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PREPARATION OF CYCLOPENTADIENES AND DIAZOCYCLOPENTADIENES *VIA* CYCLOPENTENOLONES AND CYCLOPENTENONES

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Abstract—The structure and stereochemistry of the cyclopentenolones obtained by condensation of dialkyl ketones with benzil have been studied by NMR spectroscopy. These enolones were converted into cyclopentenones and cyclopentadienes. Alkyl-substituted cyclopentadienes required phenyllithium to effect their conversion by toluenesulphonyl azide into diazo-cyclopentadienes; otherwise piperidine sufficed as base catalyst.2,3,4-Triphenyldiazocyclopentadiene was simply procured by reaction of the condensation product of benzil and phenylacetone with toluenesulphonylhydrazone followed by alkali. Cyclohexyl- and methoxy-triphenylcyclopentadienes were prepared by photolytic decomposition of diazotriphenylcyclopentadiene in cyclohexane or methanol respectively.

Diazocyclopentadienes have most commonly been made by the reaction of cyclopentadiene[1] or its derivatives[2] with toluene-*p*-sulphonyl azide. Diazo-2,3,4,5-tetraphenylcyclopentadiene has also been prepared by the action of alkali on the toluene-*p*-sulphonylhydrazone of tetraphenylcyclopentadienone.[3] Since a variety of substituted diazocyclopentadiene derivatives was required preparative routes which could lead to their formation have been studied in some detail, involving the reaction sequences shown in Scheme 1, and in particular the detailed structures of intermediates have been examined by their NMR spectra.

The reaction of benzil with ketones, which leads to the formation of cyclopentenolones (**1**), was recorded by Japp in 1885[4] and was extensively studied by him[5-7] and later by Allen and van Allan.[8] Four isomeric products (**6-9**) may result if $R \neq R'$; in the case of symmetric ketones ($R = R'$) only two isomers are possible, and if $R = R' = H$ there is only one geometric isomer. Japp had concluded[6] that all methyl alkyl ketones gave mainly products with

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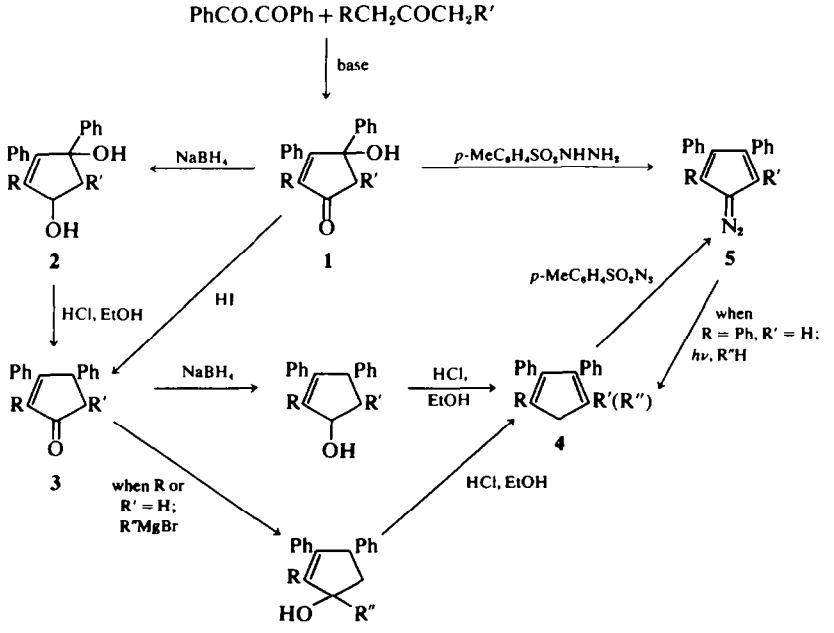
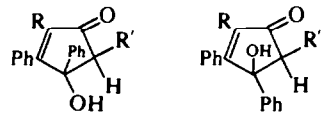


SCHEME 1



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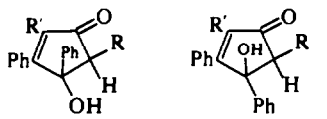

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structures **1** (R = H, R′ = Alkyl) although in the case of the products from butan-2-one he separated both isomers (**1**, R = H, R′ = Me and **1**, R = Me, R′ = H).

