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SOME HETEROCYCLIC

ANALOGUES OF

SESQUIFULVALENE

being a Thesis

presented by

FRANCIS IAN WASSON, B. Sc.,

to the

UNIVERSITY OF ST. ANDREWS

in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY



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DECLARATION

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

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

CERTIFICATE

I hereby certify that Mr. Francis Ian Wasson, B.Sc., A.R.I.C., has spent twelve terms at research work under my supervision, has fulfilled the conditions of Ordinance No.13 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Ph.D.

Director of Research.

UNIVERSITY CAREER

I entered the University of St. Andrews as an undergraduate in October 1957 and graduated B.Sc. with Second Class Honours in Chemistry in July, 1961.

The research described in this thesis was carried out between October 1961 and September 1964, during which time I held a Research Studentship awarded by the Department of Scientific and Industrial Research.

PUBLICATIONS

- (1) Preparation of a Cyclopentadienylydenepyran.

Lloyd, D. and Wasson, F.I., Chem. and Ind., 1963, 1559

- (2) The Reduction of Oximes by means of Hydrazine and Raney Nickel.

Lloyd, D., McDougall, R.H., and Wasson, F.I., J.Chem.Soc., in press.

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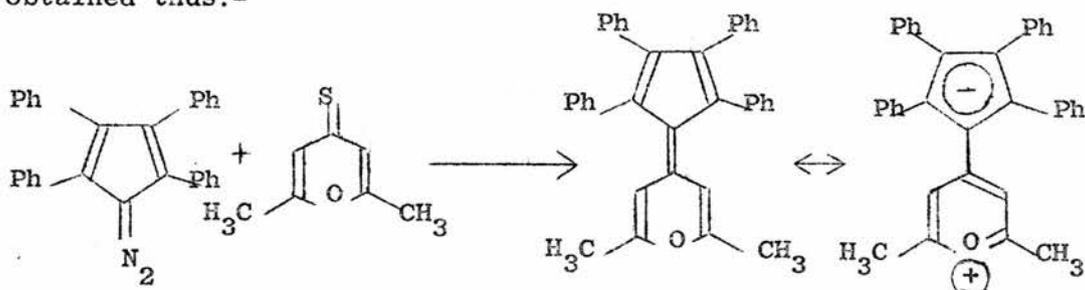
I am also grateful to Mr. Andrew Watson and Miss Joyce Ewing for assistance in determining spectra and to other members of the Technical Staff in the St. Andrews University Chemistry Department.

My thanks are also due to the Department of Scientific and Industrial Research for the award of a Research Studentship which enabled me to carry out this research.

SUMMARY

Synthetic routes leading to compounds having a cyclopentadienyliidene-pyran structure have been investigated and some of the properties of such compounds examined.

After a number of other possible synthetic routes had been examined, 4-tetraphenylcyclopentadienyliidene-2,6-dimethylpyran was obtained thus:-



The corresponding thiopyran and the pyran derived from 2,3,4-triphenyldiazocyclopentadiene were prepared by similar reactions. Evidence was found which suggested that these reactions, which were conducted in a high-boiling hydrocarbon solvent, proceed by initial decomposition of the diazo compound to the carbene followed by electrophilic attack on the sulphur atom and extrusion of sulphur.

The syntheses of phenylated diazocyclopentadienes from the diene was simplified, the use of phenyllithium in this reaction being eliminated. A new route to 2,3,4,5-tetraphenyldiazocyclopentadiene was established, involving the alkaline cleavage of 2,3,4,5-tetraphenylcyclopentadienone toluene-*p*-sulphonylhydrazone. Some electrophilic substitution reactions on 2,3,4-triphenyldiazocyclopentadiene were successfully carried out to give derivatives which were mono-substituted at the vacant position of the

five-membered ring. The position of substitution was demonstrated by the use of Nuclear Magnetic Resonance (N.M.R.) spectroscopy. In trifluoroacetic solution, the N.M.R. spectrum showed that the diazo compound was protonated in the ring, with resultant loss of aromaticity.

The ylidenepyranes were found to be stable crystalline solids, resistant to attack by bases. Reactions attempted included additions to the fulvene double-bond and electrophilic substitution reactions in the case of the triphenyl ylidenepyran. They are pseudo-bases and their most important reaction was that with acids; for instance, they formed stable perchlorates. N.M.R. spectroscopy showed that the ylidenepyranes formed only one conjugate acid, and the evidence suggests that protonation occurred at the position of the five-membered ring ortho to the pyrylium ring.

Reactions of the perchlorate of 4-tetraphenylcyclopentadienyliidene-2,6-dimethylpyran with bases were studied in some detail. According to basicity, reaction either regenerated the ylidenepyran or, in the cases of certain amines, gave rise to the corresponding dihydropyridine compound. N.M.R. and U.V. spectroscopy were used to elucidate the structures of these ylidenedihydropyridines and their conjugate acids.

A subsidiary topic which was investigated involved the use of hydrazine and Raney nickel as a general method of reducing oximes to amines. With certain exceptions, the method was found to be useful in the case of ketoximes.

CONTENTS

	Page
Declaration	(i)
Certificate	(ii)
University Career	(iii)
Publications	(iv)
Acknowledgements	(v)
Summary	(vi)

PART I

INTRODUCTION

[A] <u>AROMATIC CHARACTER</u>	1
[B] <u>AROMATIC DERIVATIVES OF CYCLOPENTADIENE</u>	
(1) Metal cyclopentadienides	6
(2) Cyclopentadienylides	8
(3) Heterocyclic analogues of sesquifulvalene	14
(4) Fulvenes	19
(5) Azulenes	20

PART II

DISCUSSION

[A] <u>DIAZOCYCLOPENTADIENES</u>	
(1) Synthesis of phenylated diazocyclopentadienes from the diene	23
Attempted extension to the synthesis of ylidenedihydropyridines	24
(2) Synthesis of phenylated diazocyclopentadienes from the dienone	24
Alkaline cleavage of toluene- <u>p</u> -sulphonylhydrazones	24
2,3,4,5-Tetraphenylcyclopentadienone toluene- <u>p</u> -sulphonylhydrazone	27

	Page
Alkaline cleavage of 2,3,4,5-tetra- phenylcyclopentadienone toluene- <u>p</u> - sulphonylhydrazone	28
Attempted one-stage synthesis of 2,3,4,5-tetraphenyldiazocyclopentadiene	29
Alkaline cleavage of dibenzyl ketone toluene- <u>p</u> -sulphonylhydrazone	30
2,3,4-Triphenylcyclopentadienone toluene- <u>p</u> -sulphonylhydrazone	30
(3) N.M.R. studies on 2,3,4-triphenyldiazo- cyclopentadiene	30
(4) Electrophilic substitution in 2,3,4- triphenyldiazocyclopentadiene	33
Bromination	34
Iodo-mercuration and iodination	35
Nitration	35
Diazo-coupling	36
(5) Reactions of 2,3,4,5-tetraphenyldiazo- cyclopentadiene with retention of nitrogen	36
Phenyl lithium	36
Hydrazine	36
Triphenylphosphine	37
β -Naphthol	39
[B] <u>PREMININARY ATTEMPTS TO SYNTHESISE CYCLOPENTADIEN- YLIDENE PYRANS</u>	
(1) Grignard reactions	40
Reaction between cyclopentadienyl magnesium bromide and 2,6-dimethyl-4-pyrone	41
Reaction between cyclopentadienyl magnesium bromide and xanthone	41
(2) Pyrylium ring formation by closure on to an acid chloride	41
Fluorene-9-carboxylic acid chloride	42
Cyclopentadiene carboxylic acid chloride	43

	Page
(3) Pyrylium ring formation by closure on to fluorene-9-aldehyde	43
(4) Michael condensation of 2,3,4,5-tetraphenylcyclopentadiene and salicylidene-acetophenone	44
The condensation with salicylidene-acetophenone	45
Attempted conversion of product	46
[C] <u>SYNTHESIS OF CYCLOPENTADIENYLIDENEPYRANS AND THIOPYRANS</u>	
(1) Reaction conditions	46
(2) Reaction mechanism	48
(3) Related reactions attempted with 2,3,4,5-tetraphenyldiazocyclopentadiene	53
2,6-Dimethyl-4-pyrone	53
Thiourea	53
m-Nitrobenzaldehyde	53
Acetic acid	54
Dibenzyl sulphide	55
(4) Reactions involving the tropylium ring	55
[D] <u>REACTIONS OF CYCLOPENTADIENYLIDENEPYRANS</u>	
(1) Structure and Stability	57
(2) Electrophilic substitution in the carbocyclic ring	60
Bromination	60
Iodo-mercuration and iodination	61
Diazo-coupling	61
(3) Additions to the fulvene double-bond	61
Phenyl lithium	62
Chlorine	63
Bromine	63
(4) Salt formation	63

	Page
[E] <u>REACTIONS OF CYCLOPENTADIENYLPYRYLIUM SALTS</u>	
(1) Formation and reaction with alkali	65
(2) Structure	65
(3) Attempted Diels-Alder additions	69
(4) Reactions of the tetraphenyl derivative with bases	69
Effect of the strength of the base	71
Benzylamine	72
<u>p</u> -Toluidine	73
Aniline	74
Phenylhydrazine	74
<u>unsymm</u> -Methylphenylhydrazine	76
Hydroxylamine; attempted reduction of product	76

PART III

EXPERIMENTAL

[A] <u>SYNTHESIS OF PHENYLATED DIAZOCYCLOPENTADIENES</u>	
(1) From the diene	
2,3,4,5-Tetraphenyldiazocyclopentadiene	79
2,3,4-Triphenyldiazocyclopentadiene	80
Attempted extension of the method to the synthesis of ylidenedihydropyridines :-	80
Cyclopentadiene and pyridine methiodide in diethylamine	
2,3,4,5-Tetraphenylcyclopentadiene and pyridine methiodide in diethylamine	
(2) From the dienone	
2,3,4,5-Tetraphenylcyclopentadienone toluene- <u>p</u> -sulphonylhydrazone	81

Alkaline cleavage of 2,3,4,5-tetra-phenylcyclopentadienone toluene- <u>p</u> -sulphonylhydrazone to 2,3,4,5-tetraphenyl-diazocyclopentadiene	82
Dibenzyl ketone toluene- <u>p</u> -sulphonylhydrazone	83
Alkaline cleavage of dibenzyl ketone toluene- <u>p</u> -sulphonylhydrazone	83
Attempted one-stage synthesis of 2,3,4,5-tetraphenyldiazocyclopentadiene	83
Reaction between 2,3,4-triphenylcyclopentadienone and toluene- <u>p</u> -sulphonylhydrazine	84

[B] PRELIMINARY ATTEMPTS TO SYNTHESISE CYCLOPENTADIENYLIDENEPYRANS

(1) Grignard reactions

Cyclopentadienyl magnesium bromide	85
Reaction between cyclopentadienyl magnesium bromide and 2,6-dimethyl-4-pyrone	85
Reaction between cyclopentadienyl magnesium bromide and xanthone	86
Oxidative cleavage of double-bond in the product	
Attempted reaction of the product with maleic anhydride	

(2) Ring-closure reactions

Reaction of fluorene-9-carboxylic acid chloride, mesityl oxide and perchloric acid	87
Reaction of fluorene-9-carboxylic acid chloride, mesityl oxide and anhydrous ferric chloride	87
Cyclopentadiene carboxylic acid chloride	87
3-Fluorenylpropiophenone	88
Reaction of 3-fluorenylpropiophenone, acetophenone and perchloric acid	89

(3) Michael condensation

Condensation of 2,3,4,5-tetraphenylcyclopentadiene and salicylidene-acetophenone 89

Attempted conversion of the product to the ylideneflavene 92

with chloranil

with perchloric acid

[C] SYNTHESIS OF CYCLOPENTADIENYLIDENEPIRANS

(1) Reactions of 2,3,4,5-tetraphenyldiazocyclopentadiene

2,6-Dimethyl-4-thiopyrone 91

2,6-Dimethyl-4-thiopyran-thione 92

Xanthione 93

(2) Reactions of 2,3,4-triphenyldiazocyclopentadiene

2,6-Dimethyl-4-thiopyrone 93

2,6-Dimethyl-4-thiopyran-thione 94

(3) Reactions of diazocyclopentadiene

Decomposition in boiling benzene 94

2,6-Dimethyl-4-thiopyrone 95

[D] OTHER REACTIONS OF PHENYLATED DIAZOCYCLOPENTADIENES

(1) Reactions of 2,3,4,5-tetraphenyldiazocyclopentadiene

Decomposition in boiling mesitylene 96

2,6-Dimethyl-4-pyrone 96

Thiourea 97

m-Nitrobenzaldehyde 97

Acetic acid 97

Dibenzyl sulphide 98

Phenyl lithium 98

Hydrazine 99

	Page
Triphenylphosphine	99
β -Naphthol	100
(2) Reactions of 2,3,4-triphenyldiazocyclopentadiene	
Bromination	100
Iodo-mercuration and iodination	101
Nitration	102
Diazo-coupling	102
Trifluoroacetic acid	102
[E] <u>REACTIONS OF CYCLOPENTADIENYLIDENEPYRANS</u>	
(1) Reactions of 4-tetraphenylcyclopentadienyldiene-2,6-dimethylpyran	
Chromium trioxide	103
Perchloric acid	103
Sulphuric acid	104
Chlorine	104
Bromine	104
Phenyl lithium	105
Maleic anhydride	105
Potassium hydroxide solution	105
Ammonia	106
Benzylamine	106
(2) Reactions of 4-(2',3',4'-triphenylcyclopentadienyldiene)-2,6-dimethylpyran	
Perchloric acid	106
Bromination	106
Iodo-mercuration and iodination	107
Diazo-coupling	108
[F] <u>REACTIONS OF 4-TETRAPHENYLCYCLOPENTADIENYL-2,6-DIMETHYL-PYRYLIUM PERCHLORATE</u>	
Maleic anhydride	108
Cyclopentadiene	108

	Page
Potassium hydroxide solution	109
Potassium hydrosulphide solution	109
Sodium cyclopentadienide	109
Hydrazine	110
Diethylamine	110
Isopropylamine	110
Ammonia	111
Benzylamine	111
Phenylhydrazine	112
<u>unsymm</u> -Methylphenylhydrazine	112
Hydroxylamine; attempted reduction of product	112
<u>p</u> -Toluidine	113
Aniline	114
<u>p</u> -Aminobenzoic acid	114
<u>p</u> -Nitroaniline	114
[G] <u>REACTIONS INVOLVING THE TROPYLIUM RING</u>	
(1) Tropylium perchlorate	115
(2) Ditropyl ether	115
(3) Tropone	115
(4) Tropone and phosphorus pentasulphide	116
(5) 2,3,4,4-Tetraphenyldiazocyclopentadiene and tropylium perchlorate	116
[H] <u>ULTRA-VIOLET SPECTRA</u>	117
[I] <u>NUCLEAR MAGNETIC RESONANCE SPECTRA</u>	120
<u>APPENDIX</u>	
REDUCTION OF OXIMES BY MEANS OF HYDRAZINE AND RANEY NICKEL	121
REFERENCES	124

SOME HETEROCYCLIC ANALOGUES OF SESQUIFULVALENE

PART I

INTRODUCTION

[A] AROMATIC CHARACTER

The development of the idea of aromaticity dates from Kekule's proposed cyclic structure for benzene.^{1,2} The concept was soon extended to include fused ring systems such as anthracene and phenanthrene and heterocyclic compounds such as furan, pyrrole and pyridine. These compounds have in common, in varying degree certain properties which distinguish them from other compounds, and which can therefore be regarded as criteria of aromaticity :-

- (1) Ease of formation of aromatic rings in the most varied reactions.
- (2) Stability of the cyclic system once formed.
- (3) Relative difficulty of effecting addition at double bonds.
- (4) Tendency to undergo electrophilic substitution reactions.
- (5) Characteristic properties of certain substituent groups (e.g. acidic aromatic hydroxyl group, weakened basicity of amino groups, lack of reactivity of halogen, etc.)

In considering aromaticity, these general properties have to be taken as a whole, as all "aromatic" compounds show variations relative to benzene. For instance, whereas pyridine is less reactive to electrophilic attack than benzene, pyrrole is more so. In benzene itself, monosubstitution by an electron withdrawing group will decrease susceptibility to electrophilic attack, whereas an

electron-donating group will enhance it. Conversely, in open-chain poly-enes some modification of double-bond character due to conjugation is evident.

Just as these chemical properties are not shown to an equal degree by all "aromatic" compounds, neither are various physical and structural properties. The latter include bond-length of C-C bonds (intermediate between single and double bonds), the equivalence of carbon atoms, the planar (or almost planar) ring, absorption of light at long wavelengths, ready polarisability, anisotropy of diamagnetic susceptibility and high resonance energy.

Notable amongst many hypotheses as to the structure of benzene were those of Kekule³ (a tautomeric equilibrium between the two possible forms having alternate single and double bonds) and Thiele⁴ (partial valencies). While the former foreshadowed theories of resonance, the latter was more in line with modern orbital theory. On either theory, however, aromatic properties would also be expected of cyclooctatetraene, but Willstätter⁵ found its properties to be entirely olefinic; furthermore, he was unable even to prepare cyclobutadiene. It was clearly not a sufficient criterion to have a cyclic system of formally conjugated bonds and Bamberger⁶ postulated that the stability of benzene derived from its six "residual valencies". Robinson⁷ suggested that the six electrons of benzene (one from each atom) form a stable system responsible for its aromatic character. This hypothesis would also include such molecules as pyrrole (four electrons from double-bonds together with a lone pair from nitrogen) and the cyclopentadienide anion, whilst excluding cyclobutadiene (only four electrons) and cyclooctatetraene (eight electrons).

The development of quantum mechanical methods in the 1930's brought a clearer insight into the problem, the contribution by Hückel^{1,2} forming the basis for the recent development of ideas

concerning aromaticity. He used the molecular orbital method, regarding all π -electrons in a conjugated system as occurring in common molecular orbitals, the number of such orbitals being equal to the number of atoms in the conjugated system. The number of bonding, antibonding and non-bonding orbitals was calculated by a solution of the wave-equation, not more than two electrons being allocated to each such orbital in accordance with the Pauli Exclusion Principle.

Calculation shows that benzene contains three bonding and three anti-bonding orbitals, and in the ground state the six π -electrons will occupy the lowest energy levels i.e. the three bonding orbitals. The π -electron energy of three isolated double bonds may be calculated similarly, and exceeds the energy in benzene by an amount which is the energy of conjugation of the aromatic ring. The unusual stability of benzene and other compounds containing a closed system of six π -electrons is thus related directly to the fact that the electrons all occupy bonding orbitals (i.e. the removal of an electron requires energy expenditure) and that there are no un-filled bonding orbitals (i.e. addition of an electron requires energy expenditure).

Hückel also dealt with the conditions under which five- and seven-membered rings can possess aromatic character. The five-membered ring C_5H_5 contains three bonding and two anti-bonding molecular orbitals. The radical C_5H_5 contains an unfilled bonding orbital, the cation $C_5H_5^+$ two, whereas in the anion $C_5H_5^-$, all are filled; in this entity the π -electrons form a closed sextet, and it should be the most stable. A satisfactory mathematical backing was thus adduced for the tendency of cyclopentadiene to form metal cyclopentadienides of considerable stability. These, and other aromatic derivatives of five-membered carbocyclic rings are discussed in subsequent sections.

A closed electron shell is possible not only in systems having six π -electrons, but also in those having two, ten, fourteen, etc. A rule may be stated in general that "Monocyclic conjugated polyolefins having the symmetry of a regular polygon possess a closed electron shell and consequently aromatic stability if the number of π -electrons is $4n + 2$ (where n is any integer)". This rule is in agreement with the experimental findings mentioned earlier that with respect to cyclobutadiene and cyclooctatetraene neither of which have $4n + 2$ π -electrons. Since there would be no resonance stabilisation if the cyclooctatetraene molecule adopted a planar configuration, it takes up the buckled form, this being the less strained. These systems, together with heptalene, pentalene and other completely conjugated cyclic systems not satisfying the Hückel condition, are termed pseudo-aromatic.

An interesting ten π -electron system,⁸ the di-potassium salt of cyclooctatetraene, has been prepared recently.⁸ That this ion can be prepared and is stable in solution is strong evidence in favour of Hückel's theory.

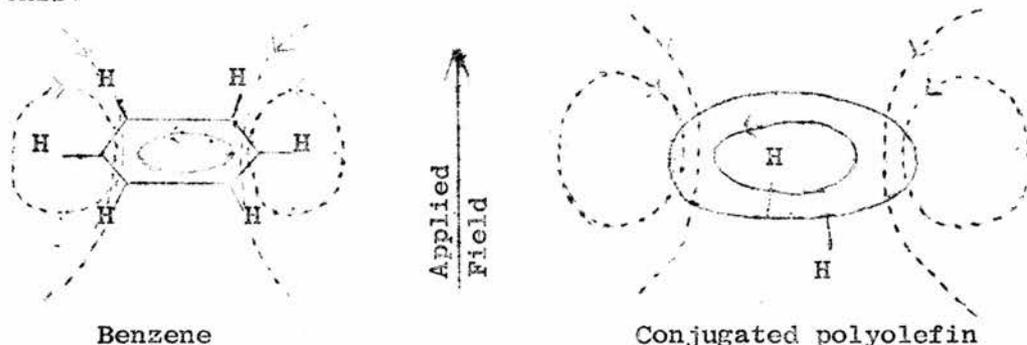
A second important criterion which must be met before the π -electrons of a poly-olefin can interact to give an aromatic system is that the molecule should be planar. Mislow⁹ pointed out that, amongst macrocyclic poly-olefins, only those having $x \geq 30$ in C_xH_x could be completely planar, due to transannular interaction. However, Sondheimer⁸ states that a study of scale drawings indicates that the C_{18} annulene (i.e. conjugated poly-olefin) is the first member after benzene in which these interactions are not extreme, and the deviation from coplanarity would not be great. He has synthesised this compound and presents evidence that it possesses aromatic character although addition reactions occur.

Resonance energies have frequently been quoted as a measure of aromaticity. They are equal to the difference between the heats of

combustion of a molecule and its constituent atoms, or between the heat of hydrogenation of the molecule and an equal number of non-resonating double-bonds. The values obtained for a particular compound can vary quite widely depending on the method used in the calculation. It is found in general that benzenoid aromatics have resonance energies in the region of 6 kcal./mole per π -electron.

Bond lengths in aromatic compounds, although lying between those of single and double-bonds, are not of much value in assessing aromaticity. Even in aromatic compounds of high resonance energy (e.g. naphthalene) individual bonds vary greatly in length.

Recently, the development of Proton Magnetic Resonance spectroscopy as a chemical weapon ¹⁰⁻¹⁴ has made possible a more definitive and quantitative criterion of aromaticity, being the ability to sustain an induced ring-current under the influence of an applied magnetic field. Diamagnetic anisotropy, mentioned at the outset as one of the physical properties exhibited by aromatic compounds is a manifestation of this.



In the case of benzene this induced field is responsible for the de-shielding of the ring protons and for the paramagnetic shift of the protons in methyl substituents.

In macrocyclic poly-olefins if planar, however, some of the protons will point into the ring and will absorb at very high field, while those pointing out will absorb at very low field. Jackman et al.¹² have shown by this method that the C₁₈ annulene is planar and aromatic, whereas the C₁₄ and C₂₄ ones are not.

Elvidge and Jackman¹¹ have confined their use of N.M.R. to certain benzenoid compounds and have used it to assess the degree of aromaticity in 2-pyridones and related systems. The ring current de-shielding effect (calculated relative to a non-aromatic model) compared with the ring de-shielding due to a benzene ring indicates that 2-pyridone, for example, has a fractional aromaticity of 31%.

Nuclear Magnetic Resonance spectra can thus give useful quantitative information to explain observed chemical facts, or, as in the case of the poly-olefins, provide a measure of aromaticity which is not easily obtained experimentally due to their instability.

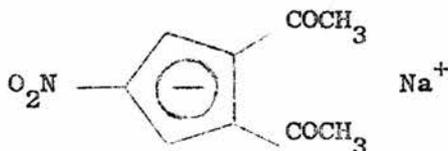
[B] AROMATIC DERIVATIVES OF CYCLOPENTADIENE

(1) Metal Cyclopentadienides

The tendency of cyclopentadiene to lose a proton to form the aromatic cyclopentadienide anion is indicated by the fact that cyclopentadiene is a stronger acid than other hydrocarbons with the exception of acetylenes. Its pK_a value of 19¹⁵ (as shown by its conversion into the potassium ion by potassium tertiary butoxide) compares with 35 for diphenyl methane, for example.

Potassium cyclopentadienide was prepared as long ago as 1901 by Thiele,¹⁶ by the action of potassium on cyclopentadiene, although he did not comment on the structure. Salts have since been obtained with alkali, alkaline-earth and rare-earth metals, and with manganese. Although the salts inflame in air and are extremely reactive, they are stable in non-hydroxylic solvents or under an

inert atmosphere. When electron-withdrawing groups are attached to the ring, the salts become stable in air e.g. Hale¹⁷ prepared the salt:-



The cyclopentadienide anion is formed³⁶ in solution in the presence of bases of moderate strength e.g. diethylamine and ethanolamine.

That these salts are entirely ionic in character is supported by physical data. The magnetic moment of the manganese salt is very close to that calculated^{19,20} for Mn²⁺ and a solution of the sodium salt in liquid ammonia has considerable conductivity.¹⁹ The equivalence of the five carbon atoms is shown in dicyclopentadienyl manganese by X-ray analysis,²¹ which shows the metal ion equidistant from all of them, the molecule having a ferrocene-like anti-prism structure.

Cyclopentadiene shows two multiplets in its Proton Magnetic Resonance spectrum¹⁰ at + 0.34 and + 4.4. p.p.m. relative to benzene as internal standard, arising from the olefinic and methylene protons respectively. The spectrum of sodium cyclopentadienide, on the other hand, consists of only one sharp peak at + 1.85 p.p.m. relative to benzene, due to the protons of the ion. This shift is thought to be due to electron density differences on the carbon atoms rather than any difference in the magnitude of the ring currents in the cyclopentadienide ion and benzene.

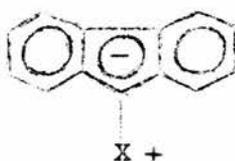
The anion shows a reactivity towards electrophilic attack markedly higher than that of benzene, but due to its aromatic nature it is much more stable than other carbanions. Water and alcohol decompose the salts, while carbon dioxide²² forms the carboxylic acid. Its high reactivity is also illustrated by the fact that deuterium exchange occurs readily,¹⁸ even in an alkaline medium, whereas pyrrole undergoes deuterium exchange only at $\text{pH} < 1$.²³

(2) Cyclopentadienylides

The cyclopentadienide ring can exist in the form of a dipolar molecule (I) as well as in salts, compounds of this type being termed cyclopentadienylides.



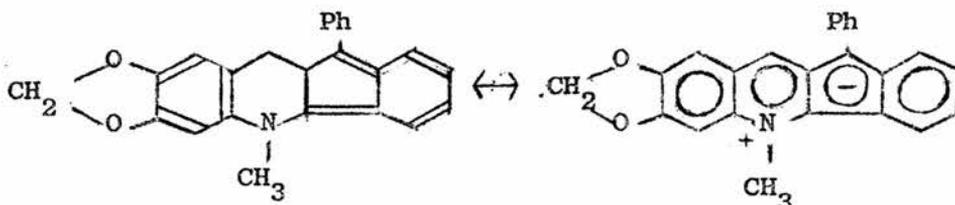
(I)



(II)

- (a) X = N₂
- (b) X = NMe₃
- (c) X = SMe₂
- (d) X = PPh₃

Armit and Robinson⁷ pointed out that in anhydronium bases such as (III), the five-membered carbocyclic ring could be stabilised by the sharing of a lone pair from the pyridine nitrogen atom (IV) as it thereby gains an aromatic sextet of electrons.



