Dioxolanones as Synthetic Intermediates. Part 1. Synthesis of α-Keto Acids, α-Keto Aldehydes, and α-Ketols

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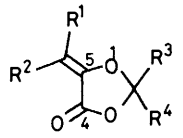
2,2-Pentamethylene-1,3-dioxolan-4-one [cyclohexanespiro-2'-(1',3'-dioxolan)-4'-one] (**10**) has been elaborated to provide 5'-ylidene derivatives using a Wittig approach. This apparently novel class of compounds is subject to nucleophilic attack at the 4-position because of strain inherent in the 5-membered ring. Thus alkaline hydrolysis leads to the formation of α-keto acids; hydride reduction of dioxolanones incorporating conjugated aryl substituents using di-isobutylaluminium hydride leads to α-keto-aldehydes; the reaction of dioxolanone (**15**) with methylmagnesium iodide gave the α-ketol (**40**).

5-Ylidene-1,3-dioxolan-4-ones (**1**) constitute a class of organic compounds that has received scant attention in the chemical literature. They are derivatives of α-keto acids in which both the keto and carboxy groups are protected in such a way that the strain inherent in the dioxolanone ring provides concurrent, specific activation of the acid carbonyl function towards nucleophilic attack. In 1898, Schiff attempted to prepare the chloralides (**2**) and (**3**) by heating chloral with ethyl acetylpyruvate and ethyl benzoylpyruvate respectively,[1] and obtained crystalline products which gave correct elemental analyses. In 1926, Bougault reported that reflux of the amide (**4**) under acidic conditions gave the dioxolanone (**5**),[2] but from the properties reported it is likely that the product was the Ehrlenmeyer lactone (**6**). Finally, in 1947, Rinderknecht and co-workers used the Schiff method to prepare the chloralides of a series of substituted pyruvic acids,[3] but it was later shown by Rossi and Schinz that the supposed chloralides from the Schiff route were, in fact, butyrolactones of type (**7**).[4]

The Schiff approach to 5-ylidene-1,3-dioxolan-4-ones was based on the analogy of the synthesis of chloralides lacking a 5-ylidene substituent from chloral and an α-hydroxy acid.[5] However, the analogy is not justified since the α-keto acid derivative (**8**) can undergo an alternative mode of reaction, initiated by attack of the enolic carbon on chloral, which can lead to the butyrolactone (**9**) after cyclisation. It is, therefore, probable that any attempted synthesis of 5-ylidene-1,3-dioxolan-4-ones (**1**) from the enolic form of an α-keto acid derivative and a carbonyl compound would give the same result and, in view of this, our approach to dioxolanones of type (**1**) has been to prepare the 1,3-dioxolan-4-one nucleus and then to introduce the 5-ylidene substituent.

The condensation of an α-hydroxy acid with a carbonyl compound, first used by Wallach,[5] remains the standard method for the preparation of 1,3-dioxolan-4-one derivatives, and the preparation of 2,2-pentamethylene-1,3-dioxolan-4-one (**10**) in 26% yield was previously achieved by condensation of glycolic acid with cyclohexanone using BF_3·Et_2O as catalyst.[6] In our hands, addition of an aqueous solution of glycolic acid to a solution of cyclohexanone in toluene containing a catalytic amount of toluene-*p*-sulphonic acid hydrate gave the dioxolanone (**10**) in 73% yield after distillation; this preparation avoided the formation of the glycolide (**11**) *via* dimerisation of glycolic acid.

The introduction of the 5-ylidene substituent by base-induced Aldol reactions failed to give a satisfactory general route and, therefore, recourse was made to a Wittig approach involving the phosphorane (**14**). Bromination of (**10**) using *N*-bromosuccinimide (NBS) in carbon tetrachloride gave a high yield of the bromide (**12**). This could be distilled but was subject to decomposition on storage, and it was, therefore, treated immediately with triphenylphosphine in toluene to give the phosphonium salt (**13**), which could be prepared and stored in large quantities. The phosphorane (**14**) could be generated from the salt (**13**) using a variety of bases, but it was found to be hydrolytically and oxidatively unstable and could only be isolated and characterised as a yellow crystalline solid ($\nu_{max.}$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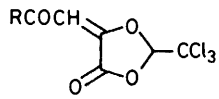
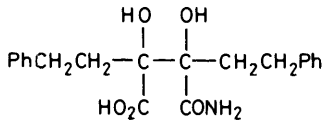

(2) R = Me
(3) R = Ph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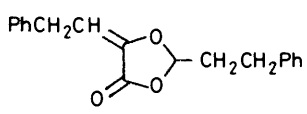
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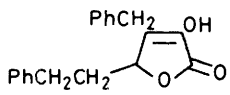
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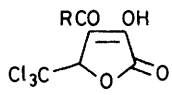
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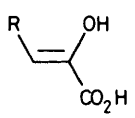
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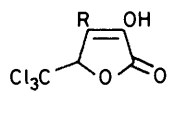
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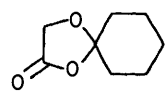

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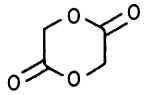

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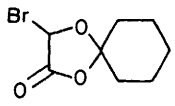

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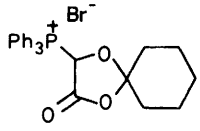

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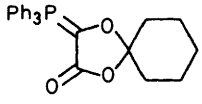
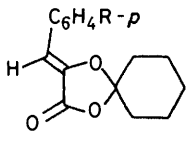
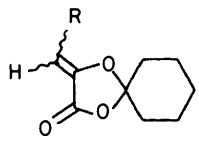


(14)

1 680 cm^{-1}) when the most stringent precautions were taken to exclude oxygen and water. In consequence, the phosphorane (**14**) was generated from the salt (**13**) under an inert atmosphere using 1,4-diazabicyclo[2.2.2]octane (DABCO) in toluene immediately before treatment with a series of aldehydes which gave the 5-ylidene-2,2-pentamethylene-1,3-dioxolan-4-ones (**15**)—(**23**). The aldehyde (**26**), required for the preparation of dioxolanone (**23**) was prepared in 3 steps from cinnamaldehyde (Scheme 1).

