CYCLOPENTADIENYLIDES

Brian Harding Freeman

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews

1971

Please use this identifier to cite or link to this item:
http://hdl.handle.net/10023/15286

CYCLOPENTADIENYLIDES

being a Thesis

presented by

BRIAN HARDING FREEMAN, B.Sc.

to the

UNIVERSITY OF ST. ANDREWS

in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY

St. Andrews
August 1971

DECLARATION

I declare that this thesis is based on the results of experiments carried out by me, that it is my own composition and has not previously been presented for a Higher Degree.

The work was carried out in the Department of Chemistry of the University of St. Andrews, under the direction of Mr. D.M.G. Lloyd, B.Sc., F.R.I.C.

CERTIFICATE

I hereby certify that Mr. BRIAN HARDING FREEMAN, B.Sc., has spent eleven terms at research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Ph.D.

Director of Research

UNIVERSITY CAREER

I entered the University of St. Andrews as an undergraduate in October 1964 and graduated B.Sc. with Second Class Honours (Class One) in Chemistry in July, 1968.

The research described in this thesis was carried out between October 1968 and August 1971, during which time I held a Research Studentship awarded by the Science Research Council.

PUBLICATIONS

(i) A Telluronium Ylide

B.H. Freeman and D. Lloyd, Chem. Comm. 1970, 924

(ii) Preparation and Reactions of Triphenylarsoniumcyclopentadienylide

B.H. Freeman and D. Lloyd, J. Chem. Soc. (C), in press

(iii) Tetraphenylcyclopentadienylides

B.H. Freeman, D. Lloyd and M.I.C. Singer, Tetrahedron, in press

ACKNOWLEDGEMENTS

I wish to thank Mr. Douglas Lloyd for providing this topic of research and for his advice and assistance throughout the last three years.

I am indebted to many members of the Chemistry Department for their cheerful help during the same period.

I am grateful to Miss Wilma Lamont and Mr. Tom McQueen for their assistance in the production of this thesis.

I wish also to thank Myfanwy for her help and encouragement during the writing of this thesis.

Finally, I gratefully acknowledge a Research Studentship from the Science Research Council.

SUMMARY

The thermal decomposition of 2,3,4,5-tetraphenyldiazocyclopentadiene in the presence of carbene acceptors having Group V and VI elements to give 2,3,4,5-tetraphenylcyclopentadienylides has been extended and the first example of a telluronium ylide has been prepared by this method.

The procedure has also been extended to other substituted diazocyclopentadienes and various new phosphonium, arsonium and sulphonium ylides have been prepared.

The reaction of diazocyclopentadienes with triphenylphosphine to give either phosphazines or phosphonium ylides has been studied and the reasons for the difference in reactivity of these diazo-compounds has been clarified to some extent. It has been shown that for phosphazine formation both lack of steric hindrance and the absence of an electron-donating group on the cyclopentadiene ring are required.

The thermal reaction of diazocyclopentadienes is assumed to proceed via a carbene-type intermediate which is then attacked by the reagent present to give an ylide. This reaction can be catalysed by the presence of copper-bronze and, in this case, can be effected either under melt conditions or in solution. The stability of the carbenoid intermediate is demonstrated by its preferential reaction with triphenylarsine rather than with benzene, which is present as the solvent.

The reaction of 2,5-diphenyldiazocyclopentadiene with triphenylarsine gives a rearranged 2,4-disubstituted product. The carbene-type intermediate in this case is presumed to rearrange before reaction with the triphenylarsine.

Some cyclopentadienylidene triphenylphosphazines have been shown to decompose thermally in the presence of triphenylphosphine to give the related triphenylphosphonium ylides.

Diazocyclopentadienes have been found to react with either hydrochloric or hydrobromic acid to give the monochloro or monobromo cyclopentadienes.

The parent, unsubstituted triphenylarsonium cyclopentadienylide has been prepared by the reaction of triphenylarsine with dibromocyclopentene and basification of the bis-arsonium salt so formed. Its properties and reactions have been studied and are found to be similar to the analogous triphenylphosphonium ylide.

The salt method for the preparation of cyclopentadienylides has also been investigated. Triphenylarsine has been shown to react with 5-bromo-1,2,3-triphenylcyclopentadiene in solution at room temperature to give the hydrobromide salt of the ylide. Various sulphides also reacted with the bromo-compound to give, in most cases, unexpected products.

The reactions of the cyclopentadienylides prepared with aldehydes have been investigated and the results are in line with previous findings. The cyclopentadienylides also readily undergo electrophilic substitution on the five-membered ring. The reaction proceeds preferentially at the 2(5)-position.

CONTENTS

PART 1

INTRODUCTION

PART 2

DISCUSSION

PART 3

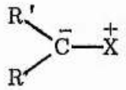
EXPERIMENTAL

PART I

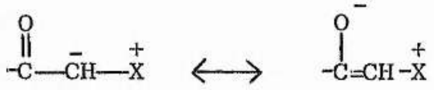
INTRODUCTION

1. YLIDES

The term 'ylide' was first introduced by Wittig[1] in 1944. Ylides have been defined[2] as compounds in which a carbanionic centre is attached directly to a heteroatom that carries a high degree of positive charge and is represented by the general formula (1)



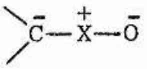
(1)



$$-\overset{\overset{O}{\|}}{C}-\bar{C}H-\overset{+}{X} \longleftrightarrow -\overset{\overset{O^{-}}{|}}{C}=CH-\overset{+}{X}$$

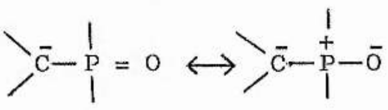
(2)

This definition is intended to include resonance hybrid molecules in which there is an important contributing structure which conforms with the original definition. Therefore molecules containing enolate structures as in (2), in which the negative charge is delocalised over the oxygen atom as well as the carbanionic centre, are also regarded as ylides. Such delocalisation affords greater stabilisation to the ylide. The definition also includes those molecular systems whose heteroatoms carry less than a formal full positive charge e.g. structures such as (3)

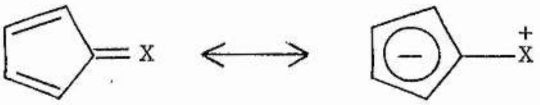


(3)

e.g.



Increased delocalisation and hence increased stability is also achieved when the carbanion is part of the cyclopentadienide, indenide or fluorenide ring systems which have stable sextets of π-electrons[3] (4)

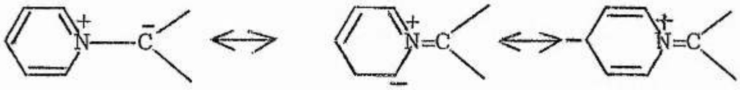


(4)

Stabilisation of ylides is a direct result of delocalisation of the non-bonded electrons on the carbanion. This can be afforded by the carbanion substituents R,R' in structure (1) as indicated, and also by the heteroatom group X as explained below. Thus many ylides are sufficiently stable to be isolated, whereas normal carbanions are seldom isolable.

The heteroatom itself is commonly nitrogen, phosphorus, arsenic, antimony or sulphur[2], but ylides where the heteroatom is bismuth[4], selenium[5], tellurium[6] or iodine[7] have also been prepared.

In the case where X is an ammonium group, it is assumed that the stabilisation of the adjacent carbanion by the heteroatom only occurs by electrostatic interaction between the opposite charges. Stability is greater when X is a pyridinium group. This is probably due to stabilisation of the carbanion by resonance interaction with the pyridinium ring (5) as well as by electrostatic interaction.



(5)

Diazo compounds (6) are special forms of nitrogen ylides which display the nucleophilicity and thermal instability associated with nitrogen ylides.

(6)

In general diazo compounds are more stable than the corresponding ammonium and pyridinium ylides.

Nitrogen is a first row element with filled 2s and 2p orbitals and has the 3s as the next available orbital. This orbital has too high an energy for any effective overlap with the non-bonded electrons of the carbanion and valence shell expansion of the nitrogen atom cannot occur. In the case of phosphorus and sulphur, which are second row elements with filled 3s and 3p orbitals, the 3d orbitals are at only a slightly higher energy level. These orbitals are thus more available for overlap with the non-bonded electrons of the carbanion moiety which results in considerable stabilisation of the ylide. The carbanion can take advantage of the ability of the phosphorus atom to expand its outer shell to accommodate ten electrons; the stabilisation afforded by a sulphonium group is similarly attributed to overlap of the carbanion with the vacant, low energy d-orbital. There is considerable experimental evidence indicating that phosphorus can use its 3d orbitals in σ-bonding and the pentacovalent phosphorus atom is well known. The involvement of the d-orbitals of phosphorus in π-bonding, although not proved, provides a satisfactory basis for much experimental evidence and therefore seems justified. In the case of sulphur there is considerable experimental evidence to support the theoretical predictions of Craig et al[8-10] that a sulphonium group should provide effective stabilisation for an adjacent carbanion by an electron-accepting conjugative mechanism. Although it is seemingly impossible to prove the accumulated evidence is best accounted for by invoking the use of the vacant, low energy 3d-orbitals of sulphur.

In the cases of arsenic and antimony whose properties are similar to those of phosphorus, similar stabilisation of the adjacent carbanion by overlap of the d-orbitals can be expected. The conversion of the arsine or stibine into a quaternary salt will contract the normally diffuse 4d and 5d orbitals and make effective overlap possible. Presumably, in the case of selenium and tellurium this argument still holds true.

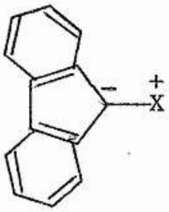
As stated above, ylides are merely a special form of carbanion. Most of the reactions of ylides depend on the use of their carbanionic properties.

The best known reaction of ylides is the Wittig reaction with carbonyl compounds to form olefins or in some cases epoxides. This reaction has been studied extensively in the case of phosphonium ylides due to its synthetic importance in the preparation of olefins. Both the carbanion and heteroatom portions of the ylide are involved in this reaction.

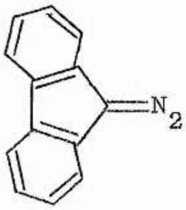
The other well-established reaction involving ylides consists of those in which only the carbanion portion is involved mechanistically. Electrophilic substitution falls into this category.

2. CYCLOPENTADIENYLIDES AND RELATED COMPOUNDS

Cyclopentadienylides (4) have only been described during the last twenty years. Since the related fluorenylides (7) had been studied forty years previously they will be considered first in the present discussion.



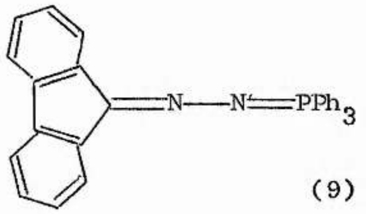
(7)



(8)

(a) FLUORENYLIDES

9-Diazofluorene (8), prepared by Staudinger[11], was the first known fluorenylide. This red solid undergoes many reactions typical of a nitrogen ylide, such as rapid reaction with nitrosobenzene[12,13] at room temperature to yield a nitrone and reactions with carbenes[14] to yield the corresponding methylene-fluorenes. Thus the diazofluorene is acting as a nucleophile and therefore essentially as an ylide. Staudinger also found that diazofluorene reacts additively with triphenylphosphine[15] to form a phosphazine (9), a reaction of stabilised diazo compounds which is now well known and which will be discussed at greater length later in this thesis.



(9)

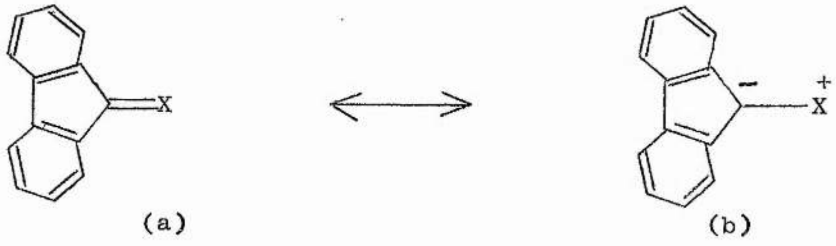
9-Dimethylsulphoniumfluorenylide (7; X = SMe_2) was prepared by Ingold and Jessop in 1930[16] and has been subsequently studied by Johnson and La Count[17]. The preparation involved the treatment of fluorenyldimethylsulphonium bromide with a base, in this case, aqueous sodium hydroxide. This method is an example of the most general method for the preparation of ylides and has been called the 'salt method'.

The same workers were unable to isolate the trimethylammoniumfluorenylide[18] (7; X = NMe_3), but it has since been prepared[1,19] by carrying out the reaction in an inert atmosphere. It is, in accord with earlier discussion, much less stable than the corresponding sulphonium ylide.

9-Pyridiniumfluorenylide (7, X = NC_5H_5) was also found to be unstable,[20] although some of its reactions have been studied[21,22]. Introduction of an electron withdrawing group into the fluorene portion of the molecule stabilises the ylide by further delocalisation of the negative charge, and pyridinium 2-nitrofluorenylide has been isolated in the absence of light and air as a blue-green solid[23].

A number of phosphonium fluorenylides have been prepared by the salt method and their chemical and physical properties have been studied. Johnson and La Count[24] have made a comparative study of triphenyl- and tri-n-butyl-phosphoniumfluorenylides. Physical and chemical studies showed that the triphenyl ylide was less basic and less nucleophilic than the tributyl ylide. The tributyl ylide reacted with aromatic aldehydes and also with activated aromatic ketones, whereas the triphenyl ylide would only react more slowly with aromatic aldehydes. This, together with the fact that the triphenyl ylide has a lower pK_a and dipole moment, shows that the triphenylphosphine group is better able to delocalise the negative charge on the carbanion than in the tri-n-butyl case[25], presumably by $p_{\pi}-d_{\pi}$ overlap.

Johnson also examined the chemical and physical properties of triphenylarsoniumfluorenylide[26], (7, X = $AsPh_3$). This ylide is slowly hydrolysed when exposed to the atmosphere and has a pK_a of 7.8 compared with 7.5 for the analogous phosphonium ylide. The arsonium ylide was found to be more reactive towards carbonyl compounds. The conclusion reached from these and other physical and chemical properties is that triphenylarsoniumfluorenylide is more basic than the phosphonium analogue and that (11(b)) contributes more to the overall structure of the arsonium ylide than does (10(b)) to the overall structure of the phosphonium ylide.



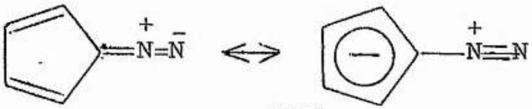
(a) (b)

X = PPh_3 (10)
= $AsPh_3$(11)

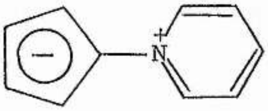
Trimethylphosphoniumfluorenylide, (7, X = PMe_3) was prepared by Wittig and Laib[27], but it was handled entirely in solution and was not isolated. The same workers attempted to prepare the stibonium analogue but could only isolate bifluorenyl from the reaction mixture.

(b) CYCLOPENTADIENYLIDES

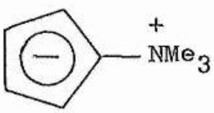
Cyclopentadienylides have been known since 1951. They owe their special stability to the delocalisation of the lone pairs of electrons on the carbanion into the five-membered ring to give a stable sextet of π-electrons (4). The first example recorded was diazocyclopentadiene (12), prepared by Doering and DePuy in 1951[28]; followed shortly by pyridinium-[29] (13), trimethylammonium-[30] (14) and triphenylphosphonium-[31] (15) cyclopentadienylides.



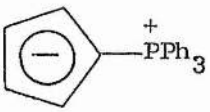
(12)



(13)



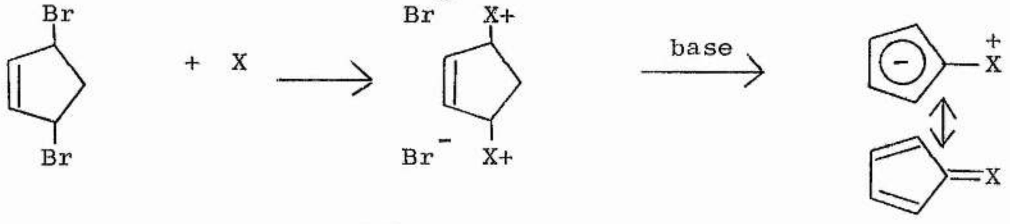
(14)



(15)

(i) Preparation

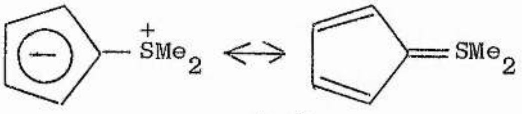
The classic salt method, which is the most general method for the preparation of ylides, has been used in a modified form in the preparation of a number of cyclopentadienylides (Scheme I)



Scheme I

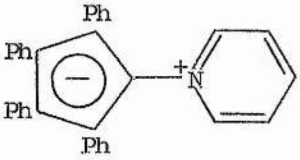
$X = NC_5H_5$, PPh_3, NMe_3, SMe_2

In 1955 Lloyd and Sneezum[29] prepared pyridiniumcyclopentadienylide (13) by the action of pyridine on dibromocyclopentene and treatment of the resulting salt with alkali. Shortly after this both the trimethylammonium-[30] (14) and the triphenylphosphonium-[31] (15) ylides were reported. More recently dimethylsulphoniumcyclopentadienylide[32] (16) has been prepared by the same method.

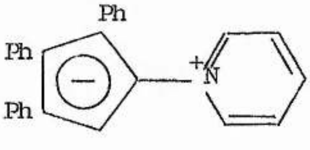


(16)

The treatment of both 5-bromo-1,2,3,4-tetraphenylcyclopentadiene[33] and 5-bromo-1,2,3-triphenylcyclopentadiene[34] with pyridine and subsequent basification led to the isolation of the appropriate ylides (17) and (18).

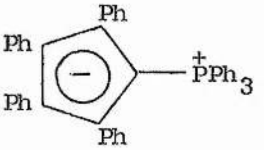


(17)

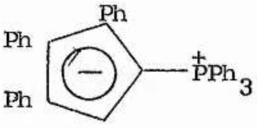


(18)

Reaction of the same bromocyclopentadienes with triphenylphosphine under slightly modified conditions[34] led to the isolation of the appropriate phosphonium ylides (19) and (20).

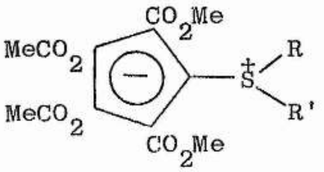


(19)



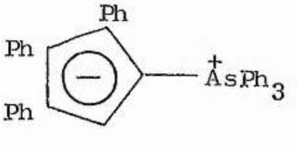
(20)

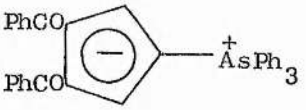
The condensation of sulphoxides with active methylene groups has been used by a number of workers[35] to prepare sulphonium ylides. Seitz[36] reacted tetracarbomethoxycyclopentadiene with various sulphoxides to obtain the corresponding sulphonium cyclopentadienylides (21).



(21)

Lloyd and co-workers[37] reported a similar reaction between triphenylarsine oxide and cyclopentadienes which resulted in the formation of the arsonium cyclopentadienylides. This condensation reaction occurred with or without electron-withdrawing groups on the ring and appears to be a more general reaction than that involving sulphoxide. Both 1,2,3-triphenylcyclopentadiene and 2,3-dibenzoylcyclopentadiene condensed with triphenylarsine oxide to give ylides (22) and (23)

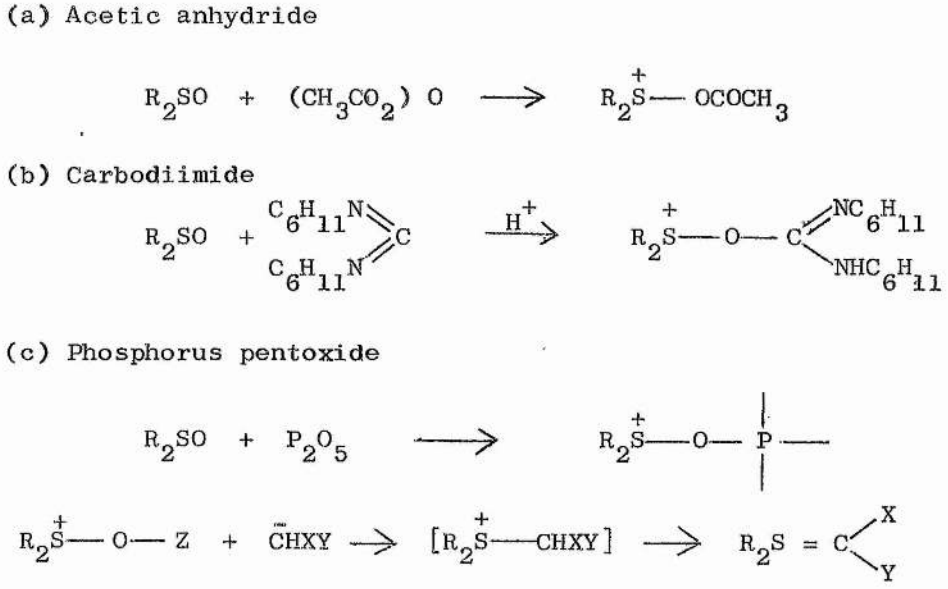




(22) (23)

McLean and Reed[38] reported an interesting variation on the sulphoxide reaction. The reaction between the trimethylsilyl derivative of cyclopentadiene and dimethyl sulphoxide afforded dimethylsulphoniumcyclopentadienylide (16) in good yield.