(III)

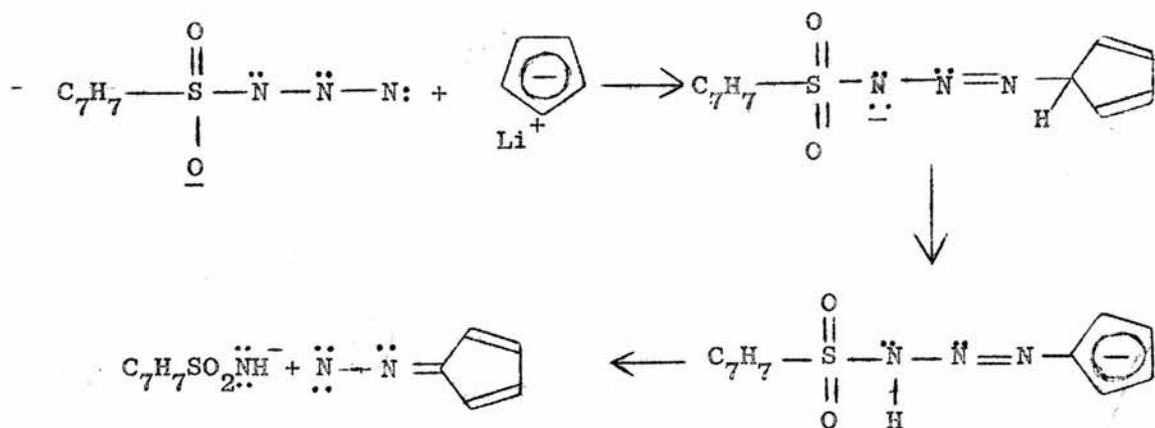
(IV)

It is only in recent years that examples of type (I) have been prepared, but fluorenylidene analogues (II) have been known longer. Ingold and Jessop²⁴ suggested a structure of type (IIb) for the transitory purple intermediate in the alkaline degradation of fluorene 9-trimethylammonium salts. They also isolated²⁵ the more stable fluorene 9-dimethylsulphonium compound (IIc), although the S-C bond is weak and the substance loses methyl sulphide readily. In the case of both compounds, more recent²⁶ dipole moment measurements show that they are highly polar, although in the case of the sulphonium compound (IIc) a fulvene structure is possible and will contribute to the hybrid, as sulphur can form a fifth valency with its vacant d-orbital. This is not possible in the case of the trimethylammonium compound which is an aromatic betaine.

Since this work was published many other fluorenylides have been prepared,²⁶⁻²⁹ most being unstable. The electron-withdrawing effect on a nitro group attached to the fluorene nucleus has a stabilising effect.²⁷ Diazofluorene³⁰ (IIa), prepared by oxidation of the hydrazone of fluorenone has a partial fluorenylide structure, although this was not recognised at the time of its first preparation, as does fluorenone peroxide.³¹

The first example of an ylide derived from cyclopentadiene was diazocyclopentadiene³³ (Ia), prepared in 1953 by Doering and DePuy.

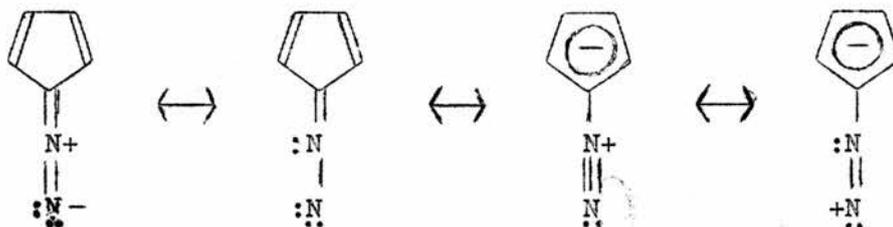
They prepared this compound by the action of p-toluene sulphonyl azide on cyclopentadienyl lithium, according to the following scheme:-



In this reaction the p-toluene sulphonyl azide satisfies three conditions:

- (1) The negative charge introduced by the carbanion is stabilised
- (2) The proton at C₁ of the ring can transfer to the exocyclic group prior to
- (3) The breakaway of the stable sulphonamide ion.

The structure of the diazocyclopentadiene was established by analysis, molecular weight determination and catalytic hydrogenation to cyclopentanone hydrazone. A strong bond in the I.R. at 4.80μ was ascribed to the $\overset{+}{\text{N}}\equiv\text{N}^-$ vibration as this region is normally assigned to triple bonds or cumulated double bonds, neither being possible in the ring. The structure of the compound may be written as:-



The U.V. maximum at 295 $m\mu$ with a long trailing absorption into the visible (accounting for the red colour of the pure liquid), is consistent with a highly conjugated system.

Pauson and Williams³⁴ have since applied this reaction satisfactorily to the synthesis of tetra- and triphenyldiazocyclopentadienes, both compounds again showing the characteristic I.R. absorption at ca. 4.80 μ . Preliminary details³⁵ of a synthesis of diazotetraphenylcyclopentadiene involving alkaline cleavage of the toluene-p-sulphonylhydrazone of tetraphenylcyclopentadienone have been given, and the method is discussed in Part II of this thesis.

A considerable simplification of the method of Doering and DePuy was described recently by Weil and Cais³⁶ who mixed cyclopentadiene and p-toluene sulphonyl azide with a base (preferably diethylamine or ethanolamine) and allowed to stand for some time at 0°C. After addition of water, the product was extracted into pentane, and its yield estimated by isolating the phosphazine⁷⁴ formed by reaction with triphenylphosphine. The action of the base is to remove a proton from the hydrocarbon, making the use of phenyl lithium unnecessary.

Diazocyclopentadiene has been decomposed by irradiation at low temperatures³⁷ and although no direct evidence of the formation of the cyclopentadienyl carbene was procured, the identification spectroscopically of fulvalene in the products makes it a likely intermediate. Organolithium reagents react³⁸ to give salts, which in turn give hitherto inaccessible azoferrocene derivatives when treated with ferrous chloride.

Cram and Partos³⁹ have made a detailed study of the electrophilic substitution reactions of diazocyclopentadiene, which take place without destruction of the ylide π -electron system. Nitration with benzoyl nitrate in acetonitrile at 0°C produced

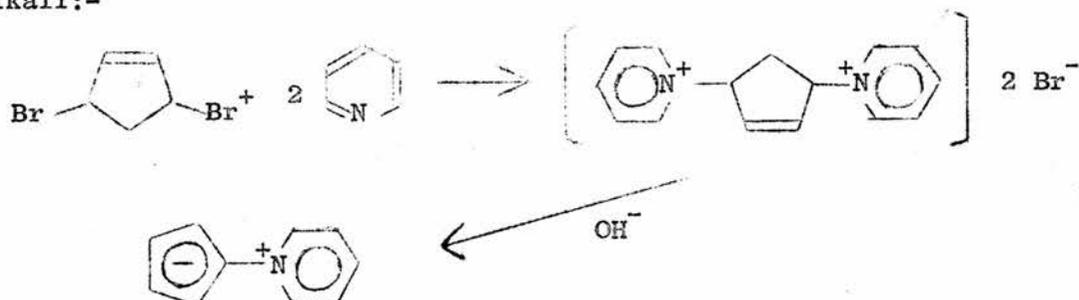
two monosubstituted derivatives, the 2-isomer predominating over the 3-isomer by a factor of two. Benzene diazonium tetrafluoroborate gave the 2-substitution product, whereas N-bromosuccinimide gave tetrabromodiazocyclopentadiene. Mercuration produced an unstable 2,5-diiodomercuri derivative which was readily converted to the diiodo compound. 1,2- addition of diazocyclopentadiene to tetracyanoethylene took place to give an unstable acid which readily lost the elements of hydrogen cyanide yielding 2-(tricyanoethylene)-diazocyclopentadiene. With dimethyl acetylene dicarboxylate, diazocyclopentadiene underwent 1,4-dipolar addition to produce a fused ring system. No evidence was obtained of the formation of Diels-Alder adducts.

In these reactions, the position of substitution was established using N.N.R. spectroscopy. Diazocyclopentadiene exhibited two multiplets of equal area at 3.3 and 4.2 τ . Since the electron-withdrawing diazo group will undoubtedly exert a stronger deshielding effect on the 2,5-positions, the 3.3 τ bond is assigned to these protons, the 4.2 τ bond to the 3,4-protons. It is of interest to note that the completely polar cyclopentadienide ion absorbs at 4.2 τ ,¹⁰ and consequently the fulvene structure must make only a very small contribution to diazocyclopentadiene. Thus almost complete carbanion character exists in the ring.

Trimethylammonium⁴⁰ and triphenylphosphonium cyclopentadienyliide⁴¹ have been prepared. Some electrophilic substitution reactions in the latter have been effected, including diazo coupling,⁴¹ 2,5-dimercuration⁴² and tribromination.⁴²

In 1955, Lloyd and Sneezum^{43,44} prepared pyridenium cyclopentadienyliide by the action of two molecules of pyridine on

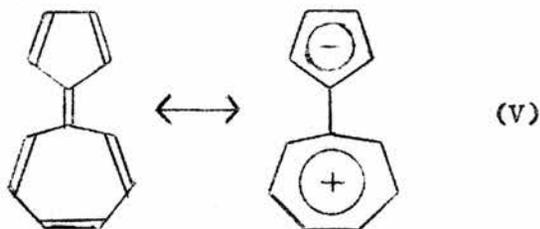
one molecule of dibromocyclopentene, followed by treatment with alkali:-



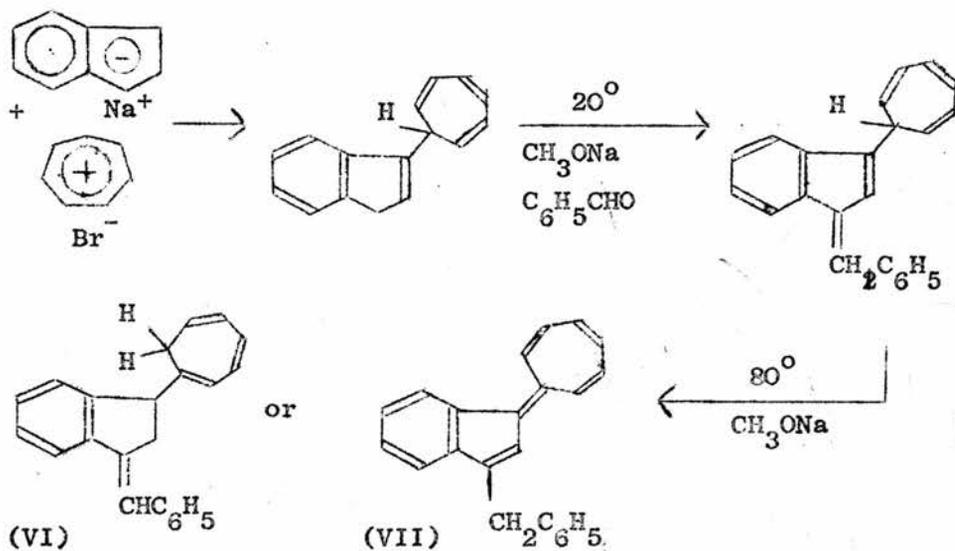
The product is a red-brown crystalline solid which readily tarnishes in air, but is quite stable under nitrogen. An interesting property is the diversity of colours of its solutions, which range, according to the polarity of the solvent, from colourless in acidic aqueous solutions to blush-purple in light petroleum. Many related compounds were prepared, using α, β and γ -picolines, 2,6-lutidine and 2,4,6-collidine as bases and indene and tetraphenylcyclopentadiene as the hydrocarbons. A modified procedure was used for indene^{29,44} starting from the mono-bromo derivative, but annelation appears to reduce the stability of the resultant ylide. The structure of pyridinium cyclopentadienylidene follows from its mode of preparation, physical properties and its quantitative hydrogenation to N-cyclopentylpiperidine.

In these compounds the nitrogen is incapable of forming a fifth covalent bond, so that the fulvene structure is impossible. As a result, their dipole moments are very high (e.g. pyridinium cyclopentadienylidene has a dipole moment of 13.5 D.⁷⁵)

(3) Heterocyclic analogues of sesquifulvalene



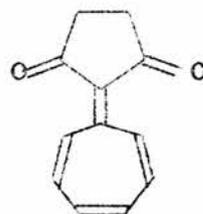
Pullman et al,⁴⁵ on the basis of molecular orbital calculations, predict a large contribution from the dipolar canonical form in cyclopentadienylenecycloheptatriene ("sesquifulvalene") (V). This canonical form contains the aromatic cyclopentadienide and tropylium nuclei, and as no steric factors are involved, the compound should be stable. Sesquifulvalene has not been synthesised yet; reaction of tropylium bromide and sodium cyclopentadienide gives the dihydro derivative which cannot be dehydrogenated. However, Prinzbach⁴⁶ has succeeded in dehydrogenating 11, 12 - dihydro 7,8,9,10-tetraphenylsesquifulvalene to tetraphenylsesquifulvalene using haloquinone, while the 8,9-diphenyl 11,12-dihydro compound gives a stable complex with the dehydrogenating agent. He prepared another⁴⁷ sesquifulvalene by a route which obviates the need for the dehydrogenation step, thus:



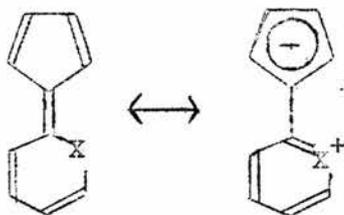
The final product was shown by N.M.R. spectroscopy to have structure (VII) rather than (VI).

Despite the prediction by Pullman *et.al.*,⁴⁵ further evidence⁴⁸ that sesquifulvalene is not highly stabilised is that the ketone (VIII) does not exist in the di-enolic form.

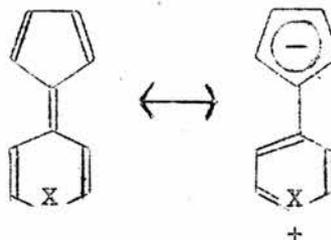
Iso- Π -electronic with the unknown sesquifulvalene are heterocyclic compounds (IX) and (X) where X = NR, O or S, and they would be expected to show some similarity in properties.



(VIII)



(IX)

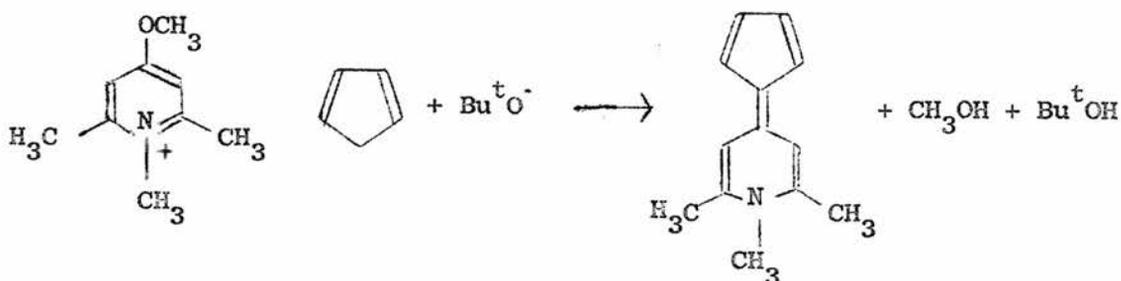


(X)

The first compounds known of the kind were 4-cyclopentadienylidenedihydropyridines, [(X); X = $\text{>NCH}_2 \cdot \text{C}_6\text{H}_5$]⁴⁹ and [(X); X = $\text{>N} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_3\text{Cl}_2$ -2,6]⁵⁰ obtained by dehydrogenative addition of cyclopentadiene to the appropriate pyridinium salt. That the benzyl compound had orientation (X) rather than (IX) was established⁵¹ by degradation and an unambiguous synthesis⁵² from 1-benzyl-4-bromopyridinium bromide.

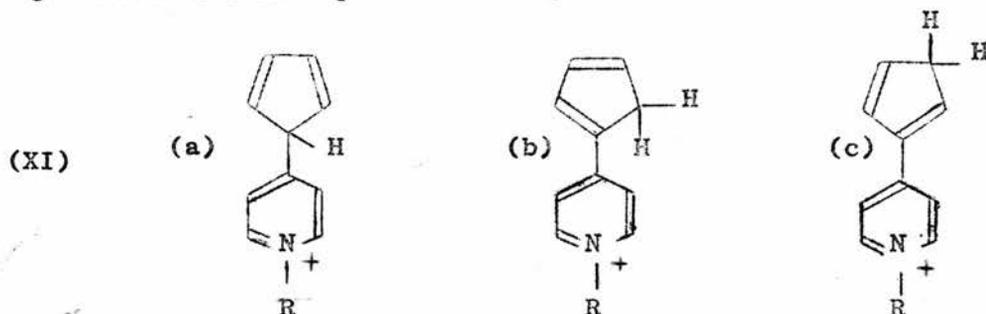
Boyd^{53,54} has prepared a number of compounds of type [(X); X = >NCH_3 or NBu^n] including indenylidene and fluorenylidene analogues, and ones having 2,6-dimethyl substituents in the pyridinium ring, by what appears to be a general method.

It involves condensation of a 4-alkoxy or 4-aryloxy pyridinium salt with a cyclopentadiene hydrocarbon in t-butyl alcohol in the presence of potassium t-butoxide e.g.



These compounds behave as typical anhydro bases, dissolving in dilute acids to give colourless solutions from which they are regenerated on basification. The stability of the products varied widely, the 4-cyclopentadienylidene compounds decomposing within a few minutes, the fluorenylidene and indenylidene compounds decomposing only in solution (but cf. Ref. ⁵²). The low solubilities of the N-methyl compounds prevented the determination of their N.M.R. spectra, but this was not the case with the N-butyl compounds. These spectra confirmed the assigned structure, coincident resonances of the 2- and 6- methyl protons and of the 5- and 7- ring protons being evidence for the axis of symmetry.

The fact that the bases gave colourless solutions in acids indicated that they are protonated in the five-membered ring, there being three structural possibilities:

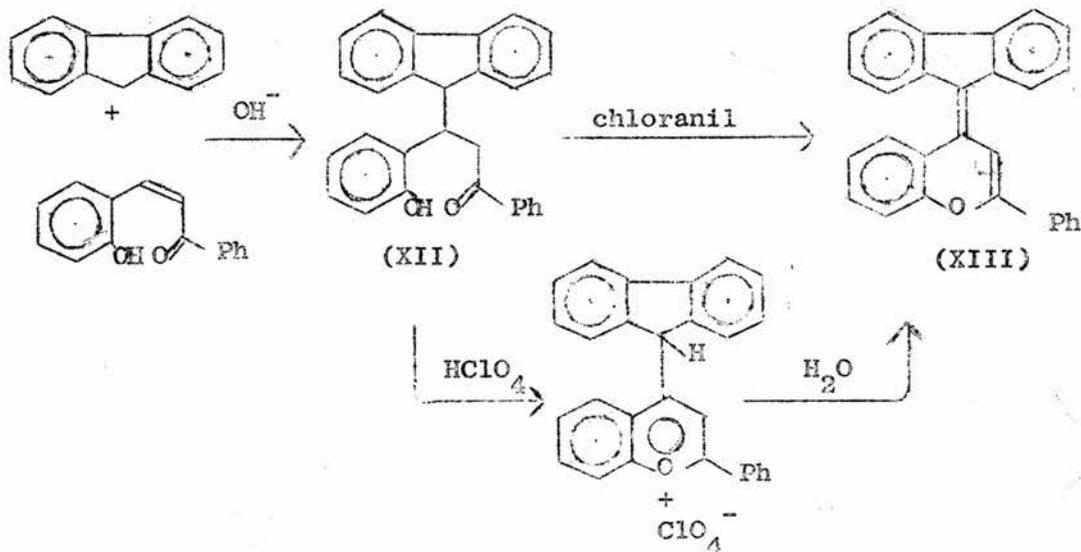


The structure could not be assigned purely on the basis of U.V. maxima, but an examination of the N.M R. spectrum showed that (XI) exists as a mixture of isomers (b) and (c).

The first 2-cyclopentadienylidenedihydropyridines [(IX); X = NR] reported⁵⁵ were benzo-derivatives obtained by dehydration and methylation from 1-(2'-pyridyl)-1-indanol and 9-(2-pyridyl)-9-fluoreno1. The fluorenylidene derivative was unstable to heat and light. 1-methyl-2-cyclopentadienylidene-1,2-dihydroquinoline is also known.⁵⁶

Berson et al.⁵⁷ obtained the parent 1-methyl-1,2-dihydropyridine [(IX); X = NCH₃] by reaction of 2-bromopyridine methiodide (1 mole) with sodium cyclopentadienide (2 moles) in 1,2-dimethoxyethane. Catalytic hydrogenation converted the product into 1-methyl 2-cyclopentylpiperidine. The position of the long wave-length absorption in the visible spectrum of this compound compared with that of its benzo and dibenzo analogues mentioned above falls in the same sequence as that expected theoretically in cyclopentadienide < indenide < fluorenylidene. This sequence is in qualitative agreement with the fact that the electronic distribution in these compounds is similar to that predicted for the parent sesquifulvene.

In the oxygen series, no compounds of type [(IX); X = O] are known, but some benzo analogues of 4-cyclopentadienylidenepyran [(X); X = O] have been reported.^{54,58} Schönberg⁵⁸ obtained 2,6-dimethyl-4-fluorenylidene pyran by refluxing 2,6-dimethyl-4-thiopyrone and diazofluorene in benzene for several hours, but did not study the product further. Boyd and Jackman⁵⁴ synthesised 4-9'-fluorenylidene flav-2-ene by a Michael Condensation of fluorene with salicylidene acetophenone, followed by dehydration, thus:-



The I.R. spectrum of (XII) exhibited intense absorption at 1670 cm^{-1} , showing that it had the keto-phenol rather than the isomeric hemiketal structure. 4-indenylidene flav-2-ene was synthesised in a similar manner, but with greater difficulty. These two compounds could not be obtained by reaction of the fluorenone with fluorenyl-lithium or indenyl magnesium bromide respectively.

Attempts by Boyd and Jackman⁵⁴ to obtain the non-annelated compound by reaction of Grignard reagents with 2,6-dimethyl-4-pyrone failed, pyrylium salts being the ultimate products. Whereas reaction of sodium cyclopentadienide with a 4-alkoxypyridinium salt is a standard synthesis^{53,54} of 4-cyclopentadienylidene dihydropyridines, an analogous reaction does not occur in the case of pyrylium salts, which are more subject to ring-opening. Thus, the product of reaction of sodium cyclopentadienide and 4-methoxy-2,6-dimethyl pyrylium perchlorate was 6-methoxy-4,8-dimethylazulene, subsequent upon attack at C-2 rather than C-4.

A tetrabenzo analogue of [(X); X = S] was obtained by Schönberg⁵⁹ on refluxing diazofluorene with thioxanthione in

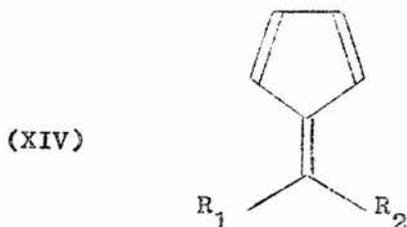
benzene.

The work described in this thesis was undertaken with a view to synthesising some non-annulated 4-cyclopentadienyldenepyran and -thiopyran compounds [(X); X = O or S], and examining their properties.

2,6-dimethyl-4-tetraphenylcyclopentadienyldenepyran and -thiopyran were obtained by reacting diazotetraphenylcyclopentadiene with 2,6-dimethyl-4-thiopyrone and 2,6-dimethyl-4-thiopyran-thione, respectively, in a high-boiling solvent. Brief details of the syntheses have been published.³⁵ Reactions of the ylidenepyran (a stable red crystalline solid) or its perchlorate which were studied included additions at the fulvene double bond, and attack by bases at the C-2 position of the heterocyclic ring. The latter provided a route to 4-tetraphenylcyclopentadienyldene-1-alkyl-1,2-dihydropyridines and related compounds.

2,6-dimethyl-4-1'-(2',3',4'-triphenylcyclopentadienyldene)-pyran was synthesised by a method similar to that used for the tetraphenyl compound, and some electrophilic substitution reactions at the C-5' position of the five-membered ring were attempted.

(4) Fulvenes



Cyclopentadiene reacts with aldehydes and ketones in an alkaline medium to form fulvenes.⁶⁰ The parent compound (XIV, R₁ = R₂ = H) has been isolated only very recently,⁷⁰ but a large number of

analogues have been studied in considerable detail. Fluorene and indene condense under the conditions specified much less readily, no doubt because annelation reduced the symmetry and stability of the ion. In general, condensation of aliphatic aldehydes is not successful, the products tending to resinify. A second method which has been used in the synthesis of fulvenes is by reacting Grignard reagents with fulvene ketones.

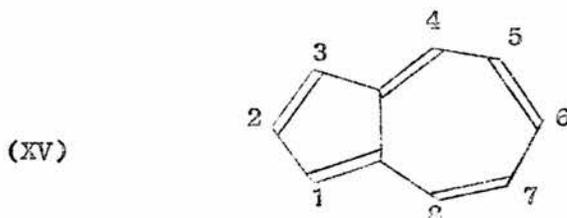
Whereas in the case of the ionic cyclopentadienides formation of the aromatic ring requires the heterolyses of a σ -bond, this is attained in the fulvenes by the energetically less difficult heterolyses of a π -bond. This tendency has an appreciable effect on the structure of the fulvenes as shown ⁶¹ by their dipole moments (e.g. 1.48 D for dimethyl fulvene). The five-membered ring acquires some negative charge, and therefore some degree of aromatic character. Calculation by molecular orbital methods ⁶² provides electron density values in accordance with these dipole moments, while valence-bond calculations ⁶³ indicate that no purely single or double bonds exist in the ring. Introduction of an electron donor substituent joined to the ring by a conjugated path will favour the dipolar form and strengthen aromatic character in the ring e.g. in 5-furyl fulvene ⁶⁴ ($\mu = 1.68$ D) and in 6-p-(NN-dimethylaminophenyl)-fulvene. ⁶⁵

The polarity of the fulvene double-bond is shown in various chemical properties. Thus, lithium aluminium hydride causes reduction of the bond ⁶⁶ and addition of organo-metallic compounds such as phenyl lithium takes place. ⁶⁷ Fulvenes can react either as dienes or as dienophiles in Diels Alder additions.

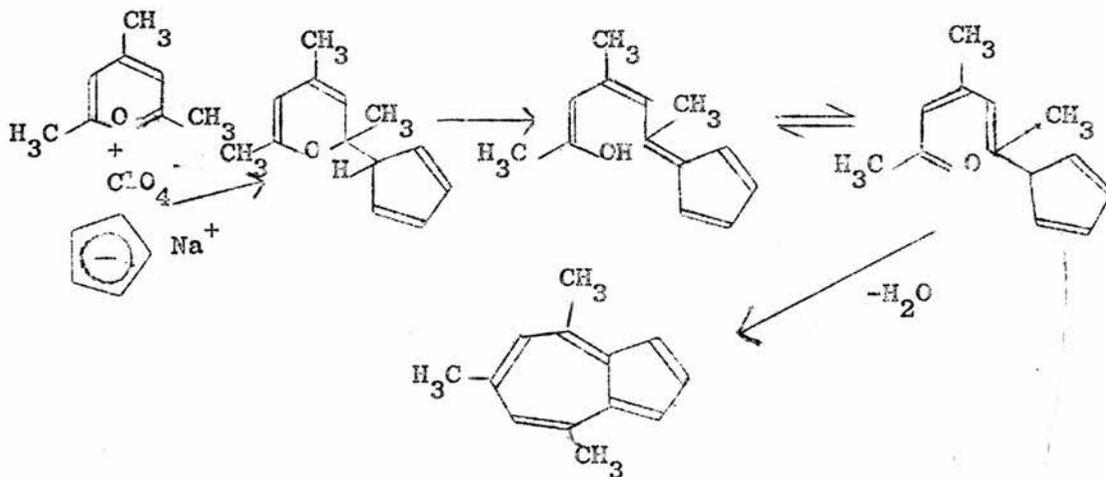
(5) Azulenes

Reduced azulenes occur widely in nature, but the first synthesis of an azulene was by Plattner and St. Pfau ⁶⁸ in 1936,

who were also the first to put forward what is now regarded as the correct structure (XV).



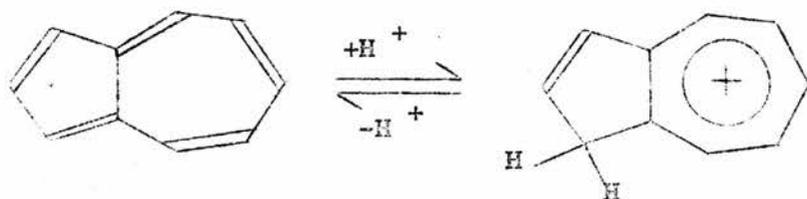
Early syntheses all involved a dehydrogenation step, but some recent methods obviate this. For instance, this reaction occurs ⁶⁹ even at room temperature:



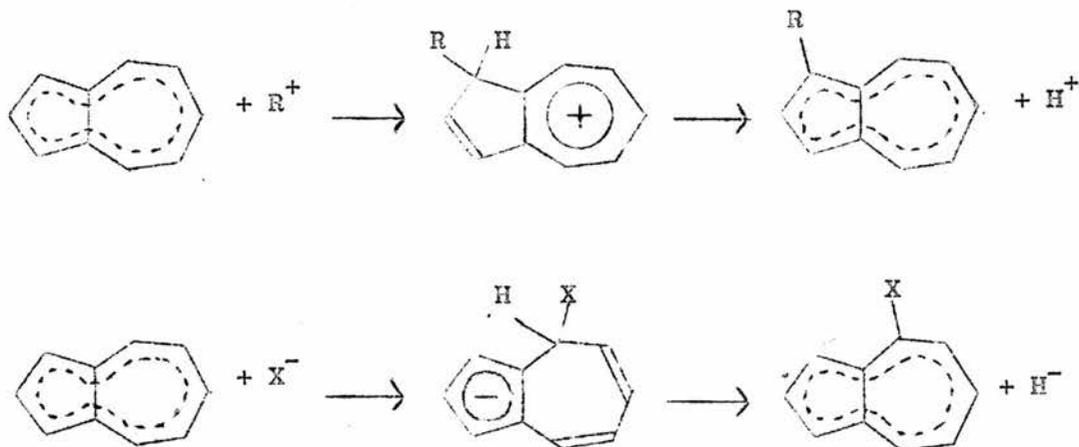
Azulene is an intensely blue solid, iso- π -electronic with naphthalene, to which it is irreversibly isomerised on heating.⁷¹ The aromatic character of azulene is confirmed by its experimentally determined resonance energy of 45 kcal./mole, and explains its ease of formation in a wide range of reactions.