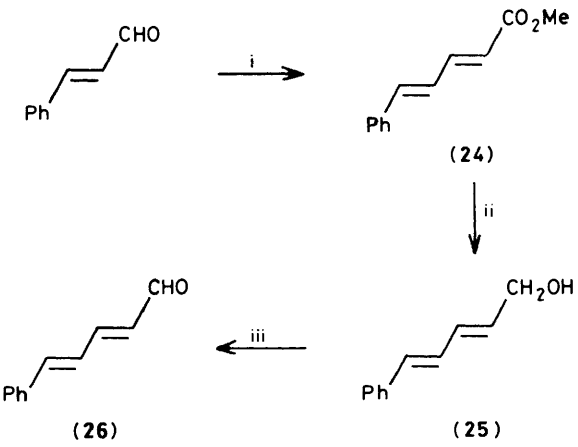


(**15**) R = H
(**16**) R = OCH_2Ph



(**17**) R = Pr
(**18**) R = Pr^i
(**19**) R = Me
(**20**) R = H
(**21**) R = CH=CHPh
(**22**) R = CH=CHMe
(**23**) R = CH=CH−CH=CHPh

The dioxolanones (**15**)—(**23**) can exist as two geometrical isomers about the exocyclic double bond. Models of the 5-arylidenedioxolanones (**15**) and (**16**) indicated that in the (*Z*)-forms the styrene moiety could be planar. However, in the alternative (*E*)-forms steric interactions between the *ortho*-hydrogen of the phenyl ring and the non-bonding orbitals of the carbonyl oxygen would lead to non-planarity and consequent loss of conjugation. The presence of two vinylic signals in the ^1H n.m.r. spectrum of the crude product from the reaction between 4-benzyloxybenzaldehyde and phosphorane (**14**) indicated that a mixture of geometrical isomers had been formed, but chromatography and recrystallisation gave a single isomer in 79% yield, and this was shown to be the (*Z*)-isomer (**16**) by *X*-ray crystallographic analysis.[7] Although the ^1H n.m.r. spectrum of the crude product of the reaction between benzaldehyde and the phosphorane (**14**) frequently showed the presence of two isomers, only a single isomer was present after

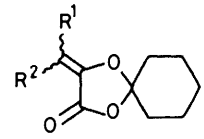


Scheme 1. *Reagents:* i, $Ph_3P{=}CHCO_2Me$; ii, DIBAH; iii, PDC

chromatography and this was also assigned as the (*Z*)-isomer (**15**).

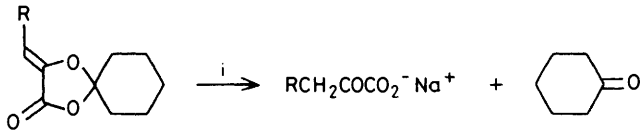
Examination of the ^1H n.m.r. spectra of the dioxolanones (**17**)—(**23**) derived from aliphatic aldehydes indicated that they were a mixture of geometrical isomers.

Attempts to induce the reaction of the phosphorane (**14**) with acetone were unsuccessful, but the more reactive 1,1,1-trifluoroacetone gave the dioxolanone (**27**). The preparation of dioxolanone (**28**) from t-butyl pyruvate indicated that the phosphorane (**14**) is also susceptible to reaction with α-keto esters. Although the dioxolanones (**27**) and (**28**) were apparently single isomers from their ^1H n.m.r. spectra, in neither case was the double bond geometry definitely assigned at this stage in the programme.



(**27**) R^1 = Me, $R^2 = CF_3$
(**28**) R^1 = Me, $R^2 = CO_2Bu^t$

The high frequency (1 775—1 795 cm^{-1}) of the lactone carbonyl absorption in the i.r. spectra of the dioxolanones (**15**)—(**23**) suggested that they should be highly susceptible to nucleophilic attack at the 4-position with subsequent extrusion of cyclohexanone. This is demonstrated by the facile alkaline hydrolysis of the dioxolanones (**15**), (**17**), and (**18**) to give high yields of the sodium salts (**29**), (**30**), and (**31**) of the corresponding α-keto acids (Scheme 2). The sodium salts gave



(**15**) R = Ph
(**17**) R = Pr
(**18**) R = Pr^i

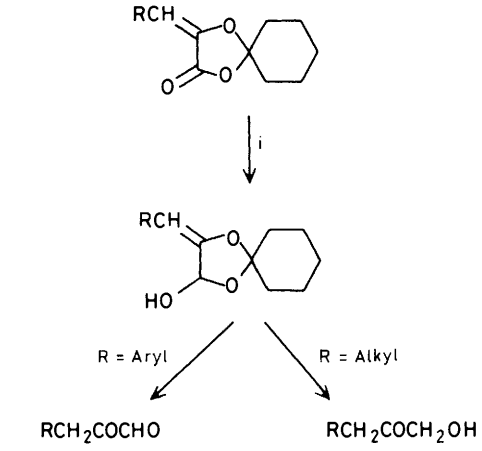
(**29**) R = Ph
(**30**) R = Pr
(**31**) R = Pr^i

Scheme 2. *Reagents:* i, NaOH–THF–H_2O

satisfactory analytical data and (**29**) and (**31**) were further characterised as the semicarbazones of the α-keto acids.

In contrast to their susceptibility to base hydrolysis, the dioxolanones (**15**) and (**17**) were found to be quite stable to aqueous acid even though acetals and 1,3-dioxolan-4-ones are hydrolysed under these conditions. Thus (**15**) was not appreciably hydrolysed in 4M-HCl at room temperature, and both (**15**) and (**17**) were unaffected by toluene-*p*-sulphonic acid in aqueous methanol at reflux. Acetal hydrolysis requires protonation of oxygen in the first step and the lone-pair electron densities on the oxygen atoms at positions 1 and 3 in (**15**) and (**17**) are reduced as a result of delocalisation.

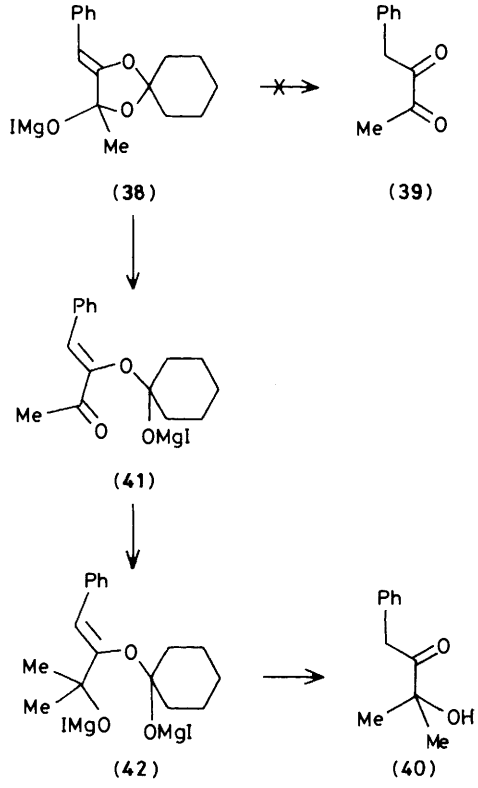
The effect of a metal hydride reducing agent on a 1,3-dioxolan-4-one has been studied by Gaylord who reported that treatment of dioxolanone (**32**) with lithium aluminium hydride (LAH) afforded isobutyl alcohol and propane-1,2-diol.[8] Di-isobutylaluminium hydride (DIBAH) is noted for its selective reduction of lactones to lactols,[9] and it was expected that reduction of 5-ylidene-2,2-pentamethylene-1,3-dioxolan-4-ones with DIBAH would furnish α-keto aldehydes (Scheme 3).



