Electrocyclic Reactions. Part III.[1] Some Reactions of 2,4-Dimethyl-1,5-diphenylpenta-1,4-dien-3-one (αα'-Dimethyldibenzylideneacetone)

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αα'-Dimethyldibenzylideneacetone (I) by treatment with hot hydrochloric acid gives *trans*-2.5-dimethyl-3.4-diphenylcyclopent-2-enone (Va). With hot hydriodic acid the minor product is the cyclopentenone (Va) and the major product is *trans*-2.5-dimethyl-*trans*-3.4-diphenylcyclopentanone (VIa). The cyclopentenone (Va) undergoes only partial reduction with hot hydriodic acid to the cyclopentanone (VIa). The results suggest a conrotatory thermal ground state electrocyclisation of a pentadienyl cation to a cyclopentenyl cation. followed by loss of a proton and ketonisation, or by reduction. The high yields of cyclic products. relative to those observed for *trans.trans*-dibenzylideneacetone. are notable.

In Part II[1] some thermal ground state electrocyclic reactions of pentadienyl cations derived from *trans,trans*-dibenzylideneacetone were reported. These reactions were found to proceed by the controtatory mode predicted by the Woodward–Hoffmann Rules for the conservation of orbital symmetry. However, treatment of *trans,trans*-dibenzylideneacetone with hydriodic acid at *ca.* 100° furnished only low yields (13%) of *trans*-3,4-diphenylcyclopentanone, with predominant production of dimeric species. We now find that αα'-dimethyldi-

benzylideneacetone with hydriodic acid at *ca.* 100° furnishes high yields (65—78%) of cyclopentane derivatives.

Yates *et al.*[2] by comparison of the u.v. maximum of *trans,trans*-dibenzylideneacetone, $\lambda_{max.}$ 330 nm (log ε 4·54), with that of benzylideneacetone, $\lambda_{max.}$ 286 nm (log 4·37) (Δλ 44), and consideration of the dipole moment,[3] concluded that the preferred conformation is the *s-cis,cis*-form. Yates *et al.*[2] similarly by comparison of the u.v. maximum of αα'-dimethyldibenzylideneacetone, $\lambda_{max.}$ 287 nm (log ε 4·44) with that of *trans,*-

[1] Part II, C. W. Shoppee and B. J. A. Cooke, *J.C.S. Perkin I,* 1972, 2271.

[2] P. Yates, N. Yoda, W. Brown, and B. Mann, *J. Amer. Chem. Soc.,* 1958, **80,** 202.

[3] J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.,* 1949, 2957.

trans-dibenzylideneacetone ($\Delta\lambda$ 43) and of benzylidene-methyl ethyl ketone, $\lambda_{max.}$ 277 nm (log ε 4·27) ($\Delta\lambda$ 10) and consideration of the i.r. spectra, concluded that the most probable conformation of $\alpha\alpha'$-dimethyldibenzylid-eneacetone is the U-shaped *s-trans,trans*-form (I). This

(II)   (I)   (III)

(IV)   (V)   (VI)
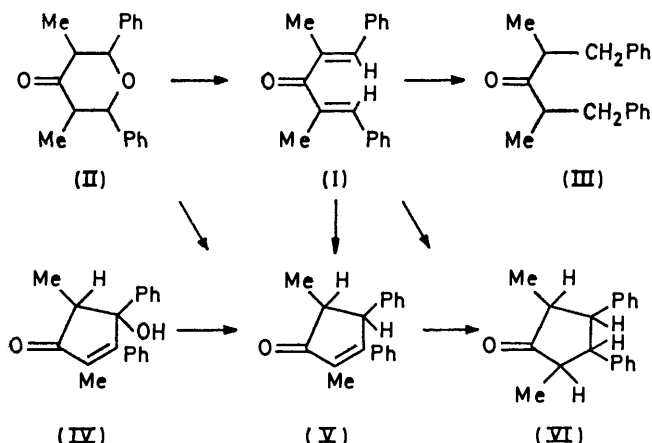
conclusion is supported by the n.m.r. spectrum; the signal given by the two methyl groups centred at δ 2·17 is split by the *trans*-vinyl protons with J 1·4 Hz, a value too large for *cis*-vinyl protons. It thus seems reasonable that reduction of (I) with hot hydriodic acid should afford, by a thermal, ground state, conrotatory, electrocyclic reaction of a derived cation, significantly higher yields of cyclic compounds than *trans,trans*-dibenzylideneacetone.