The tendency of the five-membered ring to be converted into the cyclopentadienide anion and the seven-membered ring into the tropylium cation is reflected in the dipole moment of 1.0 D.

The cyclopentadienide character of the five-membered ring is shown by the readiness with which it undergoes electrophilic substitution, first at C-1, then at C-3. Mononitration is effected by copper nitrate in acetic anhydride^{72,73} and Friedel-Craft acylation occurs without a catalyst.⁷³ In mineral acid solution addition of a proton at C-1 forms the tropylium cation:-



When electrophilic substitution occurs, the peripheral 10- π -electron system which is considered to be largely responsible for stability is destroyed. In its place, however, an aromatic sextet comes into being in the seven-membered ring of the intermediate, thereby facilitating the reaction. Conversely, during nucleophilic substitution at the C-4 or C-8 in the seven-membered ring, an aromatic cyclopentadienide ring is formed in the intermediate.



PART II

DISCUSSION

[A] DIAZOCYCLOPENTADIENES

(1) Synthesis of phenylated diazocyclopentadienes from the diene

Doering and DePuy³³ synthesised diazocyclopentadiene in 35% yield from cyclopentadienyllithium and toluene-*p*-sulphonylazide, while Pauson and Williams³⁴ used an analogous method in the preparation of 2,3,4- and 2,4,5-triphenyldiazocyclopentadienes and 2,3,4,5-tetraphenyldiazocyclopentadiene. The yields obtained for the phenylated compounds appear to have been rather higher than for diazocyclopentadiene.

Weil and Cais³⁶ found that in the synthesis of diazocyclopentadiene, phenyllithium could be replaced by almost any base (preferably diethylamine or ethanolamine) and reaction ensued on simply allowing the reactants to stand at 0° for some days.

It has been found that a similar simplification applies to the syntheses of 2,3,4-triphenyl- and 2,3,4,5-tetraphenyldiazocyclopentadienes, using diethylamine as the base. After standing at 0° for several days, the mixture was extracted with ether, and the residue from the ethereal layer chromatographed to yield 66% and 50% of the diazo compounds, respectively, after recrystallisation. The yield of tetraphenyldiazocyclopentadiene was appreciably better than that reported by Pauson and Williams, the formation of a small amount of tetracyclone also being detected in this reaction. The function of the base is to remove a proton from the hydrocarbon to form a phenylated cyclopentadiene ion, which then reacts in a manner similar to that detailed in Part I, Section [B] (2). Rapid recrystallisation of 2,3,4-triphenyldiazocyclopentadiene could be effected from cyclohexane, but prolonged boiling caused decomposition.

Attempted extension to the synthesis of ylidenedihydropyridines. -
4-cyclopentadienylidenedihydropyridines have been synthesised ⁴⁹⁻⁵⁴
by reaction of the cyclopentadienide ion with a pyridinium salt.
Since diethylamine is effective in the above reactions, it was
thought that it might also be used in the syntheses of dihydropyridines.
Hitherto, sodium or lithium cyclopentadienide or cyclopentadiene in
the presence of potassium tertiary butoxide had been used.

In the attempted condensation of cyclopentadiene with pyridine
methiodide in the presence of diethylamine some darkening of
colour was evident probably due to partial reaction, but the
methiodide was recovered unchanged in near-quantitative yield. A
possible reason for the failure of this reaction was that it
would take some days to reach completion, the anion being present
as part of an equilibrium mixture:-



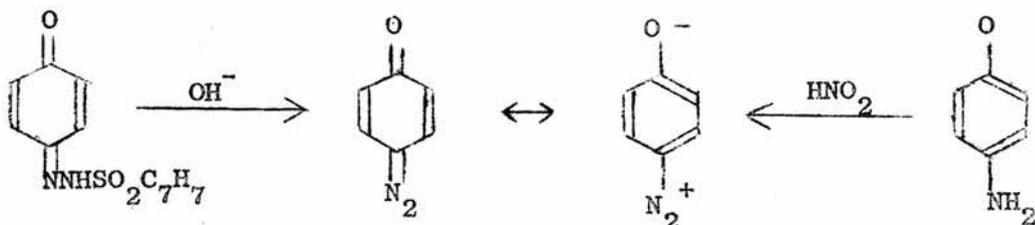
On the other hand, even at 0°, cyclopentadiene tends to polymerise
to the dimer or a polymeric material, and this competing reaction
may predominate. The product, if any, would not have great
stability.⁵⁴

No reaction was evident when tetraphenylcyclopentadiene,
pyridine methiodide and diethylamine were mixed at 0°.

(2) Synthesis of phenylated diazocyclopentadienes from the dienone

Alkaline cleavage of toluene-p-sulphonylhydrazones. - The
first reaction to be reported ⁷⁵ involving cleavage of a toluene-
p-sulphonylhydrazone by base was the conversion of p-benzoquinone
toluene-p-sulphonylhydrazone by cold aqueous alkali to the same

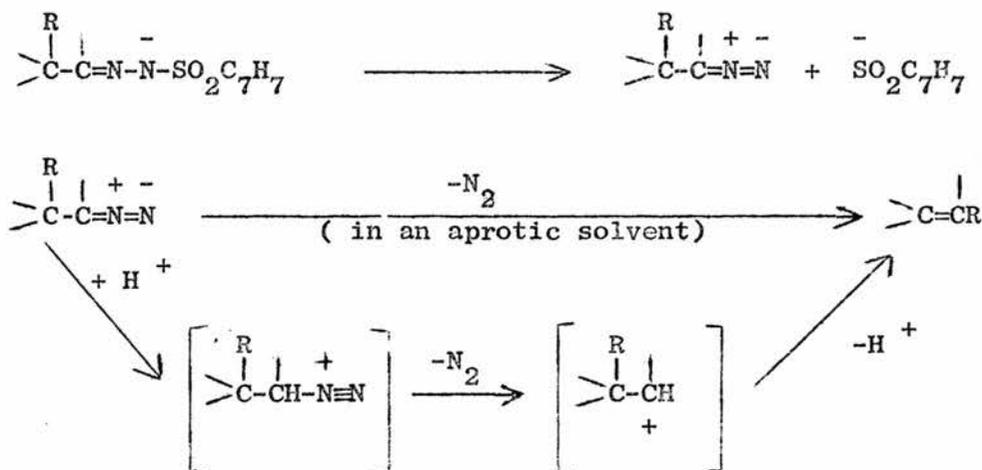
unstable p-diazooxide as is prepared by the action of nitrous acid on p-hydroxyaniline:-



Bamford and Stevens ⁷⁶ studied the decompositions of a range of tosylhydrazones using a solution of sodium in ethylene glycol. Tosylhydrazones of aliphatic ketones gave olefins (e.g. acetone tosylhydrazone afforded propylene), whereas tosylhydrazones of aromatic aldehydes or ketones gave diazo compounds or products of their decomposition; by working at low temperatures, substantial yields of the diazo compounds derived from benzaldehyde, acetophenone, benzophenone and fluorenone were obtained. The conditions they normally employed involved heating the derivative with an approximately 1.5 N solution of sodium in ethylene glycol; under these conditions the fluorenone derivative gave difluorenylidene.

They did not consider that the diazo compound was the primary product in every case. The camphor derivative was found to give an optically-active camphene as the main product, whereas diazocamphene had been shown by previous workers to decompose mainly to tricyclene, so that it was ruled out as the intermediate. However, the decomposition of diazocamphane has since been re-examined ⁷⁷, and the objection not sustained. It is now held ^{77,78,79,83} that initial decomposition of the tosylhydrazone salt to the diazo compound occurs in every case, and is followed by further reactions depending on the structure of the compound and the solvent.

Thus, in proton-rich solvents, proton transfer to the diazo compound is followed by cationic decomposition of the Wagner-Meerwein type, involving hydrogen migration or skeletal rearrangement, to give olefins. In aprotic solvents, carbenic decomposition is followed by hydrogen migration to give olefins or intramolecular insertion to give cyclopropanes. In either case, the rate-determining step is unimolecular elimination of sulphinate anion to give the diazo compound. Decomposition of tosylhydrazones by irradiation at room temperature follows a similar path, relative amounts of products obtained by carbenic and cationoid decompositions depending on the availability of protons, in agreement with the mechanistic theories outlined above. The possibilities are summarised as:-

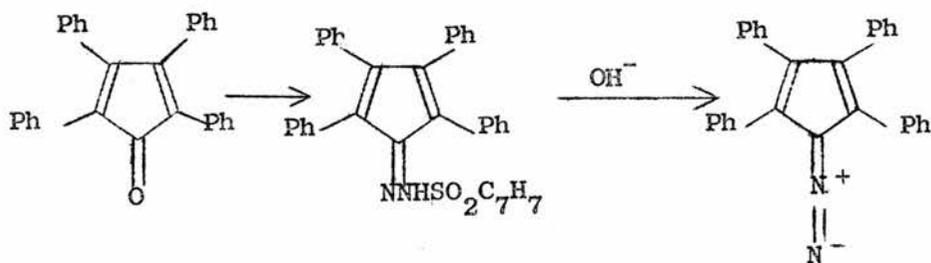


The Bamford-Stevens reaction has been widely used in the synthesis of steroids^{78,81} and has been applied to the preparation of cyclopropanes.⁸² The direction of elimination in cleavage of tosylhydrazones of simple ketones has been examined,⁷⁹ but it proved to be a rather poor preparative route.

Alkaline cleavage of tosylhydrazones has not been utilised much as a method of obtaining diazo compounds; they have

usually just been postulated or observed in the synthesis of hydrocarbons. Some aryldiazoalkanes have been obtained⁸³ by this route and it is of great value in the preparation of α -diazoketones.⁸⁴ For instance, 4,7-dimethyl-1,2-indanedione mono-tosylhydrazone, on standing at room temperature in aqueous sodium hydroxide solution, deposits the neutral diazo compound.

The preparation of 2,3,4,5-tetraphenyldiazocyclopentadienes discussed in Section [A] (1) is very simple, provided that tetraphenylcyclopentadiene is available; the preparation of this compound, however, involves a tedious four-stage synthesis. In marked contrast to this, tetraphenylcyclopentadienone (tetracyclone) may be prepared extremely easily in a high state of purity by the base-catalysed condensation of benzil and dibenzyl ketone. An efficient method of converting the dienone to the diene in reasonable yield is still to be found.⁸⁶ It was therefore considered worthwhile to examine the feasibility of the following scheme:-



The diazo compound was known to be stable, and structural considerations ruled out decompositions of the types outlined above. Fluorenone tosylhydrazone under the conditions employed⁷⁶ had given difluorenylidene in high yield; if any carbenoid decomposition of the above tosylhydrazone occurred, formation of the completely phenylated pentafulvene would be most unlikely due to steric considerations.³⁴

2,3,4,5-Tetraphenylcyclopentadienone toluene-p-sulphonylhydrazone.-
A survey of the literature showed that the only known carbonyl

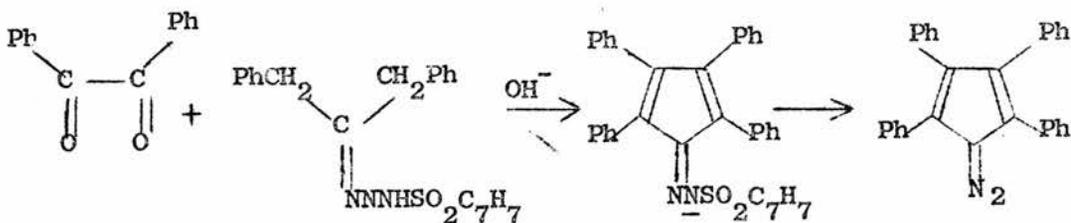
derivatives of tetracyclone were the 2,4-dinitrophenylhydrazone⁸⁵ and the 4-nitrophenylhydrazone.⁸⁶ Both compounds had been obtained only under forcing conditions, in the presence of conc. sulphuric acid and with dioxan solvent under an inert atmosphere; attempts to form the oxime and phenylhydrazone had been unsuccessful. The suppressed reactivity of the carbonyl function can be explained by the electron-withdrawing tendency of the five-membered ring.

It was found possible to prepare tetracyclone toluene-p-sulphonylhydrazone as stable copper-coloured needles, m.p. 171-172° dec., employing the forcing conditions of Josten. The product was stable to heat and acid, and was not formed in the absence of conc. sulphuric acid. The only other compound isolated in small amount after reaction, by chromatography, was tetracyclone itself; rather more of the unreacted dienone was present if the inert atmosphere was dispensed with.

Alkaline cleavage of tetraphenylcyclopentadienone toluene-p-sulphonylhydrazone. - Alkaline cleavage of the sulphonylhydrazone was effected at slightly elevated temperature, using a 3% solution of sodium ethoxide in ethanol. The red-brown residue was recrystallised from *n*-propanol to give 2,3,4,5-tetraphenyl-diazocyclopentadiene, m.p. 142-143° dec., in 64% yield. This melting point differed slightly from that given by other workers [Pauson and Williams,³⁴ m.p. 152-154° dec.; Klages and Bott,⁸⁷ m.p. 149° dec.], but was unchanged on further recrystallisations from the same or different solvents. The structure of the product was confirmed by elementary analysis, the presence of the characteristic diazo group absorption at 4.70 μ in the I.R. spectrum (c.f. Pauson and Williams,³⁴ 4.79 μ) and reaction with phenyllithium to give the phenylhydrazone (Section [A] (5)). The product gave an intense red colour with conc. sulphuric acid, in contrast to tetracyclone which gave a blue one.

Concentration of the mother liquors from the recrystallisation gave more of the diazo compound, but in an impure state. A small amount of the principal impurity was separated and found to be a white solid, m.p. 221-222.5°, elementary analysis giving figures that corresponded to $C_{32}H_{28}O_2$. 1-Propoxytetraphenylcyclopentadien-1-ol has thus formula, but is not known; it might be a product of reaction with the solvent, but insufficient time was available to confirm this structure with the small amount of material obtained.

Attempted one-stage synthesis of 2,3,4,5-tetraphenyldiazo-cyclopentadiene. - Since tetracyclone is prepared by the alkaline condensation of benzil and dibenzyl ketone, and the tosylhydrazone is cleaved to the diazo compound by alkali, it was thought the two stages might be combined into one. If dibenzyl ketone tosylhydrazone and benzil were heated together in the presence of alkali, diazo compound should be formed, provided that ring-closure took place prior to heterolysis of the N-S bond, thus:-



In the event, 1,3-diphenylpropene was formed. This is the decomposition product of dibenzyl ketone tosylhydrazone (see next section), showing that elimination of the sulphinate anion occurred prior to ring formation. Condensation of the carbonyl and methylene groups to give the cyclopentadiene ring will tend to take place less readily in this case than in the formation of tetracyclone itself. The first stage in such a condensation is

the loss of a methylene proton facilitated by electron-withdrawing groups attached to the α C-atom; the tosylhydrazone group will not exert as strong an electron-withdrawing effect as the carbonyl group, since the sulphonyl oxygen atoms are not conjugated with the methylene protons.

Alkaline cleavage of dibenzyl ketone toluene-p-sulphonylhydrazone. - Bamford and Stevens⁷⁶ decomposed this hydrazone at high temperature with a solution of sodium in ethylene glycol to give 1,3-diphenylpropene. It was found that cleavage to give this product also occurred under the influence of a 5% solution of methanolic sodium methoxide, the product being characterised as its dibromide.

2,3,4-Triphenylcyclopentadienone toluene-p-sulphonylhydrazone. - It would again be advantageous to devise a route to 2,3,4-triphenyldiazocyclopentadiene from the dienone, of which no carbonyl derivatives have been reported.

Two products were obtained from the dienone on reacting it with toluene-p-sulphonylhydrazine under the same conditions which were successfully applied to the tetraphenyl compound. Neither product was positively identified, but neither was the desired tosylhydrazone. This reaction is probably confused by the fact that the dienone can exist in stable dimeric form,³⁴ and since it was evidently not going to provide a simple route to the diazo compound, the attempt was abandoned.

(3) N.M.R. studies on 2,3,4-triphenyldiazocyclopentadiene

The N.M.R. spectrum* of this compound in deuterio-chloroform showed two signals of relative intensity 15:1. The first, at

* All N.M.R. spectra referred to in this thesis are listed in Part III, Section [I]

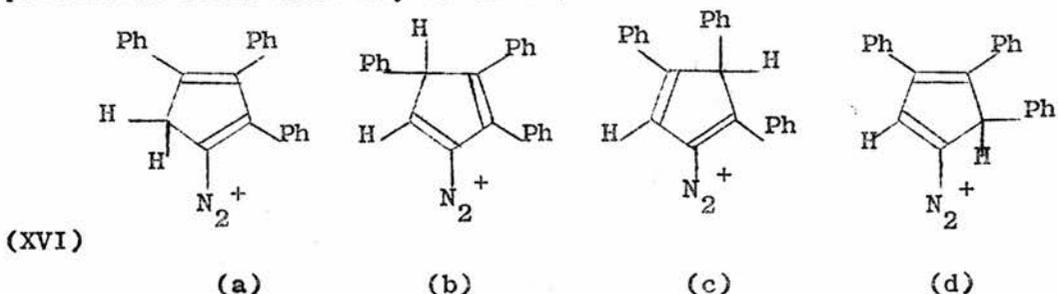
2.86 τ , was a complex peak arising from the fifteen phenyl protons, while the second, at 3.07 τ , was a sharp peak due to the single ring proton.

When the 2-4 τ region was retaken at a slow sweep-rate, no clear splitting of the complex peak could be seen. This was in agreement with the ring-current rendering the phenyl groups virtually equivalent in environment. When electron-donating substituents are attached to a benzene ring, a shielding effect on the ring-protons is observed; in this case the phenyl protons give a signal centred at 2.86 τ , compared with 2.73 τ for benzene.

The 2-(5-) protons of diazocyclopentadiene absorb at 3.3 τ .³⁹ The slight down-field shift of the signal due to the single ring-proton of 2,3,4-triphenyldiazocyclopentadiene with respect to this may be explained by an increased de-shielding effect by the diazo group. Since the negative charge may be delocalised to some extent over the phenyl substituents, the structure should be more nearly completely dipolar in character. A greater degree of positive charge will reside on the exocyclic diazo group, which will consequently exert a greater de-shielding effect on the neighbouring C-2 proton.

When the N.H.R. spectrum was taken in trifluoroacetic acid (T.F.A.), signals appeared at 2.7 τ and 5.82 τ . There was a considerable amount of background noise since the low solubility necessitated the use of high sensitivity, so that an accurate integration curve could not be obtained. The broadening of the signal due to the phenyl protons may be explained by the fact that protonation had destroyed the aromaticity of the molecule and in the absence of ring-current the phenyl protons had a greater difference in environment. In addition, the signal was centred at 2.7 τ , since the electron-donating effect of the

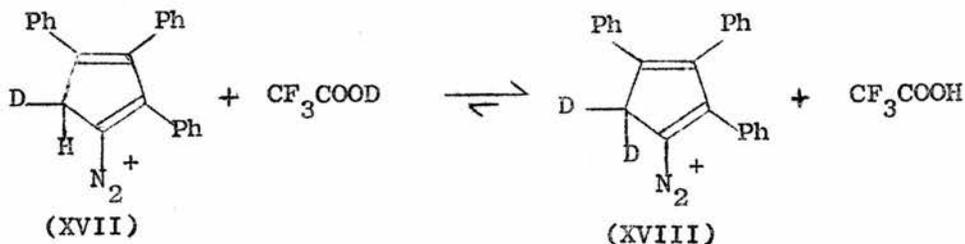
negatively charged ring had been removed. Four possible protonated structures may be drawn:-



In (b), (c), and (d) the two ring protons have very different environments and would be expected to have very different chemical shifts. Since only one other signal was observed, at 5.82 τ , (XVI) (a) is considered to be the structure, and this peak due to the two equivalent methylene protons. As would be expected, the adjacent diazo group has a de-shielding effect on these methylene protons c.f. the methylene signal of cyclopentadiene at 7.10 τ .

When the solution in T.F.A. was allowed to evaporate to dryness on a watch-glass, a yellow solid, m.p. 208-218^o, remained. The spectra and elementary analysis figures showed it to be 2-hydroxy-3,4,5-triphenylcyclopentadiene (see Part III, Section [D] (2)) arising from reaction of atmospheric moisture with the unstable diazonium salt. However, the salt appeared stable in solution for some time.

The N.M.R. spectrum of triphenyldiazocyclopentadiene in deuterio-trifluoroacetic acid (D.T.F.A.) showed only one broad signal, due to the phenyl protons, at 2.7 τ . The signal apparent at 5.82 τ in T.F.A. solution, ascribed to the methylene protons, had completely disappeared.



The initial deuterated molecule (XVII) would be expected to give a signal at ca. 5.82 τ equivalent to one proton. No such signal was observed, so rapid deuterium exchange with the solvent must have occurred, to give (XVIII). This is indicative of the high reactivity of the methylene proton.

The U.V. spectrum* of triphenyldiazocyclopentadiene had maxima at 239 $m\mu$ and 330 $m\mu$ in methnaol. After addition of a trace of perchloric acid, the spectrum showed only a single maximum at 239 $m\mu$. The disappearance of the long-wavelength band in the presence of acid was further evidence that protonation of the ring, and therefore loss of aromaticity, had occurred.

(4) Electrophilic substitution in 2,3,4-triphenyldiazocyclopentadiene

The aromatic structure of certain classes of cyclopentadiene derivatives was considered in some detail in Part I. Ease of electrophilic substitution in these compounds is of great interest as this is the characteristic mode of reaction of aromatic compounds.

Since in aromatic cyclopentadiene derivatives the ring possesses complete (cyclopentadienide) or partial(cyclopentadienylidene)

* All U.V. spectra are listed in Part III, Section [H].

anionic character, these compounds are very much more readily substituted by an electrophilic mechanism than benzene. Such substitution reactions have been examined in the cases of the anion, diazocyclopentadiene and triphenylphosphoniumcyclopentadienylide, and were discussed in Part I. The products obtained by electrophilic attack on triphenyldiazocyclopentadiene were therefore investigated. In cases where reaction occurred, the product was shown by N.M.R. spectroscopy to be mono-substituted in the only vacant position of the five-membered ring; this is in agreement with the electron density at this position being considerably higher than at the C-atoms of the phenyl substituents.

Bromination.- N-bromosuccinimide has been widely used in substituting a bromine atom at positions activated by adjacent carbonyl groups, unsaturation or other factors. With diazocyclopentadiene ¹³ the tetrabromo derivative was formed, with triphenylphosphoniumcyclopentadienylide ⁴² the tribromo derivative.

Reaction of triphenyldiazocyclopentadiene with N-bromosuccinimide at room temperature followed by chromatography of the products gave yellow crystals, m.p. 128-130^o, of a mono-bromo derivative in 48% yield. The product exhibited the characteristic diazo group absorption in its I.R. spectrum at 4.81 μ . The use of lengthy degradative procedures to establish that the compound was 5-bromo-2,3,4-triphenyldiazocyclopentadiene was obviated by the use of N.M.R. spectroscopy. The signal at 3.07 τ in the spectrum of triphenyldiazocyclopentadiene in deuterio-chloroform, ascribed to the single ring proton, had disappeared in the spectrum of the product, which was therefore mono-brominated at this position. The phenyl protons gave a complex signal at 2.81 τ , while a small peak at 8.74 τ was shown to be due to the presence of some impurity.

Iodo-mercuration and iodination.- Tetraphenyldiazocyclopentadiene reacted with mercuric acetate and sodium iodide to give a yellow monosubstituted product, showing absorption due to the diazo group at 4.73μ in its I.R. spectrum; that substitution had occurred at the vacant position of the ring was again confirmed by the N.M.R. spectrum. The signal at 3.07τ of triphenyldiazocyclopentadiene in deutereo-chloroform had disappeared, while the signal due to the phenyl protons appeared at 2.76τ . In contrast to the di-substituted compound obtained ¹³ from diazocyclopentadiene, the product appeared to be quite stable. No suitable solvent for recrystallisation could be found, but elementary analysis gave figures for N, I and H corresponding very well with the assigned structure.

The iodo-mercuri compound reacted with iodine in chloroform to give a yellow solid, m.p. $122-125^{\circ}$ (very close to the melting point of the mono-bromo compound above), isolated by chromatography. The product, which showed absorption at 4.81μ in its I.R. spectrum due to a diazo group, was less stable and decomposed slightly before the melting point was reached. Probably for this reason, together with the fact that a satisfactory recrystallisation was not achieved, the elementary analysis figures corresponded rather poorly with a mono-iodo compound. The N.M.R. spectrum again showed loss of the ring proton signal at 3.07τ , while the signal due to the phenyl protons was at 2.81τ . Two small peaks at high field show the presence of impurities in this product.

Nitration. - Two mono-nitro isomers were formed ¹³ from diazocyclopentadiene by reaction with benzoyl nitrate in acetonitrile. The triphenyl compound was not sufficiently soluble in acetonitrile for the identical conditions to be employed. The

reaction was attempted in dimethyl sulphoxide, but not crystalline products could be isolated.

Diazo-coupling.- The coupling reaction between diazocyclopentadiene and phenyldiazonium boron tetrafluoride took place in methanol, in which both reactants were soluble.¹³ The relatively low solubility of the tetraphenyl compound in methanol deterred an attempt using similar conditions. Triphenylphosphoniumcyclopentadienylide in methylene chloride couples⁴¹ with benzenediazonium chloride in aqueous solution on mixing at 0°, however, if the diazonium solution is buffered with sodium acetate to bring the pH to ca 5-6.

A similar reaction was attempted with the triphenyldiazocyclopentadiene in methylene chloride solution and buffered aqueous benzenediazonium chloride solution. The diazo compound was recovered unchanged, in high yield, while a second (unidentified) red band in the chromatogram was too polar to be a product of coupling.

(5) Reactions of 2,3,4,5-tetraphenyldiazocyclopentadiene with retention of nitrogen

Phenyl lithium.- The phenylhydrazone of tetracyclone cannot be prepared, even under forcing conditions, from the ketone (see Section [A] (2)). Pauson and Williams³⁴ reported its preparation from tetraphenyldiazocyclopentadiene by reaction with phenyl lithium, and this reaction was repeated giving a 35% yield of the dark red crystalline product.

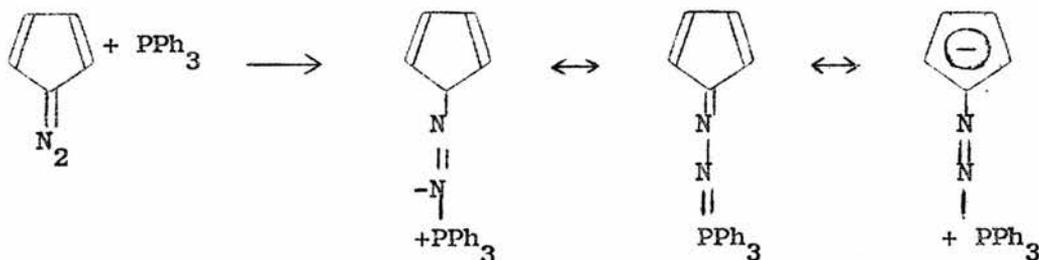
Hydrazine.- Since tetraphenyldiazocyclopentadiene can be converted into the phenylhydrazone as above, it was thought possible that the otherwise unobtainable hydrazone might result from reduction of the diazo compound; Wolff-Kishner reduction

might then provide a route to the diene. The results of Sonntag et al.⁸⁶ on the reduction of tetracyclone demonstrate that hydrogenation of the ring can take place under quite mild conditions.