Scheme 3. *Reagents:* i, DIBAH

Treatment of dioxolanones (**15**) and (**23**) with DIBAH, at −60 °C and −78 °C respectively, gave the expected products which from ^{1}H n.m.r. evidence exist in the enol forms (**33**) and (**34**). Reaction of the dioxolanone (**21**) with DIBAH under the same conditions gave what appeared to be, from the spectral and microanalytical data, a mixture of the aldehyde (**35**) and the cyclopentenone (**36**). Treatment of this mixture with aqueous sodium hydroxide gave the known cyclopentanedione (**37**).[10] 5-Ylidenedioxolanones derived from aliphatic aldehydes can be converted into α-ketols using DIBAH, probably because of the ring opening of the intermediate formed after addition of one equivalent of the reagent.

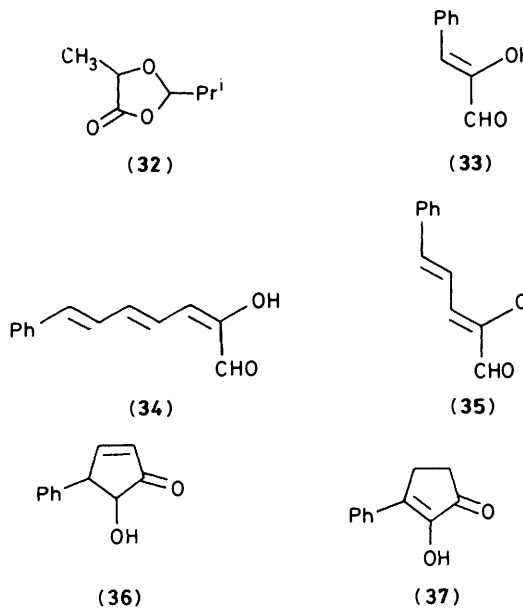
1,3-Dioxolan-4-ones react with simple alkyl Grignard reagents to give 1,2-diols.[11] It was expected that treatment of the benzylidenedioxolanone (**15**) with methylmagnesium iodide would lead initially to the intermediate (**38**) which would, on work-up, give the unsymmetrical 1,2-diketone (**39**) (Scheme 4).

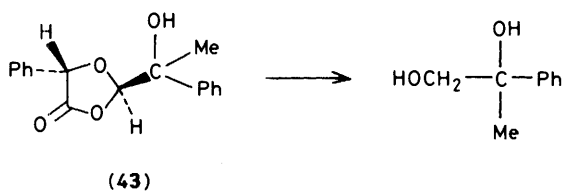


Scheme 4.

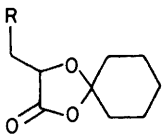
Treatment of the dioxolanone (**15**) with two equivalents of methylmagnesium iodide gave a mixture of starting material and two products. The major product was the butan-2-one (**40**) and the ^{1}H n.m.r. spectrum of the second product indicated it to be 1-methylcyclohexanol. It therefore appeared that under the conditions used the intermediate (**38**) was subject to rearrangement to give (**41**) which was further attacked by the Grignard reagent to give (**42**). Fragmentation of (**42**) would lead to formation of (**40**) *via* extrusion of cyclohexanone which itself would be subject to attack by methylmagnesium iodide to give 1-methylcyclohexanol.

It has been reported that hydrogenation of the 1,3-dioxolan-4-one (**43**) using Adams catalyst in methanol at atmospheric pressure led to complete cleavage of the dioxolanone ring (Scheme 5).[12] However, it was found that hydrogenation of the





Scheme 5. *Reagents:* i, H_2–Adams catalyst–MeOH



(**44**) R = c-C_6H_{13}
(**45**) R = Ph

dioxolanone (**15**) under these conditions led to formation of the octahydro derivative (**44**). Hydrogenation of (**15**) under milder conditions, namely 5% palladium on charcoal in ethyl acetate, led to reduction only of the exocyclic double bond with formation of the benzyldioxolanone (**45**).

Experimental

I.r. spectra, calibrated against polystyrene film at 1 603 cm^{-1}, were recorded on a Perkin-Elmer 197 spectrophotometer. 60 MHz ^1H N.m.r. spectra were recorded on Perkin-Elmer R12 and R20A spectrometers, 80 MHz on a Bruker WP80, 90 MHz on a Perkin-Elmer R32, 220 MHz on a Perkin-Elmer R34 and 300 MHz on a Varian SC300 spectrometer; chemical shifts are relative to internal $SiMe_4$ at 0.00 p.p.m. ^{13}C N.m.r. spectra were recorded at 21.1 MHz on a Bruker WP80; chemical shifts are relative to $^{13}CDCl_3$ at 76.9 p.p.m. or $(^{13}CD_3)_2CO$ at 29.2 p.p.m. U.v. spectra were recorded on a Varian Cary 118X or Pye Unicam SP8-100 spectrophotometer. Mass spectra were recorded on A.E.I. MS 902 and Kratos MS 45 spectrometers with an ionisation potential of 70 eV. Microanalyses were made on a Perkin-Elmer 240 Elemental Analyser. Melting points were determined on a Buchi 510 or a Kofler hot-stage microscope and are uncorrected as are boiling points. T.l.c. was carried out on silica gel (Fluka GF 254) and examined by u.v. light at 254 and 366 nm or by staining in iodine vapour. Preparative chromatography was performed on silica gel 60 (70—230 mesh ASTM) (Merck). Flash column chromatography was carried out on Kieselgel 60H (Merck). Unless stated otherwise all reactions were carried out at room temperature (18—24 °C). Commercially available solvents were dried by standard procedures and distilled prior to use. Tetrahydrofuran (THF) was distilled from potassium benzophenone ketyl immediately before use. Petroleum refers to the fraction boiling in the range 40—60 °C. Nitrogen was purified by passing it successively through Fieser's solution, saturated aqueous lead(II) acetate, concentrated sulphuric acid, and potassium hydroxide pellets.

Cyclohexanespiro-2′-(1′,3′-dioxolan)-4′-one (**10**).—To a solution of cyclohexanone (65.2 g, 0.67 mol) and toluene-*p*-sulphonic acid hydrate (0.15 g, 0.8 mmol) in toluene (300 ml) at reflux was added, dropwise over 4 h, a solution of glycolic acid (40.8 g, 0.54 mol) in water (20 ml). The mixture was heated for a further 5 h (the water produced in the reaction was removed *via* a Dean and Stark apparatus), cooled to room temperature, treated with anhydrous sodium acetate (0.25 g, 3 mmol), and stirred for 1 h. The mixture was filtered, and the filtrate was evaporated under reduced pressure to afford a yellow oil which was distilled to yield cyclohexanone (b.p. 20 °C, 0.5 mmHg), followed by the dioxolanone (**10**) (61.5 g, 73%) as a colourless liquid which solidified with time, b.p. 70 °C, 0.5 mmHg (lit.,[6] 74—76 °C, 15 mmHg), m.p. 30—31 °C (Found: C, 61.7; H, 7.9. Calc. for $C_{18}H_{12}O_3$: C, 61.5; H, 7.75%); $\nu_{max.}(CH_2Cl_2)$ 2 940m, 2 855w, 1 795s, and 1 105s cm^{-1}; δ_H (220 MHz, $CDCl_3$) 4.33 (2 H, s, CH_2) and 1.4—1.9 [10 H, m, $(CH_2)_5$]; *m/z* 156 (M^+, 27%).