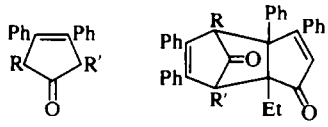
We have condensed a series of dialkyl ketones with benzil to give cyclopentenolones (**1**). When the conditions used by Japp[5-7] (a solution of benzil in excess ketone plus a small amount of 33% aqueous potassium hydroxide and a trace of ethanol kept at room temp) were employed, pentan-2-one and octan-2-one each gave mixtures of the structural isomers (**1A**, R = Et, *or* n-C_5H_{11}, R′ = H) and (**1B**, R = H, R′ = Et *or* n-C_5H_{11}). These isomers were readily distinguished from their NMR spectra since only (**1a**) have methylene groups, but it did not prove possible to establish the geometric isomerism of compounds (**1B**). On the other hand under Allen's conditions (a dilute solution of the reactants in dilute ethanolic potassium hydroxide kept at room temp)[8] pentan-2-one and heptan-2-one gave as single products the isomers (**1**, R = Et or n-Bu, R′ = H). However also under Allen's conditions octan-2-one and 4-methylpentan-2-one gave mixtures, whose NMR spectra indicated that the three isomers (**6** = **7**; **8**; **9**; R′ = H) were present but the complexity of the spectra prevented any quantitative assessment of the ratios. Each isomer suffers conformational strain due to vicinal substitutent groups and the factors governing the formation of the different isomers must necessarily be complex.

Pentan-3-one can give only geometric and not structural isomers. Under either of the above conditions the major product (70%) was isomer **7** (R = R′ = Me), and **6** (R = R′ = Me; 30%) the minor product. Since **7** is less crowded than **6** this result reflects the relative conformational strain in the two isomers, the major product being the thermodynamically more stable. The structures were assigned from the NMR spectra. The Me group attached to the sp^3 centre appears at higher field in the case of isomer **6** than in isomer **7** because in the former isomer it is shielded by the *cis*-phenyl group.

Phenylacetone also condenses readily with benzil to give a cyclopentenolone[9] but when 1-phenylbutan-2-one or 1-phenylpentan-2-one were used, a cyclopentenolone was not obtained under a variety of reaction conditions and with different bases. The reaction mixtures using ethanol as solvent contained a high proportion of unreacted ketone and ethyl benzoate, together with smaller quantities of benzaldehyde, benzoic acid and benzil. Condensations to form the cyclopentenolones appear to be either too slow or too reversible in these cases and cleavage of benzil proceeds competitively.

Attempts to condense diacetyl with a series of ketones provided no tractable products.

Reduction of **1** (R = R′ = H) with hydriodic acid gave the cyclopentenone (**3**, R = R′ = H). Structure **10** had originally been ascribed to this product[10] but the alternative structure **3** had been suggested on the basis of the UV spectrum.[11] This structure was confirmed by its NMR spectrum;[12] our results concur.



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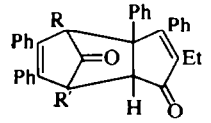

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Reduction of **1** (R = R′ = Me) with hydriodic acid gave a mixture of *cis*- and *trans*-isomers of **3** (R = R′ = Me). The major product (90%) showed an AM spectrum for the ring protons with a coupling constant $J = 3$ Hz and was therefore assigned the *trans*-structure. (For **3**, (R = R′ = H) $J_{4,5}$ (*cis*) = 7 Hz and $J_{4,5}$ (*trans*) = 2·5 Hz). The predominant product is thus the thermodynamically more stable isomer. In contrast, a preparation[12] of this enone from the diol **2** (R = R′ = Me) gave a sole product which, from its NMR spectrum, was the *cis*-isomer.

