Translated from *Uspekhi Khimii*, **49**, 1751-1773 (1980) U.D.C. 547.514.72

Arylated Cyclopentadienes and Cyclopentadienylides

Ya.N.Kreitsberga and O.Ya.Neiland

Information on the synthesis of arylated cyclopentadienes and their ylide derivatives is systematically reviewed, and the chemical reactions of the compounds are discussed. A list of 110 references is included.

CONTENTS

I.	Introduction	854
II.	Methods for the synthesis of arylated cyclopentadienes	854
III.	Chemical reactions of arylated cyclopentadienes	857
IV.	Preparation of arylated cyclopentadienylides	859
V.	Properties of arylated cyclopentadienylides	860

I. INTRODUCTION

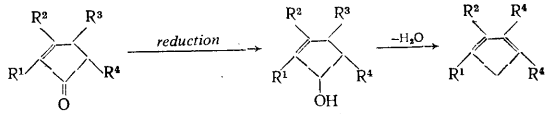
Several phenylated cyclopentadienes have found application as photosensitisers, but arylcyclopentadienes are of interest mainly as starting materials for the synthesis of cyclopentadienylides, fulvenes, ferrocenes, and other compounds.

The Review covers only those arylated cyclopentadienes in which the double bonds of the cyclopentadiene ring do not form part of an aromatic system (indenes are not covered).

II. METHODS FOR THE SYNTHESIS OF ARYLATED CYCLOPENTADIENES

1. Synthesis from Cyclopentenones

Cyclopentenones are used to obtain substituted cyclopentadienes because of the readiness with which the carbonyl group undergoes reduction and the Grignard reaction[1,2]. Cyclopent-2-enones are usually employed, for they are more stable and more readily available than cyclopent-3-enones[3]:

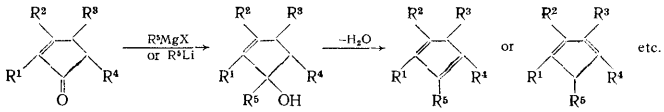


(*a*) $R^1=R^2=R^3=R^4=Ph$;
(*b*) $R^1=R^2=R^3=Ph$, $R^4=H$.

Selective reduction of the carbonyl group in the conjugated enone system is effected with lithium tetrahydroaluminate in ether at room temperature[1] or with sodium tetrahydroborate in aqueous dioxan[2]. The yields of cyclopentadienes reach 70–90% of theoretical, and the preparation can be accomplished in a single stage without isolation of the intermediate cyclopentenols. 1,2,3,4-Tetra- and 1,2,3-tri-phenylcyclopenta-1,3-dienes have been obtained in this way[1,2].

An attempt to use this method to obtain 1,2-diphenylcyclopenta-1,3-diene was unsuccessful[1,4], since 3,4-diphenylcyclopent-2-enol resinifies on acid dehydration, and the desired product is formed in small quantities, while the isomeric 3,4-diphenylcyclopent-3-enol does not eliminate water. 1,2-Diphenylcyclopenta-1,3-diene has been obtained in low yield by reducing 4-chloro-2,3-diphenylcyclopent-2-enone with lithium tetrahydroaluminate[5].

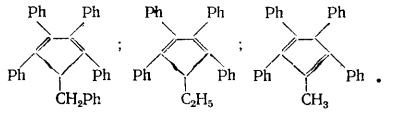
Substituted cyclopentadienes are most often obtained by treating cyclopentenones with organomagnesium and organolithium compounds and then dehydrating without isolating the intermediate carbinols[6-10]:



(*a*) $R^1=R^2=R^3=R^4=H$, $R^5=Ph$;
(*b*) $R^1=R^3=R^4=H$, $R^2=Ph$, $R^5=$ Ph or Alk; k;
(*c*) $R^1=R^2=R^3=R^4=Ph$, $R^5=$ pH or Alk; ::
(*d*) $R^4=H$, $R^1=R^2=R^3=Ph$, $R^5=p$-Me–C_6H_4–;
(*e*) $R^1=R^2=Ph$, $R^3=R^4=H$, $R^5=Ph$

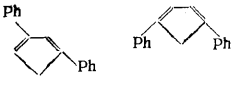
This method has been used to obtain the following cyclopenta-1,3-diene derivatives—1-phenyl[6], 1,4-diphenyl[7,8], 1,2,3,4,5-pentaphenyl[9], 1,2,3-triphenyl-4-*p*-tolyl, and 1,2,3-triphenyl[10].

The structure of the resulting cyclopentadienes cannot be predicted from that of the starting material, in the present case the cyclopentenone, since substituted cyclopentadienes that are isomeric with respect to the cyclic double bonds are in a state of thermodynamic equilibrium[3]. The potential barriers to interconversion of isomers are quite high, so that within certain temperature limits in effect only the thermodynamically more stable isomer can be isolated, but it is not so easy to predict which is the more stable form. Thus 5-benzyl- and 5-ethyl-1,2,3,4-tetraphenylcyclopenta-1,3-dienes are stable, but the methyl analogue has the structure 2-methyl-1,3,4,5-tetraphenylcyclopenta-1,3-diene[9]:



Therefore establishment of the structure of arylated cyclopentadienes requires careful examination of their proton magnetic resonance spectra.

Because of the complexity of determining the structure of the final product doubt attaches to the structure of several cyclopentadienes[7,8,11,12]. For example, it has not been established whether both isomers—1,3- and 1,4-diphenylcyclopenta-1,3-dienes

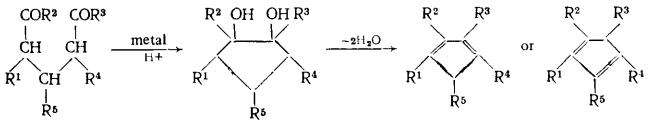


exist or only one of them. It appears more probable that only the 1,4-derivative can exist, since this structure is

supported by the ^{1}H n.m.r. spectra[8] and ozonolysis products of the diene[11], as well as by the identity of its properties with those described much earlier[7] for 1,3-diphenylcyclopenta-1,3-diene. The authors of this last work ascribe to this compound the structure of 1,3-diphenylcyclopenta-1,3-diene, although its properties conform to those of 1,4-diphenylcyclopenta-1,3-diene. However, this is contradicted by a recent report[12] that two diphenylcyclopentadienes have been obtained, giving different fulvenes on reaction with benzaldehyde.

2. Preparation of Arylated Cyclopentadienes from 1,5-Diketones

Arylated cyclopentadienes were first obtained from 1,5-diketones, in two stages. The first stage involves reductive cyclisation to cyclopentanediols (by prolonged boiling with zinc in acetic acid[13-19] or by means of aluminium amalgam in aqueous ethanol[17]). In the second stage these diols are dehydrated by boiling with alcoholic hydrochloric acid[13,14] or by fusing with oxalic acid[13,14]. The yields vary, but do not exceed 50%. Many arylcyclopentadienes have been obtained in this way[13-19]:

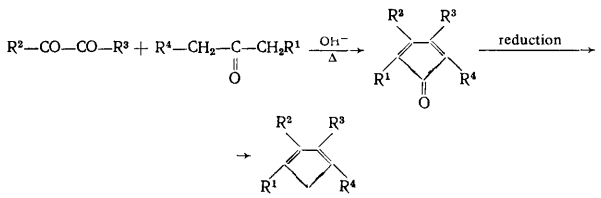


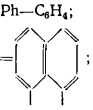
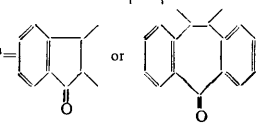
(*a*) $R^1=R^2=R^3=R^4=Ph$, $R^5=H$;
(*b*) R^1, R^2, R^3, $R^4=X-C_6H_4-$ (X=Cl, Me, OMe, NMe_2), $R^5=H$;
(*c*) $R^2=R^3=p$-MeO$-C_6H_4-$, $R^1=R^4=R^5=H$;
(*d*) $R^1=R^2=R^3=Ph$, $R^4=R^5=H$;
(*e*) $R^2=R^3=R^5=Ph$, $R^1=R^4=H$.