The primary product of the condensation of benzaldehyde and diethyl ketone with hydroxide ions is the tetrahydro-γ-pyrone [4] (II), m.p. 109°; this by the further action of hydroxide ions is converted into $\alpha\alpha'$-dimethyldibenzylideneacetone (I). The structure (I), correctly given by Vorlander and Wilcke,[5] was rejected by Japp and Maitland,[6] but has been confirmed by Yates *et al.*,[2] who report $\nu_{max.}$ 1626 cm^{-1}, by catalytic hydrogenation to 2,4-dimethyl-4,5-diphenylpentan-3-one (III), $\nu_{max.}$ 1709 cm^{-1}, identical with synthetic material. The dienone (I) with ethanolic hydrochloric acid [2,6] gives 2,5-dimethyl-3 4-diphenylcyclopent-2-enone (V), $\lambda_{max.}$ 276 nm (log ε 4·26), $\nu_{max.}$ 1698 cm^{-1}, also obtained directly from the tetrahydro-γ-pyrone (II) with ethanolic hydrochloric acid,[2,6] from the hydroxy-enone (IV),[6] and from 2,5-dimethyl-3,4-diphenyl-3,4,5-trihydroxycyclopentanone [7] with hot hydriodic acid. The reaction of the dienone (I) with hydrochloric acid has been re-examined and the reaction with hydriodic acid has been investigated using modern techniques of analysis and identification.

Treatment of the pentadienone (I) with hot ethanolic hydrochloric acid gave a 78% yield of the cyclopentenone (V), m.p. 122°. The same substance (V) was obtained in small amount from (I) by use of hot hydriodic acid and red phosphorus together with high yields of the cyclopentanone (VI), m.p. 122°. Japp and Maitland [6] describe the conversion of the tetrahydro-γ-pyrone (II) by
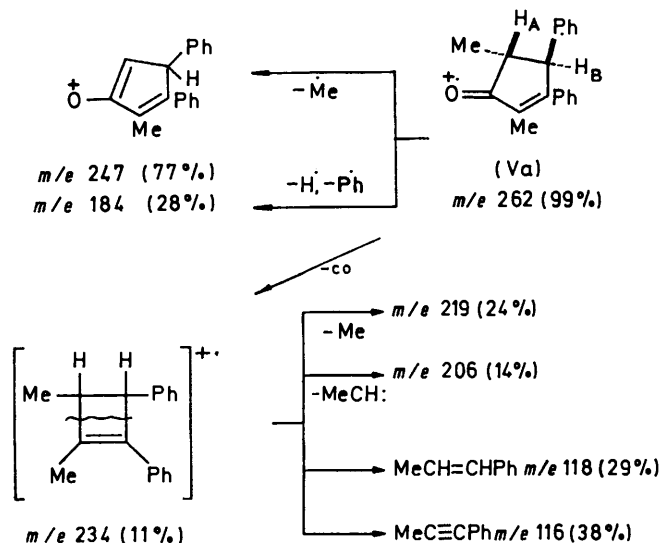
boiling fuming hydriodic acid in 5 min to a mixed crystal, m.p. 110—119°, containing *ca.* 75% (V) and *ca.* 25% (VI); we find that the cyclopentenone (V) is partly unchanged after refluxing with hydriodic acid and phosphorus for 24 h. The results are set out in the Table, the products and yields being determined by g.l.c. analysis of samples by comparison of retention times and peak areas with those of genuine specimens.