When **1** (R = Et, R′ = H) was treated with hydriodic acid it gave, in addition to the cyclopentenone (**3**, R = Et, R′ = H), a dimeric product whose NMR spectrum was consistent with it being either **11** (R = Et, R′ = H) or **11** (R = H, R′ = Et) but not the other possible isomeric adducts (**12A**, R = Et, R′ = H or **12B**, R = H, R′ = Et) since there is no evidence of spin coupling as expected in **12A** and the methylene signal of the Et group appears at too high a field for this group to be attached to an sp^2 centre. Furthermore a signal at τ 5·69 is much more reasonably explained as an olefinic proton than as a bridgehead proton, since the other bridgehead proton appears at τ 7·08.

The conversion of cyclopentenolones (**1**) into cyclopentenones (**3**) by hydriodic acid has been superceded by the sequence **1** → **2** → **3**[12] (Scheme 1). Although an extra step is involved it has proved to be a much more satisfactory method.

NMR Spectra of cyclopentenolones (1) (τ)

Solvent	R	R′	Ph	Ring CH	OH	Ring CH_2	Substituents
$CDCl_3$	H	H	2·35–3·1 (10H)	3·43 (1H)	6·13 (1H)	7·10 (2H)	
CCl_4	Me	H	2·5–3·0 (10H)		6·01 broad (1H)	7·21 (2H)	8·20 (3H)
CCl_4	Et	H	2·55–3·2 (10H)		7·00 (1H)	7·02 (2H)	7·69 (q, 2H), 8·94 (t, 3H)
$CDCl_3$	H	Et	2·4–3·2	3·47 (1H), 1 hidden	6·74		8·03 (quint.), 9·02 (t)
CCl_4	n-Bu	H	2·4–3·3 (10H)		6·13 (1H)	7·19 (2H)	7·81 (t), 8·7 (m), 9·19 (t), all broad (9H)
CCl_4	Ph	H	2·4–3·2 (15H)		7·02 (1H)	6·94 (2H)	
CCl_4	H / n-C_5H_{11}	n-C_5H_{11} / H	2·4–3·2 (10 H)	3·44 ($\frac{1}{2}$H)	7·10 (1H)	7·1–9·4 ($2\frac{1}{2}$H)	
CCl_4	Me	Me[a]	2·4–3·1	7·09 (q, J = 7·5 Hz)	7·10		8·03, 9·32 (d, J = 7·5 Hz)
	Me	Me[b]	2·4–3·1	7·30 (q, J = 7·5 Hz)	7·24		8·08, 8·80 (d, J = 7·5 Hz)

[a]Me *trans* to OH; [b]Me *cis* to OH.

NMR spectra of cyclopentenones (3) (τ)

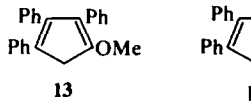
Solvent	Ph	R	—CHPh	—COCHR′	R′
$CDCl_3$	2·4–3·0	H; 3·33	5·49 (dd, J = 7, 2·5 Hz)	7·68 (dd, J = 29, 2·5 Hz)	H; 6·96 (dd, J = 19, 7Hz)
CCl_4	2·7–3·0	Et; 7·63q, 8·87t	5·68 (dd, J = 8, 3 Hz)	7·70 (dd, J = 18, 3 Hz)	H; 7·06 (dd, J = 18, 8Hz)
CCl_4	2·5–3·0	Me; 8·01	6·05 (d, J = 3 Hz)	7·59 (dd, J = 7·5, 3 Hz)	Me; 8·66 (d, J = 7·5Hz)

In addition to the previously used conversion of cyclopentenones (**3**) into cyclopentadienes (**4**) by reaction with sodium borohydride followed by ethanolic hydrogen chloride, cyclopentenones were also treated with Grignard reagents to form 1-substituted cyclopentenols which were subsequently converted into cyclopentadienes. By this latter method a number of hitherto unreported cyclopentadienes, namely 1-benzyl-, 1-ethyl-, 1-methyl- and 1 - *p* - tolyl - 2,3,4 - triphenylcyclopentadienes and 4 - benzyl - 1,2 - diphenylcyclopentadiene were prepared in good yield. In addition, the preparation of 1,2,4 - triphenylcyclopentadiene by this method, *via* 3,4 - diphenylcyclopent - 2 - en - 1 - one and phenyl magnesium bromide, was found to be superior to the method previously reported.[13] New cyclopentadienes were characterised by their conversion into fulvenes by reaction with benzaldehyde. They were also converted into 5-bromo-derivatives by reaction with N-bromosuccinimide.