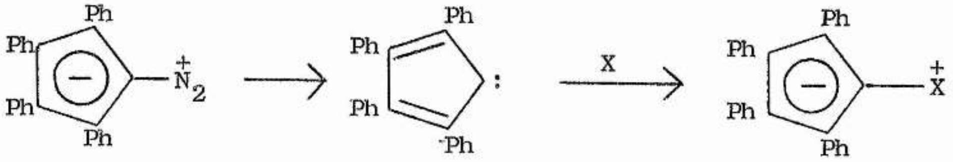
A general mechanism for the sulphoxide reaction has been put forward (Scheme II) and presumably the arsine oxide reaction follows a similar pattern.



Scheme II

The three more usual catalysts are shown in the mechanistic scheme, namely acetic anhydride, dicyclohexylcarbodiimide with a trace of phosphoric acid, or phosphorus pentoxide in triethylamine. In all cases the reaction is assumed to go through an alkoxysulphonium salt which then reacts with the carbanion of the active methylene group to give the corresponding sulphonium ylide.

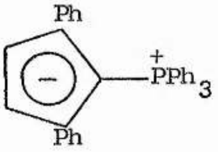
A whole series of cyclopentadienylides have been prepared by trapping the carbene formed by thermal decomposition of tetraphenyldiazocyclopentadiene with various group V and group VI nucleophiles (Scheme III)



X = NC_5H_5[39]
PPh_3[40] SPh_2[43]
$AsPh_3$[41] $SePh_2$[5]
$SbPh_3$[42] $TePh_2$[6]
$BiPh_3$[4]

Scheme III

This reaction, however, was not a completely general one. Although 2,5-diphenyldiazocyclopentadiene decomposed smoothly in triphenylphosphine to give a good yield of the ylide[40] (24), both 2,4-diphenyldiazocyclopentadiene and 2,3,4-triphenyldiazocyclopentadiene formed phosphazines[40] (25) either in solution or in low temperature melts. At higher temperatures uncontrollable decomposition set in. The reason for this startling change in reaction is not at all clear and is discussed at some length later in this thesis.



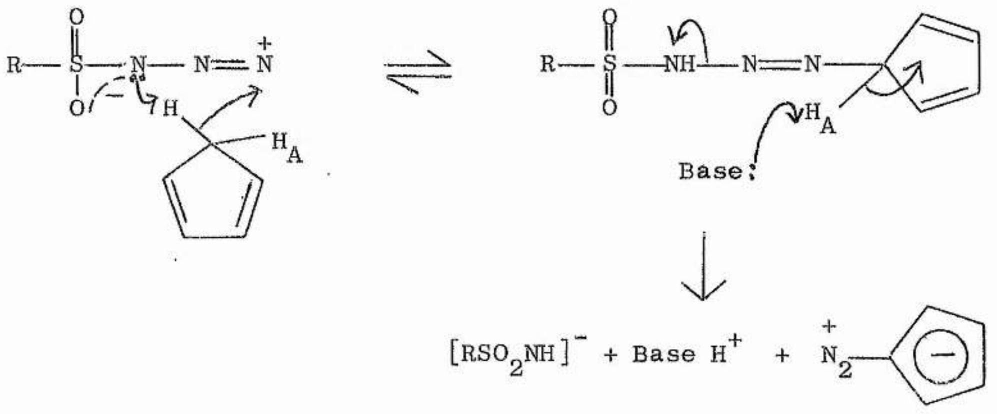
(24)

R = H or Ph

(25)

The first reported example of a cyclopentadienylide, the remarkably stable diazocyclopentadiene (12) was prepared by treating cyclopentadienyl-lithium with p-toluenesulphonylazide[28]. A more recent modification of this method[44] uses cyclopentadiene in the presence of an amine instead of the cyclopentadienyl salt. Phenylated diazocyclopentadienes have been similarly prepared[45] but a superior method has been reported by Regitz and Leidhegener[46] in which a suspension of the diene in acetonitrile is treated with p-toluenesulphonylazide in the presence of piperidine. This method gives almost quantitative yields of the required phenylated diazocyclopentadienes. However, when one or more of the phenyl groups are replaced by alkyl groups the reaction fails and the earlier method using the cyclopentadienyl salt must be used[47].

The reaction mechanism proposed[45] (Scheme IV), if correct, shows that the acidity of the proton (H_A) on the cyclopentadiene ring controls whether or not the reaction will proceed.

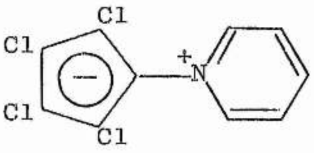


Scheme IV

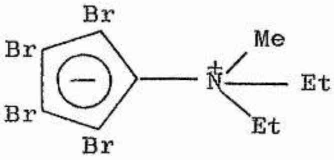
The proton (H_A) will be less acidic when alkyl groups are substituted on the ring thus causing the reaction to fail.

Tetrachlorodiazocyclopentadiene[48] and tetracyanodiazocyclopentadiene[49] have also been prepared.

Ferrocene when dissolved in pyridine and treated with either N-chlorosuccinimide or chlorine, produces pyridinium tetrachlorocyclopentadienylide (26)[50].



(26)



(27)

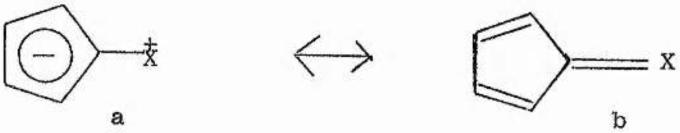
Photolysis of the diethylmethylammonium salt of ferrocene produces the ammonium ylide, which can be brominated to give diethylmethylammonium tetrabromocyclopentadienylide (27)[51].

(ii) Properties and Reactions

All cyclopentadienylides prepared to date are solids, except diazocyclopentadiene which is a remarkably stable red liquid. When diazocyclopentadienes and pyridinium cyclopentadienylides are stored under nitrogen, they appear to be stable indefinitely. Diphenylsulphonium- and diphenylselenoniumcyclopentadienylides darken slowly when exposed to light but are stable when kept in the dark. Triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide slowly hydrolyses in the air. All the phosphonium and arsonium cyclopentadienylides prepared to date appear to be stable indefinitely in the solid state.

Pyridinium cyclopentadienylides and triphenylbismuthonium-2,3,4,5-tetraphenylcyclopentadienylide are intensely coloured, usually blue-green, but pyridinium cyclopentadienylide itself is copper coloured. Diazocyclopentadienes are bright yellow or red compounds but all other cyclopentadienylides are light yellow in colour. The colours of pyridinium cyclopentadienylides in various solvents depend on the polarity of the solvents. Kosower and Ramsey[52] studied the ultra-violet and visible spectrum of pyridinium cyclopentadienylide (13) in a variety of solvents and ascribed a band at 5000 Å to intramolecular charge transfer.

Dipole moment measurements on pyridinium-[53], triphenylphosphonium- and dimethylsulphonium-[32] cyclopentadienylides (13.5D, 6.99D and 5.7D respectively) give some indication of the relative amount of $d_\pi - p_\pi$ orbital overlap in these ylides. Pyridinium cyclopentadienylide has, of course, no d-orbitals available for overlap and cannot be represented by any uncharged form. It would appear that dimethylsulphoniumcyclopentadienylide has a larger contribution from the covalent form (28b) than the corresponding triphenylphosphonium ylide.



(28)

By pK_a measurements on their series of tetraphenylcyclopentadienylides, Lloyd and Singer[54] concluded that, when the heteroatoms carry the same substituents, the effectiveness of the $p_\pi - d_\pi$ overlap in stabilising the ylides is in the order $S \approx Se > P > As > Sb$. On the other hand, purely on the basis of their reactions with carbonyl compounds and with nitrosobenzene, a reactivity sequence for the ylides could be written $Sb > As > Se > S > P$. With this series of ylides nucleophilicity did not seem to parallel basicity but the all important question of steric effects may well account for the anomalous reactivity behaviour.

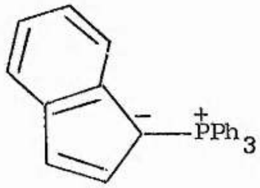
The aromatic character of diazocyclopentadiene and triphenylphosphoniumcyclopentadienylide has been confirmed both by their physical and chemical properties. The N.M.R. spectra of these ylides[55], showing an AA'BB' signal for the cyclopentadiene protons, have been resolved and the vicinal coupling constants correlated with the bond orders.

All cyclopentadienylides readily undergo electrophilic substitution. Attack occurs preferentially at the 2,5 positions presumably because a more stable transition state is involved in the reactions at these positions. Diazocyclopentadiene has been brominated, diazo-coupled and mercuriated[56]. 2,3,4-Triphenyldiazocyclopentadiene also undergoes a number of electrophilic substitution reactions; protonation in strong acid has been shown from the N.M.R. spectrum to take place at the 5-position[45].

The pyridinium, trimethylammonium- and triphenylphosphonium-cyclopentadienylides can be brominated[57,30,34] and coupled with diazonium salts[33,30,58] and the triphenylphosphonium ylide has been acetylated, formylated and nitrated[34,59].

A kinetic study on the reaction of benzylidenemalonitriles with triphenylphosphoniumcyclopentadienylide has been carried out[60].

Oda et al[61] have prepared triphenylphosphoniumindenylide (29) and compared its reactivity with that of the analogous fluorenylide and cyclopentadienylide towards dichlorocarbene.



(29)

The fluorenylide gave a 44% yield of olefin, the indenylide 8% and the cyclopentadienylide did not react. They suggest that this is due to the relative difficulty in the localisation of one electron pair on the α-carbon atom and that this explains the inertness of triphenylphosphoniumcyclopentadienylide in the Wittig reaction.

PART 2

DISCUSSION

The main objective of the work described in this thesis was to study the preparation and reactions of a variety of substituted cyclopentadienylides. The work also involved investigations of possible preparative routes to cyclopentadienes and diazocyclopentadienes using both established and novel methods.

The thermal decomposition of diazocyclopentadienes was investigated at some length and the work of Lloyd and Singer[4,5,41,42,43] was extended and clarified. The salt method and the arsine oxide condensation method were also utilised for the preparation of cyclopentadienylides.

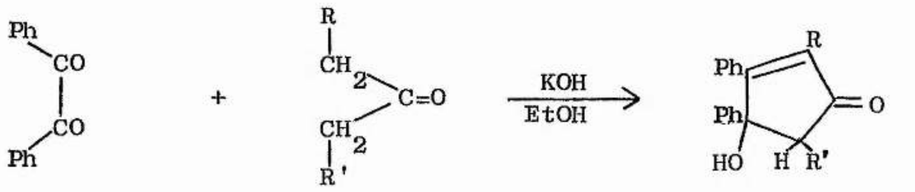
The Wittig reactions and electrophilic substitution reactions of the cyclopentadienylides which have been prepared were investigated.

For the sake of brevity some of the compounds discussed in this thesis are illustrated by formulae which in fact represent only one of the possible contributing canonical forms of the compounds in question.

I PREPARATION OF CYCLOPENTADIENES AND DIAZOCYCLOPENTADIENES

(i) CYCLOPENTADIENES

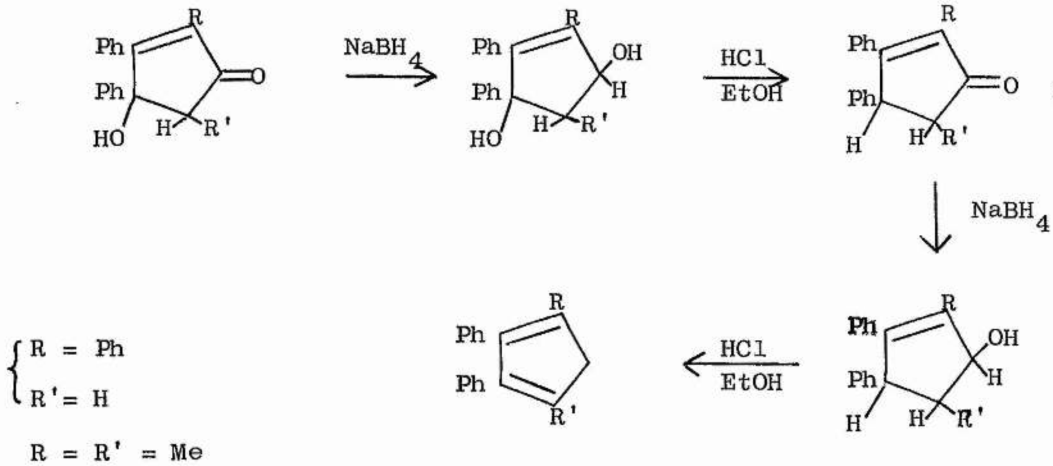
The condensation reaction between benzil and dibenzyl-, benzylmethyl, or dialkyl ketones[62] (scheme V) which leads to the formation of various substituted cyclopentenolones (30), was the starting point for the preparation of all but one of the cyclopentadienes used in these investigations.



(30)

Scheme V

In certain cases the cyclopentenolones could be converted by a series of steps[63] (scheme VI) into the respective cyclopentadienes. This method was used to prepare 1,2,3-triphenylcyclopentadiene and 1,4-dimethyl-2,3-diphenylcyclopentadiene.



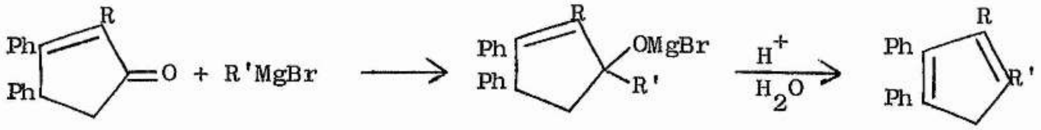
(31)

$\begin{cases} R = Ph \\ R' = H \end{cases}$

R = R' = Me

Scheme VI

The technique of adding Grignard reagents to the intermediate cyclopentenones (31)[47,64] with subsequent hydrolysis and dehydration was successful for the preparation of a number of other cyclopentadienes (scheme VII). This method of preparation of 1,2,4-triphenylcyclopentadiene was found to be superior to the method previously used[65].

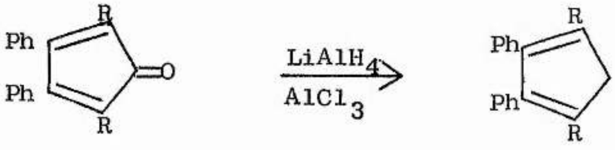


$R = H,\ R' = Ph,\ CH_2Ph,\ CH_3$

$R = Ph,\ R' = CH_3,\ C_2H_5,\ CH_2Ph,\ C_6H_4\ CH_3\underline{p}$

Scheme VII

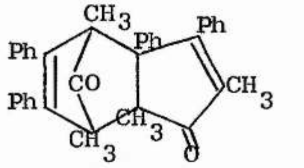
In the case of 1,2,3,4-tetraphenylcyclopentadiene[66] and 1,4-diethyl-2,3-diphenylcyclopentadiene the related monomeric cyclopentadienones could be converted into the cyclopentadienes by treatment with lithium aluminium hydride and aluminium chloride (scheme VIII).



$R = C_2H_5,\ Ph$

Scheme VIII

An attempted preparation of 1,4-dimethyl-2,3-diphenylcyclopentadiene by this method was unsuccessful. 2,5-dimethyl-3,4-diphenylcyclopentadienone exists as a dimer (32) but is reported[67] to dissociate into the monomeric form in solution at elevated temperatures.



(32)

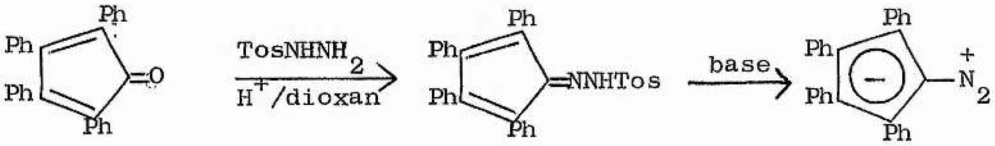
The cyclopentadienones are themselves obtained by acidic dehydration[62] of the respective cyclopentenolones or, in the case of tetraphenylcyclopentadienone, directly from the condensation of benzil with dibenzylketone. The majority of these cyclopentadienones exist as dimers and so the above method for the preparation of cyclopentadienes is very limited.

(ii) DIAZOCYCLOPENTADIENES

The established methods mentioned in Part I were used to prepare diazocyclopentadienes from cyclopentadienes. The earliest method involved the use of the cyclopentadienyl anion generated from the diene and phenyl lithium[28], but it was later found that such strongly basic conditions were not required and piperidine[46] was successfully employed as base. The latter method, however, failed to give any diazo compound when an alkyl group was attached directly to the cyclopentadiene ring. In these cases the earlier method was successfully employed.

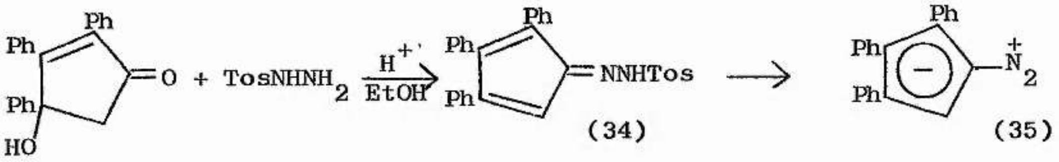
Some phenylated pyrroles have been diazotised by sodium nitrite-hydrochloric acid solutions[68]. Under similar conditions both 1,2,3,4-tetraphenylcyclopentadiene and 1,4-dimethyl-2,3-diphenylcyclopentadiene failed to give any reaction and were recovered unchanged.

Lloyd and Wasson[45] found that treatment of the readily available tetraphenylcyclopentadienone with p-toluenesulphonylhydrazine and hydrolysis of the resultant hydrazone (33) with alkali gave a good yield of 2,3,4,5-tetraphenyldiazocyclopentadiene (scheme IX)



Scheme IX

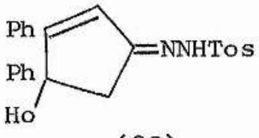
It was also discovered[47] that treatment of 2,3,4-triphenylcyclopent-2-en-4-ol-1-one with tosyl hydrazine under acid conditions gave a good yield of the respective hydrazone (34). When treated with base this tosyl hydrazone gave the diazo compound (35) in good yield (scheme X).



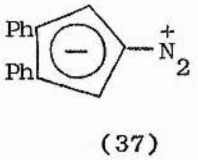
Scheme X

However neither of these methods proved to be a general route to diazocyclopentadienes. All other cyclopentadienones which were investigated appeared not to react with tosyl hydrazine under the same conditions; other cyclopentenolones gave the diazo compounds directly but in very low yields.

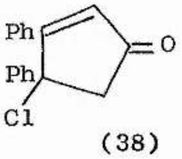
It was found that 3,4-diphenylcyclopent-2-en-4-ol-1-one reacted with tosyl hydrazine in ethanolic solution without mineral acid to give a good yield of the tosyl hydrazone (36). This reaction has since been reported in the literature[69] by Rio and Charifi who used acetic acid as solvent.



(36)



(37)



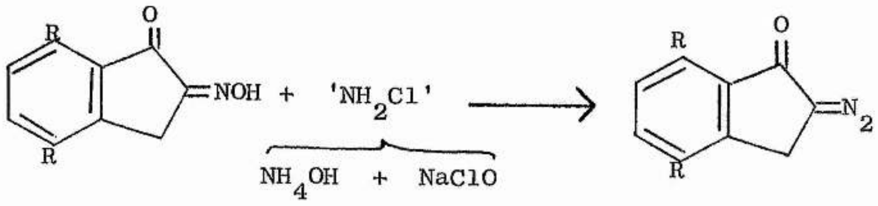
(38)

Unfortunately all attempts to convert this compound into 3,4-diphenyldiazocyclopentadiene (37) met with no real success. Attempted dehydration followed by basification gave only very small amounts of the diazo compound.

4-chloro-3,4-diphenylcyclopent-2-en-1-one (38) did not react with tosyl hydrazine under neutral or acidic conditions. Reaction of the tosyl hydrazone (36) with aluminium chloride gave the diazo compound (37) directly, but only in 13% yield.

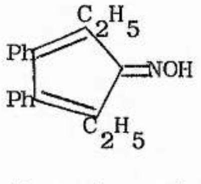
The infra-red spectrum of the mixtures of products obtained by attempted dehydration of the tosyl hydrazone (36) showed intense carbonyl absorptions. This indicates that, under the conditions used, hydrolysis of the tosyl hydrazone occurs. When 2,5-diethyl-3,4-diphenylcyclopent-2-en-4-ol-1-one reacted with tosyl hydrazine in hydrochloric acid-ethanol solution about 30% of 2,5-diethyl-3,4-diphenylcyclopentadienone was obtained. Other less substituted cyclopentadienones are known to dimerise and possibly polymerise under these conditions[62].

Diazo compounds have been obtained[70] by treatment of an oxime with 'chloramine' (scheme XI)



Scheme XI

2,5-Diethyl-3,4-diphenylcyclopentadienone reacted with hydroxylamine to give the respective oxime (39) in good yield. The reaction of this oxime with chloramine under the specified conditions gave only a very small amount of the diazo compound.



(39)

Since this reaction is only relevant for monomeric cyclopentadienones no further investigations were carried out.

II REACTIONS OF DIAZOCYCLOPENTADIENES; FORMATION OF YLIDES FROM DIAZO-COMPOUNDS AND FROM PHOSPHAZINES

(i) TETRASUBSTITUTED DIAZOCYCLOPENTADIENES

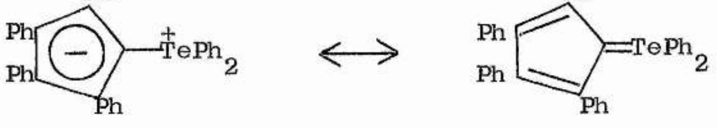
(a) 2,3,4,5-Tetraphenyldiazocyclopentadiene

It had been found that when 2,3,4,5-tetraphenyldiazocyclopentadiene was heated to about 150°C in the presence of a variety of group V and group VI nucleophiles, tetraphenylcyclopentadienylides were formed in good yields. The reaction presumably proceeds via a carbene which then attacks the nucleophile to form the ylide (see Part 1, scheme III).