In acid media 1,2,3,4- and 1,2,3,5-tetraphenylcyclopentane-1,2-diols eliminate water to form the same 1,2,3,4-tetraphenylcyclopenta-1,3-diene[15], which apparently is thermodynamically the most stable isomer.

3. Preparation of Cyclopentadienes from Cyclopentadienones

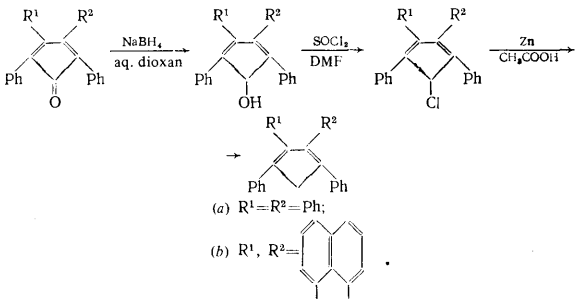
Cyclopentadienones (cyclones) are very reactive, with a strong tendency to dimerise by diene synthesis, so that mono- and di-arylcyclones can exist only as dimers[20]. Therefore cyclopentadienes can be obtained from tri- and tetra-arylcyclones, which are readily formed by the condensation of diaryl-α-diketones with αα′-diarylacetones[21-27]:



(*a*) $R^1=R^2=R^3=R^4=Ph$;
(*b*) $R^1=R^4=Ph$, $R^2=R^3=p$-Ph$-C_6H_4$;
(*c*) $R^1=R^4=n$-Ph$-C_6H_4$, $R^2=R^3=Ph$;
(*d*) $R^1=R^2=R^3=R^4=p$-Ph$-C_6H_4$;
(*e*) $R^1=R^4=Ph$, R^2, R^3=;
(*f*) $R^1=R^4=Ph$, R^2, R^3=.

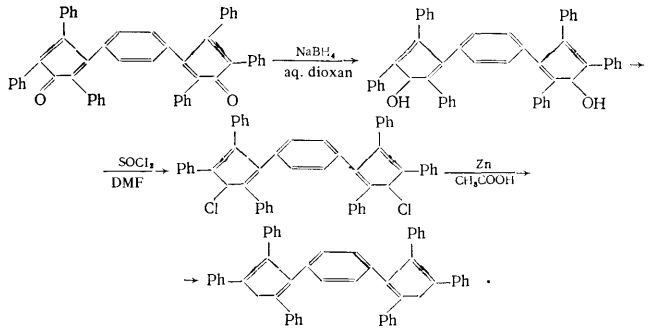
Selective reduction of the carbonyl group in tetraphenylcyclopentadienone (tetracyclone) was first attempted by Sonntag et al.[21], who obtained mixtures of various reduction products by the use of such reductants as zinc dust and lithium tetrahydroaluminate and by Clemmensen, Wolff–Kishner, or Meerwein–Pondorff reduction. Thus 5% and 12% yields of 1,2,3,4-tetraphenylcyclopenta-1,3-diene were obtained respectively on distillation with zinc dust at 270 °C and on reduction with lithium tetrahydroaluminate in dibutyl ether.

Recently, however, methods have been found for reducing tetra-arylcyclones to the corresponding cyclopentadienes. A fairly general scheme for obtaining tetra-arylcyclopentadienes is[22]



(*a*) $R^1=R^2=Ph$;
(*b*) R^1, R^2=.

Sodium tetrahydroborate in aqueous dioxan converts tetra-arylcyclones quantitatively into tetra-arylcyclopentadienols, in which the hydroxy-group is then replaced by a chlorine atom by means of Vilsmeier's reagent. The resulting tetra-arylchlorocyclopentadienes are dechlorinated with zinc in acetic acid to form tetra-arylcyclopentadienes (in 60% yield based on the cyclones). This method can be used[22] to obtain a bistetraphenylcyclopentadiene:

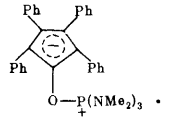


A better yield (93%) of tetraphenylcyclopentadiene was obtained[23] by the reduction of tetracyclone with a mixture of lithium tetrahydroaluminate and aluminium chloride, and a 55% yield by the two-stage reduction to 2,3,4,5-tetraphenylcyclopent-2-enol with sodium tetrahydroborate followed by elimination of water. However, other workers have been unable to repeat these experiments[24,25]. Tetraphenylcyclopentadiene is formed only on prolonged boiling in the presence of a large excess of reductant[24], and isolation of a chromatographically pure product is possible only in an inert atmosphere in the dark and at low temperatures[26]. It has proved possible to reproduce the earlier experiments[23] in only one case[26]. Extending to other cyclones the method of reduction with a mixture of lithium tetrahydroaluminate and aluminium chloride has given mixtures of products, from

which corresponding cyclopentadienes have been isolated in yields of 10–20%[24,25,27].

Tetracyclone can be reduced also with hydrazine dihydrate and dihydrochloride in diethylene glycol[26], under which conditions 1,2,3,4-tetraphenylcyclopenta-1,3-diene is formed in 80% yield.

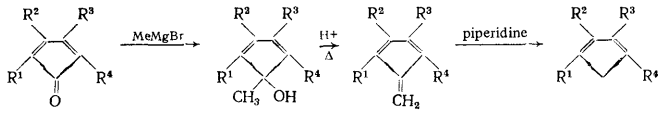
An interesting route from tetracyclone to tetraphenylcyclopentadiene was discovered[28] in an investigation of the action of tervalent phosphorus compounds on the former: with the hexamethyltriamide of phosphorous acid an unstable adduct is formed having the structure of an internal salt



This adduct is readily split by acids to form tetraphenylcyclopentadiene derivatives, but with hydrogen-donors it is reduced to 1,2,3,4-tetraphenylcyclopenta-1,3-diene in 87% yield. There have been no reports of the reactions of other cyclones with the triamide.

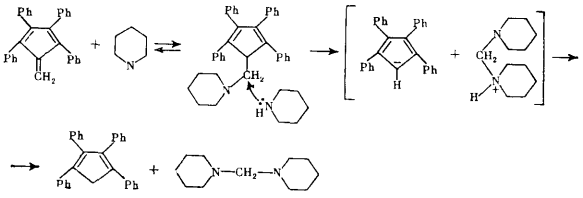
4. Fulvenes for the Preparation of Cyclopentadienes

Several tetra-arylcyclopentadienes can be obtained from tetra-arylfulvenes, which are formed by the action of methylmagnesium bromide on cyclones[29,30]:



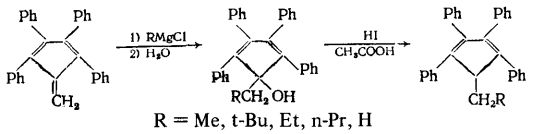
(*a*) $R^1=R^4=Ph$, $R^3=R^2=Ph$ or *p*-MeO—C_6H_4;
(*b*) $R^1=R^2=R^4=Ph$, $R^3=$ *p*-Me—C_6H_4—;
(*c*) $R^1=R^4=Ph$, $R^2=R^3=$ *p*-Me—C_6H_4— .

The mechanism



was suggested[29]. The ease of occurrence of this reaction (on boiling for a short time) is attributed to formation of the stable delocalised anion of tetraphenylcyclopentadiene. However, the reaction cannot be extended to other tetraarylcyclones ($R^2=p$-$X.C_6H_4$, where X = Cl, $(CH_3)_2N$, CH_3O), because the carbinols formed from cyclones and methylmagnesium bromide are unable to eliminate water[30].

Tetraphenylfulvene can be used to obtain alkyl- and arylalkyl-tetraphenylcyclopentadienes by the series of reactions[29,31,32]

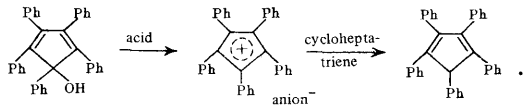


R = Me, t-Bu, Et, n-Pr, H

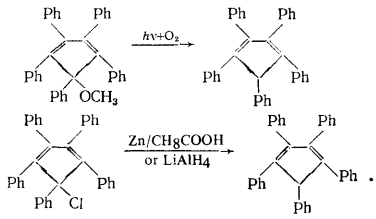
in which the yield is low. If $R=C_6H_5CH_2$ or t-C_4H_9, the carbinols are converted at high temperatures into the corresponding cyclopentadienes (*without use of a reductant*)[33].