Diazocyclopentadienes were then obtained from the different cyclopentadienes by their reactions with toluene-*p*-sulphonyl azide. The use of amines such as piperidine as condensing agents[2] was successful only for those cyclopentadienes which did not have alkyl substituents directly attached to the 5-membered ring. When such substituents were present it was necessary to revert to the earlier method[1] of first generating the lithium cyclopentadienide which then reacted with the azide.

Diazo-2,3,4,5-tetraphenylcyclopentadiene had also been prepared by reaction of the toluene-*p*-sulphonylhydrazone of tetraphenylcyclopentadienone with alkali.[3] A simple method for the preparation of diazo-2,3,4-triphenylcyclopentadiene involved treatment of the cyclopentenolone (**1**, R = Ph, R′ = H) with toluene-*p*-sulphonylhydrazine in acid. Simultaneous hydrazone formation and elimination of water ensued to provide the toluenesulphonylhydrazone of 2,3,4-triphenylcyclopentadienone which gave the diazotriphenylcyclopentadiene in good yield on treatment with base. 3,4 - Diphenylcyclopent - 2 - en - 4 - ol - 1 - one gave diazo - 3,4 - diphenylcyclopentadiene directly when heated with toluene - *p* - sulphonylhydrazine in ethanol-conc hydrochloric acid but after purification by chromatography on alumina, the yield was only 7%. Unfortunately none of these methods involving the toluene-sulphonylhydrazones of cyclopentadienones appeared to be general routes to diazocyclopentadienes.

Two further cyclopentadienes, 1-cyclohexyl-[14] and a methoxytriphenylcyclopentadiene, were obtained by photolytic decomposition of diazo-2,3,4-triphenylcyclopentadiene in cyclohexane and methanol respectively. This reaction involves formation of carbenes which insert into solvent molecules. The position of the double-bonds in the case of the methoxytriphenylcyclopentadiene was



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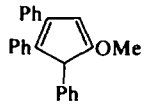

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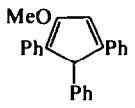

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not resolved. It could not be the 1-methoxy-compound (**13**) since the NMR spectrum showed, in addition to methoxy and phenyl signals, two singlets (each 1H). Possible structures are therefore 4-methoxy-1,2,5-triphenyl- or 2-methoxy-1,4,5-triphenyl-cyclopentadienes (**14** or **15**).

Irradiation of diazo-2,3,4-triphenylcyclopentadiene in benzene gave a triphenylbicyclo[6.3.0] undecapentaene identical with that described previously.[15] Similar irradiation with a medium pressure Hg lamp of diazotetraphenylcyclopentadiene in benzene gave a spiro-adduct, as shown by its spectra, in 57% yield; first reports of this reaction using a high pressure Hg lamp recorded the formation of a benzocycloheptatriene,[16] but very recently the isolation of a product, albeit in low yield, corresponding to ours has been reported.[17]

EXPERIMENTAL

Light petroleum had b.p. 40–60°.

Preparation of cyclopentenolones by the method of Japp.[4] Benzil (20 g) was dissolved in a mixture of the appropriate ketone (2·25 equiv) and 33% KOH aq (1 ml). When soln was complete further portions of KOH aq (5 ml) and EtOH (1 ml) were added and the mixture was kept for a minimum of 5 days. It was then washed with hot water (3 × 30 ml), and residual crystals were filtered, washed with ether (2 × 30 ml) and recrystallised from benzene. The water washings were extracted with dichloromethane and this extract was added to the benzene mother liquors and ether washings and provided further product.

