

## Cyclopentadienes, Fulvenes, and Fulvalenes. Part IV.\* 1,2-Diphenylcyclopentadienes

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Attempts to obtain 1,2-diphenylcyclopentadiene led to its Diels–Alder dimer. Evidence for dissociation of this dimer has only been obtained in its reaction with molybdenum carbonyl. By contrast, 1,4-dimethyl-2,3-diphenylcyclopentadiene and 1,2,3-trimethyl-4,5-diphenylcyclopentadiene exist as stable monomers, like all other di- and polyaryl cyclopentadienes. Exact structures have been assigned to these and other arylcyclopentadienes as well as several related cyclopentene derivatives on the basis of their n.m.r. spectra.

In the course of work on highly arylated ferrocenes<sup>1,2</sup> it was desired to have all phenyl-substituted cyclopentadienes available. Moreover, detailed examination<sup>3</sup> of the phenylation<sup>4</sup> of ferrocene with benzenediazonium salts had led to the isolation, among other products, of 1,2-diphenylferrocene. Its structure was deduced<sup>3</sup> by eliminating all other isomers as possibilities, and confirmed by study of its n.m.r. spectrum. Rosenblum and his co-workers<sup>5</sup> reached the same conclusion in a more detailed study. However, at an early stage in this work we had unsuccessfully attempted to synthesise 1,2-diphenylcyclopentadiene (I; R = Ph) in order to be able to prepare 1,2-diphenylferrocene by an independent route, and our interest in this diene was revived by the American authors' successful preparation<sup>5</sup> of the related 1,2-di-(*p*-methoxyphenyl)cyclopentadiene (I; R = *p*-MeOC<sub>6</sub>H<sub>4</sub>-).

A substance described as 1,2-(*viz.* 3,4)-diphenyl-

cyclopentadiene was prepared by Allen, Jones, and Van Allan<sup>6</sup> by the action of ethanolic potassium hydroxide on 3,4-diphenylcyclopent-2-en-1-one. However, repetition of this reaction<sup>3a</sup> had shown that the product obtained is in fact the 1,4-isomer resulting from a phenyl migration. The same rearrangement occurred<sup>3a</sup> when we attempted to prepare the diene by copper sulphate dehydration of 1,2-diphenylcyclopentan-1,2-diol (II; R = Ph).

In Rosenblum's work<sup>5</sup> the di-(*p*-methoxyphenyl)cyclopentadiene (I; R = *p*-MeOC<sub>6</sub>H<sub>4</sub>-) was obtained as a byproduct in the aluminium amalgam reduction of 1,5-di-(*p*-methoxyphenyl)pentan-1,5-dione to the analogous diol (II; R = *p*-MeOC<sub>6</sub>H<sub>4</sub>-). Presumably this diol was itself an intermediate, although its separate dehydration was not reported. However, under the same conditions we obtained only the diol (II; R = Ph) and none of the desired diene (I; R = Ph) from 1,5-diphenylpentan-1,5-dione. Dehydration of this diol (II; R = Ph) was therefore reinvestigated. Under milder conditions this gave a new hydrocarbon, also formed by

\* Part III, P. L. Pauson and B. J. Williams, *J. Chem. Soc.*, 1961, 4162.

<sup>1</sup> P. L. Pauson, *J. Amer. Chem. Soc.*, 1954, **76**, 2187.

<sup>2</sup> S. McVey and P. L. Pauson, *J. Chem. Soc.*, 1965, 4312.

<sup>3</sup> (a) G. D. Broadhead, Thesis, Sheffield University, 1956; (b) G. D. Broadhead, P. L. Pauson, and G. V. D. Tiers, unpublished observations, briefly summarised in "Non-benzenoid Aromatic Compounds," ed. D. Ginsburg, New York, 1959, p. 125.

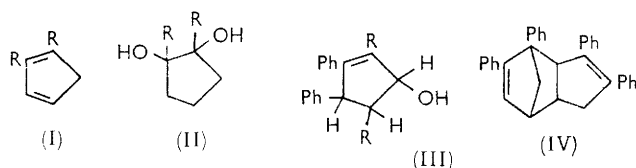
<sup>4</sup> G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 1955, 367.

<sup>5</sup> M. Rosenblum, W. G. Howells, A. K. Banerjee, and C. Bennett, *J. Amer. Chem. Soc.*, 1962, **84**, 2726.

<sup>6</sup> C. F. H. Allen, J. E. Jones, and J. A. Van Allan, *J. Org. Chem.*, 1946, **11**, 268.

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dehydration of 3,4-diphenylcyclopent-2-en-1-ol (III; R = H). This hydrocarbon had m. p. 219–221°, significantly higher than could be expected for a diphenylcyclopentadiene, and its n.m.r. spectrum was too

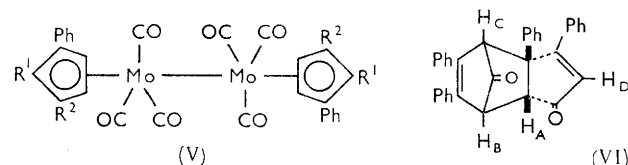


complex for such a formulation. Molecular weight determination confirmed that it is a dimer of the desired diene (I; R = Ph). Despite its reproducible and fairly sharp melting point, the n.m.r. spectrum suggests that it contains more than one isomer. Several Diels–Alder dimers are possible, and we believe that the most probable of these, dimer (IV), predominates in our product. This structure is most nearly compatible with the n.m.r. data, and by analogy with the dimers of other cyclopentadienes it may be assumed to be in the thermodynamically more stable *endo* form. When heated *in vacuo* at 200° it is converted to a low-melting yellow hydrocarbon. As this still has nearly the molecular weight expected for the dimer we regard it as the *exo* form of (IV), possibly admixed with monomer. Another, probably similar, hydrocarbon (mixture) was obtained in low yield by dehydration of 3,4-diphenylcyclopent-3-en-1-ol. However, we were unable to isolate pure monomer, and the whole product reverted to the original (*endo*) compound (IV) on standing or slow heating. More vigorous pyrolysis caused isomerisation of the monomer—presumably formed as an intermediate—to 1,4-diphenylcyclopentadiene. In several of the above preparations, the dimer (IV) was accompanied by a less soluble hydrocarbon, m. p. 265–270°, regarded as a trimer or higher polymer.