Acid catalysed reactions at *ca.* 100°

Compound	Reagent	Time (h)	Products and yields (%)
(I)	HCl	2	(V) 78 *
(I)	HI	24	(V) 4, (VI) 60 *†
(V)	HI	24	(VI) 64 ‡

* Small amounts of a solid, m.p. 273—275° (7%) also detected. † Several unidentified substances (<1%) also detected. ‡ Unchanged starting material (V) (16%) also observed.

The structure of the cyclopentenone (V) is supported by the mass spectrum; the parent peak at m/e 262 is the base peak, the next most prominent peak at m/e 247 arises from β-elimination of a methyl radical, whilst peaks observed at m/e 234, 219, 206, 184, 118, 116, 91 ($\overset{+}{C}H_2Ph$), and 77 ($\overset{+}{P}h$) may be rationalised by the fragmentations shown in the Scheme.

m/e 247 (77%)
m/e 184 (28%)

(Va)
m/e 262 (99%)

m/e 234 (11%)

m/e 219 (24%)
m/e 206 (14%)
MeCH=CHPh m/e 118 (29%)
MeC≡CPh m/e 116 (38%)

Scheme

The cyclopentenone (V) can exist in two stereoisomeric forms with H_A and H_B *cis* or *trans* (θ_{AB} 0 or 120° for a planar ring structure), but only a single isomer, m.p. 122°, has been encountered. This isomer has the *trans*-structure (Va); the n.m.r. spectrum shows two quartets centred at δ 2·45 arising from H_A, the signal of which is split by the benzylic proton H_B (J 2·5 Hz; θ *ca.* 120°) and by the three protons of the adjacent methyl group (J 7 Hz), and a set of five equally spaced lines centred at δ 4·02 (J 2 Hz) arising from H_B, the signal of which is split by the vicinal proton H_A and by the three protons of the allylic methyl group.

[4] D. Vorlander and K. Hobohm, *Ber.*, 1896, **29**, 1352, 1836.

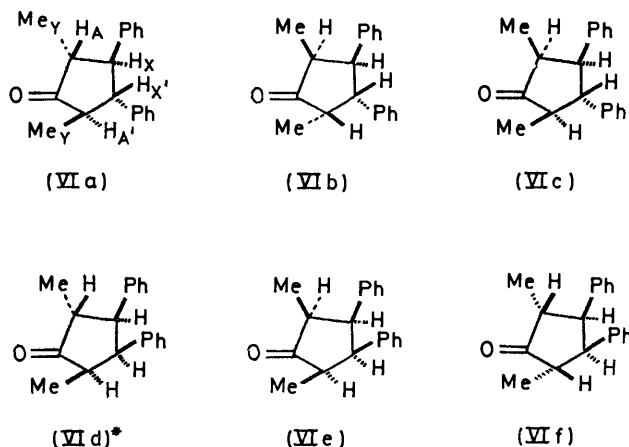[5] D. Vorlander and F. Wilcke, *Ber.*, 1898, **31**, 187.

[6] F. R. Japp and W. Maitland, *J. Chem. Soc.*, 1904, **85**, 1473.

[7] F. R. Japp and A. C. Michie, *J. Chem. Soc.*, 1903, **83**, 279, especially p. 303.

The cyclopentanone (VI) can exist in six stereoisomeric forms (VIa—f) irrespective of the precise conformation of the five-membered ring, but only a single isomer, m.p. 122°, was encountered.

(VIa)   (VIb)   (VIc)

(VId)*   (VIe)   (VIf)

* Represents a pair of enantiomers.

