

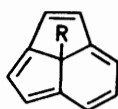
Investigation of an Electrocyclisation Route to the 7*b*H-Cyclopent[*c,d*]-indene System

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An approach to the synthesis of derivatives of 7*b*H-cyclopent[*cd*]indene ring system (1) has been explored in which two of the three rings are constructed by cyclisation reactions. The acetylenic alcohol (7) was prepared by coupling of 3-iodo-2-methylcyclopent-2-en-1-one (6) with the copper(I) salt of prop-2-ynyl alcohol tetrahydropyranyl ether. This was then converted into the *Z,E*-trienedione (2). On heating, this compound failed to undergo cyclisation; the only reaction observed was its isomerisation to the *E,E*-trienedione (10). Under forcing conditions it gave only indan-1-one.

The *cis*-double bond of the trienedione system was fixed by incorporating it into a bicyclo[2.2.1]heptadiene system. Two such derivatives, (14) and (15), were prepared; both underwent smooth electrocyclic ring-closure on heating and the ylide (15) also cyclised further to give compound (19), which incorporates the required 7*b*H-cyclopent[*cd*]indene skeleton.

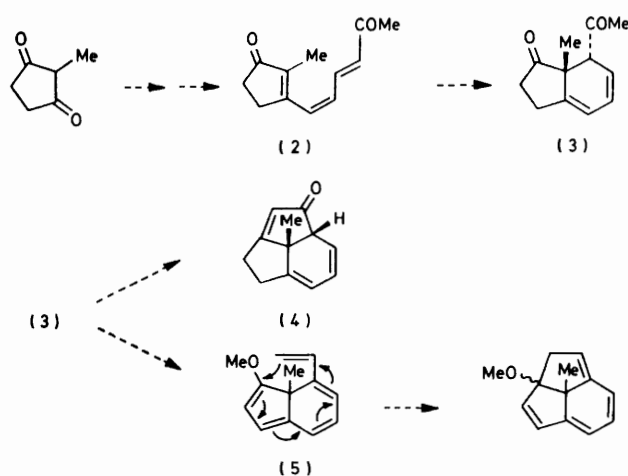
A SUCCESSFUL route to derivatives of a new tricyclic [10]annulene, the 7*b*H-cyclopent[*cd*]indene system, (1), was reported by us recently.¹ We have explored alternative routes to this ring system, and describe here our results on a method which depends on an electrocyclic



(1)

ring-closure for the construction of the six-membered ring. It is essentially an adaptation of the methodology which we have previously used to construct the 4*a*H-benzocycloheptane system,² in which the key step is an electrocyclic annelation.

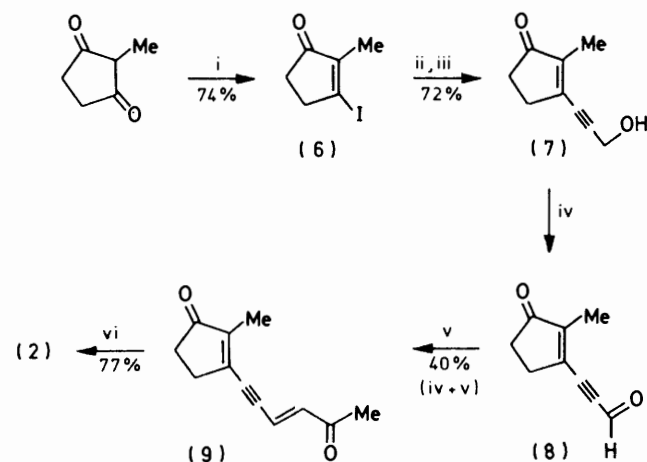
The proposed route to the 7*b*-methyl derivative of the annulene (1) is shown in outline in Scheme 1. The trienedione (2) was to be constructed from 2-methylcyclopentane-1,3-dione by adapting previously described reactions. Thermal cyclisation of the triene was then expected to give the bicyclic diketone (3) which could



SCHEME 1

then give the tricyclic ketone (4) by an internal aldol reaction. Dehydrogenation and extended enolisation reactions of the type used in our earlier work^{2,3} could then give the 1-methoxy-9*b*-methyl derivative of (1). Alternatively, the bicyclic diketone (3) could act as a precursor of the pentaenol ether (5), which could give the required system by an extended electrocyclic reaction as shown (Scheme 1).

