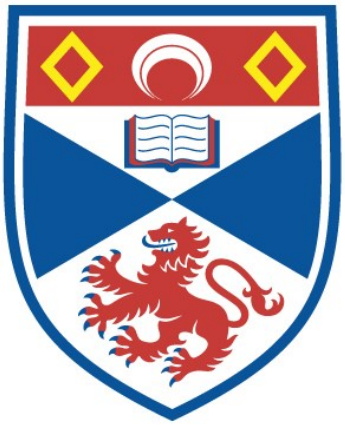
DIACYLCYCLOPENTADIENES

Nigel Wilkes Preston

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



1968

DIACYLCYCLOPENTADIENES

being a Thesis

presented by

NIGEL WILKES PRESTON, B.Sc.,

to the

UNIVERSITY OF ST. ANDREWS

in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY

DECLARATION

I declare that this thesis is a record of results of my own experiments, that it is my own composition, and that it has not previously been presented in application for a higher degree.

CERTIFICATE

I hereby certify that Mr. Nigel Wilkes Preston, 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 Queen's College, Dundee, in the University of St. Andrews, in October 1958 and graduated B.Sc. with Second Class Honours in Chemistry in June 1962.

After employment in the chemical industry as a research chemist, I entered St. Salvator's College, University of St. Andrews in October 1965 as a post-graduate student. The research described in this thesis was carried out between October 1965 and July 1968, during which time I held a Research Studentship awarded by the Science Research Council.

PUBLICATIONS

(1) Diazocyclononatetraene.

D. Lloyd and N.W. Preston,

Chem. and Ind., 1966, 1039.

(2) A New Route to Arsonium Ylides.

G.S. Harris, D. Lloyd, N.W. Preston and M.I.C. Singer,

Chem. and Ind., 1968, in press.

ACKNOWLEDGEMENTS

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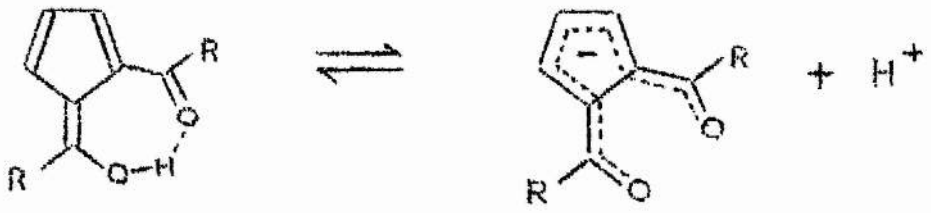
SUMMARY

A property of aromatic compounds is their preference for reaction with electrophiles by substitution rather than by addition. A number of substituted cyclopentadienes have been prepared by electrophilic substitution of the cyclopentadienide anion, a 6π-electron aromatic species. When the substituents are electron-withdrawing groups, the result is increased acidity of the cyclopentadienes, and deactivation of their anions towards further electrophilic attack.

Reaction of cyclopentadienide anion with acyl chlorides gives rise to 1,2-diacylcyclopentadienes, which appear to exist in the solid phase and in non-polar solvents almost entirely as the hydrogen-bonded enol tautomers, which are 2-acyl-6-hydroxy-fulvenes. These enols have considerable acidity, since the negative charge of their anions is delocalised:



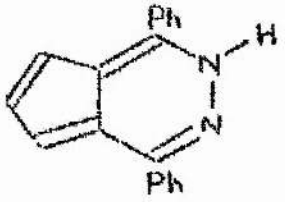
The time-averaged structure of the enol molecule is symmetrical, and it is not possible spectroscopically to distinguish the hydrogen atom at C-3 from that at C-5.

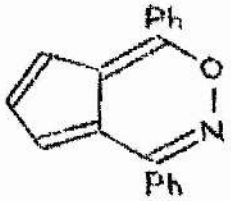
The electrophilic substitution of the 2-acyl-6-hydroxyfulvenes or their anions is of interest because of the deactivating influence of the acyl groups, together with the fact that there are three different possible sites for electrophilic substitution, viz. C-3(5), C-4 and O.

Nitrated, brominated and azo-coupled derivatives have been prepared from 2-benzoyl-6-phenyl-6-hydroxyfulvene and 2-acetyl-6-methyl-6-hydroxyfulvene. Bromination and nitration give C-4 substituted products; the monobrominated derivatives readily undergo further bromination at C-3 and C-5, since the presence of one bromine atom has little, if any, deactivating effect. The reaction between 1,2-dibenzoyl- or 1,2-diacetylcyclopentadienide anion and aryl diazonium salts gives products substituted at C-5, which are tautomeric with 2,3-diacylcyclopentadienone arylhydrazones. An O-substituted compound has been obtained from the reaction of dibenzoylcyclopentadienide anion with methyl chloroformate. Attempts to prepare triacylated cyclopentadienes by the action of acyl chlorides (without a Friedel-Crafts catalyst), or by Vilsmeier formylation of 2-acyl-6-hydroxyfulvenes, were unsuccessful.

Some possible pathways to diacyldiazocyclopentadienes and pyridinium diacylcyclopentadienylides were explored, but yielded no ylides. However, triphenylarsonium 3,4-dibenzoylcyclopentadienylide was prepared by the reaction of 2-benzoyl-6-phenyl-6-hydroxyfulvene with triphenylarsine oxide in acetic anhydride. Triphenylarsonium 3,4-dipivaloylcyclopentadienylide was similarly prepared from 2-pivaloyl-6-t-butyl-6-hydroxyfulvene.

Linn and Sharkey reported the reaction of 2-benzoyl-6-phenyl-6-hydroxyfulvene with hydrazine and with hydroxylamine to give the compounds 1,4-diphenyl-2H-cyclopenta[d]pyridazine and 1,4-diphenylcyclopenta[d]-2,3-oxazine:





Analogues have been prepared from 2-acetyl-6-methyl-6-hydroxyfulvene. These heterocyclic systems are iso-π-electronic with azulene. The 2H-cyclopenta[d]pyridazines were found to resemble azulenes in their reaction with electrophiles on the five-membered ring. Brominated and formylated derivatives were prepared, the substituents occupying the 5- or 7-position. Protonation takes place at C-5 or C-7 and the resulting methylene group is

reactive. Condensation with carbonyl compounds such as p-dimethylaminobenzaldehyde and diphenylcyclopropenone was found to occur readily.

The cyclopenta[d]-2,3-oxazines appear to be somewhat less reactive towards electrophiles than the 2H-cyclopenta[d]pyridazines, and formylation was unsuccessful. Brominated derivatives were nevertheless obtained. It is concluded, on the basis of their reactions, and the N.M.R. coupling constants of the five-membered ring protons of the brominated derivatives, that a lesser degree of π-electron delocalisation exists in the cyclopenta[d]-2,3-oxazines than in the 2-substituted cyclopenta[d]-pyridazines.

The appendix to this thesis contains an account of some reactions of the cyclononatetraenide anion, including the attempted preparation of ylides incorporating the 10 π-electron cyclononatetraenide ring.

CONTENTS

INTRODUCTION

DISCUSSION

EXPERIMENTAL

INTRODUCTION

The concept of aromaticity, historically applicable principally to benzenoid systems, achieved new status from the work of Hückel.[1] His application of molecular orbital theory to cyclic conjugated systems not only led to a deeper understanding of the properties of benzene itself, but also extended the scope of the concept to include other systems at that time either undiscovered, or unrecognised as aromatic species.

By use of modern synthetic techniques, a number of these non-benzenoid aromatic structures have become accessible, and with the appreciation of the wider implications of Hückel's predictions has come a dramatic increase in research exploiting aromaticity.

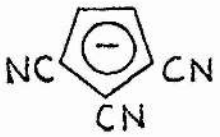
The special stability of the cyclopentadienide anion, a 6 π-electron system satisfying the requirements of the Hückel rule,[1] underlies much of the chemistry of cyclopentadiene, and is relevant to the work on substituted cyclopentadienes embodied in this thesis.

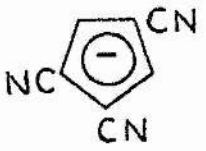
1). CYCLOPENTADIENIDE ANIONS.

The unusual acidity of cyclopentadiene has long been recognised to be a consequence of the stability of the cyclopentadienide anion (I). The acidity of substituted cyclopentadienes will

naturally depend on the extent to which the substituents confer additional stability on the anions by increasing electron delocalisation. Webster[2] has shown the effect on the acidity of the cyclopentadienide anion of progressive substitution by the -CN group. Compared with a $pK_a^{H_2O}$ of 15 for cyclopentadiene,[3] 2,3-dicyanocyclopentadiene has $pK_a^{H_2O}$ 1.11; and $pK_a^{CH_3CN}$ 10.17 for this compound compares with ca. 0 for 2,3,4,5-tetracyanocyclopentadiene and <-2 for 1,2,3,4,5-pentacyanocyclopentadiene. Similarly, 1,2,3,4,5-pentacarbomethoxycyclopentadiene[4] cannot be generated from its tetra-n-butylammonium salt by concentrated hydrochloric acid, and in aqueous solution dissolves metallic iron with liberation of hydrogen.[5]

Increased delocalisation in cyclopentadienides has a marked effect on their reactivity. Whereas cyclopentadienide[6] and, for example, methyl cyclopentadienide[7] ions resinify rapidly in air, suitably substituted ions such as dicarbomethoxycyclopentadienide[8] and nitrocyclopentadienide[9] are perfectly stable in air. Among the more highly substituted anions, tricyanocyclopentadienide requires a Friedel-Crafts catalyst for the substitution of further -CN groups; the two isomeric forms (II, III) of this ion are produced by stepwise substitution of the mono- and disubstituted anions with cyanogen chloride alone.[2]





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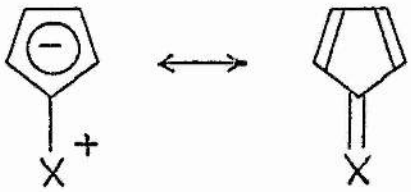

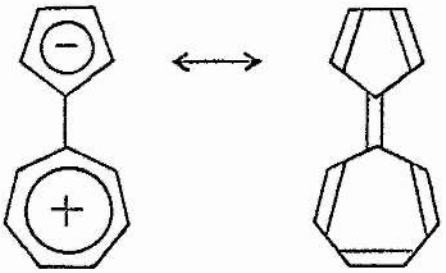

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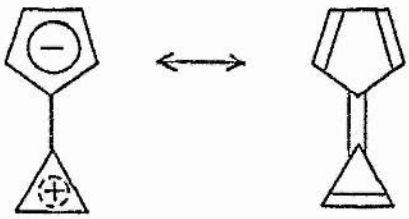

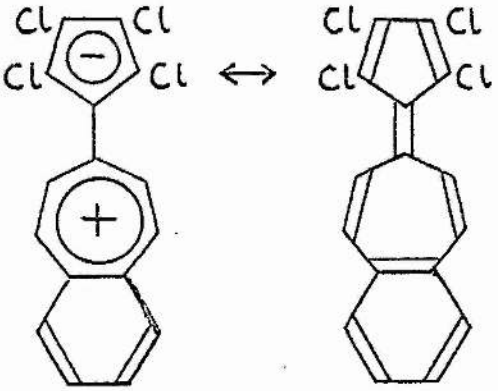

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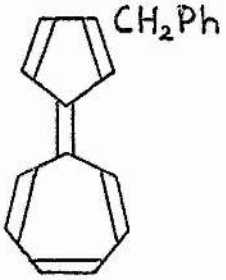


VIII

2). DIPOLAR CYCLOPENTADIENE DERIVATIVES.

In certain compounds the cyclopentadienide anion may exist in a dipolar molecule; in most cases alternative covalent structures can also be written (IV). On the basis of the classical Hückel rule, one might expect that the dipolar form should be particularly favoured in cases where both parts of the molecule can attain $4n + 2$ π-electrons, as in the sesquifulvalene (V) and calicene (VI) structures. Some, but not all, examples of these systems so far prepared show evidence of this. The benzosesquifulvalene (VII)[10] is a stable crystalline compound having a dipole moment of 5.20 D, whereas the benzylsesquifulvalene (VIII)[11] has poor stability and behaves as an olefin. Sesquifulvalene itself has been prepared only in dilute solution[11] and has not yet been isolated, which suggests that it, also, has olefinic rather than aromatic character.

The position of calicenes among aromatic compounds is uncertain. Molecular orbital calculations by the Hückel LCAO technique predict a high delocalisation energy for calicenes.[12a] On the other hand, Dewar[12b] has used more sophisticated calculations to conclude that calicenes are not aromatic, and has pointed out that the use of Hückel calculations can be misleading, since they predict a greater degree of aromatic character for fulvene than is consistent with experimental evidence (see below).

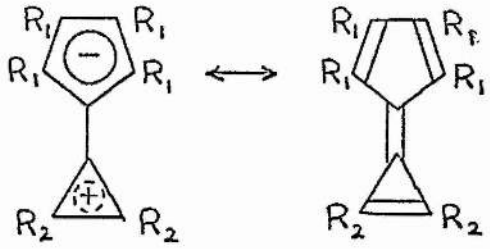
Pentatriafulvalene (calicene, VI) has not yet been prepared, but various substituted calicenes are known, some of which are known to have high dipole moments. Thus the calicenes IXa, IXb, and IXc have respective dipole moments of 7.56 ± 0.03D,[13a] 6.3 ± 0.3D,[13b] and 7.97D[13c] (also quoted as 8.1 ± 0.1D)[13d]. Certain benzo- and dibenzocalicenes[13e] have been found to show a bathochromic shift of the long-wavelength absorption in the ultraviolet spectrum with decreasing polarity of solvent. This effect has been taken to imply that the ground states of these molecules are dipolar, and consequently stabilised by solvation energy in polar solvents. Connection of this effect with the existence of a dipolar ground state is, however, questionable, since compound IXc has a high dipole moment but does not show the solvatochromic effect.[13d] Absence of the solvatochromic effect has also been noted in the case of the calicene IXd.[13f] Evidence for the aromatic character of calicenes has been found by their ability in certain cases to undergo electrophilic substitution on the five-membered ring, namely, nitration, bromination, azo-coupling, formylation and Friedel-Crafts acetylation.[14]

A number of heterocyclic analogues of sesquifulvalene, in which an ethylene unit from the 7-membered ring is replaced by an O or S atom, or by an -NR- group, (X), have been prepared.

The N-alkyl-4-cyclopentadienylidene-1,4-dihydropyridines (Xc) can be prepared from cyclopentadiene and N-alkyl-4-methoxypyridinium salts in the presence of t-butoxide ion[15,16] or from N-alkyl-,[17] or N-alkyl-4-bromopyridinium salts and cyclopentadienide anion. Use of N-alkyl-2-bromopyridinium salts in this reaction yields the N-alkyl-2-cyclopentadienylidene-1,2-dihydropyridines (XI).[18] The dipole moments of Xc ($R=CH_2Ph$) and XI ($R=CH_3$) have been found to be 8.9D and 5.2D respectively, indicating respective contributions from charged forms of approx. 27% and 25%.[19]

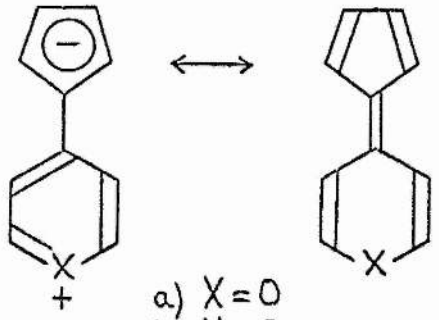
Because of the great ease with which the pyrylium ring is opened by bases, pyrylium salts cannot be used to prepare cyclopentadienylidene-pyrans; the reaction gives azulenes instead.[20]

4-Cyclopentadienylidene-pyrans can at present be obtained only by specialised reactions. Phenylated examples have been prepared by reaction of phenylated diazocyclopentadienes with pyran-4-thiones.[21] The reaction proceeds by attack at the sulphur atom of the pyranthione by the carbene generated by decomposition of the diazo-compound. Sulphur is then extruded to give the product. These ylidene-pyrans do not undergo electrophilic substitution readily.[21] Certain cyclopentadienes activated by electron-withdrawing groups, i.e. tetrachloro- and 2,3,4,5-tetracarbomethoxycyclopentadiene, condense readily with 4-pyrones



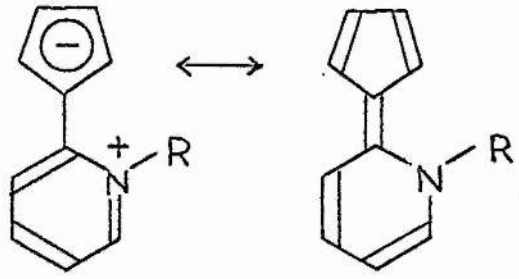
a) $R_1 = Cl$, $R_2 = n\text{-}C_3H_7$
b) $R_1 = R_2 = Ph$
c) $R_1 = Cl$, $R_2 = Ph$
d) $R_1 = Ph$, $R_2 = CH_3$

IX



a) X = O
b) X = S
c) X = NR

X



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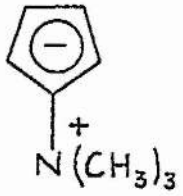

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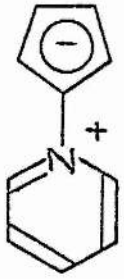

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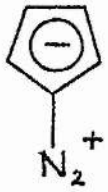

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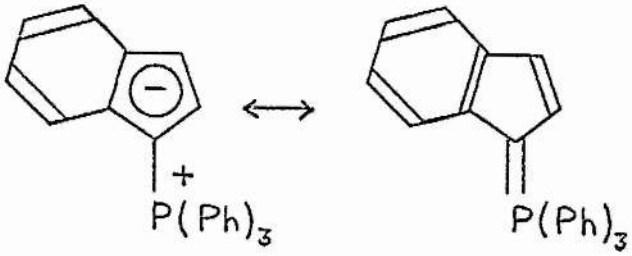

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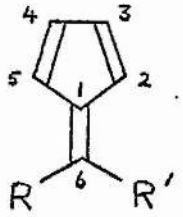
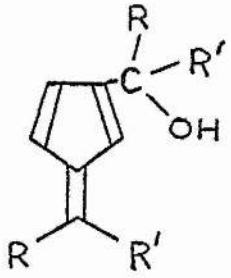


XVI



XVII

in acetic anhydride.[22] Both these reactions fail with cyclopentadiene itself.

The single example of a cyclopentadienylidene-thiin (Xb) reported to date was prepared from 2,3,4,5-tetraphenyldiazocyclopentadiene and 2,6-dimethyl-4H-thiin-4-thione.[21]

In the case of the cyclopentadienylides the cyclopentadiene ring is bonded directly to the heteroatom. The members of this class in which the heteroatom is nitrogen show the most dipolar character. For trimethylammonium cyclopentadienylide (XII)[23] no covalent form can be written, and any structure for pyridinium cyclopentadienylide (XIII)[24] which has an uncharged 5-membered ring, will obviously contribute to only a very small extent in the ground state.

The cyclopentadienylides have high melting points, (usually above 200°) and characteristically large dipole moments, that of pyridinium cyclopentadienylide being 13.5D.[25,26]

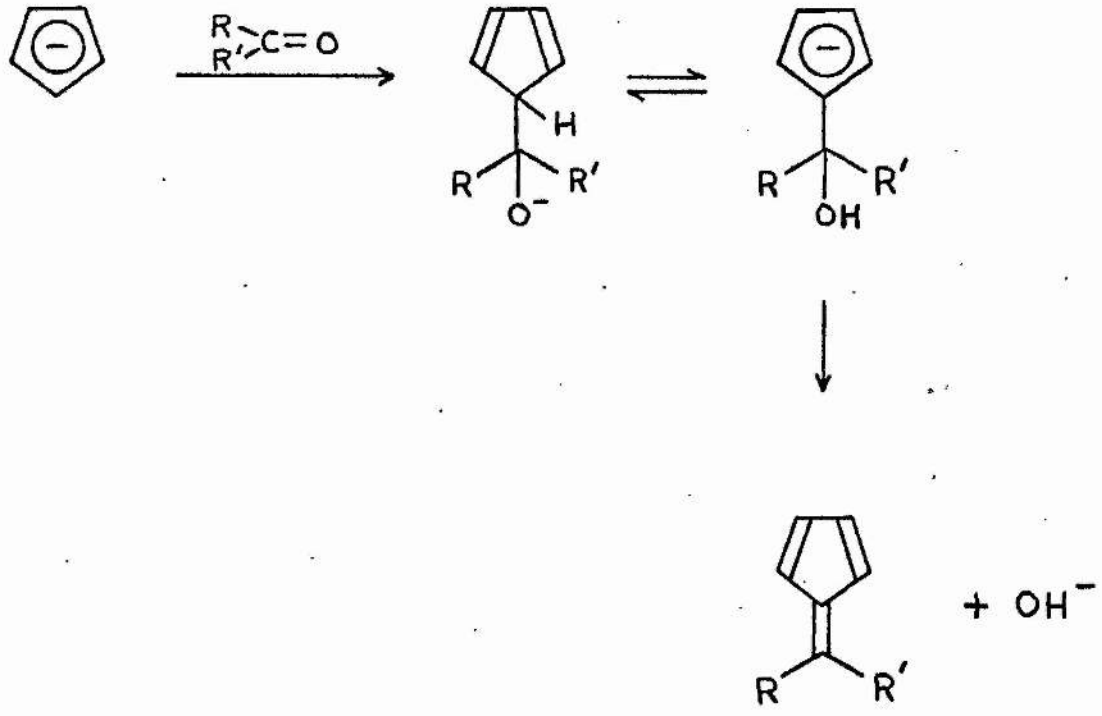
Triphenylphosphonium[27] and dimethylsulphonium[28] cyclopentadienylides have also been prepared; the phosphorus and sulphur atoms can utilise vacant d orbitals to bond covalently with the cyclopentadiene ring, and uncharged forms consequently contribute to a significant extent to the structure of these ylides. This contribution amounts to about 50% in the case of triphenylphosphonium cyclopentadienylide, as deduced from its dipole moment of 7.0D.[27]

Diazocyclopentadiene (XIV), first prepared in 1953 by Doering and DePuy,[29] is the parent of an interesting class of cyclopentadienylides, of which other members have subsequently been made. The method of Doering and DePuy, whereby toluene-_p_-sulphonyl azide is reacted with cyclopentadienide anion, has yielded triphenyl-[30-32] and tetraphenyl-diazocyclopentadienes.[32] Tetrachlorodiazocyclopentadiene is obtained from the reaction of hexachlorocyclopentadiene with hydrazine, and oxidation of the resulting hydrazone.[33,34]

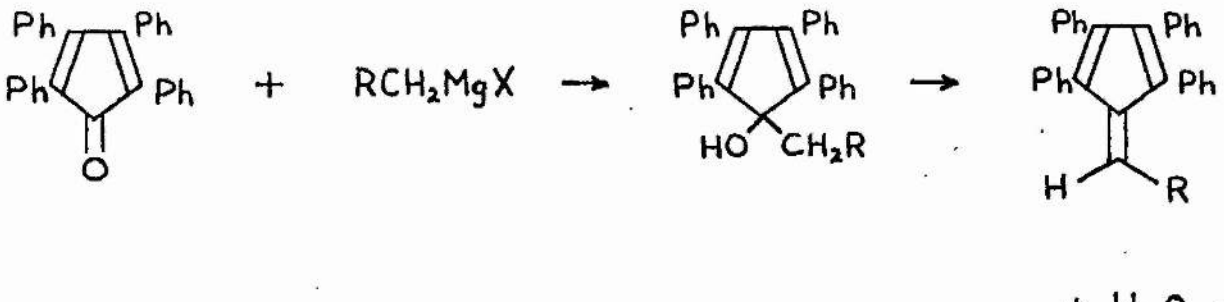
Of particular interest among the reactions of the diazocyclopentadienes is their loss of nitrogen on heating, to give carbenes. This reaction has useful synthetic possibilities and has been used to prepare some unusual cyclopentadienylides.[35] In common with other cyclopentadienylides, diazocyclopentadienes will undergo electrophilic substitution reactions. Diazocyclopentadiene itself has been brominated, nitrated, _etc_.[36] Triphenylphosphonium cyclopentadienylide has been formylated and acetylated,[37] and this compound, in common with, for example, triphenylphosphonium indenylide (XV)[38,39] and trimethylammonium cyclopentadienylide,[23] couples with diazonium salts.[40]

3). FULVENES.

The sesquifulvalenes, calicenes, and other cyclopentadienylidene compounds described above are actually special cases of fulvenes,



Scheme A



Scheme B

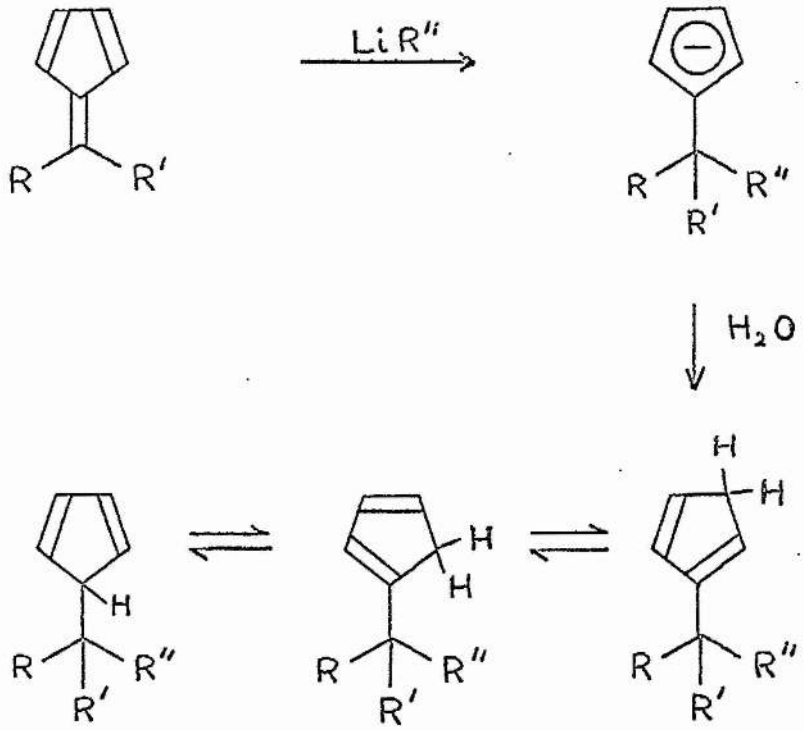
(XVI), a class of compounds of which the first examples were first prepared in 1900 by Thiele.[9] Thiele's synthesis, which is the most commonly used of the available routes to fulvenes, involves reaction of cyclopentadienide anion with carbonyl compounds[41] (Scheme A). The cyclopentadienide ion is generated from the diene by means of a base such as alkoxide ion, and since base is regenerated in the last step of the reaction, a quantity equivalent to the cyclopentadiene is not required. Certain difficulties are encountered with this synthesis, in particular with the condensation of cyclopentadiene with aliphatic aldehydes, which limit its usefulness as a general preparative method.[42] When diaryl ketones are used in which at least one aryl group is electron-withdrawing, such as 2-pyridylketones, "fulvenemethanols" (XVII) can be formed in addition to, or instead of, fulvenes, especially at low temperature. These compounds result from reaction with a second molecule of ketone of the intermediate anion shown in Scheme A.[43] Among the other reactions yielding fulvenes, the most important is the reaction of highly arylated cyclopentadienones with Grignard reagents,[44,45] exemplified in Scheme B.

The dipole moments, nuclear magnetic resonance (N.M.R.) spectra and chemical reactions of fulvenes all indicate that they are more correctly represented as olefins rather than as aromatic

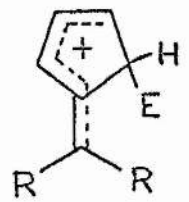
compounds. The dipole moments are small: for fulvene itself, 1.1D,[46] and for 6,6 dialkylfulvenes, ca. 1.4D.[42] These figures suggest a contribution of about 5-10% from the dipolar form. In the excited state of the molecule, this contribution is larger.[47]

That fulvenes may be considered better as olefins than as delocalised molecules is demonstrated by the size of the coupling constants (J) found in the N.M.R. spectrum: in particular, the coupling constants for the two pairs of vicinal protons on the ring. This aspect of the spectra of fulvenes has recently received attention from several workers,[48-50] and it is found that J for the pair of protons attached at the formal double bond is about 5-5.5 c/s, and for those attached at the formal single bond, about 2-2.5 c/s. These figures compare with 5.1 c/s and 1.9 c/s for the equivalent pairs of protons in cyclopentadiene.[51] The effect of greater delocalisation in the fulvenes would be to cause both these coupling constants to approach the average of the two extreme values found for fully localised cyclopentadiene, i.e. 3.5 c/s.

In their reactions, fulvenes show olefinic behaviour. With maleic anhydride they undergo Diels-Alder reactions,[52] and they react with alkyl-lithium compounds by addition to the exocyclic double bond (Scheme C; references to this reaction are contained



Scheme C

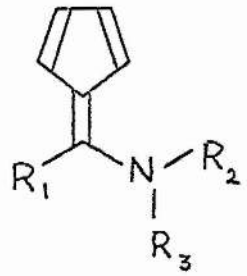


E = electrophile

XVIII

a) R = OCH_3

XIX b) R = $N(CH_3)_2$



XX

a) $R_1 = H$, $R_2 = R_3 = CH_3$

b) $R_1 = N(CH_3)_2$, $R_2 = R_3 = CH_3$

c) R_1 = Ph, R_2, R_3 = morpholine

d) $R_1 = C_2H_5$, R_2, R_3 = piperidine

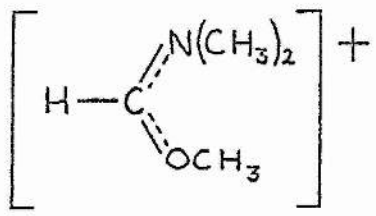
in reference 47). The action of halogens on fulvenes is somewhat obscure.[9,41,44,53] Day and Pidwerbesky, however, have identified tetrachlorinated and tetrabrominated addition products, and a tetrabrobrominated substitution product, from 6,6-diphenylfulvene,[54] but electrophilic substitution reactions of simple fulvenes are rare. 6,6-Diphenyl- and 6,6-dimethylfulvenes are attacked in the 2-position by certain electrophiles at low temperature (-80°), but the intermediate cations formed (XVIII) are stable only at low temperature, and at higher temperatures polymerise instead of forming substituted fulvenes.[55] 6,6-Diphenylfulvene has, however, been successfully formylated in the 2-position by dimethylformamide and phosphorus oxychloride.[56]

The dipole moments, and hence the degree of aromaticity, of fulvenes are increased when an electron-donating group is attached by a conjugated chain of carbon atoms to the 6-position. Thus the compounds XIXa and XIXb have dipole moments of 2.17D and 3.65D respectively. Attachment of the electron-donating group directly to the 6-position further increases the polar character of the fulvene: 6-dimethylaminofulvene (XXa) has dipole moment 4.5D, representing ca. 25% contribution from the dipolar form,[58] while for 6,6 bis-dimethylaminofulvene (XXb), the dipole moment is 5.45D.[59]

Compound XXa was first prepared by Meerwein and co-workers in 32% yield by the reaction of cyclopentadiene with dimethyl-

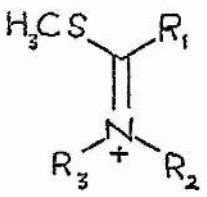
formamide-diethylacetal,[60] but was subsequently prepared in yields above 80% by the action of the complex (XXI), formed from dimethylformamide and dimethylsulphate, upon cyclopentadienide anion.[58] The reaction of cyclopentadienide anion with alkylmercaptoimmonium salts (XXII) has been used to prepare other compounds in the series (XXc&d).[59]

6-Dimethylaminofulvene has been the subject of an investigation by Downing, Ollis and Sutherland[61] into the effect of restricted rotation about the exocyclic bonds (a) and (b) (see XXIII) upon the N.M.R. spectrum. The dipolar form, in which rotation about bond (b) is impossible, would be associated with non-equivalence of the N-methyl groups; similarly the covalent form, which forbids rotation about bond (a), would be associated with non-equivalence of symmetrically placed protons on the ring. At low temperature, separate signals were observed for the N-methyl groups, which coalesced at higher temperature, and analysis of the line shapes of the coalescing signals enabled the free energy of rotation about bond (b) to be calculated. This free energy barrier was found to increase with increasing substitution of the 5-ring by (electron-withdrawing) formyl groups, an expected effect since substitution by such groups favours the dipolar form. 3,4-Diformyl-6-dimethylaminofulvene (XXIIIb), however, shows separate signals for the 2-and 5-protons, i.e.