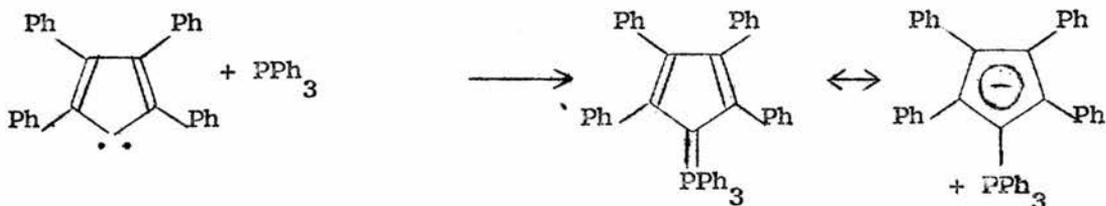
Tetraphenyldiazocyclopentadiene was refluxed with hydrazine hydrate in ethanolic solution for 2 hrs., during which time the solution had become much lighter in colour. The principal product by chromatography was a yellow solid, m.p. 68-77^o, which could not be further purified by recrystallisation. It was not stable and darkened rapidly in air, while its I.R. spectrum showed almost complete disappearance of the characteristic diazo group vibration at ca 4.8μ.

One of the nitrogen atoms had been lost, as shown by elementary analysis. Under similar conditions tetracyclone was reduced⁸⁶ to tetraphenylcyclopentane, but in this case the ring did not seem to have been reduced, the analysis figures corresponding to 1-amino-2,3,4,5-tetraphenylcyclopentadiene. The I.R. spectrum showed an amino group absorption centred at 2.9μ.

Triphenylphosphine.- Diazocyclopentadiene couples with triphenylphosphine in ethereal solution at room temperature to give the phosphazine,⁷⁴ m.p. 122-124^o, thus:-



No similar coupling reaction took place between tetraphenyl-diazocyclopentadiene and triphenylphosphine in ethereal solution either at room temperature or under reflux. Reaction was then attempted by refluxing the two components for several hours in *p*-xylene. As detailed in Section [C] (2), the diazo compound is considered to decompose to the carbene under these conditions. However, studies of the progress of other reactions indicated that this decomposition was not immediate, and it was hoped that some of the phosphazine might be formed at the elevated temperature. The tetraphenylcyclopentadienyl carbene, when formed, in addition to giving tetracyclone and other products isolated in similar reactions (see Section [C] (2)), might react with the triphenylphosphine to give 1-triphenylphosphonium-2,3,4,5-tetraphenylcyclopentadienylide:-



Steric factors, however, would seem to make the stable existence of this compound unlikely.

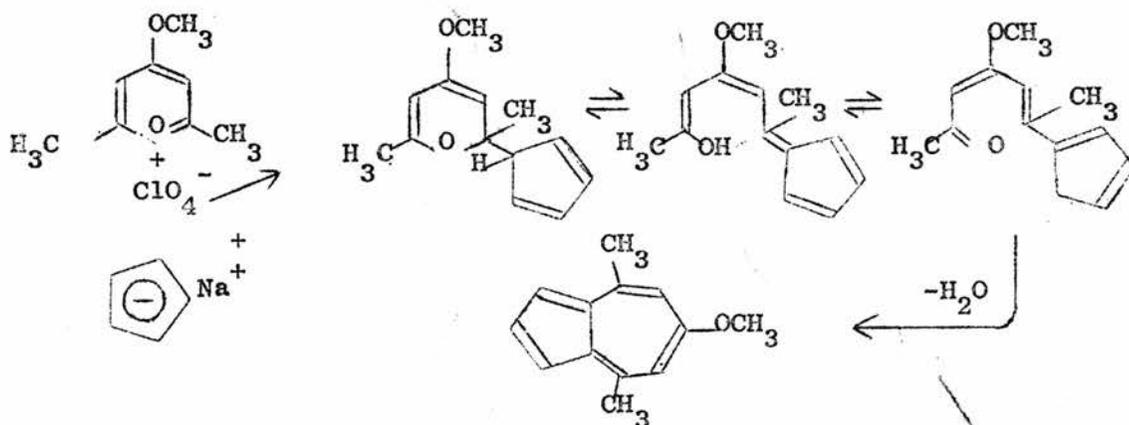
Chromatography of the products gave a yellow solid, m.p. 30-40°, which contained phosphorus and showed no diazo group absorption at ca 4.8 μ in its I.R. spectrum. Elementary analysis of this compound gave figures corresponding approximately to the tetraphenylcyclopentadienylidenephosphazine, although attempted recrystallisation caused decomposition and a very pure sample could not be obtained.

The U.V. spectrum had two maxima fairly close to those of tetraphenyldiazocyclopentadiene, as would be expected of this structure. In tetraphenyldiazocyclopentadiene, the long

[B] PRELIMINARY ATTEMPTS TO SYNTHESISE CYCLOPENTADIENYLIDENEPYRANS

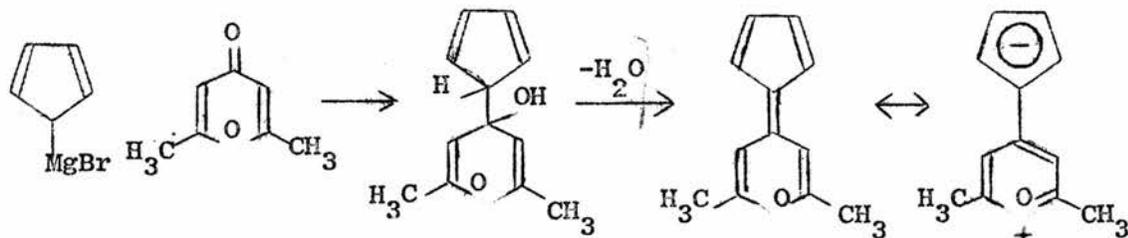
(1) Grignard reactions

It was mentioned in Part I, Section [B] (3) that a standard method of synthesising cyclopentadienylidenedehydropyridines was by reaction of sodium cyclopentadienide with a 4-methoxy-N-alkylpyridinium salt. In the case of pyrylium salts a similar reaction does not give rise to cyclopentadienylidenepyrans but azulenes, subsequent upon attack at C-2 rather than C-4,⁸⁹ thus:-



Reaction of metal cyclopentadienides with 2,6-dimethyl-4-pyrone and xanthone gave no basic products.⁵⁴

A common method of synthesising fulvenes is by reaction of a fulvene-ketone with a Grignard reagent, followed by dehydration of the resultant tertiary alcohol. A possible route to a cyclopentadienylidenepyran could therefore be as follows, since 2,6-dimethyl-4-pyrone is known to react with methyl magnesium bromide⁹⁰ :-



Sneezum⁹¹ examined this reaction briefly but obtained no promising results and did not pursue the matter further. This reaction was repeated and a similar one with xanthone attempted; in both cases a product was obtained which was shown by analysis to contain several atoms of oxygen. Simple fulvenes are known⁹² to form peroxides or bis-epoxides readily, and the products obtained may have this kind of structure. Grignard reactions were clearly not going to provide a route to cyclopentadienylidenepyrans, so the reactions were not studied further.

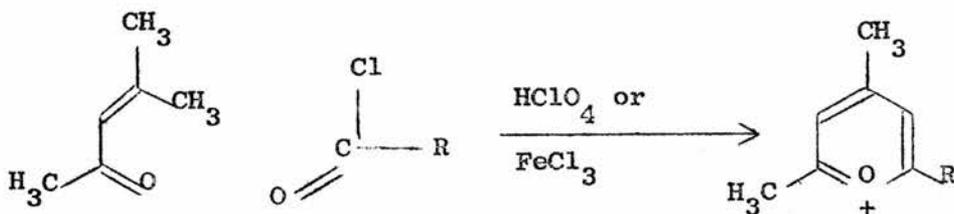
Reaction between cyclopentadienyl magnesium bromide and 2,6-dimethyl-4-pyrone.- The two reactants were refluxed briefly in ether and the oily residue obtained on removing the solvent was decomposed with ice, and mixed with dilute acid. A yellow solid of high melting point was obtained and elementary analysis gave figures corresponding to $C_{11}H_{17}O_7$. The unexpectedly high percentage of oxygen present suggested that oxidation had occurred; the formula actually corresponds to the desired cyclopentadienylidenepyrans with two peroxide groups and two molecules of water.

Reaction between cyclopentadienyl magnesium bromide and xanthone.- The reaction was carried out in a similar manner to the above, the elementary analysis figures for the yellow product corresponded to a mono-peroxide or bis-epoxide of the desired cyclopentadienylidenexanthone. Oxidative cleavage of the product with chromium trioxide gave xanthone as the only identified product. No Diels-Alder adduct could be obtained, in agreement with the conjugated diene structure of the carbocyclic ring being destroyed by peroxidation.

(2) Pyrylium ring formation by closure on to an acid chloride

Since cyclopentadienylidenepyrans did not result from the

reactions mentioned in the previous section, starting from compounds with pre-formed pyran rings, attempts were made to use modifications of some standard pyrylium ring syntheses.⁹³ One such method involves reaction of an acid chloride with an α,β -unsaturated ketone in the presence of perchloric acid or anhydrous ferric chloride:-



If, in this reaction, R = cyclopentadienyl or fluorenyl, the product expected would be the conjugate acid of a 2,4-dimethyl-6-ylidenepyran. Basification of this should give the ylidene pyran.

Fluorene-9-carboxylic acid chloride.- Fluorene-9-carboxylic acid chloride is a known compound which is fairly readily synthesised. It was therefore decided to react it with mesityl oxide in the presence of perchloric acid in the hope of getting 2,4-dimethyl-6-fluorenylpyrylium perchlorate; action of base should convert this into 2,4-dimethyl-6-fluorenylidene pyran.

Since the acid chloride is hydrolysed by water to fluorene-9-carboxylic acid and 70% perchloric acid is the most concentrated solution commercially available, it was necessary to add the calculated amount of acetic anhydride to the aqueous perchloric acid in order to take up the water.

The product of the reaction, after recrystallisation, consisted of white crystals, m.p. 246-250°, of 2,4,6-trimethylpyrylium perchlorate. This formulation was confirmed by

reacting the product with ammonium carbonate solution and characterising the resultant trimethyl pyridine as the picrate. Ring-closure had preferentially taken place with the acetic acid rather than the fluorene-9-carboxylic acid chloride.

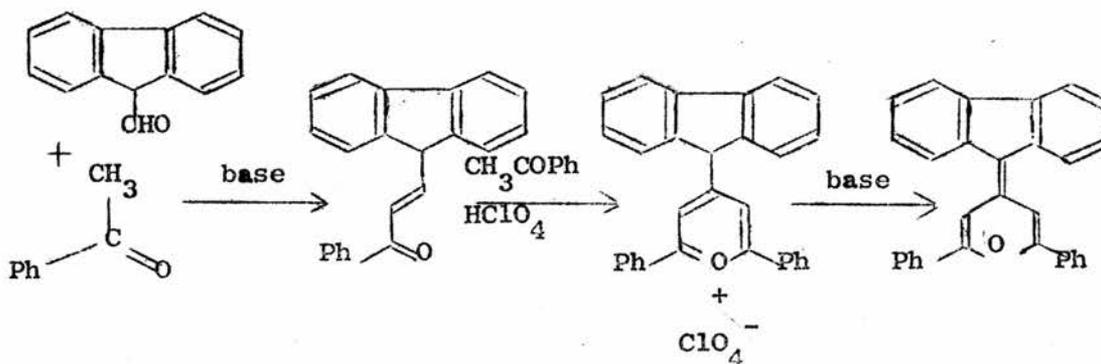
In order to circumvent the intrinsic difficulty of this reaction, the perchloric acid was replaced by freshly-sublimed anhydrous ferric chloride. The desired product was not, however, obtained.

Cyclopentadiene carboxylic acid chloride.- Cyclopentadiene carboxylic acid is known to exist normally in dimeric form.⁹⁴ Its chloride had not been prepared, but would certainly also exist as a dimer reaction of the kind under discussion.

The acid was obtained by reacting cyclopentadienyl magnesium bromide with carbon dioxide, and with thionyl chloride it gave a thick oil which was probably the dimeric acid chloride. Dicyclopentadiene and the dimeric ester are readily depolymerised thermally so an attempt to distil the oil was made but without any success.

(3) Pyrylium ring formation by closure on to fluorene-9-aldehyde

It was planned to carry out a ring-closure reaction in two stages, thus:-



(XXI)

Formation of fluorenylpropiophenone (XXI) took place readily at 25° in the presence of sodium hydroxide. (XXI) was a light yellow solid, m.p. 185-187°, giving a purple colouration with hydrazene hydrate. This colouration was probably due to formation of a pyrazolene ring, although attempts to isolate the compound were unsuccessful.

Attempts to carry out the second stage of the reaction to form the pyrylium ring were not successful. Ring-closure would probably be accompanied by the development of a red colouration due to the pyrylium perchlorate, but this did not happen, and the yellow solid obtained could not be identified.

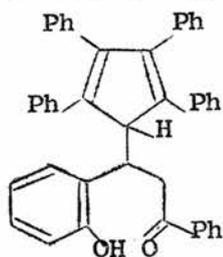
(4) Michael condensation of 2,3,4,5-tetraphenylcyclopentadiene and salicylidene-acetophenone

Boyd and Jackman⁵⁴ recently described the preparation of 4-9'-fluorenylidene-flav-2-ene by the base catalysed condensation of fluorene and salicylidene-acetophenone, followed by dehydrogenation and dehydration; the reaction sequence is considered in more detail in Part I. An analogous reaction between indene and salicylidene-acetophenone gave an adduct which was converted into the flavene, but this reaction proceeded with great difficulty and in low yield. The difficulties encountered in this reaction deterred Boyd and Jackman from attempting to prepare a Michael adduct from cyclopentadiene.

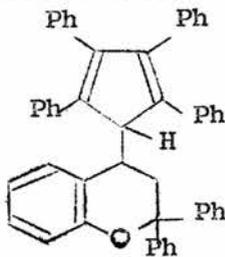
The synthesis of 4-tetraphenylcyclopentadienyldiene-2,6-dimethylpyran is discussed in Section [C]. It was hoped to prepare a related flavene compound by a Michael reaction between tetraphenylcyclopentadiene and salicylidene-acetophenone; although the results of Boyd and Jackman suggest that conversion of the adduct proceeds less readily with un-annulated

five-membered ring compound, the stability engendered by the phenyl groups might counteract this.

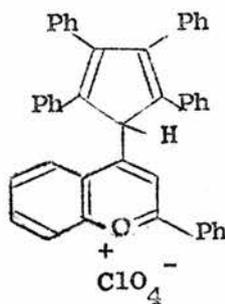
The condensation with salicylidene-acetophenone.- The highest yield of the condensation product was obtained by allowing a slight excess of tetraphenylcyclopentadiene to stand with salicylidene-acetophenone in pyridine at room temperature for several days. The reaction did not go to completion, but the condensation product was separated by its solubility in alkali and was precipitated in 25% yield on acidification. Unreacted tetraphenylcyclopentadiene could be recovered and the reaction repeated, so that the overall yield was considerably higher. Recrystallisation from aqueous methanol gave a yellow-green solid, m.p. 131-132°, for which there are two structural possibilities (XXII) and (XXIII).



(XXII)



(XXIII)



(XXIV)

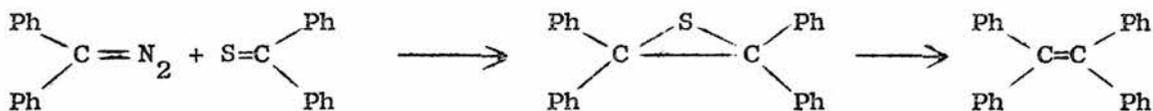
Analogous systems have been shown^{54,95} to exist as the keto-phenol rather than the isomeric hemiketal. In this case, the product showed no carbonyl absorption in its I.R. spectrum, suggesting that it had structure (XXIII); on the other hand, its solubility in alkali was typical of a phenolic hydroxyl group as in (XXII). It appears that an equilibrium mixture must exist containing only a minute amount of (XXII), undetectable in the I.R. spectrum, but that under the action of base, the equilibrium is disturbed.

Attempted conversion of product.- As with the indenyl compound,⁵⁴ attempts to dehydrogenate and dehydrate the adduct (XXIII) with chloranil were not successful, a complex with the haloquinone resulting.

An alternative possible route was to form the perchlorate (XXIV), or an isomer of it, and by the action of base convert it into the tetraphenylcyclopentadienylidene-flavene. With the indenyl compound,⁵⁴ yields of the perchlorate varied between 0 and 5%. In the case of (XXIII) a deep red colour resulted from the action of perchloric acid showing that some reaction had occurred, but the red solid obtained had a very extended melting range and analysis did not give figures corresponding well with the required product.

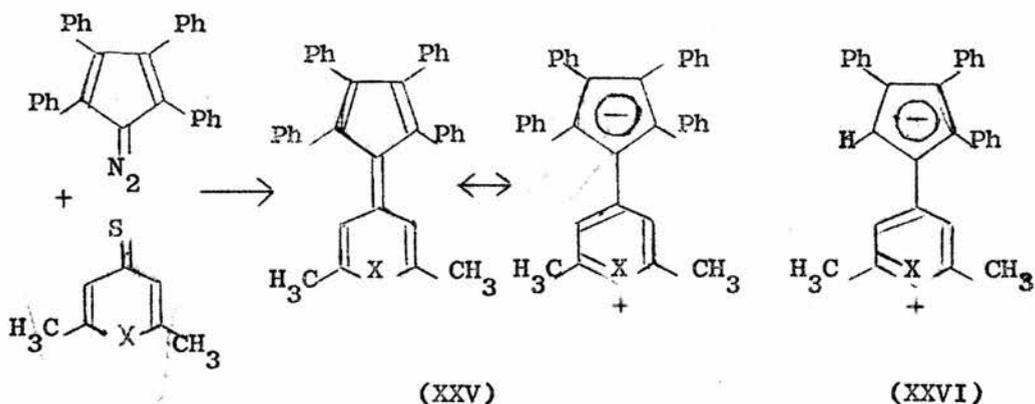
[C] SYNTHESIS OF CYCLOPENTADIENYLIDENE PYRANS AND THIOPYRANS

Standinger observed⁹⁶ that diphenyldiazomethane reacted with thiobenzophenone to give tetraphenylethylene sulphide, which readily lost sulphur to give the olefin:-



Schönberg has since applied the method⁹⁷ to a variety of diazo compounds and thioketones, in some cases the hydrocarbon being formed directly.

The following reaction was found to be successful for the preparation of 4-tetraphenylcyclopentadienylidene-2,6-dimethylpyran (XXV; X=O)



The thio-pyran (XXV; X=S) was obtained by replacing 2,6-dimethyl-4-thiopyran with 2,6-dimethyl-4-thiopyran-thione, and the method extended to obtain the triphenyl analogue (XXVI; X=O) from 2,3,4-triphenyldiazocyclopentadiene.

(1) Reaction conditions

The highest yield of 4-tetraphenylcyclopentadienylidene-2,6-dimethylpyran (XXV; X=O) was obtained by refluxing the two reactants for seven hours in *p*-cymene solution. The product formed red needles, m.p. 267-269°, purified by chromatography followed by recrystallisation from ethanol-benzene solution.

The reaction was repeated in various hydrocarbon solvents and a table showing the yields of product is included in Part III, Section [C] (1). Tetraphenyldiazocyclopentadiene melts with decomposition at 142-143°, and when the solvent used had a boiling point higher than this, the yield of (XXV; X=O) was considerably increased. A possible reason for this is that carbenic decomposition (followed by formation of (XXV; X=O) as discussed in the next section) occurs more readily at the higher temperature in preference to decomposition of the diazo compound in other ways. However, even in *p*-cymene, tetraphenyldiazocyclopentadiene took some time to decompose completely,

as was shown by periodically examining small samples by thin-layer chromatography.

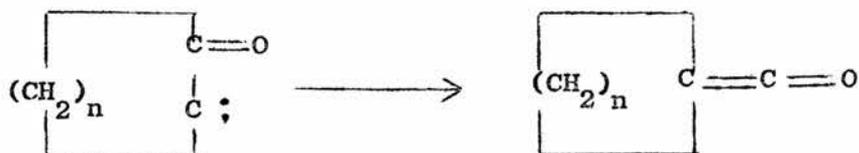
The thiopyran (XXV; X=S) and the triphenyl ylidene pyran (XXVI; X=O) were obtained in 27% and 9% yields respectively by following similar reaction conditions and working-up procedure. However, 4-triphenylcyclopentadienyldiene-2,6-dimethylthiopyran (XXVI; X=S) could be obtained only in very small amounts insufficient for adequate purification. This may be because the 2,6-dimethyl-4-thiopyran-thione used was not sufficiently pure; as mentioned in Part III, Section [C] (2) its preparation was not entirely reproducible. No reaction appeared to take place between the tetraphenyl diazo compound and xanthione.

An attempt to prepare the unphenylated 4-cyclopentadienyldiene-2,6-dimethyl pyran by refluxing 2,6-dimethyl-4-thiopyrone with diazocyclopentadiene in benzene solution was unsuccessful. Both starting materials were recovered partially unchanged, but most of the diazocyclopentadiene decomposed to a high melting polymeric material having a strong carbonyl absorption in its I.R. spectrum. This same decomposition product was obtained when diazocyclopentadiene was refluxed by itself in benzene solution, and even, after a few days, on allowing the diazo compound to stand at 0°.

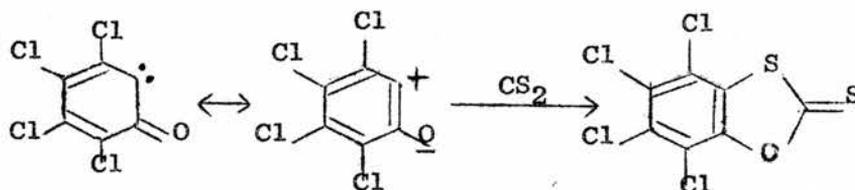
(2) Reaction mechanism

Diazo compounds have frequently been decomposed by photolysis or pyrolysis to give carbenes. These are highly reactive electrophilic species and they immediately undergo internal management or electron shift to give a more stable structure, or react with other molecules. Thus, the carbene obtained by photolysis of a cyclic diazoketone can rearrange

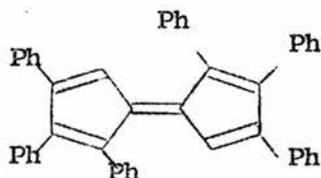
to a ketene:-



The carbene obtained from tetrachloro-o-diazquinone,⁹⁹ on the other hand, undergoes 1,3-dipolar addition with carbon disulphide after internal rearrangement of electrons:-



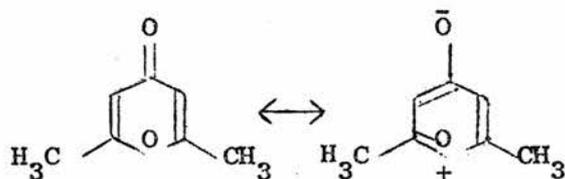
The carbene obtained from a diazocyclopentadiene cannot rearrange nor can it exist in a dipolar form, so that it would be expected to react rapidly with electron-rich centres in any other molecules present. The existence of the cyclopentadienyl carbene has not been demonstrated experimentally, but its formation has been postulated³⁷ in the low temperature photolysis of diazocyclopentadiene, since fulvalene was detected spectroscopically in the products. Pauson and Williams⁴³ have prepared 2,3,4,2',3',4'-hexaphenylfulvalene by simply refluxing 2,3,4-triphenyldiazocyclopentadiene in ethanol; from its ease of formation they concluded that it must have the relatively unhindered and almost planar trans configuration:-



Coplanarity in fulvalenes substituted at the 2,5,2',5'-positions would be impossible due to steric interactions, and attempts to prepare the 2,3,5,2',3',5'-hexaphenyl-fulvalene resulted in the formation of the dihydro compound.

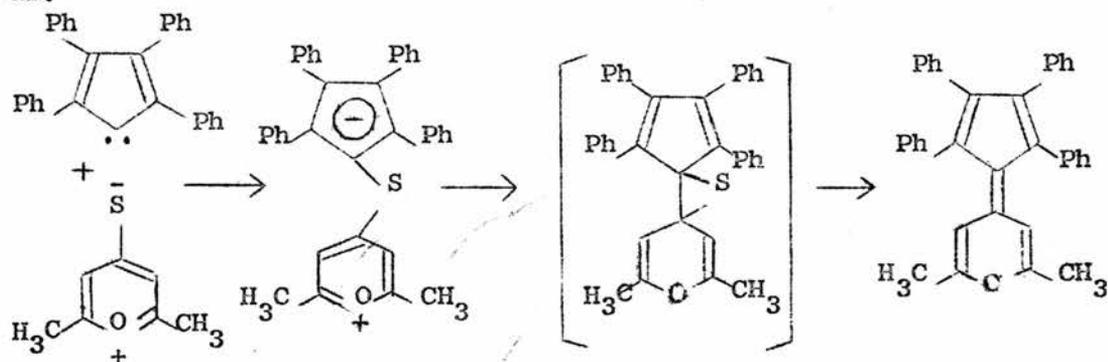
It seems likely that in the reaction of tetraphenylcyclopentadiene with 2,6-dimethyl-4 thiopyrone, the diazo compound decomposed initially to the carbene. Coupling of two such carbenic entities to give octaphenyl-fulvalene would not be possible for steric reasons, and the major product was formed by attack on 2,6-dimethyl-4-thiopyrone.

Spectroscopic studies have shown ¹⁰⁰ that 4-pyrones have a largely ketonic structure, but some contribution from the dipolar form is to be expected:-



Similar considerations apply to the structure of thiopyrones and in 2,6-dimethyl-4-thiopyrone, the highest electron density will exist at the exocyclic sulphur atom. Bearing in mind that in some related reactions the ethylene sulphides have been isolated, the mechanism in the present reaction is postulated

as:-



Sulphur was probably extruded in the elemental form, but suffered oxidation under the conditions of the experiment. The strong sulphurous smell emitted throughout tended to confirm this.

Tetracyclone was also isolated from the reaction. The formation of this compound would be expected by reaction of the carbene with atmospheric oxygen. In the attempted reaction of diazotetraphenylcyclopentadiene with 2,6-dimethyl-4-pyrone, and when the compound was heated alone in *p*-cymene, a considerable amount of tetraphenylcyclopentene was formed. Some of this compound was probably also formed in the reaction with the thiopyrone, but chromatography failed to elute it in a separate fraction. Its rate of elution in the other two reactions suggested that it came off simultaneously with the ylidene pyran and was removed from this compound in the recrystallisation. It is not certain in what way this

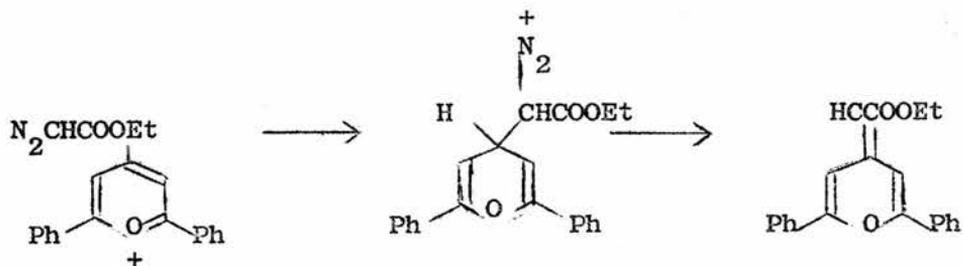
side-product was formed. However, since tetraphenylcyclopentadiene derivatives are known⁸⁶ to undergo partial hydrogenation of the ring rather readily, this may have occurred prior to carbenic decomposition of the diazo compound to give 1-diazo-2,3,4,5-tetraphenylcyclopentene. The diazo group in this molecule would no longer be stabilised by resonance interaction with the ring, and it could decompose to give the observed product.

The other similar reactions mentioned at the beginning of Section [C] probably proceed by the same kind of mechanism. In the reactions with w,3,4-triphenyldiazocyclopentadiene, the carbene resulting from the decomposition of this compound might be expected to dimerise to some extent to give the known trans-hexaphenylfulvalene.⁴³ This compound was not isolated, but its existence in small amount was probably responsible for the observed red-green fluorescence of the chromatographic fraction which was worked up to give unreacted 2,6-dimethyl-4-thiopyrone in the reaction with this compound. The fluorescence did not arise from the latter, but solutions of the fulvalene are known to show a similar effect.

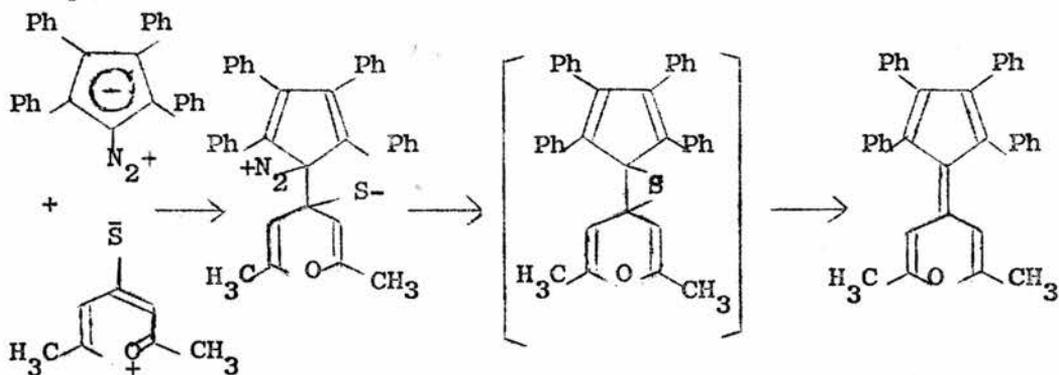
The increase in the yield of product when a solvent with a boiling point higher than the temperature at which the diazo compound melts with decomposition is used, tends to support the carbenic mechanism. The failure to obtain the desired 4-cyclopentadienylidene-2,6-dimethylpyran by reaction of diazocyclopentadiene and 2,6-dimethyl-4-thiopyrone may be the result of a tendency for the diazo compound to polymerise rather than pyrolyse to the carbene.