Synthesis of the Diketone (2).—The route used to prepare the diketone is shown in Scheme 2. 2-Methylcyclopentane-1,3-dione was converted into the iodoenone

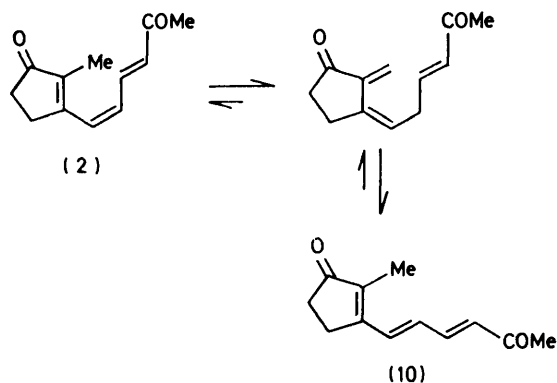


SCHEME 2 Reagents: i, $\text{Ph}_3\text{PI}_2\text{-Et}_3\text{N}$, 20 °C; ii, $\text{CuC}\equiv\text{CCH}_2\text{-OTHP-DMF}$, 125 °C; iii, TsOH-MeOH , 20 °C; iv, $\text{C}_6\text{H}_5\text{NHCl}^-\text{-CrO}_3$, 20 °C; v, $\text{Ph}_3\text{P}^+\text{CHCOMe}$, 20 °C; vi, $\text{H}_2\text{-Pd-BaSO}_4\text{-quinoline}$

(6), using the method described by Piers and Nagakura.⁴ Prop-2-ynyl alcohol was protected as its tetrahydropyranyl derivative and this was then converted into its copper(I) salt. The acetylide was found to couple smoothly with the iodoenone (6) in dimethylformamide to give, after hydrolysis, the crystalline alcohol (7). This coupling method was used only after several alternative procedures had proved unsuccessful. Cyclo-

pentane-1,3-dione was converted into its *O*-*s*-butyl ether but this failed to react with lithium or magnesium acetylides derived from protected or unprotected prop-2-ynyl alcohol, despite the fact that an analogous coupling with the corresponding butoxycyclohexenone has previously been described.⁵

Oxidation of the alcohol (7) by pyridinium chlorochromate⁶ gave cleanly the aldehyde (8), as indicated by t.l.c., but the aldehyde was found to decompose rapidly on exposure to air. A solution of the aldehyde was therefore treated directly with the ylide $\text{Ph}_3\text{P}^+\text{CHCOMe}$: the Wittig reaction took place rapidly at room temperature and the product (9) was isolated in 40% yield based on the alcohol (7).



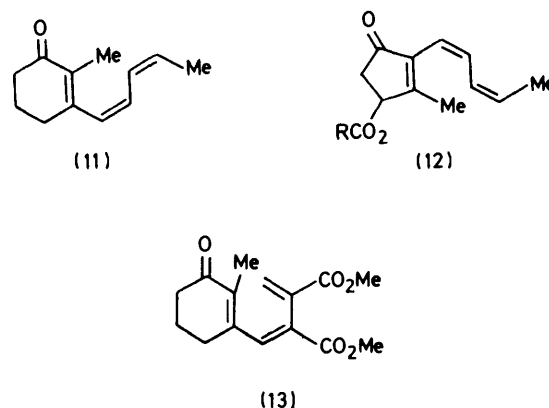
SCHEME 3

cis-Hydrogenation of the triple bond of the diketone (9) was performed using Lindlar's catalyst.^{7a} Although selective hydrogenation of similarly conjugated dienes has sometimes proved to be difficult,^{7b} because of the competitive hydrogenation of the double bonds, no such problems were encountered with the diketone (9); presumably, the additional conjugation with the carbonyl groups disfavors this competition. When a high ratio of catalyst to substrate (*ca.* 1 : 2) was used, as recommended for the semi-hydrogenation of precalciferol,⁸ the required trienedione (2) was obtained in good yield. The product was shown by n.m.r. to be contaminated with about 15% of the *E,E*-trienedione (10), but it could be obtained in a pure state by fractional crystallisation.