5. Special Methods of Preparation of Arylated Cyclopentadienes

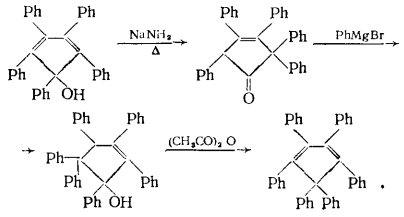
1,2,3,4,5-Pentaphenylcyclopentadiene can be obtained in two ways from 5-substituted derivatives. In the first method 1,2,3,4,5-pentaphenylcyclopenta-2,4-dienol is treated with a Lewis acid (boron trifluoride[34] or antimony pentachloride[35]) or with a strong acid, e.g. sulphuric acid[36,37], to form the pentaphenylcyclopentadienyl cation, stable only at low temperatures (−70 °C) which with a donor of a hydride ion gives 1,2,3,4,5-pentaphenylcyclopentadiene:



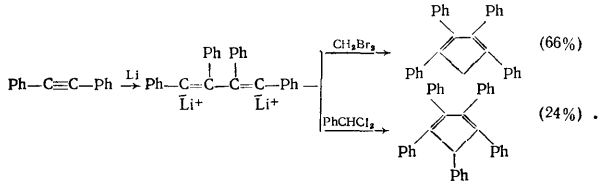
The second method may involve the photo-oxidation of 5-methoxylated[38,39] or the reduction with zinc dust or lithium tetrahydroaluminate of 5-chlorinated 1,2,3,4,5-pentaphenylcyclopenta-1,3-diene[14,38]:



Completely phenylated cyclopentadiene has been obtained by the isomerisation of 1,2,3,4,5-pentaphenylcyclopenta-2,4-dienol in the presence of sodamide into 2,2,3,4,5-pentaphenylcyclopent-3-enone, which reacts with phenylmagnesium bromide and then eliminates water to give a 30–40% yield of hexaphenylcyclopentadiene[40]:



The single-stage formation of 1,2,3,4-tetraphenylcyclopenta-1,3,diene from acetylenic compounds has still been little studied. In the presence of lithium, diphenylacetylene dimerises to form 1,4-dilithiotetraphenylbutadiene, which is alkylated by dibromomethane to give a 66% yield of tetraphenylcyclopentadiene[41]; when alkylation is effected with benzylidene dichloride, a 24% yield of 1,2,3,4,5-pentaphenylcyclopentadiene is obtained[42]:



Yields of 1,2,3,4-tetraphenylcyclopenta-1,3-diene obtained by the action of diphenylacetylene on trimethylchromium[43] or on cyclopentadienylmethylmolybdenum tricarbonyl[44] are below 5%.

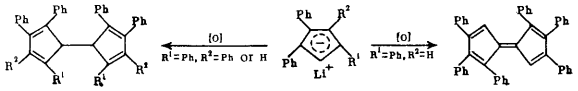
III. CHEMICAL REACTIONS OF ARYLATED CYCLOPENTADIENES

1. Acid-Base Reactions

Unsubstituted cyclopentadiene is a carbon–hydrogen acid, whose aqueous solution has $pK_a = 15.6$.[45] Such high acidity is attributed to stabilisation of the cyclopentadienyl anion by cyclic delocalisation of the six π electrons. The acidity is enhanced by the introduction of aryl substituents into the cyclopentadiene ring: thus for 8*H*-cyclopent[*a*]acenaphthylene in chloroform $pK_a = 14 \pm 0.5$.[46] For other arylated cyclopentadienes pK_a has not been determined, but their acidity is evident in reactions with bases and in many reactions involving condensation, in which they behave as containing an activated methylene group.

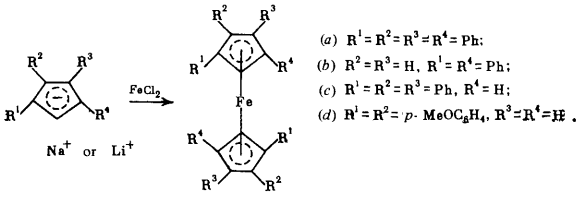
The sodium or lithium salt of 1,2,3,4-tetraphenylcyclopenta-1,3-diene is formed by the action of sodium in oxolan[47], sodamide[48,49], or sodium hydride in dimethyl sulphoxide (dimsylsodium)[47] or of phenyl-lithium or butyl-lithium[50,51]. Salts of 1,4-di- and 1,2,3,4,5-penta-phenylcyclopentadienes have been obtained by reaction of sodamide (or better dimsylsodium) with other substituted cyclopentadienes[49]. Phenyl-lithium has been used to obtain salts of 1,2,3-tri- and 1,2,3,4-tetra-phenylcyclopentadienes[49,2], and those of 1,2-di-*p*-methoxyphenylcyclopenta-1,3-diene by the action of methylmagnesium bromide[17].

Salts of arylated cyclopentadienes are readily oxidised by atmospheric oxygen and other oxidants, e.g. iodine, to form fulvalenes or, when this is prevented by steric hindrance, 1,1-dihydrofulvalenes[2]:



Salts of cyclopentadienes are therefore obtained in an inert atmosphere, and are immediately subjected to further reactions without isolation.

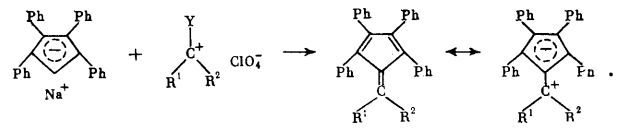
The reaction between salts of arylated cyclopentadienes and iron(II) chloride provides the only method for obtaining polyarylated ferrocenes[17,18,48,49]:



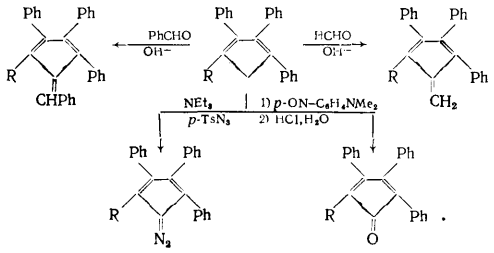
(*a*) $R^1 = R^2 = R^3 = R^4 = Ph$;
(*b*) $R^2 = R^3 = H$, $R^1 = R^4 = Ph$;
(*c*) $R^1 = R^2 = R^3 = Ph$, $R^4 = H$;
(*d*) $R^1 = R^2 = p$-$MeOC_6H_4$, $R^3 = R^4 = H$.

Almost all such compounds have been obtained in this way, with the exception of decaphenylferrocene, which was attributed[49] to steric hindrance.

The sodium and lithium salts of tetraphenylcyclopentadiene undergo nucleophilic substitution with 3,3-dichloro-1,2-diphenylcyclopropene[52], with methoxydiphenylcyclopropenylium[51], 4-chloro-2,6-dimethylthiopyrylium[53], and 2-methylthio-1,3-dithiolium[54] perchlorates, and with tropylium bromide[47] to form deeply coloured compounds of fulvene type, possessing large dipole moments:

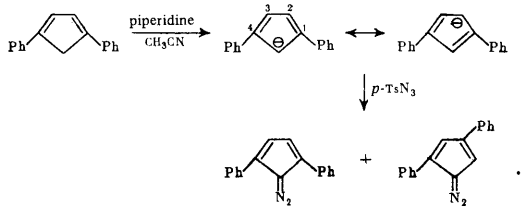


In the presence of bases arylated cyclopentadienes condense with aldehydes[12,55,56], *p*-nitrosodimethylaniline[16,56], and toluene-*p*-sulphonyl azide[3,24,50,56–59]:



The reactions with formaldehyde and benzaldehyde yield fulvenes, but that with *p*-nitrosodimethylaniline after hydrolysis gives cyclones. These reactions have been used repeatedly to characterise newly obtained cyclopentadienes[14,16,29].

