SUMMARY

The syntheses of phenyl substituted ferrocenes from the corresponding cyclopentadienes by three routes are described. The first involved treatment of the sodium salt of the cyclopentadiene with ferrous chloride and the other two involved the high temperature interaction of the cyclopentadie with iron pentacarbonyl and dicyclopentadienyldi-iron tetracarbonyl. This last route yielded the symmetrical (i.e. both rings substituted) and the unsymmetrical (i.e. one ring unsubstituted) ferrocenes, in addition to ferrocene itself. Th most notable feature of this work was the failure to obtain decaphenylferrocene. The syntheses of two new cyclopentadiene 1,4-dimethyl-2,3-diphenyl- and 1,2,5-trimethyl-3,4-diphenylcyclopentadiene, are described. These two products have been converted to the corresponding ferrocenes. Reaction of iron pentacarbonyl with 5-bromo-1,2,3,4-tetraphenyl- and 5-bromopentaphenylcyclopentadiene gave 1,2,3,4-tetraphenylcyclopentadienyliron dicarbonyl bromide and the pentaphenyl-analogue respectively. The reactions of this latter product are described in detail. Steric effects operative in this series of poly aryl ferrocenes are discussed.

In order to complete the above series, a route to the unknown hydrocarbon 1,2-diphenylcyclopentadiene was sought. The dehydration of either 1-hydroxy-3,4-diphenyl-

cyclopent-2-ene or 1,2-dihydroxy-1,2-diphenylcyclopentane was found to give the dimeric bis(1,2-diphenylcyclopentadiene). Pyrolysis of this product gave the exo-isomer, while under mo stringent conditions 1,4-diphenylcyclopentadiene was obtained Bis-(1,2-diphenylcyclopentadiene) on treatment with iron pentacarbonyl gave a black crystalline product $C_{19}H_{16}Fe(CO)_3$, structure of which was not determine, with molybdenum hexacarbonyl bis-(1,2-diphenylcyclopentadienylmolybdenum tricarbo was obtained. Attempted syntheses of 1,2-diphenylcyclopentadienes bearing a labile grouping, such as an ester or methoxy group, are described. Anhydroacetonebenzil and its substitute analogues were chosen as convenient starting materials. Durin the course of this work a new route to phenylcyclopentenones giving high yields, was developed. The N.M.R. spectra of various cyclopentadienes, phenyl substituted cyclopentenones and bis-(3,4-diphenylcyclopentadienone) are discussed and analysed. Several clarifications of dubious structures are made.

The attempted conversion of 1,1'-bis(chloromercuri)-ferrocene to 1,1'-dimethoxyferrocene is described. Reductive cleavage of methoxyferrocene followed by treatment with ferrous chloride gave only trace amounts of 1,1'-dimethoxyferrocene. The acetylation of monomethoxyferrocene, under conditions which did not promote demethoxylation, and the attempted separation of the isomeric components by vapour phase and ordinary chromatographic techniques are described. Aminomethylation of 1,1'-dimethoxyferrocene gave isomeric mixtures of mono and di-aminomethylated products. The first on rechromatography gave two components whose structures were not assigned. Reduction of the latter to dimethoxy-dimethylferrocenes followed by chromatography in petroleum ether failed to achieve any separation.

THESIS

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POLY-ARYL FERROCENES AND
RELATED COMPOUNDS

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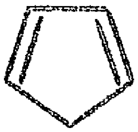
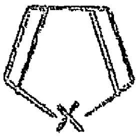
INTRODUCTION

Cyclopentadiene (I) occurs in the first runnings during the distillation of crude benzene from coal tar, this being an important commercial source.[1] It is a colourless liquid b.p. 41-42°. Cyclopentadiene bears formal analogy to the heterocyclic aromatic systems furan (II, X = O), thiophene (II, X = S) and pyrrole (II, X = NH). Unlike these cyclopentadiene is devoid of aromatic character. The unsaturated character of the diene system is so enhanced by ring strain that the pure monomer readily undergoes self condensation at room temperature to yield a crystalline dimer, dicyclopentadiene[2] (III) m.p. 32°. Monomeric cyclopentadiene is readily regenerated on heating.



(I)



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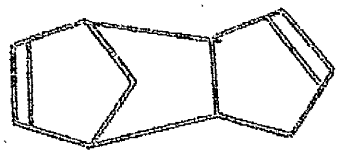
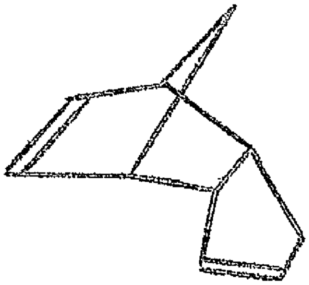


(III)

Since this dimerisation is a straightforward Diels-Alder addition, dicyclopentadiene possesses the endo configuration (IV), this is borne out by its reactions.[3]

The exo-isomer of dicyclopentadiene (V) is obtained by dimerisation at a higher temperature. Exo-dicyclopentadiene has m.p. 19.5°.



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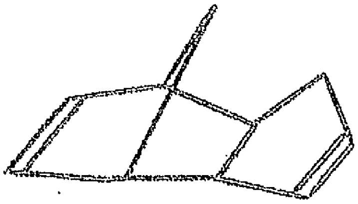
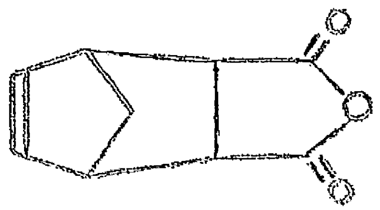


(V)

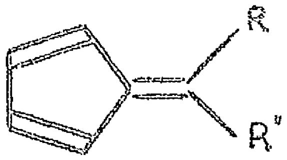
Higher polymers of cyclopentadiene, involving the condensation of 3, 4, 5 and 6-cyclopentadiene nuclei, are formed by heating the monomer to 150-200° in a sealed tube.[4,5,6]

Due to the presence of a highly reactive 1,3-diene system, cyclopentadiene readily reacts with dienophiles forming bridged ring (endomethylene) compounds.[7,8,9,10] The prime example of this is the reaction between cyclopentadiene and maleic anhydride to give cis-3,6-endomethylene-Δ^4-tetrahydrophthalic anhydride (VI).[11,12]



(VI)

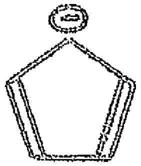
The methylene group in cyclopentadiene is highly reactive, thus it condenses with aldehydes or ketones in the presence of base to yield fulvenes (VII).[13,14] The chemistry of this class of compounds has been extensively reviewed.[15,16]



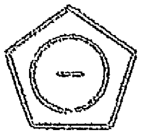
(VII)

Cyclopentadiene also reacts with methylmagnesium iodide with the formation of cyclopentadienylmagnesium iodide.

As early as 1900 Thiele recognised the acidity of cyclopentadiene by his work on cyclopentadienylpotassium,[13] a very reactive salt formed by treatment of cyclopentadiene with metallic potassium. This acidity of cyclopentadiene is attributed to the aromatic character of the cyclopentadienide anion (VIIIa).



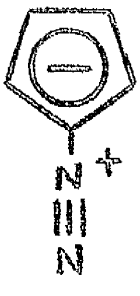
(VIIIa)



(VIIIb)

This anion possesses an aromatic sextet of electrons and is completely symmetrical, so that (VIIIa) is only one of five canonical forms, a better pictorial representation of the anion is conveyed by (VIIIb). The theoretical relationship of this anion to benzene was first put forward by Robinson[17,18] and Ingold.[19,20]

Various stable derivatives of the cyclopentadienide anion, containing a balancing positive charge within the molecule, have been isolated. These include, diazocyclopentadiene[21] (IX), pyridinium cyclopentadienylide[22] (X), the trimethylammonium[23] (XI) and triphenyl-phosphonium[24,25] (XII) analogues.



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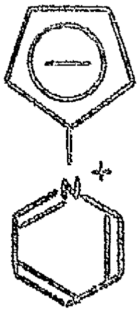

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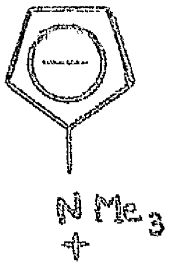

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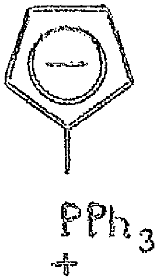


(XII)

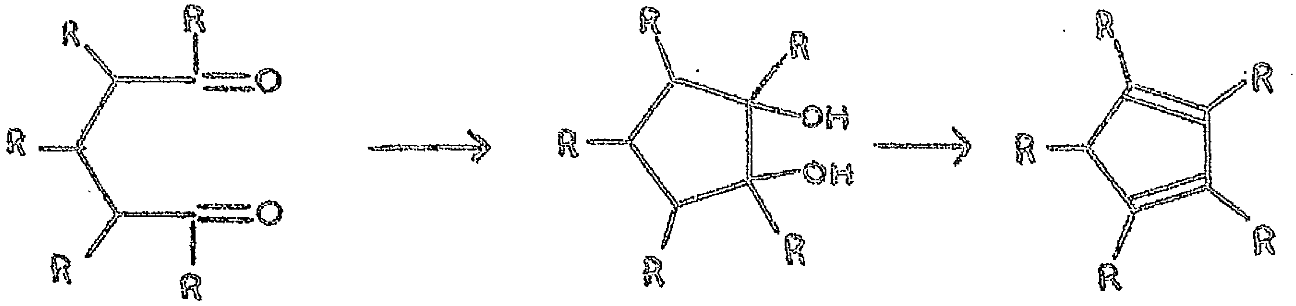
Phenyl Substituted Cyclopentadienes.

In the past alkyl substituted cyclopentadienes have not received much attention. However a Russian group recently described the preparation and properties of certain poly- methyl substituted compounds. They have shown that the structure of the substituted cyclopentadiene (or composition of the isomer mixture) depends mainly on the character of the substituent and not on the method of synthesis.

Compared with this a great deal of work has been carried out on phenyl substituted cyclopentadienes. They are all crystalline compounds with sharp melting points. The known phenyl cyclopentadienes are listed below.

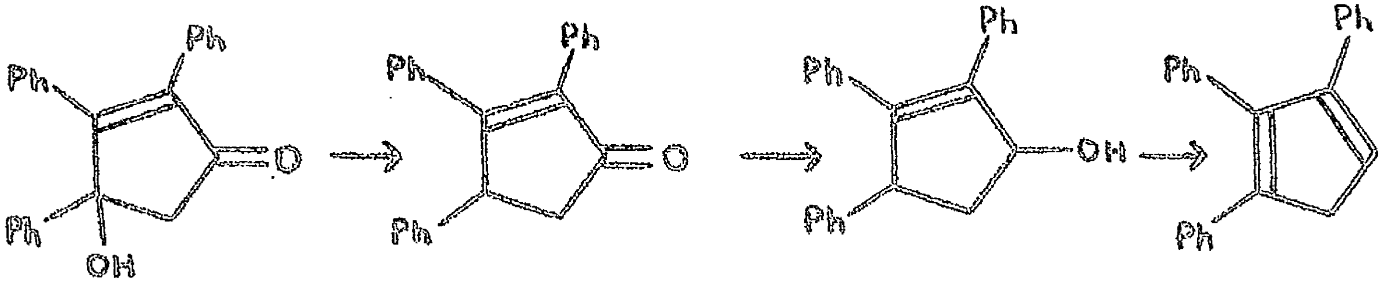
Cyclopentadiene	M.p.	Reference
monophenyl-	59-61°	27, 28
1,4-diphenyl-	158°	29
1,2,4-triphenyl-	149°	30
1,2,3-triphenyl-	157-159°	27, 31
1,2,3,4-tetraphenyl-	178°	32
1,2,3,4,5-pentaphenyl-	250°	33, 36
hexaphenyl-	172°	34

The principal method of preparation of these compounds is by pinacol reduction of a substituted 1,5-dione[35] (XIII) giving a cyclic diol (XIV), which can be dehydrated with acid to give the corresponding cyclopentadiene (XV).



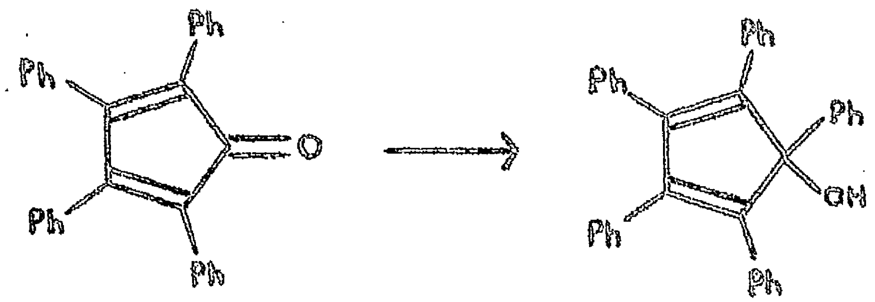
(XIII) (XIV) (XV)

By this method, 1,2,3 and 1,2,4-tri-, 1,2,3,4-tetra and 1,2,3,4,5-pentaphenylcyclopentadiene have been obtained. Pauson and Williams[31] obtained a higher yield of 1,2,3-triphenylcyclopentadiene starting from 4-hydroxy-2,3,4-triphenylcyclopent-2-enone (XVI). This was reduced first with hydriodic acid[27] to 2,3,4-triphenylcyclopent-2-enone (XVII), then with borohydride to the corresponding alcohol (XVIII), which smoothly dehydrated to give the desired cyclopentadiene (XIX).



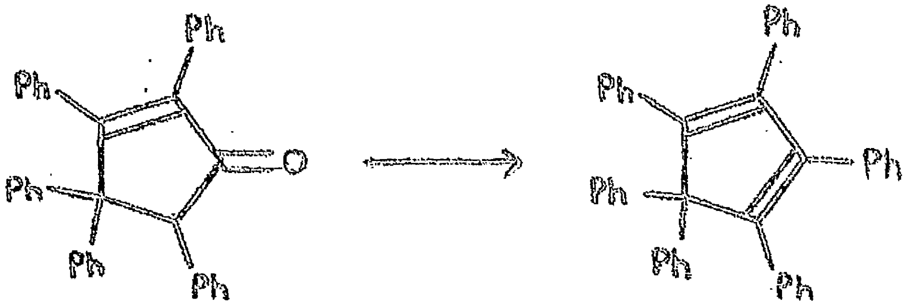
(XVI) (XVII) (XVIII) (XIX)

Pentaphenylcyclopentadiene[33] has also been obtained starting from tetracyclone (XX). Treatment with phenylmagnesium bromide gave the carbinol (XXI), which was subsequently brominated and debrominated to yield the hydrocarbon (XV, R = Ph).



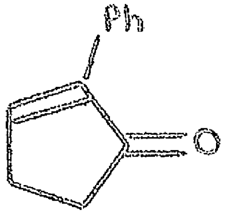
(XX) (XXI)

Pyrolysis of the carbinol (XXI) resulted in a 1,3-phenyl shift yielding the ketone (XXII), treatment of this with phenylmagnesium bromide followed by dehydration gave hexaphenylcyclopentadiene (XXIII).



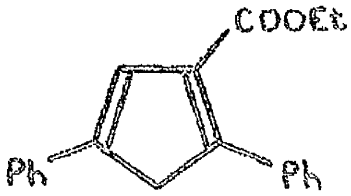
(XXII) (XXIII)

Monophenylcyclopentadiene was prepared by treatment of cyclopent-2-en-1-one with phenyllithium[27] or phenylmagnesium bromide,[28] followed by dehydration of the resulting carbinol. Riemschneider also obtained the compound by prolonged treatment of 2-phenylcyclopent-2-en-1-one (XXIV) with aluminium isopropoxide.[2

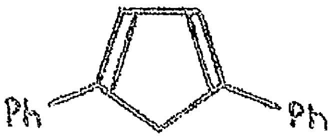


(XXIV)

1,4-Diphenylcyclopentadiene was first synthesised by Borsche and Menz,[38] who formulated the compound as the 1,3-isomer. However, Drake and Adams[29] followed the same reaction scheme and proved that the 1,4-isomer was obtained. This synthesis entailed the base catalysed condensation between β-benzoyl propionate and acetophenone to give the ester (XXV), hydrolysis gave the corresponding acid which readily lost carbon dioxide on heating to give the diene (XXVI).



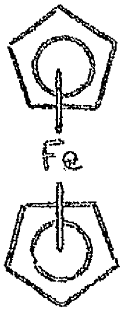
(XXV)



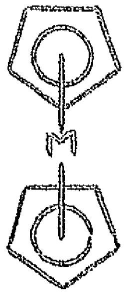
(XXVI)

Cyclopentadienyl Iron Compounds

The remarkable discovery in 1951, by two independent groups of workers, of a stable organo-iron compound[39,40], has led to the development during the last decade, of a completely new field of chemistry. In an attempted preparation of dihydrofulvalene, by the reaction of cyclopentadienylmagnesium bromide with ferric chloride, Kealy and Pauson isolated[39] dicyclopentadienyliron (XXVII). The same compound was obtained by Miller, Tebboth and Tremaine from the reaction[40] of cyclopentadiene vapour and reduced iron at 300°.



(XXVII)



(XXVIII)

The aromaticity of this new compound was recognised[41] by Woodward et al. and on this basis it was named 'ferrocene'. The organometallic chemistry of the transition metal series has been extensively developed since 1951 and the field has been summarised in numerous reviews.[42-64]

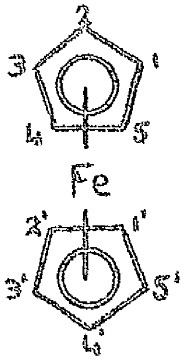
The structure of ferrocene has been described[65] as a 'molecular sandwich' or more aptly a 'Doppelkegelstruktur'.[56] It possesses a centrosymmetric structure with the two rings disposed in parallel planes about the central iron atom.[57-61] Ferrocene crystallises in the monoclinic space group $P2_{1}/c$ with two molecules in the unit cell.[57,61] Hence the metal atom lies at a centre of symmetry both within the unit cell and within the molecule.[55,57] The rings in ferrocene have the 'staggere conformation, while the analogous dicyclopentadienylruthenium (XXVIII, M = Ru)[62,63] and dicyclopentadienylosmium (XXVIII M = Os)[6 have the opposed conformation in their orthorhombic crystals. This may be attributed to the larger size of the latter two metal atoms, which reduces the repulsion between the hydrogen atoms attached to both rings.

The fact, that no rotational isomers of ferrocene derivatives bearing a substituent in each ring have ever been isolated, is strong evidence for free rotation of the rings in the molecule.[65] Even in the crystal state considerable motion of the rings, with respect to each other, is thought to occur, with the staggered conformation preferred.[61] The validity of this concept of ring rotation has been established by proton magnetic resonance studies[66] of the molecule.

Nomenclature

The ferrocene system is numbered as shown, with one ring designated by carbons 1 to 5 and the second ring 1' to 5'

(XXIX) in the same direction



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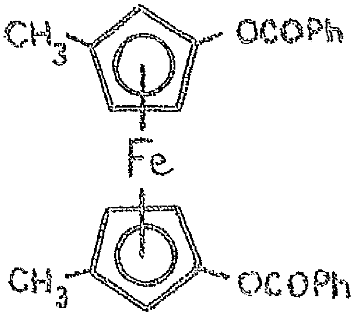

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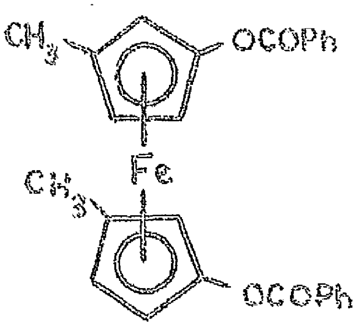
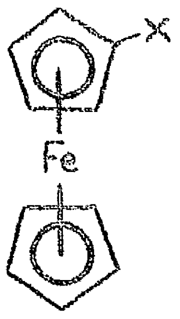


(XXXI)

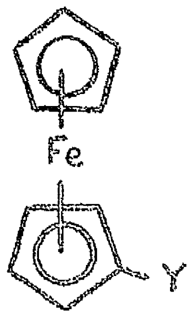
As can be seen when one ring bears a substituent, positions 2 and 5 (α positions) become equivalent as do positions 3 and 4 (β positions). It can be seen, on this system of numbering both rings in the same direction, that (XXX) and (XXXI) are stereoisomers and as such can be separated.[67] Where possible direct analogy to the benzene series is maintained; the 1,1'-disubstituted group has been termed the 'ferrocenylene' group by reference to the phenylene group (C_6H_4).

Physical Properties

Ferrocene is an orange crystalline solid, m.p. 173°, it is steam volatile and sublimes freely above 100°. The compound is diamagnetic,[65] a fact which allied to the N.M.R.[66,71,72] and infrared[68,69] spectra presents strong evidence for the high degree of symmetry in the molecule. The infrared spectrum shows a single C-H stretching band at 3075 cm.$^{-1}$, two bands at 811, 1002 cm.$^{-1}$, which have been unambiguously assigned to C-H bending vibrations and two strong bands at 1108 and 1141 cm.$^{-1}$ These have been assigned respectively to antisymmetrical ring breathing and an antisymmetrical C-C stretching mode. The presence of bands at 1002 and 1108 cm.$^{-1}$ has been found to be so characteristic of the presence of an unsubstituted cyclopentadienyl ring, that it can be employed as an empirical rule (Rosenblum's 9, 10 rule)[70] to determine the substitution pattern in substituted ferrocenes. Rosenblum also formulated the generalisation[70] that the spectra of ferrocene derivatives are additive; i.e. the spectrum of (C) for example is a composite of those of (A) and (B) with the



(A)



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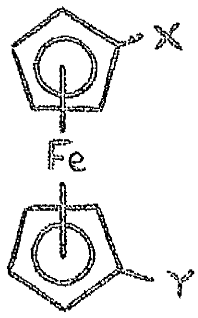


(C)

exclusion of the 9,10 bands.

Ferrocene is unaffected by acids or alkalis in the absence of oxidising agents. Nevertheless it may be oxidised to the blue monovalent ferricinium cation $(C_5H_5)_2Fe^+$, which can be precipitated as stable salts in combination with various anions.[67,74] The oxidation potential for this transformation has been measured polarographically[73] and has been found to be intermediate to those of the systems

$$[Fe(H_2O)_6]^{2+} \longrightarrow [Fe(H_2O)_6]^{3+}$$

$$[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-}$$

and of the same order as the latter. Introduction of electron withdrawing substituents into the ferrocene nucleus causes an appreciable increase in resistance to oxidation.

In contrast to its relative ease of oxidation ferrocene is remarkably stable to reduction, even under conditions which cause reduction of benzene to cyclohexane.[41] Under more severe conditions, rupture of the molecule occurs giving iron and cyclopentane.[75] Fission of the metal ring bond may also be achieved by bromination or chlorination, giving the corresponding pentahalocyclopentane,[75,76] and by alkali metals in basic solvents, such as liquid ammonia or ethylamine, to yield iron and cyclopentadiene.[77]

Aromaticity

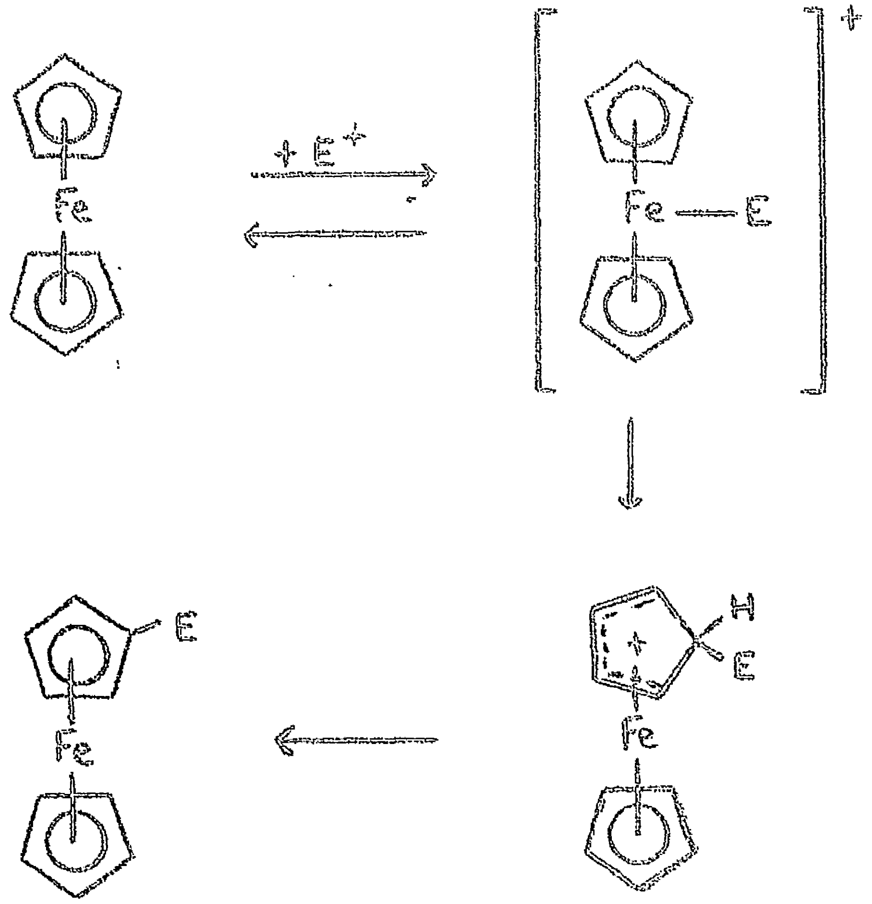
Since the discovery by Woodward *et al.*[41], that ferrocene readily undergoes Friedel-Crafts acylation under mild conditions, numerous substitution reactions have been investigated. In addition to Friedel-Crafts acylation,[63,78-84] and alkylation,[85-89] these include sulphonation,[83,90-93] mercuration,[94,95] metalation,[94,96] [1 arylation,[94,103-106] formylation,[68,80,107-109] aminomethylation[110,11 as well as various condensations with aldehydes.[83,107,110,112-114] Pauson and Morrison[115] have carried out a successful direct boronation based on a Friedel-Crafts type reaction.

No nucleophilic substitution[76] of the ring protons has ever been recorded in the ferrocene series. This has necessitated the use of indirect routes to such derivatives as nitro, nitroso[116-118] and haloferrocenes.[76,119-122]

Rosenblum has recently proposed[123] a mechanism for this electrophilic substitution. Briefly, this mechanism consists of primary attack of the electrophile at the central metal atom, followed by an internal rearrangement to the endocyclic σ-complex (XXXII) and finally expulsion of a proton to give the substituted ferrocene (XXXIII).

Competitive experiments have shown that ferrocene is the most and osmocene the least reactive of the iron, ruthenium and osmium[65] dicyclopentadienyls. The following order of reactivity[7 has also been established.

Ferrocene $\gg$ anisole $>$ cyclopentadienylmanganese tricarbonyl $>$ benzene.



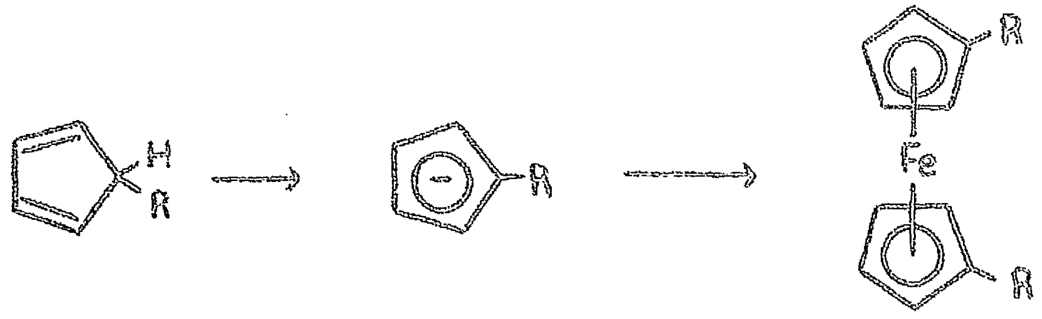
(XXXIII) (XXXII)

Synthesis of Substituted Ferrocenes

The methods for the synthesis of substituted ferrocenes can be classified into three main groups.

(1) From ferrocene via electrophilic substitution reactions as outlined in the preceding chapter.

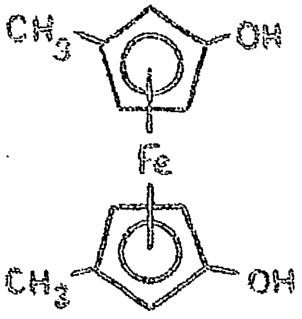
(2) By utilisation of the reaction between a substituted cyclopentadienide anion (XXXIV) and ferrous chloride. The



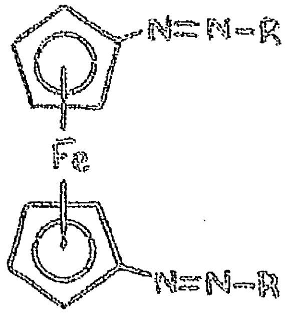
(XXXIV) (XXXV)

anion is usually obtained by the action of alkali metals or alkyl or aryllithiums on the hydrocarbon. This method is limited by the poor availability of monomeric cyclopentadienes. However it has been used extensively for the preparation of aryl substituted ferrocenes,[27,106,124,125] and 1,1'-dialkylferrocenes.[27,126,129] Unsymmetrically substituted ferrocenes can be prepared by reaction of mixed cyclopentadienyl and substituted cyclopentadienyl salts with ferrous chloride.

