14) and sodium methoxide. In our hands, the only product isolated was the cyclopentanedione enol (19), which could be isolated in pure form by extraction with base; no evidence for the co-formation of (15) and (16) [or of (17) and (18)] was obtained. Cyclopentane-1,3-diones such as (19) and (5) are readily soluble in dilute base, whereas the corresponding cyclopentene-1,3-diones [*viz.* (15)—(18), *etc.*] have negligible solubility in alkali. Consideration of the experimental procedure described by Elliott and earlier workers [5] to separate (15) and (16) from the products of reaction of (14) and sodium methoxide, suggests that (15) and (16) were not actual products of the reaction, but artefacts formed from the enol product (19) by thermal acid-catalysed isomerisation during subsequent distillation [similar to the isomerisation described for the conversion (5) ⟶ (2a)].

EXPERIMENTAL

For general experimental details see the preceding paper. G.l.c.–mass spectral data were obtained on a Varian CH5D machine, through the courtesy of the Chemistry Department, University College, Cardiff (3% OV-1, 12 ft × 2 mm column, 135°).

4-Methyl-5-n-propylcyclopent-4-ene-1,3-dione (2a).—(*a*) A mixture of 4-hydroxy-3-methyl-2-(prop-2-enyl)cyclopent-2-enone (allethrolone) (6·4 g) and pyridine hydrochloride (PHC) (64 g) was heated at 200° for 0·5 h, then cooled to 25°, and treated with 5% hydrochloric acid. The solution was filtered, and the filtrate was thoroughly extracted with ether. Evaporation of the washed (Na_2CO_3, then H_2O) and dried ether extracts left the *dione* (2a) (2·2 g, 35%), homogeneous in t.l.c. and g.l.c. (10% Apiezon, 130°), $\nu_{max.}$ (film) 1735 and 1700 cm^{-1}, τ 7·19 ($-COCH_2$), 7·56 (t, J 8, $\cdot C\cdot CH_2CH_2$), 8·00 ($\cdot CMe$), 8·4 (m, $-CH_2-$), and 9·04 (t, J 6·5, CH_2CH_3) (Found: *m/e*, 153·0835. $C_9H_{12}O_2$ requires *M*, 152·0837). It formed a *bis-2,4-dinitrophenylhydrazone*, m.p. 262—263° (nitrobenzene–ethanol) (Found: C, 49·1; H, 4·1; N, 22·4. $C_{21}H_{20}N_8O_8$ requires: C, 49·2; H, 3·9; N, 21·9%).

(*b*) Similar treatment of both 4-methoxy-3-methyl-2-(prop-2-enyl)cyclopent-2-enone (1a; R^2 = Me) and 3-hydroxy-4-methyl-5-(prop-2-enyl)cyclopent-2-enone (6) with PHC produced the same dione (mixed g.l.c., and identical i.r. and n.m.r. spectra) in comparable yields to that obtained in (*a*).

(*c*) A solution of the enone (6) (0·06 g) in 6N-hydrochloric acid (8 ml) was heated under reflux for 1·5 h, then cooled to 25° and extracted with ether. The ether extracts were washed successively with sodium carbonate solution and water, then dried and evaporated to leave the dione (*ca.* 25%), which was chromatographically and spectrally identical with that obtained in (*a*).

(*d*) A solution of allethrolone (1a; R^2 = H) (2 g) in 6N-hydrochloric acid (100 ml) was heated under reflux for 2 h, then cooled to 25° and extracted with ether. The ether extracts were washed successively with sodium carbonate solution and water, then dried and evaporated. Mixed g.l.c. and comparative spectral data showed that the

[11] G. Pattenden, L. Crombie, and P. Hemesley, *Org. Mass. Spectrometry*, 1973, **7**, 719.

residue (*ca.* 20%) was a 3 : 1 mixture of 4-methyl-5-n-propylcyclopent-4-ene-1,3-dione (2a) and 4-methyl-5-(prop-1-enyl)cyclopent-4-ene-1,3-dione (4).

