Tetrahedron. Vol. 30, pp. 2257 to 2264. Pergamon Press 1974. Printed in Great Britain

PREPARATION AND PROPERTIES OF PHENYL-SUBSTITUTED CYCLOPENTADIENYLIDES

B. H. FREEMAN and D. LLOYD*
Department of Chemistry, Purdie Building, University of St Andrews, St Andrews, Fife, Scotland

(*Received in the UK* 23 *October* 1973; *Accepted for publication November* 1973)

Abstract—Phenyl-substituted cyclopentadienylides have been prepared, for the most part by carbenic decomposition of diazocyclopentadienes copper-bronze was an effective catalyst and also enabled reaction to be carried out in solution 2,5-Diphenyldiazocyclopentadiene gave triphenylarsonium 2,4-diphenylcyclopentadienylide instead of the expected product. Electrophilic substitution (acetylation, formylation, diazo-coupling) proceeds preferentially at the 2(5)-positions, but if these sites are blocked, may take place at the 3(4)-positions. The spectra of 3(4)-acyl- and 3(4)-phenylazo-derivatives differ markedly from those of their 2(5)-analogues. Unlike their 2(5)-acyl-analogues, triphenylarsonium 3(4)-acyl-derivatives are unstable to hydrolysis.

Accounts of the chemistry of a variety of tetraphenylcyclopentadienylides[1] and 2,3,4-triphenylcyclopentadienylides[2,3] have been published; the preparation of a range of other phosphonium, arsonium and sulphonium phenyl-substituted cyclopentadienylides, and some of their properties are now recorded. They have been prepared by carbenic decomposition of different diazocyclopentadienes,[4-6] by condensation reactions with triphenylarsine oxide,[2,7,8] and the traditional salt method.

Previous work[2] had indicated that the diazocyclopentadiene → carbene method was inapplicable to diazocyclopentadienes lacking 2,5-aryl substituents.

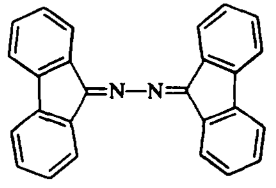
Triphenylphosphonium 2-benzyl- and 2-methyl-3,4,5-triphenylcyclopentadienylides have now been obtained by plunging an intimate mixture of the corresponding diazocyclopentadiene and triphenylphosphine into a bath at 140°. This technique appears to provide a general improvement and higher yields than those obtained by the earlier method of heating a mixture of the two reactants gradually from room temperature. It was used for the preparation of a number of other triphenylphosphonium cyclopentadienylides, eg the hitherto unreported 2,3,4 - triphenyl - 5 - *p* - tolyl - and 2,3,5-triphenyl-derivatives. 2,4-Diphenyl- and 2,3,4-triphenyl-diazocyclopentadienes, which had at first been reported to give phosphinazines rather than phosphonium cyclopentadienylides, also formed ylides when the newer method was employed with a bath temperature of 150° (cf Ref 9).

This method also proved effective for the preparation of triphenylarsonium 2 - benzyl - 3,4,5 - triphenylcyclopentadienylide, but little or no ylide was obtained from triphenylarsine and either 2 - methyl - 3,4,5 - triphenyl-, 2,3,4-triphenyl-, 2,3,5-triphenyl- or 2,5 - diphenyl - diazocyclopentadienes under these conditions. If, however, copper–bronze, powder was also mixed and heated with the reactants all these diazocyclopentadienes gave arsonium cyclopentadienylides. In addition to providing cyclopentadienylides where they could not otherwise be obtained, admixture of copper–bronze with the reactants appears in general to result in a marked increase in the yields of ylides; similar results have been noted for other types of arsonium ylides.[8]

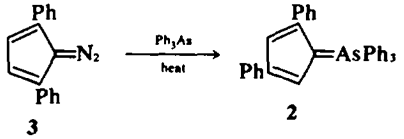
Furthermore, if a copper–bronze catalyst is used the ylide-forming reaction may be carried out at markedly lower temperatures and in solution. Thus refluxing benzene, cyclohexane or ethanol have each been used as solvents for the catalysed decomposition of diazocyclopentadienes and good yields of triphenylarsonium cyclopentadienylides have been obtained in this way. This modification, which is still being investigated, enables substrates to be used which were excluded in the 'melt' technique because they were not liquid at the melting point-decomposition temperature of the diazo-compounds.

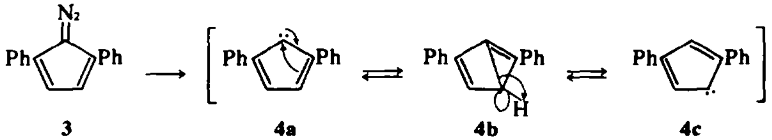
In two cases unexpected products were obtained. When diazofluorene was decomposed in the presence of triphenylarsine the ketazine **1** was formed instead of the fluorenylide. Evidence was obtained that this product resulted *via* partial formation of the arsonium ylide which reacted with more diazofluorene to give the ketazine.[8]

More surprising was the formation of triphenylarsonium 2,4-diphenylcyclopentadienylide **2** when 2,5-diphenyldiazocyclopentadiene **3** decomposed thermally in the presence of triphenylarsine. The mechanism of this rearrangement is unknown. It could involve migration of a hydrogen atom as shown in the sequence **4a–4c**; participation of a



1

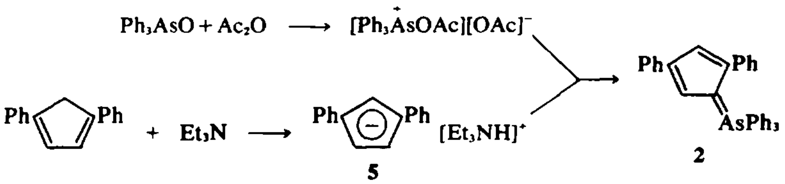




cyclopropenoid intermediate has been suggested in transformation of phenylmethylene.[10]

Formation of the ylide **2** may then result from attack of triphenylarsine on the less sterically hindered form **4c** rather than on form **4a**.