5′-Oxocyclohexanespiro-2′-(1′,3′-dioxolan)-4′-yltriphenylphosphonium Bromide (**13**).—A mixture of *N*-bromosuccinimide (94.33 g, 0.53 mol), freshly distilled cyclohexanespiro-2′-(1′,3′-dioxolan)-4′-one (78.0 g, 0.50 mol) and azobisisobutyronitrile (200 mg, 1.2 mmol) in CCl_4 (750 ml) was heated to reflux and irradiated by a 300-W tungsten lamp. The vigorous reaction was modified by switching off the lamp. After 0.5 h the pale yellow suspension was cooled to 5 °C and the white precipitate of succinimide filtered off and washed with CCl_4 (2 × 100 ml). The combined filtrate and washings were evaporated under reduced pressure to yield 5′-bromocyclohexanespiro-2′-(1′,3′-dioxolan)-4′-one (**12**) as a pale yellow, lachrymatory oil; $\nu_{max.}$(neat) 1 815 cm^{-1}; $\delta_H(CDCl_3)$ 1.58—1.86 [8 H, m, $(CH_2)_4$], 2.10 (2 H, m, CH_2), and 6.59 (1 H, s, CHBr). This was stirred at 20 °C in toluene (1 l) whilst a solution of triphenylphosphine (131.5 g, 0.50 mol) in toluene (500 ml) was added dropwise over 1 h. The stirred solution was left overnight. The colourless precipitate was filtered off, washed with toluene (2 × 100 ml), and ether (3 × 100 ml). The crude product was purified by dissolution in ethanol followed by reprecipitation with ether to afford *5′-oxocyclohexanespiro-2′-(1′,3′-dioxolan)-4′-yltriphenylphosphonium bromide* (**13**) as a colourless solid (196 g, 79%), m.p. 198 °C (Found: C, 62.9; H, 5.0; Br, 15.7; P, 6.2. $C_{26}H_{26}BrO_3P$ requires C, 62.8; H, 5.3; Br, 16.1; P, 6.2%; $\lambda_{max.}$(EtOH) 225 (ε 30 500) and 268 nm (4 700); $\nu_{max.}(CH_2Cl_2)$ 2 950s, 2 740m, and 1 795s cm^{-1}; $\delta_H[(CD_3)_2CO–D_2O]$ 7.85—8.15 (16 H, m) and 1.3—2.3 (10 H, m).

5′-Triphenylphosphoranylidenecyclohexanespiro-2′-(1′,3′-dioxolan)-4′-one (**14**).—To a suspension of the phosphonium salt (**13**) 0.497 g, 1.0 mmol) in benzene (4 ml), in a dry box under nitrogen, was added DABCO (0.112 g, 1.0 mmol) in one portion. The intense yellow mixture was shaken for 4 min and then quickly filtered to remove the hydrobromide salt of DABCO. The filtrate was evaporated under reduced pressure to leave a foamy yellow solid which was triturated with petroleum and filtered. A portion of the yellow solid was dried *in vacuo* to provide an analytical sample of the *phosphorane* (**14**) (Found: C, 74.7; H, 6.3; P, 7.5. $C_{26}H_{25}O_3P$ requires C, 75.0; H, 6.05; P, 7.45%); $\nu_{max.}$(Nujol) 1 680s cm^{-1}.

Preparation of 5′-Ylidenecyclohexanespiro-2′-(1′,3′-dioxolan)-4′-ones: General Procedure.—The phosphorane (**14**) was prepared *in situ* by addition of a solution of DABCO (1—1.05 equiv.) in toluene (*ca.* 2 ml/mmol) to a stirred slurry of the phosphonium salt (**13**) (1 equiv.) in toluene (*ca.* 3 ml/mmol) at 70—110 °C under nitrogen. The yellow colour of the phosphorane (**14**) was seen immediately and the mixture was stirred for 3—5 min before addition of the carbonyl component in toluene. On completion of the reaction, the mixture was allowed to cool and filtered to remove DABCO·HBr. The filtrate was evaporated under reduced pressure and the dioxolanones were purified (see below).

(Z)-5′-Benzylidenecyclohexanespiro-2′-(1′,3′-dioxolan)-4′-one (**15**).—The phosphorane (**14**) (35.6 mmol) was heated for 1 h with benzaldehyde (3.55 g, 33.5 mmol) in toluene (170 ml) at reflux. Work-up gave an oily solid which was triturated with petroleum (5 × 50 ml) to separate (**15**) from the insoluble triphenylphosphine oxide. Evaporation of the combined triturates and chromatography of the resulting oil on silica gel (100 g) with petroleum–ether (4:1) as eluant gave a pale yellow solid which was recrystallised from ethanol–water to give *(Z)-5′-benzylidenecyclohexanespiro-2′-(1′,3′-dioxolan)-4′-one* (**15**) as a colourless solid (5.35 g, 65%), m.p. 71—72 °C (Found: C, 73.6; H, 6.7. $C_{15}H_{16}O_3$ requires C, 73.75; H, 6.6%); $\lambda_{max.}$(EtOH) 295 (ε 37 450) and 308 nm (31 550); $\nu_{max.}(CH_2Cl_2)$ 2 940m, 1 780s, 1 670w, and 1 195s cm^{-1}; δ_H (220 MHz, $CDCl_3$) 7.25—7.75 (5 H, m), 6.48 (1 H, s, =CH), and 1.45—1.95 [10 H, m, $(CH_2)_5$]; *m/z* 244 (M^+, 42%).

(Z)-5′-(4-*Benzyloxybenzylidene*)*cyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**16**).—The phosphorane (**14**) (40 mmol) and 4-benzyloxybenzaldehyde (6.36 g, 30 mmol) were heated for 2.5 h at 70 °C in toluene (140 ml). Work-up gave a white solid which contained a mixture of geometrical isomers by ^{1}H n.m.r. The product was purified by chromatography on silica gel (300 g) with chloroform as eluant and recrystallisation from ethanol to give (Z)-5′-(4-*benzyloxybenzylidene*)*cyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**16**) (8.3 g, 79%) as a single geometrical isomer (^{1}H n.m.r.), m.p. 128—130 °C (Found: C, 75.5; H, 6.3. $C_{22}H_{22}O_4$ requires C, 75.4; H, 6.35%); $\lambda_{max.}$(EtOH) 313 nm (ε 24 000); $\nu_{max.}$($CHCl_3$) 1 775s and 1 675w cm^{-1}; δ_H (80 MHz, $CDCl_3$) 7.62 (2 H, d, *J* 8 Hz), 7.40 (5 H, m), 6.95 (2 H, d, *J* 8 Hz), 6.43 (1 H, s, =CH), 5.10 (2 H, s, OCH_2Ph), and 1.40—2.10 [10 H, m, $(CH_2)_5$]; *m/z* 350 (M^+). Evaporation and recrystallisation of the mother liquors from ethanol gave a second crop of white solid (0.84 g, 8%), shown to be a mixture of geometrical isomers (^{1}H n.m.r.).

