The Synthesis of 4-Prop-2-enyl Substituted Cyclopentane-1,3-dione Enol Esters, and an Investigation of their Structures by N.m.r. Spectroscopy

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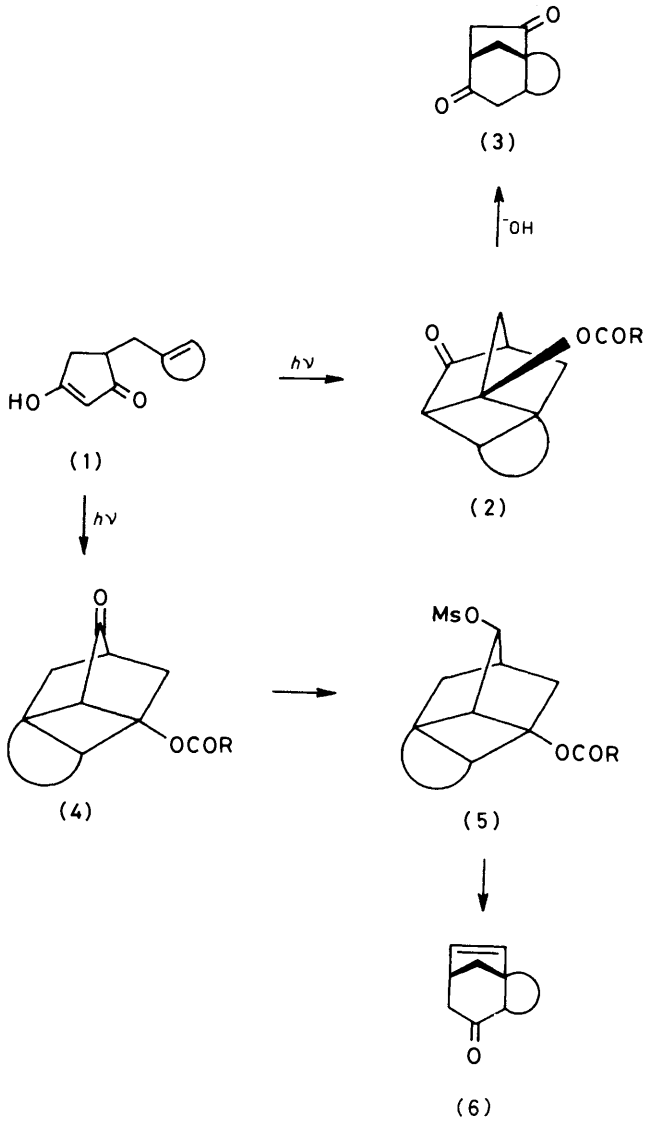
Alkylations of dianions derived from cyclopentane-1,3-dione and 2-methylcyclopentane-1,3-dione are shown to provide an expeditious route to the corresponding 4-alkylated derivatives (9). Unsymmetrical 4,5-disubstituted cyclopentane-1,3-diones(11) are more easily obtained by isomerisation of the corresponding 4-hydroxycyclopent-2-enones(10) in the presence of methanoiic sodium methoxide.

Proton and carbon-13 n.m.r. data establish that the 4-prop-2-enyl substituted cyclopentane-1,3-diones(9a—d, R = H, Me) and (11a—c) are fully enolised in solution, and that the two enolic forms [*e.g.* (18) and (19)] are undergoing rapid tautomerism. N.m.r. data also show that whereas the 2-methyl substituted diones (9a, b, d; R = Me) produce single enol acetates [*i.e.* (20), (26), and (27)] on treatment with acetic anhydride–sodium acetate, the analogues (9a, c, d; R = H) and (11a—c) instead lead to mixtures of isomeric enol acetates [*e.g.* (28)/(29); (35)/(36)]. In the case of the 4,5-disubstituted enol acetates (35), (36), and (41) ⟶ (44), the C-4, C-5 substituents are shown to have an *anti*-stereochemical relationship to one another.

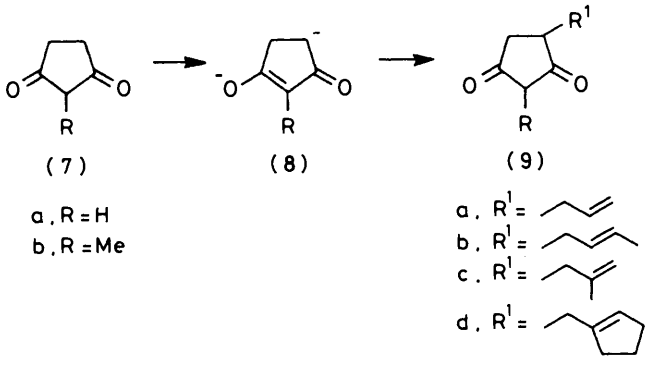
Esters derived from the enol forms (1) of 4-prop-2-enyl substituted cyclopentane-1,3-diones have been shown to be useful precursors for the construction of the bicyclo[3.2.1]-octane carbon framework [*e.g.* (3) and (6)] present in a range of biologically active natural terpenes.[1] This transformation is smoothly achieved by intramolecular [2 + 2] photocycloaddition [to (2) or (4)] followed by fragmentation, either directly [*i.e.* (2) ⟶ (3)] or after conversion into the corresponding ester mesylate (5) [*i.e.* (5) ⟶ (6)]. Although a number of methods are available for the synthesis of cyclopentane-1,3-dione, and simple 2-alkyl derivatives,[2] few investigations have been made of the synthesis of 4-prop-2-enyl substituted cyclopentane-1,3-diones. Furthermore, no systematic study of tautomerism amongst this interesting class of compound and their enol derivatives has been carried out. In connection with our photochemical route to the bicyclo[3.2.1]octane carbon framework (Scheme 1), we have examined synthetic routes to the appropriate 4-prop-2-enyl substituted cyclopentane-1,3-dione precursors (1), and investigated their tautomerism by n.m.r. spectroscopy and other methods. This paper describes these studies. In the following papers we show how these precursors can be elaborated to several substituted bicyclo[3.2.1]octanes, and also to the natural sesquiterpene zizaene, an odoriferous compound found in vetiver.