Rearrangement of the Diketone (2).—The diketone (2), when heated in xylene, failed to cyclise to the bicyclic ketone (3), and instead isomerised quantitatively to the *E,E*-trienedione (10). Attempts to achieve the desired cyclisation by heating the compound in decalin (190 °C) or by irradiating it, also resulted only in the formation of the isomer (10). This isomerisation may involve an intramolecular [1,5] hydrogen transfer (Scheme 3) which occurs in preference to cyclisation, although it has previously been demonstrated that some related trienones, (11),⁵ (12),⁹ and (13),¹⁰ can be cyclised thermally.

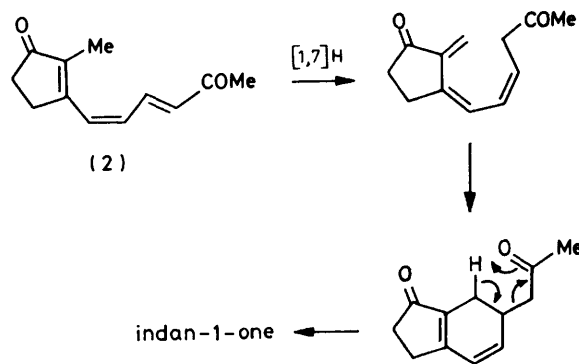
The vapour-phase pyrolysis of the dione (2) was then investigated in the hope that its isomerisation to compound (10) might be reversible at higher temperatures, allowing an irreversible cyclisation to compete. Flash

vacuum pyrolysis¹¹ of the dione at an oven temperature of 520 °C again gave compound (10) almost quantitatively. At 620 °C another component was present in the product mixture, and at 740 °C this became the



only product. It was not the diketone (3), however; it was shown to be indan-1-one by comparison with authentic material. A possible route for the formation of indan-1-one is shown in Scheme 4.

The rearrangement of the dione (2) was also investigated in the presence of a Lewis acid [tin(IV) chloride] and in the presence of a triene complexing agent (hexacarbonylchromium), with the aim of lowering the activation energy for the cyclisation. In both cases, however, the isomer (10) was the only product.

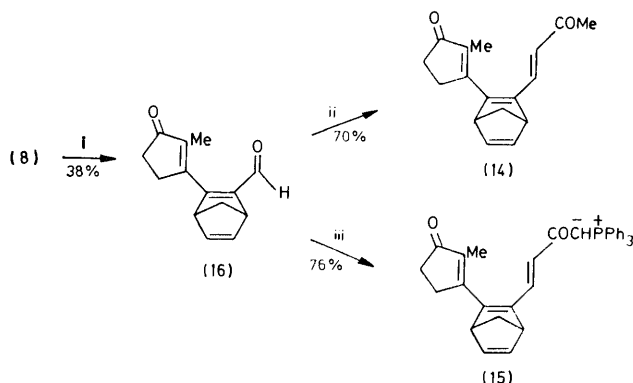


SCHEME 4

Cyclisation of Related Trienes of Fixed Geometry.—Having failed to bring about the desired cyclisation of the trienedione (2) we considered using a variety of modified or protected triene systems. Protection or modification of the carbonyl groups might make the cyclisation more favourable. A potentially more effective approach would be to protect the *cis*-double bond; for example, by its reversible incorporation into a cyclic system.

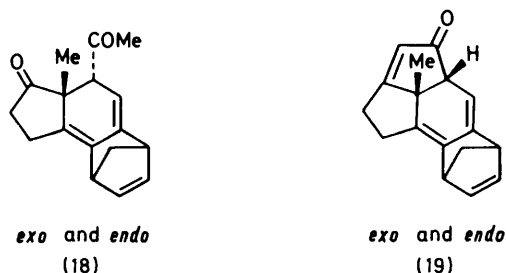
In order to determine whether compounds having fixed *cis*-geometry would undergo the required cyclisation, we prepared two model compounds, (14) and (15), by the route shown in Scheme 5. The acetylenic aldehyde (8) was intercepted *in situ* by its addition to cyclopentadiene at room temperature. The carbaldehyde (16) was isolated from the reaction as a crystalline solid, in

moderate yield. This aldehyde was converted into the diketone (14) by its Wittig reaction with the ylide $\text{Ph}_3\text{P}^+\text{CHCOMe}^-$; a similar reaction with the bisylide (17)¹² gave the derivative (15).