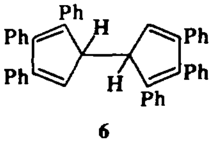
Triphenylarsonium 2,4-diphenylcyclopenta dienylide **2** was also prepared by condensation of triphenylarsine oxide with 1,4-diphenylcyclopentadiene in triethylamine in the presence of phosphorus pentoxide. If it is assumed that this reaction involves attack of an acetoxyarsonium ion on the 1,3-diphenylcyclopentadienide anion **5**,[8] then reaction again takes place preferentially at the least sterically hindered site in the ring.



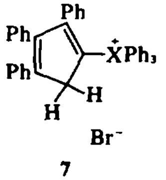
Methylphenylsulphonium cyclopentadienylides have been prepared by heating mixtures of thioanisole and 2 - benzyl - 3,4,5 - triphenyl-, 2,3,4 - triphenyl - 5 - *p* - tolyl- or 2,3,4 - triphenyl - diazocyclopentadienes. In the last two cases improved yields were again obtained when copper–bronze powder was mixed with the reactants. When diazofluorene and thioanisole were heated together the ketazine **1**, rather than an ylide, was again formed.

Diazocyclopentadienes have also proved to be useful intermediates in the preparation of cyclopentadienylides by converting them into 5-bromocyclopentadienes which may in turn be converted into cyclopentadienylides by the salt method. For example, when dry hydrogen bromide was bubbled through solutions of either 2,3,4,5-tetraphenyl- or 2,3,4-triphenyl-diazocyclopentadienes in dry ether at room temperature, the corresponding phenylated bromocyclopentadienes were obtained in good yield, presumably by nucleophilic substitution of the protonated diazocyclopentadienes. Since these two diazocyclopentadienes can be simply prepared from the readily available tetraphenylcyclopentadienone[11] and 2,3,4 - triphenylcyclopent - 2 - en - 4 - ol - 1 - one[12] respectively, this proves an attractive alternative route to the bromocyclopentadienes. Chlorocyclopentadienes were obtained similarly, but when hydrogen iodide was passed through an ethereal solution of 2,3,4-triphenyldiazocyclopentadiene the resultant product was the hexaphenyldihydrofulvalene **6**. It had been observed earlier that the reaction of iodine with lithium 1,2,3-triphenylcyclopentadienide gave a fulvalene rather than an iodotriphenylcyclopentadiene,[13] although with lithium tetraphenylcyclopentadienide iodotetraphenylcyclopentadiene was obtained.[14]

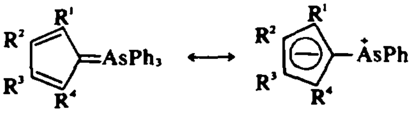
Attempts had been made previously to prepare the hydrobromide of triphenylarsonium 2,3,4-



6



7



8

triphenylcyclopentadienylide (7; X = As) by reaction of bromo-1,2,3-triphenylcyclopentadiene with triphenylarsine in a melt but they were unsuccessful, although the phosphonium analogue had been readily obtained in this way.[2] The substitution of the bromine atoms in 3,5-dibromocyclopentene by triphenylarsine was achieved by keeping a solution of the reactants in nitromethane at room temperature,[15] and this method also proved successful with the bromotriphenylcyclopentadiene, and provided an alternative method for the preparation of the ylide (8: $R^1 = R^2 = R^3 = Ph$, $R^4 = H$)[2,5] which had not previously been prepared by the salt method. Under these conditions however triphenylphosphine again only effected protodebromination of the bromotriphenylcyclopentadiene. It would seem that the more nucleophilic triphenylphosphine attacks the bromine atom in a rapid reaction (cf Ref 2), whereas triphenylarsine is not sufficiently nucleophilic to attack the bromine atom but will take part in normal nucleophilic substitution but very slowly. The phosphonium salt (7; $X{=}P$) is stable in nitromethane and so cannot be an intermediate in the protodebromination.

Bromo - 1,2,3 - triphenylcyclopentadiene also reacted with dimethyl sulphide in nitromethane at room temperature to give a low yield of the hydrobromide of dimethylsulphonium 2,3,4-triphenylcyclopentadienylide but if it was heated in refluxing dimethyl sulphide without other solvent, the product was 1-methylthio-2,3,4-triphenylcyclopentadiene, presumably formed by loss of methyl bromide from the initially formed ylide hydrobromide; the mass spectrum of this hydrobromide indicated that it lost methyl bromide very readily. When this bromotriphenylcyclopentadiene was heated with benzyl methyl sulphide in refluxing nitromethane yet another type of reaction ensued and the hexaphenyldihydrofulvalene **6** was isolated in good yield, but its mode of formation is presently not known. No reaction took place between bromotriphenylcyclopentadiene and benzyl methyl sulphide when either a solution of them in nitromethane was kept at room temperature, or they were heated together without solvent at 150°.

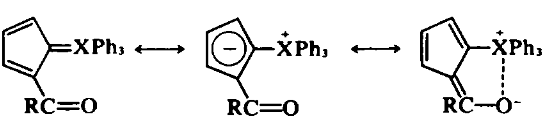
The UV spectra of all the phenyl-substituted cyclopentadienylides very closely resemble those of their tetraphenyl-analogues.[1] Unlike any previously described arsonium cyclopentadienylides, however, triphenylarsonium 2,3,5-triphenyl- and 2,4-diphenyl-cyclopentadienylides showed a small bathochromic shift in the longest wavelength absorption maximum when methylene chloride replaced methanol as solvent. Such solvatochromism has previously only been observed for pyridinium,[1,3,16] bismuthonium[1,17] and telluronium[1,18] cyclopentadienylides.