The reaction with tosyl azide involves the formation of diazocyclopentadienes, which are starting materials for many cyclopentadiene derivatives, including ylides of arylated cyclopentadienes (Section IV). It is interesting that the reaction of 1,4-diphenylcyclopenta-1,3-diene with tosyl azide in the presence of piperidine gives a mixture of 1-diazo-2,4(and 2,5)-diphenylcyclopentadienes in yields of 30% and 58% respectively[59]. The explanation is that in an intermediate species—the anion of 1,4-diphenylcyclopenta-1,3-diene—the negative charge is delocalised to give an appreciable negative charge on the $C_{(2)}$ atom[59]:



An analogous phenomenon was observed by Freeman and Lloyd[60], who obtained 2,4-diphenyl-1-triphenylarsoniopentadienylide in the reaction between 1,4-diphenylcyclopenta-1,3-diene and triphenylarsine oxide in triethylamine. The course of this reaction is also explained by formation of a conjugated anion of 1,4-diphenylcyclopentadiene. Hence it can reasonably be expected that conjugated anions of mono-, di-, and tri-arylcyclopentadienes will contain more than one nucleophilic centre, owing to delocalisation of the negative charge in the ring.

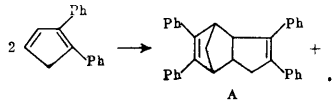
2. Arylated Cyclopentadienes in Diene Synthesis

Like other cyclopentadienes the arylated derivatives are able to undergo diene synthesis with various dienophiles, including cyclopentadienes, although the introduction of

aryl substituents results in steric hindrance to the interaction of two cyclopentadiene molecules.

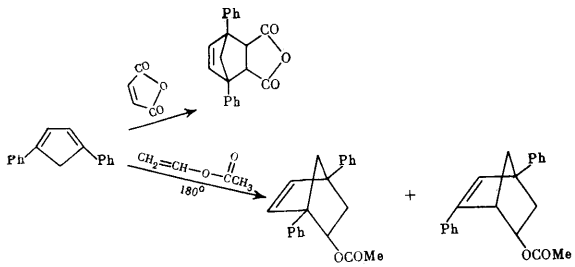
Crystalline phenylcyclopentadiene is monomeric, but its recrystallisation from ligroin leads to formation of a dimer (the structure of the latter has not been established, but dimerisation is supposed to occur by a mechanism of diene synthesis)[6].

On prolonged heating at 120 °C, 1,2-diphenylcyclopenta-1,3-diene dimerises to a mixture of products (with structure A predominating)[4,5,61]:



A

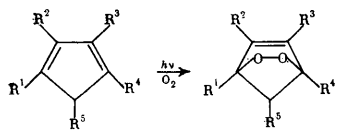
Dimerisation of the 1,4-diphenyl isomer has not been observed, although this compound readily undergoes diene synthesis with maleic anhydride[11,62] and with vinyl acetate[63]:



Dimerisation by a mechanism of diene synthesis does not take place in the presence of three or more aryl substituents. Perhaps interaction between the phenyl *ortho*-hydrogen atoms "twists" the phenyl groups out of the cyclopentadiene plane[18,64]. This impedes a frontal arrangement of two substituted cyclopentadiene molecules and formation of the transition state necessary for diene synthesis.

3. Photo-oxidation and Free Radicals of Pentaarylcyclopentadienes

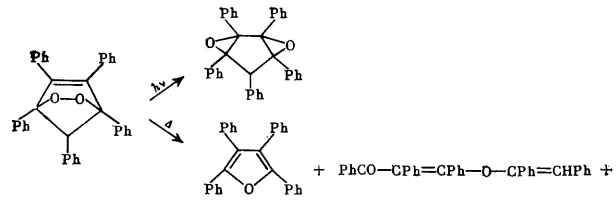
1,4-Diphenylcyclopenta-1,3-diene has been recommended[65,66] for use as a photosensitiser, and is also an oxygen-acceptor (with formation of compounds of the type MO_2). Photo-oxidation has been studied on 1,2,3,4-tetraphenylcyclopenta-1,3-diene and its alkyl derivatives[9,67], and on the 1,2,3,4,5-pentaphenyl[68] and 1,2-diphenyl[5,61] compounds. Oxygen was found to undergo 1,4 addition to the diene system to form *endo*-peroxides:



(*a*) $R^1 = R^2 = R^3 = R^4 = Ph$, $R^5 = H$, Ph, Alk;
(*b*) $R^1 = R^2 = Ph$, $R^3 = R^4 = R^5 = H$;
(*c*) $R^1 = R^2 = R^4 = R^5 = Ph$, $R^3 = Me$.

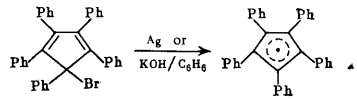
The structures of the latter have been confirmed by various chemical reactions. For example, reduction of the *endo*-peroxide of 1,2-diphenylcyclopentadiene with lithium tetrahydroaluminate gave 3,4-diphenylcyclopent-4-ene-*cis*-1,3-diol, but alkaline hydrolysis gave 4-hydroxy-3,4-diphenylcyclopent-2-enone[61].

When subjected to light or heat, *endo*-peroxides undergo further changes with fission not only of carbon–oxygen and oxygen–oxygen bonds but also of carbon–carbon bonds, so that the photo-oxidation of arylated cyclopentadienes usually gives a complicated mixture of products. For example, under the influence of light and of high temperatures the *endo*-peroxide of 1,2,3,4,5-pentaphenylcyclopentadiene undergoes the reactions[68]



The oxidation of cyclopentadienes in the dark or by means of other oxidants has not been investigated, with the exception of the oxidation of anions of tri- and tetra-phenylcyclopentadienes by iodine[2].

Many extremely stable, deeply coloured free radicals of 1,2,3,4,5-penta-arylcyclopentadienes are known. However, they have been obtained not by the direct oxidation of cyclopentadienes but by the action of silver or potassium hydroxide on penta-arylbromocyclopentadienes[14,69–76]:

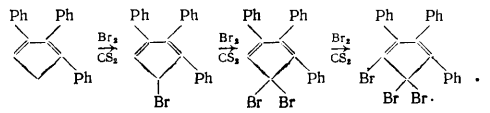


4. Halogenation of Cyclopentadienes

The action of halogens on arylated cyclopentadienes may involve either addition or substitution depending on the conditions and also on the halogenating agent used. Substitution occurs more readily.

Boiling 1,2,3-triphenylcyclopenta-1,3-diene with *N*-bromosuccinimide in tetrachloromethane for 1 h gives a mixture of the 1-bromo-2,3,4-triphenyl- and 5-bromo-1,2,3-triphenylcyclopentadienes[77]; boiling for 2 h yields 5,5-dibromo-1,2,3-triphenylcyclopenta-1,3-diene[2]. Under the same conditions 1,2,4-triphenylcyclopenta-1,3-diene forms the 5-bromo-1,2,4-triphenyl derivative[2,10].

With bromine in carbon disulphide all three hydrogen atoms in the 1,2,3-triphenylcyclopentadiene are successively replaced[2]:



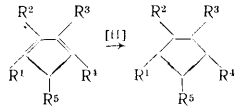
The action of bromine on the 1,2,4-triphenylcyclopentadiene involves a mechanism of addition and elimination with the formation of 2,5-dibromo-1,3,4-triphenylcyclopenta-1,3-diene[19].

With bromine both methylene hydrogen atoms in 1,2,3,4-tetraphenylcyclopenta-1,3-diene are substituted at once to give the 5,5-dibromo-derivative[13]. To obtain the monobromo-compound it is necessary to use *N*-bromosuccinimide or bromopyridinium nitrate[78]. Similarly, iodopyridinium

nitrate gives 5-iodo-1,2,3,4-tetraphenylcyclopenta-1,3-diene[78], and *S*-chloro-*S*-*p*-nitrophenyl-*N*-phenylsulphonylsulphidimine yields the corresponding 5-chloro-compound[79].

