Synthesis of Calythrone and Related Cyclopentene-1,3-diones *via* Rearrangement of 4-Ylidenebutenolides

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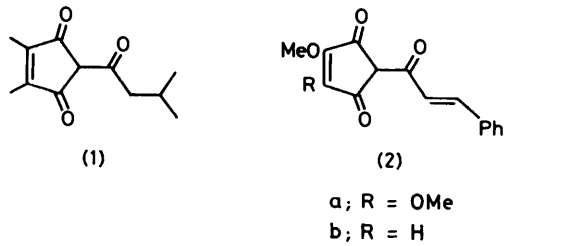
Treatment of 4-ylidenebutenolides with sodium methoxide in methanol results in rearrangement to the corresponding cyclopentene-1,3-diones in high yield. The general method is applied in a synthesis of calythrone [(1) from (18)] from *Calythrix tetragona*, and the related cyclopentene-1,3-diones [(15) from (14); (25) from (24); (27) from (26); (33) from (32); and (37) from (36)].

Attempts to rearrange the butenolide (21) to natural lucidone (2b), from *Lindera lucida* were unsuccessful, and instead led to the corresponding 4-oxo-unsaturated ester (23).

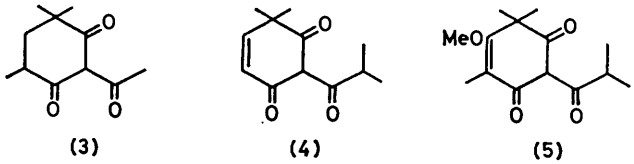
The relevance of the facile rearrangement of 4-ylidenebutenolides to cyclopentene-1,3-diones, to a possible biosynthetic route is considered.

CALYTHRONE (1),[1,2] linderone (2a),[3] and lucidone (2b) [4] are representative members of a unique group of naturally occurring β-triketones derived from a cyclopentane-1,3-dione ring. In comparison with natural β-triketones derived from cyclohexane-1,3-diones, *e.g.* angustione (3), xanthostemone (4), tasmanone (5), and humulone (6),[5,6] they have a very limited occurrence.† The biosynthesis of the cyclopentanediones (1) and (2) it has been suggested, involves ring contraction of appropriate acylphloroglucinol derivatives as a key stage.[4,7,8] Support for this comes from the observation that treatment of humulone (6) and the 1,4-quinone (8) with alkali leads to humulinic acid [9] (7) and demethyldihydrolinderone (9) [10] respectively.

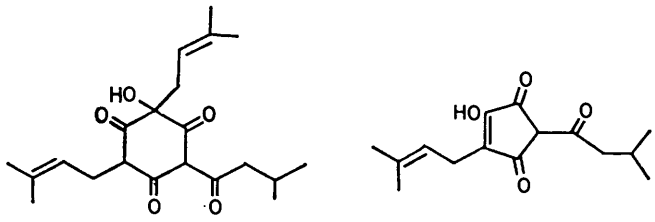


(1) (2)

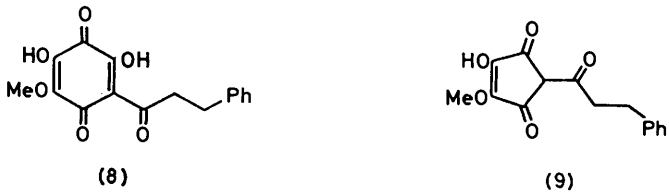
a; R = OMe
b; R = H



(3) (4) (5)

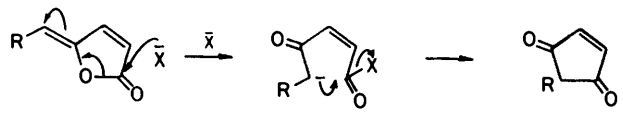


(6) (7)



(8) (9)

The 4-ylidenebutenolide ring system (10) is isomeric with the cyclopentane-1,3-dione system, and aromatic precursors have been shown to be obligatory intermediates in the biosynthesis of several natural members



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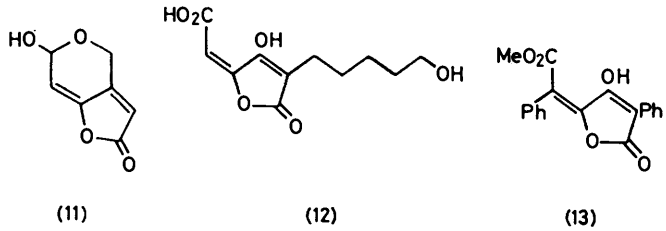