In accord with earlier work on tetraphenyl-[1] and 2,3,4-triphenyl-cyclopentadienylides,[3] the presently described triphenylarsonium cyclopentadienylides reacted with p-nitrobenzaldehyde to give good yields of fulvenes, whereas the corresponding triphenylphosphonium cyclopentadienylides did not react.

Because of the partial cyclopentadienide character of cyclopentadienylides they may undergo electrophilic substitution in the five-membered ring. Thus triphenylphosphonium and triphenylarsonium 2,3,4-triphenylcyclopentadienylides were acylated at the 5-position,[3] while unsubstituted cyclopentadienylides underwent electrophilic substitution preferentially at the 2(5)-position.[15,19–21] This preference was rationalised[15,21,22] in terms of the structures of the transition states for the substitution reactions at positions 2 and 3, which were assumed to be closely related to the σ-complexes involved in these reaction paths.

When the 2(5)-positions in the cyclopentadiene ring are blocked by substituents, acetylation may take place at the 3(4)-position. Thus triphenylphosphonium 2,5-diphenyl- and 2,3,5-triphenylcyclopentadienylides were each acetylated at the vacant 3(4)-position. In the case of 2,4-diphenylcyclopentadienylides, where both types of position in the cyclopentadiene ring are available for attack, the triphenylphosphonium compound gave a mixture of 3- and 5-acetylated products with the latter the major product, while the triphenylarsonium compound gave only the 5-acetyl-derivative, albeit in an impure state, contaminated with higher molecular weight impurities (from MS).

All the 2(5)-acetylated cyclopentadienylides show carbonyl stretching peaks in their IR spectra in the range 1560–1570 cm^{-1}. This low value is attributed to the major contribution of a canonical form **9c** wherein the negative charge is sited on the oxygen atom and there is intramolecular association between the oxygen and heteronium atoms; this contribution has been confirmed by an X-ray crystallographic examination of a 2-acetylcyclopentadienylide.[23]



9a **9b** **9c**

By contrast the carbonyl stretching peaks for 3(4)-acetylated cyclopentadienylides appear at ca 1640 cm^{-1}. Less negative charge is sited on the oxygen atom in the latter compounds and intramolecular interaction between the oxygen and hetero-atoms is not possible.

Triphenylphosphonium 2,4-diphenylcyclopentadienylide was formylated by the Vilsmeier method to give a 3,5-diformyl derivative. This diformyl compound showed IR absorptions at 1622 and 1645 cm^{-1} due to its two different carbonyl groups.

Whereas triphenylarsonium 2,3,4-triphenyl cyclopentadienylide readily formed a stable 5-formyl derivative,[3] triphenylarsonium 2,3,5-triphenylcyclopentadienylide gave a product which could not be purified satisfactorily, but gave a molecular ion peak in its mass spectrum corresponding to the expected 4-formylated derivative. From the IR spectrum of this product it appeared that hydrolysis of the formylated ylide was taking place. The corresponding 4-acetyl derivative was also unstable. Interaction between the acyl oxygen atom and the arsonium atom is not possible in these compounds and this may account for their lower stability to hydrolysis vis-a-vis their 2(5)-acyl analogues. Triphenylphosphonium 3-acetyl-2,5-diphenyl- and 3-acetyl-2,4,5-triphenylcyclopentadienylides are however stable to hydrolysis. The greater resistance to hydrolysis of the phosphonium ylides compared to their arsonium analogues may be due to a smaller contribution from dipolar canonical forms in the former case; there is ample evidence that arsonium ylides have more polar character than their phosphonium analogues (cf Refs 1, 3, 8). Likewise the lower stability of the 3(4)-acyl arsonium ylides compared with their unacylated analogues may be associated with a greater dipolar contribution in the acylated compounds.

Unsubstituted cyclopentadienylides couple readily with aryldiazonium salts, exclusively at the 2-position.[15,19] Aryldiazonium salts likewise coupled with 2,4-diphenylcyclopentadienylides exclusively at their 5-positions, and none of the 3-phenylazo-isomers were formed. However when both the 2- and 5-positions were blocked, as in 2,5-diphenyl- and 2,3,5-triphenylcyclopentadienylides, coupling took place at the 3(4)-position.

All the resultant phenylazo-products are stable red high-melting compounds. The electronic spectra of 3(4)-arylazo-derivatives are markedly different from those of the 2(5)-arylazo-derivatives, and this enabled the site of reaction to be readily identified. The maxima in the visible region occur at lower wavelengths for the 3(4)-derivatives than for their 2(5)-isomers. Both types of isomers show solvatochromism but whereas the 3(4)-isomers show a sizeable hypsochromic shift when methylene chloride (or benzene) replaces methanol as solvent, the 2(5)-isomers show a small bathochromic shift.

All these substitution reactions confirm the general pattern that electrophilic substitution in cyclopentadienylides takes place preferentially at the 2(5)-position, but can also occur at the 3(4)-position.

Acid salts of the present cyclopentadienylides were not isolated but their NMR spectra in the presence of trifluoroacetic acid show that protonation takes place, but the site of protonation is varied. Thus triphenylarsonium and triphenylphosphonium 2,5-diphenylcyclopentadienylides in acid solution both show methylene signals in their NMR spectra indicating protonation at the previously unsubstituted 3-position, but the corresponding 2,3,5-triphenylcyclopentadienylides show no methylene signal so that in these cases the unhindered position is not the site of protonation. The 2,4-diphenylcyclopentadienylides each show a methylene signal but it is not possible to decide whether protonation has occurred at the 3- or 5-positions. 2,3,4-Triphenylcyclopentadienylides are protonated at the vacant 5-position. It thus appears that protonation may take place at either the 2(5)- or 3(4)-positions, and that an unsubstituted position is often but not always the preferred site. Presumably the identity of the predominant protonated species depends on a fine balance between steric and electronic factors.