SCHEME 5 Reagents: i, cyclopentadiene, 20 °C; ii, $\text{Ph}_3\text{P}^+\text{CHCOMe}^-$, 56 °C; iii, $\text{Ph}_3\text{P}^+\text{CHCOCH}^+\text{HPPH}_3^-$ (17), 20 °C

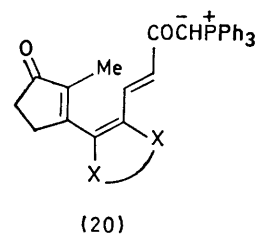
The diketone (14) cyclised in the desired manner when it was heated in bromobenzene at 156 °C. Compound (18) was isolated from the reaction mixture in 45% yield after layer chromatography. Because of the methylene bridge at C-6 and C-9 the compound is a mixture of two isomers: separate signals for the isomers could be distinguished in the n.m.r. spectrum. This clearly showed the cyclic nature of the product, with the methyl group at δ 0.91 and 1.10 in the two isomers. In the newly formed six-membered ring, the vinylic hydrogen at C-5 appears as a pair of doublets (J 6.7 Hz) at δ 5.39 and 5.42, and the methine hydrogen (H-4) is at δ 3.4, the signal being partially obscured by those from H-6 and H-9. The relationship between the signals for H-4 and H-5 was established by a decoupling experiment. In the i.r. spectrum of compound (18) the carbonyl groups absorb at 1730 and 1700 cm^{-1} ; the u.v. spectrum has maxima at 230 and 273 nm.



When the ylide (15) was heated in bromobenzene it gave a single product in 70% yield. This was assigned the structure (19) (again, it was a mixture of isomers about the methylene bridge). The methyl group in the two isomers appears at δ 1.19 and 1.27. In the fused six-membered ring the chemical shifts of the vinylic (H-9) and methine (H-9a) hydrogen atoms are similar to those of compound (18), with the resonances appearing as pairs of doublets (J 4.4 Hz) at δ 5.39/5.41 and 2.97/3.01,

the relationship between the signals being confirmed by a decoupling experiment. Two singlets are observed at δ 5.82 and 5.90 (together, 1 H) for H-2 of the five-membered ring.

Conclusions.—The experiments with the cyclopentadiene adducts (14) and (15) show that when the geometry of the central double bond of the triene system is fixed as *cis*, the thermal electrocyclic reaction takes place smoothly; moreover, in the case of the ylide (15), a second cyclisation to give the desired carbon skeleton takes place under the same conditions. In principle, therefore, this is a viable method for the synthesis of 7*bH*-cyclopent[*cd*]indene derivatives. The problem is to constrain the central double bond of the triene to be *cis* by incorporating it into a cyclic system which can subsequently be cleaved. For example, an intermediate of the general type (20) could be used, so that after cyclisation, the unwanted protective ring could be removed reductively.



Such compounds are not currently available, and the development of the route must therefore await an efficient preparation of an intermediate of this type.

EXPERIMENTAL

For general points, see ref. 2.

3-Iodo-2-methylcyclopent-2-en-1-one (6).⁴—Iodine (re-sublimed and finely divided) (23.85 g, 0.094 g-atom) was added in portions during 2 h to a stirred solution of triphenylphosphine (24.6 g, 0.094 mol) in dry acetonitrile (300 cm^3) under nitrogen. The mixture was stirred for a further 3 h, then dry triethylamine (9.52 g, 0.094 mol) was added, followed by 2-methylcyclopentane-1,3-dione¹³ (10.0 g, 0.090 mol). The mixture was stirred at room temperature for 18 h and the resulting solution was concentrated *in vacuo*. The solid residue was extracted with ethyl acetate (50 cm^3), and the insoluble triethylammonium iodide was filtered off and washed with ethyl acetate (50 cm^3). The filtrate and washings were evaporated under reduced pressure, and the residue was sublimed at 80 °C and 1 mmHg to yield the iodoenone (6) (14.76 g, 74%) as colourless needles, m.p. 51–52 °C (Found: C, 32.7; H, 3.0. Calc. for $\text{C}_6\text{H}_7\text{IO}$: C, 32.4; H, 3.15%), ν_{max} (Nujol) 1670 and 1610 cm^{-1} ; δ (60 MHz) 1.82 (3 H, t, J 2.0 Hz), 2.50 (2 H, m), and 3.00 (2 H, m). Homoallylic coupling between Me-2 and H-4,4' was observed in this and all other members of this series of compounds: this is not specifically recorded for subsequent n.m.r. spectra given below.