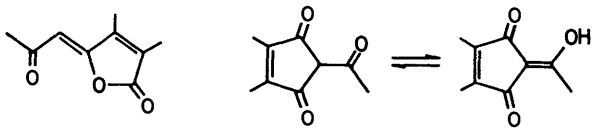
(11) (12) (13)

of this class of compound,[11] *e.g.* patulin (11) and multicolic acid (12) from polyketide-derived aromatic intermediates, and vulpinic acid (13) from phenylalanine *via* the terphenylquinone polyporic acid. The familial relationship between the 4-ylidenebutenolide and the cyclopentane-1,3-dione ring systems led us to speculate that the former may be implicated in the biosynthesis of cyclopentane-1,3-diones from aromatic precursors. To ascertain the plausibility of this supposition we have examined the isomerisation of several 4-ylidenebutenolides under basic conditions. In this paper we report the outcome of these investigations, and the development of a synthesis of natural calythrone (1) and related compounds.[12]

† The β-triketones are drawn in the ketonic forms to illustrate their similarity; they actually exist as mixtures of enolic forms.

As a model, we first examined the isomerisation of the *Z*-ylidenebutenolide (14),[13] which is readily prepared by Wittig condensation between dimethylmaleic anhydride and acetylmethylenetriphenylphosphorane in refluxing toluene.[14] The stereochemistry of (14) followed from the chemical shift of the olefinic proton (τ 4.44) in the ^{1}H n.m.r. spectrum, and comparison with data from our earlier studies.[14] Treatment of the butenolide with hot methanolic sodium methoxide [15] followed by acidification with hydrochloric acid, effected isomerisation in the anticipated sense leading to the known cyclopentenedione (15) [16] in 90% yield. Spectral data (see Experimental section) showed that the molecule exists in the exocyclic enol form shown in (16).

We next turned to the synthesis of calythrone (1) from

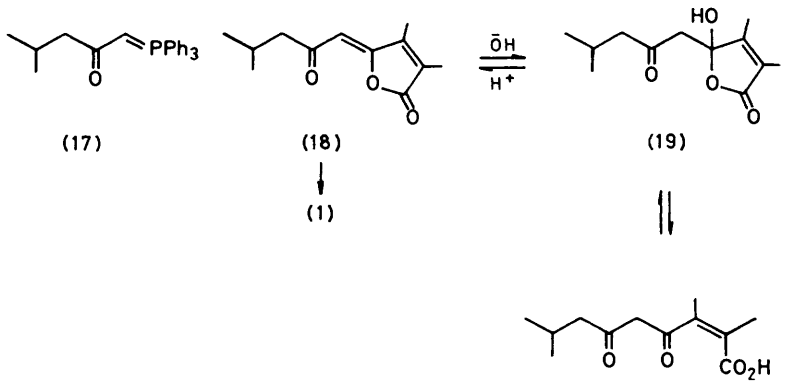


(14) (15) (16)

the butenolide (18). A Wittig condensation between dimethylmaleic anhydride and the phosphorane (17) in hot toluene led to a single isomer of the expected ylidenebutenolide, which by comparison of spectral data with (14) and other analogues was assigned the *Z*-stereochemistry (18). Treatment of the butenolide with hot methanolic sodium methoxide, in a similar manner to (14), led to calythrone (1) in 80% yield, which showed spectral data closely similar to those published for natural calythrone from the oil of *Calythrix tetragona*.[17,18] Although synthetic routes to calythrone have been published previously,[17,18] this route can be commended not only for its brevity and high overall yields over the existing routes, but also for its relevance to a possible biosynthetic route (see Discussion above).

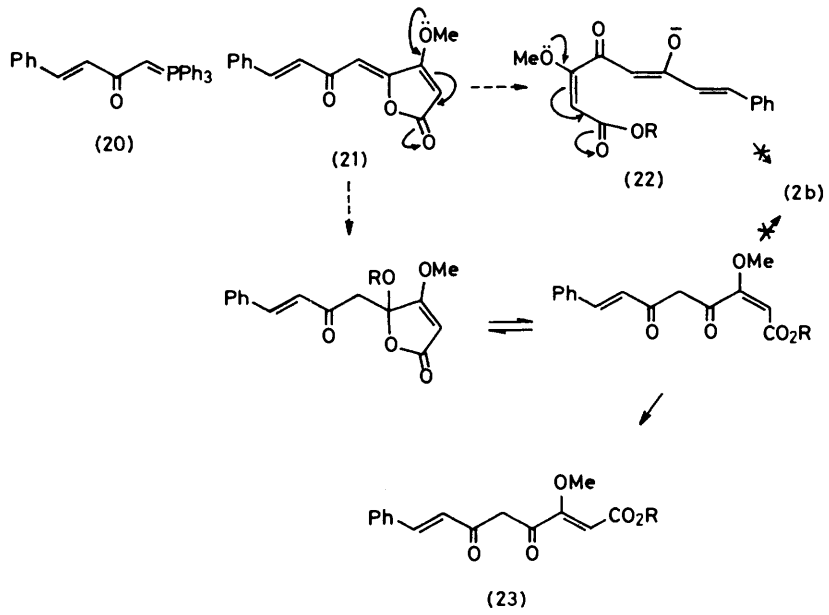
The ease with which the butenolide (18) rearranges to calythrone (1) under basic conditions was somewhat surprising, and led us to question whether the natural product actually has the butenolide structure (18), and that the cyclopentanedione (1) is an artifact produced during basic extraction and isolation.[6] In this context, it is interesting that natural calythrone was originally assigned the butenolide structure (18) by Penfold and Simonsen [1] in 1940, but this was modified to (1) by Birch and his co-workers [2] largely on the basis of i.r. and electronic absorption data. We found that simple dissolution of the butenolide (18) in aqueous sodium carbonate at room temperature for 24 h, followed by an acid work-up led to large amounts of calythrone (1) (35%) together with the ring opened 4-oxo-unsaturated acid, whose spectral data [$\nu_{max.}$ 1 750 cm^{-1}, τ 3.5 (OH)] showed that it existed in solution in the lactol form (19). Furthermore, treatment of (18) with sodium hydroxide led to only the lactol (19) which could be converted back into (18) by brief treatment with hot acid. Unfortunately, precise details of the original extraction procedure used by Penfold and Simonsen are not available. In view of its acidic (' phenolic ') properties however, it is unlikely that a basic extraction procedure was not employed in its isolation, and this feature combined with our present findings must leave some doubt as to the exact constitution (ylidenebutenolide against cyclopentenedione) of the natural product.