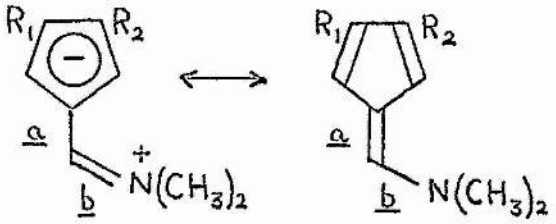
$CH_3SO_4^-$

XXI



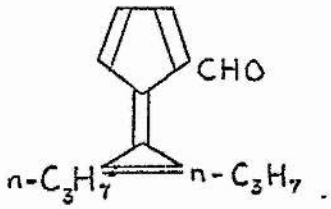
I^-

XXII

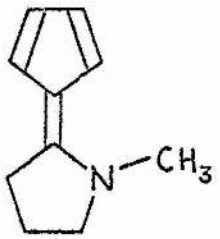


a) $R_1 = R_2 = H$

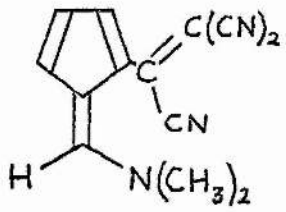
XXIII b) $R_1 = R_2 = CHO$



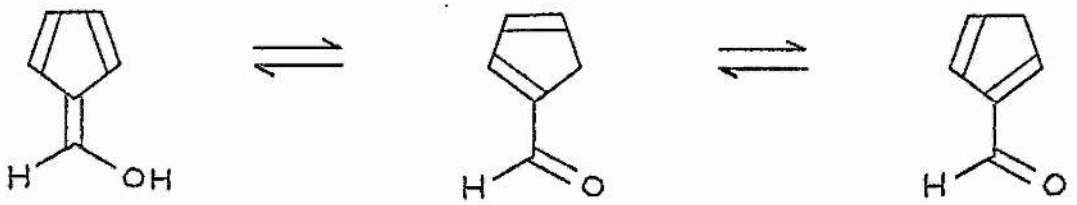
XXIV



XXV



XXVI



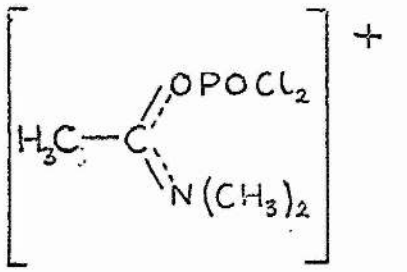
XXVII

restricted rotation about bond (a), at temperatures up to 160°. It was deduced that the free energy barrier to rotation about bond (a) for 6-dimethylaminofulvene itself, which must be greater than that for XXIIIb, is greater than 24.7 k.cal./mole at 160°, and thus greater than that for the corresponding barrier to rotation about the intercyclic bond in the calicene XXIV, which is 18.0-19.4 k.cal./mole.[14]

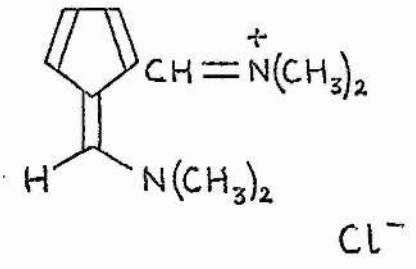
The same exercise has been carried out by Crabtree and Bertelli.[62] These workers supported their findings for bond (a), where experimental difficulties were encountered, by use of the model compound 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (XXV). Their figure for the activation energy of rotation about bond (b) for 6-dimethylaminofulvene was 13.5 k.cal./mole, compared with 15.1 k.cal./mole found by Downing *et al*.

Like other compounds possessing considerable cyclopentadienide character, 6-dimethylaminofulvene undergoes electrophilic substitution. The compound can be mono- and diacylated,[47] and with tetracyanoethylene, hydrogen cyanide is eliminated with formation of the tricyanovinyl-6-dimethylaminofulvene XXVI.[47]

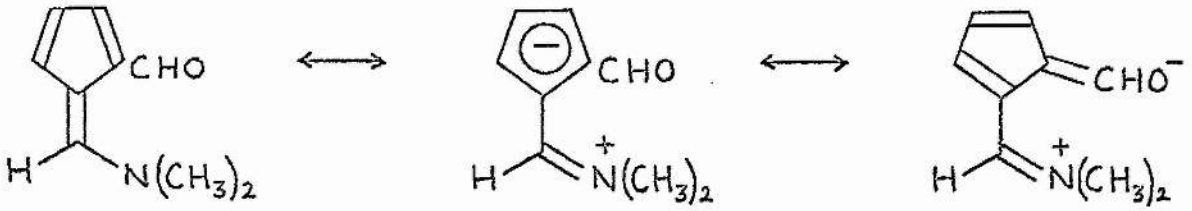
6-Dimethylaminofulvene reacts with hydroxyl ion to yield 6-hydroxyfulvene, tautomeric with formylcyclopentadiene (XXVII),[63] the ion of which is also obtainable in 93% yield by reaction of



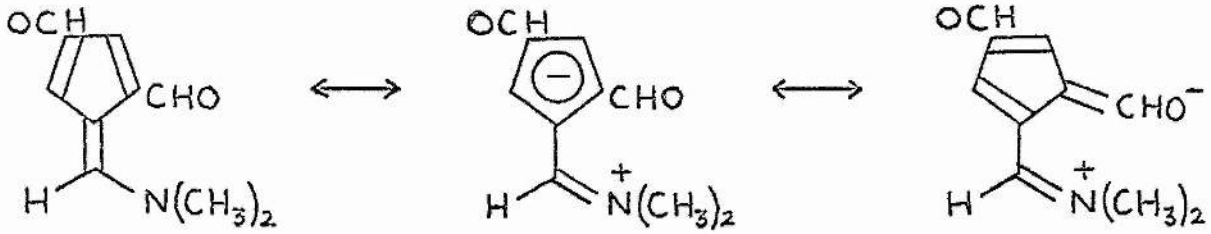
XXVIII



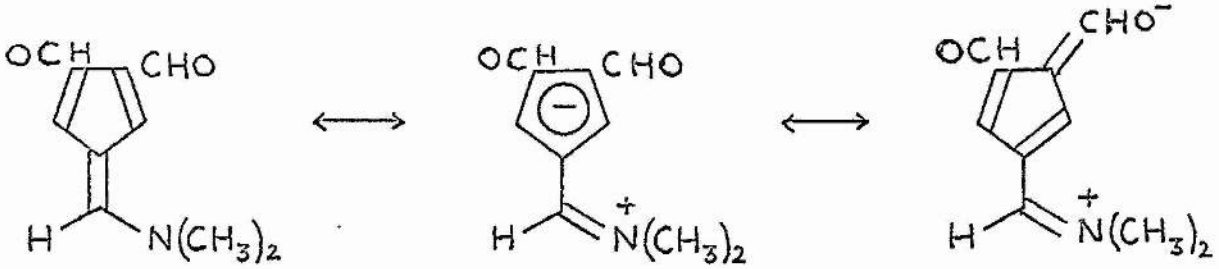
XXIX



XXX

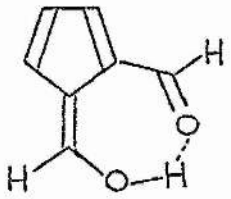


XXXI

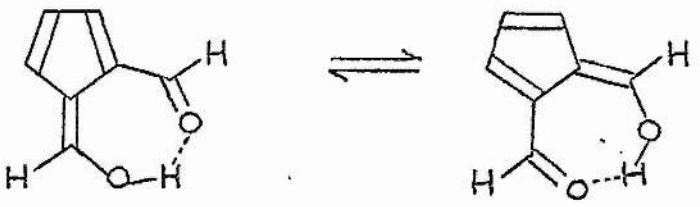


XXXII

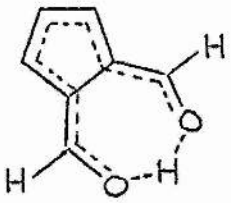
cyclopentadienide anion with ethyl formate.[63] Action of the dimethylacetamide-phosphorus oxychloride Vilsmeier complex (XXVIII) upon cyclopentadiene or upon 6-dimethylaminofulvene gives the immonium salt XXIX. This salt is the key to a number of 6-hydroxy- and 6-aminofulvene-aldehydes.[58] With base, it forms the 6-aminofulvene-monoaldehyde XXX; further reaction of XXIX with the Vilsmeier complex (XXVIII) followed by treatment of the resulting salt with base, leads to the two 6-aminofulvene-dialdehydes XXXI and XXXII. With 2N sodium hydroxide, or saturated potassium carbonate solution, compounds XXX, XXXI and XXXII give the anions of 1,2 diformyl- and the appropriate tri-formylcyclopentadienes, respectively.[58,64] Acidification of the diformylcyclopentadienide anion yields 2-formyl-6-hydroxy-fulvene (XXXIII). This 6-hydroxyfulvene is the parent of the class of compounds with which much of the work reported in this thesis is concerned. Its spectral properties [65] show that it exists in the 6-hydroxyfulvene-aldehyde form rather than in the alternative 1,2-diformylcyclopentadiene form. The infra-red (I.R.) spectrum of XXXIII does not show a distinct -OH stretching absorption, and absorption in the region of -C=O and -C=C stretching is represented by a very broad band centred at 1631cm.$^{-1}$ These features point to an extensively delocalised system with strong hydrogen bonding. This interpretation is verified in



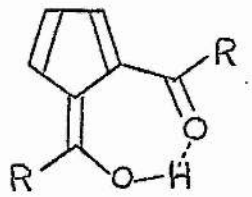
XXXIII



XXXIII a

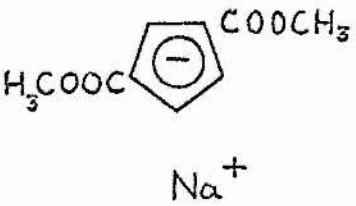


XXXIII b

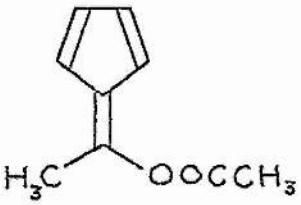


a) R = Ph
b) R = CH_3
c) R = OCH_3

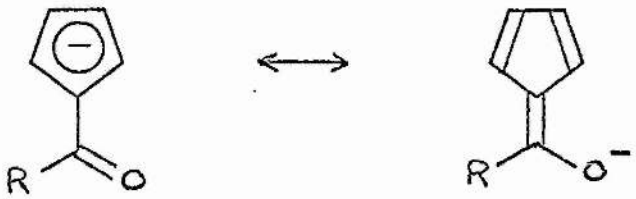
XXXIV



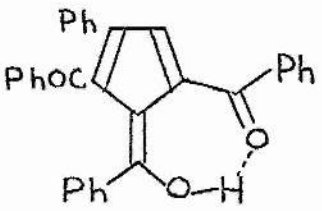
XXXV



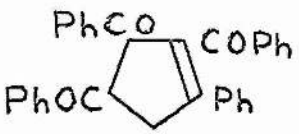
XXXVI



XXXVII



XXXVIII



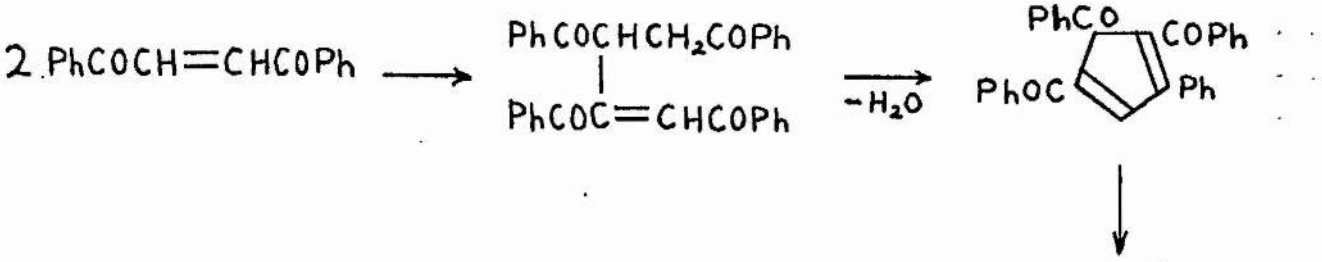
XXXIX

spectacular fashion by the N.M.R. spectrum, which indicates an almost symmetrical structure. In carbon tetrachloride solution, the two aldehyde protons appear as a doublet at 1.43 τ, and couple with the acidic enol proton which is shown as a triplet at -6.10 τ. The ring protons appear as a doublet and a triplet at 2.83 τ and 3.63 τ respectively. This spectral evidence strongly suggests that XXXIII is best considered as either a mixture of two rapidly interchanging tautomers (XXXIIIa), or as a resonance hybrid with an O-H-O bridge (XXXIIIb). The difference between these two representations has little real significance. The chemical shift of the enol proton indicates that it must be appreciably acidic, and the pK_a of XXXIII is indeed found to be 4.5.[58]

In the past ten years, other 2-aroyl- or 2-acyl-6-hydroxyfulvenes have been reported, namely 2-benzoyl-6-phenyl-6-hydroxyfulvene (XXXIVa),[66] 2-acetyl-6-methyl-6-hydroxyfulvene (XXXIVb),[67] and 2-carbomethoxy-6-methoxy-6-hydroxyfulvene (XXXIVc).[8] The latter compound was prepared as its sodium salt, which was later found to be a mixture of two compounds, the other being the 1,3 isomer (XXXV).[50] Compounds XXXIVa-c were prepared by the action of respectively, benzoyl chloride, acetyl chloride, and methyl chloroformate upon cyclopentadienide anion. The monosubstituted cyclopentadienes must be formed as intermediates,

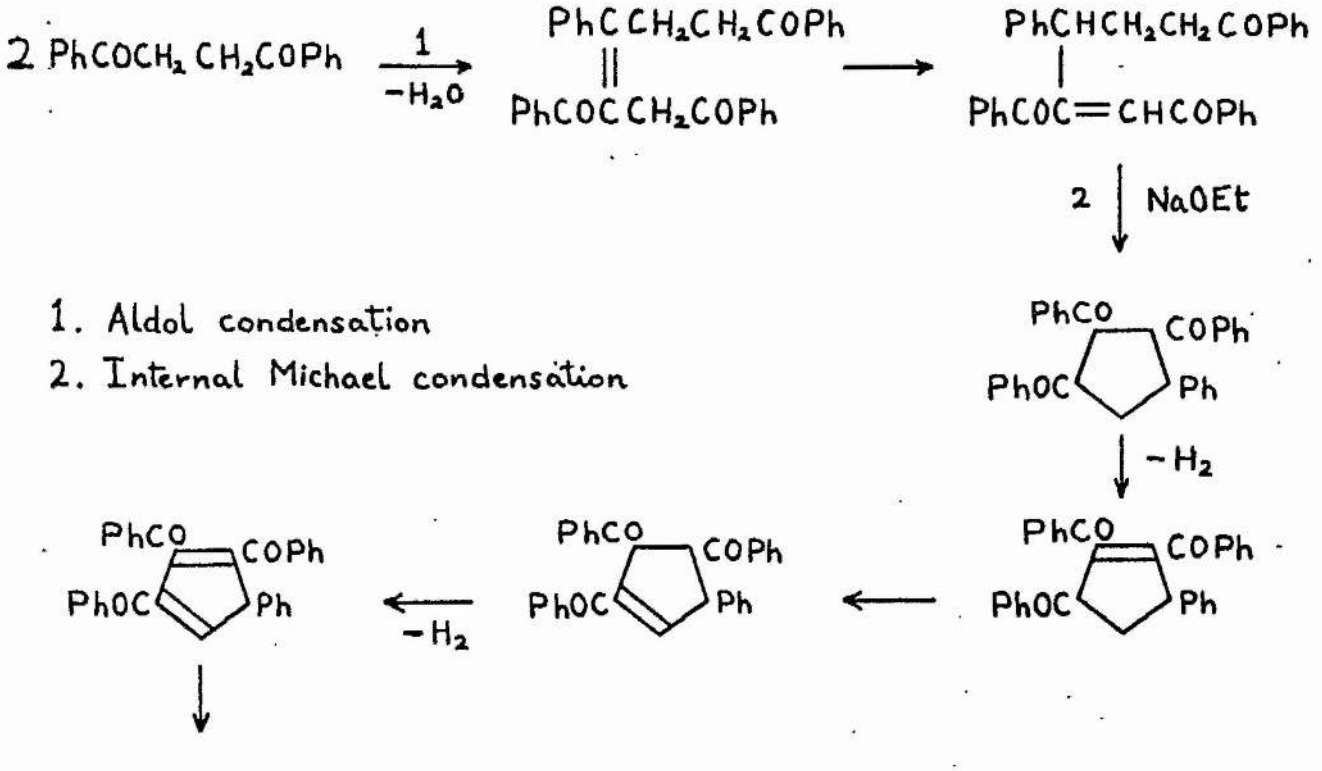
and these, being stronger acids than cyclopentadiene by virtue of their increased electron-withdrawing capacity, are converted upon formation to their anions, at the expense of unreacted cyclopentadienide anion. Thus the efficiency of these reactions is limited to a maximum of 50%. In no case was any trisubstitution found, but in the acetyl chloride reaction, XXXIVb was accompanied by an equal yield of the O-acetylated isomer, 6-methyl-6-acetoxyfulvene (XXXVI). In this connection it is interesting to note the variation in the ratio of C-acylated to O-acylated products obtained by reaction of monoacylcyclopentadienide ions (XXXVII) with acid chlorides. As mentioned above, acetylation of acetylcyclopentadienide anion yields 50% O-acetylated product; benzoylation of benzoylcyclopentadienide anion yields no O-benzoylated product, only 2-benzoyl-6-phenyl-6-hydroxyfulvene; and acetylation of formylcyclopentadienide anion yields only the O-acetylated product, 6-acetoxyfulvene.[63]

Other isolated examples of the 2-aroyl-6-hydroxyfulvene system (XXXIV) have been reported in earlier papers, sometimes in the guise of 2,3-diaroylcyclopentadienes. Fuson et al.[68] obtained 2,5-dibenzoyl-3,4,6-diphenyl-6-hydroxyfulvene (XXXVIII) and some benzene ring-substituted homologues from condensation of trans-diaroylethylenes in the presence of sodium ethoxide (Scheme D). They also observed formation of the fulvenes in



Scheme D

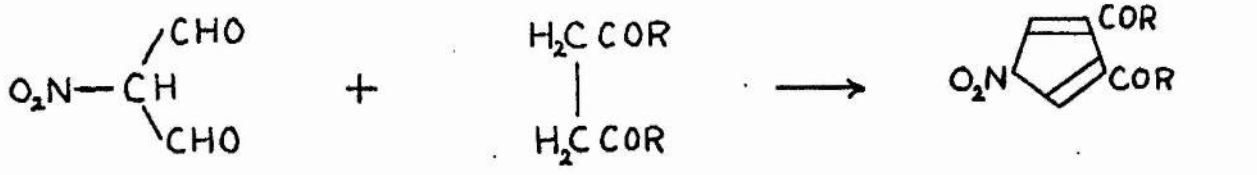
XXXVIII



1. Aldol condensation
2. Internal Michael condensation

XXXVIII

Scheme E



R = CH_3 , Ph,

p-$C_6H_4.CH_3$ or p-C_6H_4Br

Scheme F

low yield by condensing 1,2-diaroylethanes in the presence of sodium ethoxide (Scheme E). The intermediacy of cyclopentene derivatives, which yield the fulvene products by atmospheric dehydrogenation and isomerisation, was demonstrated by independent synthesis of an isomer (XXXIX) of the postulated intermediates, and its subsequent conversion to a fulvene with sodium ethoxide. The preparation of XXXVIII by Scheme D had previously been reported by Gardner and Rydon.[69] The N.M.R. spectrum of this compound was recently found to show an enol proton signal at -8.52τ.[70]

Over 50 years ago, Hale prepared "2,3-diacetyl-5-nitrocyclopentadiene"[71] and "2,3-diaroyl-5-nitrocyclopentadienes"[72] by condensation of nitromalondialdehyde with hexan-2,5-dione or 1,2-diaroylethanes in the presence of base (Scheme F). The diacetylnitrocyclopentadiene has been shown by N.M.R. to be 2-acetyl-4-nitro-6-methyl-6-hydroxyfulvene.[73]

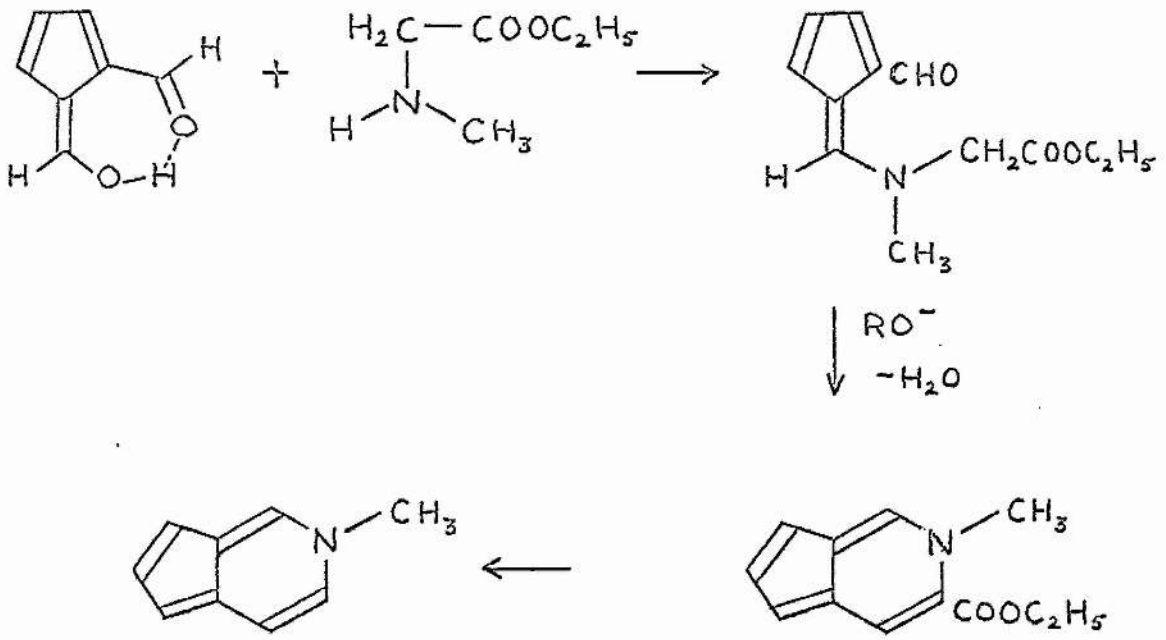
Until 1966, no cases of electrophilic substitution on the unsubstituted systems XXXIII and XXXIV had been reported; since then, reports of calicene formation from 2-benzoyl-6-phenyl-6-hydroxyfulvene[50] and of sesquifulvalene formation from this compound and from 2-acetyl-6-methyl-6-hydroxyfulvene[74] have appeared. In this thesis are reported the bromination, nitration, and azo-coupling of these two fulvenes (XXXIV a&b), and the

reaction of the anion of XXXIVa with methyl chloroformate, together with other attempted substitution reactions.

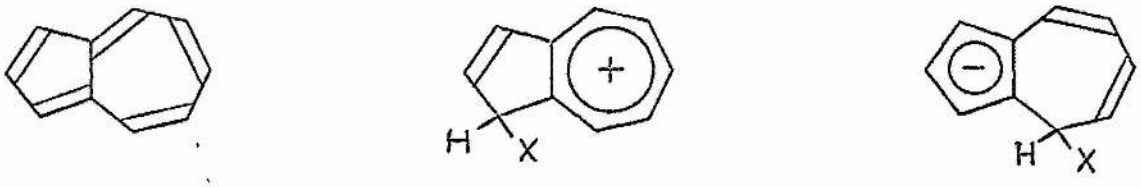
4). PSEUDOAZULENES.

The bicyclo[5.3.0.]decapentaene (azulene) system (XL) has been extensively studied, and both theoretical and synthetic aspects of its chemistry have received much attention.[75] The substitution reactions of azulene suggest that it can form alternative stabilised transition states such as XLI a&b, in which the ring not carrying the substituent group can acquire a π-electron sextet.

In recent years heterocyclic systems iso-π-electronic with azulene have been synthesised and examined for chemical behaviour and physical properties characteristic of the azulenes. Such analogues fall into two categories; those in which one or more carbons from either ring is replaced by a nitrogen atom, and which are related to azulene as pyridine, for example, is related to benzene, and those in which two adjacent carbons from the seven-membered ring are replaced by an oxygen or sulphur atom, or by an imine group, and which bear the same relationship to azulene as thiophene or pyrrole does to benzene. The two categories have been described as π-equivalent and π-excessive respectively,[76] these terms indicating whether the compounds have as many, or more π-electrons than ring atoms.



Scheme G



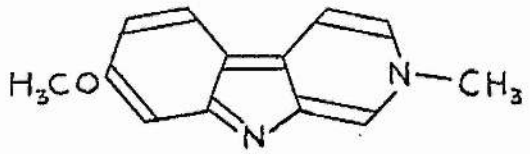
XL XLI a XLI b

XLII XLIII

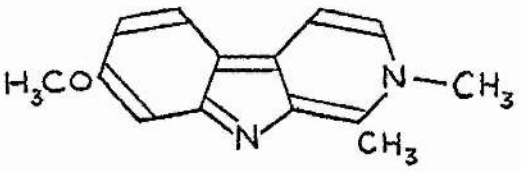
An account of the π-equivalent aza-azulenes with nitrogen atoms in the five-membered ring is inappropriate here, and may be found in reference 75; examples with nitrogen atoms in the seven-membered ring (XLII, XLIII) have recently been reported.[77,78]

The first of the π-excessive azulene analogues, methyl norharmine and methyl harmine, (XLIV, XLV), were reported by Perkin and Robinson in 1919.[79] Another early discovery was the compound XLVI,[80] produced during a search for aromatic character in novel heterocyclic systems. The π-excessive analogues of azulene, also called pseudoazulenes, can be divided into two classes, the cyclopenta[b]pyrans, -thiapyrans and N-substituted 1-pyrindines (XLVIIa-c), and the cyclopenta[c]pyrans, -thiapyrans and N-substituted 2-pyrindines (XLVIII a-c). Non-annelated examples of all the systems of type XLVII[81-85] and of type XLVIII[70,86,76,47] have now been prepared. The synthetic routes to the parent compounds of these families are long and involved, and the parent pyrans XLVIIa and XLVIIIa have not so far been synthesised. An exceptionally easy route to N-methyl-2-pyrindine, starting from 2-formyl-6-hydroxyfulvene (XXXIII), has been discovered by Hafner (Scheme G). In this way a 76% yield of the intermediate 3-carboethoxy-N-methyl-2-pyrindine has been obtained.[47]

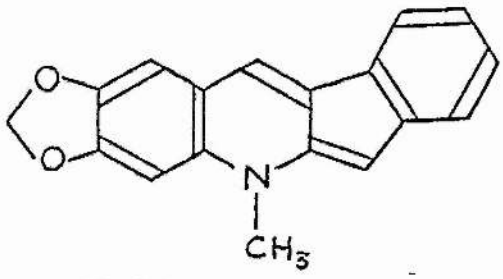
Pseudoazulenes which are unsubstituted at positions 5 and 7 have been found to undergo electrophilic attack at these



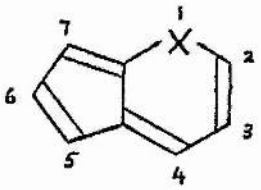
XLIV



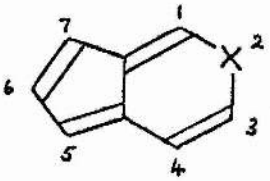
XLV



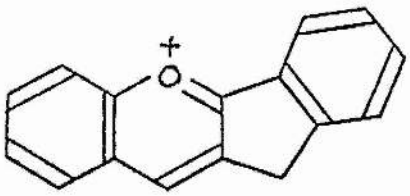
XLVI



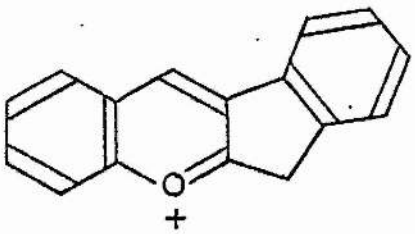
a) X = O
b) X = S
XLVII c) X = NR



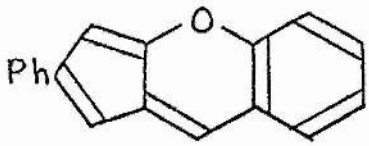
a) X = O
b) X = S
XLVIII c) X = NR



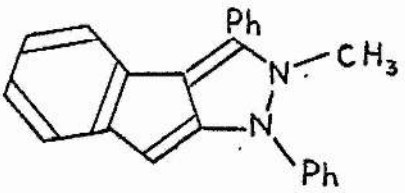
XLIX



L



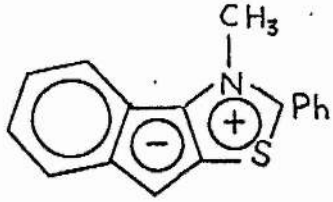
LI



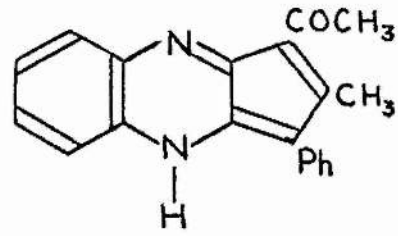
LII

positions, in common with azulene itself. The difference in reactivity of these two positions does not appear to be large, and in certain cases, such as the halogenation of the cyclopenta-thiapyrans with N-chloro- or N-bromosuccinimide, di-substituted products are readily obtained.[85,87] Monosubstituted products can be obtained, however, particularly by protonation, and the position of substitution in these compounds is not immediately obvious. The site of protonation of the pseudoazulenes has been investigated by Boyd and Ellis,[88] with particular reference to the cyclopenta[b]pyrans. Molecular Orbital (MO) calculations predict that the cyclopenta[b]pyrans will be protonated at C-5. This is supported by comparison of the N.M.R. chemical shifts of the methylene groups in the indenopyrylium salts XLIX and L with that of the methylene group in the salt arising from protonation of the benzopyran LI. MO calculations also predict C-5 as the protonation site for the other members of the cyclopenta[b] series (XLVIIb&c), and C-7 as the site for the cyclopenta[c] series of pseudoazulenes (XLVIIIa-c).

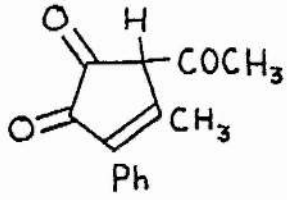
It will be seen that replacement of carbons by heteroatoms in the heterocyclic rings of the pseudoazulenes discussed above can lead to further series of structures which are iso-π-electronic with azulene. The compounds LII and LIII, which have a 5-membered heterocyclic ring corresponding to the 7-membered



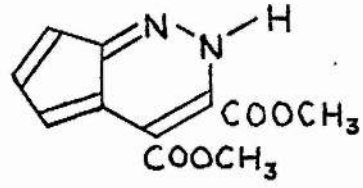
LIII



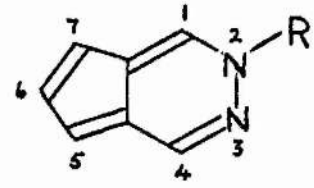
LIV



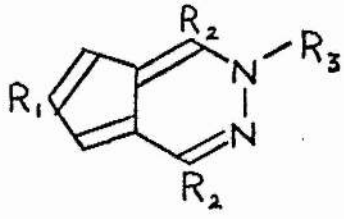
LV



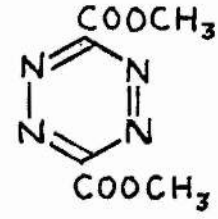
LVI



LVII



LVII a) $R_1 = NO_2$, $R_2 = CH_3$, $R_3 = H$
b) $R_1 = NO_2$, $R_2 = CH_3$, $R_3 = Ph$
c) $R_1 = NO_2$, $R_2 = Ph$, $R_3 = H$
d) $R_1 = NO_2$, $R_2 = R_3 = Ph$
e) $R_1 = R_3 = H$, $R_2 = Ph$
f) $R_1 = R_2 = R_3 = H$
g) $R_1 = R_2 = H$, $R_3 = Ph$
h) $R_1 = R_3 = H$, $R_2 = COOCH_3$



LVIII

a) R = Ph
b) R = p-C_6H_4.CH_3
LIX c) R = p-C_6H_4.Cl

carbocyclic ring in azulene, have been reported.[89] It is noteworthy that a classical structure cannot be written for LIII. LII appears to react with electrophiles at the vacant position on the cyclopentadiene ring.