When the dimer (IV) was heated with hexacarbonylmolybdenum a complex  $C_{40}H_{26}Mo_2O_6$  was formed. This must be formulated as bis(tricarbonyl-1,2-diphenylcyclopentadienylmolybdenum) (V;  $R^1 = Ph$ ,  $R^2 = H$ ). It is similar, but not identical in properties, to the isomeric 1,3-diphenyl derivative (V;  $R^1 = H$ ,  $R^2 = Ph$ ), prepared to show that no phenyl migration had occurred. This was further confirmed by lithium–ethylamine reduction of the complex (V;  $R^1 = Ph$ ,  $R^2 = H$ ). As this process causes metal–ligand cleavage at low temperature and under non-acidic conditions, it was hoped that it might finally lead to the monomeric diene (I; R = Ph); but the only crystalline component isolated from the gummy organic product was again the dimer (IV).

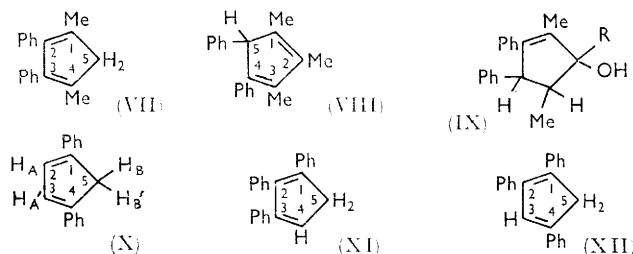
An attempt to prepare an isomer of the dimer (IV) by reduction of the diketone (VI) was unsuccessful; although it readily formed a di-hydrazone (but only a mono-2,4-dinitrophenylhydrazone), no hydrocarbon

could be isolated after subjecting the hydrazone to the Cram modification<sup>7</sup> of the Wolff–Kishner reduction. The n.m.r. spectrum of the diketone (VI) not only confirms its structure, which was, until recently,<sup>8</sup> a subject of some debate, but further establishes its stereochemistry as the *endo* isomer (VI). The resonance due to  $H_A$  appears as a doublet  $\tau$  6.87 with  $J_{H_A-H_B} = 5$  c./sec.  $H_B$  itself gives rise to a double doublet at  $\tau$  6.18, the major splitting again being 5 c./sec. A model of the *endo* isomer shows that the dihedral angle between these two hydrogens is about 30°, consistent with such a value of the coupling constant. In the *exo* isomer the corresponding angle is nearly 90°, and hence should lead<sup>9</sup> to a very small value. The minor splitting ( $J = 2$  c./sec.)



observed for  $H_B$  is due to coupling with  $H_C$ , which itself shows the corresponding doublet at  $\tau$  5.5. The large value for such a long range coupling may be due to the rigid ring system holding  $H_B$  and  $H_C$  in a fixed orientation, which allows maximum overlap of the minor lobes of the  $sp^3$  orbitals of the carbon atoms with the anti-bonding orbitals associated with the carbonyl group.<sup>10</sup> The value of  $J$  is marginally higher than would be expected (1.5 c./sec.) for homoallylic long range coupling<sup>11</sup> between these two hydrogens, although it may be argued that the rigid strained ring system would enhance this mechanism also (cf. the examples given below in the monocyclic series). The resonance of  $H_D$  is buried among that due to the phenyl protons, which give rise to four sharp peaks together with some more fragmented resonance in the region  $\tau$  2.5–3.3.

In contrast to our failure to obtain 1,2-diphenylcyclopentadiene, its di- (VII) and tri-methyl (VIII) derivatives were readily obtained by dehydration of the



alcohols (IX; R = H or Me), and were stable monomers. The apparent instability of 1,2-diphenylcyclopentadiene as a monomer is all the more difficult to understand

<sup>7</sup> D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Amer. Chem. Soc.*, 1962, **84**, 1734.

<sup>8</sup> C. F. H. Allen, *Chem. Rev.*, 1962, **62**, 662; cf. C. F. H. Allen and J. W. Gates, jun., *J. Amer. Chem. Soc.*, 1942, **64**, 2123.

<sup>9</sup> M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11; *J. Amer. Chem. Soc.*, 1963, **85**, 2870; K. L. Williamson and W. S. Johnson, *ibid.*, 1961, **83**, 4623.

<sup>10</sup> Cf. J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, 1961, **83**, 2769.

<sup>11</sup> For a review see J. Sterrhell, *Rev. Pure Appl. Chem. (Australia)*, 1964, **14**, 15.

in view of the stability of these, of 1,2-di(*p*-methoxyphenyl)cyclopentadiene,<sup>5</sup> and of all other phenyl-substituted cyclopentadienes.

The double bond positions in the dienes (VII) and (VIII) and in 1,4-diphenyl- (X), 1,2,3- (XI) and 1,2,4-triphenylcyclopentadiene (XII) have been established by study of their n.m.r. spectra. The results (excluding the phenyl protons which give broad multiplets between  $\tau$  2.2 and 3.0) and assignments are summarised in Table I.

however, has one completely unconjugated phenyl group at C<sub>5</sub>. Its structure follows unambiguously from the n.m.r. spectrum, which shows that none of the methyl groups is sufficiently strongly coupled to the methine hydrogen (H<sub>D</sub>) to admit one of the alternative structures, but the complex coupling pattern is well accounted for, for each of the three clearly resolved methyl peaks, by the assignments shown (Table 1).

Several of the above cyclopentadienes are obtained

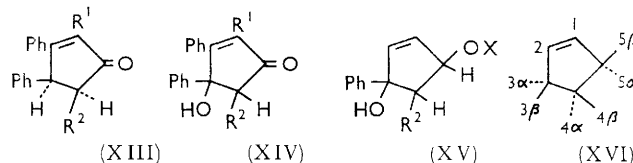
TABLE I  
N.m.r. results and assignments for the dienes (VII), (VIII), and (X—XII)