EXPERIMENTAL

Light petroleum had b.p. 40–60°. Column chromatography was carried out on either activated alumina, type H(100/200 mesh), or on silica gel, grade M60. Thin-layer chromatography was done on silica coated plates, M.N. Kieselgel G. Samples analysed by means of molecular weight determinations were pure (TLC, spectra).

Preparation of cyclopentadienylides from diazocyclopentadienes (no copper–bronze catalyst)

The diazo-compound (2 mmol) was ground together with the nucleophile (4 mmol) if the latter was a solid, or dissolved or suspended in the nucleophile (6 mmol) at 100° if it was a liquid. The mixture was placed in the reaction flask which was flushed with oxygen-free nitrogen and then plunged into a preheated bath and kept there until evolution of nitrogen had ceased. The progress of the reaction could be monitored by withdrawing test samples and recording their IR spectra to follow the disappearance of the characteristic diazo peak at ca 2050–2100 cm^{-1}. Ether or ether–light petroleum was then added to the cooled reaction mixture to precipitate the ylide. The product was filtered off and washed well with ether or ether–light petroleum.

Preparation of cyclopentadienylides from diazocyclopentadienes in the presence of copper–bronze catalyst

Copper–bronze (1 mmol) was mixed with the diazo-compound (2 mmol) and the nucleophile (4 mmol) and the melt reaction was carried out as above. The reaction mixture was cooled, chloroform was added and the solution was filtered. Solvent was evaporated and ether or ether–light petroleum was added to the residue. The ylide was then filtered off.

Preparation of triphenylarsonium 2,3,4 - triphenylcyclopentadienylide from diazo - 2,3,4 - triphenylcyclopentadiene in solution. The diazocyclopentadiene (0·640 g, 2 mmol) and triphenylarsine (1·86 g, 6 mmol) were dissolved in dry benzene (30 ml). Copper–bronze (0·15 g) was added and the mixture was heated under reflux and under nitrogen for 2 h. The hot solution was filtered and solvent was evaporated. Ether was added to the residue and the ylide was filtered off and washed with ether (0·67 g, 56%), m.p. 212–214°, mixed m.p. and spectra identical with an authentic sample. When cyclohexane or ethanol replaced benzene as solvent the yields were, respectively, 56% and 54%.

Table 1. Cyclopentadienylides prepared from diazocyclopentadienes

Ylide								Elemental analysis (%)				Molecular weight	
								Calcd.		Found		Calcd.	Found
Heteronium group	Substituents	Reaction time	Reaction temp.	Catalyst (copper bronze)	Yield (%)	m.p. °C	Recrystn. solvent	C	H	C	H		
PPh_3	2,4-Ph	10 min	150–155°	—	26	224–226	*n*-butanol	87·9	5·7	87·6	5·8		
PPh_3	2,3,4-Ph	60 min	160°	—	28	242–245	MeCN	(identical m.p., spectra, with authentic sample)					
PPh_3	2,3,5-Ph	15 min	150–155°	—	68	268–270	MeCN	88·8	5·6	88·7	5·5		
PPh_3	2-Me-3,4,5-Ph	10 min	150°	—	34	142–145	*a*					506·232	506·232
PPh_3	$2-PhCH_2-$3,4,5-Ph	15 min	155–160°	—	41	255	$MeNO_2$	89·4	5·7	89·1	6·0	644·263	644·258
PPh_3	2,3,4-Ph-5-p-MeC_6H_4	10 min	150°	—	70	320–322	$MeNO_2$—PhH	89·4	5·7	88·5	5·7	644·263	644·262
$AsPh_3$	2,4-Ph[b]	10 min	145°	cat.	18								
$AsPh_3$	2,4-Ph[c]	10 min	150°	—	19	195–197	MeCN	80·7	5·1	80·7	5·4		
		10 min	145°	cat.	35								
$AsPh_3$	2,3,4-Ph	10 min	150°	—	10	213–216	MeCN	(Identical m.p., spectra, with authentic sample)					
		10 min	130°	cat.	56								
$AsPh_3$	2,3,5-Ph	15 min	130°	cat.	67	195–197						598·164	598·165
$AsPh_3$	2-Me-3,4,5-Ph	10 min	130–135°	cat.	30	128–129		82·3	5·4	82·1	5·7		
$AsPh_3$	$2-PhCH_2-$3,4,5-Ph	15 min	150°	—	31	201–202		83·7	5·4	83·1	5·4	688·211	688·208
SMePh	2,3,4-Ph	15 min	130°	cat.	50	125–130		could not be purified satisfactorily					
SMePh	$2-PhCH_2-$3,4,5-Ph	15 min	150°	—	30	195–196		87·7	5·9	87·4	6·1	506·207	506·206
SMePh	2,3,4-Ph-5-p-MeC_6H_4	10 min	150°	—	30	185–186						506·207	506·205
		10 min	140°	cat.	61								

[a] Purified by column chromatography (silica/benzene–ethyl acetate).

[b] From diazo-2,4-diphenylcyclopentadiene.

[c] From diazo-2,5-diphenylcyclopentadiene.