The range of nucleophiles with which 2,3,4,5-tetraphenyldiazocyclopentadiene had been reacted was extended in attempts to prepare oxonium, telluronium and iodonium ylides.

When the diazo compound was decomposed in either diphenyl oxide or p-iodotoluene impure solid products were obtained which, in both cases, could not be purified or analysed satisfactorily. No evidence was found that suggested the formation of ylides.

A similar reaction in diphenyltelluride[6] yielded a solid, precipitated by ether and light petroleum (b.p. 40-60°), which from its mode of preparation, analysis and spectra was believed to be the telluronium. ylide (40)



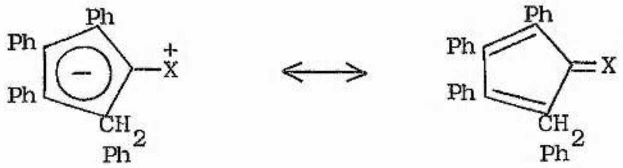
(40)

Attempts to prepare an analytically pure sample of this substance failed owing to its apparent ready decomposition. Mass spectrum of the solid at low electron voltage showed peaks corresponding to the parent ylide but the major peaks corresponded to diphenyltelluride. It appears that the ylide is cleaved in the mass spectrometer at the weak C-Te bond to give a diphenyltelluride cation, leaving the tetraphenylcyclopentadiene moiety as a neutral or negatively charged species.

The ultra-violet spectrum of the ylide (40) varies with the polarity of the solvent as do the spectra of the pyridinium- and triphenylbismuthonium-2,3,4,5-tetraphenylcyclopentadienylides but not those of the other group V and group VI heteronium ylides. The ylide (40) had a blue colour on initial precipitation, but was reprecipitated from benzene and petroleum spirit (b.p. 40-60°) as a yellow solid.

(b) 2-Benzyl-3,4,5-triphenyldiazocyclopentadiene

2-Benzyl-3,4,5-triphenyldiazocyclopentadiene reacted with triphenylphosphine, triphenylarsine and methylphenylsulphide under normal melt conditions to give the respective ylides (41,42,43) in satisfactory yields



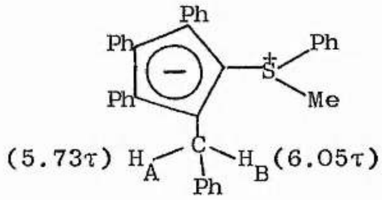
X = PPh_3 (41)
$AsPh_3$(42)
S(Me)Ph(43)
SPh_2 (44)

The ylides (41), (42) and (43), all yellow in colour, were precipitated from the cooled reaction melt by addition of ether. From analysis results before and after recrystallisation, it appears that these ylides decompose to some extent in hot solvents. Best analysis results were obtained merely by washing the precipitated ylides with ether.

2-Benzyl-3,4,5-triphenyldiazocyclopentadiene also reacted with diphenylsulphide to give the expected ylide (44). This ylide was precipitated from the cooled reaction melt by addition of ether and light petroleum (b.p. 40-60°) as an impure reddish solid in low yield, but all attempts to purify this ylide were unsuccessful.

Only a singlet peak was observed in the n.m.r. spectrum of ylide (43) indicating that free rotation occurs about the C-S bond. No change was observed in the n.m.r. spectrum on cooling the sample to -70°C. This shows that at these temperatures the ylide has some dipolar character. If there were no contribution from the dipolar canonical form then there would be two distinct geometric isomers and two methyl signals should be seen.

The peak assigned to the methylene group in the n.m.r. spectrum of ylide (43) was broadened and appeared to give an AB type signal. For steric reasons free rotation about the $C-CH_2$ bond is hindered and the protons of the methylene group are non-equivalent (43a).

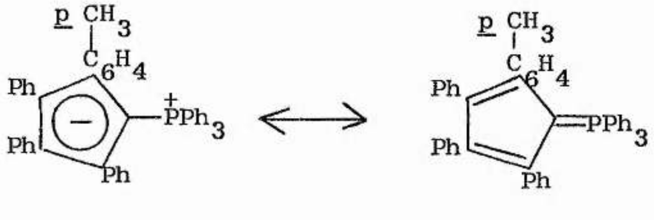


(43a)

This effect is not observed for ylides (41) (42) and (44). In these cases only phenyl groups are attached to the heteroatom and apparently the environment of the two protons, H_A and H_B are almost identical, thus giving a broad singlet. Ylides (41), (42) and (43) all gave correct molecular ion peaks in their mass spectra.

(c) 2,3,4-Triphenyl-5-p-tolyldiazocyclopentadiene

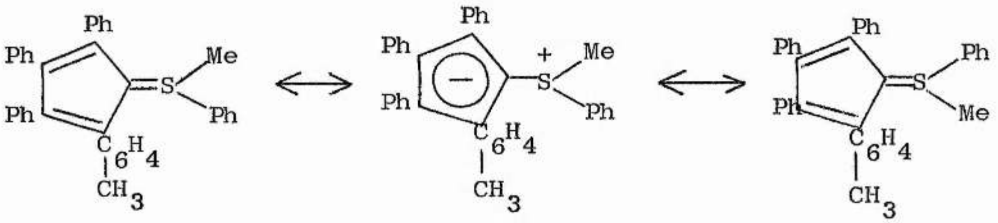
2,3,4-Triphenyl-5-p-tolyldiazocyclopentadiene was decomposed in a melt in the presence of triphenylphosphine to give a high yield of the triphenylphosphonium ylide (45)



(45)

The yellow ylide was precipitated from the cooled reaction mixture by addition of ether. It had a high melting point and was too insoluble in deuteriochloroform for the n.m.r. spectrum to be recorded. The mass spectrum of the ylide gave a large molecular ion peak allowing the accurate molecular weight to be determined.

When 2,3,4-triphenyl-5-p-tolyldiazocyclopentadiene was decomposed in methylphenylsulphide, the impure ylide (46) was obtained in poor yield as a yellow-brown solid precipitated by addition of ether and light petroleum (b.p. 40-60°)



(46)

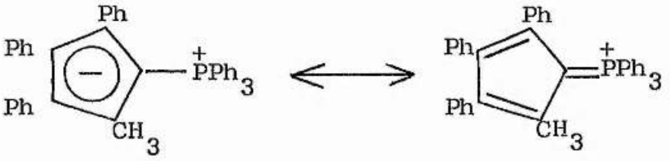
Catalytic decomposition of the diazo compound in methylphenylsulphide in the presence of copper-bronze gave a high yield of the ylide (46), which was precipitated as a pale yellow solid by ether. The n.m.r.

spectrum of this ylide showed only two methyl peaks (7.25τ, 7.75τ), indicating that rotation occurs about the C-S bond and that at the operating temperature the charged canonical form makes a contribution to the structure of the ylide. Without rotation about the C-S bond, two geometric isomers would be possible which would result in two separate signals for the S-Me protons in the n.m.r. spectrum. No change was observed in the n.m.r. spectrum in the range 0-50°C.

The mass spectrum of the ylide (46) gave a molecular ion peak, allowing its accurate molecular weight to be calculated.

(d) 2-Methyl-3,4,5-triphenyldiazocyclopentadiene

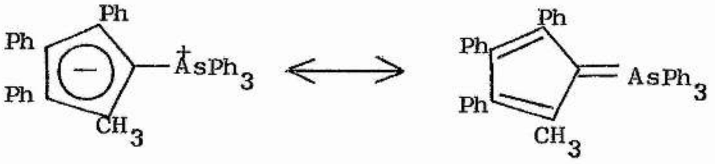
2-Methyl-3,4,5-triphenyldiazocyclopentadiene was decomposed in the presence of triphenylphosphine to give a reasonable yield of the phosphonium ylide (47)



(47)

The impure yellow ylide was precipitated from the cooled reaction mixture by addition of ether and light petroleum (b.p. 40-60°) and purified by column chromatography. Attempted recrystallisation of the ylide tended to produce a more impure product.

No ylide was isolated when 2-methyl-3,4,5-triphenyldiazocyclopentadiene was decomposed in either methylphenylsulphide or triphenylarsine. However, catalytic decomposition of the diazo compound in triphenylarsine with copper-bronze present gave a good yield of the arsonium ylide (48)



(48)

The yellow ylide (48) was precipitated by addition of ether.

The mass spectra of ylides (47) and (48) gave molecular ion peaks which enabled accurate molecular weights to be determined.

(e) 2,5-Dimethyl-3,4-diphenyldiazocyclopentadiene

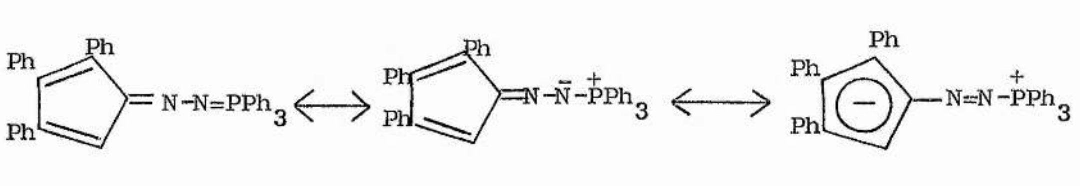
When 2,5-dimethyl-3,4-diphenyldiazocyclopentadiene was decomposed in the presence of triphenylphosphine, addition of ether to the cooled reaction mixture precipitated a number of products. A mass spectrum of the mixture gave a small m/e peak at 506 corresponding to the expected ylide. No ylide, however, was isolated. The main product isolated by column chromatography was a white solid which gave large m/e peaks at 462 and 447. This product remains unidentified.

None of the tetrasubstituted diazocyclopentadienes described above gave any indication of phosphazine formation when heated with triphenylphosphine either in solution or in a melt.

(ii) TRISUBSTITUTED DIAZOCYCLOPENTADIENES

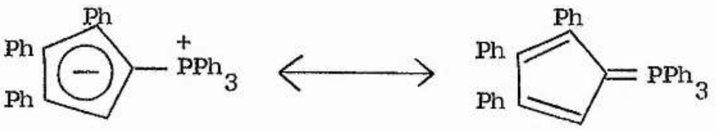
(a) 2,3,4-Triphenyldiazocyclopentadiene

When 2,3,4-triphenyldiazocyclopentadiene was heated with triphenylphosphine at 100°C, a high yield of the phosphazine (49) was obtained[34]



(49)

Despite reports to the contrary[34,40,46] at higher temperatures a reasonable yield of the ylide (50) could be obtained.

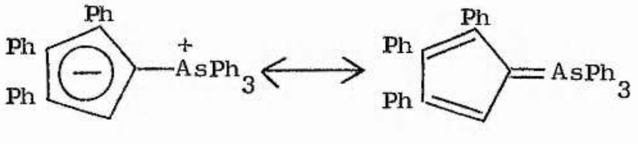


(50)

This reaction probably proceeded in a stepwise fashion. The phosphazine (49) was formed initially but at the higher temperature probably decomposed back to the diazo compound and triphenylphosphine and hence to the ylide by the normal diazo decomposition reaction. The thermal decomposition of a phosphazine into the diazo compound and triphenylphosphine is well known[71], although only one case of decomposition of a phosphazine to give an ylide has been reported[15]. Similar yields of the ylide (50) were obtained when either the diazo compound or the phosphazine itself was reacted with excess triphenylphosphine.

The ylide (50) had been previously prepared by a modified version of the salt method[34].

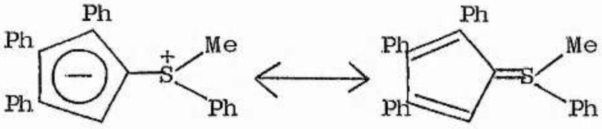
Decomposition of 2,3,4-triphenyldiazocyclopentadiene in the presence of triphenylarsine gave a low yield of the respective arsonium ylide (51)



(51)

The yield was dramatically increased by the use of copper-bronze catalysis of the reaction at a slightly lower temperature. The ylide had been previously prepared by reaction of triphenylarsine oxide with 1,2,3-triphenylcyclopentadiene[37].

Decomposition of 2,3,4-triphenyldiazocyclopentadiene in the presence of methylphenylsulphide gave a red solid, precipitated from the cooled reaction mixture by addition of ether and light petroleum (b.p. 40-60°). This solid defied all attempts at purification. Mass spectral evidence, however, indicated the presence of the expected ylide (52).



(52)

Catalytic decomposition of 2,3,4-triphenyldiazocyclopentadiene in methylphenylsulphide using copper-bronze as catalyst also failed to provide a pure product. The spectral evidence (infra-red, n.m.r. and mass spectrum) in this case did, however, point to a reasonable amount of the ylide (52) having been formed. Attempted recrystallisation and column chromatography failed to give a pure product.

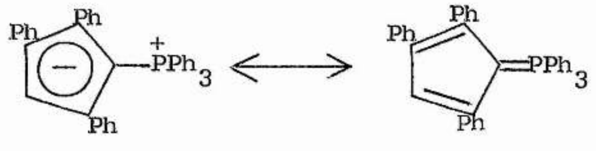
The n.m.r. spectrum of the impure ylide (52) showed only a singlet peak for the methyl protons. Upon cooling the sample to -70°C, broadening of this peak was observed. No other change was observed in the spectrum. This again indicates that, at these temperatures, the charged canonical form makes a contribution to the structure of the ylide (52). The broadening of the methyl signal may possibly be due to rotation about the C-S bond decreasing at the lower temperature. However, at this temperature, rotation is not completely inhibited.

Decomposition of 2,3,4-triphenyldiazocyclopentadiene in the presence of triphenylstibine, with or without catalyst, failed to give any evidence of the formation of any ylide.

(b) 2,3,5-Triphenyldiazocyclopentadiene

2,3,5-Triphenyldiazocyclopentadiene, unlike the 2,3,4-triphenyl analogue, was found not to react with triphenylphosphine in solution, nor did it react when heated in a melt at 100°C. In both cases the diazo compound was recovered in good yield.

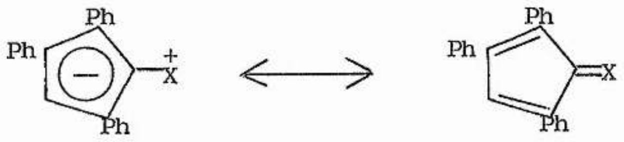
When heated with triphenylphosphine at higher temperatures, the diazo-compound decomposed smoothly to give a high yield of the respective phosphonium ylide (53)



(53)

The yellow ylide was precipitated from the cooled reaction mixture by addition of ether.

Surprisingly, in view of the reaction with triphenylphosphine, the diazo-compound did not react cleanly with either triphenylarsine, diphenylsulphide or methylphenylsuphide. Addition of a mixture of ether and light petroleum (b.p. 40-60^{o}) to the cooled reaction mixtures precipitated solids in all three cases. From mass spectral evidence these solids all contained the expected ylides (54), (55) and (56).



X = $AsPh_3$ (54)
SPh_2 (55)
$S(CH_3)Ph$ (56)

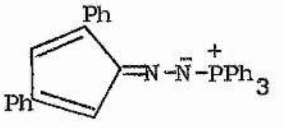
These products, however, defied all attempts at their purification. The triphenylarsonium ylide (54) was prepared in a pure state, in high yield, by decomposition of the diazo-compound using copper-bronze as a catalyst. The ylide was precipitated by addition of ether as a pale yellow solid.

Both the arsonium and phosphonium ylides gave correct molecular ion peaks in their mass spectra.

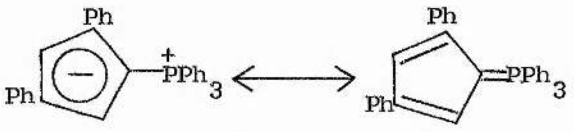
(iii) DISUBSTITUTED DIAZOCYCLOPENTADIENES

(a) 2,4-Diphenyldiazocyclopentadiene

2,4-Diphenyldiazocyclopentadiene has been reported[46] to react with triphenylphosphine to form the phosphazine (57) in solution, or when heated in a melt at controlled temperatures. At higher temperatures it was reported to decompose uncontrollably.



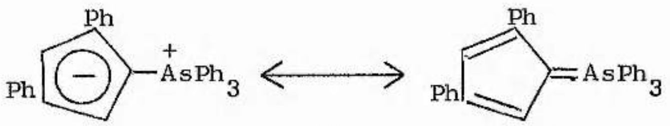
(57)



(58)

However, when 2,4-diphenyldiazocyclopentadiene was heated in the presence of excess triphenylphosphine at 150°C, the phosphonium ylide (58) was obtained in reasonable yield. The ylide was also obtained in similar yield when the phosphazine (57) was heated with excess triphenylphosphine. The reaction was assumed to proceed in a similar way to the 2,3,4-triphenyldiazocyclopentadiene reaction with triphenylphosphine. The yellow ylide was precipitated from the cooled reaction mixture by addition of ether and could be purified by recrystallisation.

Under similar conditions, no ylides were obtained when 2,4-diphenyldiazocyclopentadiene was decomposed in the presence of either triphenylarsine, diphenylsulphide or methylphenylsulphide. The triphenylarsonium ylide (59) was prepared in poor yield by catalysis of the diazo decomposition with copper-bronze. The arsonium ylide was



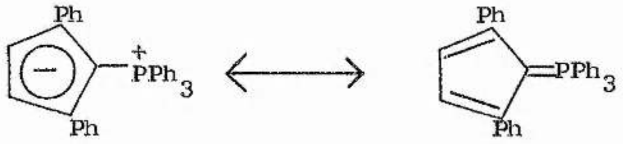
(59)

precipitated by addition of ether.

Both the phosphonium ylide (58) and the arsonium ylide (59) gave correct molecular ion peaks in their mass spectra.

(b) 2,5-Diphenyldiazocyclopentadiene

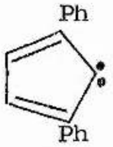
2,5-Diphenyldiazocyclopentadiene has been reported[46] to react with triphenylphosphine in a melt to give the phosphonium ylide (60) in good yield.



(60)

When the diazo-compound was decomposed under similar conditions in the presence of triphenylarsine, a poor yield of the triphenylarsonium-2,4-diphenylcyclopentadienylide (59) was obtained. This ylide was the only product obtained and there was no evidence for the presence of any of the expected 2,5-substituted product.

The method by which this rearranged product is formed is, as yet, uncertain. Presumably some rearrangement of the carbene (61) itself or of some subsequent reactive intermediate must take place.

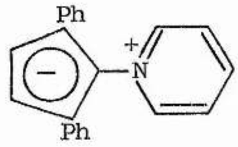


(61)

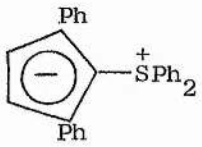
Attack of the triphenylarsine on the carbene is less hindered at the

3,4-positions. Such attack, coupled with a hydrogen shift would give the product (59). When this reaction was repeated, using copper-bronze as a catalyst, the same product was obtained in an improved yield.

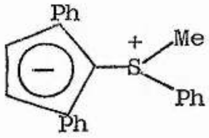
When the diazo-compound was heated under reflux in pyridine or decomposed in either diphenylsulphide or methylphenylsulphide it did not give isolable ylides. However, mass spectral evidence indicated that the ylides (62), (63) and (64) were formed to some extent.



(62)



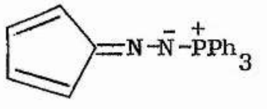
(63)



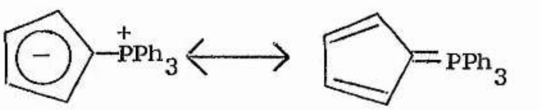
(64)

(iv) DIAZOCYCLOPENTADIENE

Diazocyclopentadiene has been reported[72] to react with triphenylphosphine either in solution or in a melt to give the very stable phosphazine (65)



(65)



(15)

The phosphazine (65) was reported not to decompose at higher temperatures to give the well known phosphonium ylide[72] (15).

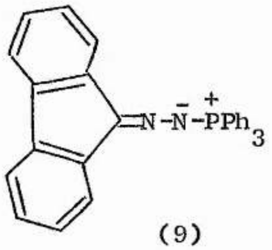
An almost quantitative yield of diazocyclopentadiene was recovered after it had been heated under reflux in pyridine for twenty-four hours[34].

No ylide was isolated when diazocyclopentadiene was decomposed in the presence of triphenylarsine or diphenylsulphide. A large amount of intractable decomposition products were obtained.

Attempted catalytic decomposition of diazocyclopentadiene using copper-bronze in triphenylarsine also gave only intractable products.

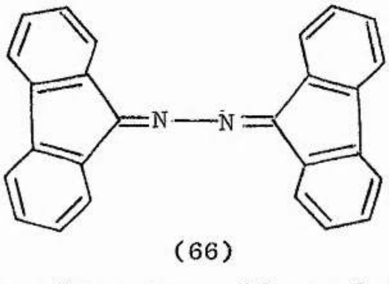
(v) DIAZOFLUORENE

When diazofluorene was heated in a melt with triphenylphosphine it gave a high yield of the phosphazine (9), which had been previously prepared[15].