3-(Tetrahydropyran-2-yloxy)prop-1-ynylcopper(I).¹⁴—A solution of copper(I) chloride (57.0 g, 0.58 mol) in aqueous ammonia (10M; 600 cm^3) was filtered and added rapidly to a cold, vigorously stirred solution of prop-2-ynyl alcohol tetrahydropyranyl ether¹⁵ in ethanol (400 cm^3). The thick

suspension was stirred at room temperature for 1 h and then diluted with water (500 cm³). The insoluble solid was filtered off and washed successively with aqueous ammonia (2M; 4 × 100 cm³), water (4 × 100 cm³), ethanol (4 × 100 cm³), and ether (4 × 100 cm³). It was then dried at 20 °C and 0.1 mmHg to give the acetylide (25.2 g, 54%) as a bright yellow solid.

3-(3-Hydroxyprop-1-ynyl)-2-methylcyclopent-2-en-1-one (7).—The copper acetylide (8.4 g, 0.0415 mol) was added in finely divided form to a solution of the iodoenone (6) (8.0 g, 0.036 mol) in dry dimethylformamide (110 cm³). The suspension was purged with nitrogen and then stirred and heated at 125 °C for 5 h. The insoluble salts were filtered off and washed with ethyl acetate (40 cm³). The filtrate and washings were concentrated to leave a liquid which was dissolved in methanol (120 cm³) containing toluene-4-sulphonic acid (0.6 g). After 24 h at room temperature, the solution was evaporated, water (100 cm³) was added to the residue, and it was extracted with ethyl acetate (3 × 50 cm³). The extract was washed with aqueous sodium carbonate, water, and saturated brine, and then dried and evaporated to leave a brown oil (5.5 g). Column chromatography (silica; ether) gave (i) unchanged iodoenone (1.30 g, 16%) and (ii) *the hydroxyenone* (7) (3.90 g, 72%), m.p. 52–54 °C (from ether–hexane) (Found: C, 71.9; H, 6.6. C₉H₁₀O₂ requires C, 72.0; H, 6.7%); ν_{\max} (KBr) 3 400, 1 690, and 1 610 cm⁻¹; λ_{\max} (EtOH) 268 nm (ϵ 17 250); δ 1.81 (3 H, 2.42 (2 H, m), 2.62 (3 H, m, 1 H exchanged on D₂O shake), and 4.56 (2 H); m/e 150 (M^+).

E-6-(2-Methyl-3-oxocyclopent-1-enyl)hex-3-en-5-yn-2-one (9).—The hydroxyenone (2.60 g, 0.0173 mol) in dry dichloromethane (15 cm³) was added to a suspension of pyridinium chlorochromate⁶ (7.3 g, 0.034 mol) in dry dichloromethane (25 cm³) under nitrogen. After 3 h the alcohol was shown by t.l.c. to have been consumed; dry ether (200 cm³) was added to the mixture and the supernatant liquor was filtered through a bed of Florisil. The solid residue was twice stirred with ether (50 cm³) for 15 min; the combined filtrate and extracts were, without further delay, concentrated to ca. 30 cm³ at room temperature. A solution of triphenylphosphonium 2-oxopropylidene (5.5 g, 0.0173 mol) in tetrahydrofuran (100 cm³) was added and the reaction mixture was left for 18 h. Column chromatography (silica, ether) gave *the dione* (9) (1.30 g, 40%), m.p. 35–37 °C (from hexane) (Found: C, 76.6; H, 6.4. C₁₂H₁₂O₂ requires C, 76.6; H, 6.4%); ν_{\max} (KBr) 1 690 and 1 610 cm⁻¹; λ_{\max} (EtOH) 238 (ϵ 7 520) and 311 nm (19 950); δ 1.93 (3 H), 2.38 (3 H), 2.54 (2 H, m), 2.76 (2 H, m), 6.68 (1 H, d, J 16.1 Hz), and 6.92 (1 H, d, J 16.1 Hz); m/e 188 (M^+).