Preparation of cyclopentenolones by the method of Allen.[5] Benzil (4·2 g) and freshly distilled ketone (2 equiv) were shaken in ethanolic KOH (0·5%, 50 ml) until the benzil had dissolved, and the mixture was kept at room temp for a minimum of 5 days. The mixture was then poured into water (100 ml). If crystals formed they were filtered off and further portions of water were added until no more solid precipitated. Otherwise the aqueous suspension was extracted with dichloromethane (100 ml; 2 × 50 ml) or ether (200 ml; 2 × 100 ml); addition of NaCl or K_2CO_3 was necessary to assist separation of the layers. The organic layer was washed with water (50 ml), dried (Na_2SO_4) and evaporated. If crystals formed they were recrystallised from benzene-light petroleum mixtures; syrups were distilled at the oil pump.

Reduction of cyclopentenolones with hydriodic acid. A previously described method was used.[9] Reduction of 2-ethyl-3,4-diphenylcyclopent-2-en-4-ol-1-one provided a product which on trituration with EtOH gave a dimer of 2-ethyl-3,4-diphenylcyclopentadiene (1·8 g, 13%) τ

2·4–3·7 (m, 20 H), 5·69 (s, 1H), 7·08 (s, 1H), 7·59 q + 8·01 q. (4H), 8·89 t + 9·25 t (6H). (Found: C, 87·7; H, 6·4. $C_{38}H_{32}O_2$ requires: C 87·7, H, 6·2%).

1-Methyl-2, 3, 4-triphenylcyclopentadiene. 2, 3, 4-Triphenylcyclopent-2-en-1-one (5·0 g) in dry benzene (80 ml) was added slowly to a stirred refluxing soln of MeMgI [from MeI (2·9 g) and Mg (0·5 g)] in ether (150 ml). When addition was complete, heating was continued for 30 min and the mixture was then poured into a soln of conc HCl (50 ml) in EtOH (100 ml). The resultant mixture was stirred at room temp for 12 hr and then evaporated until a ppt began to form. It was then cooled and filtered and the filtrate was extracted with benzene (3 × 50 ml). The benzene extract was washed with water (2 × 50 ml), $NaHSO_3$ aq (50 ml) and water (50 ml), dried (Na_2SO_4) and evaporated. Trituration of the residual gum with acetonitrile gave the *diene* as pale yellow prisms, m.p. 143° [from MeOH-MeCN (1 : 1)] (3·9 g, 78%) λ_{max} (EtOH) 237, 320 nm (ϵ = 21000, 8700), τ ($CDCl_3$) 2·89 (15H), 6·46 (2H), 7·93 (3H). (Found: C, 93·0, H, 6·2. $C_{24}H_{20}$ requires: C, 93·5; H, 6·5%).

1-Ethyl-2,3,4-triphenylcyclopentadiene. Prepared as its 1-Me analogue, but with heating for 3 hr, the product on trituration with MeOH gave the *diene* as yellow prisms, m.p. 104° (from MeOH) (66%), λ_{max} (EtOH) 238, 318 nm (ϵ = 17400, 7500), τ ($CDCl_3$) 2·87 (15H), 6·43 (2H), 7·50 (q, 2H), 8·84 (t, 3H) (Found: C, 92·8; H, 6·9. $C_{25}H_{22}$ requires: C, 93·1; H, 6·9%).

1-Benzyl-2,3,4-triphenylcyclopentadiene. Prepared as the 1-Me analogue this *diene* formed colourless needles, m.p. 120–121° (from MeCN) (77%), λ_{max} (EtOH) 239, 320 nm (ϵ = 25500, 10100), τ (CCl_4) 2·6–3·2 (20H), 6·26 (2H), 6·57 (2H) (Found: C, 93·7; H, 6·3. $C_{30}H_{24}$ requires: C, 93·7, H, 6·3%).

2,3,4-Triphenyl-1-p-tolylcyclopentadiene. Prepared as the 1-Me analogue, and further purified by chromatography on silica with benzene-light petroleum. Trituration with MeOH gave the *diene* as pale yellow crystals, m.p. 148–150° (20%), τ ($CDCl_3$) 2·6–3·2 (m, 19H), 6·05 (s, 2H), 7·76 (s, 3H).