5′-*n-Butylidenecyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**17**).—The phosphorane (**14**) (10.9 mmol) and n-butyraldehyde (1.24 g, 17.2 mmol) were heated for 45 min in toluene (60 ml) at reflux. Work-up gave an oily solid which was triturated with petroleum (4 × 50 ml) to remove the insoluble triphenylphosphine oxide. The combined triturates were evaporated under reduced pressure to give a yellow oil which was chromatographed on silica gel (100 g) with petroleum–ether (4:1) as eluant to afford 5′-*n-butylidenecyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**17**) as a colourless oil (1.9 g, 83%) (Found: C, 68.7; H, 8.3. $C_{12}H_{18}O_3$ requires C, 68.55; H, 8.65%); $\lambda_{max.}$(EtOH) 247 nm; $\nu_{max.}$(film) 2 950s, 1 780s, and 1 690w cm^{-1}; δ_H (60 MHz, $CDCl_3$) shows presence of two isomers, 5.60 (t, *J* 7 Hz) and 5.53 (t, *J* 9 Hz) (total of 1 H, =CH), pseudoquartets at 2.54 and 2.18 (2 H), 1.58—1.91 (8 H, m), 1.27—1.58 (4 H, m), and 0.93 (3 H, t, *J* 6 Hz, CH_3); *m/z* 210 (M^+, 7%).

5′-*Isobutylidenecyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**16**).—The phosphorane (**14**) (5.53 mmol) and isobutyraldehyde (2.0 g, 28 mmol) were heated for 45 min in toluene (35 ml) at reflux. Work-up gave an oily solid which was triturated with petroleum (4 × 30 ml) to remove the insoluble triphenylphosphine oxide. The triturates were evaporated under reduced pressure to give a yellow oil which was chromatographed on silica gel (30 g) with petroleum–ether (4:1) as eluant to afford 5′-*isobutylidenecyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**18**) as a colourless oil (0.91 g, 78%) which solidified on storage at −20 °C (Found: C, 68.5; H, 8.6. $C_{12}H_{18}O_3$ requires C, 68.55; H, 8.65%); $\lambda_{max.}$(EtOH) 247 nm; $\nu_{max.}$(film) 2 945s, 1 790s, 1 695w, and 1 675w cm^{-1}; δ_H (220 MHz, $CDCl_3$) shows presence of two isomers, 5.48 (d, *J* 9 Hz) and 5.35 (d, *J* 11 Hz) (total of 1 H, =CH), 3.4—3.6 (m) and 2.6—2.8 (m) (total of 1 H, CH), 1.3—1.9 [10 H, m, $(CH_2)_5$], and 0.95—1.1 [6 H, m, $(CH_3)_2$]; *m/z* 210 (M^+, 14%).

5′-*Ethylidenecyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**19**).—The phosphorane (**14**) (30 mmol) and acetaldehyde (3.3 g, 75 mmol) were heated for 45 min in toluene (100 ml) at reflux. Work-up gave an oily solid which was triturated with petroleum (4 × 50 ml) to remove the insoluble triphenylphosphine oxide. The combined triturates were evaporated under reduced pressure to give a yellow oil which was purified by chromatography on silica gel (75 g) with petroleum–ether (4:1) as eluant and Kugelrohr distillation to afford 5′-*ethylidenecyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**19**) as a colourless oil (4.62 g, 85%), b.p. 95 °C (0.04 mmHg) (Found: C, 66.2; H, 7.4. $C_{10}H_{14}O_3$ requires C, 65.9; H, 7.7%); $\lambda_{max.}$(EtOH) 247 nm (ε11 050); $\nu_{max.}$(CH_2Cl_2) 2 945s, 1 780s, 1 695w, and 1 675w cm^{-1}; δ_H (220 MHz, $CDCl_3$) shows presence of two isomers 5.62 (q, *J* 7 Hz) and 5.57 (q, *J* 8 Hz) (total of 1 H, =CH), 2.02 (d, *J* 8 Hz) and 1.77 (d, *J* 7 Hz) (total of 3 H, CH_3), and 1.40—1.85 [10 H, m, $(CH_2)_5$]; *m/z* 182.0959 (M^+, 25%, dev. 1.6).

5′-*Methylenecyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**20**).—Gaseous formaldehyde was bubbled into a solution of the phosphorane (**14**) (10 mmol) in toluene at 80 °C and caused rapid decolourisation to occur. Work-up gave an oily solid which was triturated with petroleum (4 × 50 ml) to remove triphenylphosphine oxide. The combined triturates were evaporated under reduced pressure to give a yellow oil which was purified by flash chromatography on silica gel (10 g) with petroleum–ether as eluant and Kugelrohr distillation of the resulting product to afford 5′-*methylenecyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**20**) as a colourless oil which solidified on storage at −20 °C (1.33 g, 79%), b.p. 70 °C (0.05 mmHg) (Found: C, 64.5; H, 7.1. $C_9H_{12}O_3$ requires C, 64.3; H, 7.2%); $\lambda_{max.}$(EtOH) 238 nm (ε 9 600); $\nu_{max.}$(CH_2Cl_2) 2 950s, 1 795s, and 1 670m cm^{-1}; δ_H (60 MHz, CCl_4) 5.07 and 4.73 (2 H, ABq, *J* 2 Hz, $=CH_2$), and 1.4—1.9 [10 H, m, $(CH_2)_5$]; *m/z* 168.0807 (M^+, 2%, dev. 2.0).

5′-*Cinnamylidenecyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**21**).—The phosphorane (**14**) (12.0 mmol) and cinnamaldehyde (1.60 g, 12.1 mmol) were heated for 45 min in toluene (50 ml) at reflux. Work-up gave an oily solid which was triturated with petroleum (4 × 50 ml) to remove the insoluble triphenylphosphine oxide. The combined triturates were evaporated and the residue was chromatographed on silica gel (100 g) with petroleum–ether (4:1) as eluant to afford 5′-*cinnamylidenecyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (21) as a pale yellow oil (2.90 g, 89%), $\lambda_{max.}$(EtOH) 327 nm; $\nu_{max.}$ 1 780s, 1 650w, 1 615w, and 1 600w cm^{-1}; δ_H (220 MHz, $CDCl_3$) 6.2—7.95 (8 H, m) and 1.3—2.0 (10 H, m); *m/z* 270.1258 (M^+, 7%, dev. 0.2).

5′-*Prop*-2-*enylcyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**22**).—The phosphorane (**14**) (5.53 mmol) and crotonaldehyde (2.0 g, 29 mmol) were heated for 30 min in toluene (40 ml) at reflux. Work-up gave an oily solid which was triturated with petroleum (4 × 30 ml) to remove the insoluble triphenylphosphine oxide. The combined triturates were evaporated under reduced pressure to give an orange oil which was chromatographed on silica gel (50 g) with petroleum–ether (4:1) as eluant. This afforded 5′-*prop*-2-*enylcyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4-*one* (**22**) as a colourless oil which solidified on storage at −20 °C (0.85 g, 74%), b.p. 160 °C (0.1 mmHg) (Found: C, 69.5; H, 8.0. $C_{12}H_{16}O_3$ requires C, 69.2; H, 7.7%); $\lambda_{max.}$(EtOH) 286 nm; $\nu_{max.}$(CH_2Cl_2) 2 940s, 1 780s, 1 665m, 1 655m, and 1 625w cm^{-1}; δ_H (220 MHz, $CDCl_3$) 7.0—7.75 and 5.75—6.50 (3 H, m), and 1.25—1.90 (13 H, m); *m/z* 208 (M^+, 9%).