Since this work was done, the reaction of diazoacetic ester with 2,6-diphenylpyrylium perchlorate to give the

4-carbomethoxymethylene derivative has been described.¹⁰¹ Without giving evidence for the existence of the intermediate or other explicit reasons, an ionic mechanism is suggested for this reaction, which proceeds in acetonitrile at 0°:-



A parallel ionic mechanism can be written for the reactions under discussion, involving nucleophilic attack by the C-1 atom of the five-membered ring on the C-4 atom of the thio-pyrone ring, followed by evolution of nitrogen and elimination of sulphur:-



This mechanism seems sterically most unlikely. Evidence to support electrophilic attack by the carbene rather than nucleophilic attack of the above kind comes from some of the related reactions which were attempted, and these are discussed in the next section.

(3) Related reactions attempted with 2,3,4,5-tetraphenyldiazocyclopentadiene

2,6-Dimethyl-4-pyrone.- It was thought that this compound might react in a manner analogous to the thiopyrone to give either the ylidenepyran or its epoxide (this might be expected to be rather more stable than the thiirane, which was not isolated).

Chromatography of the products, after refluxing the mixture for seven hours in p-cymene, gave 2,3,4,5-tetraphenylcyclopentene, this probably being formed by reduction of the ring prior to carbonic decomposition, as discussed in Section [C] (2). A small amount of a second product could not be purified sufficiently to obtain a reliable elementary analysis. The figures obtained were not very different from those that would be required by the epoxide of the ylidenepyran; however, the product was much too polar (requiring elution with glacial acetic acid) to have this structure. It must be concluded that since the polarity of the carbonyl group will be less than that of the thiocarbonyl group, in the former case there will not be sufficient negative charge on the oxygen atom for electrophilic attack to occur at that position.

When tetraphenyldiazocyclopentadiene was refluxed alone in p-cymene for several hours, the only products isolated were 2,3,4,5-tetraphenylcyclopentene and tetracyclone.

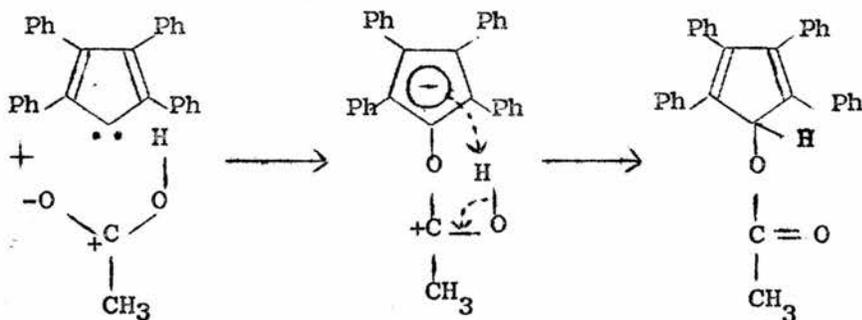
Thiourea.- It was thought that reaction with thiourea might yield diamino-tetraphenylfulvene, but the thiourea was recovered unchanged after refluxing with the diazo compound for seven hours in toluene.

m-Nitrobenzaldehyde.- If the mechanism of the reaction with thiopyrones were an ionic one as outlined in the previous

section, reaction would be facilitated by an increase in positive charge at C-4 of the thiopyrone. The diazo compound might also be expected to attack the carbonyl C-atom of m-nitrobenzaldehyde, since the combined electron withdrawing effects of the carbonyl group and the nitro group will tend to activate this position to nucleophilic attack^{*}; this position should certainly have more positive character than C-4 of the thiopyrone ring.

In practice, the m-nitrobenzaldehyde was recovered unchanged in high yield, confirming the postulated carbenic mode of decomposition of the diazo compound.

Acetic acid.- The diazo compound was refluxed in acetic acid for six hours, the only product obtained in a pure form being a pink solid, m.p. 69-72°; its analysis figures corresponded to C₃₁H₂₄O₂. The structure proposed for this compound is 1-acetoxy-2,3,4,5-tetraphenylcyclopentadiene, formed by electrophilic attack by the carbene as follows:-



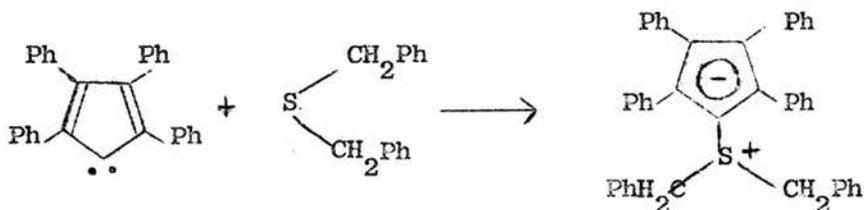
This formulation was confirmed by the I.R. spectrum which had maxima at 5.74 μ (ester C=O) and 8.15 μ (acetate C-O). The U.V. spectrum, as expected, was similar to that of

* o- or p-nitrobenzaldehyde would have been better in this reaction, as both are more activated at this position than the m- isomer. However, neither were available at the time of the experiment.

tetraphenylcyclopentadiene and tetraphenyldiazocyclopentadiene, showing that no reduction of the carbocyclic ring had taken place.

If reaction were to proceed by nucleophilic attack by the undecomposed diazo compound, the product expected would be the epoxide of 6-hydroxy-6-methyltetraphenylfulvene. This has the same empirical formula as the product, but the I.R. spectrum does not correspond.

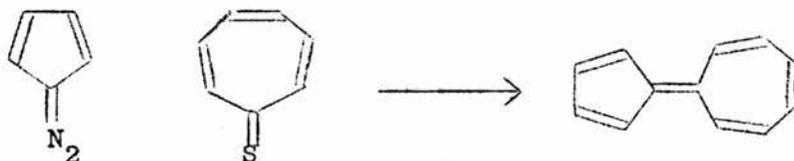
Dibenzyl sulphide.- It was hoped that reaction would provide a route to dibenzylsulphonium tetraphenylcyclopentadienylide:-



Dimethylsulphonium fluorenylide has been obtained,²⁵ but not sulphonium ylides with an un-annulated five-membered ring has been prepared. No reaction with the dibenzyl sulphide was evident, tetraphenylcyclopentene again being formed.

(4) Reactions involving the tropylium ring

Sesquifulvalene has not been prepared, the reaction between tropylium perchlorate and sodium cyclopentadienide giving the dihydro derivative (see Part I). Consideration was accordingly given to the possibility of modifying the reaction used in the synthesis of the ylidene-pyrans to synthesise sesquifulvalene, thus:-



The advantage of the method would be that no hydrogen atoms are attached to the C-1 position of either ring and formation of the dihydrosesquiifulvalene would be unlikely. The formation of the sesquiifulvalene molecule with a sulphur-bridge across the central bond would be a possibility. In order to test the validity of the method, it was intended first to attempt a reaction between thiotropone and 2,3,4,5-tetraphenyldiazocyclopentadiene which would give the known tetraphenylsesquiifulvalene. A search of the literature revealed a method¹¹² for the synthesis of substituted thiotropones by distillation of ditropylthioethers. We were subsequently informed,¹¹³ however, that the method was not applicable to the synthesis of thiotropone itself as an acidic catalyst caused decomposition to the tropylium salt and hydrogen sulphide.

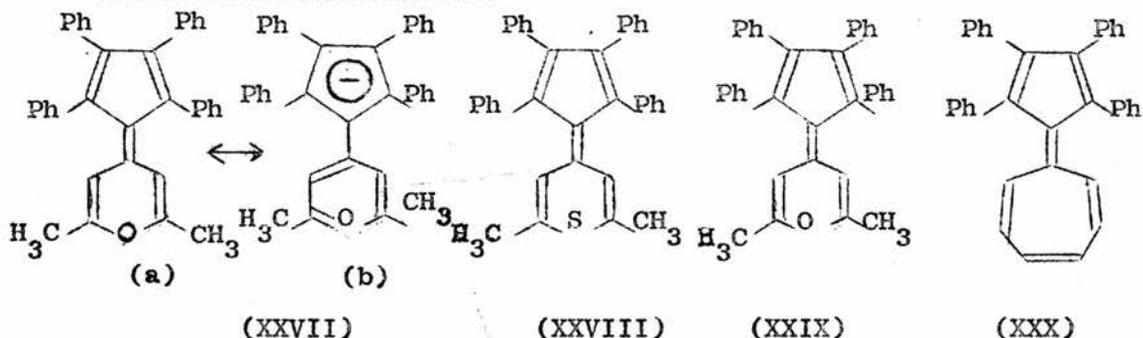
Tropone was therefore prepared from tropylium perchlorate via ditropyl ether and an attempt made to convert it into thiotropone by reaction with phosphorus pentasulphide. The only product obtained from the reaction was a yellow-brown solid which did not melt below 250^o. It was not identified, as it certainly was not the required thiotropone, but the high melting point suggested that it might be a tropylium salt. There was insufficient time to examine any other possible routes to thiotropone.

No reaction was evident between tropylium perchlorate and 2,3,4,5-tetraphenyldiazocyclopentadiene in boiling acetic acid (a polar solvent was necessary in order to dissolve the salt), the tropylium perchlorate being recovered unchanged in high yield. This provides further (negative) evidence in support of the postulated carbenic mode of reaction of the diazo compound. Since the carbene is an electrophilic species,

no tendency to attack the tropylium ion would be expected, but rather products from reaction with the solvent, etc. On the other hand, if an ionic mechanism held, electrophilic attack by the tropylium cation on C-1 of the five-membered ring would give, after elimination of a proton and nitrogen, the known tetraphenylsesquifulvalene. None of this product was formed.

[D] REACTIONS OF CYCLOPENTADIENYLIDENEPYRANS

(1) Structure and stability

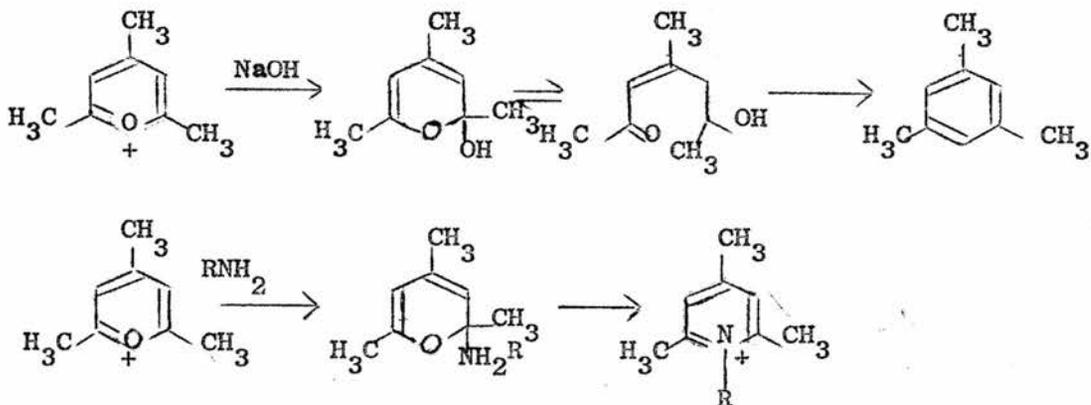


The two ylidenepyrans (XXVII) and (XXIX) form stable red needles, m.p. 267-269° and 261-262.5°, respectively, while the ylidene thiopyran (XXVIII) forms brown crystals, m.p. 239-241°. The structure of the compounds follows from their analyses and unambiguous syntheses. The two principal canonical forms of 4-tetraphenylcyclopentadienylidene-2,6-dimethylpyran may be written as (XXVII (a) \leftrightarrow (b)). The tetraphenyl heterocyclic compounds are iso- π -electronic with tetraphenylsesquifulvalene (XXX), prepared by Prinzbach.⁴⁶ It is of interest in this connection to note the close similarity in the U.V. spectra of these three compounds (see Part III, Section [H]).

Oxidative cleavage of the fulvene double-bond occurred when (XXXVII) was refluxed with chromium trioxide in acetic

acid solution. The only identified product was 2,6-dimethyl-4-pyrone; tetracyclone was not obtained so that the carbocyclic ring must undergo oxidation under the conditions used.

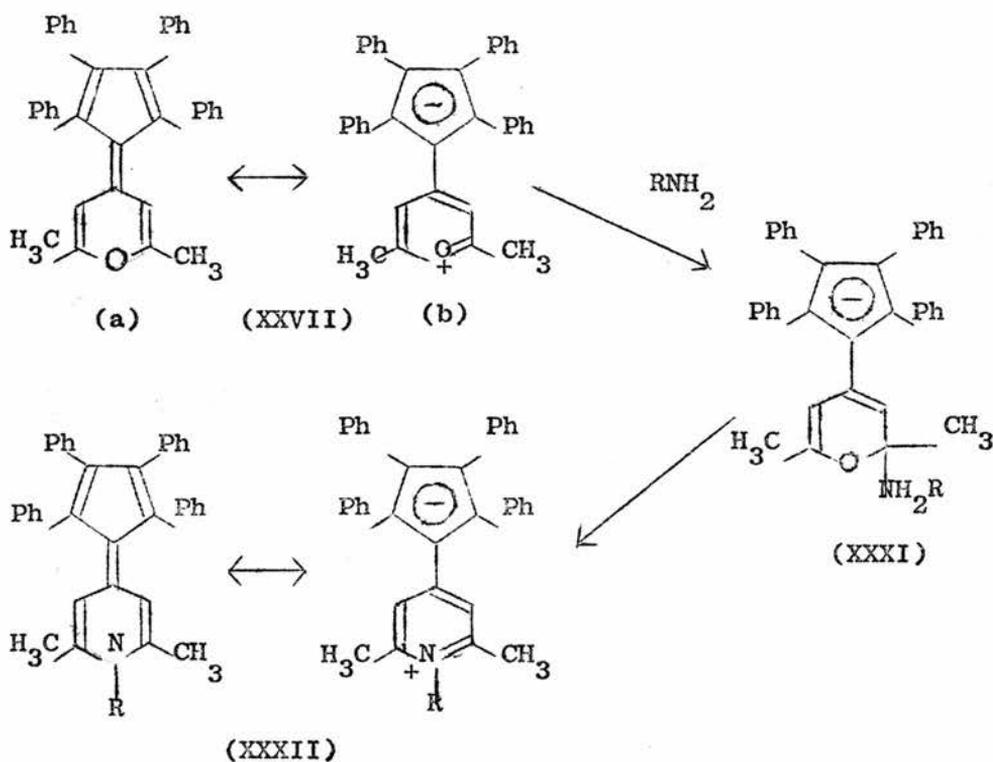
In general, bases attack pyrylium rings at C-2, the hydroxyl ion giving phenols and primary amines giving N-substituted pyridinium salts. That the initial attack occurs at C-2 is shown fairly conclusively in the reaction of sodium cyclopentadienide with trimethylpyrylium perchlorate to give 4,6,8-trimethylazulene.⁶⁹ Typical examples are the reactions of trimethylpyrylium perchlorate¹⁰¹:-



Pullman et al.⁴⁵ have predicted a large contribution from the dipolar canonical form of sesquifulvalene, and in the case of these cyclopentadienylidenepyran an identical state of affairs should exist. Since (XXVII (b)) makes a large contribution to the structure of 4-tetraphenylcyclopentadienylidene-2,6-dimethylpyran, it might be expected that this compound would be attacked by bases in a similar manner to the above but it was found to be quite unreactive towards them.

After attempted reactions with benzylamine and alcoholic sodium hydroxide solution, the ylidene pyran was recovered unchanged in nearly quantitative yield. Ammonia might be expected to give the pyridine derivative, but no reaction was found to take place even with the gas in anhydrous conditions. Potassium hydrosulphide solution failed to convert (XXVII) into the thiopyran compound (CCVIII); this was of particular note since the 2,6-dimethyl-4-thiopyran-thione used in the preparation of the latter compound was obtained from 2,6-dimethyl-4-thiopyrone by the action of potassium hydrosulphide solution.

The unreactivity to all these bases can be explained by considering the structure of the primary addition product which would be formed. This is exemplified by the case of benzylamine for which the following scheme would apply ($R=CH_2Ph$):-



The ylidenepyran (XXVII) is stabilised by resonance of the type (a) \longleftrightarrow (b), whereas the addition compound (XXXI) would have to bear a negative charge in the carbocyclic ring unstabilised by resonance interaction with the heterocyclic ring. Its formation would not, therefore, be energetically favoured. If it came into existence momentarily, electronic shifts throughout the conjugated skeleton would cause loss of benzylamine and reversion to (XXVII) rather than ring-opening and loss of water to give (XXXII).

(2) Electrophilic substitution in the carbocyclic ring

Since the dipolar form contributes to the structure of 4-(2',3',4'- triphenylcyclopentadienylidene)-2,6-dimethylpyran (XXIX), the C-2 position of the carbocyclic ring should be the most subject to electrophilic attack, The phenyl groups will be activated to some extent since they are attached to a ring bearing a partial negative charge, so that conditions would have to be mild to achieve only monosubstitution. In some of the reactions attempted some reaction occurred, but good analyses of the products could not be obtained. Similar conditions were employed as in the case of triphenyldiazocyclopentadiene (see Section [A] (4)).

Bromination.- On mixing the ylidenepyran and N-bromosuccinimide in chloroform solution, an immediate darkening in colour was evident. The residue from the main red-yellow fraction obtained by elution chromatography gave a solid which was separated into two components by fractional crystallisation. The least soluble component was unchanged ylidenepyran, while the second was a yellow solid, m.p. 126-129°. Although this melting point was fairly sharp, the elementary analysis figures showed that it was probably a mixture of the desired mono-bromo derivative and the unsubstituted compound, The percentage of bromine

found was only 3.58%, whereas the monobromo compound would require 16.7%; the carbon and hydrogen percentages likewise suggested that the solid contained only about 25% of the brominated product. It would be expected that the two compounds would have very similar polarities, and is not, therefore, surprising that they could not be separated chromatographically.

Iodo-mercuration and iodination.- An iodo-mercuration reaction identical to that successfully used with triphenyldiazocyclopentadiene (see Section [A] (4)) was attempted. Elementary analysis of the brown product, m.p. 231-235^o, again indicated that only partial reaction had occurred.

Reaction of this product with iodine, followed by chromatography and washing of the organic residue failed to give the mono-iodo derivative in a pure state. Elementary analysis showed that the product contained only one-fifth of the amount of iodine required by a mono-iodo derivative.

Diazo coupling. The ylidenepyran in methylene chloride solution was mixed with buffered aqueous benzenediazonium chloride solution. On extracting and chromatographing, the ylidenepyran was found to be unchanged.

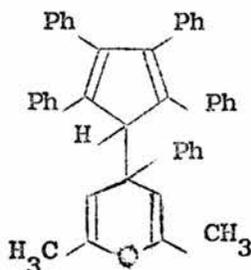
(3) Additions to the fulvene double-bond

The polarity of the exocyclic double-bond in fulvenes is shown by their reaction with such reagents as lithium aluminium hydride.⁶⁰ Phenyllithium is another such reagent and although no reactions of it with any sesquifulvalene analogue had been reported, an attempt was made to obtain a product from its reaction with 4-tetraphenylcyclopentadienyliidene-2,6-dimethylpyran (XXVII).

The structure of products obtained by reacting fulvenes

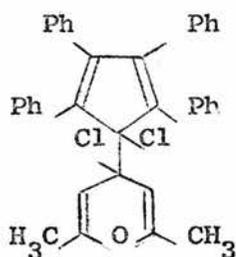
with halogens seems rather obscure.⁶⁰ In general, bromine appears to give a dibromo addition product and chlorine a tetrachloro addition product, while with some benzo-fulvenes it is claimed that substitution of chlorine in the ring takes place.

Phenyl lithium.- The reaction was attempted using a procedure similar to that used in the preparation of tetracyclone phenylhydrazone (see Section [A] (5)). Reaction at the fulvene double-bond would be expected to give a compound of this structure:-

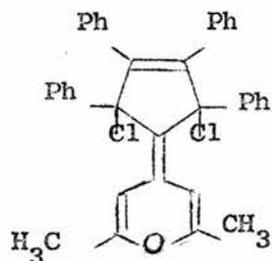


Chromatography of the products gave two coloured bands, the first yielding a very unstable yellow solid which rapidly decomposed to an oil. It was not possible to say whether this was the desired product or not, but due to steric overcrowding it might not be very stable. The structure of the product from the second, very polar band could not be elucidated definitely on the basis of its elementary analyses figures. Its U.V. spectrum had shoulders at positions close to the maxima for tetraphenylcyclopentadiene, while the long wavelength maximum in the spectrum of the ylidenepyran at 425 m μ had disappeared. This suggested that complete conjugation no longer existed in this product.

Chlorine.- Chlorine gas was passed through a solution of the ylidenepyran in dioxan. The deep red colour of the solution was immediately discharged, and the yellow product, m.p. 97° - 100° , gave an analysis corresponding fairly closely with a dichloro compound. The two most likely structures were (XXXIII) and (XXXIV).



(XXXIII)



(XXXIV)

If the structure were (XXXIV), the long wavelength maximum should be approximately the same as that of diphenylethylene ($314\text{ m}\mu$); if (XXXIII) it should be near that of tetraphenylcyclopentadiene ($335\text{ m}\mu$). In fact it occurred at $360\text{ m}\mu$, which lends support to the conclusion that the fulvene double-bond has been attacked to give (XXXIII).

Bromine.- Bromination by a chloroform solution of bromine was attempted giving a small yield of a brown solid, m.p. 175 - 195° . This product could not be purified by recrystallisation and its structure was not determined.

(4) Salt formation

The most important reaction of the ylidenepyrans was that with acids. They are pseudo-bases, and the action of acid was to cause protonation in the carbocyclic ring, with resultant loss of aromaticity. The formation and reactions of these salts are considered in the following section.

[E] REACTIONS OF CYCLOPENTADIENYLPYRYLIUM SALTS

(1) Formation and reaction with alkali

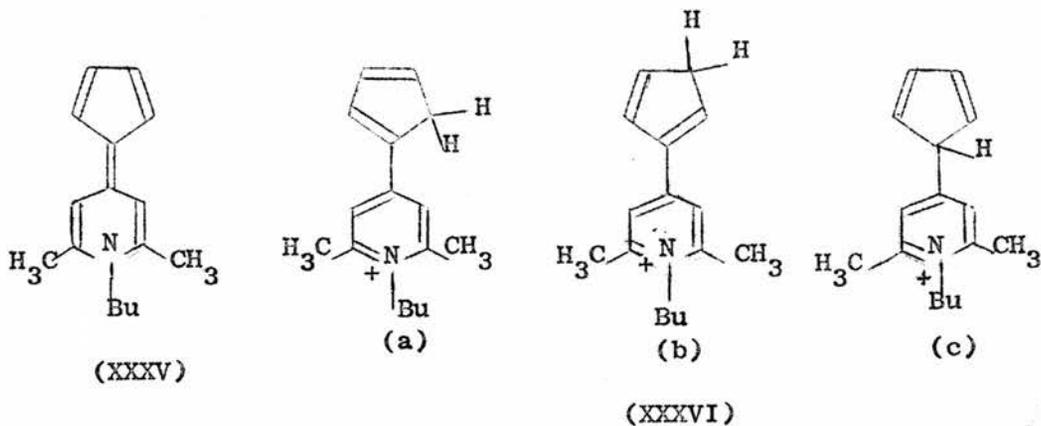
The tetraphenyl ylidenepyran (XXVII) reacted in ethereal suspension with perchloric acid to give orange crystals of the pyrylium perchlorate, m.p. 172-174^o. The product was insoluble in ether and benzene and only slightly soluble in ethanol; it appeared to be stable indefinitely in air. On boiling in ethanolic suspension it lost perchloric acid and reverted to the ylidenepyran. The triphenyl ylidenepyran (XXIX) likewise gave a perchlorate, m.p. 231-232^o.

Both these perchlorates, on shaking with alcoholic potassium hydroxide solution were quantitatively converted into the parent ylidenepyran pseudo-base.

When sulphuric acid was added to an ethereal suspension of the tetraphenyl ylidenepyran (XXVII), the orange sulphate was formed in suspension. It was not stable in air and appeared to be hygroscopic, giving an oil. The ylidenepyran was regenerated by the action of alkali on this oil.

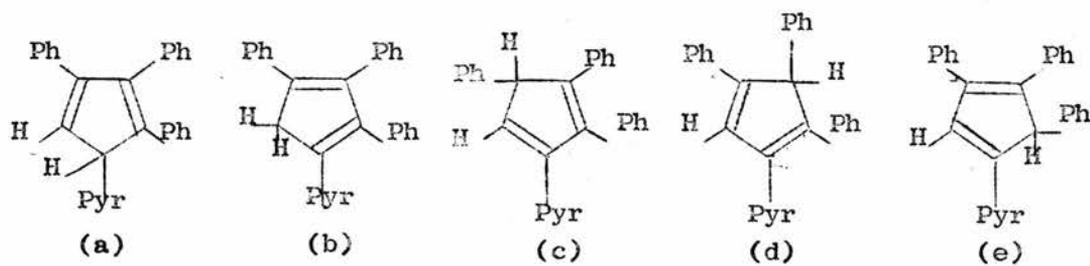
(2) Structure

Boyd and Jackman⁵⁴ have used N.M.R. spectroscopy in elucidating the structure of the conjugate acid of 1-butyl-4-cyclopentadienyliidene-2,6-dimethyl-dihydropyridine (XXXV). The spectrum of the perchlorate was recorded in T.F.A. solution, and two signals were observed due to the methylene protons of the five-membered ring. They concluded that a mixture of two conjugate acids existed (XXXVI (a) and (b)).

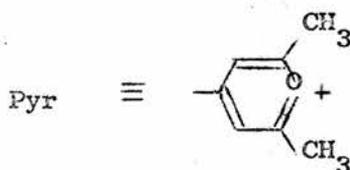


They were not able to decide which was the major constituent on the bases of chemical shifts. In the 2-cyclopentadienylidene series, Berson and Evleth⁵² also on the basis of N.M.R. spectra, found that a 7:3 mixture of two conjugate acids existed. Neither set of workers found any evidence to suggest that the third isomeric possibility (e.g. XXXVI) (c)) was present; a possible reason being that this is the least conjugated structure.

For both the ylidene pyrans (XXVII) and (XXIX), N.M.R. studies indicated that only one conjugated acid is present in T.F.A. solution. The spectra are listed in Part III, Section [I] and consideration will first be given to the structure of the conjugate acid of the triphenyl ylidene pyran (XXIX). In this compound none of the positions of the carbocyclic ring are equivalent so the following possibilities must all be considered:-



(XXXVII)



The N.M.R. spectrum exhibited three signals which will be considered in turn.

- (a) The signal at 7.45 τ could immediately be assigned to the six 2-(6-) methyl protons of the pyrylium ring.
- (b) The signal centred at 2.86 τ was assigned to the fifteen phenyl protons together with the two 3-(5-) pyrylium ring protons, which might be expected to have very similar chemical shifts. Integration gave the ratio of (a): (b) as 5.6: 17.0.
- (c) Since only one other signal arose, at 5.67 τ , the compound was assigned structure (XXXVII) (b): this is the only one in which the two protons attached to the carbocyclic ring will have identical chemical shifts. This signal, which was equivalent to two protons, appeared downfield of those arising from the methylene protons in (XXXVI), in agreement with the usual de-shielding due to a β -substituted phenyl group.

When the spectrum of the triphenyl phenyl group (XXIX) was taken in D.T.F.A, the same three signals were apparent, but with the 5.66 τ signal now equivalent to only one proton, since deuteration rather than protonation had occurred. It was of interest to notice that no deuterium exchange between the methylene proton and the solvent appeared to have taken place. This was in contrast to the case of triphenyldiazocyclopentadiene (see Section [A] (3)) when exchange occurred rapidly and completely, the relatively reduced reactivity in the case of the pyran possible being due to the electron-withdrawing property of the aromatic pyrylium ring.

The spectrum of the tetraphenyl ylidenepyran (XXVII) in T.F.A. showed three signals.