4-Benzyl-1,2-diphenylcyclopentadiene. Prepared as the 1-Me analogue, this *diene* formed pale yellow crystals, m.p. 175–176° (from MeCN). (38%), λ_{max} (CH_2Cl_2) 238, 333·5, 346 sh nm (ϵ = 11750, 41690, 38900) (Found: C, 93·3; H, 6·7. $C_{24}H_{20}$ requires: C, 93·5; H, 6·5%).

1,2,4-Triphenylcyclopentadiene. Prepared as the previous dienes from 3,4-diphenylcyclopent-2-en-1-one (17·6 g) in dry benzene (250 ml) and PhMgBr [from bromobenzene (13·25 g) and Mg (2·0 g) in ether (250 ml)] this diene formed pale yellow needles (20·0 g, 90%) on trituration with EtOH, m.p. and mixed m.p. 148–149° (lit.[13] 149°).

Formation of fulvenes from cyclopentadienes. The cyclopentadiene (0·59 g) and benzaldehyde (7 equiv) in MeOH (20 ml) were heated under reflux while a soln of Na (0·5 g) in MeOH (30 ml) was added dropwise. The solns were heated for a further 3 hr and filtered while hot. When the solns were cooled, the products separated and were filtered off, washed with MeOH and recrystallised. By this means were prepared: *1-methyl-2,3,4,6-tetraphenylfulvene,* brick-red, m.p. 205° (from cyclohexane), λ_{max} (EtOH) 243 sh, 270, 325 nm (ϵ = 18500, 21900, 20600), τ ($CDCl_3$) 2·6–3·3 (m, 21H), 3·16 (s, 3H) (Found: C, 93·7; H, 6·1. $C_{31}H_{24}$ requires: C, 93·9; H, 6·1%); *1-ethyl-2,3,4,6-tetraphenylfulvene,* red-orange, m.p. 201° (from cyclohexane) λ_{max} (EtOH) 243 sh, 260, 322 nm (ϵ = 18600, 21300, 19600), τ ($CDCl_3$) 2·5–3·4 (m, 21H), 7·60 (q, 2H), 9·42 (t, 3H) (Found: C, 93·4; H, 6·4. $C_{32}H_{26}$ requires: C, 93·6; H, 5·9%); *1-benzyl-2,3,4,6-tetraphenylfulvene,* light red needles, m.p. 152° (from chloroform), λ_{max} 240, 323 nm. (Found: C, 92·8; H, 5·9. $C_{37}H_{28}$ requires: C, 94·0; H, 6·0%; probably contaminated with fulvene oxide).

Bromination of cyclopentadienes. Molar equivalents of the cyclopentadiene (~ 1·0 g) and N-bromosuccinimide in CCl_4 (50 ml) were heated under reflux for 1 hr. The cooled mixture was filtered, and the solid was washed with CCl_4. The filtrate and washings were mixed and evaporated, and the residual gums were triturated with MeOH. This provided *5-bromo-1-methyl-2,3,4-triphenylcyclopentadiene,* orange solid (82%), m.p. 114° (dec), τ (CCl_4) 2·90 (m, 15H), 4·64 (s, 1H), 7·85 (s, 3H), decomposed on attempted recrystallisation for analysis; *5-bromo-1-ethyl-2,3,4-triphenylcyclopentadiene,* yellow microcrystals, m.p. 130° (dec)(from MeOH), λ_{max} (EtOH) 250, 256sh, 306sh, nm (ϵ 23700, 23300, 8200), τ (CCl_4) 2·93 (m, 15H), 4·53 (s, 1H), 7·37 (q, 2H), 8·88 (t, 3H) (Found: C, 75·1; H, 5·3. $C_{25}H_{21}Br$ requires: C, 74·8; H, 5·3%); *1-benzyl-5-bromo-2,3,4-triphenylcyclopentadiene,* yellow microcrystals, m.p. 98–100° (dec)(from MeCN), λ_{max} (EtOH) 245, 260sh, 345 nm (ϵ = 24700, 22000, 9700), τ (CCl_4) 2·5–3·2 (m, 20H), 4·81 (s, 1H), 6·07 (s, 2H) (Found: C, 78·9; H, 5·0, $C_{30}H_{23}Br$ requires: C, 77·8; H, 5·0%).