The 100 and 300 MHz n.m.r. spectra of this isomer exhibited four well separated resonance patterns centred at δ 7·15, 2·98, 2·45, and 1·15 with corresponding intensities of 5 : 1 : 1 : 3. These signals represent two sets of phenyl, benzylic, methine, and methyl protons, respectively, so that the stereoisomer under observation must possess a symmetrical structure (VIa, b, e, or f). In the spectra of the unsymmetrical stereoisomers (VIc, d) the number of peaks representing corresponding group protons would be nearly doubled (cf. Figure); these two
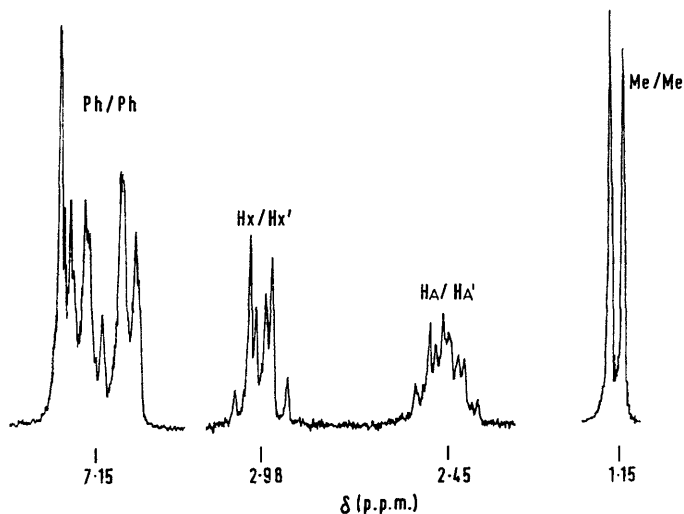

300 MHz n.m.r. spectrum of the cyclopentanone (VIa)

formulae may therefore be eliminated. The relatively narrow chemical shift range (δ 7·28—7·02) of the aromatic proton multiplet clearly indicates that the two phenyl groups have a trans-arrangement; an aromatic proton multiplet arising from two phenyl groups with an analogous cis-arrangement would be more than three times wider.[8,9] This indication is supported by the presence of the single methyl proton doublet signal at

δ 1·15 (J 7·0 Hz), i.e. the doublets of the two secondary methyl groups must coincide. The resonance positions of the benzylic, methine, and methyl protons are completely consistent only with structure (VIa). The magnitudes of the coupling constants present in the absorptions of these protons were determined by analysis of their resonance patterns as an AA′XX′Y$_3$ system (J_{AX} 12·0, $J_{XX'}$, 10·5, and J_{AY} 7·0 Hz); these values eliminate the cis,trans,cis-structure (VIb), and are fully in accord with the all-trans-structure (VIa).

The formation from the pentadienone (I) of the cyclopentane derivatives (Va) and (VIa), whose configurations are those consistent with thermodynamic control, is most readily explained by the occurrence of a thermal, ground state, conrotatory, electrocyclic reaction. In general, symmetry allowed electrocyclic reactions are subject to thermodynamic control; we suggest that the pentadienone (I) by protonation yields the pentadienyl cation (A), cyclised to the cyclopentenyl cation (B), which in the presence of hydrogen chloride can eliminate a benzylic proton to furnish the cyclopentenone (Va) with partial loss of stereochemistry, or in the presence of hydrogen iodide can undergo reduction to the cyclopentanone (VIa). However, since the cyclopentenone (Va) is partly reduced by hydrogen iodide to the cyclopentanone (VIa) (see Table), the stereochemistry of the latter may not reflect the geometry of the cyclisation.

(A)   (B)
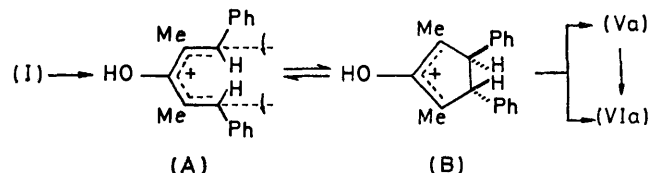
Use of deuterium iodide should distinguish between the two pathways (B) $\longrightarrow$ (VIa) and (B) $\longrightarrow$ (Va) $\longrightarrow$ (VIa); the former pathway should lead to the presence of two benzylic protons (VII), and the latter pathway to the presence of a high level of benzylic deuterons (VIII).