Compound	Solvent	Chemical shifts ( $\tau$ ) of H or CH <sub>3</sub> at ring positions: <sup>a</sup>					Coupling constants (c./sec.)	Ultraviolet maxima (m $\mu$ ) in 95% ethanol <sup>b</sup>
		1	2	3	4	5		
X	CDCl <sub>3</sub>	—	3.09	3.09	—	6.23	$J_{35} = 1.25$	235 (4.15); 350 (4.42)
XI	CDCl <sub>3</sub>	—	—	—	3.50	6.42	$J_{45} = 1.5$	240 (4.32); 308 (3.89)
XII	CDCl <sub>3</sub>	—	—	3.00 <sup>c</sup>	—	6.10	$J_{35} = 1.0$	238 (4.14); 265 (4.17); 350 (4.23)
VII	CDCl <sub>3</sub>	<i>7.97</i>	—	—	—	6.90	$J_{1'5} \leq 0.2$	237 (4.23)
VIII	CCl <sub>4</sub>	<i>8.27</i>	<i>8.10</i>	<i>7.94</i>	—	5.89	$J_{3'5} = 1.9$ $J_{1'2'} = 1.1$ $J_{1'5} = 0.95$	227 <sup>d</sup> (4.01); 301 (4.09)

<sup>a</sup> Methyl protons in italics. <sup>b</sup> Log  $\epsilon$  in parentheses. <sup>c</sup> Assignment of this band which is close to that of the phenyl protons was confirmed by spin decoupling. <sup>d</sup> Inflection.

Previously the method had only been applied to methylcyclopentadienes,<sup>12</sup> which were shown to form equilibrium mixtures of three isomers differing in double-bond positions. The arylcyclopentadienes have each been isolated in only a single crystalline form, and it is generally assumed that tautomeric change is sufficiently facile to permit the most stable isomer to be formed as the exclusive product in every case. Only in one case, however, that of 1,4-diphenylcyclopentadiene (X), has the actual position been established chemically.<sup>13</sup> The present results confirm the previous assignment based on ozonolysis. The equivalent pairs of H<sub>A</sub>, H<sub>A'</sub>, and H<sub>B</sub>, H<sub>B'</sub> each give rise to triplets, the expected pattern for an A<sub>2</sub>B<sub>2</sub> system where  $J_{AB}$  must equal  $J_{AB'}$ .<sup>14a</sup> The structures of both the triphenylcyclopentadienes, (XI) and (XII) confirm the expectation that the double bond positions will be such as to allow maximum conjugation. The assignments (Table I) all follow on first-order principles, and the ultraviolet spectra are in good agreement with these assignments. Compounds (X) and (XII) with diphenylbutadiene chromophores have highest wavelength maxima at 350 m $\mu$ , whereas the maximum at 308 m $\mu$  in the 1,2,3-triphenyl derivative (XI) may be associated with the stilbene grouping. More surprisingly, the methyl-substituted dienes lack even stilbene-like conjugation. [The peak at 301 m $\mu$  in the spectrum of the trimethyl derivative (VIII) may be assigned to the phenylbutadiene system.] The presence of a methylene group clearly establishes the structure of the dimethyl compound (VII), which at least achieves conjugation of each benzene ring separately with one double bond. The trimethyl compound (VIII),

from the corresponding cyclopentenones (XIII), and these in turn by reduction of the hydroxycyclopentenones (XIV). It was found that the traditional hydriodic acid method for the latter step gives lower yields than a two-step process: borohydride reduction to the diols (XV; X = H), followed by dehydration with alcoholic hydrogen chloride.



Treatment of the diphenylcyclopentenediol (XV; R<sup>1</sup> = R<sup>2</sup> = X = H) with dimethyl sulphate and sodium hydroxide gave its dimethyl ether, and if the hydroxide was replaced by hydride dehydration to the ketone (XIII; R<sup>1</sup> = R<sup>2</sup> = H) was the only result. No trace of a monomethyl ether was obtained. However, with acetyl or benzoyl chloride and pyridine the diol (XV; R<sup>1</sup> = R<sup>2</sup> = X = H) was readily monoacylated to give the corresponding derivatives (XV; R<sup>1</sup> = R<sup>2</sup> = H, X = COMe or COPh). The n.m.r. spectra of several of the cyclopentenones (XIII) and (XV) are recorded in Table 2. In each case the magnitude of the coupling constants reveals the stereochemical relationships of the interacting groups [indicated in the Table with reference to formula (XVI)] and the diols (XV) are thereby shown to have the oxygen atoms in *trans*-positions. In harmony with this conclusion the infrared spectra (see Experimental section) of the acyl derivatives (XV;

<sup>12</sup> S. McLean and P. Haynes, *Tetrahedron Letters*, 1964, 2385.

<sup>13</sup> N. L. Drake and J. R. Adams, jun., *J. Amer. Chem. Soc.*, 1939, **61**, 1326.

<sup>14</sup> (a) D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, 1963, **38**, 470; (b) M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1899.

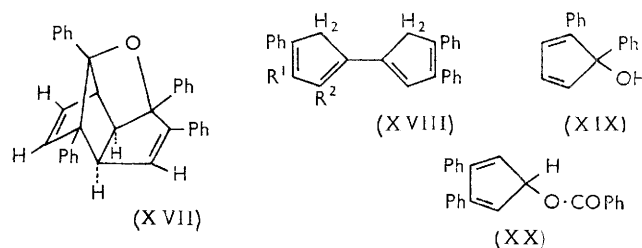
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$R^1 = R^2 = H$ ,  $X = \text{COMe}$  or  $\text{COPh}$ ) show no evidence of intramolecular hydrogen bonding.

In two of the ketones (XIII;  $R^1 = R^2 = H$  and  $R^1 = \text{Ph}$ ,  $R^2 = H$ ) the geminal coupling constants of the pair of hydrogens adjacent to the carbonyl group have values  $-18.5$  and  $-19.0$  c./sec. (a negative sign is inferred by analogy with other geminal coupling constants). The high numerical value is consistent with the  $120^\circ$  interbond angle and the presence of the adjacent carbonyl group.<sup>14b</sup>

The whole series of compounds provides examples of vicinal (3 bond) coupling constants in five membered rings. The variation of  $J_{\text{vic}}$  with dihedral angle ( $\phi$ ) can be summarised:  $\phi = 0^\circ$ ,  $J_{\text{vic}} = 6.9\text{--}7.5$  c./sec.;  $\phi = 60^\circ$ ,  $J_{\text{vic}} = 2.5\text{--}3.0$  c./sec.;  $\phi = 120^\circ$ ,  $J_{\text{vic}} = 4.0$  c./sec. These values are in reasonable agreement with

would convert the benzoate (XV;  $R^1 = R^2 = H$ ,  $X = \text{COPh}$ ) to the carbinol (XIX) or the benzoate (XX). Diels–Alder dimerisation of the former (XIX) and loss of



water (not necessarily in this order) would afford the ether (XVII). Homolytic cleavage of the ester (XX), coupling of the radical so formed, and prototropic shifts