If the second heteroatom is a nitrogen atom, and replaces one carbon instead of two, the structures obtained are simply aza-analogues of the pseudoazulenes XLVII and XLVIII. Of the large number of possible structures, only isolated examples have appeared in the literature, and very little work seems to have been done with the purpose of relating their behaviour to that of azulene. Two such examples are the purple cyclopenta[b] quinoxaline derivative LIV, prepared by condensation of o-phenylenediamine with the cyclopentenedione LV,[90] and 3,4-dicarbomethoxy-2H-cyclopenta[c]pyridazine (LVI) which is obtained by the reaction of diazocyclopentadiene with dimethylacetylene dicarboxylate.[36]

Condensation of the 6-hydroxyfulvene-2-ketones (XXXIV) with hydrazine or phenyl hydrazine yields the 2H-cyclopenta[d]pyridazine system (LVII). Compounds of this class (LVIIa-d) were first reported by Hale in 1916,[91] and other members of the series have been prepared by Linn and Sharkey (LVIIe),[66] and by Hafner and co-workers (LVIIf,g),[47] using the above reaction. Another example (LVIIh) has been obtained from the reaction of cyclopentadiene with 3,6-bismethoxycarbonyl-1,2,4,5-tetrazine (LVIII).[92]

The chemistry of this system has been little studied, but Hafner has found that LVIIf forms a resonance-stabilised anion on treatment with base, and that this anion can be alkylated on nitrogen to yield products that can also be formed by reacting 2-formyl-6-hydroxyfulvene with monosubstituted hydrazines.[47]

If the 6-hydroxyfulvene-2-ketones are condensed with hydroxylamine instead of with hydrazine, cyclopenta[d]-2,3-oxazines (LIX) are formed. Linn and Sharkey[66] prepared LIXa-c, but did not comment on their chemical behaviour.

In this thesis some electrophilic substitutions upon the 2H-cyclopenta[d]pyridazine and cyclopenta[d]-2,3-oxazine systems are presented, together with an attempt to compare the relative degrees of electron delocalisation in the two systems by the use of N.M.R. spectroscopy.

DISCUSSION

1. DIACYLCYCLOPENTADIENES.

Diacylcyclopentadienes: Tautomerism and Electrophilic Substitution.

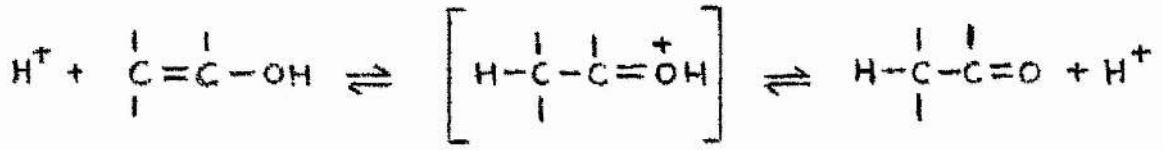
Brief mention has been made in the Introduction of the I.R. and N.M.R. spectra of the diacylcyclopentadienes, with special reference to diformylcyclopentadiene. The only unambiguous interpretation of these spectra requires the diacylcyclopentadienes to exist as enol tautomers, i.e. as 6-hydroxyfulvenes. The existence of keto-enol tautomerism in the diacylcyclopentadienes may be compared with other common examples of this phenomenon, in particular with the β-diketones.

A characteristic of the β-diketones is the very high proportion of enol form in the equilibrium mixture of tautomers. Benzoylacetone, for example, exists as 99% enol form in the absence of solvent, at 25°, while the corresponding figure for acetone is $2.5 \times 10^{-4}\%$. This difference is due almost entirely to intramolecular hydrogen bonding, which is sterically favoured in the enol form of the diketone since, in the resulting six-membered ring, the skeletal strain is minimal. When an alkyl group is attached to the carbon atom between the two carbonyl groups of a β-diketone, interference between this

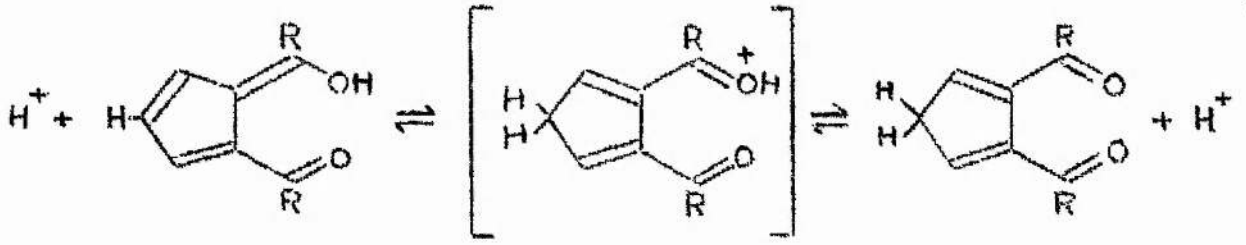
alkyl group and the neighbouring groups may distort the planarity of the conjugated enol system and thereby destabilise the enol form to a considerable extent. Thus, acetylacetone contains 80% enol tautomer, but 3 -methylpentan-2,4-dione contains only 33% enol under the same conditions. It does not appear that the enol forms of diacetyl- and dibenzoyl-cyclopentadiene are appreciably destabilised by steric interactions, or by the fact that enolisation in these compounds requires formation of a seven-membered rather than a six-membered ring, although steric effects may destabilise the enol forms of diacylcyclopentadienes having substituent groups at C-3 and C-5.

In spite of the predominance of the enol form in neutral solutions of the diacylcyclopentadienes, there is reason to believe that the percentage of keto form is increased in strongly acid solution. The lability of the enol proton is illustrated by the low-field position of its signal in the N.M.R. spectra of 2-acetyl-6-methyl-6-hydroxyfulvene and 2-benzoyl-6-phenyl-6-hydroxyfulvene in carbon tetrachloride (-8.0 τ and -8.45 τ respectively), and by the disappearance of these signals when the spectra are recorded in trifluoracetic acid.

In acidic solutions, the equilibrium between keto and enol forms involves the following mechanism:



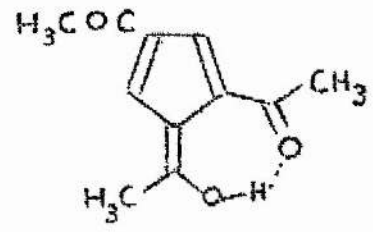
This process is aided by interaction between the hydrogen adjacent to the carbonyl group and a nucleophilic species, which may be the conjugate base of the acid employed, or merely a solvent molecule or aggregate of solvent molecules. It is reasonable to expect a similar equilibration process to occur when the 2-acyl-6-hydroxyfulvenes are dissolved in acidic solutions, possibly by the following scheme:



There is no positive evidence that the enol tautomer is protonated at C-4 as shown in the above scheme, or that the proportion of keto tautomer in equilibrium mixture in acid solution is very large. Formation of the keto tautomer involves shortening of the conjugated chain, which should cause a hypsochromic shift in the U.V. spectrum, but the U.V. spectrum of 2-benzoyl-6-phenyl-6-hydroxyfulvene in ethanol is unchanged by the addition of perchloric acid, showing that the concentration of any keto form must be low. The N.M.R. spectrum of dibenzoyl-

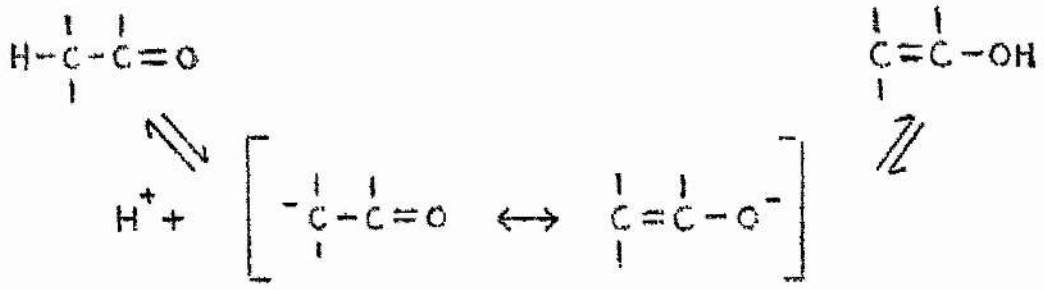
cyclopentadiene in trifluoracetic acid does not show the presence of a methylene group; the triplet shown by the hydrogen on C-4 does not represent more than one proton. This signal, however, is not found when the spectrum is run in deuteriotrifluoracetic acid, showing that exchange of the hydrogen at the 4-position does occur.

Childs, Grigg and Johnson[92] have demonstrated that electrophilic attack upon 2-acetyl-6-methyl-6-hydroxyfulvene under conditions where ionisation of the enol is discouraged leads to preferential substitution at C-4. They obtained 2,4-diacetyl-6-methyl-6-hydroxyfulvene (I) by the action of acetyl chloride in the presence of stannic chloride, in carbon disulphide solution.



I

The mechanism of the interconversion of keto and enol tautomers in the absence of acid is different from that described above. The intermediate in this case is a resonance-stabilised anion:



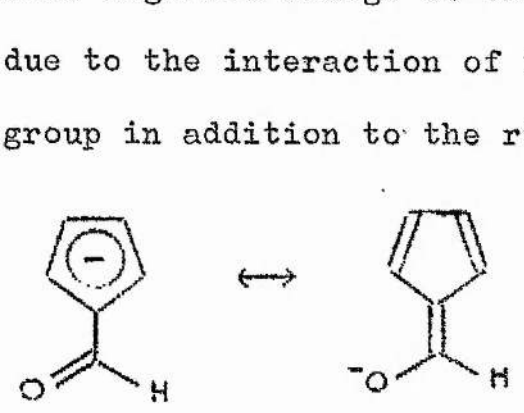
In electrophilic substitution of such a system, the species actually attacked is the anion; the first step of the reaction is the ionisation of the ketone and does not involve the electrophile. As quite strong acids (pK_a of diformylcyclopentadiene is 4.5)[58], the diacylcyclopentadienes in polar solvents should react with electrophiles by this mechanism. It is therefore not possible to draw a distinction between the reactions of a diacylcyclopentadiene and its anion with any particular electrophile, providing the same solvent is present in each case.

The position at which an enolate anion undergoes electrophilic attack will naturally be associated with the distribution of electron density within the anion, but further factors play an important part in directing the course of these reactions. When the negative charge of the anion resides mostly on the oxygen atom, kinetically-controlled reaction will lead to O-substitution; but if O-substitution requires the formation of a weak bond, then the more stable C-substituted product, obtained from thermodynamically-controlled reaction, may predominate.

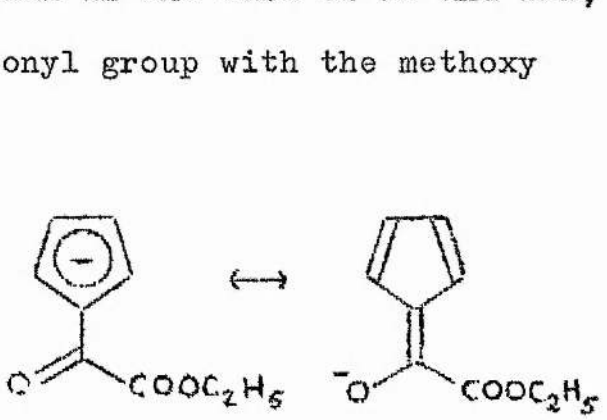
While it can be stated with some confidence that, in the anions of simple aliphatic ketones, the charge resides chiefly on oxygen, the same cannot be said of the anions of the diacylcyclopentadienes, since in these compounds the tendency of the cyclopentadiene rings to acquire a π-electron sextet will be substantial. In view of the different sites possible for electrophilic substitution in the diacylcyclopentadienide anions, these substitution reactions, hitherto unexplored, are of obvious interest. Thermodynamically-controlled C-substitution could result, in the case of the diacylcyclopentadienide anions, not only when O-substitution would lead to formation of an inherently weak bond, but also when steric hindrance from a neighboring acyl group precludes formation of an otherwise strong bond.

Attempted syntheses of ferrocenes from mono- and diacylcyclopentadienide anions have shed some light on the distribution of electron density between the five-membered ring and the acyl groups. Little and Koestler[93] were unable to prepare ferrocenes by the reaction of a series of diaroylcyclopentadienide anions with ferrous chloride, although the appropriate ferrocenes were formed when the diaroylcyclopentadienide anions were reduced to the corresponding dibenzylcyclopentadienide anions. Pauson

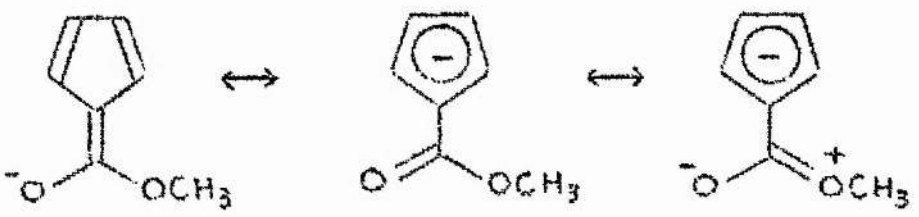
et al.[94] similarly failed to prepare ferrocenes from the anions of formylcyclopentadiene (II) and ethyloxalylcyclopentadiene (III). These failures strongly suggest that ferrocene formation is dependent upon a high concentration of negative charge on the five-membered ring of the anion, and that the syntheses failed because in the anions used, a large part of the negative charge is located on the oxygen atom. Further evidence supporting this hypothesis was provided by the preparation of a ferrocene from carbomethoxycyclopentadienide anion (IV) in moderate yield.[94] In this anion there will be more negative charge on the ring than in the case of II and III, due to the interaction of the carbonyl group with the methoxy group in addition to the ring.



II



III



IV

It is nevertheless impossible to base a complete explanation of the behaviour of monoacylcyclopentadienide anions under

electrophilic attack upon the few examples cited in connection with the ferrocene synthesis. There is no indication why the ratio of O- to C-substituted products from the acylation of formyl-, acetyl-, and benzoyl-cyclopentadienide anions should vary so greatly between the three anions (see page 15).

Nitration.

Mononitro-derivatives of diacetyl- and dibenzoyl-cyclopentadiene have been prepared by electrophilic substitution. Although nitric acid in acetic acid was ineffective, rapid reaction took place when acetic anhydride was used as solvent. Under these conditions the products decomposed readily, but at ca. 0° the decomposition was retarded and the solubility of the nitro-compounds reduced sufficiently for precipitation to occur, enabling a 72% yield of dibenzoylnitrocyclopentadiene to be isolated. Diacetylnitrocyclopentadiene, being more soluble in acetic anhydride, was more difficult to isolate before the onset of decomposition, and only a 10% yield of this compound could be obtained.

The dibenzoylnitrocyclopentadiene was too insoluble for an N.M.R. spectrum to be recorded, but the N.M.R. spectrum of the diacetyl compound showed the presence of the 6-hydroxyfulvene structure with a substituent at C-4, the doublet representing

the protons at C-3 and C-5 in unsubstituted diacetylcyclopentadiene being replaced by a two proton singlet, and the hydrogen-bonded enol proton appearing as a peak at very low field (-9.2 τ in CCl_4 solution). All the features of this spectrum correspond with the published spectrum of 2-acetyl-4-nitro-6-methyl-6-hydroxyfulvene.[73] This compound, and the corresponding dibenzoylnitrocyclopentadiene, are already known from the work of Hale,[71,72,95] although at the time of their discovery they were not recognised as 6-hydroxyfulvenes. The position of the nitro group in Hale's compounds is known from their synthesis by the condensation of nitromalondialdehyde with hexan-2,5-dione and 1,2-dibenzoylethane respectively. Comparison of the properties of Hale's compounds with those of the derivatives obtained by nitration of diacetyl- and dibenzoyl-cyclopentadiene provided additional confirmation of the identity of these nitro-compounds.

Polynitrated derivatives resulting from further substitution of the mono-nitrated compounds were not obtained, and would not be expected under the reaction conditions employed, in view of the considerable deactivation of the cyclopentadiene ring to electrophilic attack, due to the presence of the three electron-withdrawing groups.

Bromination.

Diacetyl- and dibenzoyl-cyclopentadiene were readily brominated by the action of bromine in ethanol or N-bromosuccinimide in carbon tetrachloride. Ethanolic bromine invariably gave a mixture of two derivatives, one monobrominated and the other tribrominated, even when only one molar equivalent of bromine was used. Bromination of the monobrominated compounds gave only the tribrominated compounds; another compound was formed when dibenzoylbromocyclopentadiene was brominated with a large excess of bromine, but being colourless, it was presumed to be an addition compound and was not investigated further. The absence of di- and tetra-substituted derivatives is noteworthy. Attempts to prepare them by reaction of diacetyl- and dibenzoyl-cyclopentadiene with the appropriate quantities of N-bromosuccinimide gave only the usual mixture of monobrominated and tribrominated compounds. The apparent inaccessibility of the dibrominated derivatives is particularly perplexing.

The monobrominated compounds were identified by their N.M.R. spectra as 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene and 2-acetyl-4-bromo-6-methyl-6-hydroxyfulvene. The latter compound was also found to be the monobrominated component of the mixture of two products obtained by the bromination of potassium diacetylcyclopentadienide with bromine in ethanol.

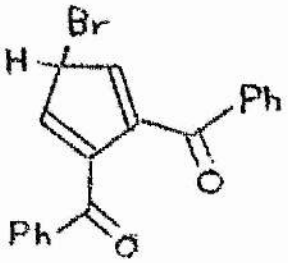
On one occasion a preparation of dibenzoyltribromocyclopentadiene by the action of ethanolic bromine on 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene yielded, besides the expected product, a few milligrams of another compound not previously encountered. Subsequent attempts to isolate this compound under a variety of reaction conditions were unsuccessful. The new compound could be recrystallised from light petroleum as golden-yellow leaflets which melted at 145-146° with decomposition. Its mass spectrum showed the presence of one bromine atom and indicated a molecular weight consistent with the formula $C_{19}H_{13}BrO_2$, implying that the compound was a monobrominated derivative of dibenzoylcyclopentadiene. TLC gave the following R_f values:

Solvent.	New Compound.	2-Benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene.
Chloroform	0.08-0.28	0.53
Benzene	0.06-0.18	0.70
Methanol	0.88	0.88

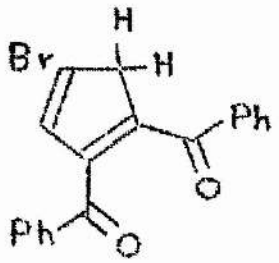
On the basis of this evidence it seems possible that the new compound is the keto tautomer of 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene. In hydrocarbon solvents and in dry chloroform the keto tautomer is stable, but in protophilic solvents such

as methanol, tautomerism to the enol form takes place. The formation of the keto tautomer can be explained by reference to the reaction conditions under which it was isolated. Ethanolic bromine was added to a solution of 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene in ethanol, and the solution was set aside, without stirring, until the product had crystallised. After bromination of the majority of the starting material, the ethanolic solution would have been sufficiently acidic on account of the liberated hydrogen bromide for an appreciable amount of the remaining monobromo-compound to be present in its keto form. The subsequent crystallisation of this form was fortuitous. In order to test the hypothesis that the proportion of keto tautomer is increased in acid solution, dibenzoylcyclopentadiene was monobrominated in trifluoracetic acid solution. The keto tautomer of dibenzoylbromocyclopentadiene (together with some enol tautomer) was identified in the reaction mixture by TLC, but during the course of the necessarily aqueous work-up, the keto tautomer gradually enolised.

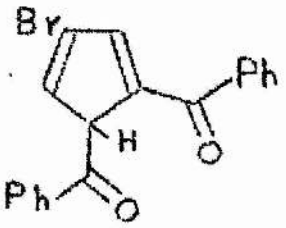
It was not possible to decide whether the keto tautomer had structure Va, Vb or Vc.



Va



Vb



Vc

The U.V. spectrum in cyclohexane is similar to that of 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene in cyclohexane, but there are significant differences. In particular, the 345mμ absorption maximum of the enol tautomer appears at 364mμ in the spectrum of the keto tautomer. This shift is in the opposite direction to that expected on the basis of the difference in conjugated chain length between the keto and enol tautomers, and offers no clue to the structure of the former.

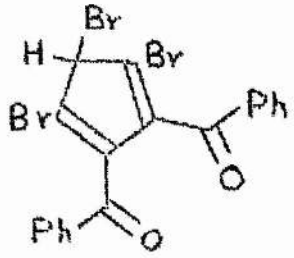
The identification of the tribrominated diacylcyclopentadienes was similarly complicated. Diacetyltribromocyclopentadiene was easily shown from its N.M.R. spectrum to be 2-acetyl-3,4,5-tribromo-6-methyl-6-hydroxyfulvene. The spectrum showed the presence of no cyclopentadiene ring protons, and the enol proton signal was visible at -9.1τ in carbon tetrachloride solution. It is interesting that the chemical shift of this proton is so different from that of the enol proton of diacetylcyclopentadiene (-8.0τ). The implied difference in acidity between the two compounds is unexpected in view of the small difference in

chemical shift (less than 0.1 τ) between the enol protons of diacetyl- and dibenzoyl-cyclopentadiene and those of their monobrominated derivatives. The chemical shifts of relevant diacylcyclopentadienes are contained in the following table:

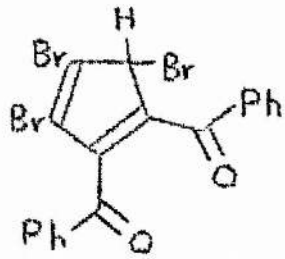
N.M.R. Spectra (in CCl_4) of Diacylcyclopentadienes: Chemical Shift of Enol Protons (τ).

Acyl Groups	Parent Compound	Monobrominated Derivative	Tribrominated Derivative
Acetyl	-8.0	-8.05	-9.1
Benzoyl	-8.45	-8.55	--
Pivaloyl	-9.2	-9.2	--

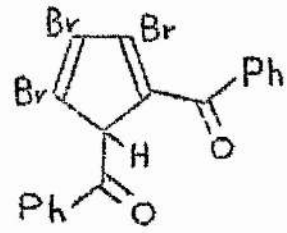
In the N.M.R. spectrum of dibenzoyltribromocyclopentadiene (in deuteriochloroform instead of carbon tetrachloride for solubility reasons) no enol proton was visible. There was, however, a single peak corresponding to somewhat less than one proton at 4.25 τ. The presence of a signal at this τ-value and the absence of the expected low-field enol proton signal suggest that dibenzoyltribromocyclopentadiene exists in the keto form, i.e. as VIa, b or c.



VI a



VI b



VI c

Destabilisation of the enol form in this compound might be explained by the distortion of the planar enol molecule by steric interaction between the phenyl groups and the bromine atoms at C-3 and C-5.

In the search for further evidence of such a steric effect, dipivaloyltribromocyclopentadiene was prepared. Treatment of dipivaloylcyclopentadiene with three molar equivalents of N-bromosuccinimide gave a mixture of mono- and tri-brominated products, as encountered in the bromination of diacetyl- and dibenzoyl-cyclopentadiene. Time did not permit the separation of these products, but the N.M.R. spectrum of the mixture (in CCl_4) could be interpreted unambiguously in terms of dipivaloyl-tribromocyclopentadiene and 2-pivaloyl-4-bromo-6-t-butyl-6-hydroxyfulvene, which were shown to be present in the approximate ratio 2.7:1. No signal for the enol proton of the tribrominated compound was visible. Since there is a difference in chemical shift of 1.1τ between the enol protons of diacetylcyclopenta-diene and its tribrominated derivative, indicating that the latter

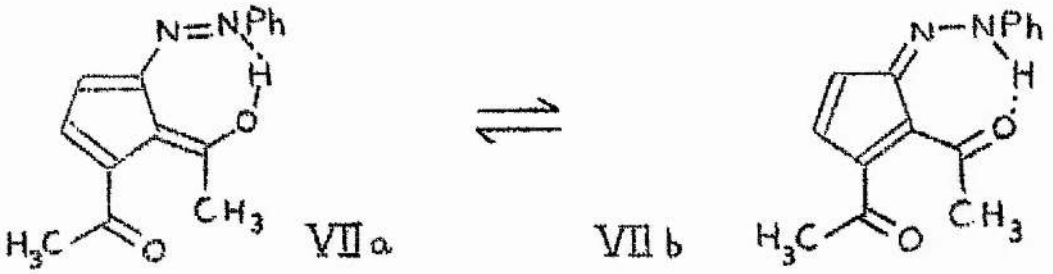
is more acidic, dipivaloyltribromocyclopentadiene might also be expected to be an appreciably stronger acid than the parent compound, and the complete absence of the labile proton signal supports this idea. Since no appreciable amount of the undissociated form appeared to be present, it proved impossible to determine whether the keto or enol form was the preferred one for this molecule.

Azo-coupling.

The monosubstituted derivatives of diacetyl- and dibenzoylcyclopentadiene obtained by nitration and bromination suggest that in the diacylcyclopentadienes, electrophilic monosubstitution normally occurs at C-4. Reactions of the diacetyl- and dibenzoyl-cyclopentadienide anions with benzene diazonium chloride were accordingly undertaken with the expectation that azo-coupling at C-4 would result. Immediate reaction occurred on adding the methanolic solutions of the anions to the ice-cold diazonium salt solution, but the yields of azo-coupled products were variable and low, probably on account of the difficulty, due to the small scale of the reactions, of exactly balancing the quantities of the reactants.

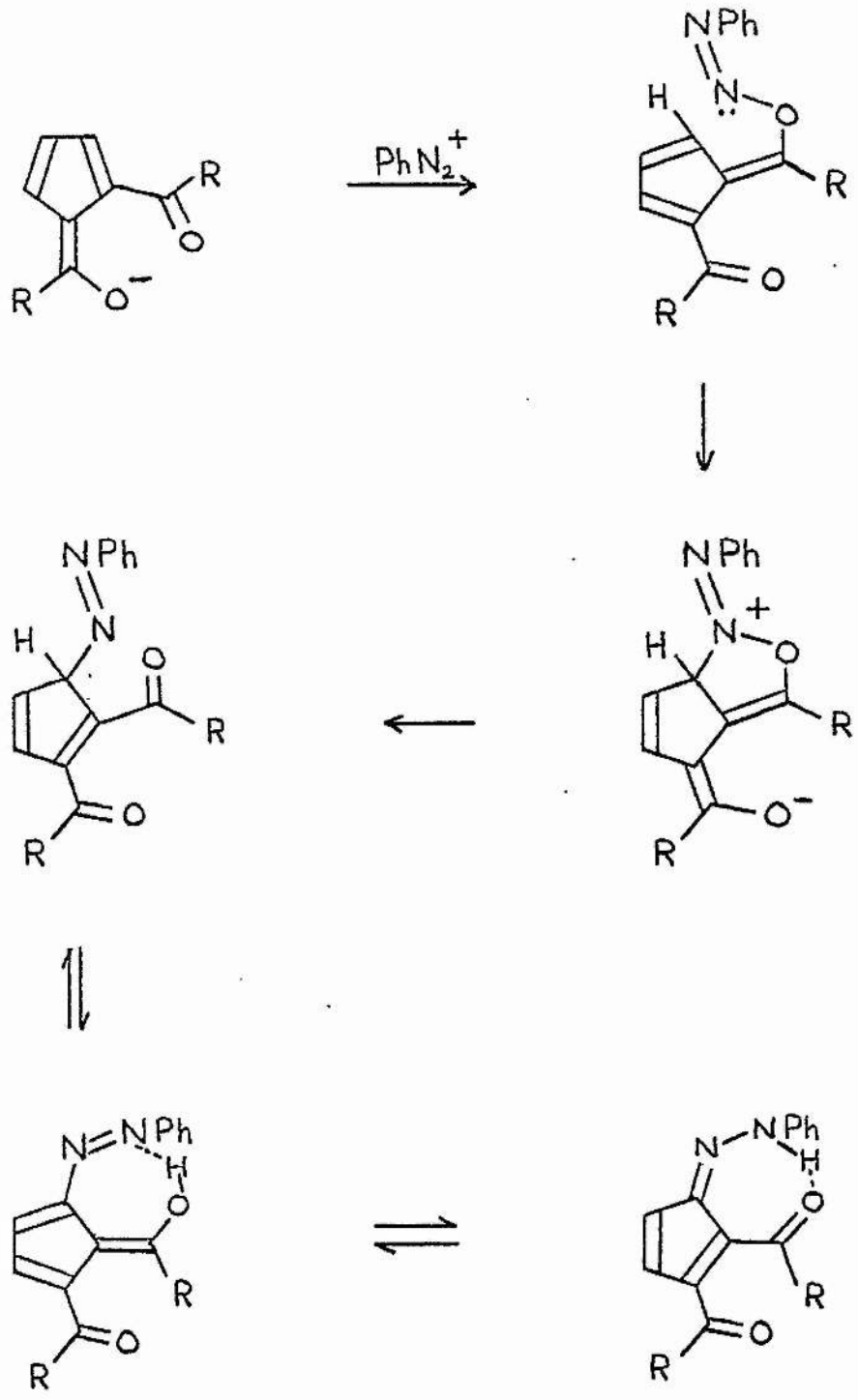
The N.M.R. spectrum of the product derived from dibenzoylcyclopentadiene was of little value for the purpose of

identification, since the peaks from the three phenyl groups and the cyclopentadiene ring protons were superimposed to form a complex multiplet in the region 2.2-3.3 τ. In the spectrum of the diacetylcyclopentadiene derivative, the phenyl protons similarly prevented analysis of the cyclopentadiene ring proton pattern, but the methyl groups were observed as two three-proton singlets. This indicates that substitution took place not at C-4, which would give a symmetrical product showing a single peak for the six methyl protons, but at C-3(5). The probable structure of this compound is therefore VIIa, b:



The low-field peak in the N.M.R. spectrum of compound VII was found at -5.6 τ (in $CDCl_3$) which is characteristic in this class for a proton between a nitrogen atom and an oxygen atom (see page 55). If the enol proton bridges two oxygen atoms, its absorption would be expected in the region of -8 τ.

Diacetylcyclopentadienide anion was also coupled with p-bromobenzene diazonium chloride and with 2,4-dibromobenzene diazonium chloride. The N.M.R. spectra of the products showed


PhN2+
NPh
H
N
O
R
O
R
R
O
R
O
NPh
H
N
O
R
R
O
NPh
H
N
+
O
R
R
O
NPh
H
N
O
R
R
O
NPh
H
N
O
R
R
O

the same features as that of compound VII. In neither spectrum could the cyclopentadiene AB system be distinguished from the phenyl proton peaks.