4-Methyl-5-[(E)-prop-1-enyl]cyclopent-4-ene-1,3-dione (4).—(*a*) A mixture of 4-methyl-5-(prop-2-enyl)cyclopent-4-ene-1,3-dione (0·2 g) [4] and PHC (2 g) was heated at 200° for 0·5 h, then cooled to 25°, and diluted with 5% hydrochloric acid (30 ml). The solution was filtered, and the filtrate thoroughly extracted with ether. The ether extracts were washed successively with sodium carbonate solution and water, and then dried. Evaporation of the ether left the *dione* (4) (30 mg, 15%), m.p. 17—22°, $\nu_{max.}$ 1735 and 1700 cm^{-1}, τ 2·52—3·12 (m, :C*H*Me), 3·71 [d, *J* 15, (*E*)-C*H*:CH-], 7·13 (-COCH$_2$-), 7·96 (:CMe), and 8·05 (d, *J* 6·5, :CH*Me*) (Found: *m/e*, 150·0676. $C_9H_{10}O_2$ requires *M*, 150·0680), homogenous in both t.l.c. and g.l.c. (10% Apiezon, 130°).

(*b*) An identical product was obtained (41%) when a solution of the same starting material (0·13 g) in 6N-hydrochloric acid (16 ml) was boiled under reflux for 1·5 h, and then worked up in the usual way.

3-Hydroxy-4-methyl-5-(prop-2-enyl)cyclopent-2-enone (6).—(a) *From 4-hydroxy-3-methyl-2-(prop-2-enyl)cyclopent-2-enone*. The alcohol was prepared (*ca.* 60%) according to the procedure of Elliott,[5] and was obtained initially as a viscous oil, b.p. 144—146° at 0·6 mmHg, n_D^{20} 1·5293 (lit.,[5] 1·5296). The oil solidified on cooling, and was recrystallised from chloroform–light petroleum (b.p. 60—80°) to give the *enol* (6) as a solid, m.p. 74—75°, $\lambda_{max.}$ (EtOH) 245 nm (ε 16,800), $\nu_{max.}$ ($CHCl_3$) 1670 and 1590 cm^{-1}, $\nu_{max.}$ (film) 2650, 2550 (OH), and 1645 cm^{-1}, τ −1·9 (OH), 4·21 (ddt, *J* 6, 10, and 17, C*H*=CH$_2$), 4·77 (:CHCO), 4·79—5·08 (m, :CH$_2$), 7·1—8·02 (4H, m), and 8·79 (d, *J* 7, ·CH*Me*) (Found: C, 71·1; H, 8·1. $C_9H_{12}O_2$ requires C, 71·0; H, 7·95%).

(b) *From 4-methyl-5-(prop-2-enyl)cyclopent-4-ene-1,3-dione* (3). A mixture of zinc amalgam [from zinc dust (1 g) and $HgCl_2$ (0·1 g) in H_2O (1·5 ml) and HCl (0·05 ml)], water (1 ml), concentrated hydrochloric acid (1·25 ml), and the dione [4] (0·2 g) was heated under reflux for 6 h, then cooled to 25° and extracted with ether. The ether extracts were washed with sodium carbonate solution (3×) and the aqueous extracts were combined, acidified with hydrochloric acid, and re-extracted with ether. Evaporation of these washed (H_2O) and dried ether extracts left the alcohol as a viscous oil (62 mg) which was spectrally (i.r. and n.m.r.) identical with an authentic sample prepared as in (a).

(c) *From 4-methoxy-3-methyl-2-(prop-2-enyl)cyclopent-2-enone*. A solution of the methyl ether (1 g) in dry dimethylformamide (DMF) (10 ml) was added to a solution of the anion from ethanethiol (1·25 g) [using NaH (0·5 g)] [6] in DMF (10 ml) and the resulting red solution was stirred at 25° for 24 h. The mixture was acidified with 10% hydrochloric acid and extracted with ether, and the ether extracts were washed with sodium carbonate solution. The aqueous layer was separated and acidified with dilute hydrochloric acid, and extraction with ether followed by evaporation of the solvent left the enol (0·43 g, 43%), homogenous in t.l.c., and spectrally (i.r. and n.m.r.) indistinguishable from that obtained in (a).

3-Hydroxy-4-methyl-5-n-propylcyclopent-2-enone (8).—(a) *From 4-hydroxy-3-methyl-2-n-propylcyclopent-2-enone* (7). A mixture of the 4-hydroxycyclopentenone (0·5 g) and PHC (5 g) was heated at 200° for 0·5 h, then cooled to 25°, and treated with 5% hydrochloric acid (35 ml). The solution was filtered, and the filtrate was thoroughly extracted with ether. The combined ether extracts were washed with saturated sodium carbonate solution, and the aqueous layer was separated, acidified with hydrochloric acid, and re-extracted with ether. Evaporation of the washed and dried ether extracts left the *3-hydroxycyclopentenone* (300 mg), as an oil, $\nu_{max.}$ (film) 2650, 2550 (OH), and 1645 cm^{-1}, τ −2·19 (OH), 4·81 (:CH), and 7·45—9·2 (12H, m) (Found: *m/e* 154·0993. $C_9H_{14}O_2$ requires *M*, 154·0994).