In certain cases substituted cyclopentadienyl salts have been prepared without isolation of the free cyclopentadiene. The most notable example of this has been the syntheses of ferrocene derivatives bearing functional groups, using the sodium enolate of methylcyclopentenone and diazocyclopentadiene[21] to give respectively dihydroxydimethylferrocene (XXXVI)[128] and the azo-ferrocenes (XXXVII R, = CH_3, C_6H_5).[129,130]

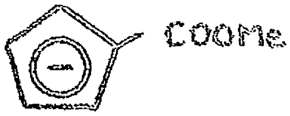


(XXXVI)



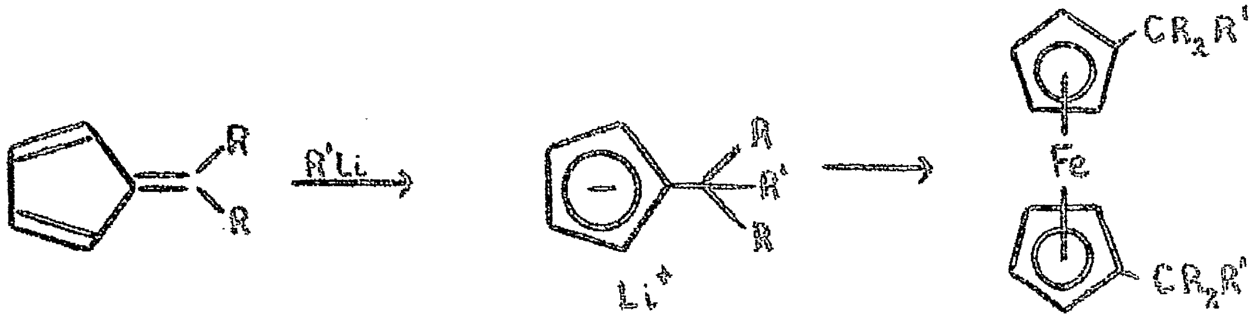
(XXXVII)

Reaction of cyclopentadienylsodium with methylchloroformate in the presence of free sodium yielded the anion (XXXVIII), which on addition of ferrous chloride gave dimethylferrocene dicarboxylate, by a similar technique 1,1'-diacetylferrocene (XXXV, R = $COCH_3$) has been obtained in low yield.[131,132]



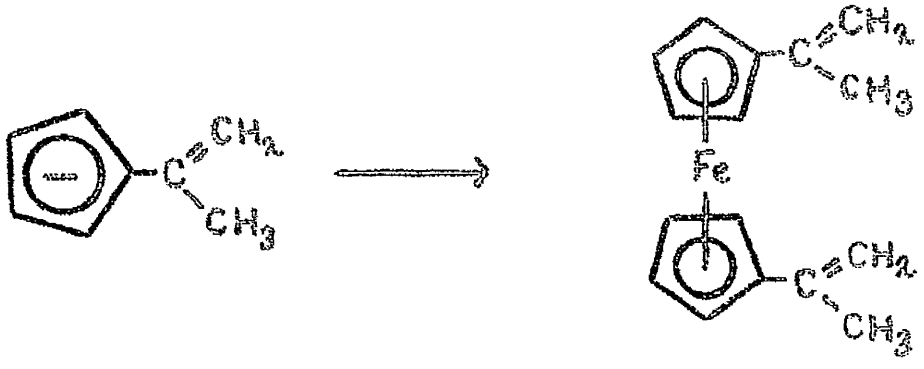
(XXXVIII)

Another important adaptation of this method has been the use of 6-substituted fulvenes in the syntheses of substituted ferrocenes.[133,134,135] Reaction of the fulvene (XXXIX, R = alkyl or aryl) with lithium aluminium hydride or alkyl or aryl lithiums gives the intermediate anion (XL) which yields the substituted ferrocene (XLI) on treatment with ferrous chloride.



(XXXIX) (XL) (XLI)

The acidic character of fulvenes, e.g. dimethylfulvene (XXXIX, $R = CH_3$), on treatment with sodamide in liquid ammonia, gives rise to anions such as (XLII) from which diisopropenylferrocene (XLIII) has been obtained.[133]



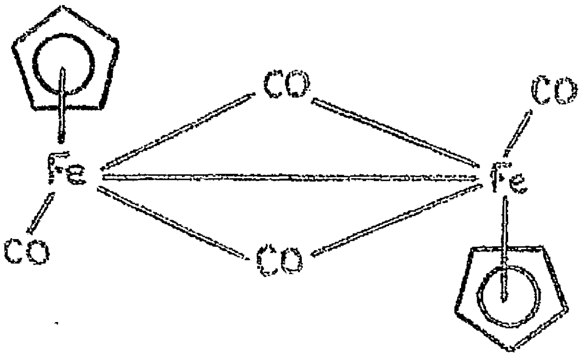
(XLII) (XLIII)

(3) The high temperature reaction of substituted cyclopentadienes with iron pentacarbonyl has been shown to yield substituted ferrocenes.[136]

Cyclopentadienyl-Iron Carbonyls.

Since the first preparation of cyclopentadienyl carbonyl compounds of molybdenum and tungsten,[137] numerous cyclopentadienyl complexes involving carbonyl and nitrosyl groups have been prepared for the transition elements of groups five to eight. It has been found that elements of odd atomic number yield compounds of formula $C_5H_5M(CO)_x$, while the even numbered members form dimers of formula $[C_5H_5M(CO)_x]_2$. The value of x corresponds to the number of pairs of electrons required for the attainment of the next inert gas configuration, it is assumed that the five-membered ring donates 6π-electrons and that the metal-metal bond contributes in the case of dimers.[138] The chemistry of this group of compounds has been extensively reviewed[42-45, 48,49] and within the present context only the chemistry of the cyclopentadienyl carbonyls of iron will be discussed.

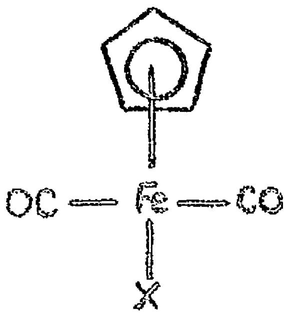
The compound dicyclopentadienyldi-iron tetracarbonyl (XLIV)[139-142] which was originally formulated as $(C_5H_5)_2Fe_2(CO)_5$,[139] is obtained by the reaction of iron pentacarbonyl and cyclopentadiene dimer in the liquid phase. An improved method of



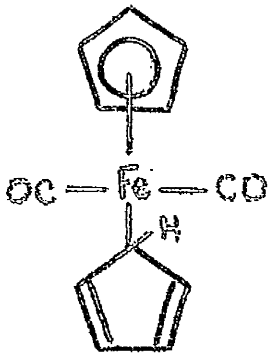
(XLIV)

preparation was achieved by the use of monomeric cyclopentadiene in a closed system.[136] The compound forms dark purple plates, m.p. 194°, insoluble in water and soluble in common organic solvents with the exception of petroleum ether. X-ray studies[143,144] have shown that the crystals are monoclinic with space group $P2_1/c$. It follows that there are two molecules per unit cell and that each molecule must possess a centre of symmetry. On the basis of this andthe infrared spectrum, which shows two distinct carbonyl frequencies, the structure has been formulated as (XLIV). The tetracarbonyl decomposes at 220° with the formation of ferrocene, the yield being improved by the addition of cyclopentadiene.

Oxidation in an aqueous medium gives the hydrated cation $[C_5H_5Fe(CO)_2H_2O]^+$. In organic solvents an anhydrous chloride (XLV, X = Cl),[141, 142] bromide (XLV, X = Br),[136,141] iodide (XLV, X = I)[136,146] and cyanide (XLV, X = CN)[142] have been obtained.

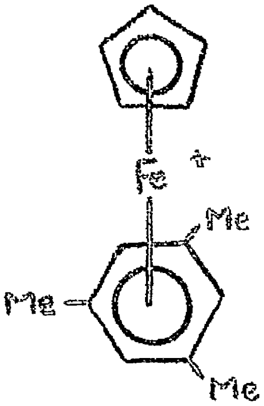


(XLV)

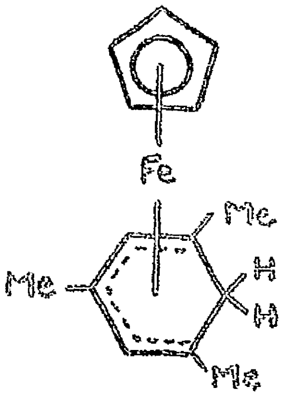


(XLVI)

These compounds also yield ferrocene on strong heating.[136] Reaction of the bromide (XLV, X = Br) with cyclopentadienyl sodium gives the unstable π-cyclopentadienyl-σ-cyclopentadienyl-iron dicarbonyl (XLVI)[156] which loses carbon monoxide very readily with the formation of ferrocene. Compounds of this type have been utilised[136] in the preparation of unsymmetrically substituted ferrocenes. Treatment of the bromide with mesitylene in the presence of a halogen acceptor such as aluminium trichloride results in the elimination of carbon monoxide and formation of the cation (XLVII).[152] This ion may be obtained as crystalline salts in conjunction with a variety of anions. Reduction of the ion with lithium aluminium hydride gives the neutral diene complex (XLVIII)[153]

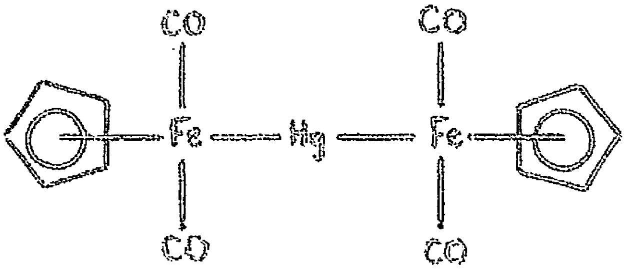


(XLVII)



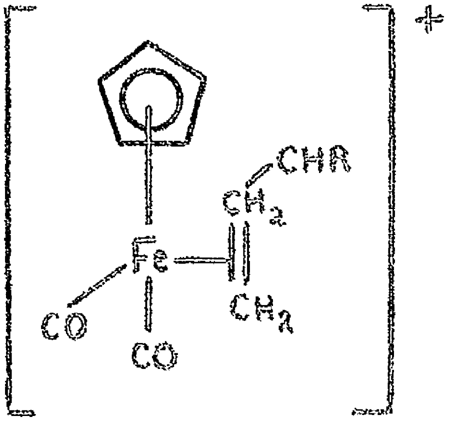
(XLVIII)

The dimeric tetracarbonyl may be reduced by sodium amalgam to the yellow anion $[C_5H_5Fe(CO)_2]^-$ which reacts with mercuric cyanide to give the yellow mercury derivative (XLIX).[140] A variety of alkyl, aryl and acyl derivatives (XLV, X = alkyl, aryl or acyl) have been prepared by reaction of this anion with the respective

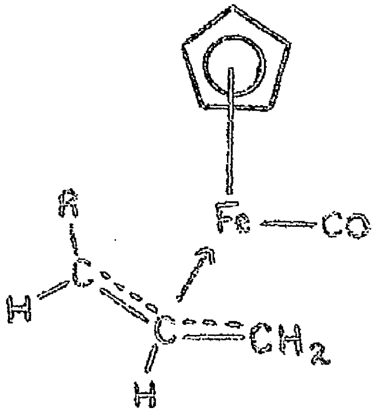


(XLIX)

halide. By similar means, allyl complexes (XLV, X = allyl) have been obtained; protonation of the allyl group affords π-ethylenic complexes (L, R = H, Me) and ultraviolet irradiation affords the π-allyl, monocarbonyl complex (LI, R = H, Me).[151]

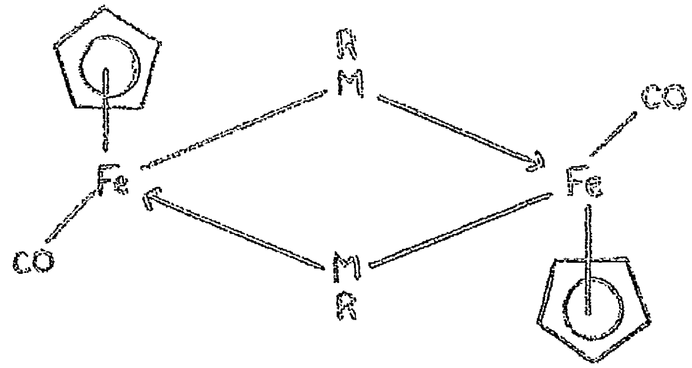


(L)



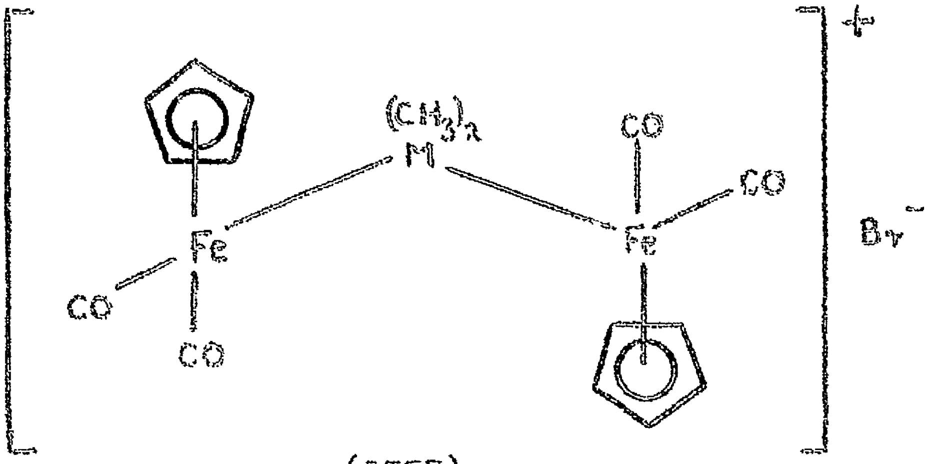
(LI)

The bridging carbon monoxide group in the tetracarbonyl (XLIV) may be replaced by other bridging ligands to give complexes which do not possess a metal-metal bond. The first instance of this was the preparation of the sulphur bridged complex



(LII)

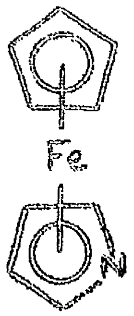
(LII, M = S; R = CH_3),[154] Hayter[155] has obtained analogous phosphorus and arsenic bridged complexes [LII, M = P, As; R = $(CH_3)_2$, $(C_6H_5)_2$] by direct interaction of the tetracarbonyl (XLIV) with tetrasubstituted biphosphines and arsines. These



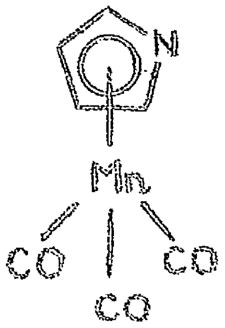
(LIII)

compounds exhibit *cis-trans* isomerism. This has recently been extended by Hayter to the preparation of singly bridged ionic complexes (LIII, M = P, As)[156] from cyclopentadienyliron dicarbonyl bromide (XLV, X = Br) and tetramethylbiphosphine and arsine.

By far the most recent development in this field has been the synthesis of aza-ferrocene (LIV),[157] by the direct interaction of cyclopentadienyliron dicarbonyl iodide (XLV, X = I) with pyrolylpotassium. Aza-ferrocene and the related pyrolylmanganese tricarbonyl (LV)[158] are distinctly less stable than their corresponding cyclopentadienyl analogues. Basic properties are retained, aza-ferrocene being more basic than the manganese complex due to the electron withdrawing effect of the carbonyl groups in the latter. Preliminary X-ray studies[159] of azaferrocene have shown that it is isomorphous with ferrocene. As yet no successful electrophilic substitution has been achieved.



(LIV)



(LV)

Bonding Theories for Ferrocene

The nature of the bonding in ferrocene and related compounds has been the subject of much controversial discussion. From the numerous publications and reviews,[42,43,49,54,162,163] two main concepts have emerged.

Fischer and his co-workers[57] visualised ferrocene as a completely new type of penetration complex. The two staggered aromatic cyclopentadienyl anions each possess three pairs of π-electrons, which interact with the central ferrous ion to form six co-ordinate covalencies (d^2sp^3 hybrids), distributed around it in a trigonal antiprism.

An alternative molecular orbital interpretation was first put forward by Dunitz and Orgel[60] and later amplified by Moffitt.[160] Briefly this theory visualises a single covalent ($d\pi - p\pi$) bond from the central metal atom to each ring as a whole, 'resonating' equally between all five carbon atoms. Any additional secondary bonding may be regarded as being very weak.

These two concepts are not as incompatible as would appear at first sight, since Linnett[161] has pointed out that the metal atom must attain the inert gas configuration. The true nature of the bonding lies somewhere between these two representations.

DISCUSSION

The work described in the following discussion is an extension of work, previously carried out by Pauson *et al.*, dealing with the syntheses of substituted ferrocenes from the corresponding cyclopentadienes. Efforts were directed particularly to the synthesis of a deca-substituted ferrocene employing various substituted cyclopentadienyliron carbonyls. The syntheses of some new cyclopentadienes is also described. An attempt was made to augment work, previously carried out by Pauson and Morrison, concerning the directive effects operative in methoxyferrocenes.

CHAPTER I

POLY-ARYL FERROCENES

The route to substituted ferrocenes via substituted cyclopentadienes was initially reported by Pauson[27] in 1954. Due to the ready availability of monomeric phenylcyclopentadienes, the above method was employed for the syntheses of various phenyl-substituted ferrocenes. In the course of this work the following compounds were prepared, 1,1'-dipheny 1,3,1',3'-tetraphenyl-, 1,2,4,1',2',4'-hexaphenyl- and 1,1'-dibenzhydrylferrocene. These were prepared either by lithiation or formation of the Grignard reagent of the diene, followed by the addition of ferric chloride. In the case of 1,2,3-triphenyl-,[27,31] 1,2,3,4-tetraphenyl-[32] and pentaphenyl- cyclopentadiene,[35,36] this technique failed to yield the corresponding ferrocene. The above results indicated that steric factors might be responsible for preventing the formation of ferrocenes having more than two phenyl groups on adjacent carbons.

However in 1955, Weinmayr reported[33] the preparation o octaphenylferrocene (LVI; $R_1 = H$; R_2, R_3, $R_4 = Ph$). The meth used was treatment of the sodium salt of tetraphenylcyclopentadiene with ferrous chloride. This suggests that the lithium salts of 1,2,3-triphenyl-, tetraphenyl- and pentaphenylcyclopentadiene were unable to reduce ferric to the ferrous state, thus explaining the earlier failures.

It was decided to investigate this further, by extending Weinmayr's technique to other phenylcyclopentadienes. Repeated attempts at the preparation of octaphenylferrocene (LVI; R_1 = H; R_2, R_3, R_4 = Ph) as described by the above author failed. An examination of the reaction conditions gave a 40% yield of 1,3,1',3'-tetraphenylferrocene from 1,4-diphenylcyclopentadiene,[29] suggesting that the conditions employed were satisfactory.

In the light of these results, a new and more powerful basic system was desirable for the preparation of the sodium salts. Treatment of anhydrous dimethylsulphoxide with sodium hydride gives the very strong base 'dimsyl' sodium[164]. The advantage of this system over sodium in liquid ammonia, as used by Weinmayr, is that anhydrous conditions are easily maintained. Consequently, application of this technique to 1,4-diphenyl-; 1,2,3-triphenyl-; and tetraphenylcyclopenta diene gave 1,3,1',3'-tetraphenyl-(LVI; R_1, R_3, R_4 = H; R_2 = P (68%); 1,2,3,1',2',3'-hexaphenyl- (LVI; R_1, R_2 = H; R_3, R_4, = Ph) (45%) and octaphenylferrocene (LVI; R_1 = H; R_2, R_3, R_4 = (20%). The addition of pentaphenylcyclopentadiene to 'dimsy sodium gave a deep purple solution. The colour was discharged on the addition of ferrous chloride, pentaphenylcyclopentadiene being recovered quantitatively. 1,4-Dimethyl-2,3-diphenylcyclopentadiene[x] on treatment with phenyl lithium

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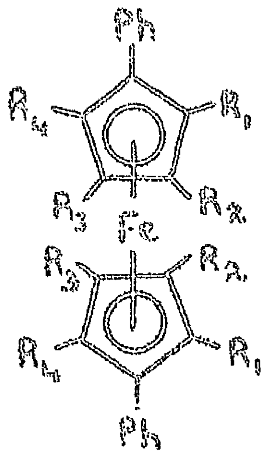
[x] See Discussion Chapter II



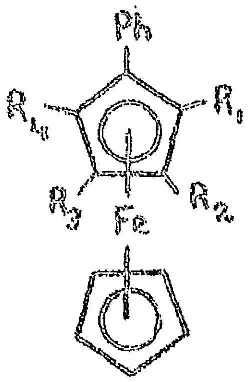
(LVI)

and ferrous chloride, gave 1,4,1',4'-tetramethyl-2,3,2',3'-tetraphenylferrocene (LVI; R_2 = H; R_1, R_3 = Me; R_4 = Ph).

It would appear from these results that earlier failures were indeed due to the poor reducing properties of the particular lithium salts. However, the fact that the yields of the above ferrocenes fall off markedly with increasing phenyl substitution, implies that formation is also inhibited by increasing steric strain. The limiting case being reached at octaphenylferrocene.

Reaction of Phenylcyclopentadienes with Iron Carbonyl Compounds.

Hallam and Pauson have reported,[136] that reaction of 1,4-diphenylcyclopentadiene with dicyclopentadienyldi-iron tetracarbonyl (XLIV) gave the unsymmetrical 1,3-diphenylferrocene (LVII; R_1, R_3, R_4 = H; R_2 = Ph).

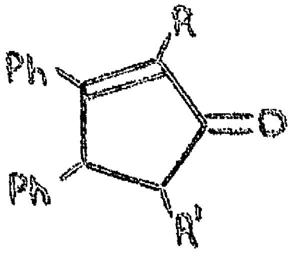


(LVII)

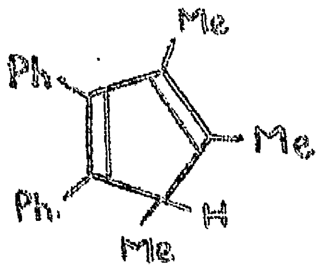
Extending this reaction to other phenyl substituted cyclopentadienes, the symmetrical (i.e. both rings substituted) and the unsymmetrical products were obtained, together with the parent compound ferrocene. Irregularities occurred in the reactions with 1,2,3-triphenyl- and pentaphenylcyclopentadiene. In the case of the former, 1,2,3-triphenylferrocene (LVII; R_1, R_2 = H; R_3, R_4 = Ph) could not be isolated. This can only be attributed to the technique employed for isolation of these products, since there is no apparent mechanistic explanation. Reaction with pentaphenylcyclopentadiene, on the other hand, failed to yield decaphenylferrocene (LVI; R_1, R_2, R_3, R_4 = Ph). An observation which is in keeping with earlier experiments. The cyclopentadienes used and the products obtained are summarised in the following table

Cyclopentadiene	FERROCENE	
	LVII	LVI
1,2,4-Triphenyl-[30]	$R_1, R_3 = H; R_2, R_4 = Ph$	$R_1, R_3 = H; R_2, R_4 =$
1,2,3-Triphenyl-	-	$R_1, R_2 = H; R_3, R_4 =$
1,2,3,4-Tetraphenyl-	$R_1 = H; R_2, R_3, R_4 = Ph$	$R_1 = H; R_2, R_3, R_4 =$
1,2,3,4,5-Pentaphenyl-	$R_1, R_2, R_3, R_4 = Ph$	-
1,2,5-Trimethyl-4,5-diphenyl- LVIX	$R_1, R_2, R_3 = Me,$ $R_4 = Ph$	$R_1, R_2, R_3 = Me;$ $R_4 = Ph$

1,2,5-Trimethyl-3,4-diphenylcyclopentadiene (LVIX) was readily obtained by reaction of 2,5-dimethyl-3,4-diphenylcyclopent-2-en-1-one[165] (LVIII, R,R' = Me) with methylmagnesium iodide and subsequent dehydration. One novel aspect of the



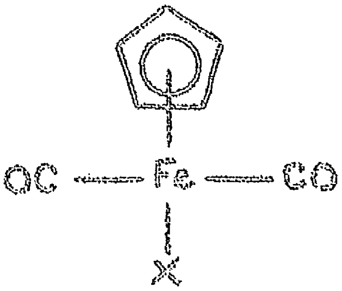
LVIII



LVIX

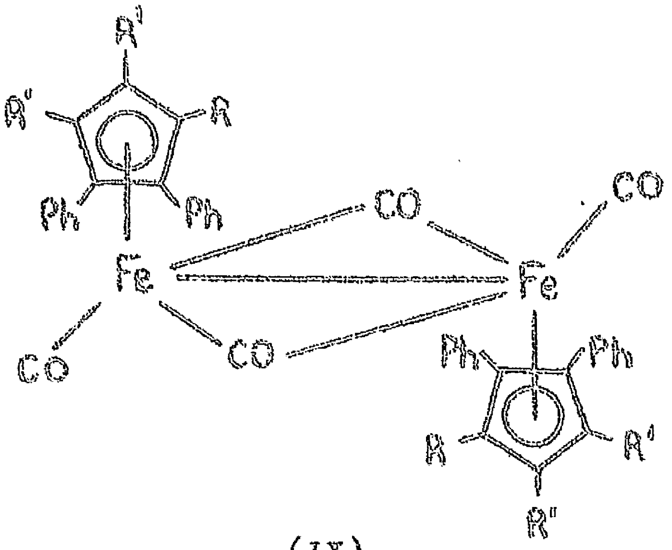
series has been the use of this compound for the preparation of the deca-substituted 1,2,3,1',2',3'-hexamethyl-4,5,4',5'-tetraphenylferrocene. Deca-ethylferrocene[190] is the only other fully substituted derivative so far reported.

The preparation of 1,2,3,4-tetraphenylferrocene (LVII; R_1 = H; R_2, R_3, R_4 = Ph) confirms the findings of a Japanese group,[166] who obtained this compound by the novel interaction of cyclopentadienyliron dicarbonyl methyl (XLV; X = Me) and diphenylacetylene.



(XLV)

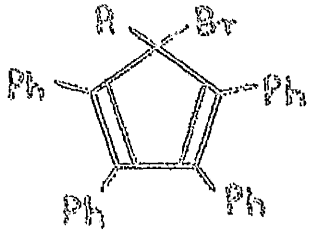
The preparation of 1,3,1',3'-tetraphenylferrocene (LVI; R_1,R_3,R_4 = H; R_2 = Ph), by the high temperature interaction of 1,4-diphenylcyclopentadiene and iron pentacarbonyl, has also been described[136] by Hallam and Pauson. Adapting this method, octaphenylferrocene (LVI; R_1 = H; R_2, R_3, R_4 = Ph) and 1,2,3,1'2',3'-hexaphenylferrocene (LVI; R_1,R_2 = H; R_3,R_4 = Ph) were obtained from the corresponding cyclopentadienes. Again pentaphenylcyclopentadiene failed to react under these conditions. Despite the fact that no other product was isolated, both these reactions were assumed to pass through a dimeric tetracarbonyl intermediate (LX; R' = H; R = Ph and R = H; R' = Ph). Attempted syntheses of



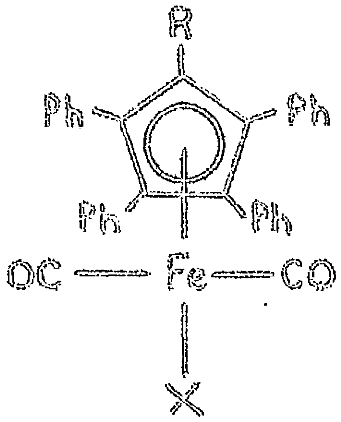
(LX)

these dimeric intermediates, by interaction of the sodium salt of the substituted cyclopentadiene with iron pentacarbonyl,[199] met with no success. However, further support for the postulated intermediates was afforded by 1,2,5-trimethyl-3,4-diphenylcyclopentadiene (LVIX), which gave bis(-1,2,3-trimethyl-4,5-diphenylcyclopentadienyl-)di-iron tetracarbonyl (LX; R,R'= Me) on treatment with iron pentacarbonyl.