(VII)   (VIII)
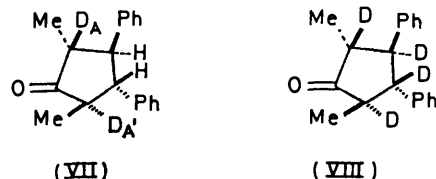
The cyclopentenone (Va) with deuterium iodide (isotopic purity 99% determined by n.m.r.) and red phosphorus at 60—65° for 24 h gave the isomer (IX; D_A 82%, D_X 84%; $\nu_{max.}$ 1695 cm^{-1}) by exchange, but suffered very little reduction to the cyclopentanone (VIII) as indicated by the i.r. spectrum of the reaction product which exhibited only a weak shoulder at $\nu_{max.}$ 1735 cm^{-1}. The n.m.r. spectrum of (IX) showed a singlet signal for the aliphatic methyl group (Me*) at δ 1·32, and another singlet signal for the vinyl methyl group (Me†) at δ 2·0.

[8] D. Y. Curtin, H. Gruen, and B. A. Shoulders, Chem. and Ind., 1958, 1205.
[9] N. S. Bhacca, unpublished results.

The pentadienone (I) with deuterium iodide and phosphorus at 60—65° for 18 h gave the cyclopentenone (IX; $D_A = D_X$ 80%; $\nu_{max.}$ 1695 cm⁻¹), together with a small amount of a cyclopentanone (?VII; $\nu_{max.}$ 1735 cm⁻¹)

(Va)   (IX)   (VIII)
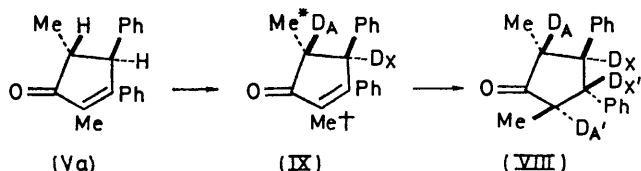
which did not permit determination of the isotopic distribution, and a little of the solid, m.p. 273—275°. In a similar experiment at 90—95° for 18 h, the products were the cyclopentenone (IX; $D_A = D_X$ 80%) the cyclopentanone (VIII; $D_A = D_{A'}$ 80%, $D_X = D_{X'}$ 67%) in the proportion 28 : 72, and a little of the solid, m.p. 275°. The limiting degree of deuteriation producible by reduction with deuterium iodide of the cyclopentenone (IX; D_A 80%, D_X 80%) should be represented by the cyclopentanone (VIII; $D_A = D_X$ 80%, $D_{A'} = D_{X'}$ 99%), which would however be indistinguishable by n.m.r. spectroscopy from (VIII; $D_A = D_X = D_{A'} = D_{X'}$ 90%). If it can be assumed that exchange of the methine and benzylic protons is 60—80% complete [(Va) ⟶ (IX)] (a low estimate in view of the exchange data described above) before reduction [(IX) ⟶ (VIII)] occurs to an appreciable extent, it follows that 13—23% of the product produced by cyclisation of the pentadienone (I) with deuterium iodide has the structure containing two benzylic protons (VII; $D_A = D_{A'}$ 80%).

The unexpected formation of the dideuteriated cyclopentenone (IX), from the dienone (I) and the cyclopentenone (Va) with deuterium iodide, suggests that the primary cyclisation product, the enol cation (D), passes to the extent of ca. 80% into the cyclopentadiene (X); this, also derivable from (Va) by enolisation,* by loss of the allylic proton yields the cyclopentadienyl anion (XI), which by deuteriation and ketonisation yields (IX). Alternatively, in the cyclopentenone (Va) activation by

* The enol (X) of the enantiomeric pair (Va) should theoretically be capable of two suprafacial [1,5] sigmatropic rearrangements to give (i) after ketonisation (Va) [d-(Va) ⟶ l-(Va); l-(Va) ⟶ d-(Va)], or (ii) after ketonisation (XII). Treatment of (Va) with a trace of methoxide ion in methanol at 65° failed predictably to yield (XII) since the conjugation energy of O=C—C=C exceeds that of Ph—C=C—Ph (cf. ref. 2).