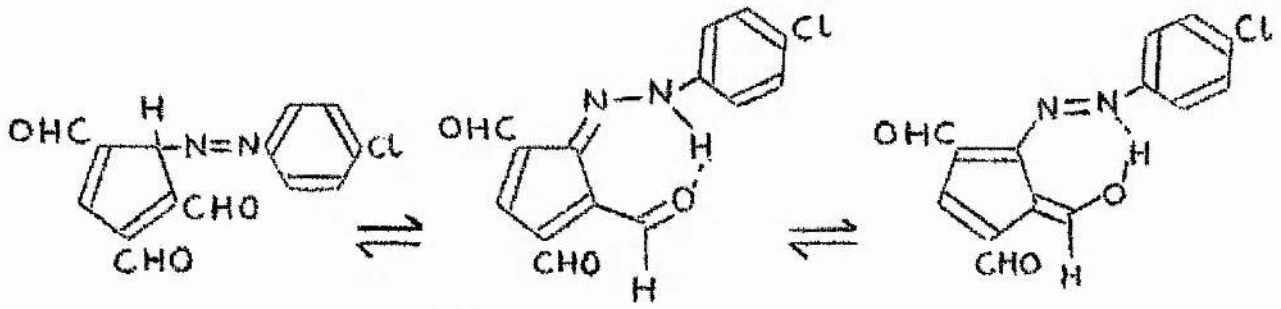
It is reasonable to conclude that in these reactions the diazonium cations do not substitute directly at C-3(5) of the diacylcyclopentadienide anions, since nitration and bromination reactions suggest that C-4 is the normally preferred site for substitution on the five-membered ring. There is also no reason to suppose that, having once substituted at C-4, the phenylazo group could migrate to C-3(5). It is therefore postulated that kinetically-controlled reaction occurs at one of the electron-rich oxygen atoms, and that partly on account of the weakness of the resulting N-O bond, rearrangement follows to give the thermodynamically-preferred C-5 substituted product. A possible mechanism for the proposed rearrangement is shown opposite. The rearrangement is facilitated, according to this mechanism, by the formation of a five-membered cyclic intermediate. There is no comparable mechanism by which the phenylazo group can transfer from the oxygen atom to C-4.

It is unlikely that the O-phenylazo intermediates from the coupling of the diacylcyclopentadienide anions rearrange by an intermolecular process, since in that event, substitution at C-4 would be expected.

The azo-coupling reaction of diacetylcyclopentadiene itself, as distinct from its anion, was investigated by allowing it to react with p-bromobenzene diazonium fluoroborate in dry acetonitrile. The product finally isolated was found to be a 5:1 mixture of 2-acetyl-5-(2,4-dibromophenyl)azo-6-methyl-6-hydroxyfulvene and 2-acetyl-5-(p-bromophenyl)azo-6-methyl-6-hydroxyfulvene.

The N.M.R. spectrum of the product suggested the presence of a mixture of two compounds, but was not conclusive owing to the coincidence of two of the methyl peaks. The presence of a dibrominated compound was demonstrated by mass spectroscopy, and its identity was confirmed by spectroscopic comparison with the product from the reaction of diacetylcyclopentadienide anion with 2,4-dibromobenzene diazonium chloride. TLC examination of the p-bromoaniline from which the diazonium fluoroborate was prepared showed contamination with 2,4-dibromoaniline, but it is surprising that the derivative of this minor contaminant should predominate in the final product. The isolation of the mixture of C-5-substituted diacylcyclopentadienes indicates that the electrophilic substitution of diacylcyclopentadienes in solvents of high dielectric constant follows the same course as that of their anions.

Hafner[58] has reported the coupling of 1,2,4-triformylcyclopentadienide anion with p-chlorobenzene diazonium fluoroborate. The product (VIII) was coupled at one of the unsubstituted ring carbons, but owing to the lack of an alternative substitution site on the ring, there is no indication whether the product was formed by substitution by the diazonium cation at carbon, with or without prior attack at oxygen, or by intramolecular rearrangement of an O-substituted intermediate.



VIII

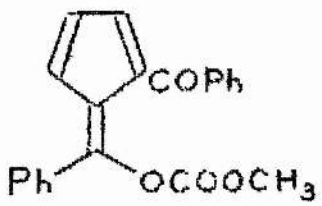
Reactions with Methyl Chloroformate and with Acyl Chlorides.

In view of the evident feasibility of electrophilic attack at oxygen in the diacylcyclopentadienide anions, it was of interest to attempt the preparation of stable O-substituted derivatives.

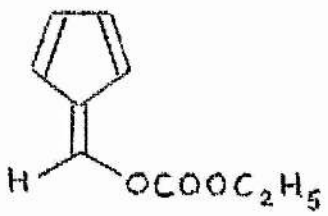
Potassium dibenzoylcyclopentadienide was found to react very readily with methyl chloroformate at reflux temperature to give a 50% yield of methyl 2-benzoyl-6-phenylfulven-6-yl carbonate (IX). This compound was identified by its N.M.R. spectrum which clearly showed the cyclopentadiene ring protons

as a twelve-peak ABX system (two peaks of the C-3 proton signal overlap). The coupling constants of the cyclopentadiene ring protons were found to be: $J_{3,4}$ 2.0, $J_{4,5}$ 5.3, $J_{3,5}$ 1.8 c/s. These figures agree in magnitude with those recorded for a number of fulvenes,[48,49,92] and such coupling constants may be regarded as characteristic of the fulvenes.

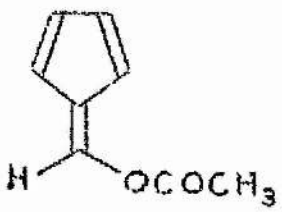
The success of this reaction is surprising in view of the failure of diacetylcyclopentadienide anion to react with acetyl chloride. It has been reported[63] that formylcyclopentadienide anion reacts exclusively at oxygen with both ethyl chloroformate and acetyl chloride to give the compounds X and XI, but the attempted reaction of diacetylcyclopentadienide anion with acetyl chloride led only to formation of tars, and a large proportion of unchanged diacetylcyclopentadiene was recovered. In contrast, it appears that diacylcyclopentadienes will undergo acylation on carbon in the presence of Friedel-Crafts catalysts (see the work of Childs, Grigg and Johnson,[92] mentioned above).



IX



X



XI

Vilsmeier formylation of dibenzoylcyclopentadiene was attempted, but no formylated products were obtained. Almost complete decomposition of the dibenzoylcyclopentadiene occurred at temperatures above ca. -20°, and at lower temperatures no reaction was observed.

Triacylcyclopentadienes are probably too deactivated to undergo acylation on carbon or on oxygen. Ploss[96] was unable to bring about reaction of benzoyl chloride with 1,2,4-triformylcyclopentadiene in pyridine, or with sodium 1,2,4-triformylcyclopentadienide.

2. YLIDES FROM DIACYLCYCLOPENTADIENES.

Diacyldiazocyclopentadienes.

The preparation and reactions of diazocyclopentadienes have already been briefly described (page 7). Recent work has shown that the reaction of the carbenic decomposition products of these compounds is considerably affected by substitution by phenyl groups at the 2- and 5-positions, possibly because of steric hindrance. 2,3,4,5-Tetraphenyldiazocyclopentadiene[35,97,98] and 2,5-diphenyldiazocyclopentadiene[97,98] afford ylides by thermal decomposition in the presence of pyridine, triphenylphosphine etc., while no ylides were obtained from the

decomposition of 2-chloro- or 2-bromo-3,4,5-triphenyldiazocyclopentadiene,[99] 3,4,5-triphenyldiazocyclopentadiene itself,[98,99] 2,4-diphenyldiazocyclopentadiene[98] or 2,3,4,5-tetrachlorodiazocyclopentadiene.[99] The striking feature of these results is the formation of ylides when the 2- and 5-positions are occupied by phenyl groups, and the failure to form ylides when only one of these positions is so occupied. This is the reverse of what might be expected if combination of the carbenes with heteroatoms is influenced by steric effects alone, and points to the existence of electronic effects, the exact nature of which has yet to be determined.

The investigation of the decomposition of diazocyclopentadienes has hitherto been limited to cases in which the diazo compounds concerned were substituted by phenyl groups, variously distributed about the ring. The decomposition of diazocyclopentadienes substituted by groups which show a marked electron-donating or -withdrawing effect with or without an accompanying steric effect is still unexplored. In this context it can be seen that examination of the decomposition of diacyldiazocyclopentadienes might provide valuable information on the mechanism of the reaction of the carbenes derived from diazocyclopentadienes. Furthermore, decomposition of diacyldiazocyclopentadienes in the presence of suitable substrates might yield some interesting new stabilised cyclopentadienylides.

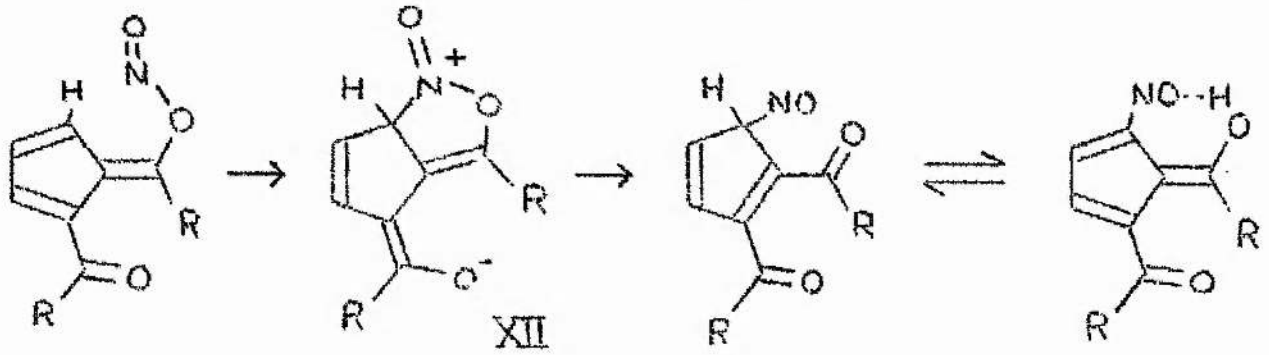
The preparation of dibenzoyldiazocyclopentadiene was accordingly attempted by a number of routes. The amine-catalysed reaction with toluene-p-sulphonyl azide failed to give the desired product. When diethylamine was added to a mixture of toluene-p-sulphonyl azide and dibenzoylcyclopentadiene, a very vigorous reaction took place which left only decomposition products. Diazocyclopentadiene[100] and phenylated diazocyclopentadienes[101] have been prepared in good yield by keeping a mixture of the cyclopentadienes, toluene-p-sulphonyl azide and diethylamine at 0^{o} for several days. When applied to dibenzoylcyclopentadiene, this modification, like the reaction at room temperature, led to decomposition products, the only effect of the lower temperature appearing to be the lowering of the reaction rate. Reaction of potassium dibenzoylcyclopentadienide with toluene-p-sulphonyl azide was equally unsuccessful. Toluene-p-sulphonyl azide was added to a suspension of the potassium salt in dry ether. No immediate reaction was observed, but on refluxing the ether, a brown colour gradually developed. The brown solid isolated from this reaction was found to contain sulphur and nitrogen (Lassaigne test).

Following the failure of the toluene-p-sulphonyl azide reactions, attempts were made to reduce the easily accessible 2-benzoyl-4-nitro-6-phenyl-6-hydroxyfulvene to the corresponding

amino compound. It was hoped that diazotisation of this amine might give 2,3,4-dibenzoyldiazocyclopentadiene. Many of the reducing agents available could not be used because of the risk of reducing the cyclopentadiene system or the carbonyl groups in addition to the nitro group. The methods of reduction eventually chosen have been employed successfully for the reduction of nitro-ketones.[102] Dibenzoylnitrocyclopentadiene reacted immediately with sodium dithionite ($Na_2S_2O_4$), but of the many coloured products formed, none was present in any quantity. Rapid reaction similarly occurred at room temperature when powdered zinc was added to a solution of the nitro compound in aqueous ethanol containing suspended ammonium chloride. Again, a mixture of products was obtained, but two dark blue-green components predominated. The yield of the products from the two reactions was too small for either reaction to be useful, and identification of the various substances obtained was not attempted.

In view of the difficulty of reducing dibenzoylnitrocyclopentadiene to dibenzoylaminocyclopentadiene, 2-benzoyl-4-nitroso-6-phenyl-6-hydroxyfulvene was considered as a precursor for the amine, and its preparation by nitrosation of dibenzoylcyclopentadiene was attempted. An interesting possibility is that nitrosation of diacylcyclopentadienes or their anions

might give products substituted at the 3-position instead of the expected 4-position, for in this case, as in the azo-coupling reaction, a cyclic intermediate (XII) can be proposed, formation of which would allow intramolecular rearrangement of an initially-formed O-nitrosated compound:



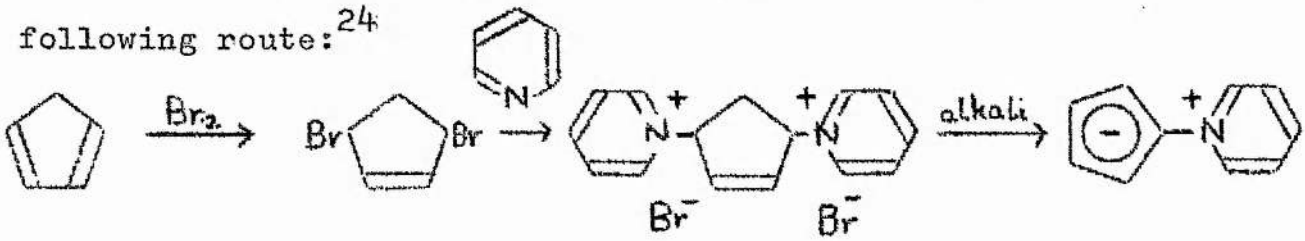
XII

A method for the direct introduction of the diazo group into aromatic nuclei was developed by Tedder *et al.* for the preparation of diazonium salts from phenols,[103] and subsequently used for the preparation of various diazo-heterocycles, including 3-[104] and 2-diazopyrroles.[105] The successful preparation of diazopyrroles, which are aza-analogues of diazocyclopentadienes, suggested the applicability of this reaction to the preparation of diacyldiazocyclopentadienes. The reaction, which takes place in an aqueous acetone solution of nitrous acid buffered to pH 3-4 by excess sodium nitrite, proceeds via the nitroso compound, so that formation of diacylnitroso-cyclopentadienes instead of diacyldiazocyclopentadienes was also possible.

When hydrochloric acid was gradually added to a solution of dibenzoylcyclopentadiene and sodium nitrite in aqueous acetone, a very rapid decomposition suddenly ensued after about half of the acid had been added. Dibenzoylcyclopentadiene was also found to decompose rapidly when ethyl nitrite gas was passed into a methanolic solution of its sodium salt. In this case, however, a dark green colour appeared before the solution became brown, which might indicate formation of an unstable nitroso derivative.

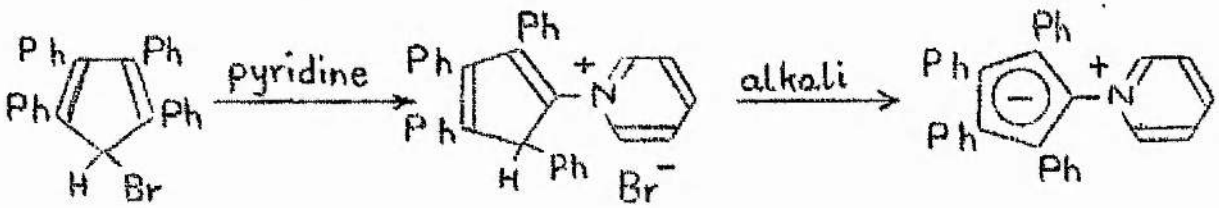
Pyridinium Ylides.

The inaccessibility of the diacyldiazocyclopentadienes prevented the attempted preparation of pyridinium diacylcyclopentadienylides by decomposition of the diazo compounds in pyridine, and other routes to the pyridinium ylides were therefore sought. Pyridinium cyclopentadienylide was prepared in 1955 by the following route:[24]



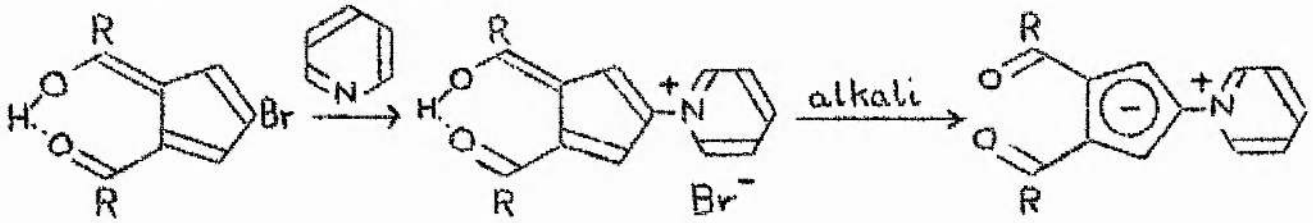
The identity of the intermediate cyclopentene-bis-pyridinium bromide, suspected by Lloyd and Sneezum,[24] was confirmed when the intermediate was isolated by Baranetskaya et al.[106]

1-Bromo-2,3,4,5-tetraphenylcyclopentadiene reacted with pyridine at room temperature to form N-(2,3,4,5-tetraphenylcyclopentadienyl)-pyridinium bromide, which, on treatment with alkali, gave pyridinium 2,3,4,5-tetraphenylcyclopentadienylide:[24]



This ylide is completely stable as a solid in the atmosphere, in contrast to the unphenylated ylide. Equally stable ylides were obtained from a reaction analogous to the above, employing 3- or 4-methylpyridine as base. With 2-methylpyridine and 2,6-dimethylpyridine the reaction was less successful, probably due to steric hindrance.[24]

The reaction between diacylbromocyclopentadienes and pyridines thus appeared to offer a possible route to diacylcyclopentadienylides:

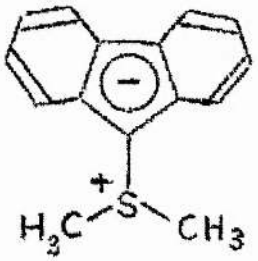


2-Acetyl-4-bromo-6-methyl-6-hydroxyfulvene gradually decomposed in pyridine solution at room temperature without formation of the intermediate N-(diacetylcyclopentadienyl)-pyridinium bromide.

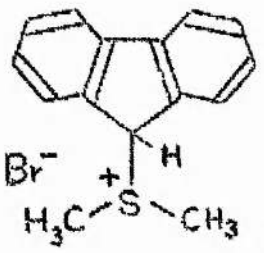
Decomposition of 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene in pyridine was somewhat slower, but again no evidence of the presence of a pyridinium salt or ylide could be found.

Sulphonium and Arsonium Ylides.

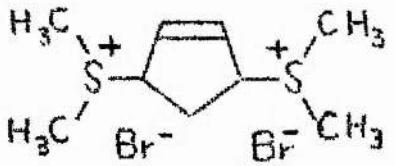
Sulphonium ylides of cyclopentadiene compounds were first made by reactions analogous to those used for the preparation of pyridinium cyclopentadienylides. Thus the preparation of dimethylsulphonium fluorenylide (XIII)[107] involved the intermediacy of fluorenyl-9-dimethylsulphonium bromide (XIV), while dimethylsulphonium cyclopentadienylide[28] was obtained from the action of alkali on cyclopentene-bis-dimethylsulphonium bromide (XV, prepared from dibromocyclopentene and dimethyl sulphide).



XIII



XIV

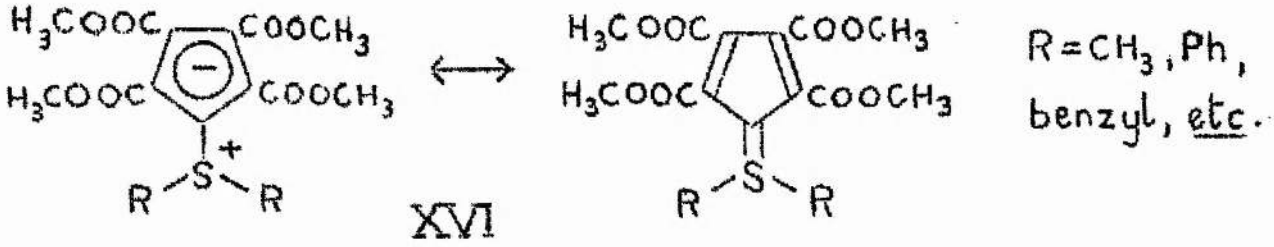


XV

Diphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide, however, has been prepared by decomposition of tetraphenyldiazocyclopentadiene in the presence of diphenyl sulphide.[108]

A recent publication of Seitz[109] reported the condensation at room temperature 2,3,4,5-tetracarbomethoxycyclopentadiene with sulphoxides in acetic anhydride. In the resulting ylides

(XVI) the dipolar form is stabilised by the electron-withdrawing carbomethoxy groups.

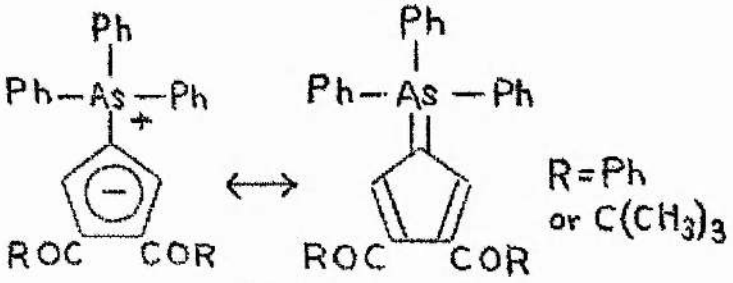


XVI

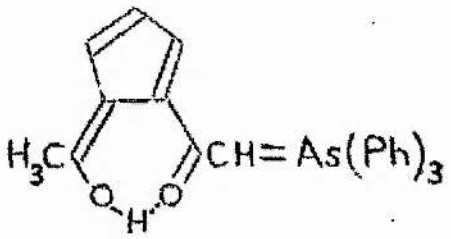
No comment was made on the degree of stabilisation of the five-membered ring necessary for ylides to be prepared by this reaction.

The success of the acetic anhydride method prompted the extension of this method to the preparation of arsonium ylides from stabilised cyclopentadienes and triphenylarsine oxide. The only arsonium cyclopentadienylide hitherto reported was formed by the decomposition of tetraphenyldiazocyclopentadiene in triphenylarsine.[35] Singer[99,110] found that 2,3,4-triphenyl-cyclopentadiene condensed with triphenylarsine oxide in acetic anhydride, giving an ylide which had been acetylated at the vacant ring position. The unacetylated ylide was obtained when the condensation was carried out in triethylamine solution in the presence of phosphorus pentoxide. No ylide was obtained from 2,3,4,5-tetraphenylcyclopentadiene; steric interference of the phenyl groups probably prevents the close approach of the bulky triphenylarsine oxide molecule.

Dibenzoylcyclopentadiene was found to form an arsonium ylide with triphenylarsine oxide in acetic anhydride. Reaction appeared to be very slow at room temperature, and after 12 hr. much unchanged dibenzoylcyclopentadiene was present, but heating for 1 hr. on a steam-bath produced a 80% yield of triphenylarsonium dibenzoylcyclopentadienylide. A 60% yield of ylide was similarly obtained from dipivaloylcyclopentadiene when the reactants were heated for 2 min. in refluxing acetic anhydride. The N.M.R. spectra of these ylides (XVII) showed a single peak for the remaining cyclopentadiene ring protons, indicative of substitution at the 4-position of the diacylcyclopentadienes.



XVII



XVIII

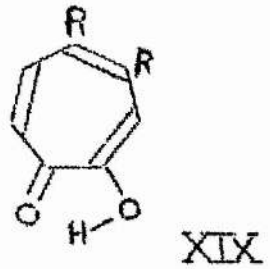
No arsonium ylide was obtained under these reaction conditions from diacetylcyclopentadiene. Although little or no reaction appeared to take place at room temperature, heating the acetic anhydride solution led to rapid decomposition of the diacetylcyclopentadiene. It is possible that in this case condensation occurred preferentially at the activated methyl groups, with subsequent decomposition of the resulting unstable product (XVIII).

Preliminary work suggests that pyridinium ylides cannot be formed by the reaction of diacylcyclopentadienes with pyridine N-oxide in acetic anhydride.

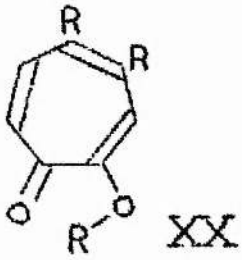
3. DIACYLCYCLOPENTADIENES: REACTIONS OF THE HYDROXYL AND CARBONYL GROUPS.

Hydroxyl Reactions.

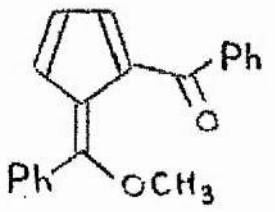
Tropolones (XIX), which have acidic hydroxyl groups, react with alkyl sulphates to form alkyl ethers (XX).[111,112]



XIX



XX



XXI

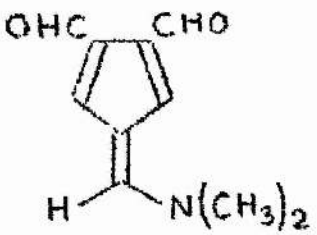
The formation of tropolone alkyl ethers is comparable with the esterification of carboxylic acids, since tropolones may be regarded as extended carboxylic acids with the hydroxyl and carbonyl functions separated by a conjugated chain through which mesomeric effects may be transmitted. Tropolone alkyl ethers are hydrolysed more easily than normal ethers, and hydrolysis takes place under the conditions used for hydrolysis of esters. Like tropolone, the 2-acyl-6-hydroxyfulvenes may be regarded as extended carboxylic acids; the validity of the

comparison was tested by heating potassium dibenzoylcyclopentadienide with dimethyl sulphate in refluxing anhydrous methanol. The colourless, water-soluble crystals which precipitated on cooling, together with an orange crystalline product, implied that reaction had occurred, but the orange compound finally isolated was found to be 2-benzoyl-6-phenyl-6-hydroxyfulvene. It is very possible that the methyl ether XXI was formed, but was hydrolysed during work-up, since it would be expected to undergo very facile hydrolysis.

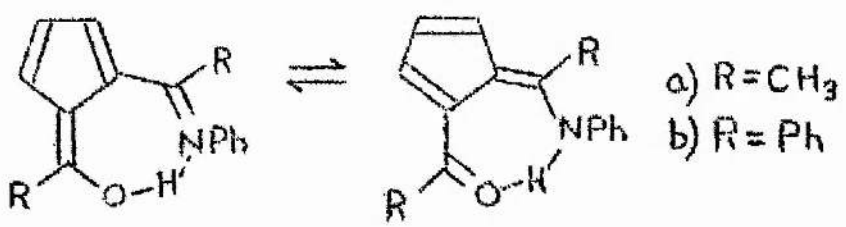
An alternative methylation procedure, in which hydrogen chloride gas was passed into an anhydrous methanolic solution of dibenzoylcyclopentadiene resulted only in decomposition of the starting material.

Carbonyl Reactions.

Hafner and co-workers[58] reported a number of reactions of the carbonyl groups in various formylcyclopentadienes, including the condensation of compound XXII with aniline in ether at room temperature.



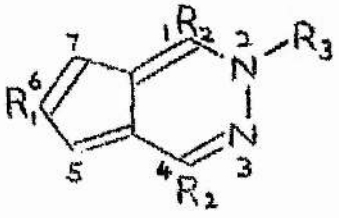
XXII



XXIII

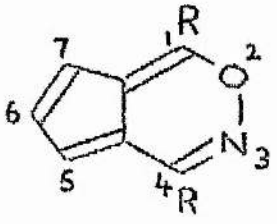
Diacetyl- and dibenzoyl-cyclopentadiene condensed with aniline to form the anils XXIIIa and b, but in this case the reaction had to be carried out in refluxing ethanol solution.[58] The hydroxyl protons in the N.M.R. spectra of XXIIIa (in CCl_4 solution) and XXIIIb (in $CDCl_3$ solution) appear at -5.7 τ and -5.6 τ respectively as broad peaks, representing the average of the two tautomeric forms. The chemical shift of the low-field protons is similar to that of the corresponding protons in the azo-coupled diacylcyclopentadienes (e.g. VII, where the shift is -5.6 τ in $CDCl_3$ solution) where the same O-H-N bonding is present.

The hitherto unreported cyclopenta[d]pyridazines XXIVa-c were prepared by reaction of the appropriately substituted cyclopentadienes with hydrazine hydrate, and XXIVd was prepared from diacetylcyclopentadiene and phenyl hydrazine. The cyclopenta[d]-2,3-oxazine XXVa was similarly prepared, from diacetylcyclopentadiene and hydroxylamine.



XXIV

a) $R_1 = R_3 = H$, $R_2 = CH_3$
b) $R_1 = Br$, $R_2 = CH_3$, $R_3 = H$
c) $R_1 = Br$, $R_2 = Ph$, $R_3 = H$
d) $R_1 = H$, $R_2 = CH_3$, $R_3 = Ph$
e) $R_1 = R_3 = H$, $R_2 = Ph$



a) R = CH_3
b) R = Ph

XXV

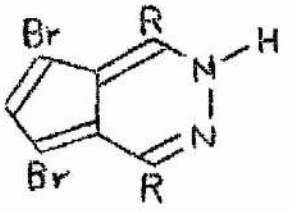
Examples of system XXIV with R_2=methyl, or examples asymmetrically substituted on the five-membered ring (see below), appear susceptible to decomposition by atmospheric oxidation or the action of strong acids, and form intense purple or green products of unknown composition. XXIVa turned slightly green on storage, and was recovered as greenish crystals after attempted recrystallisation. Bromine atoms substituted at position 6 in these compounds are unreactive; the bromine atom in XXIVb and XXIVc was not affected by boiling methanolic sodium methoxide.

4. REACTIONS OF THE 2H-CYCLOPENTA[d]PYRIDAZINES AND CYCLOPENTA[d]-2,3-OXAZINES.

The 2H-cyclopenta[d]pyridazines and cyclopenta[d]-2,3-oxazines are iso-π-electronic with azulene, and electrophilic substitution on the five-membered ring is therefore to be expected. Nitration of XXIVe[66] with nitric acid in acetic anhydride was unsuccessful, the conditions being too severe. An amorphous green substance was the only product. Reaction of ethanolic bromine with XXIVa and XXIVe gave purple or red, probably polymeric products, but by reducing the reaction time to a few seconds, yellow crystalline derivatives were obtained. The brominated derivatives of XXIVa and XXIVe were both shown to be mixtures from their elemental analyses. Mass spectroscopy

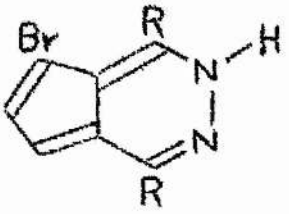
showed that the derivative of XXIVe consisted almost entirely of a dibrominated compound, slightly contaminated with unchanged starting material, and that the derivative of XXIVa was predominantly a dibrominated compound, with some monobrominated material. Bromination of XXIVa and XXIVe with one molar equivalent of N-bromosuccinimide again led to inseparable mixtures of brominated derivatives, although the proportion of monobrominated compounds was higher than when bromine was used.

Predictions on the position of electrophilic substitution in certain pseudoazulenes can be made in the light of the substitution behaviour of azulenes, and the observations of Boyd and Ellis[88] have been mentioned in the introductory section of this thesis. The formation of mixtures of mono- and dihalogenated products upon halogenation of azulene has been noted.[113] On this basis, formulae XXVI and XXVII can be assigned to the dibrominated and monobrominated derivatives of the pseudoazulenes XXIVa and XXIVe.



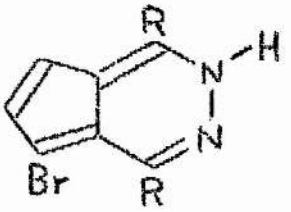
R = CH_3 or Ph

XXVI



R = CH_3 or Ph

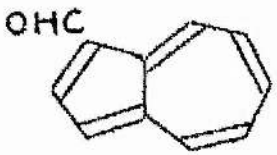
XXVII a



XXVII b

Although there is a formal difference between formulae XXVIIa and b, in fact they represent two readily interconvertible tautomeric forms; any distinction between C-5 and C-7 as the preferred site for electrophilic monosubstitution of XXIVa and XXIVe cannot in consequence be detected, since in either case the same product will result. N.M.R. evidence for the existence of prototropy in XXIVa will be presented below.

Treibs[114] prepared 1-formylazulene (XXVIII) by reaction of azulene with orthoformic ester in the presence of boron trifluoride etherate. This method was used to prepare formyl derivatives (XXIXa & b) of the 2H-cyclopenta[d]pyridazines XXIVa and XXIVe.