We next turned out attention to the synthesis of lucidone (2b),[4] which is found with linderone (2a) [3] in the fruits of the plant *Lindera lucida*. The *Z*-butenolide (21) was synthesised in a regio- and stereo-selective manner by Wittig condensation between methoxymaleic anhydride [19] and the phosphorane (20) [20] in hot benzene. To our surprise, we were unable to rearrange the butenolide to lucidone using sodium methoxide in methanol and a range of alternative basic conditions. The only product isolated, always in high yield, was the corresponding

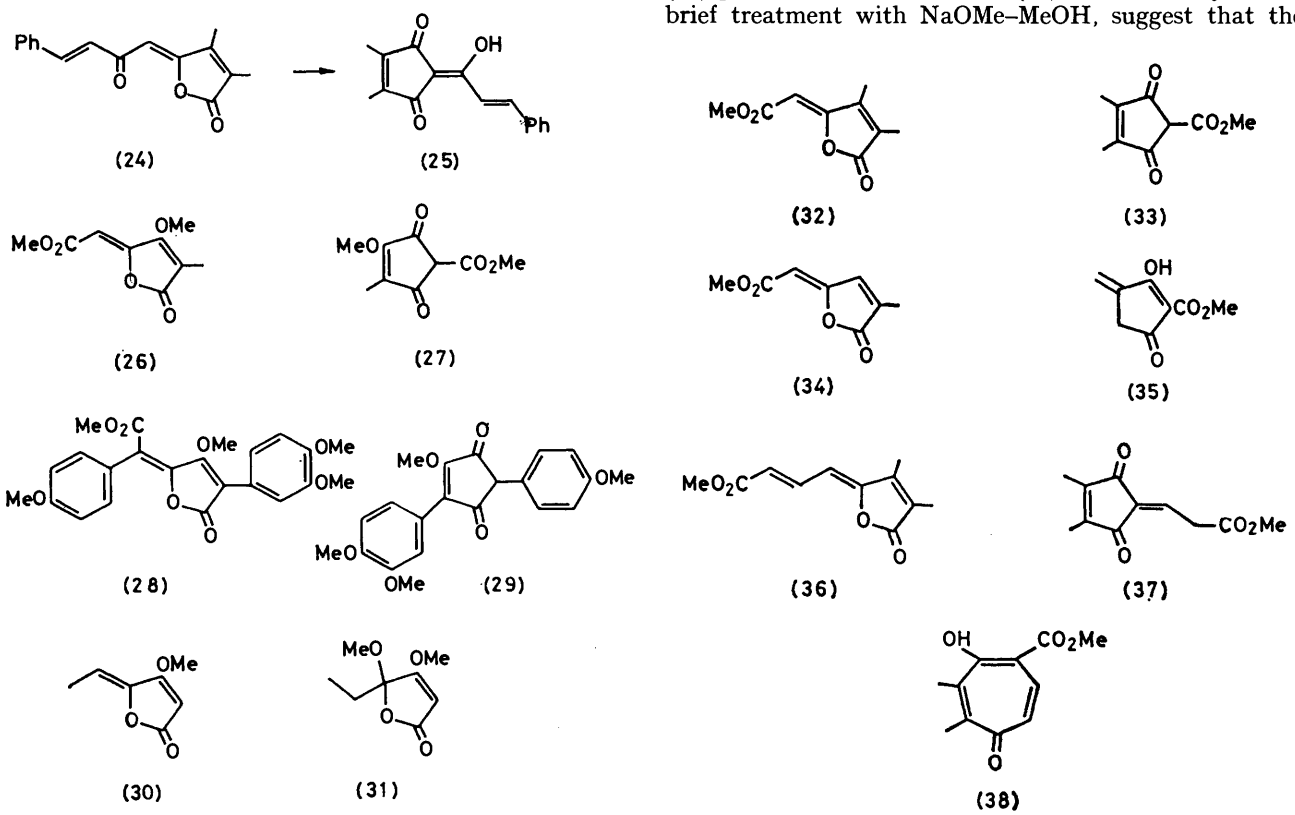


(17) (18) (19) (1)

acyclic 4-oxo-unsaturated ester (23) whose spectral data showed that it existed not only in the acyclic form ($\nu_{max.}$ 1 715 cm^{-1}), but also in the diketo-form shown (τ 6.97, $COCH_2CO$) with a *Z*-2 double bond (τ 4.28, $CH{\cdot}CO_2Me$). The result was even more surprising when it was found that the butenolide analogue (24), derived from dimethylmaleic anhydride, underwent rearrangement to the lucidone analogue (25) in 78% yield using sodium methoxide. At first sight, the failure of (21) to yield (2b) on base-catalysed rearrangement would appear to be associated with the diminished electrophilicity of the acyl groups in (21) and/or the intermediates [*e.g.* (22)] between (21) and



(2b), as a result of their vinylogous disposition relative to the 3-OMe substituents. An explanation along these lines would not be entirely compatible however with our observation that the analogous 3-OMe substituted butenolide (26) [14] is smoothly rearranged to (27) in NaOMe, or with the observation by Edwards and Gill [21] that rearrangement of the pulvinate (28) with methanolic potassium hydroxide produces the cyclopentenedione (29) in 34% yield. These results, taken together with the observation that the simple ethylidenebutenolide (30) produces the lactol ether (31) in excellent yield on brief treatment with NaOMe–MeOH, suggest that the failure of (21) to undergo rearrangement to lucidone is closely associated with the more facile $E \longrightarrow Z$ isomerisation about the C-2 double bond in the intermediate (22); isomerisation to the Z-configuration (23) clearly pre-