2-Benzyl-1-diazo-3,4,5-triphenylcyclopentadiene. Toluene-*p*-sulphonyl azide (0·75 g) and piperidine (1 ml) were added successively to a soln of 1-benzyl-2 3,4-triphenylcyclopentadiene (1·3 g) in MeCN (50 ml). The mixture was stirred at 40° for 90 min. The *diazocyclopentadiene* (0·84 g, 60·5%) was filtered off and washed with MeOH and formed fine yellow needles, m.p. 153° (dec)(from MeCN), λ_{max} (EtOH) 241, 325 nm (ϵ = 22800, 10300), τ ($CDCl_3$) 2·60–3·0 (m, 20H), 5·94 (s, 2H) (Found: C, 88·2; H, 5·2. $C_{30}H_{22}N_2$ requires: C, 87·8; H, 5·4%).

Diazo-2,3,4-triphenyl-5-p-tolylcyclopentadiene. Prepared as the benzyltriphenyl- analogue, but with a reaction time of 3 hr, this *diazo-compound* (65%) had ν_{max} (nujol) 2070 cm^{-1} (N_2); λ_{max} (CH_2Cl_2) 251, 334·5 nm (ϵ = 43500, 38400); τ ($CDCl_3$) 2·8–3·1 (m, 19H), 7·70 (s, 3H) (Found: C, 88·0; H, 5·5, N, 6·7. $C_{30}H_{22}N_2$ requires: C, 87·8; H, 5·4; N, 6·8%).

Diazo-2-methyl-3,4,5-triphenylcyclopentadiene. 1-Methyl-2,3,4-triphenylcyclopentadiene (12 g) in dry benzene (100 ml) was added slowly (30 min) to a soln of PhLi [prepared from bromobenzene (12 ml) and Li (1·5 g)] in dry ether (100 ml) under dry N_2. The mixture was heated under reflux for 2 hr and then toluene-*p*-sulphonyl azide (13·5 g) in ether (200 ml) was added during 1 hr. The mixture was stirred overnight and then poured into water (400 ml). The organic layer was separated, combined with the benzene washings (2 × 200 ml) of the aqueous layer and dried (Na_2SO_4). Evaporation of the solvent left a residue which was triturated with MeOH to give the yellow *diazocyclopentadiene* (12·7 g, 86%), m.p. 147° (dec) (from MeCN), τ ($CDCl_3$) 2·6–3·2 (m, 15H), 7·72 (s, 3H) (Found: C, 86·8; H, 5·4; N, 7·9. $C_{24}H_{18}N_2$ requires: C, 86·2; H, 5·4; N, 8·4%).

Diazo-2,5-dimethyl-3,4-diphenylcyclopentadiene. Prepared as the methyl-triphenyl-analogue, this *diazo-compound* (51%) had m.p. 105–106° (from MeOH) ν_{max} (nujol) 2080 cm^{-1} (N_2); λ_{max} (CH_2Cl_2) 248, 318 nm (ϵ = 41400, 40500); τ ($CDCl_3$) 2·7–3·1 (m, 10H), 7·80 (s, 6H) (Found: C, 84·0; H, 6·3; N, 9·3. $C_{19}H_{16}N_2$ requires: C, 83·8; H, 5·9; N, 10·3%). N-analysis was consistently low because of slight decomposition and formation of

dimethyldiphenylcyclopentadiene on recrystallisation from hot solvents).

Diazo - 2, 3, 4 - triphenylcyclopentadiene from 2, 3, 4 - triphenylcyclopent - 2 - en - 4 - ol - 1 - one. The enolone (6·0 g), toluene - *p* - sulphonylhydrazone (4·0 g) and conc HCl (1 ml) in EtOH (200 ml) were heated under reflux for 30 min. The mixture was cooled and KOH aq (10 g in 20 ml) and ether (100 ml) were added. It was heated for a further 2 hr. Diazo-compound (3·7 g), m.p. 166° (dec), was filtered off from the cooled mixture. The filtrate was washed with ether (2 × 200 ml, 1 × 100 ml), the combined ether extracts were washed thrice with $CaCl_2$ aq and dried ($CaCl_2$). Ether was evaporated and the residue was dissolved in hot nitromethane. When the soln cooled more diazo-compound (0·7 g) separated out (total yield, 74·5%).