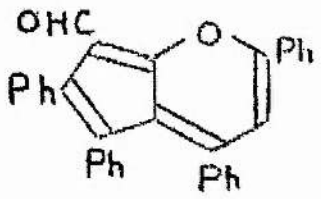
XXVIII

a) R = CH_3
b) R = Ph

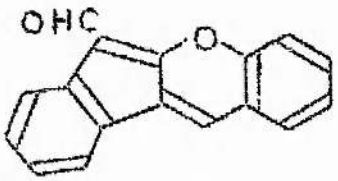
XXIX

The N.M.R. spectra (in trifluoracetic acid) of XXIXa and b are consistent with the proposed structure. That of XXIXa is particularly informative, showing well-separated signals for the two methyl groups, the vicinal cyclopentadiene ring protons, and the formyl proton. In neither spectrum was the imine proton signal visible.

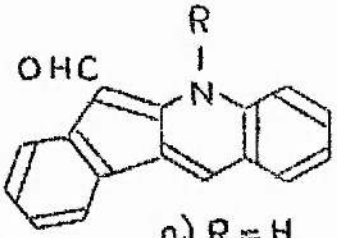
The I.R. spectra of XXIXa and b show the carbonyl absorption as a somewhat broadened peak centred at 1608 cm.$^{-1}$ Similar low frequencies for the carbonyl absorptions of pseudoazulene aldehydes have been observed for compounds XXX (1619 cm.$^{-1}$),[82] XXXI (1600 cm.$^{-1}$),[115] and XXXIIa and b (1610 cm.$^{-1}$ and 1600 cm.$^{-1}$)[116] respectively.



XXX



XXXI

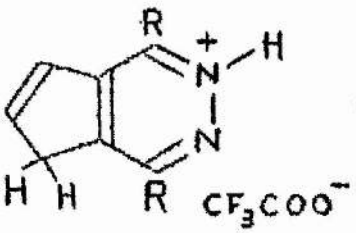


XXXII

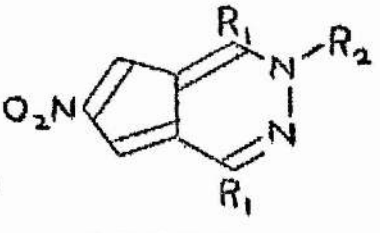
a) R = H
b) R = CH_3

1-Formylazulene[117] and pseudoazulene aldehydes (e.g. XXXI[115]) have been found to undergo the usual carbonyl condensation reactions. Similarly XXIXa formed a yellow 2,4-dinitrophenylhydrazone.

Protonation of the 2H-cyclopenta[d]pyridazines at C-5(7) is demonstrated by their N.M.R. spectra in trifluoracetic acid. The spectra of compounds XXIVa-e show a two-proton singlet due to the methylene group formed on protonation (XXXIII). No such methylene signal was observed in the spectra of the nitro compounds XXXIVa-c,[91] or of the aldehydes XXIXa and b; the presence of the electron-withdrawing groups on the five-membered ring presumably makes the hydrogen atoms of the methylene group more acidic in these cases.



XXXIII

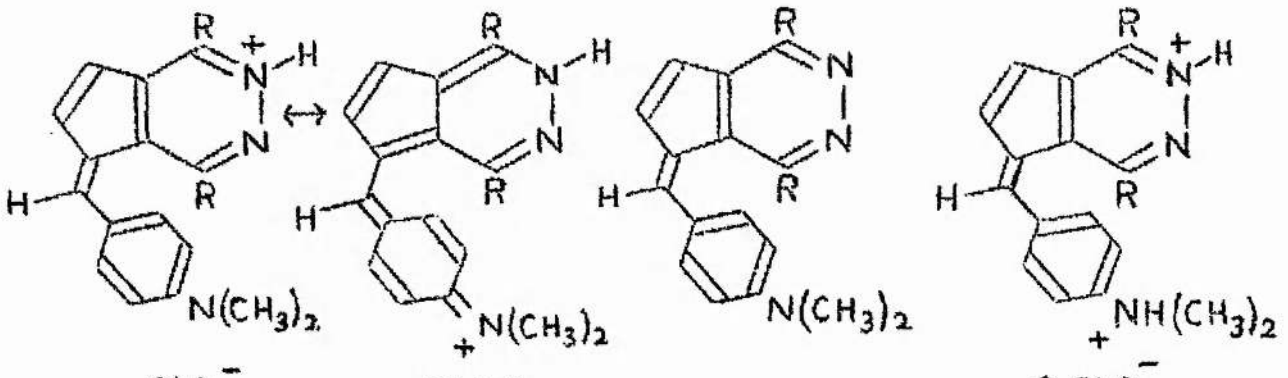


XXXIV

a) $R_1 = CH_3$, $R_2 = H$
b) $R_1 = Ph$, $R_2 = H$
c) $R_1 = CH_3$, $R_2 = Ph$

The methylene group of the protonated 2H-cyclopenta[d]-pyridazines is reactive, and condensation occurs between these salts and carbonyl compounds. The crystalline perchlorates of XXIVa and e reacted with p-dimethylaminobenzaldehyde immediately at room temperature in acetic acid or methanol solution (acetic anhydride was not necessary) to form the compounds XXXVa and b. These compounds, which gave intense blue-purple solutions in alcohols, could be isolated in an impure state by precipitation with ether, but could not be recrystallised, and in consequence satisfactory elemental analyses were not obtained. The purple solutions became red on addition of alkali, the original colour being restored on acidification. In the presence of a high concentration of perchloric or hydrochloric acid, the purple solutions faded to pale yellow or colourless. When the decolorised solutions were diluted with alcohol, the purple colour reappeared. The red, and the yellow or colourless solutions are attributed, respectively, to the deprotonated (XXXVI) and protonated (XXXVII) forms of XXXV. XXXVI (R=Ph) was isolated, but in an impure condition.

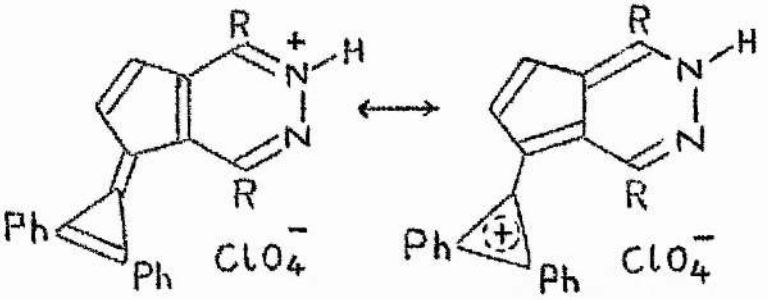
As with XXXVb, satisfactory recrystallisation proved to be impossible.



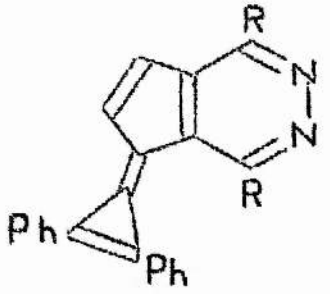
XXXV XXXVI XXXVII

Blue or purple condensation products werealso prepared by reaction of the brominated 2H-cyclopenta[d]pyridazines XXIVb and c with p-dimethylaminobenzaldehyde, although in these examples hot acetic acid was required to effect the condensation. The perchlorates of the nitro compounds XXXIVa and b reacted still less readily, formation of the coloured products being slow even in hot acetic anhydride solution. None of these products was obtained pure.

Another example of the facile condensation of the salts of 1,4-diphenyl- and 1,4-dimethyl-2H-cyclopenta[d]pyridazine (XXIVa and e) is provided by reaction of the perchlorates of XXIVa and e with diphenylcyclopropenone. Both perchlorates reacted in warm (50°) acetic anhydride, and a reaction time of 5 min. was sufficient for compounds XXXVIIIa and b to be formed in ca. 80% yield.



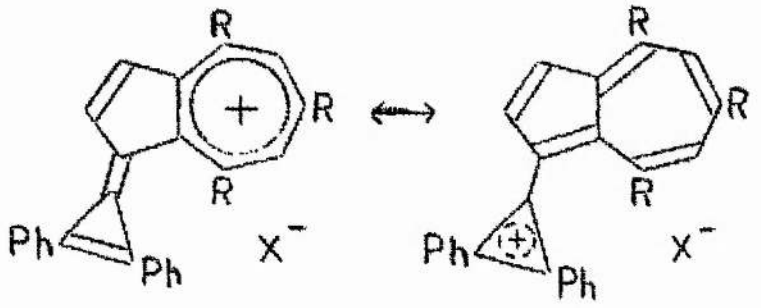
XXXVIII a) R = CH_3 b) R = Ph



XXXIX R = CH_3 or Ph

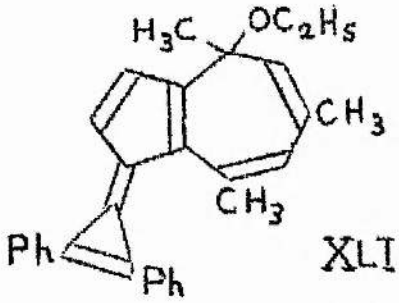
Elemental analysis suggested that XXXVIIIa crystallised from methanol as the monohydrate, having taken up water from the solvent. A weak -OH stretching absorption was visible in the I.R. spectrum, and N.M.R. showed the absence of methanol of crystallisation. Attempts to deprotonate XXXVIIIa and b with triethylamine to give the calicenes XXXIX were unsuccessful, and only tars were isolated.

Carbocyclic analogues of XXXVIII have been reported. A 93% yield of XLa was prepared from azulene and 1,2-diphenyl-3-ethoxycyclopropenium fluoroborate.[118] 4,6,8-Trimethylazulene reacted with 1,2-diphenyl-3,3-dichlorocyclopropene to give XLb, isolated in 67% yield as the perchlorate (XLc).[119]



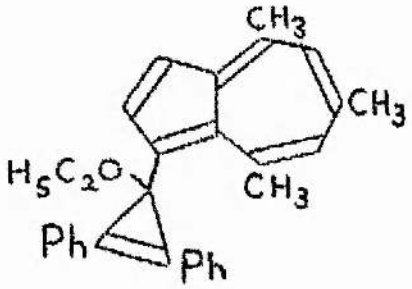
XL a) R = H, X = BF_4
b) R = CH_3, X = Cl
c) R = CH_3, X = ClO_4

When treated in boiling ethanol with triethylamine, XLc gave the azulene XLII, and not a calicene such as XLI.[119]



XLI

XLII



The cyclopenta[d]-2,3-oxazines appear to be less reactive towards electrophiles than are the corresponding 2H-cyclopenta-[d]pyridazines. This decreased reactivity implies decreased electron density at the C-5(7) positions, associated with decreased annular delocalisation of the π-electrons in the five-membered ring. On the evidence of the reactions investigated, the cyclopenta[d]-2,3-oxazines resemble azulenes less than do the 2H-cyclopenta[d]pyridazines. 1,4-Diphenylcyclopenta[d]-2,3-oxazine[66] (XXVb) was not formylated by orthoformic ester/boron trifluoride etherate under conditions which led to seemingly instantaneous formylation of the 2H-cyclopenta[d]-pyridazines XXIVa and e.

The salts of the cyclopenta[d]-2,3-oxazines XXVa and b evidently dissociate readily. The N.M.R. spectrum of XXVb in trifluoracetic acid did not show the methylene singlet expected as the result of protonation on the five-membered ring. Although the possibility of protonation on nitrogen cannot be discounted,

it seems likely that XXVb is protonated on carbon but rapidly exchanges protons with trifluoracetic acid, in common with the nitro-2H-cyclopenta[d]pyridazines XXXIVa and b. A perchlorate of XXVb was isolated as yellow needles, but appeared to dissociate without the presence of a high concentration of perchloric acid. On exposure to the atmosphere, it rapidly lost perchloric acid and reverted to orange crystals of XXVb. This difficulty in the isolation of the perchlorate complicated the reaction of diphenylcyclopropenone with the oxazinium cation derived from XXVb. Condensation of XXVb with diphenylcyclopropenone was found to occur in acetic anhydride containing a large excess of trichloracetic acid, and a product was isolated as the perchlorate salt by addition of perchloric acid. The yield isolated was low (18%), but the product was seen to decompose to a considerable extent while in contact with the reaction mixture in which excess perchloric acid was present. 1,4-Dimethylcyclopenta[d]-2,3-oxazine (XXVa) reacted under the same conditions as XXVb, but the product decomposed so readily on addition of perchloric acid, that only tarry material could be isolated.

Both 1,4-dimethyl- and 1,4-diphenylcyclopenta[d]-2,3-oxazine were smoothly monobrominated on the five-membered ring by the action of one molar equivalent of N-bromosuccinimide,

and no mixtures with dibrominated compounds were obtained. The position of electrophilic substitution in the cyclopenta[d]-2,3-oxazines will be discussed below.

5. N.M.R. SPECTRA OF THE PSEUDOAZULENES.

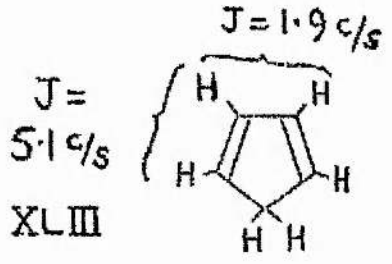
A well-recognized property of aromatic rings is the delocalisation of their π-electrons, achieved through the presence of overlapping atomic p-orbitals which form a continuous planar molecular orbital in which the π-electrons are free to move. Under the influence of an applied magnetic field, the π-electrons circulate around the ring, thereby inducing a secondary magnetic field in a direction such that it opposes the applied field within the ring, and reinforces it outside the ring. A proton in these two locations thus experiences respectively a shielding, and deshielding effect, relative to a proton placed in similar environments in which no ring-current exists. The N.M.R. spectrum of a compound having protons affected in this way will show the signals of shielded protons at higher chemical shift, and those of deshielded protons at lower chemical shift, than would be expected from the shifts of analogous open-chain polyolefins, in which no ring-current is possible. This example of diamagnetic anisotropy is characteristic of aromatic compounds, and allows the definition of an aromatic compound as one which

will sustain an induced ring current.[120] It has been suggested that the magnitude of the ring-current reflects the degree of delocalisation of the π-electrons, and is thus a measure of aromatic character.

Elvidge and Jackman[120] used the comparison of ring-currents to estimate the degree of aromatic character in the 2-pyridones, and concluded that such compounds have ca. 35% of the aromaticity of benzene. This result was obtained by comparison of the chemical shift of protons attached to the 2-pyridone ring with the shift encountered in benzene (in which π-electron delocalisation is complete), and with the shifts calculated for fully-localised model structures. The usefulness of this method depends on the judicious choice of shifts to represent the fully-aromatic and non-aromatic ends of the chemical shift scale. In the case of six-membered monocyclic systems, choice of the completely-delocalised compound for the aromatic end of the scale presents no difficulty; benzene is perfectly suitable. On the other hand, calculation of the shifts attributable to the protons of the completely-localised model structures requires the use of chemical shifts of comparable protons in known compounds, the choice of which is generally controversial.[121,122] Furthermore, an objection to the validity of the method on theoretical grounds has been raised by Musher.[123]

The extension of the chemical shift method of comparison of ring-currents to fused aromatic ring systems introduces further complications, for the protons attached to one ring will be affected to some extent by the circulation of π-electrons in a neighbouring ring, and suitable corrections must be applied to the observed chemical shifts. An important practical consideration is that all N.M.R. spectra should be recorded using the same solvent and concentration of solute, since these factors affect the chemical shift. Low solubility of the compounds under investigation may therefore preclude the use of the chemical shift method.

An alternative method, more appropriate to the estimation of aromatic character in systems incorporating cyclopentadiene rings, is based on the analysis of the N.M.R. spectrum of cyclopentadiene carried out by Manatt and Elleman.[51] These workers calculated that the vicinal coupling constants for the vinyl protons have the figures shown in figure XLIII. Since cyclopentadiene is fully localised, these figures represent the extreme values associated with a non-aromatic five-membered ring system. In compounds which are known from dipole moment measurements or other data to have a degree of delocalisation, the values of



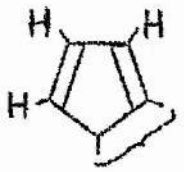
XLIII

the corresponding coupling constants are found to converge; it is reasonable to expect that in a fully-delocalised system this convergence is carried to a point where both coupling constants have the same value, which is the average of the values shown in figure XLIII (i.e. 3.5 c/s). This assumption cannot, of course, be tested by reference to the cyclopentadienide anion which, for reasons of symmetry, must be fully delocalised, because this very symmetry requires that the N.M.R. spectrum shall consist of only one peak. The 1,2-dicarbomethoxycyclopentadienide anion has an N.M.R. spectrum showing the three ring-protons as an AB_2 system with J=3.5 c/s.[50]

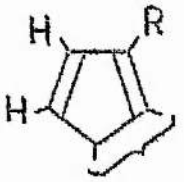
The similarity of the vicinal coupling constants in the fulvenes[48-50] to those of cyclopentadiene supports the chemical evidence that fulvenes resemble olefins rather than delocalised systems (see Introduction, page 9). In more general terms, there is a relationship between π-bond order and size of vicinal proton coupling constants in five-membered ring compounds which possess some aromatic character. A similar correlation between bond order and vicinal proton coupling constants has been reported for a series of six-membered ring aromatic compounds.[124] Smith et al.[125] produced an approximately linear plot of π-bond order against vicinal coupling constant for a variety of five-membered rings, including

fulvenes, cyclopentadienylides and fused-ring systems such as azulene and the pentalene dianion. The bond orders for the various compounds were obtained from molecular orbital calculations.

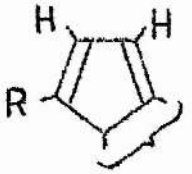
It is considered that the above results justify the qualitative comparison of the extent of delocalisation in the 2-substituted cyclopenta[d]pyridazines (XXIV) and the cyclopenta[d]-2,3-oxazines (XXV) on the basis of the vicinal coupling constants of the protons on the five-membered ring. Determination of the coupling constants does not call for complicated computation, since the unsubstituted compounds have only three adjacent protons (XLIV), and the alternatives for the monosubstituted compounds, only two protons (XLV, XLVI).



XLIV



XLV



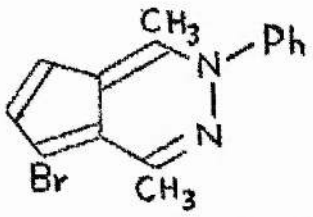
XLVI

As previously mentioned, chemical evidence leads to the suggestion that there is less delocalisation of the π-electrons in the five-membered ring of the cyclopenta[d]-2,3-oxazines than in the 2-substituted cyclopenta[d]pyridazines. This should be further demonstrated by the vicinal coupling constant

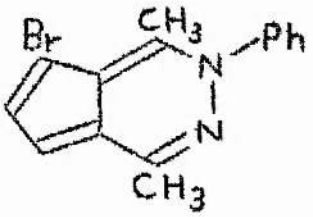
(J_{vic}) for the protons at positions 6 and 7 (see formula XXV, page 55) in the oxazines, which would be larger than J_{vic} for the corresponding protons in comparable pyridazines. J_{vic} for the oxazine protons at positions 5 and 6 would then be smaller than J_{vic} for the corresponding pyridazine protons. In the case of cyclopenta[d]-2,3-oxazines monosubstituted on the five-membered ring, the existence of an appreciable difference between $J_{5,6}$ and $J_{6,7}$ would enable the position of monosubstitution to be determined.

The N.M.R. spectrum of 1,4-dimethyl-2H-cyclopenta[d]-pyridazine (XXIVa) in acetone shows an AB_2 system with J = 3.6 c/s for the protons at positions 5,6 and 7. Such a spectrum either could be due to a fully-delocalised system, or could represent the time-averaged spectrum of a mixture of rapidly-interchanging prototropic forms in which the bonds are completely fixed. The N-phenylated cyclopenta[d]pyridazine XXIVd was therefore prepared, since in this compound the possibility of prototropy is eliminated. The 5-H, 6-H and 7-H signals in its N.M.R. spectrum (CCl_4 solution) were found to form a multiplet which was insufficiently resolved for coupling constants to be measured. It was thus necessary to prepare a monosubstituted derivative of XXIVd in order to obtain a coupling constant which could yield meaningful

information on the 2-substituted cyclopenta[d]pynidazine system. Reaction of XXIVd with one molar equivalent of N-bromosuccinimide gave a mixture of three products, of which one could be separated by column chromatography. The N.M.R. spectrum of this compound identified it as the 5,7-dibromo derivative. Although the remaining compounds could not be separated, elemental analysis of the mixture showed them to be monobrominated, and the N.M.R. spectrum of the mixture showed separate signals attributable to 5-bromo- (XLVII) and 7-bromo-2-phenylcyclopenta[d]pyridazine (XLVIII). The five-membered ring protons appeared as two AB systems with J = 4.4 c/s and 3.7 c/s. The former was assigned to compound XLVII, the latter to compound XLVIII. Integration of the remaining signals supported this assignment.



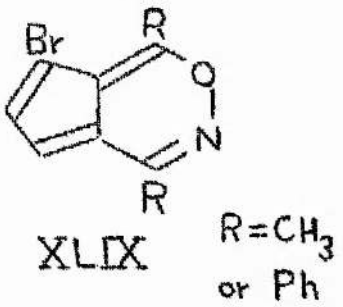
XLVII



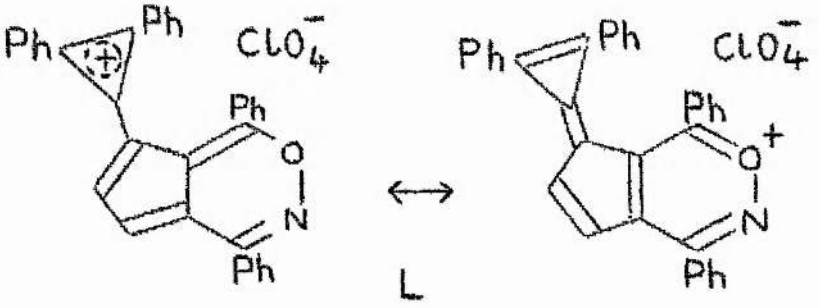
XLVIII

The N.M.R. spectrum of 1,4-dimethylcyclopenta[d]-2,3-oxazine (XXVa) in carbon tetrachloride showed a well-resolved ABX system for the five-membered ring protons, although the resolution in acetone was found to be poor. The following

coupling constants were found: $J_{5,6}$ = 2.9 c/s, $J_{6,7}$ = 4.4 c/s. The N.M.R. spectrum of the monobrominated derivative of XXVa showed an AB system with J = 3.1 c/s. It is therefore concluded that electrophilic monosubstitution in the cyclopenta[d]-2,3-oxazines takes place at C-7, which implies that the correct formulae for the products from the monobromination of XXVa and b, and the reaction of XXVb with diphenylcyclopropenone, are XLIX and L.

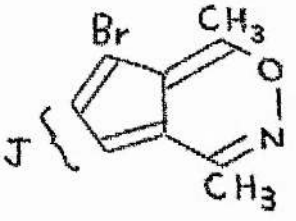


XLIX R=CH$_3$ or Ph

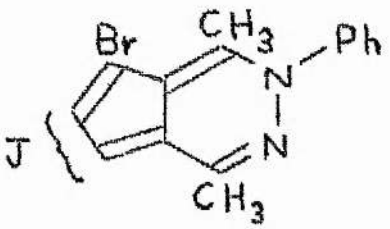


L

An indication of the relative delocalisation of the 2-substituted cyclopenta[d]pyridazine and cyclopenta[d]-2,3-oxazine systems is afforded by comparison of J_{vic} for the formal single bonds in the 7-brominated derivatives:



J = 3·1 c/s



J = 3·7 c/s

The larger value for the pyridazine shows that there is more double-bond character in the formal single bond than is present in the corresponding bond of the oxazine. No quantitative

conclusions can be drawn, however, since these heterocyclic structures bear insufficient resemblance to cyclopentadiene. Moreover, the observed coupling constant is larger than the figure of 3.5 c/s estimated for a fully-delocalised cyclopentadiene structure.

Analysis of the N.M.R. spectrum of XXVa (CCl_4 solution) reveals that the 5-H signal is approximately 0.2 τ up-field of the 7-H signal. This is surprising in view of the evidence for preferential electrophilic attack at C-7.

The chemical shift of an aromatic proton is affected by several factors,[126] probably the most important of which are the anisotropic ring-current effect, and the shielding influence of the local charge density at the carbon to which the proton is bonded. In XXVa all the ring-protons must be affected to an equal extent by the ring-current, so it might be supposed that the observed shifts of these protons reflect the relative concentration of charge on C-5, C-6 and C-7. By this reasoning, the proton most readily substituted by electrophiles would be expected to show the highest chemical shift. The presence of a heteroatom in an aromatic ring causes polarisation of the σ-bonds,[126] and the resulting electric field contributes to the effective field at any particular proton, and hence affects its chemical shift. It appears likely that this effect is

responsible for the unexpected shift sequence of the ring-protons of XXVa. Alternatively, the formation of an excited transition-state during the process of electrophilic substitution may be accompanied by a redistribution of charge so as to favour substitution at C-7. Such a possibility would be not incompatible with the observed N.M.R. spectrum of XXVa, which is only associated with the ground state of the molecule.

EXPERIMENTAL

1. Materials and Procedures.

Light petroleum had boiling point 60-80° unless otherwise stated. Solvents were dried as follows:

Acetonitrile was distilled from phosphorus pentoxide.

Chloroform was passed through a column of activated alumina, then distilled.

Ether was part-dried over calcium chloride, then refluxed over sodium and distilled.

Ethanol was refluxed with sodium and diethyl succinate, then distilled.

Methanol was refluxed with sodium and dimethyl phthalate, then distilled.

Tetrahydrofuran was refluxed over sodium, then distilled. If not used immediately, it was stored in a desiccator.

Cyclopentadiene was prepared by thermal cracking of the dimer in a flask fitted with platinum gauze in the side-arm. The cyclopentadiene monomer was stored at *ca.* -25° and used within 24 hr. of preparation.

Column chromatography was carried out on Spence Type H alumina (100/200 mesh), or on Whatman SG 31 silica.

Silica used for thin layer chromatography was Kieselgel G (E. Merck or Macherey, Nagel & Co.).

Infra-red spectra were run on Grubb-Parsons Type G.S.-2A and Perkin-Elmer 257 instruments. Perkin-Elmer 127 and 227 instruments were also used for semi-quantitative and comparative purposes.

Ultra-violet and visible spectra were run on a Unicam SP 800 spectrophotometer.

N.M.R. spectra were run at ca. 34° on a Perkin-Elmer R10 spectrometer (60 Mc./sec.).

Melting points are uncorrected.

2. Preparation of Diacylcyclopentadienes.

2-Benzoyl-6-phenyl-6-hydroxyfulvene ("dibenzoylcyclopentadiene").

Dibenzoylcyclopentadiene was prepared by the method of Linn and Sharkey.[66] All stages of the synthesis were carried out under nitrogen.

A solution of phenyl lithium was prepared in the usual manner from bromobenzene (62.8g.) and lithium (5.6g.) in ether (300 ml.). To this solution cyclopentadiene (26.4g.) was slowly added. An immediate and mildly exothermic reaction produced a white suspension of lithium cyclopentadienide. The suspension was cooled with ice and stirred vigorously, and benzoyl chloride (56.4g.) was added dropwise. Stirring was continued for 0.5 hr. after the addition

was complete, and aqueous acetic acid was added. The ether layer was separated, and combined with ether washings of the aqueous layer. After drying (Na_2SO_4), the ether and as much as possible of the acetic acid and unreacted benzoyl chloride were removed by evaporation under reduced pressure. A tarry residue remained, from which the crude product began to crystallise. The whole of the residue was recrystallised from light petroleum (b.p. 40-60°) (charcoal) to give dibenzoylcyclopentadiene (19.4g., 35.4%) as yellow crystals, m.p. 100-101° (lit.[66] 102-103°).

2-Acetyl-6-methyl-6-hydroxyfulvene ("diacetylcyclopentadiene"). This preparation was essentially identical to that described by Riemschneider and Krüger,[67] and also by Hafner, Schultz and Wagner.[63]

A solution of sodium cyclopentadienide was made by the addition, with stirring, of cyclopentadiene (25.6g.) to cooled tetrahydrofuran (THF) (110 ml.) containing granulated sodium (9.0g.), under nitrogen. The stirred solution was cooled in ice, and acetyl chloride (30.7g.) in THF (40 ml.) was added dropwise, after which the reaction mixture was stirred for a further 2 hr. The mixture was poured into water (2000 ml.) and extracted three times with ether. The combined ether extracts were washed with water, dried (Na_2SO_4) and evaporated to give a dark, viscous residue which was

distilled under reduced pressure (water pump). A yellow distillate, consisting of a mixture of diacetylcyclopentadiene and 6-methyl-6-acetoxyfulvene, was collected at 95-122°. The distillate was dissolved in ether (120 ml.) and thoroughly extracted with 1N sodium hydroxide (130 ml.). The aqueous solution was washed with ether and acidified with hydrochloric acid. The resulting emulsion was extracted with ether, and the ether solution was dried (Na_2SO_4) and evaporated to give a yellow oil (4.5g., 15%), which partially crystallised to a yellow crystalline mass of diacetylcyclopentadiene (3.2g.), slightly contaminated with a brown impurity.

2-Pivaloyl-6-t-butyl-6-hydroxyfulvene ("dipivaloylcyclopentadiene")

Cyclopentadiene (13.2g.) was added to a solution of phenyl lithium, prepared from bromobenzene (31.4g.) and lithium (2.8g.), in dry ether (300 ml.). A nitrogen atmosphere was maintained above the reaction mixture. The resulting suspension of lithium cyclopentadienide was cooled in ice and stirred vigorously as pivaloyl chloride (24.1g.) was added over a period of 45 min. After the addition was complete, the mixture was stirred for a further 30 min. and as much as possible of the unreacted lithium was removed. Ethanol was then added to dispose of any remaining lithium fragments, and the mixture was acidified with acetic acid and washed with water (1000 ml.). After drying (Na_2SO_4), the ether and other

volatiles were removed by evaporation under reduced pressure, leaving a dark brown oily residue. This was dissolved in light petroleum and partially purified by passage through a column of alumina, followed by boiling with decolourising charcoal. On evaporation of solvent, there remained a yellow crystalline mass of dipivaloylcyclopentadiene (9.2g., 39.3%), contaminated with a brown impurity. Three recrystallisations from methanol gave an analytical sample, yellow prisms, m.p. 90-91°. $C_{15}H_{22}O_2$ requires C 76.90, H 9.89%. Found: C 77.03%, H 9.98%.

3. Nitration of Dibenzoylcyclopentadiene.

Conc. nitric acid in acetic acid. Dibenzoylcyclopentadiene (0.5g.) was dissolved in glacial acetic (25 ml.), and conc. nitric acid (0.15 ml., approx. 1 molar equivalent), dissolved in glacial acetic acid (1 ml.) was added. The mixture was left at room temperature for 24 hr., after which addition of water precipitated a yellow solid. The crude solid was identified by its melting point (95-96°) as unreacted dibenzoylcyclopentadiene.

Nitric acid/acetic anhydride. Dibenzoylcyclopentadiene (0.5g.) was dissolved in acetic anhydride (30 ml.). The solution was cooled to 2°, and maintained at this temperature while conc. nitric acid (0.30 ml.) in acetic anhydride (1 ml.) was added dropwise,

with stirring. After 2 min., a solid precipitated, and after a further 8 min. the reaction mixture began to darken. At this point the solid was filtered off, washed with water, and dried in a vacuum desiccator over potassium hydroxide. Yield: 2-benzoyl-4-nitro-6-phenyl-6-hydroxyfulvene (0.42g., 72.2%) as a yellow granular solid. An analytical sample, yellow prisms, m.p. 236-237° after darkening, (lit.[72] 237-238° decomp.), was obtained by recrystallisation from acetone. Calculated for $C_{19}H_{13}NO_4$: C 71.47%, H 4.10%, N 4.39%. Found: C 71.57%, H 3.98%, N 4.41%.

4. Nitration of Diacetylcyclopentadiene.

Nitric acid/acetic anhydride. Conc. nitric acid (0.15 ml.) in acetic anhydride (1 ml.) was added to a solution of diacetylcyclopentadiene (0.5g.) in acetic anhydride (0.5 ml.), cooled to -10°. The mixture was warmed to room temperature, when the colour began to darken rapidly, and a product crystallised. Filtration and washing with water gave 2-acetyl-4-nitro-6-methyl-6-hydroxyfulvene (68 mg., 10.4%) as almost colourless needles. A sample recrystallised from ethyl acetate had melting point (193° decomp., lit.[95] 195° decomp.), N.M.R. and I.R. spectra identical to those of an authentic sample of 2-acetyl-4-nitro-6-methyl-6-hydroxyfulvene prepared from nitromalondialdehyde and hexan-2,5-dione.