TABLE 2  
N.m.r. results and assignments for cyclopentene derivatives

Derivative of cyclopentene (XVI)	Solvent	Chemical shifts ( $\tau$ ) of H, OH, or $\text{CH}_3$ at ring positions: <sup>a</sup>						Coupling constants (c./sec.)	
		1	3 $\beta$	4 $\alpha$	4 $\beta$	5 $\alpha$	5 $\beta$		
2,3 $\alpha$ -Diphenyl-5-oxo	$\text{CCl}_4$	3.33	5.42	7.66	7.04	—	—	$J_{1,3\beta} = 2$ ;	$J_{3\beta,4\beta} = 7.5$ ; $J_{3\beta,4\alpha} = 3.0$ ; $J_{4\alpha,4\beta} = 18.5$
1,4 $\alpha$ -Dimethyl-2,3 $\alpha$ -diphenyl-5-oxo	$\text{CDCl}_3$	7.92	5.37	9.26	7.09	—	—	$J_{1,3\beta} = 2.2$ ;	$J_{3\beta,4\beta} = 7.5$ ; $J_{4\alpha',\beta_1} = 7.5$
1,2,3 $\alpha$ -Triphenyl-5-oxo	$\text{CDCl}_3$	—	5.42	7.38	6.80	—	—	$J_{3\beta,4\beta} = 6.9$ ;	$J_{3\beta,4\alpha} = 3.0$ ; $J_{4\alpha,4\beta} = 19.0$
2,3 $\alpha$ -Diphenyl-3 $\beta$ ,5 $\alpha$ -di-hydroxy	$\text{CDCl}_3$	3.49	$\sim 8.4$	7.72	7.16	$\sim 8.4$	4.80	$J_{1,5\beta} = 2.5$ ;	$J_{4\beta,5\beta} = 6.9$ ; $J_{4\alpha,5\beta} = 4.0$ ; $J_{4\alpha,4\beta} = 15.0$
2,3 $\alpha$ -Diphenyl-3 $\beta$ -hydroxy-5 $\alpha$ -acetoxy	$\text{CDCl}_3$	3.58	7.42	7.69	7.21	8.01	4.11	$J_{1,5\beta} = 2.7$ ;	$J_{4\beta,5\beta} = 7.0$ ; $J_{4\alpha,5\beta} = 4.0$ ; $J_{4\alpha,4\beta} = 15.0$
2,3 $\alpha$ -Diphenyl-3 $\beta$ -hydroxy-5 $\alpha$ -benzoyloxy	$\text{CDCl}_3$	3.43	7.49	7.51	7.12	—	3.88	$J_{1,5\beta} = 2.7$ ;	$J_{4\beta,5\beta} = 6.9$ ; $J_{4\alpha,5\beta} = 4.0$ ; $J_{4\alpha,4\beta} = 14.7$
1,2,3 $\alpha$ -Triphenyl-3 $\beta$ ,5 $\alpha$ -di-hydroxy	$\text{CDCl}_3$	—	$\sim 8.1$	7.54	7.11	$\sim 8.1$	4.49	$J_{4\beta,5\beta} = 7.0$ ;	$J_{4\alpha,5\beta} = 4.0$ ; $J_{4\alpha,4\beta} = 15.0$

<sup>a</sup> Methyl protons in italics.

the recognised equation<sup>9</sup> relating the vicinal coupling constant and dihedral angle. Both the allylic (4 bond) and homoallylic (5 bond) couplings in the ketones (XIII;  $R^1 = R^2 = H$  and  $R^1 = R^2 = \text{Me}$ , respectively) are slightly greater (2.0 and 2.2 c./sec.) than would be expected.

All the compounds in Table 2 have a phenyl group in the position arbitrarily designated 3 $\alpha$  and one at position 2. The shielding of the 4 $\alpha$  hydrogens relative to 4 $\beta$  is readily explained if we assume that the plane of the 3 $\alpha$ -phenyl group is nearly normal to that of the cyclopentene ring, due to steric interference with the 2-phenyl ring. The 4 $\alpha$ -hydrogen then lies above the plane of the 3 $\alpha$ -phenyl ring.

Refluxing the benzoyl derivative (XV;  $R^1 = R^2 = H$ ,  $X = \text{COPh}$ ) with oxalic acid in benzene gave a mixture of the ketone (XIII;  $R^1 = R^2 = H$ ) (27%), an ether  $\text{C}_{34}\text{H}_{26}\text{O}$  (49%) and a hydrocarbon  $\text{C}_{34}\text{H}_{26}$  (8%). On the basis of their n.m.r. and i.r. spectra and the following postulated mechanisms of formation, we formulate these last two tentatively as the bridged ether (XVII) and the dihydrofulvalene (XVIII;  $R^1$  or  $R^2 = \text{Ph}$ ;  $R^2$  or  $R^1 = H$ ), respectively. Loss of benzoic acid or water

x

would give the hydrocarbon (XVIII;  $R^1 = \text{Ph}$ ,  $R^2 = H$ ). Its u.v. maximum at  $380\text{ m}\mu$  strongly suggests the fully conjugated structure. The methylenes resonate as a doublet at  $\tau 6.8$ ; splitting must result either from allylic coupling or from a chemical shift difference if the molecule has undergone a phenyl migration to the unsymmetrical structure (XVIII;  $R^2 = \text{Ph}$ ,  $R^1 = H$ ).

#### EXPERIMENTAL

N.m.r. spectra were obtained on a Perkin-Elmer R-10 spectrometer operating at 40 or 40.004 Mc./sec. Unless otherwise stated, spectra were obtained in  $\text{CDCl}_3$  as solvent with tetramethylsilane added as internal standard. The temperature was  $33.5^\circ$ . In all cases integrated intensities were obtained and agreed, within experimental error, with the assignments made.