cludes intramolecular acylation within the enolate leading to lucidone.

As a corollary to these investigations we also examined the rearrangement of the butenolide esters (32), (34), and (36). Treatment of (32) with NaOMe–MeOH resulted in smooth rearrangement to the cyclopentenedione (33), whereas the butenolide (34), under identical conditions led to largely the α-methylenedione (35) resulting from simultaneous rearrangement and allylic isomerisation. The rearrangement of the butenolide (36) containing additional unsaturation in the side chain, produced entirely the cyclopentenedione (37). Interestingly we were unable to detect the presence of the isomeric seven-ring dione (38) in the crude reaction mixture from (36).

EXPERIMENTAL

For general experimental details see ref. 14.

Z-4-Acetylmethylene-2,3-dimethylbut-2-en-4-olide (14).—A solution of dimethylmaleic anhydride (0.63 g) and acetylmethylenetriphenylphosphorane (1.6 g) [22] in dry toluene (50 ml) was heated under reflux for 16 h, and then evaporated to dryness under reduced pressure. Chromatography on silica, using ether–hexane (4 : 1) as eluant gave the butenolide (0.55 g, 66%) which crystallised from light petroleum (b.p. 60—80 °C) as colourless needles, m.p. 107—109 °C (lit.,[13] m.p. 109 °C), $\lambda_{max.}$ (EtOH) 284 nm; $\nu_{max.}$ (KBr) 1 780, 1 665, and 1 630 cm^{-1}; τ 4.44 (:CH), 7.47 (COMe), 7.91 (:CMe), and 8.01 (:CMe).

Rearrangement of 4-Ylidenebut-2-enolides to Cyclopent-4-ene-1,3-diones: General Procedure.—A solution of the 4-ylidenebutenolide (0.1 g) in dry methanol (5 ml) was added to a solution of sodium methoxide (from 0.1 g sodium) in methanol (25 ml), and the resulting orange-coloured solution was heated under reflux for 1 h and then poured onto ice–water (30 ml) and acidified to pH 1.0 with 2M-hydrochloric acid. The methanol was removed by evaporation, and the residue was then extracted with ether. Evaporation of the dried extracts left the dione which was purified by distillation or crystallisation.