The inefficacy of all direct methods for the preparation of decaphenylferrocene (LVI; R_1,R_2,R_3,R_4 = Ph), prompted the syntheses of intermediate carbonyl compounds, possessing the pentaphenylcyclopentadienyl ring π-bonded to iron. Consequently, by analogy with the preparation of allyl-iron tricarbonyl iodide,[167] 1,2,3,45-pentaphenylcyclopentadienyliron dicarbonyl bromide (LXII; R = Ph; X = Br) was obtained directly by refluxing 5-bromopentaphenylcyclopentadiene (LXI; R = Ph)[52] and iron pentacarbonyl in benzene. Under similar conditions



(LXI)



(LXII)

5-bromo-1,2,3,4-tetraphenylcyclopentadiene (LXI; R = H)[52] failed to react. However it did react with iron pentacarbonyl on refluxing in chlorobenzene, to give a low yield of 1,2,3,4-tetraphenylcyclopentadienyliron dicarbonyl bromide (LXII; R = H; X = Br). The efficiency of this reaction in the case of 5-bromopentaphenylcyclopentadiene is probably due to the enhanced stability of the pentaphenylcyclopentadienyl anion, which facilitates the elimination of a bromonium ion.

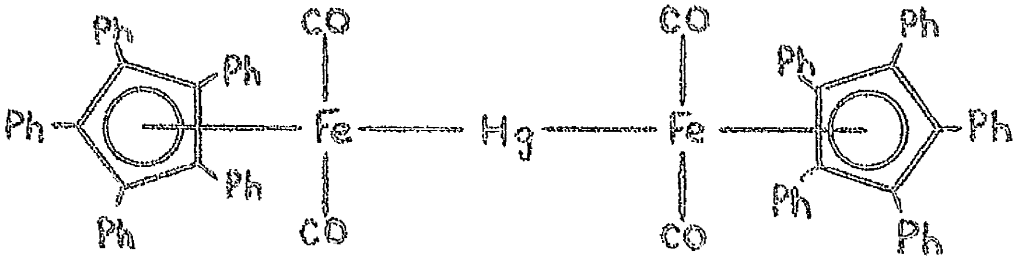
It has also been found that high temperature interaction of 5-bromopentaphenylcyclopentadiene with iron pentacarbonyl gives moderate yields of pentaphenylcyclopentadiene.

Reactions of Pentaphenylcyclopentadienyliron Dicarbonyl Bromide (LXII; R = Ph; X = Br).

As has already been stated, the primary interest in this compound lay in its potential as an intermediate in the formation of decaphenylferrocene (LVI; R_1, R_2, R_3, R_4 = Ph). Accordingly all initial efforts were concentrated in this direction.

In the case of the parent compound, cyclopentadienyliron dicarbonyl bromide (XLV; X = Br), pyrolysis[136] yields ferrocene. Pyrolysis of pentaphenylcyclopentadienyliron dicarbonyl bromide (hereafter referred to as 'the bromide') (LXII; R = Ph; X = Br) failed to yield the expected ferrocene, the products being pentaphenylcyclopentadiene and a red crystalline material, which had no carbonyl absorption in the infrared. Due to the technique employed for isolation of the above product i.e. reduction of a benzene solution to small bulk followed by precipitation with petroleum ether, quantities sufficient for a structural investigation were unobtainable. Chromatographic techniques proved abortive, since the red material on adsorption on alumina and subsequent elution with ether-benzene gave a deep blue solid, readily soluble in petroleum ether. On account of the meagre yields obtained and difficulties of purification, no conclusions have been drawn as to a possible explanation for this phenomenon.

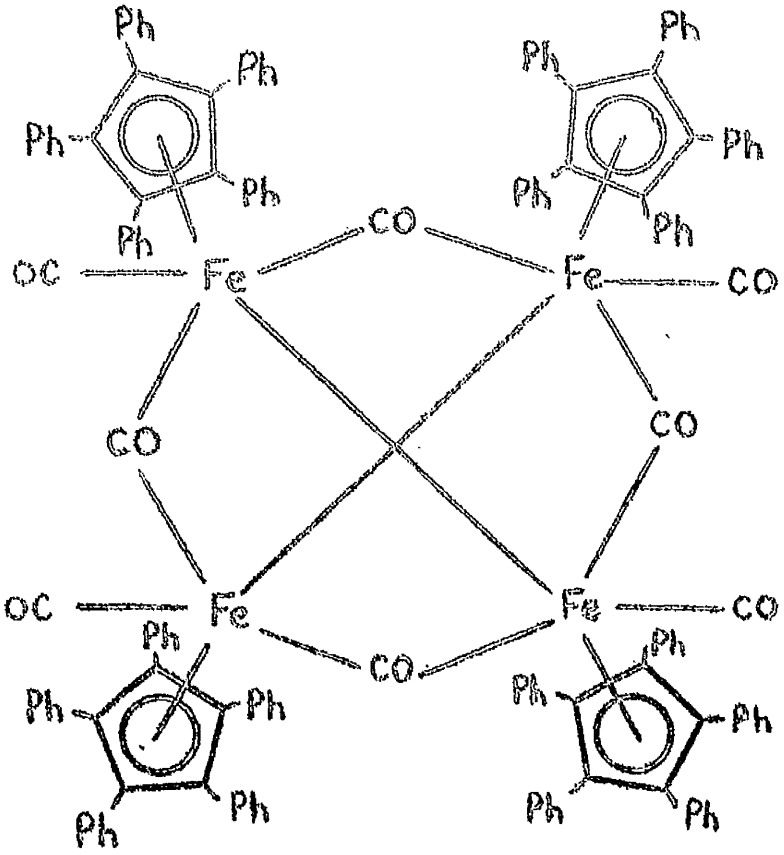
It was felt that bis-(pentaphenylcyclopentadienyl-)di-iron tetracarbonyl (LX; R,R' = Ph) would be more suitable for pyrolysis, since rupture of an iron-iron bond should occur more readily than rupture of an iron-bromine bond. Thus, treatment of the bromide (LXII; R = Ph; X = Br) with sodium amalgam gave two products. One was identified as bis-(pentaphenylcyclopentadienyliron dicarbonyl)mercury (LXIII). The shift in the carbonyl stretching frequencies in the infrared is compatible



(LXIII)

with the formation of a metal-metal bond i.e. a shift from 2040, 2000 cm.$^{-1}$ for the bromide to 1970, 1930 for (LXIII). The major product obtained was an insoluble green solid, which decomposed in a few days and could not be obtained pure. As a consequence, analytical data have not been obtained. However an examination of the infrared spectrum revealed the presence of two carbonyl stretching frequencies, i.e. 1965 and 1786 cm.$^{-1}$. The former is consistent with a terminal carbonyl group attached to a metal, which is bonded to another metal and the latter is typical of a bridging carbonyl group between two metal atoms.

The remainder of the spectrum is indicative of the presence of a pentaphenylcyclopentadienyl group. Summing up the infrared evidence, it would appear that this compound is in fact bis-(pentaphenylcyclopentadienyl-)di-iron tetracarbonyl (IX; R,R' = Ph). On the other hand the colour and insolubility are not compatible with this explanation. A more rational interpretation of this latter criterion is provided by a tetrameric structure, (LXIV) being one of the many possibilities. However, until the compound can be purified and an accurate

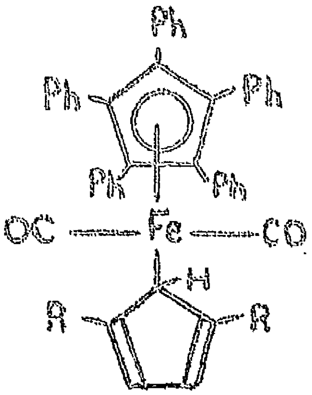


(LXIV)

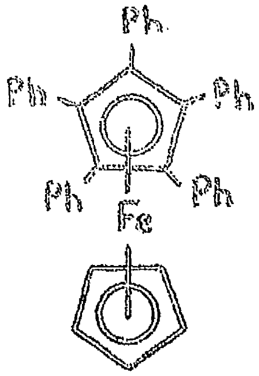
molecular weight determination carried out, no definite conclusions can be drawn. Pyrolysis of both these products yielded pentaphenylcyclopentadiene, verifying the presence of the pentaphenylcyclopentadienyl group.

Reduction of the bromide (LXII; R = Ph; X = Br) with sodium borohydride in water gave, after acidification, π-1,2,3,4,5 pentaphenylcyclopentadienyliron dicarbonyl hydride (LXII; R = Ph; X = H) as a yellow crystalline solid, m.p. 277-279°(d). It is stable in air for a few hours, unlike previously reported analogues.[136] The same compound has been claimed by Hubel[168] from the reaction of pentaphenylcyclopentadiene and iron pentacarbonyl, a reaction which incidentally could not be repeated. The infrared spectra of these two compounds are identical, although Hubel reports a melting point of 160-180°. The apparent discrepancy in the melting points is probably a function of the rate of heating, since it has been found that to minimise decomposition of the materials melting points must be carried out fairly rapidly. Proof of the hydride structure was provided by the preparation from the hydride (LXII; R = Ph; X = H) of 1,2,3,4,5-pentaphenylcyclopentadienyliron dicarbonyl mercuri-halides (LXII; R = Ph; X = HgCl and HgI), in direct analogy with Nyholm's work on rhodium hydrides.[169] These compound form stable orange crystalline solids.

Treatment of the bromide (LXII; R = Ph; X = Br) with cyclopentadienylsodium gave the expected π-1,2,3,4,5-pentaphenyl-σ-cyclopentadienyliron dicarbonyl (LXV; R = H). This compound



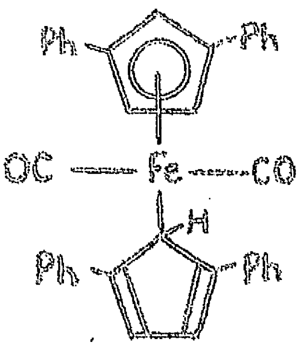
(LXV)



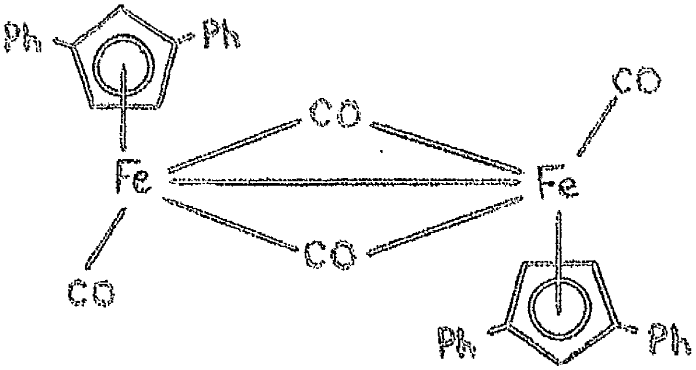
(LXVI)

is much more stable at room temperature than the parent compound (LVI),[136] however it readily loses carbon monoxide on strong heating to yield 1,2,3,4,5-pentaphenylferrocene (LXVI).

The obvious extension to the above would be the use of phenylcyclopentadienylsodium salts in the same role. This was duly carried out with the following results. 1,4-Diphenylcyclopentadienylsodium on interaction with the bromide (LXII; R = Ph; X = Br) yielded pentaphenylcyclopentadiene and 1,3;1',3'-tetraphenylferrocene (LVI; R_1,R_3,R_4 = H; R_2 = Ph). There are two possible mechanistic explanations, involving initially the formation of the expected π-σ complex (LXV; R = Ph).



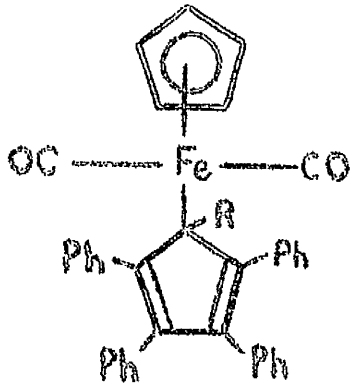
(LXVII)



(LXVIII)

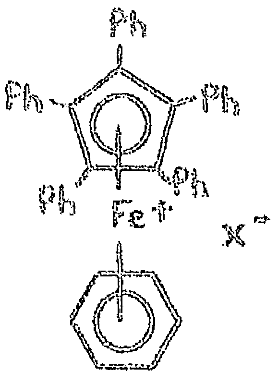
The pentaphenylcyclopentadienyl group could be displaced by another molecule of 1,4-diphenylcyclopentadienylsodium, to give an unstable symmetrical π-σ complex (LXVII), which could lose carbon monoxide giving the ferrocene. Alternatively, the dicarbonyl (LXV; R = Ph) could decompose to the intermediate bis-(1,3-diphenylcyclopentadienyl-)di-iron tetracarbonyl (LXVIII), then to the ferrocene.

It was anticipated that identical treatment with more heavily substituted aryl-cyclopentadienyl salts would give similar results. However reaction of the bromide (LXII; R = Ph; X = Br) with the alkali salts of 1,2,3-triphenyl-; 1,2,3,4-tetraphenyl- and pentaphenylcyclopentadiene led to isolation of pentaphenylcyclopentadiene and the same green solid discussed previously. It would seem reasonable to infer that formation of the expected π-σ complex in these three latter cases is inhibited by steric effects. A postulate which was further exemplified by attempts to prepare π-σ complexes (LXIX; R = H or Ph) in which the π-bonded ring was unsubstituted and the σ-bonded ring substituted. This was carried out by reaction of cyclopentadienyliron dicarbonyl bromide (XLV; X = Br) with the alkali salts of tetra- and pentaphenylcyclopentadiene. The only product isolated being dicyclopentadienyldi-iron tetracarbonyl (XLIV). This aspect will be more fully debated in the next chapter.



(LXIX)

The bromide (LXII; R = Ph; X = Br) readily forms very stable π-arene complexes (LXX) on treatment with benzene and aluminium trichloride in the usual manner.[152]



(LXX)

The salt is obtained initially as the bromide (LXX, X = Br), insoluble in water, a fact which can be accounted for by the large organic residue surrounding the metal atom. Nevertheless it is readily soluble in aqueous acetone, in which medium the iodide (LXX; X = I) and the reineckate (LXX; X = rein) were prepared.

Steric Effects in Poly-Aryl Ferrocenes.

From the results discussed in the preceding chapters two significant points are apparent.

1. In the symmetrical ferrocenes (i.e. both rings identical) the limit to further phenyl substitution in either ring is four.

2. For a ferrocene to bear five phenyl groups on one ring, steric effects apparently dictate that the other ring cannot contain phenyl substituents.

It can readily be seen from models that the phenyl groups in these compounds cannot be coplanar with each other or with the ring, due to steric interaction between the hydrogens in the ortho position. The molecules most probably assume a propeller like configuration,[27] the phenyl groups forming the blades of the propeller.

On this basis it does not seem reasonable that the propeller configuration should be limited to four phenyl groups. The inclusion of a fifth phenyl group should not alter the arrangement in any way. This infers that these products would be stable if formed and that steric effects interfere with formation under the reaction conditions employed. This is exemplified by the series of reactions dealing with the attempted preparation of π-σ complexes.

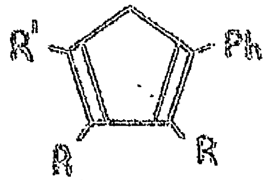
CHAPTER II

ATTEMPTS TO SYNTHESISE 1,2-DIPHENYLCYCLOPENTADIENE

Before proceeding to the discussion of the above topic, it is felt that the N.M.R. spectra of certain known phenyl substituted cyclopentadienes warrant comment at this point. Spectra were obtained for 1,4-diphenyl-, 1,2,4-triphenyl- and 1,2,3-triphenylcyclopentadiene. Resonance values, integrals and assignments are reported in the Appendix.

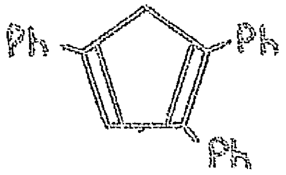
The principal objective of these N.M.R. studies was to determine the position of the double bonds relative to the phenyl substituents.

The spectrum of 1,4-diphenylcyclopentadiene (LXXI; R = H; R' = Ph) was perfectly straightforward, confirming Drake and Adams' earlier evidence[29] for the 1,4-configuration. 1,2,3-Triphenylcyclopentadiene (LXXI; R' = H; R = Ph) was also confirmed by its spectrum. The pertinent features being a triplet at 3.5τ corresponding to one olefinic proton (C_4) coupled with the methylene group (C_5) and a doublet at 6.4τ for the methylene group coupled with the olefinic proton. The 1,2,4-isomer had a more complicated spectrum, the most peculiar feature being the integral. The ratio of aromatic + olefinic/alkyl was found to be 12.5, which is intermediate

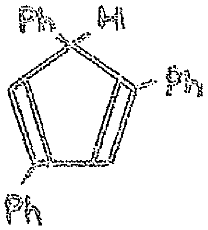


(LXXI)

between that for structure A (8) and B (17). It is therefore



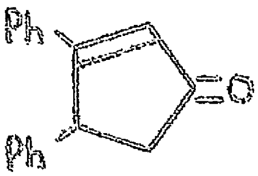
A



B

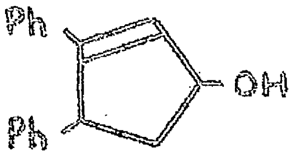
proposed that this isomer is an equimolar mixture of A and B.

The only phenyl-substituted cyclopentadiene which has not been isolated is the 1,2-diphenyl-compound (LXXVI; R = Ph). It has been claimed in the literature by Allen <u>et al.</u>[170] who obtained a diphenylcyclopentadiene by treatment of 3,4-diphenylcyclopent-2-en-1-one(LXXII)[57,171] with ethanolic potash. However Broadhead and Pauson[172] showed that a rearrangement had taken place and the product was actually the 1,4-isomer (LXXI; R = H; R' = Ph).

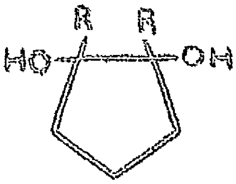


(LXXII)

The latter authors also endeavoured to dehydrate 1-hydroxy-3,4-diphenylcyclopent-2-ene (LXXIII)[172] and 1,2-diphenylcyclopentan-1,2-diol (LXXIV; R = Ph).[173,174] In the first case unchanged starting material was recovered and in the latter, rearrangement again took place to give (LXXI; R = H; R' = Ph). By employing more drastic conditions



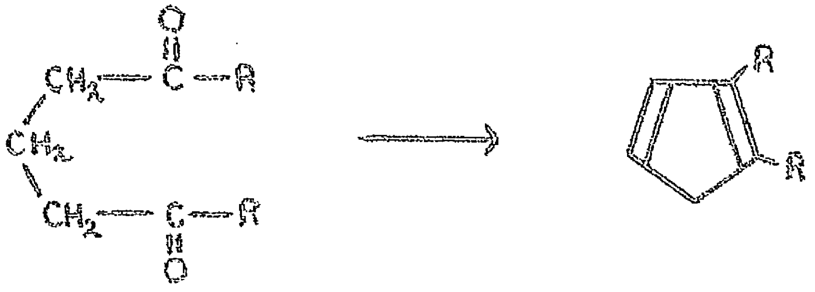
(LXXIII)



(LXXIV)

Horspool and Pauson[175] obtained two products from the dehydration of (LXXIII) with ethanol and hydrochloric acid. These compounds were consistent with hydrocarbons of formula $(C_{17}H_{14})_n$, however no conclusions were drawn as to the value of n or possible structures.

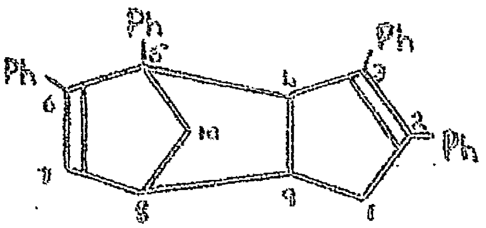
The synthesis of 1,2-bis-(p-methoxyphenyl-)cyclopentadiene (LXXVI; R = C_6H_4OMe), by treatment of the diketone (LXXV; R = C_6H_4OMe) with aluminium amalgam, has recently been reported.[124] The route is probably <u>via</u> the cyclic diol (LXXIV; R = C_6H_4OMe) which is consequently dehydrated, possibly during distillation of the products from the



(LXXV) (LXXVI)

reaction mixture, a point which has apparently been overlooked by the authors.

This re-awakened interest in the elusive hydrocarbon 1,2-diphenylcyclopentadiene (LXXVI; R = Ph). Application of the above technique to the unsubstituted analogue (LXXV; R = Ph) yielded only the cyclic diol (LXXIV; R = Ph).[173,174] Subsequent dehydration with ethanol and hydrochloric acid gave one of the hydrocarbons $(C_{17}H_{14})_n$ previously isolated by Horspool and Pauson. Accurate molecular weight determination gave a formula $C_{34}H_{28}$. It was therefore concluded that the compound is a dimer of 1,2-diphenylcyclopentadiene (LXXVII). The probable structure (LXXVII) was assigned on the basis of



(LXXVII)

the N.M.R. spectrum which was analysed as follows.

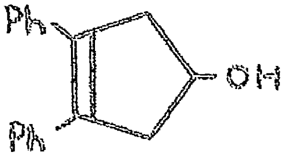
2.6 - 3τ - corresponding to 20 aromatic protons

4.05 τ (d) - corresponding to the olefinic proton on C_7 coupled with the tertiary proton on C_8

6.7 - 7.6τ - a hump assigned to the alkyl protons on carbons 1,4,5,8,9 and 10.

On the basis of this evidence it seems reasonable to postulate that the second, relatively insoluble, product[178] obtained by dehydration of (LXXIII) is a trimer or tetramer of 1,2-diphenylcyclopentadiene.

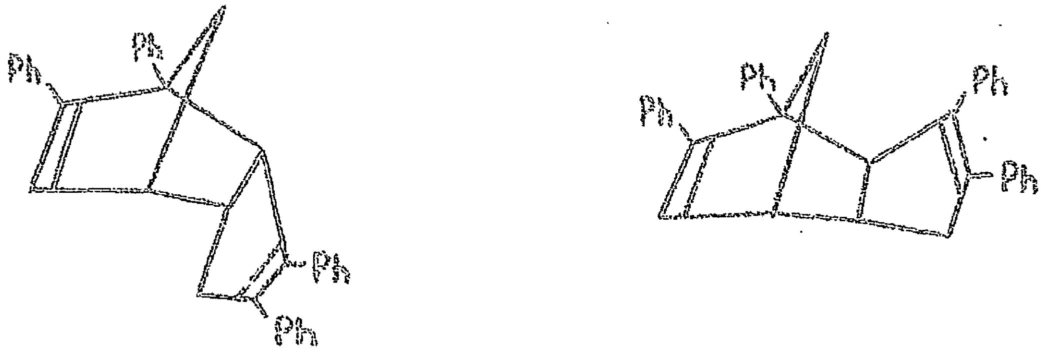
The dimer (LXXVII) was also obtained by treatment of the diketone (LXXV; R = Ph) with zinc and acetic acid. Chugaev reaction[198] on the methyl xanthate of (LXXIII) and reaction of (LXXII) with aluminium isopropoxide[28] failed to yield any hydrocarbon. It was hoped that dehydration of 1-hydroxy-3,4-diphenylcyclopent-3-ene (LXXVIII)[189] might yield the desired



(LXXVIII)

monomer due to the different position of the double bond, i.e. one form of conjugation might be more susceptible to dimerisation. However, dehydration was not realised by alcoholic hydrogen chloride. The more rigorous method of sulphuric in acetic acid yielded a trace amount of a hydrocarbon which was thought to be isomeric with (LXXVII). It would appear that dehydration with ethanol and hydrochloric acid is more applicable when the hydroxyl group is in the α-position to the double bond.

Cracking of the dimer (LXXVII) now appeared to be the most likely method of procuring the pure monomer (LXXVI; R = Ph). Heating under vacuum at 200° produced a bright yellow solid with a much lower melting point. Analysis gave a formula $C_{34}H_{28}$, infrared, ultraviolet and N.M.R. spectra are similar to (LXXVII) which reforms on slow heating. The two products are probably the *endo* and *exo*-isomers (A) and (B).

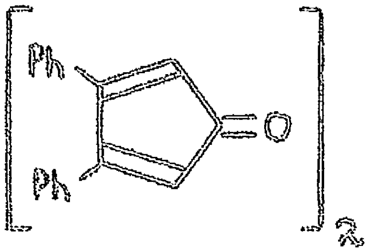


A

B

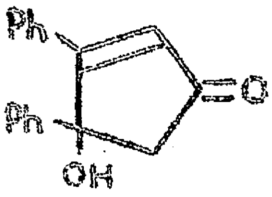
(LXXVII)

By analogy with known examples, the *endo*-isomer should be the more thermally stable. This configuration (A) is assigned to the first product obtained by dehydration. The pyrolysis product has the *exo*-configuration (B). Pyrolysis of the dimer (LXXVII) under more drastic conditions yielded 1,4-diphenylcyclopentadiene (LXXI; R = H; R' = Ph). It is possible that retro Diels-Alder reaction took place to give 1,2-diphenylcyclopentadiene (LXXVI; R = Ph), which under the conditions rearranged to the 1,4-isomer.

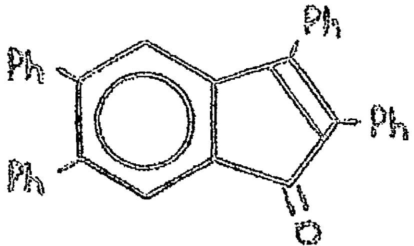


(LXXIX)

By reduction of the undissociable dimer of 3,4-diphenylcyclopentadienone (LXXIX),[176] it was hoped, by comparison of the ultraviolet and infrared spectra, to provide structural confirmation of the dimer (LXXVII). Before commencing this project, the structure of (LXXIX) had to be determined unequivocally. Since its discovery[176] in 1887 by dehydration of anhydroacetonebenzil (LXXX) many contradictory statements have been made concerning the correct structure. Briefly it was initially formulated by

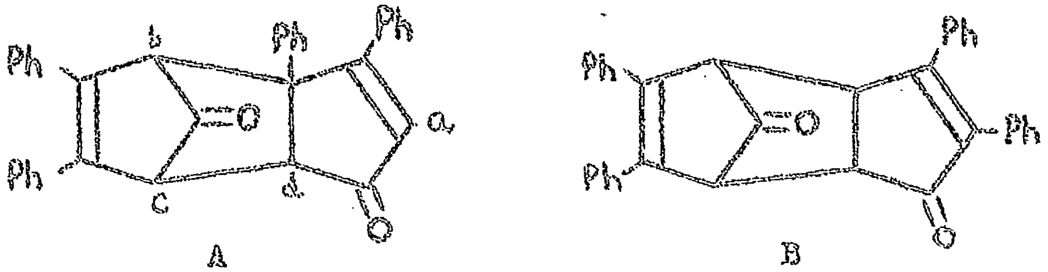


(LXXX)



(LXXXI)

Japp and Burton[176] as (LXXIXA). However Allen and Gates[177] found that decarbonylation followed by dehydrogenation gave the indenone (LXXXI). Consequently they formulated the structure as (LXXIXB). This was later retracted[178] in favour of (LXXIXA) by analogy with other known examples.[179] The formation of the



A B

(LXXIX)

indenone (LXXXI) being accounted for by a 1,3-phenyl shift.

An N.M.R. study (see Appendix) of the compound verified the initial formulation (LXXIXA). Analysis of the spectrum is as follows.

$2.65 - 3.08\tau$ - aromatic + olefinic proton (a)

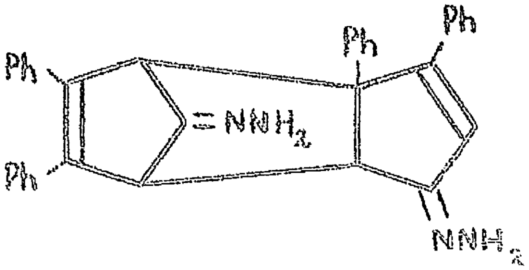
5.5τ - doublet for proton [b] split by long range coupling with [c]

6.14τ - double doublet - proton [c] coupled with [d] and [b]

$J_{CD} \sim 4.5$ c.p.s. $J_{BC} \sim 1.8$ c.p.s.

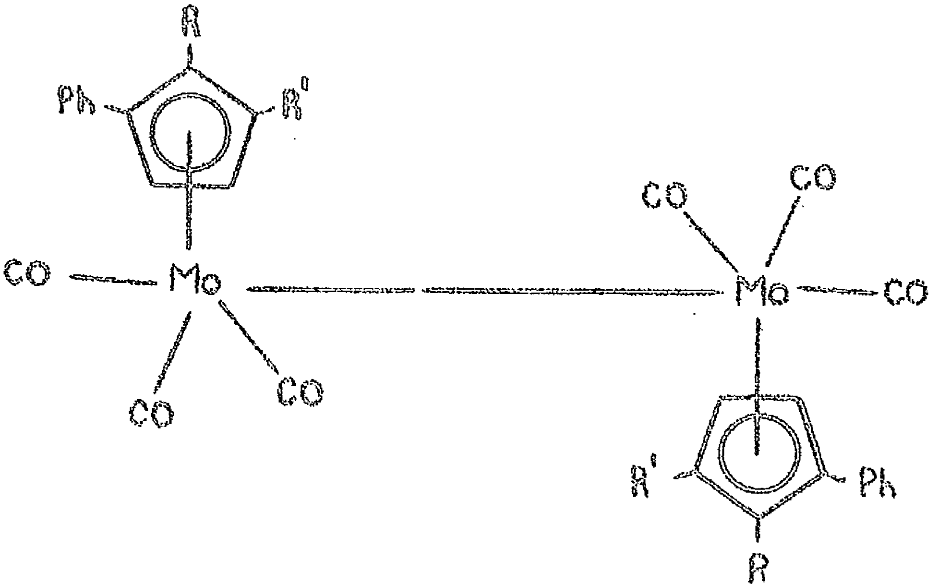
6.85τ - proton [d] split by coupling with [c].