5. Bromination of Dibenzoylcyclopentadiene.

Bromine in ethanol. Dibenzoylcyclopentadiene (0.5g.) was dissolved in ethanol (40 ml.). The solution was swirled by hand as bromine (0.29g.) in ethanol (5 ml.) was slowly added. The solution darkened soon after the addition was complete, and crystallisation started after 10 min. The mixture was kept at 0° until no further crystallisation occurred, and the crystalline precipitate was filtered off. It consisted of two compounds, one yellow, the other orange. These were separated by washing the mixed crystals with light petroleum (b.p. 40-60°), in which the orange compound was virtually insoluble; evaporation of the light petroleum left almost pure 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene (0.34g., 52.7%). Recrystallisation from ethanol gave yellow needles, m.p. 147-148° decomp. $C_{19}H_{13}BrO_2$ requires C 64.62%, H 3.71%, Br 22.62%. Found: C 64.51%, H 3.86%, Br 22.77%

The orange compound (0.15g., 16.1%) was recrystallised from light petroleum as orange blades, m.p. 146-147° decomp. Elemental analysis showed it to be a dibenzoyltribromocyclopentadiene: $C_{19}H_{11}Br_3O_2$ requires C 44.66%, H 2.17%. Found: C 44.67%, H 2.17%.

N-Bromosuccinimide. Dibenzoylcyclopentadiene (0.5g.) was refluxed with N-bromosuccinimide (0.97g., 3 molar equivalents) in carbon tetrachloride (10 ml.) for 2.5 hr. Filtration of the

resulting succinimide and evaporation of solvent left a red-brown oil. Thin layer chromatography (TLC) with chloroform as solvent showed the presence of 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene and of the dibenzoyltribromocyclopentadiene obtained with bromine as described above. No other products were present.

N-Bromosuccinimide: attempted dibromination. Dibenzoylcyclopentadiene (0.2g.) was refluxed for 45 min. with N-bromosuccinimide (0.260g., 2 molar equivalents). Examination of the reaction mixture by TLC ($CHCl_3$ solvent) showed the presence of 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene and dibenzoyltribromocyclopentadiene only.

Bromine in acid solution. Bromine (0.29g.) in acetic acid (5 ml.) was added dropwise at room temperature to a stirred solution of dibenzoylcyclopentadiene (0.5g.) in trifluoracetic acid (5 ml.). Copious fumes of hydrogen bromide were evolved. After 5 min. the mixture was diluted with ether (50 ml.) and washed with water (3 x 50 ml.), and the ether layer was dried (Na_2SO_4). TLC ($CHCl_3$ solvent) showed the presence of 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene, and of another compound, identified as its keto tautomer (see Discussion section). Partial separation of the latter was achieved by chromatography on an alumina column. The first yellow band, eluted with benzene, contained 2-benzoyl-4-

bromo-6-phenyl-6-hydroxyfulvene. A second yellow band was eluted with 1:1 ether/benzene and contained the keto tautomer, but this gradually enolised during the course of the work-up.

6. Bromination of Diacetylcyclopentadiene.

Bromine in ethanol. Diacetylcyclopentadiene (0.55g.) was dissolved in ethanol (5 ml.) and bromine (0.59g.) in ethanol (4 ml.) was added dropwise at room temperature. Crystallisation soon started, and the mixture was kept at -15° until crystallisation was complete. Filtration yielded yellow needles (0.60g.). These were shown by N.M.R. to be a mixture of 2-acetyl-4-bromo-6-methyl-6-hydroxyfulvene and 2-acetyl-3,4,5-tribromo-6-methyl-6-hydroxyfulvene. Elemental analysis indicated that the ratio of monobrominated to tribrominated product was 3.8:1, corresponding to a 49.3% yield of the former and a 13.1% yield of the latter. The monobrominated compound was separated by column chromatography on silica (eluted with ethyl acetate). Recrystallisation from light petroleum (b.p. 40-60°) gave yellow needles, m.p. 112-113°. $C_9H_9BrO_2$ requires C 47.19%, H 3.96%. Found: C 46.48%, H 3.85%.

The diacetyltribromocyclopentadiene could not be obtained pure from this reaction, and an analytical sample was obtained from the product of bromination of 2-acetyl-4-bromo-6-methyl-6-hydroxyfulvene (see below).

Reaction of diacetylcyclopentadienide anion with bromine in ethanol. A solution of diacetylcyclopentadienide anion was prepared by dissolving potassium hydroxide (0.21g.) and diacetylcyclopentadiene (0.55g.) in ethanol (10 ml.). The solution was stirred rapidly and bromine (0.59g.) in ethanol (4 ml.) was added over 8 min. The reaction mixture was cooled in ice-water for 0.5 hr., during which time the product crystallised. The precipitate, consisting of the product and potassium bromide, was filtered, washed with water and dried in a vacuum desiccator to give yellow needles (0.47g.). TLC examination of the filtrate showed that only 2-acetyl-4-bromo-6-methyl-6-hydroxyfulvene and 2-acetyl-3,4,5-tribromo-6-methyl-6-hydroxyfulvene were present; N.M.R. examination of the crystalline product showed that it consisted of a mixture of the same two compounds.

Attempted dibromination and tetrabromination with N-bromosuccinimide. Diacetylcyclopentadiene (0.20g.) in carbon tetrachloride (10 ml.) was refluxed with N-bromosuccinimide (0.475g., 2 molar equivalents) for 70 min. TLC (chloroform and benzene solvents) showed that the only products present in the filtered reaction mixture were 2-acetyl-4-bromo-6-methyl-6-hydroxyfulvene and 2-acetyl-3,4,5-tribromo-6-methyl-6-hydroxyfulvene.

In another experiment, diacetylcyclopentadiene (0.20g.) in carbon tetrachloride (10 ml.) was refluxed with N-bromosuccinimide (0.95g., 4 molar equivalents). After 2 hr., no further reaction appeared to be taking place, and a considerable proportion of the N-bromosuccinimide remained. The reaction mixture was filtered and examined by TLC. Again, 2-acetyl-4-bromo-6-methyl-6-hydroxyfulvene and 2-acetyl-3,4,5-tribromo-6-methyl-6-hydroxyfulvene were the only products present.

7. Bromination of Dipivaloylcyclopentadiene.

Tribromination with N-bromosuccinimide. Dipivaloylcyclopentadiene (0.5g.) and N-bromosuccinimide (1.14g., 3 molar equivalents) were refluxed in carbon tetrachloride (15 ml.) for 1 hr. After cooling and filtration of the succinimide, the solvent was evaporated to leave a viscous brown oil which slowly crystallised. This was recrystallised from a small quantity of methanol to give yellow prisms, 0.29g. Cooling the mother liquor to -25° gave an additional 0.12g. The N.M.R. spectrum of the product showed it to consist of a mixture of 2-pivaloyl-3,4,5-tribromo-6-t-butyl-6-hydroxyfulvene and 2-pivaloyl-4-bromo-6-t-butyl-6-hydroxyfulvene in the approximate ratio 2.7:1. Further recrystallisation from methanol gave a mixture of yellow and almost colourless prisms. Analysis of the almost colourless material showed it to be the

tribrominated compound. $C_{15}H_{19}Br_3O_2$ requires C 38.25%, H 4.06%. Found: C 38.65%, H 4.06%

8. Bromination of 2-Acetyl-4-bromo-6-methyl-6-hydroxyfulvene.

Bromine in ethanol. 2-Acetyl-4-bromo-6-methyl-6-hydroxyfulvene (0.1g.) was mixed with ethanol (5 ml.) and ether was added until the solid dissolved. Bromine (0.15g., 2 molar equivalents) was added at room temperature. The mixture was left to stand for 2 hr. during which time the product crystallised. Filtration gave 2-acetyl-3,4,5-tribromo-6-methyl-6-hydroxyfulvene (0.055g., 32.5%). This was recrystallised from light petroleum (b.p. 40-60°) to give yellow needles, m.p. 167°. $C_9H_7Br_3O_2$ requires C 27.94%, H 1.83%. Found: C 28.16%, H 2.10%.

9. Azo-coupling of Dibenzoylcyclopentadienide Anion.

Benzene diazonium chloride. Aniline (0.61g.) was mixed with conc. hydrochloric acid (1.7 ml.) and water (0.5 ml.); more water was added until the precipitate of aniline hydrochloride almost dissolved. The solution was cooled in ice as sodium nitrite (0.48g.) in water (3 ml.) was added. Ice cooling was continued and the diazonium salt solution was agitated as a cold solution of potassium dibenzoylcyclopentadienide (1.2g.) in methanol (15 ml.) was added dropwise. The resulting deep red precipitate (1.16g.)

was filtered, washed with water and dried (vacuum desiccator). It was then dissolved in benzene/light petroleum and chromatographed on a silica column. The first band, eluted with 1:1 light petroleum/benzene, gave dibenzoylcyclopentadiene. After a second (pink) band, the azo-coupled product was obtained as a red band, eluted with benzene. Evaporation of the solvent left 2-benzoyl-5-phenylazo-6-phenyl-6-hydroxyfulvene (0.27g., 18.5%) as purple-brown prisms, m.p. 170°. $C_{25}H_{18}N_2O_2$ requires C 79.34%, H 4.80%. Found: C 78.68%, H 5.23%.

In this preparation, and in the azo-coupling reactions that follow, the bands eluted before the product contained negligible amounts of material.

10. Azo-coupling of Diacetylcyclopentadienide Anion.

Benzene diazonium chloride. Aniline (0.30g.) was mixed with conc. hydrochloric acid (0.6 ml.) and water (1 ml.). The aniline hydrochloride thus formed was cooled well in ice and stirred vigorously, and an ice-cold solution of sodium nitrite (0.25g.) in water (3 ml.) was added, followed after 5 min. by a cooled solution of sodium diacetylcyclopentadienide, prepared from diacetylcyclopentadiene (0.5g.) and potassium hydroxide (0.19g.) in water (10 ml.). The brown reaction mixture was diluted to 25 ml. with water and extracted with ether (25 ml.). The ether

extract was washed with water, dried (Na_2SO_4), then evaporated. The residue was taken up in benzene and applied to an alumina column. The product was eluted with 1:4 ether/benzene as the fourth band (red), after elution of two yellow bands followed by one purple band. Evaporation of solvent left brown needles (70 mg., 8.3%), which were recrystallised from ether to give 2-acetyl-5-phenylazo-6-methyl-6-hydroxyfulvene, m.p. 125.5-126°. $C_{15}H_{14}N_2O_2$ requires C 70.87%, H 5.55%. Found: C 70.52%, H 5.32%.

p-Bromobenzene diazonium chloride. p-Bromoaniline (1.15g.) was dissolved in conc. hydrochloric acid (1.1 ml.) diluted with water (10 ml.). The solution was cooled in ice and sodium nitrite (0.46g.) in water (5 ml.) was slowly added, with stirring. The temperature was kept near 0° by addition of solid carbon dioxide. The diazonium salt solution was stirred and kept at 0-3° during the addition of a solution of sodium diacetylcyclopentadienide made from diacetylcyclopentadiene (1.0g.) and sodium metal (0.154g.) dissolved in methanol (10 ml.). After the addition was complete, stirring was continued for 10 min. and the reaction mixture was poured into water (50 ml.). The product was extracted with ether (8 x 50 ml.), the combined ether extracts were dried (Na_2SO_4) and evaporated. The residue was dissolved in benzene and applied to an alumina column. After elution of three yellow or orange bands,

a fourth (red) band was eluted with benzene. Evaporation gave 2-acetyl-5-(p-bromophenyl)azo-6-methyl-6-hydroxyfulvene (0.85g., 38.3%) as red needles. An analytical sample, m.p. 148-150°, was prepared by recrystallisation from ether. $C_{15}H_{13}BrN_2O_2$ requires C 54.09%, H 3.93%, N 8.41%. Found: C 53.62%, H 3.89%, N 8.28%. This compound was also prepared by the reaction of diacetylcyclopentadienide anion with p-bromobenzene diazonium fluoroborate in acetonitrile.

2,4-Dibromobenzene diazonium chloride. Conc. hydrochloric acid (0.6 ml.) was diluted with water (10 ml.) and mixed with 2,4-dibromoaniline (0.83g.). The mixture was warmed briefly to form the hydrochloride. It was then cooled to 0°, and a solution of sodium nitrite (0.21g.) in water (5 ml.) was slowly added. The cold diazonium salt solution was stirred vigorously and a solution of sodium diacetylcyclopentadienide, prepared from diacetylcyclopentadiene (0.5g.) and sodium metal (0.076g.), in methanol (10 ml.), was added dropwise. The temperature of the reaction mixture was maintained at 0-3° throughout the formation and coupling of the diazonium salt. After a further 10 min. the deep red-brown reaction mixture was poured into water (100 ml.) and extracted with benzene (2 x 50 ml.). The combined benzene extracts were washed with water and dried (Na_2SO_4). After

evaporation of solvent, the residue was chromatographed on an alumina column. Three orange bands were eluted, followed by a red band (eluted with benzene), which, on evaporation, yielded 2-acetyl-5-(2,4-dibromophenyl)azo-6-methyl-6-hydroxyfulvene (0.38g., 27.6%). Recrystallisation from ether gave red needles, m.p. 178-178.5° decomp. $C_{15}H_{12}Br_2N_2O_2$ requires C 43.73%, H 2.94%, N 6.80%. Found: C 43.44%, H 3.00%, N 6.65%.

Reaction of diacetylcyclopentadiene with p-bromobenzene diazonium fluoroborate. p-Bromobenzene diazonium fluoroborate (1.8g.), made from p-bromoaniline, later found to be contaminated with 2,4-dibromoaniline, was dissolved in acetonitrile (10 ml., freshly distilled from P_2O_5) and added to a stirred, ice-cold solution of diacetylcyclopentadiene (1.0g.) in dry acetonitrile (10 ml.). Stirring and cooling were continued for 2.25 hr. The dark brown solution was diluted with water (20 ml.) and extracted with ether (2 x 50 ml.). The combined ether extracts were dried (Na_2SO_4) and evaporated to give a residue which was dissolved in benzene and chromatographed on an alumina column. Three yellow bands were eluted, followed by a red band (eluted with benzene), which yielded a purple-brown crystalline product (0.12g.). N.M.R. showed that this product was a mixture of 2-acetyl-5-(2,4-dibromophenyl) azo-6-methyl-6-hydroxyfulvene and 2-acetyl-5-(p-bromo-

phenyl)azo-6-methyl-6-hydroxyfulvene in the approximate ratio 5:1. Mass spectroscopy confirmed the presence of the dibrominated compound. An analytical sample, purple-brown needles, m.p. 163-164°, prepared by recrystallisation from ether, contained 45.60% carbon, corresponding to a mixture of 82% of the dibrominated compound and 18% of the monobrominated compound.

11. Reaction of Dibenzoylcyclopentadienide Anion with Methyl Chloroformate.

Potassium dibenzoylcyclopentadienide (0.60g.) was refluxed with methyl chloroformate (5 ml.) for 3 min. Almost immediately an orange colour appeared, which darkened to brown. The solution was diluted with chloroform (20 ml.), and the precipitate of potassium chloride was filtered off. Solvent was removed under reduced pressure to leave a brown residue, which crystallised. It was washed with a little ether to leave orange-red crystals of methyl 2-benzoyl-6-phenylfulven-6-yl carbonate (0.368g., 57.6%). Recrystallisation from carbon tetrachloride gave red prisms, m.p. 131°. $C_{21}H_{16}O_4$ requires C 75.88%, H 4.85%. Found: C 75.69%, H 4.75%.

12. Attempted Acylation of Diacylcyclopentadienes.

Formylation. A mixture of phosphorus oxychloride (12g.) and dimethyl formamide (6 ml.) was added over 0.5 hr. to a solution of dibenzoylcyclopentadiene (1.0g.) in dimethyl formamide (30 ml.) at room temperature, with stirring and exclusion of moisture. The mixture was stirred for 1 hr., then poured onto ice. When the ice had melted, it was made alkaline with 2N sodium hydroxide, and extracted with ether. Much brown ether-insoluble material separated at this stage. Evaporation of the dried (Na_2SO_4) ether solution left a residue of tarry decomposition products.

This attempted formylation was repeated at lower temperatures. At -8°, the result was the same as at room temperature, only decomposition products being obtained. In another experiment, the formylating mixture was added at $-70/-60^{\circ}$, and the reaction mixture was warmed to 0° over a period of 2 hr. and then worked up as described above. No reaction occurred at very low temperature, but above -20° the usual decomposition started. Work-up gave unreacted dibenzoylcyclopentadiene in $>50\%$ yield.

Acetylation. Sodium (0.077g.) was dissolved in methanol (10 ml.) and diacetylcyclopentadiene (0.50g.) was added. The solution was evaporated to dryness under reduced pressure and

the solid sodium diacetylcyclopentadienide was dissolved in THF (20 ml., freshly distilled from sodium). Acetyl chloride (0.27g.) was added and the solution was refluxed for 15 min., during which time it became brown. Evaporation of solvent left a brown oil which had the odour of acetyl chloride. Column chromatography on alumina gave a single yellow band, from which diacetylcyclopentadiene (0.24g.) was isolated.

13. Attempted Preparation of Ylides and their Precursors.

A. Dibenzoyldiazocyclopentadiene.

Amine-catalysed reactions with toluene-p-sulphonyl azide. Dibenzoylcyclopentadiene (2.0g.) was mixed with toluene-p-sulphonyl azide (1.44g.) and diethylamine (0.75 ml.) was added at room temperature. A strongly exothermic reaction immediately occurred, in which the reactants were decomposed. Subsequently, ether or a large excess of diethylamine were used to dilute the mixture and moderate the reaction, and a lower reaction temperature was also employed.

Dibenzoylcyclopentadiene (0.5g.) was mixed with diethylamine (5 ml.), and the flask was cooled in ice. Toluene-p-sulphonyl azide (0.4g.) dissolved in diethylamine (5 ml.) was added, and the reaction mixture was stored at ca. -15° for 5 days. Work-up of the red-brown mixture afforded no tractable

products. A small proportion of the original dibenzoylcyclopentadiene was recovered by column chromatography.

The same result was obtained when pyridine (5 ml.) was used in place of the diethylamine. In this case, however, greenish tars were produced.

Reaction of dibenzoylcyclopentadienide anion with toluene-p-sulphonyl azide. Dibenzoylcyclopentadiene (0.5g.) and potassium hydroxide (0.1g.) were dissolved in methanol (10 ml.) and the solution was refluxed for 10 min. and evaporated to dryness. The potassium salt was suspended in dry ether and toluene-p-sulphonyl azide azide (0.25g.) in a little dry ether was added. No change was observed, and the mixture was refluxed for 7.5 hr., in the course of which a brown colour developed. Addition of ether precipitated a brown amorphous solid, which was soluble in water and methanol, but virtually insoluble in ether. Its I.R. spectrum showed that it was contaminated by toluene-p-sulphonyl azide, but no absorption attributable to a diazo compound was found. A Lassaigne test was carried out on the brown solid, after the azide had been removed by thorough washing with ether. Sulphur and nitrogen were found to be present.

B. 2-Benzoyl-4-amino-6-phenyl-6-hydroxyfulvene.

Reduction with sodium dithionite ($Na_2S_2O_4$). 2-Benzoyl-4-nitro-6-phenyl-6-hydroxyfulvene (0.2g.) was dissolved with warming in water (15 ml.) containing acetone (5 ml.) and sodium hydroxide (0.05g.). Sodium dithionite (1g.) in water (10 ml.) was added. An immediate darkening to red-brown was observed and a tarry scum separated. Repeated extraction with ether produced an intensely purple ether solution which was evaporated to yield a blackish tar. TLC (chloroform solvent) and column chromatography on alumina succeeded only in separating a large number of coloured products, each in very small yield, among which a blue-green substance was prominent.

Reduction with zinc. 2-Benzoyl-4-nitro-6-phenyl-6-hydroxy-fulvene (0.2g.) was dissolved in ethanol (20 ml.) containing water (2 ml.) and a suspension of ammonium chloride (0.5g.). Finely powdered zinc (1g.) was then added to the stirred mixture. A red colour was immediately produced, which darkened to brown and ultimately to dark green. After 5 hr., the reaction mixture was filtered and diluted with water (250 ml.) to precipitate dark green flocculent material. Column chromatography on alumina separated this into a number of brownish products, plus a green-black solid (36 mg.) as the major component. This solid was, however, further resolved into two components by TLC.

Identification of the various products was not attempted, since the very low yields obtained showed that this reaction was unsuitable for the reduction of 2-benzoyl-4-nitro-6-phenyl-6-hydroxyfulvene.

C. Dibenzoylnitrosocyclopentadiene.

Nitrous Acid. Dibenzoylcyclopentadiene (1g.) was dissolved in acetone (100 ml.) and a solution of sodium nitrite (10g.) in water (50 ml.) was added. The mixture was swirled by hand as conc. hydrochloric acid (7 ml.), diluted with water to 25 ml., was added in portions. There was no evidence of reaction until about half the acid had been added, when the solution suddenly became dark red-brown. This experiment was not pursued further.

Ethyl nitrite. Ethyl nitrite gas was generated by addition of an ethanol/conc. sulphuric acid mixture to sodium nitrite in aqueous ethanol (Organic Syntheses, Collective Volume II, page 204). The gas, dried by passage through a column of calcium chloride, was passed for 0.5 hr. through a solution of sodium dibenzoylcyclopentadienide, prepared from dibenzoylcyclopentadiene (1g.) and sodium (0.1g.) in dry methanol (20 ml.). The colour of the solution darkened rapidly, first to dark green, then to dark brown. Dilution with water (500 ml.) followed by

ether extraction gave an ether solution from which nothing could be obtained except dibenzoylcyclopentadiene and brown tarry material. Acidification of the aqueous phase afforded more ether-soluble material, but column chromatography of this gave only a number of decomposition products and a little dibenzoylcyclopentadiene.

D. Pyridinium Ylides.

Reaction of 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene with pyridine. 2-benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene (0.1g.) was dissolved in pyridine (2 ml.) and heated on a water-bath at 60-70° for 1.5 hr. Samples of the reaction mixture were examined every 30 min. These showed only the gradual conversion of the dibenzoylbromocyclopentadiene to a tarry material.

Reaction of 2-acetyl-4-bromo-6-methyl-6-hydroxyfulvene with pyridine. 2-acetyl-4-bromo-6-methyl-6-hydroxyfulvene (0.2g.) was dissolved in pyridine (1 ml.) and left to stand at room temperature. The colour darkened quite rapidly, and after 2.5 hr. was deep red-brown. After 24 hr., the brown reaction mixture was examined by TLC, and only a brown decomposition product and unchanged diacetylbromocyclopentadiene were found.

E. Arsonium Ylides.

Triphenylarsonium 3,4-dibenzoylcyclopentadienylide. Triphenylarsine oxide (0.20g.) was dissolved in acetic anhydride (10 ml.) and dibenzoylcyclopentadiene (0.17g.) was added. The yellow solution was heated on a steam-bath for 1 hr., and then diluted with ether, whereupon the product crystallised (0.29g., 80.7%). Recrystallisation from ethanol gave almost colourless needles of triphenylarsonium 3,4-dibenzoylcyclopentadienylide, m.p. 233-234° decomp. $C_{37}H_{27}AsO_2$ requires C 76.83%, H 4.71%. Found: C 76.69%, H 4.41%.

Reaction of triphenylarsine oxide with diacetylcyclopentadiene. Triphenylarsine oxide (0.21g.) was dissolved in acetic anhydride (10 ml.) and diacetylcyclopentadiene (0.10g.) was added. The solution was heated on a steam-bath for 1 hr., by which time it had become dark brown. Addition of ether precipitated nothing, but a whitish emulsion was formed.

This experiment was nepeated, but the reaction mixture was left overnight at room temperature instead of being heated. There was very little change in appearance, and TLC showed that a large proportion of the diacetylcyclopentadiene was still present. The mixture was heated on a steam-bath for 10 min., cooled, and diluted with ether. As before, only an emulsion

was obtained. The ether was evaporated and the acetic anhydride was hydrolysed by addition of water and a few drops of pyridine. The aqueous solution was extracted with methylene chloride (2 x 15 ml.), the extract was dried (Na_2SO_4) and evaporated, and the residue was dissolved in a little ethanol. Addition of perchloric acid followed by ether caused precipitation of a flocculent yellow substance (0.19g.). This was filtered and washed with ether. N.M.R. showed an extremely high ratio of phenyl protons to methyl protons, suggesting that the solid was contaminated triphenylarsine oxide rather than the perchlorate salt of triphenylarsonium diacetylcyclopentadienylide.

Triphenylarsonium 3,4-dipivaloylcyclopentadienylide. Triphenyl arsine oxide (0.40g.) and dipivaloylcyclopentadiene (0.29g.) were refluxed for 2 min. in acetic anhydride (5 ml.). On cooling, crystals appeared. The brown mixture was diluted with ether (5 ml.), and light petroleum (b.p. 40-60°) was added to complete the precipitation. The colourless needles thus obtained were filtered and dried in vacuo, to give triphenylarsonium 3,4-dipivaloylcyclopentadienylide (0.405g., 60.7%). Recrystallisation from isopropanol gave a crystalline powder, m.p. 229-230°. $C_{33}H_{35}AsO_2$ requires C 73.58%, H 6.55%. Found: C 73.23%, H 6.83%.

14. Diacylcyclopentadienes: Reactions of the Hydroxyl and Carbonyl Groups.

Dimethyl sulphate. Potassium dibenzoylcyclopentadienide (0.57g.) was mixed with anhydrous methanol (5 ml.) and dimethyl sulphate (0.27g.), and refluxed for 20 min. On cooling, a mixture of orange prisms and colourless needles crystallised. The colourless crystals were dissolved out by washing with water. The remaining orange crystals were identified (m.p. and mixed m.p.) as dibenzoylcyclopentadiene.

Methanol/hydrogen chloride gas. Dibenzoylcyclopentadiene (1g.) was finely powdered and stirred with anhydrous methanol (20 ml.). Dry hydrogen chloride gas was passed through the suspension for 0.75 hr. The solid gradually dissolved and the solution darkened to brown-black. The solvent was evaporated under reduced pressure and the residue was chromatographed on an alumina column. Only unreacted dibenzoylcyclopentadiene and tars were obtained.

Condensation of dibenzoylcyclopentadiene with aniline. Dibenzoylcyclopentadiene (1.0g.) and aniline (1.0g., 4 molar equivalents) were dissolved in hot ethanol (10 ml.) and refluxed for 6 hr. On cooling, the monoanil of dibenzoylcyclopentadiene crystallised in yellow and orange modifications, but the yellow

form slowly disappeared and was replaced by the orange form. The orange crystals (0.96g., 75.3%) were filtered, washed with a little cold isopropanol, and dried under vacuum. Recrystallisation from methanol gave orange needles, m.p. 156-157°. $C_{25}H_{19}NO$ requires C 85.94%, H 5.48%, N 4.01%. Found: C 85.45%, H 5.29%, N 3.98%.

Condensation of diacetylcyclopentadiene with aniline. Diacetylcyclopentadiene (0.93g.) and aniline (1.15g., 2 molar equivalents) were refluxed in ethanol (3 ml.) for 2 hr. The solvent was removed by evaporation under reduced pressure, and the brown oil that remained was dissolved in light petroleum and applied to an alumina column. The product was contained in the first (yellow) band, eluted with 1:1 benzene/light petroleum. On evaporation of the solvent, the monoanil of diacetylcyclopentadiene crystallised as yellow needles (0.91g., 65.1%). An analytical sample, yellow needles, m.p. 68°, was prepared by recrystallisation from a little methanol. $C_{15}H_{15}NO$ requires C 79.98%, H 6.71%. Found: C 80.36%, H 6.81%.

Condensations with hydrazine: (i) diacetylcyclopentadiene. Diacetylcyclopentadiene (1.0g.) and hydrazine hydrate (99-100%, 1 ml.) were dissolved in ethanol (10 ml.) and the solution was refluxed for 1 hr. and then cooled. Water was added dropwise

until the product crystallised. Filtration and vacuum drying gave almost colourless needles of 1,4-dimethyl-2H-cyclopenta[d]-pyridazine (0.73g., 74.8%). This compound could not be crystallised without some decomposition taking place, but a sample precipitated from the reaction mixture, m.p. 170° decomp., gave satisfactory elemental analyses without further purification. $C_9H_{10}N_2$ requires C 73.92%, H 6.89%, N 19.16%. Found: C 73.98%, H 6.81%, N 18.99%.

(ii) 2-Acetyl-4-bromo-6-methyl-6-hydroxyfulvene. 2-Acetyl-4-bromo-6-methyl-6-hydroxyfulvene (0.39g.), dissolved in ethanol (10 ml.) containing hydrazine hydrate (99-100%, 0.5 ml.) was refluxed for 2 hr. The reaction mixture was filtered, and a few drops of water were added to induce crystallisation. A precipitate of colourless needles of 1,4-dimethyl-6-bromo-2H-cyclopenta[d]pyridazine (0.35g., 59.8%) was obtained. This compound decomposed easily and recrystallisation was not attempted; an analytical sample, m.p. 170-171° decomp., was taken from the initial precipitate. $C_9H_9BrN_2$ requires C 48.01%, H 4.03%, Br 35.50%, N 12.45%. Found: C 48.02%, H 4.18%, Br 35.44%, N 12.25%.

(iii) 2-Benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene. 2-Benzoyl-4-bromo-6-phenyl-6-hydroxyfulvene (0.6g.) was partly

dissolved in hot ethanol (30 ml.) and hydrazine hydrate (99-100%, 0.5 ml.) was added, whereupon the remaining solid immediately dissolved. The solution was refluxed for 1 hr., in the course of which, yellow crystals were formed. After cooling, the crystalline precipitate of 1,4-diphenyl-6-bromo-2H-cyclopenta-[d]pyridazine (0.53g., 89.0%) was filtered and washed with a little ethanol. An analytical sample was prepared by recrystallisation from acetone, as yellow prisms which gradually decomposed above 215° without melting. $C_{19}H_{13}BrN_2$ requires C 65.34%, H 3.75%, Br 22.89%, N 8.02%. Found: C 66.02%, H 3.92%, Br 22.88%, N 7.91%.

Condensation of diacetylcyclopentadiene with phenylhydrazine. Diacetylcyclopentadiene (1.0g.) and sodium hydroxide (0.27g.) were dissolved in ethanol (20 ml.). Phenylhydrazine hydrochloride (0.96g.) was added, and the mixture was refluxed for 0.5 hr. The brown solution containing a precipitate of sodium chloride was poured into water (100 ml.) and extracted with ether (2 x 50 ml.). The combined ether extracts were washed with water and dried (Na_2SO_4). Evaporation of the solvent yielded a viscous brown oil that did not crystallise. This was dissolved in benzene and applied to an alumina column. The first (yellow) band, eluted with benzene, gave 1,4-dimethyl-2-phenyl-cyclopenta[d]pyridazine (1.27g., 85.6%) as a yellow oil,

which eventually crystallised. Recrystallisation from ethanol at low temperature gave yellow platelets, m.p. 70-71°. $C_{15}H_{14}N_2$ requires C 81.06%, H 6.35%. Found: C 80.90%, H 6.49%.

Condensation of diacetylcyclopentadiene with hydroxylamine. Diacetylcyclopentadiene (1.0g.), hydroxylamine hydrochloride (1.0g.) and potassium hydroxide (0.8g.) were refluxed in ethanol (15 ml.) for 2.5 hr. (in subsequent preparations, 1 hr. was found to be sufficient). A white precipitate of potassium chloride was formed. The mixture was diluted with water (150 ml.) and extracted with ether (3 x 20 ml.), and the combined ether extracts were washed with water and dried (Na_2SO_4). Evaporation of the ether left crude 1,4-dimethyl-cyclopenta[d]-2,3-oxazine (0.94g.) as a golden-yellow oil. This was purified by distillation at 0.2 mm. (external temperature 60-65°). The distillate was a yellow oil, which crystallised to yellow prisms, m.p. 24-25°. C_9H_9NO requires C 73.43%, H 6.16%, N 9.52%. Found: C 73.23%, H 6.37%, N 9.45%.