Methyl 5-*Phenylpenta*-2,4-*dienoate* (**24**).—Methyltriphenylphosphoranylideneacetate (17.0 g, 50.9 mmol) and cinnamaldehyde (6.41 g, 48.6 mmol) were heated for 4 h in toluene (200 ml) at reflux under nitrogen. The solvent was evaporated and the residue was triturated with petroleum (3 × 100 ml) to remove the insoluble triphenylphosphine oxide. The combined triturates were evaporated under reduced pressure to give a yellow solid which was purified by flash chromatography on silica gel (50 g) with petroleum–ether as eluant and recrystallisation from petroleum (b.p. 60—80 °C) to afford (**24**) as colourless crystals (5.87 g, 64%), m.p. 70—71 °C (lit.,[13] 71 °C); $\nu_{max.}$(CH_2Cl_2) 1 715s, 1 630s, 1 620m, and 1 600w cm^{-1}; δ_H (60 MHz, CCl_4) 7.21—7.50m, 6.80—6.90m and 5.85—5.95m (total of 9 H), and 3.70 (3 H, s, OMe); *m/z* 188 (M^+, 48%).

5-*Phenylpenta*-2,4-*dienol* (**25**).—To a solution of the ester (**24**) (0.95 g, 5.05 mmol) in toluene (45 ml) at −60 °C under nitrogen, was added DIBAH [7 ml of a 25% (w/w) solution in toluene, equivalent to 11.1 mmol]. The reaction mixture was allowed to attain room temperature during overnight stirring, before addition of saturated aqueous NH_4Cl (4 ml). After 30 min the mixture was filtered and the filtrate dried ($MgSO_4$), filtered, evaporated under reduced pressure, and recrystallised from dichloromethane–petroleum (b.p. 60—80 °C) to give (**25**) (0.66 g, 82%), m.p. 78—79 °C; $\nu_{max.}(CH_2Cl_2)$ 3 610m, 2 980m, 1 620m, and 1 600w cm^{-1}; δ_H (220 MHz, $CDCl_3$) 6.90—7.25 (5 H, m), 5.50—6.80 (4 H, m), and 4.00 (2 H, d, *J* 6 Hz, CH_2); *m/z* 160.0886 (M^+, 58%, dev. −0.2) and 129.0697 ($M^+ - CH_2OH$, 82%, dev. −0.7).

5-*Phenylpenta*-2,4-*dienal* (**26**).—Pyridinium dichromate (1.63 g, 4.34 mmol) was added to a solution of the alcohol (**25**) (0.46 g, 2.88 mmol) in dry dichloromethane (20 ml) under nitrogen. The mixture was stirred for 7 h at room temperature, poured into ether (80 ml), and filtered through $MgSO_4$. The filtrate was evaporated under reduced pressure and the resulting yellow oil was flash chromatographed on silica gel (15 g) with chloroform as eluant to afford (**26**) as a pale yellow oil (0.313 g, 69%), $\nu_{max.}(CH_2Cl_2)$ 1 680s, 1 625m, and 1 610w cm^{-1}; δ_H (220 MHz, $CDCl_3$) 9.62 (d, *J* 7 Hz) and 9.55 (d, *J* 7 Hz) (total of 1 H, CHO), and 5.90—7.60 (9 H, m); *m/z* 158.0734 (M^+, 72%, dev. 0.2) and 129.0702 (M^+ − CHO, 100% dev. −0.2).

5′(5-*Phenylpenta*-2,4-*dienylidene*)*cyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**23**).—The phosphorane (**14**) (2 mmol) and the aldehyde (**26**) (0.30 g, 1.9 mmol) were heated for 45 min in toluene (19 ml) at reflux. Work-up gave an oily solid which was triturated with petroleum (3 × 25 ml) to remove triphenylphosphine oxide. The combined filtrates were evaporated under reduced pressure and the resulting orange oil was chromatographed on silica gel (18 g) with petroleum–ether (4:1) as eluant to afford 5′(5-*phenylpenta*-2,4-*dienylidene*)*cyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**23**) as a pale yellow oil (0.51 g, 91%). $\lambda_{max.}$(EtOH) 353 nm (ε 49 500); $\nu_{max.}(CH_2Cl_2)$ 1 775s, 1 650w, 1 630m, 1 610m, and 1 600w cm^{-1}; δ_H (220 MHz, $CDCl_3$) 6.20—7.55 (10 H, m) and 1.40—2.00 (10 H, m); *m/z* 296.1420 (M^+, 7%, dev. 0.8).

5′(1-*Trifluoromethylethylidene*)*cyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**27**).—The phosphorane (**14**) (4 mmol) and 1,1,1-trifluoroacetone (4.0 g, 36 mmol) were heated for 30 min in toluene (35 ml) at reflux. Work-up gave an oily solid which was triturated with petroleum (4 × 30 ml) to remove the insoluble triphenylphosphine oxide. The triturates were evaporated under reduced pressure to give a yellow oil which was chromatographed on silica gel (25 g) with petroleum–ether (4:1) as eluant to afford 5′-(1-*trifluoromethylethylidene*)*cyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**27**) as a colourless oil (0.71 g, 70%) (Found: C, 53.0; H, 5.5; F, 23.1. $C_{11}H_{13}F_3O_3$ requires C, 52.8; H, 5.25; F, 22.8%); $\nu_{max.}(CH_2Cl_2)$ 1 800s and 1 680m cm^{-1}; δ_H (60 MHz, CCl_4) 1.95 (3 H, s, CH_3) and 1.50—1.90 [10 H, m, $(CH_2)_5$]; *m/z* 250 (M^+, 9%).

5′-(1-*t*-*Butoxycarbonylethylidene*)*cyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**28**).—The phosphorane (**14**) (40 mmol) and t-butyl pyruvate (5.82 g, 40.4 mmol) were heated for 1 h in toluene (140 ml) at reflux. Work-up gave an oily solid which was triturated with petroleum (4 × 60 ml) to remove triphenylphosphine oxide. The combined triturates were evaporated under reduced pressure and the residue was chromatographed on silica gel (100 g) with petroleum–dichloromethane (3:1) as eluant and recrystallised from dichloromethane–petroleum (b.p. 60—80 °C) to afford 5′-(1-*t*-*butoxycarbonylethylidene*)*cyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**28**) as colourless crystals (6.3 g, 56%) m.p. 99—100 °C (Found: C, 63.8; H, 8.0. $C_{15}H_{22}O_5$ requires C, 63.8; H, 7.85%); $\lambda_{max.}$(EtOH) 256 nm (ε 12 100); $\nu_{max.}(CH_2Cl_2)$ 1 790s and 1 720s cm^{-1}; δ_H (220 MHz, $CDCl_3$) 1.97 (3 H, s, CH_3), 1.65—1.85 [10 H, m, $(CH_2)_5$], and 1.53 (9 H, s, Bu^t); *m/z* 282.1465 (M^+, 1%, dev. −0.2), 209.0811 (M^+ − OBu^t, 13% dev. −0.3), and 181.0861 ($M^+ - CO_2Bu^t$, 4%, dev. −0.4).