Table 2. Spectral data of cyclopentadienylides

Ylide		Ultraviolet (solvent) λ_{max} nm (log ϵ)	PMR (solvent) τ multiplicity, (relative intensity)[a]
Heteronium group	Substituents		
PPh$_3$	2,4-Ph	(CH$_2$Cl$_2$) 233(4·38), 291(4·40) (MeOH) 215, 290	(CDCl$_3$) 2·2–3·4 m, 3·67 m (CDCl$_3$—CF$_3$CO$_2$H) 2·2–2·8m, 6·10s
PPh$_3$	2,5-Ph		(CDCl$_3$) 2·2–3·4m, 3·55d (*J* 6Hz) (CDCl$_3$—CF$_3$CO$_2$H) 2·2–2·8m, 6·13s
PPh$_3$	2,3,4-Ph	(EtOH) 286(4·30)	(CF$_3$CO$_2$H) 2·0–3·2m (30), 5·88s (2)
PPh$_3$	2,3,5-Ph	(CH$_2$Cl$_2$) 233·5(4·42), 278sh(4·32), 296(4·33) (MeOH) 226, 277sh, 295	(CDCl$_3$—CF$_3$CO$_2$H) 2·2–3·2m, 3·65s
PPh$_3$	2-Me-3,4,5-Ph	(EtOH) 227, 286	(CDCl$_3$) 2·2–3·5m (30), 8·28s (3)
PPh$_3$	2-PhCH$_2$-3,4,5-Ph	(PhH) 292(4·40) (CH$_2$Cl$_2$) 233·5(4·46), 291·5(4·42)	(CDCl$_3$) 2·3–3·5m(35), 6·45s (2)
PPh$_3$	2,3,4-Ph-5-*p*-MeC$_6$H$_4$	(PhH) 291 (CH$_2$Cl$_2$) 233·5(4·47), 292(4·48)	
AsPh$_3$	2,4-Ph	(CH$_2$Cl$_2$) 232·5(4·26), 273sh(4·25) 309(4·30) (MeOH) 215, 300	(CDCl$_3$) 2·4–3·3m, 3·65d (*J* 2·5 Hz)[b] (CF$_3$CO$_2$H) 2·2–3·8m, 6·12s
AsPh$_3$	2,3,4-Ph	(EtOH) 288(4·35)	(CF$_3$CO$_2$H) 2·2–3·3m(30), 5·64s(2)
AsPh$_3$	2,3,5-Ph	(CH$_2$Cl$_2$) 233(4·34), 303(4·34) (MeOH) 213, 296	(CDCl$_3$—CF$_3$CO$_2$H) 2·2–3·2m, 3·65s
AsPh$_3$	2-Me-3,4,5-Ph	(CH$_2$Cl$_2$) 234(4·31), 2·66(4·24), 273(4·25), 296(4·29)	(CDCl$_3$) 2·3–3·6m(30), 8·15s(3)
AsPh$_3$	2-PhCH$_2$-3,4,5-Ph	(CH$_2$Cl$_2$)233(4·35), 296(4·29)	(CDCl$_3$) 2·4–3·6m(35), 6·40s(2)
SMePh	2,3,4-Ph		(CDCl$_3$) 2·4–3·4m(21), 6·98s(3)
SMePh	2-PhCH$_2$-3,4,5-Ph	(CH$_2$Cl$_2$) 233·5(4·24), 293(4·39)	(CDCl$_3$) 2·6–3·2m(25) 5·73, 6·05 AB system (2), 7·32s(3)
SMePh	2,3,4-Ph-5-*p*-MeC$_6$H$_4$	(MeOH) 212, 291	(CDCl$_3$) 2·6–3·2m(24), 7·27s(3), 7·75s(3)

[a] Relative intensities are not given where integration of the peaks is confused by overlapping.

[b] Part of AB system.

Thermal decomposition of diazofluorene in the presence of carbene acceptors. Diazofluorene (0·39 g, 2 mmol) and triphenylarsine (1·23 g, 4 mmol) were ground together, put into a reaction flask which was flushed with nitrogen, and plunged into a bath at 140°. After 15 min the reaction mixture was cooled. Addition of ether precipitated fluorenone ketazine as red crystals (0·57 g, 80%), m.p. and mixed m.p. 272–274° (lit[24] m.p. 276–277°). When thioanisole replaced triphenylarsine the ketazine was again obtained but in lower yield (0·143 g, 20%); precipitation with ether was less efficient in this case.

Triphenylarsonium 2,4-diphenylcyclopentadienylide from 1,4-diphenylcyclopentadiene and triphenylarsine oxide. Phosphorus pentoxide (1·0 g) was added to a mixture of 1,4-diphenylcyclopentadiene (1·53 g, 7 mmol), triphenylarsine oxide (2·25 g, 7 mmol) and triethylamine (40 ml) and the mixture was heated under reflux for 24 h. After 4 h further phosphorus pentoxide (0·5 g) was added. Water (100 ml) was added to the reaction mixture and the resultant suspension was extracted with methylene chloride. The extract was washed well with water, dried (Na$_2$SO$_4$), and the solvent was evaporated. Trituration of the residue with ether–ethanol gave the ylide (55%), m.p. 193–195° (from acetonitrile), identical with that obtained from triphenylarsine and 2,4- or 2,5-diphenyldiazocyclopentadienes.

Reaction of diazotetraphenylclopentadiene with hydrogen bromide. Diazotetraphenylcyclopentadiene (0·99 g, 2·5 mmol) was dissolved in dry ether (30 ml) and dry hydrogen bromide gas, together with oxygen-free nitrogen, was bubbled through the solution at room temperature for 2 h. The yellow precipitate (0·90 g, 80%) of 5-bromo-1,2,3,4-tetraphenylcyclopentadiene was then filtered off and washed with ether, and had m.p. 195–197° [from chloroform–methanol (1:1)] (lit[25] 190–191°) (Found: C, 77·8; H, 4·9. Calc. for C$_{29}$H$_{21}$Br: C, 77·5; H, 4·7%).