5. Hydrogenation of Arylated Cyclopentadienes

The hydrogenation of arylated cyclopentadienes to cyclopentane derivatives is used to establish and confirm the structure of cyclopentadienes obtained for the first time[11,13,19,80]:



(*a*) R^1 = R^4 = Ph, R^2 = R^3 = R^5 = H;
(*b*) R^1 = R^4 = *p*-Me—C_6H_4; R^2 = R^3 = R^5 = H;
(*c*) R^2 = R^3 = R^5 = Ph, R^1 = R^4 = H;
(*d*) R^1 = R^2 = R^3 = R^4 = Ph, R^5 = H.

Hydrogenation is effected with hydrogen in the presence of a catalyst—Raney nickel[80] or palladium black[11]—or with hydriodic acid in the presence of red phosphorus[13,19].

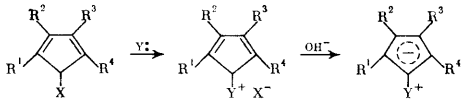
IV. PREPARATION OF ARYLATED CYCLOPENTADIENYLIDES

Much information has been published on the preparation and properties of tri- and tetra-arylcyclopentadienylides, but only in 1974 were the first diarylcyclopentadienylides—1-triphenylphosphonio- and 1-triphenylarsonio-2,4- and -2,5-diphenylcyclopentadienylides—described[60], since when 1-*N*-pyridinio-2,3- and -3,4-diphenylcyclopentadienylides have been obtained[22]. Ylides of monoarylcyclopentadienes are at present unknown.

Two main methods—the salt method and the decomposition of diazocyclopentadienes—have been used to obtain arylated cyclopentadienylides. In addition, triphenylarsoniocyclopentadienylides have been obtained by condensing substituted cyclopentadienes with triphenylarine oxide in the presence of bases[60,77] or phosphorus pentoxide[81].

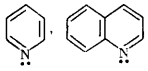
1. Salt Method

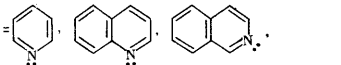
In the salt method onium salts of arylated cyclopentadienes are treated with bases to abstract the proton. Its limits of applicability depend on the accessibility of the onium salts[82]. These can be obtained in three ways, firstly from halogen derivatives of the substituted cyclopentadiene[60,77,83–86]:

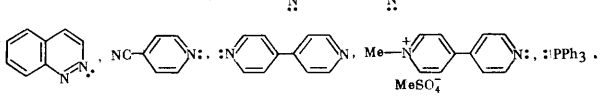


X = Cl or Br;

(a) R^1 = R^2 = R^3 = Ph, R^4 = H, Y: = , :PPh_3, :$AsPh_3$, :SMe_2, :S=C(NR$_2$)(NR$_2$);

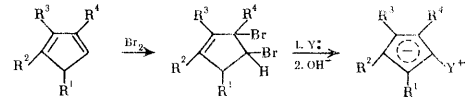
(b) R^1 = R^2 = R^3 = R^4 = Ph, Y: = , :PPh_3, :S=C(NR$_2$)(NR$_2$);

(c) R^1 = R^4 = Ph, R^2, R^3 = , Y: = ;

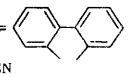
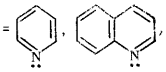


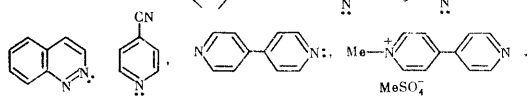
$MeSO_4^-$

In the second process an onium salt of an arylated cyclopentadiene is obtained by the action of a base on a dibromocyclopentene[24,87]:



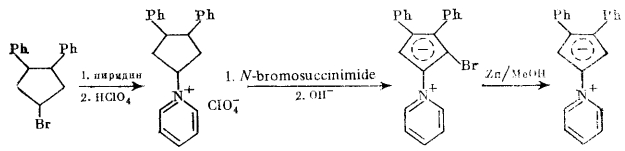
(*a*) R^1 = R^4 = H, R^2 = R^3 = Ph, Y: = ;

(*b*) R^1 = R^4 = Ph, R^2, R^3 = , Y: = ,



$MeSO_4^-$

The starting compound in the third method is a halogenated cyclopentane, but in this case it is necessary also to dehydrogenate the onium salt[24]:

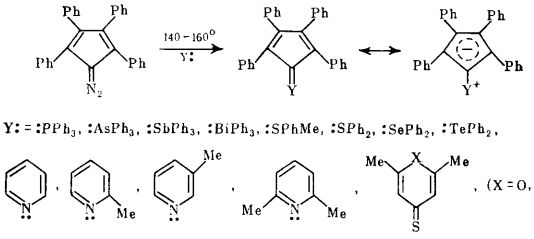


In all cases aqueous–ethanolic sodium hydroxide was used as the base.

Two limitations have been found in obtaining onium salts of arylated cyclopentadienes, the first involving steric hindrance to nucleophilic substitution of the bromine atom. If the cyclopentadiene ring contains 2- and 5-phenyl substituents, the yield of onium salts in the reaction of the corresponding bromocyclopentadiene with 2-methyl- or 2,6-dimethyl-pyridine is 6%, but with quinoline reaction does not occur[84]. From the corresponding chlorocyclopentadiene and quinoline the onium bond is formed in low yield[85], but when the decomposition of diazocyclopentadienes is used, a method in which steric hindrance is absent from the reactant species (a carbene), onium salts are obtained in good yields[88]. The second limitation is due to dehalogenation in the reaction of halogenated cyclopentadienes with triphenylphosphine in acid solvents. This reaction involves the formation not of onium salts but of the original substituted cyclopentadienes[77,85], which is attributed to attack by triphenylphosphine on the bromine atom.

2. Decomposition of Diazocyclopentadienes

The thermal decomposition of arylated diazocyclopentadienes in the presence of nucleophilic species has been used to obtain a number of tetraphenylcyclopentadienylides[59,86,88,90–99], since diazotetraphenylcyclopentadiene itself is readily obtainable[88]:



With copper bronze powder as catalyst the temperature can be lowered and the reaction conducted in such solvents as benzene, cyclohexane, and ethanol, when the yield of ylides is increased[60].

1-Triphenylphosphonio- and 1-triphenylarsonio-2,3,4-triphenylcyclopentadienylides have been obtained by the catalytic decomposition of 1-diazo-2,3,4-triphenylcyclopentadiene[60], although it had been reported earlier[77] that the decomposition of diazocyclopentadienes could not be used to obtain onium betaines of cyclopentadienes unsubstituted at position 2 or 5.

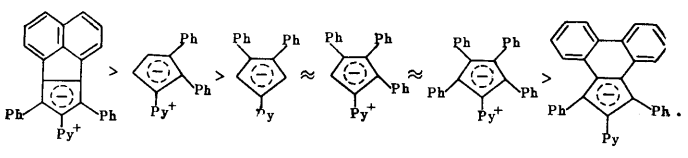
The decomposition of 1-diazo-2,5-diphenylcyclopentadiene in the presence of triphenylphosphine and triphenylarsine yields respectively 1-triphenylphosphonio- and 1-triphenylarsonio-2,4-diphenylcyclopentadienylides. The explanation proffered[60] is that positions 3 and 4 in the intermediate 1-carbene of 2,5-diphenylcyclopentadiene are sterically more favourable than position 1 to nucleophilic attack by triphenylphosphine or triphenylarsine.

Theoretically ylides can be formed from diazo-compounds in two ways. The nucleophile (triphenylphosphine, triphenylarsine, etc.) may add initially to the diazo-compound, and the resulting adduct breaks down to the ylide with the evolution of nitrogen. Alternatively the ylide may be formed via the carbene, which is partly supported by thermogravimetric investigation of these reactions[100].