(X)

(Va)   (XII)
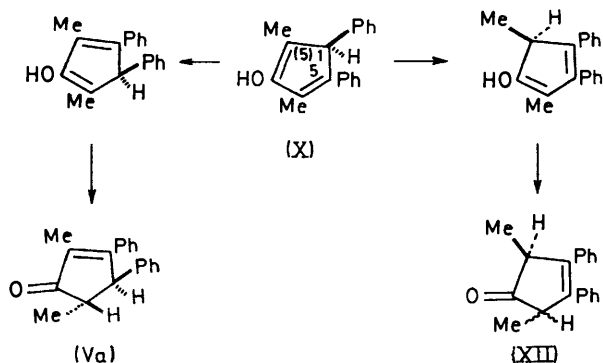
the carbonyl group of both the adjacent position and the nonadjacent vinylogous position may be responsible for dideuteriation.

(X)   (XI)   (IX)
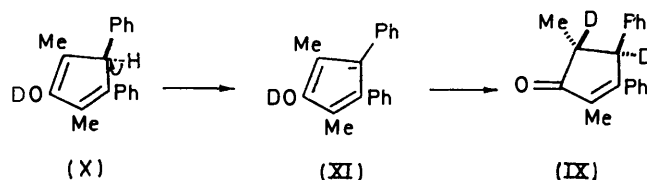
From the above evidence it appears that at least 13% and probably 23% of the cyclopentanone (VII) is produced by a conrotatory, ground state, electrocyclic reaction (I) ⟶ (C) ⟶ (D) ⟶ (VII) with preserva-

(C)   (D)
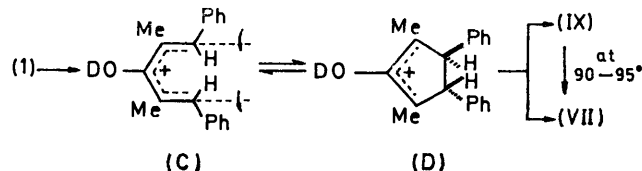
tion of the stereochemistry of the cyclisation. This conclusion is supported by the observation that the dienone (I) with deuterium iodide at 60—65° yields some cyclopentanone (VII), i.e. in conditions under which the cyclopentenone (IX) is effectively not reduced. This conclusion may presumably be extended to the conrotatory, ground state, electrocyclic reaction sequence (I) ⟶ (A) ⟶ (B) ⟶ (VIa).

EXPERIMENTAL

For general experimental directions see *J. Chem. Soc.*, 1959, 345, M.p.s were determined with a Thomas 40 hot-stage apparatus and are corrected. U.v. absorption spectra in ethanol solution were measured with a Beckman Acta III spectrometer, whilst i.r. absorption spectra (in chloroform solution † unless otherwise specified) were measured with Beckman IR 18 and IR 33 spectrometers. N.m.r. spectra were measured with Varian A60 and XL100 instruments in deuteriochloroform with tetramethylsilane as internal reference. Mass spectra were measured with a Varian-MAT 311 double-focusing spectrometer. Column chromatography was performed using aluminium oxide (Woelm neutral). T.l.c. was carried out using silica gel G or F (Merck); plates prepared with silica gel G were developed by exposure to iodine vapour, whilst plates made with silica gel F were examined in u.v. light. G.l.c. was carried out with a Beckman GC45 chromatograph fitted with a flame ionisation detector and a 6 ft × ⅛ in column packed with 5% XE60 substrate employing a helium flow rate of 40 ml min⁻¹ and temperature programming from 120 to 220 °C.

2,4-*Dimethyl*-1,5-*diphenylpenta*-1,4-*dien*-3-*one* ($\alpha\alpha'$-*Dimethyldibenzylideneacetone*) (I).—Pentan-3-one and benzaldehyde were treated with base according to the procedure of Yates et al.[2] (cf. refs. 5 and 6) to afford 2,4-dimethyl-1,5-diphenylpenta-1,4-dien-3-one, m.p. 128° (lit., 127·5—128°;[2] 122°;[5] 128°[6]), δ 2·17 (6H, d, *J* 1·4 Hz), 7·36 (2H, s, vinyl H), and 7·48 (10H, m, ArH).