(9)

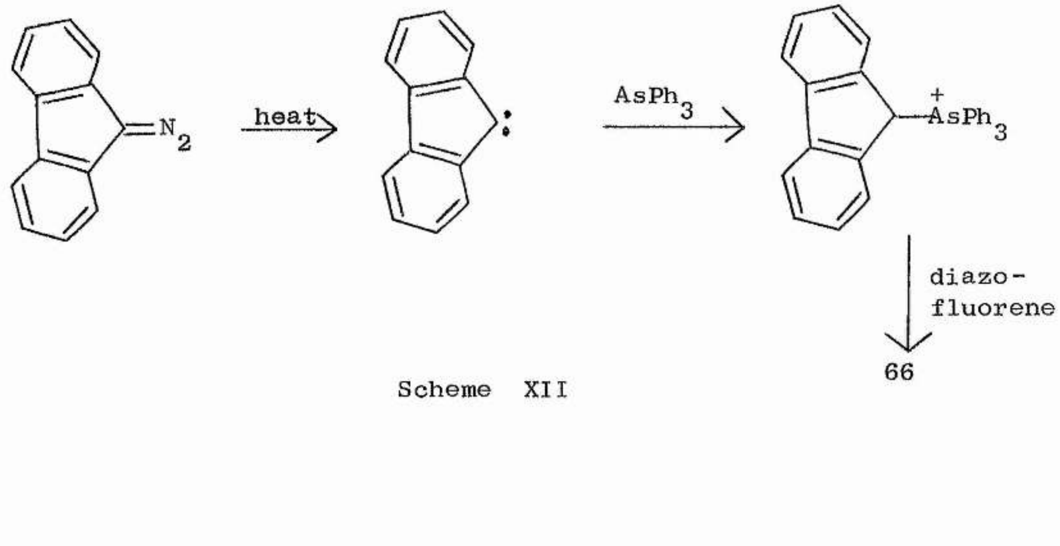
When diazofluorene was heated in a melt with either triphenylarsine or diphenylsulphide, the product isolated was fluorenone ketazine (66).



(66)

In neither case was there any evidence for the formation of the expected arsonium or sulphonium ylide.

It seemed possible that the fluorenone ketazine was formed by reaction of the ylide with further diazofluorene (scheme XII).

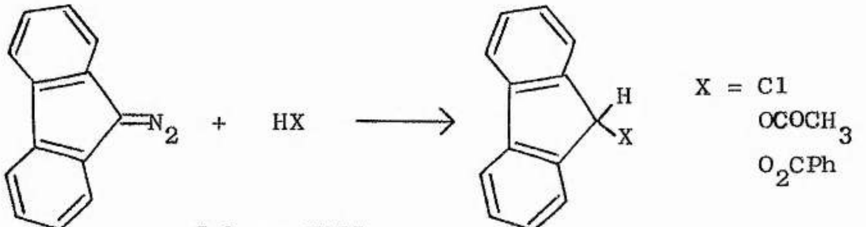


Scheme XII

It has since been shown[73], in this laboratory, that triphenylarsoniumfluorenylide will react with diazofluorene in solution at room temperature, to give an almost quantitative yield of fluorenone ketazine.

(vi) REACTIONS OF DIAZOCYCLOPENTADIENES WITH ACIDS

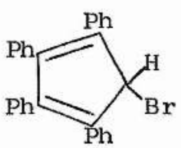
Staudinger first reported in 1916[74] that the reaction between diazofluorene and various acids gave the appropriate 9-substituted derivatives (scheme XIII).



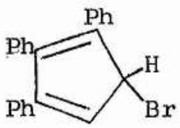
Scheme XIII

5-Bromo-1,2,3,4-tetraphenylcyclopentadiene and 5-bromo-1,2,3-triphenylcyclopentadiene are both useful intermediates for the preparation of ylides by the salt method (see Part 1) and are normally prepared by reaction of the respective phenylated cyclopentadienes with N-bromosuccinimide[34,75]. Since the preparation of both 2,3,4,5-tetraphenyl- and 2,3,4-triphenyl-diazocyclopentadienes is less tedious than the preparation of the respective phenylated cyclopentadienes (see Part 2, I (ii)), the preparation of the 5-bromo derivatives could be simplified if they could be obtained directly from the diazo compounds.

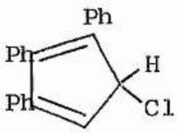
The reaction between 2,3,4,5-tetraphenyldiazocyclopentadiene and hydrogen bromide was carried out in ether solution at room temperature and a high yield of 5-bromo-1,2,3,4-tetraphenylcyclopentadiene (67) was obtained.



(67)

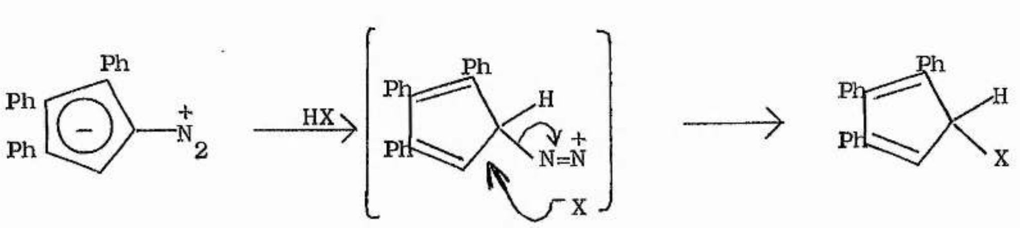


(68)



(69)

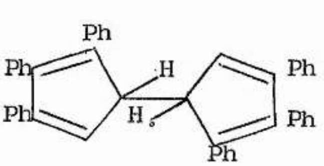
Under the same conditions 2,3,4-triphenyldiazocyclopentadiene provided 5-bromo-1,2,3-triphenylcyclopentadiene (68) in 52% yield. With hydrogen chloride a 64% yield of 5-chloro-1,2,3-triphenylcyclopentadiene (69) was obtained. The reaction mechanism in these cases is assumed to proceed by nucleophilic substitution rather than via a carbene (scheme XIV)



Scheme XIV

A possible alternative mechanism is via a cyclopentadienyl radical and a bromonium radical.

In an attempt to provide a better leaving group at position 5, 2,3,4-triphenyldiazocyclopentadiene was treated with hydrogen iodide. The only product obtained was 1,2,3,1',2',3'-hexaphenyl-5,5'-dihydrofulvalene (70)



(70)

The dihydrofulvalene had been previously prepared by Pauson and Williams[76].

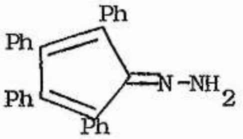
(vi) SURVEY OF REACTIONS OF DIAZOCYCLOPENTADIENES

All the diazocyclopentadienes used in these investigations did not decompose below a specific decomposition temperature. No reaction was observed, for example, when 2,3,4-triphenyldiazocyclopentadiene was heated for 7 hours with methylphenylsulphide at 90-100°C, and the diazo-compound could be recovered in good yield.

Better results were obtained in the melt reactions by plunging the solid mixture or suspension into a preheated bath, rather than by heating the mixture slowly to the required temperature, which was normally about 150°C. Kaiser et al[77] found a similar effect when decomposing ethyldiazoacetate with α-methylstyrene. In that case, a greater yield was obtained by adding the reactants to refluxing xylene than by mixing the olefin and diazo-compound at 0°C and heating slowly. The effect must presumably be due to the suppression of competing side reactions or decomposition which takes place during the slow heating process. These side reactions probably take place at temperatures just below the diazo decomposition temperature.

Nearly all the diazocyclopentadienes used, reacted under melt conditions with triphenylphosphine to give a certain amount of the respective triphenylphosphonium ylide. The yield from the reaction is higher when the cyclopentadiene part of the molecule is more crowded, especially at the 2 and 5 positions. The steric crowding will hinder nucleophilic attack by the bulky triphenylphosphine to form a phosphazine and thus allows the competing decomposition of the diazocyclopentadiene to proceed smoothly to form the intermediate carbene. The higher temperatures or longer periods of heating required, when the reaction proceeds via a phosphazine, causes greater amounts of intractable decomposition products to be formed.

Singer[34] provided evidence that steric crowding hinders phosphazine formation by reacting 2,3,4,5-tetraphenyldiazocyclopentadiene with the less bulky tri-n-butylphosphine. Although the phosphazine itself was not isolated from this reaction the hydrazone (71) which was isolated was presumed to have been formed by hydrolysis of the phosphazine; such hydrolyses are well established.

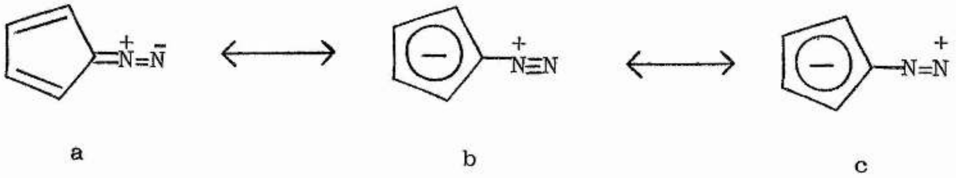


(71)

However, since tri-n-butylphosphine is also much more nucleophilic than triphenylphosphine, possible electronic factors cannot be discounted.

If steric factors are of major importance, it would be expected that 2-methyl-3,4,5-triphenyldiazocyclopentadiene and 2,5-dimethyl-3,4-diphenyldiazocyclopentadiene would form phosphazines under forcing conditions, especially when the ease of formation of the phosphazine from 2,3,4-triphenyldiazocyclopentadiene is considered. In fact, neither compound forms a phosphazine. However, both 2-chloro- and 2-bromo-3,4,5-triphenyldiazocyclopentadienes form phosphazines under forcing conditions[34]. The inductive electron-donating effect of the alkyl groups will hinder nucleophilic attack by the triphenylphosphine, whereas the electron-withdrawing effects of the halogen atoms will facilitate nucleophilic attack.

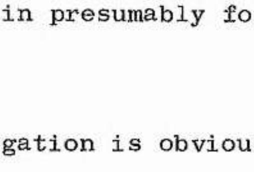
If one considers the resonance canonical forms of diazocyclopentadiene (scheme XV), two effects are apparent.



Scheme XV

An electron-donating group will tend to result in a greater contribution from form (a), thus hindering nucleophilic attack on the nitrogen atom and strengthening the C-N bond so that nitrogen will be lost less readily. An electron-withdrawing group will have an opposite effect. From the evidence above it appears that the hindering or facilitating of nucleophilic attack is the overriding electronic effect.

In order to provide further evidence to support this argument, an attempt was made to nitrate 2,3,4-triphenyldiazocyclopentadiene and to react the product with triphenylphosphine. Although, after the nitration, only a small amount of impure diazo-compound was obtained, it reacted with triphenylphosphine in solution to give the hydrazone (72)

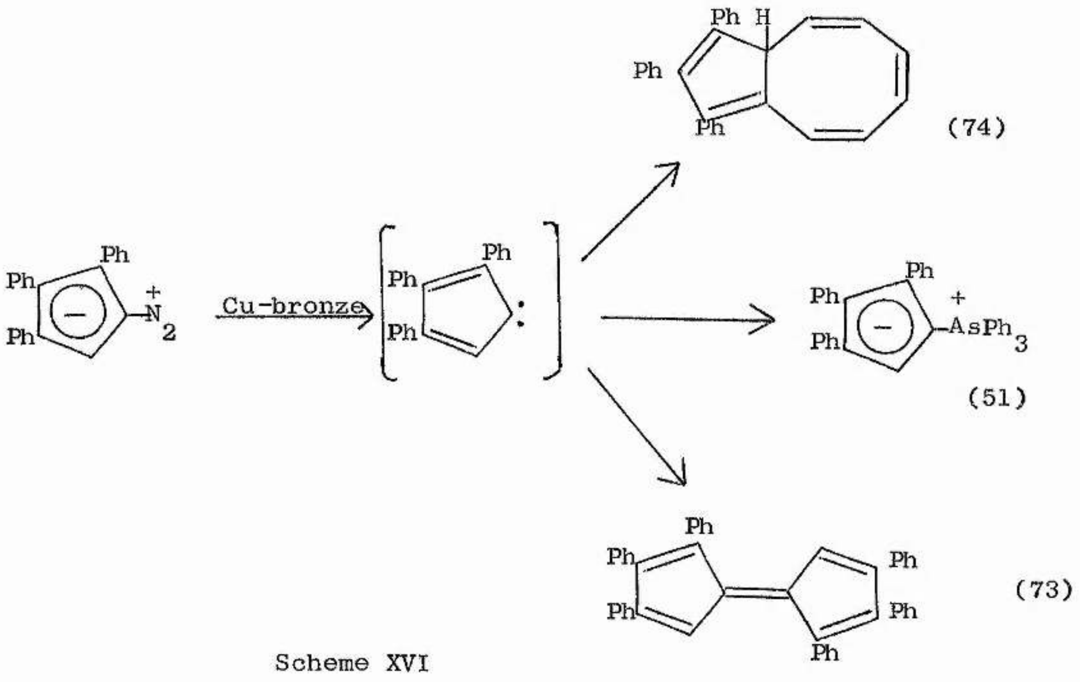


(72)

The hydrazone was again presumably formed by the hydrolysis of the phosphazine.

Further investigation is obviously required to provide a fuller explanation, but the evidence presently available seems to show that for phosphazine formation both lack of steric hindrance to the approaching triphenylphosphine and the absence of any electron-donating group on the cyclopentadiene is required. A series of reactions using para-substituted tetraaryldiazocyclopentadienes and possibly para-substituted triarylphosphines might clarify the problem.

The use of copper-bronze as a catalyst for the decomposition of diazocyclopentadienes has been shown to be very useful for the preparation of both arsonium and sulphonium cyclopentadienylides. Only a limited number of reactions using this catalyst were studied. One particularly interesting reaction was the decomposition of 2,3,4-triphenyldiazocyclopentadiene in a refluxing benzene solution of triphenylarsine and in the presence of copper-bronze. This reaction gave a good yield of the triphenylarsonium ylide (51). This demonstrates that the carbene or carbenoid formed, certainly with copper-bronze as a catalyst, is a reasonably stable reactive intermediate and that it reacts preferentially with triphenylarsine rather than either with benzene or with itself (scheme XVI)

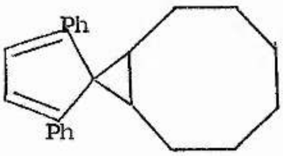


Scheme XVI

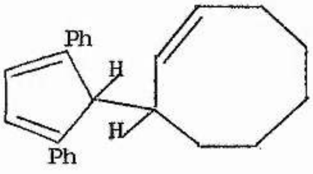
2,3,4-Triphenyldiazocyclopentadiene has been decomposed in refluxing ethanol to give the fulvalene (73)[76], and photolytic decomposition of the same diazo-compound in benzene gave the product (74)[78].

Dalton and Liebmann[71] found, by e.s.r. studies on the thermal decomposition of diazo-compounds, that the ratio of products depended on the inherent stability of the intermediate carbene formed. It seems possible that the cyclopentadienylidene carbenes are reasonably stable intermediates and therefore it is not unreasonable that they may rearrange before further reaction, as in the reaction between 2,5-diphenyldiazocyclopentadiene and triphenylarsine. This may also explain why some diazocyclopentadienes give only very small or no yields of ylides when they are decomposed in the presence of various heteronium nucleophiles. In these cases the preferential reaction of the carbene may not lead to ylide formation.

When 2,5-diphenyldiazocyclopentadiene was decomposed in cyclooctene it gave normal addition products, probably a mixture of isomers (75) and (76)



(75)



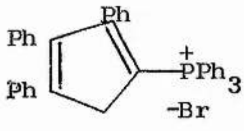
(76)

The molecular ion peak for the crude solid product was correct for either of these two compounds.

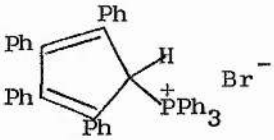
The photolysis of tetraphenyldiazocyclopentadiene with cycloheptene gave similar products[79].

III SALT METHOD FOR THE PREPARATION OF CYCLOPENTADIENYLIDES

Lloyd and Singer[34] found that 5-bromo-1,2,3-triphenylcyclopentadiene and 5-bromo-1,2,3,4-tetraphenylcyclopentadiene reacted with triphenylphosphine under melt conditions to give high yields of the ylide salts (77) and (78)



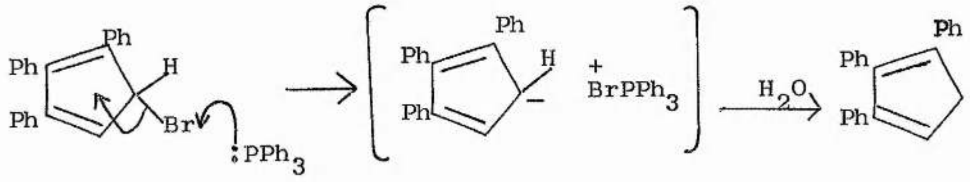
(77)



(78)

Gagan and Lloyd[47] found that this reaction worked equally well for 1-methyl-, 1-ethyl- and 1-benzyl-5-bromo-2,3,4-triphenylcyclopentadienes.

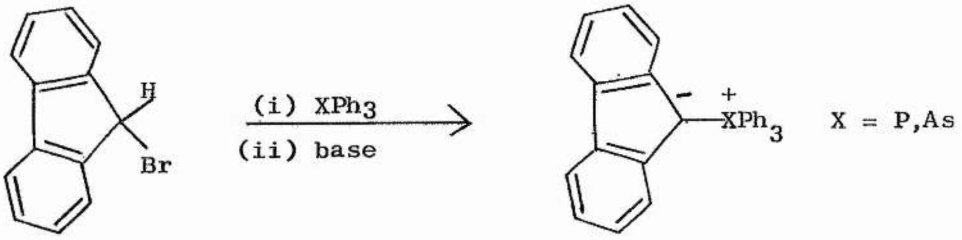
In all cases when the two reactants were heated together in nitromethane solution, the only product obtained in good yield was the cyclopentadiene itself. It was suggested[34] that the triphenylphosphine attacked not the carbon atom but the bromine, giving an intermediate carbanion which gained a proton from the solvent or from water in the solvent to give the cyclopentadiene (scheme XVII)



Scheme XVII

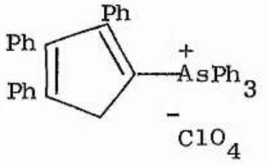
When triphenylarsine was used no reaction took place under melt conditions, presumably due to the low nucleophilicity of triphenylarsine. Singer[34] also found that no reaction took place in refluxing nitromethane.

Since the salt method had been used in nitromethane solution to prepare both the triphenylphosphonium-[24] and triphenylarsonium-[26] fluorenylides (scheme XVIII), the reaction was reinvestigated.



Scheme XVIII

It was found that when a solution of 5-bromo-1,2,3-triphenylcyclopentadiene and triphenylarsine in nitromethane was stirred at room temperature for 40 hours, the ylide salt (79) could be isolated as the perchlorate in 40% yield



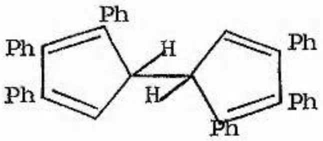
(79)

There was no evidence that any diene was formed in the reaction. However, when triphenylphosphine was employed under identical conditions, a 70% yield of the cyclopentadiene was again obtained.

It would seem that the more nucleophilic triphenylphosphine attacks the bromine atom in a rapid reaction, thus forming the diene in solution, whereas the triphenylarsine is not sufficiently nucleophilic to attack the bromine atom but will undergo normal nucleophilic substitution in a slow process. The phosphonium bromide salt (77) was found to be stable in nitromethane solution showing that this was not an intermediate in the diene formation.

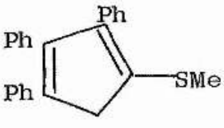
Methylphenylsulphide and benzylmethylsulphide did not react with

5-bromo-1,2,3-triphenylcyclopentadiene when mixtures of the reactants were heated together in a melt. However, when the bromo-compound and benzylmethylsulphide were heated together in refluxing nitromethane, a 50% yield of the dihydrofulvalene (70) was obtained. The same reactants in nitromethane at room temperature appeared to undergo little or no reaction.

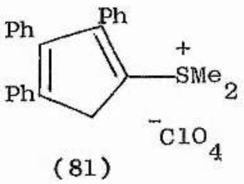


(70)

When 5-bromo-1,2,3-triphenylcyclopentadiene was heated in excess refluxing dimethylsulphide, yet another different and surprising product was obtained, namely 1-methylthio-2,3,4-triphenylcyclopentadiene (80)



(80)



(81)

At room temperature in nitromethane, dimethylsulphide reacted with the bromo-compound to give the ylide salt, isolated as the perchlorate (81) in very low yield. The mass spectrum of the perchlorate (81) showed a large m/e peak at 340, which corresponds to the thioether (80) cation. It is probable that the bromide salt was formed initially in both cases but decomposed thermally to give the thioether (80) and methyl bromide.

The ylide salts (77), (78) and (79) have all been converted into the respective ylides by treatment with base[34].

Although the reactions of bromocyclopentadienes seem to be very varied it appears that some triphenylphosphonium-, triphenylarsonium- and possible some dialkylsulphonium-cyclopentadienylides can be prepared using the salt method.

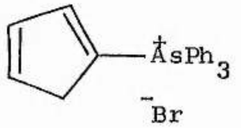
IV REACTIONS OF TRIPHENYLARSINE OXIDE AND SULPHOXIDES

The condensation reaction between cyclopentadienes and sulphoxides[36] or arsine oxides[37] failed to provide a large number of new cyclopentadienylides.

1,4-Diphenylcyclopentadiene reacted with triphenylarsine oxide in triethylamine, using phosphorus pentoxide as catalyst, to give a good yield of triphenylarsonium-2,4-diphenylcyclopentadienylide (59). This ylide was also prepared by the 'diazo method' (see Part 2, II (iii)).

In the cases of fluorene, 1,2,4-triphenylcyclopentadiene and 1-benzyl-2,3,4-triphenylcyclopentadiene very little or no reaction was observed with triphenylarsine oxide, in acetic anhydride or in triethylamine and phosphorus pentoxide. Little or no reaction appeared to take place between cyclopentadiene itself and triphenylarsine oxide in triethylamine and phosphorus pentoxide.