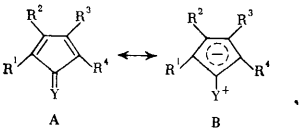
V. PROPERTIES OF ARYLATED CYCLOPENTADIENYLIDES

1. Physical Properties and Structure

Arylated cyclopentadienylides are crystalline, sparingly soluble in water, ethanol, ether, and hexane, and soluble in benzene and chloroform. Phosphonium, arsonium, sulphonium, and selenonium ylides are stable, and decompose only when illuminated. Pyridinium, other *N*-heteronium, and stibonium ylides are stable in the solid state, but decompose in solution. Telluronium and bismuthonium ylides decompose slowly in the solid state, but rapidly in solution[86, 101]. The stability of ylides depends not only on the onium moiety but also on the aryl substituents in the cyclopentadiene ring. For example, known pyridium ylides of arylated cyclopentadienes can be arranged in the stability sequence



The stability of ylides is usually explained[86] by the nature of the bond between the heteroatom and the five-membered ring, which in turn depends on the charge distribution in the molecule (on the "contribution" by the dipolar structure B):



Increase in the volume of the heteroatom enhances the diffuse character of the *d*-orbital, while the efficiency of interaction between the 2*p*-electrons of the carbanion and the vacant *d*-orbitals of the heteroatom diminishes (the contribution by structure A decreases). The stability diminishes also as electrostatic interaction between carbanion and onium heteroatom becomes weaker (with decrease in the electronegativity of the heteroatom, with lengthening of the carbon–heteroatom bond).[86] Arylated cyclopentadienylides are less stable if aryl or onium substituents are "twisted" out of the cyclopentadiene plane owing to the steric hindrance in the molecule.

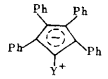
Table 1. Long-wavelength absorption by tetraphenylcyclopentadienylides[85,86].

Y	PPh_3	$AsPh_3$	$SbPh_3$	$BiPh_3$	SPh_2
λ_{max}, nm (solvent)	288* (EtOH)	291* (EtOH)	349 ($CHCl_3$)	525 (EtOH); 596 (benzene)	292*; 328*(sh** (EtOH)

Y	$SePh_2$	$TePh_2$		
λ_{max}, nm (solvent	294*; 347* (sh**) (EtOH)	335 (MeOH) 347 (benzene)	538 (EtOH) 595 (benzene)	587 (EtOH) 645 (benzene)

*Absorption maximum independent of solvent (solvatochromism not observed).
**sh = shoulder.

Table 2. Long-wavelength absorption by pyridinium ylides of arylated cyclopentadienes[22].

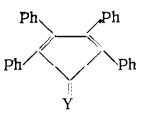


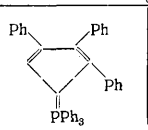
λ_{max} in						
Benzene	572	582	589	590	630	650
Ethanol	530	530	547	535	572	590

The structure of an ylide can best be characterised by X-ray examination, but only a few ylides of unsubstituted cyclopentadiene have been studied in this way[102–104].

All ylides are yellow with the exception of *N*-heteronium and bismuthonium ylides, which in the crystalline form are intensely coloured ($\lambda_{max} \cong 500-800$ nm) [85,87,101] (Table 1). With several ylides (Y = $(C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, $(C_6H_5)_2S$, $(C_6H_5)_2Se$) the longer-wavelength absorption maximum is independent of the solvent, but negative solvatochromism is observed with bismuthonium and telluronium ylides of tetraphenylcyclopentadiene[86] and with all *N*-heteronium ylides of arylated cyclopentadienes[22,77,85,87] (Table 2). Slight solvatochromism has been found in 1-triphenylphosphonio-2,3,5-tri- and -2,4-di-phenylcyclopentadienylides[60]. It is assumed that betaines in which solvatochromism is observed have structure B in the ground state, or that the contribution by this structure is large, and that the longer-wavelength absorption is due to intramolecular charge transfer.

Table 3. Dipole moments of arylated cyclopentadienylides[105].



Y	μ, D	Y	μ, D
SPh_2	6.69		6.99
SPhMe	6.90		
PPh_3	7.75		
$AsPh_3$	8.32		
$SbPh_3$	2.2		

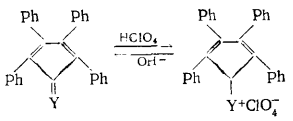
Dipole moments in benzene solution at 25 °C have been determined for several tetra- and 2,3,4-tri-phenylcyclopentadienylides (Table 3)[105]. The results indicate that the contribution by the ionic structure (B) increases in the series of betaines with sulphonio < phosphonio < arsonio. The low dipole moment of triphenylstiboniotetraphenylcyclopentadienylide is explained by association of the betaine with the solvent or with itself[105]. The dipole moment is larger in tetra- than in tri-phenylcyclopentadienylides and ylides of unsubstituted cyclopentadiene[106]; hence substitution by phenyl groups increases the contribution by the ionic structure in the ground state of the molecules.

Ionisation potentials have been determined for several ylides of 7,9-diphenyl-8*H*-cyclopent[*a*]acenaphthylene by spectrophotometric examination of intermolecular charge-transfer complexes[85]. These ylides are found to constitute a novel class of strong electron-donors with ionisation potentials of 6.7–6.75 eV.

2. Reactions of Arylated Cyclopentadienylides

(*a*) Acid-base reactions

Arylated cyclopentadienylides are bases, forming with acids such as perchloric, hydrobromic, etc. salts that are readily hydrolysed to the original ylides:



Y=PPh_3, $AsPh_3$, $SbPh_3$, Py .

This procedure is the only method for purifying ylides that are unstable in solution[86]. However, several cyclopentadienylides of diphenylsulphonium[107], diphenyselenonium, and diphenyltelluronium are too weak bases to be protonated by mineral acids.

Table 4. Acidity constants pK_a of protonated forms of arylated cyclopentadienylides[101,107].

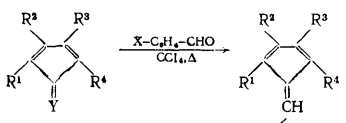
Tetraphenylcyclopentadienylides			2,3,4-Triphenylcyclopentadienylides	
Y=PPh_3	Y=$AsPh_3$	Y=$SbPh_3$	Y=PPh_3	Y=$AsPh_3$
5.3	7.6	7.6	4.2	5.6

Acidity constants of the protonated forms in 95% ethanol have been determined for several tetra- and 2,3,4-triphenylcyclopentadienylides[101,107]. Table 4 shows that the basicity of the ylides is closely related to the polarity of the molecule. The basicity diminishes in the sequence stibonio > arsonio > phosphonio with decrease in the degree of interaction of the 2*p*-electrons of the anion with the vacant orbitals of the heteroatom. Values of pK_a are smaller for tri- than for tetra-phenylcyclopentadienylides, which indicates greater thermodynamic stability of the former[101].

The site of protonation depends on the structure of the ylide. Investigation of the proton magnetic resonance spectra of cyclopentadienylides in trifluoroacetic acid has established[60,101] that the unsubstituted carbon atom is protonated, for example positions 5 and 3 respectively in 2,3,4-tri- and 2,5-di-phenylcyclopentadienylides. On the other hand, 2,3,5-triphenylcyclopentadienylides are not protonated in the vacant position 4, as the n.m.r. spectra do not contain the signal of a methylene group.

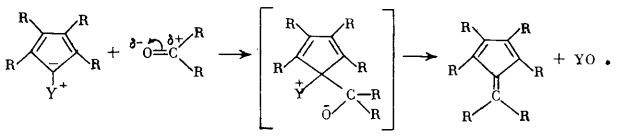
(*b*) Reaction with a polar double bond

Reactions with aldehydes and with *p*-nitrosobenzene have been studied for tri- and tetra-phenylcyclopentadienylides[60,83,86,101]. Only triphenylarsonium, triphenylstibonium, and thiouronium ylides react with benzaldehyde or *p*-nitrobenzaldehyde, forming fulvenes:

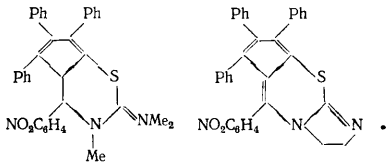


Y=$AsPh_3$, $SbPh_3$, S—CN $(HMe)_2$;
R^1=R^2=R^3=Ph, R^4=Ph or H .