Reactions of diazo-2,3,4-triphenylcyclopentadiene with hydrogen halides. (a) Diazotriphenylcyclopentadiene (0·80 g, 2·5 mmol) was treated with hydrogen bromide gas in an identical manner to its tetraphenyl-analogue and gave 5-bromo-1,2,3-triphenylcyclopentadiene (0·49 g, 53%), m.p. 150° [from chloroform–methanol (1:1)] (lit[2] 150–152°) (Found: C, 74·0; H, 4·6. Calc. for C$_{23}$H$_{17}$Br: C, 73·9; H, 4·6%). (b) Hydrogen chloride was used instead of hydrogen bromide. After 2 h solvent was evaporated and the residue was triturated with methanol to give 5-*chloro-1,2,3-triphenylcyclopentadiene* (0·53 g, 65%), golden needles (from nitromethane), m.p. 155–156°, λ_{max} (CH$_2$Cl$_2$) = 242·5, 321 nm (log ϵ = 4·37, 3·91) (Found: C, 84·0; H, 5·3. C$_{23}$H$_{17}$Cl requires C, 84·0; H, 5·2%). (c) Hydrogen iodide replaced hydrogen bromide. The solution was stirred for 12 h. Solvent was evaporated and the residue was triturated with methanol to give yellow-green needles (55%) m.p. 255–258° (from acetone) of the hexaphenyldihydrofulvalene **6**, identical spectra to those of an authentic specimen.

Triphenyl - (2,3,4 - *triphenylcyclopentadienyl)arsonium perchlorate and triphenylarsonium* 2,3,4 - *triphenylcyclopentadienylide.* A suspension of 5 - bromo - 1,2,3 - triphenylcyclopentadiene (0·373 g, 1 mmol) and triphenylarsine (0·306 g, 1 mmol) in nitromethane (25 ml) was stirred at room temperature for 40 h. Solvent was then removed in vacuo, and ether (15 ml) was added. The precipitate was filtered off and suspended in methanol, and perchloric acid (60%, 0·2 ml) was added, followed by ether (20 ml). The pale yellow precipitate of triphenyl(triphenylcyclopentadienyl)arsonium perchlorate (0·28 g, 40%) was filtered off and had m.p. and mixed m.p. 220–223° (from n-propyl alcohol) (lit[2] m.p. 225–226°). This perchlorate was converted into the corresponding arsonium ylide by treatment with sodium hydroxide.[2]

Reaction of 5 - *bromo* - 1,2,3 - *triphenylcyclopentadiene with dimethyl sulphide*

(a) Bromotriphenylcyclopentadiene (0·410 g) in excess dimethyl sulphide was heated under reflux for 48 h. Excess dimethyl sulphide was evaporated and the residue was dissolved in the minimum of benzene and chromatographed on alumina. Benzene–light petroleum (1:1) eluted a yellow band from which the solvent was removed. Trituration of the residue with methanol gave yellow solid 1 - *methylthio* - 2,3,4 - *triphenylcyclopentadiene* (0·23 g, 63%), m.p. 150–152° [from chloroform–methanol (1:1)], λ_{max} (CH_2Cl) = 242, 264 sh, 349 nm (log ϵ = 4·27,—,3·84), τ ($CDCl_3$) 2·6–3·0 m (15H), 6·25 s (2H), 7·60 s (3H) (Found: C, 85·0; H, 5·9. $C_{24}H_{20}S$ requires C, 84·7; H, 5·9%).

(b) Bromotriphenylcyclopentadiene (0·80 g), dimethyl sulphide (0·2 ml), and nitromethane (35 ml) were stirred at room temperature for 23 h. Remaining bromo-compound (0·22 g) was filtered off and the solution was evaporated. The residue was dissolved in ethanol (5 ml) and perchloric acid (70%, 0·2 ml) was added, followed by ether (10 ml). The pale yellow precipitate of dimethyl - (2,3,4 - triphenylcyclopentadienyl)sulphonium perchlorate (0·10 g, 13%) was filtered off and washed well with ether and had m.p. 153–155°. (Found: C, 64·2; H, 5·0. $C_{25}H_{23}ClO_4S$ requires C, 66·0; H, 5·1%. Recrystallisation proved to be impossible because of partial decomposition in hot solvents).

Reaction of 5 - *bromo* - 1,2,3 - *triphenylcyclopentadiene with benzyl methyl sulphide.* Bromotriphenylcyclopentadiene (0·373 g, 1 mmol), benzyl methyl sulphide (0·137 g, 1 mol) and nitromethane (20 ml) were heated under reflux for 2 h. The precipitate was filtered off from the cooled solution and was 1,2,3,1′,2′,3′ - hexaphenyl - 5,5′ - dihydrofulvalene **6** (0·15 g, 51%), m.p. 261–263° (from acetone) (lit[13] m.p. 268–270°) (Found: C, 94·1; H, 5·7. Calc. for $C_{46}H_{34}$: C, 94·2; H, 5·8%).

No reaction took place between these reactants when a solution in nitromethane was kept at room temperature or when they were heated together without solvent at 150°.

Reactions of cyclopentadienylides with p-nitrobenzaldehyde

(a) A solution of triphenylarsonium 2,3,5 - triphenylcyclopentadienylide (0·538 g, 1 mmol) and p-nitrobenzaldehyde (0·15 g, 1 mmol) in carbon tetrachloride (25 ml) was heated under reflux for 5 h. Solvent was evaporated and the residue was dissolved in a minimum of benzene and chromatographed on silica. Elution with benzene gave a dark red band which, after removal of solvent, was recrystallised from nitromethane to give 6 - p - *nitrophenyl* - 2,3,5 - *triphenylfulvene* (0·36 g, 84%), m.p. 211–214°, λ_{max} (CH_2Cl_2) = 235 sh, 271, 343 nm (log ϵ = 4·22, 4·50, 4·34), λ_{max} (MeOH) = 210, 267, 336 nm (Found: M 427·157. $C_{30}H_{21}NO_2$ requires M 427·157). Benzene–methanol (4:1) eluted triphenylarsine oxide (0·292 g, 87%).