It has been reported[80] that cyclopentadienyl magnesium bromide reacted with triphenylarsine oxide and, after treatment with hydrobromic acid, gave a quantitative yield of the arsonium ylide salt (82)



(82)

Attempts to repeat this reaction failed to give any of the reported product. Present work indicated that the main product obtained by Nesmeyanov et al contained ethyl groups; the time allowed for the exchange Grignard reaction between ethyl magnesium bromide and cyclopentadiene in the Russian work was in fact much too short to permit complete exchange to have taken place.

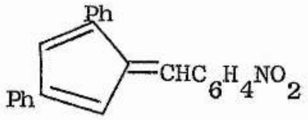
The reaction between cyclopentadienyl lithium and triphenylarsine oxide in both ether and tetrahydrofuran solutions was also investigated. In both cases some reaction appeared to occur but no pure product was isolated. Some product was obtained which from its n.m.r. spectrum appeared to contain some small amount of the expected ylide.

Attempted condensations of methylphenylsulphoxide or dimethylsulphoxide with 1,2,3-triphenylcyclopentadiene were also unsuccessful despite the use of all the usual catalysts for these reactions. Formation of the cyclopentadienyl salt before reaction with the sulphoxide also failed to give any ylide as product.

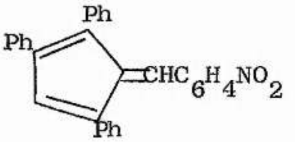
V REACTIONS OF CYCLOPENTADIENYLIDES

(i) WITTIG REACTION

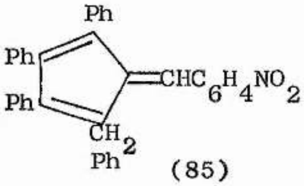
All the triphenylarsonium cyclopentadienylides reacted with p-nitrobenzaldehyde to give good yields of the expected fulvenes. Fulvenes (83), (84) and (85) were prepared by this method.



(83)



(84)



(85)

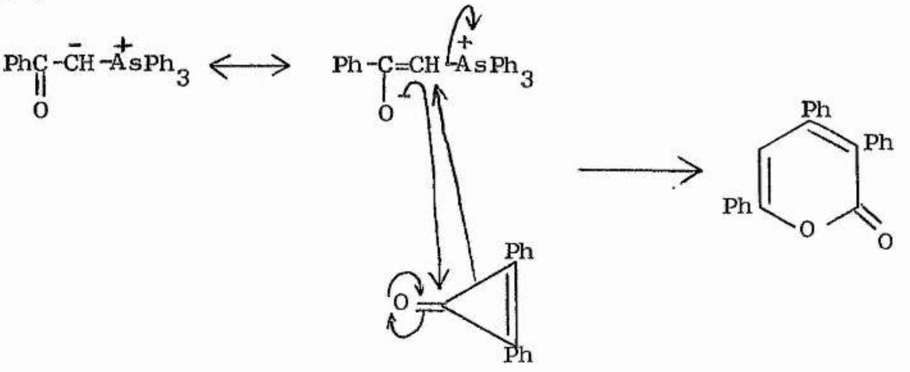
These fulvenes, all red-orange in colour, gave correct molecular ion peaks in their mass spectra.

The triphenylphosphonium cyclopentadienylides did not react with p-nitrobenzaldehyde even after they had been heated in refluxing carbon tetrachloride for several hours.

These results conform with the findings of Lloyd and Singer[34,54] who explained the difference in reactivity in terms of the effectiveness of d_π-p_π overlap in the carbon-heteroatom bond, suggesting that the order of effectiveness is $S > P > As > Sb$. The greater amount of d_π-p_π overlap in the C-P bond makes the ylide less nucleophilic and thus less reactive. No alternative explanation has been put forward.

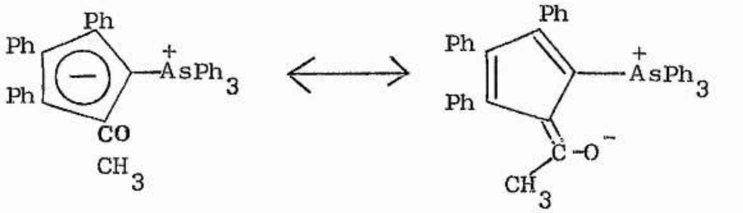
Diphenyltelluronium-2,3,4,5-tetraphenylcyclopentadienylide did not react with p-nitrobenzaldehyde after 18 hours in refluxing carbon tetrachloride, nor could any pure product be isolated when the ylide was heated with nitrosobenzene. Apparently decomposition superseded any reaction in both cases.

Unlike some other arsonium ylides prepared in this laboratory[73], triphenylarsonium-2,3,4-triphenylcyclopentadienylide did not react with diphenylcyclopropenone, even after several hours in refluxing benzene. Triphenylarsonium phenacylide and other β-carbonyl arsonium ylides have been reacted with diphenylcyclopropenone to give substituted pyrones[73] (scheme XIX)



Scheme XIX

It was hoped that triphenylarsonium-2-acetyl-3,4,5-triphenylcyclopentadienylide (86) might react by a similar mechanism to give a tropone derivative

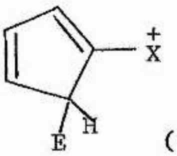


(86)

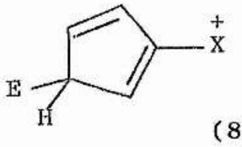
However no reaction was observed after the reactants had been heated under reflux in benzene or in nitromethane for several hours. The ylide (86) was recovered in almost quantiative yield.

(ii) ELECTROPHILIC SUBSTITUTION

By virtue of the high charge density on the five-membered ring cyclopentadienylides are prone to electrophilic attack. This attack occurs preferentially at the 2(5)-position since the transition stage for this reaction is linearly conjugated (87), whereas, for reaction at the 3(4)-position the transition stage must be cross-conjugated (88)



(87)

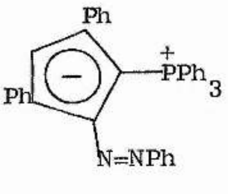


(88)

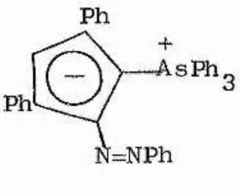
This suggests that electrophilic substitution may take place at any site in the five-membered ring but that reaction at the 2(5)-position is preferred.

(a) Diazo coupling

Triphenylphosphonium- and triphenylarsonium-2,4-diphenylcyclopentadienylides both reacted with benzene diazonium chloride to give the 2-phenylazo-derivatives (89) and (90)



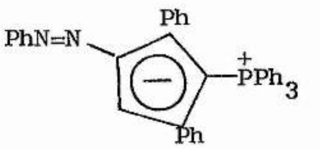
(89)

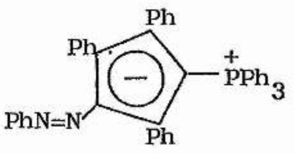


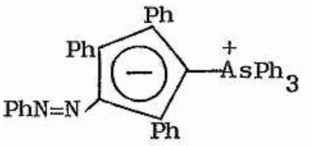
(90)

These red crystalline solids have very similar electronic spectra ($\lambda_{max} \sim 480$ mμ). They are both stable high melting solids and could be purified by recrystallisation. Both ylides (89) and (90) gave correct molecular ion peaks in their mass spectra.

The 3-phenylazo derivatives (91), (92) and (93) were all obtained by reaction of the respective ylides with benzene diazonium chloride


(91)


(92)

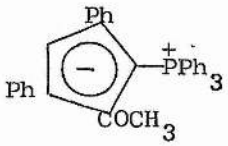

(93)

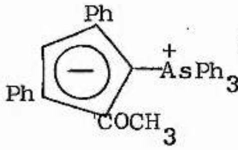
These red-orange crystalline solids have maxima in the visible region at lower wavelength than the 2-phenylazo compounds. They are again stable, fairly high melting solids which give molecular ion peaks in their mass spectra.

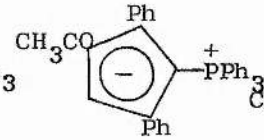
Although the above ylides all readily reacted with benzene diazonium chloride to give monosubstituted products, reaction occurred, where possible, at the 2(5)-position.

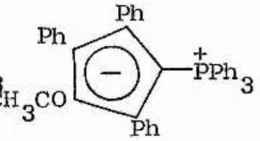
(b) Acetylation

Triphenylphosphonium- and triphenylarsonium-2,4,-diphenylcyclopentadienylide, triphenylphosphonium-2,5-diphenylcyclopentadienylide and triphenylphosphonium-2,3,5-triphenylcyclopentadienylide all reacted with acetic anhydride to give, respectively, the acetyl derivatives (94), (95), (96) and (97)

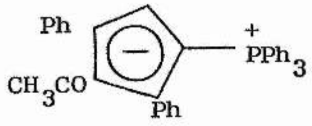

(94)


(95)


(96)


(97)

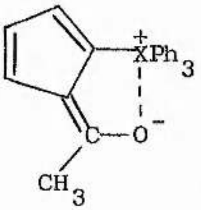
All the ylides(94-97) were isolated by column chromatography as pale coloured solids. The n.m.r. spectrum of (94) showed that it was not pure but also contained about 25% of the 3-acetyl derivative (98)



(98)

The arsonium ylide (95) defied all attempts at purification, but the n.m.r. spectrum of the impure ylide had only a single peak for the acetyl protons, showing that it was not contaminated by the 3-acetyl isomer. Ylides (96) and (97) both gave single peaks for the acetyl protons.

The infra-red spectra of the 3(4)-acetyl ylides (96) and (97) had carbonyl absorption peaks at about 1640 cm^{-1}, whereas the 2(5)-acetyl ylides (94) and (95) absorbed in the range 1560-70 cm^{-1}. Ylide (98), as an impurity in the sample of ylide (94), gave a carbonyl absorption at about 1625 cm^{-1}. The polarisation of the carbon-oxygen bond in these compounds is exaggerated even further when the carbonyl group is in close proximity to the hetero-atom, presumably by interaction between the positive hetero-atom and the negative oxygen in canonical structure (99)



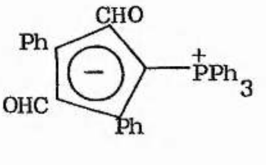
(99)

The pure acetyl derivatives appear to be stable although slight darkening occurs in the presence of light and air.

Attempted acetylation of triphenylarsonium-2,3,5-triphenylcyclopentadienylide failed to give any isolable product.

(c) Formylation

Triphenylphosphonium-2,4-diphenylcyclopentadienylide was formylated by reaction with phosphorus oxychloride in dimethylformamide and subsequent basification. The product was the diformylated ylide (100)

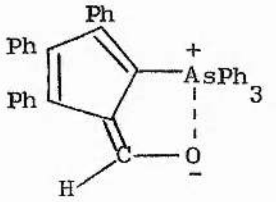


(100)

This ylide was a stable pale yellow solid. Its infra-red spectrum showed carbonyl absorptions at 1620 cm^{-1} and 1640 cm^{-1}. Its n.m.r. spectrum in deuteriochloroform showed the formyl protons at 0.60τ and 0.80τ. Each peak was split into a doublet ($J \sim 1c/s$), probably by long range coupling of the two formyl protons. The ylide was high melting and gave a correct molecular ion peak in its mass spectrum.

Attempted formylation of triphenylarsonium-2,3,5-triphenylcyclopentadienylide gave an impure product which could not be obtained pure by column chromatography. The bright yellow product obtained gave a peak at 3400 cm^{-1} on the infra-red spectrum apparently due to a hydroxyl group and a very broad carbonyl absorption at 1590-1630 cm^{-1}. The mass spectrum of this solid gave a molecular ion peak for the expected formylated product but the major peaks were at m/e 376 and below. A peak at 0.35τ on the n.m.r. spectrum may be due to the formyl proton. It seems possible from the infra-red spectrum that some hydrolysis of the product has taken place. Electron-withdrawal by the carbonyl group would make the arsenic more electropositive and thus more prone to hydrolysis. This would also explain why it was not possible to isolate the acetyl derivative of the same ylide.

In contrast, the triphenylarsonium-2-acetyl-3,4,5-triphenylcyclopentadienylide made by Singer[34] is stable. This may be due to the interaction between the positive arsenic and the negative oxygen in canonical structure (101)



(101)

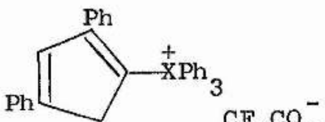
Such interaction is not possible for the 2,3,5-triphenyl isomer and may account for the different stabilities of the two isomers.

Attempted formylation of triphenylarsonium-2,4-diphenylcyclopentadienylide also gave an impure product. In this case there was no evidence for any hydrolysis of the product having taken place.

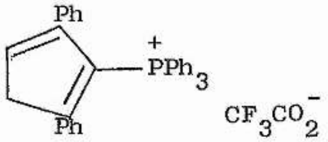
(d) Protonation

Although crystalline salts were not isolated, protonation of the cyclopentadienylides was shown to take place by their n.m.r. spectra in trifluoroacetic acid.

Addition of a few drops of trifluoroacetic acid to triphenylphosphonium- or triphenylarsonium-2,4-diphenylcyclopentadienylides in deuteriochloroform gave, in both cases, a peak at about 6.1τ due to the methylene group in structure (102).



(102)



(103)

Similar treatment of triphenylphosphonium-2,5-diphenylcyclopentadienylide also gave a methylene peak indicating that protonation takes place at the 3(4)-position (103) in this case.

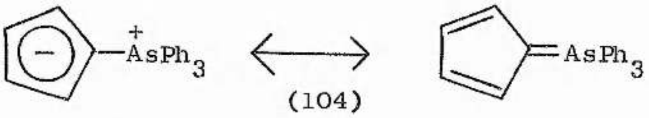
The n.m.r. spectra of solutions of triphenylphosphonium- or triphenylarsonium-2,3,5-triphenylcyclopentadienylides, when treated with trifluoroacetic acid, did not have a methylene peak, indicating that protonation does not take place at the 3(4)-positions in these cases.

VI UNSUBSTITUTED ARSONIUM CYCLOPENTADIENYLIDES

(a) Preparation and Properties

Various cyclopentadienylides unsubstituted in the five-membered ring have been prepared by reaction of suitable nucleophiles with dibromocyclopentene and subsequent basification of the salt formed (see Part I).

The arsonium cyclopentadienylide (104) has now been prepared by keeping a solution of dibromocyclopentene and triphenylarsine at room temperature for ten days and treating the cyclopentene bis-arsonium salt so obtained with base



(104)

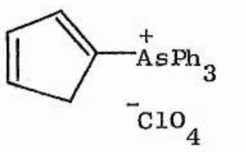
If the initial reactants were heated together in a solvent, as in the preparation of the phosphonium analogue, none or almost none of the ylide was obtained.

The spectra (u.v., i.r., and n.m.r.) of the ylide (104) closely resemble those of the phosphonium analogue. The ylide is colourless when freshly prepared but slowly reddens on exposure to light and air or on attempted recrystallisation.

The n.m.r. spectrum of a solution in deuteriochloroform shows no change when the solution is shaken with deuterium oxide but addition of a few drops of trifluoroacetic acid causes the complete disappearance of the signals due to the hydrogen atoms on the five-membered ring, thus showing that each position in this ring is readily deuteriated (or protonated) in strong acid. Addition of a few drops of deuterioethanol also causes a slow decrease in the intensity of these signals together with an increase in the signal due to the hydroxyl group.

(b) Reactions

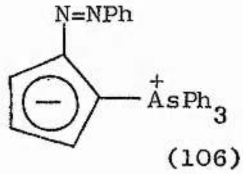
The ylide (104) is soluble in mineral acid. Addition of perchloric acid followed by ether to a solution of the ylide in acetic acid precipitated the crystalline perchlorate (105)



(105)

The n.m.r. spectrum of the perchlorate (105) had a broad singlet at 6.4τ due to the methylene group.

The five-membered ring is thus susceptible to electrophilic attack. This was further shown by its coupling reaction with benzene diazonium chloride. The product had u.v. and n.m.r. spectra closely resembling those of the product obtained analogously from the phosphonium ylide[58]. The phosphonium compound was shown conclusively to have undergone reaction at the 2-position and the product from ylide (104) was assumed therefore to have structure (106)



(106)

As before electrophilic substitution occurs preferentially at the 2(5)-position.

Bromination, nitration and acylation of ylide (104) were also investigated but, although reaction obviously ensued in each case, no single pure products were obtained.

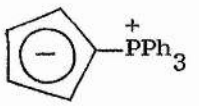
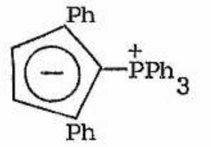
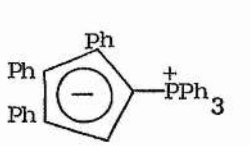
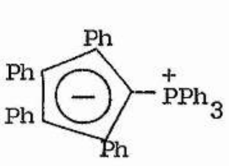
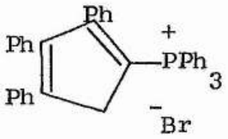
The ylide (104) reacted with p-nitrobenzaldehyde to give a high yield of triphenylarsine oxide and a small amount of triphenylarsine, but the fulvene which was assumed to be formed apparently reacted further, possibly by dimerisation, to give two presently uncharacterised products. Both of these products, however, gave large peaks in their mass spectra at m/e-199 which is the molecular weight of the expected fulvene. Similar results were obtained with benzaldehyde and cinnamaldehyde.

Tri-p-tolyl- and tri-p-anisylarsoniumcyclopentadienylides were also prepared in a similar fashion and had similar properties.

VII PHOSPHORUS-31 N.M.R. SPECTRA

A study of ^{31}P n.m.r. chemical shifts of a series of ylides might have been expected to shed light on the electron density about the phosphonium atom.

The ^{31}P n.m.r. spectra of some phosphonium cyclopentadienylides were recorded and the results obtained are shown in the table below.

YLIDE	CHEMICAL SHIFT
	- 12.8
	- 11.2
	- 13.7
	- 11.7
	- 12.9
Ph_3P	+ 5.5

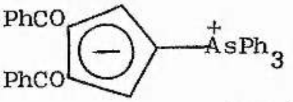
The chemical shifts are shown with reference to phosphoric acid and the solvent used in all cases was methylene chloride.

There appears to be little change in chemical shift with the number of phenyl groups attached to the cyclopentadiene nucleus. There is , however, greater shielding of the phosphorus atom when phenyl groups are in both the 2 and 5 positions. The bromide salt has a similar chemical shift to the ylide itself, a situation identical to that reported by Speziale and Ratts[81] for their β-ketophosphonium ylides. This result implies that the electron density on the phosphorus atom is the same in each case and infers that there is little, if any, p_{π}-d_{π} bonding in the P-C bond of the ylide. From all other evidence this is not the case and an alternative explanation of the ^{31}P n.m.r. results is needed, but has not yet been provided.

VIII MISCELLANEOUS REACTIONS

(a) Attempted preparation of a phosphonium ylide using triphenylphosphine oxide.

3,4-Dibenzoylcyclopentadiene reacted very readily with triphenylarsine oxide[37] in acetic anhydride to give a high yield of triphenylarsonium-3,4-dibenzoylcyclopentadienylide (107)

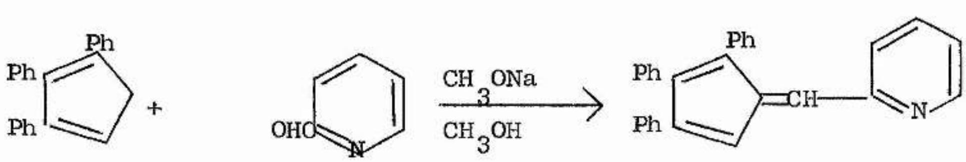


(107)

Under similar conditions, but with a longer reaction time, triphenylphosphine oxide gave no reaction. Obviously, in this case, the strength of the P-O bond is too high for reaction to occur.

(b) Preparation of a 6-pyridyl fulvene.

The condensation reaction between pyridine-2-aldehyde and 1,2,3-triphenylcyclopentadiene occurred under normal conditions and a 88% yield of the fulvene was obtained (scheme XX)



Scheme XX

IX FURTHER STUDIES IN CYCLOPENTADIENYLIDE CHEMISTRY

The results described in the previous pages suggest further work which could be carried out on these cyclopentadiene derivatives. Some of the possible extensions of the work are now discussed briefly.

(i) Physical Studies

Mass spectral data of the cyclopentadienylides could be used to correlate the strength of the carbon-hetero-atom bond. The primary breakdown of these ylides is the breaking of the carbon-hetero-atom bond giving the hetero-atom containing portion as a positive fragment. The simple ratio of molecular ion peak height to the m/e peak height for the hetero-atom moiety should give a relative measure of the strength of the bond. These results might be correlated with dipole moment or pK_a values.

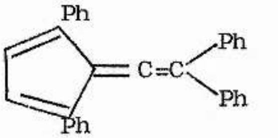
Variable temperature n.m.r. spectra of unsymmetric methylphenylsulphonium cyclopentadienylides, only briefly investigated in this present work, would be very useful for a study of the bonding in the C-S bond. The amount of free rotation about the C-S bond must be due to the contribution of the charged single bond canonical form. When the molecule is cooled it would be expected to 'freeze' into the covalent forms and give two peaks for the S-methyl protons in the two possible geometric isomers. The variation of the spectra with temperature should thus provide information about the C-S bonding.

X-ray studies on some cyclopentadienylides prepared are being undertaken by Professor Ferguson at the University of Guelph, Ontario.

(ii) Chemical Studies

Further studies of various catalysts for the decomposition of diazocyclopentadienes may provide many more cyclopentadienylides. The copper-bronze catalysed reaction, having been noted only at a late date, was all too briefly studied in this present work. In particular, the preparation of sulphonium cyclopentadienylides may be facilitated by the use of catalysts and this method could provide the ylides required for the variable temperature n.m.r. work suggested above.