*Reaction of 3,4-Diphenylcyclopent-2-en-1-one with Sodium Hydroxide.*—Following Allen *et al.*,<sup>6</sup> 3,4-diphenylcyclopent-3-en-1-one (14 g., 0.06 mole) was dissolved in ethanol (100 ml.) containing potassium hydroxide (8.4 g., 0.15 mole). The mixture was heated under reflux for 15 hr., then diluted with water and extracted with ether. The ether extract was washed until neutral, dried, and evaporated, and the residue chromatographed on alumina. The product,



isolated in low yield, was identified as 1,4-diphenylcyclopentadiene<sup>13</sup> by its m. p. 161°, undepressed by mixing with an authentic sample, and by comparison of its i.r. spectrum and mixed m. p. of its picrate<sup>13</sup> with authentic material.

**Dehydration of 1,2-Diphenylcyclopentan-1,2-diol (II; R = Ph) with Copper Sulphate.**—1,2-Diphenylcyclopentan-1,2-diol (0.2 g., 0.008 mole) and anhydrous copper sulphate (0.5 g., 0.03 mole) were heated under vacuum (0.01 mm.) to 180–210° (bath temp.) for 1 hr. Working up as in the preceding experiment yielded a trace of 1,4-diphenylcyclopentadiene.

**3,4-Diphenylcyclopent-2-en-1-ol (III; R = H).**—(a) To a suspension of 3,4-diphenylcyclopent-2-en-1-one (XIII; R<sup>1</sup> = R<sup>2</sup> = H) (10 g., 0.04 mole) in methanol (125 ml.) was added sodium borohydride (1.2 g.) dissolved in water (5 ml.). A vigorous reaction took place. The mixture was left for 1 hr. and then warmed on a steam-bath until most of the solvent had evaporated. On cooling, an oil separated and soon crystallised. Recrystallisation from cyclohexane gave a product (3.1 g., 78%), m. p. 103–105°,  $\nu_{\max}$  (KCl disc) 3390 cm.<sup>-1</sup> (OH), suitable for further reactions. Further purification raised the m. p. to 107–108.5°, depressed to 95° by the initial ketone (m. p. 107.5–109.5°) (Found: C, 86.6; H, 6.9. C<sub>17</sub>H<sub>16</sub> requires C, 86.4; H, 6.8%).

(b) To a solution of the ketone (XIII; R<sup>1</sup> = R<sup>2</sup> = H) (9.0 g., 0.038 mole) in a mixture of dry toluene (50 ml.) and isopropanol (30 ml.) was added a solution of aluminium isopropoxide (30 g., 0.148 mole) in toluene (60 ml.) and isopropanol (130 ml.), and the whole heated with stirring at 80° for 3 hr. and then at 100° for 19 hr., with slow distillation of solvent, while maintaining a constant volume by dropwise addition of isopropanol. The solution was then concentrated under reduced pressure, added to 20% NaOH, and extracted with ether. The ethereal solution was washed to neutrality, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. Chromatography of the residue on alumina afforded unchanged ketone (4 g., 45%), eluted with ligroin–benzene, and the carbinol (3 g., 33%), eluted by ether, m. p. 104–106°, undepressed by admixture with a sample prepared by method (a).

**3,4-Diphenylcyclopent-3-en-1-ol.**—This was conveniently obtained using sodium borohydride in place of lithium aluminium hydride,<sup>15</sup> but in somewhat lower yield. Following the above procedure with 3,4-diphenylcyclopent-3-en-1-one<sup>15</sup> (4.5 g., 0.019 mole) and sodium borohydride (0.6 g.) gave the desired carbinol (3.0 g., 66%), m. p. 102–104° (lit.<sup>15</sup> 102.5–103.5°),  $\nu_{\max}$  (KCl disc) 3413 cm.<sup>-1</sup> (OH).

**2,5-Dimethyl-3,4-diphenylcyclopent-2-en-1-ol (III; R = Me).**—This carbinol was obtained similarly from the corresponding ketone (XIII; R<sup>1</sup> = R<sup>2</sup> = Me) (2 g.) with sodium borohydride (0.24 g.). It formed colourless prisms (1.8 g., 90%) from cyclohexane, m. p. 102–104°,  $\nu_{\max}$  (KCl disc) 3340 cm.<sup>-1</sup> (OH) (Found: C, 86.6; H, 7.7. C<sub>19</sub>H<sub>20</sub>O requires C, 86.3; H, 7.6%).

**3,4-Diphenylcyclopent-2-en-1,4-diol (XV; R<sup>1</sup> = R<sup>2</sup> = X = H).**—This was obtained from the ketone (XIV; R<sup>1</sup> = R<sup>2</sup> = H) (2.45 g.) by the same procedure employing sodium borohydride (0.3 g.). Crystallisation from benzene gave the diol (2.46 g., 96%) as colourless plates, m. p. 149–151°,  $\nu_{\max}$  (KCl disc) 3390 cm.<sup>-1</sup> (OH) (Found: C, 79.9; H, 6.4. C<sub>17</sub>H<sub>16</sub>O<sub>2</sub> requires C, 80.9; H, 6.3%). The diol (2.54 g., 0.01 mole) in benzene–pyridine (1 : 1, 8 ml.) was treated with benzoyl chloride (1.3 g., 0.01 mole) at 0°. The mixture was left at room temperature for 30 min., then poured into water and extracted with ether. The extract was washed

in turn with water, dil. hydrochloric acid, 10% sodium hydrogen carbonate, and again water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. The benzoate (XV; R<sup>1</sup> = R<sup>2</sup> = H, X = C(Ph) (2.9 g., 82%) crystallised from benzene–light petroleum, m. p. 112–114°,  $\nu_{\max}$  (KCl disc) 1695 cm.<sup>-1</sup> (CO), 3460 cm.<sup>-1</sup> (OH);  $\nu_{\max}$  (CCl<sub>4</sub>) 1719 cm.<sup>-1</sup> (CO) 3605 cm.<sup>-1</sup> (OH) (Found: C, 80.5; H, 5.3. C<sub>24</sub>H<sub>20</sub>O<sub>3</sub> requires C, 80.8; H, 5.6%). Similar reaction of the diol (5.0 g., 0.02 mole) with acetyl chloride (1.58 g., 0.02 mole) afforded the acetate (XV; R<sup>1</sup> = R<sup>2</sup> = H, X = COMe) (4.76 g., 82%) which crystallised from cyclohexane, m. p. 103–105°,  $\nu_{\max}$  (KCl) 1709 cm.<sup>-1</sup> (CO), 3448 cm.<sup>-1</sup> (OH);  $\nu_{\max}$  (CCl<sub>4</sub>) 1740 cm.<sup>-1</sup> (CO), 3610 cm.<sup>-1</sup> (OH) (Found: C, 77.4; H, 6.4. C<sub>19</sub>H<sub>18</sub>O<sub>3</sub> requires C, 77.5; H, 6.1%). The diol (5.08 g., 0.02 mole) in methanol (50 ml.) was treated with dimethyl sulphate (2.5 g., 0.02 mole) followed by aqueous sodium hydroxide (4 ml., 20%). After refluxing for 1 hr. the mixture was poured into water and extracted with ether. The washed and dried (Na<sub>2</sub>SO<sub>4</sub>) extract was evaporated, and the residue chromatographed on silica gel. Benzene–ether (9 : 1) eluted 1,4-dimethoxy-3,4-diphenylcyclopent-2-ene (2.6 g., 86%) which distilled at 175° (bath temp.)/0.01 mm. as a colourless oil,  $\nu_{\max}$  (liquid film) 1115, 1093 cm.<sup>-1</sup> (C–O–C) (Found: C, 80.9; H, 7.2. C<sub>19</sub>H<sub>20</sub>O<sub>2</sub> requires C, 81.4; H, 7.1%). Benzene–ether (1 : 1) eluted unchanged diol (1.9 g.).