We began our investigations of synthetic routes to 4-prop-2-enyl substituted cyclopentane-1,3-diones by first examining the alkylation of bis-anions derived from the commercially available cyclopentane-1,3-diones (7a) and (7b).[3] γ-Alkylations of dianions derived from β-keto esters, and ω-alkylations of poly-anions derived from poly-β-ketones are both well documented and useful procedures in synthesis.[4] We therefore expected the cyclic ' variants ' of these reactions to proceed in a similar straightforward manner.

The dianions (8) were generated from the cyclopentane-1,3-diones (7) following treatment with n-butyl-lithium (2 equiv.) in tetrahydrofuran at −78 °C in the presence of hexamethylphosphoramide. Addition of the alkylating agent at −78 °C and warming to 25 °C, followed by quenching and work-up then led to the 4-alkylated derivatives (9). The 4-alkylated diones were easily purified by extraction into aqueous sodium carbonate followed by acidification and re-extraction with ether. In this manner a range of 4-prop-2-enyl substituted cyclopentane-1,3-diones and 4-prop-2-enyl substituted 2-



Scheme 1.



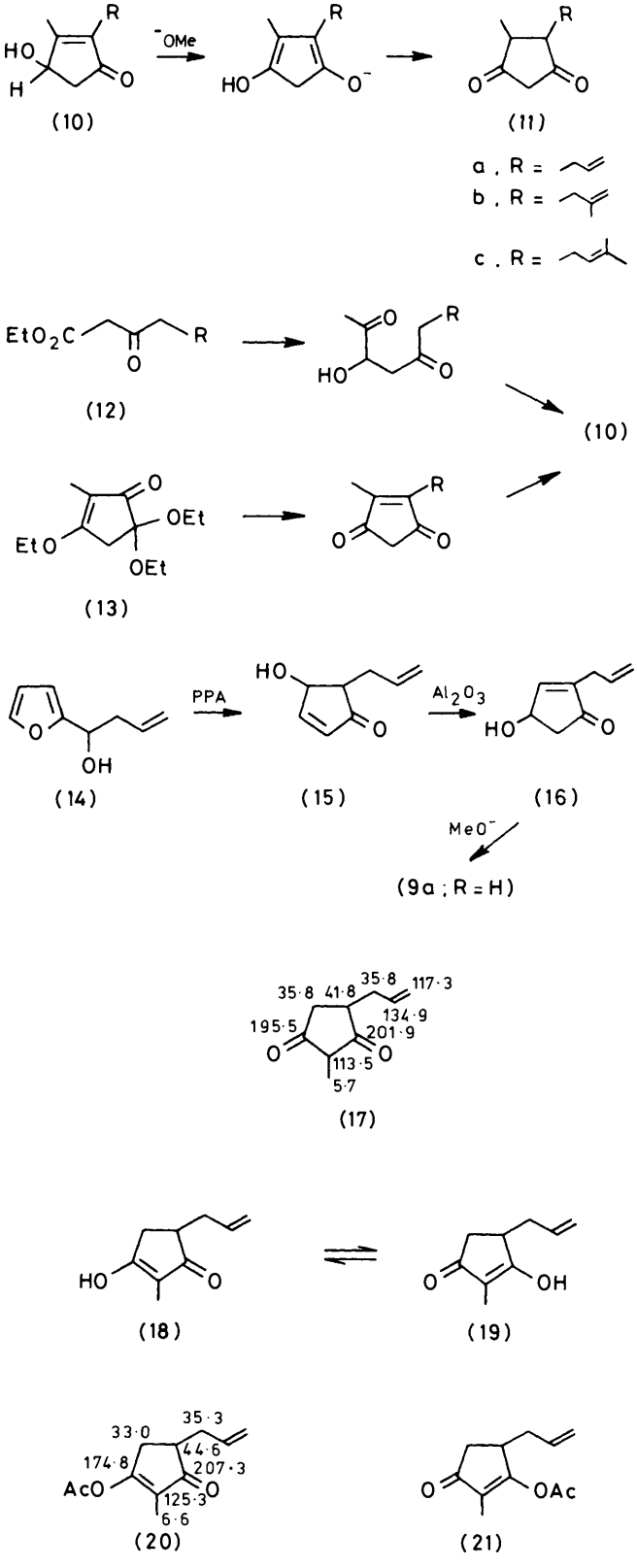
methylcyclopentane-1,3-diones were synthesised (*i.e.* 9a—d, R = H, Me). After preliminary publication of this route to 4-substituted cyclopentane-1,3-diones, Koreeda *et al.*[5] showed that the isobutyl ether derived from cyclopentane-1,3-dione can be used in a similar manner for the preparation of symmetrical 4,5-disubstituted cyclopentane-1,3-diones.

Neither of the above procedures is useful for the synthesis of unsymmetrical 4,5-disubstituted cyclopentane-1,3-diones [*e.g.* (11)]. A preparatively useful route to this type of molecule is by isomerisation of the corresponding 4-hydroxycyclopent-2-enone (10) in the presence of methanolic sodium methoxide. This novel isomerisation was first investigated in detail by Elliott,[6] and later by ourselves.[7] The required 2-prop-2-enyl substituted 4-hydroxycyclopent-2-enones (10) are most conveniently obtained starting from the corresponding β-keto esters (12) or the triethoxycyclopentenone (13) by procedures which are well documented.[8] Heating the hydroxycyclopentenones in the presence of hot methanolic sodium methoxide then produced the unsymmetrical diones (11a—c) in good yield. During the course of our studies we also synthesised 2-allyl-4-hydroxycyclopent-2-enone (16) by rearrangement of the furanol (14) in the presence of polyphosphoric acid [to (15)] followed by isomerisation.[9] Treatment of the 4-hydroxycyclopent-2-enone (16) with *cold* methanolic sodium methoxide then provided the same cyclopentane-1,3-dione (9a; R = H) obtained by direct allylation of the dianion (8a) derived from cyclopentane-1,3-dione.