Difficulty has been experienced in judging the reactivity of the various phosphonium cyclopentadienylides in the Wittig reaction. They do not react with p-nitrobenzaldehyde or with nitrosobenzene[54]. Various stable phosphonium ylides have been found to react with ketenes[82-4]. When triphenylphosphonium-2,5-diphenylcyclopentadienylide was reacted with diphenylketene, a low yield of the allene (108) was obtained



(108)

This red compound gave a correct molecular ion peak in the mass spectrum and a complex peak at 1910 cm^{-1} on the infra-red spectrum.

Further studies of this type of reaction and investigation of the properties of the allenes formed may give many interesting results.

PART 3

EXPERIMENTAL

I MATERIALS AND APPARATUS

Ultra-violet and visible spectra were measured with a Unicam S.P. 800 instrument.

Infra-red spectra were obtained with a Perkin-Elmer 257 instrument.

N.m.r. spectra were carried out on a Perkin-Elmer R10 spectrometer operating at 60 Mc/sec or a Varian HA100 spectrometer operating at 100 Mc/sec.

Microanalyses were carried out by Mr. J.R. Bews in the Department of Chemistry at St. Andrews University.

Mass spectra were recorded and molecular weights determined on an A.E.I., M.S.902 instrument.

Column chromatography was carried out on either activated alumina, Type H 100/200 mesh or silica gel, Grade M.60.

Thin layer chromatography was done on silica (M.N. Kieselgel G) coated plates.

Samples analysed by means of molecular weight determinations were pure (t.l.c., spectra) unless otherwise indicated.

Light petroleum refers to light petroleum boiling in the range 40-60°C.

II PREPARATION OF CYCLOPENTADIENES

(i) 1,2,4-Triphenylcyclopentadiene

3,4-Diphenylcyclopent-2-en-1-one (17.6 g) in dry benzene (250 ml) was added slowly to phenyl magnesium bromide, prepared from bromobenzene (13.25 g) and magnesium (2.0 g), in refluxing ether (250 ml). After addition was complete, the mixture was heated under reflux for a further ½-hr. The reaction mixture was then poured into a solution of conc. hydrochloric acid (230 ml) in ethanol (400 ml). The single phase system was stirred at room temperature for 12 hr. and then evaporated until a precipitate began to form. The mixture was well cooled and filtered and the filtrate was extracted with benzene (3 x 200 ml). The extract was washed with water, aqueous sodium bisulphite and again with water. It was then dried ($CaCl_2$) and the solvent evaporated. The residue was triturated with ethanol. 1,2,4-Triphenylcyclopentadiene (20.0 g, 90%) was obtained as pale yellow needles, m.p. 148-9°C (lit. 149°C[65]) from ethanol. The product did not depress the melting point of an authentic sample.

(ii) 4-Benzyl-1,2-diphenylcyclopentadiene

The above procedure was followed starting from 3,4-diphenylcyclopent-2-en-1-one (7.55 g) and benzyl chloride (7.0 g). The diene was obtained from the evaporated benzene extract by trituration with acetonitrile. 4-Benzyl-1,2-diphenylcyclopentadiene (3.8 g, 38%) was obtained as pale yellow crystals, m.p. 175-6°C from acetonitrile.
(Found C, 93.3; H, 6.7. $C_{24}H_{20}$ requires C, 93.5; H, 6.5%)

(iii) 4-Methyl-1,2-diphenylcyclopentadiene

The same procedure was used, starting from 3,4-diphenylcyclopent-2-en-1-one (3.37 g) and methyl iodide (2.9 g) , and yielded 4-methyl-1,2-diphenylcyclopentadiene, recrystallised from acetonitrile as pale yellow crystals (2.06 g, 62%), m.p. 76-7°C (lit. 78-82°C[64])

(iv) 1,2,3-Triphenyl-4-p-tolylcyclopentadiene

The above procedure was followed, starting from 2,3,4-triphenylcyclopent-2-en-1-one (11.7 g) and p-bromotoluene (7.22 g). The evaporated benzene extract was taken up again in the minimum amount of benzene and applied to a silica column, prepared with benzene-petroleum spirit (1:1). Benzene-petroleum spirit (1:1) eluted a yellow band which, when the solvents were removed, was triturated with methanol and recrystallised from methanol to give 1,2,3-triphenyl-4-p-tolylcyclopentadiene (2.9 g, 20%) as pale yellow crystals, m.p. 148-50°C. This cyclopentadiene was reacted with tosyl azide without further purification (see Part 3, III (i)).

(v) 1,4-Diethyl-2,3-diphenylcyclopentadiene

To a stirred solution of 2,5-diethyl-3,4-diphenylcyclopentadienone (0.844 g, 3 m.moles) in dry ether (60 ml), aluminium chloride (0.798 g, 6 m.moles) was added, followed by lithium aluminium hydride (0.228 g, 6 m.moles). The mixture was heated to reflux for 6 hr. The excess hydride was decomposed with dil. hydrochloric acid, and the mixture was extracted with ether and dried (Na_2SO_4). The solvent was removed to give the crude diene (0.72 g, $\sim$ 87%). All attempts to crystallise this diene were unsuccessful.

(v) Other Cyclopentadienes

1,4-Diphenylcyclopentadiene was prepared by the method of Drake and Adams[85].

1-Benzyl- and 1-methyl-2,3,4-triphenylcyclopentadienes were prepared, as previously, by the Grignard method[47].

1,2,3-Triphenylcyclopentadiene and 1,4-dimethyl-2,3-diphenylcyclopentadiene were prepared by the method of Bladon *et al*[63].

III PREPARATION AND ATTEMPTED PREPARATION OF DIAZOCYCLOPENTADIENES

(i) 2,3,4-Triphenyl-5-p-tolyldiazocyclopentadiene

The method of Regitz and Liedhegener[46] was used, but with a 3 hr. reaction time. The filtered product was recrystallised from acetonitrile to give 2,3,4-triphenyl-5-*p*-tolyldiazocyclopentadiene (65%), m.p. 142-3°C. (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%) ν_{max}(nujol)2070 cm^{-1} (diazo group)

(ii) 2,5-Dimethyl-3,4-diphenyldiazocyclopentadiene

1,4-Dimethyl-2,3,-diphenylcyclopentadiene (9.3 g) in dry benzene (100 ml) was added slowly to a solution of phenyl lithium, prepared from bromobenzene (12 ml) and lithium (1.5 g) in dry ether (100 ml), under a dry nitrogen atmosphere. The mixture was heated under reflux for 2 hr. and then tosyl azide (13.5 g) in ether (200 ml) was added during 1 hr. The mixture was stirred overnight and was then poured into water (400 ml). The organic layer was separated and combined with the benzene washings (2 x 200 ml) of the aqueous layer. The organic layer was dried (Na_2SO_4) and the solvent was removed. Trituration and recrystallisation of the residue with methanol gave 2,5-dimethyl-3,4-diphenyldiazocyclopentadiene (5.22 g; 51%), m.p. 105-6°C.

(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%) ν_{max} (nujol) 2080 cm^{-1} (diazo group)

This product was contaminated by a small amount of 1,4-dimethyl-2,3,-diphenylcyclopentadiene caused by recrystallisation of the compound from hot solvents.

(iii) Other diazocyclopentadienes

2,3,4-Triphenyldiazocyclopentadiene and 2,3,4,5-tetraphenyldiazocyclopentadiene were prepared as previously described via the tosyl hydrazone[47,45].

All other diazocyclopentadienes used were prepared as previously described via methods (i) or (ii).

(iv) Tosyl hydrazone of 3,4-diphenylcyclopent-2-en-4-ol-1-one

3,4-Diphenylcyclopent-2-en-4-ol-1-one (1.93 g) and tosyl hydrazine (1.7 g) were taken up in ethanol (100 ml) and the solution was heated under reflux for 5 hr. The precipitate from the cooled solution was filtered off and recrystallised from ethanol to give the tosyl hydrazone (2.29 g, 71%) as fine white needles, m.p. 200-1°C.

(Found, C, 69.2; H, 5.3; N, 6.5. $C_{24}H_{22}O_3N_2S$ requires C, 68.9; H, 5.3; N, 6.7%)

The product was identical with a sample prepared by the method of Rio and Charifi[69]

ν_{max} (nujol) -OH, 3390 cm^{-1}, -NH, 3210 cm^{-1}

All attempts to dehydrate the above product failed to give any tractable material. Dehydrating agents used were conc. hydrochloric acid-ethanol, conc. sulphuric acid-dry dioxan, conc. sulphuric acid-acetic anhydride and iodine-benzene.

(v) 2,5-Diethyl-3,4-diphenylcyclopentadienone oxime

Hydroxylamine hydrochloride (2.5 g) and sodium acetate (4.0 g) were dissolved in water (10 ml). 2,5-Diethyl-3,4-diphenylcyclopentadienone (7.35 g) in ethanol (40 ml) was added and the mixture was heated under

reflux for 4 hr. The solution was poured into water (100 ml) and extracted with chloroform (3 x 50 ml). The chloroform extract was washed with water, dried (Na_2SO_4) and the solvent was removed. The residue was dissolved in the minimum amount of benzene and applied to a silica column made up in light petroleum. The first band, eluted from the column by benzene-light petroleum (1:1), after removal of the solvents, gave unreacted starting material (0.77 g, 10.5%). A second band, eluted with benzene, gave, after removal of the solvent, 2,5-diethyl-3,4-diphenylcyclopentadienone oxime (5.46 g, 70%), recrystallised from ethanol as orange crystals, m.p. 172-3°C.
(Found C, 83.4; H, 7.2; N, 4.4. $C_{21}H_{21}NO$ requires C, 83.2; H, 6.9; N, 4.6%)

(vi) 2-Nitro-3,4,5-triphenyldiazocyclopentadiene

2,3,4-Triphenyldiazocyclopentadiene (3.82 g) was added to a cooled solution of silver nitrate (2.04 g) in acetonitrile (40 ml). A cooled solution of benzoyl chloride (1.69 g) in acetonitrile (10 ml) was added slowly, keeping the temperature $< 5^\circ C$. The solution was stirred at $< 5^\circ C$ for 2 hr., filtered, diluted with water and extracted with ether (3 x 30 ml). The ether extract was washed with water, dil. sodium carbonate solution and again with water and dried (Na_2SO_4). The solvent was removed and the residue was taken up in the minimum amount of benzene and applied to an alumina column. The product, after elution with benzene and removal of the solvent, was triturated with methanol to give 2-nitro-3,4,5-triphenyldiazocyclopentadiene (0.10 g, 2.3%) as a brown solid, m.p. 152-4°C. ν_{max} 2120 cm^{-1} (diazo group).

The product was not purified further but reacted immediately with triphenylphosphine (see V (iv)).

IV PREPARATION OF YLIDES FROM DIAZOCYCLOPENTADIENES AND FROM PHOSPHAZINES

Melt Reactions - General Procedure

(a) For solid nucleophiles

The diazo compound (2 m.mole) and the nucleophile (4 m.mole) were ground together as a powder. The mixture was placed in a reaction flask and flushed with oxygen-free nitrogen. It was then plunged into a preheated oil-bath and kept there until all the nitrogen had been evolved. The reaction could be followed by infra-red spectroscopy which showed the disappearance of the diazo absorption. Ether or ether-light petroleum was added to the cooled reaction mixture to precipitate the product which was then filtered off and washed well with the same solvent or solvent mixture.

(b) For liquid nucleophile

The diazo compound (2 m.mole) was dissolved / suspended in the nucleophile (6 m.mole) at 100°C. The reaction was then carried out as above.

(c) For copper-bronze catalysis

Copper-bronze (1 molar equiv. 2 m.moles) was mixed with the original starting materials and the melt reaction was carried out as above. Chloroform was added to the cooled reaction mixture and the solution was filtered. The solvent was removed from the filtrate and ether or ether-light petroleum was added to the residue, as above.

(i) Diphenyltelluronium-2,3,4,5-tetraphenylcyclopentadienylide

Bath temperature = 150°

Time of reaction = 10 min

The ylide was precipitated by addition of ether-light petroleum, m.p. 175°C from benzene-light petroleum

(Found C, 74.7; H, 4.7. $C_{41}H_{30}Te$ requires C, 75.7; H, 4.6%)

(ii) Triphenylphosphonium-2-benzyl-3,4,5-triphenylcyclopentadienylide

Bath temperature = 155-60°

Time of reaction = 15 min

The ylide was precipitated by addition of ether as a yellow solid (0.522 g, 40.5%), m.p. 255°C from nitromethane.

(Found C, 89.1; H, 6.0. $C_{48}H_{37}P$ requires C, 89.4; H, 5.7% Molecular weight 644.258; requires 644.263)

(iii) Triphenylarsonium-2-benzyl-3,4,5-triphenylcyclopentadienylide

Bath temperature = 150°C

Time of reaction = 15 min

The ylide was precipitated by ether as a yellow solid (0.420 g, 30.5%), m.p. 201-2°C.

(Found C, 83.1; H, 5.4. $C_{48}H_{37}As$ requires C, 83.7; Y, 5.4% Molecular weight 688.208; requires 688.211)

(iv) Methylphenylsulphonium-2-benzyl-3,4,5-triphenylcyclopentadienylide

Bath temperature = 150°C

Time of reaction = 15 min

The ylide was precipitated by addition of ether as a pale yellow solid (0.304 g, 30%),m.p. 195-6°C.

(Found C, 87.4; H, 6.1. $C_{37}H_{30}S$ requires C, 87.7; H, 5.9% Molecular weight 506.206; requires 506.207)

(v) Diphenylsulphonium-2-benzyl-3,4,5-triphenylcyclopentadienylide

Bath temperature = 150°C

Time of reaction = 10 min

The impure ylide was precipitated by addition of ether and light petroleum as a yellow solid (0.22 g, $\sim$19%).

All attempts to purify this compound further were unsuccessful.

(vi) Triphenylphosphonium-2,3,4-triphenyl-5-p-tolylcyclopentadienylide

Bath temperature = 150°C

Time of reaction = 10 min

The ylide was precipitated by addition of ether as a yellow solid (0.902 g, 70%), m.p. 320-2°C from nitromethane-benzene

(Found C, 88.5; H, 5.7. $C_{48}H_{37}P$ requires C, 89.4; H, 5.7% Molecular weight 644.262; requires 644.263)

Best analysis figures were obtained for this ylide before recrystallisation.

(vii) Methylphenylsulphonium-2,3,4-triphenyl-5-p-tolylycyclopentadienylide

(a) Bath temperature = 150°C

Time of reaction = 10 min

The impure ylide was precipitated by addition of ether and light petroleum as a yellow solid (0.34 g, $\sim$ 30%), m.p. 176-85°C.

(b) Copper-bronze catalyst

Bath temperature = 140°C

Time of reaction = 10 min

The ylide was precipitated by addition of ether as a pale yellow solid (0.682 g, 61%), m.p. 185-6°C.

(Molecular weight 506.205. $C_{37}H_{30}S$ requires 506.207)

(viii) Triphenylphosphonium-2-methyl-3,4,5-triphenylcyclopentadienylide

Bath temperature = 150°C

Time of reaction = 10 min

The impure ylide was precipitated by addition of ether and light petroleum (0.38 g, ~34%), and purified by column chromatography on silica using benzene-ethyl acetate as eluent, m.p. 142-5°C.

(Molecular weight 506.232. $C_{42}H_{33}P$ requires 506.232)

(ix) Triphenylarsonium-2-methyl-3,4,5-triphenylcyclopentadienylide

Copper-bronze catalyst

Bath temperature = 130-5°C

Time of reaction = 10 min

The ylide was precipitated by addition of ether as a yellow solid (0.370 g, 30.2%), m.p. 128-9°C

(Found C, 82.1; H, 5.7. $C_{42}H_{33}As$ requires C, 82.3; H, 5.4%)

(x) Triphenylphosphonium-2,3,5-triphenylcyclopentadienylide

Bath temperature = 150-5°C

Time of reaction = 15 min

The ylide was precipitated by addition of ether as a yellow solid (0.753 g, 68%), m.p. 268-70°C from acetonitrile

(Found C, 88.7; H, 5.5. $C_{41}H_{31}P$ requires C, 88.8; H, 5.6%)

(xi) Triphenylarsonium-2,3,5-triphenylcyclopentadienylide

Copper-bronze catalyst

Bath temperature = 130°C

Time of reaction = 15 min

The ylide was precipitated by addition of ether as a pale yellow solid (0.805 g, 67%), m.p. 195-7°C

(Molecular weight 598.165. $C_{41}H_{31}As$ requires 598.164)

(xii) Triphenylphosphonium-2,3,4-triphenylcyclopentadienylide

Bath temperature = 160°C

Time of reaction = 60 min

The ylide was precipitated by addition of ether as a green-yellow solid (0.310 g, 28%), m.p. 242-5°C (lit. 240-3°C[34]) from acetonitrile. The product did not depress the melting point of an authentic sample.

This ylide was also obtained in similar yield by heating together 2,3,4-triphenylcyclopentadienylidene triphenylphosphazine and triphenylphosphine under the same conditions as used for the preparation starting from the diazo-compound.

(xiii) Triphenylarsonium-2,3,4-triphenylcyclopentadienylide

(a) Bath temperature = 150°C

Time of reaction = 10 min

The ylide was precipitated by additon of ether as a pale coloured solid (0.120 g, 10%)

(b) Copper-bronze catalyst

Bath temperature = 130°C

Time of reaction = 10 min

The ylide was precipitated by addition of ether as a pale yellow solid, (0.627 g, 52.5%), m.p. 213-6°C (lit 198-200°C[37]) from acetonitrile.

(c) Copper-bronze catalyst in benzene solution.

2,3,4-Triphenyldiazocyclopentadiene (0.640 g, 2 m.mole) and triphenylarsine (1.84 g, 6 m.mole) were dissolved in dry benzene (30 ml). Copper-bronze (0.15 g) was added to the solution and the mixture heated under reflux under nitrogen for 2 hr. The solution was filtered and the solvent removed. Addition of ether to the residue gave a precipitate which was filtered off and washed well with ether to give triphenylarsonium-2,3,4-triphenylcyclopentadienylide as a pale yellow solid (0.42 g, 35%), m.p. 212-4°C.

The spectra of each of the products from (a), (b) and (c) were identical to those of the ylide which had been prepared previously[37].

(xiv) Methylphenylsulphonium-2,3,4-triphenylcyclopentadienylide

(a) Bath temperature = 150°C

Time of reaction = 10 min

The crude product was precipitated by addition of ether and light petroleum as a brown solid.

(b) Copper-bronze catalyst

Bath temperature = 130°C

Time of reaction = 15 min

The impure ylide was precipitated by addition of ether and light petroleum as a dark yellow solid (0.42 g, $\sim$ 50%), m.p. 125-30°C.

All attempts to purify this product further were unsuccessful.

(xv) Triphenylphosphonium-2,4-diphenylcyclopentadienylide

Bath temperature = 150-5°C

Time of reaction = 15 min

The ylide was precipitated by addition of ether as a greeny-yellow solid (0.249 g, 26%), m.p. 224-6°C from n-butanol

(Found C, 87.6; H, 5.8. $C_{35}H_{27}P$ requires C, 87.9; H, 5.7%)

This ylide was also obtained in similar yield by heating together 2,4-diphenylcyclopentadienylidene triphenylphosphazine and triphenylphosphine under the same conditions.

(xvi) Triphenylarsonium-2,4-diphenylcyclopentadienylide

A From 2,5-diphenyldiazocyclopentadiene:

(a) Bath temperature = 150°C

Time of reaction = 10 min

The ylide was precipitated by addition of ether as a yellow solid (0.202 g, 19.3%)

(b) Copper-bronze catalyst

Bath temperature = 145°C

Time of reaction = 10 min

The ylide was obtained as above (0.368 g, 35.2%)

B From 2,4-diphenyldiazocyclopentadiene:

Copper-bronze catalyst

Bath temperature = 145°C

Time of reaction = 10 min

The ylide was obtained as above (0.184 g, 17.6%)

m.p. 195-7°C from acetonitrile

(Found C, 80.7; H, 5.4. $C_{35}H_{27}As$ requires C, 80.7; H, 5.1%)

V OTHER REACTIONS OF DIAZOCYCLOPENTADIENES AND OF DIAZOFLUORENE

(i) Reaction of diazofluorene with triphenylphosphine

Diazofluorene was heated with triphenylphosphine under the normal melt conditions (see section IV)

Bath temperature = 150°C

Time of reaction = 5 min

Addition of ether to the cooled reaction mixture precipitated fluorenylidene triphenylphosphazine as a bright yellow solid (0.790 g, 87%), m.p. 209-10°C (lit. m.p. 209-10°C[15])

(ii) Reaction of diazofluorene with triphenylarsine

Diazofluorene was heated with triphenylarsine under the normal melt conditions

Bath temperature = 140°C

Time of reaction = 15 min

Addition of ether to the cooled reaction mixture precipitated fluorenone ketazine as red crystals (0.570 g, 80%), m.p. 272-4°C (lit. m.p. 276-7°C[86])

(iii) Reaction of diazofluorene with diphenylsulphide

Under the same conditions as (ii), diphenylsulphide reacted with diazofluorene to give fluorenone ketazine (0.143 g, 20%). Precipitation of the product was not so effective with ether in this case, giving a much reduced yield.

(iv) 2-Nitro-3,4,5-triphenyldiazocyclopentadiene and triphenylphosphine

2-Nitro-3,4,5-triphenyldiazocyclopentadiene (0.040 g) and triphenylphosphine (0.030 g) were dissolved in acetonitrile (2 ml). The solution was warmed for 5 min and the solvent was removed. The residue was taken up in the minimum amount of benzene and applied to a silica column, prepared in benzene. Benzene eluted a red band which, after removal of the solvent, gave 2-nitro-3,4,5-triphenylcyclopentadienone hydrazone as red crystals, (0.025 g, 62%), m.p. 168-70°C from nitromethane.