E,Z-6-(2-Methyl-3-oxocyclopent-1-enyl)hexa-3,5-dien-2-one (2).—The dione (9) (0.80 g, 4.26 mmol) in AnalaR ethyl acetate (25 cm³) was stirred with 5% palladium on charcoal (75 mg). The suspension was filtered and the filtrate was added to a pre-hydrogenated suspension of Lindlar's catalyst (400 mg) in ethyl acetate (10 cm³) containing quinoline (75 mg). The mixture was then hydrogenated at 1 atm. Hydrogen was taken up steadily during 15 min, after which time 101 cm³ (1.06 mol) had been absorbed. The catalyst was filtered off and washed with a little ethyl acetate, and the solvent was then removed from the filtrate to leave a yellow solid. Trituration with ether gave two crops (0.46 g, and 0.08 g) of the crude *E,Z*-dione, which was shown by n.m.r. to be contaminated with ca. 15% of the *E,E*-isomer (10). The mother liquors gave a further 0.08 g of the mixture; the total yield was 0.62 g (77%). Crystal-

lisation of the main crop material from dichloromethane–hexane and sublimation at 80–85 °C and 0.02 mmHg gave an analytical specimen of the *E,Z*-dione (2) as pale yellow aggregates, m.p. 98–100 °C (Found: C, 76.0; H, 7.3. C₁₂H₁₄O₂ requires C, 75.8; H, 7.4%); ν_{\max} (KBr) 1 685, 1 670 (C=O), 1 595, and 1 580 (C=C) cm⁻¹; λ_{\max} (EtOH) 237 (ϵ 6 180) and 322 nm (23 750); δ 1.82 (3 H), 2.31 (3 H), 2.51 (2 H, m), 2.92 (2 H, m), 6.35 (1 H, d, $J_{3,4}$ 15.5 Hz, H-3), 6.49 (1 H, t, $J_{4,5}$ 12.0, $J_{5,6}$ 12.0 Hz, H-5), 6.71 (1 H, d, J 12.0 Hz, H-6), and 7.59 (1 H, dd, J 15.5 and 12.0 Hz, H-4); m/e 190 (M^+).

Rearrangement of the Dione (2).—(a) *In xylene.* The pure *E,Z*-trienedione (120 mg) was heated in dry xylene (3 cm³) at 138 °C under nitrogen for 24 h. The solvent was removed and the residue was sublimed to give *E,E*-6-(2-methyl-3-oxocyclopent-1-enyl)hexa-3,5-dien-2-one (10) (110 mg, 92%) as pale yellow aggregates, m.p. 120–122 °C (from ether) (Found: C, 75.5; H, 7.3. C₁₂H₁₄O₂ requires C, 75.8; H, 7.4%); ν_{\max} (KBr) 1 680 (C=O), 1 650 and 1 610 (C=C) cm⁻¹; λ_{\max} (EtOH) 322 nm (ϵ 44 650); δ 1.85 (3 H), 2.33 (3 H), 2.50 (2 H, m), 2.72 (2 H, m), 6.36 (1 H, d, $J_{3,4}$ 15.6 Hz, H-3), 6.77 (1 H, dd, $J_{5,6}$ 15.6 Hz, $J_{4,5}$ 11.1 Hz, H-5), 7.13 (1 H, d, J 15.6 Hz, H-6), and 7.32 (1 H, dd, J 15.6 and 11.1 Hz, H-4); m/e 190 (M^+).

(b) *In decalin.* The *E,Z*-dione (20 mg) was heated in dry decalin (1 cm³) under nitrogen at 190 °C for 6 h and gave only the *E,E*-dione (10) (i.r., t.l.c.).