2-Acetyl-4,5-dimethylcyclopent-4-ene-1,3-dione (15).—By the general procedure, rearrangement of *Z*-4-acetylmethylene-2,3-dimethylbut-2-en-4-olide gave the dione (90%) which crystallised from light petroleum (b.p. 60—80 °C) as pale yellow needles, m.p. 50—52 °C (lit.,[16] m.p. 51—52 °C), $\lambda_{max.}$ (MeOH) 240 and 267 nm; $\lambda_{max.}$ (MeOH–NaOH) 239 and 275 nm; $\nu_{max.}$ (KBr) 1 705, 1 658, and 1 640 cm^{-1}; τ 7.66 [:C(OH)Me], 8.05 (2× :CMe).

Z-4-Isobutyrylmethylene-2,3-dimethylbut-2-en-4-olide (18). —(*a*) A solution of dimethylmaleic anhydride (0.63 g) and isobutyrylmethylenetriphenylphosphorane (1.8 g) [23] in dry toluene (30 ml) was heated under reflux for 16 h, and then evaporated to dryness under reduced pressure. Chromatography on silica, using ether–hexane (4 : 1) as eluant gave the butenolide (0.75 g, 72%) as a brown oil, n_D [28] 1.3675, $\lambda_{max.}$ (EtOH) 286 nm (ε 19 650); $\nu_{max.}$ (film) 1 785, 1 760, and 1 645 cm^{-1}; τ 4.41 (:CH), 7.2d (*J* 7, CH_2), 7.6—7.8 m ($CHMe_2$), 7.91 (2× :CMe), 9.02d (*J* 7, Me_2 CH); δ 198.9, 168.8, 155.6, 148.4, 128.6, 105.9(d), 52.1(t), 24.8(d), 22.6(q), 10.0(q), and 9.18(q) p.p.m. (Found: *m/e* 208.1122. $C_{12}H_{16}O_3$ requires: *M* 208.1101).

(*b*) A mixture of 4-hydroxy-4-isobutyrylmethyl-2,3-dimethylbut-2-enolide (19) (0.05 g), acetic acid (0.6 ml), acetic anhydride (1.2 ml), and concentrated sulphuric acid (0.2 ml) [24] was heated at 100 °C for 2 h and then diluted with water (5 ml), washed with 10% sodium hydrogen carbonate solution, and extracted with chloroform. Evaporation of the dried chloroform extracts left the butenolide (0.031 g) showing spectral data identical with those of an authentic specimen.

2-Isobutyryl-4,5-dimethylcyclopent-4-ene-1,3-dione (*Calythrone*) (1).—By the general procedure, rearrangement of *Z*-4-isobutyrylmethylene-2,3-dimethylbut-2-en-4-olide gave calythrone (80%) as a yellow oil, $\lambda_{max.}$ (MeOH) 240 (ε 21 300) and 265 nm (20 800); $\lambda_{max.}$ (MeOH–NaOH) 240 (ε 18 150) and 276 nm (21 800); $\nu_{max.}$ (film) 1 780, 1 760, 1 705, and 1 655 cm^{-1}; τ 7.32d (*J* 7, CH_2), 7.92br ($CHMe_2$), 8.01 (2× :CMe), and 9.01 d (*J* 7, Me_2CH); δ 200.8, 192.1, 151.0, 146.3, 104.1, 39.8t, 27.2d, 8.9q, and 8.2q p.p.m. [*m/e* 208.1098 (26%), 166(9), 152(100), 151(93), 124(16), 95(11), 79(21), and 70(20). $C_{12}H_{16}O_3$ requires *M* 208.1101]. The copper derivative was prepared, and had m.p. 208—210 °C (lit.,[1] m.p. 208 °C).

A solution of the butenolide (18) (0.1 g) in ether (25 ml) was shaken overnight at 25 °C with a 10% solution of sodium hydrogencarbonate (20 ml). The aqueous layer was then acidified and extracted with ether. Evaporation of the ether left a 1 : 2 mixture (by ^1H n.m.r.) of calythrone and 4-hydroxy-2,3-dimethyl-4-(isobutyrylmethyl)but-2-enolide (19) (0.043 g).

4-Hydroxy-4-isobutyrylmethyl-2,3-dimethylbut-2-enolide (19).—A suspension of *Z*-2,3-dimethyl-4-(isobutyrylmethylene)but-2-en-4-olide (0.063 g) in 2M-sodium hydroxide (10 ml) was stirred at 25° for 2 h, and then acidified with 2M-sulphuric acid and extracted with ether. Evaporation of the ether left the lactol (0.05 g) as a yellow oil, n_D [21] 1.4712, $\lambda_{max.}$ ($CHCl_3$) 270 nm (ε 4 600); $\nu_{max.}$ (film) 3 350, 1 750, and 1 690 cm^{-1}; τ 3.5 (OH), 7.22 ($COCH_2CO$), 7.58 d (*J* 7, $CHCH_2CO$), 7.72—7.83 m ($CHMe_2$), 8.06 (:CMe), 8.19 (:CMe), and 9.07 d (*J* 7, Me_2CH) (*m/e* 226.1200. $C_{12}H_{18}O_4$ requires *M* 226.1205).