- (a) A signal at 7.56 τ was assigned to the six 2-(6-) methyl protons of the pyrylium ring.
- (b) A double peak with maxima at 2.68 τ and 2.84 τ was assigned to the twenty phenyl protons and two 3-(5-) pyrylium ring protons. Signals (a) and (b) had relative intensities 6.3:22.
- (c) A signal equivalent to approximately one proton at 4.5 τ . This was considered to arise from a proton at C-2 of the carbocyclic ring, since this structure is the most highly conjugated (c.f. (XXXVII) (b)) and by analogy with the case of the triphenyl compound above.

The U.V. spectra of both the tetra- and triphenyl ylidenepyrylium perchlorates and of the triphenyl ylidenethiopyrylium perchlorate appeared to be rather anomalous, all showing a maximum at longer wavelength than the parent pseudo-bases. Since the latter are fully conjugated and

protonation at any position whatever can only interrupt this conjugation, the observed bathochromic shift may be due to some form of intermolecular interaction.

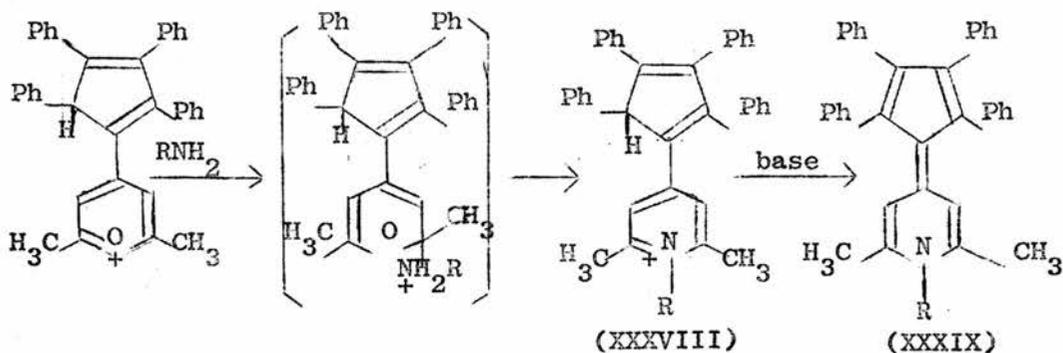
(3) Attempted Diels Alder additions

4-Tetraphenylcyclooctadienyliidene-2,6-dimethylpyran did not react with maleic anhydride, which was not surprising as the carbocyclic ring is considered to have partial aromatic character and so would not behave as a conjugated diene.

The conjugate perchlorate was also found to react neither as a diene nor as a dienophile in attempted reactions with maleic anhydride and with cyclopentadiene, respectively. This suggests that interaction of the double-bonds of the carbocyclic ring with the heterocyclic ring may occur, and provides an added reason why the perchlorate cannot be protonated at C-1' (c.f. (XXXVII) (a)).

(4) Reaction of the tetraphenyl derivative with bases

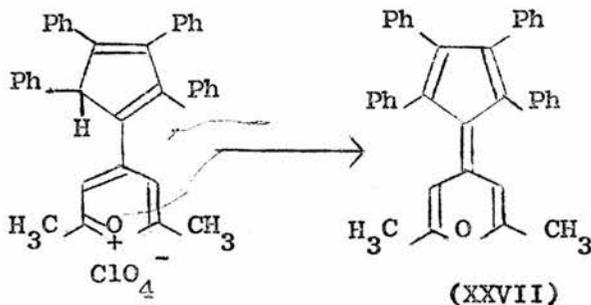
In Section [B] (1), it was argued that the stability of the parent ylidenepyran to attack by bases was due to the fact that the initial addition compound would have to bear a negative charge in the five-membered ring and its formation would not be energetically favoured. This consideration does not apply in the case of the perchlorates as they are protonated in the carbocyclic ring. A generalised reaction for the tetraphenyl compound with, for instance, primary amines can be visualised, the reaction sequence being as in Scheme (A):-



REACTION SCHEME (A)

Action of base on the resultant N-pyridinium salt (XXXVIII) should give the parent dihydropyridine compound (XXXIX); presence of excess of the amine should be sufficient to effect this. If the hydroxide ion, the hydrosulphide ion or ammonia were to react with the perchlorate in an analogous manner, the products expected would be a cyclopentadienylphenol, the thiopyran (XXVIII) and a cyclopentadienylpyridine respectively.

An alternative mode of reaction with bases involves loss of perchloric acid to give the parent ylidenepyran, thus:-



REACTION SCHEME (B)

Effect of the strength of the base.- Which of the two reaction schemes followed was found to depend on the strength of the base used. Since potassium hydroxide solution and potassium hydrosulphide solution followed Scheme (B), whereas benzylamine and p-toluidine followed Scheme (A) it was at first thought to depend on whether the base was an anion or a neutral molecule. No rational explanation for this could be discovered by a more detailed consideration of the mechanism, and further experiments showed that it did not hold true: ammonia and iso-propylamine, although uncharged molecules, followed Scheme (B). It now seems certain that the critical factor is the strength of the attacking base, only those having a pK_b value within certain limits following Scheme (A). The results are collected in the following table:-

BASE	pK_b	SCHEME FOLLOWED
hydroxide ion		(B)
hydrosulphide ion		
cyclopentadienide ion		
hydrazine		
diethylamine	2.9	
isopropylamine	3.5	
ammonia	4.75	
benzylamine	5.2	(A)
phenylhydrazine		
methylphenylhydrazine		
hydroxylamine		
<u>p</u> -toluidine	9.0	
aniline	9.3	(B)
<u>p</u> -aminobenzoic acid	12.0	
<u>p</u> -nitroaniline	13.0	

↓
DECREASING BASICITY

A competitive reaction between the two schemes may exist, but without a more detailed study it is impossible to say why the reaction is dependent on basicity in the manner shown. The cases in which reaction resulted in the formation of a new molecule are now considered in more detail.

Benzylamine.- When the pyrylium perchlorate was suspended in anhydrous benzene at room temperature and an excess of benzylamine added the precipitate dissolved to give a deep red solution, which was refluxed for an hour. Reaction presumably formed (XXXVIII; $R = CH_2Ph$) initially, which would be insoluble in the solvent, and in the presence of excess aniline this was immediately converted into (XXXIX; $R = CH_2Ph$). This product 1-benzyl-4-tetraphenylcyclopentadienyliene-2,6-dimethyldihydro-pyridine, was isolated in 49% yield as deep red crystals, m.p. 217-220°.

When this product was suspended in ether and a little 73% perchloric acid added, a yellow precipitate immediately formed but rapidly decomposed to a separate red layer. The yellow precipitate was presumably the corresponding pyridinium salt (XXXVIII; $R = CH_2Ph$). Since the reaction was, of necessity, performed on a very small scale a slight excess of perchloric acid may have been added, and the salt may have dissolved in this to give the separate red layer rather than actually decomposing.

The N.M.R. spectrum of the product (XXXIX; $R = CH_2Ph$) was taken in T.F.A., in which solvent it would be expected to be protonated. There was enough of the compound to make up only a very weak (1.5%) solution. Therefore, the signals obtained were not sufficiently strong relative to the background noise for a reliable integration to be obtained; also, it was

not possible to pick up a signal due to the single proton attached to the carbocyclic ring expected at ca 4.0 - 5.0 τ . A complex double-peak at 2.65/2.88 τ was assigned to all twenty-six phenyl protons together with two 3-(5-) pyridinium ring protons; a signal at 7.6 τ to the 2-(6-) methyl protons; and a smaller signal at 7.3 τ to the methylene protons of the benzyl group.

The U.V. spectrum of (XXXIX; R = CH₂Ph) was taken in methanol, and in methanol containing a trace of perchloric acid; in the latter case the long wavelength maximum was at shorter wavelength. This is in agreement with protonation interrupting conjugation in the latter case. However, the maximum was at longer wavelength than that of tetraphenylcyclopentadiene, so some conjugation must exist between the five-membered ring and the heterocyclic ring i.e. protonation was at C-2' or C-3'. The N.M.R. spectrum in this case gave no information to assist in deciding between the two possibilities, but again it is pointed out that protonation at C-2' gives the most highly conjugated molecule.

This compound, and others obtained by reaction with amines, were completely stable, in contrast to some of the unphenylated ylidenedihydropyridines.^{53,54}

p-Toluidine.- Reaction of the pyrylium perchlorate with p-toluidine was carried out in an identical manner to the above, giving a 25% yield of 1-p-methylphenyl-2,6-dimethyl-4-tetraphenylcyclopentadienylylidenedihydropyridine (XXXIX; R = C₆H₄CH₃) as dark red needles, m.p. 262-264°.

The U.V. spectrum of this product again showed a shift to shorter wavelength of the long wavelength maximum in the

presence of acid, indicating protonation at either C-2' or C-3' of the five-membered ring. The N.M.R. spectrum in T.F.A. indicated that only one conjugate acid was present. The spectrum was analysed as follows.

- (a) A twin peak at 2.65 τ / 2.81 τ was assigned to the twenty-four phenyl protons and the two 2-(6-) pyridinium ring protons.
- (b) A signal at 7.52 τ was assigned to the nine methyl protons.
- (c) A signal at 4.5 τ was assigned to the single proton attached to the five-membered ring.

Integration gave the relative intensities as 26:8.3:1.2 compared with the required 26:9:1.

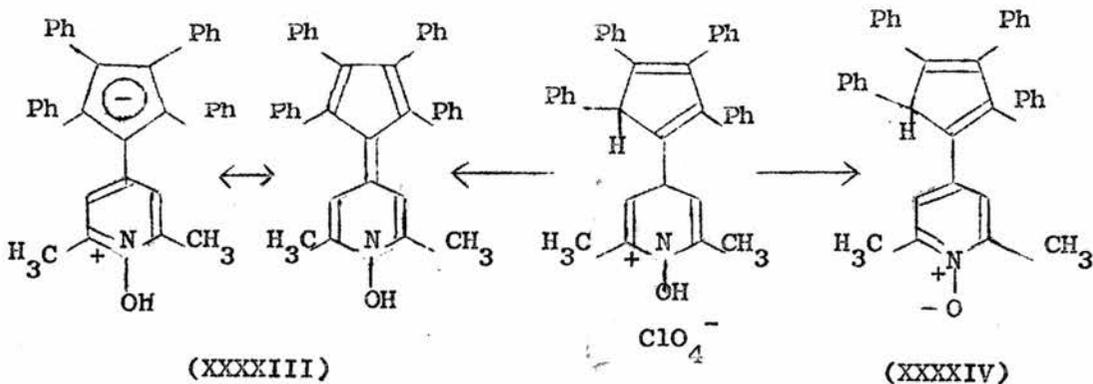
Aniline.- Aniline reacted with the ylidene-pyrylium perchlorate under identical conditions to the above to give a red solution, but working up gave only an oily red solid. This could not be purified sufficiently for its identity to be established.

Phenylhydrazine.- On addition of a slight excess of phenylhydrazine, a suspension of the pyrylium perchlorate dissolved to give a clear red solution, but on refluxing this a bright yellow precipitate was formed immediately. Analysis indicated that this yellow solid was 1-anilino-4 tetraphenyl-cyclopentadienyl-2,6-dimethylpyridinium perchlorate (XXXX) which was formed in 89% yield, m.p. 200-201^o. Shaking of this product with ethanolic alkali and working up the red solution obtained provided a red solid, m.p. 118-120^o. This solid was formed by removal of perchloric acid, which could have occurred in two ways:-

unsymm-methylphenylhydrazine.-- Reaction of the ylidene-pyrylium perchlorate with unsymm-methylphenylhydrazine proceeded with the isolation of the pseudo-base (XXXIX; R = N(CH₃)Ph) directly. It was formed in 57% yield as a brick-red solid, m.p. 142-144^o, and it did not appear to be completely stable on standing at room temperature exposed to air.

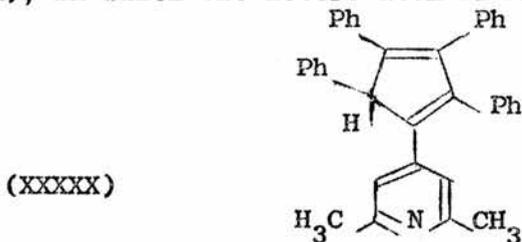
The U.V. spectra in methanol and in methanol with a trace of perchloric acid added are given in Part III, Section [H]. It is noticeable that in both cases they closely resemble the spectrum of the corresponding compound derived from phenylhydrazine. In this case, however, there is no hydrogen attached to the exocyclic nitrogen atom in the perchlorate which could be removed by base to give a betaine structure, so that the pseudo-base must have the fully conjugated form (c.f. XXXXI).

Hydroxylamine.-- The ylidene-pyrylium perchlorate reacted with hydroxylamine (liberated from an alcoholic solution of the hydrochloride by the addition of a slight excess of alkali) to give a red solution. It turned yellow on refluxing and the product obtained was an unstable yellow solid, m.p. 97-103^o, which decomposed to an oil on attempted recrystallisation. The product could not be purified effectively by washing, but elementary analysis indicated that it contained one atom of nitrogen. The N-hydroxypyridinium salt (XXXIX; R = OH) which would be the initial reaction product, again could have lost a molecule of perchloric acid in two possible ways to give (XXXIII) or (XXXIV).



The U.V. spectrum of the final product (XXXIX; R = OH) when taken in acidic solution had a long wavelength maximum in the same region of the spectrum as other similar compounds already considered. Contrary to the other cases, however, this maximum was at slightly longer wavelength than that in neutral solution. The completely conjugated structure (XXXXIII) could be ruled out as (XXXIX; R = OH) would be expected to absorb at shorter wavelength than this. Structure (XXXXIV) would be expected to absorb at similar wavelength as its conjugated skeleton is the same. The rather unstable product was therefore considered to have this N-oxide structure.

It would clearly be of interest to prepare compound (XXXXX), in which the hetero-atom is not quaternised.



It was impossible to prepare this compound from the pyrylium analogue by the action of ammonia, as already discussed, since this reagent caused regeneration of the ylidene pyran. It was thought that an alternative route might be provided by reduction of its N-oxide (XXXXIV). Reaction with benzyl chloride followed by treatment with alkali, and reaction with phosphorus pentachloride are standard methods of achieving reduction of pyridine N-oxides. Attempts were made by both methods, but in both cases only an oily brown decomposition product was obtained, similar in appearance to that formed on attempted recrystallisation of the N-oxide.

PART III

EXPERIMENTAL

[A] SYNTHESIS OF PHENYLATED DIAZOCYCLOPENTADIENES

(1) From the diene

2,3,4,5-Tetraphenyldiazocyclopentadiene.- Tetraphenylcyclopentadiene (5 g.), toluene-p-sulphonylazide (2.7 g.) and diethylamine (12.5 ml.) were mixed, some heat being evolved. On being allowed to stand for ten days at 0°, a red precipitate was formed. Water (70 ml.) was added, and the mixture was extracted with ether several times. The combined ethereal extracts were washed several times with water, dried (Na₂SO₄) and the solvent removed. The residue, dissolved in the minimum quantity of benzene, was applied to an alumina column*. Elution with a 1:1 mixture of benzene and 80-100° petroleum ether brought off two distinct bands:

- (1) The first band was yellow, and on removing the solvent and washing the residue with methanol, yielded 2,3,4,5-tetraphenyldiazocyclopentadiene (3.5g.; 66%) as yellow crystals, m.p. 143-144° dec.^t On standing for a few days the crystals became red in colour, but the melting point remained constant. The product exhibited intense absorption in its I.R. spectrum at 4.70μ, arising from the diazo group.

* All column chromatography was done using Type H 100/120 mesh activated alumina.

^t All melting points are corrected.

- (2) The second band was purple in colour and yielded a few mg. of tetraphenylcyclopentadienone (hereafter referred to as tetracyclone).

2,3,4-Triphenyldiazocyclopentadiene.- 2,3,4-Triphenylcyclopentadiene (7.7g.), toluene-p-sulphonylazide (4.75g.) and diethylamine (25 ml.) were mixed and allowed to stand at 0° for a week. Water (100 mls.) was added, and the mixture extracted several times with benzene. The combined extracts were washed several times with water, dried (Na₂SO₄), and reduced in volume by evaporation. On applying the solution to an alumina column and eluting with a 1:1 mixture of benzene and 100-120° petroleum ether, the first band (yellow) gave a yellow solid, m.p. 153-157°. Rapid crystallisation from cyclohexanone gave yellow crystals of 2,3,4-triphenyldiazocyclopentadiene (5.2g.; 50%), m.p. 159-159.5° (boiling in solution for longer than a very few minutes caused partial decomposition to a dark-coloured solid). The product showed intense absorption in its I.R. spectrum at 4.80μ.

Attempted extension of the method to the synthesis of ylidenedihydropyridines

Cyclopentadiene and pyridine methiodide in diethylamine.- Cyclopentadiene (13.4g.) pyridine methiodide (4g.) and diethylamine (17 ml.) were mixed and allowed to stand for two days at 0°, during which time the mixture became dark in colour. Filtration separated a dark solid, but on refluxing this in ethanolic solution with charcoal screening, filtering, and removing solvent, a yellow solid consisting of unreacted pyridine methiodide in nearly quantitative amount was obtained.

2,3,4,5-Tetraphenylcyclopentadiene and pyridine methiodide in diethylamine.- 2,3,4,5-Tetraphenylcyclopentadiene (2g.),

pyridine methiodide (1.19g.) and diethylamine (20 ml.) were mixed and allowed to stand at 0°. No darkening in colour took place and the 2,3,4,5-tetraphenyldiazocyclopentadiene was filtered off unchanged after several days.

(2) From the dienone

2,3,4,5-Tetraphenylcyclopentadienone toluene-p-sulphonylhydrazone.- Toluene-p-sulphonylhydrazine (10.56g.) and conc. sulphuric acid (20 ml.) in dioxan (130 ml.) were placed in a three-necked flask fitted with a gas inlet tube, condenser and dropping funnel, and the solution brought to reflux. A continuous stream of oxygen-free nitrogen was passed through the vessel while a solution of tetracyclone (21.77g.) in dioxan (750 ml.) was added during 1 hr. Refluxing was continued for a further 2 hrs., the solution was then cooled and, with vigorous stirring, poured into water (7 l.). The light red-brown coloured precipitate was filtered off, washed once with water, then warm ethanol, to give 26.25g. (66%) of tetracyclone toluene-p-sulphonylhydrazone as copper-coloured needles, m.p. 171-172° dec.

The product obtained in this way was found to be fairly pure as shown by chromatography using benzene as eluent. The only impurity detected was tetracyclone, and this in trace amount. A sample was prepared for analysis by recrystallising twice from ethanol (Found: C, 77.24; H, 5.17; N, 4.96; S, 5.67. $C_{36}H_{28}O_2N_2S$ requires: C, 78.26; H, 5.07; N, 5.07; S, 5.80).

The product appeared to be completely stable in air, and was not decomposed by hydrochloric acid in ethanol. The reaction was repeated in an identical manner, but without the presence of the inert atmosphere. In this case the proportion

of unreacted tetracyclone in the products was found to be considerably higher, and the yield of toluene-p-sulphonylhydrazone, after purification, was reduced to 46%.

No reaction occurred in the absence of conc. sulphuric acid, using ethanol as the solvent. Tetracyclone (6.2g.) and toluene-p-sulphonylhydrazine (3g.) were dissolved in boiling ethanol (600 ml.) and the solution refluxed for two hours. On cooling, unchanged tetracyclone precipitated out.

Alkaline cleavage of 2,3,4,5-tetraphenylcyclopentadienone toluene-p-sulphonylhydrazone to 2,3,4,5-tetraphenyldiazocyclopentadiene.- Tetracyclone toluene-p-sulphonylhydrazone (9.3g.) was suspended in anhydrous ether (250 ml.) and a 3% solution of sodium ethoxide in ethanol (250 ml.) was added. The resulting dark solution was stirred mechanically for 2 hrs. on a warm water bath, so that it refluxed gently. The solution was cooled and washed with several portions (250 ml.) of water. The ethereal layer was dried (Na_2SO_4), and evaporated (care: frothing) to give a red-brown solid residue (6.2g.). Recrystallisation from n-propanol gave red crystals of 2,3,4,5-tetraphenyldiazocyclopentadiene (4.25g.; 64%), m.p. 142-143^o dec. (Found: C, 87.97; H, 5.16; N, 6.76. $\text{C}_{29}\text{H}_{20}\text{N}_2$ requires C, 87.88; H, 5.05; N, 7.07.). The product had an intense absorption band in its I.R. spectrum at 4.70 μ , arising from the diazo group. It gave an intense red colouration with conc. sulphuric acid, whereas tetracyclone gave a deep blue colouration.

Concentration of the mother liquors from the recrystallisation yielded a further crop of product, but examination with a microscope showed this to be contaminated with a white impurity. The latter was isolated, by its

relative insolubility in ether, as a white solid, m.p. 221-222.5° to a red melt. (Elementary analysis gave figures corresponding to $C_{32}H_{28}O_2$; 1-propoxytetraphenylcyclopentadienol has this formula).

Cleavage was also effected by ethanolic potassium hydroxide solution (5%).

Dibenzyl ketone toluene-p-sulphonylhydrazone.- Dibenzyl ketone (11.11g.) and toluene-p-sulphonylhydrazine (10g.) were dissolved in ethanol (1 l.) and refluxed for 15 mins. The precipitate (16.8g.) obtained on cooling, together with a further precipitate (4.4g.) obtained on evaporation of the solvent, was recrystallised from ethanol to give a white solid (15.4g.; 86%) of dibenzyl ketone toluene-p-sulphonylhydrazone, m.p. 181-182° (Found: C, 70.03; H, 5.75; N, 7.35; S, 8.52. $C_{22}H_{22}N_2O_2S$ requires: C, 69.84; H, 5.82; N, 7.41; S, 8.46).

Alkaline cleavage of dibenzyl ketone toluene-p-sulphonylhydrazone.- The toluene-p-sulphonylhydrazone (3.44g.) in anhydrous dioxan (100 ml.) was mixed with 5% methanolic sodium methoxide solution (25 ml.), and refluxed for 5 hrs. Water and ether were added and the yellow organic layer separated, washed with water, dried (Na_2SO_4) and solvent removed on a water-bath. The residual yellow liquid distilled at 55°/10 mm. to give colourless 1,3-diphenylpropene, identified as the dibromide, m.p. 108-110°.

Attempted one-stage synthesis of tetraphenyldiazocyclopentadiene.- Benzil (2.1g.) and dibenzyl ketone toluene-p-sulphonylhydrazone (3.78g.) were dissolved in anhydrous dioxan. After addition of 5% methanolic sodium methoxide solution (25 ml.), the solution was refluxed for

4 hrs., with mechanical stirring. The yellow solution was poured into water and extracted with ether. The yellow residual oil (1.63g.) was distilled and the distillate identified as 1,3-diphenylpropene, as above.

Reaction between 2,3,4-triphenylcyclopentadienone and toluene-p-sulphonylhydrazine.- Toluene-p-sulphonylhydrazine (0.24g.) and conc. sulphuric acid (0.5 ml.) in dioxan (5 ml.) were brought to reflux. 2,3,4-Triphenylcyclopentadienone (0.38g.) was added portionwise and refluxing continued for 2.5 hrs. The solution was poured into water, and the grey precipitate, after filtration and drying was applied in benzene solution to an alumina column.

A green band, eluted with ethanol, yielded a green solid (0.214g.), m.p. 163-167° after two recrystallisations from ethanol (Found: C, 81.63; H, 5.89; N, 2.98; S, 6.02, corresponding approximately to $C_{31}H_{27}NSO$; the desired toluene-p-sulphonylhydrazone, $C_{30}H_{24}N_2SO_2$, requires C, 75.63; H, 5.04; N, 5.88; S, 6.72). Carbonyl group absorption was present in the I.R. spectrum at 5.85μ .

A much more polar red band was eluted with acetic acid, but on coming into contact with the eluent it changed its colour to dark blue. The blue solid, (0.045g.), m.p. 161-167°, obtained on working this fraction up gave a blue solution in alcoholic hydrochloric acid solution and a red solution in alcoholic potassium hydroxide solution. No absorption band appeared in the carbonyl group region of the I.R. spectrum either in carbon tetrachloride solution (blue) or in alkalene alcoholic solution (red). (Found: C, 87.68%; H, 5.14%; N, 1.43%; S, 3.34%).

[B] PRELIMINARY ATTEMPTS TO SYNTHESISE CYCLOPENTADIENYLIDENE PYRANS

(1) Grignard Reactions

Cyclopentadienyl magnesium bromide.- The method is that of Peters.⁹⁴

Magnesium (24g.) was placed in a dry three-necked flask fitted with a condenser and mechanical stirrer. Ethyl bromide (109g.) in ether (625 ml.) was run in slowly, and reaction was initiated by the addition of a small crystal of iodine, when cooling became necessary. The formation of ethyl magnesium bromide was completed by refluxing for several hours. Freshly distilled monomeric cyclopentadiene (70g.) was added, and the solution refluxed for 20 hrs until the evolution of ethane ceased. This solution was then used in the subsequent reactions.

Reaction between cyclopentadienyl magnesium bromide and 2,6-dimethyl-4-pyrone.- 2,6-dimethyl-4-pyrone (5.9g.) was added to a portion of the above solution of cyclopentadienyl magnesium bromide equivalent to 3.4g. of cyclopentadiene and the resultant red solution was refluxed briefly, with mechanical stirring. The dark coloured oily solid which remained on evaporating off the solvent was decomposed by ice to give a yellow solid. Addition of dil. sulphuric acid to this product formed a yellow-red oily solid which was separated by decantation and converted into a yellow precipitate (darkened ca. 240° , m.p. 300°) on triturating with ether. It was very soluble in acetic acid, dioxan and acetone, slightly soluble in ethanol and ether.

The elementary analysis figures corresponded approximately to the formula $C_{11}H_{17}O_7$, and the reaction was not studied further. This formula corresponded to

that of the desired product, 4-cyclopentadienylidene-2,6-dimethylpyran, with two peroxide groups and two molecules of water.

Cyclopentadienyl magnesium bromide and xanthone.- Xanthone (21g.) in benzene (50 ml.) was added to a portion of the above ethereal solution of cyclopentadienyl magnesium bromide equivalent to 7.5g. of cyclopentadiene. The mixture was refluxed for 1 hr. The yellow residue obtained on evaporation of the solvent in vacuo was shaken with an ice-cold 1:1 aqueous solution of sulphuric acid, forming a brown solid. This was filtered off and dried in vacuo.

The dark brown solid partially sublimed to colourless crystals at ca 110^o, and melted at 151-167^o; the sublimed portion had a similar melting range. The product was insoluble in ether and benzene, but soluble in ethanol, acetone, dioxan and acetic acid. An analysis sample was prepared by precipitation from acetic acid solution by the addition of water, and the figures obtained corresponded to a mono-peroxide of cyclopentadienylidenexanthene. (Found: C, 78.25; H, 4.18. C₁₈H₁₂O₃ requires C, 78.27; H, 4.35).

The product (2g.) was dissolved in acetic acid (25 ml.) and chromium trioxide (2g.) added. After refluxing for 1 hr. the mixture was cooled, filtered, and dirty white crystals, m.p. 167-174^o, were obtained by addition of water to the filtrate. Recrystallisation from aqueous ethanol gave xanthone, m.p. and mixed m.p. 171-174^o.

An attempt to form a Diels Alder adduct with maleic anhydride failed.

(2) Ring-closure reactions

Reaction of fluorene-9-carboxylic acid chloride, mesityl oxide and perchloric acid.- Fluorene-9-carboxylic acid chloride (1.23g.) and 70% perchloric acid (1.5 ml.) in acetic anhydride (4.5 ml.) were mixed at 0°. Mesityl oxide (0.57g.) was added and the mixture swirled as reaction took place. After heating on a steam-bath for 1 hr., the solution was cooled, giving a brown crystalline mass. The solid was filtered off and recrystallised from acetic acid, then ethanol to give white crystals, m.p. and mixed m.p. 246-250°, of 2,4,6-trimethylpyrylium perchlorate. The structure of the product was confirmed by reacting it in the cold with ammonium carbonate solution to give 2,4,6-trimethylpyridine, identified as the picrate, m.p. 152-156° (155-156°).

Reaction of fluorene-9-carboxylic acid chloride, mesityl oxide, and anhydrous ferric chloride.- The above reaction was repeated using freshly sublimed anhydrous ferric chloride in place of the perchloric acid in acetic anhydride. A solid brown product was obtained, but it could not be recrystallised, and elementary analysis indicated that it was not the desired product.

Cyclopentadiene carboxylic acid chloride.- The acid was prepared by the method of Peters.⁹⁴ Carbon dioxide gas, dried by passing through conc. sulphuric acid, was bubbled for 2 hrs. through a solution of cyclopentadienyl magnesium bromide in ether, prepared as above from 70g. of cyclopentadiene. A thick green oil separated from the clear ethereal layer. Water and then sulphuric acid were added, the oil reacting vigorously, to give two clear

layers containing a suspended solid. The solid was filtered off and taken up in aqueous ammonia, filtered and reprecipitated by the addition of acid. Recrystallisation from methanol gave dimeric cyclopentadiene-9-carboxylic acid (2.01g.; 2%) m.p. 216-219°.