It has been reported[176] that the dimer [LXXIX] does not react with phenylhydrazine. However the author has obtained a mono-2,4-dinitrophenylhydrazone, with the bridging carbonyl unattacked and a di-hydrazone (LXXXII). Attempted Wolff-Kishner reduction of this hydrazone at room temperature[180] did not afford the anticipated isomer of the hydrocarbon (LXXVII).



(LXXXII)

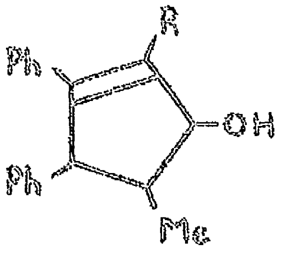
Direct interaction of bis-(1,2-diphenylcyclopentadiene) (LXXVII) with metal carbonyls produced the following results. Treatment with iron pentacarbonyl in a closed system yielded a black crystalline compound $C_{19}H_{16}Fe(CO)_3$. Various attempts to isolate the organic fragment met with no success. The N.M.R. spectrum [see Appendix] could not be analysed, it considts of the normal aromatic resonance and two singlets at 4.74 and 5.85 τ relative ratios being 8.65:0.5:1.2. By contrast, reaction of the dimer (LXXVII) with molybdenum hexacarbonyl gave the purple bis-(1,2-diphenylcyclopentadienyl)di-molybdenum hexacarbonyl (LXXXIII; R' = H; R = Ph). It appeared possible that a 1,2-phenyl shift had occurred to give the 1,3-phenyl isomer (LXXXIII;



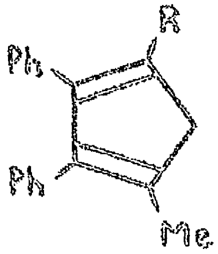
(LXXXIII)

R = H; R' = Ph); synthesis of the latter by reaction of 1,4-diphenylcyclopentadiene (LXXI; R = H; R' = Ph) with molybdenum hexacarbonyl proved that this was not the case. Reductive cleavage of the 1,2-diphenyl-compound (LXXXIII; R' = H; R = Ph) was carried out with lithium in ethylamine, however dimerisation again took place giving bis-(1,2-diphenylcyclopentadiene) (LXXVII).

The apparent existence of 1,2-diphenylcyclopentadiene in the dimeric form (LXXVII) prompted investigation of possible methyl substituted analogues. Thus reduction of 2,5-dimethyl-3,4-diphenylcyclopent-2-en-1-one (LVIII; R, R' = Me) afforded the corresponding alcohol (LXXXVIII; R = Me), dehydration of which gave monomeric 1,4-dimethyl-2,3-diphenylcyclopentadiene (LXXXIV; R = Me); the structure was verified by N.M.R. (see Appendix). This probably involved a rearrangement of the secondary carbonium

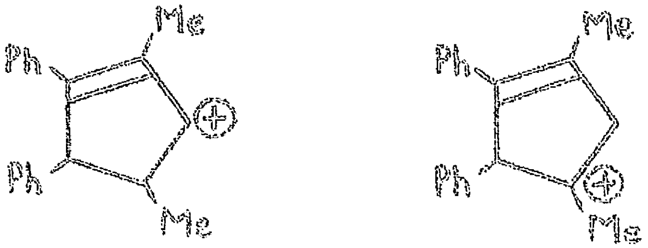


(LXXXVIII)



(LXXXIV)

ion (LXXXVA) to the more stable tertiary form (LXXXVB) prior to elimination of the proton. Identical reduction of the less



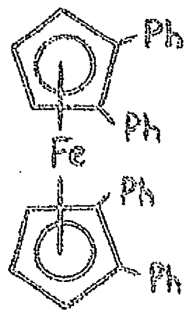
A

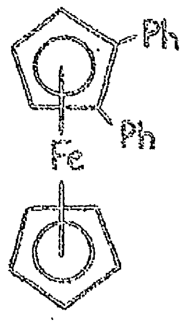
B

(LXXXV)

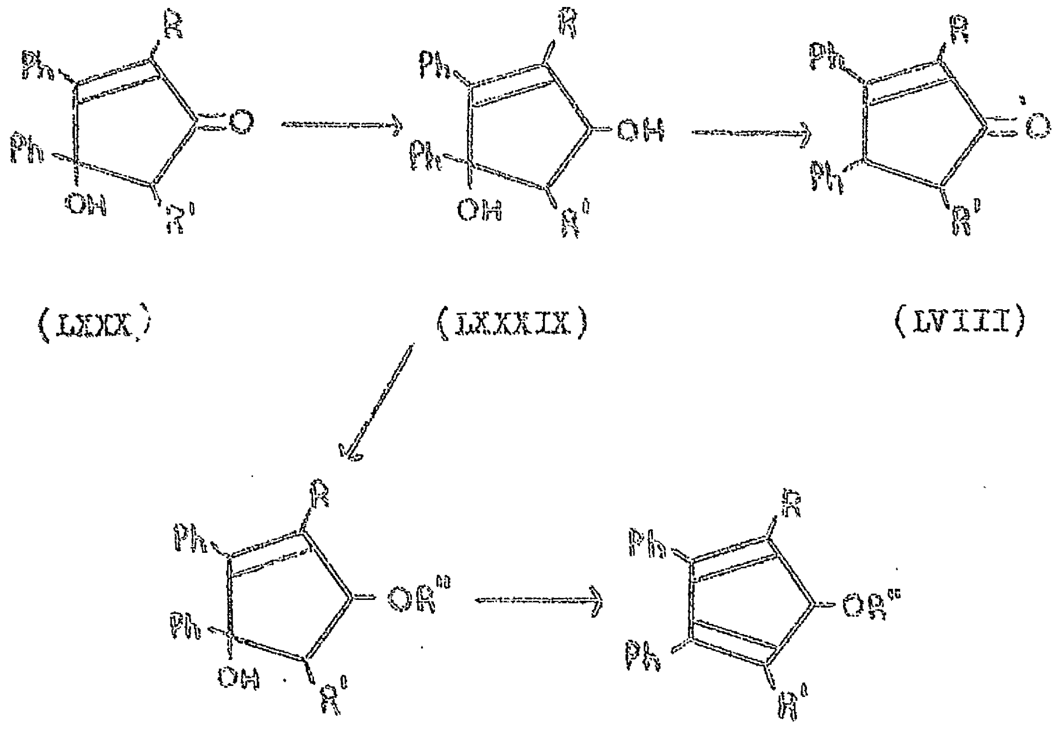
hindered 5-methyl-3,4-diphenylcyclopent-2-en-1-one (LVIII; R = H; R' = Me) gave a colourless oil which is probably a mixture of epimers. Dehydration of this crude material with alcoholic hydrogen chloride gave a gum from which the pure monomer 1-methyl-2,3-diphenylcyclopentadiene (LXXXIV; R = H) could not be isolated.

One of the principal reasons, for the desire to obtain 1,2-diphenylcyclopentadiene (LXXVI, R = Ph), was the direct synthesis of 1,2,1',2'-tetraphenylferrocene (LXXXVI) and the unsymmetrical 1,2-diphenylferrocene (LXXXVII); the latter is of particular importance for comparison with the alleged 1,2-diphenylferrocene obtained by arylation.[105-106,123] Consequently efforts were now directed to the syntheses of aryl-cyclopentadienes having a labile grouping, such as ester or methoxy, which could be removed after conversion to the desired ferrocene.


(LXXXVI)


(LXXXVII)

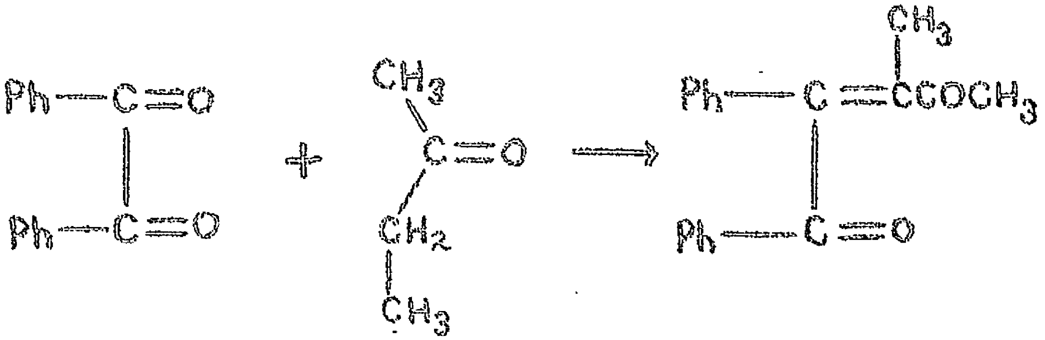
The route chosen for the above was via anhydroacetone-benzil (LXXX ; R,R' = H),[181] parallel syntheses were carried out on 2-phenylanhydroacetonebenzil (LXXX ; R' = H; R = Ph),[51] 2,5-dimethylanhydroacetonebenzil (LXXX ; R,R' = Me)[182,165] and the 5-methyl analogue (LXXX ; R = H; R' = Me).[182,183] All were



(LXXX) (LXXXIX) (LVIII)

(XC) (XCI)

readily obtained by the literature methods, with the exception of the 5-methyl compound (LXXX ; R = H; R' = Me). Application of the conditions reported[183] by Japp, i.e. treatment of benzil (XCII) and methyl ethyl ketone (XCIII) with aqueous sodium hydroxide at 80°, gave the diketone (XCIV). However use of alcoholic potassium hydroxide in the cold yielded the desired product (N.B. Japp reports[183] the preparation of 2-methylanhydroacetonebenzil (LXXX ; R' = H; R = Me) under these conditions).



(XCII) (XCIII) (XCIV)

The first step in the proposed synthesis was reduction of the anhydroacetonebenzil (LXXX) to the diol (LXXXIX). Benzoylation of the secondary alcohol group followed by dehydration of the tertiary hydroxyl should give the desired cyclopentadiene (XCI). All four compounds employed were readily reduced to the respective diols with sodium borohydride. These diols, as might be expected, dehydrate very readily with alcoholic hydrogen chloride to give the ketones (LVIII). The reaction could probably proceed by either 1,4-elimination of water to give (XCVA) which would rearrange to the ketone or by straight 1,2-elimination to give (XCVB) which could also rearrange. This constitutes a

A B

(XCV)

new route to 3,4-diphenylcyclopent-2-en-1-one[37,171,182] (LVIII; R,R' = H), the 2,5-dimethyl,[165] 2-phenyl-[31] and 5-methyl analogues.[197] The high yields (~90%) obtained compensate for the two stage process involved. The literature methods[37,165,171,182,197] by hydriodic acid reduction of (LXXX) afford yields of only 50%.

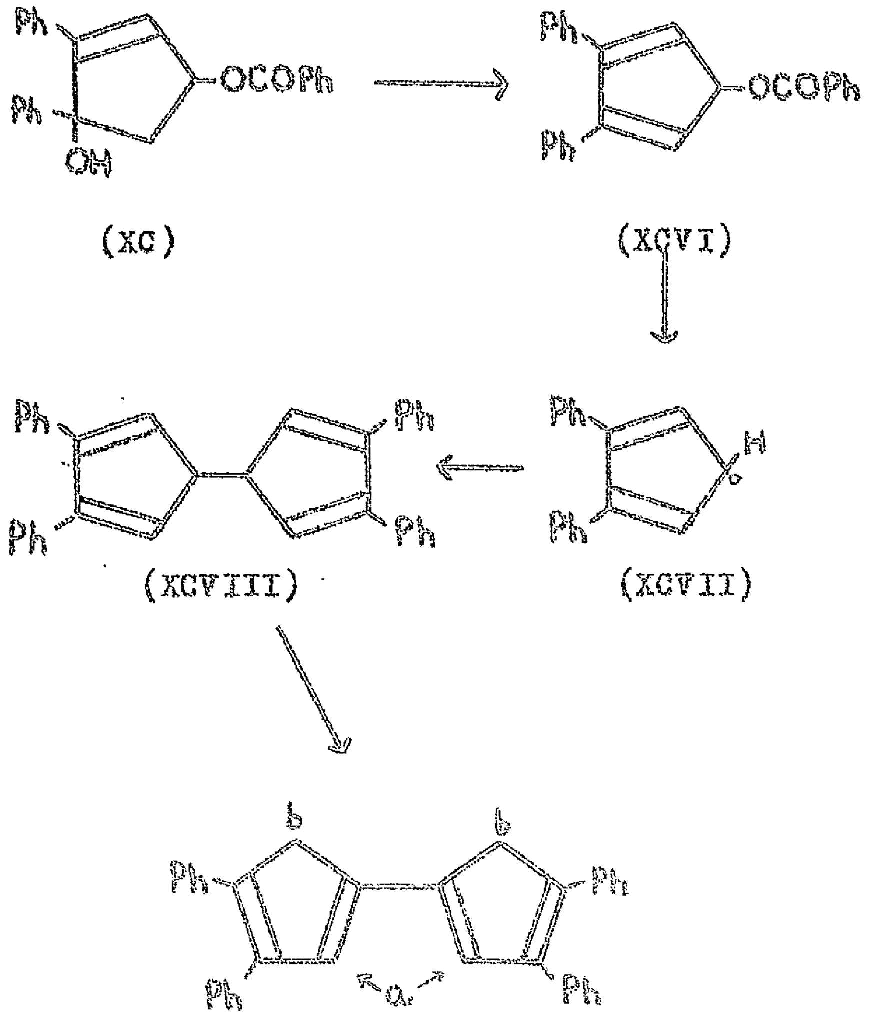
Attempted benzoylation of 1,4-dihydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-ene (LXXXIX; R,R' = Me) and the 2-phenyl analogue (LXXXIX; R' = H; R = Ph) resulted in dehydration to the respective cyclopentenones (LVIII). However 1,4-dihydroxy-3,4-diphenylcyclopent-2-ene (LXXXIX; R,R' = H) on treatment with acetyl chloride and benzoyl chloride yielded the respective acetyl (XCI; R,R' = H; R'' = $COCH_3$) and benzoyl (XCI; R,R' = H; R'' = COPh) derivatives. The success in this latter case may be attributed to the fact that the hydroxy group in the 1 position is less hindered by bulky alkyl or aryl substituents. Treatment of both these derivatives with alcoholic hydrogen chloride resulted in initial hydrolysis of the ester group, followed by dehydration of the reformed diol (LXXXIX; R,R' = H) to give the corresponding cyclopentenone (LVIII; R, R' = H). Despite this, dehydration under milder conditions, i.e. anhydrous oxalic acid in benzene gave, in addition to the cyclopentenone (LVIII; R,R' = H), two major products. The first, eluted with petroleum ether-benzene, was a yellow hydrocarbon which gave blue-green fluorescent solutions.

Analysis indicated an empirical formula of $C_{34}H_{26}$. The compound appears to be a dihydrofulvalene derivative of 1,2-diphenylcyclopentadiene (LXXVI; R = Ph). Examination of the ultraviolet and N.M.R. spectra (see Appendix) indicated (XCIXA) as the most probable structure. The ultraviolet max. at 380 mu can be accounted for by extension of the conjugated system across four double bonds. The N.M.R. spectrum has been analysed as follows

2.6 - 2.85τ - Aromatic protons and olefinic protons [a]

6.79 τ - methylene protons [b]. This peak appears to be a doublet, split possibly by some long range coupling effect.

Relative intensities are 5.9:1. The mechanism involved is probably initial dehydration of the tertiary hydroxyl group to give the cyclopentadiene ester (XCVI). Then cleavage of the labile ester group to yield the radical (XCVII), followed by radical coupling to give the dihydrofulvalene (XCVIII), which could then rearrange to the more fully conjugated form (XCIXA). Despite the evidence in favour of this latter structure, one must not ignore the possibility of a 1,2-phenyl shift to give the isomers (XCIXB) and (XCIXC). The N.M.R. spectra of these would be similar to that of (XCIXA).



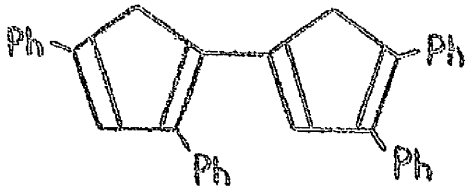
(XC)

(XCVI)

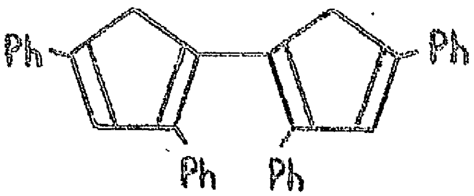
(XCVIII)

(XCVII)

(XCIXA)



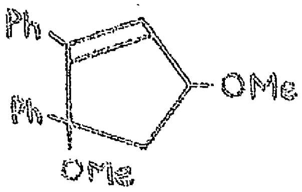
(XCIXB)



(XCIXC)

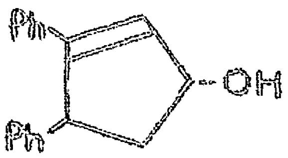
The second product obtained by dehydration of (XC) was a colourless crystalline ether $C_{34}H_{26}O$, which exhibits maxima in the infrared at 1066 and 1033 cm.$^{-1}$ The N.M.R. spectrum (see Appendix) has not been analysed.

It has become obvious that attempted dehydration of this ester (XC) leads to loss of the ester grouping. Consequently attempts were made to introduce a methoxy group at position 1. Treatment of the diol (LXXXIX) with sodium hydride and dimethyl sulphate once again promoted dehydration to the cyclopentenone (LVIII; R,R' = H). Use of sodium hydroxide as base gave a 50% yield of the diether (C). The N.M.R. spectrum of this product is reported in the Appendix.

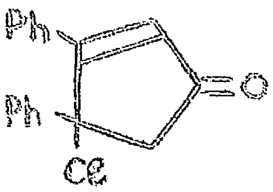


C

The above abortive results only serve to illustrate the futility of this technique. Consequently two attempts were made to obtain 1,2-diphenylcyclopentadienes containing a halogen substituent. Both routes, i.e. attempted bromination of (LXXIV) with N-bromosuccinimide and reduction of (CI)[188] with sodium borohydride, resulted in dehydrohalogenation to give the



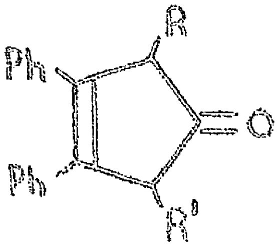
(LXXIII)



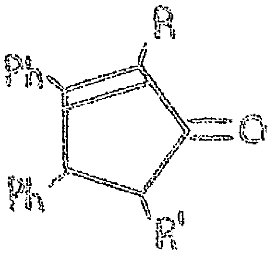
(CI)

dimer of 3,4-diphenylcyclopentadienone (LXXIX).

<u>Phenylcyclopentenones.</u>



A



B

R = Me, Ph and H

R' = Me, H and H

These compounds were first prepared by Japp and his Co-workers,[171,176,181,183,187] by hydriodic acid reduction of the corresponding anhydroacetonebenzil (LXXX) . The structure was initially formulated as (A). Support for this formulation was later given by Ruhemann *et al.*[184,185] The structure remained unchallenged for many years, until three groups presented ultraviolet evidence[165,186,187] in favour of the more likely structure (B). It does not seem reasonable to postulate a shift of the double bond from the 2 to the 3 position on reduction of the hydroxyl group.

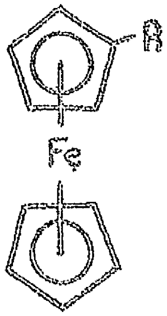
The author has recorded and analysed the spectra obtained from a few of these compounds. (see Appendix). The evidence verifies structure (B). The determining factor being the presence of a peak at 3.33τ in the N.M.R. spectrum of 3,4-diphenylcyclopent-2-en-1-one (LVIII, R, R' = H), which has been assigned to the olefinic proton. Structure A has no olefinic proton. The peak at 3.33τ is absent in the 2,5-dimethyl- (LVIII; R,R' = Me) and 2-phenyl- (LVIII; R' = H, R = Ph) analogues, thus authenticating the original assignment. Supporting proof has recently been afforded[189] by the independent synthesis of isomer (A).

CHAPTER III

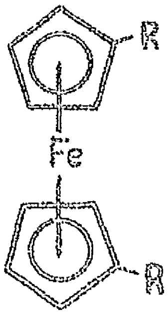
METHOXYFERROCENES

Attempts to Prepare 1,1'-Dimethoxyferrocene

The existing methods for the preparation of methoxyferrocenes (CII and CIII; R = OMe), via the boronic acids,[116,120,122] give moderate yields of monomethoxy-(CII; R = OMe)[191] and small amounts of 1,1'-dimethoxyferrocene (CIII; R = OMe).[192]

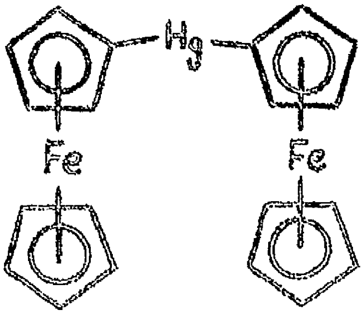


(CII)



(CIII)

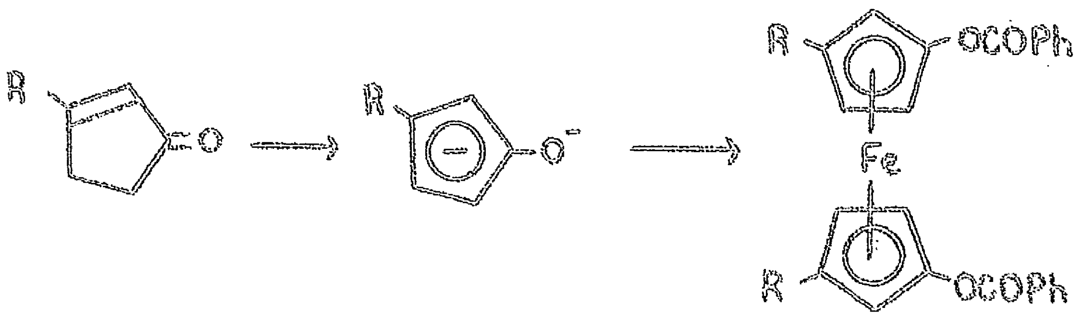
In order to obtain sufficient quantities of the latter, more direct methods of preparation were sought. Bis(1,1'-chloromercuri)ferrocene (CIII; R = HgCl)[94] was chosen as a convenient starting material. During the preparation of this product, diferrocenylmercury (CIV)[94] was obtained in 22% yield. Previous authors have not reported the isolation of this compound under these conditions.



(CIV)

Treatment of (CIII; R = HgCl) with ethyl-lithium is reported[102] to give moderate yields of 1,1'-dilithioferrocene (CIII; R = Li). Boronation of this mixture with tri-n-butyl borate gave 1,1'-ferrocenylenediboronic acid [CIII; R = $B(OH)_2$] in 12% yield, which shows no improvement over existing methods. Conversion of (CIII; R = HgCl) to di-iodoferrocene (CIII; R = I)[76] followed by acetoxylation yielded trace amounts of the expected acetoxy compound (CIII; R = $OCOCH_3$).[192] This route, via acetoxyferrocene, to the methoxy has been successfully utilised[191,192] in the case of bromo-and chloroferrocenes. The above failure is probably due to the decreased solubility of di-iodoferrocene in aqueous solvents. This was borne out by the preparation of monoacetoxyferrocene (CII; R = $OCOCH_3$)[191] from iodoferrocene (CII; R = I).[76]

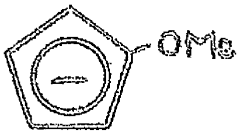
Benson and Lindsey[126] have successfully prepared derivatives of 'hydroxymetallocenes' from the cyclopentenone (CV; R = Me). This novel synthesis was achieved by treatment of



(CV) (CVI) (CVII)

(CV; R = Me) with excess sodium in liquid ammonia to give the double anion (CVI; R = Me), which reacted with ferrous chloride to yield the ferrocene derivative (CVII; R = Me), isolated as the mixture of stereoisomeric benzoates. Use of cyclopentenone[201] (CVIII; R = H) and dimsyl sodium[164] under the above conditions failed to yield the anticipated product. Morrison and Pauson[115] reported a similar result employing sodium in liquid ammonia as the basic medium.

The preparation[111] of 1,1'-disubstituted ferrocenes from the monosubstituted compound, by reductive cleavage followed by treatment with ferrous chloride, has been utilised for the preparation of 1,1'-bis(dimethylaminomethyl)ferrocene (CIII; R = CH_2NMe_2). Application of this technique to methoxyferrocene (CII; R = OMe) gave only a 4% yield of 1,1'-dimethoxyferrocene (CIII; R = OMe). Due to this, one must doubt the stability of the methoxycyclopentadienide anion (CVIII) in a strongly basic medium.

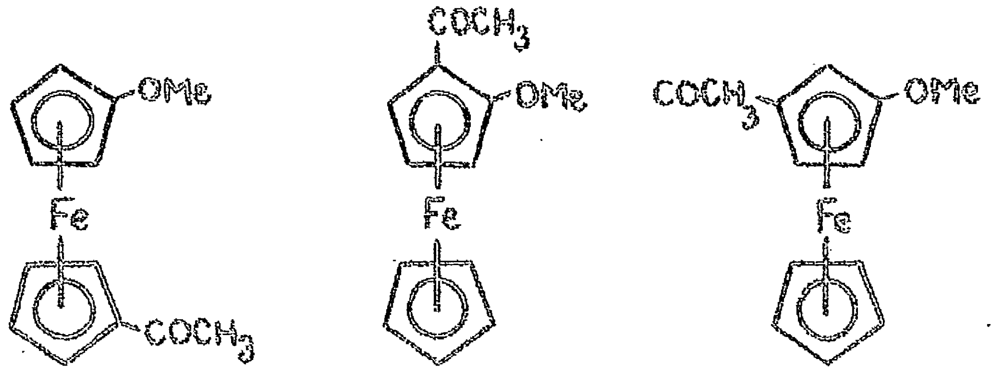


(CVIII)

Acetylation of Mono-methoxyferrocene (CII, R = OMe).

Friedel-Crafts acetylation of mono-methoxyferrocene (CII; R = OMe) has been shown to cause demethoxylation.[193] Thus accurate isomer ratios could not be obtained by this method due to possible preferential demethoxylation of one particular isomer. The mixture of acetyl-methoxyferrocenes (CIX) obtained could only be separated by reduction to the corresponding ethyl-methoxy derivatives followed by chromatography in petroleum ether. The reductive techniques employed[116] gave yields of 50%. Hence another preferential factor is introduced which could lead to erroneous isomer ratios.

It was deemed necessary to attempt acetylation by a technique which would not promote demethoxylation and to separate the isomeric mixture without resorting to reduction. It was found that use of the system, acetic anhydride-phosphoric

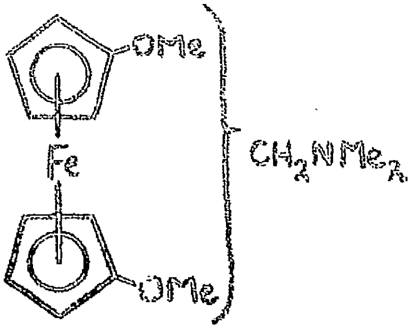


(CIX)

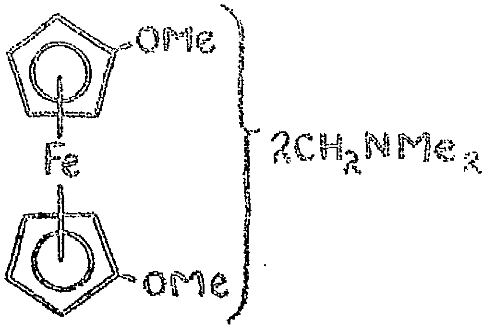
acid[194] did not result in demethoxylation. Attempted separation of the acetylated isomers (CIX), by vapour phase chromatography, gave a total of seven peaks, thought to be due to decomposition of the isomeric mixture at the column temperature. Attempted separation by ordinary chromatographic techniques also resulted in decomposition.

Amino-methylation of Di-methoxyferrocene (CIII; R = OMe).