Cinnamoylmethylenetriphenylphosphorane (20).—Bromination of benzylideneacetone with pyrrolidone hydrotribromide, according to the method of Awang and Wolfe,[20a] led to bromomethyl styryl ketone, τ 2.32 d (*J* 17, :CH), 2.36—2.84 (m, 5 H), 3.08 (d, *J* 17, :CH), and 5.95 (CH_2), which on reaction with triphenylphosphine gave the corresponding phosphonium salt, m.p. 246—247 °C, τ 1.72 (d, *J* 16, CHPh), 2.02—2.54 (m, 15 H), 2.65 (PhCH:), 2.94 (dd, *J* 16 and 3, PhCH:CH), 4.07 (d, *J* 12, CH_2P).

A solution of sodium hydroxide (2 g) in water (20 ml) was added to a suspension of the phosphonium salt (12.2 g) in water (350 ml) and methanol (250 ml), and the mixture was stirred at 25 °C for 10 h and then extracted with benzene (2 × 200 ml). Evaporation of the benzene and crystallisation of the black tarry residue from glyme gave the phosphorane as yellow cubes, m.p. 147—149 °C (lit.,[20b] m.p. 99—102 °C), ν_{max} (KBr) 1 630 cm^{-1}; τ 2.2—2.8 (m, 21 H), 3.08 (d, *J* 16, PhCH:CH), and 4.93 (d, *J* 6, CHP) (Found: C, 82.5; H, 5.8; P, 7.5. $C_{28}H_{23}OP$ requires C, 82.7; H, 5.7; P, 7.6%).

Methoxymaleic Anhydride.—A mixture of 2-methoxyfumaric acid (9.12 g) and thionyl chloride (100 ml) was stirred at 25 °C for 1 h and then at 60 °C for 24 h. Distillation gave the anhydride (5.6 g, 65%) as a pale yellow liquid,[19] b.p. 105—110 °C/0.5 mmHg, n_D [32] 1.4840, $\lambda_{max.}$ ($CHCl_3$) 264 nm (ε 6 800); $\nu_{max.}$ (film) 1 860 and 1 780 cm^{-1}; τ 4.17 (:CH) and 5.9 (OMe) (*m/e* 128.0106. $C_5H_4O_4$ requires *M* 128.0110).

Z-4-Cinnamoylmethylidene-3-methoxybut-2-en-4-olide (21).—A solution of methoxymaleic anhydride (0.34 g) and cinnamoylmethylenetriphenylphosphorane (1 g) in dry benzene (100 ml) was heated under reflux in a nitrogen atmosphere for 16 h, and then evaporated to dryness under reduced pressure. Chromatography on silica, using ether–hexane (4 : 1) as eluant gave the butenolide (0.38 g, 56%) as a yellow solid which crystallised from methanol as yellow plates, m.p. 149—150 °C, $\lambda_{max.}$ ($CHCl_3$) 274infl (ε 16 300), 296 (19 900), and 325infl nm (16 000); $\nu_{max.}$ (KBr) 1 795 and 1 618 cm^{-1}; τ 2.2—2.76 (m, 7 H, PhCH:CH), 4.03 [C(OMe):C*H*], 4.6 (:CH), and 6.0 (OMe) (Found: C, 70.2; H, 4.9. $C_{15}H_{12}O_4$ requires C, 70.1; H, 5.2%).

Methyl 3-Methoxy-8-phenyl-4,6-dioxo-octa-2,7-dienoate (23; R = Me).—A solution of *Z*-4-cinnamoylmethylidene-3-methoxybut-2-en-4-olide (0.1 g) in methanol (20 ml) was added to a solution of sodium methoxide (from 0.1 g sodium) in methanol (5 ml), and the resulting orange coloured solution was heated under reflux for 10 min, and then poured onto ice–water and acidified to pH 1.0 with 2M-hydrochloric acid. The solution was extracted with ether, and the ether extracts were then dried and evaporated to leave the ester (0.085 g) as a yellow oil, $\lambda_{max.}$ ($CHCl_3$) 350 nm; $\nu_{max.}$ (film) 1 715 cm^{-1}; τ 2.4 d (*J* 16, :CH), 3.16 (d, *J* 16 :CH), 2.36—2.84 (m, 5 H), 4.28 [C(OMe):CH], 6.35 [:C(OMe)], 6.7 (OMe), and 6.97 ($COCH_2CO$) (*m/e* 288.0985, $C_{16}H_{16}O_5$ *M* 288.0998).

When potassium t-butoxide was used instead of sodium methoxide, the corresponding t-butyl ester, τ 8.72 (CMe_3), was obtained, and treatment with sodium thiophenoxide in methanol gave (23; R = Me). When the butenolide (21) was heated in pyridine or triethylamine for several hours, or when it was heated *in vacuo* (0.1 mmHg) between 140 and 180 °C for 2 h only starting material was recovered.