**2,3,4-Triphenylcyclopent-2-en-1,4-diol (XV; R<sup>1</sup> = Ph, R<sup>2</sup> = X = H).**—Reduction of the ketone (XIV; R<sup>1</sup> = Ph, R<sup>2</sup> = H) (10 g., 0.03 mole) by the same method using sodium borohydride (1 g.) afforded this diol (9.6 g., 96%) as colourless plates, crystallising from benzene, m. p. 172–174°,  $\nu_{\max}$  (KCl disc) 3360 cm.<sup>-1</sup> (OH) (Found: C, 84.9; H, 6.5. C<sub>22</sub>H<sub>20</sub>O<sub>2</sub> requires C, 84.1; H, 6.1%).

**5-Methyl-3,4-diphenylcyclopent-2-en-1,4-diol (XV; R<sup>1</sup> = X = H, R<sup>2</sup> = Me).**—Similar reduction of the ketone (XIV; R<sup>1</sup> = H, R<sup>2</sup> = Me) (14 g., 0.053 mole) with sodium borohydride (1.7 g.) gave this diol (12.5 g., 90%) as colourless needles, crystallising from benzene, m. p. 200–202°,  $\nu_{\max}$  (KCl disc) 3356 cm.<sup>-1</sup> (OH) (Found: C, 80.5; H, 7.1. C<sub>18</sub>H<sub>18</sub>O<sub>2</sub> requires C, 81.2; H, 6.8%).

**2,5-Dimethyl-3,4-diphenylcyclopent-2-en-1,4-diol (XV; R<sup>1</sup> = R<sup>2</sup> = Me, X = H).**—Analogous reduction of the ketone (XIV; R<sup>1</sup> = R<sup>2</sup> = Me) (10 g., 0.036 mole) with sodium borohydride (1.2 g.) gave this diol (9.4 g., 94%) as colourless needles crystallising from benzene, m. p. 140–142°,  $\nu_{\max}$  (KCl disc) 3448 cm.<sup>-1</sup> (OH) (Found: C, 80.8; H, 7.1. C<sub>19</sub>H<sub>20</sub>O<sub>2</sub> requires C, 81.4; H, 7.1%).

**Dehydration of the Diols (XV) to the Ketones (XIII).**—(a) Each of the above diols was dehydrated by heating under reflux for 1 hr. in a mixture of conc. hydrochloric acid (1 part) and ethanol (10 parts). Dilution of the resulting solutions gave the known ketones (XIII) (90–95%) identified by m. p. and mixed m. p. with authentic samples. In one case (XV; R<sup>1</sup> = X = H, R<sup>2</sup> = Me) the ketone (XIII; R<sup>1</sup> = H, R<sup>2</sup> = Me) (85%) was identified by its m. p. 75–77°, and by formation of a 2,4-dinitrophenylhydrazones, m. p. 202–204° (Found: N, 12.8. C<sub>24</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub> requires N, 13.1%).

(b) In an attempt to obtain the mono-methyl ether (XV; R<sup>1</sup> = R<sup>2</sup> = H, X = Me), the diol (XV; R<sup>1</sup> = R<sup>2</sup> = X = H) (3.5 g., 0.014 mole) in tetrahydrofuran (40 ml.) was treated with sodium hydride (0.66 g., 0.014 mole; 50% dispersion) and the mixture heated under reflux for 2 hr.; dimethyl

<sup>15</sup> E. J. Corey and H. Uda, *J. Amer. Chem. Soc.*, 1963, **85**, 1788.

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sulphate (1.76 g., 0.014 mole) in tetrahydrofuran (5 ml.) was then added, and heating continued for 30 min. After pouring into water, extraction with ether, evaporation of the dried extract, and crystallisation from cyclohexane, 3,4-diphenylcyclopent-2-en-1-one (XIII;  $R^1 = R^2 = H$ ) (3.1 g., 95%), m. p. and mixed m. p. 109–110° was obtained.

(c) In an attempt to convert the diol (XV;  $R^1 = R^2 = Me$ ,  $X = H$ ) (10 g., 0.036 mole) into a benzoate, dehydration to the ketone (XIII;  $R^1 = R^2 = Me$ ) (8.8 g., 94%) resulted. The reaction was carried out by mixing a cooled solution of the diol in benzene–pyridine (1:1; 30 ml.) with benzoyl chloride (4.5 g., 0.032 mole), and allowing the mixture to stand at room temperature for 30 min. After pouring into water, extracting with ether, and evaporating the washed and dried extract, the residue was chromatographed on silica gel in benzene. The product had m. p. 114–116°, undepressed by an authentic specimen.

**1,4-Dimethyl-2,3-diphenylcyclopentadiene** (VII).—The carbinol (III;  $R = Me$ ) (0.5 g., 1.9 mmole) and concentrated hydrochloric acid (1.2 ml.) in methanol (15 ml.) were heated under reflux for 1 hr. On cooling, the diene (0.3 g., 65%) separated. Recrystallisation from methanol gave pale yellow needles, m. p. 89–90° (Found: C, 93.5; H, 7.1.  $C_{19}H_{18}$  requires C, 92.7; H, 7.1%).