Formation of the latter is explained[86] by nucleophilic addition of the ylide to the carbonyl group with further change in the resulting adduct:

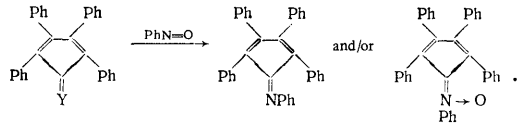


The reaction between 1-thiouronio-2,3,4-triphenylcyclopentadienylide and *p*-nitrobenzaldehyde yields mainly strongly coloured products having the structure[83]



This is attributed[83] to attack by the aldehyde at the unsubstituted position 5 (not position 1) in the cyclopentadiene ring followed by attack on one of the nitrogen atoms. Ylides having $Y = (C_6H_5)_3P$, $(C_6H_5)_2S$, $(C_6H_5)_2Se$, $(C_6H_5)_2Te$ do not react with aldehydes.

Ylides of tetra-arylcyclopentadienes react with nitrosobenzene to form the tetra-arylcyclopentadienone anil, [its *N*-oxide], or a mixture of the two[83,86,101]:



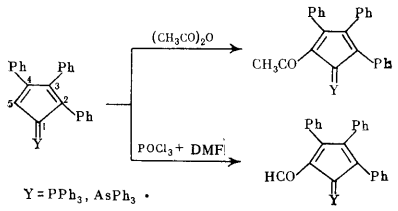
Diphenysulphonio- and -selenonio-tetraphenylcyclopentadienylides, when boiled with nitrosobenzene in tetrachloromethane for 18 h, form the anil *N*-oxides of tetraphenylcyclopentadienone in 5% and 80% yields respectively. Under the same conditions triphenylarsoniotetraphenylcyclopentadienylide forms a mixture of the anil and the anil *N*-oxide (respective yields 35% and 48%), but the corresponding stibonio-ylide forms only the anil *N*-oxide (yield 80%) even with a shorter period of boiling[86].

2,3,4-Triphenylcyclopentadienylides are more reactive than their tetraphenyl analogues towards polar double bonds, although the former are less basic: i.e. the nucleophilicity of the ylides (Sb > As > Se > S > P) does not parallel their basicity (Sb > As > P ≫ S ≅ Se) owing to the great sensitivity of nucleophilic reactions to steric factors[107].

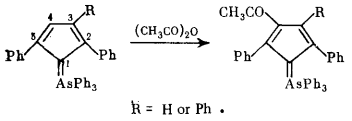
(*c*) Electrophilic substitution

Electrophilic substitution in ylides of unsubstituted cyclopentadiene have been well studied[106,108–110], and arylated cyclopentadienylides are found to follow the same pattern. Substitution occurs more readily at position 2(5), but if this site is occupied, it occurs at position 3(4),[60] which is explained by the more favourable transition state with substitution in position 2(5).[108]

1-Triphenyl-phosphonio- and -arsonio-2,3,4-triphenylcyclopentadienylides are acylated by acetic anhydride[81] and undergo Vilsmeier formylation[101] to the corresponding 5-substituted ylides:



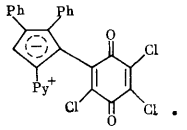
2,5-Di- and 2,3,5-tri-phenylcyclopentadienylides are acylated at position 4:[60]



1-Triphenylphosphonio-2,4-diphenylcyclopentadienylide forms a mixture of 3- and 5-acylated products in which the latter isomer predominates, but Vilsmeier formylation gives the disubstituted 3,5-diformyl-2,4-diphenyl-1-triphenylphosphoniocyclopentadienylide[60].

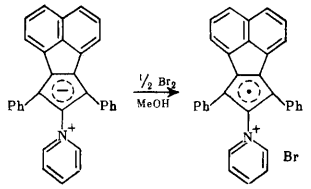
Azo-coupling has been investigated in 1-phosphonio- and 1-arsonio-2,4-di-, -2,5-di-, and -2,3,4-tri-phenylcyclopentadienylides. The products are quite stable red 2(5)-azo-compounds[60].

1-*N*-Pyridinio-3,4-diphenylcyclopentadienylide reacts with *p*-chloranil to form as electrophilic substitution product a stable betaine having two absorption bands in the visible (at 480–520 and 800 nm). The former absorption maximum exhibits negative solvatochromism, but the latter is independent of the solvent. Thus the interesting phenomenon is observed of simultaneous intramolecular charge transfer from the 3,4-diphenylcyclopentadiene anion to the onium substituent (~500 nm) and to the 2-substituent (~800 nm):[22]



(*d*) Oxidation

N-Heteronium, stibonium, telluronium, and bismuthonium ylides of arylated cyclopentadienes are relatively unstable[24,86,101]. Their instability is connected with their ready oxidisability by atmospheric oxygen, since they are more stable in an inert atmosphere. However, the decomposition (atmospheric oxidation) products of ylides have not yet been studied. It has been shown merely[22] that oxidation by bromine of 8-*N*-pyridinio-7,9-diphenyl-8*H*-cyclopent[*a*]-acenaphthylenylide gives a salt of a radical-cation:



In the crystalline state the yellowish-green product is extremely stable, but it decomposes readily in solution.