Dimeric cyclopentadiene-9-carboxylic acid (0.5g.) and thionyl chloride (2.4 ml.) in carbon tetrachloride (1.5 ml.) were refluxed for 4 hrs. During this time the white solid slowly dissolved to give a brown solution. Removal of solvent in vacuo gave a viscous brown oil. Attempts to distil this at pressures down to 0.1 mm. failed, the oil merely charring at high temperature.

3-Fluorenyl-propiofenone.- Sodium hydroxide (3g.) was dissolved in a mixture of water (18 ml.) and ethanol (10 ml.), and the solution cooled. Acetophenone (5.6g.) and fluorene-9-aldehyde (9.0g.) were added, with mechanical stirring, the temperature being kept steady at 25°. The immediate purple colouration soon disappeared and after 20 mins. a white solid began to form. After stirring for 3 hrs., the mixture was allowed to stand overnight at 0°, by which time it had become a thick paste. The filtrate was washed with water until the washings were neutral to litmus, then with a little cold ethanol, to give 3-fluorenyl-propiofenone (4.25g.; 31%), m.p. 185-187° (Found: C, 89.73 ; H, 5.33 ; $C_{22}H_{16}O$ requires: C, 89.19 ; H, 5.40.).

When shaken with hydrazine hydrate, 3-fluorenyl-propiofenone gave a purple colouration, which could not be extracted into ether, and was destroyed on acidification. It may be due to the formation of a basic pyrazoline, but attempts to isolate this failed.

Reaction of 3-fluorenyl-propiofenone, acetophenone and perchloric acid.- 3-Fluorenyl-propiofenone (1 g.), acetophenone (0.39g.) and 70% perchloric acid (0.5 ml.) were dissolved in acetic anhydride (50 ml.) and the red solution was refluxed for 2 hrs., by which time it had become darker in colour. The solution was cooled, neutralised with sodium carbonate solution, and the mixture extracted with benzene. The dark benzene layer was washed twice with water, dried (Na_2SO_4) and the solvent removed. The oily solid residue was converted into a brown powder, m.p. $< 310^\circ$, by washing with ethanol, but its structure could not be elucidated (Found: C, 73.74; H, 4.31).

(3) Michael condensation

Condensation of salicylidene-acetophenone and 2,3,4,5-tetraphenylcyclopentadiene.- Potassium hydroxide (2g.) in water (2 ml.) was added to a suspension of tetraphenylcyclopentadiene (4 g.; a 15% molar excess) and salicylidene-acetophenone (2.1g.) in pyridine (30 ml.). After allowing to stand at room temperature for 8 days, the suspension was poured into dil. hydrochloric acid solution (100 ml.) and the mixture filtered to give an oily brown solid, which was washed with water. The solid was warmed with a solution of potassium hydroxide (4g.) in methanol (100 ml.). Part of the solid dissolved to give a dark solution, while a yellow solid remained in suspension. The yellow solid was removed by filtration and, after recrystallisation with charcoal screening from acetic acid, was identified as unreacted tetraphenylcyclopentadiene (1.75g.; 45%), m.p. $175-178^\circ$. The solution was neutralised with 1:1 aqueous acetic acid, whereupon a light brown solid (1.73g.) m.p. $110-120^\circ$, was precipitated. Recrystallisation from 90% aqueous methanol gave

a yellow-green solid (1.73g.; 25%), m.p. 131-132° consisting of the desired condensation product, w-tetraphenylcyclopentadienyl-w-o-hydroxyphenylpropiophenone (Found: C, 87.04; H, 5.27. $C_{44}H_{34}O_2$ requires C, 88.89; H, 5.72). This product showed no absorption between 5 μ and 6 μ in its I.R. spectrum.

The use of a slight excess of tetraphenylcyclopentadiene, as above, was found to improve the yield of the condensation product. When equivalent amounts of the two reactants were used, the yield was reduced to 17%. The reaction was repeated, but with the difference that instead of allowing the mixture to stand for some days at room temperature, it was refluxed for 4 hrs. An identical working-up procedure was used, but only 0.075g. (1.6%) of the condensation product resulted.

Attempted conversion of product to the ylidene flavene.- The condensation product from the Michael reaction (0.2g.) and chloranil (0.0835g.) were dissolved in xylene (15 ml.), and the solution refluxed for 40 mins. After standing overnight, the precipitated quinol was filtered off, and the solvent removed in vacuo. The red residue was recrystallised twice from ethanol to give a yellow solid, m.p. 170-180°. Further recrystallisations failed to raise the m.p., or make it any sharper. A Lassaigne test gave a positive result for chlorine and elementary analysis gave figures in agreement with this product being a complex with the haloquinone. (Found: C, 39.10; H, 1.62. Chloranil requires C, 29.3. Condensation product requires C, 88.89; H, 5.72).

An ice-cold solution of the condensation product (0.292g.) in ether (10 ml.) and acetic anhydride (2 ml.) was slowly treated with 72% perchloric acid (0.2 ml.) and the resulting deep red solution left overnight at 0°. A small amount

of red solid formed and was separated by decantation and washed well with ether. The solid turned yellow and progressively melted between 170° and 320°, and its elementary analysis did not correspond to any recognisable product.

[C] SYNTHESIS OF CYCLOPENTADIENYLIDENEPYRANS

(1) Reactions with 2,3,4,5-tetraphenyldiazocyclopentadiene

2,6-Dimethyl-4-thiopyrone.- 2,3,4,5-Tetraphenyldiazocyclopentadiene (0.5g.) and 2,6-dimethyl-4-thiopyrone (0.2g.; a 12% molar excess) were dissolved in p-cymene (20 ml.; first purified by distilling twice from sodium). The solution was refluxed gently for 7 hrs. The solvent was removed in vacuo and the residue applied to an alumina column in the minimum volume of benzene.

A dark yellow layer, eluted with a 7:3 mixture of benzene: 60-80° petroleum ether, gave a residue which on recrystallisation from a 9:1 mixture of ethanol: benzene provided deep red crystals (0.10g.; 16.7%) of 4-tetraphenylcyclopentadienylidene-2,6-dimethylpyran, m.p. 267-269°. (Found: C, 89.69; H, 6.06. $C_{36}H_{28}O$ requires C, 90.79; H, 5.87).

A second purple layer was eluted with benzene and, after one recrystallisation from acetic acid yielded tetracyclone (0.03g.; 6%), m.p. 216-218°.

In two repetitions of this experiment, the yields obtained were both 14%. In other hydrocarbon solvents with lower boiling points, the yields were reduced, while no reaction occurred in ethanol, the reactants being largely recovered unchanged. The average yields obtained are listed in the table.

solvent	boiling point	yield of pyran
benzene	80°	5.5%
toluene	110°	8.7%
mesitylene	165°	13.0%
p-cymene	177°	14.9%
ethanol	78°	nil

Samples removed periodically during the course of the reaction and tested by thin layer chromatography showed no increase in the amount of product after the first few hours. Chromatography on a plate coated with silica, and elution with a 7:3 mixture of 60-80° petroleum ether:ether gave four coloured spots. These were identified, as shown, by comparison with pure samples.

yellow  ylidenepyran
blue  diazo compound
very faint yellow  thiopyrone
brown  -----

2,6-Dimethyl-4-thiopyran-thione.- 2,3,4,5-Tetraphenyldiazo-cyclopentadiene (0.5g.) and 2,6-dimethyl-4-thiopyran-thione were dissolved in mesitylene (15 ml.) and the solution was refluxed for 7 hrs. The solvent was removed in vacuo, and the brown residue dissolved in the minimum quantity of benzene and applied to an alumina column.

The first red layer, eluted with a 7:3 mixture of benzene: 60-80° petroleum ether, gave brown crystals (0.167g.; 27%) of 4-tetraphenylcyclopentadienylidene-2,6-dimethylthiopyran, m.p. 239-241°. (C₃₆H₂₈S requires C, 87.80; H, 5.69; S, 6.50. Two elementary analyses of different samples were obtained, the first being acceptable for C, but not S, while in the second the reverse held: (a) C, 88.74; H, 6.25; S, 4.12. (b) C, 80.5; H, 5.38; S, 6.97).

Xanthione.- 2,3,4,5-Tetraphenyldiazocyclopentadiene (1.5g.) and xanthione (0.89g.; 10% molar excess) were dissolved in mesitylene (40 ml.) and the solution was refluxed for 7 hrs. The solvent was removed in vacuo and the residue dissolved in the minimum volume of benzene and applied to an alumina column.

Elution with a 7:3 mixture of benzene:100-120° petroleum ether gave two fractions. The first (dark blue) band yielded a black solid (0.665g.), m.p. 80-95°, which went into an oil on attempted recrystallisation. This decomposition product did not show the characteristic diazo group absorption band at ca 4.8 μ in its I.R. spectrum. The second (green) band gave beautiful long red needles (0.45g.), m.p. 155.5-157.5° to a green melt, on two recrystallisations from ethanol. Despite its appearance, elementary analysis indicated that this material was unreacted xanthione (lit. m.p. 155-156°).

Reactions with 2,3,4-triphenyldiazocyclopentadiene

2,6-Dimethyl-4-thiopyrone.- 2,3,4-Triphenyldiazocyclopentadiene (1.5g.) and 2,6-dimethyl-4-thiopyrone (0.65g.) were dissolved in mesitylene (50 ml.). The solution was brought slowly to the boiling point and gently refluxed for 6 hrs. The solvent was removed in vacuo and the residue applied to an alumina column in the minimum volume of benzene.

Two coloured bands were eluted with a 7:3 mixture of benzene:100-120° petroleum ether. The first (green-yellow) band gave a green solution showing some red fluorescence. Several recrystallisations of the residue from ethanol with charcoal screening gave unreacted 2,6-dimethyl-4-thiopyrone (0.01g.). The second (dark red-yellow) band yielded a dark red solid, m.p. 252-258°, on evaporation of the solvent. Two recrystallisations from a 9:1 mixture of ethanol:benzene

gave red needles (0.17g. ; 9%) of 4-1'-(2',3',4'-triphenyl-cyclopentadienylydene)-2,6-dimethylpyran, m.p. 261-262.5°. (Found: C, 83.18; H, 5.88. $C_{30}H_{24}O$ requires C, 90.0; H, 6.0).

A repetition of this experiment gave a slightly higher yield (10.5%).

2,6-Dimethyl-4-thiopyran-thione.- The reaction was carried out in a manner exactly similar to that in the previous section, but chromatography isolated only a minute trace of a high melting product. There was insufficient for purification to be carried out.

The failure of this reaction may have been due to the 2,6-dimethyl-4-thiopyran-thione being insufficiently pure. It was prepared as follows by the method of Aindt et al.¹⁰² A 50% solution of potassium hydrosulphide was prepared by saturating a solution of potassium hydroxide (5.9g.) in water (10 ml.) with hydrogen sulphide at 0°. 2,6-Dimethyl-4-thiopyrone (1g.) in boiling alcohol (8 ml.) was treated with a portion (6 ml.) of the potassium hydrosulphide solution, heated for 4 mins., a further portion (3 ml.) of the solution added, and heated for 2 mins. On cooling orange needles separated and were collected and recrystallised from ethanol (0.33g.; 29%), m.p. 116-117°.

In a second reaction, the yield was greatly reduced, and in a third no product at all was obtained on cooling. The purity of the starting material in these reactions appeared to be critical, as in both these cases it has been standing in sunlight for some time and some decomposition may have occurred.

(3) Reactions of diazocyclopentadiene

Decomposition in boiling benzene.- Diazocyclopentadiene (1.2g.) was dissolved in anhydrous benzene (20 ml.) and the solution was

refluxed for 4 hrs., during which time a brown solid was precipitated. The solid was filtered off and found to be a polymeric decomposition product (0.024g.), m.p. $\leq 300^{\circ}$, showing strong carbonyl absorption in its I.R. spectrum. The mother liquor was applied to an alumina column, the only band eluted with benzene containing unreacted diazocyclopentadiene b.p. 46-48^o/50 m.m.

2,6-Dimethyl-4-thiopyrone.- Diazocyclopentadiene (1.2g.; 20% molar excess) and 2,6-dimethyl-4-thio-pyrone (1.52g.) were dissolved in anhydrous toluene (20 ml.) and the solution was refluxed. An immediate darkening in colour became evident and a brown precipitate began to form. After 4 hrs., the solution was cooled and the brown precipitate was filtered off. On standing overnight, more of this precipitate formed, giving a total of 0.034g. It was a polymeric material, m.p. $\leq 310^{\circ}$, have an intense carbonyl absorption band in its I.R. spectrum.

The clear solution was evaporated in vacuo, and the residue dissolved in benzene and applied to an alumina column. Elution with benzene gave three distinct fractions:-

- (a) The first fraction yielded a small amount of unreacted diazocyclopentadiene, b.p. 46-48^o/50mm.
- (b) The second fraction yielded a brown polymeric solid (0.003g.) m.p. 300° . This solid gave no colouration with perchloric acid, and had a strong carbonyl absorption band in its I.R. spectrum.
- (c) The third band yielded unreacted 2,6-dimethyl-4-thiopyrone (0.463 g.)

[D] OTHER REACTIONS OF PHENYLATED DIAZOCYCLOPENTADIENES

(1) Reactions of 2,3,4,5-tetraphenyldiazocyclopentadiene

Decomposition in boiling mesitylene.- 2,3,4,5-Tetraphenyldiazocyclopentadiene (0.3g.) was dissolved in mesitylene (15 ml.) and the solution refluxed for 7 hrs. Solvent was removed at reduced pressure, the residue dissolved in a small amount of benzene and applied to an alumina column.

Elution with benzene brought off two bands. The first (yellow) band gave a pale yellow solid, which on recrystallisation from ethanol formed waxy white tetraphenylcyclopentene (0.13g.; 45%), m.p. 95-98°. (Found: C, 92.67; H, 6.74. $C_{29}H_{24}$ requires C, 93.55; H, 6.45). The product gave no colouration with conc. sulphuric acid and exhibited intense blue fluorescence in U.V. light. The latter phenomenon, together with its appearance and solubility in ethanol serve to distinguish from 2,3,4,5-tetraphenylcyclopentadiene.

2,6-Dimethyl-4-pyrone.- 2,3,4,5-Tetraphenyldiazocyclopentadiene (0.3g.) and 2,6-dimethyl-4-pyrone (0.11g.; 20% molar excess) were dissolved in p-cymene (15 ml.) and the solution was refluxed for 7 hrs. The solvent was removed in vacuo, and the residue dissolved in a small volume of benzene and applied to an alumina column.

A yellow band, eluted with benzene, gave a residue on evaporation which was purified by charcoal screening in ethanolic solution, from which an almost white solid was precipitated by the addition of water. The solid (m.p. 95-98°) was tetraphenylcyclopentene, identified as in the previous section. A second yellow band was eluted by acetic acid, the eluate being worked up to give a yellow solid (0.05g.), m.p. 70-90°. This small amount could not be

purified sufficiently for meaningful elementary analysis figures to be obtained; they corresponded to $C_{13}H_{11}O$.

Thiourea.- 2,3,4,5-Tetraphenyldiazocyclopentadiene (0.1g.) and thiourea (0.039g.; 100% molar excess) were dissolved in boiling toluene (10 ml.). After refluxing the solution for 7 hrs., it was cooled to yield white needles of unreacted thiourea (0.032g.; 85%), m.p. 179-180°.

m-Nitrobenzaldehyde.- 2,3,4,5-Tetraphenyldiazocyclopentadiene (0.1g.) and m-nitrobenzaldehyde (0.038g.) were dissolved in p-cymene (5 ml.) and the solution was refluxed for 7 hours. The solvent was removed, and the residue eluted in an alumina column with benzene. The first (pale yellow) band yielded, after recrystallisation of the residue from aqueous ethanol, pale yellow crystals (0.0328g.); 85%) of unchanged m-nitrobenzaldehyde, m.p. 58-60°.

Acetic acid.- 2,3,4,5-Tetraphenyldiazocyclopentadiene (0.25g.) was dissolved in glacial acetic acid (40 ml.) and the solution was refluxed for 6 hrs. The residue on removing the solvent in vacuo, was dissolved in the minimum volume of benzene and applied to an alumina column.

A 7:3 mixture of benzene: 100-120° petroleum ether eluted three bands.

- (a) A yellow band, yielding a red oil. This was dissolved in ethanol and precipitated as a chocolate-coloured solid by addition of water. Recrystallisation from aqueous ethanol yielded a pale pink solid (0.029g.- 11%), m.p. 69-72°, the elementary analysis figures corresponding to 1-acetoxy-2,3,4,5-tetraphenylcyclopentadiene.

[Found: C, 22.66; H, 5.67; N, nil. $C_{31}H_{24}O$ requires C, 26.91; H, 5.61]. The I.R. spectrum had maxima at 5.74μ (ester C=O) and 8.15μ (acetate C-O).

- (b) A red band, yielding a red oil on removing the solvent. Recrystallisation gave a brown solid, (0.0007g.) m.p. $45-60^{\circ}$. The yield of this product was too small to make identification possible.
- (c) A third yellow-green band gave a small amount of a yellow oil, which could not be crystallised.

Dibenzyl sulphide. - 2,3,4,5-Tetraphenyldiazocyclopentadiene (0.25g.) and dibenzyl sulphide (0.147g.; 10% molar excess) were dissolved in mesitylene (10 ml.) and the solution was refluxed for 6 hrs. Removal of solvent and elution with benzene on an alumina column gave only one distinct red-yellow band. After recrystallisation from aqueous ethanol, the residue from this was again identified as tetraphenylcyclopentene.

Phenyl lithium.- Lithium (0.12g.) and anhydrous ether (4 ml.) were placed in a 100 ml. three-necked flask fitted with a condenser, mechanical stirrer and dropping funnel. The flask had first been dried as for a Grignard reaction, and a slow stream of oxygen-free nitrogen was passed through it. Stirring was started, and redistilled bromobenzene (1.28g.) in anhydrous ether (2 ml.) was run in dropwise. Reaction ensued on gentle warming and stirring was continued for 0.5 hrs., by which time most of the metal had dissolved.

2,3,4,5-Tetraphenyldiazocyclopentadiene (0.72g.) in anhydrous benzene (25 ml.) was now added dropwise, with the development of a violet colour in the solution. After stirring for 1 hr., ice and hydrochloric acid were added. The organic layer was separated, washed to neutrality, dried

(Na_2SO_4) and the solvent removed to leave a dark oily residue. One recrystallisation from n-propanol gave deep red crystals of tetracyclone phenylhydrazone (0.3g.; 35%), m.p. $264-266^\circ$ ($266-268^\circ$).

Hydrazine.- 2,3,4,5-Tetraphenyldiazocyclopentadiene (0.2g.) and 85% hydrazine hydrate solution (0.05 ml.) were dissolved in ethanol. The solution was refluxed for 2 hrs., during which time it became lighter in colour. Water was added, and the mixture extracted several times with ether. The combined ethereal extracts were washed with water, dried (Na_2SO_4) and the solvent evaporated off. The residue was eluted with benzene in an alumina column.

The first fraction was yellow and was worked up to give a yellow solid, m.p. $68-77^\circ$, after precipitating from ethanolic solution by the addition of water. It was not stable and darkened rapidly on standing in air. Elementary analysis indicated that it might be 1-amino-2,3,4,5-tetraphenylcyclopentadiene. [Found: C, 89.78; H, 5.22; N, 4.84. $\text{C}_{29}\text{H}_{23}\text{N}$ requires C, 90.39; H, 5.97; N, 3.64]. The I.R. spectrum showed a broad amino-group absorption band at 2.9μ .

Triphenylphosphine.- No reaction took place between 2,3,4,5-tetraphenyldiazocyclopentadiene and triphenylphosphine in ethereal solution, either at room temperature or at the boiling point, unchanged diazo compound being recovered in each case.

2,3,4,5-Tetraphenyldiazocyclopentadiene (0.2g.) and triphenylphosphine (0.133g.) were refluxed for 1 hr. in benzene (5 ml.). Chromatography of the solution in an alumina column separated two components. The first yellow band contained unchanged diazo compound (0.12g.; 60%), m.p. $138-142^\circ$,

and the second band contained a few mgs. of tetracyclone.

Diazo compound (0.1g) and triphenylphosphine (0.068g.) were refluxed in p-cymene (5 ml.) for 7 hrs. The solvent was removed in vacuo and the residue was applied to an alumina column in benzene. The first band eluted with a 7:3 mixture of benzene; 80-100° petroleum ether gave a deep yellow oil on evaporation of the solvent. It was dissolved in ethanol, and a yellow precipitate (0.016g.) m.p. 30-40°, obtained on addition of a few drops of water. Addition of further water merely precipitated an oily brown solid. Elementary analysis of the yellow product, which showed no diazo group absorption at ca 4.8 μ , gave figures corresponding approximately to tetracyclone triphenylphosphazine (Found: C, 87.64; H, 6.25; N, 3.17; P, 3.34. $C_{47}H_{25}N_2P$ requires C, 85.7; H, 5.33; N, 4.25; P, 4.71).

β -naphthol.- 2,3,4,5-Tetraphenyldiazocyclopentadiene (0.1g) and β -naphthol (0.18g ; 5 molar equivalents) were dissolved in benzene (12 ml.) and the solution was refluxed for 6 hrs. The solution was washed many times with 2N aqueous sodium hydroxide solution to remove β -naphthol, then water, dried (Na_2SC_4) and the solvent removed in vacuo. The residue was washed with ethanol to give unchanged diazo compound.

(2) Reactions of 2,3,4-triphenyldiazocyclopentadiene

Bromination.- N-bromosuccinimide (0.056g.) was added portionwise to a solution of 2,3,4-triphenyldiazocyclopentadiene (0.0g.) in chloroform (6 ml.). The solution was shaken and allowed to stand for 0.5 hrs., during which time it became much darker in colour. Water was added and the mixture extracted twice with ether. The combined

ethereal extracts were washed several times with water, dried (Na_2SO_4), and applied to an alumina column in benzene. The principal yellow band gave, after recrystallisation from methanol, yellow crystals, m.p. $128-130^\circ$, of 5-bromo-2,3,4-triphenyldiazocyclopentadiene (0.0606g.; 48%). λ_{max} (diazo) was at 4.81μ . (Found: C, 69.39; H, 4.65; Br, 19.50. $\text{C}_{23}\text{H}_{15}\text{N}_2\text{Br}$ requires C, 69.17; H, 3.76; Br, 20.05).

Iodo-mercuration and iodination.- 2,3,4-Triphenyldiazocyclopentadiene (0.20g.) was added to a solution of mercuric acetate (0.20g.) in dimethyl sulphoxide (10 ml.). This solution, after standing for 20 mins. at 40° , was added to an ice-cold solution of sodium iodide (0.095g.) in ethanol (3 ml.). After standing at 0° for five minutes, water (4 ml.) was added, precipitating a yellow solid which was washed twice with water and twice with ethanol, separating the solid by centrifugation on each occasion. The elementary analysis figures for the product (0.274g.; 68%), m.p. $145-147^\circ$ dec., correspond to 5-iodomercuric-2,3,4-triphenyldiazocyclopentadiene, although the value for C was high. (Found: C, 47.58; H, 2.91; N, 4.36; I, 19.71. $\text{C}_{23}\text{H}_{15}\text{N}_2\text{HgI}$ requires C, 42.68; H, 2.47; N, 4.33; I, 19.64). λ_{max} (diazo) was at 4.73μ .

The above iodo-mercuri derivative (0.20g.) was suspended in chloroform (10 ml.) in a centrifuge tube and treated portionwise with iodine (0.077g.). The mixture was stirred for 1 hr. at room temperature and centrifuged. The filtrate was washed with dil. aqueous sodium thiosulphate solution, dried (Na_2SO_4) and the solvent removed. Elution of the residue with benzene in an alumina column brought off a single yellow band, which yielded a yellow solid (0.08g.), m.p. $122-125^\circ$, λ_{max} (diazo) at 4.81μ . The product decomposed slightly on heating before the m.p. was reached (Found: C, 69.71;

H,4.51; N,4.71; I,21.30. 5-iodo-2,3,4-triphenyldiazocyclopentadiene requires C,61.88; H,3.36; N,6.23; I,28.48).

Nitration.- 2,3,4-Triphenyldiazocyclopentadiene (0.2g.) and silver nitrate (0.104g.) were dissolved in the minimum volume of dimethyl sulphoxide at room temperature. The resultant solution was added dropwise to benzoyl chloride (0.088g.) in dimethyl sulphoxide (2 ml.). After 2 hrs., water was added and the mixture extracted several times with ether. The continued extracts were dried (Na_2SO_4) and the solvent removed. The residue was eluted in an alumina column with benzene, the principal yellow band giving a dark uncrystallised oil.

Diazo-coupling.- A solution of benzenediazonium chloride was made from aniline (1g.), conc. hydrochloric acid (2.75 ml.) and sodium nitrite (0.8g.) in the usual manner. Sodium acetate was added to raise the pH of the solution to ca 5.

2,3,4-Triphenyldiazocyclopentadiene (0.1g.) in methylene chloride (4 ml.) was added to a portion of this benzenediazonium chloride solution (an excess) at 0° , with stirring. After 0.5 hrs., an excess of 5% aqueous sodium hydroxide solution was added, and the organic layer separated. It was washed with water, dried (Na_2SO_4), dissolved in a small amount of benzene and applied to an alumina column. The principal (yellow) band on elution with benzene contained unreacted diazo compound. A second, considerably more polar layer, contained only a minute trace of some unidentified product.

Trifluoroacetic acid.- Since 2,3,4-triphenyldiazocyclopentadiene was not sufficiently soluble in carbon tetrachloride or deuterio-chloroform for its N.M.R. spectrum to be determined in these solvents, trifluoroacetic acid (T.F.A.) was used. The molecule was found to be protonated in this solvent, and the

spectrum is discussed in Part II, Section [A] (3).

On allowing the solvent to evaporate off on a watch glass, a green residue remained. In a few minutes, the colour had changed to yellow, and the solution in ethanol was yellow with some green fluorescence. A yellow solid, m.p. $177-180^{\circ}$ was precipitated from the ethanolic solution by the addition of water. Elementary analysis gave figures corresponding to 1-hydroxy-2,3,4-triphenylcyclopentadiene (Found: C, 80.59; H, 5.49; N, nil; $C_{23}H_{18}O$ requires C, 89.03; H, 5.81). The product had a broad hydroxyl group absorption band centred at 2.93μ in its I.R. spectrum.

[E] REACTIONS OF CYCLOPENTADIENYLIDENEPYRANS

(1) Reactions of 4-tetraphenylcyclopentadienylidene-2,6-dimethylpyran

Chromium trioxide.- The ylidenepyran (0.03g.) and chromium trioxide (0.06g.) were dissolved in acetic acid (10 ml.) and the solution was refluxed. The red solution, which immediately turned green was refluxed for an hour, water added, and the organic products extracted with benzene. The benzene layer was washed with water, dried (Na_2SO_4) and solvent removed to give, after one recrystallisation from benzene-petroleum ether, 2,6-dimethyl-4-pyrone (0.0037g., 50%), m.p. $128-132^{\circ}$.

Perchloric acid.- The ylidenepyran (0.05g.) was suspended in anhydrous ether (7 ml.) and two drops of 73% perchloric acid were added. After standing at 0° for 2 hrs., filtration separated orange crystals, which were washed with ether, of 4-tetraphenylcyclopentadienyl-2,6-dimethylpyrylium perchlorate (0.0567g.; 83.4%), m.p. $172-174^{\circ}$ (Found: C, 73.76; H, 5.63; Cl, 6.94. $C_{36}H_{29}ClO_4$ requires C, 74.93; H, 5.03; Cl, 6.16).

The product was found to be completely stable in air, but on refluxing it in ethanolic suspension it was converted back to the ylidenepyran.

Sulphuric acid.- The ylidenepyran (0.05g.) was suspended in anhydrous ether (7 ml.) and conc. sulphuric acid (1 drop) added. After standing overnight at 0°, filtration of the resultant orange precipitate was attempted, but as the solid was being sucked dry in the filter funnel it turned into a dark oily solid. This was shaken with ethanolic potassium hydroxide solution, water added, and the mixture extracted with benzene. Evaporation of the benzene gave regenerated ylidenepyran.

Chlorine.- Chlorine gas was passed for 10 mins. through a solution of the ylidenepyran (0.05g.) in dioxan (10 ml.) during which time it became pale yellow in colour. Most of the solvent was removed in vacuo, water added, and the mixture extracted with benzene. The benzene layer was dried (Na_2SO_4) and evaporated to give a green oil, which was dissolved in ethanol and precipitated as a yellow solid (0.053g.); 91%), m.p. 85-100°, by the addition of water. The sample for analysis was prepared by dissolving in ethanol and precipitating with water as yellow crystals, m.p. 97-100°, of a dichloro addition product. (Found: Cl, 26.10. $\text{C}_{36}\text{H}_{28}\text{Cl}_2\text{O}$ requires Cl, 22.96.).