Sodium Phenylpyruvate (**29**).—A solution of NaOH (0.145 g, 3.63 mmol) in water (5 ml) was added over 20 min to a solution of dioxolanone (**15**) (0.93 g, 3.82 mmol) in THF (10 ml) under nitrogen. After 18 h the homogenous reaction mixture was evaporated under reduced pressure to afford a white solid which was washed with ether (3 × 15 ml) to remove cyclohexanone and unchanged (**15**) and freeze dried for 24 h to give *sodium phenylpyruvate* (**29**) (0.66 g, 89%), m.p. 220—230 °C (decomp.) (Found: C, 53.1; H, 4.5. $C_9H_7O_3Na{\cdot}H_2O$ requires C, 52.9; H, 4.45%); $\nu_{max.}$(Nujol) 3 500—2 500s, br, 2 950s, and 1 600s, br cm^{-1}; semicarbazone, m.p. 177—177.5 °C (EtOH–water) lit.,[14] 180 °C) Found: C, 54.0; H, 4.8; N, 19.1. $C_{10}H_{11}N_3O_3$ requires C, 54.3; H, 5.0; N, 19.0%); *m/z* 221.0805 (M^+, 35%, dev. 0.5) and 176.0811 ($M^+ - CO_2H$, 19%, dev. −1.2).

Sodium 2-*Oxohexanoate* (**30**).—A solution of NaOH (0.337 g, 8.4 mmol) in water (10 ml) was added over 20 min to the dioxolanone (**17**) (1.89 g, 9 mmol) in THF (10 ml) under nitrogen. After 18 h the homogenous mixture was evaporated under reduced pressure to give a white solid which was washed with ether (4 × 10 ml) and dried *in vacuo* (130 °C) to afford *sodium* 2-*oxohexanoate* (**30**) (0.97 g, 76%), m.p. 235 °C (decomp.) (Found: C, 47.6; H, 6.2; Na, 14.8. $C_6H_9NaO_3$ requires C, 47.3; H, 6.0; Na, 15.1%); $\nu_{max.}$(Nujol–hexachlorobutadiene) 2 955m, 2 930m, 2 870w, 1 705s, 1 640s, and 1 625s cm^{-1}.

Sodium 4-*Methyl*-2-*oxopentanoate* (**31**).—A solution of NaOH (0.185 g, 4.6 mmol) in water (5 ml) was added over 20 min to a solution of the dioxolanone (**18**) (1.02 g, 4.86 mmol) in THF (10 ml) under nitrogen. After 18 h the homogenous mixture was evaporated under reduced pressure to give a white solid which was washed with ether (3 × 10 ml) and dried *in vacuo* (130 °C) to afford *sodium* 4-*methyl*-2-*oxopentanoate* (**31**) (0.51 g, 73%), m.p. 295—300 °C (decomp.) (Found: C, 47.3; H, 5.9. $C_6H_9NaO_3$ requires C, 47.3; H, 6.0%); $\nu_{max.}$(Nujol–hexachlorobutadiene) 2 950s, 2 870s, 1 710s, and 1 630s cm^{-1}; semicarbazone, *m/z* 187.0974 (M^+, 1%, dev. 1.7) and 142.0969 ($M^+ - CO_2H$, 100%, dev. −1.1).

2-*Oxo*-3-*phenylpropanal* (**33**).—To a solution of the dioxolanone (**15**) (0.112 g, 0.46 mmol) in toluene (25 ml) at −60 °C under nitrogen, was added DIBAH [0.6 ml of a 25% (w/w) solution in toluene, equivalent to 0.95 mmol] over 5 min. After 20 min at −60 °C the reaction was quenched by addition of 10% aqueous citric acid (20 ml) and allowed to attain room temperature. The aqueous layer was washed with toluene (2 × 5 ml) and the combined organic layers were dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give an off-white solid (73 mg) which was sublimed *in vacuo* (85—90 °C, 0.1 mmHg) to afford (**33**) (51 mg, 75%), m.p. 118—119 °C (lit.,[15] 118—120 °C); $\lambda_{max.}$(EtOH) 310 nm; $\lambda_{max.}$(EtOH + 2M-NaOH) 355 nm; $\nu_{max.}(CH_2Cl_2)$ 3 440m, 1 670s, and 1 645s cm^{-1}; δ_H (220 MHz, $CDCl_3$) 9.3 (1 H, s, CHO), 7.9—7.95 (2 H, m), 7.4—7.55 (3 H, m), 6.7 (1 H, s, exchanges with D_2O, OH), and 6.2 (1 H, s, =CH); *m/z* 148.0527 (M^+, 80%, dev. 0.3) and 119.0484 (M^+ − CHO, 36%, dev. −1.2).

2-*Oxo*-7-*phenylhepta*-4,6-*dienal* (**34**).—To a solution of the dioxolanone (**23**) (0.348 g, 1.18 mmol) in toluene (50 ml) at

−78 °C under nitrogen was added DIBAH [0.9 ml of a 25% (w/w) solution in toluene, equivalent to 1.43 mmol] over 5 min. After 20 min at −78 °C the reaction was quenched by addition of 10% aqueous citric acid (5 ml), allowed to attain room temperature, and diluted with ether (50 ml) and brine (60 ml). The combined organic layers were washed with water (2 × 40 ml), dried ($MgSO_4$), filtered, and evaporated under reduced pressure to afford a brown oily solid which was chromatographed on silica gel (20 g) with chloroform as eluant to give *2-oxo-7-phenylhepta-4,6-dienal* (**34**) as a yellow solid (0.115 g, 49%), m.p. 124—125 °C; $\lambda_{max.}$(EtOH) 361 nm (ε 43 000); $\lambda_{max.}$(EtOH + 2M-NaOH) 408 nm (ε 38 300); $\nu_{max.}$(CH_2Cl_2) 3 460m, 1 665s, 1 635s, and 1 600s cm^{-1}; δ_H (220 MHz, $CDCl_3$) 9.10 (1 H, s, CHO) and 5.95—7.55 (11 H, m); *m/z* 200.0840 (M^+, 55%, dev. 0.3), 182.0723 ($M^+ - H_2O$, 8%, dev. −0.9), and 171.0811 (M^+ − CHO, 87%).