Aminomethylation of dimethoxyferrocene (CIII, R = OMe) was carried out by Morrison and Pauson[115] who obtained isomeric mixtures of mono- (CX) and diaminomethylated (CXI) products. No attempt was made at that time to separate the isomers.



(CX)



(CXI)

The author has repeated this experiment with a similar result. The mixture of mono-aminomethylated products (CX), will be termed mixture 1 and that of the diaminomethylated (CXI), mixture 2. Careful chromatography of mixture 1 gave two fractions designated components A and B. The N.M.R. spectra (see Appendix of both these components indicate the presence of two methoxy groups. This fact is borne out by analysis of the methiodides obtained from these two components. However due to the presence of medium 9,10 bands in the infra-red spectrum of A, one must be wary of making any definite assignments on spectral evidence.

Chromatography of mixture 2 did not effect any resolution. Reduction to the corresponding dimethyl-dimethoxy isomers could only be accomplished in 50% yield and the product obtained thus, was not completely separated on chromatography in petroleum ether.

EXPERIMENTAL

Experimental Procedures

Melting Points. These were determined using a Gallenkamp melting point apparatus and are uncorrected. Melting points of all organometallic compounds were measured in sealed capillaries evacuated to about 20 mm. pressure.

Infrared Spectra were recorded as 1% potassium chloride discs.

N.M.R. Spectra were run in deuterochloroform on a Perkin-Elmer 40 M/C Spectrometer.

Molecular Weights were determined cryoscopically in benzene.

Reagents. Petroleum ether used was the fraction b.p. 60-80°. Ferrous chloride was prepared by reduction of anhydrous ferric chloride in refluxing chlorobenzene.[196] Chromatographies were carried out on alumina (Spence Grade H), which had been partially deactivated by exposure to the atmosphere for 6 hr., and on silica gel (Hopkin and Williams M.F.C. Grade). All reactions involving organometallic compounds were carried out under an atmosphere of nitrogen, which had been deoxygenated with Fieser's solution and dried with concentrated sulphuric acid.

CHAPTER I

POLY- ARYL FERROCENES

1,3,1',3'-Tetraphenylferrocene (LVI; R_1,R_3,R_4=H; R_1=Ph).

(a) Sodamide was prepared from sodium (0.5 g., 0.022 mole) in liquid ammonia (50 ml.) containing ferric nitrate (0.2 g.). 1,4-Diphenylcyclopentadiene[29] (2.18 g., 0.01 mole) was added, followed about an hour later by anhydrous ferrous chloride (3.0 g., 0.023 mole). Xylene (25 ml.) was added, the ammonia allowed to distil off and the mixture was stirred at room temperature overnight. The precipitate which formed was filtered and washed with hot xylene. Removal of the solvent yielded an orange solid, which crystallised from acetone to give orange-red prisms of 1,3,1',3'-tetraphenylferrocene (0.9 g., 40%), m.p. 220-222° [Lit.[27] 220-222°].

(b) 1,4-Diphenylcyclopentadiene[29] (1.6 g., 7.3 mmole) in tetrahydrofuran (50 ml.) was added to dimsyl sodium, {prepared from sodium hydride (0.52 g., 50% dispersion, 0.01 mole) in dimethylsulphoxide (6 ml.) according to the method of Corey[164]} and the resulting mixture was stirred for 1 hr. Ferrous chloride (0.63 g., 5.0 mmole) was added and the mixture was stirred overnight. The reaction mixture was filtered and washed with tetrahydrofuran. Removal of the solvent gave 1,3,1',3'-tetraphenylferrocene[27] (1.2 g., 68%). After crystallisation from acetone the compound had m.p. 220-222°.

Octaphenylferrocene (LVI; R_1=H; R_2,R_3,R_4=Ph).

(a) 1,2,3,4-Tetraphenylcyclopentadiene[82] (5.2 g., 0.014 mole) in tetrahydrofuran (100 ml.) was added to dimsyl sodium,[164] [from sodium hydride (1.04 g., 50% dispersion, 0.02 mole) in dimethyl sulphoxide (8 ml.)] and the mixture was maintained at 40°C with stirring for 2 hr. Ferrous chloride (1.25 g., 0.01 mole) was added and the mixture was stirred overnight. Filtration, followed by evaporation of the solvent yielded a brown substance. Chromatography in benzene on alumina gave octaphenylferrocene (1.0 g., 20%) as deep red prisms, m.p. 322° [Lit.[83] 322°].

(b) Tetraphenylcyclopentadiene (3.7 g., 0.01 mole) and iron pentacarbonyl (1.5 ml., 0.01 mole) were heated in an autoclave, under carbon dioxide, at 180° for 4 hr. The residue was extracted with hot benzene. After removal of the solvent the product was chromatographed in benzene on alumina. A small yellow band, separating first, contained starting material. This was followed by a large red band yielding octaphenylferrocene[83] (1.2 g., 32%). After recrystallisation from chlorobenzene the product had m.p. 322°. No depression of m.p. was observed on admixture with the compound obtained in (a).

1,2,3,1',2',3'-Hexaphenylferrocene (LVI; R_1,R_2=H; R_3,R_4=Ph).

(a) 1,2,3-Triphenylcyclopentadiene[31] (2.06 g., 7 mmole) in tetrahydrofuran (50 ml.) was added to dimsyl sodium,[164] [from sodium hydride (0.52 g., 50% disp., 0.01 mole) in dimethylsulphoxide (6 ml.)] and the mixture was stirred for 1 hr. Ferrous chloride (0.63 g., 5.0 mmole) was added. The reaction was carried out as described above yielding 1,2,3, 1',2'3'-hexaphenylferrocene (1 g., 45%) which recrystallised from chlorobenzene as red prisms, m.p. 266-268°. (Found: C,86.1; H,5.5. $C_{46}H_{34}Fe$ requires C,86.0; H,5.3%).

(b) 1,2,3- Triphenylcyclopentadiene (3 g., 0.01 mole), and iron pentacarbonyl (1.5 ml., 0.01 mole) were treated as described above in the preparation (b) of octaphenylferrocene. This yielded 1,2,3,1',2',3'-hexaphenylferrocene (0.75 g., 21%). After recrystallisation from chlorobenzene the product had m.p. 266-268°, undepressed on admixture with the product described in (a).

Attempted Preparation of Decaphenylferrocene (LVI; R_1,R_2,R_3,R_4=Ph).

(a) 1,2,3,4,5-Pentaphenylcyclopentadiene[36] (2.23 g., 5.0 mmole) in tetrahydrofuran (50 ml.) was added to dimsyl sodium,[164] [from sodium hydride (0.24 g. 50% dispersion, 5.0 mmole) in dimethylsulphoxide (4 ml.)] and the mixture was stirred for 2 hr. A deep purple colour developed. Ferrous chloride (0.32 g., 2.5 mmole) was added and after a few minutes the purple colouration disappeared. After stirring overnight, pentaphenylcyclopentadiene (1.8 g., 81%) was recovered unchanged.

(b) 1,2,3,4,5-Pentaphenylcyclopentadiene (4.5 g., 0.01 mole) and iron pentacarbonyl (1.5 ml., 0.01 mole) were heated in an autoclave, under carbon dioxide, at 185° for 4 hr. Extraction of the residue yielded only unchanged diene (4 g., 89%).

Similar reactions, carried out at 150° and 135°, also resulted in isolation of unchanged diene.

1,4,1',4'-Tetramethyl-2,3,2',3'-tetraphenylferrocene(LVI; R_2=H, R_1,R_3=Me; R_4=Ph).

1,4-Dimethyl-2,3-diphenylcyclopentadiene[x] (1.23 g., 5.0 mmole) in benzene (25 ml.) was added to phenyllithium, [prepared in ether from lithium (0.07 g., 0.01 g. atom) and bromobenzene (0.8 g., 5 mmole)] and the mixture was refluxed for 2 hr. Ferrous chloride (0.32 g., 2.5 mmole) was added and the stirring continued overnight. Hydrolysis, followed by separation of the organic layer and removal of the solvent gave an orange gum, which crystallised on the addition of

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[x] The synthesis of this compound is described in Experimental Chapter II.

acetone. Recrystallisation from acetone gave 1,4,1',4'-tetramethyl-2,3,2',3'-tetraphenylferrocene (0.63 g., 46%) as orange-red prisms, m.p. 232-233° [Found: C,83.2; H,6.8. $C_{38}H_{34}Fe$ requires C,83.3; H,6.2%].

1,2,5-Trimethyl-3,4-diphenylcyclopentadiene (LVIX).

2,5-Dimethyl-3,4-diphenylcyclopent-2-en-1-one[165] (17 g., 0.065 mole) in benzene (125 ml.) was added to methyl magnesium iodide, [prepared from magnesium (2.4 g., 0.1 g. atom) and methyl iodide (15 g., 0.1 mole) in ether (50 ml.)]. The mixture was stirred at room temperature overnight and was finally refluxed for 1 hr. It was then poured onto ice-ammonium chloride mixture and extracted with ether. The ethereal extract was dried over sodium sulphate. Removal of the ether yielded an orange yellow gum. Chromatography on alumina in petroleum ether gave a yellow oil which crystallised from methanol on scratching. Recrystallisation from the same solvent gave 1,2,5-trimethyl-3,4-diphenylcyclopentadiene (3.5 g., 21%) as colourless prisms, m.p. 87-89°. (Found: C,91.8; H,8.0. $C_{20}H_{20}$ requires C,92.3; H,7.7%). N.M.R. data are given in the Appendix.

Bis-(1,2,3-trimethyl-4,5-diphenylcyclopentadienyl)-di-iron tetracarbonyl (LX; R,R'= Me).

1,2,5-Trimethyl-3,4-diphenylcyclopentadiene (1.3 g., 5 mmole) and iron pentacarbonyl (0.75 ml., 5 mmole) were heated in an autoclave (40 ml.), under carbon dioxide, at 150° for 4 hr. Extraction of the residue with hot benzene, followed by removal of the solvent gave a black crystalline mass. Recrystallisation from benzene yielded bis-(1,2,3-trimethyl-4,5-diphenylcyclopentadienyl)di-iron tetracarbonyl (0.9 g., 48.5%) m.p. 330° (d). Infrared maxima in the carbonyl region 1953, 1773 cm.$^{-1}$ (Found: C,70.8; H,5.4. $C_{44}H_{38}Fe_2O_4$ requires C,71.2; H,5.1%).

Attempted Preparation of 1,2,3,1',2',3'-Hexamethyl-4,5,4',5'-tetraphenylferrocene. (LVI; R_1,R_2,R_3 = Me; R_4 = Ph).

1,2,5-Trimethyl-3,4-diphenylcyclopentadiene (2.25 g., 8.5 mmole) in benzene (20 ml.) was added to phenyllithium (0.01 mole) in ether (10 ml.) and the mixture was refluxed for 2 hr. Ferrous chloride (0.63 g., 5 mmole) was added and stirring continued overnight. The mixture was poured into water and extracted with ether. The extract was dried (Na_2SO_4) and the solvent was removed to yield unchanged starting material.

A similar result was obtained using dimsyl sodium in place of phenyllithium.

Reaction of Substituted Cyclopentadienes with Di-cyclopentadienyl Di-iron Tetracarbonyl.

These reactions were carried out by heating the substituted cyclopentadiene and the tetracarbonyl (1:1 molar ratio) in an autoclave (40 ml.), under carbon dioxide, at 180° for 3 hr. The reaction mass was extracted with benzene, the solvent removed and the products were filtered through a short column of alumina in benzene. In all cases this yielded ferrocene and a dark red oil. Fractional crystallisation of this from acetone separated the two ferrocenes, i.e. with one ring substituted and with both rings substituted. In every case, except the reactions with 1,2,3-triphenylcyclopentadiene and pentaphenylcyclopentadiene, two products were obtained. The results of the series are summarised in Table I. Physical constants and analytical data are listed in Table II. Authenticity of known compounds isolated was established by melting point and mixed melting point.

Reaction of 1,4-Diphenylcyclopentadienylsodium with Iron Pentacarbonyl.

To dimsyl sodium [prepared from sodium hydride (0.38 g., 7 mmole) and dimethyl sulphoxide (4 ml.)] was added 1,4-diphenylcyclopentadiene (1.6 g., 7 mmole) in anhydrous tetrahydrofuran (60 ml.) and the mixture was stirred for 1 hr. Iron pentacarbonyl (1.1 ml., 7 mmole) was added, and the mixture was refluxed overnight. The reaction mass was then acidified with acetic acid, filtered and the solvent removed. Crystallisation of the residue from ethanol gave 1,4-diphenylcyclopentadiene (1.3 g., 81%), m.p. and mixed m.p. 156-158°.

Reaction of Substituted Cyclopentadienes with Dicyclopentadienyldi-iron Tetracarbonyl

Substituted Cyclopentadiene	Amount of Tetracarbonyl	PRODUCTS	
1,2,4-Triphenyl-[30] 0.73 g., 2.5 mmole	0.9 g., 2.5 mmole	1,2,4-Triphenylferrocene 0.41 g., 37%	1,2,4,- 1',2',4'-Hexaphenylferrocene[27] 0.06 g.,7%
1,2,3-Triphenyl- 0.73 g., 2.5 mmole	0.9 g., 2.5 mmole	-	1,2,3,- 1',2',3'-Hexaphenylferrocene 0.09 g., 10%
1,2,3,4-Tetraphenyl- 0.9 g., 2.5 mmole	0.9g., 2.5 mmole	1,2,3,4-Tetraphenyl ferrocene 0.53 g., 43%	1,2,3,4,1',2',3',4',-Octaphenylferrocene 0.14 g., 15%
1,2,3,4,5-Pentaphenyl- 1.1 g., 2.5 mmole	0.9 g., 2.5 mmole	1,2,3,4-Pentaphenylferrocene trace amount	-
1,2,5-Trimethyl-3,4-diphenyl- 0.4 g., 1.6 mmole.	0.6 g., 1.6 mmole	1,2,3-Trimethyl-4,5-diphenylferrocene 0.23 g., 40%	1,2,3,1',2',3'-Hexamethyl-4,5,4',5'-tetraphenylferrocene 40 mg., 9%

TABLE II

Physical Characteristics and Analytical Data for New Ferrocenes

Ferrocene	Colour	M.P.	Analytical Data
1,2,4-Triphenyl- LVII; $R_1, R_3 = H$ $R_2, R_4 = Ph$	orange prisms	167–169°	Found: C,81.3; H,5.9 $C_{28}H_{22}Fe$ requires C,81.2; H,5.3%
1,2,3,4,5-Pentaphenyl- LVII; $R_1, R_2, R_3, R_4 = Ph$	orange yellow needles	m.p. and * mixed m.p. 356–358°	
1,2,3,4-Tetraphenyl[166] LVII; $R_1 = H$ $R_2, R_3, R_4 = Ph$	orange red prisms	226°	Found: C,82.7; H,5.8. $C_{34}H_{26}Fe$ requires C,82.9; H,5.4%
1,2,3-Trimethyl-4,5-diphenyl- LVII; $R_1, R_2, R_3 = Me$ $R_4 = Ph$	golden yellow needles	204–206°	Found: C,79.2; H,7.0 $C_{25}H_{24}Fe$ requires C,78.9; H,6.3%
1,2,3,1',2',3'-Hexamethyl-4,5,4',5'-tetraphenyl- LVI; $R_1, R_2, R_3 = Me$ $R_4 = Ph$	red prisms	192–193°	Found: C,83.6; H,7.5 $C_{40}H_{38}Fe$ requires C,83.6; H,6.6%

* Mixed melting point with sample prepared on p.84

Reaction of Tetraphenylcyclopentadienylsodium with Iron Pentacarbonyl

1,2,3,4-Tetraphenylcyclopentadiene (3.7 g., 0.01 mole) was added to sodamide [prepared from sodium (0.23 g., 0.01 g. atom) and liquid ammonia (25 ml.)] and the resulting mixture was stirred for 2 hr. Iron pentacarbonyl (1.5 ml., 0.01 mole) in anhydrous tetrahydrofuran (100 ml.) was added and the mixture was refluxed overnight. The reaction mass was acidified with acetic acid, filtered and the solvent was removed under reduced pressure. The residue was chromatographed in benzene on alumina yielding unchanged tetraphenylcyclopentadiene (3.3 g., 90%).

1,2,3,4-Tetraphenylcyclopentadienyliron Dicarbonyl Bromide (LXII; R = H; X = Br).

5-Bromo-1,2,3,4-tetraphenylcyclopentadiene[32] (1.0 g., 2.2 mmole) and iron pemtacarbonyl (0.5 ml., 3.3 mmole) were refluxed in chlorobenzene (20 ml.) for 2 hr. Carbon monoxide was evolved and the solution turned dark red. Filtration, followed by removal of the solvent yielded a dark brown residue. Chromatography in benzene on alumina gave a small amount of a purple compound. Recrystallisation from methylene chloride-petroleum ether gave 1,2,3,4-tetraphenylcyclopentadienyliron dicarbonyl bromide, as dark red prims, m.p. 175-177° (d) (Found: C, 67.7; H, 4.3. $C_{31}H_{21}BrFeO_2$ requires C, 66.3; H, 3.8%). Infrared max. in the carbonyl region 2041 and 2000cm.$^{-1}$

Attempted Reaction of 5-Bromopentaphenylcyclopentadiene with Iron Pentacarbonyl

5-Bromopentaphenylcyclopentadiene[32] (1.0 g., 2 mmole) and a slight excess of iron pentacarbonyl were heated in an autoclave at 150° for 4 hr. The reaction mass was extracted with benzene; removal of the solvent gave a pale yellow solid. Recrystallisation from ethyl acetate gave colourless needles of pentaphenylcyclopentadiene (0.5 g., 59%), m.p. and mixed m.p. 253-255°.

1,2,3,4,5-Pentaphenylcyclopentadienyliron Dicarbonyl Bromide (LXII; R = Ph; X = Br).

5-Bromopentaphenylcyclopentadiene (6.5 g., 0.012 mole) and iron pentacarbonyl (2.0 ml., 0.013 mole) were refluxed in benzene (150 ml.) for 2 hr. The mixture was filtered and reduced to small bulk in a vacuum. The product crystallised out and was collected by filtration. Recrystallisation from methylene chloride-petroleum ether gave 1,2,3,4,5-pentaphenylcyclopentadienyliron dicarbonyl bromide as dark red needles (5.0 g., 65%), m.p. > 360° with decomposition from 230°. (Found: C, 69.9; H, 4.2; Fe, 8.8. $C_{37}H_{25}BrFeO_2$ requires C, 69.7; H, 3.9; Fe, 8.8%). I.R. max. in the carbonyl region 2040 and 2000 $cm.^{-1}$

Pyrolysis of the Above Product

1,2,3,4,5-Pentaphenylcyclopentadienyliron dicarbonyl bromide (0.5 g.) was heated (200°, 0.1 mm.) for 2 hr. The residue was extracted with benzene, the extract was reduced to small bulk and the addition of petrol yielded a red solid (0.05 g.). Recrystallisation from chlorobenzene gave deep red needles, m.p. 264-266° (Found: C, 52.6, 53.1; H, 3.7, 3.0%).

Some of this red product (35 mg.) was chromatographed on alumina. Benzene eluted a small green band giving a green fluorescent solution. Removal of the solvent gave a yellow solid (~ 3 mg.), insufficient for identification. Benzene-ether (2:1) eluted a blue band giving a blue solid (12.5 mg.) m.p. 110-130°. The compound was soluble in petroleum ether from which it could be precipitatedby cooling to -70°

Reaction of 1,2,3,4,5-Pentaphenylcyclopentadienyliron Dicarbonyl Bromide with Sodium Amalgam.

1,2,3,4,5-Pentaphenylcyclopentadienyliron dicarbonyl bromide (1 g., 1.5 mmole) in anhydrous tetrahydrofuran (40 ml.) was stirred with sodium amalgam (1.52 g., 1%, 1.5 mmole) for 2 hr. A green precipitate formed. This was removed by filtration giving a green powder (0.5 g.), m.p. >360° (d). This compound was insoluble in common solvents and had I.R. max. in the carbonyl region 1965 and 1786 cm.$^{-1}$. Chromatography of the filtrate on alumina in benzene gave bis-(1,2,3,4,5-pentaphenylcyclopentadienyliron dicarbonyl)mercury (0.3 g., 30%), which crystallised as orange prisms, m.p. 262-264° from methylene chloride. (Found: C, 67.0; H, 3.9; Fe, 7.7 . $C_{74}H_{50}Fe_2HgO_4$ requires C, 67.6; H, 3.8; Fe, 8.5%), I.R. max. in the carbonyl region 1970 and 1931 cm.$^{-1}$

Pyrolysis of the Above Insoluble Green Solid.

The green solid (0.2 g.) was heated (200°; 1.0 mm.) for 2 hr. The residue was extracted with benzene; removal of the solvent gave a yellow residue. Crystallisation from ethyl acetate gave pentaphenylcyclopentadiene, m.p. and mixed m.p. 251-254°.

Pyrolysis of Bis-(1,2,3,4,5-pentaphenylcyclopentadienyliron dicarbonyl)mercury.

Bis-(1,2,3,4,5-pentaphenylcyclopentadienyliron dicarbonyl) mercury was heated (200°, 1 mm.) as above. Once again pentaphenylcyclopentadiene m.p. 251-253° was the only product isolated.

1,2,3,4,5-Pentaphenylcyclopentadienyliron Dicarbonyl Hydride

To 1,2,3,4,5-pentaphenylcyclopentadienyliron dicarbonyl bromide (1.0 g., 1.5 mmole) in tetrahydrofuran (30 ml.) was added sodium borohydride (excess) in water (3 ml.) and the mixture was stirred for 3 hr. The aqueous layer was withdrawn; the tetrahydrofuran was acidified with glacial acetic acid and on cooling in ice a yellow crystalline product separated. Recrystallisation from tetrahydrofuran acidified with glacial acetic acid yielded <u>1,2,3,4,5-pentaphenylcyclopentadienyliron dicarbonyl hydride</u> as yellow prisms, m.p. 277-279°(d). (Found: C,75.8; H,5.0. $C_{37}H_{26}FeO_2$ requires C,79.0; H,4.7%). I.R. max. in the carbonyl region at 2000 and 1942 cm.$^{-1}$. An accurate analysis of this compound could not be obtained due to its unstable nature.

<u>1,2,3,4,5-Pentaphenylcyclopentadienyliron Dicarbonyl Mercuri-halides.</u>

An acidified tetrahydrofuran solution of 1,2,3,4,5-pentaphenylcyclopentadienyliron dicarbonyl hydride was treated with a saturated ethanolic solution of the respective mercuric halide. The resulting mixture was shaken for 10 min., the crystalline mercuri-halide was filtered off and recrystallised from aqueous tetrahydrofuran. The following compounds were obtained.

<u>1,2,3,4,5-Pentaphenylcyclopentadienyliron Dicarbonyl Mercuri-chloride (LXII: R = Ph; X = HgCl)</u>

as yellow orange needles, m.p. > 360° with decomposition from 150° (Found: C,57.0; H,3.8; Fe,7.4, $C_{37}H_{25}ClFeO_2$ requires C,56.0; H,3.2; Fe,7.1%). I.R. max. in the carbonyl region at 2000 and 1970 cm.$^{-1}$

1,2,3,4,5-Pentaphenylcyclopentadienyliron icarbonyl ercuri-iodide (LXII; R = Ph; X = HgI).

as orange needles, m.p. 245° (decomp. with effervesence). (Found: C,52.5; H,3.6; Fe,6.5. $C_{37}H_{25}FeIO_2$ requires C,50.2; H,2.8; Fe,6.3%). I.R. max. in the carbonyl region at 2010 and 1960 cm.$^{-1}$

π-1,2,3,4,5-Pentaphenylcyclopentadienyl-σ-cyclopentadienyl-iron Dicarbonyl (LXV; R = H).

Cyclopentadiene (0.132 g., 2.0 mmole) was added to dispersed sodium (0.230 g., 20% dispersion, 2 mmole) in anhydrous tetrahydrofuran and the mixture was stirred for 1 hr. 1,2,3,4,5-Pentaphenylcyclopentadienyl iron dicarbonyl bromide (1.276 g., 2 mmole) in tetrahydrofuran (50 ml.) was then added and stirring continued for a further 2 hr. An orange precipitate formed, which was filtered and recrystallised from methylene chloride to give π-1,2,3,4,5-pentaphenylcyclopentadienyl-σ-cyclopentadienyl-iron dicarbonyl (0.8 g.) as orange red prisms, m.p. 343-345° (d). Another (0.2 g.) was obtained from the filtrate, total yield (1.0 g., 78%). (Found: C,79.6; H,5.0; Fe,9.0. M.W. 622 $C_{42}H_{30}FeO_2$ requires C,81.0; H,4.8; Fe,9.0%; M.W. 623). I.R. max in the carbonyl region at 2010 and 1961 cm.$^{-1}$

1,2,3,4,5-Pentaphenylferrocene

π-1,2,3,4,5-Pentaphenylcyclopentadienyl-σ-cyclopentadienyliron dicarbonyl (0.2 g.) was heated (200°, 0.5 mm.) for

1.5 hr. The residue was extracted with benzene and the solvent was removed to yield an orange yellow solid. Crystallisation from chlorobenzene gave 1,2,3,4,5-pentaphenylferrocene (0.175 g. 95%) as orange needles, m.p. 356-358° (Found: C,84.6; H,5.9; M.W., 518. C$_{40}$H$_{30}$Fe requires C,84.8; H,5.3%; M.W. 566).

Reaction of 1,2,3,4,5-Pentaphenylcyclopentadienyliron Dicarbonyl Bromide with 1,4-Diphenylcyclopentadienylsodium.

To dimsyl sodium [prepared from sodium hydride (0.11 g., 50% dispersion, 2 mmole) and dimethylsulphoxide (2 ml.)] was added 1,4-diphenylcyclopentadiene (0.44 g., 2 mmole) in anhydrous tetrahydrofuran (20 ml.) and the mixture was stirred for 1 hr. 1,2,3,4,5-Pentaphenylcyclopentadienyliron dicarbonyl bromide (1.276 g., 2 mmole) in tetrahydrofuran (30 ml.) was added and stirring continued for a further 1 hr. The mixture was then refluxed for 4 hr., filtered and the solvent was removed. The residue was extracted with hot acetone and filtered yielding pentaphenylcyclopentadiene (0.65 g., 73%) m.p. and mixed m.p. 252-254°. Removal of the solvent from the filtrate, followed by chromatography of the residue on alumina in benzene gave 1,3,1',3'-tetraphenylferrocene (0.1 g., 20%), m.p. 221-223°, undepressed on admixture with an authentic specimen.

Reaction of 1,2,3,4,5-Pentaphenylcyclopentadienyliron Dicarbonyl Bromide with 1,2,3-Triphenylcyclopentadienyllithium.

To phenyllithium [prepared in ether from lithium (0.023 g., 0.003 g. atom) and bromobenzene (0.25 g., 1.6 mmole)] was added 1,2,3-triphenylcyclopentadiene (0.5 g., 1.65 mmole) and the resulting mixture was refluxed for 3 hr. 1,2,3,4,5-Pentaphenylcyclopentadienyliron dicarbonyl bromide (0.95 g., 1.5 mmole) was added and the mixture was stirred for 1 hr. Filtration gave a green solid (0.12 g.) m.p. 360° (d). I.R. max in the carbonyl region at 1965 and 1786 cm.$^{-1}$, the infrared spectrum is identical with that of the green solid obtained on treatment of the bromide with sodium amalgam (p. 81). Removal of the solvent from the filtrate gave a colourless residue. Chromatography in benzene on alumina gave, after fractional crystallisation from acetone, 1,2,3-triphenylcyclopentadiene and pentaphenylcyclopentadiene, m.p.s and mixed m.p.s were identical with authentic samples.

Reaction of 1,2,3,4,5-Pentaphenylcyclopentadienyliron Dicarbonyl Bromide with 1,2,3,4-Tetraphenylcyclopentadienylsodium.

To dimsyl sodium [prepared from sodium hydride [0.24 g., 50% dispersion, 5 mmole) and dimethylsulphoxide (3 ml.)] was added tetraphenylcyclopentadiene (1.85 g., 5 mmole) in anhydrous tetrahydrofuran (50 ml.) and the mixture was stirred for 1hr. 1,2,3,4,5-Pentaphenylcyclopentadienyliron dicarbonyl bromide (3.19 g., 5 mmole) in tetrahydrofuran (100 ml.) was added and the stirring continued for a further 2 hr. Filtration gave the same green solid (1.2 g.) as described in the previous experiment. Removal of the solvent from the filtrate gave, after chromatography in benzene on alumina, tetracyclone m.p. and mixed m.p. 219-220°, and a yellow solid presumably a mixture of tetra-and pentaphenylcyclopentadiene.

Reaction of 1,2,3,4,5-Pentaphenylcyclopentadienyliron Dicarbonyl Bromide with 1,2,3,4,5-Pentaphenylcyclopentadienylsodium.