(Molecular weight 367.133. $C_{23}H_{17}N_3O_2$ requires 367.132)

(v) 2,5-Diphenyldiazocyclopentadiene and cyclooctene

2,5-Diphenyldiazocyclopentadiene (0.30 g) and cyclooctene (0.6 g) were heated under a nitrogen atmosphere at 145°C for 20 min. Addition of benzene-methanol (1:1) to the cooled mixture precipitated a brown solid. The solid was dissolved in the minimum amount of benzene and applied to a silica column prepared in benzene. A band was eluted by benzene which, after removal of the solvent and trituration with methanol, gave a light brown solid which was apparently a mixture of the spiro adduct and 5-(cyclo-oct-2-enyl)-1,4-diphenylcyclopentadiene (0.24 g, $\sim$ 60%).

(Molecular weight 326.203. $C_{25}H_{26}$ requires 326.203)

(vi) 2,3,4,5-Tetraphenyldiazocyclopentadiene and hydrogen bromide

2,3,4,5-Tetraphenyldiazocyclopentadiene (0.99 g, 2.5 m.mole) was dissolved in dry ether (30 ml) and dry hydrogen bromide gas, together with oxygen-free nitrogen, was bubbled through the solution. After 2 hr. at room temperature, the yellow precipitate was filtered off, washed with ether and recrystallised from chloroform-methanol (1:1) to give 5-bromo-1,2,3,4-tetraphenylcyclopentadiene (0.90 g, 80%), m.p. 195-7°C (lit. m.p. 190-1°C[75]).

(Found C, 77.8; H, 4.9. Calc.for $C_{29}H_{21}Br$ C, 77.5; H, 4.7%)

(vii) 2,3,4-Triphenyldiazocyclopentadiene and hydrogen bromide

Under identical conditions to (vi) above, 2,3,4-triphenyldiazocyclopentadiene (0.80 g, 2.5 m.mole) reacted with hydrogen bromide to give 5-bromo-1,2,3-triphenylcyclopentadiene (0.49 g, 52.5%), m.p. 150°C (lit. 150-2°C[34])
(Found C, 74.0; H, 4.6. Calc. for $C_{23}H_{17}Br$ C, 73.9; H, 4.6%)

(viii) 2,3,4-Triphenyldiazocyclopentadiene and hydrogen chloride

2,3,4-Triphenyldiazocyclopentadiene (0.80 g, 2.5 m.mole) reacted with hydrogen chloride following the above procedure. After removal of the solvent, the residue was triturated with methanol and recrystallised from nitromethane to give 5-chloro-1,2,3-triphenylcyclopentadiene as golden needles (0.53 g, 64.5%), m.p. 155-6°C
(Found C, 84.0; H, 5.3. $C_{23}H_{17}Cl$ requires C, 84.0; H, 5.2%)

(ix) 2,3,4-Triphenyldiazocyclopentadiene and hydrogen iodide

2,3,4-Triphenyldiazocyclopentadiene (0.32 g, 1 m.mole) was dissolved in dry ether (30 ml) and hydrogen iodide (0.38 g, 3 m.mole) was added. The solution was stirred at room temperature for 12 hr. After removal of the solvent, the dark residue was triturated with methanol and recrystallised from acetone to give 1,2,3,1',2',3'-hexaphenyl-5,5'-dihydrofulvalene as yellow-green needles (0.16 g, 55%) m.p. 255-8°C (lit. 268-70°C[76]).

This compound although impure had identical spectra to those of the compound prepared in Section VI, (iii).

VI SALT METHOD FOR THE PREPARATION AND ATTEMPTED PREPARATION OF CYCLOPENTADIENYLIDES

(i) 5-Bromo-1,2,3-triphenylcyclopentadiene and triphenylarsine

5-Bromo-1,2,3-triphenylcyclopentadiene (0.373 g, 1 m.mole) and triphenylarsine (0.306 g, 1 m.mole) were suspended in nitromethane (25 ml) and the mixture was stirred at room temperature for 40 hr. The solvent was removed under vacuum, ether (15 ml) was added and the precipitate was filtered off. The white solid was suspended in methanol and perchloric acid (0.2 ml, 60%) was added. Ether (20 ml) was added, the precipitate filtered off and washed well with ether to give triphenyl-(2,3,4-triphenylcyclopentadienyl)-arsonium perchlorate as a pale yellow solid (0.28 g, 40%), m.p. 220-3°C (lit. m.p. 225-6°C[34]) from n-propanol. The product did not depress the melting point of an authentic sample. This perchlorate could be converted into the respective arsonium ylide by treatment with sodium hydroxide[34].

(ii) 5-Bromo-1,2,3-triphenylcyclopentadiene and dimethylsulphide

(a) 5-bromo-1,2,3-triphenylcyclopentadiene (0.410 g) was refluxed in excess dimethylsulphide for 48 hr. The excess dimethylsulphide was removed at the water pump. The residue was dissolved in the minimum amount of benzene and applied to an alumina column, prepared with light petroleum. Benzene-light petroleum (1:1) eluted a yellow band which, after removal of the solvents, was triturated with methanol and recrystallised from chloroform-methanol (1:1) to give 1-methylthio-2,3,4-triphenylcyclopentadiene as a yellow solid (0.23 g, 63%), m.p. 150-2°C.

(Found C, 85.0; H, 5.9. $C_{24}H_{20}S$ requires C, 84.7; H, 5.9%)

(b) 5-Bromo-1,2,3-triphenylcyclopentadiene (0.80 g) and dimethylsulphide (0.2 ml) were stirred in nitromethane (35 ml) for 23 hr. The solution was filtered to give unreacted bromo compound (0.22 g, 27.5%). The residue, after the solvent had been removed, was taken up in ethanol (5 ml) and perchloric acid (0.2 ml, 70%) was added. Ether (10 ml) was then added and the precipitate filtered off and washed well with ether to give dimethyl-(2,3,4-triphenylcyclopentadienyl)-sulphonium perchlorate as a pale yellow solid (0.10 g, 13%), m.p. 153-5°C. (Found C, 64.2; H, 5.0. $C_{25}H_{23}SClO_4$ requires C, 66.0; H, 5.1%) The product tended to decompose in hot solvents.

(iii) 5-Bromo-1,2,3-triphenylcyclopentadiene and benzylmethylsulphide

5-Bromo-1,2,3-triphenylcyclopentadiene (0.373 g, 1 m.mole) and benzylmethylsulphide (0.137 g, 1 m.mole) were heated in refluxing nitromethane (20 ml) for 2 hr. The precipitate was filtered from the cooled solution and recrystallised from acetone to give 1,2,3,1',2',3'-hexaphenyl-5,5'-dihydrofulvalene as yellow needles (0.15 g, 51%), m.p. 261-3°C (lit. m.p. 268-70°C[76])

(Found C, 94.1; H, 5.7. Calc. for $C_{46}H_{34}$ C, 94.2; H, 5.8%)

5-Bromo-1,2,3-triphenylcyclopentadiene did not react with benzylmethylsulphide or with methylphenylsulphide at room temperature in nitromethane, nor was there any reaction when the reactants were heated together at 150°C.

VII REACTIONS OF TRIPHENYLARSINE OXIDE AND SULPHOXIDES WITH CYCLOPENTADIENES

(i) 1,4-Diphenylcyclopentadiene and triphenylarsine oxide

(a) The method of Lloyd and Singer[34] was employed. The two reactants were heated under reflux in triethylamine, with phosphorus pentoxide as catalyst, for 24 hr. The product, recrystallised from acetonitrile, was triphenylarsonium-2,4,-diphenylcyclopentadienylide (55%), m.p. 193-5°C, indentical with that prepared in section IV (xvi)

(b) The reactants were also heated under reflux in acetic anhydride[34] for 10 min. No ylide product was isolated from the reaction mixture.

(ii) Other cyclopentadienes and triphenylarsine oxide

Using either of the above methods (a) or (b), 1,2,4-triphenylcyclopentadiene, 1-benzyl-2,3,4-triphenylcyclopentadiene or fluorene did not react with triphenylarsine oxide.

(iii) 1,2,3-Triphenylcyclopentadiene and dimethylsulphoxide

No reaction took place when 1,2,3-triphenylcyclopentadiene was heated with dimethylsulphoxide either in refluxing acetic anhydride, triethylamine with phosphorus pentoxide, or with dicyclohexylcarbodiimide and anhydrous phosphoric acid[35].

VIII REACTIONS OF CYCLOPENTADIENYLIDES

(i) WITTIG REACTION WITH p-NITROBENZALDEHYDE

General method

The ylide (1 m.mole) ~~as~~ and p-nitrobenzaldehyde (1 m.mole) were heated under reflux in carbon tetrachloride (25 ml).

(a) Triphenylphosphonium-2,3,5-triphenylcyclopentadienylide

After 20 hr., the solvent was removed and the residue was triturated with ether to give unreacted starting ylide (0.46 g, 84%).

(b) Triphenylphosphonium-2-benzyl-3,4,5-triphenylcyclopentadienylide

After 17 hr., some of the starting ylide was recovered by an identical method to (a) (0.25 g, 39%). Some decomposition had taken place in this reaction, but there was no evidence of any fulvene formation.

(c) Triphenylphosphonium-2,5-diphenylcyclopentadienylide

After 16 hr., the starting ylide was recovered by the above procedure (0.41 g, 85%).

(d) Triphenylarsonium-2,3,5-triphenylcyclopentadienylide

After 5 hr., the solvent was removed and the residue was taken up in the minimum amount of benzene and applied to a silica column, prepared with benzene. Elution with benzene gave a dark red band which, after removal of the solvent, was recrystallised from nitromethane to give 6-p-nitrophenyl-2,3,5-triphenylfulvene (0.36 g, 84%), m.p. 211-4°C. (Molecular weight 427.157. $C_{30}H_{21}NO_2$ requires 427.157)

A pale yellow band eluted by benzene-methanol (4:1) gave, after removal of the solvents and recrystallisation from water, triphenylarsine oxide hydrate (0.296 g, 87%)

(e) Triphenylarsonium-2-benzyl-3,4,5-triphenylcyclopentadienylide

Under identical conditions to those described above in paragraph (d), 6-p-nitrophenyl-2-benzyl-3,4,5-triphenylfulvene was obtained as orange-brown crystals (0.517 g, 62%), m.p. 192°C
(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%)

Triphenylarsine oxide hydrate (0.114 g, 33.5%) was also obtained as in paragraph (d).

(f) Triphenylarsonium-2,4-diphenylcyclopentadienylide

After 15 hr., the solvent was removed and the residue was taken up in the minimum amount of benzene and applied to a silica column, prepared in benzene. Elution with benzene gave a red band which, after the solvent was removed, was recrystallised from nitromethane to give 6-p-nitrophenyl-2,4-diphenylfulvene as dark red crystals (0.120 g, 34%), m.p. 130-2°C.
(Molecular weight 351.126. $C_{24}H_{17}NO_2$ requires 351.125.

A second band eluted with benzene gave, after the solvent was removed and the residue triturated with methanol, a yellow solid (0.06 g) which was not identifed, m.p. 165-70°C

Triphenylarsine oxide hydrate (0.161 g, 47%) was also obtained as in paragraph (d).

(g) Diphenyltelluronium-2,3,4,5-tetraphenylcyclopentadienylide

Diphenyltelluronium-2,3,4,5-tetraphenylcyclopentadienylide (0.122 g) and p-nitrobenzaldehyde (0.0285 g) in carbon tetrachloride (10 ml) were heated under reflux for 18hr.

Neither the expected fulvene nor unreacted ylide was isolated from the reaction mixture. Thin layer chromatography of the products gave no evidence for any fulvene formation and decomposition of the ylide was apparently the overriding reaction.

(ii) DIAZO COUPLING

The method of Ramirez and Levy[58], for the reaction of triphenylphosphoniumcyclopentadienylide with benzene diazonium chloride, was used in all cases with a ½-hr reaction time. The products were all recrystallised from benzene-methanol.

(a) Triphenylphosphonium-2,4-diphenylcyclopentadienylide

The product, triphenylphosphonium-2-phenylazo-3,5-diphenylcyclopentadienylide, was a red crystalline solid (90%), m.p. 245°C (Molecular weight 582.220. $C_{41}H_{31}N_2P$ requires 582.222)

(b) Triphenylarsonium-2,4-diphenylcyclopentadienylide

The product, triphenylarsonium-2-phenylazo-3,5-diphenylcyclopentadienylide, was a red crystalline solid (85%), m.p. 238-40°C (Molecular weight 626.171. $C_{41}H_{31}AsN_2$ requires 626.170)

(c) Triphenylphosphonium-2,5-diphenylcyclopentadienylide

The product, triphenylphosphonium-3-phenylazo-2,5-diphenylcyclopentadienylide, was an orange crystalline solid (90%), m.p. 190-2°C (Molecular weight 582.223 . $C_{41}H_{31}N_2P$ requires 582.222)

(d) Triphenylphosphonium-2,3,5-triphenylcyclopentadienylide

The product, triphenylphosphonium-3-phenylazo-2,4,5-triphenylcyclopentadienylide was a red-brown crystalline solid (60%), m.p. 243°C (Molecular weight 658.254. $C_{47}H_{35}N_2P$ requires 658.254)

(e) Triphenylarsonium-2,3,5-triphenylcyclopentadienylide

The product, triphenylarsonium-3-phenylazo-2,4,5-triphenylcyclopentadienylide was a red-brown crystalline solid (55%), m.p. 218°C (Molecular weight 702.210. $C_{47}H_{35}N_2As$ requires 702.202)

(iii) ACETYLATION

(a) Triphenylphosphonium-2,4-diphenylcyclopentadienylide

A solution of triphenylphosphonium-2,4-diphenycyclopentadienylide (0.478 g, 1 m.mole) 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 well shaken. After 1 hr., the mixture was extracted with chloroform (3 x 20 ml), washed with water and the extract was dried (Na_2SO_4). After the solvent had been removed, the residue was taken up in the minimum amount of benzene and applied to a silica column, prepared in benzene. The column was eluted with increasing proportions of chloroform to benzene. A dark band was eluted by chloroform-benzene (1:1) which, after the solvents had been removed, was triturated with ether to give a mixture of triphenylphosphonium-2-acetyl-3,5-diphenylcyclopentadienylide and triphenylphosphonium-3-acetyl-2,4-diphenylcyclopentadienylide (0.20 g, 38%) in a ratio of approx 3:1 (by n.m.r.), m.p. (of mixture) ~225°C (Molecular weight 520.196. $C_{37}H_{29}OP$ requires 520.196)

(b) Triphenylarsonium-2,4-diphenylcyclopentadienylide

Triphenylarsonium-2,4-diphenylcyclopentadienylide (0.522 g, 1 m.mole) was treated as in the above procedure (a), with a 3 min. reaction time.

Chloroform-benzene (7:3) eluted a dark band which, after the solvents had been removed, gave triphenylarsonium-2-acetyl-3,5-diphenylcyclopentadienylide as a dark yellow impure solid (0.275 g). This product was not obtained as a pure compound and its mass spectrum showed high molecular weight impurities.

(c) Triphenylphosphonium-2,5-diphenylcyclopentadienylide

Triphenylphosphonium-2,5-diphenylcyclopentadienylide (0.478 g, 1 m.mole) was treated by the above procedure (a), with a 15 min reaction time.

Chloroform-benzene (1:1) eluted a dark band which, after the solvents had been removed, was triturated with ether to give triphenylphosphonium-3-acetyl-2,5-diphenylcyclopentadienylide (0.19 g, 36%), m.p. 208-10°C.

(Molecular weight 520.196. $C_{37}H_{29}OP$ requires 520.196)

(d) Triphenylphosphonium-2,3,5-triphenylcyclopentadienylide

Triphenylphosphonium-2,3,5-triphenylcyclopentadienylide (0.554 g, 1 m.mole) was treated by the above procedure (a), with a 30 min reaction time.

Chloroform-benzene (1:1) eluted a band which, after the solvents had been removed, was triturated with ether to give triphenylphosphonium-3-acetyl-2,4,5-triphenylcyclopentadienylide (0.28 g, 47%), m.p. 243-5°C
(Molecular weight 596.229. $C_{43}H_{33}OP$ requires 596.227)

(e) Triphenylarsonium-2,3,5-triphenylcyclopentadienylide

Triphenylarsonium-2,3,5-triphenylcyclopentadienylide was also treated by the above procedure (a), with a 15 min reaction time. However, no ylide was isolated by column chromatography.

The acetyl compounds from paragraph (a), (c), and (d) were obtained in a pure condition (t.l.c. spectra), as pale yellow solids, merely by washing the product well with ether.

(iv) FORMYLATION

(a) Triphenylphosphonium-2,4-diphenylcyclopentadienylide

A suspension of triphenylphosphonium-2,4-diphenylcyclopentadienylide (0.478 g, 1 m.mole) in dimethylformamide (5 ml) was treated with phosphorus oxychloride (0.15 ml, ca 2 m.moles) . The clear solution was warmed at 60°C for 15 min before a 2N solution of sodium hydroxide (5 ml) was added and the mixture was quenched with water (50 ml). The mixture was extracted with benzene (3 x 20 ml) and the benzene solution was washed well with water and dried (Na_2SO_4). Evaporation of the solvent and trituration of the residue with ether gave triphenylphosphonium-2,4-diformyl-3,5-diphenylcyclopentadienylide (0.24 g, 45%), m.p. 233-6°C.

(Molecular weight 534.173. $C_{37}H_{27}O_2P$ requires 534.175)

(b) Triphenylarsonium-2,4-diphenylcyclopentadienylide
Triphenylarsonium,2,3,5-triphenylcyclopentadienylide

Each of the arsonium ylides was treated under the same conditions as (a). Although reaction obviously took place, in neither case were pure products isolated.

(v) PROTONATION (see n.m.r. tables)

A solution of the ylide in deuteriochloroform was placed in a n.m.r.

tube and treated with a few drops of trifluoroacetic acid. The n.m.r. spectrum was then run under normal operating conditions.

IX TRIPHENYLARSONIUMCYCLOPENTADIENYLIDE

(i) Preparation

A solution of dibromocyclopentene, prepared from cyclopentadiene (0.9 g) and bromine (2.2 g) in chloroform (2 ml) was added to a solution of triphenylarsine (8.42 g) in nitromethane (50 ml) and the mixture was stirred at room temperature for 10 days. The solvent was removed under reduced pressure and the resultant dark oil was extracted with warm water (3 x 25 ml). The combined aqueous extracts were cooled and basified with aqueous sodium hydroxide (5N). A precipitate formed which was filtered off, washed well with water, dried (vacuum dessicator), suspended in ether-light petroleum (1:1) and filtered off again, giving the pale yellow triphenylarsoniumcyclopentadienylide (1.40 g, 28%), m.p. > 220°C.

(Molecular weight 370.071. $C_{23}H_{19}As$ requires 370.070)

(ii) Salt formation with perchloric acid

Perchloric acid (60%, 0.1 ml) was added to a solution of triphenylarsoniumcyclopentadienylide (0.20 g) in the minimum quantity of glacial acetic acid. A yellow precipitate formed slowly. Ether (10 ml) was added and the salt was filtered off and washed well with ether to give the buff perchlorate (0.224 g, 88%), m.p. ca 200°, from methanol. (Found, C 58.6; H, 4.4. $C_{23}H_{20}AsClO_4$ requires C, 58.5; H, 4.3%)

(iii) Diazo coupling

The method of Ramirez and Levy[58] was again used.

Trituration of the residue with methanol gave triphenylarsonium-2-phenylazocyclopentadienylide as a red-orange solid which, recrystallised from benzene-methanol, formed orange crystals (70%), m.p. ca 220°C (Found C, 73.1; H, 5.0, N, 6.3. $C_{29}H_{23}AsN_2$ requires C, 73.4; H, 4.9; N, 5.9%)

(iv) Attempted Wittig Reaction with aldehydes

Equivalent amounts of triphenylarsoniumcyclopentadienylide and aldehyde were dissolved in chloroform and the mixture was heated under reflux for 4-20 hr. After removal of the solvent, the reaction products were chromatographed on silica using, in turn, light petroleum, benzene and ethyl acetate as eluents. With p-nitrobenzaldehyde, triphenylarsine (10%), triphenylarsine oxide (80%), and two other major products were obtained. Both the latter products gave major fragmentation peaks at m/e = 199. With benzaldehyde and cinnamaldehyde similar results were obtained.

X MISCELLANEOUS REACTIONS

(i) Triphenylphosphonium-2,5-diphenylcyclopentadienylide and diphenylketene

Triphenylphosphonium-2,5-diphenylcyclopentadienylide (0.478 g, 1 m.mole) and diphenylketene (0.214 g, 1 m.mole + 10% excess) were dissolved in dry benzene (25 ml) under a nitrogen atmosphere. The solution was heated under reflux for 2 hr and the solvent was then removed. The residue was taken up in the minimum amount of benzene and applied to a silica column, prepared in benzene. A red band was eluted by benzene which, when the solvent was removed, gave 6-(diphenylmethylene)-2,5-diphenylfulvene, as a red oil (0.040 g, 10.3%). This product did not crystallise.

ν_{max} 1910 cm^{-1} (complex)

(ii) Diphenyltelluronium-2,3,4,5-tetraphenylcyclopentadienylide and nitrosobenzene

A solution of diphenyltelluronium-2,3,4,5-tetraphenylcyclopentadienylide (0.1 g) and nitrosobenzene (0.0164 g) in benzene (10 ml) was heated under reflux for 18 hr. After removal of the solvent the residue was taken up in the minimum amount of benzene and applied to an alumina column, prepared in light petroleum. Petroleum-benzene (10:1) eluted a band which, after the solvents had been removed, gave diphenyltelluride (0.0109 g, 25%). No other product was isolated in a pure state from the column. Apparent decomposition of the initial ylide had taken place.