(b) Under identical conditions, triphenylarsonium 2 - benzyl - 3,4,5 - triphenyl - cyclopentadienylide gave 2 - benzyl - 6 - p - *nitrophenyl* - 3,4,5 - *triphenylfulvene*, orange-brown crystals, (0·517 g, 62%), m.p. 192°, λ_{max} (CH_2Cl_2) = 235·5, 269·5, 334 nm (log ϵ = 4·32, 4·43, 4·26), τ ($CDCl_3$) 2·0–2·2 m and 2·6–3·5 m (25H), 6·33 s (2H) Found: C, 85·7; H, 5·3; N, 2·6. $C_{37}H_{27}NO_2$ requires C, 85·9; H, 5·2; N, 2·7%).

(c) Under identical conditions save that the mixture was heated for 15 h, triphenylarsonium 2,4-diphenylcyclopentadienylide gave 6 - p - *nitrophenyl* - 2, 4 - *diphenylfulvene*, dark red crystals (0·12 g, 34%), m.p. 130–132° λ_{max} (CH_2Cl) = 268, 361 nm (log ϵ = 4·29, 4·12), λ_{max} (MeOH) = 224, 268, 352 nm (Found: M 351·126. $C_{24}H_{17}NO_2$ requires M 351·125).

(d) Triphenylphosphonium 2,5-diphenyl-, 2,3,5-triphenyl- or 2 - benzyl - 3,4,5 - triphenyl - cyclopentadienylides, heated with *p*-nitrobenzaldehyde for up to 20 h, were recovered unchanged in high yield.

Acetylation of cyclopentadienylides

(a) A solution of triphenylphosphonium 2,4 - diphenylcyclopentadienylide (0·478 g, 1 mmol) in acetic anhydride (10 ml) was heated under reflux for 10 min. Water (30 ml) was added to the cooled solution and the mixture was shaken well. After 1 h it was extracted with chloroform (3 × 20 ml). The extract was washed with water and dried (Na_2SO_4) and the solvent was removed. The residue was dissolved in a minimum of benzene and chromatographed on silica. It was eluted with increasing proportions of chloroform to benzene. A 1:1 mixture eluted a dark band, which, after removal of solvent, was triturated with ether to give a mixture (0·20 g, 38%), m.p. ca 225°, (approx. 3:1; from NMR spectrum), of *triphenylphosphonium* 2 - *acetyl* - 3,5 - *diphenylcyclopentadienylide* and *triphenylphosphonium* 3 - *acetyl* - 2,4 - *diphenylcyclopentadienylide*, ν_{max} (CO) = 1566 (major product), 1624 cm^{-1} (minor product), τ ($CDCl_3$) 2·2–3·3 m (25H), 3·90 s and 3·95 s (1H), 8·10 s (minor) and 8·22 s (major) (3H) (Found: M 520·196. $C_{37}H_{29}OP$ requires M 520·196).

(b) Triphenylphosphonium 2,5 - diphenylcyclopentadienylide (0·478 g, 1 mmol), treated as in (a), but with a reaction of time of 15 min, gave *triphenylphosphonium* 3 - *acetyl* - 2,5 - *diphenylcyclopentadienylide* (0·19 g, 36%) m.p. 208–210°, ν_{max} (CO) = 1640 cm^{-1}, λ_{max} (CH_2Cl_2) = 234, 287 nm (log ϵ = 4·42, 4·45), τ ($CDCl_3$) 2·2–3·4 m (26H), 8·05 s (3H) (Found: M 520·196. $C_{37}H_{29}OP$ requires M 520·196).

(c) Triphenylphosphonium 2,3,5 - triphenylcyclopentadienylide (0·554 g, 1 mmol), treated as in (a) but with a reaction time of 30 min, gave *triphenylphosphonium* 3 - *acetyl* - 2,4,5 - *triphenylcyclopentadienylide* (0·28 g, 47%), m.p. 243–245°, ν_{max} (CO) = 1643 cm^{-1}, λ_{max} (CH_2Cl_2) = 234, 279 nm (log ϵ = 4·39, 2·79), τ ($CDCl_3$) 2·3–3·6 m (30H), 8·30 s (3H) (Found: M 596·229. $C_{43}H_{33}OP$ requires M 596·227).

(d) Triphenylarsonium 2,4 - diphenylcyclopentadienylide (0·522 g, 1 mmol) was treated as in (a) but with a reaction time of 3 min. Chloroform–benzene (7:3) eluted triphenylarsonium 2 - acetyl - 3,5 - diphenylcyclopentadienylide as a dark yellow solid (0·275 g); mass spectra showed the presence of high mol wt impurities,

ν_{max} (CO) = 1560 cm^{-1}, τ ($CDCl_3$) 2·2–3·4 m (25H), 3·60 s (1H), 8·12 s (3H).

Triphenylphosphonium 2,4 - diformyl - 3,5 - diphenylcyclopentadienylide. A suspension of triphenylphosphonium 2,4 - diphenylcyclopentadienylide (0·478 g, 1 mmol) in dimethylformamide (5 ml) was treated with phosphoryl chloride (0·15 ml, ca 2 mmol). The solution was warmed at 60° for 15 min. Aqueous sodium hydroxide (2N, 5 ml) was then added. The mixture was diluted with water (50 ml) and extracted with benzene (3 × 20 ml). The extract was washed well with water and dried (Na_2SO_4), and solvent was evaporated. Trituration of the residue with ether gave the *diformylcyclopentadienylide* (0·24 g, 45%), m.p. 233–236°, ν_{max} (CO) = 1622, 1645 cm^{-1}, λ_{max} (CH_2Cl_2) = 233·5, 287, 338 nm (log ϵ = 4·48, 4·65, 4·21), τ ($CDCl_3$) 2·2–3·2 m (25H), 0·60 d (1H), and 0·80 d (1H) J = 1 Hz) (Found: M 534·173. $C_{37}H_{27}O_2P$ requires M 534·175).