Investigations of tautomeric equilibria amongst acyclic 1,3-dicarbonyl compounds, using n.m.r. spectroscopy (both ^1H and ^{13}C), have been extensive.[10] By contrast, with a few exceptions,[11] little is known about tautomerism in cyclopentane-1,3-diones.

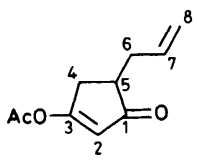
Both i.r. ($\nu_{max.}$ 2 700—3 515, 1 515—1 620 cm^{-1}) and ^1H n.m.r. spectroscopy [δ 11.56(OH), 1.66 (:CMe)] of 2-methyl-4-prop-2-enylcyclopentane-1,3-dione (9a; R = Me) establish that the dione is fully enolised in solution, and that the two enolic forms (18) and (19) are undergoing rapid tautomerism. The latter feature is also corroborated in the ^{13}C n.m.r. spectrum where only one set of carbon resonances are observed; these data are summarised on formula (17). Significantly, C-2 in the dione occurs as a singlet at δ 113.5 p.p.m. indicating its sp^2 character. A distinction between the C-1 and C-3 carbonyl carbon atoms in (9a; R = Me) was made on the basis of preferential deshielding of C-3 by the α-propenyl side chain. The remaining resonances were readily assigned from inspection and comparison of shift data, and also from decoupled spectra.

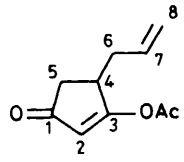
Treatment of the dione (9a; R = Me) with acetic anhydride in the presence of sodium acetate afforded a single enol acetate, homogeneous in g.l.c. and t.l.c. analysis. The enol



acetate showed one set of resonances in both the ^1H n.m.r. and the ^{13}C n.m.r. spectra. Significantly the vinyl methyl protons resonated as an ' apparent ' triplet (homoallylic coupling *ca.* 1.5 Hz) in the ^1H n.m.r. spectrum indicating structure (20) for the enol acetate, rather than (21). The relative shifts (δ 33.0 and 44.6 p.p.m.) of C-4 and C-5 in the ^{13}C n.m.r. spectrum of

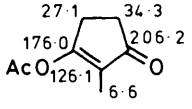
Table ^{13}C N.m.r. data (p.p.m. from $SiMe_4$)





Carbon atom	(26)	(28)	(29)	(30a)	(31a)	(30b)	(31b)	(35)	(36)	(41)	(42)	(37)	(38)
1	207.8	208.8	206.1	208.2	205.6	208.6	205.8	206.8	208.0	207.7	210.2	205.8	207.2
2	125.3	115.4	116.1	115.6	116.5	115.3	116.0	114.4	115.0	114.3	114.8	103.0	102.5
3	174.9	178.8	181.3	178.6	180.3	178.6	181.0	180.9	178.8	180.8	179.6	192.7	190.5
4	33.0	32.7	39.5	34.3	39.9	34.9	40.9	44.6	41.0	45.5	41.6	45.8	53.6
5	45.4	43.3	32.7	43.6	38.8	42.6	38.9	48.6	52.2	47.4	51.1	48.4	40.7
6	34.2	34.2	34.2	35.0	36.0	39.4	39.4	35.6	34.7	40.8	39.5	35.1	35.6
7	127.7	141.8	140.9	134.7	133.8	143.2	142.3	135.1	134.2	143.2	142.9	134.5	135.5
8	127.4	125.7	126.7	117.2	118.0	112.0	112.8	117.3	117.9	112.6	113.3	117.6	116.9
2-Me	6.6												
7/8-Me	17.8					22.2	22.2						
4/5 Me								15.6	17.4			16.0	17.4

[δ 166.2—166.5 (O $COCH_3$); 21.3 ($OCOCH_3$) p.p.m.]



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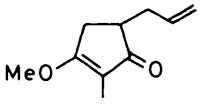

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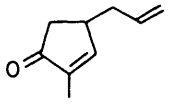

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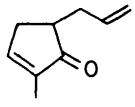

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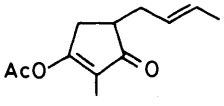

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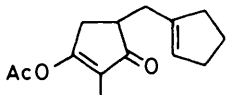
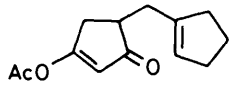


(27)

(9d; R = H)

Ac_2O | NaOAc



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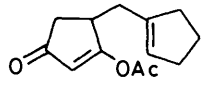

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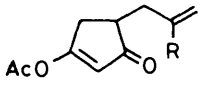

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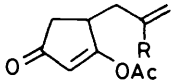


(31)

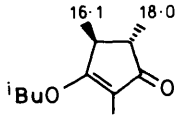
a, R = H; b, R = Me

the enol acetate, compared to those found in the model compound (22) (δ 27.1 and 34.3 p.p.m.) also support formulation (20) for the prop-2-enyl substituted acetate (*i.e.* C-5 more deshielded since it bears the propenyl side-chain). Additional confirmation of this formulation was obtained when the corresponding enol methyl ether (23) (also a single isomer) prepared from (9a; R = Me) was converted into the cyclopent-2-enone (24) [rather than (25)] on reduction with lithium aluminium hydride followed by an acid work-up.

Both the 4-but-2-enyl and the 4-cyclopent-1-enylmethyl substituted cyclopentane-1,3-diones (9b; R = Me) and (9d; R = Me), also led to single enol acetates on treatment with acetic anhydride–sodium acetate. The enol esters displayed closely similar n.m.r. data to those recorded for (20), thereby supporting a similar structural assignment, *i.e.* (26) and (27) respectively (see Table for ^{13}C n.m.r. data).