(iii) 6-(α-pyridyl)-1,2,3-triphenylfulvene

1,2,3-Triphenylcyclopentadiene (1.47 g, 5 m.mole) and pyridine-2-aldehyde (1.07 g, 10 m.mole) were dissolved in methanol (25 ml). A solution of sodium methoxide, prepared from sodium (1.5 g) and methanol (50 ml), was added and the mixture was heated under reflux for 2 hr. The solution was cooled and the precipitated filtered off and recrystallised from acetonitrile to give 6-(α-pyridyl)-1,2,3-triphenylfulvene (1.65 g, 87%), m.p. 182-4°C.

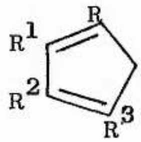
(Found C, 90.9; H, 5.2; N, 3.6. $C_{29}H_{21}N$ requires C, 90.9; H, 5,5; N, 3.6%)

XI SPECTRA

(i) N.M.R. SPECTRA

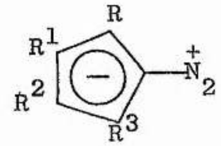
Chemical shifts (τ) are given in p.p.m. relative to tetramethylsilane as internal standard, with relative intensities in parentheses. Deuteriochloroform was the solvent unless otherwise stated

(a) Cyclopentadienes



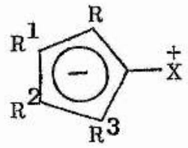
R	R^1	R^2	R^3			
Ph	Ph	Ph	$C_6H_4CH_3\underline{p}$	2.6-3.2(19)m	6.05(2)s	7.76(3)s
Ph	Ph	Ph	CH_2Ph	2.6-3.2(20)m	6.26(2)s	6.57(2)s
Ph	Ph	Ph	CH_3	2.7-3.1(15)m	6.46(2)s	7.93(3)s
Ph	Ph	Ph	SCH_3	2.6-3.0(15)m	6.25(2)s	7.60(3)s
CH_3	Ph	Ph	CH_3	2.6-3.2(10)m	6.87(2)s	7.95(6)s
C_2H_5	Ph	Ph	C_2H_5	2.6-3.2(10)m	6.85(2)s	7.35-8.0(4) m 8.6-9.2(6) m
Ph	Ph	H	CH_3	2.6-2.9(10)m	6.65(2)s	$\underbrace{3.72(1)q \quad 7.60(3)d}_{J\sim 1c/s}$

(b) Diazocyclopentadienes



R	R^1	R^2	R^3		
Ph	Ph	Ph	$-C_6H_4CH_3\underline{p}$	2.8-3.1(19)m	7.70(3)s
Ph	Ph	Ph	CH_2Ph	2.6-3.0(20)m	5.94(2)s
Ph	Ph	Ph	CH_3	2.6-3.2(15)m	7.72(3)s
CH_3	Ph	Ph	CH_3	2.7-3.1(10)m	7.80(6)s

(c) Cyclopentadienylides



(i) $X = PPh_3$

R	R^1	R^2	R^3		
Ph	Ph	Ph	CH_2Ph	2.3-3.5(35)m	6.45(2)s
Ph	Ph	Ph	CH_3	2.2-3.5(30)m	8.28(3)s
Ph	H	H	Ph	2.2-3.4 m	3.55 d (J_{pH} = 6 c/s)
Ph	H	Ph	H	2.2-3.4 m	3.67 m
Ph	CHO	Ph	CHO	2.2-3.2(25)m	$\underbrace{0.60(1)d \quad 0.80(1)d}_{J\sim 1c/s}$
Ph	Ph	CH_3CO	Ph	2.3-3.6(30)m	8.30(3)s
Ph	H	CH_3CO	Ph	2.2-3.4(26)m	8.05(3)s
Ph	CH_3CO	Ph	H	2.2-3.3(25)m	$\left.\begin{matrix}3.95\\3.90\end{matrix}\right\}(1)d \quad \left.\begin{matrix}8.10\\8.22\end{matrix}\right\}(3)s$
Ph	H	Ph	CH_3CO		

(ii) $X = AsPh_3$

R	R^1	R^2	R^3		
Ph	Ph	Ph	CH_2Ph	2.4-3.6(35)m	6.40(2)s
Ph	Ph	Ph	CH_3	2.3-3.6(30)m	8.15(3)s
Ph	H	Ph	H	2.4-3.3 m	3.65 d(part of AB system $J\sim 2.5$ c/s)
Ph	H	Ph	CH_3CO	2.2-3.4(25)m	3.60(1)s 8.12(3)s
H	H	H	H	2.3-2.6(15)m	3.4-3.8(4)m (AA'BB' system)
H	H	H	N_2Ph	2.4-2.8 m	3.0-3.3 m 3.55 t 4.02 q

(iii) $X = S(CH_3)Ph$

R	R^1	R^2	R^3		
Ph	Ph	Ph	CH_2Ph	2.6-3.2(25)m	$^{5.73}_{6.05}$(2) AB system 7.32(3)s
Ph	Ph	Ph	$C_6H_4CH_3$p	2.6-3.2(24)m	7.27(3)s 7.75(3)s
Ph	Ph	Ph	H	2.4-3.4(21)m	6.98(3)s

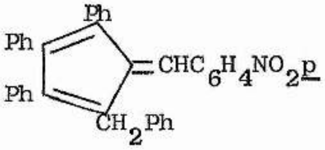
(iv) X = $As(C_6H_4CH_3\underline{p})_3$

H	H	H	H	2.3-2.9(12)m	3.5-3.8(4)m	AA'BB'system	7.60(9)s

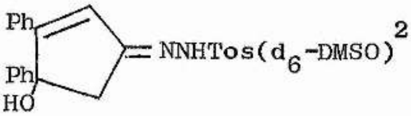
(v) X = $As(C_6H_4OCH_3\underline{p})_3$

H	H	H	H	2.3-3.1(12)m	3.5-3.9(4)m	AA'BB'system	6.20(9)s

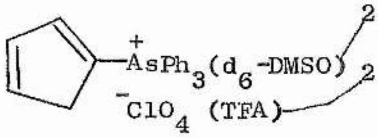
(d) Miscellaneous compounds



2.0-2.2 } (25)m 6.33(2)s
2.6-3.5



2.1-3.1(14)m 3.70(1)s 6.54(1)s 6.97(2)s 7.65(3)s



2.2(15)m 6.0(2)s

2.2(15)m 6.40(2)s

(e) Cyclopentadienylides with trifluoroacetic acid (Protonation)

X = PPh_3

$\underline{R}$	$\underline{R}^1$	$\underline{R}^2$	$\underline{R}^3$		
Ph	H	Ph	H	2.2-2.8m	6.10s
Ph	H	H	Ph	2.2-2.8m	6.13s
Ph	Ph	H	Ph	2.3-3.1m	

X = $AsPh_3$

Ph	H	Ph	H	2.2-2.8m	6.12s
Ph	Ph	H	Ph	2.2-3.2m	3.65s

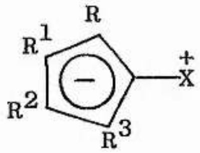
m = multiplet, q = quartet, t = triplet, d = doublet.

Relative intensities are not given in those cases where integration of the peaks is confused, either by background noise or by overlapping of two peaks.

(ii) U.V. SPECTRA

λ_{max} is given in millimicrons. Extinction coefficient is given as log ϵ in parentheses (sh denotes shoulder)

(a) Cyclopentadienylides



(i) X = PPh_3

R	R^1	R^2	R^3		
Ph	Ph	Ph	CH_2Ph	(benzene)	292(4.40)
				(CH_2Cl_2)	233.5(4.46), 291.5(4.42)
Ph	Ph	Ph	$C_6H_4CH_3$p	(benzene)	291
				(CH_2Cl_2)	233.5(4.47), 292(4.48)
Ph	Ph	Ph	CH_3	(EtOH)	227, 286
Ph	Ph	H	Ph	(CH_2Cl_2)	233.5(4.42), 278sh(4.32), 296 (4.33)
				(MeOH)	226, 277sh, 295
Ph	H	Ph	H	(CH_2Cl_2)	233 (4.38), 291(4.40)
				(MeOH)	215, 290
Ph	CHO	Ph	CHO	(CH_2Cl_2)	233.5(4.48), 287(4.65), 338 (4.21)
				(EtOH)	213, 287, 338
Ph	H	Ph	N_2Ph	(CH_2Cl_2)	233.5(4.41), 262(4.40), 481 (4.29)
				(MeOH)	212, 259, 476
				(benzene)	280, 484
Ph	H	N_2Ph	Ph	(CH_2Cl_2)	233.5(4.42),261sh(4.29),266sh (4.27), 408(432)
				(MeOH)	213, 338, 450
				(benzene)	277, 400
Ph	Ph	N_2Ph	Ph	(CH_2Cl_2)	234(4.16), 267(4.43), 404(4.35)
				(MeOH)	214, 255sh, 430
Ph	CH_3CO	H	Ph	(CH_2Cl_2)	234(4.42), 287(4.45)
				(MeOH)	220, ~ 295, ~ 310sh
Ph	CH_3CO	Ph	Ph	(CH_2Cl_2)	234(4.39), 279(4.42)
				(MeOH)	222, 276

(2) $X = AsPh_3$

Ph	Ph	Ph	CH_2Ph	(CH_2Cl_2)	233(4.35), 296(4.29)
Ph	Ph	Ph	CH_3	(CH_2Cl_2)	234(4.31),266(4.24),273(4.25),296(4.29)
Ph	Ph	H	Ph	(CH_2Cl_2)	233(4.34), 303(4.34)
				(MeOH)	213, 296
Ph	H	Ph	H	(CH_2Cl_2)	232.5(4.26),273sh(4.25),309(4.30)
				(MeOH)	215, 300
Ph	H	Ph	N_2Ph	(CH_2Cl_2)	236(4.41), 266(4.50), 489(4.40)
				(MeOH)	214, 262, 484
Ph	Ph	N_2Ph	Ph	(CH_2Cl_2)	234(4.53),265sh, 416(4.27)
H	H	H	H	(CH_3CN)	227(4.15), 246 (4.01)
H	H	H	N_2Ph	(CH_3CN)	224(4.61), 250sh(4.28), 456(4.32)

(3) $X = S(CH_3)Ph$

Ph	Ph	Ph	CH_3Ph	(CH_2Cl_2)	233.5(4.24), 293(4.39)
Ph	Ph	Ph	$C_6H_4CH_3\underline{p}$	(MeOH)	212, 291

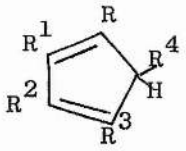
(4) $X = TePh_2$

Ph	Ph	Ph	Ph	(benzene)	280, 347
				(MeOH)	252, 280sh, 335

(b) Diazocyclopentadienes ($X = N_2$)

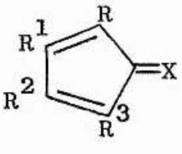
Ph	Ph	Ph	$C_6H_4CH_3\underline{p}$	(CH_2Cl_2)	251(4.35), 334.5(3.84)
				(MeOH)	210, 255, 333
CH_3	Ph	Ph	CH_3	(CH_2Cl_2)	248(4.14), 318(4.05)

(c) Cyclopentadienes



R	R^1	R^2	R^3	R^4		
Ph	Ph	H	CH_2Ph	H	(CH_2Cl_2)	238(4.07),333.5(4.62),346sh(4.59)
Ph	Ph	Ph	H	Cl	(CH_2Cl_2)	242.5(4.37), 321(3.91)
Ph	Ph	Ph	SMe	H	(CH_2Cl_2) (MeOH)	242(4.27), 264sh, 349(3.84) 240, 347

(d) Fulvenes etc



R	R^1	R^2	R^3	X		
Ph	Ph	Ph	CH_2Ph	$CHC_6H_4NO_2$*p*	(CH_2Cl_2)	235.5(4.32),269.5(4.43),334(4.26)
Ph	Ph	H	Ph	$CHC_6H_4NO_2$*p*	(CH_2Cl_2) (MeOH)	235sh(4.22),271(4.50),343(4.34) 210, 267, 336
Ph	H	Ph	H	$CHC_6H_4NO_2$*p*	(CH_2Cl_2) (MeOH)	268(4.29), 361(4.12) 224, 268, 352
C_2H_5	H	H	C_2H_5	NOH	(CH_2Cl_2)	260.5(4.39), 294sh(4.05)
Ph	Ph	Ph	H	$CH-C_5H_5N$	(CH_2Cl_2) (MeOH)	238(4.35),270(4.47),353(4.54) 222, 264, 347
Ph	H	H	Ph	$C=CPh_2$	(MeOH)	214, 250, 270sh, 425

REFERENCES:-

1. G. Wittig and G. Felletschin, Annalen, 1944, 555, 133
2. A.W. Johnson, 'Ylid Chemistry', Academic Press, N.Y. and London (1966)
3. E. Hückel, Z. Physik, 1931, 70, 204; 1931, 72, 310
4. D. Lloyd and M.I.C. Singer, Chem. Comm., 1967, 1042
5. D. Lloyd and M.I.C. Singer, Chem. Comm., 1967, 390
6. B.H. Freeman and D. Lloyd, Chem. Comm., 1970, 924
7. O. Nieland and B. Karele, J. Org. Chem. USSR, 1965, 1, 1884; 1965, 1, 1888
8. D.P. Craig, A. Maccoll, R.S. Nyholm, L.E. Orgel and L.E. Sutton, J. Chem. Soc., 1954, 332
9. D.P. Craig, Chem. Soc. Special Publ., 1958, No. 12, 343
10. D.P. Craig and E. Magnusson, J. Chem. Soc., 1956, 4895
11. H. Staudinger and O. Kupfer, Ber., 1911, 44, 2197
12. H. Staudinger and K.Miescher, Helv. Chim. Acta, 1919, 2, 554
13. A.W. Johnson, J. Org. Chem., 1963, 28, 252
14. H. Reimlinger, Angew. Chem., 1962, 74, 153
15. H. Staudinger and J. Meyer, Helv. Chim. Acta, 1919, 2, 619
16. C.K. Ingold and J.A. Jessop, J. Chem. Soc., 1930, 713
17. A.W. Johnson and R.B. LaCount, Chem. and Ind., 1958, 1440
18. C.K. Ingold and J.A. Jessop, J. Chem. Soc., 1929, 2357
19. W.R. Bamford, T.S. Stevens and J.W. Wright, J. Chem. Soc., 1952, 4334
20. F. Krollpfeiffer and K. Schneider, Annalen, 1937, 530, 34
21. L.A. Pinck and G.E. Hilbert, J. Amer. Chem. Soc., 1946, 68, 2011
22. F. Kröhnke, Chem. Ber., 1950, 83, 253
23. A. Novelli and A.P.G. de Valera, Ciencia e Invest(Buenos Aires), 1948, 82; (Chem. Abs., 1948, 42, 5912)

24. A.W. Johnson and R.B. LaCount, Tetrahedron,1960, 9, 130

25. A.W. Johnson, S. Yen Lee, R.A. Swor and L.D. Royer, J. Amer. Chem. Soc., 1966, 88, 1953

26. A.W. Johnson, J. Org. Chem., 1960, 25, 183

27. G. Wittig and H. Laib, Annalen, 1953, 580, 57

28. W. von E. Doering and C.H. DePuy, J. Amer. Chem. Soc., 1953, 75, 5955

29. D. Lloyd and J.S. Sneezum, Chem. and Ind., 1955, 1221

30. W. Spooncer, Dissert; Univ. of Washington 1955; Chem. Abs., 1956 50, 10664

31. F. Ramirez and S. Levy, J. Org. Chem., 1956, 21, 488

32. H. Behringer and F. Sheidl, Tetrahedron Letters, 1965, 1757

33. D. Lloyd and J.S. Sneezum, Tetrahedron, 1958, 3, 334

34. D. Lloyd and M.I.C. Singer, Unpublished results; J. Chem. Soc. (C) in press.

M.I.C. Singer, Ph.D. Thesis 1968, University of St. Andrews

35. See A.F. Cook and J.G. Moffat, J. Amer. Chem. Soc., 1968, 90, 740, and references cited therein.

36. G. Seitz, Chem. Ber., 1968, 101, 585

37. G.S. Harris, D. Lloyd, N.W. Preston and M.I.C. Singer, Chem. and Ind., 1968, 1483

38. S. McLean and G.W.B. Reed, Canad. J. Chem., 1970, 48, 3110

39. I.B.M. Band, D. Lloyd, M.I.C. Singer and F.I. Wasson, Chem. Comm., 1966, 544

40. D. Lloyd, M.I.C. Singer, M. Regitz and A. Liedhegener, Chem. and Ind., 1967, 324

41. D. Lloyd and M.I.C. Singer, Chem. and Ind., 1967, 510

42. D. Lloyd and M.I.C. Singer, Chem. and Ind., 1967, 787

43. D. Lloyd and M.I.C. Singer, Chem. and Ind., 1967, 118

44. T. Weil and M. Cais, J. Org. Chem., 1963, 28, 2472

45. D. Lloyd and F.I. Wasson, J. Chem. Soc. (C), 1966, 408

46. M. Regitz and A. Liedhegener, Tetrahedron, 1967, 23, 2701

47. D. Lloyd and J.M.F. Gagan, Unpublished results

48. H. Disselnkötter, Angew. Chem. (Internat. Edtn.), 1964, 3, 379

49. O.W. Webster, J. Amer. Chem. Soc., 1965, 87, 1820

50. V.A. Nefedov, Zhur. Obshchei. Khim., 1966, 36, 1508

51. A.N. Nesmeyanov, V.A. Sazonova, V.I. Romanenko, V.N. Postnov, G.P. Zol'nikova, V.A. Blinova and R.M. Kalyanova, Doklady Akad. Nauk. SSSR, 1967, 173, 589

52. E.M. Kowoser and B.G. Ramsey, J. Amer. Chem. Soc., 1959, 81, 856

53. D.N. Kursanov and N.K. Barenetskaia, Izvest. Akad. Nauk. SSSR, 1958, 362

54. D. Lloyd and M.I.C. Singer, Chem. and Ind., 1968, 1277

55. W.B. Smith, W.H. Watson and S. Chiranjeevi, J. Amer. Chem. Soc., 1967, 89, 1438

56. D.J. Cram and R.D. Parkos, J. Amer. Chem. Soc., 1963, 85, 1273

57. D.N. Kursanov, N.K. Baranetskaia and Z.N. Parnes, Izvest. Akad. Nauk. SSSR, 1961, 140

58. F. Ramirez and S. Levy, J. Amer. Chem. Soc., 1957, 79, 6167

59. Z. Yosida, S. Yoneda, Y. Murata and H. Hashimoto, Tetrahedron Letters, 1971, 1523

60. E. Lord, M.P. Naan and C.D. Hall, J. Chem. Soc. (B), 1970, 1401

61. Y. Ito, M. Okano and R. Oda, Tetrahedron, 1966, 22, 2615

62. C.F.H. Allen and J.A. Van Allan, J. Amer. Chem. Soc., 1950, 72, 5165

63. P. Bladon, S. McVey and P.L. Pauson, *J. Chem. Soc.* (C), 1966, 306

64. see G. Rio and M. Charifi, *Compt. Rend.*, 1969, **286** (C), 1960

65. F.R. Newmann, *Annalen*, 1898, **302**, 236

66. M.P. Cava and K. Narasimhan, *J. Org. Chem.*, 1969, **34**, 3641

67. C.F.H. Allen and J.A. Van Allan, *J. Amer. Chem. Soc.*, 1942, **64**, 1260

68. H.P. Patel, Ph.D. Thesis, Sheffield 1963

69. G. Rio and M. Charifi, *Bull. Soc. Chim. France*, 1970, 3585

70. M.P. Cava, R.L. Little and D.R. Napier, *J. Amer. Chem. Soc.*, 1958, **80**, 2257

71. see D.R. Dalton and S.A. Liebmann, *Tetrahedron*, 1969, **25**, 3321

72. F. Ramirez and S. Levy, *J. Org. Chem.*, 1958, **23**, 2036

73. D. Lloyd and I. Gosnay, Unpublished results

74. H. Staudinger and A. Gaule, *Ber.*, 1916, **49**, 1951

75. H. Kainer, *Annalen*, 1952, **578**, 232

76. P.L. Pauson and B.J. Williams, *J. Chem. Soc.*, 1961, 4153

77. C. Kaiser, B.M. Lister, C.L. Zirkle, A. Burger, C.S. Davis, T.J. Delia and L. Zirngibl, *J. Med. Pharm. Chem.*, 1962, **5**, 1243

78. H. Dürr and G. Scheppers, *Chem. Ber.*, 1970, **103**, 380

79. H. Dürr and G. Scheppers, *Chem. Ber.*, 1967, **100**, 3236

80. N.A. Nesmeyanov, V.V. Pravdina and O.A. Reutov, *Doklady Akad. Nauk. SSSR*, 1964, **155**(6), 1364

81. A.J. Speziale and K.W. Ratts, *J. Amer. Chem. Soc.*, 1963, **85** 2790

82. D.A. Phipps and G.A.Taylor, *Chem. and Ind.*, 1968, 1279

83. Z. Hamlet and W.D. Barker, *Synthesis*, 1970, **2**(10), 543

84. H.J. Bestmann and H. Hartnung, Chem. Ber., 1966, 99, 1198

85. N.L. Drake and J.R. Adams, J. Amer. Chem. Soc., 1939, 61, 1326

86. E.E. Schweizer, G.J. O'Neill and J.N. Wemple, J. Org. Chem., 1964, 29, 1744.