15. Bromination of 2H- and 2-Phenyl-cyclopenta[d]pyridazines.

A. 1,4-Diphenyl-2H-cyclopenta[d]pyridazine.[66]

Bromine in ethanol. Bromine (0.29g., 1 molar equivalent) in ethanol (2 ml.) was added to 1,4-diphenyl-2H-cyclopenta[d]-pyridazine (0.5g.), dissolved in ethanol (50 ml.). After 0.5

min. the mixture started to darken rapidly, and it was poured into water (250 ml.). A yellow solid (0.57g.) precipitated, which was filtered, dried, and recrystallised from methanol at low temperature to give yellow needles. Elemental analysis indicated that the product consisted almost entirely of a dibrominated compound, probably 1,4-diphenyl-5,7-dibromo-2H-cyclopenta[d]pyridazine, instead of the expected 1,4-diphenyl-5(7)-bromo-2H-cyclopenta[d]pyridazine. $C_{19}H_{12}Br_2N_2$ requires C 53.3%, H 2.8%, Br 37.3%, N 6.55%. Found: C 55.4%, H 3.5%, Br 35.4%, N 5.9%. Mass spectroscopy supported this conclusion by showing the presence of a dibrominated 1,4-diphenyl-2H-cyclopenta[d]pyridazine, slightly contaminated with starting material. No sign of a monobrominated compound was found.

N-Bromosuccinimide. 1,4-diphenyl-2H-cyclopenta[d]pyridazine (0.5g.) was refluxed with N-bromosuccinimide (0.33g., 1 molar equivalent) in carbon tetrachloride (40 ml.) for 15 min. The precipitated succinimide was filtered and the solvent was evaporated to give a yellow crystalline product which was recrystallised from methanol as yellow needles (0.5g.). Elemental analysis showed that a high proportion of the product was polybrominated: $C_{19}H_{13}BrN_2$ requires C 65.34%, H 3.75%, N 8.02%. Found: C 56.81%, H 3.02%, N 7.09%. No separation of the brominated products could be achieved by TLC.

B. 1,4-Dimethyl-2H-cyclopenta[d]pyridazine.

Bromine in ethanol. Bromine (0.29g., 1 molar equivalent) in ethanol (3 ml.) was added to 1,4-dimethyl-2H-cyclopenta[d]-pyridazine (0.27g.) in ethanol (2 ml.). Immediately a yellow solid precipitated, which was filtered after a few seconds. It was found that the product rapidly decomposed if left in contact with the reaction mixture for any length of time. Recrystallisation from ethanol gave yellow crystals (0.15g.). Elemental analysis indicated that partial polybromination had occurred. $C_9H_9BrN_2$ requires Br 35.5%; $C_9H_8Br_2N_2$ requires Br 78.3%. Found: Br 54.5%. Mass spectroscopy showed the presence of $C_9H_8Br_2N_2$, with a smaller amount of $C_9H_9BrN_2$. These compounds were probably 1,4-dimethyl-5,7-dibromo-2H-cyclopenta[d]pyridazine and 1,4-dimethyl-5(7)-bromo-2H-cyclopenta[d]pyridazine.

N-Bromosuccinimide. 1,4-dimethyl-2H-cyclopenta[d]pyridazine (0.3g.) was dissolved in carbon tetrachloride (40 ml.) and refluxed with N-bromosuccinimide (0.36g., 1 molar equivalent). After 10 min. a purple colour began to develop, indicating decomposition. The mixture was quickly filtered, and on cooling the filtrate, buff needles (0.38g.) crystallised. These were purified by low temperature recrystallisation from acetone, giving pale yellow needles, which slowly turned purple on

exposure to the atmosphere. Elemental analysis showed that the product was a mixture of brominated compounds. $C_9H_9BrN_2$ requires C 48.0%, H 4.0%, N 12.45%; $C_9H_8Br_2N$ requires C 35.55%, H 2.65%, N 9.2%. Found: C 38.1%, H 2.9%, N 9.95%. The presence of 1,4-dimethyl-5(7)-bromo-2H-cyclopenta[d]pyridazine as a major component of the mixture was established by N.M.R.

C. 1,4-Dimethyl-2-phenyl-cyclopenta[d]pyridazine.

N-Bromosuccinimide. 1,4-Dimethyl-2-phenyl-cyclopenta[d]-pyridazine (0.30g.) was refluxed with N-bromosuccinimide (0.24g., 1 molar equivalent) in carbon tetrachloride (10 ml.) for 15 min. The red-brown solution was cooled, filtered and evaporated to leave a residue which was dissolved in light petroleum and applied to an alumina column. A yellow band was eluted with 3:1 light petroleum/benzene, and a second yellow band with 1:1 light petroleum/benzene.

On evaporation of solvent, the first band gave a yellow crystalline deposit of a dibrominated 1,4-dimethyl-2-phenyl-cyclopenta[d]pyridazine (0.12g., 23.4%), considered on the basis of its N.M.R. spectrum to be 1,4-dimethyl-5,7-dibromo-2-phenyl-cyclopenta[d]pyridazine. Low temperature recrystallisation from ethanol gave yellow needles, m.p. 135-136°. $C_{15}H_{12}Br_2N_2$ requires C 47.42%, H 3.18%, N 7.37%. Found: C 47.79%, H 3.18%, N 7.38%.

The second band, on evaporation of solvent, left a mixture of 1,4-dimethyl-5-bromo-2-phenyl-cyclopenta[d]pyridazine and 1,4-dimethyl-7-bromo-2-phenyl-cyclopenta[d]pyridazine (0.22g., 54.1%) as a viscous yellow oil which crystallised with difficulty. The compounds were identified by their N.M.R. spectra, but could not be separated by column or thin layer chromatography. The mixture was chromatographed once more on an alumina column to remove traces of the dibrominated compound, and then recrystallised from ethanol at low temperature as a yellow crystalline powder. $C_{15}H_{13}BrN_2$ requires C 59.82%, H 4.35%, N 9.30%. Found: C 59.53%, H 4.49%, N 9.15%.

16. Attempted Nitration of 1,4-Diphenyl-2H-cyclopenta[d]pyridazine.

Conc. nitric acid (0.3 ml.) in acetic anhydride (1 ml.) was added dropwise to 1,4-diphenyl-2H-cyclopenta[d]pyridazine (0.5g.) in acetic anhydride (30 ml.). Immediately a deep green colour was produced. Work-up yielded only an amorphous green substance, which was not further investigated.

17. Formylation of 2H-Cyclopenta[d]pyridazines.

1,4-Diphenyl-2H-cyclopenta[d]pyridazine. Boron trifluoride etherate (0.3 ml.) was added dropwise to a stirred solution of

1,4-diphenyl-2H-cyclopenta[d]pyridazine (0.2g.) and triethyl orthoformate (1.8g.) in dry ether (40 ml.). A white precipitate, contaminated with a purple decomposition product, was formed. On addition of ice (20g.) and a few drops of 0.880 ammonia, the white precipitate dissolved and was replaced by a yellow precipitate. The ether, containing the yellow precipitate, was separated from the aqueous phase and evaporated to dryness. The solid residue was recrystallised from methanol (charcoal) to give 1,4-diphenyl-5(7)-formyl-2H-cyclopenta[d]-pyridazine (0.13g., 58.9%) as a yellow crystalline powder. An analytical sample, recrystallised from methanol, had m.p. 280-281°. $C_{20}H_{14}N_2O$ requires C 80.54%, H 4.73%. Found: C 80.24%, H 4.77%

1,4-Dimethyl-2H-cyclopenta[d]pyridazine. Boron trifluoride etherate (0.5 ml.) was added dropwise to a solution of 1,4-dimethyl-2H-cyclopenta[d]pyridazine (0.1g.) and triethyl orthoformate (0.89g.) in dry ether (50 ml.), and the mixture was shaken for 2 min. Ice (25g.) and a few drops of 0.880 ammonia were added, the mixture was shaken again, and the ether layer was separated. The aqueous layer was saturated with sodium sulphate and extracted with ether (3 x 25 ml.). These extracts were combined with the ether phase of the reaction mixture and

dried (Na_2SO_4). Evaporation of the ether left a whitish solid which was recrystallised from benzene (charcoal) to give 1,4-dimethyl-5(7)-formyl-2H-cyclopenta[d]pyridazine (69 mg., 57.9%) as an almost colourless crystalline powder. An analytical sample, recrystallised from benzene, had m.p. 192-193° decomp. $C_{10}H_{10}N_2O$ requires C 68.95%, H 5.79%. Found: C 68.68%, H 5.93%.

18. Protonation of 2H-Cyclopenta[d]pyridazines.

The perchlorate salts of 1,4-dimethyl-2H-cyclopenta[d]pyridazine, 1,4-diphenyl-2H-cyclopenta[d]pyridazine, 1,4-dimethyl-6-bromo-2H-cyclopenta[d]pyridazine and 1,4-diphenyl-6-bromo-2H-cyclopenta[d]pyridazine were obtained by solution of the pyridazines in acetic acid, followed by addition of perchloric acid (60%) and ether. The perchlorates crystallised as colourless or yellow needles. The above pyridazines are protonated on C-5 or C-7, as shown by their N.M.R. spectra in trifluoracetic acid.

In the case of 1,4-dimethyl-6-nitro-2H-cyclopenta[d]pyridazine[91] and 1,4-diphenyl-6-nitro-2H-cyclopenta[d]pyridazine,[91] hot acetic acid was necessary for solution, and the perchlorates appeared to hydrolyse readily. N.M.R. did not showed that these nitrated pyridazines are ~~not~~ protonated on the five-membered ring.

19. Condensation of 5(7)H-Cyclopenta[d]pyridazinium Perchlorates with Diphenylcyclopropenone.

1,4-Diphenyl-5(7)H-cyclopenta[d]pyridazinium perchlorate. Diphenylcyclopropenone (0.16g.) and 1,4-diphenyl-5(7)H-cyclopenta[d]pyridazinium perchlorate (0.21g.) in acetic anhydride (10 ml.) were warmed at 50° for 5 min. On cooling, the product began to crystallise. Precipitation was completed by addition of ether. Recrystallisation of the precipitate from methanol gave 1,4-diphenyl-5(7)-diphenylcyclopropenylidene-cyclopenta[d]-pyridazinium perchlorate (0.28g., 88.2%) as yellow needles. An analytical sample, recrystallised from methanol, exploded at 246°. $C_{34}H_{23}ClN_2O_4$ requires C 73.07%, H 4.15%. Found: C 72.63%, H 4.07%.

1,4-Dimethyl-5(7)H-cyclopenta[d]pyridazinium perchlorate. Diphenylcyclopropenone (0.17g.) and 1,4-dimethyl-5(7)H-cyclopenta[d]pyridazinium perchlorate (0.20g.) in acetic anhydride (3 ml.) were warmed at 50° for 5 min. The yellow product crystallised from the reaction mixture on cooling. Ether was added to complete the precipitation. The precipitate was recrystallised from methanol to give 1,4-dimethyl-5(7)-diphenylcyclopropenylidene-cyclopenta[d]pyridazinium perchlorate (0.28g., 79.4%) as yellow needles. An analytical sample, m.p. 216° decomp., was

prepared by recrystallisation from methanol. The I.R. spectrum showed -OH absorption, and elemental analysis suggested that the salt took up water from the solvent to crystallise as the monohydrate. $C_{24}H_{19}ClN_2O_4$ requires C 64.19%, H 4.96%; $C_{24}H_{19}ClN_2O_4.H_2O$ requires C 63.56%, H 4.73%. Found: C 63.66%, H 4.65%.

20. Condensation of 5(7)H-cyclopenta[d]pyridazinium Perchlorates with p-Dimethylaminobenzaldehyde.

1,4-Diphenyl-5(7)H-cyclopenta[d]pyridazinium perchlorate reacted at carbon 5(7) with p-dimethylaminobenzaldehyde with elimination of H_2O when the perchlorate salt was added to an equimolar quantity of p-dimethylaminobenzaldehyde in acetic acid or methanol solution at room temperature. The resulting product, which gave an intense blue-purple solution in alcohol, was precipitated as a blue-black powder by addition of ether. It could not be recrystallised, and gave unsatisfactory N.M.R. spectra and elemental analyses.

In the same way, blue-black products were obtained by the reaction of 1,4-dimethyl-, 1,4-dimethyl-6-bromo-, and 1,4-diphenyl-6-bromo-5(7)H-cyclopenta[d]pyridazinium perchlorates. The brominated salts reacted slightly less readily than the unsubstituted salts, and hot acetic acid was used. The

perchlorates of 1,4-dimethyl-6-nitro-, and 1,4-diphenyl-6-nitro-2H-cyclopenta[d]pyridazine did not react in acetic acid alone, but reacted slowly in hot acetic acid/acetic anhydride mixture. None of the products could be obtained analytically pure.

21. Bromination of Cyclopenta[d]-2,3-oxazines.

1,4-Diphenylcyclopenta[d]-2,3-oxazine.[66] 1,4-Diphenylcyclopenta[d]oxazine (0.3g.) was dissolved in carbon tetrachloride (30 ml.) and N-bromosuccinimide (0.20g., 1 molar equivalent) was added. The mixture was refluxed for 15 min. and cooled. The precipitated succinimide was filtered, and the filtrate was evaporated to give 1,4-diphenyl-7-bromocyclopenta[d]-2,3-oxazine as an orange oil which rapidly crystallised. Recrystallisation from a little methanol gave orange platelets (0.32g., 82.6%), m.p. 82-83°. $C_{19}H_{12}BrNO$ requires C 65.16%, H 3.46%. Found: C 65.04%, H 3.52%.

1,4-Dimethylcyclopenta[d]-2,3-oxazine. 1,4-dimethyl-cyclopenta[d]-2,3-oxazine (0.27g.) and N-bromosuccinimide (0.33g., 1 molar equivalent) in carbon tetrachloride (10 ml.) were refluxed for 15 min. On cooling, succinimide crystallised. This was filtered, and the filtrate evaporated to leave yellow needles

of 1,4-dimethyl-7-bromocyclopenta[d]-2,3-oxazine. The product was recrystallised from ethanol (low temperature) as yellow needles (0.32g., 77.2%), m.p. 72-73°. C_9H_8BrNO requires C 47.80%, H 3.57%. Found: C 47.97%, H 3.85%. The same compound was obtained by the reaction of 1,4-dimethylcyclopenta[d]-2,3-oxazine with bromine in ethanol.

22. Attempted Formylation of 1,4-Diphenylcyclopenta[d]-2,3-oxazine.

Boron trifluoride etherate (0.5 ml.) was added dropwise to a stirred solution of 1,4-diphenylcyclopenta[d]-2,3-oxazine (0.1g.) and triethyl orthoformate (0.89g.) in dry ether (20 ml.). After 10 min., ice (20g.) and a few drops of 0.880 ammonia were added. When the ice had melted, the ether layer was separated, washed with water and dried (Na_2SO_4). Removal of solvent left yellow needles. TLC (ethyl acetate and benzene solvents) showed that this yellow product was in fact the starting material. The yellow needles were recrystallised from ethanol as orange platelets, which were shown (m.p. and mixed m.p.) to be unchanged 1,4-diphenylcyclopenta[d]-2,3-oxazine.

23. Condensation of 1, 4-Diphenylcyclopenta[d]-2,3-oxazine with Diphenylcyclopropenone.

1,4-Diphenylcyclopenta[d]-2,3-oxazine (0.2g.) was mixed with diphenylcyclopropenone (0.15g.), trichloracetic acid (1.0g.) and acetic anhydride (5 ml.). The mixture was warmed slightly to dissolve the oxazine, and set aside at room temperature for 1 hr. Ether was then added, followed by a few drops of perchloric acid (70%). A yellow precipitate was formed, but partly decomposed within a few seconds. The supernatant liquor was quickly decanted, and the precipitate was washed with, and then recrystallised from, methanol, to give orange needles of 1,4-diphenylcyclopenta[d]-2,3-oxazin-7-yl diphenyl cyclopropenium perchlorate (0.11g., 18.6%). An analytical sample, m.p. 189-190° decomp., was prepared by recrystallisation from methanol. $C_{34}H_{22}ClNO_5$ requires C 72.93%, H 3.96%. Found: C 72.41%, H 3.89%.

TABLES

U.V., VISIBLE AND N.M.R. SPECTRA

U.V. and Visible Spectra.

Absorption maxima are quoted in millimicrons; log ϵ values are given in parentheses.

All spectra were recorded in ethanol except those marked *, when cyclohexane was used as solvent.

sh. denotes a shoulder.

N.M.R. Spectra.

Chemical shifts are given in τ units, relative to tetramethylsilane as internal standard.

Concentrations were ca. 0.4 M, or saturated in cases of insufficient solubility.

bs = broad singlet

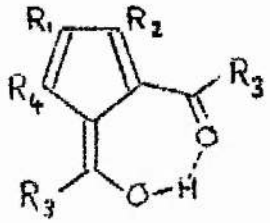
d = doublet

dd = double doublet

m = multiplet

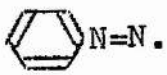
s = singlet

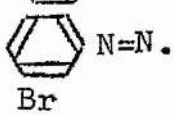
t = triplet



Ia $R_1 = R_2 = H$, $R_3 = Ph$, $R_4 = PhN{=}N$.

Ib $R_1 = R_2 = H$, $R_3 = CH_3$, $R_4 = PhN{=}N$.

Ic $R_1 = R_2 = H$, $R_3 = CH_3$, $R_4 = Br$  $N{=}N$.

Id $R_1 = R_2 = H$, $R_3 = CH_3$, $R_4 = Br$  $N{=}N$.

Ie $R_1 = R_2 = R_4 = H$, $R_3 = CH_3$.

If $R_1 = R_2 = R_4 = H$, $R_3 = C(CH_3)_3$.

Ig $R_1 = R_2 = R_4 = H$, $R_3 = Ph$.

Ih $R_1 = Br$, $R_2 = R_4 = H$, $R_3 = CH_3$.

Ii $R_1 = R_2 = R_4 = Br$, $R_3 = CH_3$.

Ij $R_1 = Br$, $R_2 = R_4 = H$, $R_3 = C(CH_3)_3$.

Ik $R_1 = R_2 = R_4 = Br$, $R_3 = C(CH_3)_3$.

Il $R_1 = Br$, $R_2 = R_4 = H$, $R_3 = Ph$.

Im Keto tautomer of Il.

In Dibenzoyltribromocyclopentadiene, structure unknown.

Table I.

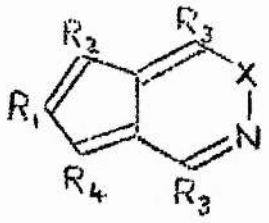
2-Acyl-6-hydroxyfulvenes: U.V. and Visible Spectra.

Ia	244 (4.26), 266 (4.24), 450 (4.45)
Ib	258 (4.39), 274 sh.(4.20), 488 (4.33)
Ic	262 (4.37), 488 (4.35)
Id	248 sh. (4.23), 267 (4.33), 472 (4.35)
If	253 (4.17), 334 (3.96), 397 (3.98)
Ih	257 (4.39), 329 (4.00), 404 (3.91)
Ii	258 (4.24), 347 (4.21), 400 (4.00)
Il	273 (4.20), 285 (4.21), 346 (3.95), 432 (4.08)
Il*	269 (-), 288 (-), 345 (-), 434 (-)
Im*	288 (4.16), 364 (3.97), 430 (4.03)
In	244 (4.27), 344 (4.04)

Table II.

2-Acyl-6-hydroxyfulvenes: N.M.R. Spectra.

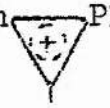
	Solvent	
Ia	$CDCl_3$	-5.1(bs)1H, 2.2-3.3(m)17H.
Ib	$CDCl_3$	-5.6(bs)1H, 2.3-2.9(m)7H, 7.28(s)3H, 7.43(s)3H
Ic	$CDCl_3$	-5.45(bs)1H, 2.4-2.9(m)6H, 7.30(s)3H, 7.40(s)3H.
Id	$CDCl_3$	-4.85(bs)1H, 2.2-2.8(m)5H, 7.33(s)3H, 7.40(s)3H.
Ie	CCl_4	-8.0(s)1H, 2.8(d)2H, 3.75(t)1H, 7.5(s)6H. $J_{3,4(4,5)} = 3.9$ c/s.
If	CCl_4	-9.2(s)1H, 2.52(d)2H, 3.75(t)1H, 8.53(s)18H. $J_{3,4(4,5)} = 4.1$ c/s.
Ig	CCl_4	-8.45(s)1H, 2.1-2.75(m)10H, 2.85(d)2H, 3.65(t)1H. $J_{3,4(4,5)} = 3.8$ c/s.
Ih	CCl_4	-8.05(s)1H, 2.9(s)2H, 7.5(s)6H.
Ii	CCl_4	-9.1(s)1H, 7.2(s)6H.
Ij	CCl_4	-9.2(s)1H, 2.62(s)2H, 8.52(s)18H.
Ik	CCl_4	8.8(s)18H.
Il	CCl_4	-8.55(s)1H, 2.0-2.6(m)10H, 2.95(s)2H.
In	$CDCl_3$	2.1-2.8(m)10H, 4.25(s) ca. 0.5H.

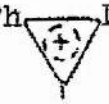


IIa $R_1 = R_2 = R_4 = H$, $R_3 = CH_3$, X = NH.

IIb $R_1 = Br$, $R_2 = R_4 = H$, $R_3 = CH_3$, X = NH.

IIc $R_1 = Br$, $R_2 = R_4 = H$, $R_3 = Ph$, X = NH.

IId $R_1 = R_4 = H$, R_2 =  (ClO_4^-), $R_3 = CH_3$, X = NH.

IIe $R_1 = R_4 = H$, R_2 =  $(ClO_4)^-$, $R_3 = Ph$, X = NH.

IIf $R_1 = R_4 = H$, $R_2 = CHO$, $R_3 = CH_3$, X = NH.

IIg $R_1 = R_4 = H$, $R_2 = CHO$, $R_3 = Ph$, X = NH.

IIh $R_1 = R_2 = R_4 = H$, $R_3 = CH_3$, X = NPh.

IIi $R_1 = H$, $R_2 = R_4 = Br$, $R_3 = CH_3$, X = NPh.

IIj $R_1 = R_2 = H$, $R_3 = CH_3$, $R_4 = Br$, X = NPh.

IIk $R_1 = R_4 = H$, $R_2 = Br$, $R_3 = CH_3$, X = NPh.

IIl $R_1 = R_2 = R_4 = H$, $R_3 = CH_3$, X = O.

IIm $R_1 = R_4 = H$, $R_2 = Br$, $R_3 = CH_3$, X = O.

IIn $R_1 = R_4 = H$, $R_2 = Br$, $R_3 = Ph$, X = O.

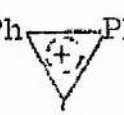
IIo $R_1 = R_4 = H$, R_2 =  $(ClO_4)^-$, $R_3 = Ph$, X = O.

Table III.

2-Substituted Cyclopenta[d]pyridazines and Cyclopenta[d]-2,3-oxazines: U.V. and Visible Spectra.

IIa	247 (4.46), 261 sh. (4.20), 307 (3.68)
IIb	252 (4.59), 268 sh. (4.18), 300 (3.64)
IIc	259 (4.48), 277 (4.46), 317 sh. (3.79)
IId	215 (4.38), 260 (4.37), 327 (4.06), 398 (4.48)
IIe	258 (4.64), 412 (4.44)
IIf	242 (4.25), 246 (4.26), 251 (4.24), 257 (4.21), 260 sh. (4.14), 286 (4.03), 322 (3.98), 372 (4.00)
IIg	240 (4.44), 258 sh. (4.34), 298 (4.26), 339 (4.05), 392 (3.75)
IIh	248 (4.44), 256 sh. (4.41), 276 (4.31), 310 (3.79), 380 (3.28)
IIi	254 (4.37), 278 (4.45), 317 (3.90), 326 sh. (3.88), 400 (3.39)
IIl	230 (4.16), 260 (4.00), 312 (3.63), 321 sh. (3.58), 345 sh. (3.17)
IIm	231 (4.11), 237 sh. (4.08), 261 (4.10), 267 sh. (4.07), 315 (3.66), 326 sh. (3.60), 374 (3.30)
IIn	241 (4.33), 287 (4.23), 334 (3.88)
IIo	238 (4.55), 283 (4.42), 338 (4.22)

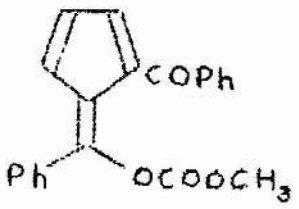
Table IV.

2-Substituted Cyclopenta[d]pyridazines and Cyclopenta[d]-2,3-oxazines: N.M.R. Spectra

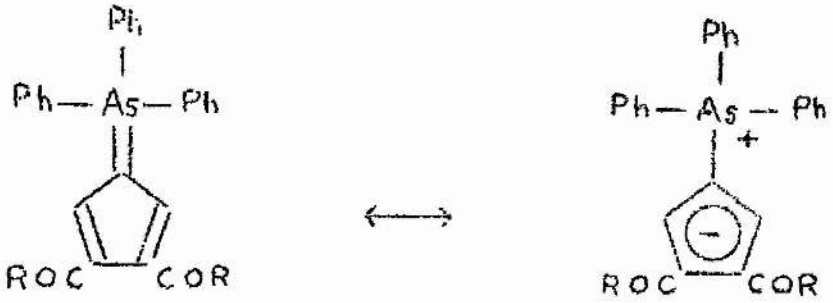
	Solvent	
IIa	Acetone	2.77(t)1H, 3.25(d)2H. (Ring protons only). $J_{5,6(6,7)}$ = 3.6 c/s.
	TFA	2.3(d)1H, 2.65(d)1H, 6.0(s)2H, 7.0(s)6H. $J_{5,6(6,7)}$ = 6 c/s.
IIb	TFA	2.60(s)1H, 5.82(s)2H, 7.03(s)3H, 7.07(s)3H.
IIc	TFA	1.8-2.4(m)11H, 5.60(s)2H.
IId	TFA	1.43(d)1H, 1.4-2.2(m)10H, 2.27(d)1H, 6.80(s)6H. $J_{5,6(6,7)}$ = 4.4 c/s.
IIf	TFA	0.98(s)1H, 1.85(d)1H, 2.67(d)1H, 6.73(s)3H, 6.95(s)3H. $J_{5,6(6,7)}$ = 5.2c/s.
IIh	CCl_4	2.4-2.95(m)6H, 3.1-3.45(m)2H, 7.42(s)3H, 7.55(s)3H.
IIi	CCl_4	2.4-2.9(m)5H, 2.95(s)1H, 7.22(s)6H.
IIj	CCl_4	2.4-2.9(m)5H, 2.98(d)1H, 3.38(d)1H, 7.20(s)3H, 7.60(s)3H. $J_{6,7}$ = 4.4c/s.
IIk	CCl_4	2.4-2.9(m)5H, 2.91(d)1H, 3.53(d)1H, 7.25(s)3H, 7.48(s)3H. $J_{5,6}$ = 3.7 c/s.
IIl	CCl_4	2.95(dd)1H, 3.17(dd)1H, 3.37(dd)1H, 7.33(s)3H, 7.53(s)3H. $J_{5,6}$ = 2.9 c/s, $J_{6,7}$ = 4.4 c/s, $J_{5,7}$ = 1.1 c/s.
IIm	CCl_4	3.00(d)1H, 3.53(d)1H, 7.07(s)3H, 7.57(s)3H. $J_{5,6}$ = 3.1 c/s.

IIIa R = CH_3

IIIb R = Ph



IV



Va R = Ph

Vb R = $C(CH_3)_3$

Table V.

Miscellaneous: U.V. and Visible Spectra.

IIIa	266 (4.40), 345 (4.07), 415 (4.19).
IIIb	237 (4.19), 289 (4.21), 358 (4.04), 434 (4.27).
IV	237 (4.17), 323 (4.25).
Va	220 (4.63), 241 sh. (4.38), 270 (4.08), 299 (4.29), 348 sh. (4.08).
Vb	220 (4.59), 264 (4.06), 270 (4.09), 304 (4.21).

Table VI.

Miscellaneous: N.M.R. Spectra

	Solvent	
IIIa	CCl_4	-5.7(bs)1H, 2.4-2.9(m)7H, 3.63(t)1H, 7.42(s)3H, 7.50(s)3H.
IIIb	$CDCl_3$	-5.6(bs)1H, 2.0-3.7(m)17H, 3.73(t)1H.
IV	$CDCl_3$	1.95-2.75(m)10H, 3.07(dd)1H, 3.38(dd)1H, 3.53(dd)1H, 6.30(s)3H. $J_{3,4}$ = 2.0 c/s, $J_{4,5}$ = 5.3 c/s, $J_{3,5}$ = 1.8 c/s.
Va	$CDCl_3$	2.2-3.0(m)25H, 3.15(s)2H.
Vb	$CDCl_3$	2.1-2.4(m)15H, 3.67(s)2H, 8.75(s)18H.

APPENDIX

REACTIONS OF THE CYCLONONATETRAENIDE ANION

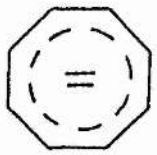
Cyclooctatetraenide Dianion and Cyclononatetraenide Anion.

On the basis of the Hückel rule, aromaticity is to be expected for carbocyclic compounds which have a closed shell of $4n + 2\ \pi$-electrons where n is any integer. Thus where n = 0, we have the cyclopropenium cation, and where n = 1, the cyclopentadienide anion, benzene, and the tropylium cation, all of which are recognised to have aromatic character. That the Hückel rule may be extended to cases where n = 2 has been amply demonstrated by the preparation of the cyclooctatetraenide dianion (I) and the cyclononatetraenide anion (II).

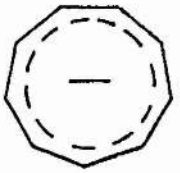
Although the reaction of cyclooctatetraene with alkali metals was reported in 1948,[127] it was not until 1960 that the product of this electron-transfer reaction was shown to be a planar aromatic dianion.[128] A suggestion to this effect was, however, made in 1956 on the basis of magnetic susceptibility measurements.[129] The N.M.R. spectrum of the cyclooctatetraenide dianion is a single peak, virtually coincidental with that of cyclooctatetraene itself. If the dianion were to consist of a mixture of rapidly interchanging structures, having the shape of the cyclooctatetraene molecule (III), the dianion signal would appear appreciably up-field of that of cyclooctatetraene, on account of the increased shielding produced by addition of electrons to the cyclooctatetraene molecule. The

observed chemical shift of the dianion peak is thus presumably due to a compensating down-field displacement, of the kind associated with the effect of the diamagnetic ring-current induced in aromatic molecules.