Like the 2,4-disubstituted cyclopentane-1,3-diones (9a, b and d; R = Me), i.r. and n.m.r. spectral data on the 4-cyclopent-1-enylmethylcyclopentane-1,3-dione (9d; R = H) showed that the molecule exists in solution as a mixture of rapidly interconverting enolic forms. On acetylation however, the dione afforded an approximately 1 : 1 mixture (by integration of ^1H n.m.r. resonances) of the two enol acetates (28) and (29). The two enol acetates are easily distinguished in the ^1H n.m.r. spectrum where the cyclopentenone ring olefinic proton in (28) is observed as an ' apparent ' triplet (allylic coupling *J ca.* 1.5 Hz) at δ 6.12, whereas the same proton in enol acetate (29) is observed as a doublet (*J ca.* 1) at δ 6.19. A partial separation of the isomeric enol acetates was achieved by a combination of pressure liquid and thin layer chromatography, and this permitted us to assign all of the carbon atoms in the ^{13}C n.m.r. spectra of the esters (see Table). In a similar manner, the 4-substituted cyclopentane-1,3-diones (9a; R = H) and (9c; R = H) led to approximately 1 : 1 mixtures of the corresponding isomeric enol acetates (30) and (31) respectively, on treatment with acetic anhydride–sodium acetate.

Although the 4,5-disubstituted cyclopentane-1,3-diones (11a) (11b) and (11c) can exist as mixtures of *syn*- and *anti*-diastereoisomers, their ^1H n.m.r. spectra each revealed only



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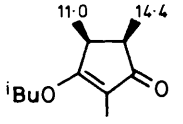

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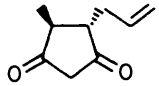


(34)

one secondary methyl absorbance (*J* 7, δ *ca.* 1.23) which showed no further splitting in the presence of lanthanide shift reagents. These data indicated that only one diastereoisomer was present, and the *anti*-stereochemistry for each dione is supported by comparison of the positions of the secondary methyl carbon atoms in their ^{13}C n.m.r. spectra (δ 16.8) with those of the model *anti*- and *syn*-cyclopentane-1,3-dione enol ethers (32) and (33) (see data on formulae).[5]

Acetylation of the dione (11a), using acetic anhydride in the presence of sodium acetate, gave rise to a 1 : 1 mixture of isomeric enol acetates, which by inspection and comparison of n.m.r. data with those of the analogues (20), (30), and (31), were assigned structures (35) and (36) respectively. In the ^{13}C n.m.r. spectrum (see Table for shift data), the C-4/5 methyl carbon atoms in the mixture occur at δ 17.4 and 15.6 p.p.m., which by comparison with (32) and (33), again suggests that the C-4, C-5 substituents in the isomeric enol acetates are *anti*- to each other. This was corroborated when the dione (11a) was converted into the corresponding mixture of enol methyl ethers, and the latter transformed into a mixture of cyclopentenones by reduction with lithium aluminium hydride. Thus, treatment of the *anti*-dione (34) with potassium carbonate–dimethyl sulphate, led to a 1 : 1 mixture of the two *anti*-enol methyl ethers (37) and (38) which showed C-4/5 methyl carbon atom resonances at δ 16.0 and 17.4 p.p.m. respectively. Reduction of this mixture, followed by acid treatment then led to the two cyclopentenones (39) and (40) whose structures followed from their n.m.r. spectral data.

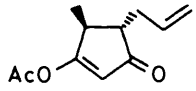
In a similar manner, the *anti*-cyclopentane-1,3-diones (11b) and (11c), on acetylation produced comparable amounts of the two possible corresponding *anti*-enol acetates, *i.e.* (41)/(42) and (43)/(44) respectively.

Significantly, irradiations of the approximate 1 : 1 mixtures of enol acetates derived from (9a, c, d, R = H) and (11a—c) produce intramolecular cycloadducts [*i.e.* (2) or (4)] derived from only the 5-prop-2-enyl isomers [*i.e.* (28), (30a), (30b), (35), (41), and (43)]. Since the 4-prop-2-enyl isomers (29), (31a), (31b), (36), (42), (44) are consumed during the photocycloadditions, equilibration between the isomeric enol acetates, possibly by a process not unrelated to the photo-Fries reaction, must be quite rapid during the irradiations. These and other photochemical studies involving cyclopentane-1,3-dione enol acetates are described in the accompanying papers.[12]

Experimental

^{1}H N.m.r. spectra were determined on a Jeol JNM-MH 100 spectrometer, or at 250 MHz on a Bruker WM PFT instrument, as dilute solutions in $CDCl_3$ with internal $SiMe_4$ reference. ^{13}C N.m.r. spectra were recorded at 20 °C with a JEOL-PS-100 spectrometer operating at 25.15 MHz interfaced with a Nicolet 1085 20K computer.

Solutions were dried over magnesium sulphate, unless otherwise indicated, and solvents were evaporated under reduced pressure. All solvents for chromatography were redistilled. G.l.c. analyses were made on 5 ft × $\frac{1}{8}$ in columns packed with 10% SE-30 on Diatomite. Ether refers to diethyl ether throughout.