† Carbonyl frequencies are ca. 15 cm⁻¹ lower than those observed in carbon tetrachloride.[10]

[10] A. R. H. Cole, *Rev. Pure Appl. Chem.*, 1954, **4**, 119.

Reaction of the Pentadienone (I) *with Ethanolic Hydrochloric Acid.*—The pentadienone (I) (310 mg) was dissolved in 95% ethanol (30 ml) containing conc. hydrochloric acid (40 drops) and the solution was refluxed for 2 h. The solution by standing overnight at 25° deposited material of high molecular weight (40 mg), m.p. 273—275° (sublimation and decomp.), which was removed by filtration.* The filtrate was evaporated to dryness in a vacuum to yield *trans*-2,5-dimethyl-3,4-diphenylcyclopent-2-enone (Va) (242 mg), m.p. 122° (from aqueous methanol) (lit., 122°; [2] 122° [6]), $\nu_{max.}$ 1695, 1630, 1610, and 1385 cm^{-1}, δ 1·45 (3H, d, *J* 7·2 Hz), 2·12 (3H, d, *J* 2 Hz, allylic Me), 3·45 (1H, octet, all *J* 2·5 Hz, H$_A$), 4·02 (1H, quintet, all *J* 2 Hz, H$_B$), 7·25 (5H, m, ArH), and 7·38 (5H, m, ArH). For mass spectrum, see Discussion section.

Reaction of the Pentadienone (I) *with Hydrogen Iodide.*—The pentadienone (I) (0·5 g) was refluxed with 45% hydriodic acid (7 ml) and red phosphorus (0·4 g) for 24 h. The cooled mixture was diluted and extracted with chloroform (3 × 10 ml); the extract was washed with sodium hydrogen carbonate solution, with water, dried over potassium carbonate, and evaporated. The resulting material (345 mg), $\nu_{max.}$ 1735, 1715, 1695, 1602, and 1380 cm^{-1}, by dissolution in chloroform gave a solid,* m.p. 273—275° (with sublimation and decomp.) in 7% yield. The filtrate was completely evaporated and the product subjected to g.l.c. analysis on XE 60 columns (temperature programmed from 120 to 220°). Two major components were detected together with several trace substances (*ca.* 1%): (*a*) *trans*-2,5-dimethyl-*trans*-3,4-diphenylcyclopentanone (VIa) (300 mg, 60%); t_R 6·3 min), m.p. 121·5—122·5° (from benzene–pentane) (lit., [2,6] m.p. 122°), $\nu_{max.}$ 1735, 1600, and 1372 cm^{-1}, *m/e* 264 (*M*$^+$), 178 (PhC≡CPh), 118 (100%, PhCH=CHMe), and 91 (PhĊH$_2$), for 100 and 300 MHz n.m.r. spectra, see Discussion section; the 2,5-dibromo-derivative, prepared according to the directions of Japp and Maitland,[6] had m.p. 191—194° (decomp.) (from benzene–methanol) [lit.,[6] m.p. 192° (decomp.)], δ 2·16 (6H, s, 2 Me), 3·84 (2H, s, 2 PhC*H*), and 7·30 (10H, m, ArH). The n.m.r. spectrum shows that its structure corresponds to (VIa) with the two methine protons replaced by two bromine atoms; (*b*) *trans*-2,5-dimethyl-3,4-diphenylcyclopent-2-enone (Va) (17 mg, 4%; t_R 7 min), m.p. and mixed m.p. 122°, whose i.r. and n.m.r. spectra were identical with those of the specimen described above.

Reduction of trans-2,5-*Dimethyl*-3,4-*diphenylcyclopent-2-enone* (Va) *with Hydrogen Iodide.*—The ketone (Va) (242 mg) was refluxed with 48% hydriodic acid (5 ml) and red phosphorus (250 mg) for 24 h. The usual isolation procedure furnished a semisolid (155 mg), which crystallised on standing. N.m.r. analysis by comparison of the integrated peaks of signals centred at δ 2·45 and 1·15 [corresponding to (Va) and (VIa)] showed the product to consist of 16% of the cyclopentenone (Va) and 84% of the cyclopentanone (VIa). Recrystallisation from benzene–pentane gave a mixed crystal, m.p. 115—117°, which had m.p. 116—117° when

mixed with a genuine specimen of the cyclopentanone (VIa), m.p. 122°.