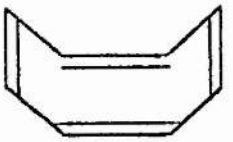
The cyclooctatetraenide dianion, although stable in solution, reacts immediately and sometimes explosively on exposure to air or moisture. It reacts with two moles of electrophilic reagents to give disubstituted cyclooctatrienes, which generally rearrange in a variety of ways.[130] No reactions of the dianion are known in which the π-electron decet is retained. An interesting reaction of the cyclooctatetraenide dianion gives access to the bicyclo-[6.1.0]nonatriene system (IV). Katz and Garratt[131] have prepared the parent hydrocarbon, and its anti-9-chloro, 9,9-dichloro, and anti- 9-methoxy derivatives (IVa-d) from the dianion and methylene chloride, chloroform, carbon tetrachloride, and dichloromethyl methyl ether respectively. The mechanism of this reaction is not fully understood. The reaction of dipotassium cyclooctatetraenide with chloroform yields anti-9-chlorobicyclo[6.1.0]nonatriene with the syn isomer (IVe) present in trace quantities only,[131] or as 16-22% of the total product.[132] 9-Chlorobicyclo[6.1.0.]nonatriene is also obtainable by the action of chlorocarbene (from methylene chloride and methyl lithium) on cyclooctatetraene. The product in this case is a mixture of syn and anti isomers, the ratio of syn



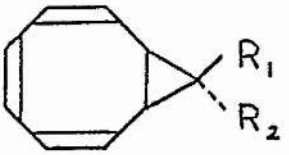
I



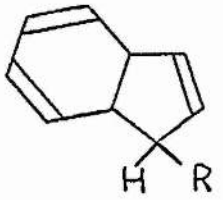
II

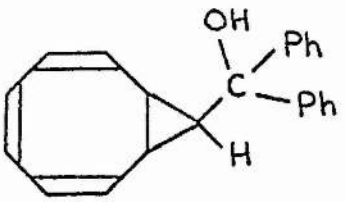


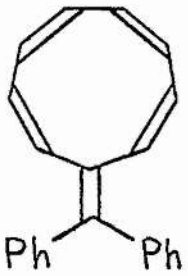
III



IV a) $R_1 = R_2 = H$
b) $R_1 = Cl$, $R_2 = H$
c) $R_1 = R_2 = Cl$
d) $R_1 = OCH_3$, $R_2 = H$
e) $R_1 = H$, $R_2 = Cl$







a) R = H
b) $R = CH_3$
V c) R = COOH

VI

VII

to anti being 3:1.[132] The different stereochemistry of the products from the two reactions is difficult to explain if it is assumed that the reaction between cyclooctatetraenide dianion and chloroform involves cyclooctatetraene and chlorocarbene as combining intermediates.

Bicyclo[6.1.0]nonatrienes having suitable leaving groups at the 9-position react with alkali metals in dry, inert atmospheres to give the cyclononatetraenide anion. Thus a solution of the potassium salt in tetrahydrofuran (THF) has been obtained from the action of potassium metal on a THF solution of IVd. The preferred method of preparation of the cyclononatetraenide anion, however, appears to be the reaction of lithium metal with the 9-chlorobicyclo[6.1.0]nonatrienes (IVb&e) in THF; this was the original synthesis reported independently from two laboratories in 1963.[133,134] The yield of cyclononatetraenide anion from this reaction is 60-65%, deduced from N.M.R. spectra.[132] A 38% yield of sodium cyclononatetraenide has also been obtained from the reaction of IVa with methylsulphinyl carbanion.[132]

The alkali metal cyclononatetraenides have not been isolated as solids, and resemble the cyclooctatetraenide salts in their stability in solution in an inert atmosphere and their great reactivity towards oxygen and moisture. The tetraethylammonium salt, prepared from the lithium salt and tetraethylammonium chloride, is a white

solid, recrystallisable from anhydrous acetonitrile, and, although moisture-sensitive, appears to be inert to anhydrous oxygen.[132]

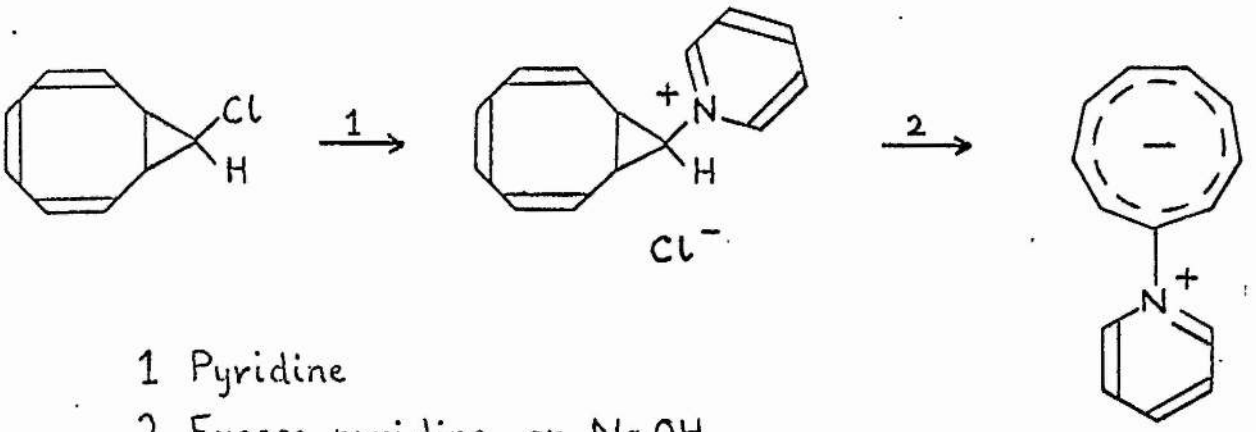
As with the cyclooctatetraenide dianion, the N.M.R. spectrum of the cyclononatetraenide anion confirms its aromatic nature; it also shows that its shape must be that of a regular nonagon. The single peak observed indicates that all the hydrogen atoms are exactly equivalent and excludes the possibility of a planar ring with re-entrant angles, since the hydrogen atoms inside the ring of such a system would give rise to a separate signal at higher field than that of the hydrogens outside. The chemical shift of the cyclononatetraenide peak (ca. 3.0 τ) shows that it is not due to a mixture of rapidly interchanging valence tautomers of bicyclic anions such as the anions of 8,9-dihydroindene (Va) or bicyclo-[6.1.0]nonatriene (IVa).

As a vinylogue of the cyclopentadienide anion, cyclononatetraenide anion might, on first considerations, be expected to undergo the same extensive range of substitution reactions; but, unlike substituted cyclopentadienes, the cyclononatetraene compounds resulting from such reactions should be considerably destabilised by ring-strain. It has been shown[131,132] that reaction of cyclononatetraenide anion with water gives cyclononatetraene, which rapidly rearranges to a valence tautomer, 8,9-dihydroindene (Va). Similarly, reaction of the anion with methyl

iodide and with carbon dioxide has produced 1-methyl-8,9-dihydroindene (Vb) and 1-carboxy-8,9-dihydroindene (Vc).[131]

In the light of this demonstrated instability of cyclononatetraene, it might be inferred that isolable cyclononatetraene derivatives in which the 9-membered ring is retained would be limited to those classes in which a high degree of resonance stabilisation is conferred by contributing forms which possess the planar, aromatic cyclononatetraenide system.

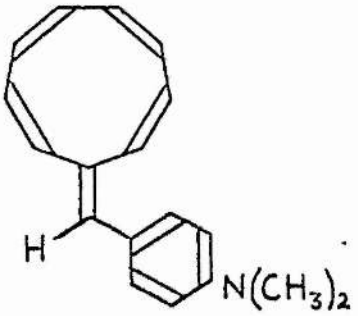
It might further be expected that successful syntheses would avoid the presence of cyclononatetraenes as long-lived intermediates. This limitation suggests that bicyclo[6.1.0]nonatriene compounds might be useful starting materials for the preparation of cyclononatetraene derivatives. The chlorocyclononatetraenide anion has been prepared in ca. 50% yield by the action of lithium metal in THF upon 9,9-dichlorobicyclo[6.1.0]nonatriene (IVc).[132] The attempted dehydration of diphenylbicyclo[6.1.0]nonatrien-9-ylcarbinol (VI) to the fulvenoid derivative (VII) of cyclononatetraene has been reported.[135] Base-catalysed elimination of water failed to take place, and acid-catalysed dehydration was precluded by the sensitivity of compound VI to acid. With fluoroboric acid, a red mixture of decomposition products was immediately obtained, from which was recovered an 88% yield of 1,1,4-triphenylbuta-1,3-diene.



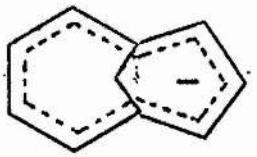
1 Pyridine

2 Excess pyridine or NaOH

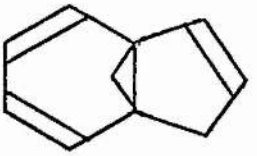
Scheme 1



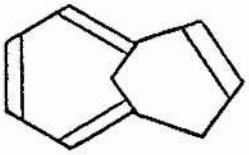
VIII



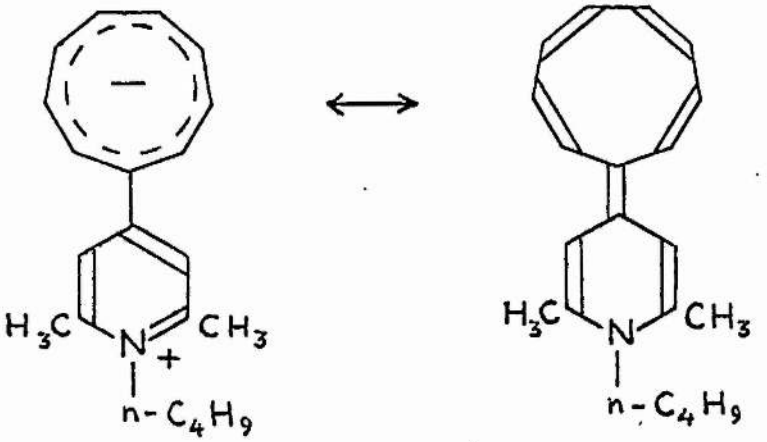
IX



X



XI



XII

To date, no confirmed reports of the preparation of cyclononatetraene compounds, other than the cyclononatetraenide salts cited above, have appeared in the literature. There exists, however, an unsubstantiated claim that the fulvenoid compound VIII has been obtained as the crystalline product of the reaction of cyclononatetraenide anion with p-dimethylaminobenzaldehyde.[136]

Another possible route to compounds possessing an aromatic 9-membered carbocyclic ring is offered by the recent synthesis[137] of the bridged cyclononatetraenide anion IX by the action of methylsulphinyl carbanion on tricyclo[4.3.1.$0^{1,6}$]deca-2,4,7-triene (X). Evidence of the existence of a ring-current in the anion IX is afforded by the up-field shift of the absorption representing the cyclopropane methylene protons in X, from 8.6 τ and 10.0 τ in the olefin to 10.7 τ and 11.2 τ in the anion. In addition, an increase in the geminal coupling constant of this AB system from 3 c/s to 7.5 c/s accompanies the transition to the aromatic anion.

It is observed that protonation of anion IX gives the original tricyclic triene X, and not the strained bridged cyclononatetraene XI. The 1,6-methano-cyclononatetraenide ion thus appears to suffer from the same disadvantage as the unbridged cyclononatetraenide ion as far as the formation of 9-membered ring derivatives is concerned: in both cases the strain incurred by de-aromatisation is relieved

by skeletal rearrangement. Tricyclo[4.3.1.$0^{1,6}$]deca-2,4,7-trienes, however, would probably be acceptable intermediates in the reactions of anion IX, since the corresponding 10 π-electron aromatic systems should be obtainable from them by the action of base. The analogous reactions of 8,9-dihydroindene compounds would not be expected to occur. Cyclononatetraenide anion could not be obtained from 8,9-dihydroindene by the action of methylsulphinyl carbanion.[132]

There follows an account of some attempted reactions of the cyclononatetraenide anion. Shortage of time prevented a thorough examination of the products obtained; the sensitivity of the intermediate species to air and moisture, the small scale of the reactions and consequent repetitive work, all helped to slow the rate of progress.

Preparation of the Cyclononatetraenide Anion: Experimental.

The chosen route to cyclononatetraenide anion was that of Katz and Garratt.[131] 9-Chlorobicyclo[6.1.0]nonatriene was prepared as follows: cyclooctatetraene (12g.) was dissolved in tetrahydrofuran (100 ml., freshly distilled from sodium). This solution was stirred and cooled and the theoretical quantity of potassium metal (9.0g.) was added in small pieces under a nitrogen atmosphere. Solution of the potassium was rapid and exothermic, and accompanied by the formation of a deep red-brown colour. After 4.5 hr., the

intensely coloured solution of cyclooctatetraenide dianion was filtered under nitrogen through a plug of glass wool into a 250 ml. dropping funnel. Although the reaction was repeated many times, sometimes with different amounts of potassium, the quantity of potassium dissolved was always between 5.4 and 5.9g., indicating an average conversion of 63% of cyclooctatetraene to the dianion.

The dianion solution was added over a period of 45 min. to 100 ml. of vigorously stirred chloroform. The reaction mixture was kept at -20° to -10°, and a nitrogen atmosphere was maintained over both the reaction mixture and the cyclooctatetraenide dianion solution. The mixture was stirred for a further 2 hr., while it warmed to room temperature. After addition of a little ethanol to remove any fragments of potassium present, the mixture was poured into water (1500 ml.) and washed thoroughly, then dried (Na_2SO_4). The solvent was evaporated off under reduced pressure at 25-30° to leave a dark brown viscous residue, which was distilled. After rejection of the first few drops of distillate, 9-chloro-bicyclo[6.1.0] nonatriene was collected, b.p. 25-27° (0.2 mm.). The N.M.R. spectrum showed J_{AX_2} = 4.3 c/s for the cyclopropane ring protons, identifying the product as the anti isomer (IVb). LaLancette and Benson[132] have assigned the syn structure to the isomer having a coupling constant of 7.6 c/s for the cyclopropane AX_2 system, and the anti structure to the isomer where this coupling

constant is 4.3 c/s. The best yield of anti-9-chlorobicyclo [6.1.0]nonatriene was 5.92g. (69.6% based on cyclooctatetraenide dianion, 45.2% based on cyclooctatetraene.

To generate the cyclononatetraenide anion, the theoretical quantity of lithium metal was added in small pieces to 9-chlorobicyclo[6.1.0]nonatriene dissolved in dry THF, and the flask was securely stoppered under nitrogen and shaken mechanically until reaction was complete. A reaction time of 6 hr. was usually employed, which was more than sufficient. A mildly exothermic reaction started within 10 min., which was counteracted by ice-water cooling. At the same time a colour, either red or green, developed in the reaction mixture and rapidly intensified. The final colour of the cyclononatetraenide anion solution was dark purple-brown or green-black.

Pyridinium Cyclononatetraenylide.

Numerous attempts to prepare pyridinium cyclononatetraenylide from 9-chlorobicyclo[6.1.0]nonatriene by reaction scheme 1 resulted in formation of only trace quantities of an ylide product. After several totally unsuccessful preparations employing reaction times of a few days, 9-chlorobicyclo[6.1.0]nonatriene (1.0g.) was stored in a closed vessel with pyridine (0.5 ml., 1 equivalent) at approx. -15° for 3 months, after which time the reaction mixture

consisted of a red-brown solution and precipitate. When the solution was shaken with water, a heavy oil separated. This oil, when dissolved in various solvents, gave solutions of different colours, depending on the polarity of the solvent: in carbon tetrachloride, pale blue, in benzene, purple, in acetone, red-purple, in ethanol, red. This hypsochromic shift of the absorption with increase of solvent polarity is characteristic of the pyridinium cyclopentadienylides and is attributed to the stabilisation by solvation of a dipolar ground state that otherwise would be destabilised relative to an uncharged excited state.[138]

The bulk of the oil was shown by N.M.R. to be unchanged 9-chlorobicyclo[6.1.0]nonatriene; the quantity of ylide present was too small to permit its isolation and further examination.

The extreme slowness of the reaction of the nonatriene at low temperature is understandable in view of the low reactivity of cyclopropyl halides. It was necessary to keep the reaction mixture cold in order to preserve the 9-chlorobicyclo[6.1.0] nonatriene, which is reported to isomerise to 1-chloro-8,9-dihydroindene.[132]

1-n-Butyl-2,6-dimethyl-4-cyclononatetraenylidene-1,4-dihydropyridine (XII).

A solution of cyclononatetraenide anion in THF (10 ml.) was prepared from 9-chlorobicyclo[6.1.0]nonatriene (1.4g.) and lithium metal

(0.2g.) as described above. The unreacted lithium was removed under nitrogen, and a solution of 1-n-butyl-2,6-dimethyl-4-ethoxypyridinium perchlorate (1.4g., 1 molar equivalent) in THF (25 ml.) was added. A red colour was immediately produced. After 0.5 hr. the red mixture was poured into water (250 ml.) and extracted with benzene (3 x 50 ml.). The combined benzene extracts were dried (Na_2SO_4) and evaporated, and the residue was chromatographed on a column of alumina. Elution with benzene gave a yellow solution which, on evaporation, left a yellow oil (0.36g.). No other products were obtained. U.V. and N.M.R. examination of this oil showed it to be predominantly 8,9-dihydroindene. It would therefore appear that reaction between the pyridinium salt and cyclononatetraenide anion leads to tarry decomposition products only, the 8,9-dihydroindene arising from the quenching of unreacted cyclononatetraenide anion with water on work-up.

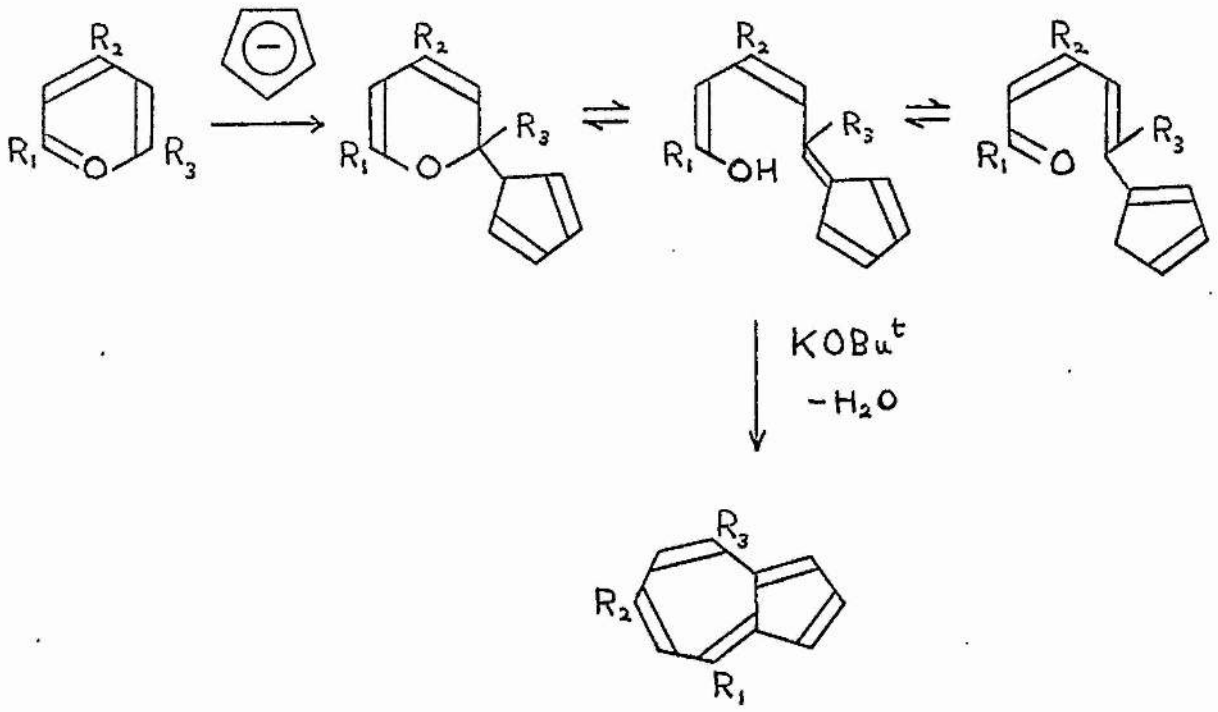
The analogous reaction of cyclopentadiene with 1-methyl-4-alkoxypyridinium salts in the presence of t-butoxide ion has successfully given 4-cyclopentadienylidene-1,4-dihydropyridines.[15]

Reaction of Cyclononatetraenide Anion with Benzophenone.

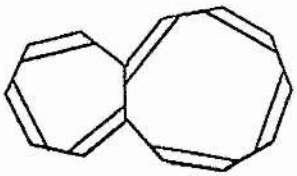
To a THF solution of lithium cyclononatetraenide (40 ml.), prepared from 9-chlorobicyclo[6.1.0]nonatriene (2g.), a solution of benzophenone (1.8g., 1 molar equivalent) in dry THF (70 ml.) was added

under nitrogen, with stirring, over a period of 50 min. The colour of the reaction mixture gradually changed through blue and green to orange-brown. After 18 hr. the THF solution was concentrated under reduced pressure, diluted with water, and extracted with chloroform. The chloroform extract was dried (Na_2SO_4) and evaporated to leave an orange-red oil which was chromatographed on an alumina column. Two yellow bands were eluted, the first with a 1:1 mixture of ether and light petroleum ether (b.p. 40-60°), the second with methanol. The latter band was shown by its U.V. spectrum to contain 8,9-dihydroindene, probably the product of protonation of unreacted cyclononatetraenide anion. The first band, however, yielded on evaporation of solvent, a small amount of an orange substance, together with much unreacted benzophenone. Examination of this orange product, which may have been a fulvenoid compound, was not possible, as it could not be separated from benzophenone.

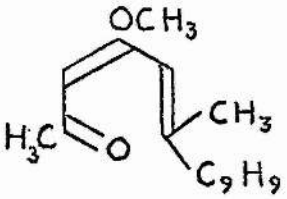
Another preparation was carried out, employing cyclohexanone in place of benzophenone, since in this case unreacted ketone could be separated from any product by formation of its bisulphite addition compound. No tractable product was obtained from this reaction.



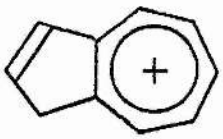
Scheme 2



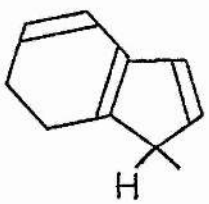
XIII



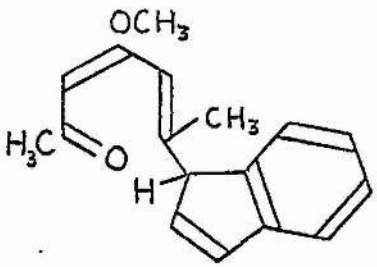
XIV



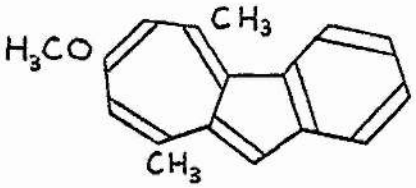
XV



XVI



XVII



XVIII

Reaction of Cyclononatetraenide Anion with a Pyrylium Salt.

The azulene synthesis of Hafner,[20] in which cyclopentadienide anion reacts with a pyrylium salt, has already been mentioned (page 5). The reaction follows the course shown in Scheme 2. The analogous reaction of the cyclononatetraenide anion was therefore of interest, as it offered the possibility of synthesis of the azulene vinylogue XIII.

A THF solution of lithium cyclononatetraenide, prepared in the usual way from 9-chlorobicyclo[6.1.0]nonatriene (2.0g., 13m.mole) was added to a stirred suspension of 2,6-dimethyl-4-methoxypyrylium perchlorate (2.2g., 9 m.mole) in dry THF (15 ml.) under nitrogen, over a period of 0.5 hr. The temperature of the reaction mixture rose during the course of the addition from -20° to -3°. After a further 2 hr., the THF was evaporated off and the residue was taken up in light petroleum, washed with water, and dried ($CaCl_2$). Removal of the solvent left a viscous orange-red oil (1.8g.), which could be distilled ($152\text{-}6^{\circ}$, 0.3 mm.). This oil was thought to correspond to the uncyclised intermediate in Hafner's azulene synthesis (see Scheme 2), and elemental analysis and molecular weight determination indeed indicated a compound compatible with the structure XIV ($C_{17}H_{20}O_2$ requires C 79.69%, H 7.81%, mol. wt. 256. Found: C 80.63%, H 7.78%, mol. wt. 254. These figures do not exclude a dehydrogenation product of XIV: $C_{17}H_{18}O_2$ requires C 80.30%, H 7.13%, mol. wt. 254).

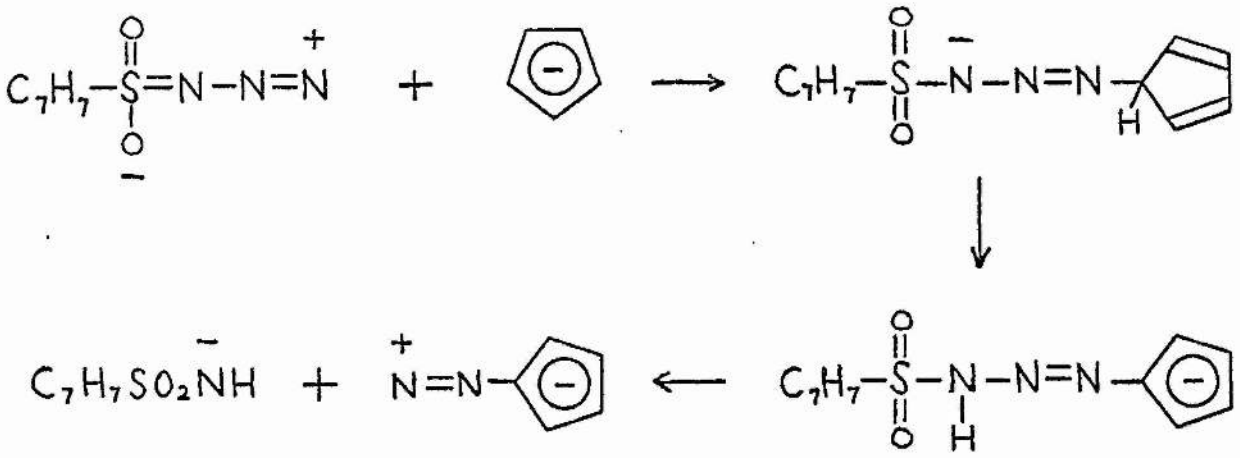
The final step of the Hafner azulene synthesis is the addition of potassium t-butoxide, which brings about cyclisation with elimination of H_2O. Treatment of the oil XIV with t-butoxide ion under nitrogen gave an intensely purple solid, which was soluble in acetone (purple solution) and alcohols (orange-brown solutions). The purple product appeared to be stable for an indefinite time under nitrogen, but decomposed completely in a few seconds on exposure to air.

It became evident that this purple compound could not be the desired cyclononatetraene derivative XIII when it was found that treatment with dilute aqueous acid, or even with water, regenerated the oil XIV. The interconversion of the purple compound and oil XIV bears a superficial resemblance to the reversible protonation of intensely coloured azulenes to the corresponding azulenium cations (XV), but strongly acidic conditions are required for the formation of the azuleniumcations, and correspondingly weak basic conditions for regeneration of the azulenes, i.e. the reverse of the conditions necessary to effect the interconversion in this case.

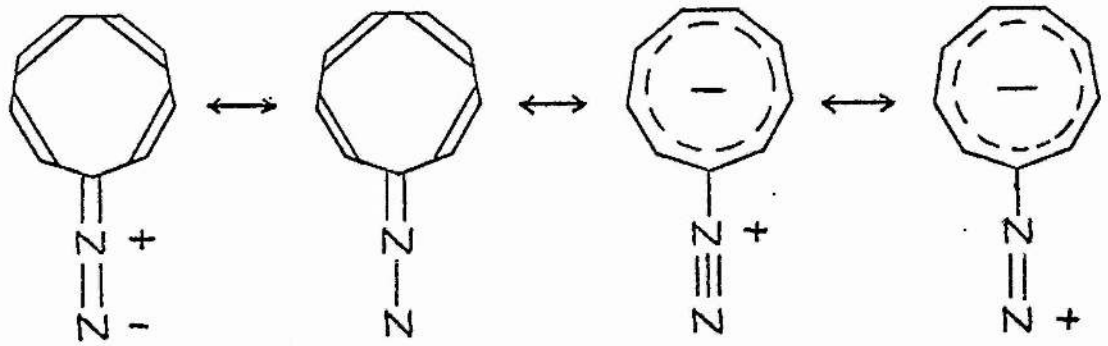
The most plausible explanation of this acid-base reaction is that the purple compound, unstable to air, is an anionic species, and that the stable orange-red oil is its conjugate acid, with the structural formula XIV. The nature of the C_9H_9 fragment in XIV must now be considered. The possibilities are that the bicyclo

[6.1.0]nonatriene structure is present in the oil, and valence tautomerises to the cyclononatetraenide structure in the anion; that the cyclononatetraene ring is present in both oil and anion; and that the indene skeleton is present in both oil and anion. According to Katz and Garratt,[131] the bicyclo[6.1.0]nonatriene chromophore is characterised by an absorption maximum at 248 ± 3 mμ in the U.V. spectrum. Such an absorption maximum was not found in the spectrum of the oil. The presence of a 9-membered ring which survives the protonation-deprotonation cycle is inconsistent with the behaviour of the cyclononatetraenide anion, which, on protonation, is known to collapse irreversibly to give 8,9-dihydroindene. It is concluded that the C_9H_9 residue in XIV probably consists of a dihydroindene system, in which rearrangement of the initially-formed 8,9-dihydroindene residue has produced a structure containing a cyclopentadiene ring, e.g. XVI. Such a structure would offer the maximum opportunity for charge delocalisation in the anion.

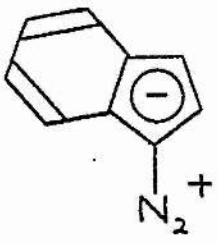
The further possibility that XIV contains an indenyl group, formed by atmospheric oxidation, cannot be ruled out. This compound (XVII) or a tautomer, or its cyclised derivative, the benzazulene XVIII, should be formed by the reaction of 2,6-dimethyl-4-methoxy-pyrylium perchlorate with sodium indenide. This reaction was carried out under nitrogen, and an orange colour was initially produced, suggesting that the expected attack by the anion at the



Scheme 3



XIX



XX

2-position of the pyrylium salt and subsequent ring opening took place. Spontaneous decomposition ensued, however, and neither the substituted indene XVII nor the benzazulene XVIII could be isolated from the decomposed reaction mixture. It is noteworthy that, after this reaction had been attempted, the failure of the reaction of sodium indenide and 2,4,6-trimethylpyrylium perchlorate to give 4,6,8-trimethyl-1,2-benzazulene was reported.[139]

Diazocyclononatetraene.

The reaction used by Doering and DePuy[29] to prepare diazocyclopentadiene from cyclopentadienide anion and toluene-p-sulphonyl azide is shown in Scheme 3. This reaction is the obvious choice for an attempt to prepare the interesting compound diazocyclononatetraene (XIX). As in the other derivatives of cyclononatetraene referred to above, there is the very real possibility that the 9-membered ring compound might be unstable relative to the corresponding dihydroindene derivative. In the ylides of cyclononatetraene, however, the dipolar nature of the compounds and consequent stabilisation of the 9-membered ring would minimise the tendency towards valence tautomerism.

A solution of toluene-p-sulphonyl azide (4.86g., 1.5 molar equivalents.) in dry ether (5 ml.) was added, over a period of 5 min., to a cooled, agitated solution of lithium cyclononatetraenide

in dry THF (10 ml.) prepared from 9-chlorobicyclo[6.1.0]nonatriene (2.5g.). A nitrogen atmosphere was maintained above the reaction mixture. The following day the mixture was poured into water (250 ml.) and the resulting emulsion was extracted thoroughly with ether. The combined ether extracts were dried (Na_2SO_4) and evaporated down. Examination of the I.R. spectrum of the residue in the region of 4.8μ showed the presence of a diazo compound in addition to unreacted toluene-p-sulphonyl azide. Diazo compounds are characterised by a strong absorption close to 4.8μ, due to C = N = N stretching. Azides also absorb strongly in this region (N = N = N asymmetric stretching).

Partial purification of the diazo product was achieved by chromatography on an alumina column. The first (yellow) band, eluted with light petroleum (b.p. 80-100°) was found to contain the diazo compound. Evaporation of the solvent gave a very small quantity (perhaps 100 mg.) of an impure orange-red oil, one impurity being identified by N.M.R. as indene. A twice-chromatographed sample was dissolved in light petroleum (b.p. 40-60°) and its I.R. spectrum was recorded. The absorption of the diazo group was found at 4.77μ.

Time did not permit the proof of the structure of this compound. It was intended that, after the compound had been prepared in suitable quantity and in a satisfactory state of purity, it should

be hydrogenated and the product compared with an authentic sample of cyclononanone hydrazone. The possibility thus still remains that an indene skeleton is present in the diazo compound. One alternative, however, has been excluded. Diazoindene (XX) was prepared by the diethylamine-catalysed reaction of indene with toluene-p-sulphonyl azide.[100] The diazo group in this compound was found to absorb at 4.82μ in light petroleum (b.p. 40-60°) solution. The azide absorption of toluene-p-sulphonyl azide in this solvent was found at 4.74μ.

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