Pentaphenylcyclopentadienylsodium was prepared from 1,2,3,4,5-pentaphenylcyclopentadiene (2.23 g., 5 mmole) and dimsyl sodium (5 mmole). Treatment with 1,2,3,4,5-pentaphenylcyclopentadienyliron dicarbonyl bromide (3.19 g., 5 mmole), under the same conditions as above, gave the same green solid (1.4 g.) and pentaphenylcyclopentadiene, m.p. and mixed m.p. 251-254°.

Reaction of Tetraphenylcyclopentadienyllithium with Cyclopentadienyliron Dicarbonyl Bromide.

Tetraphenylcyclopentadiene (1.7 g., 4 mmole) in benzene (20 ml.) was added to phenyllithium [prepared from lithium (0.056 g., 0.008 g. atom) and bromobenzene (0.628 g., 4 mmole) in ether (5 ml.)] and the mixture was refluxed for 2 hs. Cyclopentadienyliron dicarbonyl bromide (1.04 g., 4 mmole) in anhydrous tetrahydrofuran (40 ml.) was added and the whole stirred overnight. The reaction mass was filtered and the solvent removed under reduced pressure. Chromatography in benzene on alumina resulted in the separation of two compounds

1. Unchanged tetraphenylcyclopentadiene (1.62 g., 95%) m.p. and mixed m.p. 175-177°.

2. Dicyclopentadienyldi-iron tetracarbonyl (0.46 g., 68%), m.p. 192°, undepressed on admixture with an authentic sample.

Reaction of 1,2,3,4,5-Pentaphenylcyclopentadienylsodium with Cyclopentadienyliron Dicarbonyl Bromide.

Pentaphenylcyclopentadienylsodium was prepared from 1,2,3,4,5-pentaphenylcyclopentadiene (2.23 g., 5 mmole) and dimsyl sodium (5 mmole) in tetrahydrofuran (40 ml.). Cyclopentadienyliron dicarbonyl bromide (1.28 g., 5 mmole) in tetrahydrofuran (20 ml.) was added and the mixture stirred for 2 hr. The mixture was worked up as described above to yield pentaphenylcyclopentadiene (2.1 g., 94%) m.p. and mixed m.p. 250-253°, and dicyclopentadienyldi-iron tetracarbonyl (0.85 g., 72%), m.p. 191°, undepressed on admixture with an authentic specimen.

π-1,2,3,4,5-Pentaphenylcyclopentadienyl-π-benzeneiron Bromide (LXX; X = Br).

1,2,3,4,5-Pentaphenylcyclopentadienyliron dicarbonyl bromide (1 g., 1.5 mmole) and aluminium trichloride (0.20 g., 1.5 mmole) were refluxed in benzene (30 ml.) for 1 hr. The mixture was poured into water, precipitating an orange solid which was removed by filtration and was crystallised from acetone to give π-1,2,3,4,5-pentaphenylcyclopentadienyl-π-benzeneiron bromide (0.75 g., 75%) as orange prisms, m.p. 256-258°(d). (Found: C,75.3; H,5.3; Fe,8.5. $C_{41}H_{31}BrFe$ requires C,74.5; H,4.7; Fe,8.2%).

Treatment of aqueous acetone solutions of the above salt with aqueous acetone solutions of ammonium reineckate and potassium iodide gave respectively,

π-1,2,3,4,5-pentaphenylcyclopentadienyl-π-benzeneiron reineckate (LXX; X=rein) as bright red needles, m.p. 219-221°(d), and π-1,2,3,4,5-pentaphenylcyclopentadienyl-π-benzeneiron iodide (LXX; X = I) as orange needles. After recrystallisation from aqueous acetone the compound had m.p. 253-254°(d). (Found: C,69.2; H,4.9; Fe,8.1. $C_{41}H_{31}FeI$ requires C,69.7; H,4.4; Fe,7.9%).

CHAPTER II

ATTEMPTS TO SYNTHESISE

1,2 DIPHENYLCYCLOPENTADIENE

1-Hydroxy-3,4-diphenylcyclopent-2-ene (LXXVII)

3,4-Diphenylcyclopent-2-en-1-one[37] (10 g., 0.04 mole) was suspended in methanol (125 ml.), sodium borohydride (1.2 g.) in water (5 ml.) was added and the mixture was allowed to react for 1hr. at room temperature. It was then warmed on the steam bath to ensure completion of the reaction and at the same time most of the solvent was allowed to evaporate. On cooling an oil separated out, which quickly crystallised. Recrystallisation from cyclohexane gave 1-hydroxy-3,4-diphenylcyclopent-2-ene (3.1 g., 78%) m.p. 103-105° (Lit.[196] 107-108.5°C). ν_{max}(KCl) 3390 cm^{-1} (OH).

Bis-(1,2-diphenylcyclopentadiene)(LXXVII)

Concentrated hydrochloric acid (4.8 ml.) was added to 1-hydroxy-3,4-diphenylcyclopent-2-ene (2.36 g., 0.01 mole) in ethanol (44 ml.). The mixture was refluxed for 1hr. and the product (0.6 g.) was removed by filtration. Extraction with hot petroleum ether followed by filtration gave a yellow insoluble hydrocarbon (0.06 g.) m.p. 265-270°. (Found: C,92 3; H,6.7. $(C_{17}H_{14})n$ requires C,93.5; H,6.5%). Removal of the solvent from the filtrate gave a yellow powder. Recrystallisation from petroleum ether yielded bis-(1,2-diphenyl-cyclopentadiene) (0.52 g., 35%) as a fine microcrystalline powder m.p. 219-221°. (Found: C,93.7; H,6.7; M.W.,453. $C_{34}H_{28}$ requires C,93.5; H,6.5%; M.W.436).

The infrared spectra of these two products are identical. Ultra-violet and N.M.R. data for the latter are reported in the Appendix.

Reaction between 1,5-Diphenylpentan-1,5-dione and Aluminium Amalgam[124]

1,5-Diphenylpentan-1,5-dione[175] (25 g., 0.1 mole) was dissolved in ethanol-water (900 ml., 2:1). 6 g. batches of aluminium amalgam were added twice daily over a period of 14 days. The reaction mixture was filtered, poured into water (5l.) and extracted with ether (total volume 3l.). Evaporation of the ether yielded a yellow gum (24.5 g.). Chromatography on alumina failed to yield any hydrocarbon, the major product being 1,2-dihydroxy-1,2-diphenylcyclopentane m.p. 102-104° [Lit.[175] 103-104°]

Dehydration of 1,2-Dihydroxy-1,2-diphenylcyclopentane (LXXIV; R = Ph).

1,2-Dihydroxy-1,2-diphenylcyclopentane[175] (4.72 g., 0.01 mole) was dissolved in ethanol (75 ml.), concentrated hydrochloric acid (5 ml.) was added and the mixture was refluxed for 2 hr. On cooling a red gum separated. The mother liquor was decanted and the gum was crystallised from petroleum ether. Recrystallisation from petroleum ether gave a small yield of bis-(1,2-diphenylcyclopentadiene) m.p. 218-220°, undepressed on admixture with product isolated from the dehydration of 1-hydroxy-3,4-diphenylcyclopent-2-ene.

Reaction of 1,5-Diphenylpentan-1,5-dione with Zinc and Acetic Acid

1,5-Diphenylpentan-1,5-dione (4.0 g., 0.016 mole) was refluxed in acetic acid (75 ml.) and zinc (15 g.) was added in small portions over 3hr. The mixture was refluxed for a further 2hr., then filtered hot onto ice and the inorganic residue was washed with a further 80 ml. of hot acetic acid. The mixture was extracted with ether, the ether layer was washed with water, dilute sodium bicarbonate, water and dried over sodium sulphate. Removal of the ether gave an orange oil (2.2 g.). Chromatography in petroleum ether on alumina gave bis-(1,2-diphenylcyclopentadiene) (0.15 g.). Recrystallised from petroleum ether the compound had m.p. 218-220°, undepressed on admixture with an authentic sample. Benzene and benzene-ether solutions eluted a further five bands which were not investigated.

Methyl Xanthate[190] of 1-Hydroxy-3,4-diphenylcyclopent-2-ene

To sodium hydride (2.1 g., 50% dispersion, 0.0438 mole) in ether (25 ml.) was added 1-hydroxy-3,4-diphenylcyclopent-2-ene (7.08 g., 0.03 mole) in ether (75 ml.) and the mixture was refluxed for 3hr. Carbon disulphide (2.91 g., 0.0438 mole) was added and refluxing continued for 3hr. This was followed by the addition of methyl iodide (5.76 g., 0.0438 mole) and the mixture was refluxed a further 3hr. It was then poured into water, a little ether was added and the ethereal layer was withdrawn. Removal of the solvent from the dried (Na_2SO_4)

extract gave an orange oil. Chromatography on silica gel in benzene gave the crude xanthate (8.54 g.) as an orange gum. No further attempt was made to purify this material.

Attempted Pyrolysis of the above Xanthate

The above xanthate (4.0 g.) was heated (200°, 0.1 mm.) in a sausage flask for 2hr. No distillate was collected in the side arm. Extraction of the residue followed by chromatography on alumina, with petroleum ether as eluent, failed to yield any hydrocarbon fragment.

Reduction of 3,4-Diphenylcyclopent-2-en-1-one with Aluminium Isopropoxide^{28}

3,4-Diphenylcyclopent-2-en-1-one (9.0 g., 0.038 mole) was dissolved in dry toluene (50 ml.) and dry isopropanol (30 ml.) and the insoluble material was removed by filtration. This was combined with a solution of aluminium isopropoxide (30 g., 0.148 mole) in dry toluene (60 ml.) and dry isopropanol (130 ml.). The mixture was stirred and heated at 80° for 3hr. The temperature of the bath was raised to 100° and the mixture of isopropanol and acetone was distilled continuously, via a long column, for 19hr. The liquid volume in the flask was kept constant by the dropwise addition of isopropanol. The solution was concentrated in a vacuum, then added to sodium hydroxide solution (20%) and extracted with ether. The ethereal solution was washed to neutrality and dried over sodium sulphate. Removal of the ether gave a red oil (7.1 g.). Chromatography on alumina yielded two fractions. Petroleum ether-benzene (1:3) eluted 3,4-diphenylcyclopent-3-en-1-one (4 g., 45%) m.p. 108-110°, undepressed on admixture with an authentic specimen. Ether eluted 1-hydroxy-3,4-diphenylcyclopent-2-ene (3 g., 33%). After recrystallisation from cyclohexane the compound had m.p. 104-106, undepressed on admixture with an authentic sample.

1-Hydroxy-3,4-diphenylcyclopent-3-ene (LXXVIII)

3,4-Diphenylcyclopent-3-en-1-one[189] (4.5 g., 0.019 mole) was suspended in methanol (75 ml.), sodium borohydride (0.6 g.) in water (2 ml.) was added and the mixture was allowed to react at room temperature for 1hr. It was then heated on the steam bath and the solvent was allowed to evaporate. After 1hr. the mixture was poured into water and extracted with ether. The ethereal extract was washed with water and dried over sodium sulphate. Removal of the ether gave a red oil which crystallised from benzene-petroleum ether on scratching. Recrystallisation from cyclohexane gave prisms of 1-hydroxy-3,4-diphenylcyclopent-3-ene (3.0 g., 66%) m.p. 102-104° [Lit.[189] 102.5-103.5], ν_{max} (KCl) 3413 cm^{-1} (OH)

Attempted Dehydration of 1-Hydroxy-3,4-diphenylcyclopent-3-ene

(a) With alcoholic hydrogen chloride.

1-Hydroxy-3,4-diphenylcyclopent-3-ene (0.5 g., 2.1mmole) was dissolved in ethanol (11 ml.), concentrated hydrochloric acid (1.2 ml.) was added and the mixture was refluxed for 1hr. It was then poured into water and extracted with ether. The ethereal layer was washed with water and dried over sodium sulphate. Removal of the ether gave a red oil which crystallised on the addition of petroleum ether. Recrystallisation from petroleum ether gave unchanged starting material (0.39 g., 78%) m.p. 101-103°.

(b) Sulphuric acid/acetic acid.

1-Hydroxy-3,4-diphenylcyclopent-3-ene (0.5 g., 2.1mmole) in acetic acid (10 ml.) was heated with concentrated sulphuric acid (1 ml.) for 15 min. The mixture was poured into water and extracted with ether. The ethereal extract was washed with dilute sodium bicarbonate solution, water and dried (Na_2SO_4). Removal of the solvent gave a red oil, which on chromatography on alumina in petroleum ether gave a yellow solid (0.02 g.) m.p. 105-110°, which had a similar infrared spectrum to bis-(1,2-diphenylcyclopentadiene). It is believed to be isomeric with this dimer.

Pyrolysis of Bis-(1,2-diphenylcyclopentadiene)

(a) Bis-(1,2-diphenylcyclopentadiene) (0.2 g., 0.5mmole) was heated (200° 0.1 mm.) for 2hr. in a water cooled sublimation apparatus. A yellow compound, was collected on the cold finger condensor, m.p. 85-95°C. The compound does not have a sharp melting point due to the fact that it reforms the original bis-(1,2-diphenylcyclopentadiene) on slow heating.

This is believ.d to be the exo-form of bis-(1,2-diphenylcyclopentadiene). (Found, C,92.5; H,6.6; M.W., 374. $C_{34}H_{28}$ requires, C,93.5; H,6.5%; M.W., 436).

(b) Bis-(1,2-diphenylcyclopentadiene) (0.5 g., 1.1mmole) was heated under nitrogen(360°) in a flask with a long side arm. An oily crystalline compound was collected in the side arm. Recrystallisation from ethanol gave 1,4-diphenylcyclopentadiene as pale yellow plates m.p. 156-158°, undepressed on admixture with an authentic sample.

Preparation of Derivatives of Bis-(3,4-diphenylcyclopentadienone)

(a) 2,4-Dinitrophenylhydrazone

Addition of 2,4-dinitrophenylhydrazine solution to an ethanolic solution of bis-(3,4-diphenylcyclopentadienone)[176] gave a bright red precipitate. Recrystallisation from ethanol containing a few drops of ethyl acetate gave the mono-2,4-dinitrophenylhydrazone of bis-(3,4-diphenylcyclopentadienone) as red needles m.p. 248-250° with considerable decomposition from 200°. (Found: N,8.9. $C_{40}H_{28}N_4O_5$ requires N,8.7%). ν_{max}(KCl) 1773 cm^{-1}.

(b) Hydrazone (LXXXII)

Bis-(3,4-diphenylcyclopentadienone) (1.1 g., 2.5mmole) was dissolved in hydrazine hydrate (20 ml.) and the mixture was refluxed for 9hr. An oil formed, the mother liquor was decanted and the oil was recrystallised from ethanol giving the di-hydrazone of bis-(3,4-diphenylcyclopentadienone) (0.8 g., 68% m.p. 155-161°. (Found: N, 10.4. $C_{34}H_{30}N_4$ requires N, 11.4%).

Attempted Reduction of the above Hydrazone

To a rapidly stirred mixture of freshly sublimed potassium tertiary butoxide (2 g.) in anhydrous dimethylsulphoxide (5 ml.), was added in small portions over 3hr., the above hydrazone (2 g., 4 mmole). The mixture was shaken with a methylene chloride: water mixture. The organic layer was separated and dried over calcium chloride. Removal of the solvent gave a red oil. Chromatography on alumina failed to yield any hydrocarbon fragment.

Reaction between Bis-(1,2-diphenylcyclopentadiene) and Iron Pentacarbonyl

Bis-(1,2-diphenylcyclopentadiene) (2.2 g., 5 mole) and iron pentacarbonyl (1.5 ml., 0.01 mole) were heated in an autoclave, under carbon dioxide, at 200° for 4hr. The reaction mass was extracted with benzene. The solvent was reduced to small bulk, addition of petrol gave a dark brown solid. This material was chromatographed on alumina in benzene to give a black crystalline solid. Recrystallisation from methylene chloride-petroleum ether gave black needles m.p. 264-266° (d). (Found: C,68.5; H,4.2; Fe,15.3; M.W., 466. $C_{22}H_{16}FeO_3$ requires C,68.4; H,4.6; Fe,14.6; M.W., 386). I.R.$_{max}$ in the carbonyl region at 2041 and 1980 cm^{-1}. The N.M.R. spectrum is reported in the Appendix.

Bis-(1,2-diphenylcyclopentadienylmolybdenum tricarbonyl) (LXXXIII; R' = H; R = Ph).

Bis-(1,2-diphenylcyclopentadiene) (1.1 g., 2.5 mmole) and molybdenum hexacarbonyl (1.2 g., 5 mmole) were heated in an autoclave, under carbon dioxide, at 200° for 24 hr. Extraction of the reaction mass with benzene, followed by removal of the solvent gave a purple solid. Chromatography in petroleum ether on alumina gave,

1. Unchanged hydrocarbon (0.25 g., 22%), m.p. 218-220°.
2. A deep purple solid (0.5 g., 20%) was eluted with petroleum ether-benzene (4:1). Recrystallisation from benzene-petroleum ether gave <u>bis-(1,2-diphenylcyclopentadienylmolybdenum tricarbonyl)</u> as purple needles, m.p. 341-345° (decomp. from 310°) (Found: C, 61.9; H, 3.2; O, 11.7. $C_{40}H_{26}Mo_2O_6$ requires C, 61.5; H, 3.3; O, 12.1%). Infrared max. in the carbonyl region at 2030, 1961 and 1905 cm.$^{-1}$.

Reaction of Bis-(1,2-diphenylcyclopentadienylmolybdenum tricarbonyl) with Lithium in Ethylamine.

A solution of bis-(1,2-diphenylcyclopentadienylmolybdenum tricarbonyl) (0.5 g., 0.58 mmole) in anhydrous ethylamine (10 ml.) was poured onto lithium metal (0.1 g., 0.014 g. atom) during 5 min. The mixture was stirred for 20 min. and then poured onto ice-water. Extraction with ether followed by removal of the solvent from the dried ($MgSO_4$) extract gave an orange gum. Chromatography on alumina in petroleum ether gave a small amount of bis-(1,2-diphenylcyclopentadiene), m.p. 217-219°.

Bis-(1,3-diphenylcyclopentadienylmolybdenum tricarbonyl) (LXXXIII; R = H; R' = Ph).

Treatment of 1,4-diphenylcyclopentadiene (1.06 g., 5 mmole) with molybdenum hexacarbonyl (1.2 g., 5 mmole) in the manner described above yielded a black gum. Chromatography on alumina in benzene gave a purple oil (1.1 g.). This was rechromatographed on alumina with petroleum ether as eluent. A small yellow band separated first, presumably unchanged starting material. Benzene eluted a dark purple band yielding a purple solid. Crystallisation from benzene-petroleum ether gave bis-(1,3-diphenylcyclopentadienylmolybdenum tricarbonyl) (0.9 g., 36%) as purple prisms, m.p. 284-286°, mixed m.p. with the 1,2-isomer 240-249°. (Found: C,62.1; H,3.9. $C_{40}H_{26}Mo_2O_6$ requires C,61.5; H,3.3%). Infrared max. in the carbonyl region 2028, 1980 and 1942 cm.$^{-1}$.

1-Hydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-ene (LXXXVIII R = Me).

2,5-Dimethyl-3,4-diphenylcyclopent-2-en-1-one[165] (2 g., 7.5 mmole) was suspended in methanol (30 ml.), sodium borohydride (0.24 g.) in water (1.5 ml.) was added and the mixture was allowed to react at room temperature for 1 hr. It was then heated on the steam bath and most of the solvent was allowed to evaporate. An oil separated. The mixture was poured into water and extracted with ether. Removal of the solvent from the dried (Na_2SO_4) extract gave a yellow oil, which crystallised on the addition of cyclohexane. Recrystallisation from cyclohexane gave *1-hydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-ene* (1.8 g., 90%) as colourless prisms, m.p. 102-104° (Found: C,86.6; H,7.7. $C_{19}H_{20}O$ requires C,86.3; H,7.6%). $\nu_{max.}$ (KCl) 3340 cm.$^{-1}$ (OH).

1,4-Dimethyl-2,3-diphenylcyclopentadiene (LXXXIV; R = Me).

1-Hydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-ene (0.5 g., 1.9 mmole) and concentrated hydrochloric acid (1.2 ml.) were heated to reflux in methanol (15 ml.) for 1 hr. On cooling a pale yellow crystalline material separated. Recrystallisation from methanol gave pale yellow needles of *1,4-dimethyl-2,3-diphenylcyclopentadiene* (0.3 g., 65%), m.p. 89-90° (Found: C,93.5; H,7.1. $C_{19}H_{18}$ requires C,92.7; H,7.1%). N.M.R. data are recorded in the Appendix.

5-Methylanhydroacetonebenzil (LXXX; R = H, R' = Me).

To a mixture of benzil (60 g., 0.29 mole) and methyl ethyl ketone (21.6 g., 0.3 mole) was added potassium hydroxide (3 g.) in ethanol (10 ml.). After stirring for 5 hr. the mixture solidified. The solid material was washed well with water and then with ether to remove impurities. Recrystallisation from methanol gave colourless prisms of 5-methylanhydroacetonebenzil (41.5 g., 55%), m.p. 180° [Lit.[183] m.p. 180°].

1,4-Dihydroxy-5-Methyl-3,4-diphenylcyclopent-2-ene (LXXXIX; R = H, R' = Me).

5-Methylanhydroacetonebenzil (14 g., 0.053 mole) in methanol (200 ml.) was reduced in the manner described previously, with sodium borohydride (1.7 g.) in water (11 ml.). On cooling a crystalline material separated. Filtration, followed by recrystallisation from benzene gave 1,4-dihydroxy-5-methyl-3,4-diphenylcyclopent-2-ene (12.5 g., 90%) as colourless needles, m.p. 200-202° (Found: C, 80.5; H, 7.1. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%). $\nu_{max.}$ (KCl) 3356 cm.$^{-1}$ (OH).

5-Methyl-3,4-diphenylcyclopent-2-en-1-one (LVIII, R = H, R' = Me)

Concentrated hydrochloric acid (7 ml.) was added to 1,4-dihydroxy-5-methyl-3,4-diphenylcyclopent-2-ene (2.1 g., 8 mmole) in ethanol (70 ml.) and the mixture was heated to reflux for 1 hr. It was then diluted with water and extracted with ether. Removal of the dried (Na_2SO_4) solvent from the extract gave a yellow oil which crystallised slowly. Recrystallisation from petroleum ether gave 5-methyl-3,4-diphenylcyclopent-2-en-1-one (1.65 g., 85%) as colourless needles, m.p. 75-77° [Lit.[197] 77°].

It formed a 2,4-dinitrophenylhydrazone, m.p. 202-204° (Found: N, 12.8. $C_{24}H_{20}N_4O_4$ requires N, 13.1%).

1-Hydroxy-5-methyl-3,4-diphenylcyclopent-2-ene (LXXXVIII; R = H)

5-Methyl-3,4-diphenylcyclopent-2-en-1-one (1.5 g., 6 mmole) in methanol was reduced with sodium borohydride (0.21 g.), in water (1.5 ml.), as previously described. The mixture was poured into water and extracted with ether. Removal of the solvent from the dried (Na_2SO_4) extract yielded 1-hydroxy-5-methyl-3,4-diphenylcyclopent-2-ene (1.3 g., 87%) as a colourless oil which failed to crystallise from the usual solvents. This oil is probably a mixture of stereoisomers. $\nu_{max.}$ (liquid) 3373 cm.$^{-1}$ (OH).

Attempted Dehydration of the above Crude Material.

The crude alcohol (1.2 g.) was dissolved in ethanol (30 ml.), concentrated hydrochloric acid (2.5 ml.) was added and the mixture was refluxed for 1 hr., diluted with water and extracted with ether. Removal of the solvent from the dried (Na_2SO_4) extract gave a red gum. Chromatography on alumina in benzene-petrol (1:9) failed to yield any crystalline monomeric hydrocarbon.

1,4-Dihydroxy-2,3,4-triphenylcyclopent-2-ene (LXXXIX; R'=H; R = Ph

2-Phenylanhydroacetonebenzil[81] (10 g.; 0.03 mole) was dissolved in methanol (150 ml.), sodium borohydride (1 g.) in water (6 ml.) was added and the mixture was allowed to react at room temperature for 1 hr. It was then heated on the steam bath and most of the solvent was allowed to evaporate. A solid separated, this was filtered off and recrystallised from benzene giving 1,4-dihydroxy-2,3,4-triphenylcyclopent-2-ene as colourless plates (9.6 g., 96%), m.p. 172-174° (Found: C,84.9; H,6.5. $C_{23}H_{20}O_2$ requires C,84.1; H,6.1%). $\nu_{max.}$(KCl disc) 3360 cm.$^{-1}$ (OH).

Dehydration of 1,4-Dihydroxy-2,3,4-triphenylcyclopent-2-ene.

1,4-Dihydroxy-2,3,4-triphenylcyclopent-2-ene (0.2 g.) was dissolved in ethanol (5 ml.), concentrated hydrochloric acid (0.5 ml.) was added and the mixture was refluxed for 1 hr. Cooling, followed by the dropwise addition of water gave 2,3,4-triphenylcyclopent-2-en-1-one[51] (0.178 g., 95%), which crystallised from petroleum ether as needles, m.p. and mixed m.p. 141-143°. $\nu_{max.}$(KCl) 1704 cm.$^{-1}$ (C=O)

Attempted Benzoylation of 1,4-Dihydroxy-2,3,4-triphenylcyclopent-2-ene.

1,4-Dihydroxy-2,3,4-triphenylcyclopent-2-ene (7 g., 0.021 mole) was dissolved in benzene-pyridine (1:1, 30 ml.), benzoyl chloride (3 g., 0.021 mole) was added slowly with cooling. The mixture was allowed to stand at room temperature for 30 min., then it was poured into water and extracted with ether. The ethereal extract was washed with water, dilute hydrochloric acid, 10% sodium bicarbonate solution, water and dried over sodium sulphate. Removal of the ether gave a yellow gummy solid. Crystallisation from petroleum ether yielded 2,3,4-triphenylcyclopent-2-en-1-one, m.p. 140-142°, undepressed on admixture with an authentic sample.

1,4-Dihydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-ene (LXXXIX; R, R'=Me).

2,5-Dimethylanhydroacetonebenzil[165] (10 g., 0.036 mole) was dissolved in methanol (150 ml.), sodium borohydride (1.2 g.) in water (8 ml.) was added and the mixture was allowed to react at room temperature for 1 hr. It was then heated on the steam bath and most of the solvent was allowed to evaporate. An oil separated which crystallised on cooling. Recrystallisation from benzene gave *1,4-dihydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-ene* as colourless needles (9.4 g., 94%), m.p. 140-142°. (Found: C, 80.8; H, 7.1. $C_{19}H_{20}O_2$ requires C, 81.4; H, 7.1%). $\nu_{max.}$ (KCl) 3448 cm.$^{-1}$ (OH).

Dehydration of 1,4-Dihydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-ene.

1,4-Dihydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-ene (0.3 g.) was dissolved in ethanol (10 ml.), concentrated hydrochloric acid (1 ml.) was added and the mixture was refluxed for 1 hr. Cooling, followed by the dropwise addition of water gave 2,5-dimethyl-3,4-diphenylcyclopent-2-en-1-one[165] (0.26 g., 93%) which crystallised from cyclohexane as colourless plates, m.p. 114-116°, undepressed on admixture with an authentic sample. $\nu_{max.}$ (KCl) 1695 cm.$^{-1}$ (C=O).

Attempted Benzoylation of 1,4-Dihydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-ene.

1,4-Dihydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-ene (10 g., 0.036 mole) was dissolved in benzene-pyridine (1:1, 30 ml.), benzoyl chloride (4.5 g., 0.032 mole) was added with cooling and the mixture was allowed to stand at room temperature for 30 min. It was then poured into water and extracted with ether. The ethereal extract was washed with water, dilute hydrochloric acid, 10% sodium bicarbonate solution, water and dried over sodium sulphate. Removal of the ether gave a yellow gum. Chromatography on silica gel in benzene afforded 2,5-dimethyl-3,4-diphenylcyclopent-2-en-1-one (8.8 g., 94%). After recrystallisation from cyclohexane the compound had m.p. 114-116°, undepressed on admixture with an authentic sample.

1,4-Dihydroxy-3,4-diphenylcyclopent-2-ene (LXXXIX, R,R' = H).

Anhydroacetonebenzil[181] (2.54 g., 0.01 mole) was suspended in methanol (60 ml.), sodium borohydride (0.3 g.) in water (2 ml.) was added and the mixture was allowed to react at room temperature for 1 hr. It was then heated on the steam bath and most of the solvent was allowed to evaporate. After 20 min. a colourless crystalline solid separated. The mixture was cooled and filtered. Recrystallisation from benzene gave 1,4-dihydroxy-3,4-diphenylcyclopent-2-ene as colourless crystalline plates (2.46 g., 96%), m.p. 149-151°. (Found: C,79.9; H,6.4. $C_{17}H_{16}O_2$ requires C,80.9; H,6.3%). $\nu_{max.}$(KCl) 3390 $cm.^{-1}$ (OH).