**1,2,3-Trimethyl-4,5-diphenylcyclopentadiene** (VIII).—The ketone (XIII;  $R^1 = R^2 = Me$ ) (17 g., 0.065 mole) in benzene (125 ml.) was added to methylmagnesium iodide [prepared from magnesium (2.4 g., 0.1 g. atom) and methyl iodide (15 g., 0.1 mole) in ether (50 ml.)]. After stirring at room temperature overnight, the mixture was heated under reflux for 1 hr., then poured on to a mixture of ice and ammonium chloride and extracted with ether. The dried ( $Na_2SO_4$ ) ether extract on evaporation yielded an orange-yellow gum. This was chromatographed on alumina, in petrol, to give a yellow oil which crystallised from methanol. **1,2,5-Trimethyl-3,4-diphenylcyclopentadiene** (3.5 g., 21%) formed colourless prisms, m. p. 87–89° (Found: C, 91.8; H, 8.0.  $C_{20}H_{20}$  requires C, 92.3; H, 7.7%).

**Bis-(1,2-diphenylcyclopentadiene)** (IV).—(a) *From the carbinol* (III;  $R = H$ ). A mixture of concentrated hydrochloric acid (4.8 ml.) and 3,4-diphenylcyclopent-2-en-1-ol (III;  $R = H$ ) (2.36 g.) in ethanol (44 ml.) was heated under reflux for 1 hr., and the product removed by filtration of the hot suspension obtained. Extraction of the residue with hot ligroin left a yellow insoluble hydrocarbon (the "trimer") (0.06 g.), m. p. 265–270° (Found: C, 92.3; H, 6.7.  $(C_{17}H_{14})_n$  requires C, 93.5; H, 6.5%). Evaporation of the filtrate gave the dimer (IV) (0.52 g., 35%), which forms an almost colourless microcrystalline powder from ligroin m. p. 219–222°,  $\lambda_{max}$  260 (log  $\epsilon$  3.87), 276 m $\mu$  (log  $\epsilon$  4.33) (Found: C, 93.7; H, 6.7%;  $M$  (cryoscopic in benzene), 453.  $C_{34}H_{28}$  requires C, 93.5; H, 6.5%;  $M$ , 436). The same product was obtained in an experiment in which methanol replaced ethanol, whilst only a trace of the "trimer" was isolated from an experiment in the latter solvent at room temperature (48 hr.), and again from an experiment using sulphuric acid in place of hydrochloric acid.

An attempt to effect the dehydration with phosphorus oxychloride in pyridine solution at room temperature (64 hr.) gave only tarry products and a trace of unchanged carbinol (III;  $R = H$ ).

(b) *From 1,2-diphenylcyclopentan-1,2-diol* (II;  $R = Ph$ ). The diol (4.72 g.) was dissolved in ethanol (75 ml.), concentrated hydrochloric acid (5 ml.) was added, and the

mixture was heated under reflux for 2 hr. The dimer (IV), m. p. 218–220°, undepressed by admixture with the above product, was isolated in low yield from the gum which separated on cooling. The same product (0.15 g.) was formed, presumably by dehydration of the same diol formed as an intermediate, when 1,5-diphenylpentan-1,5-dione (4 g.) and zinc (15 g., added in small portions) were heated under reflux for 5 hr. in acetic acid (75 ml.).

**Dehydration of 3,4-Diphenylcyclopent-3-en-1-ol.**—(a) *With hydrogen chloride.* Treatment of this carbinol (0.5 g.) as described for the  $\Delta^2$ -isomer above led to its recovery (0.39 g., 78%), substantially unchanged.

(b) *With sulphuric acid.* The carbinol (0.5 g.) was heated in acetic acid (10 ml.) containing concentrated sulphuric acid (1 ml.) for 15 min. The mixture was poured into water, extracted with ether, and the washed ( $NaHCO_3$ ) and dried ( $Na_2SO_4$ ) extract evaporated. The residual oil was chromatographed on alumina in ligroin to give a yellow solid (20 mg.), m. p. 105–110°, having a similar i.r. spectrum to, and believed to be isomeric with, the dimer (IV).

**Pyrolysis of Bis-(1,2-diphenylcyclopentadiene)** (IV).—(a) *At 200°.* The dimer (0.2 g., 0.5 mmole) was heated to 200°/0.1 mm. in a sublimation apparatus with a water-cooled cold-finger. The sublimate, m. p. 85–95°, is regarded as the *exo* form of bis-(1,2-diphenylcyclopentadiene), possibly admixed with monomeric 1,2-diphenylcyclopentadiene (Found: C, 92.5; H, 6.6%;  $M$  (cryoscopic in benzene), 374.  $C_{34}H_{28}$  requires C, 93.5; H, 6.5%;  $M$ , 436). It reformed the *endo* isomer (IV) on slow heating.

(b) *At 360°.* The dimer (IV) (0.5 g.) was heated in a flask with a long side arm under a nitrogen atmosphere at 360°. The compound which gradually collected in the side-arm was recrystallised from ethanol and identified as 1,4-diphenylcyclopentadiene by its i.r. spectrum, m. p. and mixed m. p. with an authentic sample.

**Derivatives of the Diketone** (VI).—(a) **2,4-Dinitrophenylhydrazones.** Addition of alcoholic 2,4-dinitrophenylhydrazine sulphate to a solution of the diketone (VI) in the same solvent gave a bright red precipitate of the mono-2,4-dinitrophenylhydrazone, crystallising from ethyl acetate, m. p. 248–250° (decomp.),  $\nu_{max}$  (KCl disc) 1773  $cm^{-1}$  (CO) (Found: N, 8.9.  $C_{40}H_{28}N_4O_5$  requires N, 8.7%).

(b) **Dihydrazone.** A mixture of the diketone (VI) (1.1 g.) and aqueous hydrazine (20 ml.) was heated under reflux for 9 hr. The resultant oil was separated by decantation and crystallised from ethanol, giving the dihydrazone (0.8 g., 68%), m. p. 155–161° (Found: N, 10.4.  $C_{34}H_{30}N_4$  requires N, 11.4%). No hydrocarbon could be obtained on chromatography of the product from this hydrazone (2 g.) added over 3 hr. to a solution of potassium t-butoxide (2 g.) in dimethylsulphoxide (5 ml.) (cf. ref. 7).