Z-4-Cinnamoylmethylidene-2,3-dimethylbut-2-en-4-olide (24).—A solution of dimethylmaleic anhydride (0.32 g) and cinnamoylmethylenetriphenylphosphorane (1 g) in dry benzene (100 ml) was heated under reflux for 4 days, and then evaporated to dryness *in vacuo*. Chromatography on silica, using ether–hexane (4 : 1) as eluant gave the butenolide (0.42 g, 65%) as a yellow solid which crystallised from methanol as yellow needles, m.p. 194—196 °C, $\lambda_{max.}$ ($CHCl_3$) 302 (ε 19 800) and 333infl nm (10 100); $\nu_{max.}$ (KBr) 1 775 and 1 632 cm^{-1}; τ 2.26 (d, *J* 16, PhC*H*:), 2.48 (d, *J* 16, PhCH:C*H*), 2.28—2.64 (m, 5 H), 4.25 (:CH), 7.9 (:CMe), and 8.0 (:CMe) (Found: C, 75.3; H, 5.4%; *m/e* 254.0959. $C_{16}H_{14}O_3$ requires C, 75.5; H, 5.6%; *M* 254.0943).

In one experiment a small amount of the corresponding *E*-isomer was separated by chromatography (eluted first). It recrystallised from methanol as yellow needles, m.p. 105—108 °C, $\lambda_{max.}$ ($CHCl_3$) 318 nm; $\nu_{max.}$ ($CHCl_3$) 1 770, 1 650, and 1 620 cm^{-1}; τ 2.28—2.72 (m, 6 H), 3.12 (d, *J* 16, PhCH:C*H*), 3.45 (COCH), 7.75 (:CMe), and 8.0 (:CMe), and isomerised to the *Z*-isomer (24) on heating above its melting point.

2-(α-*Hydroxy cinnamylidene*)-4,5-*dimethylcyclopent*-4-*ene*-1,3-*dione* (25).—By the general procedure, rearrangement of *Z*-4-cinnamoylmethylidene-2,3-dimethylbut-2-en-4-olide gave the diene (78%) which crystallised from aqueous ethanol as yellow needles, m.p. 115—117 °C, $\nu_{max.}$ (MeOH) 234 (ε 23 900), 349 (33 300), 361infl (28 900), and 384 nm (13 600); $\lambda_{max.}$ (NaOH–MeOH) 234 (ε 25 000), 285 (15 400), 303infl (12 500), and 347 nm (18 950); $\nu_{max.}$ (KBr) 1 700, 1 650, 1 635, and 1 597 cm^{-1}, τ 2.3—2.7 (m, 7 H, PhCH:CH), 8.0 (2× :CMe); δ 200.8, 192.0, 166.2, 151.3, 147.3, 142.2(d), 135.0, 130.4(d), 128.8(d), 128.5(d), 117.7d, 102.8, 8.95(q), and 8.4(q) p.p.m. (Found: C, 75.2; H, 5.8%; *m/e* 254.0959. $C_{16}H_{14}O_3$ requires C, 75.5; H, 5.6%; *M*, 254.0943).

4-*Methoxy*-2-*methoxycarbonyl*-5-*methylcyclopent*-4-*ene*-1,3-*dione* (27).—By the general procedure, rearrangement of 3-methoxy-4-methoxycarbonylmethylidene-2-methylbut-2-enolide [14] gave the dione (90%) as a liquid, $\nu_{max.}$ (film) 1 760, 1 725, 1 690, and 1 625 cm^{-1}; τ 5.78 (OMe), 6.32 (OMe), 8.13 (:CMe) (Found: *m/e* 198.0539, $C_9H_{10}O_5$ requires *M*, 198.0528). Attempted purification by distillation under reduced pressure led to substantial amounts (>50%) of 4-methoxy-5-methylcyclopent-4-ene-1,3-dione, τ 5.74 (OMe), 7.27 (2 H), and 8.10 (:CMe) (Found: *m/e* 140.0488. $C_7H_8O_3$ requires *M*, 140.0473).

4-*Ethylidene*-4-*methoxybut*-2-*enolide* (30).—4-Ethylidene-4-hydroxybut-2-enolide [25] was converted into the corresponding tetrabutylammonium salt, m.p. 138—140 °C, according to the procedure of Wengel *et al.*,[26] which was then treated with dimethyl sulphate giving the corresponding methyl ether (97%). Recrystallisation from n-hexane gave the 4-methoxybutenolide as colourless needles, m.p 69—70 °C, $\lambda_{max.}$ (EtOH) 259 nm; $\nu_{max.}$ (KBr) 1 760 and 1 605 cm^{-1}; τ 4.6 q (*J* 7.5, :C*H*CH_3), 4.9 (:CH), 6.1 (OMe), and 8.15 (d, *J* 7.5, :CH*Me*) (Found: C, 59.9; H, 5.7. $C_7H_8O_3$ requires C, 60.0; H, 5.8%).