Reaction of the Pentadienone (I) *with Deuterium Iodide.* (*a*) The pentadienone (I) (200 mg), red phosphorus (200 mg), and deuterium iodide (10 ml; 57% solution in D$_2$O; isotopic purity 99% by n.m.r.) were sealed in an ampoule containing a magnetic stirrer and heated in an oil-bath at 60—65° for 18 h. The ampoule was cooled, opened, and the contents were diluted with deuterium oxide (15 ml); the product was extracted with chloroform (3 × 25 ml), the extract filtered, dried (MgSO$_4$), and evaporated in a vacuum to give a greenish semisolid (205 mg), $\nu_{max.}$ 1735w and 1695s cm^{-1}. The product was dissolved in the minimum amount of boiling methanol, and the solution on standing at 20° deposited crystals (38 mg), shown by n.m.r. analysis to be a mixture of the cyclopentenone (IX), the cyclopentanone (?VII) of undetermined isotopic constitution, and the compound, C$_{38}$H$_{40}$O$_4$ (possibly deuteriated), of unknown structure. The residue from the mother liquor was shown by n.m.r. analysis to consist of the cyclopentenone (IX; D$_A$ = D$_X$ 80%).

(*b*) The pentadienone (I) (500 mg), red phosphorus (500 mg), and deuterium iodide (10 ml) were heated together similarly at 90—95° for 18 h. The product, crystallised from methanol, gave the compound, C$_{38}$H$_{40}$O$_4$, m.p. 271—273° (47 mg); the residue (400 mg) from the mother liquor, $\nu_{max.}$ 1735s, 1710sh, and 1695m cm^{-1}, by n.m.r. analysis by comparison of the areas of the methyl group signals at δ 1·13 [corresponding to (VIII)] and at δ 1·32 and 2·0 [corresponding to (IX)], consisted of a mixture of 72% (VIII) and 28% (IX), together with a small undetermined amount of the compound C$_{38}$H$_{40}$O$_4$; comparison of the area of the signal at δ 2·9 due to benzylic protons with that at δ 1·13 due to methyl protons showed that the average isotopic content of benzylic deuterium in (VIII) was 67%. The isotopic purity of methine deuterium in (VIII) and in (IX) was calculated from the areas of the corresponding peaks to be 80—90%; no signal due to a benzylic proton in (IX) at δ 3·95 was detected.

Reduction of trans-2,5-*Dimethyl*-3,4-*diphenylcyclopent-2-enone* (Va) *with Deuterium Iodide.*—Using the sealed ampoule procedure, the cyclopentenone (100 mg), red phosphorus (100 mg), and deuterium iodide (5 ml) were heated at 60—65° for 24 h. Dilution with deuterium oxide, and extraction with chloroform gave a greenish semisolid (87 mg), $\nu_{max.}$ 1735sh, w and 1695s cm^{-1}. N.m.r. analysis of the crude product showed it to consist of (IX) containing 84 and 82% deuterium at the 4- and 5-positions respectively.

Attempted Isomerisation of trans-2,5-*Dimethyl*-3,4-*diphenylcyclopent-2-enone* (Va) *to* 2,5-*Dimethyl*-3,4-*diphenylcyclopent-3-enone* (XII).—The cyclopentenone (Va) (19 mg) was heated with 0·24N-sodium methoxide at 65° for 1·5 h; the solution was cooled, diluted with water, neutralised with 2N-hydrochloric acid, and extracted with chloroform. The product (18·7 mg) was unchanged (Va), $\nu_{max.}$ 1695 cm^{-1}; no selective absorption at *ca.* 1740 cm^{-1} was observed.