(b) The same product was obtained (*ca.* 40% conversion) when the 4-hydroxycyclopentenone was heated in 6N-hydrochloric acid for 1·5 h, followed by isolation of the acidic product.

(c) *From 5-methyl-4-n-propylcyclopent-4-ene-1,3-dione*. The dione (0·8 g) was treated with Zn–Hg [from Zn (4 g)] in hydrochloric acid (5 ml) and water (4 ml) in an identical manner to that described for the corresponding 5-(prop-2-enyl)dione. Isolation of the acidic product produced the 3-hydroxycyclopentenone (0·4 g) spectrally indistinguishable from that obtained in (a).

4-Hydroxy-3-methyl-2-n-propylcyclopent-2-enone (7).—A solution of allethrolone (5·2 g) in ethyl acetate (100 ml) was hydrogenated at 25° and at atmospheric pressure in the presence of 10% palladium on charcoal (0·25 g), until 1 mol. equiv. of hydrogen had been absorbed. The mixture was filtered, and the filtrate was evaporated to leave the *cyclopentenone* (7) (5·2 g, 98%) as an oil, b.p. 110—120° at 0·5 mmHg, $\nu_{max.}$ (film) 3430, 1685, and 1642 cm^{-1}, τ 5·35 (1H, m), 5·65br (OH), 7·28 (dd, *J* 6 and 18, -C*H*H·CO), 7·81 (dd, *J* 2 and 18, -CH*H*·CO), 7·87 (t, *J* 6·5, :C·C*H*$_2$), 7·95 (:CMe), 8·26—9·0 (2H, m), and 9·16 (t, *J* 6·5, CH$_2$C*H*$_3$) (Found: *m/e*, 154·0989. $C_9H_{14}O_2$ requires *M*, 154·0994).

4-(n-Butyl)-5-methylcyclopent-4-ene-1,3-dione (2b).—Treatment of 2-[(*Z*)-but-2-enyl]-4-hydroxy-3-methylcyclopent-2-enone (0·3 g) [1] with PHC (3 g) in an identical manner to that described for the 2-(prop-2-enyl) analogue gave the *dione* (2b) (0·06 g, 22%), as a homogenous (t.l.c., g.l.c.) oil, $\nu_{max.}$ 1735 and 1700 cm^{-1}, τ 7·19 (-COC*H*$_2$), 7·56 (t, *J* 7, :C·CH$_2$), 7·99 (:CMe), 8·4—8·9 (4H, m), and 9·07 (t, *J* 6·5, CH$_2$C*H*$_3$) (Found: *m/e*, 166·1003. $C_{10}H_{14}O_2$ requires *M*, 166·0994).

4-Methyl-5-n-pentylcyclopent-4-ene-1,3-dione (2c).—Treatment of 4-hydroxy-3-methyl-2-[(*Z*)-pent-2-enyl]cyclopent-2-enone (0·2 g) [1] with PHC (2 g) in an identical manner to that described for the side-chain analogues gave the *dione* (2c) (0·05 g, 30%) as a homogenous (t.l.c., g.l.c.) oil, $\nu_{max.}$ 1735 and 1700 cm^{-1}, τ 7·18 (COCH$_2$), 7·55 (t, *J* 7, :C·CH$_2$), 7·97 (:CMe), 8·2—8·9 (6H, m), and 9·05 (t, *J* 6·5, CH$_2$C*H*$_3$) (Found: *m/e*, 180·1156. $C_{11}H_{16}O_2$ requires *M*, 180·1150).

3-Hydroxy-4-methyl-5-[(Z)-penta-2,4-dienyl]cyclopent-2-enone (19).—A sample of (+)-4-hydroxy-3-methyl-2-[(*Z*)-penta-2,4-dienyl]cyclopent-2-enone (14) was obtained by dehydration of the crystalline hydrate; [12] the alcohol showed one peak in g.l.c. and displayed i.r. and n.m.r. spectral data identical with those described previously.[4,11] A solution of the alcohol (0·75 g) in methanol (5 ml) was treated with a solution of sodium methoxide [from Na (0·13 g)] in methanol (5 ml) and the mixture was boiled under reflux for 18 h. The methanol was removed *in vacuo*, and the residue was dissolved in water. The aqueous solution was washed with ether to remove neutral products, acidified with hydrochloric acid, and re-extracted with ether. Evaporation of the dried ether extracts left the *3-hydroxycyclopent-2-enone* (19) (0·3 g, 40%) as a yellow glass, $\nu_{max.}$ (film) 3350, 2700, and 2580 cm^{-1} (1700—1600 cm^{-1} obscured), τ

[12] M. Elliott, *J. Chem. Soc.*, 1964, 5225.