(c) *Other isomerisations.* The *E,Z*-dione was converted in good yield into the *E,E*-isomer in the following experiments: (i) irradiation in benzene at 45 °C for 10 h using Rayonet 400-W lamps at 300 nm; (ii) heating under reflux in dioxan with hexacarbonylchromium; (iii) heating under reflux in benzene with tin(IV) chloride; (iv) sublimation through a hot tube at 520 °C and 0.005 mmHg.

Flash Pyrolysis of the Dione (2).—The *E,Z*-dione (120 mg) was vapourised at 80 °C and 0.005 mmHg and the vapour was passed through a hot tube¹¹ at 740 °C onto a cold finger. The pyrolysate (70 mg, 84%) was a single component (t.l.c.). Filtration through silica gave indan-1-one, m.p. 30–34 °C (i.r., t.l.c.), m/e 132 (M^+); 2,4-dinitrophenylhydrazones, m.p. 258–259 °C (lit.,¹⁶ m.p. 258 °C). Pyrolysis at 620 °C gave a mixture of indan-1-one and the *E,E*-dione (10).

3-(2-Methyl-3-oxocyclopent-1-enyl)bicyclo[2.2.1]hepta-2,5-diene-2-carbaldehyde (16).—A solution of the aldehyde (8) in dichloromethane (35 cm³) and ether (230 cm³) was obtained as described above from the alcohol (7) (2.20 g, 0.0147 mol). The volume of the solution was reduced to 80 cm³, cyclopentadiene (12 cm³) was added, and the solution was left at room temperature for 20 h. Evaporation followed by column chromatography (silica; ether) gave *the carbaldehyde* (16) (1.20 g, 38%), m.p. 79–81 °C (from ether) (Found: C, 78.3; H, 6.5. C₁₄H₁₄O₂ requires C, 78.5; H, 6.5%); ν_{\max} (KBr) 1 690 and 1 640 cm⁻¹; λ_{\max} (EtOH) 232 (ϵ 12 350) and 302 nm (7 200); δ (CDCl₃) 1.72 (3 H), 2.19 (2 H), 2.50 (2 H, m), 2.70 (2 H, m), 3.88 (1 H, br s), 4.17 (1 H, br s), 6.81 (1 H, m), 6.99 (1 H, m), and 9.71 (1 H); m/e 214 (M^+) and 186 ($M^+ - CO$).

E-4-[3-(2-Methyl-3-oxocyclopent-1-enyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl]but-3-en-2-one (14).—The aldehyde (16) (400 mg, 1.87 mmol) and triphenylphosphonium 2-oxopropylidene (600 mg, 1.89 mmol) were heated under nitrogen in tetrahydrofuran under reflux for 48 h. Evaporation followed by column chromatography (silica; ether) gave *the dione* (14) (330 mg, 70%) as a yellow oil; ν_{\max} 1 685, 1 660,

and 1 590 cm^{-1} ; δ 1.67 (3 H), 2.10 (2 H), 2.21 (3 H), 2.45 (2 H, m), 2.5—2.7 (2 H, m), 3.82 (2 H, m), 6.24 (1 H, d, *J* 15.5 Hz), 6.77 (1 H, m), 6.87 (1 H, m), and 7.13 (1 H, d, *J* 15.5 Hz).