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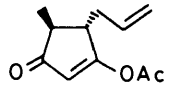

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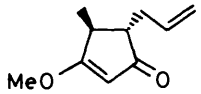

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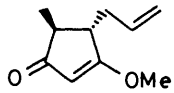

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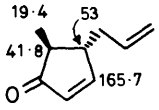

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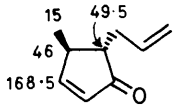

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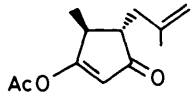

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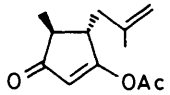
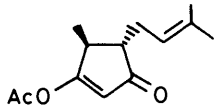
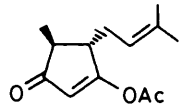


(42)



(43)



(44)

4-*Prop*-2-*enyl Substituted Cyclopentane*-1,3-*diones* via *Alkylation of Bis-anions Derived from Cyclopentane*-1,3-*dione and* 2-*Methylcyclopentane*-1,3-*dione: General Procedure (with M. Mellor)*.[3]—A solution of n-butyl-lithium (8.4 mM; 2.1 equiv.) in hexane was added over 5 min to a stirred solution of the cyclopentane-1,3-dione (4 mM) in hexamethylphosphoramide (3.4 ml) and tetrahydrofuran (25 ml) at −78 °C. The mixture was stirred at −78 °C for 20 min and then treated dropwise over 5 min with the alkylating agent (1.1 equiv.). The mixture was stirred at −78 °C for 1 h, and then allowed to warm to 25 °C when it was diluted with dilute hydrochloric acid. The aqueous layer was separated, and then washed with ether (3 × 15 ml). The combined organic layers were extracted with 10% aqueous sodium carbonate solution (5 × 10 ml), and the combined aqueous layers were then acidified (6M-HCl) and extracted with ether (4 × 10 ml). Evaporation of the washed (water) and dried ether extracts then left the dione which was used without further purification. Satisfactory microanalyses could not be obtained on any of the diones, because of the ease with which the molecules underwent oxidation.

4-*Prop*-2-*enylcyclopentane*-1,3-*dione* (9a; R = H).—By the general procedure, alkylation of cyclopentane-1,3-dione with allyl bromide gave the dione (50%) as an almost colourless oil, $\lambda_{max.}$ (EtOH) 241 nm; $\nu_{max.}$ (film) 2 670—3 250, 1 640, and 1 520—1 625 cm^{-1}; δ 11.94 (OH), 5.45—5.96 (m, C*H*:CH_2) 5.34 (CO·C*H*:), 4.9—5.23 (m, :CH_2), and 1.97—2.93 (m, 5 H) (Found: M^+, *m/z* 138.0682; $C_8H_{10}O_2$ requires *M*, 138.0681).

4-(2-*Methylprop*-2-*enyl*)*cyclopentane*-1,3-*dione* (9c; R = H).—By the general procedure, alkylation of cyclopentane-1,3-dione with 2-methylallyl chloride gave the dione (72%) as a pale yellow solid, m.p. 65—67 °C (decomp.), $\lambda_{max.}$ (EtOH) 240 nm; $\nu_{max.}$ (KBr) 2 700—3 350, 1 645, and 1 530—1 630 cm^{-1}; δ 11.94(OH), 5.28 (COCH:), 4.59—4.83 (m, :CH_2), 1.75—2.99 (m, 5 H), and 1.74 (:CMe) (Found: M^+, *m/z* 152.0836. $C_9H_{12}O_2$ requires *M*, 152.0837).

4-*Cyclopent*-1-*enylmethylcyclopentane*-1,3-*dione* (9d; R = H).—By the general procedure, alkylation of cyclopentane-1,3-dione with 1-(bromomethyl)cyclopentene [13] gave the dione (29%) as a yellow solid, m.p. 95—105 °C, $\nu_{max.}$ ($CHCl_3$) 2 730—3 350, 1 640, and 1 550—1 620 cm^{-1}; δ 10.36 (OH), 5.29—5.38 (m, 2 × :CH), 2.45—3.0 (m, 4 H), 2.0—2.45 (m, 3 H), and 1.7—2.0 (m, 2 H); δ_C 205.6, 201.2, 141.6, 126.0(d), 105.0(d), 42.3(d), 37.8(t), 35.2(t), 33.6(t), 32.5, and 23.5 p.p.m. (Found: *M*, *m/z* 178.1000. $C_{11}H_{14}O_2$ requires *M*, 178.0994).

2-*Methyl*-4-*prop*-2-*enylcyclopentane*-1,3-*dione* (9a; R = Me).—By the general procedure, alkylation of 2-methylcyclopentane-1,3-dione with allyl bromide gave the dione (51%) as an amorphous solid, m.p. 71—73 °C, $\lambda_{max.}$ (EtOH) 243 nm; $\nu_{max.}$ ($CHCl_3$) 2 665—3 515, 1 640, and 1 515—1 620 cm^{-1}; δ 11.56 (OH), 5.19—5.83 (m, ·CH:CH_2), 4.65—5.07 (m, CH_2), 1.75—2.84 (m, 5 H), and 1.66 (:CMe); δ_C see formula (17) (Found: M^+, *m/z* 152.0830; $C_9H_{12}O_2$ requires *M*, 152.0837).

4-*But*-2-*enyl*-2-*methylcyclopentane*-1,3-*dione* (9b; R = Me).—By the general procedure, alkylation of 2-methylcyclopentane-1,3-dione with *E*-1-bromobut-2-ene, gave the dione (50%) as an amorphous solid, m.p. 85—88 °C, $\nu_{max.}$ ($CHCl_3$) 2 650—3 450, 1 640, and 1 520—1 625 cm^{-1}; δ 9.46(OH), 5.1—5.84 (m, 2 × :CH), 1.9—2.88 (m, 5 H), and 1.73br (2 × :CMe) (Found: *M*, *m/z* 166.0992. $C_{10}H_{14}O_2$ requires *M*, 166.0993).