Reaction of cyclopentadienylides with benzene diazonium chloride. The method of Ramirez and Levy[24] was used with a reaction time of 30 min. The products, listed below, were all recrystallised from benzene–methanol

(a) *Triphenylphosphonium 2 - phenylazo - 3,5 - diphenylcyclopentadienylide*, red crystals (90%), m.p. 245°, λ_{max} (CH_2Cl_2) = 233·5, 262, 481 nm (log ϵ = 4·41, 4·40, 4·29), λ_{max} (PhH) = 280, 484 nm, λ_{max} (MeOH) = 212, 259, 476 nm (Found: M 582·220. $C_{41}H_{31}N_2P$ requires M 582·222).

(b) *Triphenylphosphonium 3 - phenylazo - 2,5 - diphenylcyclopentadienylide*, orange crystals (90%), m.p. 190–192°, λ_{max} (CH_2Cl_2) = 233·5, 261 sh, 266 sh, 408 nm (log ϵ = 4·42, 4·29, 4·27, 4·32), λ_{max} (PhH) = 277, 400 nm, λ_{max} (MeOH) = 213, 338, 450 nm (Found: M 582·223. $C_{41}H_{31}N_2P$ requires M 582·222).

(c) *Triphenylphosphonium 3 - phenylazo - 2,4,5 - triphenylcyclopentadienylide*, red-brown crystals (60%), m.p. 243°, λ_{max} (CH_2Cl_2) = 234, 267, 404 nm (log ϵ = 4·16, 4·43, 4·35), λ_{max} (MeOH) = 214, 255 sh, 430 nm (Found: M 658·254. $C_{47}H_{35}N_2P$ requires M 658·254).

(d) *Triphenylarsonium 2 - phenylazo - 3,5 - diphenylcyclopentadienylide*, red crystals (85%), m.p. 238–240°, λ_{max} (CH_2Cl_2) = 236, 266, 489 nm (log ϵ = 4·41, 4·50, 4·40). λ_{max} (MeOH) = 214, 262, 484 nm (Found: M 626·171. $C_{41}H_{31}AsN_2$ requires M 626·170).

(e) *Triphenylarsonium 3 - phenylazo - 2,4,5 - triphenylcyclopentadienylide*, red-brown crystals (55%), m.p. 218°, λ_{max} (CH_2Cl_2) = 234, 265 sh, 416 nm (log ϵ = 4·53, —, 4·27) (Found M 702·210. $C_{47}H_{35}AsN_2$ requires M 702·202).

Acknowledgements—We are grateful to the S.R.C. for the award of a research scholarship to B. H. F. We thank Drs E. E. Ernstbrunner and I. Gosney for valuable discussions.

REFERENCES

[1] B. H. Freeman, D. Lloyd and M. I. C. Singer, *Tetrahedron* **28**, 343 (1972)

[2] D. Lloyd and M. I. C. Singer, *J. Chem. Soc.* (*C*) 2941 (1971)

[3] D. Lloyd and M. I. C. Singer, *Tetrahedron* **28**, 353 (1972)

[4] D. Lloyd, M. I. C. Singer, M. Regitz and A. Liedhegener, *Chem. & Ind.* 324 (1967); M. Regitz and A. Liedhegener, *Tetrahedron* **23**, 2701 (1967)

[5] D. Lloyd and M. I. C. Singer, *Chem. & Ind.* 510 (1967)

[6] D. Lloyd and M. I. C. Singer, *Ibid.* 118 (1967)

[7] G. S. Harris, D. Lloyd, N. W. Preston and M. I. C. Singer, *Chem. & Ind.* 1483 (1968)

[8] I. Gosney and D. Lloyd, *Tetrahedron* **29**, 1697 (1973)

[9] B. H. Freeman, D. Lloyd and M. I. C. Singer, *Ibid.* **30**, 211 (1974)

[10] W. M. Jones, R. C. Joines, J. A. Myers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis and A. B. Turner, *J. Am. Chem. Soc.* **95**, 826 (1973)

[11] D. Lloyd and F. I. Wasson, *Chem. & Ind.* 1559 (1963), *J. Chem. Soc.* (*C*) 408 (1966)

[12] B. H. Freeman, J. M. F. Gagan and D. Lloyd, *Tetrahedron* **29**, 4307 (1973)

[13] P. L. Pauson and B. J. Williams, *J. Chem. Soc.* 4153 (1961)

[14] *Idem, Ibid.* 4158 (1961)

[15] B. H. Freeman and D. Lloyd, *J. Chem. Soc.* (*C*), 3164 (1971)

[16] D. Lloyd and J. S. Sneezum, *Chem. & Ind.* 1221 (1955); *Tetrahedron* **3**, 334 (1958); E. M. Kosower and B. G. Ramsey, *J. Am. Chem. Soc.* **81**, 856 (1959)

[17] D. Lloyd and M. I. C. Singer, *Chem. Comm.* 1042 (1967)

[18] B. H. Freeman and D. Lloyd, *Ibid.* 924 (1970)

[19] F. Ramirez and S. Levy, *J. Org. Chem.* **21**, 1333 (1956); **23**, 2035 (1958)

[20] Z. Yoshida, S. Yoneda, Y. Murata and H. Hashimoto, *Tetrahedron Letters* 1523 (1971)

[21] D. Lloyd and M. I. C. Singer, *Chem. & Ind.* 786 (1971)

[22] D. J. Cram and R. P. Partos, *J. Am. Chem. Soc.* **85**, 1273 (1963)

[23] G. Ferguson, D. F. Rendle, D. Lloyd and M. I. C. Singer, *Chem. Comm.* 1647 (1971)

[24] E. E. Schweizer, G. J. O'Neill and J. N. Wemple, *J. Org. Chem.* **29**, 1744 (1964)

[25] H. Kainer, *Liebigs Ann.* **578**, 232 (1952)

[26] F. Ramirez and S. Levy, *J. Am. Chem. Soc.* **79**, 6167 (1957)