REFERENCES

1. G.Rio and J.Mion-Coatleven, Bull.Soc.chim.France 3774 (1966).
2. P.Pauson and B.Williams, J.Chem.Soc., 4153 (1961).
3. A.N.Elizarova, "Khimiya Tsiklopentenonov" (The Chemistry of Cyclopentenones), Nauka, Moscow, 1966, p.150.
4. P.Bladon, S.McVey, and P.Pauson, J.Chem.Soc.C, 306 (1966).
5. G.Rio and M.Charifi, Bull.Soc.chim.France, 3585 (1970).
6. R.Riemschneider and R.Nerin, Monatsh., **91**, 829 (1960).
7. W.Borsche and W.Menz, Ber., **41**, 190 (1908).
8. D.Farnum, A.Mostashari, and A.Hagedorn, J.Org. Chem., **36**, 699 (1971).
9. G.Rio and G.Sanz, Bull.Soc.chim.France, 3775 (1966).
10. B.Freeman, J.Gagan, and D.Lloyd, Tetrahedron, **29**, 4307 (1973).
11. N.Drake and J.Adams, J.Amer.Chem.Soc., **61**, 1326 (1939).
12. G.A.Chukhadzhyan, Zh.I.Abramyan, G.M.Tonyan, and V.A.Matosyan, Zhur.Org.Khim., **10**, 1994 (1974).
13. J.Wislicenus and H.Carpenter, Annalen, **302**, 223 (1898).
14. K.Ziegler and B.Schnell, Annalen, **445**, 266 (1925).
15. E.Auerbach, Ber., **36**, 993 (1903).
16. L.Mehr, E.Becker, and P.Spoerri, J.Amer.Chem. Soc., **77**, 984 (1955).
17. M.Rosenblum, W.Howells, A.Banerjee, and C.Bennett, J.Amer.Chem.Soc., **84**, 2726 (1962).
18. P.Pauson, J.Amer.Chem.Soc., **76**, 2187 (1954).
19. F.Newman, Annalen, **302**, 237 (1898).
20. M.Ogliaruso, M.Romanelli, and E.Becker, Chem.Rev., **65**, 261 (1965).
21. N.Sonntag, S.Linder, E.Becker, and P.Spoerri, J.Amer.Chem.Soc., **75**, 2283 (1953).
22. Ya.N.Kreitsberga, Candidate's Thesis, Riga Polytechnic Institute, 1977.
23. M.Cava and K.Narashimhan, J.Org.Chem., **34**, 3641 (1969).
24. H.Czwikla, Dissertation Technische Universität, Hannover, 1971.
25. W.Ried, W.Merkel, and H.Herrmann, Annalen, **750**, 91 (1971).
26. H.Bandara, N.Rajasckera, and S.Sotheeswaren, Tetrahedron, **30**, 2587 (1974).
27. W.Ried and H.Herrmann, Tetrahedron, **769**, 201 (1974).
28. M.Gallagher and I.Jenkins, J.Chem.Soc.C, 2605 (1969).
29. D.Taber, E.Becker, and P.Spoerri, J.Amer.Chem. Soc., **76**, 776 (1954).
30. K.Kun and P.Spoerri, J.Amer.Chem.Soc., **77**, 4676 (1955).
31. A.Bonagura, M.Meyers, S.Storfer, and E.Becker, J.Amer.Chem.Soc., **76**, 6122 (1954).
32. S.Linder, E.Becker, and P.Spoerri, J.Amer.Chem. Soc., **75**, 5972 (1953).
33. R.Fuson and O.York, J.Org.Chem., **18**, 570 (1953).
34. R.Bresloy, H.WonChang, R.Hill, and E.Wasserman, J.Amer.Chem.Soc., **89**, 1112 (1967).
35. H.Volz, Tetrahedron Letters, 1899 (1964).
36. R.Breslow and H.WonChang, J.Amer.Chem.Soc., **83**, 3727 (1961).
37. R.Breslow and H.WonChang, J.Amer.Chem.Soc., **85**, 2033 (1963).
38. G.Rio and A.Ranjon, Compt.rend., **254C**, 2997 (1962).
39. C.Dufraisse, G.Rio, and A.Liberles, Compt.rend., **256**, 1873 (1963).
40. A.Youssef and M.Ogliaruso, J.Org.Chem., **37**, 2601 (1972).
41. F.Leavitt, T.Manuel, and F.Johnson, J.Amer.Chem. Soc., **82**, 5099 (1960).
42. E.Braye, W.Hubel, and Y.Caplier, J.Amer.Chem.Soc., **83**, 4406 (1961).
43. M.Tsutsui, J.Amer.Chem.Soc., **81**, 6090 (1959).
44. A.Nakamura and N.Hagihara, Nyppon Kagaku Zasshi, **84**, 344 (1963).
45. A.Streitwieser and L.Lebenzahl, J.Amer.Chem.Soc., **98**, 2188 (1976).
46. K.Yamamoto, M.Morioka, and I.Murata, Tetrahedron Letters, 3009 (1975).
47. H.Prinzbach, D.Seip, L.Knothe, and W.Faist, Annalen, **698**, 34 (1966).
48. V.Weinmayr, J.Amer.Chem.Soc., **77**, 3012 (1955).
49. S.McVey and P.Pauson, J.Chem.Soc., 4312 (1965).
50. F.Klages and K.Bott, Chem.Ber., **97**, 735 (1964).
51. T.Eicher and A.Loscher, Z.Naturforsch., **21b**, 295 (1966).
52. E.Bergmann and J.Arganat, Chem.Comm., 512 (1965).
53. B.Eistert and J.Arackal, Chem.Ber., **108**, 2397 (1975).
54. A.Lüttringhaus, H.Berger, and H.Prinzbach, Tetrahedron Letters, 2121 (1965).
55. W.Dilthey and P.Huchtemann, J.prakt.Chem., **154**, 238 (1940).
56. P.Pauson and B.Williams, J.Chem.Soc., 4162 (1961).
57. F.Klage, K.Bott, P.Hegenberg, and H.Jung, Chem. Ber., **98**, 3765 (1965).
58. D.Lloyd and F.Wasson, J.Chem.Soc.C, 408 (1966).
59. M.Regitz and A.Liedhegener, Tetrahedron, **23**, 2701 (1967).
60. B.Freeman and D.Lloyd, Tetrahedron, **30**, 2257 (1974).
61. G.Rio and M.Charifi, Compt.rend., **268**, 1960 (1961).
62. K.Leppanen, Ann.Acad.Sci.Fennicae, Ser.A, **11**, 50 (1965).
63. K.Leppanen, Suomen Kem., **B44**, 384 (1971).
64. G.Evrard, P.Piret, G.Germain, and M.Van Meerssche, Acta Cryst., **27B**, 661 (1971).
65. G.Schenck and W.Müller, Naturwiss., **41**, 474 (1954).
66. G.Schenck, Naturwiss., **41**, 452 (1954).
67. C.Dufraisse, G.Rio, and J.Basselier, Compt.rend., **246C**, 1640 (1958).
68. J.Basselier and J.LeRouse, Compt.rend., **286**, 970 (1960).
69. D.Reitz, J.Chem.Phys., **34**, 701 (1961).
70. H.Kurreck and W.Broser, Chem.Ber., **98**, 11 (1965).
71. K.Möbius, Z.Naturforsch., **20a**, 1117 (1965).
72. W.Broser, H.Korreck, and P.Siegle, Chem.Ber., **99**, 2246 (1966).
73. C.Tuzun, Comm.Fac.Sci.Univ.Ankara, Ser.B, **13**, 53 (1966).
74. W.Broser, P.Siegle, and H.Kurreck, Chem.Ber., **101**, 69 (1968).
75. W.Broser, J.Reusch, H.Kurreck, and P.Siegle, Chem. Ber., **102**. 1715 (1969).
76. D.Janzen and H.Kurreck, Tetrahedron Letters, 5231 (1972).
77. D.Lloyd and M.Signer, J.Chem.Soc.C, 2941 (1971).
78. H.Kainer, Annalen, **578**, 232 (1952).

79. S.S.Trach and N.S.Zefirov, Zhur.Org.Khim., **10**, 219 (1974).
80. A.V.Strashnenko and S.V.Zavgorodnyi, Zhur.Org. Khim., **3**, 91 (1967).
81. G.Harris, D.Lloyd, N.Preston, and M.Singer, Chem. and Ind., 1483 (1968).
82. A.W.Johnson, "Ylid Chemistry" (Translated into Russian), Mir, Moscow, 1969, p.58.
83. D.Lloyd, R.Millar, H.Lumbroso, and C.Liegeois, Tetrahedron, **33**, 1379 (1977).
84. D.Lloyd and J.Sneezum, Tetrahedron, 334 (1958).
85. Ya.N.Kreitsberga, V.E.Kampar, and O.Ya.Neiland, Zhur.Org.Khim., **11**, 1508 (1975).
86. B.Freeman, D.Lloyd, and M.Singer, Tetrahedron, **28**, 343 (1972).
87. Ya.N.Kreitsberga, O.Ya.Neiland, and V.E.Kampar, Zhur.Org.Khim., **11**, 1941 (1975).
88. D.Lloyd and M.Singer, J.Chem.Soc.C, 2939 (1971).
89. D.Lloyd, M.Singer, M.Regitz, and A.Liedhegener, Chem. and Ind., 324 (1967).
90. D.Lloyd and M.Singer. Chem. and Ind., 510 (1967).
91. D.Lloyd and M.Singer, Chem. and Ind., 787 (1967).
92. D.Lloyd and M.Singer, Chem.Comm., 1042 (1967).
93. D.Lloyd and M.Singer, Chem. and Ind., 118 (1967).
94. D.Lloyd and M.Singer, Chem.Comm., 390 (1967).
95. B.Freeman and D.Lloyd, Chem.Comm., 924 (1970).
96. I.Band, D.Lloyd, M.Singer, and F.Wasson, Chem. Comm., 544 (1966).
97. D.Lloyd and F.Wasson, Chem. and Ind., 1559 (1963).
98. D.Lloyd and F.Wasson, J.Chem.Soc.C, 1086 (1966).
99. G.Seitz, Angew.Chem., **81**, 518 (1969).
100. B.Freeman, G.Harris, and B.Kennedy, Chem.Comm., 913 (1972).
101. D.Lloyd and M.Singer, Tetrahedron, **28**, 353 (1972).
102. H.Anmon, G.Wheeler, and P.Watts, J.Amer.Chem. Soc., **95**, 6158 (1973).
103. Z.Yoshida, S.Yoneda, T.Yato, and M.Hazawa, Tetrahedron Letters, 873 (1973).
104. V.G.Andrianov and Yu.T.Struchkov, Izv.Akad. Nauk SSSR, Ser.Khim., 687 (1977).
105. H.Lumbroso, D.Lloyd, and G.Harris, Compt.rend., **278C**, 219 (1974).
106. Z.Yoshida, S.Yoneda, and I.Murata, J.Org.Chem., **38**, 3537 (1973).
107. D.Lloyd and M.Singer. Chem. and Ind., 1277 (1968).
108. D.Lloyd and M.Singer, Chem. and Ind., 786 (1971).
109. Z.Yoshida, S.Yoneda, I.Murata, and H.Hashimoto, Tetrahedron Letters, 1523 (1971).
110. Z.Yoshida, S.Yoneda, and M.Hazama, J.Org.Chem., **37**, 1364 (1972).

Riga Polytechnic Institute