4-*Cyclopent*-1-*enylmethyl*-2-*methylcyclopentane*-1,3-*dione* (9d; R = Me).—By the general procedure, alkylation of 2-methylcyclopentane-1,3-dione with 1-(bromomethyl)cyclopentene [13] gave the dione (32%) as a solid, m.p. 107—110 °C, $\lambda_{max.}$ (EtOH) 245 nm; $\lambda_{max.}$ (KBr) 2 600—3 450, 1 670, and 1 520—1 640 cm^{-1}; δ 10.6(OH), 5.35 (m, :CH), 1.29—2.97 (m, 11 H), 1.66 (:CMe); δ_C 202.9, 195.9, 141.9, 125.8(d), 113.0, 41.3, 36.6(t), 35.2(t), 32.5(t), 23.5(t), and 5.8(q) p.p.m. (Found: *M*, *m/z* 192.1169. $C_{12}H_{16}O_2$ requires *M*, 192.1150).

anti-4-*Methyl*-5-*prop*-2-*enylcyclopentane*-1,3-*dione* (11a).—The dione was prepared as described previously [7] and showed δ 12.4 (OH), 5.43—6.17 (m, CH:CH_2), 5.23 (COCH:), 4.93—5.22 (m, :CH_2), 1.98—3.0 (m, 4 H), and 1.23 (d, *J* 7, CH*Me*); δ_C 204.4, 202.7, 134.7(d), 117.6(t), 104.1(d), 51.2(d), 43.3(d) 35.3(t), and 16.8(q) p.p.m.

anti-4-*Methyl*-5-(3-*methylbut*-2-*enyl*)*cyclopentane*-1,3-*dione* (11c).—A solution of 4-hydroxy-3-methyl-2-(3-methylbut-2-enyl)cyclopent-2-enone (0.25 mol) * in dry methanol (50 ml) was added to a solution of sodium (0.32 g-atom) in methanol (500 ml), and the deep red solution was heated under reflux for 21 h. The mixture was cooled, and the methanol was then removed under reduced pressure. The residue was diluted with water, and the solution was then washed with ether and acidified with 6M-hydrochloric acid. The aqueous solution was extracted with ether (6 × 50 ml), and the combined ether extracts were then washed (water), dried, and evaporated to leave the *dione* (78%) as a red oil, $\nu_{max.}$ (film) 2 750—3 350, 1 640, and 1 590 cm^{-1}; δ 6.88 (OH), 5.22 (COCH:), 5.07 (m, Me_2C:C*H*), 2.64—3.1 (m, 1 H), 2.0—2.6 (m, 3 H), 1.71 (:CMe), 1.63 (:CMe), and 1.18 (d, *J* 7, CHMe) (Found: *M*, *m/z* 180.1152. $C_{11}H_{16}O_2$ requires *M*, 180.1150).

anti-4-*Methyl*-5-(2-*methylprop*-2-*enyl*)*cyclopentane*-1,3-*dione* (11b).—The dione was prepared (84%) from 4-hydroxy-3-methyl-2-(2-methylprop-2-enyl)cyclopent-2-enone [14] by treatment with sodium methoxide in methanol, according to the procedure described for the analogue (11a). It showed b.p. 134—138/°C 0.3 mmHg, $\lambda_{max.}$ 239 nm; $\lambda_{max.}$ (film) 2 670—3 400, 1 640, and 1 585 cm^{-1}; δ 11.1 (OH), 5.27 (d, *J* 2, COCH:), 4.65—4.9 (m, :CH_2), 1.95—3.12 (m, 4 H), 1.8 (:CMe), and 1.21 (d, *J* 7.5, CH*Me*) (*m/z* 166).

4-*Hydroxy*-2-*prop*-2-*enylcyclopent*-2-*enone* (16).—Treatment of 2-furfuraldehyde with the Grignard reagent derived from allyl bromide, by the usual procedure, gave 2-(1-hydroxybut-3-enyl)furan (73%), b.p. 83—85 °C/15 mmHg, $\nu_{max.}$ (film) 3 390 cm^{-1}; δ 7.46 (d, *J* 1.5, OCH:), 6.4 (m, OCH:C*H*), 6.3 (m, OCH:C*H*), 5.63—6.1 (m, C*H*:CH_2), 5.05—5.35 (m, :CH_2), 4.76 (t, *J* 6.5, C*H*OH), 2.76 (OH), and 2.64 (dd, *J* 2 and 7, CH_2) (Found: *M*, *m/z* 138.0681. $C_8H_{10}O_2$ requires *M*, 138.0681).

Rearrangement of the furanol in polyphosphoric acid, according to the procedure of Piancatelli *et al.* [9] produced 4-hydroxy-5-prop-2-enylcyclopent-2-en-1-one (15) (30%), $\nu_{max.}$ (film) 3 480, 1 690, and 1 640 cm^{-1}; δ 7.8 (dd, *J* 1.5 and 6, C*H*:CHCO), 6.38 (d, *J* 6, :*CH*CO), 5.74—6.2 (m, C*H*:CH_2), 5.12—5.44 (m, :CH_2), 4.89 (C*H*OH), 3.55(OH), and 2.12—2.9 (m, 3 H), which was then isomerised to the hydroxycyclopentenone on alumina. The hydroxycyclopentenone showed, $\lambda_{max.}$ (EtOH) 239.5 nm; $\nu_{max.}$ (film) 3 480, 1 710, 1 690, and 1 645 cm^{-1}; δ 7.55 (m, :C*H*·CHOH), 5.81—6.3 (m, C*H*:CH_2), 5.04—5.49 (m, :CH_2), 4.39 (C*H*OH), 3.08 (d, *J* 6, CH_2CO), 2.3—2.8 (m, 2 H), and 3.52 (OH) (Found: *M*, *m/z* 138.0681. $C_8H_{10}O_2$ requires *M*, 138.0681).

The 4-hydroxycyclopentenone was rearranged in methanolic sodium methoxide solution at 0 °C to 4-prop-2-enylcyclopentane-1,3-dione (9a; R = H) (60%) which showed identical spectral data with those obtained for the same dione prepared by allylation of cyclopentane-1,3-dione, described above.

Cyclopentane-1,3-*dione Enol Acetates: General Procedure.*—A solution of the dione (50 mM) in acetic anhydride (40 ml) containing anhydrous sodium acetate (20 mM) was stirred at 25 °C for 24 h; the excess of acetic anhydride and acetic acid were then removed under reduced pressure. The residue was diluted with water (150 ml) and extracted with ether (4 × 50 ml). The combined ether extracts were washed with aqueous sodium carbonate (5 × 25 ml) and water (2 × 25 ml), and then dried and evaporated to leave the enol acetate which was purified by distillation or by chromatography (yields 80—98%).