E-Triphenylphosphonium 4-[3-(2-Methyl-3-oxocyclopent-1-enyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl]-2-oxobut-2-enylide (15).—2-Oxotrimethylene-1,3-bis(triphenylphosphonium) chloride¹² (1.02 g, 1.57 mmol) was added to a solution of butanol-free potassium *t*-butoxide¹⁷ (352 mg, 3.14 mmol) in dry dimethyl sulphoxide (6 cm^3) under nitrogen. The yellow mixture was stirred at room temperature for 1 h after which a solution of the aldehyde (16) (330 mg, 1.54 mmol) in dimethyl sulphoxide (5 cm^3) was added. The dark solution was left at room temperature under nitrogen for 18 h after which it was poured into saturated brine (40 cm^3). The emulsion was extracted with dichloromethane ($2 \times 20 \text{ cm}^3$) and the organic phase was washed with water, dried, and evaporated. The residue was shaken with ethyl acetate (20 cm^3) and hydrochloric acid (2*M*; 20 cm^3). The organic phase was separated and extracted again with hydrochloric acid ($3 \times 10 \text{ cm}^3$). The combined acidic extracts were washed with ether and basified; the product was then taken up by washing the aqueous solution with dichloromethane ($3 \times 15 \text{ cm}^3$). The organic phase, after washing and drying, was evaporated to leave the crude *ylide* (0.60 g, 76%). Crystallisation gave the *ylide* as a yellow solid, m.p. 188—190 °C (decomp.) (from ethyl acetate) (Found: C, 81.2; H, 6.0. $\text{C}_{35}\text{H}_{31}\text{O}_2\text{P}$ requires C, 81.7; H, 6.3%); ν_{max} (KBr) 1 675 and 1 610 cm^{-1} ; δ 1.78 (3 H), 2.07 (2 H), 2.38 (2 H, m), 2.5—2.9 (2 H, m), 3.87 (2 H, m), 5.30 (1 H), 6.55 (1 H, d, *J* 15 Hz), 6.78 (1 H, m), 6.87 (1 H, m), 7.25 (1 H, d, *J* 15 Hz), and 7.4—7.8 (15 H).

Thermal Rearrangement of the Dione (14).—The butenone (14) (220 mg) was heated in bromobenzene (10 cm^3) under reflux in a nitrogen atmosphere for 24 h. The solvent was removed. T.l.c. showed the presence of one major product which was isolated by layer chromatography (silica; ether). This gave *trans*-(2,3,3*a*,4,6,9-hexahydro-6,9-methano-3*a*-methyl-3-oxo-1*H*-benz[e]inden-4-yl)ethanone (18) as a mixture of diastereoisomers about the 6- and 9-positions: it was a clear oil (99 mg, 45%); ν_{max} (film) 1 730 and 1 700 cm^{-1} ; λ_{max} (EtOH) 230 (ϵ 8 630) and 273 nm (3 120); δ 0.91 and 1.10 (together, 3 H, Me-3*a*), 1.49 and 1.86 (together, 2 H, both m, H-10 and 10'), 1.95 and 2.08 (together, 3 H, COMe), 2.5—2.9 (4 H, m), 3.40 (3 H, m), 5.41 (1 H, t, *J* 6.7 Hz, H-5), and 6.15 (2 H, m, H-7 and H-8). Irradiation at δ 3.40 caused collapse of the apparent triplet at 5.41 to a pair of singlets at δ 5.39 and 5.42.

Thermolysis of the Ylide (15).—The *ylide* (15) (200 mg) was heated under nitrogen in dry bromobenzene (10 cm^3) for 20 h. The solvent was removed under reduced pressure and the sole non-polar product was isolated by layer chromatography (silica; ether) as an oil (65 mg, 70%) which solidified with time; m.p. 97—103 °C. This was assigned the structure *cis*-3,4,5,8,9*a*,9*b*-hexahydro-5,8-methano-9*b*-methyl-1*H*-cyclopenta[gh]benz[e]inden-1-one (19), a mixture of diastereoisomers about the 5- and 8-positions; ν_{max} (Nujol) 1 695 and 1 625 cm^{-1} ; δ 1.19 and 1.27 (together, 3 H, Me-9*b*), 1.35, 1.60, 1.72, and 1.86 (together, 2 H, all d, H-10, 10'), 2.40—2.92 (4 H, H-3, 3', 4, 4'), 2.97 and 3.01 (together, 1 H, both d, *J* 4.4 Hz, H-9*a*), 3.30 (2 H, m, H-5,8), 5.40 (1 H, t, *J* 4.4 Hz, H-9), 5.82 and 5.90 (together, 1 H, H-2), and 5.95, 6.10, and 6.20 (together, 2 H, all m, H-6 -7). Irradiation of the apparent triplet at δ 5.40 (a superimposed pair of doublets) caused the doublets at δ 2.97 and 3.01 to collapse to singlets, *me* 236 (*M*⁺).

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