Dehydration of 1,4-Dihydroxy-3,4-diphenylcyclopent-2-ene.

1,4-Dihydroxy-3,4-diphenylcyclopent-2-ene (2.54 g., 0.01 mole) was dissolved in ethanol (70 ml.), concentrated hydrochloric acid (7.5 ml.) was added and the mixture was refluxed for 1 hr. It was then poured into water and extracted with ether. The ethereal extract was washed with water and dried over sodium sulphate. Removal of the ether gave a yellow gum, which crystallised on the addition of petroleum ether. Recrystallisation from petroleum ether yielded 3,4-diphenylcyclopent-2-en-1-one (2.1 g., 90%), m.p. and mixed m.p. 107-109°.

1-Benzoyloxy-4-hydroxy-3,4-diphenylcyclopent-2-ene (XC, R,R'= H, R'' = COPh)

1,4-Dihydroxy-3,4-diphenylcyclopent-2-ene (2.54 g., 0.01 mole) was dissolved in benzene pyridine (1:1, 8 ml.), benzoyl chloride (1.3 g., 0.01 mole) was added at 0° and the mixture was allowed to react at room temperature for 30 min. It was then poured into water and extracted with ether. The ethereal extract was washed with water, dilute hydrochloric acid, 10% sodium bicarbonate solution, water and finally dried over sodium sulphate. Removal of the solvent gave a yellow oil (2.9 g., 82%) which crystallised on scratching from benzene-petroleum ether. Recrystallisation from benzene-petroleum ether gave 1-benzoyloxy-4-hydroxy-3,4-diphenylcyclopent-2-ene, m.p. 112-114° (Found: C,80.5; H,5.3. $C_{24}H_{20}O_3$ requires C,80.8; H,5.6%). $\nu_{max.}$ (KCl) 1695 cm.$^{-1}$ (C=O), 3460 cm.$^{-1}$ (OH). N.M.R. data are reported in the Appendix.

Dehydration of 1-Benzoyloxy-4-hydroxy-3,4-diphenylcyclopent-2-ene.

(a) 1-Benzoyloxy-4-hydroxy-3,4-diphenylcyclopent-2-ene (0.5 g.) was dissolved in ethanol (11ml.), concentrated hydrochloric acid (1.2 ml.) was added and the mixture was refluxed for 1 hr. It was then reduced to half bulk and an oil separated, which crystallised on cooling to give a yellow solid (0.31 g., 94%). Recrystallisation from petroleum ether gave 3,4-diphenylcyclopent-2-en-1-one as colourless needles, m.p. 102-104° [Lit.[182] 108-110°], undepressed on admixture with an authentic sample.

(b) 1-Benzoyloxy-4-hydroxy-3,4-diphenylcyclopent-2-ene (7.1 g., 0.02 mole) was dissolved in benzene (600 ml.) and refluxed for 12 hr. through a Soxhlet apparatus containing anhydrous oxalic acid. The mixture was then poured into water and the benzene layer separated. It was washed several times with 10% sodium bicarbonate solution, then with water and finally dried over sodium sulphate. Removal of the solvent gave an orange gum which was chromatographed on silica gel to give :

(1) A yellow crystalline product (0.34 g., 8%) eluted by petroleum ether-benzene (3:1). Recrystallisation from acetone gave yellow needles, m.p. 238-239° [Found: C,92.7; H,6.0 M.W., 326. $C_{34}H_{26}$ requires C,94.0; H,6.0%; M.W., 434). N.M.R. data are reported in the Appendix.

(2) 3,4-Diphenylcyclopent-2-en-1-one (0.6 g., 27%), m.p. and mixed m.p. 103-105°.

(3) Benzene-petroleum ether (1:1) gave a colourless crystalline solid (1.1 g., 49%) which recrystallised from acetone as fine needles, m.p. 207-209° [Found: C,91.0; H,6.0. $C_{34}H_{26}O$ requires C,90.8; H,5.8%). N.M.R. spectrum is reported in the Appendix. $\nu_{max.}$(KCl) 1066 and 1033 cm.$^{-1}$

<u>1-Acetoxy-4-hydroxy-3,4-diphenylcyclopent-2-ene (XC; R,R' = H; R'' = $COCH_3$).</u>

1,4-Dihydroxy-3,4-diphenylcyclopent-2-ene (5.0 g., 0.02 mole) was dissolved in benzene:pyridine (1:1, 14 ml.), acetyl chloride (1.58 g., 0.02 mole) was added slowly with cooling. The mixture was allowed to stand at room temperature for 30 min., then it was poured into water and extracted with ether. The ethereal extract was washed with water, 10% sodium bicarbonate solution, dilute hydrochloric acid, water and finally dried over sodium sulphate. Removal of the solvent gave a yellow oil, which crystallised on the addition of cyclohexane to give 1-acetoxy-4-hydroxy-3,4-diphenylcyclopent-2-ene (4.76 g., 82%). After recrystallisation from cyclohexane the compound had m.p. 103-105° (Found: C,77.4; H,6.4. $C_{19}H_{18}O_3$ requires C,77.5; H,6.1%). $\nu_{max.}$ (KCl) 1709 cm.$^{-1}$ (C=O), 3448 cm.$^{-1}$ (OH). N.M.R. data are reported in the Appendix.

Dehydration of 1-Acetoxy-4-hydroxy-3,4-diphenylcyclopent-2-ene.

1-Acetoxy-4-hydroxy-3,4-diphenylcyclopent-2-ene (0.5 g.) was dissolved in ethanol (11ml.), concentrated hydrochloric acid (1.2 ml.) was added and the mixture was refluxed for 1 hr. It was then poured into water and extracted with ether. The ethereal extract was washed with water and dried over sodium sulphate. Removal of the solvent gave 3,4-diphenylcyclopent-2-en-1-one (0.36 g., 90%), m.p. and mixed m.p. 97-101°, Recrystallisation from petroleum ether raised the melting point to 102-104° [Lit.[182] 108-110°].

Attempted Preparation of 4-Hydroxy-1-methoxy-3,4-diphenylcyclopent-2-ene.

(a) 1,4-Dihydroxy-3,4-diphenylcyclopent-2-ene (5.08 g., 0.02 mole) was dissolved in methanol (50 ml.), dimethyl sulphate (2.5 g., 0.02 mole) was added, followed by sodium hydroxide (4 ml., 20% solution). The mixture was refluxed for 1 hr., then it was poured into water and extracted with ether. The ethereal extract was washed with water and dried over sodium sulphate. Removal of the ether gave an orange oil which was chromatographed on silica gel. Benzene-ether (9:1) eluted a yellow viscous liquid. Distillation at (175° (bath), 0.01 mm.) gave 1,4-dimethoxy-3,4-diphenylcyclopent-2-ene (2.6 g., 86%) as a colourless oil (Found: C,80.9; H,7.2. $C_{19}H_{20}O_2$ requires C,81.4; H,7.1%). $\nu_{max.}$ (liquid) 1115, 1093 cm.$^{-1}$ (C-O-C), N.M.R. data are reported in the Appendix. Benzene-ether (1:1) eluted starting material (1.9 g.).

(b) 1,4-Dihydroxy-3,4-diphenylcyclopent-2-ene (3.5 g., 0.014 mole) was dissolved in anhydrous tetrahydrofuran (40 ml.) sodium hydride (0.66 g., 50% dispersion, 0.014 mole) was added and the mixture was refluxed for 2 hr. Dimethyl sulphate (1.76 g., 0.014 mole) in tetrahydrofuran (5 ml.) was added and the mixture was refluxed a further 30 min. It was then poured into water and extracted with ether. The ethereal extract was washed with water and dried over sodium sulphate. Removal of the ether gave a yellow oil, which crystallised on the addition of cyclohexane. Recrystallisation from cyclohexane gave 3,4-diphenylcyclopent-2-en-1-one (3.1 g., 95%), m.p. and mixed m.p. 109-110°.

Attempted Reaction of 1-Hydroxy-3,4-diphenylcyclopent-2-ene with N-Bromosuccinimide.

1-Hydroxy-3,4-diphenylcyclopent-2-ene (1.17 g., 5 mmole) and N-bromosuccinimide (1.25 g.,) were refluxed in carbon tetrachloride (50 ml.) for 1 hr. Filtration gave a dark red solution and removal of the solvent under reduced pressure yielded a dark red oil. No attempt was made purify this material, which was dehydrated directly with concentrated hydrochloric acid (2 ml.) in ethanol (40 ml.). A dark brown precipitate formed which was filtered and recrystallised from benzene to give bis-1,2-diphenylcyclopentadienone), m.p. 200°(d). $\nu_{max.}$(KCl 1773 and 1695 cm.$^{-1}$

Attempted Reaction of 4-Chloro-3,4-diphenylcyclopent-2-en-1-one[189] with Sodium Borohydride.

4-Chloro-3,4-diphenylcyclopent-2-en-1-one (2.68 g., 0.01 mole) was suspended in methanol (60 ml.), sodium borohydride (0.3 g.,) in water (2 ml.) was added and the mixture was allowed to react at room temperature for 10 min. It was then reduced to small bulk on the steam bath. On cooling a colourless crystalline product separated. Filtration followed by recrystallisation from benzene gave bis-(1,2-diphenylcyclopentadienone), m.p. 200°(d).

CHAPTER III

METHOXYFERROCENES

Chloromercuriferrocene and 1,1'-Bis(chloromercuri)-ferrocene[94] (CII, CIII, R = HgCl).

Ferrocene (47 g., 0.25 mole) and mercuric acetate (77 g., 0.25 mole) were dissolved in ether methanol (1:1, 2 l.) and the mixture was left for 14 days with occasional shaking. The reaction mixture was filtered and the precipitate was washed with ether: methanol. Recrystallisation of the precipitate from xylene gave diferrocenyl mercury[94] (15 g.; 22%), m.p. 210-215°, undepressed on admixture with an authentic sample. To the filtrate, an aqueous solution of potassium chloride (0.25 mole) was added yielding an orange yellow precipitate.

Filtration gave a mixture of mono and di-mercurichlorides. Soxhlet extraction for 6 days yielded mono-chloromercuriferrocene (7.7 g., 7%) and bis(-chloromercuri-)ferrocene (40 g., 25%).

Attempted Preparation of 1,1'-Dibromoferrocene[76] (CIII, R = Br)

1,1'-Bis(chloromercuri)-ferrocene (6.54 g., 0.01 mole) and bromine (4 g., 0.025 mole) were refluxed in chloroform (200 ml., for 30 min. The mixture was poured into sodium thiosulphate solution and extracted with ether. The ethereal extract was washed with water and dried (Na_2SO_4), removal of the solvent failed to yield any of the expected product.

1,1'-Diiodoferrocene.[76] (CIII; R = I).

1,1'-Bis(chloromercuri)-ferrocene (6.55 g., 0.01 mole) and iodine (12.9 g., 0.025 mole) were refluxed in chloroform (250 ml.)

for 30 min. The chloroform was decanted off and the black viscous residue was extracted (×6) with boiling ethanol. The ethanol extracts were combined with aqueous sodium thiosulphate and the precipitate was removed by filtration. The precipitate was dissolved in ether. This was filtered and dried (Na_2SO_4). Removal of the solvent, followed by chromatography of the residue on silica gel in benzene, gave 1,1'-di-iodoferrocene (1.11 g., 26%) as a red oil.

Attempted Preparation of 1,1'-Ferrocenylene Di-acetate[192] ($CIII$; $R = OCOCH_3$).

(a) 1,1'-Di-iodoferrocene (1 g.) was refluxed with copper acetate (2.5 g.) in ethanol for 15 min. The mixture was poured into water and extracted with ether. The ethereal extract was washed with water, 5% potassium hydroxide solution, water and finally dried (Na_2SO_4). Removal of the solvent gave unchanged 1,1'di-iodoferrocene (0.95 g., 95%).

(b) 1,1'-Di-iodoferrocene (0.95 g.) was dissolved in 50% aqueous tetrahydrofuran (200 ml.), copper acetate (2.5 g.) was added and the mixture was refluxed for 30 min. The mixture was worked up as described above to give a red oil. An infrared spectrum of this oil showed a weak carbonyl absorption at 5.8 μ probably due to a trace of 1,1'ferrocenylene diacetate.

When the above procedure was repeated using water as the solvent medium, the carbonyl absorption increased, however only by a marginal amount.

Iodoferrocene[76] (CII, R = I).

Chloromercuriferrocene (3.3 g., 8.0 mmole) was dissolved in hot xylene (200 ml.) and mixed with a hot solution of iodine (10 g.) in xylene (100 ml.), immediate precipitation occurred. The mixture was cooled, filtered and the precipitate was washed with alcohol. The precipitate was then shaken with aqueous sodium thiosulphate and extracted with ether. Removal of the solvent gave iodoferrocene(0.6 g., 24%), m.p. 46-48° [Lit.[76] 44-45°].

Ferrocenylacetate.[191] (CII, R = $OCOCH_3$).

Iodoferrocene (0.6 g., 1.45 mmole) was dissolved in aqueous methanol (150 ml.), copper acetate (1.3 g.) was added and the mixture was refluxed for 15 min. It was then diluted with water and extracted with ether. The ethereal extract was washed with water, 5% potassium hydroxide solution, water and finally dried (Na_2SO_4). Removal of the ether gave an orange oil. Crystallisation from petroleum ether gave ferrocenylacetate (0.317 g., 67%), m.p. 62-64°, [Lit.[191] 64.5-66°].

Cyclopent-2-en-1-one.[201] (CV; R = H).

A three necked flask, fitted with a dropping funnel, fractionating column and nitrogen inlet, was heated in a metal bath to 300°. Dicyclopentadienol[200,201] (48.5 g.) was added dropwise during 6 hr. and the distillate was collected in a flask at -70°. Redistillation gave cyclopent-2-en-1-one (b.p. 24.5° 2 mm.) (15.5 g., 66%).

Attempted Preparation of 1,1'-Dimethoxyferrocene (CIII; R = OMe)

To dimsyl sodium, [prepared by the method of Corey,[164] from sodium hydride (18.2 g., 50% dispersion, 0.35 mole) and dimethylsulphoxide (145 ml.)], cyclopent-2-en-1-one (14.5 g., 0.175 mole) in anhydrous tetrahydrofuran (50 ml.) was added dropwise during 30 min. The mixture was stirred a further 3 hr., then freshly prepared anhydrous ferrous chloride (11.2 g., 0.088 mole) was added in small portions over 30 min., followed by anhydrous tetrahydrofuran (150 ml.). The mixture was stirred overnight, then a solution of sodium hydroxide (5 g.) in water (250 ml.) was added and the mixture was stirred for 30 min. The solid material was removed by filtration under nitrogen and the filtrate was refluxed with dimethylsulphate (25.2 g., 0.2 mole) for 30 min. The mixture was poured into water (2 l.) and extracted with chloroform. The extract was washed well with water and dried ($CaCl_2$). Removal of the solvent gave a yellow gummy solid which was insoluble in petroleum ether and was therefore not investigated.

1,1-Dimethoxyferrocene (CIII; R = OMe)

A solution of methoxyferrocene (4.32 g., 0.02 mole) in anhydrous ethylamine (100 ml.) was poured on to lithium metal (3.0 g., 0.43 g. atom) as rapidly as the vigorous reaction would allow (~ 5 min).[111] The mixture was stirred for 20 min., then ferrous chloride, from ferric chloride (6 g., 0.04 mole) was added and stirring continued overnight. It was then poured into water and extracted with ether, which was dried ($MgSO_4$) and removed to give an orange gummy solid, which on chromatography yielded.

1. ferrocene (0.905 g., 21.8%), m.p. and mixed m.p. 74-76°.
2. monomethoxyferrocene[191] (1.38 g., 32%), m.p. 40-42.5°.
3. dimethoxyferrocene[192] (0.105 g., 4%) identified by its infrared spectrum.

Ferrocenylboronic acid and 1,1'-Ferrocenylenediboronic acid.[115,120,122]

(a) To butyllithium (0.043 mole) was added 1,1'-bis-(chloromercuri-)ferrocene (6.5 g., 0.01 mole) and the mixture stirred at room temperature for 1 hr.[102] This was then filtered through a glass wool plug into a dropping funnel and added dropwise to butyl borate (13.8 g., 0.06 mole) in ether (20 ml.) at -70° over 2 hr. The mixture was then allowed to come to room temperature (1.5 hr.), destroyed with aqueous sodium hydroxide (10%, 100 ml.) and filtered. Theether layer was extracted with aqueous sodium hydroxide (10%) and the extracts combined (total volume; 400 ml.). Acidification with sulphuric acid (10%) yielded a yellow precipitate, filtration followed by washing with water and petroleum ether gave 1,1'-ferrocenylenediboronic acid (0.5 g., 8.5%) as a yellow powder.

(b)[115] To a stirred slurry of ferrocene (37.2 g., 0.2 mole), fine aluminium powder (50 g., 1.85 mole), freshly ground aluminium trichloride (3 g., 0.0225 mole) and methyl iodide (1 ml.) in dry petroleum ether (350 ml.) under nitrogen at -30° was added dropwise, over a period of 40 min., boron trichloride (100 g., 0.852 mole). The reaction mixture was then stirred a further 4 days and the remaining boron trichloride distilled off under reduced pressure. The reaction mass was then suction filtered through kieselguhr, under carbon dioxide, and the aluminium powder washed carefully with petroleum ether. The red coloured filtrate of ferrocene, ferrocenylboronyl dichloride and 1,1'-ferrocenylene bis(boronyldichloride) was hydrolysed at 0° by dropwise addition of water (containing a few drops of titanous chloride) to the stirred solution. The mixture of boronic acids was filtered off and washed with petroleum ether and water to neutrality (Congo red). Extraction with ether left only a trace amount of 1,1'-ferrocenylenediboronic acid. Evaporation of the dried (Na_2SO_4) ether extract afforded ferrocenylboronic acid (12.0 g., 26%).

Acetylation of Monomethoxyferrocene

Methoxyferrocene (3.5 g., 0.0138 mole), acetic anhydride (0.87 g., 8.5 mmole), polyphosphoric acid (30 g.) were stirred under nitrogen at 45° for 2 hr. The mixture was then poured into water and extracted with ether. The ethereal extract was washed with water, sodium bicarbonate solution, water and finally dried (Na_2SO_4). Removal of ether gave a deep red oil (2.68 g.). Chromatography on alumina in benzene gave

(a) an oily solid (0.532 g.) eluted with benzene and having no carbonyl absorption in the infrared,

(b) a deep red oil (1.909 g.; 45%) eluted very slowly by benzene consisting of the three mono-acetylated methoxyferrocenes.

Rechromatography of (a) in petroleum ether gave unchanged monomethoxyferrocene (0.461 g., 13%).

Fraction (b) was distilled (150° bath; 0.02 mm.) and separation attempted by vapour phase chromatography. Three principal peaks with smaller peaks superimposed were obtained. This was thought to be due to partial decomposition at the column temperature (200°). When 1.357 g. of (b) was rechromatographed on a column (72" x 1.2") in benzene no apparent separation was achieved.

Aminomethylation of 1,1'-dimethoxyferrocene.[115]

1,1'-Dimethoxyferrocene (1.16 g., 4.75 mmole), methylene bis-dimethylamine (1.94 g., 19 m.mole) and a catalytic amount of 85% phosphoric acid in glacial acetic acid (30 ml.) were stirred at 100° for 15 hr. under nitrogen. After removal of most of the acetic acid, the solution was basified to pH10 with 10N sodium hydroxide solution and extracted with ether. The extract was dried and evaporated to yield an oil (0.968 g.) which was chromatographed on alumina to yield

(a) a dark orange oil (0.343 g.) eluted with ether consisting of isomeric monoaminomethylated methoxyferrocenes.

(b) a red oil (0.608 g.) eluted with ether:methanol (99:1) consisting of isomeric diaminomethylated methoxyferrocenes.

(a) (0.343 g.) was rechromatographed in ether on a column (60" x 0.6"), 25 ml. fractions were collected.

Fraction No.	Weight mg.	Fraction No.	Weight mg.
1	0.5	21	2.5
2	1.5	22	2.5
3	9.0	23	0.5
4	15.5	24	0.5
5	22	25	1.5
6	19	26	3
7	18	27	3
8	18	28	2
9	15	29	2
10	12	30	3
11	10	31	2
12	10	32	2.5
13	9	33	2
14	8.5	34	2
15	5	35	2
16	6	36	2
17	3.5	37 (column extruded)	91
18	3		
19	3		
20	0.5		

From this table it appears that the mixture consists of two components. Fractions 1-20 were bulked and considered to be component (A) (0.211 g.), fractions 23-36 were bulked and designated component (B) (0.118 g.). N.M.R. and infrared data for these are recorded in the Appendix. Component (A) gave a methiodide, m.p. 126-127° (Found: C,43.2; H,5.4; N,2.9. $C_{16}H_{24}FeNO_2$ requires C,43.1; H, 5.4; N,3.1%). Component (B) gave a methiode, m.p. 150-152° (Found: C,42.7; H,5.8; N,2.8. $C_{16}H_{24}FeNO_2$ requires C,43.1; H,5.4; N,3.1%).

Rechromatography of (b) failed to achieve any separation.

Reduction of Bis-(dimethylaminomethyl)-dimethoxyferrocenes.

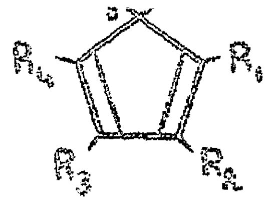
Reduction of Bis-(dimethylaminomethyl)-dimethoxyferrocenes.

To a solution of the aminomethylated product (b) (0.608 g., 1.7 mmole) in dry benzene (30 ml.) was added portionwise over a period of 10 min., methyliodide (0.895 g., 6.3 mmole) in dry benzene (10 ml.). On each addition the solution was shaken vigorously and after the final addition the mixture was refrigerated for 12 hr. The precipitate was filtered off and the filtrate evaporated to dryness giving a combined yield of methiodide (1.09 g., 100%).

To freshly ground sodium amalgam (175 g.) prepared from sodium (34 g.) and mercury (40 ml.) was added, with cooling in an ice bath, a solution of the methiodide (1.09 g.) in water (50 ml.). After addition of benzene (20 ml.) the mixture was heated on the steam bath for 3 hr., during which time the evolution of trimethylamine was noted. After cooling the mixture was extracted with benzene, dried ($CaCl_2$) and evaporated to yield an oil (0.4615 g.). An infrared spectrum of this product showed stronghydroxyl absorption at 2.9 u. The product was once again reacted in benzene-water with sodium amalgam (100 g.) for 5 hr. The mixture was worked up as before yielding an oil (0.434 g.). Chromatography on alumina in petroleum ether gave a mixture of dimethyl-dimethoxyferrocenes (0.255 g., 55%) as a brown oil. Rechromatography on alumina in petroleum ether failed to resolve the mixture.

APPENDIX

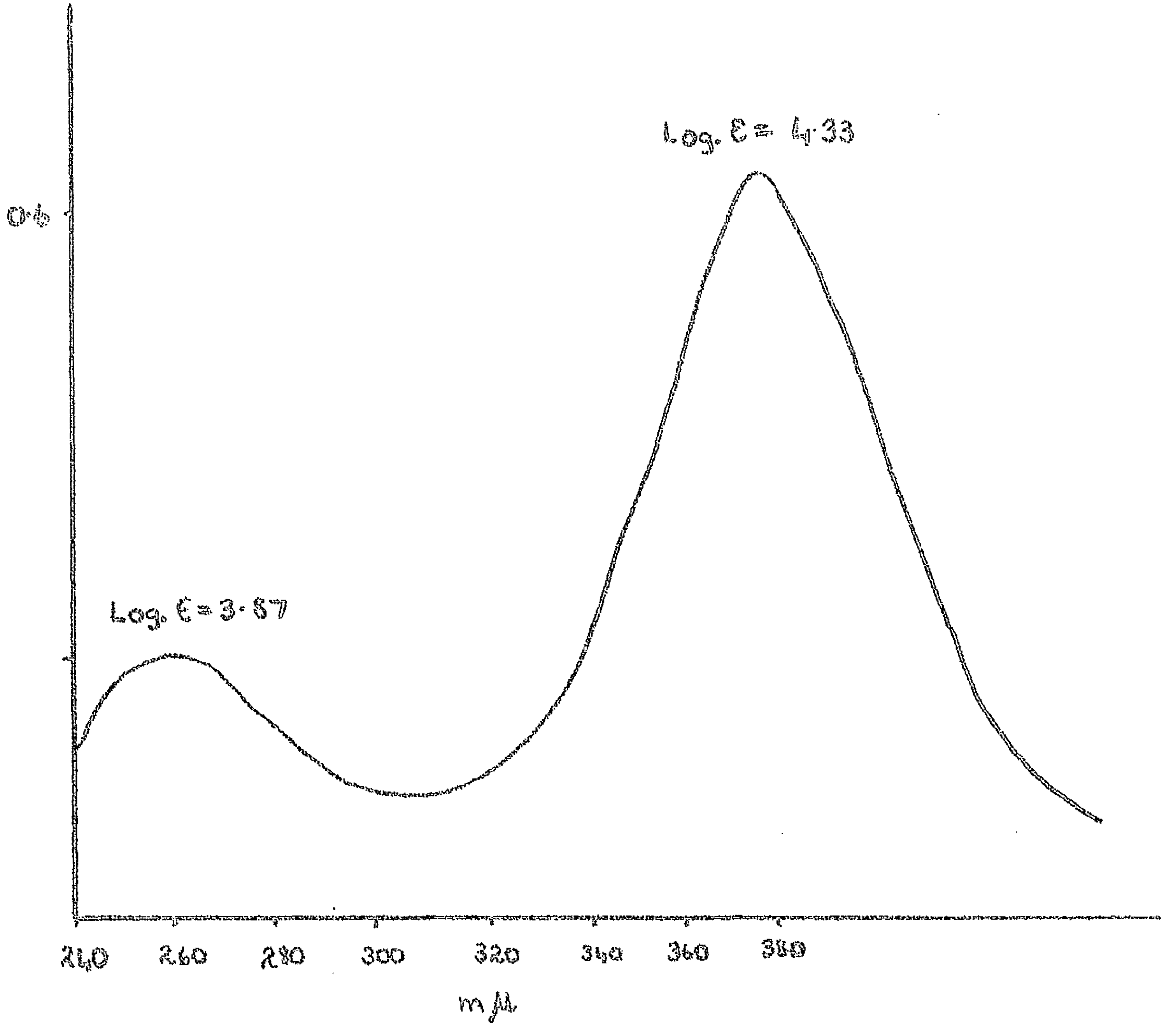
N.M.R. Spectra of Phenyl Substituted Cyclopentadienes



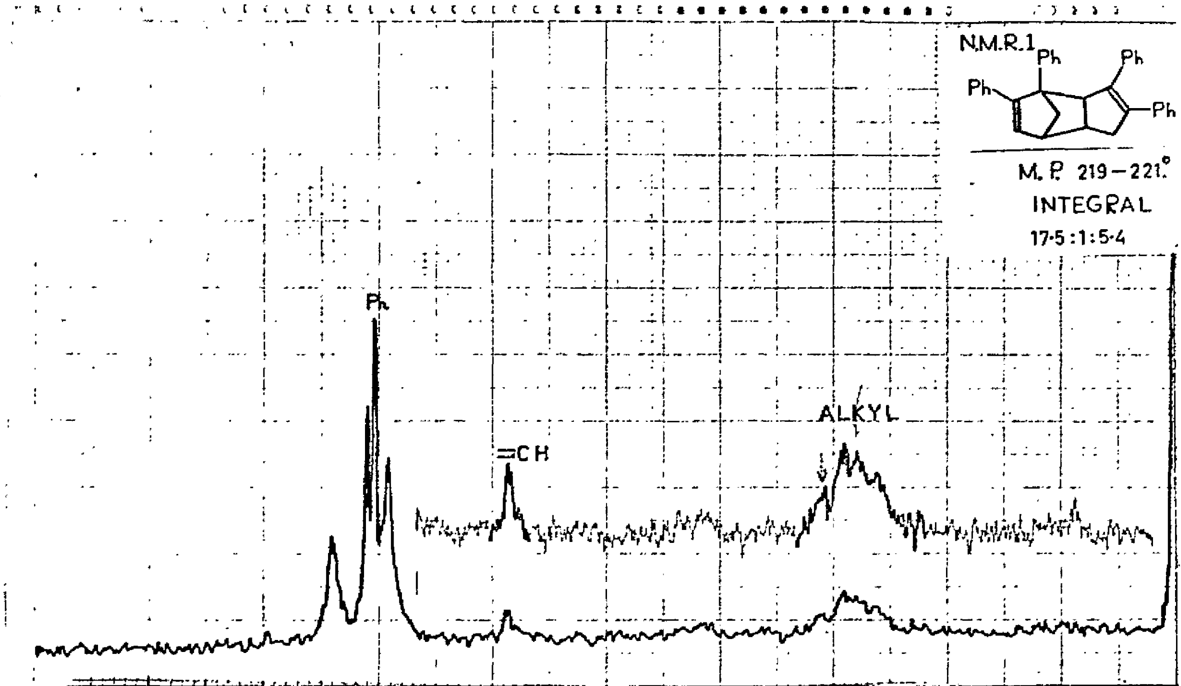
Cyclopentadiene	τ Value	Relative Intensity	Assignment
1,4-Diphenyl- R_1, R_4 =Ph; R_2, R_3, R_5 =H	2.4-3 (m) 3.13 6.28	5.77 0.99 1.0	Phenyl- -10 Olefinic C_2, C_3 ~ 2 Methylene C_5 ~ 2
1,2,4-Triphenyl- R_1, R_2, R_4 =Ph, R_3, R_5 =H	2.5-3.1 (m) 6.12	12.51 1	Phenyl and olefinic-16 or 17 Methylenic ~ 2 or 1
1,2,3-Triphenyl- R_1, R_2, R_3 =Ph, R_4, R_5 =H	2.6-3.1 (m) 3.5 (t) 6.4 (d)	16.05 1 1.88	Phenyl ~ 15 Olefinic C_4 ~ 1 Methylene C_5 ~ 2
1,4-Dimethyl-2,3-diphenyl- R_1, R_4 =Me; R_2, R_3 =Ph; R_5 =H	2.6-3.1 (m) 6.89 7.98	5.7 1.0 3.0	Phenyl- C_2, C_3 ~ 10 Methylene C_5 ~ 2 Methyls C_1, C_4 ~ 6
1,2,5-Trimethyl-3,4-diphenyl R_1, R_2, R_5 =Me; R_3, R_4 =Ph	2.8-3.1 (m) 5.87 (m) 7.93 (d) 8.1 (t) 8.27	11.3 1 9.25	Phenyl, C_3, C_4 ~ 10 Proton on C_5 ~ 1 Methyl " " ~ 9

d = doublet t = triplet m = multiplet.