4-*Ethyl*-3,4-*dimethoxybut*-2-*enolide* (31).—Treatment of 4-ethylidene-3-methoxybut-2-enolide in methanol with sodium methoxide, according to the general procedure gave the dimethoxybut-2-enolide (86%) as a colourless liquid, b.p. 95—100 °C at 10.02 mmHg, $\lambda_{max.}$ (EtOH) 223 (ε 10 300) nm; $\nu_{max.}$ 3 120, 2 980, 2 950, and 1 765 cm^{-1}; τ (CCl_4) 4.93 (1 H), 6.14 (:COMe), 6.92 (OMe), 7.99—8.38 (m, 2 H), and 9.14 (t, *J* 7.5, CH_2CH_3); δ 177.4, 169.6, 107.2, 91.5(d), 59.6(q), 50.8(q), 28.6(t), and 7.0(q) p.p.m. (Found: *m/e* 143.034 76 $C_6H_7O_4$ requires *M*, 143.034 44; *m/e* 172 not observed).

2-*Methoxycarbonyl*-4,5-*dimethylcyclopent*-4-*ene*-1,3-*dione* (33).—By the general procedure, rearrangement of 4-methoxycarbonylmethylidene-2,3-dimethylbut-2-enolide [14] gave the dione (79%) as a colourless liquid, b.p. 100—105 °C/0.05 mmHg, $\nu_{max.}$ (film) 1 755, 1 720, 1 695, and 1 635 cm^{-1}; τ (CCl_4) 6.32 (OMe), 6.42 (1 H), 7.95 (2× :CMe) (Found: *m/e* 182.0590. $C_9H_{10}O_4$ requires *M*, 182.0580).

2-*Methoxycarbonyl*-4-*methylenecyclopentane*-1,3-*dione* (35).—By the general procedure, rearrangement of 4-methoxycarbonyl-2-methylbut-2-enolide,[14] gave the dione (96%); τ 3.9 (m, :CH), 4.42 (m, :CH), 6.07 (OMe), and 6.89 (m, 2 H) contaminated with the isomeric 2-methoxycarbonyl-4-methylcyclopent-4-ene-1,3-dione (25%), τ 2.67 (:CH), 6.11 (1 H), 6.15 (OMe), and 7.77 (:CMe).

4-(3-*Methoxycarbonylprop*-2-*enylidene*)-2,3-*dimethylbut*-2-*en*-4-*olide* (36).—A solution of dimethylmaleic anhydride (0.63 g) and 3-methoxycarbonylprop-2-enylidenetriphenylphosphoranylide (1.8 g) [27] in dry benzene (100 ml) was heated under reflux for 3 days, and then evaporated to dryness under reduced pressure. Chromatography on silica, using ether–hexane (4 : 1) as eluant gave the *E,E*-butenolide (0.5 g, 48%) which crystallised from methanol as yellow needles, m.p. 148—149 °C, $\lambda_{max.}$ ($CHCl_3$) 320 nm; $\nu_{max.}$ (KBr) 1 760, 1 700, 1 635, and 1 605 cm^{-1}; τ 2.32 (dd, *J* 16, 12, $MeO_2C{\cdot}CH{:}CH$), 4.01 (d, *J* 16, $MeO_2C{\cdot}CH$), 4.23 (d, *J* 12, O·C:CH), 6.24 (OMe), 7.92 (:CMe), and 8.04 (:CMe) (Found: C, 63.3; H, 5.8. $C_{11}H_{12}O_4$ requires C, 63.5; H, 5.8%).

2-*Methoxycarbonylethylidene*-4,5-*dimethylcyclopent*-4-*ene*-1,3-*dione* (37).—A suspension of *E,E*-4-(3-methoxycarbonylprop-2-enylidene)-2,3-dimethylbut-2-en-4-olide (0.1 g) in

methanol (15 ml) was added to a solution of sodium methoxide (from 0.1 g sodium) in methanol (5 ml), and the deep-red coloured solution was heated under reflux for 0.25 h and then poured onto ice–water and acidified to pH 1.0 with 2M-hydrochloric acid. The solution was extracted with ether, and the ether extracts were then dried and evaporated to leave the dione (0.09 g, 90%) as a yellow oil, $\nu_{max.}$ (film) 1 735 and 1 685 cm^{-1}; τ 3.06 (t, J 7, $CHCH_2$), 5.9 (d, J 7, CH_2CO_2Me), 6.08 (OMe), and 7.73 (2× .CMe), (M, m/e 208.0747. $C_{11}H_{12}O_4$ requires M, 208.0736).

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