Bromine.- A 1% solution of bromine in chloroform (an excess) was added to the ylidenepyran (0.05g.) in carbon tetrachloride (5 ml.), with the immediate formation of a red oil. The solvent was taken off in vacuo, and the residual red oil dissolved in benzene, the solution washed with water, dried (Na_2SO_4), and evaporated to leave a residue which on washing with ethanol gave a brown solid (0.017g.) m.p. 175-195°.

This solid could not be recrystallised.

Phenyl lithium. - The ylidenepyran (0.1g.) in anhydrous benzene (8 ml.) was added dropwise to a solution of phenyl lithium in ether, prepared as in Section [D] (1) from lithium (0.012g.) and bromobenzene(1.28g.). The rusty-red coloured solution was stirred for 2 hrs. until it had become golden yellow in colour. Dil. hydrochloric acid was added and the organic layer separated, washed with water, dried (Na_2SO_4) and evaporated. The residue was applied to an alumina column in benzene.

A band eluted with a 7:3 mixture of benzene:80-100° petroleum ether gave a dark residue which was dissolved in ethanol and precipitated as a yellow solid by the addition of water. The yellow solid rapidly decomposed to an oily brown solid which could not be purified. A second very polar brown band was eluted with acetic acid, and the fraction worked up to yield a yellow solid (0.038g.), m.p. 150-152° after recrystallisation from ethanol.(Found: C, 84.80; H, 5.90).

Maleic anhydride.- No Diels Alder addition product was formed when the ylidenepyran and an excess of maleic anhydride were refluxed for several hours in benzene.

Potassium hydroxide solution.- After refluxing for several hours in a 5% alcoholic potassium hydroxide suspension, the ylidenepyran was filtered off and found to be unchanged.

Potassium hydrosulphide solution.- The ylidenepyran was suspended in a 50% aqueous solution of potassium hydrosulphide (made by saturating a solution of potassium hydroxide (5.9g.) in water (10 ml.) with H_2S at 0°) and the suspension refluxed for a few minutes. Filtration and washing with ethanol gave unchanged ylidenepyran.

Ammonia.- The ylidenepyran was unchanged after boiling for 3 hrs. suspended in a 1:1 mixture of ethanol and .800 ammonia solution.

The ylidenepyran (0.04g.) was suspended in warm tert.-butanol (15 ml.) and a stream of ammonia gas passed through for 3 hrs. After cooling, water was added and the mixture extracted several times with benzene. The residue from the combined extracts was washed with ethanol to afford unreacted ylidenepyran (0.035g.; 87%) m.p. 264-269°.

Benzylamine.- The ylidenepyran (0.06g.) in anhydrous benzene (5 ml.) was added to benzylamine (0.03 ml.). After refluxing for 1 hr., the solvent was removed, and the residue washed three times with ethanol to give unchanged ylidenepyran (0.54g.; 90%), m.p. 267-269°.

(2) Reactions of 4-(2',3',4'-tetraphenylcyclopentadienylidene)-2,6-dimethylpyran

Perchloric acid.- The ylidenepyran (0.05g.) was suspended in anhydrous ether (7 ml.) and 73% perchloric acid (2 drops) was added. After allowing to stand at 0° overnight, filtration and washing with ether gave orange coloured 4-(2',3',4'-triphenylcyclopentadienyl)-2,6-dimethylpyrylium perchlorate. (0.0566g.; 90%), m.p. 231-232°. (Found : C, 71.45; H, 4.89; Cl, 7.03. $C_{30}H_{25}ClO_5$ requires C, 71.93; H, 5.00; Cl, 7.09).

The action of alkali on this perchlorate was to regenerate the ylidenepyran, as for the tetraphenyl compound.

Bromination.- N-bromosuccinimide (0.045g.) in chloroform (9 ml.) was added to the ylidenepyran (0.1g.) in chloroform (4 ml.), an immediate darkening in colour taking place. After 0.5 hrs., water and ether were added and the organic layer

separated, washed several times with water, dried (Na_2SO_4) and evaporated. The residue was dissolved in benzene and applied to an alumina column.

The residue from the main red-yellow band, eluted with 7:3 benzene: 100-120° petroleum ether was separated into two components by fractional crystallisation from ethanol. The least soluble component was unreacted ylidenepyran (0.01g.; 10%), m.p. 266-269°; the more soluble one, separated from the combined mother liquors, after addition of water, by centrifugation, was a yellow solid (0.018g.), m.p. 126-129°. (Found: C, 87.19; H, 5.97; Br, 3.58. A mono-bromo derivative requires C, 75.16; H, 4.80; Br, 16.7).

Iodo-mercuration and iodination.- The ylidenepyran (0.1g.) in chloroform (9 ml.) was added to mercuric acetate (0.0798g.) in dimethyl sulphoxide (3 ml.). After standing at 40° for 20 mins., the solution was added to an ice-cold solution of sodium iodide (0.0375g.) in ethanol (2 ml.). After standing at 0° for 10 mins., water and more chloroform were added and the organic layer separated, washed many times with water, dried (Na_2SO_4), and the solvent removed to give a brown solid (0.086g.), m.p. 231-235°. (Found: C, 69.42; H, 4.92. Monoiodo-mercuri derivative requires C, 50.70, H, 3.24).

The above solid (0.075g.) was suspended in chloroform (4 ml.) in a centrifuge tube and iodine (0.011g.) added portionwise. After standing at room temperature for 2 hrs., the mixture was centrifuged and the filtrate washed twice with dil. sodium thiosulphate solution, dried (Na_2SO_4) and evaporated. The residue from the main (dark yellow band) obtained on eluting with a 7:3 mixture of benzene:100-120° petroleum ether was washed with a little ethanol to give a

dark red solid (0.013g.), m.p. 127-132°. (Found: C, 88.20; H, 6.07; I, 5.10. Mono-iodo derivative requires C, 70.59; H, 4.51; I, 24.90).

Diazo-coupling.- A solution of the ylidenepyran (0.05g.) in methylene chloride (5 ml.) was added, at 0°, to an excess of benzenediazonium chloride solution, buffered at approximately pH 6 with sodium acetate. After 0.5 hrs., 5% sodium hydroxide solution was added, the organic layer separated, washed twice with water, dried (Na_2SO_4) and applied in benzene to an alumina column. The principal (yellow) band eluted with a 1:1 mixture of benzene:100-120° petroleum ether yielded unreacted ylidenepyran (0.039g. ; 78%), m.p. 255-260°.

[F] REACTIONS OF 4-TETRAPHENYLCYCLOPENTADIENYL-2,6-DIMETHYL-PYRYLIUM PERCHLORATE

Maleic anhydride.- The pyrylium perchlorate (0.056g.) and maleic anhydride (0.013g.; 2 molar equivalents) were refluxed for 2.5 hrs. suspended in anhydrous benzene (5 ml.) . After reaction, the pyrylium perchlorate, m.p. 171-172°, was recovered unchanged.

The pyrylium perchlorate (0.07g.) and maleic anhydride (an excess) were refluxed for 2 hrs. in anhydrous toluene. In this solvent, the perchlorate dissolved to a considerable extent, and on cooling and filtering, a solid was obtained which melted at 160-172°. By the action of alkali, however, this was quantitatively converted into 4-tetraphenylcyclopentadienyldiene-2,6-dimethylpyran, indicating that no Diels Alder reaction had occurred.

Cyclopentadiene.- The pyrylium perchlorate (0.03g.) was suspended in anhydrous benzene (8 ml.) and a large excess of freshly distilled cyclopentadiene (0.1g.) was added.

After standing, with occasional stirring, for 0.5 hrs. at room temperature, the suspension was refluxed for 0.5 hours to give a red solution. After refluxing again briefly with added decolourising charcoal, the solution was filtered, washed with dil. potassium hydroxide solution, then water, dried (Na_2SO_4) and evaporated. Washing of the residue with ethanol gave the tetraphenyl ylidenepyran, m.p. $265-269^\circ$, showing again that no adduct had been formed.

Potassium hydroxide solution.- The pyrylium perchlorate (0.04g.) was suspended in a 10% aqueous solution of sodium hydroxide (10 ml.) and the suspension refluxed for 3 hrs. Cooling and filtration followed by washing with water and ethanol gave the tetraphenyl ylidenepyran (0.032g.; 96%), m.p. $266-269^\circ$.

Potassium hydrosulphide solution.- A 50% solution of potassium hydrosulphide was made by saturating a solution of potassium hydroxide (5.9g.) in water (10 ml.) with hydrogen sulphide at 0° .

A portion (0.1 ml.) of this solution was added to the pyrylium perchlorate (0.015g.) in boiling ethanol (5 ml.). After 5 mins., another portion (0.1 ml.) of the potassium hydrosulphide solution was added, and after refluxing for a further 5 minutes, the suspension was cooled and filtered. Recrystallisation from a 9:1 mixture of ethanol:benzene gave a red solid, m.p. $253-254^\circ$. Despite the low melting point, elementary analyses showed that the compound contained no sulphur, and was the tetraphenyl ylidenepyran (m.p. $267-269^\circ$).

Sodium cyclopentadienide.- Sodium (0.7g.) and tetrahydrofuran (10 ml.) were placed in a three-necked flask filled with a dropping funnel, mechanical stirrer and gas

inlet tube. With a slow stream of oxygen-free nitrogen passing through the vessel, and mechanical stirring, freshly distilled cyclopentadiene (2g.) was added portionwise, with cooling on an ice-bath. The resulting 3M solution of sodium cyclopentadienide was purple in colour.

The pyrylium perchlorate (0.03g.) was added, and stirring; was continued for 1 hr. The red solution was poured into water and extracted three times with benzene. The combined benzene extracts were washed with water and a certain amount of polymeric material removed by filtration. The solution was dried (Na_2SO_4) and the solvent removed, leaving an oily residue. This was washed with ethanol to give a few mg. of the tetraphenyl ylidene-pyran, m.p. $265-268^\circ$.

Hydrazine.-- The pyrylium perchlorate (0.03g.) was suspended in benzene (8 ml.) and 99% hydrazine hydrate solution (0.05 ml.) was added. The resulting dark red solution was refluxed for 1 hr., washed with dil. aqueous potassium hydroxide solution and water, dried (Na_2SO_4) and the solvent removed in vacuo. Washing of the residue with ethanol gave a nearly quantitative yield of the tetraphenyl ylidene-pyran, m.p. $260-269^\circ$.

Diethylamine.-- The pyrylium perchlorate (0.047g.) in benzene (5 ml.) had an excess of diethylamine added, and the solution was refluxed for 1 hr. The solution was cooled, washed with dil. aqueous sodium hydroxide solution and water, dried (Na_2SO_4) and the solvent removed in vacuo. Recrystallisation of the residue from a 9:1 mixture of ethanol:benzene gave an almost quantitative yield of the tetraphenyl ylidene-pyran, m.p. $267-269^\circ$.

Isopropylamine.-- The pyrylium perchlorate (0.07g.) was

suspended in benzene (10 ml.) and iso-propylamine (0.04 ml.) added, giving a red solution, which was refluxed briefly. It was cooled, washed with dilute aqueous potassium hydroxide solution and water, dried (Na_2SO_4) and solvent removed in vacuo to give the tetraphenyl ylidene-pyran, m.p. 267-269° in almost quantitative yield.

Ammonia.- The pyrylium perchlorate (0.08g.) was suspended in t-butanol, and ammonia gas bubbled through for 4 hrs., precipitating ammonium perchlorate. Water (30 ml.) was added and the resultant red-yellow precipitate filtered off. It was washed with water and recrystallised from a 9:1 mixture of ethanol and benzene to give the tetraphenyl ylidene-pyran (0.035g., 77%), m.p. 262-264°. (Found: C, 89.99; H, 5.73; N, nil; $\text{C}_{36}\text{H}_{28}\text{O}$ requires C, 90.95; H, 6.10).

Benzylamine.- The pyrylium perchlorate (0.08g.) was suspended in anhydrous benzene (10 ml.) at room temperature and benzylamine (0.06 ml.) was added, the suspended solid immediately dissolving to give a deep red solution. It was refluxed for 1 hr., cooled, washed with dil. sodium hydroxide solution and water, dried (Na_2SO_4) and the ether evaporated off to give a red solid, m.p. 150-210°. It gave a red-green dichroic solution in ethanol and two recrystallisations from this solvent gave deep red crystals (0.045g.; 49%), m.p. 217-220°, of 1-benzyl-4-tetraphenylcyclopentadienyli-dene-2,6-dimethyldihydropyridine. (Found: C, 88.79; H, 6.04; N, 2.40. $\text{C}_{43}\text{H}_{35}\text{N}$ requires C, 91.33; H, 6.19; N, 2.48).

The ylidenedihydropyridine (0.02g.) was suspended in ether (4 ml.) and 73% perchloric acid (0.02 ml.) added. A yellow precipitate (presumably of the corresponding pyrylium perchlorate) formed immediately, but decomposed in a few

minutes to a red oil, immiscible in the ether.

Phenylhydrazine.-- The pyrylium perchlorate (0.055g.) was suspended in anhydrous benzene (7 ml.) and a slight excess of phenylhydrazine (0.03 ml.) was added. The suspension dissolved to a red solution, and a yellow precipitate formed immediately on refluxing. The precipitate was filtered off and washed with benzene to give the corresponding N-phenylaminopyridinium perchlorate (0.0653g.; 89%), m.p. 200-201°. (Found: C, 74.50; H, 5.09; N, 4.44; Cl, 5.78. $C_{42}H_{35}N_2ClO_4$ requires C, 75.62; H, 5.25; N, 4.20; Cl, 5.33).

A red solution formed when a portion of the above pyridinium perchlorate was shaken with dil. ethanolic potassium hydroxide solution. Water was added and the mixture extracted several times with ether, the combined extracts washed with water, dried (Na_2SO_4) and the solvent removed to leave the N-phenylaminodihydropyridine analogue as a red solid, m.p. 118-120°.

Unsymm.-methylphenylhydrazine.-- The pyrylium perchlorate (0.04g.) was suspended in anhydrous benzene (6 ml.) and a slight excess of unsymm.-methylphenylhydrazine (0.03 ml.) added. A red solution was formed on refluxing briefly, and this was washed with dil. aqueous sodium hydroxide solution and water, dried (Na_2SO_4) and solvent removed to give the N-methylphenylaminodihydropyridine compound as a brick red solid (0.0275g.; 57%), m.p. 142-144°, after washing with ethanol. (Found: C, 88.34; H, 6.21; N, 4.64. $C_{43}H_{36}N_2$ requires C, 88.96; H, 6.21; N, 4.83). This product had decomposed slightly after standing at room temperature for a few days.

Hydroxylamine.-- The pyrylium perchlorate (0.05g.) was suspended in anhydrous benzene (7 ml.). An ethanolic

solution containing an excess of hydroxylamine hydrochloride made just alkaline by the addition of potassium hydroxide was added to give a deep red solution, which turned yellow on being refluxed. After 0.5 hrs., the solution was cooled, washed several times with water, dried (Na_2SO_4) and evaporated in vacuo. The residue was dissolved in ethanol and a yellow solid (0.027g., 66%), m.p. 97-103° precipitated on addition of water.

Although it was stable at room temperature, any attempted recrystallisation of this product caused it to decompose to a brown oily solid. Physical data (see Part II) indicated that it had an N-oxide structure, but good elementary analysis figures could not be obtained (Found: C, 79.01; H, 5.22; N, 2.95. $\text{C}_{36}\text{H}_{29}\text{NO}$ requires C, 87.98; H, 5.91; N, 2.86.).

Attempts were made to reduce this product as follows.

- (1) The N-oxide (0.02g.) was dissolved in acetonitrile (3 ml.) and benzyl chloride (0.02 ml.) added. After refluxing for 0.5 hrs., removal of solvent in vacuo left a brown oily residue. This could not be purified, and after refluxing with aqueous ethanolic sodium hydroxide solution, it remained unchanged.
- (2) The N-oxide (0.015g.) was dissolved in chloroform and phosphorus pentachloride (0.02g.) added. The solution was refluxed for 0.5 hrs., washed repeatedly with water, dried and solvent removed in vacuo. Washing of the green residue with cold ethanol gave only a brown oily solid.

p-toluidine.— The pyrylium perchlorate (0.075g.) was suspended in anhydrous benzene (5 ml.) and p-toluidine (0.03g.) in benzene (5 ml.) added. The resulting clear red

solution was refluxed for 0.5 hrs., cooled, washed with dil. aqueous potassium hydroxide solution and water, dried (Na_2SO_4) and the solvent removed. Two recrystallisations of the residue from ethanol gave dark red needles (0.022g.; 25%), m.p. 262-264°, of 4-tetraphenylcyclopentadienyldiene-1-p-methylphenyl-2,6-dimethyldihydropyridine (Found: C, 89.07; H, 5.85; N, 2.73. $\text{C}_{43}\text{H}_{35}\text{N}$ requires C, 91.33; H, 6.19; N, 2.48).

Aniline.- The pyrylium perchlorate (0.04g.) was suspended in anhydrous benzene (5 ml.) and aniline (0.06 ml.) added. The clear red solution which resulted was refluxed for 1 hr., cooled, washed with dil. aqueous sodium hydroxide solution and water, dried (Na_2SO_4) and the solvent evaporated off. It did not prove possible to purify the oily red residue, by washing or recrystallisation, sufficiently for elementary analysis to be worthwhile.

p-aminobenzoic acid.- An excess of p-aminobenzoic acid (0.028g.) was added to a suspension of the pyrylium perchlorate (0.056g.) in anhydrous benzene (7 ml.). A few drops of ethanol were added to dissolve the p-aminobenzoic acid and the mixture was refluxed for 1 hr. The clear red solution was washed with dil. aqueous potassium hydroxide solution and water, dried (Na_2SO_4), and the solvent removed in vacuo. The red residue was washed with ethanol, and found to be the tetraphenyl ylidene-pyran, m.p. 266-269°.

p-Nitroaniline.- An excess of p-nitroaniline (0.048g.) was added to a suspension of the pyrylium perchlorate (0.1g.) in anhydrous benzene (7 ml.). A dark red solution was formed on refluxing. After 0.5 hrs., it was cooled, washed with dil. aqueous sodium hydroxide solution and water, dried (Na_2SO_4) and the solvent evaporated off. The

residue was washed with ethsnol to give a red solid (0.065g.), m.p. 257-259°. The I.R. spectrum of this compound showed no absorption in the regions normally associated with vibrations arising from a nitro group, and elementary analysis indicated that, despite the low melting point, it was the tetraphenyl ylidenepyran. (Found: C, 90.71; H, 6.10. $C_{36}H_{28}O$ requires C, 90.79; H, 5.89).

[G] REACTIONS INVOLVING THE TROPYLIUM RING

(1) Tropylium perchlorate

Cycloheptatriene (24 ml.) was added to a boiling solution of chloranil (39.36g.) and 70% perchloric acid (26.8 ml.) in glacial acetic acid (1200 ml.) and the brown solution boiled for 2 mins. It was cooled under cold, running water and dry ether (2,400 ml.) added to dissolve the precipitated quinol. The residual tropylium perchlorate was filtered off, washed with ether (600 ml.) and recrystallised, with charcoal screening, from glacial acetic acid (1,200 ml.) to give white crystals (27.8g.; 75%).

(2) Ditropyl ether

Tropylium perchlorate (10g.) was neutralised with excess cold sodium bicarbonate solution, whereupon ditropyl ether formed as an oily layer. This was extracted with ether and the solution dried (Na_2SO_4). Removal of solvent in vacuo gave ditropyl ether (3.54g. ; 61%). This product was used in the preparation of tropone without further purification.

(3) Tropone

The method of Ikemi et al.¹⁰³ involving distillation of ditropyl ether in the presence of a minute trace of acid was found to be very unsatisfactory, only a few drops of

product being obtained. The method of Ter Borg et al.¹⁰⁴ was used, as follows.

Chromatographic silica-gel was treated with fuming nitric acid on a steam bath for an hour. The mixture was diluted with distilled water and filtered. The residue was washed three times with water and dried over conc. sulphuric acid in a dessicator for 24 hrs. Ditropyl ether (3.54g.) and acid silica gel (0.212g.) were placed in a distillation flask and heated at 150 ml. pressure. Distillation of cycloheptatriene commenced at approximately 65°, and the temperature was gradually raised and pressure reduced to 120°/15 mm. At this temperature and pressure, tropone distilled over (1.1g.; 58%).

(4) Tropone and phosphorus pentasulphide

Tropone (0.3g.) and phosphorus pentasulphide (0.8g.) were refluxed in benzene (20 ml.) for 1 hr. The mixture was filtered hot, and the filtrate evaporated to give a brown residue, which was treated with warm ammonium sulphide solution to ensure removal of any phosphorus pentasulphide still present. The residue was washed with water to give a yellow-brown solid (0.26g.), m.p. \leftarrow 250°.

(5) 2,3,4,5-Tetraphenyldiazocyclopentadiene and tropylium perchlorate

The diazo compound (0.2g.) and tropylium perchlorate (0.096g.) were dissolved in acetic acid (15 ml.) at the boiling point. After refluxing for 5 hrs., the solvent was removed in vacuo and the brown residue stirred with hot benzene (10 ml.). Cooling and filtration gave yellow

crystals (0.025g.; 88%) of unreacted tropylium perchlorate, m.p. 298-304° dec., after recrystallisation, with charcoal screening, from acetic acid.

[H] ULTRA-VIOLET SPECTRA

All spectra were recorded in methanol; those in acid solution after the addition of a trace of 72% perchloric acid solution. Two spectra which were in the literature are included for purposes of comparison.

λ_{\max} is given in millimicrons.

ϵ is the molar extinction coefficient.

sh. denotes a shoulder.

TABLE I

Compound	λ_{\max}	
2,4,6-trimethylpyrylium perchlorate(a)	232	286
2,3,4,5-tetraphenylcyclopentadiene(b)	262	335
2,3,4,5-tetraphenyldiazocyclopentadiene	255	332
2,3,4,5-triphenyldiazocyclopentadiene	239	330
in acid solution	239	-

(a) Taken from Ref. 105.

(b) Taken from Ref. 86 (in cyclohexane).

TABLE II

Compounds in the table are numbered as in Part II, p. 57.

	max (ϵ)		
(XXVII) in acid solution	261 (22,050)	301 (14,700)	425 (31,700) 481 (29,800)
(XXIX) in acid solution	260 305		417 481
(XXVIII) in acid solution	270 309		473 505
(XXXII; R=CH ₂ Ph) in acid solution	262 (17,300)	289 (17,300)	469 (30,950) 413 (15,100)
(XXXII; R=C ₆ H ₄ CH ₃) in acid solution	262 (23,070)		425 (32,450) 389 (28,600)
(XXXII; R=NHPh) in acid solution	262 (27,250)	289 (27,350)	472 (49,400) 427 (18,750)
(XXXII; R=N(CH ₃)Ph)(c) in acid solution	235 (27,500)	263 (20,450)	288 (21,650)
	231 (57,400)	263 (22,850)	474 (41,300) 433 (29,500)
(XXXII; R=OH) in acid solution	261 (16,550)		362 (14,450) 397 (12,700)

(c) This compound was not very stable, and the short wavelength maximum may have been due to some decomposition product.

TABLE III

Compound	λ_{max}	
Products of reaction between 2,3,4,5-tetraphenyldiazocyclo- pentadiene and:		
triphenylphosphine	250 <u>sh.</u>	321 <u>sh.</u>
in acid solution	250 <u>sh.</u>	321 <u>sh.</u>
acetic acid	249	342
trifluoroacetic acid	246 <u>sh.</u>	
Dichloro adduct XXXIII	247 <u>sh.</u>	360 <u>sh.</u>

[I] NUCLEAR MAGNETIC RESONANCE SPECTRA

Chemical shifts are given in p.p.m. relative to tetramethylsilane as internal standard. Relative intensities are given in brackets.

Compound	Solvent	Conc.	Signals (τ)
2,3,4-triphenyldiazocyclopentadiene	CDCl_3	3%	2.86(15) 3.07(1)
	T.F.A.	4%	2.7(<u>ca</u> 15) 5.82(1)
	D.T.F.A.	4%	2.7
5-bromo-2,3,4-triphenyldiazocyclopentadiene	CDCl_3	4%	2.81 8.74(small)
5-iodo-2,3,4-triphenyldiazocyclopentadiene	CDCl_3	4%	2.76
5-iodo-mercuri-2,3,4-triphenyldiazocyclopentadiene (XXVII)	CDCl_3	4%	2.81 7.4(small) 8.4(small)
	T.F.A.	4%	2.68) (22.4) 4.5(1.0) 2.84) 7.56(6.6)
(XXIX)	T.F.A.	15%	2.86(19) 5.67(2) 7.45(6.3)
	D.T.F.A.	15%	2.84(17) 5.66(0.97) 7.44(5.4)
(XXXII; R= $\text{C}_6\text{H}_4\text{CH}_3$)	T.F.A.	1%	2.65) (26) 4.5(1.2) 2.81) 7.52(8.3)
(XXXII); R= CH_2Ph	T.F.A.	1.5%	2.65) 7.3 7.6 2.88)
(XXXII); R=OH	CDCl_3	1.7%	2.75) 7.67 3.06)

APPENDIX

THE REDUCTION OF OXIMES BY MEANS OF HYDRAZINE AND RANEY NICKEL

The use of hydrazine in the presence of metal catalysts for the reduction of nitro-compounds and esters of nitric and nitrous acids was described by Kuhn.¹⁰⁶ Balcom and Furst¹⁰⁷ showed that hydrazine in the presence of Raney nickel was an excellent and convenient reagent for the reduction of nitro-compounds; this reagent has also been applied to nitriles.¹⁰⁸

A report¹⁰⁹ of the reduction of an oxime to an amine, suggested the present investigation into the generality of the reaction. The results, listed in the table, show that saturated ketoximes are normally **reduced under** simple conditions, the yields of amines often being comparable with those obtained by reduction with lithium aluminium hydride.¹¹⁰ Two typical aldoximes which were investigated were not reduced.

In the case of α,β -unsaturated ketoximes a pyrazoline was produced instead of an amine, e.g. 3,5,5-trimethylpyrazoline was obtained from the oxime of mesityl oxide.

Biacetylmonoxime and pentan-2,4-dioxime formed nickel complexes instead of amines under the standard conditions but 2,5-diaminohexane was obtained from hexan-2,5-dione dioxime.

Oxime Reduced	Percentage yield of amine	Oxime Reduced	Percentage yield of amine
Acetone	36	Fluorenone	94
Cyclopentanone	27	1,2-benzo-3-hydroxy-fluorenone	97
Cyclohexanone	65	Mesityl oxide	<u>a</u>
Cycloheptanone	29	Isophorone	<u>a</u>
Menthone	90	Carvone	<u>a</u>
Carvomenthone	36	Biacetyl monoxime	<u>b</u>
Dihydrocarvone	8	Pentan-2,4-dione dioxime	<u>b</u>
Fenchone	6	Hexan-2,5-dione dioxime	31
Camphor	0	n-Heptaldehyde	0
Benzophenone	45	Benzaldehyde	0

a: pyrazoline formed.

b: nickel complex formed

Reduction of oximes to amines.- In a typical run, the oxime (0.02 mole.) and hydrazine hydrate (64%, 6 ml.) were dissolved in ethanol (50 ml.). Raney nickel sludge W-4 ¹¹¹ was then added in portions to maintain a steady reaction. When reaction subsided, excess hydrazine was decomposed by refluxing until evolution of ammonia ceased (ca 4 hrs.). The solution was then filtered and the amine was normally isolated by passing gaseous hydrogen chloride through the solution. Alternatively, the water-insoluble amines could be obtained directly by adding water to the ethanolic solution. The amines were characterised by suitable derivatives.

Attempted reduction of mesityl oxide oxime.- To a mixture of mesityl oxide oxime (11.81g.) and hydrazine (64%, 30 ml.) in ethanol (100 ml.) Raney nickel sludge was added as

above. After filtration and the addition of hydrogen chloride, the solution was concentrated, water added and the solution washed with ether. The aqueous solution was then basified and extracted again with ether. The dried ethereal extract was fractionally distilled, giving a colourless oil, b.p. 80-84°/45 m.m., whose I.R. spectrum was identical with that of an authentic specimen of 3,5,5-trimethylpyrazoline.

Attempted reduction of pentan-2,4-dione dioxime.- Raney nickel sludge was added to a mixture of pentan-2,4-dione dioxime (7.28g.) and hydrazine (64%, 14 ml.) in ethanol (250 ml.) as above. On refluxing to decompose excess hydrazine the solution became brown. After filtration, the solution was boiled with decolourising charcoal, filtered again and concentrated. An orange nickel-containing solid, m.p. $> 300^{\circ}$, was obtained.

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