3-*Acetoxy*-2-*methyl*-5-*prop*-2-*enylcyclopent*-2-*en*-1-*one* (20).—The ester showed $\lambda_{max.}$ (EtOH) 234 nm (ε 12 000); $\nu_{max.}$ 1 770, 1 700, 1 665, and 1 640 cm^{-1}; δ 5.47—5.94 (m, C*H*:CH_2), 4.87—5.16 (m, :CH_2), 2.01—3.13 (m, 5 H), 2.27 (OAc), and 1.62 (t, *J* 1.5, :CMe); δ_C see formula (20).

3-*Acetoxy*-2-*methylcyclopent*-2-*en*-1-*one* (22).—The ester showed b.p. 58—64 °C/0.3 mmHg (lit.,[11b] b.p. 66—67.5 °C/0.5 mmHg), $\nu_{max.}$ (film) 1 765, 1 705, and 1 660 cm^{-1}; δ 2.76—2.96 (m, $COCH_2$), 2.53 (dt, *J* 6 and 2, CH_2C:), 2.32 (OAc), and 1.67 (t, *J* 2, :C*Me*); δ_C see formula (22).

* Kindly donated by Dr. J. Martel (Roussel Uclaf).

3-*Acetoxy*-5-*but*-2-*enyl*-2-*methylcyclopent*-2-*en*-1-*one* (26).—The ester showed $\lambda_{max.}$ (EtOH) 236 nm (ε 12 500); $\nu_{max.}$ (film) 1 775, 1 705, and 1 665 cm^{-1}; δ_C see Table (Found: *M*, *m/z* 208.1112. $C_{12}H_{16}O_3$ requires *M*, 208.1100).

3-*Acetoxy*-5-*cyclopent*-1-*enylmethyl*-2-*methylcyclopent*-2-*en*-1-*one* (27).—The ester showed $\lambda_{max.}$ (EtOH) 237 nm (ε 13 600); $\nu_{max.}$ (film) 1 770, 1 700, and 1 660 cm^{-1}; δ 5.35 (m, C:C*H*CH_2), 1.51—3.08 (m, 11 H), 2.3 (OAc), and 1.63 (t, *J* 1.5, :C*Me*) (Found: *M*, *m/z* 234.1236. $C_{14}H_{18}O_3$ requires *M*, 234.1256).

2-*Methyl*-4-*prop*-2-*enylcyclopent*-2-*en*-1-*one* (24).—Treatment of 2-methyl-4-prop-2-enylcyclopentane-1,3-dione with dimethyl sulphate in hot acetone in the presence of anhydrous potassium carbonate, in the usual manner, gave 3-methoxy-2-methyl-5-prop-2-enylcyclopent-2-en-1-one (23) (93%), b.p. 60—65 °C/0.05 mmHg, $\lambda_{max.}$ (EtOH) 253 nm (ε 11 000); $\nu_{max.}$ (film) 1 695 and 1 640 cm^{-1}; δ 6.0—7.47 (m, :CH), 4.95—5.25 (m, :CH_2), 4.0 (OMe), 2.01—3.05 (m, 5 H), and 1.64 (:CMe).

Reduction of the enol methyl ether, with lithium aluminium hydride in ether, followed by treatment of the crude product with dilute sulphuric acid (2 h at 25 °C) then gave the cyclopentenone (65%) as an odoriferous oil, $\lambda_{max.}$ (EtOH) 231 nm; $\nu_{max.}$ 1 715 and 1 645 cm^{-1}; δ 5.28—5.79 (m, C*H*:CH_2), 4.91 (m, :C*H*·CH), 4.68—4.87 (m, :C*H*$_2$) 1.7—2.9 (m, 5 H), 1.59 (d, *J* 2, :CMe) (Found: *M*, *m/z* 136. $C_9H_{12}O$ requires *M*, 136).

3-*Acetoxy*-5-*prop*-2-*enylcyclopent*-2-*en*-1-*one* (30a) and 3-*Acetoxy*-4-*prop*-2-*enylcyclopent*-2-*en*-1-*one* (31a).—The esters were obtained as a 1 : 1 mixture which showed n_D^{22} 1.4885, $\lambda_{max.}$ (EtOH) 235 nm; $\nu_{max.}$ (film) 1 785, 1 705, 1 640, and 1 605 cm^{-1}; δ 6.19 (d, *J* 1, COC*H*:) [isomer (31a)], 6.12 (dd, *J ca.* 1, COCH:) [isomer (30a)], 5.49—5.97 (m, C*H*:CH_2), 4.95—5.25 (m, :CH_2), 1.95—3.18 (m, 5 H), and 2.33 (OAc), 2.3 (OAc); δ_C see Table (Found: *m/z* 180.0776. $C_{10}H_{12}O_{23}$ requires *M* 180.0786).

3-*Acetoxy*-5-(2-*methylprop*-2-*enyl*)*cyclopent*-2-*en*-1-*one* (30b) *and* 3-*Acetoxy*-4-(2-*methylprop*-2-*enyl*)*cyclopent*-2-*en*-1-*one* (31b).—The esters were obtained as a 1 : 1 mixture which showed $\lambda_{max.}$ 239.5 nm (ε 12 500); $\nu_{max.}$ 1 785, 1 705, 1 645, and 1 600 cm^{-1}; δ 6.26 (d, *J* 1, COC*H*:) [isomer (31b)], 6.21 (dd, *J* 1, COC*H*:) [isomer (30b)], 4.7—4.95 (m, :CH_2), 1.91—3.3 (m, 5 H), 2.33 (OAc), 2.35 (OAc), and 1.78br (:CMe); δ_C see Table (Found: *M*, *m/z* 194.0963. $C_{11}H_{14}O_3$ requires *M*, 194.0943).