**Bis-(tricarbonyl-1,2-diphenylcyclopentadienylmolybdenum)** (V;  $R^1 = Ph$ ,  $R^2 = H$ ).—The dimer (IV) (1.1 g., 2.5 mmole) and hexacarbonylmolybdenum (1.2 g., 5 mmole) were heated in an autoclave under carbon dioxide at 200° for 24 hr. Extraction with benzene, evaporation, and chromatography of the product in ligroin on alumina gave unchanged hydrocarbon (IV) (0.25 g., 22%), followed on elution with ligroin–benzene (4:1) by the complex (V;  $R^1 = Ph$ ,  $R^2 = H$ ) (0.5 g., 20%). This formed purple needles from benzene–ligroin, m. p. 341–345° (decomp.),  $\nu_{max}$  in the metal-carbonyl region at 2020, 1961, and 1905  $cm^{-1}$  (Found: C, 61.9; H, 3.2; O, 11.7.  $C_{40}H_{28}Mo_2O_6$  requires C, 61.5; H, 3.3; O, 12.1%). Adding a solution of this complex (0.5 g., 0.58 mmole) in anhydrous ethylamine

(10 ml.) over 5 min. to lithium metal (0.1 g., 0.014 g. atom) and stirring for 20 min. gave, after pouring the mixture on to ice, extracting and chromatographing, a small amount of bis-(1,2-diphenylcyclopentadiene) (IV), m. p. 217—219°.

*Bis-(tricarbonyl-1,3-diphenylcyclopentadieneylmolybdenum)* (V;  $R^1 = H$ ,  $R^2 = Ph$ ).—This was obtained in the same manner as its isomer (above), from 1,4-diphenylcyclopentadiene (1.06 g., 5 mmole) and hexacarbonylmolybdenum (1.2 g., 5 mmole). On crystallisation from benzene–ligroin, the *complex* (V;  $R^1 = H$ ,  $R^2 = Ph$ ) (0.9 g., 36%) formed purple prisms, m. p. 284—286° (depressed by the above isomer to 240—249°),  $\nu_{\max}$  in the metal–carbonyl region at 2028, 1980, and 1942  $\text{cm}^{-1}$  (Found: C, 62.1; H, 3.9.  $C_{40}H_{26}Mo_2O_6$  requires C, 61.5; H, 3.3%).

*5-Methyl-3,4-diphenylcyclopent-2-en-1-one* (XIII;  $R^1 = H$ ,  $R^2 = Me$ ).—This ketone, required (see above) for the preparation of the corresponding diol, was prepared by a modification of the method of Japp and Knox,<sup>16</sup> since, in our hand, their procedure gave only the uncyclised 3-methyl-1,2-diphenylpent-2-en-1,4-dione. A mixture of benzil (60 g., 0.29 mole) and methyl ethyl ketone (21.6 g., 0.3 mole) was stirred with potassium hydroxide (3 g.) in ethanol (10 ml.) for 5 hr. The resulting solid was washed with water and then ether, and crystallised from methanol. The ketone (41.5 g., 55%) formed colourless prisms, m. p. 180° (lit.,<sup>16</sup> 180°). *N.B.* Japp and Knox<sup>16</sup> report the formation of the isomeric 2-methyl-3,4-diphenylcyclopent-2-en-1-one (XIII;  $R^1 = Me$ ,  $R^2 = H$ ) by essentially this procedure (!). Sodium borohydride reduction of the ketone (XIII;  $R^1 = H$ ,  $R^2 = Me$ ) (1.5 g.) gave the corresponding carbinol as a colourless oil (1.3 g., 87%),  $\nu_{\max}$  (liquid film) 3373  $\text{cm}^{-1}$  (OH), possibly a mixture of stereoisomers, but dehydration of this crude carbinol with ethanol–hydrochloric acid failed to give a crystalline hydrocarbon.

*Dehydration of 1-Benzoyloxy-3,4-diphenylcyclopent-2-en-*

*4-ol* (XV;  $R^1 = R^2 = H$ ,  $X = C(Ph)$ ).—(a) The benzoate (0.5 g.) on refluxing in ethanol (11 ml.) with concentrated hydrochloric acid (1.2 ml.) for 1 hr. gave the ketone (XIII;  $R^1 = R^2 = H$ ) (0.31 g., 94%) probably *via* hydrolysis to the diol (XV;  $R^1 = R^2 = X = H$ ). The corresponding acetate (XV;  $R^1 = R^2 = H$ ,  $X = COMe$ ) behaved similarly.

(b) A solution of the benzoate (7.1 g.) in benzene (600 ml.) was refluxed through a Soxhlet apparatus containing anhydrous oxalic acid for 12 hr. The mixture was poured into water, the organic layer washed with 10% sodium hydrogen carbonate solution and with water, and dried ( $Na_2SO_4$ ). After evaporation, the residual gum was chromatographed on silica gel. Ligroin–benzene (3:1) eluted a *hydrocarbon* (0.34 g., 8%), m. p. 238—239° (Found: C, 92.7; H, 6.0%;  $M$  (cryoscopic in benzene), 326.  $C_{34}H_{26}$  requires C, 94.0; H, 6.0%;  $M$ , 434). Its n.m.r. spectrum showed only a peak at  $\tau$  6.8 (doublet) ( $CH_2$ ) and a complex pattern in the phenyl (+ olefin) region at  $\tau$  2.5—3.0. The ketone (XV;  $R^1 = R^2 = H$ ) (0.6 g., 27%) was eluted next, followed, on elution with ligroin–benzene (1:1), by the *ether* (XVII?) (1.1 g., 49%). This crystallised from acetone as fine colourless needles, m. p. 207—209°,  $\nu_{\max}$  (KCl) 1066 and 1033  $\text{cm}^{-1}$  (C—O) (Found: C, 91.0; H, 6.0.  $C_{34}H_{26}O$  requires C, 90.8; H, 5.8%). Its n.m.r. spectrum showed complex patterns in the phenyl ( $\tau$  2.5—3.1), olefinic  $\tau$  3.7 and 4.2, and saturated C—H region ( $\tau$  6.3—7.0), with relative intensities 20:2:0.8:2.6, compatible, within the limits of error, with structure (XVII).

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<sup>16</sup> F. R. Japp and J. Knox, *J. Chem. Soc.*, 1905, **87**, 673; F. R. Japp and A. N. Meldrum, *ibid.*, 1901, **79**, 1024.