U.V. SPECTRUM OF BIS-(1,2-DIPHENYLCYCLOPENTADIENE).



N.M.R.1



M.P. 219–221°

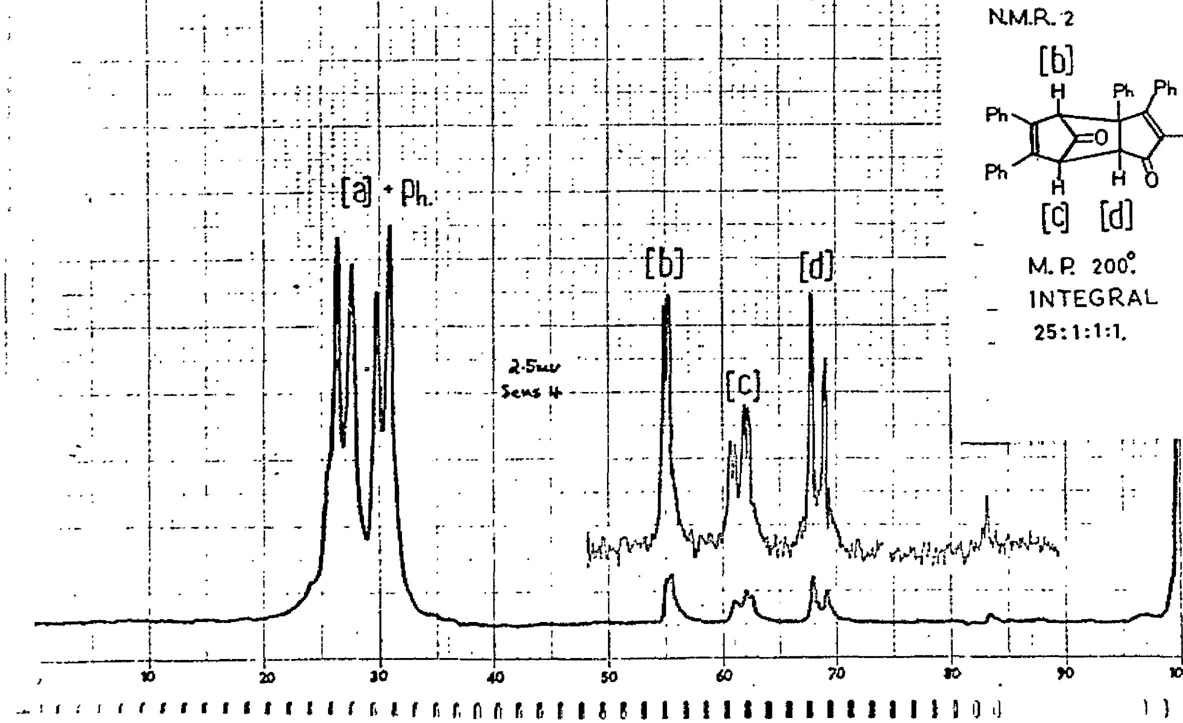
INTEGRAL

17·5:1:5·4

CONCN. 22mg/0.5cc
SOLVENT CCl4
NUC. H FREQ. 40
REF. STD. TMS
SCALE FACTOR. C/S PER UNIT. 4
SWEEP RATE. C/S PER SEC 320/m
DECADE SET. REF. TO STD.
R.F. FIELD. 2mV
R.F. GAIN. 1
SENSITY. 1
SAMPLE TUBE.
DATE. 5-12-62

T.C. 0·1

N.M.R. 2



M.P. 200°.

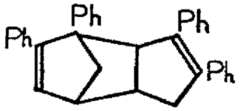
INTEGRAL

25:1:1:1.

CONCN.
SOLVENT. CDCl3
NUC. H FREQ. 40
REF. STD. TMS
SCALE FACTOR C/S PER UNIT 4
SWEEP RATE. C/S PER SEC. 320/m
DECADE SET. REF. TO STD.
R.F. FIELD. 2mv
R.F. GAIN. ½
SENSITY. 1
SAMPLE TUBE.
DATE 8.12.62.

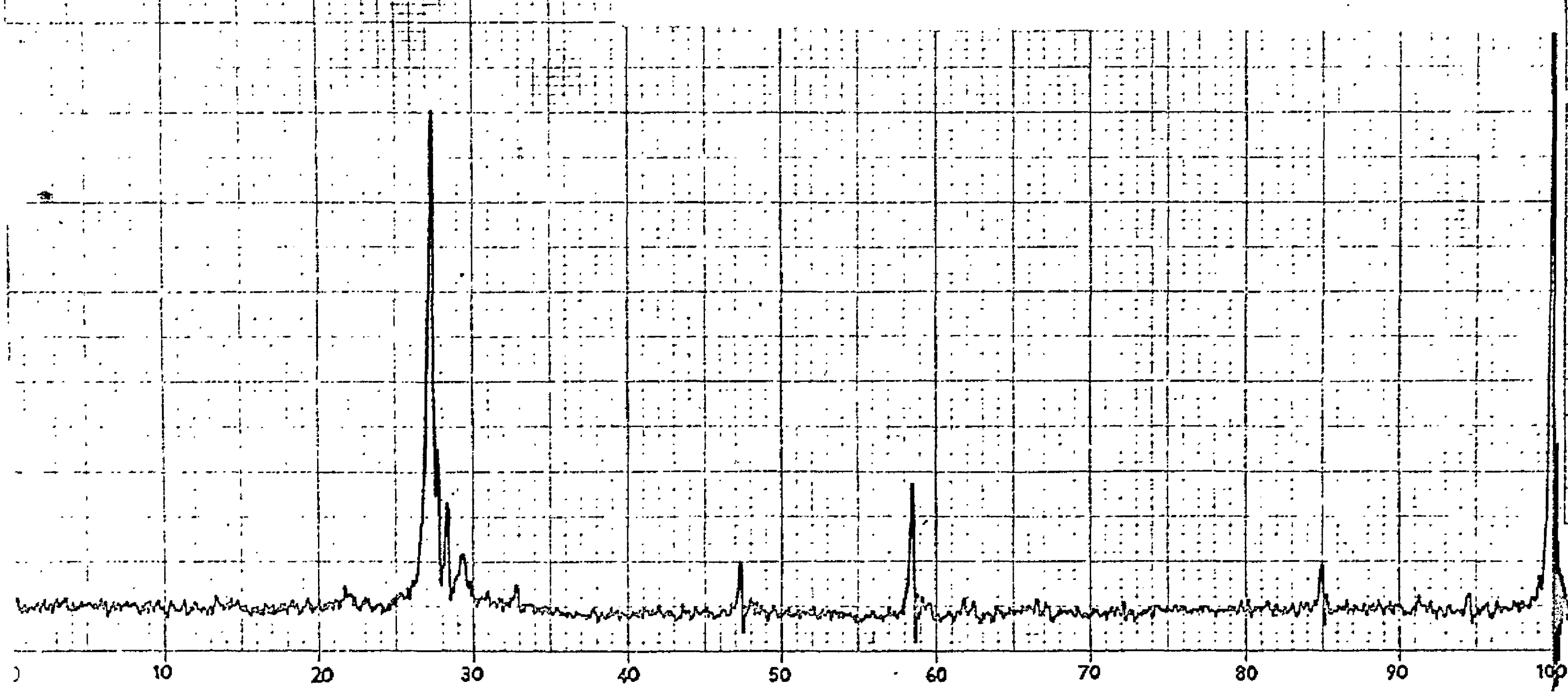
T.C 0·1

N.M.R. 3

PRODUCT FROM  AND $Fe(CO)_5$ M.P. 264-266°

INTEGRAL

8·65:0·5:1·2



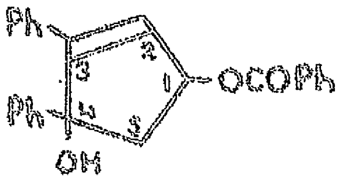
CONCN. Sat
SOLVENT CS_2
NUC. H FREQ. 40
REF STD. TMS
SCALE FACTOR. C/s PER UNIT. 4
SWEEP RATE. C/s PER SEC. 16
DECADE SET. REF. TO STD.
R.F. FIELD. 2.5mV
R.F. GAIN. 1
SENSITY. 1
SAMPLE TUBE.
DATE. 4.6.63

T.C 0.1.

PART No. OS—NR 7025

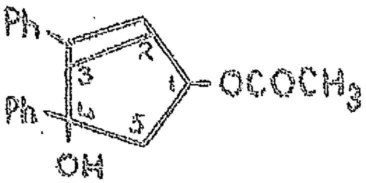
PERKIN ELMER LTD., BEACONSFIELD, BUCKS

N.M.R. Spectrum of



τ Value	Relative Intensity	Assignment
1.9–2.9	15.9	Phenyl– ~15
3.43 (d)	1	Proton on C_2 ~ 1
3.88 (qu)	1	Proton on C_1 ~ 1
7.33 (d.d.)	1.93	Protons on C_5 ~ 2
7.49	1	OH proton C_4 ~ 1

N.M.R. Spectrum of



τ Value	Relative Intensity	Assignment
2.4–2.9 (m)	10.9	Phenyl ~10
3.58 (d)	1	Proton on C_2 ~ 1
4.12 (qu)	0.86	Proton on C_1 ~ 1
7.32 (d)	3.0	Proton on C_5 ~ 1
7.43		OH proton C_4 ~ 1
7.5 (d)		Proton on C_5 ~ 1
8.0	3.4	Methyl group ~ 3

d = doublet

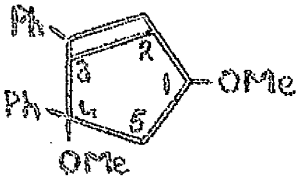
m = multiplet

d.d. = double doublet

q = quartet

qu = quintuplet

N.M.R. Spectrum of

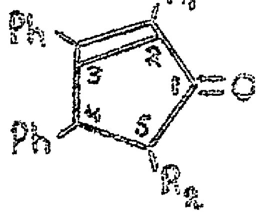


τ Value	Relative Intensity	Assignment	
2.60–2.94	12.5	Phenyl	~10
5.51 (d)	1	Olefinic proton on C_2	~ 1
6.07 (m)	1	Proton on C_3	~ 1
6.64 6.72	6.4	Methoxy protons	~ 6
7.12 (m)	1.8	C_5 methylene group	~ 2

d = doublet

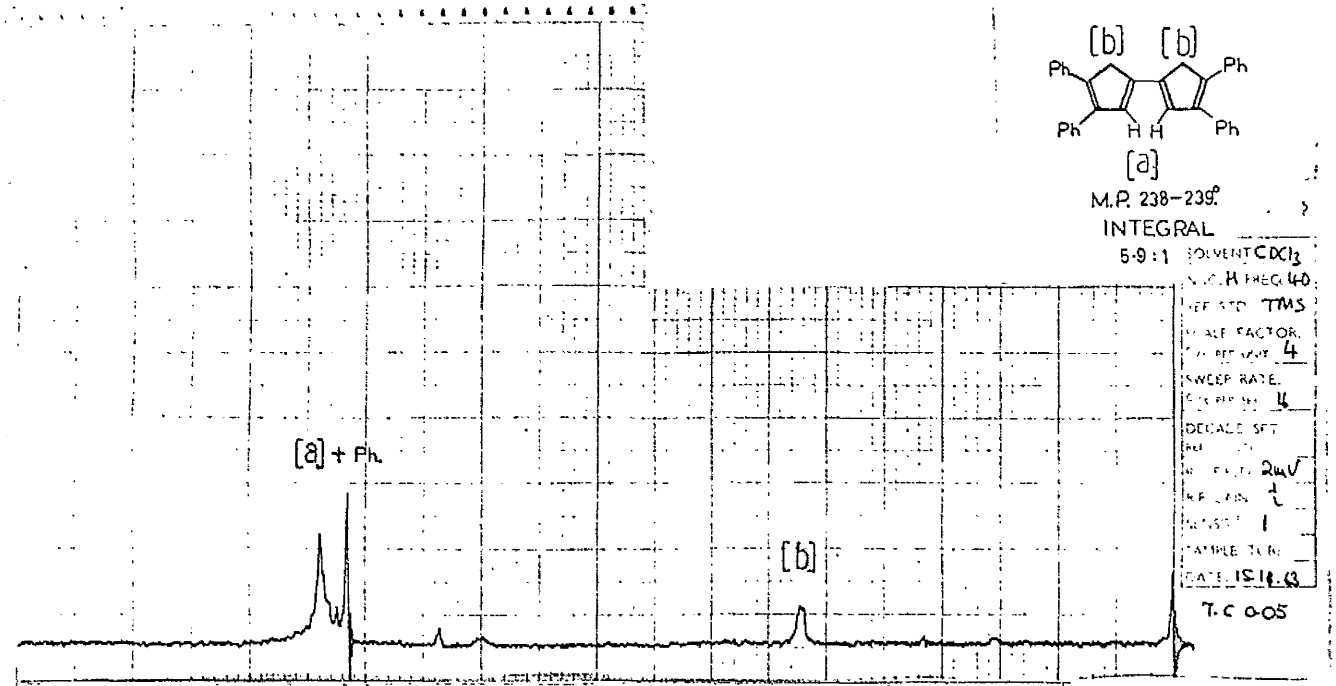
m = multiplet

N.M.R. Spectrum of Phenylsubstituted Cyclopentenones



Cyclopentenone	τ Value	Relative Intensity	Assignment	
3,4-diphenylcyclopent-2-en-1-one	2.5-2.84 (m)	10.7	Phenyl	~10
R_1, R_2 = H	3.33 (d)	1	Olefinic C_2	~ 1
	5.43 (m)	1	Proton on C_4	~ 1
	7.18 (d)	0.88	Proton on C_5	~ 1
	7.51 (d)	0.88	Proton on C_5	~ 1
2,3,4-triphenylcyclopent-2-en-1-one	2.55-3.2	18.7	Phenyl	~15
	5.43 (q)	1	Proton on C_4	~ 1
R_1 = Ph, R_2 = H	6.95 (d)	1	Proton on C_5	~ 1
	7.23 (d)	1	Proton on C_5	~ 1
2,5-dimethyl-3,4-diphenyl-cyclopent-2-en-1-one	2.65-3.15	10.9	Phenyl-	~10
	5.48 (q)	0.8	Proton on C_4	~ 1
R_1, R_2 = Me	7.18 (q)	1	Proton on C_5	~ 1
	7.92 (d)	3.15	Methyl group on C_2	~ 3
	9.25 (d)	2.7	Methyl group on C_5	~ 3

d = doublet   q = quartet   m = multiplet



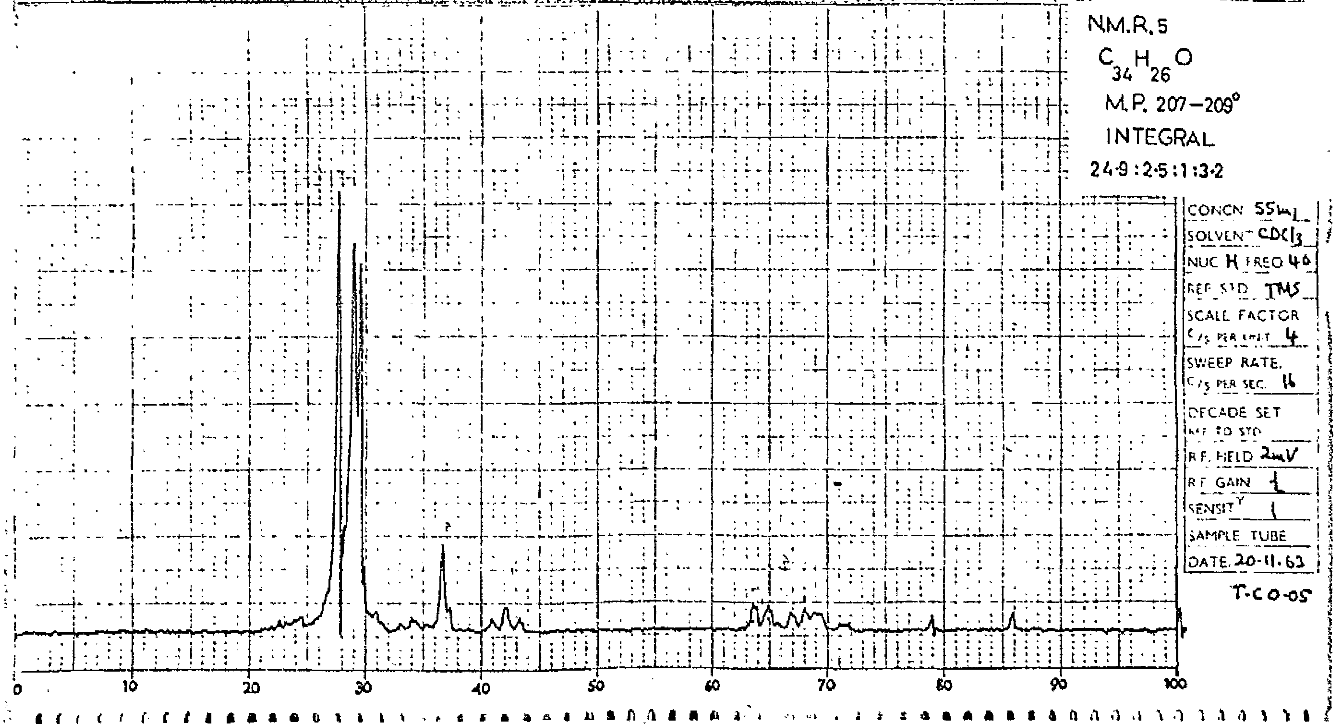
M.P. 238–239°

INTEGRAL

5·9 : 1

SOLVENT $CDCl_3$
NUC H FREQ 40
REF STD TMS
SCALE FACTOR C/S PER UNIT 4
SWEEP RATE C/S PER SEC 16
DECADE SET REF TO STD
R.F. FIELD 2mV
R.F. GAIN 1
SENSIT^Y 1
SAMPLE TUBE
DATE 15.11.63

T.C 0·05



N.M.R. 5

$C_{34}H_{26}O$

M.P. 207–209°

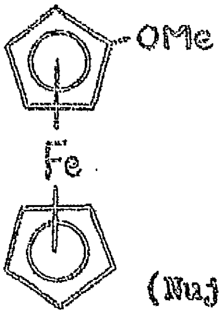
INTEGRAL

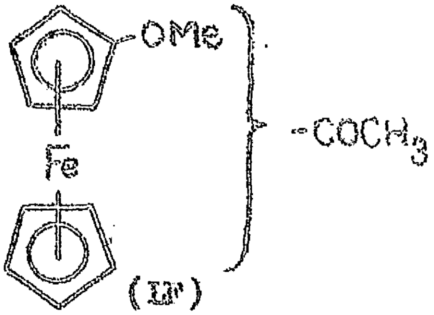
24·9 : 2·5 : 1 : 3·2

CONCN 55mg
SOLVENT $CDCl_3$
NUC H FREQ 40
REF STD TMS
SCALE FACTOR C/S PER UNIT 4
SWEEP RATE C/S PER SEC. 16
DECADE SET REF TO STD
R.F. FIELD 2mV
R.F. GAIN 1
SENSIT^Y 1
SAMPLE TUBE
DATE 20-11-63

T·C 0·05

Infrared maxima for methoxyferrocene and acetylmethoxyferrocenes below 2000 cm.$^{-1}$

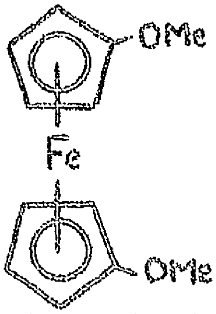




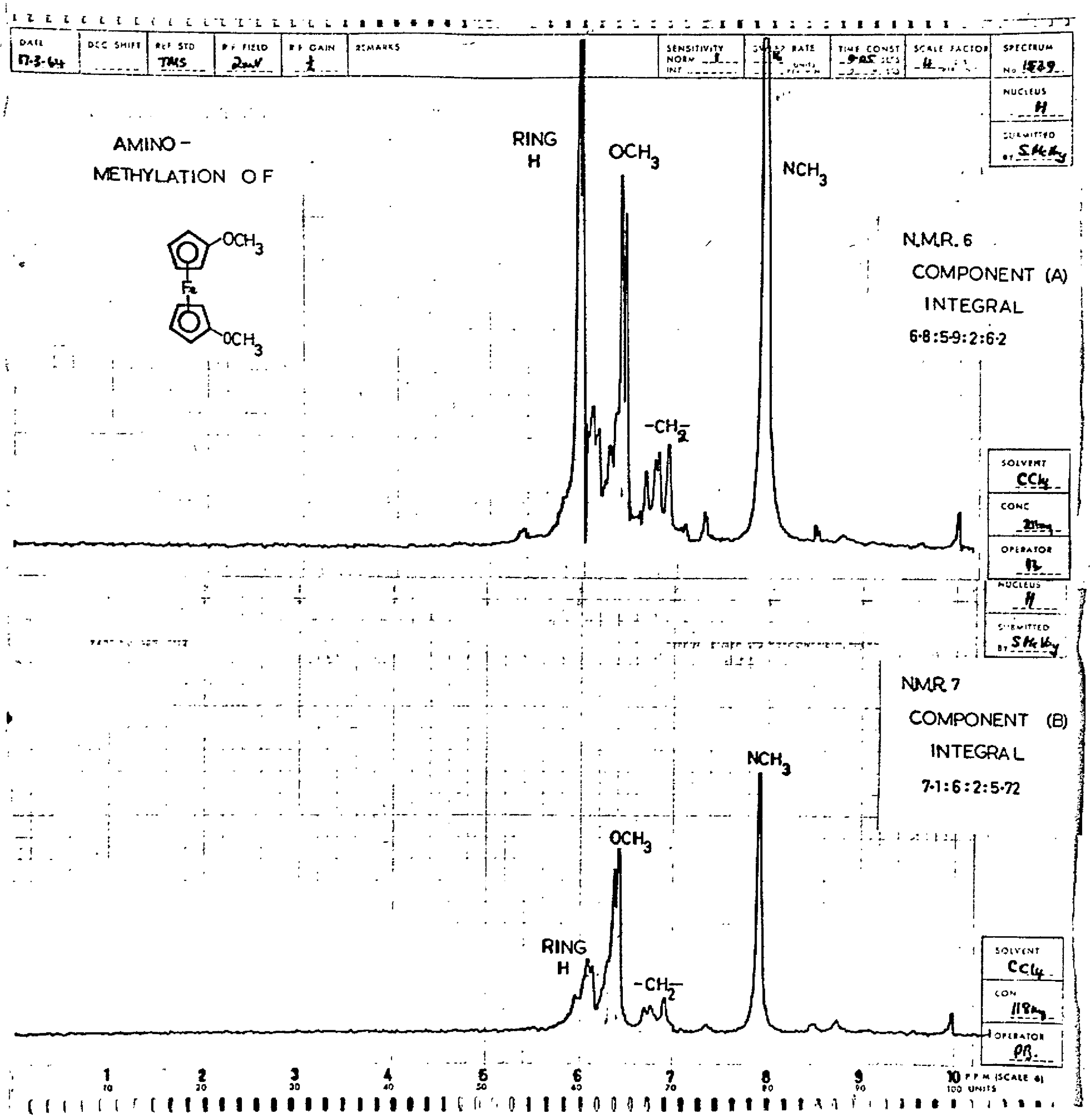
(Nujol)	(Lr)
–	1661 (vs)
1493 (s)	1493 (vs)
1466 (s)	–
1456 (s)	1453 (s)
1429 (vs)	1429 (s)
1410 (m)	–
1377	1377 (s)
–	1361 (s)
–	1274 (vs)
1244 (m)	1250 (s)
–	1111 (m)
1104 (s)	1104[b] (w)
1058 (vs)	1053 (vs)
–	1032 (m)
1012 (vs)	1010 (s)
1000 (s)	1000[b] (m)
–	960 (w)
914 (s)	914 (w)
–	890
832 (s)	–
821 (s)	813
804 (vs)	–

a = doublet b = shoulder

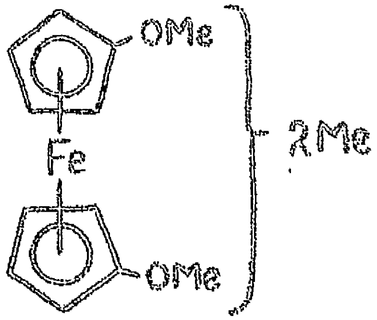
Infrared maxima for dimethoxyferrocene and dimethylaminomethylated product below 2000 cm.$^{-1}$

	Component (A)	Component (B)
1493 (vs)	1493 (vs)	1493 (vs)
–	1475 (s)	1475 (s)
1450^b (s)	1451^b (s)	1451 (s)
1428 (s)	1422 (s)	1425 (s)
1374 (s)	1381 (w)	1376 (m)
–	1351 (w)	1351 (w)
–	1316 (vw)	1316 (vw)
–	1286 (m)	1286 (m)
1250 (s)	1250 (m)	1247 (vs)
1235^b (s)	–	–
1198 (m)	1212 (m)	1214 (m)
–	1170 (m)	1174 (m)
1149 (w)	1149 (m)	1149 (m)
–	1115 (m)	1116 (m)
–	1105 (s)	1104 (w)
1053 (s)	1047^a (s)	1056 (s)
1044^b (s)	1036 (s)	1036^b (s)
1012 (s)	1020^a (s)	1018^a (s)
–	1000 (s)	–
–	990^a (w)	946 (w)
921 (s)	925^a (w)	926^b (w)
862 (w)	881 (w)	917 (m)
823^b (m)	843 (s)	842 (m)
816 (s)	813 (s)	813 (s)

a = doublet, b = shoulder


DATE 17-3-64
DEC SHIFT
REF STD TMS
R F FIELD 2mV
R F GAIN ½
REMARKS
SENSITIVITY NORM 1
SWEEP RATE
TIME CONST 9·05
SCALE FACTOR 4
SPECTRUM No 1529
NUCLEUS H
SUBMITTED BY S.McK.y
AMINO-
METHYLATION OF
OCH3
Fe
OCH3
RING H
OCH3
NCH3
-CH2-
N.M.R. 6
COMPONENT (A)
INTEGRAL
6·8:5·9:2:6·2
SOLVENT CCl4
CONC 211mg
OPERATOR R.
NUCLEUS H
SUBMITTED BY S.McK.y
NMR 7
COMPONENT (B)
INTEGRAL
7·1:6:2:5·72
NCH3
OCH3
RING H
-CH2-
SOLVENT CCl4
CON 118mg
OPERATOR P.B.
1
2
3
4
5
6
7
8
9
10
P P M (SCALE 6)
100 UNITS

Infrared maxima for mixed dimethyl-dimethoxyferrocenes below 2000 cm.$^{-1}$



(Liquid Film

1493	(s)
1475	(s)
1418	(s)
1376	(m)
1277	(s)
1227	(w)
1190^{a}	(m)
1142	(s)
1052	(s)
1034	(s)
943	(w)
921	(w)
859^{b}	(w)
816	(m)
792^{a}	(w)
704	(m)

a = doublet, b = shoulder

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