Diazo - 3,4 - diphenylcyclopentadiene from 3,4 - diphenyl - cyclopent - 2 - en - 4 - ol - 1 - one. The enolone (2·5 g) and toluene - *p* - sulphonylhydrazone (2·2 g) in EtOH (150 ml) were warmed until soln was complete. Conc HCl (0·5 ml) was added and the mixture was heated under reflux for 30 min and then kept at room temp overnight. EtOH was evaporated and the residue was partitioned between benzene (100 ml) and water (50 ml). The benzene soln was evaporated and then chromatographed on alumina. Benzene eluted a first band of the *diazocyclopentadiene* (0·16 g, 7%), orange thick needles, m.p. 108° (from EtOH), λ_{max} (EtOH), 231, 326 nm (ϵ = 19200, 9800), τ (CCl_4) 2·90 (m, 10H), 3·32 (s, 2H) (Found: C, 83·7; H, 4·5; N, 11·6. $C_{17}H_{12}N_2$ requires: C, 83·6; H, 4·9; N, 11·5%).

Photolysis of diazo-2,3,4-triphenylcyclopentadiene in solvents. A soln of the diazo-compound (0·5 g) was placed in a pyrex irradiation vessel fitted with a magnetic stirrer and in an atmosphere of N_2. The medium pressure 100-watt mercury lamp was in a central silica unit dipping below the surface of the soln. Irradiation was carried out at room temp, and the progress of reaction was assessed by monitoring samples by UV spectra and TLC. When reaction was complete, solvent was evaporated and the products were chromatographed on alumina. In this way were obtained, from cyclohexane (750 ml, 2 hr irradiation), 1-cyclohexyl-2,3,4-triphenylcyclopentadiene (0·33 g, 58%), m.p. 163–164° [from acetone-MeOH (1 : 1)], (lit.[14] 162–163°) λ_{max} (EtOH) 237, 319 nm (ϵ = 22200, 10000); τ ($CDCl_3$) 2·7–3·2 (m, 15H), 6·44 (s, 2H) 8·0–9·0 (m, 11H). (Found:C, 92·7; H, 7·6 Calc. for $C_{29}H_{28}$: C, 92·5; H, 7·5%); from MeOH (600 ml, 100 min) a *methoxytriphenylcyclopentadiene* (0·15 g, 20%), (from EtOH), λ_{max} (EtOH) 234, 280 sh nm (ϵ = 23900, 11100), τ ($CDCl_3$) 2·3–3·1 (m, 15H), 4·37 (s, 1H), 4·58 (s, 1H), 6·47 (s, 3H). (Found: C, 88·8; H, 6·3. $C_{24}H_{20}O$ requires: C, 88·8; H, 6·2%); from benzene (750 ml, 1 hr) 9,10,11-triphenyl-1H-bicyclo [6.3.0] undecapentaene (0·35 g, 61%), m.p. 157° [from EtOH-benzene (1 : 1)] (lit.[13] 155–160°); identical UV and NMR spectra[15]) (Found: C, 94·1; H, 5·9. Calc. for $C_{29}H_{22}$: C, 94·0; H, 6·0%).

1, 2, 3, 4-*Tetraphenylspiro* [4,6] *undeca*-1, 3, 6, 8, 10-*pentaene.* Similar photolysis of diazotetraphenylcyclopentadiene (0·5 g) in benzene (750 ml) gave the spiroundecapendaene, (0·32 g, 57%) m.p. 115° (from MeOH) (lit.[17] 110–112°), λ_{max} (EtOH) 250, 275 sh (ϵ = 33200, 16700) (Found: C, 94·2; H, 6·0. Calc. for $C_{35}H_{26}$: C, 94·1; H, 5·9%).

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