3·35 (dd, J 16 and 10, $H_2C{:}CH{\cdot}CH$), 3·98 (dd, J 11, $HC{:}CH{\cdot}CH$), 4·7 ($:CHCO$), *ca.* 4·5—5·0 (partly obscured, 3 × $:CH$), 7·0—8·0 (4H, m), and 8·8 (m, Me) (Found: *m/e*, 178·0998. $C_{11}H_{14}O_2$ requires M, 178·0994).

Evaporation of the ether extracts containing the neutral products of reaction, gave starting alcohol only (0·20 g, 20% recovery), showing identical g.l.c. and spectral data with an authentic specimen.

Reaction of (+)-4-*Hydroxy*-3-*methyl*-2-[(Z)-*penta*-2,4-*dienyl*]*cyclopent*-2-*enone* (14) *with PHC*.—The starting alcohol[4] was shown to contain traces of (1b; R^2 = H) (*ca.* 2%) and of (1c; R^2 = H) (*ca.* 1%) in g.l.c. analysis. A mixture of the alcohol (2·14 g) and PHC (21·4 g) was heated at 200° for 0·5 h, then cooled to 25°, and treated with 5% hydrochloric acid. The solution was filtered, and the filtrate was thoroughly extracted with ether. Evaporation of the washed (Na_2CO_3, then H_2O) and dried ether extracts left a mixture of cyclopentenediones (0·15 g, *ca.* 7%), largely homogenous in t.l.c., but showing three major peaks in g.l.c. in the approximate proportions 1 : 3 : 6. Tentative assignments were made on the basis of n.m.r. data on the dione mixture, and these data, combined with some mixed g.l.c. and particularly g.l.c.–m.s. data enabled the following assignments to be made to the components of the mixture.

(*a*) 4-Methyl-5-[(*E*)-pent-1-enyl]cyclopent-4-ene-1,3-dione (17) (eluted last, *ca.* 60% total g.l.c. integral), τ 2·85 (dt, J 15 and 7, $HC{:}CH{\cdot}CH_2$), 3·71 [d, J 15, (*E*)–$CH{:}CH$], 7·12 ($COCH_2$), and 7·9 ($:CMe$), *m/e* 178 (100%), 163 (20), 150 (23·5), 149 (19·3), 136 (27·6), 135 (39·5), 124 (32·1), 121 (41), 108 (52), 107 (35), 93 (28), 91 (41), 80 (48), 79 (85), 77 (61), and 66 (45).

(*b*) 4-Methyl-5-(pent-2-enyl)cyclopent-4-ene-1,3-dione (16) (eluted second) which co-chromatographed with an authentic specimen from previous work[4] and displayed *m/e* 178, 163, 150, 136, 135, 124, 121, 108, and 96.

(*c*) 4-Methyl-5-[pent-3-(or 4-)enyl]cyclopent-4-ene-1,3-dione (18) or (15) (eluted first), *m/e* 178 (21%), 163 (2·5), 150 (12), 149 (4·6), 136 (7), 135 (5·6), 132 (4·1), 124 (22), 121 (5·8), 117 (2·9), 108 (5·2), 107 (4·9), 96 (10), 9·3 (511), and 91 (7·4).

G.l.c.–m.s. data also revealed the presence of small amounts of (i) 4-methyl-5-n-pentylcyclopent-4-ene-1,3-dione (2c) (only partly resolved in g.l.c. from the second peak) which co-chromatographed with an authentic sample, and displayed *m/e* 180, and (ii) 4-n-butyl-5-methylcyclopent-4-ene-1,3-dione (2b) (eluted before the first peak) which co-chromatographed with an authentic sample and displayed *m/e* 166 (5·8%), 151 (7·6), 139 (8·4), 138 (88·4), 137 (14), 124 (100), 123 (39), 109 (12·7), 96 (37), 95 (44), 82 (36), and 81 (22), in the product of reaction, which both resulted from acid-catalysed transformations of the alcohols (1b; R^2 = H) and (1c; R^2 = H) respectively, present in the starting alcohol.

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