3-*Acetoxy*-5-*cyclopent*-1-*enylmethylcyclopent*-2-*en*-1-*one*(28) *and* 3-*Acetoxy*-4-*cyclopent*-1-*enylmethylcyclopent*-2-*en*-1-*one* (29).—The esters were obtained as a 1 : 1 mixture which showed $\nu_{max.}$ 1 780, 1 700, 1 635, and 1 600 cm^{-1}; δ 6.21 (d, *J* 1.5 COC*H*:) [isomer (29)], 6.14 (dd, *J ca.* 1.5, COC*H*:) [isomer (28)], 5.4 (m, CH_2C*H*:), and 1.6—3.3 (m, 11 H), 2.3 (OAc); δ_C see Table. A partial purification (⩾ 75%) of each enol acetate was achieved by repetitive pressure column elution and thin layer chromatography on silica gel using ether–light petroleum (b.p. 60—80 °C) (1 : 1) as eluant.

3-*Acetoxy*-4-*methyl*-5-*prop*-2-*enylcyclopent*-2-*en*-1-*one* (35) *and* 3-*Acetoxy*-5-*methyl*-4-*prop*-2-*enylcyclopent*-2-*en*-1-*one* (36).—The esters were obtained as a 1 : 1 mixture which showed b.p. 104—106 °C/1 mmHg, $n_D^{22.5}$ 1.4890, $\lambda_{max.}$ (EtOH) 234 (ε 13 100) and 287 nm (ε 270); $\nu_{max.}$ (film) 1 785, 1 705, 1 645, and 1 600 cm^{-1}; δ 6.19 (m, CO·CH:), 5.5—5.96 (m, C*H*:CH_2), 4.94—5.22 (m, :CH_2), 1.9—2.9 (m, 4 H), 2.31 (OAc), and 1.23, 1.18 (d, *J* 7.5, CH*Me*, two isomers); δ_C see Table; (Found: *M*, *m/z* 194.0946. $C_{11}H_{14}O_3$ requires *M* 194.0963).

5-*Methyl*-4-*prop*-2-*enylcyclopent*-2-*en*-1-*one* (39) *and* 4-*Methyl*-5-*prop*-2-*enylcyclopent*-2-*en*-1-*one* (40).—Treatment of 4-methyl-5-prop-2-enylcyclopentane-1,3-dione with dimethyl sulphate in hot acetone in the presence of anhydrous potassium carbonate, in the usual manner, gave a mixture of the two enol methyl ethers (37) and (38) (73%), b.p. 80—83 °C/0.1 mmHg, $\lambda_{max.}$ (EtOH) 244 nm (ε 11 500); $\nu_{max.}$ (film) 1 690, 1 640, and 1 595 cm^{-1}; δ 5.54—5.98 (m, C*H*:CH_2), 5.25 (d, *J* 2, COCH:), 4.96—5.22 (m, :CH_2), 3.86 (OMe), 1.94—2.69 (m, 4 H), and 1.22, 1.18 (d, *J* 7.5, CH*Me*, two isomers); δ_C see Table (Found: *M*, *m/z* 166.0993; $C_{10}H_{14}O_2$ requires *M*, 166.0994).

Reduction of the enol ether mixture with lithium aluminium hydride in ether, followed by treatment of the crude product with dilute sulphuric acid (2 h at 25 °C) then gave an approximate 1 : 1 mixture of the two enones (39) and (40) (64%), $\lambda_{max.}$ (EtOH) 219 nm; δ 7.56 and 7.48 (dd, *J* 2 and 8, COCH: C*H*, two isomers), 6.11 and 6.05 (d, *J* 8, COC*H*:CH, two isomers), 5.54—6.0 (m, C*H*:CH_2), 4.92—5.22 (m, :CH_2), 1.83—2.85 (m, 4 H), and 1.21, 1.18 (d, *J* 8, CH*Me*, two isomers), δ_C see formulae (39) and (40).

3-*Acetoxy*-4-*methyl*-5-(2-*methylbut*-2-*enyl*)*cyclopent*-2-*en*-1-*one* (43) *and* 3-*Acetoxy*-5-*methyl*-4-(2-*methylbut*-2-*enyl*)*cyclopent*-2-*en*-1-*one* (44).—The esters were obtained as a 1 : 1 mixture which showed $\lambda_{max.}$ (EtOH) 243 nm (ε 16 500); $\nu_{max.}$ ($CHCl_3$) 1 780, 1 705, and 1 590 cm^{-1}; δ 6.25 (m, COCH:), 5.0—5.3 (m, Me_2C:CH), 2.95—3.28 (m, 1 H), 1.88—2.85 (m, 3 H), 2.34 (OAc), 1.74 (:CMe), 1.66 (:CMe), and 1.22, 1.20 (d, *J* 7, CH*Me*, two isomers) (Found: *M*, *m/z* 222.1231. $C_{13}H_{18}O_3$ requires *M*, 222.1256).

3-*Acetoxy*-4-*methyl*-5-(2-*methylprop*-2-*enyl*)*cyclopent*-2-*en*-1-*one* (41) and 3-*Acetoxy*-5-*methyl*-4-(2-*methylprop*-2-*enyl*)-*cyclopent*-2-*en*-1-*one* (42).—The esters were obtained as a 1 : 1 mixture which showed b.p. 125—130 °C/1.5 mmHg, $\lambda_{max.}$ (EtOH) 233 nm (ε 12 900); $\lambda_{max.}$ (film) 1 775, 1 700, and 1 645 cm^{-1}; δ 6.2 (m, COCH:), 4.81 (m, :CH_2), 1.93—2.87 (m, 4 H), 2.33 (OAc), 1.81 (:CMe), and 1.26, 1.18 (d, *J* 7, CH*Me*, two isomers); δ_C see Table (Found: *M*, *m/z* 208.1120. $C_{12}H_{16}O_3$ requires *M*, 208.1100).

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