2-Oxo-5-phenylpent-4-enal (**35**) *and 5-Hydroxy-4-phenylcyclopenta-2-en-1-one* (**36**).—To a solution of the dioxolanone (**21**) (0.6 g, 2.2 mmol) in toluene (120 ml), at −78 °C under nitrogen, was added DIBAH [2.8 ml of a 25% (w/w) solution in toluene, equivalent to 4.4 mmol] over 5 min. After 20 min at −78 °C the reaction was quenched with 10% aqueous citric acid (15 ml) and allowed to attain room temperature. The aqueous layer was washed with ether (3 × 25 ml) and the combined organic layers were dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give a yellow solid (0.37 g) which was sublimed *in vacuo* (*ca.* 100 °C, 0.1 mmHg) to afford a hygroscopic yellow solid (0.175 g, 46%), m.p. 75—95 °C (Found: C, 75.5; H, 6.0. $C_{11}H_{10}O_2$ requires C, 75.8; H, 5.8%); $\lambda_{max.}$(EtOH) 337 nm; $\nu_{max.}$(CH_2Cl_2) 3 550w, 3 450w, 1 720s, 1 665m, 1 630m, and 1 605w cm^{-1}; δ_H (220 MHz, $CDCl_3$) 9.17 (0.3 H, s), 7.20—7.70 (6.6 H, m), 6.88 (s) and 6.95 (s) (total of 0.3 H), 6.65—6.85 (br s, 0.1 H, exchanges with D_2O), 6.30—6.40 (0.6 H, m), 6.18 (s) and 6.12 (s) (total of 0.3 H), 4.08—4.14 (0.7 H, m), 3.95—4.02 (0.7 H, m), and 3.60—3.95 (br s, 0.4 H, exchanges with D_2O); *m/z* 174.0682 (M^+, 100%, dev. 0.2), 156.0555 ($M^+ - H_2O$, 10%, dev. −2.0), and 145.0650 (M^+ − CHO, 37%, dev. 0.2).

3-Phenylcyclopentane-1,2-dione (**37**).—Sodium hydroxide (30 mg, 0.75 mmol) in water (2 ml) was added to a solution of (**35**) and (**36**) (107 mg, 0.61 mmol) in ethanol (15 ml). After 5 min the mixture was acidified (pH 4) with 2M-HCl and evaporated under reduced pressure to afford a yellow oily solid which was triturated with ether (3 × 10 ml). The combined triturates were dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give a yellow solid which was recrystallised from benzene–petroleum (b.p. 60—80 °C) to give (**37**) as white crystals (67 mg, 63%), m.p. 190—191 °C (lit.,[10] 190—191 °C) (Found: C, 75.7; H, 5.6. Calc. for $C_{11}H_{10}O_2$ C, 75.8; H, 5.8%); $\lambda_{max.}$(EtOH) 309 nm (ε 29 050); $\lambda_{max.}$(EtOH + 2M-NaOH) 356 nm (ε 23 350); $\nu_{max.}$(CH_2Cl_2) 3 460m, 1 695s, and 1 645s cm^{-1}; δ_H (80 MHz, $CDCl_3$) 7.80—8.05 (2 H, m), 7.25—7.50 (3 H, m), 6.55 (1 H, s, exchanges with D_2O), 2.75—2.95 (2 H, m), and 2.45—2.65 (2 H, m); *m/z* 174.0693 (M^+, 100%, dev. 1.3).

3-Hydroxy-3-methyl-1-phenylbutan-2-one (**40**).—A solution of methyl iodide (3.27 g, 25.16 mmol) in ether (20 ml) was added over 25 min to magnesium turnings (0.60 g, 24.69 mg-atom) under nitrogen. After a further 35 min a solution of the dioxolanone (**15**) (2.44 g, 10 mmol) in ether (20 ml) was added dropwise over 35 min and a vigorous reaction occurred. After 19 h the mixture was treated with saturated aqueous NH_4Cl, the ethereal layer was separated, and the aqueous layer washed thrice with ether. The combined organic layers were dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give a dark liquid (2.35 g), a portion (1.01 g) of which was chromatographed on silica gel (80 g). Elution with ether–petroleum (1:9 initially, followed by 1:1) gave successively, unchanged (**15**), 1-methylcyclohexanol, and finally *3-hydroxy-3-methyl-1-phenylbutan-2-one* (**40**) (0.326 g, 42%), b.p. *ca.* 100 °C (0.05 mmHg); $\lambda_{max.}$(EtOH) 215 nm (ε 3 500); $\nu_{max.}$(film) 3 450s, 1 705s, and 1 605w cm^{-1}; δ_H (220 MHz, $CDCl_3$) 7.18—7.42 (5 H, m), 3.88 (2 H, s), 3.00—4.00 (1 H, v br s, exchanges with D_2O), and 1.42 (6 H, s); *m/z* 178.0983 (M^+, 4%, dev. −0.6) and 160.0891 ($M^+ - H_2O$, 30%, dev. 0.1).

5′-Cyclohexylmethylcyclohexanespiro-2′-(1′,3′-dioxolan)-4′-one (**44**).—A solution of the dioxolanone (**15**) (1.01 g, 4.12 mmol) in methanol (20 ml) was treated with Adams catalyst (0.20 g) and the mixture was stirred under hydrogen for 6 h. The solution was filtered through Celite and evaporated under reduced pressure to give a slightly discoloured oil (1.01 g) which was chromatographed on silica gel (50 g) with ether–petroleum (1:4) as eluant to give *5′-cyclohexylmethylcyclohexanespiro-2′-(1′,3′-dioxolan)-4′-one* (**44**) as a colourless oil (0.91 g, 87%), b.p. *ca.* 110 °C (0.4 mmHg); $\nu_{max.}$(film) 2 930s, 1 790s, and 1 220s cm^{-1}; δ_H (220 MHz, $CDCl_3$) 4.43 (1 H, ABq) and 0.79—2.70 (23 H, m); *m/z* 252.1768 (M^+, 100%, dev. 1.7).

5′-Benzylcyclohexanespiro-2′-(1′,3′-dioxolan)-4′-one (**45**).—A solution of the dioxolanone (**15**) (2.0 g, 8.20 mmol) in ethyl acetate (40 ml) was treated with 5% palladium on charcoal (0.19 g) and stirred under hydrogen for 18 h. The mixture was filtered through Celite and the filtrate evaporated under reduced pressure to give a colourless oil (2.01 g). A portion (0.23 g) of the product was microdistilled to give *5-benzylcyclohexanespiro-2′-(1′,3′-dioxolan)-4′-one* (**45**) (0.20 g, 87%), b.p. *ca.* 120 °C (0.35 mmHg) (Found: C, 73.2; H, 7.45. $C_{15}H_{18}O_3$ requires C, 73.15; H, 7.35%), $\nu_{max.}$(film) 1 785s, 1 605w, and 1 220s cm^{-1}; δ_H (220 MHz, $CDCl_3$) 7.14—7.44 (5 H, m), 4.64 (1 H, ABq, J_{AX} 4.42 Hz, J_{BX} 6.1 Hz), 3.17 (1 H, ABq, J_{AX} 4.42 Hz, J_{AB} 14.5 Hz), 3.04 (1 H, ABq, J_{AB} 14.5 Hz, J_{BX} 6.1 Hz), and 1.16—1.94 (10 H, m); *m/z* 246 (M^+).

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